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THE UNIVERSITY OF ALBERTA

THERMODYNAMIC MODELLING OF COMPLEX AQUEOUS SOLUTIONS

by

Ⓒ GOUR SADAY CHOUDHURY

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF
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IN
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled **THERMODYNAMIC MODELLING OF COMPLEX AQUEOUS SOLUTIONS** submitted by **GOUR SADAY CHOUDHURY** in partial fulfilment of the requirements for the degree of **DOCTOR OF PHILOSOPHY** in **FOOD ENGINEERING**.

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Dedicated to

- my beloved parents

ABSTRACT

The primary objective of this study was to present a novel approach for the thermodynamic treatment of fluids produced by cellular processes. Such fluids are normally an aqueous mixture in which water is the major component. In essence, the aim was to adapt a thermodynamic model to the study of complex aqueous solutions in order to predict the activity coefficient of the components. Considering the complex nature of such solutions, this study was focussed on the carbohydrate-water system.

The UNIFAC group contribution method of Fredenslund *et al.* (1975, 1977) was evaluated in terms of its ability to predict the activity coefficients of components in a binary glucose-water system. The model performed poorly when applied to aqueous glucose solutions. The values of the parameters reported by Gmehling *et al.* (1982) could not represent the binary glucose-water system. The lack of fit with the expreimental data was extremely high. Revision of the parameter values for the OH group led to significant improvements in the predictions. A free-volume correction was necessary for water in the concentrated range.

The model with the revised parameter values for the OH group was employed to estimate the equilibrium properties of aqueous solutions of fructose, common disaccharides and mixtures of sugars. The predictions were reasonably quantitative for solutions of fructose and mixtures of

sugars but were unsatisfactory for solutions of sucrose, maltose and lactose. The lack of a defined functional group for the cyclic sugar molecules appeared to be a major problem. Possible approaches to increase the domain of validity of the model were examined.

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Table of Contents

List of Tables

List of Figures

List of Symbols

Symbol	Description
a	Activity
a_{mn}	Group interaction parameter
A	Empirical Constant
A	Helmholtz energy
A^E	Excess Helmoltz energy
b	Proportionality constant
B	Empirical Constant
$\bar{c}_p^E$	Excess partial molar heat capacity
C	Empirical Constant
C_p^E	Excess heat capacity
C1	Sugar conformation
D	Empirical Constant
E	Empirical Constant
f	Fugacity
f°	Standard state fugacity
g	Molar Gibbs free energy
$\bar{g}$	Partial molar Gibbs free energy
$\bar{g}^E$	Excess partial molar Gibbs free energy
G	Gibbs free energy
G^E	Excess Gibbs free energy
h	Molar enthalpy
$\bar{h}$	Partial molar enthalpy
$\bar{h}^E$	Excess partial molar enthalpy

H	Enthalpy
H	Henry's constant
H^E	Excess enthalpy
K	Proportionality constant
K_{eq}	Equilibrium distribution coefficient
m	Molality
n	Number of moles
P	Pressure
P^s	Saturation pressure
P_{ref}	Pressure at reference state
q_i	Area parameter of component i
Q_k	Area parameter of group k
r_i	Volume parameter of component i
R	Universal gas constant
R_k	Area parameter of group k
s	Molar entropy
$\bar{s}$	Partial molar entropy
$\bar{s}^E$	Excess partial molar entropy
S	Entropy
S^E	Excess entropy
T	Temperature in K
TMD	Temperature of maximum density
T_f	Freezing point temperature
T_m	Melting point temperature
T_t	Triple point temperature

T_{ref}	Temperature at reference state
U	Internal energy
U^E	Excess internal energy
v	Molar volume
$\bar{v}$	Partial molar volume
$\tilde{v}$	Reduced volume
$\bar{v}^E$	Excess partial molar volume
$v_{glucose}$	Molar volume of glucose
V	Volume
V^E	Excess Volume
w	Weight fraction
W	Weight
x	Liquid phase mole fraction
X_m	Mole fraction of group m
y	Vapor phase mole fraction
z	Coordination number
1C	Sugar conformation
3c	Number of external degrees of freedom per molecule

Greek

α	Sugar anomer
β	Sugar anomer
γ	Activity coefficient
γ^C	Combinatorial activity coefficient

γ^{FV}	Free-volume activity coefficient
γ^{R}	Residual activity coefficient
Γ_k	Activity coefficient of group k
ΔC_f	Change in specific heat upon fusion
ΔE	Change in activation energy
ΔG	Change in Gibbs free energy
ΔG^E	Change in excess Gibbs free energy
Δh_f	Molar enthalpy of fusion at freezing point
ΔH	Change in enthalpy
ΔH^E	Change in excess enthalpy
Δs_f	Molar entropy of fusion at melting point
ΔS	Change in entropy
ΔS^E	Change in excess entropy
θ	Freezing point depression
θ_i	Area fraction of component i
μ	Chemical potential
μ°	Chemical potential at reference state
ν	Number of groups
σ^2	Sample variance
ϕ	Osmotic coefficient
ϕ_i	Volume fraction of component i
χ^2	Chi-square
ψ_{mn}	Group interaction parameter

Superscripts

C	Combinatorial
E	Refers to excess property
f	Refers to freezing point
FV	Free-volume
m	Refers to melting point
O	Refers to standard state
R	Residual
S	Saturation
t	Refers to triple point
*	Refers to unsymmetric convention

Subscripts

eq	Refers to equilibrium
P	Refers to constant pressure
i	Refers to component
k	Refers to functional group
m	Refers to functional goup
mn	Refers to functional gropus 'm' and 'n'
Ref	Refers to reference state

1. INTRODUCTION

1.1 Complex Aqueous Solutions

Fluids processed in food industries are mostly of biological origin produced by cellular processes. Such fluids are typically aqueous mixtures of proteins, carbohydrates, minerals, lipids, vitamins and traces of other constituents like enzymes, fatty acids, amino acids, peptones, nitrogeneous bases, gases and other volatile components. Milk is one such complex fluid produced in the mammary tissue that contains on average 87.5% water, 4.8% carbohydrate, 3.8% fat, 3.2% protein, 0.7% minerals and traces of other minor ingredients (Brunner, 1976).

The study of complex aqueous solutions is important in understanding many processes that take place when biological compounds combine, react with each other or change shape in an aqueous environment. The reactivity of a compound with another is affected by its interaction with water. According to Wolfenden (1978), the evolution of biological catalysts was intensely influenced by the solvation effects. The preferential extraction of activated intermediates rather than the substrates themselves from solvent water is needed for the action of enzymes in substrate transformation (Wolfenden, 1972, 1976). Study of aqueous systems will aid in understanding the observed affinities of active sites and other biological receptors for ligands such as substrates and intermediates. It will be of interest to know why these ligands have an absolute tendency to leave water and enter a featureless cavity. This might then lead to inference about the presence of specific attractive or repulsive interactions between these ligands and the sites at which they are attached (Wolfenden, 1978).

1.2 Need for a Thermodynamic Treatment

The majority of foods are aqueous mixtures of which water is the most abundant component and its activity is therefore of crucial importance as a quality parameter (Choudhury and Le Maguer, 1985). It plays a vital role in influencing microbial growth (Gould, 1985; Troller, 1980), kinetics of chemical and biochemical reactions (Labuza, 1980; Schwimmer, 1980), enzyme activity (Drapron, 1985), food rheology (Karel, 1975, 1985; Moreyra and Peleg, 1981; Peleg, 1985), food spoilage (Loncin, *et al.*, 1968), packaging and drying of foods (Gall, 1983; Roth and Loncin, 1985). The amount and activity of water determine the state of aggregation and mobility of various food components (Karel, 1985). Figure 1.1 shows the influence of the activity of water on chemical, enzymatic and microbiological changes, overall stability and moisture sorption properties of food products (Rockland and Nishi, 1980). Thus, it is apparent that the estimation of water activity in a food system which has a dominant role in determining the properties and performance of a wide range of manufactured food products is of paramount importance.

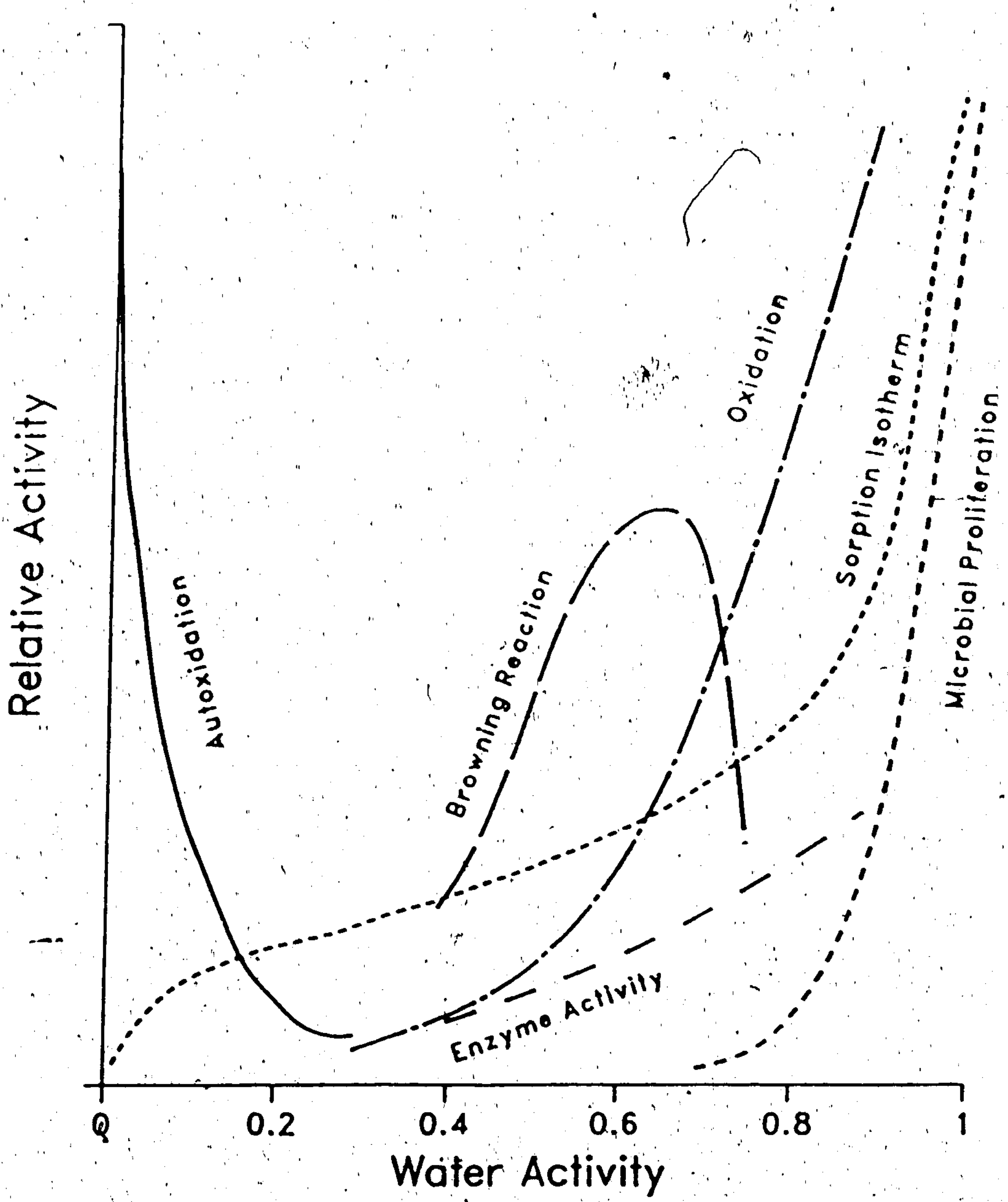


Figure 1.1 Diagramatic illustration of the influence of water activity on the rate of various important microbiological, physical, chemical and biochemical changes that place in food systems (Adapted from: Rockland and Nishi, 1980).

In a modern food processing plant, complex aqueous mixtures are converted into varieties of products employing a chain of unit operations. Table 1.1 lists the type of thermodynamic data used in these operations, most of which deal with the removal of water, the major component, from the food systems. Drying and freezing are two methods available for long term preservation of food in which the activity of water is lowered by evaporation (or sublimation) and crystallisation of the major component (water) in the food system. Evaporation is another unit operation used extensively in the removal of water from liquid food mixtures. The aqueous extraction of sugar from sugar beets and leaching of water-soluble ingredients from ground coffee beans depend on strong and specific interactions between the solute and the solvent water. The process selectively removes one or more components from a complex mixture. In crystallization the solution containing the solute to be crystallized is concentrated and usually cooled until the solute concentration becomes greater than its solubility at that temperature. Food industries in general produce large volumes of waste water. Treatment of waste water has become acute in recent years because of the imposition of government regulations and an increased need for energy conservation. All these operations require quantitative information on thermodynamic properties of water and aqueous mixtures.

Table 1.1 Unit operations in the food processing industry that require thermodynamic data.

Unit Operations	Type of Thermodynamic Data	Examples of Products
Drying	Enthalpy, latent heat, specific heat, volumetric properties, thermal conductivity, thermal diffusivity and sorption data.	Dried grains, dried fruits and vegetables, corn starch, sugar and pasta products; dried milk and milk products, breakfast cereals, soup and cake mixes.
Thermal Processing	Thermal conductivity, specific heat, enthalpy and latent heat.	Canned fruits, vegetables, meat and fish; pasteurized and sterilized milk.
Evaporation	Boiling point, phase diagram, specific heat, latent heat, enthalpy, vapor pressure and volumetric data.	Concentrated milk, fruit juices, tomato sauce and paste. A major intermediate step in the manufacture of sugar and whey powder
Crystallization	Phase diagram, solubility.	Sugar, table salt and fruit juice concentrates.

Table 1.1 Contd.

Unit Operations	Type of Thermodynamic Data	Examples of Products
Freezing and Freeze Drying	Freezing point, phase-diagram, specific heat, latent heat, thermal conductivity and volumetric data.	Frozen fruits and fruit juices, vegetables, meat and fish; freeze-dried coffee and flavour compounds.
Extraction	Activity coefficient, distribution coefficient and equilibrium composition.	Vegetable oil from oilseeds, cocoa butter from cocoa beans, sugar from sugar beets and sugar cane, decaffeinated coffee, desalting of pickles.
Distillation	Activity coefficient, vapor-liquid equilibrium composition, latent heat, enthalpy and heat capacity.	Distilled liquor and volatile flavour compounds.

The aqueous solubility of various compounds is still a poorly understood phenomenon, in spite of its growing need and importance in food processing, pharmacy and other applied chemical disciplines. The prediction of the solubility limit of components in an aqueous solution is a difficult task. The elevation of boiling point and osmotic pressure and depression of freezing point and vapor pressure depend on the number of solute particles in the mixture. No method is available for estimating the aqueous solubility of solutes and the colligative properties from a consideration of the structure and physical properties of the components. In planning the processing of a biofluid it is also important to know the behaviour of the system with the nature and composition of the phases that appear when one cools, heats, or removes water from actual liquid foods. The final composition of each phase depends on the temperature, pressure, the chemical nature and concentration of the substances in the mixture. This knowledge is necessary to predict the true composition of the food after operations such as freezing, freeze-drying, evaporation, distillation and membrane separation (Le Maguer, 1981). This requires information on the activity coefficient of the solution components over the composition and temperature ranges of interest.

One important facet of food engineering is concerned with design of equipment and processes for efficient conversion of large quantities of raw materials into finished products. Such an endeavour demands quantitative knowledge of the properties (Table 1.1) of raw materials to be processed which, in a food industry, is usually an aqueous mixture of components produced by an animal or a plant. These bulk raw materials are rarely in pure form. In design work quantitative estimates of partial equilibrium properties are required and it is frequently necessary to estimate these thermodynamic properties from severely limited experimental data (Reid *et al.*, 1977). Volumetric, energetic or transport properties are computed when one is interested in the property of the mixture as a whole, whereas in phase-equilibrium calculations, one must know the partial properties of individual components that constitute the mixture. The prediction of phase-equilibria relations in process design is usually more difficult and less accurate than prediction of other properties (Reid, *et al.*, 1977). Because of the complexity of aqueous mixtures and the difficulty in obtaining reliable experimental equilibrium data, simple physical models have proved to be useful for representing phase equilibria in a thermodynamically consistent way. Not only do such models provide efficient tools for data reduction, but they also provide sound guidelines for estimation of other equilibrium mixture properties such as liquid-liquid equibria from vapor-liquid equilibria and vice versa or multicomponent vapor-liquid equilibrium from equilibrium data for binary systems.

1.3 Objectives of this Study

The thermodynamic treatment of complex aqueous solutions is of interest for rational design and development of food processes. Through a systematic and deeper understanding of the properties of biofluids, processes for manufacture, preservation and storage of food products can be designed efficiently and economically. The number of complex fluids processed in food industries is large. The composition of such aqueous mixtures is ever changing due to their biological origin. Any factor that affects cellular processes will change the composition of the mixture produced by a living cell. It is therefore unreasonable to determine the effect of such composition variation of various components on the thermodynamic properties of the mixture on a regular basis. Further, it requires appreciable skill, money, experience and patience for obtaining good experimental data. It is, therefore, an economic necessity to have an efficient mathematical tool to describe the effects of composition and temperature on the thermodynamic properties of biofluids and to generate phase-equilibrium data.

The activity coefficient of components, which is directly related to excess Gibbs free energy, reflects the deviation from ideal behaviour. It plays a key role in the calculation of phase equilibria and is suited for applications in which the behaviour of a particular component of the solution is of special interest, as in the distribution of a component between two phases or in the chemical reaction of a component in the solution (Friedman, 1960). Thermodynamics relates the effect of pressure on the activity coefficient to the partial molar volume and the effect of temperature to the partial molar enthalpy (Reid *et al.*, 1977). Activity coefficients in liquid mixtures can be calculated from a model which expresses the excess Gibbs energy of the mixture as a function of composition and temperature (Abrams and Pransnitz, 1975).

It is needless to reiterate the importance of the thermodynamic properties of biofluids in engineering design of equipment and processes and the necessity for the prediction of the activity coefficient of each component in complex aqueous solutions. This study thus aims at contributing to the area of thermodynamic treatment of complex aqueous solutions through the following objectives:

1. Review the present state of our knowledge of aqueous solution of nonelectrolytes.
2. Present a novel approach for the thermodynamic treatment of complex aqueous solutions.
3. Review the available thermodynamic models for multicomponent solutions of nonelectrolytes such as an aqueous solution of carbohydrates.
4. Adaptation of a suitable model to the study of aqueous solutions, especially that of the carbohydrates. This will involve modification of parameters in such a model to reflect the strong intermolecular interaction in an

aqueous environment.

5. Estimation of equilibrium mixture properties of complex solutions using the adapted/modified model.
6. Prediction of water activity, freezing point, solubility limit and partial equilibrium properties of an aqueous mixture.
7. Finally, to suggest possible extension of this work based on the experience gained in the present study.

2. REVIEW OF LITERATURE

2.1 Water: The Universal Solvent

Water is the most abundant compound on the earth's surface and forms a vital and necessary component of all living organisms. Life cannot exist, even for a limited period, in the absence of water which constitutes 70-90% of the weight of all living organism (Franks, 1972).

As confirmed by experimental investigations and quantum mechanical calculations, the water molecule can be represented by an oxygen atom at the center of a regular tetrahedron (Figure 2.1) which has hydrogen nuclei (protons, deuterons or tritons) at two of its vertices and "lone pair" electrons in orbitals directed towards the other two (Frank, 1974). The X-ray study of liquid water by Morgan and Warren (1938) indicated essentially the tetrahedral nature of the water structure. This tetrahedral arrangement is possible only in water. It mimicks the ionic structure of quartz with one H between every two oxygen instead of one oxygen between every two silicons (Bernal and Fowler, 1933). The most important molecular feature underlying the properties of liquid and solid water is its capacity to form intermolecular hydrogen bonds (Rahman and Stillinger, 1973). In the liquid state at 0°C, each water molecule is hydrogen bonded at any given time with an average of about 3.6 other water molecules, whereas in ice (common crystalline form ice I) each water molecule is hydrogen bonded with exactly four

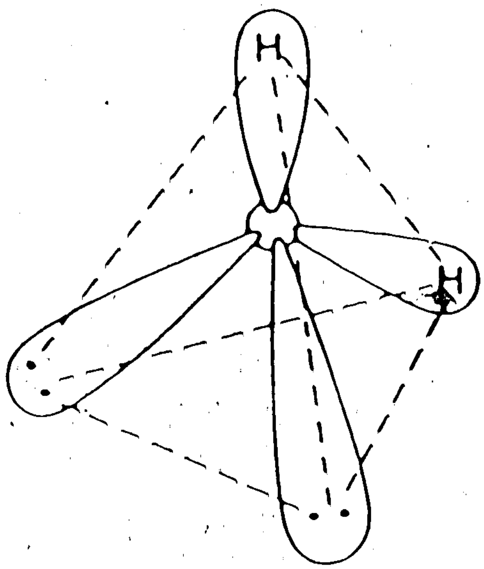


Figure 2.1 Geometric representation of the distribution of nuclei and electron in a water molecule (Adapted from: Frank, 1974).

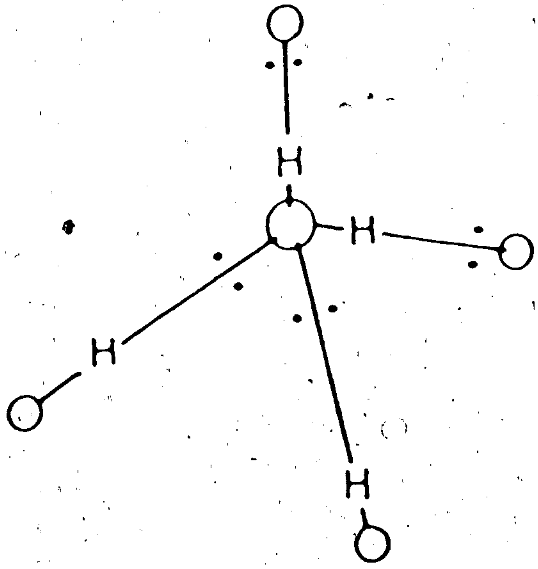


Figure 2.2 Pictorial representation of the hydrogen bond as the attraction of an H atom from one molecule to a lone pair of another (Adapted from: Frank, 1974).

nearest neighbours in a regular lattice having an average oxygen-oxygen distance of 0.276 nm. The oxygen-oxygen distance in liquid water is about 0.29 nm at 15°C and 0.305 nm at 83°C. The specific distribution of electrons in the water molecule is responsible for strong intermolecular attraction in the form of hydrogen bonding between neighbouring water molecules (Lehninger, 1978). The energy levels of the water molecules vary with the number of hydrogen bonds they form (Figure 2.3). Liquid water consists of a random hydrogen-bonded network with frequent strained and broken bonds, that are continually subject to spontaneous restructuring (Stillinger, 1977). The half-life of each hydrogen bond is only 10^{-11}s (Lehninger, 1978). According to Rao (1972) cyclic as well as open dimers and polymers may be present in liquid water. A large variety of distorted hydrogen bonds with a distribution of energies may be associated with each of these species. The linear dimer is more stable than the cyclic and bifurcated structures of the water dimer. However, the latter forms are stable enough to contribute to water structure. Many models have been proposed for the structure of liquid water, but none has been completely verified experimentally.

Water has abnormal physical properties when compared with other compounds of similar electronic structure. A molecule of water, like CH_4, NH_3, and HF has ten electrons. Water has the highest van der Waals constant 'a' corresponding to the greatest intermolecular attraction, and

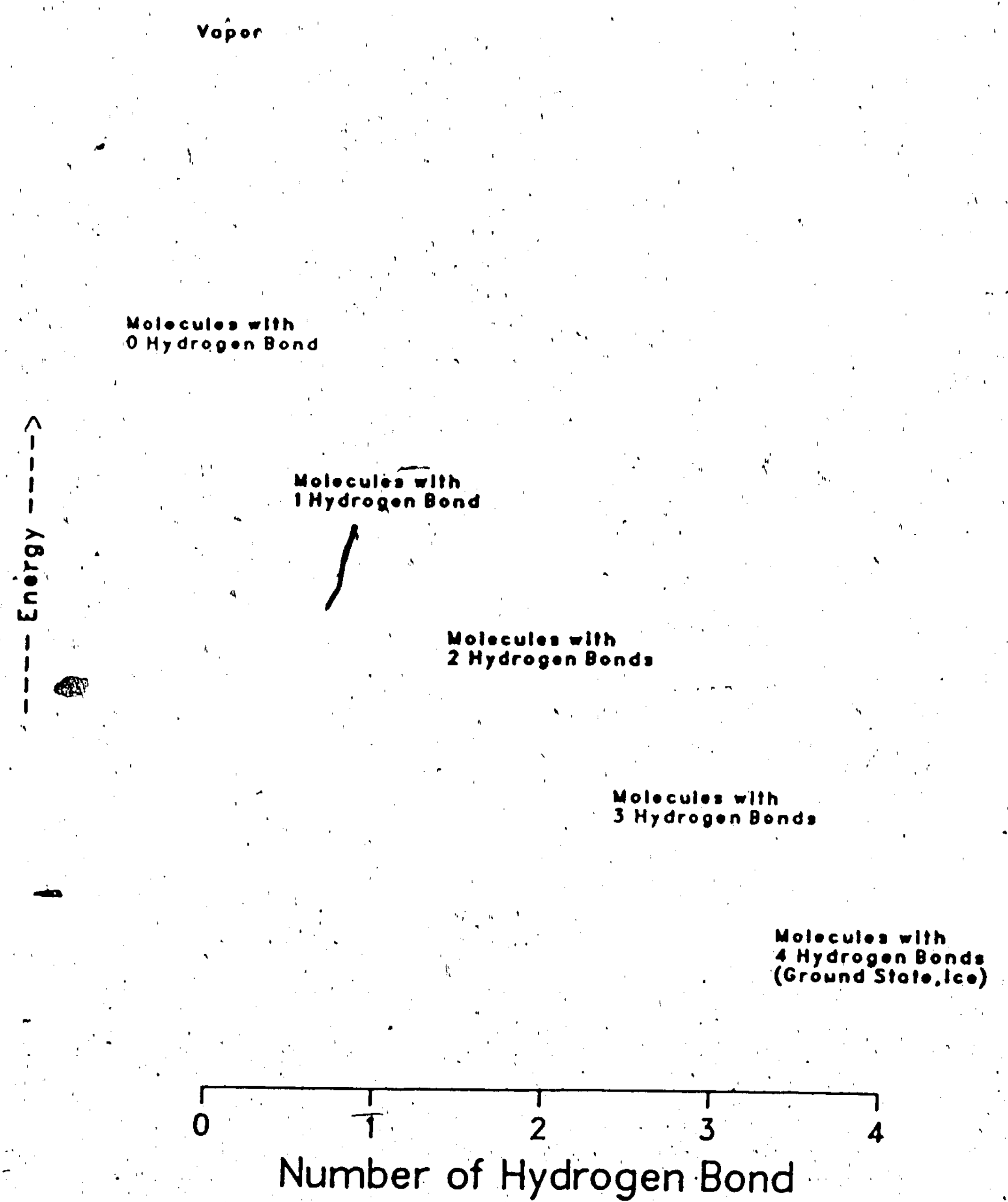


Figure 2.3 Schematic representation of energy levels for water molecules in liquid water (Adapted from: Nemethy and Scheraga, 1962a).

the lowest 'b' corresponding to the smallest distance between molecular centres. The high internal cohesion of water is due to the presence of dipoles and the geometrical possibility of fitting the molecules together (Bowler and Fowler, 1933).

Water has a high melting point, boiling point, heat of vaporization, heat of fusion and surface tension when compared with similar hydrides (H_2S, NH_3) and common liquids (acetone, methanol etc). The high intermolecular forces and relatively high internal cohesion are responsible for these unusual properties of water (Lehninger, 1978). Water has anomalous physical properties as a solvent, some of which are: contraction upon melting, density maximum at 3.98°C, isothermal compressibility minimum, high dielectric constant, high constant volume heat capacity and viscosity reduction upon pressurization. Any theory for liquid water must rationalize these observations, if not predict them quantitatively (Stillinger, 1977).

The water content of biological fluids such as plasma, saliva, and gastric juices is between 99-97.5% (Franks, 1972). Its primary role in biology is as a solvent and constituent of interfaces. It has a dominant role in the production and maintenance of active forms of biological molecules (Stillinger, 1977). It promotes biological hydrolysis in which proteins and carbohydrates are catabolized and the anabolism of these compounds give rise to the biosynthesis of water (Franks, 1972).

The thermodynamic and transport properties of water play a key role in many biochemical and industrial processes. Much of the industrial production would not exist without water. Unlike other solvents, water demonstrates a capability to discriminate between various solutes according to their nature and functional groups (Cabani and Gianni, 1979). The high degree of order, caused by hydrogen bonding, is the dominant feature of liquid water that is responsible for its general solution properties. The high degree of polarity of water along with its temperature dependent high degree of order have frustrated any attempt to use the classical solution theory for the treatment of aqueous solutions (Getzen, 1976). The strikingly unique solution properties of this universal solvent are closely related to its structure and will be highlighted in the section on aqueous solutions that follows.

2.2 Aqueous Solutions

A large body of information is available on the properties of aqueous solution of electrolytes since most effort in the past has been devoted to the study of ionic solutions. This is largely due to the fact that an acceptable theory existed against which experimental results could be tested (Franks *et al.*, 1972). The Debye-Hückel theory dominated the study of aqueous electrolyte solution from around 1920 to near the end of the 1950's. This theory treated ions as point charges (later as charged spheres) and took no direct account of the solvent other than considering it to be a homogeneous dielectric. Deviations from ideal behaviour were assumed to be due only to long range electrostatic forces between ions. To improve the predictive power of this model further refinements were eventually added to include ion-ion pairing and ion hydration (Wilhoit, 1980).

Recent years have witnessed an increased interest in the study of aqueous nonelectrolyte solutions. The impetus for this interest has come from the realization of the biochemical and physicochemical importance of water as a solvent and its prevalence in many industrial processes. This renewal of interest is mainly due to the availability of refined experimental methods for the direct and indirect measurements of enthalpies, heat capacities and volumetric properties. Although a rigorous treatment of concentrated solutions remains a distant goal of solution theory (Stokes and Robinson, 1966), the developments in statistical thermodynamics and computer simulation have facilitated the analysis of solute-solute and solute-solvent interactions in dilute solutions (Franks, 1985).

A full description of the properties of a solution requires information about three different interactions that contribute to the total potential energy: solvent-solvent, solvent-solute and solute-solute interactions (Franks, 1983). In concentrated solution the behaviour of the system is very complex and depends not only on the interaction of the solute molecules with the solvent but also with each other (Butler, 1937). As the concentration of the solute is decreased the solute-solute interaction becomes less important and in a dilute solution the measured properties of the system are dominated by those of the solvent which makes it difficult to investigate experimentally the solvation and solute-solute interaction. The concentration dependence of a thermodynamic property is a measure of solute-solute effects, whereas the extrapolation of the same property at the limit of infinite dilution provides an estimate of solute-solvent (solvation) interactions. In an electrolyte solution the system is further complicated by the fact that each solute ionises into at least two distinguishable species (Franks, 1983). Although a large volume of information has been gathered on molecular interaction from experimental measurements on aqueous solutions (Wilhoit, 1980), most of the available informaton on solute-water interactions is based on circumstantial experimental evidence or on comparison of water with some reference solvent (Franks, 1983).

2.2.1 Classification of Solutes in Aqueous Solutions

When solute molecules are introduced into water, they perturb the predominantly tetrahedral arrangement of water molecules, usually referred to as water structure (Franks, 1977) by increasing or decreasing the distribution of hydrogen bonds (Desnoyers, 1982). Solvation by water may thus be interpreted as a response of the labile and geometrically diverse random network to various perturbations caused by different solutes. Solutes may induce hydrogen bonds to form ('structure makers') or to break ('structure breakers'). In addition to these effects solutes may locally alter the distribution of hydrogen bond polygons, or perhaps alter the frequency with which different portions of the random network interpenetrate (Stillinger, 1977).

Based on the influence upon water structure Frank (1965) classified the solutes into four categories according to the type of structural interaction they have with solvent water. These are ionic, chemically inert, hydrogen bonding and polyfunctional.

A. Ionic Solutes

Ionic solutes (Na^+, Cl^- etc.), in general produce a structure breaking effect, presumably by "depolymerization" which increases the fluidity of liquid water (Frank and Evans, 1945). This structure breaking effect arises due to the disorder created in an intermediate region between primary hydrate water, oriented in some radial pattern about the ionic charge, and the region which the more distant water imposes upon itself (Frank, 1965). The water structure in this intermediate region is broken down, or melted, or depolymerised as compared to pure water (Frank and Evans, 1945). Based on entropy data, Frank and Wen (1957) assigned a structure-altering influence to a considerable number of ions. Cations smaller or more highly charged than K^+ are net structure formers, and become more strongly so if the ion is smaller and more highly charged. K^+ is slightly structure-breaking on balance, and this tendency increases through Rb^+ and Cs^+. F^- is a structure-former, and the other halide anions are structure-breakers. The larger the ion, the greater is the structure breaking tendency. NO_3^- and ClO_4^- are strongly structure breaking, and SO_4^- is less so. OH^- appears to be a structure former. In the case of small or multiply charged ions (e.g., Li^+, F^-, Mg^{++}), larger regions of near-neighbour water is immobilized which produces marked 'structure-making' effects on entropy (Frank, 1965).

Samoilov (1957) contradicted the idea of using hydration number to describe the hydration by ions in view of the large discrepancies in the value of hydration number for the same ion reported by various researchers. The main quantitative measure of ion hydration in solution is the change in activation energy (ΔE) of the exchange of the closest water molecules due to the influence of the dissolved ion. A procedure was developed for computing the value of ΔE for individual ions from experimental data of self-diffusion in water and of the temperature coefficients of the ion mobilities in solutions. It was shown that for Li^+ and Na^+, $\Delta E > 0$ and for K^+, Cs^+, Cl^-, $\Delta E < 0$. In the latter case the water molecules near the dissolved ion became more mobile than in pure water and the phenomenon was described as "negative hydration".

B. Hydrogen Bonding Solutes

These solutes exert comparatively less influence in modifying water structure, except when specific geometrical effects are involved. Since water is predominantly a hydrogen bonded network, any solute that forms hydrogen bonds will simply mimick the solvent, displaying no special effects on water structure. An example of such a solute is NH_3 which might have a modest role in cluster formation (Frank, 1965). An exception to this general behaviour is urea which is known to be a marked structure breaker (Rupley, 1964), even though its polarity and hydrogen bonding capability is similar to that of water (Frank, 1965). This peculiar behaviour appeared to arise from geometrical effects, the triangular shape of urea preventing it from entering into the four coordinated clusters of water, with their tetrahedral bonding. Rupley (1964) postulated that urea, like an ion, may orient the neighbouring water molecules around it, preventing them from participating in a hydrogen-bonded water cluster which induces a region of disorder about the solvated solute molecule. Finar *et al.* (1972) observed from NMR studies of aqueous urea solutions that urea destroys the long-range order characteristic of pure water. It has also been shown that urea-water hydrogen bonding interactions are very short-lived and no urea self-association exists in solution. The disruption of water structure is expected to influence the conformation of water-soluble polymers such as proteins by altering the nature of polymer-water interactions and may be responsible for the denaturation of proteins by urea. Since the poor solubility of hydrocarbons in water is largely due to the ordering of the solvent, the solubilization of hydrocarbons by urea may manifest a destruction of water structure (Rupley, 1964).

C. Chemically Inert Solutes

The thermodynamic properties of aqueous solutions of chemically inert solutes are influenced to a great extent by the strikingly unique structural features of liquid water. These solutes, like others, also display water structure modifying characteristics. Rare gases, hydrocarbons and alkyl halides fall into this category (Frank, 1965). Based on experimental data, Frank and Evans (1945) presented a physical picture of aqueous solutions containing chemically inert solutes. At room temperature a dissolved atom of rare gas or non-polar molecule modifies the water structure in the direction of greater "crystallinity" - the water builds a microscopic iceberg around it. The larger the foreign atom or molecule the greater is the size of the iceberg. The "freezing" of water by these solutes results in loss of heat and entropy beyond what would be expected from the norms established for nonaqueous solutions. The heat adds on to the otherwise smaller heat of solution of the inert gas, giving rise to a considerable positive ΔH of vaporization. The exceptionally large ΔS of vaporization is the outcome of the loss of entropy. The "melting" of these "icebergs" with an increase in temperature can account for the high partial molar heat capacity of these gases in water, which may exceed 251 J/degree mol. The magnitude of this effect is a function of the size of the icebergs originally formed and it is greatest for the rare gas Rn. The existence of crystalline hydrates of rare gases and hydrocarbons supports the concept of iceberg formation by these solutes. The formation of solid hydrates by these solutes also reflects that the geometric and energetic relations between the nonpolar solute and the water molecules have no natural antagonism to complex formation (Frank and Evans, 1945). The most detailed theory of the behaviour of aqueous solution of hydrocarbons has been given by Nemethy and Scherega (1962b) in their classical work on structure of water and hydrophobic bonding in proteins. The structural changes brought about by a hydrocarbon molecules in a aqueous solution is an increase in "ice-likeness". This increased "ice-likeness" results from the effects of the van der Waals interaction between water and solute molecules, the measure of which is given by the amount of hydrogen bonding which is increased in the immediate neighbourhood of the solute over its average value in pure water. This hydrogen-bonded network extends around part of the solute molecule, creating an incomplete cage.

The speculation of increased "ice-likeness" or formation of "iceberg" provides a pictorial explanation for the observation of Butler (1937) that the insolubility of non-polar solutes in water is an entropy, rather than an energy effect. Larger non-polar molecules, because of their stronger van der Waals force fields around them, are strongly held in any condensed phase, including aqueous solution than do the small ones, and consequently produce larger icebergs in water. This results in greater loss of entropy and hence poor solubility. The plot of solubility against temperature shows a minimum for most gases in water. This was attributed to the fact that these solutes alter the structure of water to an extent so as to devoid it of most of its pecularity as a solvent (Frank and Evans, 1945).

Eley (1939) theorized that the energy and entropy of solution of an inert gas molecule in water can be accounted for by two consecutive processes: (i) the formation of a cavity and (ii) the entry of the gas molecule into the cavity. All inert gases show a negative temperature coefficient of solubility and the plots of ln(s) against 1/T are distinctly curved. The negative temperature coefficient and its rapid increase to zero as the temperature is raised to 80°C, is to be elucidated mainly by the energy and entropy associated with the cavity formation and loss of translational movement. The positive temperature coefficient observed for some gases above 100°C, is to be accounted for by the large energy required to form a cavity at these temperatures, which surpasses the solute-solvent attraction (Eley, 1939).

A plausible explanation for the large negative entropies of solution of the rare gases in water was offered by Claussen and Polglase (1952) based on the structures of inert gas hydrates. The water molecules occupy the corner of a polyhedral clathrate and the inert molecules occupy the void space inside. The angle formed by any three water molecules attached by hydrogen bonds is close to the tetrahedral angle found in water molecules in ordinary ice. These structures are fairly stable with the central inert solute molecule preventing it from collapsing into liquid water structure, thus forming a highly ordered state which accounts for the large negative entropies of solution. A positive support for such an explanation was offered by Klots and Benson (1963) in the study of the isotopic effect in the solution of oxygen and nitrogen in distilled water. Although the notion of clathrate cages is useful in explaining experimental data, such cages, if or when formed about non-polar solute molecules or residues, are fragmentary or transitory and resemble real clathrates only by analogy (Frank, 1965). A convincing picture emerges from all these studies revealing that the chemically inert solutes bring about a short-range ordering of the solvent water molecules around solute molecules.

D. Polyfunctional Solutes

The interactions which predominate in solutions of polyfunctional solutes are complex and difficult to interpret (Frank, 1965). In such a complex solution each functional group is able to interact independently and differently with solvent water contributing to the observed properties (Franks and England, 1975). In the case of solutions of molecules possessing polyfunctional groups capable of hydrogen bonding to the solvent, both hydration (the direct hydrogen-bonding interaction) and long-range water-water interactions determine the properties of the system. Hydration effects due to solute-solvent hydrogen bonding are expected to be highly orientation-specific and depend sensitively on the stereochemistry of the hydration sites. The conformation of the solute might therefore be one of the key factors influencing such hydration effects (Franks *et al.*, 1972; Franks *et al.*, 1973; Franks, 1977). Such conformation effects were demonstrated to exist in sugar solutions in which marked differences were observed in hydration behaviour between axial and equatorial OH groups (Tait *et al.*, 1972; Franks *et al.*, 1973).

The study of the solutions of amino acids and proteins, though complex, is of great practical and theoretical interest. In amino acid solutions, the positively charged amino group of one zwitterion can interact with the negatively charged carbonyl group of the second molecule. This charge-charge interaction between solvated amino acid molecules as well as the contribution from the perturbation of water structure determines the behaviour of the system (Wegrzyn *et al.*, 1984). According to Kresheck and Benjamin (1964) glycine behaves as a structure breaker and higher aliphatic homologs behave as structure makers. In protein solution, the polyfunctional protein molecule can interact with solvent water by virtue of various functional groups, such as peptide bonds, ionizable groups (COO^-, NH_3^+, polar groups (OH, SH) and apolar hydrocarbon side chains (Franks and England, 1975). In an attempt to illustrate the nature of the complex problem encountered in protein solution, Alagona *et al.* (1973) undertook the study of formamide, a representative molecule having the biochemical peptide linkage. The presence of carbonyl and amino groups in this molecule suggests *a priori* the possibility of formation of two types of association with water: one in which the water molecule acts as a proton donor in a hydrogen bond to the carbonyl oxygen, the other in which the water acts as a proton acceptor in hydrogen bonding to the N-H bonds. Based on the binding energies at the minima, it was shown that neither CH hydrogen-bonding, nor π-bonding above the amino group appear to correspond to an appreciable probability of hydration, although a small attraction for water does exist in these regions. A review by Pullman and Pullman (1975) provides detailed information on hydration of biomolecules and the effect of solvent on the conformational properties of such molecules. Franks and England (1975) reviewed the role of solvent interaction in protein conformation and concluded that protein conformation stability is closely linked with the properties of the solvent system.

2.2.2 Excess Functions and Solution Behavior

According to Franks (1983), the sign and magnitude of excess functions provide a convenient way to classify liquid mixtures. The excess Gibbs energy change of mixing, defined by

$$\Delta G^E = \Delta H^E - T\Delta S^E$$

is composed of an enthalpic and an entropic contribution. For mixture of chemically similar and symmetrical molecules the excess Gibbs energy is likely to be small, positive and symmetrical about a mole fraction of 0.5. But the excess function diagrams can be quite complex for molecules of dissimilar sizes or where there are specific interactions, such as hydrogen-bonding. Aqueous solutions, the excess function diagrams of which are even more complex, fall roughly into two categories, characterized by the relative magnitudes of ΔH^E and $T\Delta S^E$ (Franks *et al.*, 1973). The deviations from Raoult's law in non-aqueous mixtures are determined by the sign of ΔH^E, i.e. $|\Delta H^E| > T|\Delta S^E|$. But in mixtures where the interactions between a non-polar group and water predominate, the sign of ΔG^E is determined by ΔS^E, i.e, $T|\Delta S^E| > |\Delta H^E|$. Such behaviour is manifested by an aqueous mixture of alcohols, amines and ethers which exihibit positive deviations from Raoult's law in spite of large negative heats of mixing. Based on the relative magnitudes of excess mixing functions, aqueous mixtures of various solutes are classified into two major groups as shown in Table 2.1 (Frank, 1965). Table 2.2 (Franks, 1983;

Table 2.1 Classification of aqueous solutions based on the magnitudes of excess entropy and enthalpy of mixing. (Adapted from: Franks, 1968).

$\lvert\Delta H^E\rvert > T\lvert\Delta S^E\rvert$	$\lvert\Delta H^E\rvert < T\lvert\Delta S^E\rvert$
Amides	Alcohols
Carbohydrates	Amines
Dimethyl sulphoxide	Dioxan (?)
Glycerol	Ethylene oxide
Glycerides (?)	Glycols
Hydrogen peroxide	Hexamethylene tetramine (?)
Nitriles	(Hydrocarbons)
Polyamino compounds	Ketones
Polyhydroxy compounds	Polyoxyethylene derivatives
Urea	Pyridine bases

Table 2.2 Excess Thermodynamic properties and phase behaviour in aqueous solutions (Adapted from: Franks, 1983; Rowlinson and Swinton, 1982).

Aqueous Solutions of	Excess Functions					Phase behaviour
	H^E	G^E	TS^E	V^E	C_p^E	
Nitriles, Ketones	+	+	−	+	−	Complete miscibility or upper critical demixing
Ethers, Alcohols, Amines	+or−	+	−	−	+	Upper critical demixing, tending to closed loop
Sec-, tert- amines, Cyclic ethers, Polyethers	−	+	−	−	+	Closed loop
Urea, H_2O_2, Polyols	−	−	−	−	≈ 0	Completely miscible
Sugars						Completely miscible up to the solubility limit

Rowlinson and Swinton, 1982) summarizes the various types of behaviour observed in aqueous mixtures. Cassel and Wood (1974) used excess enthalpy to classify solutes into two groups. If heats of dilution are used to classify solutes as structure-making or structure-breaking (Frank and Robinson, 1940; Frank and Wen, 1957), then at low concentrations, those solutes which have positive excess enthalpies are structure-making and ones that have negative excess enthalpies are structure-breaking. Based on this scheme, glycine and urea were classified as structure-breakers, while sucrose was classified as a structure-maker (Cassel and Wood, 1974).

2.3 Water Affinity of Non-Electrolytes

Water affinity can be defined as the attraction of a compound or a functional group for water by noncovalent forces. Strictly speaking, virtually all molecules are attracted to water by dispersion forces (Wolfenden, 1983). In the vapor phase, for example, isolated methane molecules show modest affinity for water molecules (Ungemach and Schaefer, 1974); even at the interface between liquid octane and water a net attractive force exists (Harkins and Cheng, 1921). As stated by Wolfenden (1983) and Wolfenden *et al.*, (1981), the absolute affinity of a compound for an aqueous environment can be evaluated by the following methods:

a. Determining the equilibrium constant for transfer of a compound from the dilute vapor phase to a very dilute aqueous, solution in which each solute is surrounded by solvent.

b. Measuring the vapor pressure of a compound over dilute aqueous solutions.

c. Measuring the solubilities of a gas under known pressure.

d. Determining the concentration of less volatile compounds in the gas space over solutions of known concentrations.

e. Determining the concentration of highly polar solutes in measured volumes of inert gas bubbled through an aqueous solution of known concentration.

Based on the relative magnitude of the affinity for watery surrounding, compounds and functional groups are qualitatively classified as "hydrophilic" and "hydrophobic". The distinctive difference in thermodynamic properties of these two types of solutes is reflected in Table 2.3 (Franks, 1983).

2.3.1 Hydrophilic Nature of Organic Molecules

A molecule or a functional group is considered to be hydrophilic when it demonstrates measurable affinity for aqueous environment, although not all molecules or functional group exhibit the same degree of affinity. Hine and Mookerjee (1975) considered the tendency of a molecule to go from the gas phase to a dilute aqueous solution to be a measure of its intrinsic hydrophilic character. This

Table 2.3 Comparison of polar and hydrophobic solutes based on the limiting thermodynamic excess functions (Adapted from: Franks, 1983).

Excess Functions and Other Properties	Solutes	
	Polar	Hydrophobic
Free energy	−	+
Enthalpy	−	+ or −
Entropy	−, $T\|\Delta S\|<\|\Delta H\|$	−, $T\|\Delta S\|>\|\Delta H\|$
Heat capacity	− (≃0)	+
Volume	− (small)	−
Expansivity (at low temp.)	+	−
Compressibility	− (large for ions)	− (small)
Shift in TMD	−	+

character is better understood in terms of molecular structure, and depends, to a large extent, on the presence of polar centres in a molecule that are capable of forming hydrogen-bonds with solvent water (Hine and Mookerjee, 1975). To be hydrophilic, the attractive force between the molecule and the water should be strong enough to overcome the self-cohesive properties of water (Wolfenden, 1983).

In an attempt to correlate the hydrophilicity with the number of hydrogen-bond forming centres in a molecule Wolfenden (1983) found that ethyl acetate, acetic acid, acetamide and methyl quanidine (with one, two, three and four such groups, respectively) seem to lie in the order expected on this basis. Acetaldehyde and acetone show identical hydrophilic character as evidenced from the values of their water-to-vapor distribution coefficient. Similar hydrophilicity exhibited by ketones and esters suggest that the ester bridge oxygen atom confers little affinity for water. Wolfenden and Williams (1983) reported comparable observations for phosphate esters. It was shown that triethylphosphine oxide (in which ester oxygens are replaced by methylene groups) is slightly more hydrophilic than trimethyl phosphate. While comparing phosphoric acid with carboxylic acid, it was also demonstrated that the $\equiv P=O$ function appears to be considerably more hydrophilic than the $>C=O$ function.

The hydrophilic nature of a molecule can be altered by replacement or substitution of an atom or a functional group by another. The hydrophilic character is marginally increased by replacement of hydrogen by deuterium on carbon of the carbonyl group in N-methylformamide (Wolfenden and Kirkman, 1983), and β to the carbonyl group in acetone, ethyl acetate, and p-nitroacetanilide (Kovach and Quinn, 1983). The water affinity of hydrocarbons can be considerably enhanced by increasing unsaturation, branching and ring formation (McAuliffe, 1966). Polar functional groups such as OH, COOH and NH_2 increase considerably the affinity of organic compounds (Butler, 1937). Acetamide is more hydrophilic than uncharged acetic acid. Wolfenden (1978) studied the effect of N-methylation of acetamide, which is expected to reduce its hydrophilicity. Instead, it increases the hydrophilic nature of acetamide. However, introduction of a second methyl group slightly decreases its hydrophilicity. Nevertheless, after second substitution, N,N-dimethyl acetamide is substantially more hydrophilic than acetic acid itself. This unusual hydrophilic character of amides was explained by Wolfenden (1978) as due to the peptide bond that represents an extreme among uncharged functional group in the degree to which it is stabilized by solvent water. The great hydrophilic character of the peptide bond is associated mainly with the hydrogen bonding of the solvent to the carbonyl oxygen atom rather than the NH group. Similar behaviour is displayed by amines, with methylamine exhibiting greater hydrophilic character than either ammonia or dimethylamine. It is thus apparent that maximum hydrophilicity is displayed by a molecule of amide and amine that can form two kinds of hydrogen bonds, one as a proton donor and the other as a proton acceptor.

The free energy of transfer of organic compounds from the gas phase to the aqueous solution is approximately an additive function of the groups that constitute the compounds (Butler *et al.*, 1933, 1935; Butler and Ramchandani, 1935). Cabani and Gianni (1979) proposed a method for prediction of free energies of transfer of organic compounds from vapor to water based on molecular structure.

Hine and Mookerjee (1975) reported the hydrophilicity (defined as water-to-vapor distribution coefficient at 25°C) of 292 organic compounds based on molecular structure by considering bond and group contributions, and compared them with experimentally determined values. Major deviations arising from distant polar interactions were observed for polyfunctional compounds. Alkyl-substituted pyrazines were found to be less hydrophilic compared with pyridine which contain only one ring nitrogen. This is a reflection of the ability of pyridine nitrogen atoms to accept hydrogen bonds from water. The hydrogen bonding ability of these nitrogen atoms, which depends on the electron density at the nitrogen, decreases by substitution of electron withdrawing groups (Taft *et al.*, 1969). For 1,3-propanediol, Bone *et al.* (1983) reported a value for the water-to-vapor distribution which was ten-fold higher than expected from the correlations of Hine and Mookerjee (1975). This difference was attributed to probable weak intermolecular hydrogen bonding between vicinal diols in the vapor phase. The hydrophilic character of p-nitrophenol was found to be much higher than that predicted from bond and group contributions. Unlike pyrrole and cyclopentadiene, imidazole was found to be extremely hydrophilic (Wolfenden, *et al.*, 1981). The high hydriphilic nature of these compounds was presumed to be due to one polar group acting as a proton donor, while the other as a proton acceptor. These effects are expected to strengthen each other electronically, so that hydrogen bonds at one end are stronger than they would be if those at the other end were not present (Wolfenden, 1983).

Extreme departure from the principle of the additive contribution of constituent functional groups on hydrophilic character of a compound may occur if one of the groups is highly polar or ionic (Wolfenden, 1983). Hydrophilicity of NH_4^+ progressively decreases with increasing methylation, the free energy of hydration changing by approximately 79.5 kJ/mol from ammonium ion to trimethyl amine (Arnett *et al.*, 1972). But the free energies of solvation of uncharged ammonia, methyl amine and dimethyl amine are nearly the same, and only 9.6 kJ/mol more negative than that of trimethyl amine (Wolfenden, 1983). Such striking effects of methylation on solvation of ions have also been revealed by Kebarle (1975) from studies on gas phase acidities of normal aliphatic carboxylic acids and by Arnett and Chawla (1979) from studies on hydration of pyridines and pyridinium ions. It appears reasonable to assume that the alkyl substituents may serve as "sinks" for delocalization of charge and stabilize the ionized group in the vapor phase. A second reason for such effect is due to volume or steric hindrance for solvation - the alkyl substituents being the impediment for the access of solvent water to the ionized groups (Kebarle, 1975). A different explanation for this effect was postulated by Kauzmann *et al.*, (1962) based on the observation of volume change accompanying the ionization of a series of normal carboxylic acids in water. This evidence indicated that the hydrocarbon substituents influence the structure of water in the neighbourhood of the ionizing group. The departure from the addivity of functional group principle arises from the interactions among the regions of water surrounding different parts of the solute. This explanation of the behaviour of alkyl substituents also gained support from the study of Lewis and Wolfenden (1973) on the hydration of aliphatic aldehydes.

2.3.2 Hydrophobic Nature of Organic Molecules

A molecule or a functional group is considered to be hydrophobic when it displays very little or no affinity for an aqueous environment. Hydrophobic compounds in general, are apolar in nature and are much less soluble in water than in organic solvents (Frank and Franks, 1968). When a hydrophobic solute is introduced into water, the water molecules tend to organize around the solute and imprison it in a hydrogen-bonded cage similar to clathrate hydrates (Desnoyers, 1982). A rearrangement of water networks takes place to accommodate the space-filling hydrophobic entity, without the necessity of breaking bonds (Stillinger, 1977). This process results in a reduction of the spatial, orientational and dynamic degrees of freedom of the neighbouring water molecules leading to a crystal-like state of water. This effect is known as "hydrophobic hydration". The structural changes in water by an apolar molecule or residue is reflected in the thermodynamic excess functions, both at infinite dilution and at finite concentration. The solution properties that are characteristic of hydrophobic hydration are negative TS^E, negative limiting excess partial molar volumes ($\bar{V}_2^E$), and positive excess partial molar heat capacities ($\bar{C}_{P_2}^E$). A negative $\bar{V}_2^E$ indicates a net shrinkage while a positive $\bar{C}_{P_2}^E$ implies that the "quasi-crystalline structures" produced by the addition of a hydrophobic solute are thermally more labile than pure water. For a homologous series both $\bar{V}_2^E$ and $\bar{C}_{P_2}^E$ are linear functions of the number of CH_2 groups in the solute molecule. Hydrophobic hydration is accompanied by a reduction in the diffusion rates of the structured water molecules (Franks, 1983).

When two apolar molecules are allowed to interact, they agglomerate and share a single cavity with a smaller surface area than the total attributable to two separated cavities, thus easing the entropic 'discomfort' created in the water (Stillinger, 1977). This tendency of non-polar compounds to adhere to each other in water is known as "hydrophobic interaction" or "hydrophobic bonding" and is indeed a partial reversal of the entropically unfavourable hydrophobic hydration (Tanford, 1973). This behaviour of apolar molecules might stem from the affinity of hydrophobic compounds for each other, from cohesive properties of water, or from a combination of both of these attributes (Wolfenden and Lewis, 1976).

The hydrophobicity of an apolar organic molecule can be increased by increasing the chain length. Wolfenden and Lewis (1976) reported an approximately five-fold increase in the value of the distribution coefficient ($K_{eq} = C_{nonpolar\ solvent}/C_{water}$) for each increment of one methylene group in going up a homologous series of normal alkanes. This effect of increasing chain length is a reflection of an enhanced tendency of the paraffin to be excluded by water and a strong influence of hydrophobic interactions on the distribution of apolar solutes between water and nonpolar solvents. The free energy of transfer is approximately a linear function of the number of carbon atom present and is insensitive to the nature of the non-polar solvent (Frnaks and Evans, 1945). In general, it was observed that the free energy of transfer corresponds to 3347-3766 J (water -> hydrocarbon) and 628 J (water -> vapor) for each increment of one methylene group in the homologous series of n-alkanes, n-1-alkenes, n-1-chloroalkanes, n-alkyl acetates, n-1-aminoalkanes and n-1-alcohols (Butler, 1937; McAuliffe, 1966; Hine and Mookerjee, 1975; Wolfenden and Lewis, 1976).

The meager solvent capacity of water for apolar solutes and the steady decrease of aqueous solubility in going up a homologous series are the most distinct features of aqueous solutions of nonpolar organic compounds (Butler, 1937). The poor aqueous solubility of apolar solutes was ascribed by Cabani and Gianni (1979) exclusively to entropic effects, probably related to the structural changes brought about by these solutes. The negative solution entropies observed in such solutions are in agreement with the above interpretation (Claussen and Polglase, 1952; Franks, 1973). It is expected that certain hydrophilic groups (OH, NH_2, COOH, etc.) will bestow appreciable solubility to hydrocarbons (Butler, 1937). However, Hertz and Radle (1973) did not observe marked difference in the state of hydration of the carbonyl proton in formic acid and that in the methyl group.

In an attempt to quantify hydrophobicity on a molecular basis Nemethy and Scheraga (1962b) presented a thermodynamic treatment based on the behaviour of aqueous hydrocarbon solutions. The thermodynamic parameters were derived from models developed for pure water (Nemethy and Scheraga, 1962a) using statistical thermodynamics. These parameters were developed to take into account the intermolecular forces, the restriction on internal bond rotation and changes in the water structure. Ben-Naim (1971) developed a more fundamental approach for estimating the strength of the hydrophobic interaction using statistical thermodynamics. In this approach the hydrophobic interaction was defined as the indirect part of the work associated with the process of bringing the two solute particles from infinity to a specified separation. It is hoped that this model will enable one to gain insight into the molecular origin of the phenomenon and relating it to particular structure of liquid water.

A different hypothesis of the hydrophobic interaction has been proposed by Friedman and Krishnan (1973). This approach incorporates in the interaction potential of two solute molecules a core repulsion ~~term~~ and an attraction term originating from an overlap of the two solute hydration spheres with subsequent partial relaxation of the hydration sphere to bulk water. This model lends itself to a comparison with experimentally determined thermodynamic quantities (Franks *et al.*, 1976; Clark *et al.*, 1977).

Interaction between the apolar side chain of amino acid residues in protein play a dominant role in structure and conformational stability of proteins (Kauzmann, 1959; Scheraga, 1961; Franks and England, 1975). Hydrophobic aggregation can range from molecular or residue pair interaction to micelle or bilayer membrane formation. The attractive component of the free energy of micellization arises entirely from hydrophobic effects (Tanford, 1974).

Hydrophobic interaction provides a significant contribution for the *in vivo* stability of biological macromolecules and for self-assembly of biological structures, such as membranes, multi-subunit enzyme systems and viruses (Franks, 1983).

2.4 Aqueous Solutions of Carbohydrates

The carbohydrates, in general, are defined as the polyhydroxy aldehydes, ketones, alcohols, acids, their simple derivatives, and their polymers that have polymeric linkages of the acetal type (Pigman and Horton, 1972). Sugars are polyhydroxy aldehydes and ketones that conform to the general formula $C_n(H_2O)_x$, where x equals n or n-1. They are classified according to two schemes: a chemical and a structure-constitution classification. According to chemical classification, sugars can either be reducing or non-reducing whereas the structures-constitution classification divides them into mono-, di-, oligo- and polysaccharides. The monosaccharides are further sub-classified based on number of carbon atoms (tetroses, pentoses, hexoses, etc.) and ring forms (pyranose and furanose). The oligo- and polysaccharides can either be homogeneous or heterogeneous (Shallenberger, 1982).

2.4.1 Crystal Structure and Hydrogen Bonding

Carbohydrates are polar molecules that cohere in the solid state by an extensive system of intermolecular hydrogen bonding. The hardness and high density of sugar crystals suggest that the packing arrangement is dictated mainly by the hydrogen bonding and van der Waals forces play a meager role in binding the molecules together. In the case of glucose, all the five available hydrogen atoms per molecule are involved in the formation of a complete system of strong hydrogen bonds (McDonald and Beevers, 1950, 1952; Ferrier, 1960, 1963; Chu and Jeffrey, 1968; Brown and Levy, 1979). Extensive intermolecular hydrogen bonding has also been reported in the crystal structure of α-D-glucose monohydrate (Killean *et al.*, 1962) and β-D-fructose (Kanters *et al.*, 1977; Takagi and Jeffrey, 1977). Jeffrey and Mitra (1983) described in detail the hydrogen-bonding patterns observed in pyranose and pyranoside. Based on the analysis of hydrogen-bond lengths by neutron or X-ray diffraction in the unsubstituted mono- and disaccharide crystals, Jeffrey and Lewis (1978) revealed that 70% of the hydrogen-bonds in these crystals are of the donor-acceptor type. The length of the hydrogen-bond from the anomeric hydroxyl is shorter than the mean value for the nonanomeric hydroxyls (Jeffery and Takagi, 1978). The hydroxyl groups attached to anomeric carbon atoms should be stronger than the average H-bond donor and weaker than the average H-bond acceptor (Tse and Newton, 1977).

According to Jeffrey (1973), intramolecular hydrogen bonds are rare in carbohydrate crystals. The geometrical arrangement of the hydroxyl groups on adjacent carbon atoms excludes the possibility of intramolecular H-bond formation. While the OH--O distance is appropriate, the OH--O angle which is less than 120° is unfavourable for intramolecuar H-bonding. This geometrical restriction also prevents the H-bond formation between the ring oxygen and a hydroxyl group in the same molecule. The disaccharides are the exceptions. The intramolecular hydrogen bonds between hydroxyls and oxygen of different monosaccharide units have been reported for sucrose (Brown and Levy, 1963; Hanson *et al*., 1973), β-cellobiose (Chu and Jeffrey, 1968), α-lactose monohydrate (Fries *et al*., 1971), methyl-β-D-maltoside (Chu and Jeffrey, 1967) and methyl-β-D-cellobioside (Ham and Williams, 1970). No intramolecular H-bonds have been reported in three trisaccharides viz., 1-kestose (Jeffrey and Park, 1972), raffinose pentahydrate (Berman, 1970) and planteose dihydrate (Rohrer, 1972). But such H-bonds have been reported in cellotetrose (Poppleton and Mathieson, 1968) and are often postulated in model structures of polysaccharides (Carlstrom, 1962). All polysaccharides have amorphous regions in the solid state where molecules or chain segments are in a jumbled or disorganized arrangement with intermolecular forces and intermolecular hydrogen bonding only partially satisfied because of the random spatial arrangement (Whistler, 1973).

2.4.2 Solvation of Carbohydrates

Carbohydrates are polar, hydrophilic, polyhydroxy molecules capable of interacting with solvent and with each other through hydrogen bonding. Such interactions are very sensitive to the spatial and orientational correlations between hydrogen bonding groups in the solvent and the solute (Franks, 1979; Franks and Pedley, 1983). The spacings and orientations of the polar group relative to the OH geometry in water determine to a large extent the ease of forming sugar-water hydrogen bond when a sugar molecule is introduced in the solvent water (Franks, 1983). The study by Dunfield and Whittington (1977) revealed a strong hydrogen bonding between the sugar hydroxyl and adjacent water molecules in the aqueous solutions. The detailed NMR and infrared studies of Casu and Reggiani (1966) also suggest extensive hydrogen bonding between glucose and DMSO, the hydrogen bond strength being different for the various OH groups on different carbon atoms. In an aqueous solution the hydration interaction competes with the hydrogen bonding between water molecules. It therefore seems reasonable to speculate that solute molecules which can interact with the solvent without major perturbations in the predominantly tetrahedral water structure are likely to interact preferentially. The hexose sugars in their pyranose forms constitute a group of molecules that are similar, both physically and chemically but differ in the location of hydration sites. The difference is reflected in the distribution of axial and equatorial OH groups on carbon atoms 1-4 (Franks, 1977). Solvation interactions are determined by the solvent structure compatibility. In aqueous sugar solutions such compatibility is associated with the equatorial OH group which will be more strongly hydrated than the axial group and therefore any hydration contribution to the anomeric equilibrium favours the β-anomer (Kabayama and Patterson, 1958; Tait *et al.*, 1972; Franks, 1979). The distances between equatorial OH groups on pairs of alternate carbon atoms (i.e., 1,3 and 2,4) in pyranose sugars are identical with the distance of the second peak in the water pair correlation function, implying that the equatorially substituted sugars can interact with water with a minimum of perturbation (Kabayama *et al.*, 1958). The interaction of equatorial OH groups with water leads to quite specific and long-lived hydration structure (Franks, 1979). The negative ΔH for mutarotation of sugars (D-xylose, cellobiose, D-glucose, lactose monohydrate, maltose monohydrate) reported by Kabayama *et al.* (1958) is also in agreement with the notion of greater hydration for equatorial hydroxyl groups than for axial groups (Kabayama and Patterson 1958). According to Bociek and Franks (1979), the steric compatibility is reflected in the lower and concentration independent activation energy observed for β-glucose.

In dilute solutions the solute-solute interactions are effectively screened by the hydration spheres that shield the solute molecules and closely resemble pure water (Franks *et al.*, 1972). However, with increase in concentration the hydrated solute molecules progressively draw close to each other and at a certain concentration (≃ 35-40% w/w for D-fructose, D-glucose and D-sucrose) the repartition of carbohydrates occurs indicating the beginning of prenucleation (Mathlouthi, 1981). In case of sucrose, a twisting of the glycosidic linkage, C_1-O-C_2, takes place as the solute molecules draw closer leading to the form of the molecule found in the crystal with two intramolecular hydrogen bonds (Brown and Levy, 1963; Hanson *et al.*, 1973).

The hydration interaction is a temperature dependent process and the average number of water molecules hydrogen bonded to sugar vary with the temperature of the solution. At lower temperatures, the influence of solvent structure compatibility is more pronounced and different sugars interact with the solvent in specific ways. However, at higher temperatures this characteristic behaviour is lost. Based on dielectric and nuclear magnetic relaxation studies, Tait *et al.*, (1972) suggested that at 80°C, glucose, galactose and ribose exist as monohydrates in solution.

The solute-solvent interactions in aqueous sugar solutions are known to induce a short range order of water molecules in the vicinity of sugars and a long range order in the bulk water. These interactions also contribute to the conformational equilibria that exist in aqueous solutions of carbohydrates (Mathlouthi, 1984). Numerous studies have been carried out on solute-solvent interactions in aqueous solutions of carbohydrates. Different techniques that have been employed in the study of the hydration behaviour of carbohydrates are NMR (Harvey *et al.*, 1976; Harvey and Symons, 1978; Bociek and Franks, 1979), nuclear magnetic relaxation (Suggett *et al.*, 1976), dielectric relaxation (Suggett and Clark, 1976), nuclear magnetic and dielectric relaxation (Tait *et al.*, 1972; Suggett, 1976), laser Raman spectroscopy (Mathlouthi *et al.*, 1980a, 1980b, 1980c), calorimetry (Franks *et al.*, 1973), pycnometry and dilatometry (Garrod and Herrington, 1970). The estimate of the hydration numbers (defined as the number of water molecules hydrogen bonded to the sugar) seems to vary with the technique of investigation. For example, the hydration number of glucose varies from 2.7 (Suggett and Clark, 1976) to 11 (Harvey *et al.*, 1976) and from 5 to 21 (Allen *et al.*, 1974) for sucrose. The hydration number reported for other sugars are 3.9±0.4 for mannose, 2.5±0.4 for ribose and 5.0±0.4 for maltose (Suggett, 1976). The hydration interaction has a pronounced influence on conformational and anomeric equilibria that exist in sugar solutions and will be highlighted in the next section on the conformations of carbohydrates in aqueous solution.

According to Whistler (1973), all polysaccharides have affinity for water and the amorphous region in the polysaccharide structure has numerous unsatisfied hydrogen bonding positions which can interact with water. When a soluble polysaccharide is introduced into water, the water molecules quickly penetrate the amorphous region and hydrates the available polymer sites. Segments of polysaccharide thus become fully solvated and move towards solution by kinetic action, splitting more interpolysaccharide bonds and forming polysaccharide-water bonds. The dissolution of all polysaccharides proceeds through an intermediate gel state where most of the polysaccharide chains are fully solvated and solubilized while a few segments are still attached to other polysaccharide chains which are not yet completely solvated. When the polysaccharide molecules are fully solubilized, they become completely surrounded by a layer of partially immobilized water molecules. Aqueous solubility of polysaccharides varies depending on the type of polysaccharide chain. Highly branched polysaccharides are very soluble in water while the linear homopolysaccharides are usually insoluble due to the fit of molecules and their preference for partial crystallization. The hydration behaviour of polysaccharides can be altered by chemical modification of the polysaccharide chains. The hydration can be improved by providing anionic groups or by placing substituents on the linear structure which reduce the fit of one polysaccharide to another.

2.4.3 Conformational and Anomeric Equilibria

In solid state the hexopyranoses can assume one of the two chair and six boat conformations (Reeves, 1951). The chair shape is thermodynamically the most stable conformation that the pyranoid ring can assume (Hassel and Ottar, 1947). However, the possibility of a boat conformation in some of the pyranoses have been reported (Reeves, 1954; Reeves and Blouin, 1957). The chair conformations of pyranose rings are generally observed in C1 and rarely in 1C (Reeves, 1950; Jeffrey, 1973). The furanose rings can occur in several variations of twist and envelope conformations (Jeffrey, 1973). In di-, oligo- and polysaccharides, the conformations of the pyranose or furanose monomer may be slightly distorted (Cox *et al.*, 1935; Reeves and Blouin, 1957).

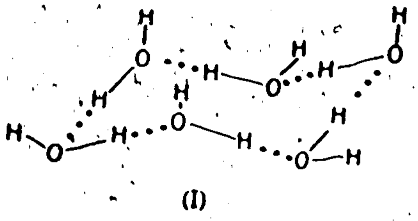
When a crystalline carbohydrate molecule is dissolved in water it may undergo one or more of the following stereochemical transformations (Franks, 1977):

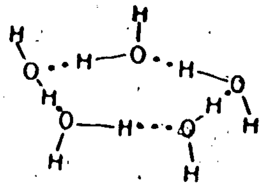
a. Simple mutarotation or anomerization, e.g., α-glucose ↔ β-glucose.

b. Conformational equilibria exhibited by the monosaccharides, e.g., C1 pyranose ↔ 1C pyranose, pyranose ↔ furanose.

c. Rotation about the glycosidic linkage exhibited by di- or oligosaccharides.

In aqueous sugar solutions the pyranoid ring may assume one of the two chair forms or the less stable flexible skew and boat forms; the furanoid ring may be in one of the envelope or twist forms. The chain form is known to be energetically more favourable than the skew and boat forms (Angyal, 1969). The majority of D-sugars in aqueous solution exist preponderantly in the C1 conformation (Reeves, 1951). According to Perlin (1966), the better fit of the pyranose ring into the components (I) of the tridymite structure of water partly accounts for the intrinsic stability of its structure in aqueous solution, although both (I) and (II) are the favoured forms of the polymerised structure of water (Minton, 1970).


(I)


(II)

Favoured structures of polymerised water

The conformation of the sugar which is most compatible (in terms of H-bond formation) with the tetrahedral arrangement of water molecules increasingly becomes the most favoured form as the temperature is lowered (Franks *et al.*, 1972). The equilibrium composition of an aqueous sugar solution depends on temperature and is governed by the intrinsic free energies of various anomers and conformers (Table 2.4). An approximate calculation of the free energies can be done by adding the values of all the non-bonded

Table 2.4 Predominant conformations and calculated interaction energies of D-aldopyranoses in aqueous solutions (Adapted from: Angyal, 1969).

Aldose	Conformations found by		Calc. Int. Energies (kJ/mol)	
	NMR[a]	Calculation[b]	C1	1C
α-D-Allose	C1	C1	16.32	22.38
β-D-Allose	C1	C1	12.34	25.31
α-D-Altrose	C1, 1C	C1, 1C	15.27	16.11
β-D-Altrose	C1	C1	14.02	22.38
α-D-Arabinose	1C	1C	13.39	8.58
β-D-Arabinose		C1, 1C	12.13	10.04
α-D-Galactose	C1	C1	11.92	26.36
β-D-Galactose	C1	C1	10.46	32.43
α-D-Glucose	C1	C1	10.04	27.41
β-D-Glucose	C1	C1	8.58	33.47
α-D-Gulose	C1	C1	16.74	19.87
β-D-Gulose	C1	C1	12.76	22.8
α-D-Iodose	C1, 1C	C1, 1C	18.2	16.11
β-D-Iodose		C1	16.95	22.38
α-D-Lyxose	C1, 1C	C1, 1C	8.58	10.88
β-D-Lyxose	C1	C1	10.46	14.85
α-D-Mannose	C1	C1	10.46	23.22
β-D-Mannose	C1	C1	12.34	32.01
α-D-Ribose	C1, 1C	C1, 1C	14.43	14.85
β-D-Ribose	C1, 1C	C1, 1C	10.46	12.97
α-D-Talose	C1	C1	14.85	24.69
β-D-Talose		C1	16.74	33.47
α-D-Xylose	C1	C1	8.16	15.06
β-D-Xylose	C1	C1	6.69	16.32

[a] From: Lemieux and Stevens (1966), Rudrum and Shaw (1965), Angyal and Pickles (1972).

[b] From: Angyal, 1968.

interactions and the anomeric effect (Angyal, 1968). The amomeric effect was explained by Edward (1955) in terms of the repulsive interaction between the equatorial carbon-oxygen dipole and the dipole formed as the resultant of the two carbon-oxygen dipoles in the pyranose ring. The non-bonded interactions are determined by the number of axial groups, adjacent equatorial groups, 1,3-diaxial interactions, and the anomeric effect. Although various forms of the same molecule coexist in equilibrium, usually one conformation predominates which determines the physical properties of the solution. But the chemical reactions may proceed through another conformation. The introduction of a substituent group or the formation of a glycosidic bond which changes the anomeric effect may alter the predominant conformation (Angyal, 1969).

Most sugars exist and react in the pyranose form. The conformations of the aldopyranoses have been investigated by NMR spectroscopy (Rudrum and Shaw, 1965; Lemieux and Stevens, 1966; Angyal and Pickles, 1972). The chair form favoured by various aldopyranoses appears to be controlled by the disposition of the bulkiest substituent, the hydroxymethyl group, which tends to assume the equatorial position. Accordingly, all the β-anomers exist preponderantly in C1 conformation, as the alternative, 1C conformation appears to be highly destabilized by the syn-diaxial interaction between the anomeric hydroxyl and axial hydroxymethyl group. Although this interaction is not found in 1C conformation of the α-anomers, most of the α-anomers adopt the C1 conformation, presumably because of a favourable anomeric effect. The conformations of the aldopentopyranoses, which do not have hydroxyl methyl group at C-5, are determined by the disposition of the hydroxyl groups (Angyal, 1969).

The α:β ratio at equilibrium varies from sugar to sugar. Angyal (1968) used the free energy values of pyranoses in Table 2.4 to predict their α:β ratio in aqueous solutions. The predicted and the experimentally determined ratios together with the calculated energies of two anomeric chair forms of each aldose are listed in Table 2.5. The agreement between the calculated and the experimentally determined values was found satisfactory in view of all the approximations involved in the calculation. In case of furanoses the anomer in which the OH group on C-1 and C-2 are *trans* predominates over the *cis*-1,2 anomer, although the α:β ratio varies from sugar to sugar as can be seen in Table 2.6 (Angyal, 1969).

The furanose:pyranose ratio of a sugar at equilibrium is determined by the difference between the free energies of the two ring forms. Generally the five membered rings are less stable than the six-membered ones. Glucose, mannose and xylose have very little furanose forms in equilibrium mixture since the pyranose forms have low free energies. But in some cases considerable amount of furanoses have been reported in equilibrium. One such sugar is 3-deoxy-glucose

Table 2.5 Conformational free energies and the equilibrium proportions of the α-anomer in aqueous solutions of D-aldopyranoses (Adapted from: Angyal, 1969).

Aldose	Free energy (kJ/mol)		% α-Pyranose[a]	
	α-form	β-form	Calculated[b]	Found by NMR[c]
Allose	16.11	12.34	18	20
Altrose	14.02	14.02	50	44
Arabinose	8.16	9.2	60	63
Galactose	11.92	10.46	36	27
Glucose	10.04	8.58	36	36
Gulose	16.11	12.76	21	22
Iodose	15.27	16.74	64	46
Lyxose	7.74	10.04	72	71
Mannose	10.46	12.34	68	67
Ribose	12.97	9.62	20.5	26
Talose	14.85	16.74	68	58
Xylose	7.95	6.69	37	33

[a] Percentage of the two pyranose forms only

[b] From: Angyal, 1968.

[c] From: Lemieux and Stevens (1966), Rudrum and Shaw (1965), Angyal and Pickles (1972).

Table 2.6 Equilibrium proportions (%) of the pyranose and furanose forms of aldoses in aqueous solution at 40°C[a] (Adapted from: Angyal, 1969).

Aldose	Pyranose		Furanose	
	α	β	α	β
D-Allose	18	70	5	7
D-Altrose	27	40	20	13
D-Arabinose	63	34	–	–
D-Iodose	31	37	16	16
D-Ribose	20	56	6	18
D-Talose	40	29	20	11
D-Glycero-D-guloheptose	10	88	–	–
3-Deoxy-D-arabinohexose	47.5	52.5	0	0
3-Deoxy-D-ribohexose	26	46	6	22

[a] From: Lemieux and Stevens (1966), Angyal and Pickles (1972).

which in aqueous solution has 28% furanose form in equilibrium (Angyal and Pickles, 1972). The most unfavourable interaction in the furanose ring is the one between O-3 and the side-chain on C-4, when these are in *Cis* to each other. Sugars (with the only exception of iodose) which have this interaction do not contain detectable amount of furanose in the equilibrium mixture (Angyal, 1969).

The conformations of di-, oligo- and polysaccharides are also strongly influenced by the solvent water (Franks, 1977, 1979; Rees and Thom, 1977; Whistler, 1973). In case of a disaccharide the conformation of the two sugar units relative to one another is defined in terms of two dihedral angles ϕ and ψ. The rotation about the glycosidic linkage adds two more degrees of freedom that determine the solvent compatibility of the sugar (Franks, 1977, 1979). In aqueous solutions of di- and oligosaccharides the conformation of the glycosidic linkage in the crystalline state is often but not always preferred (Rees and Thom, 1977). According to Bock and Lemieux (1982), sucrose shows a strong conformational preference about the glycosidic linkage in solution that is similar to that in the crystalline state. As suggested by Rees and Thom (1977), water favours 'folded' conformations for methyl β-maltoside, α,α- trehalose and cyclohexa-amylose in which the sugar rings shield C-H bonds and expose OH groups to water so as to assume a form that is more compatible with the water structure. The conformation of polysaccharides varies depending upon their chemical structure. Polysaccharides in solution may adopt secondary structures such as helices, tertiary structures formed by the union of double or triple helices and even quaternary structures from the cross linking of tertiary structures (Whistler, 1973).

An unified theoretical or semi-theoretical treatment of conformational equilibria that exist in carbohydrate solution is difficult because of the very small energy differences between anomers, conformers and epimers (Franks, 1979).

2.4.4 Thermodynamic Studies

The macroscopic thermodynamic properties of the polyfunctional carbohydrate solutions are determined by weak intermolecular forces which are more difficult to deal with both experimentally and theoretically than strong interactions. Literature relating to the thermodynamic study of carbohydrate solutions is rather sparse. The majority of the studies that have been carried out are on colligative properties of sugar solutions and measurement of partial molar quantities. A few thermal studies of sugar solutions are also on record.

The earliest thermal studies have been the measurements of the heats of solution of anhydrous α-glucose and anhydrous sucrose (clifford *et al.*, 1930), the heats of combustion and free energies of α-D-glucose and α-D-glucose hydrate at 25°C (Huffman and Fox, 1938), the calorimetric investigation of the inversion of sucrose Sturtevant (1937) an the heat of mutarotation of D-glucose (Sturtevant, 1941; Rowe and Parks, 1946). Vallender and Perman (1931) reported the heat of dilution of aqueous solution of cane sugar. The specific heats of glucose glass and liquids have been measured by Parks *et al.* (1928) and Nelson and Newton (1941). The heats of solution of pure α-D-glucose crystals at 25°C have been reported by Rowe and Parks (1946). The heats of mutarotation of D-glucose, D-xylose, lactose, maltose and cellobiose have also been measured calorimetrically by Kabayama *et al.* (1958). Taylor and Rowlinson (1955) determined the heats of solution, heats of dilution at 25°C and vapor pressures from 25-65°C of aqueous glucose solutions. Other thermal investigations reported are heat of mixing of aqueous solutions of glucose and sucrose (Cassel and Wood, 1974), excess enthalpies of ternary mixture of water, sucrose and mannitol at 25°C (Stroth and Schönert, 1977), heat of mixing of aqueous solutions of mannitol (Tasker and Wood, 1982a,b); freezing temperatures of aqueous solution of sugar alcohols (Spitzer, *et al.*, 1984) and sugars (CRC, 1983-84).

The partial molar volumes for a number of mono-, di-, oligo- (tri-, tetra-, penta-, hexa-, hepta-), and polysaccharides and their derivatives in water at 25°C have been reported by Shahidi *et al.* (1976) who showed that these values can be calculated from van der Waals volumes of the molecules if shrinkage due to hydrogen-bonding is taken into account. Data on apparent and partial molal volumes and compressibilities of mono-, di-, and trisaccharides, sugar alcohols and related polyhydroxy compounds are also available (Garrod and Herrington, 1970; Franks *et al.*, 1972; Høiland and Holvik, 1978). Stroth and Schönert (1977) reported the excess volumes of binary mixtures of water + mannitol and ternary mixtures of water, sucrose and mannitol at 25°C.

The isopiestic method has been used to measure the vapor pressure and osmotic coefficients of some sugar solutions. Scatchard *et al.* (1938) used the isopiestic method to measure the osmotic coefficient of aqueous sucrose solutions. Dunning *et al.* (1951) measured the vapor pressure of pure sucrose solution at various temperatures (65-95°C). Stokes and Robinson (1966) reported osmotic coefficients of aqueous glucose and sucrose solutions at 25°C from isopiestic measurements. The activity coefficients in aqueous solutions of sucrose, mannitol, xylose and maltose have also been measured by the isopiestic vapor pressure method (Robinson and Stokes, 1961; Uedaira and Uedaira, 1969). Robinson *et al.* (1970) used isopiestic method to determine the activity coefficients of the solutes in the ternary mixtures of water, sucrose and sodium chloride. Audu *et al.* (1978) used a bubbling method while Ruegg and Blanc (1981) employed an electronic hygrometer to determine the activity of water in aqueous solutions of a number of sugars, their mixtures and honey. Extensive freezing point data are available (CRC, 1983-84) which can be used to compute directly the activity of water in sugar solutions.

The phase equilibria studies on record are limited to ternary diagrams at 30°C for water-sugar-inorganic salts and water-sugar-sugar systems (Kelly, 1954a, b, c, d, e) binary phase diagram of D-glucose-water between -30 and +62°C (Young, 1957) and of D-fructose-water system between -30 and +40°C (Young *et al.*, 1952).

The study of the thermodynamic behaviour of aqueous polysaccharide solutions is still in its infancy. Reid (1979) reviewed the thermodynamics of dilute and concentrated polysaccharide solutions, ion-polysaccharide interactions, gelation and sorption. Most of the solution studies are limited to anionic polysaccharides, perhaps because of the enhanced solubility of such charged polymers.

It is evident that limited progress has been made in the thermodynamic study of aqueous carbohydrate solutions in spite of the fact that the interactions of carbohydrate molecules with water, with each other, with ions and other chemical compounds lie at the basis of many natural phenomena which are utilized, in somewhat crude manner, in food processing and other industries (Franks, 1979). It is hoped that the future will see an increased interest in this area with the newly developed and refined experimental methods which will make detailed studies possible.

2.5 Modelling of Complex Aqueous Solutions

The primary objective of modelling liquid mixtures is to develop an efficient mathematical tool for prediction of activity coefficients of components in such mixtures. Although considerable advances have been made in the thermodynamic treatment of liquid mixtures, a general unified approach is still a distant goal of solution theory. Most of the theoretical work in the past has been on liquid solutions of nonpolar spherical molecules with equivalent size and shape. Prausnitz *et al.* (1986) reviewed the solution theories that are useful for and restricted to particular types of mixtures. Many equations relating the excess Gibbs energy (G^E) to composition have been proposed. Some of the earlier expressions for G^E that have been in use are Margules (two-, three- and four-suffix), van Laar, Redlich-Kister, Scatchard-Hildebrand and Flory-Huggins models. The introduction of the local composition concept by Wilson (1964) led to the development of the more powerful and flexible expressions such as Wilson, NRTL and UNIQUAC (Fredenslund and Rasmussen, 1985). All these expressions have a strong empirical flavor and contain temperature dependent adjustable parameters (Reid *et al.*, 1977). For moderately nonideal mixtures, all models for G^E are well suited and give good results. But for strongly nonideal binary mixtures, the recent models such as Wilson, NRTL and UNIQUAC are more reliable than the older ones. These three equations can also be extended to multicomponent systems. A more detailed discussion on the G^E models mentioned above is offered by Prausnitz *et al.* (1986). The pioneering work of Pierotti *et al.* (1959) initiated the group-contribution theories. The two models that calculate activity coefficients from structural group contributions are ASOG (Derr and Deal, 1969) and UNIFAC (Fredenslund *et al.*, 1975). These two methods are similar in principle but differ in detail. The UNIFAC model has become very popular in recent years and is being widely applied for phase-equilibrium and other calculations (Rasmussen, 1983).

The treatment of aqueous solutions encountered in food systems is, however, largely unexplored. A few attempts have been made to develop equations for the prediction of water activity in isolated cases. Money and Born (1951) proposed an empirical equation for sugar solutions relating the equilibrium humidity value with molar concentration. An empirical equation, relating vapor pressure to temperature, was also derived for sucrose solution by Dunning *et al.* (1951). Norrish (1966) proposed an eqation for the activity coefficient of water as a function of concentration in confectionery syrups. Apart from the practical use of predicting equilibrium relative humidity at a given concentration, this equation yields significant information about the nature of solute-solvent interaction. Ross (1975) used the Gibbs-Duhem equation to derive an expression for the activity of water at constant temperature and pressure. According to this equation the water activity of a complex solution is given by the product of the water activity values of the aqueous solutions of each component, when measured at the same molality as in the complex solution. A refinement of Ross's equation was proposed by Ferro Fontan and Chirife (1981) for predicting the water activity of nonelectrolyte mixtures. It is thus apparent that there is, as yet, no satisfactory model that can predict the activity coefficients of all the components of a complex aqueous solution.

It was therefore felt necessary to look for a thermodynamic model which will be most suitable to the study of complex aqueous solutions encountered in food systems. The adapted model should possess the ability to predict the activity coefficients of each of the components and the behaviour of aqueous systems for which little or no experimental data are available. The present study is an attempt to achieve these objectives.

3. SOLUTION MODELLING WITH UNIFAC-FV MODEL

The goal of solution modelling is to predict the thermodynamic properties of mixtures in terms of intermolecular forces and fundamental liquid structure. It is desirable to estimate the equilibrium properties of mixture from pure component properties. In essence, the primary objective of solution modelling is to estimate the numerical values of the activity coefficients of components in a mixture (Prausnitz *et al.* 1986) using thermodynamically consistent correlations. The development of efficient mathematical models for liquid mixtures with good predictive power has been the subject of numerous studies. Many models have been proposed, most of which follow phenomenological, semiempirical considerations and entail approximations (Hu *et al.*, 1984). In practice one has to introduce parameters in a model, since theory in its present state only gives some indications of the form of a fundamental function and suggests where to introduce parameters and their physical meaning, if any (Renon, 1978).

3.1 Thermodynamic Framework

3.1.1 Chemical Potential and Fugacity

For an open system the Gibbs free energy (G) is a function of temperature (T), pressure (P) and the composition of the system $(n_1,\ldots,n_k)$, i.e.

$$G = G(T, P, n_1, \ldots, n_k) \qquad [3.1]$$

The total differential of the Gibbs free energy is:

$$dG = \left[\frac{\partial G}{\partial T}\right]_{P,n_i} dT + \left[\frac{\partial G}{\partial P}\right]_{T,n_i} dP + \left[\frac{\partial G}{\partial n_1}\right]_{T,P,n_{j\neq 1}} dn_1 + \ldots$$

$$\ldots + \left[\frac{\partial G}{\partial n_k}\right]_{T,P,n_{j\neq k}} dn_k \qquad [3.2]$$

Since,

$$\left[\frac{\partial G}{\partial T}\right]_{P,n_i} = -S = -\text{Entropy} \quad \text{and} \quad \left[\frac{\partial G}{\partial P}\right]_{T,n_i} = V = \text{Volume} \qquad [3.3]$$

we get

$$dG = -SdT + VdP + \sum_{i=1}^{k} \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_{j\neq i}} dn_i \qquad [3.4]$$

The chemical potential (μ_i) for a component i is defined as

$$\mu_i \equiv \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_{j\neq i}} \qquad [3.5]$$

Then Eq. (3.4) becomes

$$dG = -SdT + VdP + \sum_{i=1}^{k} \mu_i dn_i \qquad [3.6]$$

From the definition of internal energy (U), enthalpy (H), and Helmholtz energy (A) it can be shown that :

$$dU = TdS - PdV + \sum_{i=1}^{k} \mu_i dn_i \qquad [3.7]$$

$$dH = TdS + VdP + \sum_{i=1}^{k} \mu_i dn_i \qquad [3.8]$$

$$dA = -SdT - PdV + \sum_{i=1}^{k} \mu_i dn_i \qquad [3.9]$$

Therefore, the definition of μ_i and equations (3.7), (3.8) and (3.9) lead to

$$\mu_i = \left[\frac{\partial U}{\partial n_i}\right]_{S,V,n_{j\neq i}} = \left[\frac{\partial H}{\partial n_i}\right]_{S,P,n_{j\neq i}} = \left[\frac{\partial A}{\partial n_i}\right]_{T,P,n_{j\neq i}} \qquad [3.10]$$

Since the independent variables T and P for the Gibbs free energy are also arbitrarily chosen as the independent variables in defining partial molar quantities, the chemical potential (μ_i), is the partial molar Gibbs energy ($\bar{g}_i$) but not the partial molar internal energy, enthalpy or Helmholtz energy (Prausnitz *et al.*, 1986).

From Euler's theorem we get

$$G = \sum_{i=1}^{k} n_i \bar{g}_i \qquad [3.11]$$

where, $\bar{g}_i$ is the partial molar Gibbs free energy of component i. Differentiation of Eq. (3.11) gives

$$dG = \sum_{i=1}^{k} \bar{g}_i dn_i + n_i d\bar{g}_i \qquad [3.12]$$

$$\text{or, } dG = \sum_{i=1}^{k} \mu_i dn_i + n_i d\mu_i \qquad [3.13]$$

Equations (3.6) and (3.13) when combined yield the general Gibbs-Duhem equation:

$$SdT - VdP + \sum_{i=1}^{k} n_i d\mu_i = 0 \qquad [3.14]$$

For a pure substance i, equation (3.14) relates the chemical potential to the temperature and pressure by the differential equation

$$d\mu_i = -s_i dT + v_i dP \qquad [3.15]$$

where, s_i is the molar entropy and v_i is the molar volume of component i. Integrating Eq. (3.15) and solving for μ_i at some temperature T and pressure P, we get

$$\mu_i(T,P) = \mu_i(T_{ref},P_{ref}) - \int_{T_{ref}}^{T} s_i dT + \int_{P_{ref}}^{P} v_i dP \qquad [3.16]$$

The subscript 'ref' refers to some arbitrary reference state. The two integrals on the right side of Eq. (3.16) can be evaluated from the thermal and volumetric data over the temperature range T_{ref} to T and the pressure range P_{ref} to P. However, the chemical potential of the system at the reference state $\mu_i(T_{ref}, P_{ref})$ is not known. Therefore the chemical potential at a state of interest $\mu_i(T, P)$ can only be expressed relative to its value at the arbitrary reference state designated by T_{ref} and P_{ref}. The need for a reference state arises from our inability to compute an absolute value of the chemical potential which complicates the use of thermodynamics in practical applications (Prausnitz *et al.* 1986).

The chemical potential is an abstract quantity and it is difficult to relate it to the physical world unless expressed in terms of some auxiliary function which might be more easily identifed with the physical reality. The concept of fugacity provides such an auxiliary function (Prausnitz *et al.*, 1986). For an ideal gas at constant temperature, Eq. (3.15) can be written as

$$\left[\frac{\partial \mu_i}{\partial P}\right] = v_i \qquad [3.17]$$

Substituting the ideal-gas equation (v_i = RT/P) and integrating at constant temperature we get,

$$\mu_i - \mu_i^o = RT\ln\frac{P}{P^o} \qquad [3.18]$$

Equation (3.18) is valid only for pure, ideal gases. To generalize it for any system, whether solid, liquid, or gas, pure or mixed, ideal or nonideal, Lewis introduced a function f, called the fugacity (or escaping tendency). For a component undergoing an isothermal change in any system Eq. (3.18) takes the form

$$\mu_i - \mu_i^\circ = RT\ln\frac{f}{f_i^\circ} \qquad [3.19]$$

where both μ_i° and f_i° refers to the standard state and when one is chosen the other is automatically fixed. Fugacity is a "corrected pressure" (these corrections are due to nonidealities) which for a pure, ideal gas is equal to the pressure (P) and for a component i in a mixture of ideal gases is equal to the partial pressure (y_iP) of that component. Since all systems, pure or mixed, approach the limiting ideal-gas behaviour at very low pressure, the definition of fugacity is completed by the limit

$$\frac{f_i}{y_iP} \rightarrow 1 \text{ as } P \rightarrow 0 \qquad [3.20]$$

where y_i is the mole fraction of the component i. As stated by Prausnitz *et al.* (1986), the relation between chemical potential (μ_i) and fugacity (f_i) is a conceptual instrument in performing the translation from thermodynamic to physical variables. The transition from pure thermodynamics to the theory of intermolecular forces is possible through the notion of fugacity. Both the chemical potential and the fugacity provide the fundamental equation of phase equilibria. For two phases α and β at equilibrium we have

$$\mu_i^\alpha = \mu_i^\beta \qquad [3.21]$$

$$f_i^\alpha = f_i^\beta \qquad [3.22]$$

Equations (3.21) and (3.22) are equivalent and from a strictly thermodynamic standpoint, one is not preferable to the other. But Eq. (3.22) is preferred in cases where one wishes to apply thermodynamics to physical problems.

3.1.2 Activity and Activity Coefficient

The activity (a_i) of a component i is defined as the ratio of the fugacity of i at some temperature (T), pressure (P) and composition (x) to the fugacity of i in the standard state, a state which is at the same temperature as that of the mixture and at some arbitrary condition of pressure (P°) and composition (x°):

$$a_i(T,P,x) = \frac{f_i\{T,P,x\}}{f_i^\circ\{T,P^\circ,x^\circ\}} \qquad [3.23]$$

As can be seen in Eq. (3.23) the activity of a substance in its standard state is unity, $a^\circ = 1$. From Eq. (3.19) we get,

$$\mu_i = \mu_i^\circ + RT\ln\frac{f_i}{f_i^\circ} \qquad [3.24]$$

$$\text{or, } \mu_i = \mu_i^\circ + RT\ln a_i \qquad [3.25]$$

$$\text{or, } a_i = \exp\left[\frac{\mu_i - \mu_i^\circ}{RT}\right] \qquad [3.26]$$

Equation (3.26) indicates that the activity provides a measure of the differenece between the chemical potential of the substance at the state of interest and that at its standard state. The relative fugacity or the activity therefore gives an indication of how 'active' a substance is relative to its standard state (Prausnitz *et al.*, 1986).

The activity coefficient (γ_i) of a component i is defined as the ratio of the activity (a_i) of i to some convenient measure of its concentration which is usually the mole fraction (x_i):

$$\gamma_i = \frac{a_i}{x_i} \qquad [3.27]$$

$$\therefore \; a_i = x_i \gamma_i \qquad [3.28]$$

when the composition is expressed in a mole fraction, the activity coefficient is sometimes referred to as the rational activity coefficient and when expressed in molality, the activity coefficient is called the practical activity coefficient (Klotz and Rosenberg, 1974). The numerical value of the activity coefficient depends both on the standard state and on the units of expressing concentration (Hougen *et al.* 1954).

3.1.3 Solutions: Ideal Behaviour and Nonideality

A solution is a homogeneous one-phase system, solid, liquid or gaseous, containing more than one component dispersed on a molecular scale. In dilute solutions the component present in the largest amount is ordinarily referred to as the solvent, while those components, one or more, present in relatively small amounts are called solutes. But for thermodynamic treatment of a solution it is immaterial to define components as solute and solvent.

It follows from Eq. (3.28) that the fugacity of any component i in a liquid solution is related to its mole fraction x_i by an equation of the form:

$$f_i^L = \gamma_i x_i f_i^\circ \qquad [3.29]$$

where γ_i is the activity coefficient of i and f_i° is the fugacity of i at some arbitrary condition of temperature (T°), pressure (P°) and composition (x°) known as standard state (Prausnitz, 1986).

An ideal solution is one in which all intermolecular forces and the molecular volume of each species are the same, and for a range of conditions the activity coefficient γ_i of any component i in Eq. (3.29) is exactly equal to unity. Since the activity coefficient and the standard state fugacity are intimately related, the definition of solution ideality ($\gamma_i = 1$) is complete when the choice of standard state is clearly indicated. Two choices of standard states are in use, one leads to an ideal solution in the sense Raoult's law while the other leads to an ideal solution in the sense of Henry's Law (Prausnitz *et al*. 1986).

In an ideal solution the fugacity of every component is proportional to some suitable measure of its concentration (usually the mole fraction). At constant temperature (T) and pressure (P), the fugacity of any component i in an ideal solution is given by

$$f_i^L = K_i x_i \qquad [3.30]$$

where K_i is a proportionality constant dependent on temperature and pressure but independent of x_i. If f_i^o in Eq. (3.28) is replaced by K_i then $\gamma_i = 1$, and we get

$$f_i^L = f_i^o x_i \qquad [3.31]$$

If Eq. (3.31) holds for the entire range of concentration ($x_i = 0$ to $x_i = 1$), the solution is said to be ideal in the sense of Raoult's Law. It is apparent from the boundary condition at $x_i = 1$ that the proportionality constant K_i for such a solution is equal to the fugacity of the pure liquid i at the solution temperature. If the fugacities in Eq. (3.31) are set equal to the partial pressure of the component i we obtain the ideal solution law known as Raoult's Law:

$$P_i = P_i^s x_i \qquad [3.32]$$

where P_i and P_i^s are respectively the partial and saturation pressure of component i at the solution temperature.

In an infinitely dilute solution ($x_i \simeq 0$) the proportionality constant K_i is not equal to the fugacity of pure liquid i and if Eq. (3.30) holds, the solution is said to be ideal in the sense of Henry's Law which states that

$$P_i = H_i x_i \qquad [3.33]$$

where P_i and H_i are respectively the partial pressure and Henry's constant for the component i at the temperature of the solution.

The strict definition of an ideal solution requires that the solution obeys the ideal law ($f_i^L = K_i x_i$) and that the formation of such a solution from pure components occurs without evolution or absorption of heat and without change of volume. The ideal solution laws such as Raoult's and Henry's are inherently limited to mixtures of interchangeable components or to sufficiently dilute solutions (Flory, 1970) and are experimentally observed to be approached by liquid solutions as the components resemble one another more and more closely (Levine, 1978). Mixtures of chemically stable nonelectrolytes in the limit of very large dilution behave as ideal dilute solutions (Prausnitz *et al.*, 1986).

Mixtures of real fluids exhibit nonideal behaviour. This departure from ideality results from different size and shape of the constituent molecules and from the interaction between unlike molecules. The measure of the degree of departure is given by the activity coefficient of the components. The deviation from ideality can be described most conveniently by the use of excess functions to represent the thermodynamic properties of the mixtures of real fluids (Friedman, 1960).

3.1.4 Standard States and Normalization of Activity Coefficients

A. Choice of Standard State

A judicious selection of standard state is necessary for successful application of thermodynamics to real systems (Prausnitz *et al.* 1986). The choice is arbitrary and is dictated by convenience. The temperature of the standard state is not a fixed reference value and is the same as that of the system under study. The pressure and the concentration of a component in the standard state are conveniently chosen such that the activity coefficient γ_i assumes values close to unity. For certain systems, the standard state of a component cannot be attained experimentally and therefore represents a hypothetical state. For the same component, different standard states may be selected for use in different systems (Hougen *et al.* 1954).

Experience in the past has proved the convenience of certain choices of standard states which have generally been adopted and are in common use (Hougen *et al.* 1954 and Klotz and Rosenberg, 1974).

Gases.

Two choices generally used are:

1. The pure component gas in its ideal state, and 1 atm pressure i.e., at system temperature the gas has a fugacity of 1 atm.

$$\therefore \quad a = \frac{f}{f^{o}} = \frac{f}{1} = |f| \qquad [3.34]$$

Since for an ideal gas fugacity is numerically equal to pressure, we get

$$a = |f| = P \qquad [3.35]$$

and in mixtures of gases showing ideal-gas behavior the activity of each component is numerically equal to its partial pressure.

2. The pure component gas at the temperature and pressure of the system. In this case, the activity of each component becomes equal to its mole fraction in ideal solutions.

Liquids and Solids

(i) Pure Substances

a. Pure liquid or solid at a pressure of 1 atm and at system temperature. This standard state reduces to a hypothetical one when the vapor pressure of pure component exceeds 1 atm. The activity of a pure solid or pure liquid becomes unity at a pressure of 1 atm. However, the assumption of unit activity for pure solid may not be valid at times since its activity may be greatly altered by small impurities, by lack of equilibrium in the crystal structure and by crystal size (Hougen *et al.* 1954).

b. For liquids the standard state may also be taken as pure liquid at the temperature and pressure of the system. This state becomes hypothetical at temperatures above the critical or saturation temperature of the pure liquid.

(ii) <u>Solutions</u>

a. Pure component at the temperature and pressure of the solution

$$f_{i(\mathrm{std.\ state})} = f^{\circ}_{i(\mathrm{at}\ x_i = 1)} \qquad [3.36]$$

$$a_{i(\mathrm{std.\ state})} = a^{\circ}_{i} = \frac{f^{\circ}_{i}}{f^{\circ}_{i}} = 1 \qquad [3.37]$$

The activity of a component in any solution of finite concentration must be less than unity and is equal to its mole fraction in an ideal solution (i.e., $\gamma_i = 1$). In a liquid solution the standard state of component may become hypothetical if the pure component is not liquid at the temperature and pressure of the solution.

b. For components of limited solubility, it is desirable to choose the standard state in such a way that the activity of the component will reduce to its mole fraction in very dilute solution where Henry's Law is applicable. Thus,

$$\frac{a_i}{x_i} \rightarrow 1 \text{ as } x_i \rightarrow 0 \qquad [3.38]$$

This standard state is not the state of infinite dilution but a hypothetical liquid state which is defined by reference to the behaviour of the component at infinite dilution (Hougen *et al.* 1954).

When concentration is expressed in molality scale a standard state may be chosen such that the activity of a component approaches its molality in the limit of infinite dilution, i.e.,

$$\frac{a_i}{m_i} \rightarrow 1 \text{ as } m_i \rightarrow 0 \qquad [3.39]$$

This standard state is called "hypothetical one-molal solution" and will have the properties that a one-molal solution would have if it obeyed the limiting Henry's Law. A component in this standard state has a fugacity that a one-molal solution would have if it obeyed the limiting law at the temperature and pressure of the system (Klotz and Rosenberg, 1974).

B. Symmetric and Unsymmetric Conventions

If follows from the discussion in the preceeding sections (3.1.2 and 3.1.3) that for an ideal solution

$$a_i = x_i \quad , \qquad [3.40]$$

$$\text{or, } \gamma_i = 1 \qquad [3.41]$$

Since a solution can be ideal either in the sense of Raoult's law or in the sense of Henry's Law, the activity coefficients may be normalized (i.e., become unity) in two different ways leading to symmetric and unsymmetric conventions of normalization (Prausnitz *et al.* 1986).

(i) Symmetric Convention of Normalization

If the activity coefficients are defined with reference to an ideal solution in the sense of Raoult's Law, we get

$$\gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1 \qquad [3.42]$$

This normalization hold for both solute and solvent and is easily extended to multicomponent solutions.

(ii) Unsymmetric Convention of Normalization

If the activity coefficients are defined with reference to an ideal dilute solution in the sense of Henry's Law, we get

$$\gamma_1 \rightarrow 1 \text{ as } x_1 \rightarrow 1 \text{ (solvent)} \qquad [3.43]$$

$$\gamma_2^* \rightarrow 1 \text{ as } x_2 \rightarrow 0 \text{ (solute)} \qquad [3.44]$$

The asterisk (*) in γ_2^* is used to distinguish it form symmetrically normalized activity coefficients and in this case normalization is not same for solute and solvent. The extension of unsymmetric normalization to multicomponent solutions is not simple and needs more care (Prausnitz *et al*. 1986).

Relationship Between the Two Conventions

In a binary system γ_2 and γ_2^* are defined as

$$\gamma_2 = \frac{f_2}{x_2 f_{pure\ 2}} \qquad [3.45]$$

$$\gamma_2^* = \frac{f_2}{x_2 H_{2,1}} \qquad [3.46]$$

$$\therefore \quad \frac{\gamma_2}{\gamma_2^*} = \frac{H_{2,1}}{f_{pure\ 2}} \qquad [3.47]$$

Since, $\lim_{x_2 \to 0} \gamma_2^* = 1$ [3.48]

$$\therefore \quad \lim_{x_2 \to 0} \gamma_2 = \frac{H_{2,1}}{f_{pure\ 2}} \qquad [3.49]$$

$$\therefore \quad \frac{\gamma_2}{\gamma_2^*} = \lim_{x_2 \to 0} \gamma_2 \qquad [3.50]$$

By similar argument, it can be shown that

$$\frac{\gamma_2}{\gamma_2^*} = \lim_{x_2 \to 1} \gamma_2^* \qquad [3.51]$$

Equations (3.50) and (3.51) relates the two activity coefficients, one normalized by symmetric convention and the other by unsymmetric convention. The limit on the right side of Eq. (3.50) represents a physical situation, whereas the limit on the right side of Eq. (3.51) may correspond to a hypothetical state whenever component 2 cannot exist as a pure liquid at the temperature of the solution. Consequently Eq. (3.50) is the preferred one and is more useful.

3.1.5 Excess Functions and Thermodynamic Modelling

The excess functions are the most convenient measure of the extent of deviation of real liquid mixtures from ideal bahavior (Klotz and Rosenberg, 1974). Most of these functions are extensive and are thermodynamic properties of solutions which are in excess of those of an ideal solution at the same condition of temperature, pressure and composition (Prausnitz *et al.* 1986).

The excess Gibbs free energy function is defined by

$$G^E \equiv G_{(\text{actual solution at } T,P,x)} - G_{(\text{ideal solution at } T,P,x)} \qquad [3.52]$$

Other excess functions such as excess Helmholtz energy (A^E), excess enthalpy (H^E), excess entropy (S^E), excess internal energy (U^E), and excess volume (V^E) can also be defined similarly. Thermodynamic relations between these extensive excess functions and their partial derivatives are identical to those of the total functions:

$$G^E = H^E - TS^E \qquad [3.53]$$

$$A^E = U^E - TS^E \qquad [3.54]$$

$$H^E = U^E - PV^E \qquad [3.55]$$

$$\left(\frac{\partial G^E}{\partial T}\right)_{P,x} = - S^E \qquad [3.56]$$

$$\left(\frac{\partial G^E/T}{\partial T}\right)_{P,x} = - \frac{H^E}{T^2} \qquad [3.57]$$

$$\left(\frac{\partial G^E}{\partial P}\right)_{P,x} = - V^E \qquad [3.58]$$

The definition of partial molar excess functions and their relationships with total excess function are analogous to those used for partial molar thermodynamic properties. For example,

$$\bar{g}_i^E = \left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} \qquad [3.59]$$

$$G^E = \sum_{i}^{k} n_i \bar{g}_i^E \qquad [3.60]$$

where $\bar{g}_i^E$ is the partial molar excess Gibbs free energy of component i.

Excess functions may be positive or negative and their sign indicates the type of deviation from ideal behavior. For example, a solution with a positive excess Gibbs free energy is said to exhibit a positive deviation from ideality and vice versa (Prausnitz *et al*. 1986).

The partial molar excess Gibbs energy, because of its direct relationship with the activity coefficient, is the most useful thermodynamic function in solution modelling. At constant temperature and pressure, for a component i in solution, it follows from Eq. (3.19).

$$\bar{g}_{i(real)} - \bar{g}_{i(ideal)} = RT\ln\frac{f_{i(real)}}{f_{i(ideal)}} \qquad [3.61]$$

Since,

$$\bar{g}_i^E = \bar{g}_{i(real)} - \bar{g}_{i(ideal)} \qquad [3.62]$$

$$\therefore \quad \bar{g}_i^E = RT\ln\frac{f_{i(real)}}{f_{i(ideal)}} \qquad [3.63]$$

Again, from Eq. (3.30) we get

$$f_{i(ideal)} = K_i x_i \qquad [3.64]$$

$$\therefore \quad \bar{g}_i^E = RT\ln\frac{f_{i(real)}}{K_i x_i} \qquad [3.65]$$

If we set the standard-state fugacity f_i° equal to K_i, Eq. (3.23) and Eq. (3.28) lead to

$$a_i = \gamma_i x_i = \frac{f_i}{K_i} \qquad [3.66]$$

Substitution of Eq. (3.66) into Eq. (3.65) gives.

$$\bar{g}_i^E = RT\ln\frac{a_i}{x_i} \qquad [3.67]$$

$$\therefore \quad \bar{g}_i^E = RT\ln\gamma_i \qquad [3.68]$$

Again, it follows from Eq. (3.60)

$$g^E = RT\sum_i^k x_i \ln\gamma_i \qquad [3.69]$$

where, g^E is the excess molar Gibbs energy. The temperature and pressure derivatives of activity coefficient are related to partial molar excess enthalpy and partial molar excess volume respectively. It follows from equations (3.57) and (3.58) that for a component i in solution,

$$\left[\frac{\partial \ln\gamma_i}{\partial T}\right]_{P,x} = -\frac{\bar{h}_i - h_{pure\ i}}{RT^2} = -\frac{\bar{h}_i^E}{RT^2} \qquad [3.70]$$

$$\left[\frac{\partial \ln\gamma_i}{\partial P}\right]_{T,x} = \frac{\bar{v}_i - v_{pure\ i}}{RT^2} = \frac{\bar{v}_i^E}{RT^2} \qquad [3.71]$$

where $\bar{h}_i^E$ and $\bar{v}_i^E$ are respectively the partial molar excess enthalpy and partial molar excess volume of component i in solution.

Equations (3.68) and (3.69) reflect the intimate relationship between activity coefficient and excess Gibbs energy and are the most useful equations in thermodynamic modelling of solutions. It is thus apparent that one can estimate the thermodynamic properties of a mixture if a suitable model is available for the prediction of activity coefficients. One of the models for the prediction of activity coefficients in nonelectrolyte solutions is UNIFAC, a detailed description of which is presented in the next section.

3.2 The UNIFAC Model

The UNIFAC (UNIQUAC Functional Group Activity Coefficient) is a group-contribution method originally developed by Fredenslund *et al.* (1975) for the prediction of liquid-phase activity coefficient in a nonelectrolyte, nonpolymeric solution. It is applicable at low to moderate pressures and at temperatures between 300 to 425 K (Gmehling *et al.* 1982). In concept, it is similar to ASOG (Analytical Solution of Groups) correlation proposed by Derr and Deal (1969), and is a consequence of the UNIQUAC model developed by Abrams and Prausnitz (1975).

It is one of the popular models for prediction of activity coefficients (Rasmussen, 1983; Thomas and Eckert, 1984). Its popularity stems from the group-contribution approach of the model and that in general it gives reasonably good predictions of activity coefficients. With the knowledge of 20-100 functional groups the properties of thousands of multicomponent mixtures can be predicted (Reid *et al.*, 1977). The type of organic molecules encountered in fluids of biological origin appear to be amenable to treatment by the UNIFAC group contribution method.

3.2.1 Fundamental Assumptions and General Features

The UNIFAC like any other group contribution method is based on two fundamental assumptions (Reid *et al.* 1977):

a. *Additivity*: the physical property of a compound is the sum of the contributions made by the molecule's constituent functional groups.

b. *Absence of environmental effect*: each functional group is assumed to act independently as an individual entity and its contribution within a molecule is not influenced by any other group. This assumption renders the group-contribution models unable to distinguish between details in the molecular structure as in isomers (Fredenslund and Rasmussen, 1985). However, this assumption is seldom valid since functional groups within a molecule do influence each other.

In this method the parameters characterizing interaction between functional groups are obtained by suitable reduction of experimentally obtained activity coefficient data in nonelectrolyte systems, and these parameters are then used for the prediction of activity coefficients in other systems which have not been studied experimentally but contain the same functional groups (Fredenslund *et al.*, 1975).

3.2.2 The Model Equations

The UNIFAC model was developed by combining the 'solution-of-groups' concept and the UNIQUAC model for liquid phase activity coefficients (Fredenslund *et al.*, 1975). The volume change accompanying the mixing of nonelectrolytes is normally small. This small volume change can have a significant effect on entropy and enthalpy of mixing. These two effects approximately cancel in the excess Gibbs energy making it insensitive to volume changes. This allows for the replacement of the excess Helmholtz energy at constant temperature and volume by the excess Gibbs energy at constant temperature and pressure, i.e. $(A^E)_{T,V} \approx (G^E)_{T,P}$. This substitution enables the development of a theory based on Guggenheim's (1952) lattice model of a liquid (Le Maguer, 1981). The extension of Guggenheim's theory to mixtures of molecules of different size and shape by using Wilson's (1964) local composition concept resulted in the development of the UNIQUAC equation (Abrams and Prausnitz, 1975). The UNIFAC model is similar to the UNIQUAC equation; the only difference is that the liquid mixture is considered to be made up of structural groups which add up to form the component molecules. The standard state of the components in these two models is the pure liquid at the solution temperature.

According to the UNIFAC model, the activity coefficient of a component which reflects the nonideal behavior of a molecule in solution can be broken into two independent parts, one associated with the differences in molecular sizes and the other with the interactions among the functional groups. The activity coefficient of a component i is given by:

$$\ln\gamma_i = \underbrace{\ln\gamma_i^C}_{\text{(Combinatorial)}} + \underbrace{\ln\gamma_i^R}_{\text{(Residual)}} \qquad [3.72]$$

The combinatorial part of the activity coefficient is derived from the pure component properties such as group volume and area parameters and is exactly the same as that of the UNIQUAC equation:

$$\ln\gamma_i^c = \ln\frac{\phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_j x_j l_j \qquad [3.73]$$

Where,

$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$ = Component volume fraction

$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}$ = Component area fraction

$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$

x_i = Mole fraction of component i

z = Coordination Number, set equal to 10

The pure component structural parameters r_i and q_i are calculated as the sum of the group volume and area parameters:

$r_i = \sum_k \nu_k^{(i)} R_k$ = Component volume parameter

$q_i = \sum_k \nu_k^{(i)} Q_k$ = Component area parameter

where $\nu_k^{(i)}$ is the number of groups of type in molecule i. The structural parameters (R_k and Q_k) of the functional groups are obtained from the van der Waals group volume (V_{wk}) and surface area (A_{wk}), given by Bondi (1968):

$R_k = \frac{V_{wk}}{15.17}$ = Group volume parameter

$Q_k = \frac{A_{wk}}{2.5x10^9}$ = Group area parameter

where V_{wk} and A_{wk} are respectively the van der Waals volume and area of group k. The normalization factors 15.17 and 2.5×10^9 are determined by the volume and surface area of a CH_2 unit in polyethylene (Abrams and Prausnitz, 1975). The values of R_k and Q_k for various functional groups encountered in nonelectrolyte solutions are listed in a number of publications (Gmehling *et al.*, 1982; Herskowitz and Gottlieb, 1981; Skjold-Jørgensen *et al.*, 1979 and Fredenslund *et al.*, 1977, 1975)

The residual part of the activity coefficient is a function of group external surface area (Q_k), group fractions (X_k), temperature (T) and group interaction parameters (a_{mn}) in pure components as well as in mixtures. $\mathrm{Ln}\gamma_i^R$ is given by:

$$\ln\gamma_i^R = \sum_k \nu_k^{(i)}\left[\ln\Gamma_k - \ln\Gamma_k^{(i)}\right] \qquad [3.74]$$

The group activity coefficient is:

$$\ln\Gamma_k = Q_k\left[1 - \ln\{\sum_m \theta_m\psi_{mk}\} - \sum_m \{\frac{\theta_m\psi_{km}}{\sum_n \theta_n\psi_{nm}}\}\right] \qquad [3.75]$$

Where,

$\theta_m = \dfrac{Q_m X_m}{\sum_n Q_n X_n}$ = Area fraction of group m

$X_m = \dfrac{\Sigma_n x_n \nu_{mn}}{\sum_n x_n \sum_m \nu_{mn}}$ = Mole fraction of group m

x_n = Mole fraction of component n

$$\psi_{mn} = \exp\left[-\frac{U_{mn} - U_{nn}}{RT}\right] = \exp\left[-\frac{a_{mn}}{T}\right]$$

= Group interaction parameter

Extensive lists of group interaction parameters (a_{mn}) are available in the published literature (Macedo *et al.*, 1983; Gmehling *et al.*, 1982; Herskowitz and Gottlieb, 1981; Skjold-Jørgensen *et al.*, 1979 and Fredenslund *et al.*, 1977, 1975)

3.2.3 Free-volume Correction and Other Modifications

The UNIFAC model is derived using the two-liquid theory which is concerned only with the effect of exchanging nearest neighbours and neglects changes in rotational and vibrational motions which molecules experience upon mixing. This theory does not explicitly take into account changes in free volume accompanying the process of mixing (Brandani and Prausnitz, 1981; Oishi and Prausnitz, 1978). The local structure which determines the equilibrium thermodynamic properties of liquid mixtures depends upon the forces between molecules and on their form and volume which change with composition (Flory, 1965). A null volume change upon mixing can not be assumed since the free volume of a molecule in the pure state is different from that in a mixture. Therefore, 'equation-of-state contribution' or free-volume effects can not be neglected while dealing with polymers and polyatomic molecules of various sizes and spatial forms (Maurer and Prausnitz, 1978).

Oishi and Prausnitz (1978) added a correction term to the UNIFAC model to take into account the changes in free-volume caused by mixing in polymer solutions. The UNIFAC model with the free-volume correction takes the form:

$$\ln\gamma_i = \ln\gamma_i^{UNIFAC} + \ln\gamma_i^{FV} \qquad [3.76]$$

$$\text{or, } \ln\gamma_i = \ln\gamma_i^{C} + \ln\gamma_i^{R} + \ln\gamma_i^{FV} \qquad [3.77]$$

The free-volume term ($\ln\gamma_i^{FV}$) can be calculated by an expression developed using the 'equation-of-state' theory of Flory (1970) and is given by:

$$\ln\gamma_i^{FV} = 3c_i \ln\left[\frac{(\tilde{v}_i^{1/3} - 1)}{(\tilde{v}_m^{1/3} - 1)}\right] - c_i\left[\left\{\frac{\tilde{v}_i}{\tilde{v}_m} - 1\right\}\left\{1 - \frac{1}{\tilde{v}_i^{1/3}}\right\}^{-1}\right] \qquad [3.78]$$

Where,

$\tilde{v}_i = \dfrac{v_i}{15.17br_i}$ = Reduced volume of component i

$\tilde{v}_m = \dfrac{\Sigma_i v_i x_i}{15.17b\Sigma_i r_i x_i}$ = Reduced volume of mixture

v_i = Molar volume of component i

x_i = Mole fraction of component i

b = proportionality constant of the order of unity

$3c_i$ = Number of external degrees of freedom per molecule of component i

Equation (3.77) is known as the UNIFAC-FV model which is used in our study of thermodynamic modelling of aqueous carbohydrate solutions.

The UNIFAC, like any other local composition models does not possess the ability to give an accurate representation of the excess Gibbs energy and excess enthalpy simultaneously. The model in its original form is also unable to represent vapor-liquid and liquid-liquid equilibria simultaneously (Fredenslund and Rasmussen, 1985; Skjold-Jergensrn, 1982, 1980). A fundamental deficiency in the model is the arbitrary choice of the volume and surface area of methylene in polyethylene as the normalizing factors (Rasmussen, 1983). In order to overcome these limitations and to improve the predictive power of the UNIFAC model various modifications have been attempted, and in most cases, these are empirical in nature with little or no physical meaning. Skjold-Jørgensen *et al.* (1982) introduced a composition variation of the interaction energies so that the association and solvation effects can be taken into account. This modification lead to quantitative representation of the vapor-liquid equilibrium (VLE) data and semi-quantitative representation of binary and ternary liquid-liquid equilibrium (LLE) data. The simultaneous representation of the VLE and H^E was achieved by making the coordination number 'z' temperature dependent (Skjold-Jørgensen *et al.*, 1980). Kikic *et al.* (1980) modified the combinatorial part of the UNIFAC by replacing r_i with $r_i^{2/3}$ in the Flory-Huggins part of the S-G combinatorial and obtained much improved predictions of activity coefficients in mixtures of saturated hydrocarbons. In an attempt to overcome most of the serious limitations of the original UNIFAC, Fredenslund and Rasmussen (1985) developed an advanced group-contribution model called SUPERFAC. This model is based on UNIFAC with numerous changes to incorporate all the suggested modifications of Skjold-Jørgensen *et al.* (1982, 1980) and Kikic *et al.* (1980). In addition, the group-interaction parameters and the association and solvation parameters are also considered temperature dependent. This model has better predictive capability for mixtures containing large variation of size and shape.

The numerous attempts to improve the flexibility and predictive power of the UNIFAC model by extending its application to a variety of diverse systems furnish valuable insight into special phenomena and areas where experimental information is urgently needed. It is hoped that the mathematical equations will gradually become more accurate, finally leading to an unified general model for solutions.

4. MODELLING OF AQUEOUS CARBOHYDRATE SOLUTIONS

Carbohydrates are organic compounds made up of carbon, oxygen and hydrogen atoms. In the molecular assembly these elements constitute functional groups which are amenable to treatment by the UNIFAC group-contribution method.

Glucose, an aldohexose, is by far the most abundant and important monosaccharide since it is the monomer unit of many di-, oligo- and polysaccharides and has a special role in many biological processes. Other aldohexoses are isomers of glucose and have similar physical and chemical properties. The ketohexoses also have similar properties; the only difference is that the reducing carbonyl group in keto-sugars is in the keto form, whereas in aldo-sugars it is in the aldehyde form. Further, the functional groups that combine to form a glucose molecule and those that constitute any other carbohydrate molecule are, with minor variation, alike. However, the number of such groups needed to form different carbohydrate molecules may be different. It is expected that the solution behavior of any aqueous monosaccharide solution will follow a similar pattern as that of an aqueous glucose solution. It was therefore decided to model the glucose-water system which should provide enough information and experience to model other carbohydrate-water systems. The UNIFAC model proposed by Fredenslund *et al*. (1975, 1977) was used in this study.

4.1 Experimental Data on Glucose-Water System

The experimental values of activity coefficients are calculated from freezing point, osmotic coefficient and vapor pressure data on aqueous glucose solutions. The mathematical equations used to treat these data are:

a. **Activity coefficient of water from freezing point measurements (Wall, 1974):**

$$\ln\gamma_w = -\left[\, 9.692\times10^{-3}\theta + 0.495\times10^{-6}\theta^2 + \ldots\ldots\ldots \right] - \ln x_w \qquad [4.1]$$

Where,

$\theta = T_0 - T$ = freezing point depression

γ_w = activity coefficient of water

x_w = mole fraction of water

The activity coefficients of water together with the freezing point depression values are shown in Table A1.1 (Appendix 1).

b. **Activity coefficients of water from osmotic coefficient measurements (Stokes and Robinson, 1966):**

$$\ln\gamma_w = -\left[\frac{\phi\times m}{55.51} + \ln x_w\right] \qquad [4.2]$$

where,

ϕ = osmotic coefficient

m = mola~~l~~ity of the solution

The activity coefficient of water together with the osmotic coefficients of glucose solution at 25°C are presented in Table A1.2.

c. **Activity coefficients of water from vapor-pressure measurements (Van den Berg and Bruin, 1981):**

$$\ln\gamma_w = -\left[\frac{P_w}{P_w^s}\right] - \ln x_w \qquad [4.3]$$

where,

P_w = equilibrium vapor pressure of water over the system at solution temperature.

P_w^s = Saturation vapor pressure of pure water at solution temperature.

The activity coefficients of water at different temperatures (25, 35, 45, 55 and 65°C) and the corresponding vapor pressures are presented in Table A1.3.

Ruegg and Blanc (1981) measured the activity of water (a_w) directly using an electronic hygrometer and developed an equation by regression analysis for calculation of a_w in glucose solutions within the concentration range 1.2-7.2 m (moles/kg water). The equation is:

$$a_w = 1.0042 - 0.02011m \qquad [4.4]$$

The calculated values of activity coefficient of water (γ_w) using this equation are presented in Table A1.4.

d. **Activity Coefficients of Glucose:**

The activity coefficients of glucose can be obtained from the activity coefficients of water by rearrangement and integration of Gibbs-Duhem equation (Klotz and Rosenberg, 1974). At constant temperature and pressure, it can be shown from Eq. (3.14) that

$$d\ln\gamma_2 = -\frac{x_1}{x_2}\, d\ln\gamma_1 \qquad [4.5]$$

which, on integration gives

$$\ln\gamma_2^* = -\int_0^{\ln\gamma_1} \frac{x_1}{x_2}\, d\ln\gamma_1 \qquad [4.6]$$

This integration can be performed by expressing $\ln\gamma_1$ as a polynomial function in x_2 of the form:

$$\ln\gamma_1 = Ax_2^2 + Bx_2^3 + \ldots\ldots \qquad [4.7]$$

and evaluating the integral analytically from a concentration of 0 to x_2. When the osmotic coefficient data of Stokes and Robinson (1966) for water was used, the best fit was obtained with an equation of the following form:

$$-\ln\gamma_w = Ax_g^2 + Bx_g^3 - Cx_g^4 + Dx_g^5 - Ex_g^6 \qquad [4.8]$$

Integration of equation (4.5) then gives

$$\begin{aligned}\int_0^{\ln\gamma_g^*} d\ln\gamma_g^* &= \int_0^{x_g} \frac{x_w}{x_g}\left[\frac{d\{-\ln\gamma_w\}}{dx_g}\right]dx_g \\ &= \int_0^{x_g} \Big[2A - (2A-3B)x_g - (3B+4C)x_g^2 + \\ &\qquad (4C+5D)x_g^3 - (5D+6E)x_g^4 + 6Ex_g^5\Big]\, dx_g \qquad [4.9]\end{aligned}$$

Therefore, the activity coefficient of glucose $\ln\gamma_g^*$ is given by:

$$\ln\gamma_g^* = 2Ax_g - \left[\frac{2A-3B}{2}\right]x_g^2 - \left[\frac{3B+4C}{3}\right]x_g^3 + \left[\frac{4C+5D}{4}\right]x_g^4$$

$$- \left[\frac{5D+6E}{5}\right]x_g^5 + Ex_g^6 \qquad [4.10]$$

The activity coefficients of glucose obtained at different concentrations (x_g) using the method described above are shown in Tables A1.5, A1.6 and A1.7 (Appendix 1).

Another method of obtaining the activity coefficient of glucose is by evaluating the integral on the right side of equation (4.7) by the extrapolation method described by Klotz and Rosenberg (1974).

e. The excess partial molar enthalpies and entropies

The excess partial molar enthalpies of glucose and water are reported by Taylor and Rowlinson (1955). The excess partial molar entropies are calculated from these data using the following equations:

$$\bar{g}^{E}_{water} = RT\ln\gamma_{water} \qquad [4.11]$$

$$\bar{g}^{E*}_{glucose} = RT\ln\gamma^{*}_{glucose} \qquad [4.12]$$

$$T\bar{s}^{E}_{water} = \bar{h}^{E}_{water} - \bar{g}^{E}_{water} \qquad [4.13]$$

$$T\bar{s}^{E*}_{glucose} = \bar{h}^{E*}_{glucose} - \bar{g}^{E*}_{glucose} \qquad [4.14]$$

The excess partial molar Gibbs energy, enthalpy and entropy of water and glucose are presented in Table A1.8 and A1.9 respectively.

4.2 Modelling of Glucose-Water System

Glucose is a six-membered ring compound that predominantly exists in the C1 chair conformation and mutarotates to an equilibrium mixture of 5 tautomeric forms (Figure 4.1) in aqueous solution. All these tautomers contribute to the measured property of glucose solution. However, as can be seen in Table 4.1, the pyranose forms predominate and the relative amounts of various forms change little with temperature.

4.2.1 Assignment of Functional Groups

The functional groups that make up the glucose-water mixture are shown in Figure 4.2. The group composition together with their volume (R_k) and area (Q_k) parameters is presented in Table 4.2. Glucose molecules display no aromaticity; all the assigned functional groups are therefore assumed to be of the aliphatic type. Since UNIFAC cannot distinguish the structural differences among isomers, the glucose-water system is assumed to be composed of two components: water and glucose having the functional groups shown in Table 4.2. The matrix of group-interaction parameters for the constituent functional groups reported by Gmehling *et al.* (1982) is shown in Table 4.3.

4.2.2 Evaluation of the Applicability of the UNIFAC Model

The activity coefficients of water and glucose in an aqueous glucose solution at 25°C were calculated using the UNIFAC model (Eq. 3.72) and the parameters presented in

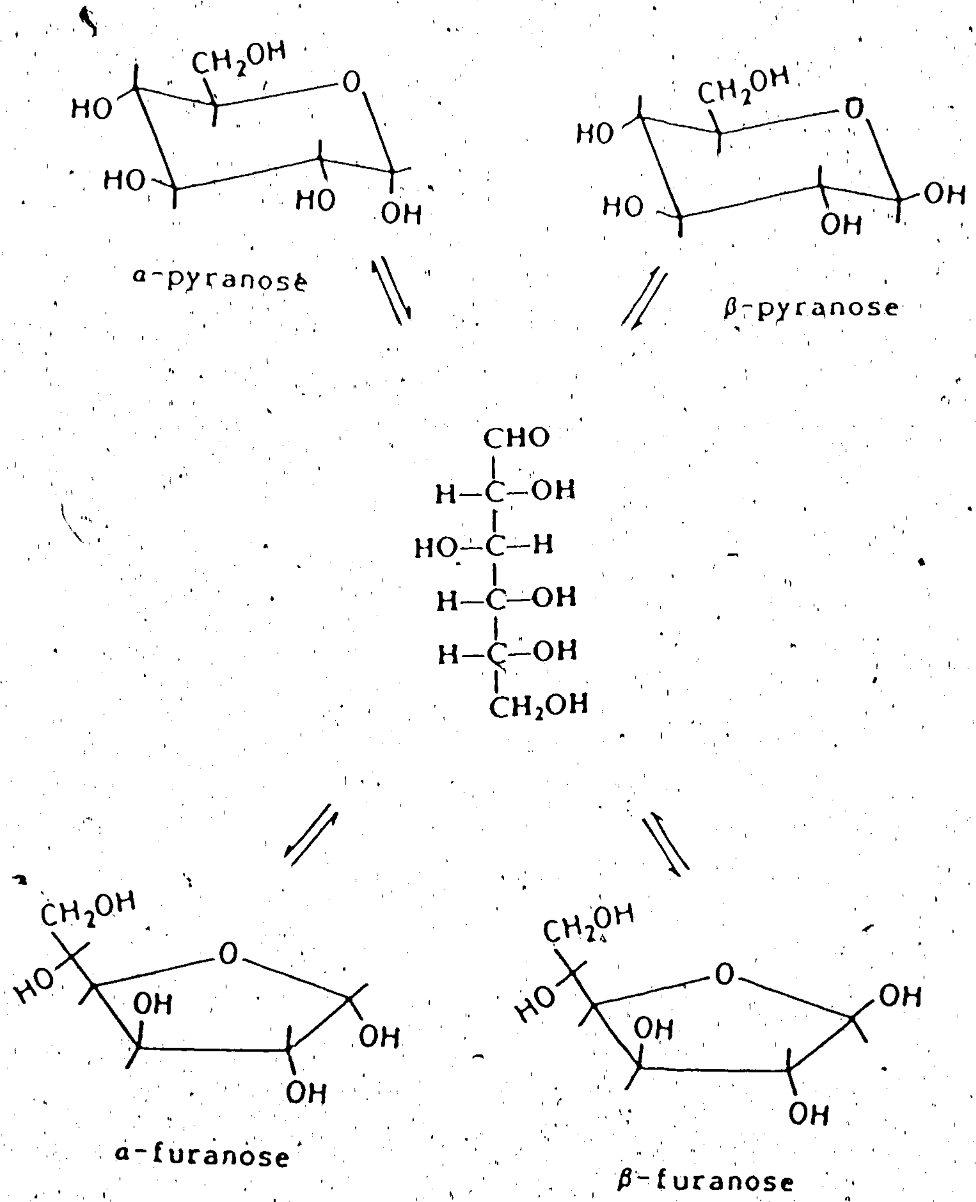


Figure 4.1 Tautomeric equilibrium that exists in aqueous glucose solution (Adapted from: Shallenberger, 1982).

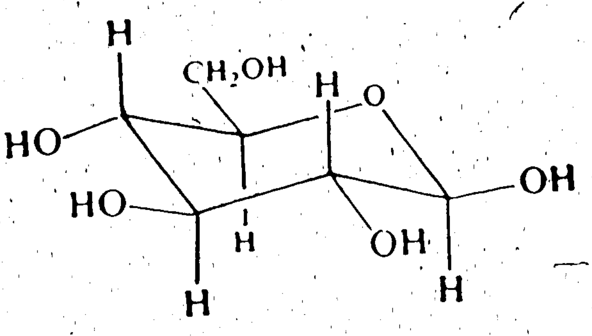
Table 4.1 The equilibrium composition of glucose tautomers at different temperatures.

Tautomer	Composition (%) at		
	20°C[a]	25°C[b]	43°C[c]
α-pyranose	36.4	37	37.30
β-pyranose	63.6	63	62.51
α-furanose	-	-	0.05
β-furanose	-	-	0.14

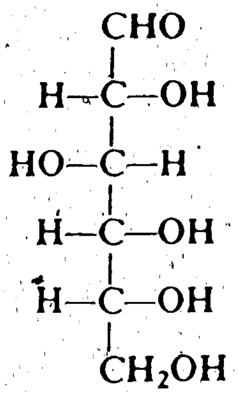
[a] From: Isabell and Pigman (1937)

[b] From: Frank (1979)

[c] From: William and Allerhand (1977)



OR



Glucose

.Functional groups:

CH_2, CH, OH, CHO

H_2O

Water

Functional group:

H_2O

Figure 4.2 The functional groups that constitute the mixture of glucose and water.

Table 4.2 The area and volume parameters of functional groups in a binary solution of glucose and and water.

Components	Functional Groups	Number of Groups (ν_k)	Volume Parameter (R_k)	Area Parameter (Q_k)
Glucose	CH_2	1	0.6744	0.540
	CH	4	0.4469	0.228
	OH	5	1.0000	1.200
	CHO	1	0.9980	0.948
Water	H_2O	1	0.9200	1.400

Parameter values from: Gmehling *et al.* (1982)

Table 4.3 The group-interaction parameters (a_{mn})

Groups	CH_2	CH	OH	H_2O	CHO
CH_2	0.0	0.0	986.5	1318.0	677.0
CH	0.0	0.0	986.5	1318.0	677.0
OH	156.4	156.4	0.0	353.5	441.8
H_2O	300.0	300.0	-229.1	0.0	-257.3
CHO	505.7	505.7	-404.8	232.7	0.0

Parameter values from: Gmehling *et al.* (1982)

Tables 4.2 and 4.3. In these calculations the standard states of the two components were respectively taken as pure water and hypothetical pure liquid glucose at solution temperature. Many sets of calculations were carried out and in each set a change in the group composition of the glucose molecule was considered. The three major variations in the group composition of a glucose molecule that are possible include:

a. A molecule of α- or β-glucose is expected to have the group composition shown in Figure 4.2. Therefore the first set of calculation was done with the group composition shown in Table 4.2-4.3, referred to as as 'Glucose {CHO}' in Figures 4.3-4.10.

b. In the second set a variation of the functional group was tried in order to ascertain whether the ring oxygen has the characteristics of an aldehyde or an ether group. The CHO (aldehyde) group in Tables 4.2-4.3 was replaced by a CH-O (ether) group, referred to as 'Glucose {CH-O}' in Figures 4.3-4.10.

c. One of the common crystalline states of glucose is its monohydrate and therefore a molecule of water was added to the glucose molecule in the third set, referred to as 'Glucose Monohydrate' in Figures 4.3-4.10.

The estimates of the activity coefficients (γ_i) and activities (a_i) were compared with the experimental values (obtained from osmotic coefficient data of Stokes and Robinson, 1966) in Figures 4.3-4.6. The results of the calculation demonstrated poor prediction of the activity coefficients of both the components (Figures 4.3 and 4.4) when glucose(CHO or CH-O) and water were considered as the molecular species in the solution. The variation of the logarithm of activity coefficient ($\ln\gamma_i$) with mole fraction of water (x_w) showed opposite trend when compared with the experimental values. This poor prediction of γ_i is, however, not reflected in the activity-mole fraction plots (Figures 4.5 and 4.6) which at least showed the right trend. For water, the experimental and predicted values of the activity coefficient were very close to unity so that the activity of water in dilute solutions numerically approaches the values of the mole fraction of water (x_w). However, as the concentration of glucose increases the divergence between the experimental and predicted values becomes greater and greater (Figure 4.5). But in the case of glucose, the prediction of its activity was poor even in dilute solution (Figure 4.6).

The quality of prediction of both activity coefficient and activity was significantly improved when the molecular species in solution were changed to glucose monohydrate and water (Figures 4.3-4.6). In the dilute region the prediction of the activity coefficient of water was comparatively better than that of the glucose (Figures 4.3 and 4.4).

The excess partial molar entropies and enthapies were predicted using the combinatorial (C) and residual (R) parts of the activity coefficients according to the following equations:

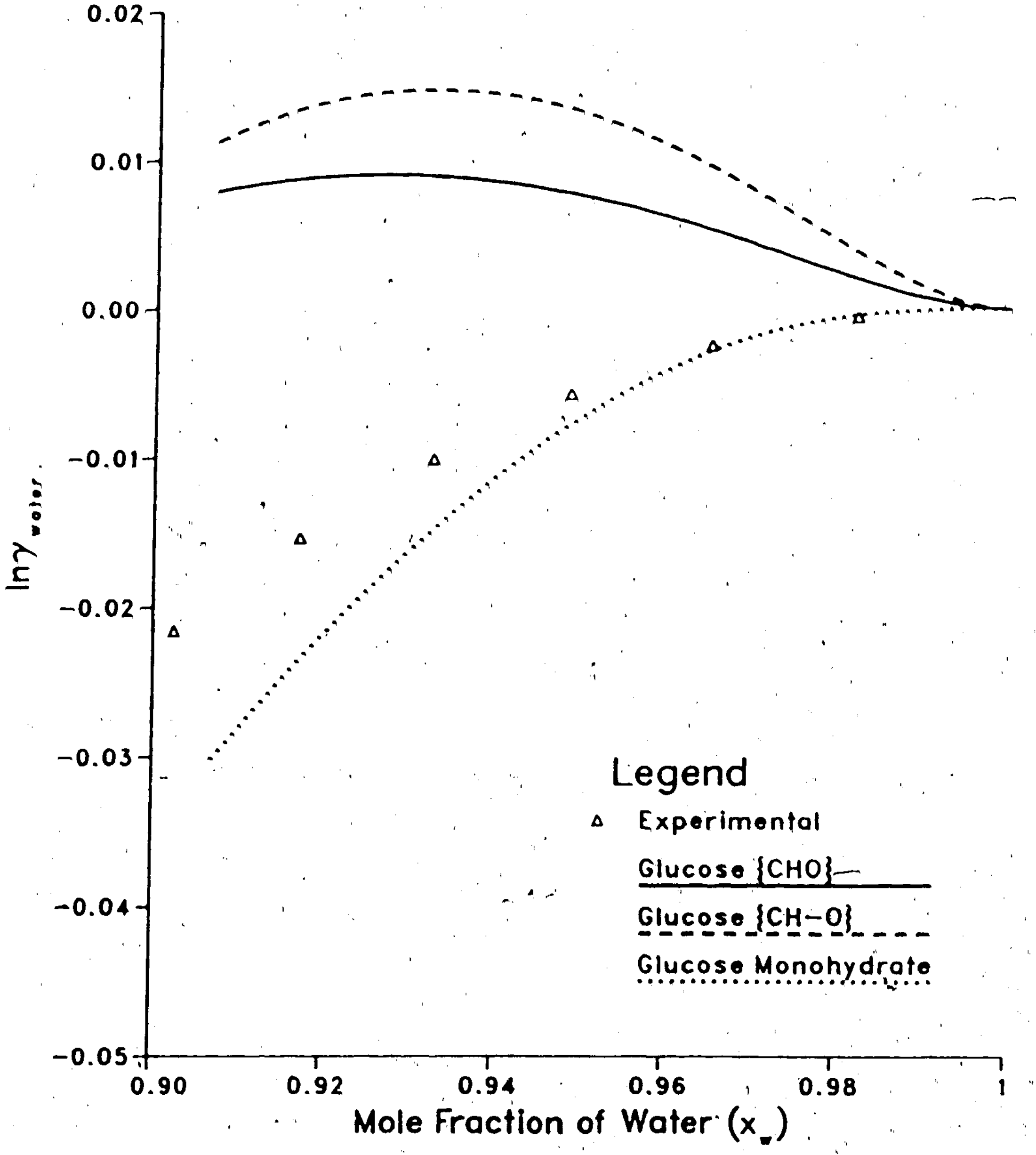


Figure 4.3 The experimental and predicted values of the activity coefficient of water at 25°C. The experimental values were obtained from the osmotic coefficient data of Stokes and Robinson (1966). The predicted values were generated using the UNIFAC model (Eq. 3.72) and the values of the parameters presented in Tables 4.2-4.3.

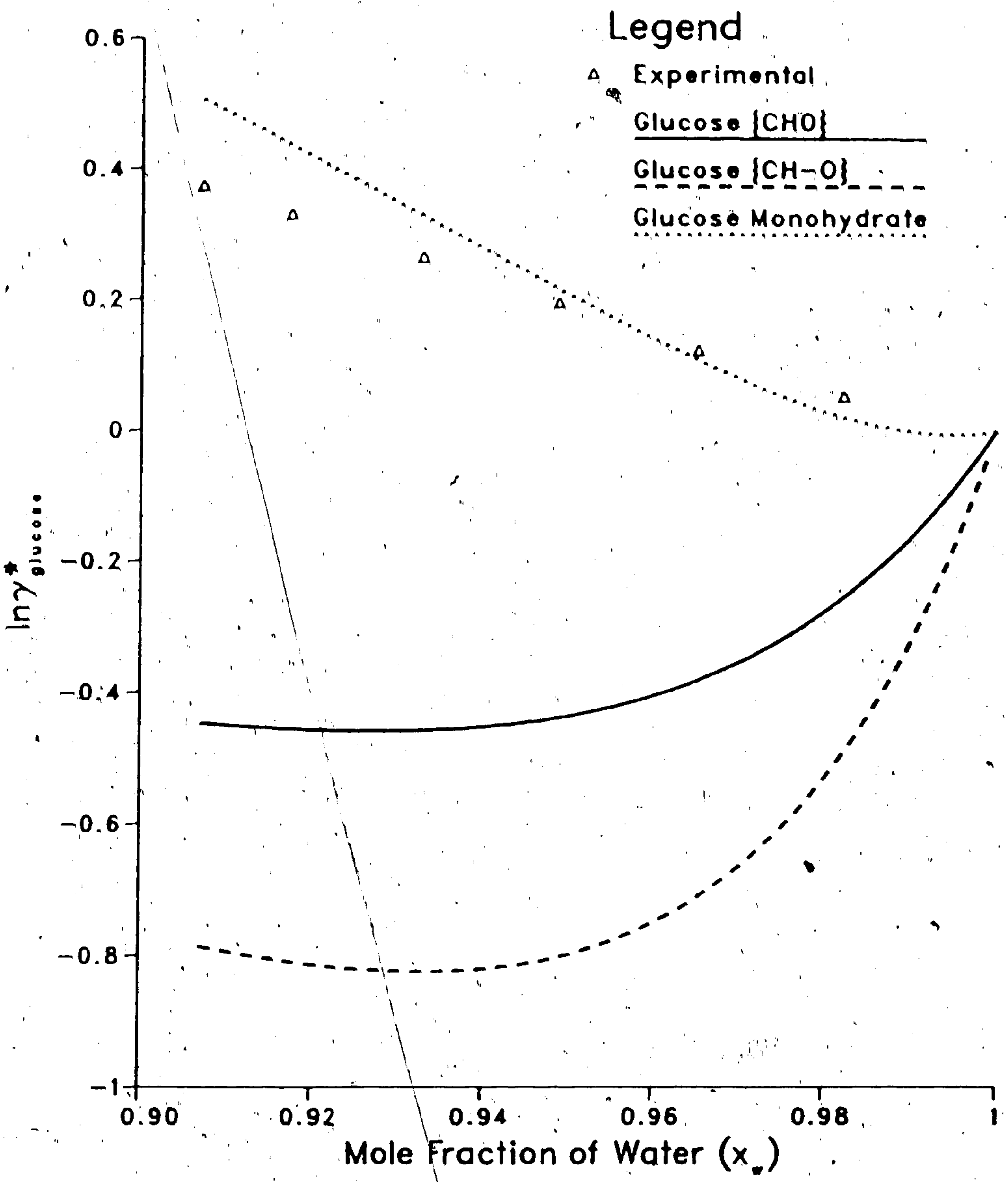


Figure 4.4 The experimental and predicted values of the activity coefficient of glucose at 25°C. The experimental values were obtained by applying the Gibbs-Duhem equation to the osmotic coefficient data of Stokes and Robinson (1966). The predicted values were generated using the UNIFAC model (Eq. 3.72) and the values of the parameters presented in Tables 4.2-4.3.

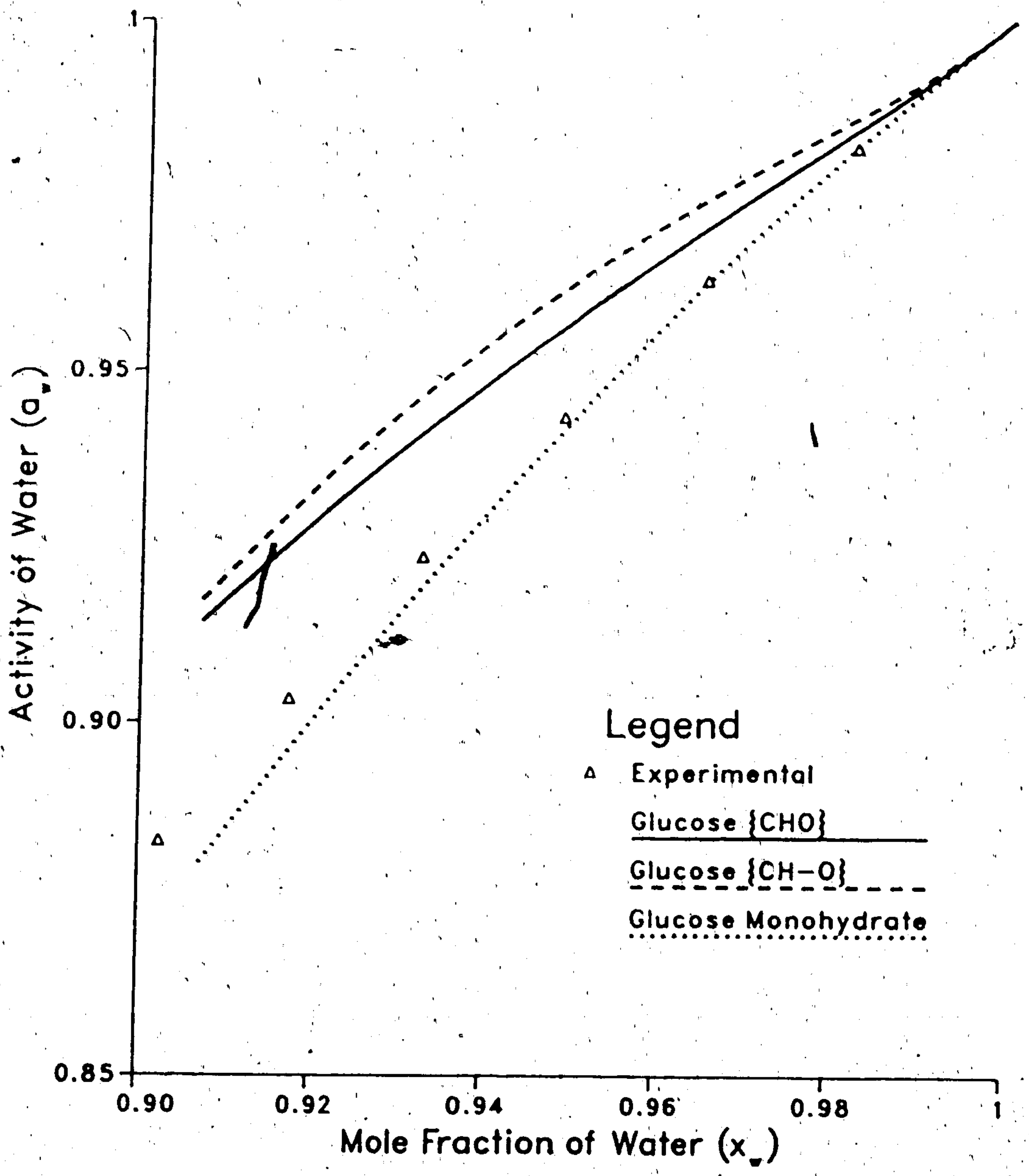


Figure 4.5 The experimental and predicted values of the activity of water at 25°C. The experimental values were obtained from the osmotic coefficient data of Stokes and Robinson (1966). The predicted values were generated using the UNIFAC model (Eq. 3.72) and the values of the parameters presented in Tables 4.2-4.3.

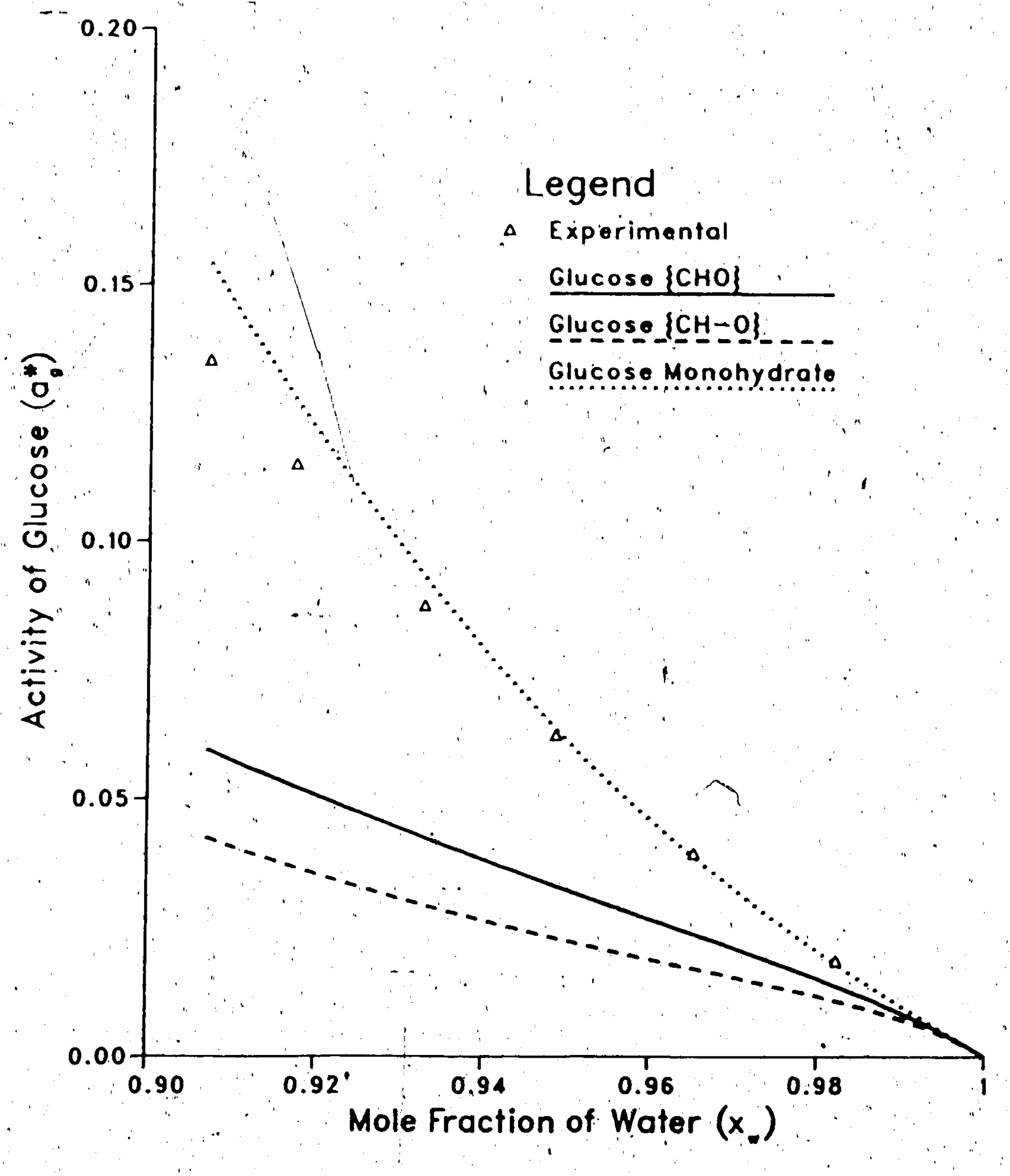


Figure 4.6 The experimental and predicted values of the activity of glucose at 25°C. The experimental values were obtained by applying the Gibbs-Duhem equation to the osmotic coefficient data of Stokes and Robinson (1966). The predicted values were generated using the UNIFAC model (Eq. 3.72) and the values of the parameters presented in Tables 4.2-4.3.

$$T\bar{s}^{E}_{water} = -RT\ln\gamma^{C}_{water} \qquad [4.15]$$

$$T\bar{s}^{E*}_{glucose} = -RT\ln\gamma^{C*}_{glucose} \qquad [4.16]$$

$$\bar{h}^{E}_{water} = RT\ln\gamma^{R}_{water} \qquad [4.17]$$

$$\bar{h}^{E*}_{glucose} = RT\ln\gamma^{R*}_{glucose} \qquad [4.18]$$

The experimental and the predicted values are compared in Figures 4.7-4.10. In every case (Figures 4.7-4.10) the predicted $T\bar{s}^{E}$-x and $\bar{h}^{E}$-x relationship displayed an opposite trend when compared with the experimentally observed behavior. With increase in glucose concentration the predicted $T\bar{s}^{E}$ and $\bar{h}^{E}$ values for water increased positively while the experimental values increased negatively as shown in Figures 4.7 and 4.9. As can be seen in Figures 4.8 and 4.10 the reverse was found to be true for glucose.

The partial molar excess Gibbs energy ($\bar{g}^{E}_{i} = RT\ln\gamma_{i} = \bar{h}^{E}_{i} - T\bar{s}^{E}_{i}$) is a composite function of enthalpic and entropic contributions. Since lnγi is obtained by adding the combinatorial ($\ln\gamma^{C}_{i}$) and residual ($\ln\gamma^{R}_{i}$) parts, these two contributions may cancel each other or balance in a way so as to leave an apparently well-behaved $\ln\gamma_{i}$-x or a_{i}-x relationship. This appeared to be the case when glucose monohydrate and water were considered as the molecular species in the binary solution.

Several other structural variations were also investigated. In one case the dimer of glucose (diglucose)

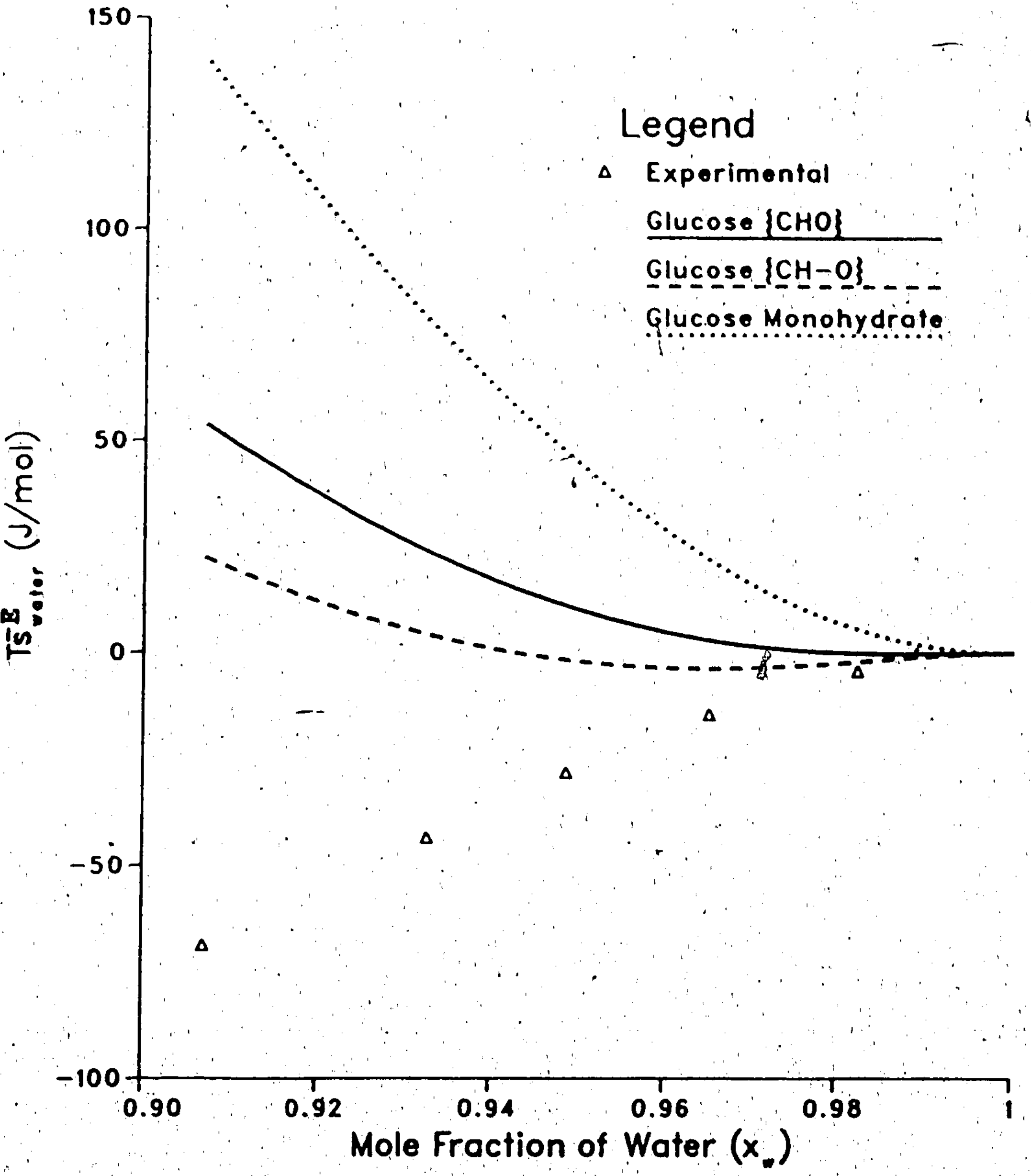


Figure 4.7 The experimental and predicted values of the excess partial molar entropy of water at 25°C. The experimental values were obtained from the data of Taylor and Rowlinson (1955); Stokes and Robinson (1966). The predicted values were generated using the combinatorial part of the UNIFAC model (Eq. 3.72) and the values of the parameters presented in Tables 4.2-4.3.

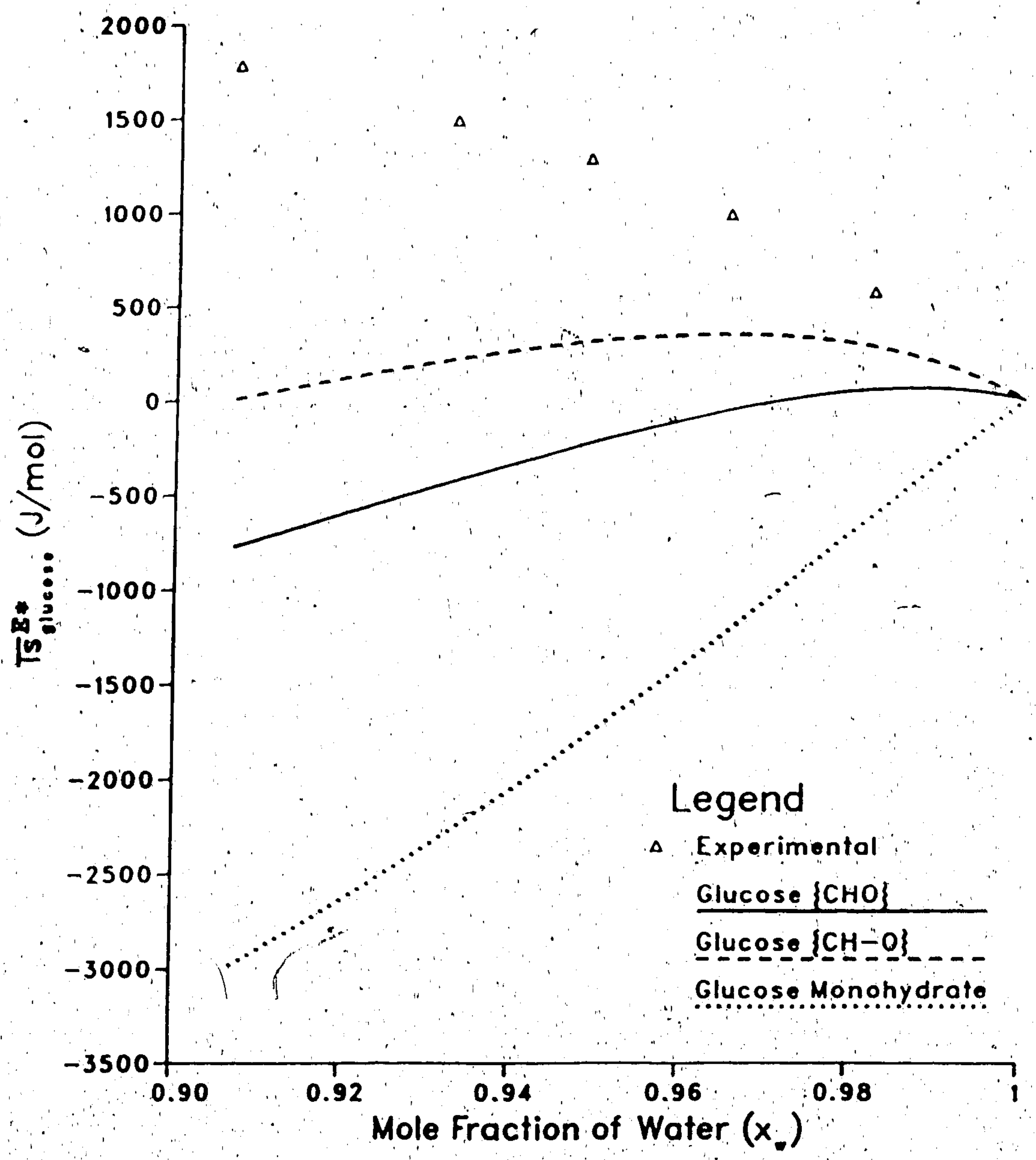


Figure 4.8 The experimental and predicted values of the excess partial molar entropy of glucose at 25°C. The experimental values were obtained from the data of Taylor and Rowlinson (1955); Stokes and Robinson (1966). The predicted values were generated using the combinatorial part of the UNIFAC model (Eq. 3.72) and the values of the parameters presented in Tables 4.2-4.3.

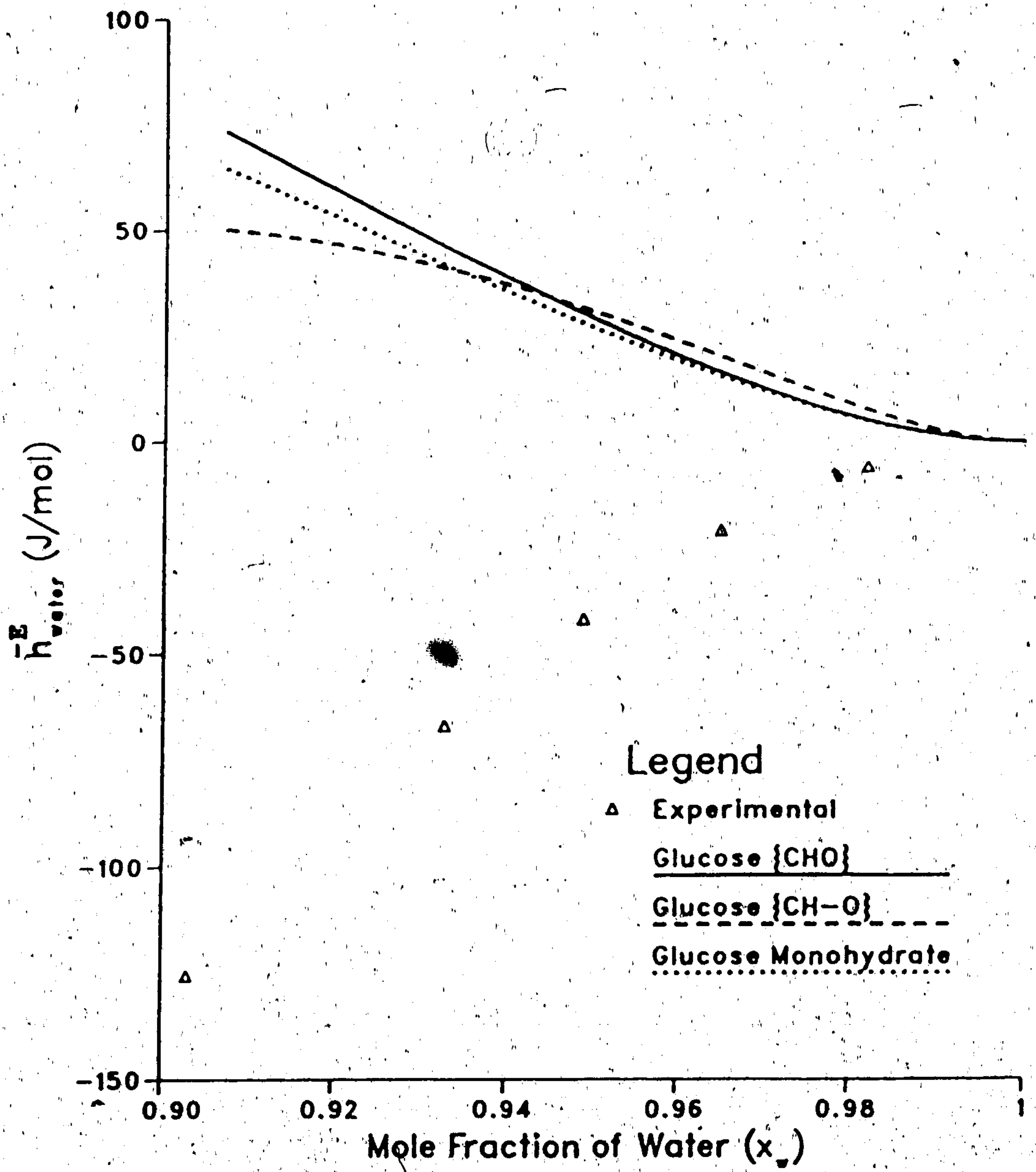


Figure 4.9 The experimental and predicted values of the excess partial molar enthalpy of water at 25°C. The experimental values were obtained from the data of Taylor and Rowlinson (1955). The predicted values were generated using the residual part of the UNIFAC model (Eq. 3.72) and the values of the parameters presented in Tables 4.2-4.3.

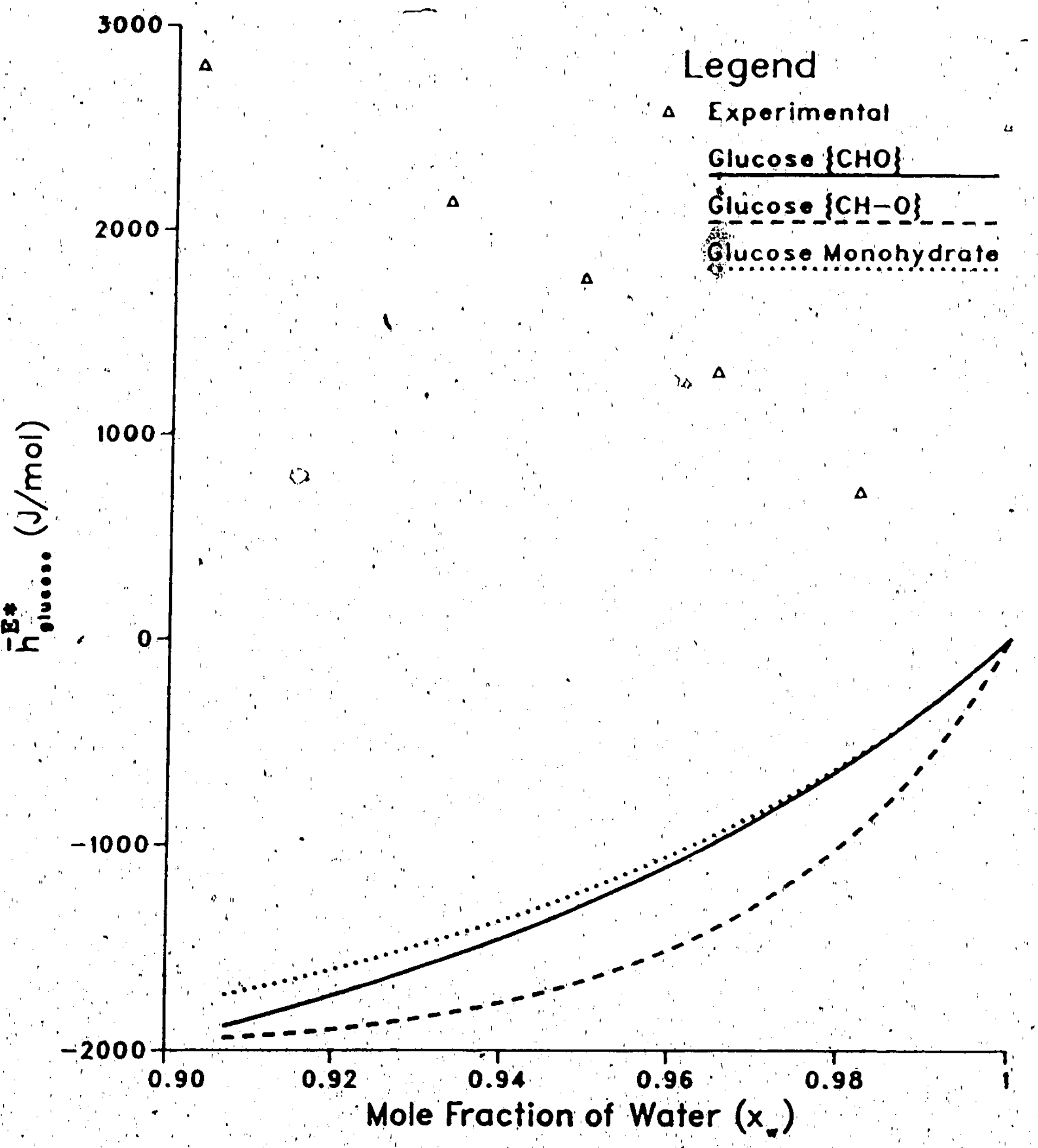


Figure 4.10 The experimental and predicted values of the excess partial molar enthalpy of glucose at 25°C. The experimental values were obtained from the data of Taylor and Rowlinson (1955). The predicted values were generated using the residual part of the UNIFAC model (Eq. 3.72) and the values of the parameters presented in Tables 4.2-4.3.

and water were considered as the molecular species in the solution, while in another case structural constraint on the accessibility of the OH groups was assessed by making some of these groups unavailabe for interaction with other functional groups. It was observed that the prediction of the activity coefficient of components in each case was poorer compared to the three major sets of calculation shown in Figures 4.3-4.10.

One plausible explanation for the failure of the UNIFAC model to predict the behaviour of the glucose-water system is perhaps the parameters used in the calculation do not represent the system well and therefore need modification. Further, considering the disparity in the molecular size and nature of glucose and water molecules, it would probably be necessary to include the free-volume effects in the computation of the activity coefficients. An attempt was therefore made to modify or reevaluate the UNIFAC parameters and to add the free-volume contribution to describe the binary system of glucose and water.

4.3 Adaptation of the UNIFAC-FV Model to the Glucose-Water System

The results in the previous section and the illustrations in Figures 4.7-4.10 clearly reveal that the parameters used in the computation of both the combinatorial ($\ln\gamma_i^C$) and the residual ($\ln\gamma_i^R$) parts of the activity coefficient are unable to predict the excess partial molar entropy and enthalpy of the components. Consequently, the volume (R_k) and area(Q_k) parameters of the functional groups shown in Table 4.2 (for computation of $\ln\gamma_i^C$) and the group-interaction parameters presented in Table 4.3 (for computation of $\ln\gamma_i^R$) need to be considered for modification.

According to Skjold-Jørgensen (1982) the R_{OH} and Q_{OH} were artifically increased compared to the values based on van der Waals volume and surface area given by Bondi (1968). In order to obtain better agreement for systems containing water and lower alcohols, Anderson and Prausnitz (1978) used q' instead of q for water and alcohols in the computation of the residual part of the UNIQUAC equation. The optimum value of q' (the surface of interaction) was found to be much lower than q (the geometrical external surface) used in the original equation, suggesting that the intermolecular attraction is dominated by the OH group (Prausnitz *et al.*, 1986). Glucose is a polar molecule containing 5 OH groups and has high affinity for an aqueous environment as demonstrated by the lowering of vapor pressure of water (Taylor and Rowlinson, 1955). According to Franks (1983) the behavior of the highly polar compounds is dominated by hydrogen bonding between water and the solute molecules. It therefore seems reasonable to speculate that the property of the glucose-water system will be dominated by the characteristics of the OH group and its interaction with water. Further, the values of the three parameters R_k, Q_k and a_{mn} for the functional groups CH_2, CH, CHO and H_2O have been successfully utilized to predict the activity coefficients of components in a variety of systems

(Fredenslund *et al.*, 1977). Consequently, an atttempt was made to estimate the volume (R_k) and area (Q_k) parameters of the OH group and the parameter representing its interaction with water viz. a_{OH,H_2O} and $a_{H_2O,OH}$ using the experimental data up to the solubility limit of glucose. In doing so, the entropic and enthalpic contributions to the excess Gibbs energy were matched independently with the combinatorial and residual parts of the activity coefficients. The chemical properties of glucose in solution (reactions with Br_2 + H_2O, HNO_3, $C_6H_5NHNH_2$, Ac_2O and HCN) indicate that the ring oxygen has the characteristics of an aldehyde (CHO) group. Therefore, CHO group was chosen to represent the ring oxygen in subsequent calculations.

Glucose is a polyatomic molecule with a much bigger molecular size and different spatial form compared with a molecule of water. This dissimilarity of molecular size cannot be ignored and the volume change accompanying the process of mixing should be accounted for through the free-volume correction. In order to compute the free-volume contribution to the component's activity coefficient using Eq. (3.78), the information on molar volumes of both the components and the value of the constants b, c_1, and c_2 should be known. The molar volume of water is available in published literature (CRC, 1983-1984); but the molar volume of liquid glucose and the value of the constants need to be estimated.

4.3.1 Estimation of the UNIFAC and Free-volume Parameters

The values of the UNIFAC and free-volume parameters were determined using a Simplex search technique described by Toupin (1986). It is a derivative free, sequential or direct search method based on weighted least-square minimization of the objective function. This sequential search procedure developed by Nelder and Mead (1965a, b) is an extension of the Simplex method originally introduced by Spendley *et al.* (1962). A detailed description of the Simplex algorithm is provided by Toupin (1986).

The objective function used for the least-square fitting is a chi-square (χ_2) statistic of the form:

$$\chi^2 = \sum_i W_i \left[Y_i^{Expt.} - Y_i^{Pred.} \right]^2 \qquad [4.19]$$

$$= \sum_i \frac{1}{\sigma_i^2} \left[Y_i^{Expt.} - Y_i^{Pred.} \right]^2 \qquad [4.20]$$

where σ_i^2 is an unbiased estimate of the ith sample variance or the estimate of error in the data point $Y_i^{Expt.}$.

The optimum values of the parameters associated with the structural contribution (combinatorial and free-volume) of the molecules to the activity coefficients were estimated using the entropy data of the glucose-water system. The objective function used for these parameters was of the form:

$$\chi^2 = \sum_i W_i \left[\{T\bar{S}_i^E\}^{Expt.} - \{T\bar{S}_i^E\}^{Pred.} \right]^2 \qquad [4.21]$$

where,

$$\{T\bar{S}_i^E\}^{Pred.} = -\left[RT\{\ln\gamma_i^C + \ln\gamma_i^{FV}\}^{Pred.}\right] \qquad [4.22]$$

The optimized value of Q_{OH} found in this step was used in the computation of $(\ln\gamma_i^R)$ for optimization of a_{OH,H_2O} and $a_{H_2O,OH}$ in the next step. Since these parameters are associated with the energy of interaction of the constituent structural groups, the optimization was carried out with enthalpy data on the glucose-water system. The objective function used in this case was of the form:

$$\chi^2 = \sum_i W_i\left[\{\bar{h}_i^E\}^{Expt.} - \{RT\ln\gamma_i^R\}^{Pred.}\right]^2 \qquad [4.23]$$

The entropy and enthalpy data (Tables A1.8 and A1.9) at 25°C on both water and glucose were used in the optimization of the parameters. As can be seen in Table A1.8 and A1.9 the data for glucose are several times higher than those for water. In order to avoid the least square procedure anchoring the solution to the data set of glucose only, a weight of 100 was used on the data set for water.

A constrained Simplex search was carried out for the parameters R_{OH}, Q_{OH}, b and c_2 in order to restrict these parameters to assume only positive values. Since the group-interaction parameters can assume any value, positive or negative, an unconstrained search was carried out in the latter case. It was observed that the value of R_{OH} (=0.97) determined by the least-squares procedure was very close to its reported value of 1.0 (Gmehling *et al.*, 1982) whereas Q_{OH} changed drastically. It was therefore felt that the value of R_{OH} be retained to its original value of 1.0 and only Q_{OH} which appeared to be a very important and sensitive parameter be optimized using the entropy data. This speculation appears to be reasonable in view of the observation made by Anderson and Prausnitz (1978) in their study of systems containing lower alcohols using UNIQUAC equation.

The optimized values of the parameters together with the associated errors are presented in Table 4.4. Of the UNIFAC parameters, Q_{OH} was found to be very sensitive. A small change in Q_{OH} changed the prediction drastically. The optimum value of Q_{OH} was found to be lower than that reported by Gmehling *et al.* (1982). This finding is in agreement with Anderson and Prausnitz (1978) who also found a lower value of q for alcohols. As can be seen in Table 4.4, the error on the parameter $a_{H_2O,OH}$ is significantly high indicating that the parameter does not play a key role in prediction of the activity coefficients.

As suggested in published literature (Oishi and Prausnitz, 1978; Nocon *et al.*, 1983), the value of the constant c_1 was set equal to 1.0. The values of b and c_2 were estimated using the Simplex search technique. The error on the parameter c_2 is large and fitting calculations showed that the results were insensitive to a change in the value of b and c_2 in the vicinity of 1.0. Therefore the values of all the free-volume parameters were set equal to 1.0. This

Table 4.4 The estimates of the UNIFAC and Free-volume parameters determined by the Simplex search technique.

UNIFAC PARAMETERS

Parameter	Reported Value[a]	Estimated Value	Standard Error
Q_{OH}	1.20	1.097	0.008
a_{OH,H_2O}	353.5	-169.6	3.16
$a_{H_2O,OH}$	-229.1	-6.1	5.92

FREE-VOLUME PARAMETERS

Parameter	Estimated Value	Standard Error	Value used in Calculation
b	0.97	0.067	1.0
c_1	-	-	1.0
c_2	0.87	0.509	1.0

[a] Parameter values from: Gmehling *et al.* (1982)

assumption is in agreement with Alessi *et al.* (1982) who used a value of 1.1 for c_2 (for solute) in order to estimate the UNIFAC parameters from infinite dilution activity coefficients.

4.3.2 Estimation of Molar Volume of Liquid Glucose

Several additive methods are available for the estimation of liquid molar volume at the normal boiling points (Partington, 1949). A numerical value is assigned to each element and certain bond linkages so that the molar volume at the normal boiling point is obtained by the addition of these values in a manner shown below. The volume increment for carbon, hydrogen and oxygen published by Le Bas (1915) are:

	cm^3/mol
Carbon	14.8
Hydrogen	3.7
Oxygen	7.4

Glucose has 6 carbon atoms, 12 hydrogen atoms and 6 oxygen atoms. The molar volume of liquid glucose at normal boiling point estimated by the method of Le Bas is given by

$$v_{glucose} = 6\times14.8 + 12\times3.7 + 6\times7.4 = 177.6\ cm^3/mol$$

This estimate of $v_{glucose}$ is used as the molar volume of liquid glucose with the assumption that a change in temperature does not affect this value of $v_{glucose}$.

4.3.3 Results with the Revised Parameters

The activity coefficients, activities and excess partial molar properties (entropy and enthalpy) were predicted using the new parameters and the UNIFAC-FV model (Eq. 3.77). The results are shown in Figures 4.11-4.18. For both water and glucose, the $\ln\gamma_i$-x_i relationship displayed the correct trend when compared with the experimentally observed behavior (Figures 4.11 and 4.12). However, the agreement with the experimental values was poor with a high average error (106% for water and 34% for glucose) over the concentration (x_w) range of 0.9 to 1.0. As demonstrated in Figures 4.13 and 4.14, the model can estimate the activities of water and glucose which are in good agreement with the experimental values. The average errors in the estimates are 0.3% for water and 8% for glucose over the entire concentration (x_w) range mentioned above. In the case of water, the UNIFAC model without free-volume correction provides a better estimate of its activity in the dilute region, up to a mole fraction (x_w) of 0.95 (Figure 4.13). As the glucose concentration increases, the free-volume effects become important and in the concentrated region the prediction of a_w is better with the free-volume correction. This is also indicated in the $\ln\gamma_w$-x_w plot (Figure 4.11). But for glucose, the free-volume contribution to the prediction of its activity was found to be negligible (Figures 4.12 and 4.14).

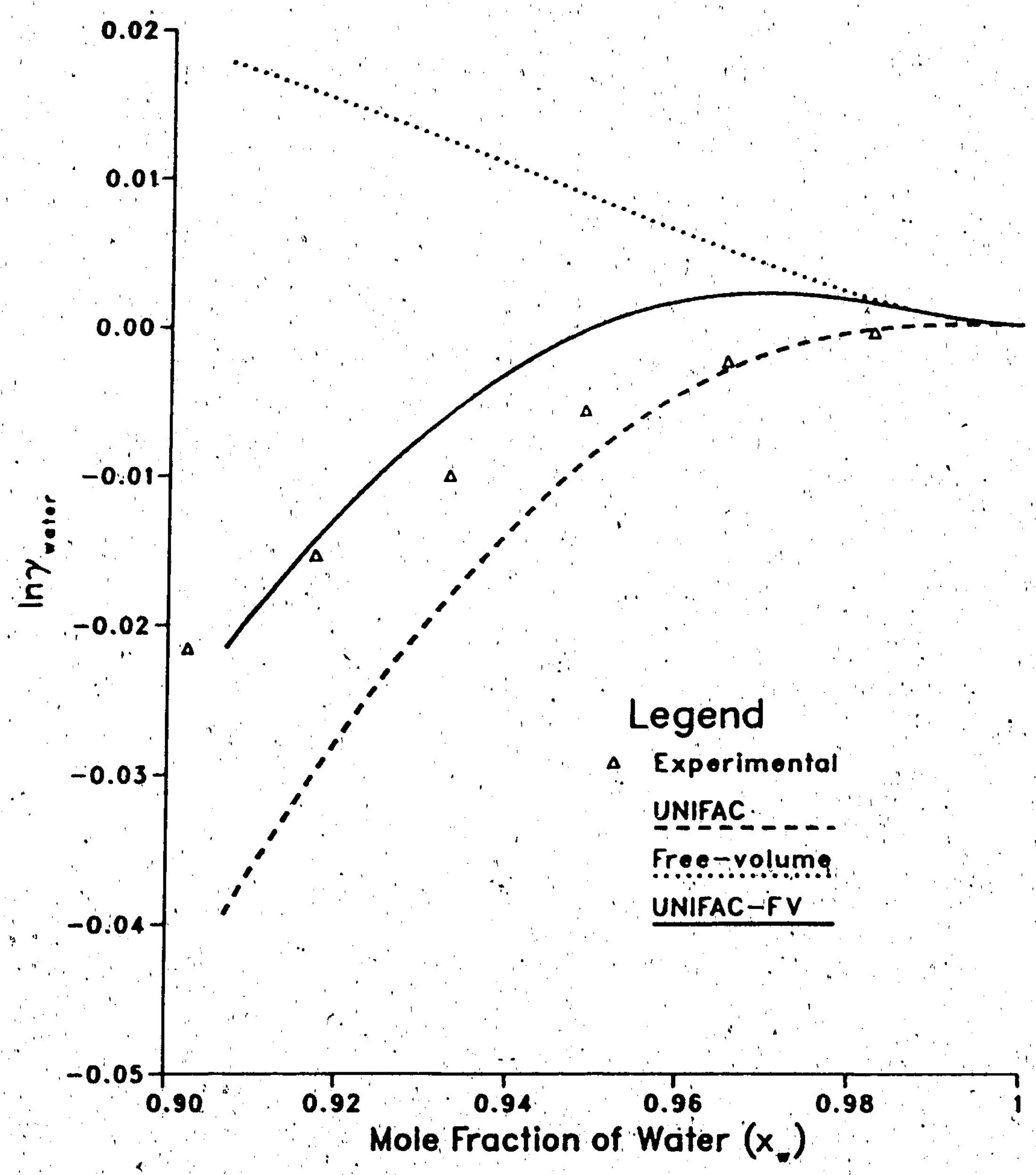


Figure 4.11 The experimental and predicted values of the activity coefficient of water at 25°C. The experimental values were obtained from the osmotic coefficient data of Stokes and Robinson (1966). The predicted values were generated using the UNIFAC-FV model (Eq. 3.77) and the new values of the parameters presented in Table 4.4.

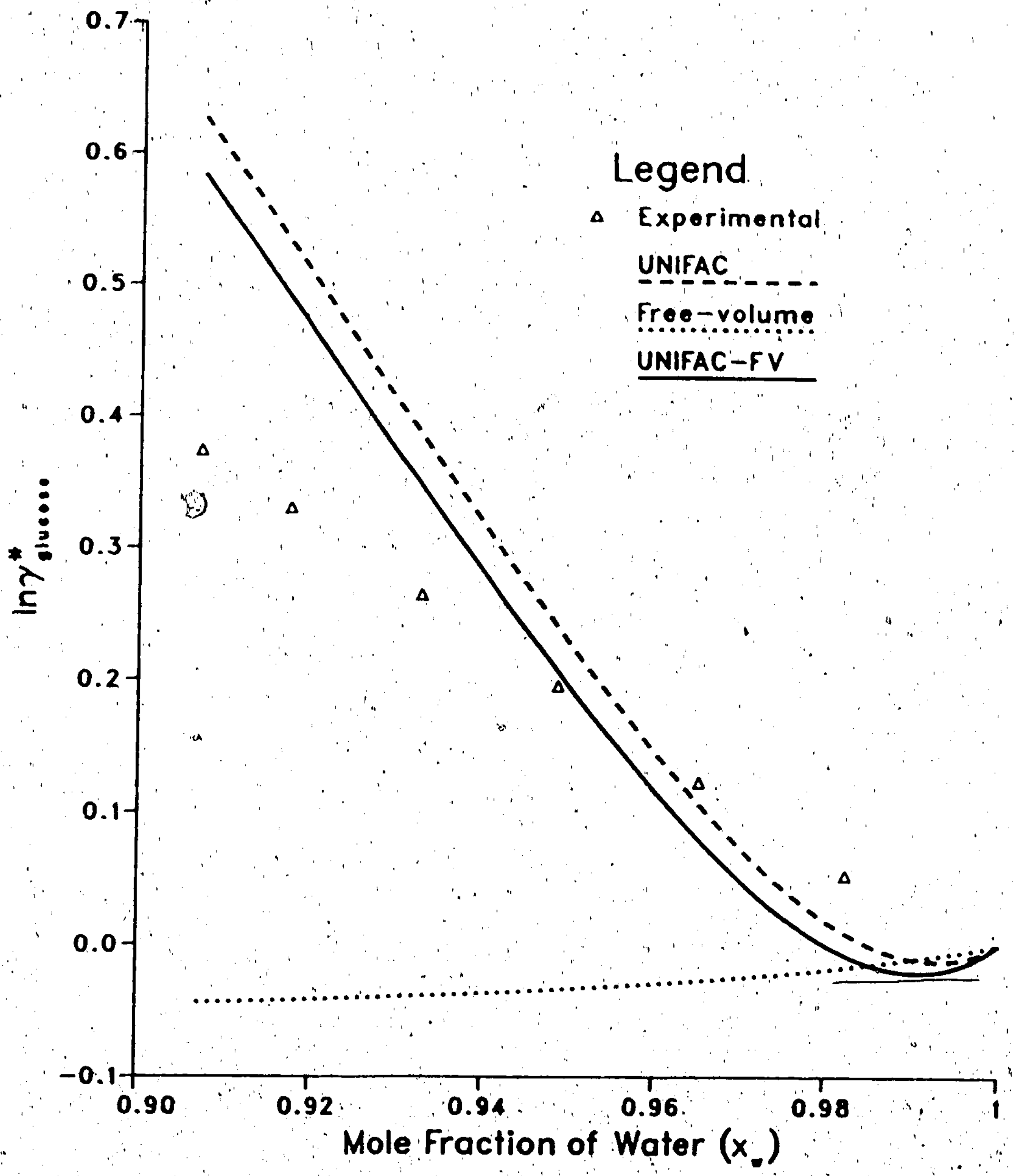


Figure 4.12 The experimental and predicted values of the activity coefficient of glucose at 25°C. The experimental values were obtained by applying the Gibbs-Duhem equation to the osmotic coefficient data of Stokes and Robinson (1966). The predicted values were generated using the UNIFAC-FV model (Eq. 3.77) and the new values of the parameters presented in Table 4.4.

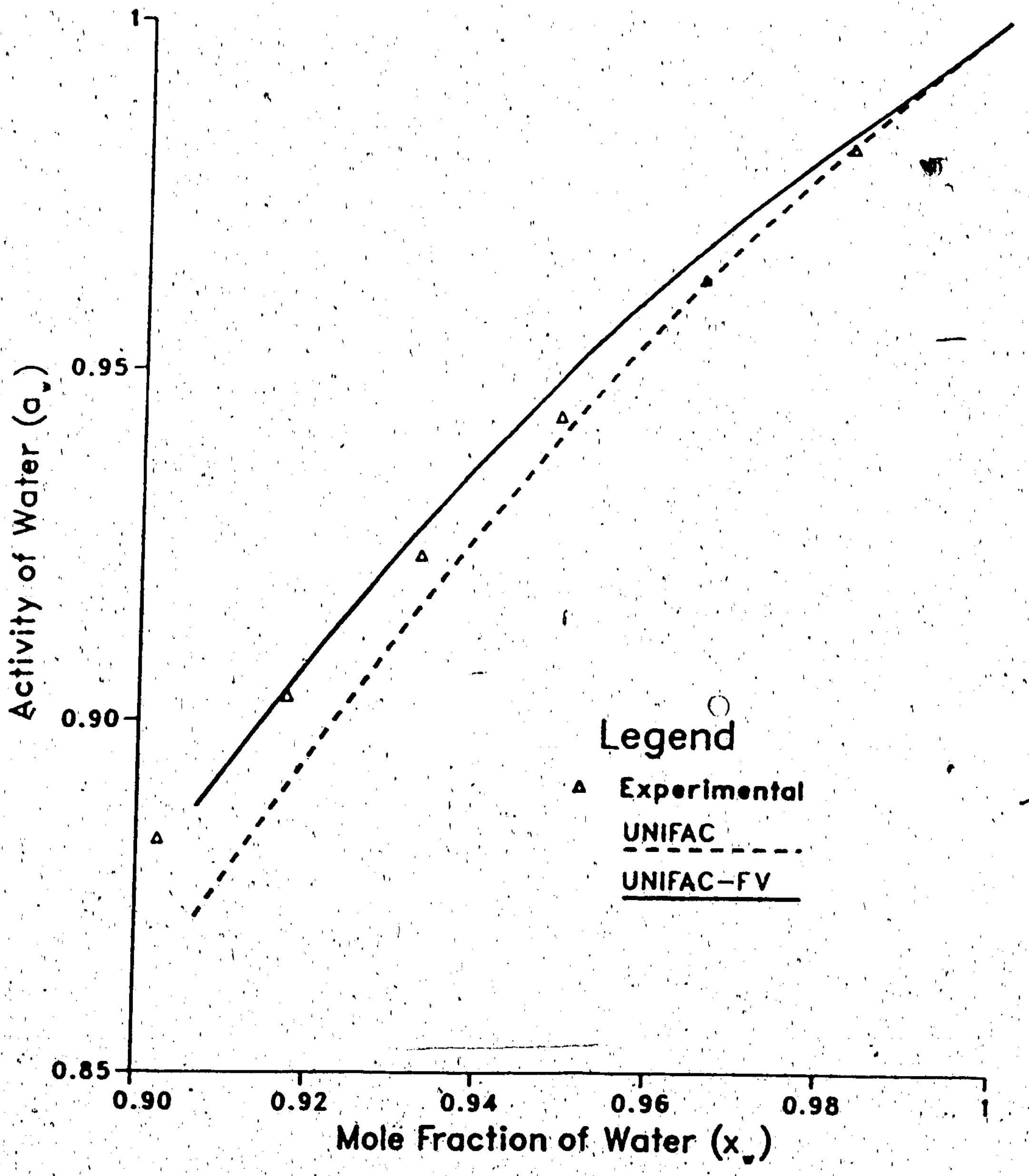


Figure 4.13 The experimental and predicted values of the activity water at 25°C. The experimental values were obtained from the osmotic coefficient data of Stokes and Robinson (1966). The predicted values were generated using the UNIFAC-FV model (Eq. 3.77) and the new values of the parameters presented in Table 4.4.

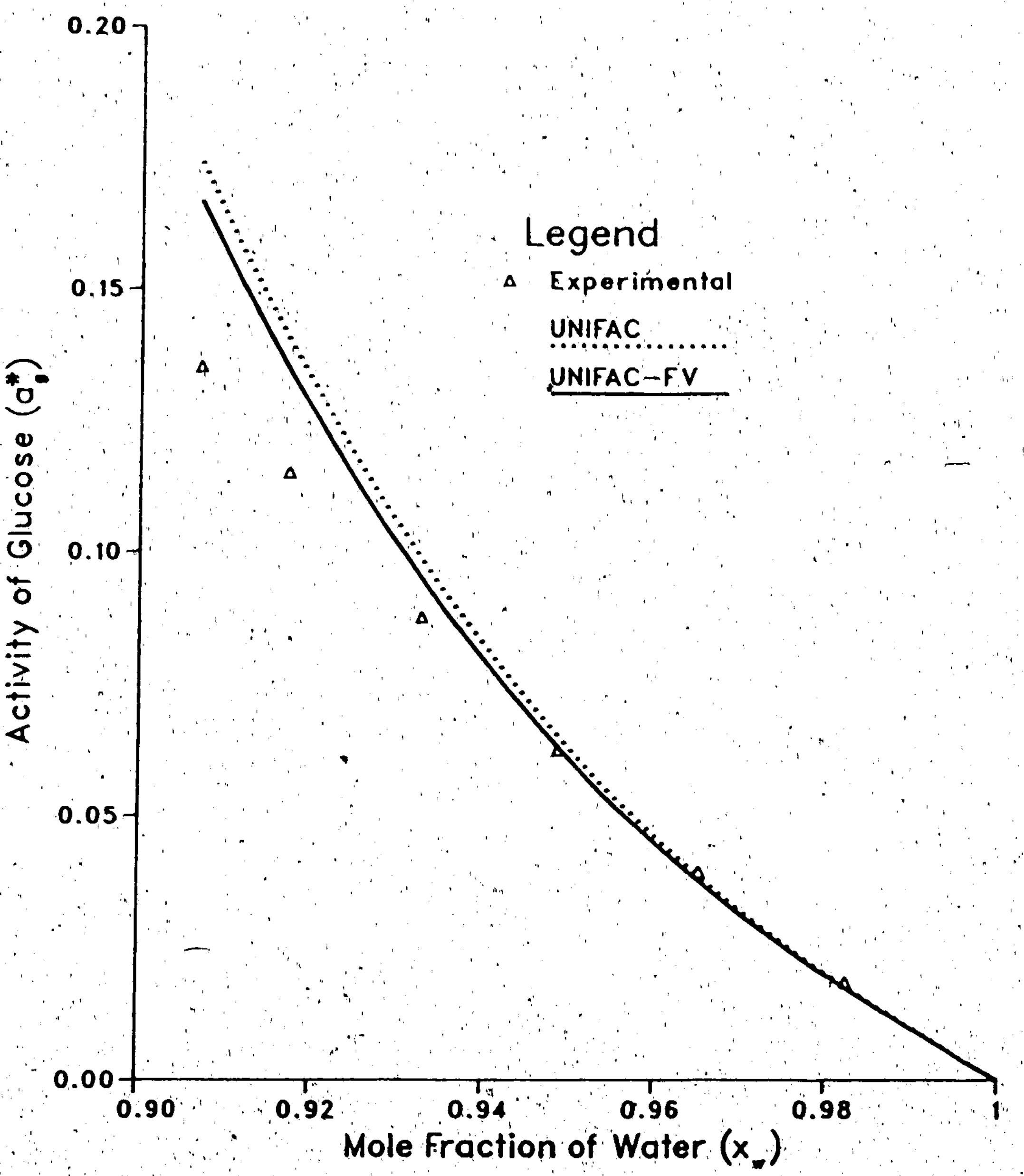


Figure 4.14 The experimental and predicted values of the activity of glucose at 25°C. The experimental values were obtained by applying the Gibbs-Duhem equation to the osmotic coefficient data of Stokes and Robinson (1966). The predicted values were generated using the UNIFAC-FV model (Eq. 3.77) and the new values of the parameters presented in Table 4.4.

As can be seen in Figures 4.15 and 4.16 the agreement between the experimental and predicted values of the excess partial molar entropies is poor with a high average error (49% for water and 22% for glucose) over the concentration range shown, although the general shape of the $T\bar{s}^E$-x curves can be considered valid. For water, the free-volume correction is necessary to get the proper behavior of the predicted $T\bar{s}_w^E$-x_w curve in the concentrated glucose solution. It appears the the model with the new parameters give good estimates of excess partial molar enthalpies for both glucose and water (Figures 4.17 and 4.18). The average errors on the estimates are 3% for water and 2% for glucose over the entire concentration (x_w) range of 0.9 to 1.0. It thus gives enough evidence that the new parameter values, which were indeed necessary to describe the interaction between OH and H_2O in an aqueous environment, lead to considerable improvements in the predictions.

The poor prediction of activity coefficients appears to arise from the model's inability to describe accurately the entropic contribution which depends on the size and shape of the constituent molecules. This probably stems from the fundamental assumption of the model that the functional groups (CH_2, CH, OH, etc.) behave identically no matter which molecule they come from. This assumption of the absence of influence of the neighboring groups is seldom valid and is particularly so in case of polar molecules. As stated by Skjold-Jørgensen *et al*. (1982), the UNIFAC model, based on solution-of-groups concept simplifies matter too

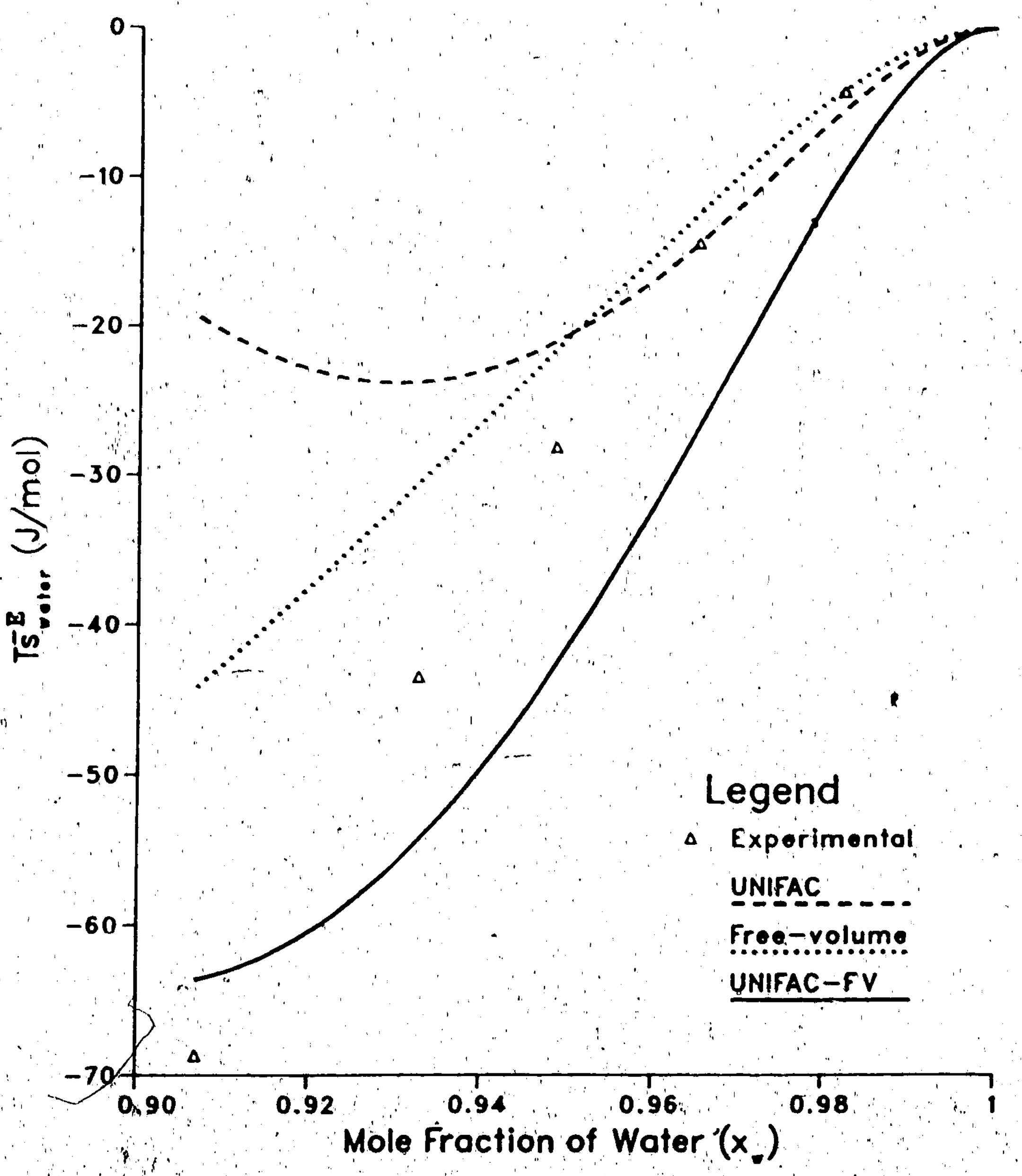


Figure 4.15 The experimental and predicted values of the excess partial molar entropy of water at 25°C. The experimental values were obtained from the data of Taylor and Rowlinson (1955); Stokes and Robinson (1966). The predicted values were generated using the combinatorial part of the UNIFAC-FV model (Eq. 3.77) and the new values of the parameters presented in Table 4.4.

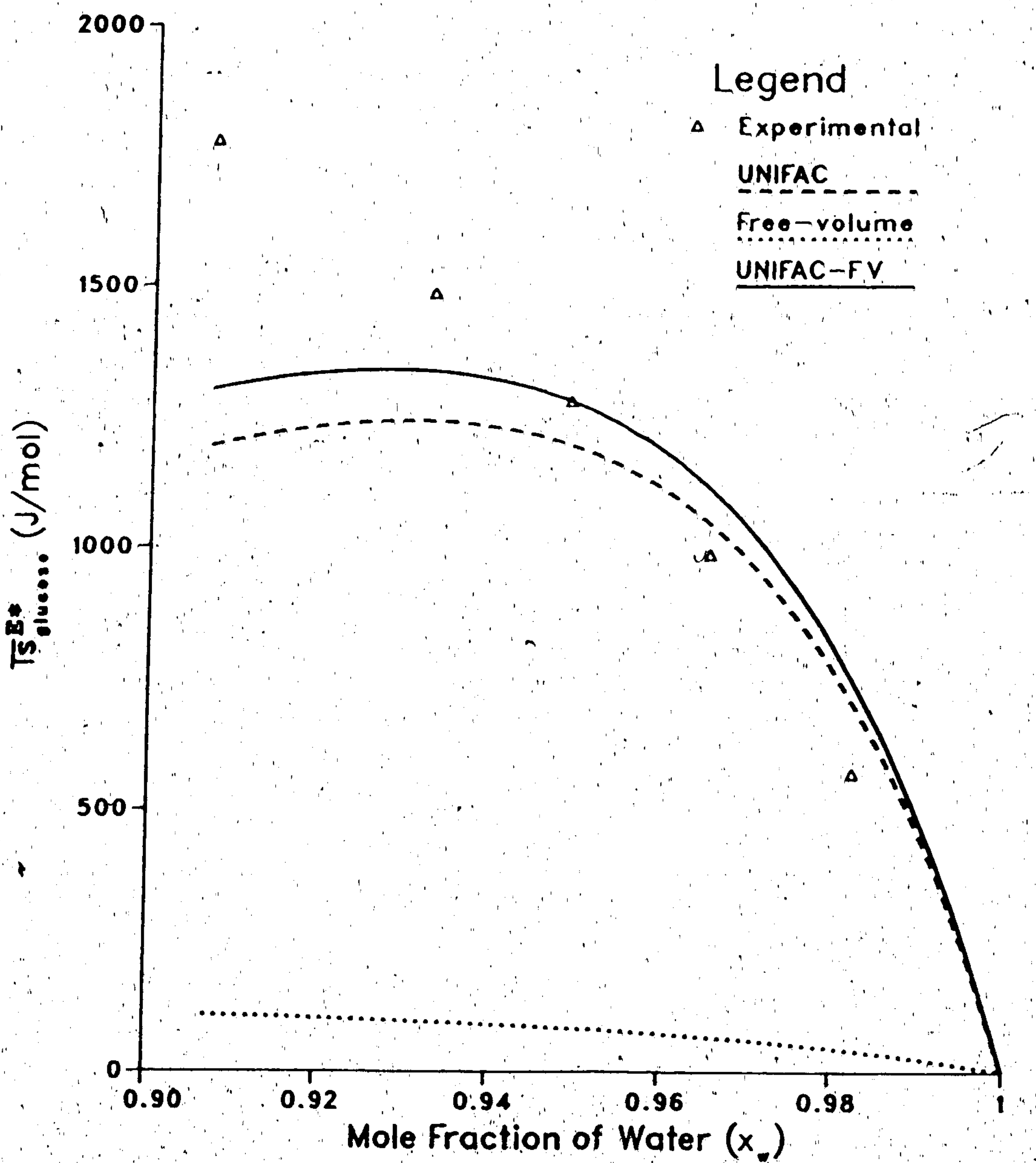


Figure 4.16 The experimental and predicted values of the excess partial molar entropy of glucose at 25°C. The experimental values were obtained from the data of Taylor and Rowlinson (1955); Stokes and Robinson (1966). The predicted values were generated using the combinatorial part of the UNIFAC-FV model (Eq. 3.77) and the new values of the parameters presented in Table 4.4.

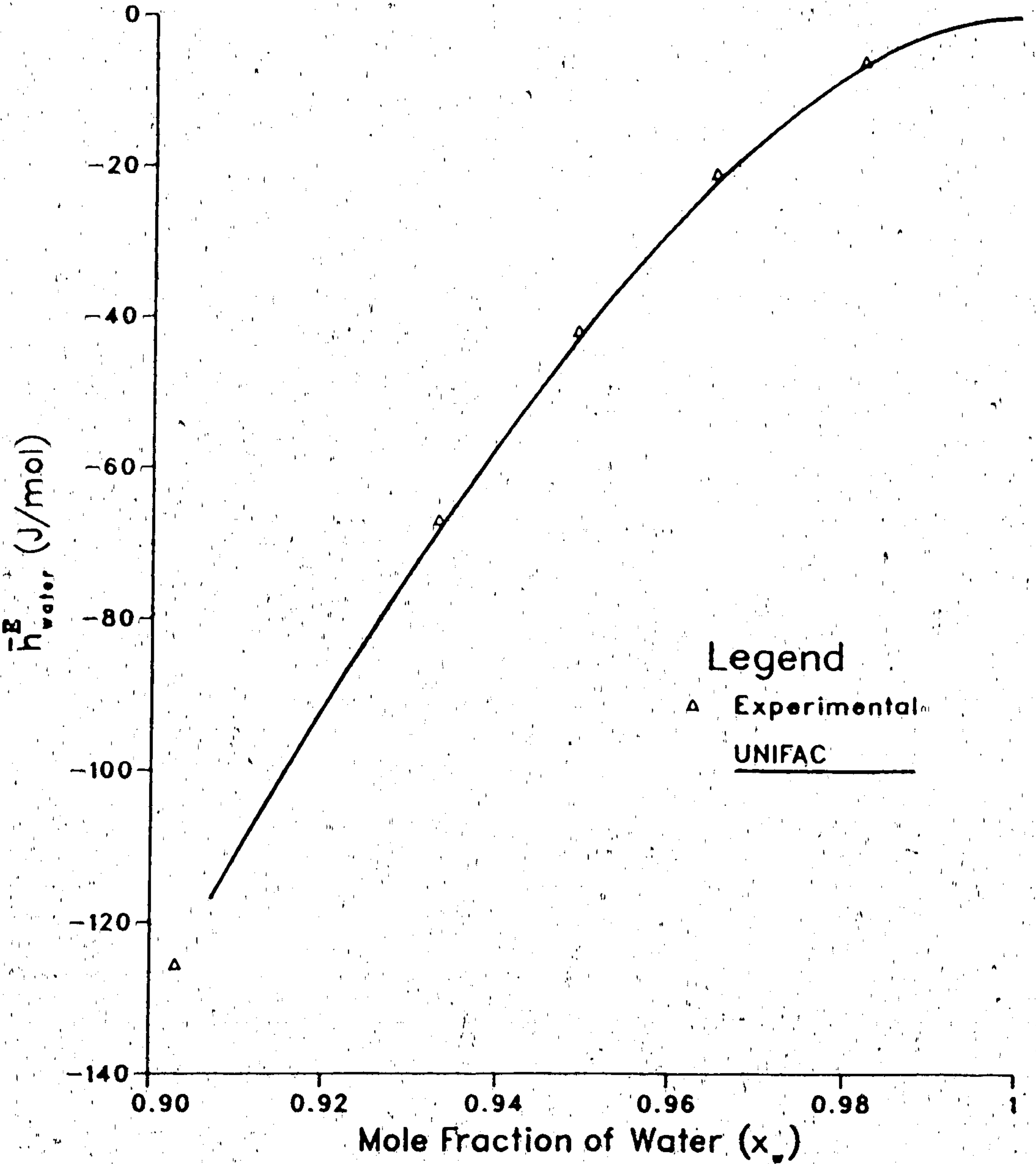


Figure 4.17 The experimental and predicted values of the excess partial molar enthalpy of water at 25°C. The experimental values were obtained from the data of Taylor and Rowlinson (1955). The predicted values were generated using the residual part of the UNIFAC-FV model (Eq. 3.77) and the new values of the parameters presented in Table 4.4.

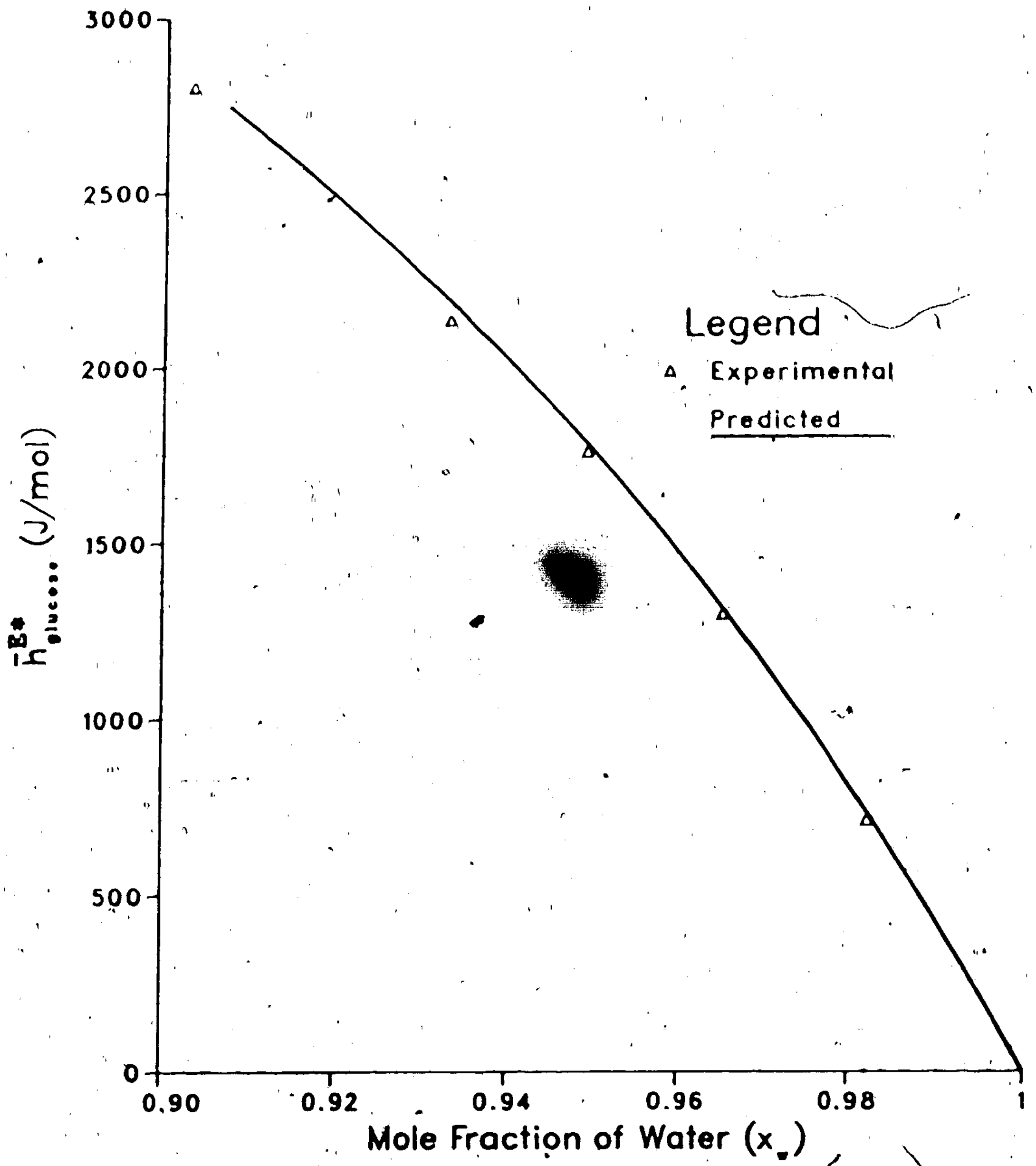


Figure 4.18 The experimental and predicted values of the excess partial molar enthalpy of glucose at 25°C. The experimental values were obtained from the data of Taylor and Rowlinson (1955). The predicted values were generated using the residual part of the UNIFAC-FV model (Eq. 3.77) and the new values of the parameters presented in Table 4.4.

radically. The model has no provision to describe the 'proximity effects', i.e., the fact that two strongly polar groups situated on two neighboring carbon atoms will have different properties than if the groups are spaced far apart (Fredenslund and Rasmussen, 1985). Sugar molecules are polar and in aqueous solution the solvation effects contribute significantly to the conformational free energies of these molecules. Solvation structures exist in such solution, the detailed properties of which are intimately related to the spatial and orientational correlations between hydrogen bonding sites of the solute and solvent molecules (Frank, 1983). The non-idealities, according to Skjold-Jørgensen *et al.* (1982), often arise from such specific interactions as solvation and association and the model in its original form has no provision to describe such stereospecific effects. Fredenslund and Rasmussen (1985) attempted to account for association and solvation by introducing empirical parameters ('α' for association and 'β' for solvation) in the model 'SUPERFAC'. This effort has been abandoned in view of the fact that the association parameter 'α' was found to be system-dependent instead of being a 'pure-group' property and the solvation parameter 'β' was found to yield erratic prediction of multicomponent phase behavior from parameters based on binary information only. The primary reason of such failures is that the parameters are empirical in nature since, according to Franks (1983), there is no theoretical approach from which the orientation-specific or even orientation-averaged interactions might be calculated and compared with measured thermodynamic excess functions.

The results of this study indicate that the new values of the parameters have led to substantial improvements in the predictive power of the UNIFAC-FV model. The model with the new parameters was applied to estimate the equilibrium properties of a number of aqueous carbohydrate systems. The general applicability of the model in the computation of the equilibrium properties is evaluated in the next chapter.

4.4 General Remarks

The UNIFAC-FV model, inspite of its serious limitations, is able to perform satisfactorily in estimating the thermodynamic properties of the components in aqueous glucose solution. The model is, however, far from being complete and further refinements are undoubtedly necessary in order to improve its predictive power by taking into account the specific interactions such as association and solvation. It is hoped that the developments in molecular physics and solution modelling will eventually lead to an unified and general model for aqueous solution based on 'solution-of-groups' concept.

5. PREDICTION OF EQUILIBRIUM PROPERTIES

The UNIFAC-FV model with the revised parameters was employed to test its power as a predictive tool in estimating the equilibrium properties of a number of sugar solutions. The three different systems studied were:

a. Glucose-water system.
b. Mannitol-water system.
c. Aqueous solutions of fructose and three common dissacharides found in food systems.
d. Aqueous solutions of mixtures of sugars.

5.1 Application to Glucose-Water System

The group composition and the parameter values used in the computation of equilibrium properties of aqueous glucose solutions were those presented in the previous chapter (Tables 4.2-4.4)

5.1.1 The Variation of the Activity Coefficient with Temperature

The activity coefficient of water and glucose were estimated at two different temperatures (25° and 65°C) and were compared with the experimental values reported by Taylor and Rowlinson (1955). The results are illustrated in Figures 5.1 and 5.2. In both cases (water and glucose), it was observed that the model can predict the temperature variation, although the fit with the experimental data was not satisfactory. In the light of what has been discussed in

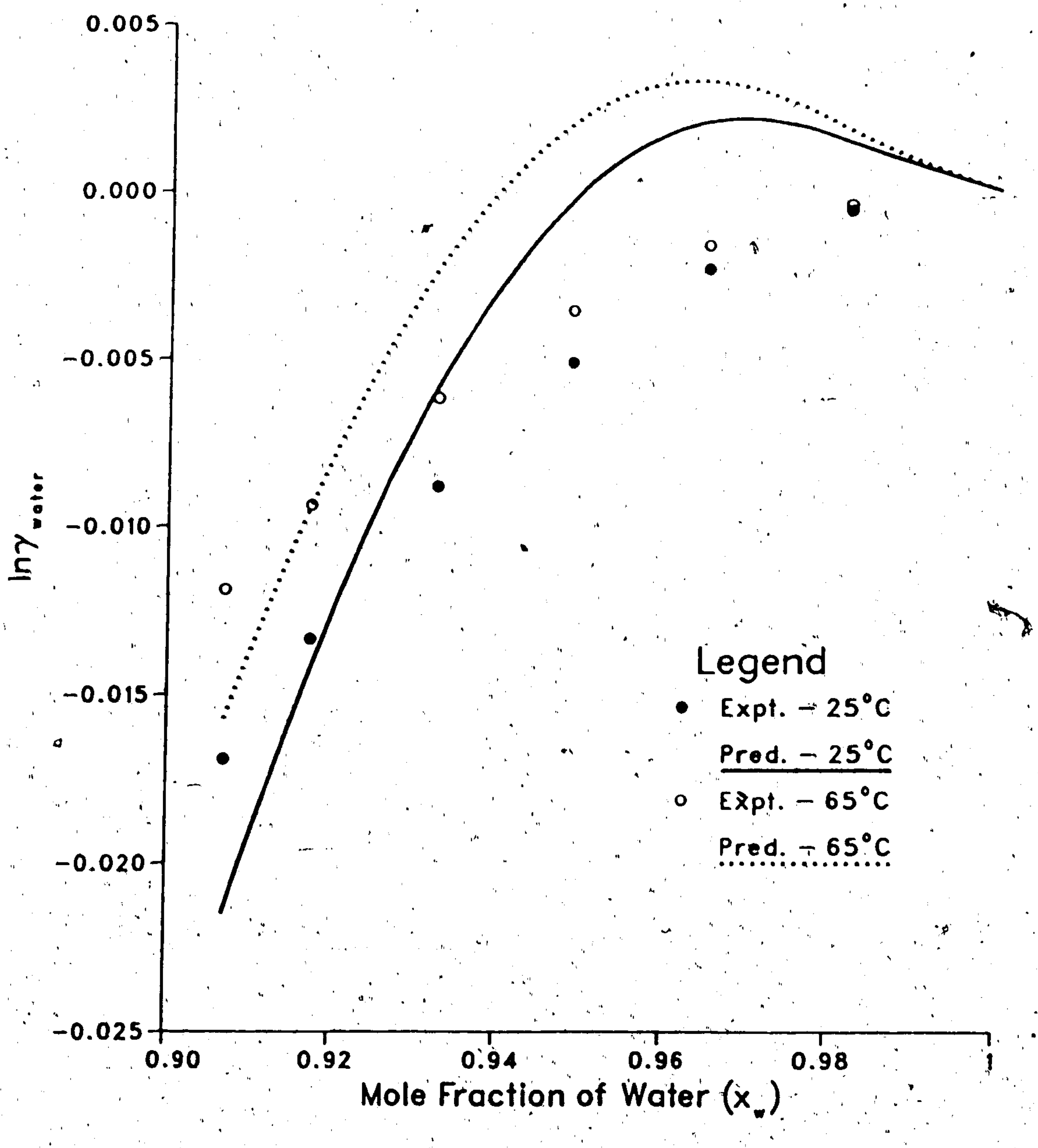


Figure 5.1 The variation of the activity coefficient of water with temperature. The experimental values were obtained from the vapor pressure data of Taylor and Rowlinson (1955).

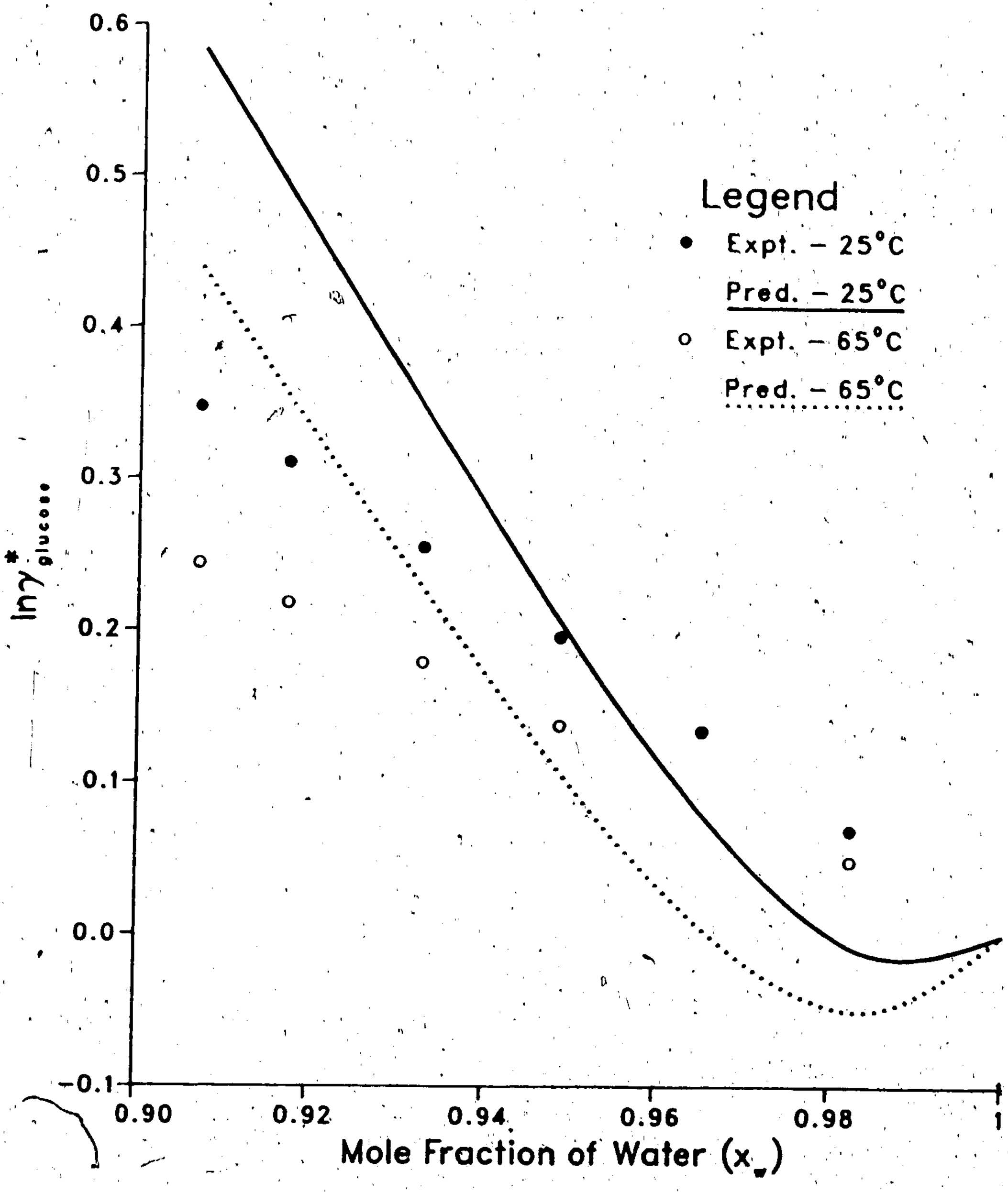


Figure 5.2 The variation of the activity coefficient of glucose with temperature. The experimental values were obtained by applying the Gibbs-Duhem equation to the vapor pressure data of Taylor and Rowlinson (1955).

the previous chapter and illustrated in Figures 4.16 and 4.17, this lack of fit with the experimental data results from the inability of the model to describe accurately the entropic contribution to the activity coefficients. The extent of estimated temperature variation was found to be similar to that observed experimentally. The divergence between the two predicted curves (at 25° and 65°C) increases with an increase in glucose concentration. This is in agreement with the experimentally observed behavior (Figures 5.1 and 5.2). It is therefore expected that an improvement in the estimation of the activity coefficient will lead to a better prediction of its temperature variation.

5.1.2 Prediction of Freezing Points

The depression of the freezing point of a solvent is a strong function of the intermolecular forces between solute and solvent. The fundamental thermodynamic equation that governs the equilibrium between two phases (solid ice and liquid water) at a particular temperature and pressure is given by:

$$f_w^s = f_w^o \qquad [5.1]$$

where,

f_w^s = fugacity of pure ice

f_w^o = fugacity of pure liquid water

When a solute is added to the system and if it dissolves only in the liquid phase, then the fugacity of the solvent water will be lowered, i.e.,

$$f_w < f_w^o \qquad [5.2]$$

For equilibrium to reestablish, f_w^s must also decrease. This can be achieved by decreasing the temperature. The fugacity of the liquid solvent is decreased by a drop in temperature as well as by the addition of the solute (Klotz and Rosenberg, 1974). However, the equilibrium is reestablished if

$$df_w^s = df_w^o \qquad [5.3]$$

and once the equilibrium is reached, we get

$$f_w^s = f_{w\ (\text{in solution})} \qquad [5.4]$$

$$\text{or,}\ f_w^s = \gamma_w x_w f_w^o \qquad [5.5]$$

where,

x_w = mole fraction of water

γ_w = liquid phase activity coefficient of water

f_w^o = standard state fugacity of water to which γ_w refers.

The standard state fugacity (f_w^o) is the fugacity of the pure liquid subcooled water at the freezing temperature.

It follows from equation (5.5) that the liquid phase activity of water is given by:

$$a_v = \frac{f_v^s}{f_v^o} \qquad [5.6]$$

The ratio of the fugacities can be calculated from the equation (Hildebrand and Scott, 1962):

$$\ln\frac{f_v^s}{f_v^o} = -\frac{\Delta h_f}{R}\left[\frac{T_f - T}{T_f T}\right] + \frac{\Delta C_f}{R}\left[\frac{T_f - T}{T_f T} - \ln\frac{T_f}{T}\right] \qquad [5.7]$$

where,

Δh_f = heat of fusion of water at freezing point (J/mol)

R = universal gas constant (J/mol K)

T_f = freezing point of water (K)

ΔC_f = change of specific heat upon fusion (J/mol K)

Therefore, the liquid phase activity of water is given by

$$\ln a_v = -\frac{\Delta h_f}{R}\left[\frac{T_f - T}{T_f T}\right] + \frac{\Delta C_f}{R}\left[\frac{T_f - T}{T_f T} - \ln\frac{T_f}{T}\right] \qquad [5.8]$$

All the parameters except the temperature (T) on the right-hand side of equation (5.8) are known for water.

The freezing points of glucose solution at various concentrations were estimated by an iterative approach using the IMSL subroutine 'ZSCNT'. The freezing point is the temperature at which the activity of water (a_v) estimated by the UNIFAC-FV model converges with the a_v value determined from equation (5.8). Good agreement with the experimental data (CRC, 1983-1984) was observed with an average error of less than 7% over the concentration range shown in Figure 5.3.

5.1.3 Prediction of Solubility

As stated by Prausnitz *et al.* (1986), the solubility of a chemical substance is strongly influenced by intermolecular forces between solute and solvent. Other factors also play a large role in determining the solubility.

The thermodynamic equation of equilibrium for two phases that exists at the solubility limit is given by:

$$f_{2\,(\text{pure solid})} = f_{2\,(\text{solute in solution})} \qquad [5.11]$$

$$\text{or, } f_{2\,(\text{pure solid})} = \gamma_2 x_2 f_2^{\circ} \qquad [5.12]$$

where,

x_2 = solubility (mole fraction) of the solute in solution

γ_2 = liquid phase activity coefficient of the solute

f_2° = standard state fugacity of the solute to which γ_2 refers.

From equation (5.12) we get

$$x_2 = \frac{f_{(\text{pure solid})}}{\gamma_2 f_2^{\circ}} = \frac{f_2^{s}}{\gamma_2 f_2^{\circ}} \qquad [5.13]$$

As can be seen in equation (5.7), the solubility of a compound not only depends on the activity coefficient but

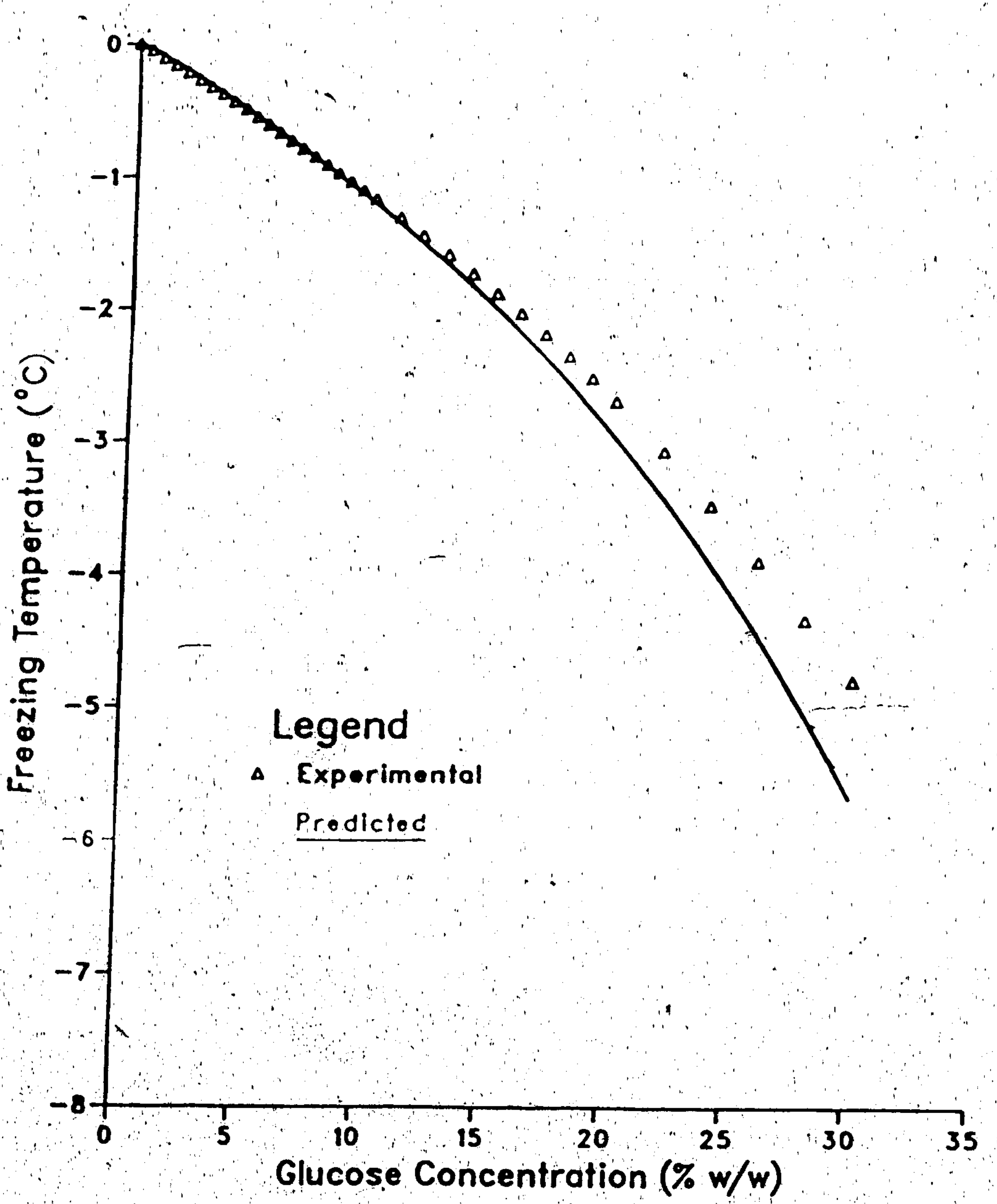


Figure 5.3 The experimental and predicted values of the freezing temperature of glucose solutions. The experimental values were obtained from the CRC (1983-1984) tables on freezing point depression.

also on the ratio of the two fugacities (f_2^s/f_2^o). Although the choice of the standard state is arbitrary, it is convenient to define the standard state fugacity (f_2^o) as the fugacity of the pure, subcooled liquid at the temperature of the solution at some specified pressure.

The two fugacities (f_2^s and f_2^o) in equation (5.13) are independent of the nature of the solvent and can be calculated (by following a thermodynamic cycle) from the equation similar to (5.7)(Prausnitz *et al.*, 1986):

$$\ln\frac{f_2^s}{f_2^o} = -\frac{\Delta h_f}{R}\left[\frac{T_t - T}{T_f T}\right] + \frac{\Delta C_f}{R}\left[\frac{T_t - T}{T_f T} - \ln\frac{T_f}{T}\right] \qquad [5.14]$$

where,

Δh_f = enthalpy of fusion of the solute at triple point (J/mol)

R = universal gas constant (J/mol K)

T_t = triple point temperatures of the solute (K)

ΔC_f = change in specific heat upon fusion (J/mol K)

The first term on the right-hand side of equation (5.14) is dominant; the remaining two, of opposite sign, have a tendency to approximately cancel each other, especially if the temperature (T) of the solution is not far from the triple-point (T_t). Since there is very little difference between the triple point and the normal melting point for most substances, it is a common practice to substitute the normal melting temperature (T_m) for the triple point temperature (T_t). Therefore, according to Prausnitz *et al.* (1986), it is sufficient in many cases to calculate the fugacity ratio using the following equation:

$$\ln\frac{f_2^s}{f_2^o} = -\frac{\Delta s_f}{R}\left[\frac{T_m}{T} - 1\right] \qquad [5.15]$$

where,

Δs_f = entropy of fusion of the solute (J/mol K)

Equation (5.13) then reduces to

$$x_2 = \frac{1}{\gamma_2}\left[\exp\{-\frac{\Delta s_f}{R}(\frac{T_m}{T} - 1)\}\right] \qquad [5.16]$$

$$\text{or, } a_2 = \exp\left[-\frac{\Delta s_f}{R}\{\frac{T_m}{T} - 1\}\right] \qquad [5.17]$$

If the entropy of fusion (Δs_f), the melting temperature and activity coefficient of the solute (γ_2) are known, its solubility can be estimated from equation (5.16).

The melting temperatures of different tautomers of glucose are available in the literature (CRC, 1983) and the activity coefficient of glucose (γ_g) can be calculated using the UNIFAC-FV model; but the entropy of fusion of glucose tautomers are not available in the published literature and therefore need to be estimated.

A. Estimation of the Entropy of Fusion of Glucose Tautomers

The entropy of fusion of glucose tautomers were determined using the Simplex search technique (Toupin, 1986). The objective function used was of the form:

$$\chi^2 = \sum_i W_i \left[x_g^{\text{Expt.}} - x_g^{\text{Pred.}} \right]^2 \qquad [5.18]$$

The predicted value of the solubility limit of glucose ($x_g^{\text{Pred.}}$) was obtained by an iterative method using the equation:

$$a_g - x_g\gamma_g = 0 \qquad [5.19]$$

The activity of glucose (a_g) was obtained from the equation (5.17) for a given value of Δs_f and γ_g was calculated using the UNIFAC-FV model. The IMSL subroutine 'ZREAL1' was used to obtain the value of x_g by iteration. The experimental values of the solubility limit ($x_g^{\text{Expt.}}$) of glucose tautomers at different temperatures published by Young (1957) were used in the optimization. The estimated values of the entropy of fusion together with the associated errors are presented in Table 5.1. Since the melting temperatures of α- and β-glucose differs only by 4°, their crystal structures are expected to be similar. The density of α-glucose crystals is 1.563 g/cm^3 (McDonald and Beevers, 1950) and that of β-glucose is 1.535 g/cm^3 (Ferrier, 1960). The activity coefficients of these two isomers refer to the same standard state i.e. pure, subcooled liquid glucose with the group composition shown in Figure 4.2. Therefore, the difference in the entropy of fusion (Table 5.1) appears to be due to the differences in the melting temperature which apparently arises from minor differences in the crystal structure of the two isomers. Glucose monohydrate has a much higher entropy of fusion compared with the values for α- or

Table 5.1 The melting temperatures and the estimates of the entropy of fusion of α-glucose, β-glucose and glucose monohydrate.

Anomer	Melting Temperature (°C)	Entropy of Fusion (J/mol K)	
		Estimated Value[a]	Standard Error
α-Glucose	146	19.31	0.37
β-Glucose	150	14.53	0.29
Glucose Monohydrate	86	47.43	0.99

[a] Determined by the Simplex optimization technique.

β-glucose. Greater dissimilarity in the crystal structure of monohydrate compared to α- or β-isomers of glucose might have contributed to this high Δs_f value. Unlike the crystals of α- and β-glucose which have four molecules per unit cell (McDonald and Beevers, 1950, 1952; Ferrier, 1960, 1963; Chu and Jeffrey, 1968; Brown and Levy, 1979), glucose monohydrate has two molecules per unit cell (Killean *et al.*, 1962). The density of the crystals is 1.512 g/cm^3. The difference in crystal structures is also reflected in the melting temperatures of monohydrate and the two isomers of glucose (Table 5.1). The melting temperature of glucose monohydrate is much lower than those of α- and β-glucose. It therefore seems reasonable to obtain a higher value of entropy of fusion for glucose monohydrate.

The solubility limit of the glucose tautomers at different temperatures were then predicted using the UNIFAC-FV model, equations (5.17) and (5.19) and estimated entropies of fusion. The results are presented in Figure 5.4. The solubility limits of α- and β-glucose were predicted with an average error of 12% and 10% respectively over the temperature range shown in Figure 5.4 whereas, the average error for glucose monohydrate was close to 24%. Further refinement of the model is expected to lead to better predictions of the solubility limit.

One advantage of having a suitable model for prediction of the activity coefficients is that it provides a method for the estimation of the entropy of fusion of sugar molecules, which are difficult to determine experimentally

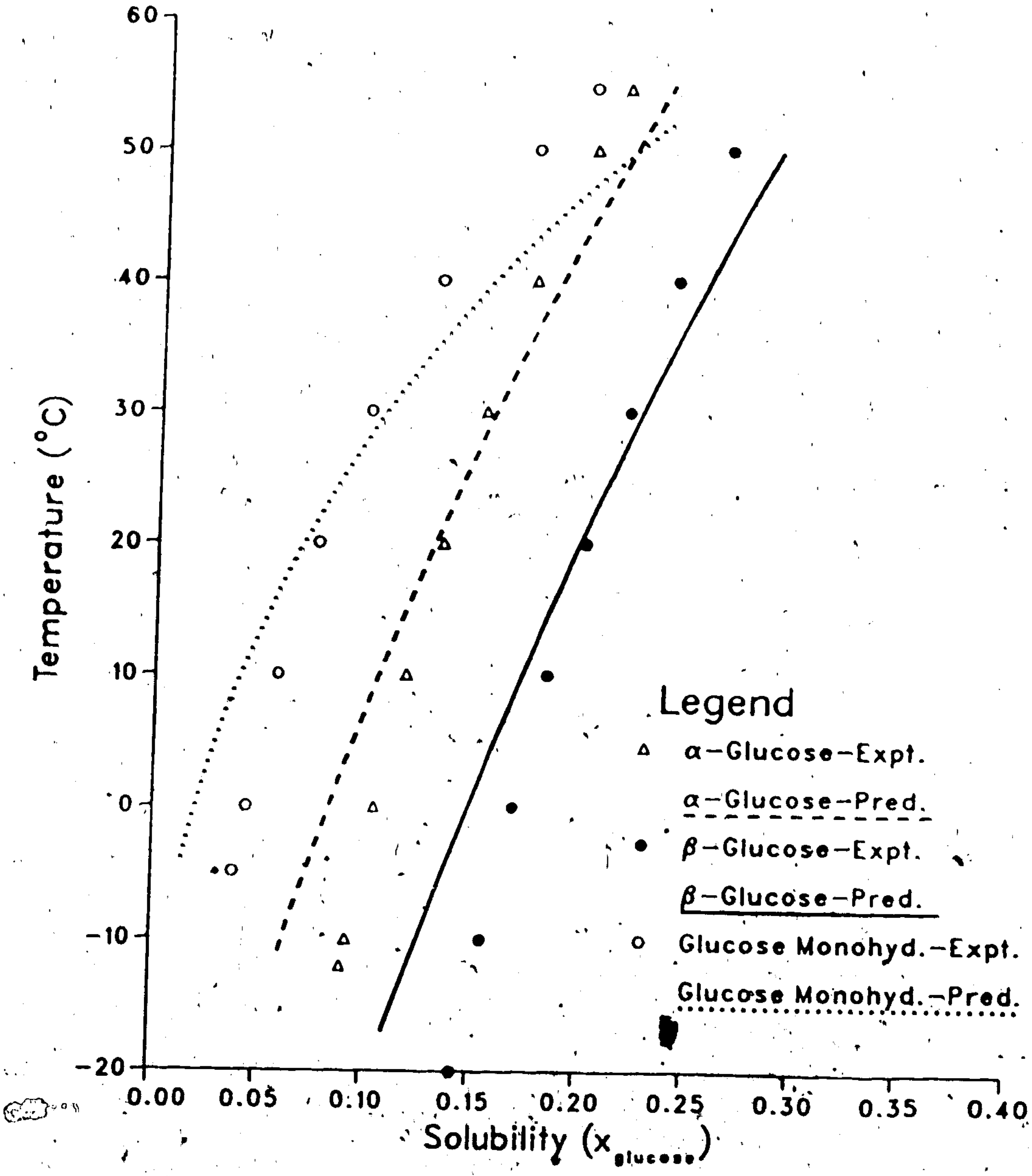


Figure 5.4 The experimental and predicted values of the solubility limit of α-glucose, β-glucose and glucose monohydrate. The experimental values were obtained from the solubility data of Young (1957).

since these molecules decompose before melting. This method will, however, require the information on the solubility limit at various temperatures.

5.1.4 Modelling of Solid Glucose - Water System

An attempt was made to estimate the activity of water (a_w) in a binary mixture of glucose crystals and water employing the UNIFAC model (Eq. 3.72) and the new parameters obtained in this study. It is difficult to conceive of a situation where a model (UNIFAC), developed for liquid mixtures can be applied to a solid-vapor system. As stated by Le Maguer (1985), the concept of solution can be extended to a mixture where water is scarce and the system as a whole has the appearance of solid if suitable assumptions (discussed below) are made.

Considering the 'group-contribution' approach of the UNIFAC model, it may not present any major difficulty if the group composition of the mixture can be estimated and if it is assumed that the characteristics of these groups are not altered with a change in the state of the molecules.

A. Experimental Data on Solid Glucose - Water System

The sorption data reported by Smith *et al.* (1981) were used to calculate the experimental value of the water activity at different temperatures (40, 45, 55, 65 and 75°C). The following equation was used to convert the partial pressure of water at different temperatures to the activity of water:

$$a_w = \left[\frac{P_w}{P_w^s} \right] \qquad [5.9]$$

where,

P_w = Equilibrium vapor pressure of water over the system at solution temperature.

P_w^s = Saturation vapor pressure of pure water at solution temperature.

The calculated values of the activity of water together with the reported value of partial pressure of water at different temperatures are presented in Table A1.11 (Appendix 1). The partial pressure values were generated from the sorption isotherms of glucose at different temperatures using an electronic digitiser.

B. Fundamental Assumptions and Group Composition

The crystals of α-D- and β-D-glucose are made up of unit cells of four molecules held together by a complex system of strong hydrogen bonds. All the five available hydrogen atoms per molecule are involved in the formation of intermolecular hydrogen bonds which are equally strong in all directions (McDonald and Beevers, 1950, 1952; Ferrier, 1960, 1963; Chu and Jeffrey, 1968; Brown and Levy, 1979). A pictorial representation of the unit cell is presented in Figure 5.5. Since all the OH groups are involved in binding the molecules together, it is resonable to speculate that such an arrangement in the unit cells presents a hydrophobic surface to the water molecules.

As elaborated by Le Maguer (1985), the following assumptions were made in extending the concept of solution

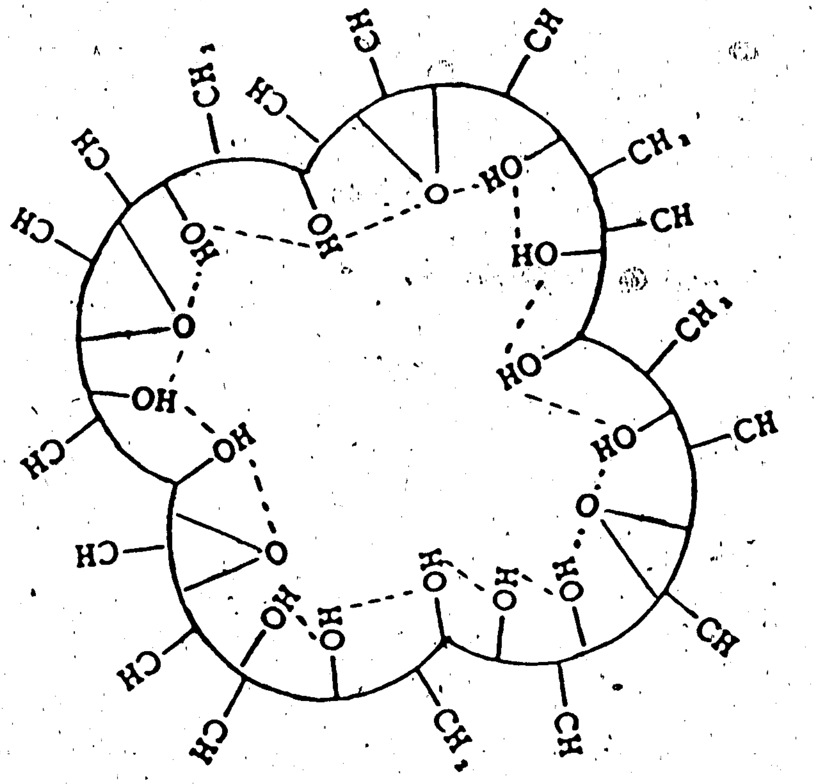


Figure 5.5 Pictorial representation of an unit cell of glucose crystal.

and employing the UNIFAC to the binary mixture of glucose crystal and water:

a. The water molecules and the unit cells of glucose crystal are considered as the components of the mixture.

b. The characteristics of the functional groups are the same in liquid and solid states.

c. The physical process of adding or removing a unit cell is equivalent to the infinitesimal mathematical increment.

d. All the unit cells making up the mixture have the same specific properties and therefore the observed extensive properties are simply proportional to the number of unit cells in the mixture.

The group-composition of the binary mixture is presented in the Table 5.2. All the functional groups constituting the unit cell are considered in the calculation of component's volume parameter ($r_{unit\ cell}$). But in the computation of the area parameter ($q_{unit\ cell}$) and the residual part of the activity coefficient ($\ln\gamma_i^R$) only the groups that are present on the surface of the unit cell which are able to interact are considered. It was found that the number of OH groups (ν_{OH}) available on the surface of interaction is a function of temperature and the concentration of water given by the equation:

$$\nu_{OH} = \exp\left[A + \frac{B}{T} + C \times w \right] \qquad [5.10]$$

where,

Table 5.2 The functional group composition of glucose crystal - water mixture.

Components	Functional Groups	Number of groups (ν_k) considered in the computation of component's Volume Parameter	Number of groups (ν_k) considered in the computation of component's Area Parameter
Unit cell of Glucose Crystal.	CH_2	4	4
	CH	16	16
	OH	20	$f(T,w)^a$
	CHO	4	0
Water	H_2O	1	1

[a] T = Temperature in K, w = Weight fraction of water.

w = Weight fraction of water

T = Temperature in K

A, B, C = optimized constants for the binary system of glucose crystal and water.

The optimized value of the parameters for OH group (viz., Q_{OH}, a_{OH,H_2O} and $a_{H_2O,OH}$) and the value of the parameters (R_k, Q_k, a_{mn}) for other groups presented in Table 4.2 and 4.3 were used in this computation. The constants A, B and S were determined by the Simplex search technique using the data in Table A1.10. The estimated value of the parameters together with the associated errors are presented in Table 5.3.

C. Prediction of Water Activity

The activities of water at different temperatures (40, 45, 55, 65 and 75°C) were estimated using the UNIFAC model (Eq. 3.72) and the revised values of the UNIFAC parameters shown in Table 4.4. The number of OH groups (ν_{OH}) available for interaction on the surface of the unit cell of glucose crystal was estimated using the equation (5.10) and the constants presented in Table 5.3. The estimated values of the water activity were converted to partial pressure of water using equation (5.9). The results presented in Figure 5.6 show good agreement with experimental values with an average error of less than 7% over the entire range of temperature (40-75°C) and concentration (w_w) of water (1.0×10^{-5}-11.0×10^{-5}).

An interesting feature of this study is that the number of available OH groups (ν_{OH}) per unit cell of glucose crystal increases with an increase in temperature and

Table 5.3 The estimates of the constants of the equation 4.25 that determines the number of OH groups available on the surface of the unit cell of glucose crystal at a particular temperature and water concentration.

Parameter	Estimated Value[a]	Standard Error
A	2.48	0.038
B	-506.18	12.667
C	1534.96	57.365

[a]Determined by the Simplex optimization technique.

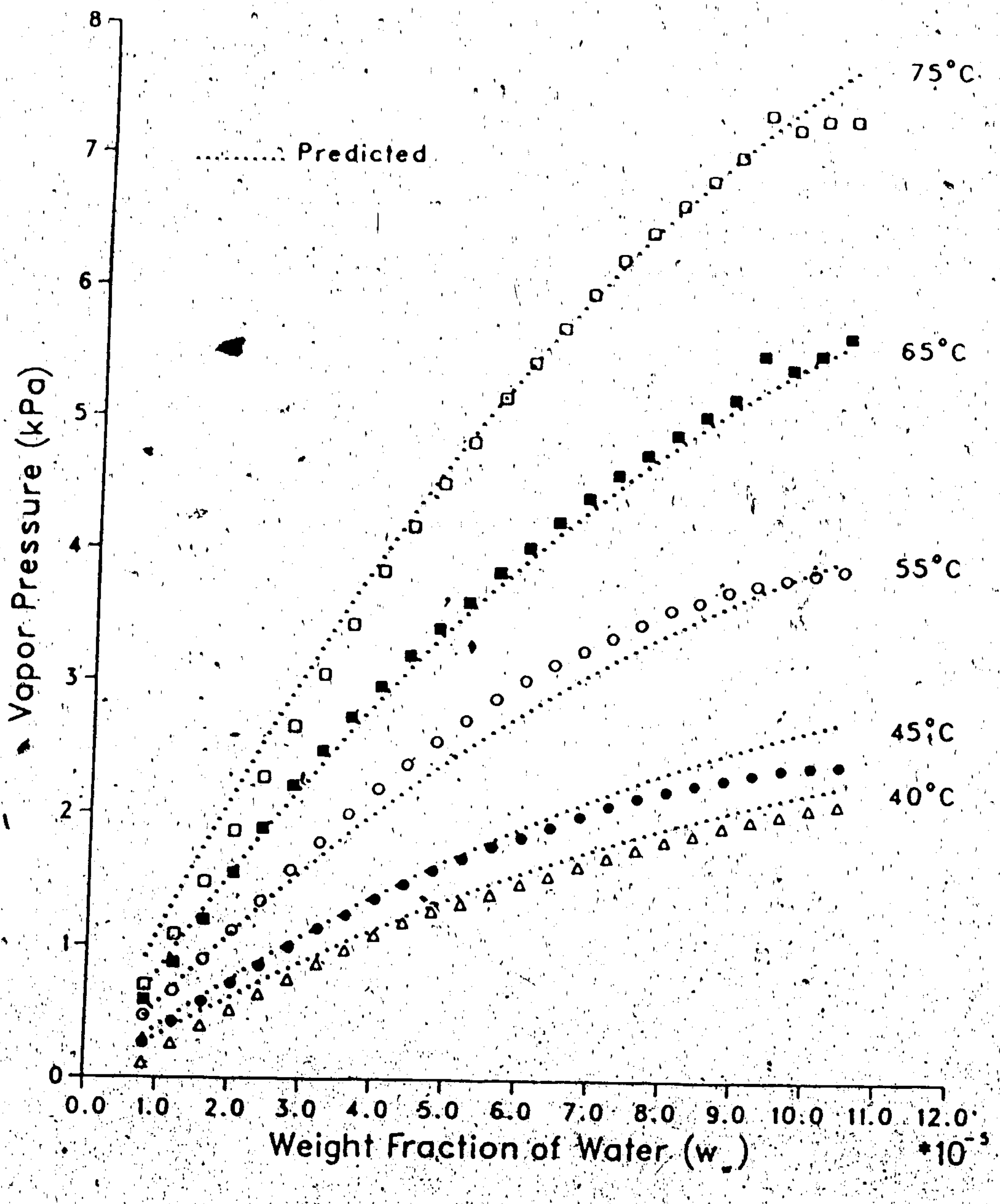


Figure 5.6 The experimental and predicted values of the vapor pressure of water in a binary system of glucose crystal and water. The experimental values were generated from the sorption isotherm of glucose reported by Smith *et al.* (1981) using an electronic digitiser.

concentration of water (w_w). This phenomenon can be compared with the "opening" of the unit cells of glucose crystal to form individual molecules before it goes into solution. An increase in temperature or water concentration induces breaking of the intermolecular hydrogen bonds thus making more OH groups available for interaction with water. This speculation, if found true, may provide a useful tool to estimate water sorption isotherm at very low water concentration if the crystal structure and the group composition of the solid under investigation are known.

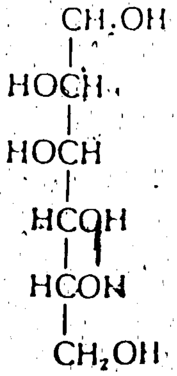
5.2 Application to Mannitol-Water System

The UNIFAC-FV model with the revised parameter values for the OH group was evaluated in terms of its predictive power to estimate the equilibrium properties of the mannitol-water system. The functional group composition of the binary mixture is presented in Table 5.4. The values of the group volume (R_k), area (Q_k) and interaction parameters used in the calculation were those reported by Gmehling *et al.* (1982), except the revised values of Q_{OH}, a_{OH,H_2O} and $a_{H_2O,OH}$ determined in this study. The molar volume of mannitol was estimated using the Le Bas additive method. The values of the free-volume parameters used were those shown in Table 4.4 (Chapter 4).

5.2.1 Prediction of Water Activity

The activity of water (a_w) in aqueous mannitol solutions was predicted and compared with experimental

Table 5.4 The functional group composition of the binary system of mannitol and water together with their volume and area parameters (Parameter values from: Gmehling *et al.*, 1982)



D-Mannitol[a]

Components	Functional Groups	Number of Groups (ν_k)	Volume Parameter (R_k)	Area Parameter (Q_k)
	CH_2	1	0.6744	0.540
Mannitol	CH	3	0.4469	0.228
	OH	5	1.0000	1.097[b]
Water	H_2O	1	0.9200	1.400

[a] Structure adapted from Lehninger (1978).

[b] Determined in this study

values reported by Robinson and Stokes (1961). The result of the prediction is illustrated in Figure 5.7. The model provides good estimates of a_w with an average error of 0.2% over the concentration range shown in Figure 5.7.

5.2.2 Prediction of Freezing Point

The freezing points of aqueous mannitol solutions were estimated using the procedure elaborated in section 5.1.2. The result of the prediction illustrated in Figure 5.8 shows good agreement with the experimental data (CRC, 1983-1984). The average error over the concentration and temperature ranges studied (Figure 5.8) was less than 9%.

5.3 Application to Aqueous Solutions of Fructose and Disaccharides

In an attempt to evaluate the general applicability to carbohydrate systems, the UNIFAC-FV model with the revised parameter for the OH group was employed to estimate the equilibrium properties of the aqueous solutions of fructose and three disaccharides (sucrose, maltose and lactose) commonly found in food systems. The group composition of the sugar molecules are presented in Tables 5.5-5.8. The values of the group volume (R_k), area (Q_k) and interaction parameters used in the calculation were those reported by Gmehling *et al.* (1982), except the revised values of Q_{OH}, a_{OH,H_2O} and $a_{H_2O,OH}$ determined in this study. The molar volume of the constituent sugar molecules were estimated using the Le Bas additive method. The values of the free-volume

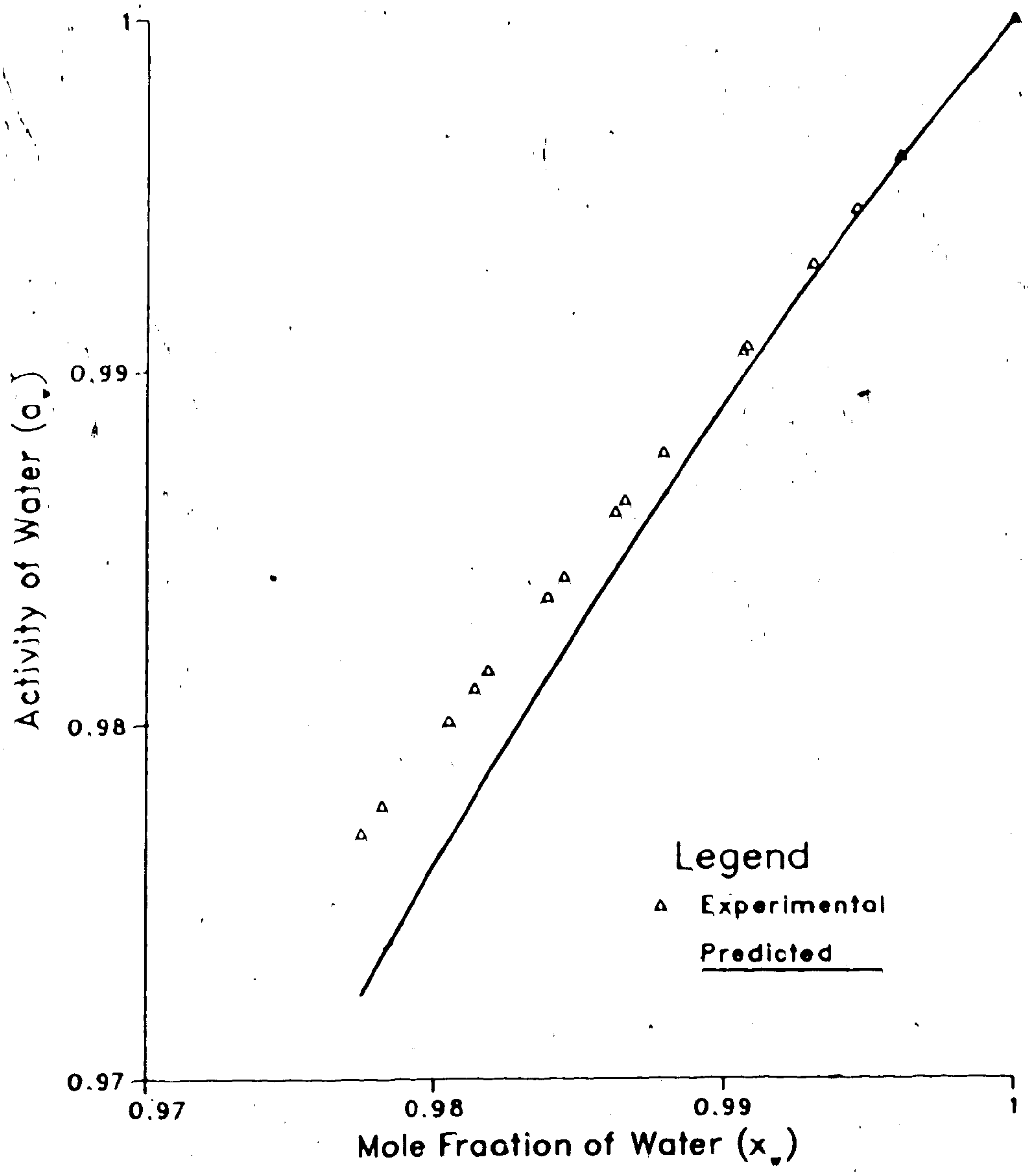


Figure 5.7 The experimental and predicted values of the activity of water in mannitol solutions at 25°C. The experimental values were generated from the osmotic coefficient data of Robinson and Stokes (1961).

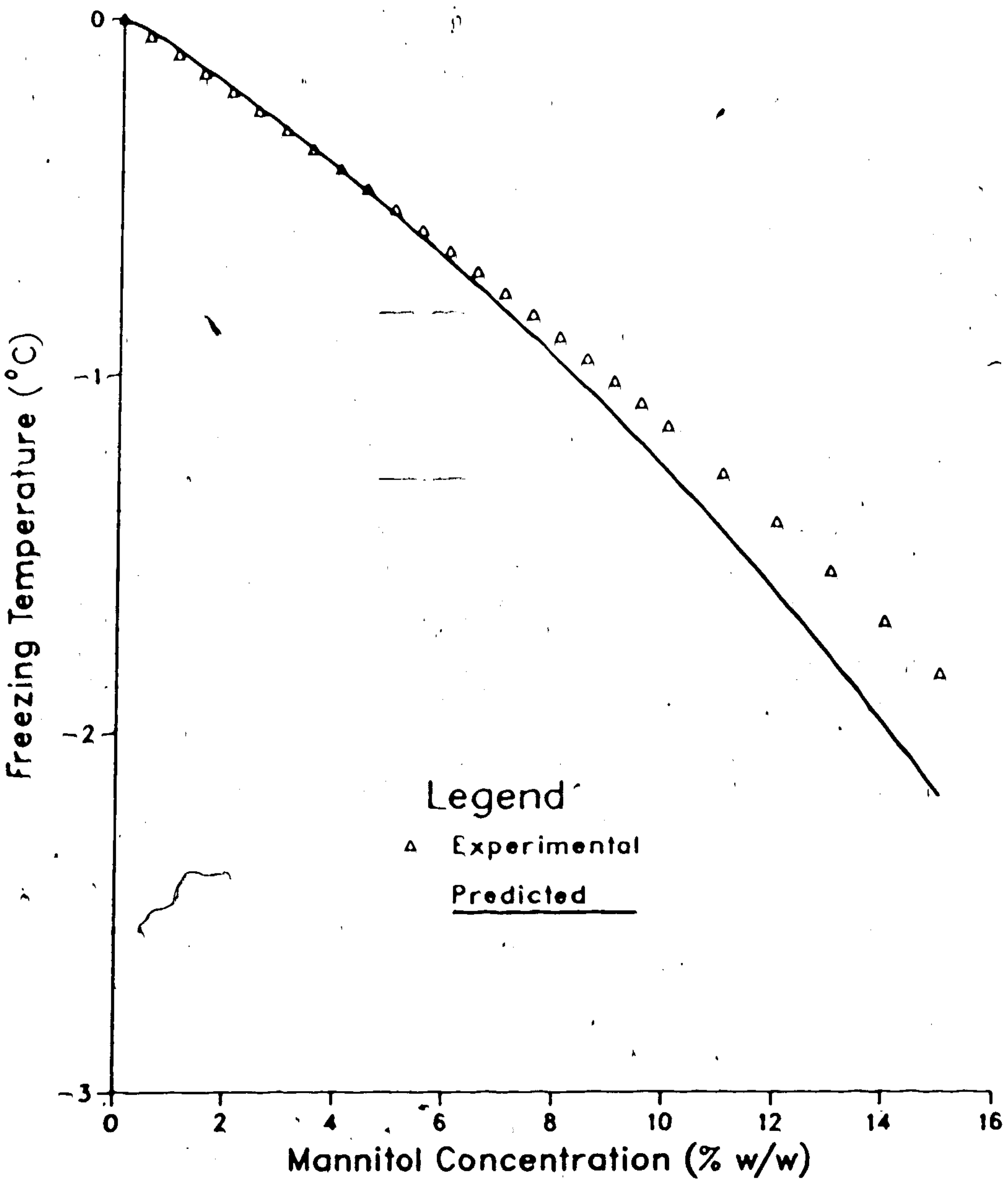
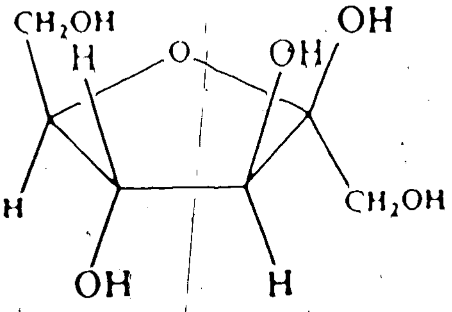


Figure 5.8 The experimental and predicted values of the freezing temperature of mannitol solutions. The experimental values were obtained from the CRC (1983-1984) tables on freezing point depression.

Table 5.5 The functional group composition of the binary system of fructose and water together with their volume and area parameters (Parameter values from: Gmehling *et al.*, 1982)



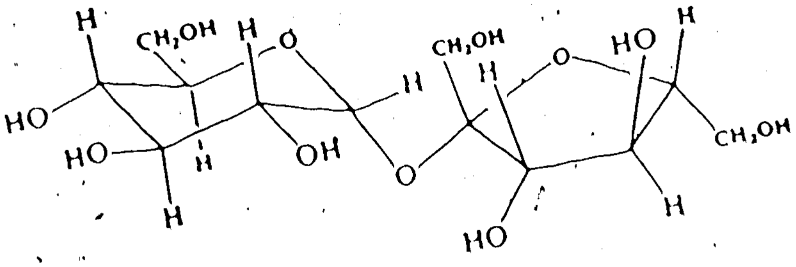
β-Fructose[a]

Components	Functional Groups	Number of Groups (ν_k)	Volume Parameter (R_k)	Area Parameter (Q_k)
Fructose	CH_2	1	0.6744	0.540
	CH	3	0.4469	0.228
	OH	5	1.0000	1.097[b]
	CH_2CO	1	1.4457	1.180
Water	H_2O	1	0.9200	1.400

[a] Structure adapted from Morrison and Boyd (1976).

[b] Determined in this study

Table 5.6 The functional group composition of the binary system of sucrose and water together with their volume and area parameters (Parameter values from: Gmehling *et al.*, 1982)



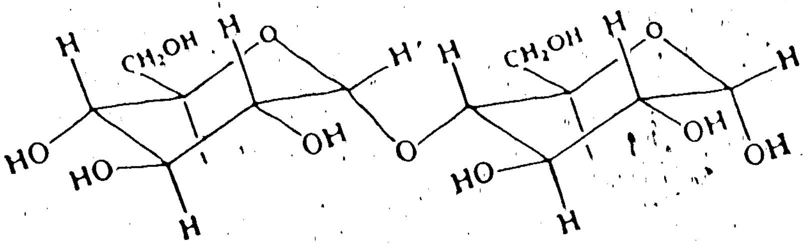
Sucrose[a]

Components	Functional Groups	Number of Groups (ν_k)	Volume Parameter (R_k)	Area Parameter (Q_k)
Sucrose	CH_2	2	0.6744	0.540
	CH	6	0.4469	0.228
	OH	8	1.0000	1.097[b]
	CH_2CO	1	1.4457	1.180
	CHO	2	0.9980	0.948
	(or CH-O)	(2)	(0.6908)	(0.468)
Water	H_2O	1	0.9200	1.400

[a] Structure adapted from Morrison and Boyd (1976).

[b] Determined in this study

Table 5.7 The functional group composition of the binary system of maltose and water together with their area and volume parameters (Parameter values from: Gmehling *et al.*, 1982)



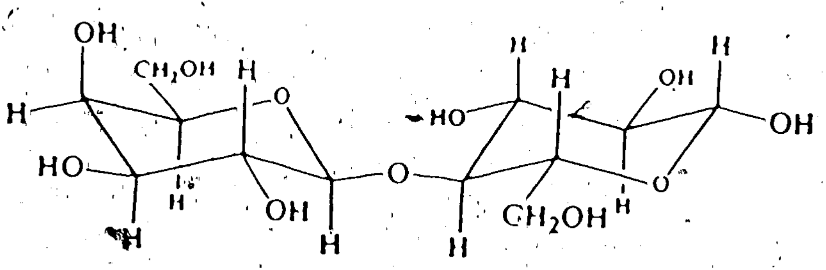
α-Maltose[a]

Components	Functional Groups	Number of Groups (ν_k)	Volume Parameter (R_k)	Area Parameter (Q_k)
Maltose	CH_2	2	0.6744	0.540
	CH	7	0.4469	0.228
	OH	8	1.0000	1.097[b]
	CHO	3	0.9980	0.948
	(or CH-O)	(3)	(0.6908)	(0.468)
Water	H_2O	1	0.9200	1.400

[a] Structure adapted from Morrison and Boyd (1976).

[b] Determined in this study

Table 5.8 The functional group composition of the binary system of lactose and water together with their area and volume parameters (Parameter values from: Gmehling *et al.*, 1982)



β-Lactose[a]

Components	Functional Groups	Number of Groups (ν_k)	Volume Parameter (R_k)	Area Parameter (Q_k)
	CH_2	2	0.6744	0.540
	CH	7	0.4469	0.228
Lactose	OH	8	1.0000	1.097[b]
	CHO	3	0.9980	0.948
	(or CH-O)	(3)	(0.6908)	(0.468)
Water	H_2O	1	0.9200	1.400

[a] Structure adapted from Morrison and Boyd (1976).

[b] Determined in this study

parameters used were those shown in Table 4.4 (Chapter 4).

5.3.1 Prediction of Water Activity

The activity of water (a_w) in aqueous solutions of fructose, sucrose, maltose and lactose was predicted and compared with the published experimental values (Stokes and Robinson, 1966; Rüegg and Blanc, 1981; Miracco *et al.*, 1981). The results of the prediction are illustrated in Figures 5.9-5.12. The model provides a good estimate of a_w in the dilute solution of fructose (Figure 5.9), but with an increase in concentration the departure from the experimental values becomes larger and larger. In the case of sucrose, the agreement with the experimental values was not satisfactory (Figure 5.10) even in the dilute region. The prediction of water activity was poor for both maltose and lactose solutions (Figures 5.11 and 5.12). The results seem to indicate a deficiency in the flexibility of the group contribution model. The functional groups which add together to form the sugar molecules may not be representative since these molecules exist in 5- or 6-membered ring conformations in solution and the groups selected to represent these molecules were of the open chain aliphatic type. For example, the aldehyde (CHO) group was selected to include one CH group and the ring oxygen between two carbon atoms in the glucose molecule. As can be seen in Figure 4.7 (Chapter 4), a CH-O-CH group may be a better choice to represent the ring oxygen between the two carbon atoms. In case of fructose, the CH_2CO group was considered

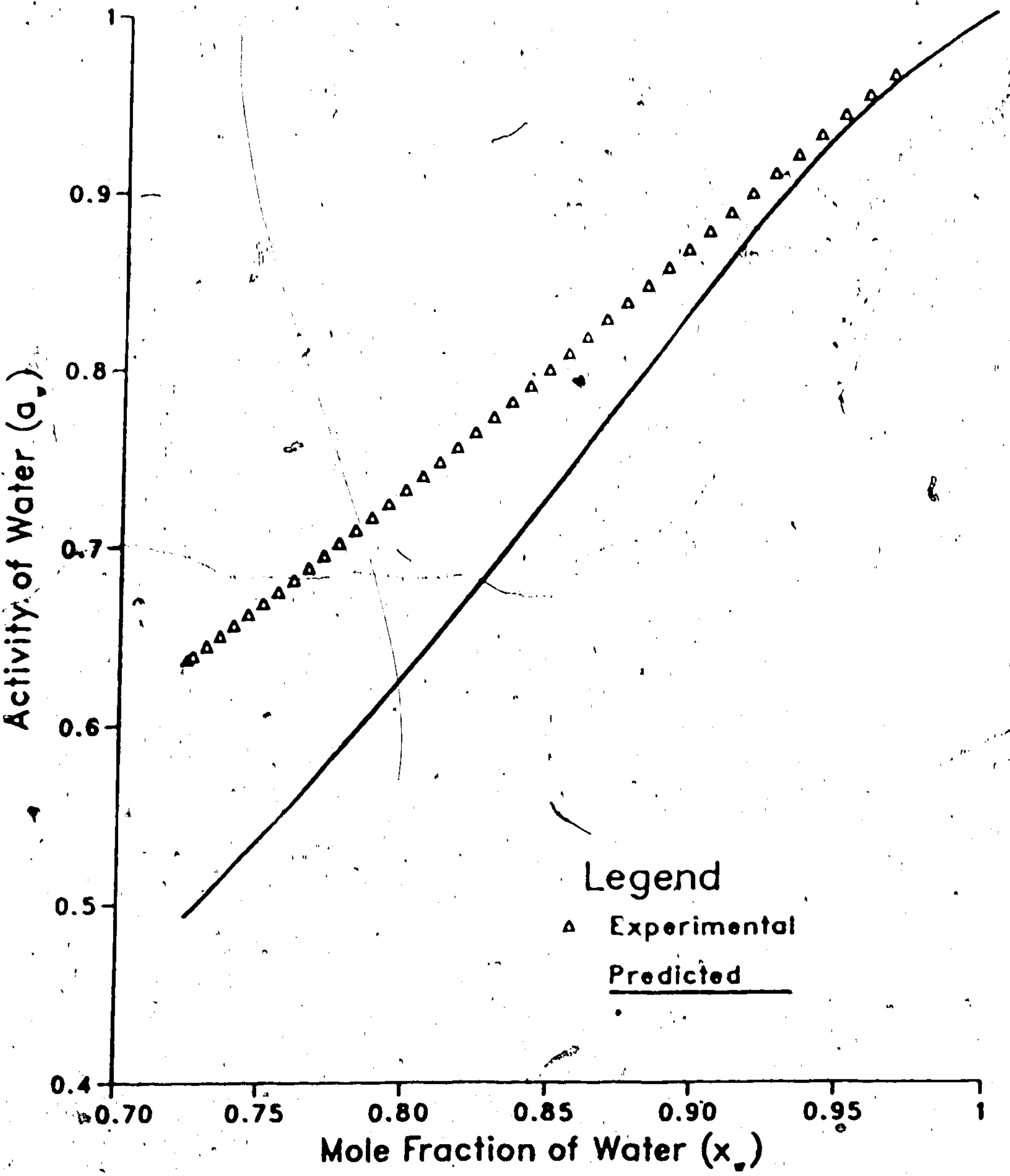


Figure 5.9 The experimental and predicted values of the activity of water in fructose solutions at 25°C. The experimental values were generated from the regression equation of Rüegg and Blanc (1981).

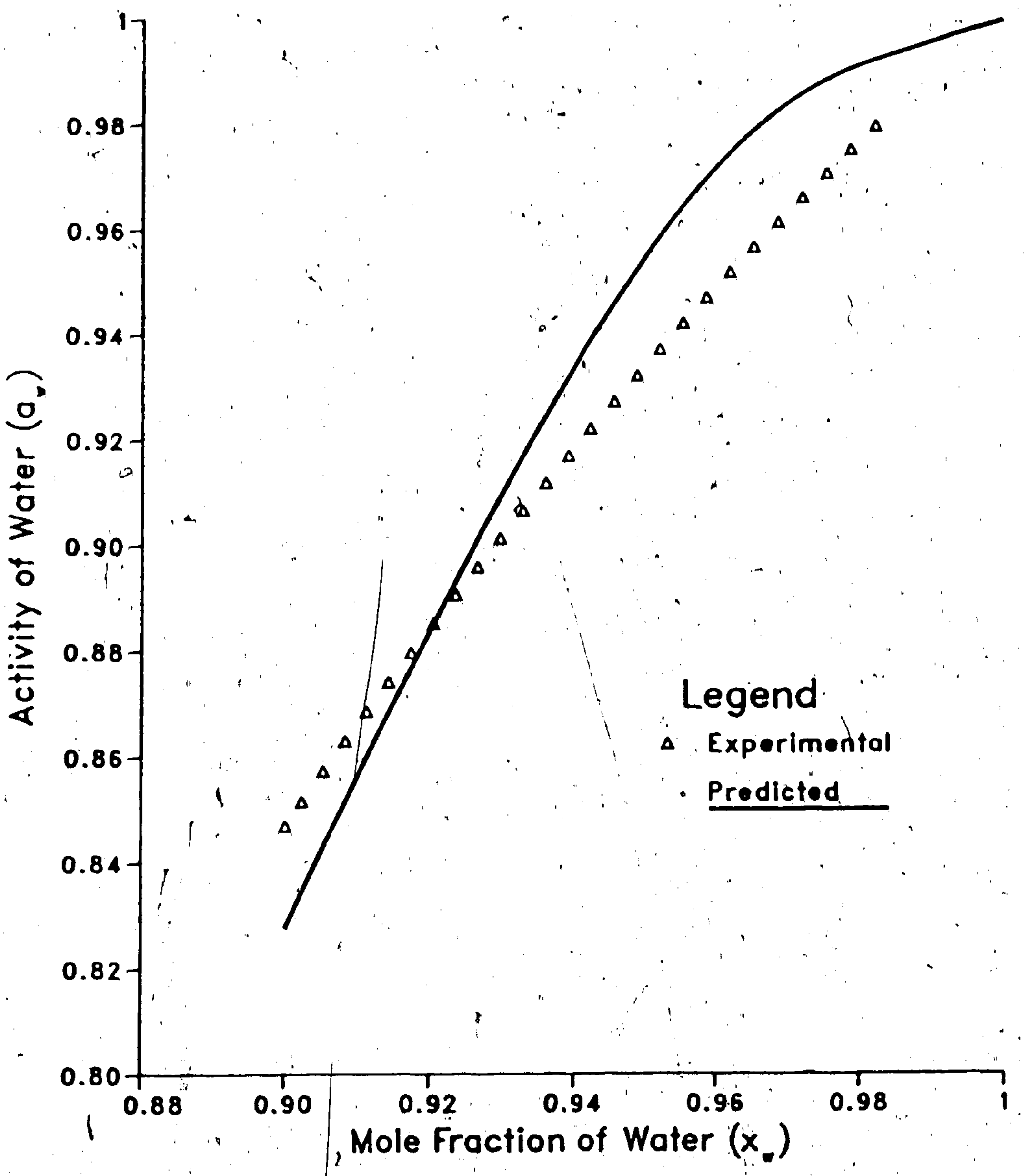


Figure 5.10 The experimental and predicted values of the activity of water in sucrose solutions at 25°C. The experimental values were generated from the regression equation of Rüegg and Blanc (1981).

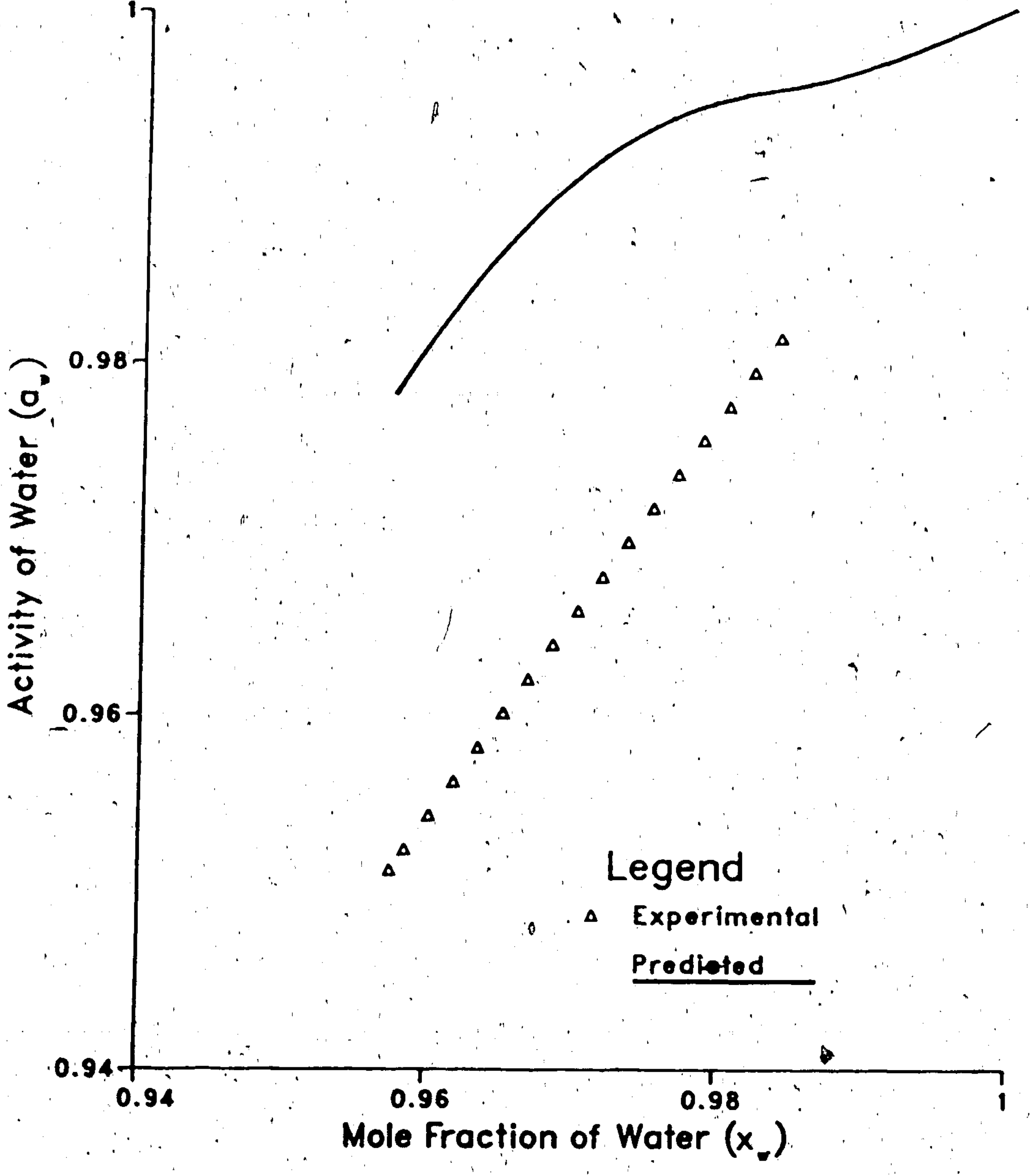


Figure 5.11 The experimental and predicted values of the activity of water in maltose solutions at 25°C. The experimental values were generated from the regression equation of Rüegg and Blanc (1981).

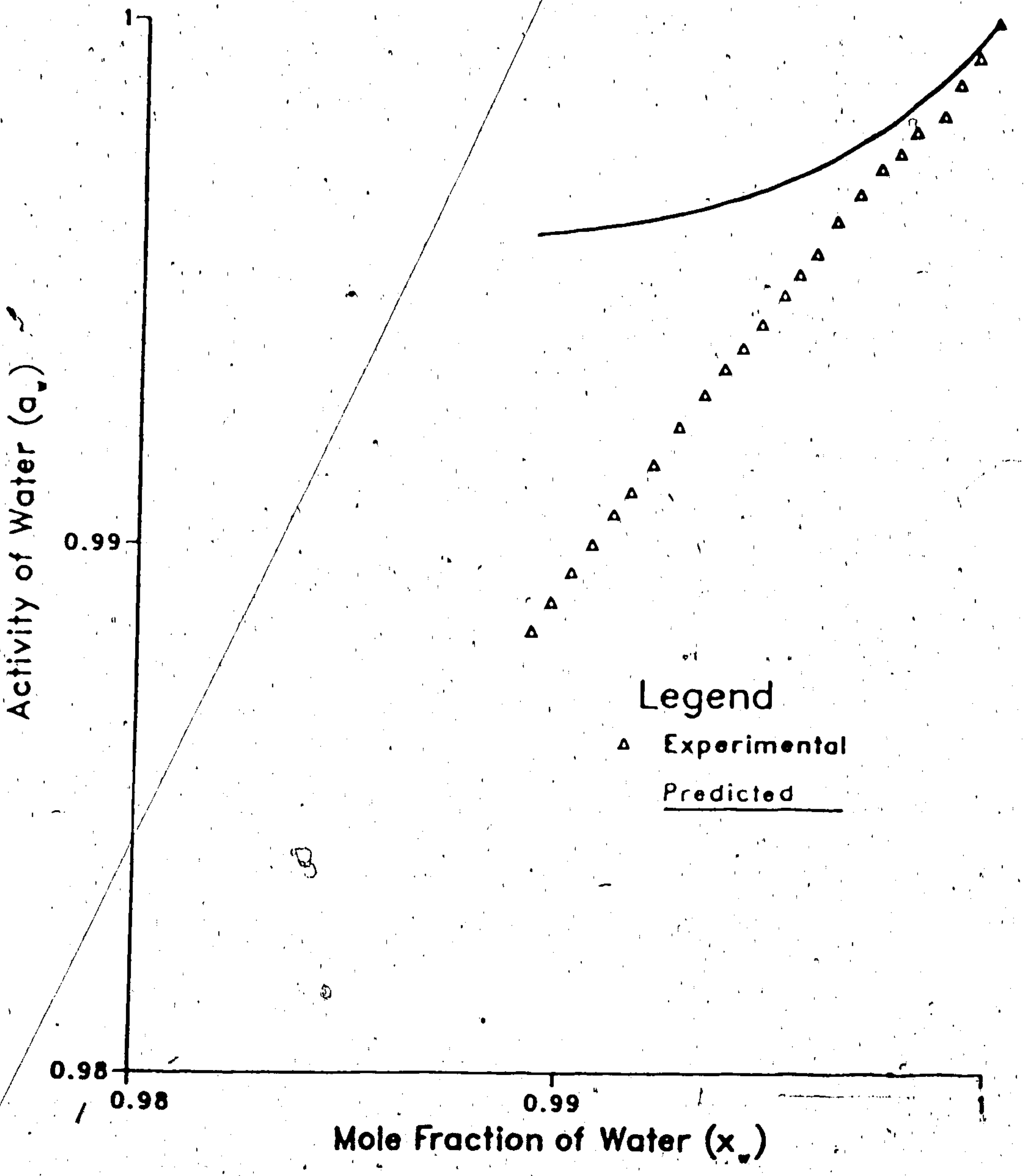


Figure 5.12 The experimental and predicted values of the activity of water in lactose solutions at 25°C. The experimental values were generated from the plot of water activity against lactose concentration reported by Miracco *et al.* (1981) using an electronic digitiser.

to represent a CH_2 group, one carbon atom and the ring oxygen between two carbon atoms. The CO group in CH_2CO/CHO is a keto group with a double bond between carbon (C) and oxygen (O). Sugars in the open chain form contain a CO group with double bond between C and O. But in solution open chain forms are found in traces (Table 4.1) and therefore the solution properties are dictated by the ring form of the sugar molecules. The model can describe the behaviour of aqueous mannitol (a six membered open chain compound) solutions. This indicates that the model's failure to estimate the equilibrium properties of fructose and three other disaccharides is primarily due to unavailability of functional groups to describe the ring compounds. It is therefore expected that defining two new groups viz. CH-O-CH and $C-O-CH_2$ to depict the ring oxygen between two carbon atoms in aldoses and ketoses respectively will improve the predictive power of the model.

5.3.2 Prediction of Freezing Point

The freezing points of binary sugar (fructose, sucrose, maltose and lactose) solutions were predicted using the procedure elaborated in section 5.1.2. Figure 5.13 indicates good agreement with experimental data for fructose solutions in the concentration range studied. However, the prediction was not satisfactory for the disaccharide solutions (Figures 5.14-5.16). Several variations in the group composition of the disaccharide molecules were investigated. In one case the aldehyde group (CHO) was replaced by an ether group

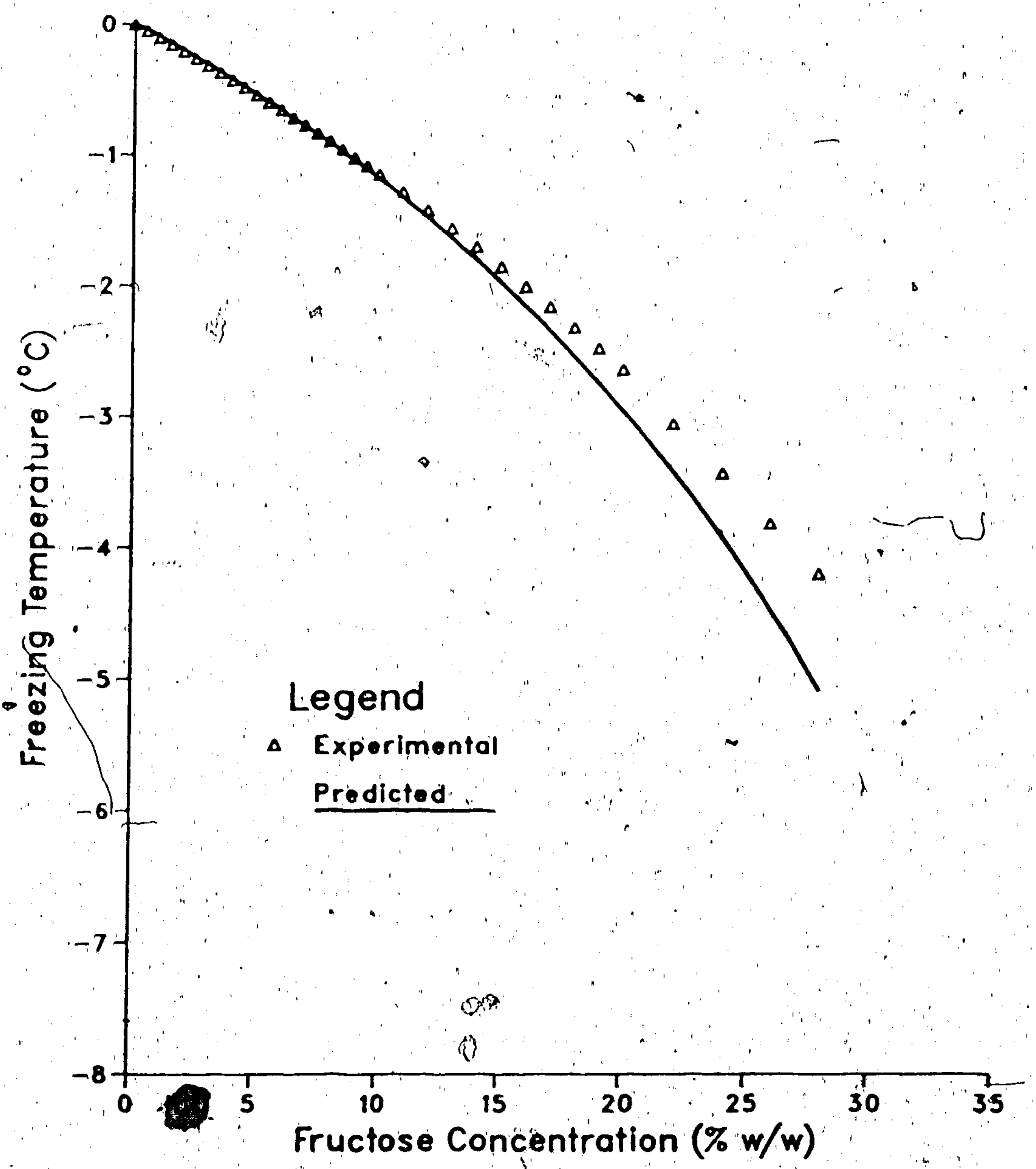


Figure 5.13 The experimental and predicted values of the freezing temperature of fructose solutions. The experimental values were obtained from the CRC (1983-1984) tables on freezing point depression.

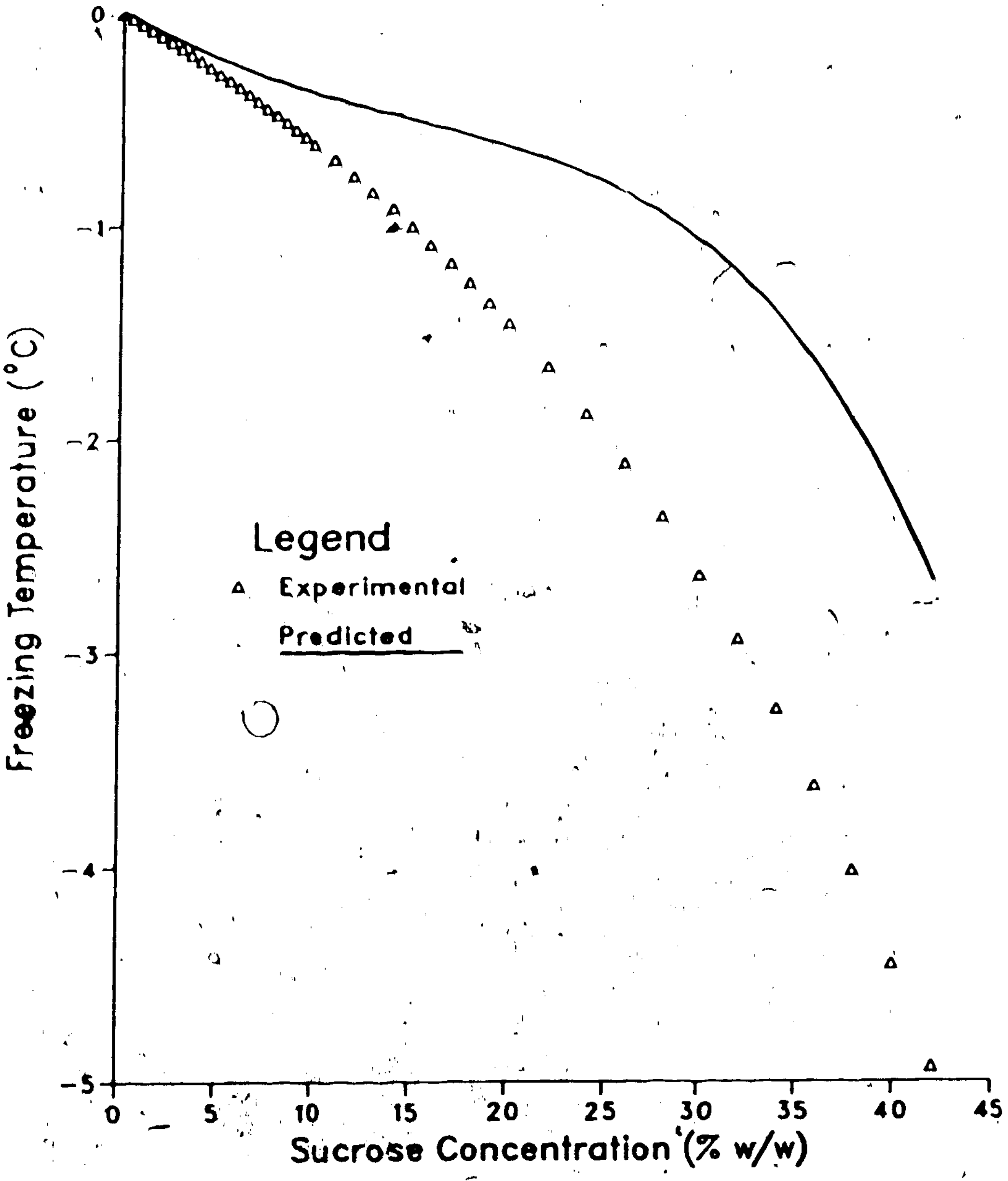


Figure 5.14 The experimental and predicted values of the freezing temperature of sucrose solutions. The experimental values were obtained from the CRC (1983-1984) tables on freezing point depression.

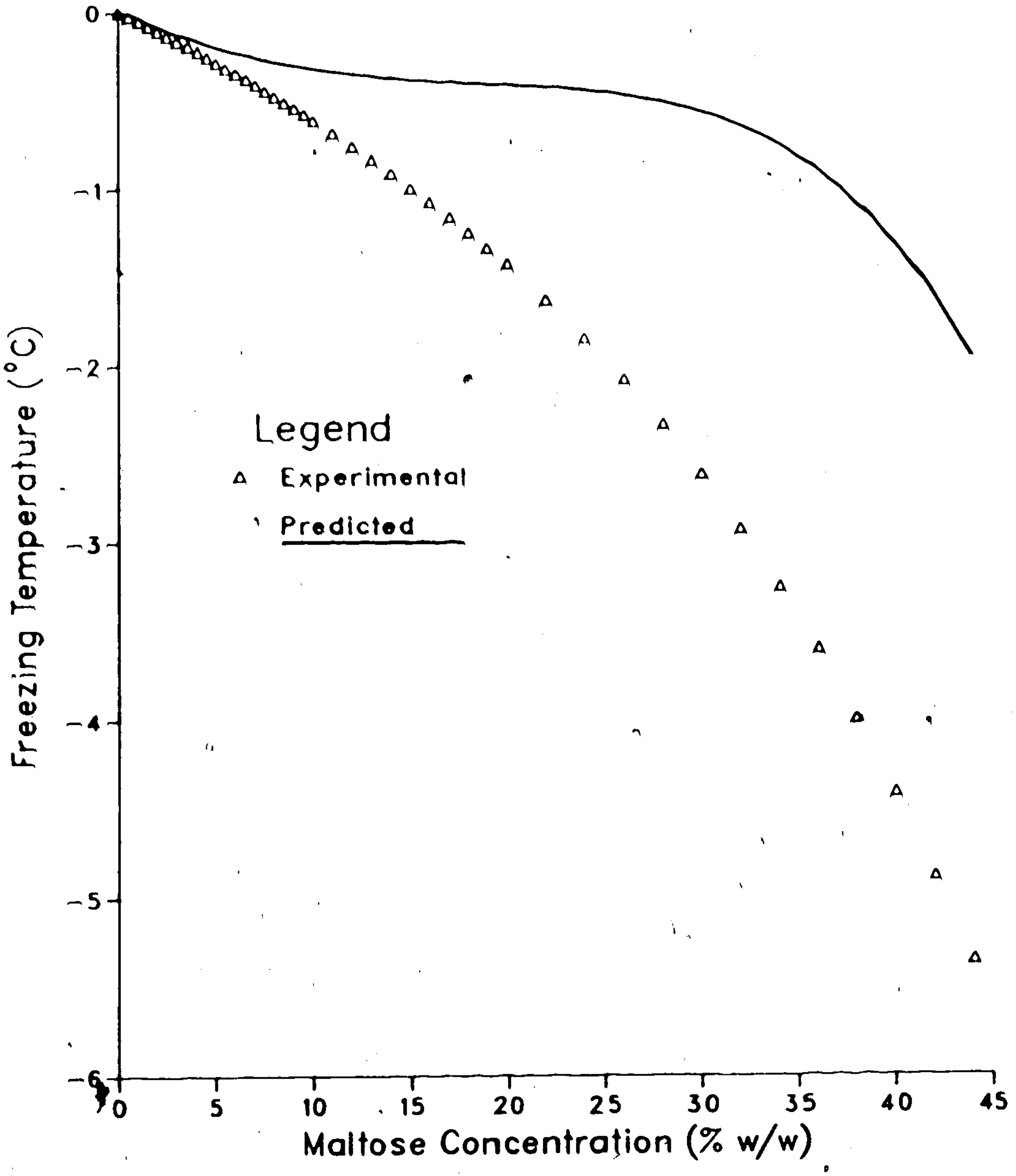


Figure 5.15 The experimental and predicted values of the freezing temperature of maltose solutions. The experimental values were obtained from the CRC (1983-1984) tables on freezing point depression.

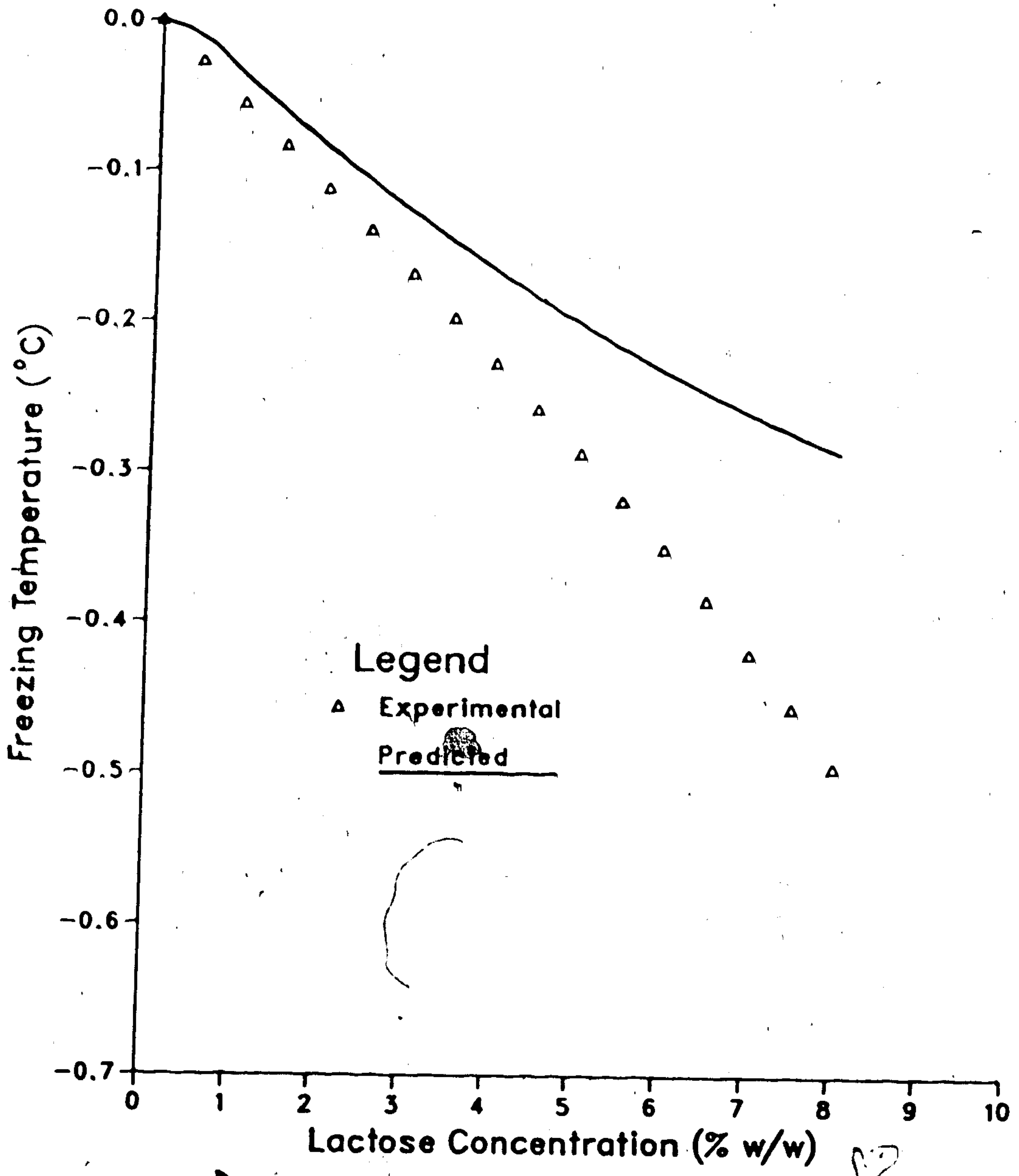


Figure 5.16 The experimental and predicted values of the freezing temperature of lactose solutions. The experimental values were obtained from the CRC (1983-1984) tables on freezing point depression.

(CH-O) while in another case a mixture of CHO and CH-O was considered. None of these group compositions could improve the prediction of freezing temperatures of aqueous disaccharide solutions. As elaborated in the previous section, the definition of the new group CH-O-CH will also describe the glycosidic linkage through an oxygen atom between two monosaccharide units of the disaccharides and is expected to improve the predictions.

5.4 Application to Mixtures of Sugars

In order to test the performance of the model in multicomponent systems, the activity of water was estimated in mixtures of sugars resembling the composition of honey. The freezing curves of orange and apple juices were also determined. These fruit juices were assumed to be an aqueous [illegible]ure of sugar molecules that are normally present in these juices. A small amount of soluble solids made up of components other than the sugars considered in this calculation study was neglected. The group composition of the constituent molecules u~~sed in~~ the calculation were those presented in Tables 5.5-5.8.

5.4.1 Prediction of Water Activity

The activity of water in solutions of a mixture of sugars resembling the composition of honey was predicted using the UNIFAC-FV model. The compositions of the solutions with various proportions of the sugars present are shown in Table 5.9. The estimated values of the activity of water at

Table 5.9 The composition of aqueous solutions containing mixture of sugars resembling the typical sugar make-up of honey (Adapted From: Rüegg and Blanc, 1981).

Total Solid (TS) (% w/w)	Proportion of sugars (% w/w)			
	Glucose (40% of TS)	Fructose (48% of TS)	Sucrose (2% of TS)	Maltose (10% of TS)
72.0	28.80	34.560	1.440	7.20
73.9	29.56	35.472	1.478	7.39
75.9	30.36	36.432	1.518	7.59
78.0	31.20	37.440	1.560	7.80
79.8	31.92	38.304	1.596	7.98
81.9	32.76	39.312	1.638	8.19
84.0	33.60	40.320	1.680	8.40
85.8	34.32	41.184	1.716	8.58
87.9	35.16	42.192	1.758	8.79

25°C were compared with the experimental values reported by Rüegg and Blanc (1981). The results in Figure 5.17 show a moderately good fit with an average error of less than 20% over the concentration range studied. Any improvement in the estimation of the activity coefficients of the components will make the predictions better.

5.4.2 Prediction of Freezing Curves

The freezing curves of orange and apple juices were predicted using the procedure described in section 5.1.2. The composition of the juices with different proportions of sugars is presented in Table 5.10. The predicted freezing curves were compared with the experimental data reported by Heiss and Schachinger (1949). As can be seen in Figure 5.18, the fit with experimental data for orange juice is very good up to a concentration of 30% (w/w) solid. The divergence from the experimental values in the higher concentration range appears to arise from a high amount of sucrose present in the orange juice (Table 5.10). This is most likely the case in view of the failure of the model to accurately predict the activity of water (Figure 5.10) and freezing point depression (Figure 5.14) in binary sucrose solutions. Also, as shown in Table 5.10, the components in the orange juice (in 1.3% of soluble solid) not included in the calculation might have contributed to this lack of fit in the higher range of concentration. However, for apple juice, an excellent fit was obtained with an average error of less than 9% over the concentration range shown in Figure 5.19.

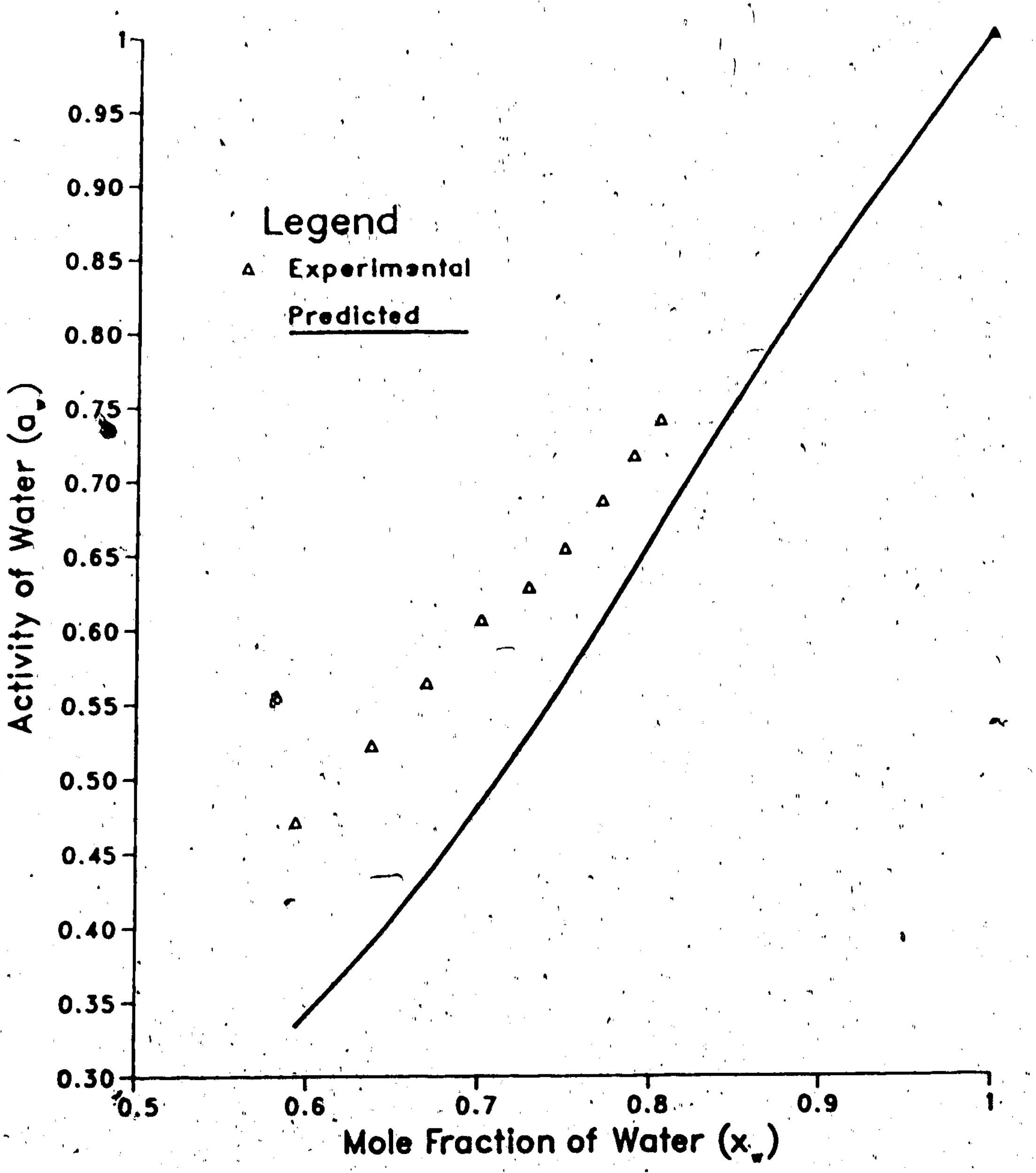


Figure 5.17 The experimental and predicted values of the activity of water at 25°C in solutions of mixtures of sugars resembling the composition of honey. The experimental values were reported by Rüegg and Blanc (1981).

Table 5.10 The amount of major sugars in orange and apple juices (Notter *et al.*, 1959; Watt and Merrill, 1963).

Type of Fruit Juice	Total Dissolved		Proportions of major sugars		
	Solids (% w/w)	Sugars (% w/w)	Glucose (% w/w)	Fructose (% w/w)	Sucrose (% w/w)
Orange	11.7	10.4	23.9	21.2	54.8
Apple	12.2	12.0	14.8	62.4	22.7

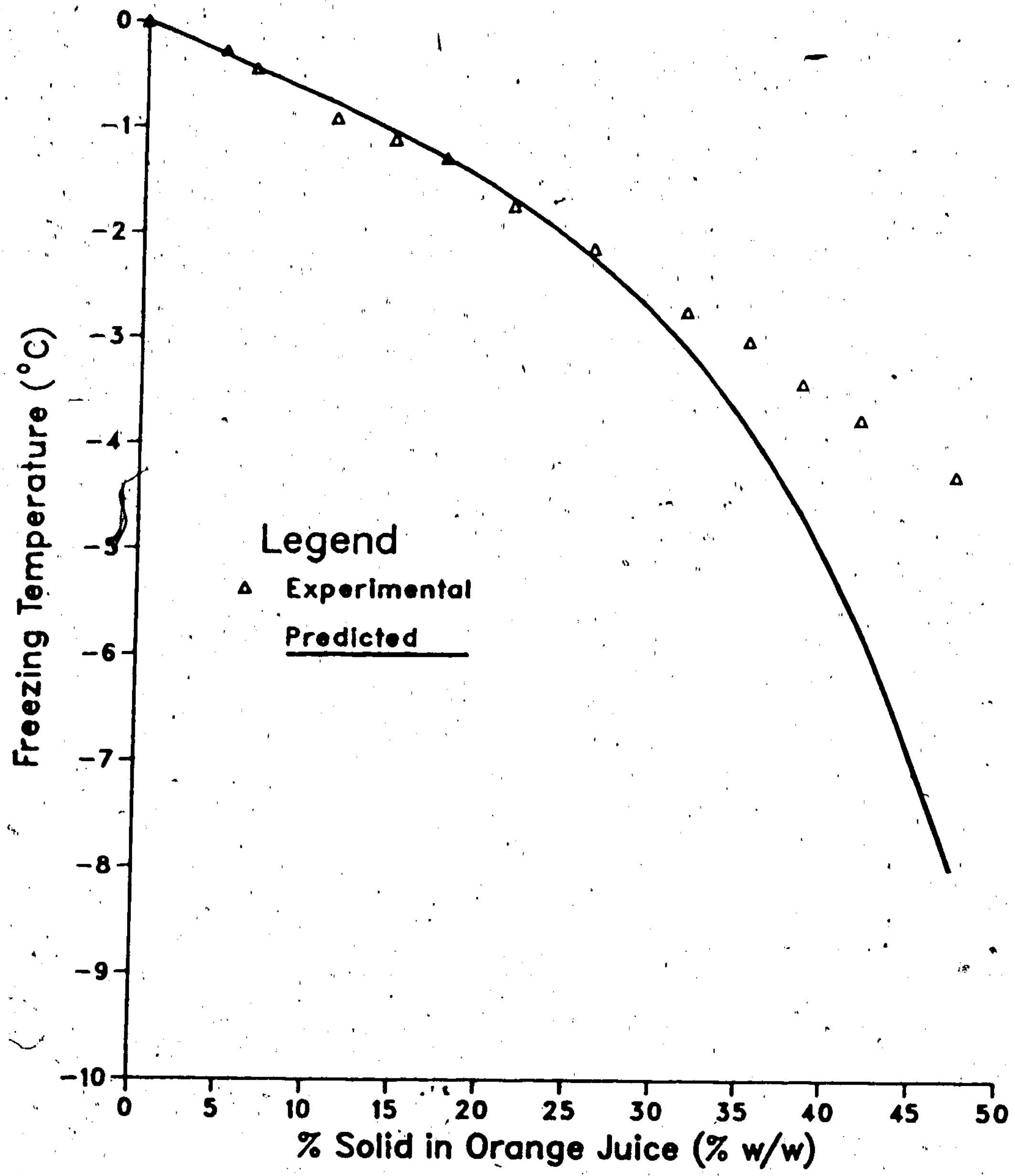


Figure 5.18 The experimental and predicted freezing curves of orange juice. The experimental values were generated from the freezing curve of orange juice reported by Heiss and Schachinger (1949) using an electronic digitiser.

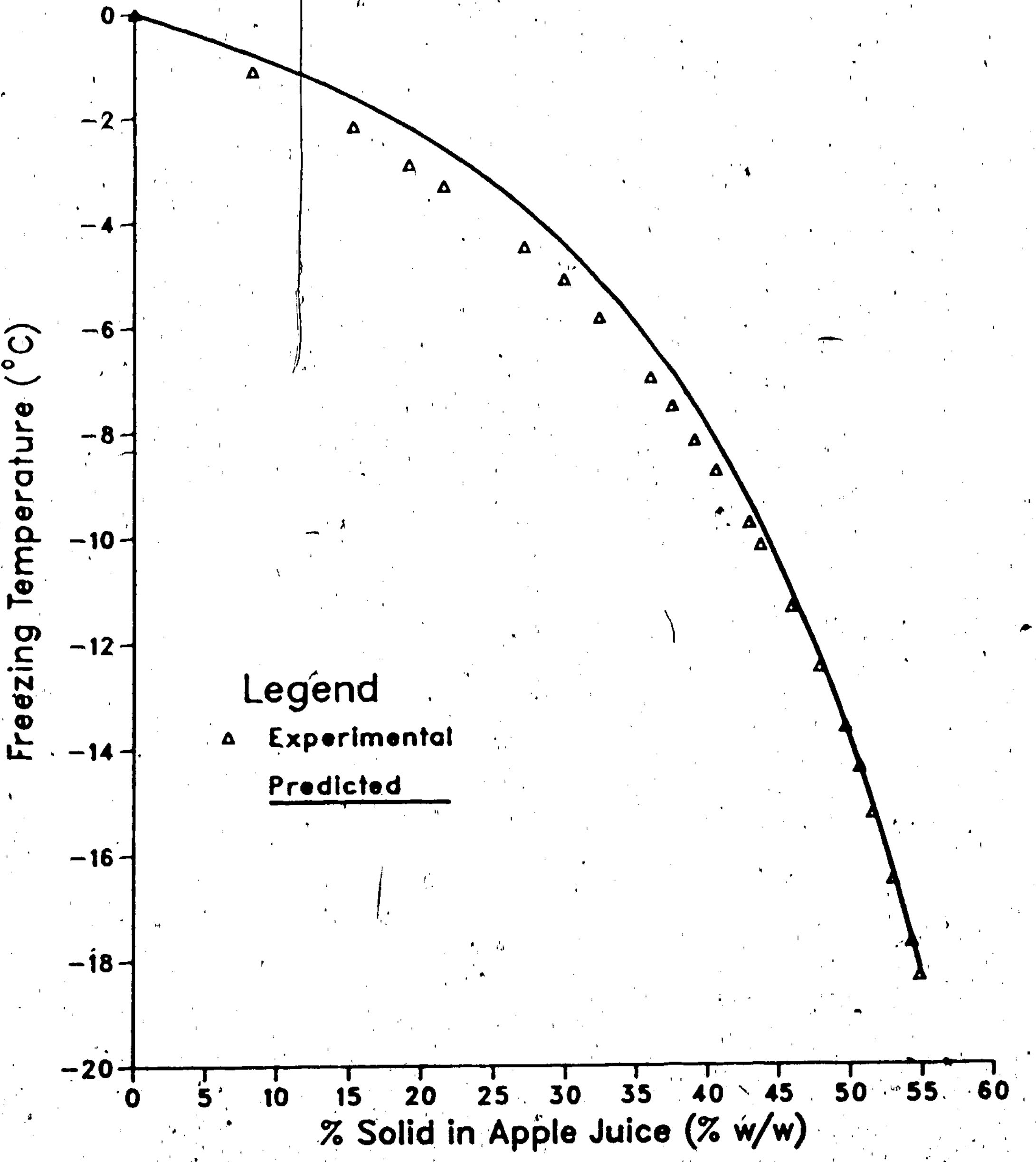


Figure 5.19 The experimental and predicted freezing curves of apple juice. The experimental values were generated from the freezing curve of orange juice reported by Heiss and Schachinger (1949) using an electronic digitiser.

5.5 General Comments

The estimations of the equilibrium properties of a number of aqueous carbohydrate solutions indicate that the model has the capability of predicting these properties. There is room for further refinement of the model to improve its flexibility and predictive power. To do this, a greater effort is needed to generate experimental data on a variety of aqueous carbohydrate systems. These will facilitate accurate estimation of the parameter values of the model.

6. SUMMARY AND CONCLUSIONS

The results of this study provided valuable and interesting information on the modelling of carbohydrate solutions. The UNIFAC group-contribution method of Fredenslund *et al.* (1975, 1977) with the parameter values reported by Gmehling *et al.* (1982) gave erratic results when applied to the glucose-water system. Many combinations of functional group compositions for glucose were evaluated. In all cases predictions were found to be unsatisfactory and none of the combinations could represent the experimantal data. An inspection of the glucose molecule indicates that its solution properties will be dominated by the five hydroxyl (OH) groups which have strong affinity for aqueous environments. Published literature (Anderson and Prausnitz, 1978; Skjold-Jørgensen, 1982; Prausnitz *et al.*, 1986) indicated that the parameter values for the OH group were unable to represent the behavior of aqueous systems containing molecules with OH group. This prompted a reevaluation of the volume (R_k) and area (Q_k) parameters of the OH group and the parameter describing its interaction with water. The revised parameters led to substantial improvements in the predictions of activity coefficients of water and glucose in binary systems. A free-volume correction was necessary for water in the concentrated range. This correction was, however, insignificant for glucose.

To extend the validity of the model with revised parameters (for the OH group), the equilibrium properties of aqueous solutions of fructose and common disaccharides were predicted. The model was also extended to systems containing mixtures of sugars. The properties of aqueous solutions of fructose and mixtures of sugars were predicted with limited success. The model, in general, performed poorly in disaccharide-water systems. This could possibly have been circumvented to an extent by including experimental data on a variety of aqueous carbohydrate systems. Experimental data on sugar solutions are not plentiful which limit such an endeavor. It is felt that the fundamental assumption of the independence of the functional groups from those in the surrounding milieu is most inappropriate in aqueous solutions of carbohydrates. Another difficulty arises from the lack of defined cyclic groups to represent the molecules of sugar. Sugar molecules are polar and in solution exist in 5- or 6-membered ring conformations. As stated by Thomas and Eckert (1984), UNIFAC is incapable of handling polar molecules with a cyclic backbone. The choice of the aldehyde (CHO) and keto (CH_2CO) group to describe the ring oxygen therefore seems inappropriate. A natural extension of this work would be to define new functional groups to describe the ring oxygen and estimate the new values of the parameters. Future work should also examine whether the ring oxygen in the monosaccharide and the glycosidic oxygen which links two monosaccharides have the same characteristics. This will require extensive experimental data, which are scarce on aqueous solutions of carbohydrates. Therefore more efforts are needed in obtaining experimental data on such systems.

Solvation of sugars in aqueous solution is a well known phenomenon. It is desirable that the model should have provision to describe such phenomena. Attempts, with limited success, are presently being made to account for phenomena such as solvation and association.

It is reasonable to conclude from the present study that despite many limitations in the group-contribution method, UNIFAC can be adapted to aqueous solutions of carbohydrates. Further work is undoubtedly necessary to increase the domain of its validity. Defining new groups should lead to significant improvements in the predictive power of the model. Further refinements to include proximity and other intermolecular effects is desirable. This might lead to more complex mathematical expressions. But with the advent of high speed computers, mathematical complexity is no longer an obstacle. It is hoped that the future will witness more progress in molecular physics and solution modelling leading to a unified and general treatment of complex aqueous solutions.

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1. APPENDIX 1 : EXPERIMENTAL DATA

Table A1.1 The freezing point data on aqueous glucose solution together with the calculated activity coefficients of water (Adapted from: CRC, 1983-1984).

Anhydrous Glucose (% w/w)	Mole Fraction of Water (x_w)	Freezing Point Depression ($\theta = T_0 - T$)	Logarithm of Activity Coefficient $\ln\gamma_w$	Activity Coefficient of Water γ_w
0.5	0.9995	0.047	4.684E-5	1.00005
1.0	0.9990	0.107	-2.752E-5	0.99997
1.5	0.9985	0.158	-0.979E-5	0.99999
2.0	0.9980	0.214	-3.560E-5	0.99996
2.5	0.9974	0.270	-5.641E-5	0.99994
3.0	0.9969	0.323	-4.306E-5	0.99996
3.5	0.9964	0.377	-3.425E-5	0.99997
4.0	0.9959	0.433	-3.960E-5	0.99996
4.5	0.9953	0.490	-4.935E-5	0.99995
5.0	0.9948	0.549	-7.310E-5	0.99993
5.5	0.9942	0.608	-9.140E-5	0.99991
6.0	0.9937	0.668	-1.138E-4	0.99987
6.5	0.9931	0.729	-1.404E-4	0.99986
7.0	0.9925	0.790	-1.612E-4	0.99984
7.5	0.9920	0.851	-1.762E-4	0.99982
8.0	0.9914	0.913	-1.950E-4	0.99981

Table A1.1 Contd.

Anhydrous Glucose (% w/w)	Mole Fraction of Water (x_w)	Freezing Point Depression ($\theta = T_0 - T$)	Logarithm of Activity Coefficient $\ln\gamma_w$	Activity Coefficient of Water γ_w
8.5	0.9908	0.975	-2.078E-4	0.99979
9.0	0.9902	1.038	-2.242E-4	0.99978
9.5	0.9896	1.102	-2.442E-4	0.99976
10.0	0.9890	1.167	-2.676E-4	0.99973
11.0	0.9878	1.303	-3.534E-4	0.99966
12.0	0.9865	1.443	-4.518E-4	0.99955
13.0	0.9853	1.586	-5.521E-4	0.99945
14.0	0.9840	1.731	-6.439E-4	0.99936
15.0	0.9827	1.880	-7.455E-4	0.99925
16.0	0.9813	2.033	-8.560E-4	0.99914
17.0	0.9799	2.190	-9.744E-4	0.99903
18.0	0.9785	2.353	-1.119E-3	0.99888
19.0	0.9771	2.521	-1.279E-3	0.99872
20.0	0.9756	2.696	-1.473E-3	0.99853
22.0	0.9726	3.073	-2.016E-3	0.99799
24.0	0.9694	3.480	-2.698E-3	0.99731
26.0	0.9661	3.900	-3.342E-3	0.99666
28.0	0.9626	4.337	-3.976E-3	0.99603
30.0	0.9589	4.794	-4.613E-3	0.99540

Table A1.2 The osmotic coefficient data on aqueous glucose solution together with the calculated activity coefficients of water (Adapted from: Stokes and Robinson, 1966)

Molality of Anhydrous Glucose (m)	Mole Fraction of Water (x_w)	Osmotic Coefficient (ϕ)	Logarithm of Activity Coefficient $\ln\gamma_w$	Activity Coefficient of Water γ_w
1.0	0.9823	1.020	-5.206E-4	0.99948
2.0	0.9652	1.050	-2.435E-3	0.99757
3.0	0.9487	1.079	-5.679E-3	0.99434
4.0	0.9328	1.105	-1.004E-2	0.99001
5.0	0.9174	1.128	-1.536E-2	0.98476
6.0	0.9025	1.149	-2.156E-2	0.97867
7.0	0.8880	1.166	-2.827E-2	0.97212
7.5	0.8810	1.173	-3.176E-2	0.96874

Table A1.3 The vapor pressure data on aqueous glucose solution together with the calculated activity coefficients of water (Adapted from: Taylor and Rowlinson, 1955)

Temperature (°C)	Mole Fraction of Water (x_w)	Vapor Pressure (mm Hg)	Logarithm of Activity Coefficient $\ln\gamma_w$	Activity Coefficient of Water γ_w
25	0.9882	23.476	1.367E-5	1.00001
	0.9492	22.563	6.120E-4	1.00061
	0.9239	21.727	-1.013E-2	0.98992
	0.9066	21.151	-1.809E-2	0.98207
	0.9050	21.117	-1.794E-2	0.98222
	0.8909	20.668	-2.373E-2	0.97655
	0.8696	19.943	-3.523E-2	0.96538
	0.8402	19.002	-4.918E-2	0.95201
	0.8050	17.751	-7.448E-2	0.92823
35	0.9239	38.666	-7.716E-3	0.99231
	0.9239	38.590	-9.683E-3	0.99036
	0.9049	37.504	-1.745E-2	0.98270
	0.8907	36.781	-2.110E-2	0.97912
	0.8788	36.097	-2.642E-2	0.97393
	0.8695	35.484	-3.291E-2	0.96763
	0.8395	33.619	-5.179E-2	0.94953
	0.8046	31.585	-7.174E-2	0.93078

Table A1.3 Contd.

Temperature (°C)	Mole Fraction of Water (x_w)	Vapor Pressure (mm Hg)	Logarithm of Activity Coefficient $\ln\gamma_w$	Activity Coefficient of Water γ_w
45	0.9237	65.86	-8.099E-3	0.99193
	0.9237	65.80	-9.010E-3	0.99103
	0.9047	63.95	-1.674E-3	0.98339
	0.8905	62.74	-2.003E-3	0.98017
	0.8692	60.59	-3.067E-3	0.96978
	0.8397	57.80	-4.330E-3	0.95763
	0.8041	54.11	-6.595E-3	0.93618
55	0.9237	108.15	-8.136E-3	0.99190
	0.9045	105.18	-1.498E-2	0.98513
	0.8904	102.97	-2.050E-2	0.97971
	0.8690	100.12	-2.424E-2	0.97605
	0.8394	95.24	-3.956E-2	0.96122
	0.8038	89.19	-6.185E-2	0.94002
65	0.9237	172.06	-6.781E-3	0.99324
	0.9047	167.69	-1.172E-2	0.98835
	0.8902	163.98	-1.794E-2	0.98222
	0.8687	159.45	-2.150E-2	0.97873
	0.8389	151.57	-3.728E-2	0.96341
	0.8031	142.34	-5.650E-2	0.94507

Table A1.4 The activity coefficients of water from the water activity data measured with electronic hygrometers (Adapted from: Rüegg and Blanc, 1981)

Molality (moles per kg of water)	Mole Fraction of Water (x_w)	Water Activity (a_w)	Logarithm of Activity Coefficient $\ln\gamma_w$	Activity Coefficient of Water γ_w
1.5	0.9737	0.9740	3.558E-4	1.00036
2.0	0.9652	0.9640	-1.289E-3	0.99871
2.5	0.9569	0.9539	-3.117E-3	0.99689
3.0	0.9487	0.9438	-5.132E-3	0.99488
3.5	0.9407	0.9338	-7.332E-3	0.99269
4.0	0.9328	0.9238	-9.721E-3	0.99033
4.5	0.9250	0.9137	-1.230E-2	0.98778
5.0	0.9174	0.9037	-1.507E-2	0.98505
5.5	0.9098	0.8936	-1.803E-2	0.98213
6.0	0.9025	0.8835	-2.118E-2	0.97904
6.5	0.8952	0.8735	-2.453E-2	0.97577
7.0	0.8880	0.8634	-2.808E-2	0.97231

Table A1.5 The activity coefficients of glucose calculated from the activity coefficients of water using Gibbs-Duhem equation and osmotic coefficient data at 25°C. The integration was performed analytically by expressing $\ln\gamma_w$ as a polynomial function in x_g.

Mole Fraction of Glucose (x_g)	Logarithm of Activity Coefficient of Water $\ln\gamma_w$	Logarithm of Activity Coefficient of Glucose $\ln\gamma_g^*$	Activity Coefficient of Glucose γ_g^*
0.0177	-4.770E-4	0.0526	1.0540
0.0212	-8.001E-4	0.0660	1.0682
0.0246	-1.166E-3	0.0799	1.0832
0.0280	-1.576E-3	0.0941	1.0986
0.0314	-2.029E-3	0.1085	1.1146
0.0348	-2.526E-3	0.1230	1.1309
0.0381	-3.067E-3	0.1376	1.1475
0.0414	-3.652E-3	0.1521	1.1643
0.0447	-4.281E-3	0.1666	1.1813
0.0480	-4.956E-3	0.1810	1.1984
0.0513	-5.675E-3	0.1953	1.2156
0.0545	-6.440E-3	0.2094	1.2329

Table A1.5 Contd.

Mole Fraction of Glucose (x_g)	Logarithm of Activity Coefficient of Water $\ln\gamma_w$	Logarithm of Activity Coefficient of Glucose $\ln\gamma_g^{\bullet}$	Activity Coefficient of Glucose $\gamma_g^{\bullet}$
0.0577	-7.250E-3	0.2234	1.2503
0.0609	-8.106E-3	0.2372	1.2677
0.0641	-9.008E-3	0.2509	1.2852
0.0672	-9.956E-3	0.2645	1.3027
0.0703	-1.095E-2	0.2778	1.3203
0.0734	-1.199E-2	0.2911	1.3379
0.0765	-1.308E-2	0.3042	1.3556
0.0796	-1.422E-2	0.3272	1.3733
0.0826	-1.540E-2	0.3301	1.3911
0.0857	-1.664E-2	0.3429	1.4090
0.0887	-1.792E-2	0.3555	1.4269
0.0916	-1.925E-2	0.3680	1.4448
0.0930	-1.986E-2	0.3736	1.4529

Table A1.6 The activity coefficients of glucose calculated from the activity coefficients of water using Gibbs-Duhem equation and vapor pressure data at different temperatures. The integration was performed analytically by expressing $\ln\gamma_w$ as a polynomial function in x_g.

Temperature (°C)	Mole Fraction of Glucose (x_g)	Logarithm of Activity Coefficient of Water $\ln\gamma_w$	Logarithm of Activity Coefficient of Glucose $\ln\gamma_g^*$	Activity Coefficient of Glucose γ_g^*
25°C	0.0118	-2.725E-4	0.0459	1.0470
	0.0508	-5.051E-3	0.1938	1.2139
	0.0761	-1.134E-2	0.2866	1.3318
	0.0934	-1.707E-2	0.3485	1.4170
	0.0950	-1.766E-2	0.3542	1.4250
	0.1091	-2.330E-2	0.4038	1.4975
	0.1304	-3.328E-2	0.4772	1.6115
	0.1598	-4.998E-2	0.5755	1.7781
	0.1950	-7.442E-2	0.6889	1.9915
35°C	0.0761	-1.060E-2	0.2680	1.3074
	0.0951	-1.656E-2	0.3316	1.3932
	0.1093	-2.187E-2	0.3783	1.4598
	0.1212	-2.689E-2	0.4168	1.5172
	0.1305	-3.118E-2	0.4466	1.5630
	0.1605	-4.716E-2	0.5405	1.7168
	0.1954	-6.989E-2	0.6455	1.9069

Table A1.6 Contd.

Temperature (°C)	Mole Fraction of Glucose (x_g)	Logarithm of Activity Coefficient of Water $\ln\gamma_w$	Logarithm of Activity Coefficient of Glucose $\ln\gamma_g^*$	Activity Coefficient of Glucose γ_g^*
45°C	0.0763	-9.853E-3	0.2484	1.2820
	0.0953	-1.537E-2	0.3072	1.3596
	0.1095	-2.029E-2	0.3503	1.4196
	0.1308	-2.896E-2	0.4138	1.5125
	0.1603	-4.349E-2	0.4991	1.6472
	0.1959	-6.495E-2	0.5981	1.8187
55°C	0.0763	-8.954E-3	0.2258	1.2533
	0.0955	-1.403E-2	0.2798	1.3228
	0.1096	-1.848E-2	0.3187	1.3753
	0.1310	-2.640E-2	0.3766	1.4573
	0.1606	-3.967E-2	0.4544	1.5752
	0.1962	-5.921E-2	0.5444	1.7235
65°C	0.0763	-8.003E-3	0.2018	1.2236
	0.0953	-1.249E-2	0.2495	1.2834
	0.1098	-1.657E-2	0.2853	1.3302
	0.1313	-2.370E-2	0.3373	1.4011
	0.1611	-3.568E-2	0.4072	1.5027
	0.1969	-5.329E-2	0.4880	1.6291

Table A1.7 The activity coefficients of glucose calculated from the activity coefficients of water using Gibbs-Duhem equation and water activity data measured at 25°C using electronic hygrometer. The integration was performed analytically by expressing $\ln\gamma_w$ as a polynomial function in x_g.

Mole Fraction of Glucose (x_g)	Logarithm of Activity Coefficient of Water $\ln\gamma_w$	Logarithm of Activity Coefficient of Glucose $\ln\gamma_g^{\bullet}$	Activity Coefficient of Glucose $\gamma_g^{\bullet}$
0.0431	-3.117E-3	0.0105	1.0106
0.0513	-5.132E-3	0.0526	1.0540
0.0593	-7.332E-3	0.0911	1.0954
0.0672	-9.721E-3	0.1261	1.1344
0.0750	-1.230E-2	0.1587	1.1720
0.0826	-1.507E-2	0.1904	1.2097
0.0902	-1.803E-2	0.2221	1.2487
0.0975	-2.118E-2	0.2539	1.2890
0.1048	-2.453E-2	0.2854	1.3291
0.1120	-2.808E-2	0.3113	1.3652

Table A1.8 The partial excess molar properties of water in aqueous glucose solution at 25°C (Adapted from: Taylor and Rowlinson, 1955; Stokes and Robinson, 1966).

Mole Fraction of Water (x_w)	Logarithm of Activity Coefficient $\ln\gamma_w$	$\bar{g}^E_{water}$ (J/mol)	$\bar{h}^E_{water}$ (J/mol)	$T\bar{s}^E_{water}$ (J/mol)
0.9823	-5.469E-4	-1.4	-5.7	-4.3
0.9788	-8.267E-4	-2.0	-8.0	-6.0
0.9754	-1.161E-3	-2.9	-10.7	-7.8
0.9720	-1.547E-3	-3.8	-13.7	-9.9
0.9686	-1.986E-3	-4.9	-17.0	-12.1
0.9652	-2.475E-3	-6.1	-20.6	-14.5
0.9619	-3.014E-3	-7.5	-24.5	-17.0
0.9586	-3.601E-3	-8.9	-28.6	-19.6
0.9553	-4.235E-3	-10.5	-32.9	-22.4
0.9520	-4.916E-3	-12.2	-37.4	-25.3
0.9487	-5.643E-3	-14.0	-42.2	-28.2
0.9455	-6.414E-3	-15.9	-47.1	-31.2
0.9423	-7.228E-3	-17.9	-52.1	-34.2
0.9391	-8.085E-3	-20.0	-57.3	-37.3

Table A1.9 Contd.

Mole Fraction of Water (x_w)	Logarithm of Activity Coefficient $\ln\gamma_w$	$\bar{g}^E_{water}$ (J/mol)	$\bar{h}^E_{water}$ (J/mol)	$T\bar{s}^E_{water}$ (J/mol)
0.9359	-8.984E-3	-22.3	-62.7	-40.4
0.9328	-9.923E-3	-24.6	-68.1	-43.5
0.9297	-1.090E-2	-27.0	-73.6	-46.6
0.9266	-1.192E-2	-29.5	-79.2	-49.7
0.9235	-1.298E-2	-32.2	-84.9	-52.8
0.9204	-1.407E-2	-34.9	-90.7	-55.8
0.9174	-1.520E-2	-37.7	-96.5	-58.8
0.9143	-1.637E-2	-40.6	-102.3	-61.8
0.9113	-1.757E-2	-43.5	-108.2	-64.6
0.9084	-1.880E-2	-46.6	-114.1	-67.5
0.9070	-1.937E-2	-48.0	-116.7	-68.7

Table A1.9 The partial excess molar properties of glucose in aqueous solution at 25°C (Adapted from: Taylor and Rowlinson, 1955; and Stokes and Robinson, 1966).

Mole Fraction of Glucose (x_g)	Logarithm of Activity Coefficient $\ln\gamma_g^*$	$\bar{g}^{E*}_{glucose}$ (J/mol)	$\bar{h}^{E*}_{glucose}$ (J/mol)	$T\bar{s}^{E*}_{glucose}$ (J/mol)
0.0177	0.0529	130.4	699.8	569.4
0.0212	0.0664	163.6	827.7	664.1
0.0246	0.0804	198.1	950.8	752.7
0.0280	0.0948	233.3	1069.0	835.8
0.0314	0.1094	268.9	1182.4	913.4
0.0348	0.1241	304.9	1290.8	985.9
0.0381	0.1389	341.1	1394.4	1053.3
0.0414	0.1538	377.0	1493.2	1116.1
0.0447	0.1685	413.0	1587.3	1174.4
0.0480	0.1832	448.7	1677.1	1228.4
0.0513	0.1978	484.1	1762.7	1278.6
0.0545	0.2122	519.1	1844.4	1325.4

Table A1.9 Contd.

Mole Fraction of Glucose (x_g)	Logarithm of Activity Coefficient $\ln\gamma_g^*$	$\bar{g}^{E*}_{glucose}$ (J/mol)	$\bar{h}^{E*}_{glucose}$ (J/mol)	$T\bar{s}^{E*}_{glucose}$ (J/mol)
0.0577	0.2265	553.8	1922.6	1368.9
0.0609	0.2407	588.0	1997.6	1409.8
0.0641	0.2548	621.9	2069.9	1447.9
0.0672	0.2687	655.6	2139.7	1484.1
0.0703	0.2825	688.6	2207.6	1519.0
0.0734	0.2962	721.6	2274.1	1552.5
0.0765	0.3097	754.0	2339.7	1585.6
0.0796	0.3232	786.3	2404.8	1618.5
0.0826	0.3365	818.2	2469.9	1651.7
0.0857	0.3498	850.0	2535.8	1685.8
0.0887	0.3629	881.2	2602.9	1721.6
0.0916	0.3759	912.2	2671.7	1759.5
0.0930	0.3817	926.1	2703.4	1777.3

Table A1.10 The sorption data on solid glucose and water together with the calculated values of the activity of water (Adapted from: Smith *et al.*, 1981)

Temperature (°C)	Weight Fraction of Water (x_w)	Partial Pressure of Water (Pa)	Activity of Water (a_w)
40°C	7.9999E-06	1.1146E+02	1.4897E-02
	1.2000E-05	2.6346E+02	3.5211E-02
	1.6000E-05	3.9519E+02	5.2817E-02
	2.0000E-05	5.1678E+02	6.9068E-02
	2.3999E-05	6.3838E+02	8.5320E-02
	2.7999E-05	7.4984E+02	1.0022E-01
	3.1999E-05	8.7144E+02	1.1647E-01
	3.5999E-05	9.7277E+02	1.3001E-01
	3.9998E-05	1.0842E+03	1.4491E-01
	4.3998E-05	1.1856E+03	1.5845E-01
	4.7998E-05	1.2666E+03	1.6928E-01
	5.1997E-05	1.3274E+03	1.7741E-01
	5.5997E-05	1.3984E+03	1.8689E-01
	5.9996E-05	1.4794E+03	1.9772E-01
	6.3996E-05	1.5402E+03	2.0585E-01
	6.7995E-05	1.6111E+03	2.1533E-01
	7.1995E-05	1.6821E+03	2.2481E-01
	7.5994E-05	1.7429E+03	2.3294E-01
	7.9994E-05	1.8037E+03	2.4106E-01
	8.3993E-05	1.8543E+03	2.4783E-01
	8.7992E-05	1.9151E+03	2.5596E-01
	9.1992E-05	1.9658E+03	2.6273E-01
	9.5991E-05	2.0063E+03	2.6815E-01
	9.9990E-05	2.0570E+03	2.7492E-01
	1.0399E-04	2.0874E+03	2.7898E-01

Table 4.15 Contd.

Temperature (°C)	Weight Fraction of Water (x_w)	Partial Pressure of Water (Pa)	Activity of Water (a_w)
45°C	7.9999E-6	2.6346E+02	2.7103E-02
	1.2000E-5	4.2559E+02	4.3782E-02
	1.6000E-5	5.7758E+02	5.9418E-02
	2.0000E-5	7.1944E+02	7.4012E-02
	2.3999E-5	8.5117E+02	8.7564E-02
	2.7999E-5	9.9303E+02	1.0216E-01
	3.1999E-5	1.1349E+03	1.1675E-01
	3.5999E-5	1.2362E+03	1.2718E-01
	3.9998E-5	1.3578E+03	1.3969E-01
	4.3998E-5	1.4693E+03	1.5115E-01
	4.7998E-5	1.5706E+03	1.6158E-01
	5.1997E-5	1.6618E+03	1.7096E-01
	5.5997E-5	1.7530E+03	1.8034E-01
	5.9996E-5	1.8239E+03	1.8764E-01
	6.3996E-5	1.9050E+03	1.9598E-01
	6.7995E-5	1.9861E+03	2.0432E-01
	7.1995E-5	2.0671E+03	2.1266E-01
	7.5994E-5	2.1279E+03	2.1891E-01
	7.9994E-5	2.1786E+03	2.2412E-01
	8.3993E-5	2.2293E+03	2.2933E-01
	8.7992E-5	2.2698E+03	2.3350E-01
	9.1992E-5	2.3103E+03	2.3767E-01
	9.5991E-5	2.3509E+03	2.4184E-01
	9.9990E-5	2.3711E+03	2.4393E-01
	1.0399E-4	2.3813E+03	2.4497E-01

Table 4.15 Contd.

Temperature (°C)	Weight Fraction of Water (x_w)	Partial Pressure of Water (Pa)	Activity of Water (a_w)
55°C	7.9999E-06	4.6612E+02	2.9192E-02
	1.2000E-05	6.5864E+02	4.1249E-02
	1.6000E-05	8.9170E+02	5.5845E-02
	2.0000E-05	1.1146E+03	6.9806E-02
	2.3999E-05	1.3376E+03	8.3767E-02
	2.7999E-05	1.5706E+03	9.8363E-02
	3.1999E-05	1.7834E+03	1.1169E-01
	3.5999E-05	1.9962E+03	1.2502E-01
	3.9998E-05	2.1887E+03	1.3707E-01
	4.3998E-05	2.3711E+03	1.4850E-01
	4.7998E-05	2.5434E+03	1.5928E-01
	5.1997E-05	2.7055E+03	1.6944E-01
	5.5997E-05	2.8676E+03	1.7959E-01
	5.9996E-05	3.0095E+03	1.8848E-01
	6.3996E-05	3.1311E+03	1.9609E-01
	6.7995E-05	3.2324E+03	2.0244E-01
	7.1995E-05	3.3338E+03	2.0878E-01
	7.5994E-05	3.4351E+03	2.1513E-01
	7.9994E-05	3.5466E+03	2.2211E-01
	8.3993E-05	3.6073E+03	2.2592E-01
	8.7992E-05	3.6884E+03	2.3099E-01
	9.1992E-05	3.7391E+03	2.3417E-01
	9.5991E-05	3.7796E+03	2.3671E-01
	9.9990E-05	3.8201E+03	2.3924E-01
	1.0399E-04	3.8505E+03	2.4115E-01

Table 4.15 Contd.

Temperature (°C)	Weight Fraction of Water (x_w)	Partial Pressure of Water (Pa)	Activity of Water (a_w)
65°C	7.9999E-06	5.8771E+02	2.3172E-02
	1.2000E-05	8.7144E+02	3.4359E-02
	1.6000E-05	1.1957E+03	4.7143E-02
	2.0000E-05	1.5503E+03	6.1127E-02
	2.3999E-05	1.8847E+03	7.4311E-02
	2.7999E-05	2.2090E+03	8.7095E-02
	3.1999E-05	2.4725E+03	9.7483E-02
	3.5999E-05	2.7258E+03	1.0747E-01
	3.9998E-05	2.9588E+03	1.1666E-01
	4.3998E-05	3.1919E+03	1.2585E-01
	4.7998E-05	3.3946E+03	1.3384E-01
	5.1997E-05	3.5972E+03	1.4183E-01
	5.5997E-05	3.8201E+03	1.5062E-01
	5.9996E-05	4.0127E+03	1.5821E-01
	6.3996E-05	4.2052E+03	1.6580E-01
	6.7995E-05	4.3876E+03	1.7299E-01
	7.1995E-05	4.5599E+03	1.7978E-01
	7.5994E-05	4.7118E+03	1.8578E-01
	7.9994E-05	4.8638E+03	1.9177E-01
	8.3993E-05	5.0057E+03	1.9736E-01
	8.7992E-05	5.1374E+03	2.0256E-01
	9.1992E-05	5.4718E+03	2.1574E-01
	9.5991E-05	5.3705E+03	2.1175E-01
	9.9990E-05	5.4820E+03	2.1614E-01
	1.0399E-04	5.6137E+03	2.2133E-01

Table 4.15 Contd.

Temperature (°C)	Weight Fraction of Water (x_w)	Partial Pressure of Water (Pa)	Activity of Water (a_w)
	7.9999E-06	6.9918E+02	1.7885E-02
	1.2000E-05	1.0842E+03	2.7735E-02
	1.6000E-05	1.4794E+03	3.7843E-02
	2.0000E-05	1.8645E+03	4.7693E-02
	2.3999E-05	2.2698E+03	5.8061E-02
	2.7999E-05	2.6548E+03	6.7911E-02
	3.1999E-05	3.0500E+03	7.8020E-02
	3.5999E-05	3.4250E+03	8.7610E-02
	3.9998E-05	3.8303E+03	9.7978E-02
	4.3998E-05	4.1647E+03	1.0653E-01
	4.7998E-05	4.4889E+03	1.1483E-01
	5.1997E-05	4.8030E+03	1.2286E-01
75°C	5.5997E-05	5.1374E+03	1.3142E-01
	5.9996E-05	5.4110E+03	1.3841E-01
	6.3996E-05	5.6745E+03	1.4515E-01
	6.7995E-05	5.9379E+03	1.5189E-01
	7.1995E-05	6.2014E+03	1.5863E-01
	7.5994E-05	6.4041E+03	1.6382E-01
	7.9994E-05	6.6168E+03	1.6926E-01
	8.3993E-05	6.7992E+03	1.7392E-01
	8.7992E-05	6.9816E+03	1.7859E-01
	9.1992E-05	7.3059E+03	1.8688E-01
	9.5991E-05	7.1944E+03	1.8403E-01
	9.9990E-05	7.2654E+03	1.8585E-01
	1.0399E-04	7.2654E+03	1.8585E-01

9. APPENDIX 2 : COMPUTER PROGRAMS

9.1 UFACFV

This program calculates the activity coefficient or activity of components in a multicomponent mixture. For aqueous solutions, water is considered as component one. A detail listing of the program is given below:

```
C****************************************************************
C
C      PROGRAM  : UFACFV (IN DOUBLE PRECISION)
C                 UNIFAC WITH FREE VOLUME CORRECTION
C
C      PURPOSE  : To calculate estimates of activity of components in
C                 an aqueous solution of biological origin
C      METHOD   : Combines the Solution-of-Functional-Groups concept
C                 with a model for activity coefficients based on an
C                 extension of the Quasi-Chemical theory of liquid
C                 mixtures (UNIQUAC) and free volume theory
C      NOTES    : The variables are described in the subroutine
C                 where they are used
C               : Uses concentration in mole-fraction unit and
C                 temperature in degree kelvin.
C
C      KEY REFERENCES :
C
C          (1) Fredenslund,A.,Jones,R.L.,Prausnitz,J.M.,AICHE J.
C                21,1086(1975).
C          (2) Abrams,D.S.,Prausnitz,D.M.,AICHE J.21,116(1975).
C          (3) Skjold-Jorgensen,S.,Kolbe,B.,Gmehling,J.,Ramussen,
C                P.,I.E.C.Proc.Des.Dev.,18(4),714(1979).
C          (4) Gmehling,J.,Rasmussen,P.,Fredenslund,A.,I.E.C.Proc.
C                Des.Dev.,21(1),118,(1982).
C
C      PROGRAMED BY : Gour Choudhury
C
C****************************************************************
C
C Declare real and integer variables
C
      REAL*8  A(90,90), RK(90), QK(90), T(90), B, C(90), VM(90),
     &        XC(90,90), CRNU(90,90), GLUNFV(200,90), ACTVTY(200,90)
      INTEGER NU(90,90), NGC(90,90), NPG(90), NSG(90), NC, NG, NT,
     &        IT, NXCSET, MCOUNT, ICOUNT, NRQ, NCOMP, NSYSTM
C
C Declare common variables
C
      COMMON/ DF1 /VM, C, B
      COMMON/ DU1 /NC, NG
```

```
        COMMON/  DU2  /RK,  QK,  NRQ
        COMMON/  DU3  /NU
        COMMON/  DU4  /NGC,  NPG,  NSG
        COMMON/  DU5  /XC
        COMMON/  DU6  /A,  T
        COMMON/  DU7  /NSYSTM,  IT,  NT,  NXCSET,  MCOUNT
        COMMON/  DU8  /CRNU
C
C Call DDATA, and DUFV to obtain the UNIFAC AND FREE-VOLUME
C contributions to the activity coefficient of the components.
C
        CALL  DDATA
        CALL  DUFV   (GLUNFV)
        STOP
        END
C*****************************************************************
C
C         Subroutine  :  DDATA
C
C         Purpose      :  Reads the input data from the following files:
C
C       FFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFF
C       F
C       F                       SUMMARY  OF  DATA  FILES
C       F                       .........................
C       F     1=RKQK       :  NRQ,  R  and  Q  values  of  groups
C       F     2=AMN        :  Group  interaction  parameters
C       F     3=FVDATA   :  NCOMP,  B,  c(i),  and  VM(i)   of
C       F                    components.
C       F     4=GCODE      :  NC,  NG,  and  Group  code  numbers
C       F     5=NEW        :  Total  no.  of  each  group  in  a  component
C       F     6=NEWCR      :  Total  no.  of  each  group  in  a  component
C       F                  used  for  computation  of  molecular  area
C       F                  parameter  and  group  fractions
C       F     7=TMOLEF   :  Temperature,  no.  of  mole  fraction  sets
C       F                  and  mole  fractions  of  various  components
C       F     8=GCV        :  Group  code  vectors
C       FFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFFF
C
C*****************************************************************
C
        SUBROUTINE  DDATA
C
C ...................Description  of  variables....................
C
C NRQ      =  Total  no.  of  groups  for  which  'R'  and  'Q'  are  known
C RK       =  Group  volume  parameter
C QK       =  Group  area  parameter
C A(M,N)  =  Group  interaction  parameter
C B          =  Proportionality  constant  used  in  the  calculation  of
C             reduced  volume
C ĉ(I)     =  Constant  used  in  the  expression  of  external  degrees  of
C             freedom  in  free-volume  computation
C VM       =  Molar  volume  of  the  components
C NC       =  Total  no.  of  components
C NG       =  Total  no.  of  groups
```

```
C NGC      = Group code numbers
C NU       = No. of a particular type of group in a component
C T        = Temperature of the solution in degrees kelvin
C NPG      = Code no. of primary groups
C NSG      = Code no. of secondary groups
C NXCSET = Total no. of component mole fraction sets to be computed
C XC       = Mole fraction of each component
C IS       = Index of do-loops for no. of sets of mole fractions
C NCOMP   = Number of component
C NSYSTM = Number of systems
C
         REAL*8    A(90,90), RK(90), QK(90), T(90), B, C(90), VM(90),
     &             XC(90,90), CRNU(90,90)
         INTEGER   NU(90,90), NGC(90,90), NPG(90), NSG(90), NC, NG,
     &             NT, IT, NXCSET, MCOUNT, ICOUNT, NRQ, NCOMP, NSYSTM
C
         COMMON/  DF1  /VM, C, B
         COMMON/  DU1  /NC, NG
         COMMON/  DU2  /RK, QK, NRQ
         COMMON/  DU3  /NU
         COMMON/  DU4  /NGC, NPG, NSG
         COMMON/  DU5  /XC
         COMMON/  DU6  /A, T
         COMMON/  DU7  /NSYSTM, IT, NT, NXCSET, MCOUNT
         COMMON/  DU8  /CRNU
C
C Statement that allows format-free reading and writing of
C both real and integer data.
C
         LOGICAL *1 FREE(1)/'*'/
C
C Read volume and surface area parameters for various groups
C from the file 'RKQK'.
C
         READ(1,FREE) NRQ
         DO 10 I = 1, NRQ
            READ(1,FREE) RK(I), QK(I)
   10    CONTINUE
C
C Read a(m,n) values from the file 'AMN'.
C
         READ(2,FREE) ((A(M,N), N = 1, 43), M = 1, 43)
C
C Read number of components, the constants B, C(i), and molar
C volumes of the components from the file 'FVDATA'.
C
         READ(3,FREE) NCOMP, B
         DO 20 J = 1, NCOMP
            READ(3, FREE) C(J), VM(J)
   20    CONTINUE
C
         READ(4,FREE) NSYSTM
C
C Set Do-loop to read the input data for all the component in
C the solution
C
```

```
      DO 70 IN = 1, NSYSTM
C
C Read no. of components and total no. of functional groups in
C the solution from the file 'GCODE'
C
      READ(4,FREE) NC, NG
C
C Read the code no. (serial no.) of each group in the solution for
C each of the component and the no.(how many) of such group for
C each component from the files "GCODE" and "NEW" respectively
C
      DO 30 J = 1, NC
         DO 30 I = 1, NG
         READ(4,FREE) NGC(I,J)
         READ(5,FREE) NU(I,J)
         READ(6,FREE) CRNU(I,J)
   30 CONTINUE
C
C Read temperature, total no. of mole fractoion sets and the mole
C fractions of components from the file 'TMOLEF'.
C
      READ(7,FREE) NT
      READ(7,FREE) (T(IT), IT=1,NT)
      READ(7,FREE) NXCSET
      MCOUNT = 0
      DO 60 L = 1, NT
         DO 50 IS = 1, NXCSET
         MCOUNT = MCOUNT + 1
            DO 40 J = 1, NC
            READ (7,FREE) XC(MCOUNT,J)
   40       CONTINUE
   50    CONTINUE
   60 CONTINUE
C
C Read primary and secondary group code nos. from the file 'GCV'
C
      READ(8,FREE) (NSG(I),I = 1, NG)
      READ(8,FREE) (NPG(I),I = 1, NG)
C
   70 CONTINUE
      RETURN
      END
C*********************************************************************
C
C     Subroutine : DUFV
C
C     Purpose    : Computes the UNIFAC and FREE-VOLUME contribution
C                  to the activity coefficients of the components
C                  in aqueous solution
C
C*********************************************************************
C
      SUBROUTINE DUFV (GLUNFV)
C
C Variables and their dimension for the combinatorial part of
C the activity coefficient
```

```
C
      REAL*8   RK(90), QK(90), RC(90), QC(90), RG(90,90), QG(90,90),
     &         CL(90), XC(90,90), THETAC(90), PHIC(90), CLOGC(90),
     &         CRNU(90,90)
C
C Variables and their dimension for the residual part of the
C activity coefficient
C
      REAL*8   XP(90,90), XGM(90,90), XM(90), SUMXP(90), SUMXM,
     &         SUMQXP(90), A(90,90), SHY(90,90), SUMQXM, T(90),
     &         SUMTSP(90,90)
      REAL*8   SUMTSM(90), TEMPP(90), TSPP1(90,90), TSPP(90,90),
     &         TSPM(90), THETAP(90,90), THETAM(90), THETAT, PHIT, XL
      REAL*8   GLOGP(90,90), GLOGM(90), DIFLOG(90,90), RLOGC(90)
C
C Variables and their dimension for the free-volume contribution
C to the activity coefficient of the components
C
      REAL*8   B, C(90), VM(90), LNGFV(200)
C
C Variables and their dimensions for the total activity coefficient
C
      REAL*8   CLGAMA(90), GLNO(90), GLUNFV(200,90), ACTVTY(200,90)
C
C Global integer variables and their dimensions
C
      INTEGER NRQ, NGC(90,90), NU(90,90), NPG(90), NSG(90), NXCSET,
     &         NSYSTM, NT, IT, MCOUNT, ICOUNT
C
C Common variables
C
      COMMON /DF1/ VM, C, B
      COMMON/ DU1 /NC, NG
      COMMON/ DU2 /RK, QK, NRQ
      COMMON/ DU3 /NU
      COMMON/ DU4 /NGC, NPG, NSG
      COMMON/ DU5 /XC
      COMMON/ DU6 /A, T
      COMMON/ DU7 /NSYSTM, IT, NT, NXCSET, MCOUNT
      COMMON/ DU8 /CRNU
C
C Do-loop to calculate the activity coefficient of all the
C components in the solution
C
      ICOUNT = 0
      DO 200 I = 1, NSYSTM
C
      MCOUNT = 0
      DO 190 IT = 1, NT
      DO 180 IS = 1, NXCSET
      MCOUNT = MCOUNT + 1
C
      CALL DRQLC   (RK, QK, RG, QG, NGC, RC, QC, CL, SUMXP, SUMXM,
     &               THETAT, PHIT, XL, CRNU, MCOUNT)
      CALL DTPHI   (RC, QC, THETAT, PHIT, THETAC, PHIC, MCOUNT)
      CALL DCOMB   (RC, QC, PHIT, THETAT, CL, XL, CLOGC)
```

```
      CALL DGFRP   (SUMXP, SUMXM, QG, XP, XGM, SUMQXP, CRNU, MCOUNT)
      CALL DGFRM   (NSG, XGM, XM, QK, SUMQXM)
      CALL DAFP    (QG, XP, SUMQXP, THETAP)
      CALL DAFM    (NSG, QK, XM, SUMQXM, THETAM)
      CALL DINPAR (NPG, IT, A, T, SHY
      CALL DTSHYP (NPG, THETAP, SHY, TEMPP, SUMTSP)
      CALL DTSHYM (NPG, NSG, SHY, THETAM, SUMTSM)
      CALL DSSUMP (NPG, THETAP, SHY, SUMTSP, TSPP1, TSPP)
      CALL DSSUMM (NPG, NSG, THETAM, SHY, SUMTSM, TSPM)
      CALL DGLNP   (QG, SUMTSP, TSPP, GLOGP)
      CALL DGLNM   (QK, NSG, SUMTSM, TSPM, GLOGM)
      CALL DDLNM   (NSG, GLOGP, GLOGM, DIFLOG)
      CALL DRES    (NSG, CRNU, DIFLOG, RLOGC)
      CALL DFREEV (MCOUNT, RC, LNGFV)
C
C Check for the activity coefficient at infinite dilution when
C mole fraction of water = 1.0D0
C
      IF (XC(MCOUNT,1) .NE. 1.0D0) GO TO 130
      DO 120 J = 2, NC
         GLNO(J) = CLOGC(J) + RLOGC(J) + LNGFV(J)
  120 CONTINUE
      GO TO 180
C
  130 CLGAMA(1) = CLOGC(1) + RLOGC(1) + LNGFV(1)
      DO 140 K = 2, NC
         CLGAMA(K) =  (CLOGC(K) + RLOGC(K) + LNGFV(K)) - GLNO(K)
  140 CONTINUE
C
      DO 170 L = 1, NC
        GLUNFV(MCOUNT,L) = CLGAMA(L)
  170 CONTINUE
      CALL ACVTY (GLUNFV, ACTVTY)
C
  180 CONTINUE
  190 CONTINUE
C
  200 CONTINUE
      RETURN
      END
C***********************************************************
C
C      Subroutine  : DRQLC
C
C      Purpose     : Computes 'r','q' and 'l' values of the
C                    components
C
C***********************************************************
C
      SUBROUTINE DRQLC (RK, QK, RG, QG, NGC, RC, QC, CL, SUMXP,
     &                 SUMXM, THETAT, PHIT, XL, CRNU, MCOUNT)
C
C .....................DESCRIPTION OF VARIABLES...................
C
C RC        = Component area parameter
C QC        = Component volume parameter
```

```
C CL          = 'l' value of a component
C SUMXP       = Sum of NU values for all the groups in a component
C               in pure state for calculation of group fraction in
C               pure compounds
C SUMXM       = Same as above in mixture
C THETAT      = Sum of the product of 'QC' and 'XC' of components
C               for calculation of component area fractions
C PHIT        = Sum of the product of 'RC' and 'XC' of components
C               for calculation of component volume fractions
C XL          = Sum of the product of 'XC' and 'l' values of components
C CRNU        = Variable used in calculation of molecular area
C               parameter and group fractions
C
      REAL*8      RK(90), QK(90), RC(90), QC(90), CL(90), RG(90,90),
     &            QG(90,90), SUMXP(90), XC(90,90), SUMXM, THETAT,
     &            PHIT, XL, CRNU(90,90)
      INTEGER     NGC(90,90), NU(90,90), NC, NG, MCOUNT
C
      COMMON/ DU1 /NC, NG
      COMMON/ DU3 /NU
      COMMON/ DU5 /XC
C
C INITIALIZE
C
      THETAT = 0.0D0
      PHIT = 0.0D0
      XL = 0.0D0
C
      SUMXM = 0.0D0
      DO 70 J = 1, NC
      RC(J) = 0.0D0
      QC(J) = 0.0D0
      SUMXP(J) = 0.0D0
      DO 60 I = 1, NG
      IF(NGC(I,J) .NE. 0) GO TO 50
      RG(I,J) = 0.0D0
      QG(I,J) = 0.0D0
      GO TO 60
 50   N3 = NGC(I,J)
      RG(I,J) = RK(N3)
      QG(I,J) = QK(N3)
      RC(J) = RC(J) + RG(I,J)*NU(I,J)
      QC(J) = QC(J) + QG(I,J)*CRNU(I,J)
      SUMXP(J) = SUMXP(J) + CRNU(I,J)
 60   CONTINUE
      CL(J) = 5.0*(RC(J)-QC(J))-(RC(J)-1)
      THETAT = THETAT + QC(J)*XC(MCOUNT,J)
      PHIT = PHIT + RC(J)*XC(MCOUNT,J)
      XL = XL + CL(J)*XC(MCOUNT,J)
      SUMXM = SUMXM + SUMXP(J)*XC(MCOUNT,J)
 70   CONTINUE
      RETURN
      END
```

```
C*************************************************************
C
C       Subroutine  :  DTPHI
C
C       Purpose      : Computes 'THETA' and 'PHI' values for each
C                        component of the solution
C
C*************************************************************
C
        SUBROUTINE DTPHI (RC, QC, THETAT, PHIT, THETAC, PHIC, MCOUNT)
C
C ...................DESCRIPTION OF VARIABLES....................
C
C THATAC  = Area fraction of a component
C PHIC    = Volume fraction of a component
C
        REAL*8      RC(90), QC(90), THETAC(90), PHIC(90), XC(90,90),
     &              THETAT, PHIT
        INTEGER     NU(90,90), NC, NG, MCOUNT
C
        COMMON/ DU1 /NC, NG
        COMMON/ DU3 /NU
        COMMON/ DU5 /XC
C
        DO 80 J = 1, NC
        THETAC(J) = (QC(J)*XC(MCOUNT,J))/THETAT
        PHIC(J) = (RC(J)*XC(MCOUNT,J))/PHIT
 80     CONTINUE
        RETURN
        END
C*************************************************************
C
C       Subroutine  :  DCOMB
C
C       Purpose      : Computes combinatorial ln gamma of each component
C                       in the solution
C
C*************************************************************
C
C
        SUBROUTINE DCOMB (RC, QC, PHIT, THETAT, CL, XL, CLOGC)
C
C ...................DESCRIPTION OF VARIABLES....................
C
C CLOGC  = Combinatorial ln gamma of components
C
        REAL*8     RC(90), QC(90), CL(90), CLOGC(90), PHIT, THETAT, XL
        REAL*8     FAC1, FAC2
C
        INTEGER  NC, NG
C
        COMMON/ DU1 /NC, NG
C
        DO 90 J = 1, NC
        FAC1 = RC(J)/PHIT
        FAC2 = QC(J)/THETAT
```

```
      CLOGC(J)  =  DLOG(FAC1)+5.0*QC(J)*DLOG(FAC2/FAC1)+CL(J)-FAC1*XL
C     WRITE(11,88), CLOGC(J)
C  88 FORMAT(' ', D16.7)
   90 CONTINUE
      RETURN
      END
C**************************************************************
C
C       Subroutine  :  DGFRP
C
C       Purpose     :  Computes group fractions in all the components
C                      in pure state
C
C**************************************************************
C
      SUBROUTINE DGFRP (SUMXP, SUMXM, QG, XP, XGM, SUMQXP, CRNU,
     &                         MCOUNT)
C
C ....................DESCRIPTION OF VARIABLES....................
C
C XP      = Group fraction in pure components
C XGM      = Intermediate variable in computation of group fraction
C          in mixture
C SUMQXP = Sum of the product of 'Q' and 'XP' in pure compound
C
      REAL*8       XC(90,90), SUMXP(90), SUMXM, QG(90,90), XP(90,90),
     &             XGM(90,90), SUMQXP(90), CRNU(90,90)
      INTEGER      NU(90,90), NC, NG, MCOUNT
C
      COMMON/ DU1 /NC, NG
      COMMON/ DU3 /NU
      COMMON/ DU5 /XC
C
      DO 110 J = 1, NC
      SUMQXP(J) = 0.0D0
      DO 100 I = 1, NG
      XP(I,J) = CRNU(I,J)/SUMXP(J)
      XGM(I,J) = (XC(MCOUNT,J)*CRNU(I,J))/SUMXM
  100 SUMQXP(J) = SUMQXP(J) + (XP(I,J)*QG(I,J))
  110 CONTINUE
      RETURN
      END
C**************************************************************
C
C       Subroutine  :  DGFRM
C
C       Purpose     :  Computes group fractions in the mixture
C
C**************************************************************
C
      SUBROUTINE DGFRM (NSG, XGM, XM, QK, SUMQXM)
C
C ....................DESCRIPTION OF VARIABLES....................
C
C XM     = Group fraction in mixture
C SUMQXM = Sum of the product of 'Q' and 'XM' in mixture
```

```
C
      REAL*8    XGM(90,90), XM(90), QK(90), SUMQXM
      INTEGER    NSG(90), NC, NG
C
      COMMON/ DU1 /NC, NG
C
      SUMQXM = 0.0D0
      DO 130 I = 1, NG
      K = NSG(I)
      XM(I) = 0.0D0
      DO 120 J = 1, NC
 120 XM(I) = XM(I) + XGM(I,J)
      IF (NSG(I) .EQ. 0) GO TO 130
      SUMQXM = SUMQXM + (QK(K)*XM(I))
 130 CONTINUE
      RETURN
      END
C****************************************************************
C
C     Subroutine : DAFP
C
C     Purpose    : Computes area fraction of a particular group in
C                  a compound in pure state
C
C****************************************************************
C
C
      SUBROUTINE DAFR (QG, XP, SUMQXP, THETAP)
C
C ..................DESCRIPTION OF VARIABLES...................
C
C THETAP = Area fraction of a particular group in a compound in
C        pure state
C
      REAL*8    QG(90,90), XP(90,90), SUMQXP(90), THETAP(90,90)
C
      INTEGER   NC, NG
C
      COMMON/ DU1 /NC, NG
C
C Calculate "THETA" values for all the groups in pure compounds
C
      DO 140 J = 1, NC
      DO 140 I = 1, NG
      THETAP(I,J) = (QG(I,J)*XP(I,J))/SUMQXP(J)
 140 CONTINUE
      RETURN
      END
```

```
C***************************************************************
C
C      Subroutine : DAFM
C
C      Purpose    : Computes area fraction of a particular group in
C                   mixture
C
C***************************************************************
C
       SUBROUTINE DAFM (NSG, QK, XM, SUMQXM, THETAM)
C
C ..................DESCRIPTION OF VARIABLES...................
C
C THETAM = Area fraction of a particular group in mixture
C
       REAL*8    QK(90), XM(90), SUMQXM, THETAM(90)
       INTEGER   NSG(90), NC, NG
C
       COMMON/ DU1 /NC, NG
C
C Calculate "THETA" values for all the groups in the mixture
C
       DO 150 I = 1, NG
       IF (NSG(I) .EQ. 0) GO TO 150
       L = NSG(I)
       THETAM(I) = (QK(L)*XM(I))/SUMQXM
   150 CONTINUE
       RETURN
       END
C***************************************************************
C
C      Subroutine : DINPAR
C
C      Purpose    : Computes group interaction parameter for
C                   all possible interactions in the mixture
C
C***************************************************************
C
       SUBROUTINE DINPAR (NPG, IT, A, T, SHY)
C
C ..................DESCRIPTION OF VARIABLES...................
C
C SHY    = Group interaction parameter
C
       REAL*8    A(90,90), SHY(90,90), T(90)
       REAL*8    DEXP
       INTEGER   NPG(90), IT, NC, NG
C
       COMMON/ DU1 /NC, NG
C
       DO 170 J = 1, NG
       IF (NPG(J) .EQ. 0) GO TO 170
       NP = NPG(J)
C
       DO 160 I = 1, NG
       IF (NPG(I) .EQ. 0) GO TO 160
```

```
         MP = NPG(I)
         SHY(MP,NP) = DEXP(-(A(MP,NP)/T(IT)))
  160  CONTINUE
  170  CONTINUE
         RETURN
         END
C****************************************************************
C
C       Subroutine : DTSHYP
C
C       Purpose    : Computes sum of the products of 'THETA' and 'SHY'
C                    values for various groups in pure compounds
C
C****************************************************************
C
         SUBROUTINE DTSHYP (NPG, THETAP, SHY, TEMPP, SUMTSP)
C
C...................DESCRIPTION OF VARIABLES....................
C
C TEMPP  = Intermediate variable in the computation of SUMTSP
C SUMTSP = Sum of the products of 'THETA' and 'SHY' values in pure
C          compounds
C
         REAL*8    THETAP(90,90), SHY(90,90), TEMPP(90), SUMTSP(90,90)
         INTEGER   NPG(90), NC, NG
C
         COMMON/ DU1 /NC, NG
C
         DO 210 K = 1, NC
         DO 200 J = 1, NG
         NP = NPG(J)
         IF(THETAP(J,K) .NE. 0.0D0) GO TO 180
         SUMTSP(J,K) = 0.0D0
         GO TO 200
  180  TEMPP(J) = 0.0D0
         DO 190 I = 1,NG
         MP = NPG(I)
         IF(THETAP(I,K) .EQ. 0.0D0) GO TO 190
         TEMPP(J) = TEMPP(J) + THETAP(I,K)*SHY(MP,NP)
  190  CONTINUE
         SUMTSP(J,K) = TEMPP(J)
  200  CONTINUE
  210  CONTINUE
         RETURN
         END
C****************************************************************
C
C       Subroutine : DTSHYM
C
C       Purpose    : Computes sum of the products of 'THETA' and 'SHY'
C                    values for various groups in mixture
C
C****************************************************************
C
         SUBROUTINE DTSHYM (NPG, NSG, SHY, THETAM, SUMTSM)
C
```

```
C ...........................DESCRIPTION OF VARIABLES......................
C
C SUMTSM = Sum of the products of 'THETA' & 'SHY' values in mixture.
C
      REAL*8    THETAM(90), SHY(90,90), SUMTSM(90)
      INTEGER    NPG(90), NSG(90), NC, NG
C
      COMMON/ DU1 /NC, NG
C
      DO 230 J = 1, NG
      IF (NPG(J) .EQ. 0) GO TO 230
      NP = NPG(J)
      NS = NSG(J)
      SUMTSM(NS) = 0.0D0
      DO 220 I = 1, NG
      IF (NPG(I) .EQ. 0) GO TO 220
      MP = NPG(I)
      MS = NSG(I)
      SUMTSM(NS) = SUMTSM(NS) + THETAM(I)*SHY(MP,NP)
 220  CONTINUE
 230  CONTINUE
      RETURN
      END
C*************************************************************************
C
C     Subroutine : DSSUMP
C
C     Purpose    : Computes second sum to be used in the computation
C                  of ln gamma of groups in pure compounds
C
C*************************************************************************
C
      SUBROUTINE DSSUMP (NPG, THETAP, SHY, SUMTSP, TSPP1, TSPP)
C
C ......................DESCRIPTION OF VARIABLES....................
C
C TSPP1  = Intermediate variable in the computation of TSPP
C TSPP   = Second sum to be used in the computation of ln gamma
C         of groups in pure compounds .
C
      REAL*8    THETAP(90,90), SHY(90,90), TSPP1(90), SUMTSP(90,90),
     &          TSPP(90,90)
      INTEGER   NPG(90), NC, NG
C
      COMMON/ DU1 /NC, NG
C
      DO 270 K = 1, NC
      DO 260 J = 1, NG
      NP = NPG(J)
      IF(THETAP(J,K) .NE. 0.0D0) GO TO 240
      TSPP(J,K) = 0.0D0
      GO TO 260
  240 TSPP1(J) = 0.0D0
      DO 250 I = 1, NG
      MP = NPG(I)
      IF(THETAP(I,K) .EQ. 0.0D0) GO TO 250
```

```
         TSPP1(J) = TSPP1(J) + (THETAP(I,K)*SHY(NP,MP))/SUMTSP(I,K)
  250 CONTINUE
      TSPP(J,K) = TSPP1(J)
  260 CONTINUE
  270 CONTINUE
      RETURN
      END
C***************************************************************
C
C     Subroutine  :  DSSUMM
C
C     Purpose     : Computes second sum to be used in the computation
C                   of ln gamma of groups in mixture
C
C***************************************************************
C
      SUBROUTINE DSSUMM (NPG, NSG, THETAM, SHY, SUMTSM, TSPM)
C
C ..................DESCRIPTION OF VARIABLES...................
C
C TSPM    = Second sum to be used in the computation of ln gamma
C           of groups in mixture
C
      REAL*8     THETAM(90), SHY(90,90), SUMTSM(90), TSPM(90)
      INTEGER    NPG(90), NSG(90), NC, NG
C
      COMMON/ DU1 /NC, NG
C
      DO 290 J = 1, NG
      IF (NPG(J) .EQ. 0) GO TO 290
      NP = NPG(J)
      NS = NSG(J)
      TSPM(NS) = 0.0D0
      DO 280 I = 1, NG
      IF (NPG(I) .EQ. 0) GO TO 280
      MP = NPG(I)
      MS = NSG(I)
      TSPM(NS) = TSPM(NS) + (THETAM(I)*SHY(NP,MP))/SUMTSM(MS)
  280 CONTINUE
  290 CONTINUE
      RETURN
      END
C***************************************************************
C
C     Subroutine  :  DGLNP
C
C     Purpose     : Computes ln gamma of groups in pure compounds
C
C***************************************************************
C
      SUBROUTINE DGLNP (QG, SUMTSP, TSPP, GLOGP)
C
C ..................DESCRIPTION OF VARIABLES...................
C
C GLOGP   = Ln gamma of groups in pure compounds
C
```

```
      REAL*8     QG(90,90),SUMTSP(90,90),TSPP(90,90),GLOGP(90,90)
      REAL*8     DLOG
C
      INTEGER    NC, NG
C
      COMMON/ DU1 /NC, NG
C
      DO   310  J  =  1,  NC
      DO   310  I  =  1,  NG
      IF(SUMTSP(I,J)  .NE.  0.0D0)  GO  TO  300
      GLOGP(I,J)  =  0.0D0
      GO  TO  310
  300 GLOGP(I,J)  =  QG(I,J)*(1.0D0-DLOG(SUMTSP(I,J))-TSPP(I,J))
  310 CONTINUE
      RETURN
      END
C*****************************************************************
C
C        Subroutine  :  DGLNM
C
C        Purpose      :  Computes  ln  gamma  of  groups  in  mixture
C
C*****************************************************************
C
      SUBROUTINE  DGLNM  (QK,  NSG,  SUMTSM,  TSPM,  GLOGM)
C
C  .....................DESCRIPTION  OF  VARIABLES.....................
C
C GLOGM   =  Ln  gamma  of  groups  in  mixture
C
      REAL*8     QK(90),  SUMTSM(90),  TSPM(90),  GLOGM(90),  DLOG
      INTEGER     NSG(90), NC,  NG
C
      COMMON/  DU1  /NC,  NG
C
      DO  320  I  =  1,  NG
      IF  (NSG(I)  .EQ.  0)  GO  TO  320
      NS  =  NSG(I)
      GLOGM(NS)  =  QK(NS)*(1.0D0-DLOG(SUMTSM(NS))-TSPM(NS))
  320 CONTINUE
      RETURN
      END
C*********************************************************************
C
C        Subroutine  :  DDLNM
C
C        Purpose      :  Computes  difference  between  ln  gamma  of  groups
C                        in  mixture  and  in  pure  state
C
C*********************************************************************
C
      SUBROUTINE  DDLNM  (NSG,  GLOGP,  GLOGM,  DIFLOG)
C
C  .....................DESCRIPTION  OF  VARIABLES....................
C
C DIFLOG   =  (ln  gamma  of  grp.  in  mixture)  -  (ln  gamma  grp.  in  pure
```

```
C                                                       compound)
C
      REAL*8    GLOGP(90,90), GLOGM(90), DIFLOG(90,90)
      INTEGER   NSG(90), NC, NG
C
      COMMON/ DU1 /NC, NG
C
C
      DO  330 J = 1, NC
      DO  330 I = 1, NG
      IF (NSG(I) .EQ. 0) GO TO 330
      NS = NSG(I)
      DIFLOG(NS,J) = GLOGM(NS) - GLOGP(I,J)
  330 CONTINUE
      RETURN
      END
C*******************************************************************
C
C     Subroutine : DRES
C
C     Purpose    : Computes residual ln gamma of components in
C                  in mixture
C
C*******************************************************************
C
      SUBROUTINE DRES (NSG, CRNU, DIFLOG, RLOGC)
C
C ..................DESCRIPTION OF VARIABLES.....................
C
C RLOGC   = Residual ln gamma of components in mixture
C
      REAL*8    CRNU(90,90), DIFLOG(90,90), RLOGC(90)
      INTEGER   NSG(90), NU(90,90), NC, NG
C
      COMMON/ DU1 /NC, NG
      COMMON/ DU3 /NU,
C
      DO 350 J = 1, NC
      RLOGC(J) = 0.0D0
      DO 340 I = 1, NG
      NS = NSG(I)
      IF(CRNU(I,J) .EQ. 0.0D0) GO TO 340
      RLOGC(J) = RLOGC(J) + CRNU(I,J)*DIFLOG(NS,J)
  340 CONTINUE
  350 CONTINUE
      RETURN
      END
C*******************************************************************
C
C     Subroutine : DFREEV
C
C     Purpose    : Computes free-volume contribution to the activity
C                  coefficients of components in mixture
C
C*******************************************************************
C
```

```
      SUBROUTINE DFREEV (MCOUNT, RC, LNGFV)
C
C ....................DESCRIPTION OF VARIABLES......................
C
C B            = Proportionality constant
C C            = Constant related to the external degree of freedom
C                for each component
C VM           = Molar volume of the components
C VMX,        = Intermediate variable used in the calculation of the
C RCX           reduced volume of the mixture
C VR           = Reduced volume of the components
C VRM          = Reduced volume of the mixture
C F1,F2,     = Intermediate variable used in the calculation of the
C F3,F4        ln gamma (free-volume)
C LNGFV       = Free-volume activity coefficeint
C
C Declare real and integer variables and their dimension
C
      REAL*8   B, C(90), RC(90), VM(90), XC(90,90)
      REAL*8   P, F1, F2, F3, F4, DLOG, LNGFV(90)
      REAL*8   VMX, RCX, VR(90), VRM
C
      INTEGER NC, NG, MCOUNT
C
C Declare common variables
C
      COMMON/ DU1 /NC, NG
      COMMON/ DU5 /XC
      COMMON /DF1/ VM, C, B
C
C Expdnent "P" to be used in the calculation of ln gamma (FV)
C
      P = 1.0D0 / 3.0D0
C
C Initialize and set do-loops for the number of components
C
      VMX = 0.0D0
      RCX = 0.0D0
      DO 400 J = 1, NC
C
C Compute reduced volume of the components
C
      VR(J) = VM(J) / (15.17D0 * B * RC(J))
      VMX = VMX + (VM(J) * XC(MCOUNT,J))
      RCX = RCX + (RC(J) * XC(MCOUNT,J))
  400 CONTINUE
C
C Compute the reduced volume of the mixture
C
        VRM = VMX / (15.17 * B * RCX)
C
C Compute ln gamma (FV) for solvent and solutes
C
        DO 450 K = 1, NC
C
      F1 = (3.0D0*C(K)) * DLOG((VR(K)**P-1.0D0) / (VRM**P-1.0D0))
```

```
          F2 = (VR(K) / VRM) - 1.0D0
          F3 = 1.0D0 / (1.0D0 - (1.0D0 / (VR(K)**P)))
          F4 = C(K) * (F2 * F3)
          LNGFV(K) = F1 - F4
  450   CONTINUE
        RETURN
        END
C************************************************************
C
C     Subroutine : ACVTY
C
C     Purpose    : To compute estimates of activity of components
C                  in an aqueous solution of biological origin
C
C************************************************************
C
        SUBROUTINE ACVTY (GLUNFV, ACTVTY)
C
C Declare real and integer variables
C
        REAL*8     GLUNFV(200,90), GAMMA(200,90), ACTVTY(200,90),
     &               XC(90,90)
        INTEGER  MCOUNT, NC, NG
C
C Declare common variables
C
        COMMON/ DU1 /NC, NG
        COMMON/ DU5 /XC
        COMMON/ DU7 /NSYSTM, IT, NT, NXCSET, MCOUNT
C
C Do-loop to compute the activity coefficient and activity over
C the composition range and for the temperatures provided
C
           DO 500 J = 1, NC
            GAMMA(MCOUNT,J) = DEXP(GLUNFV(MCOUNT,J))
            ACTVTY(MCOUNT,J) = GAMMA(MCOUNT,J) * XC(MCOUNT,J)
  500     CONTINUE
        RETURN
        END
```

9.1.1 Input Data for the Program UFACFV

The data given here are for binary glucose-water system.

```
FILE NO. & NAME

1 = RKQK --------- The group volume and area parameters as reported
                   by Gmehling et al. (1982)

FILE NO. & NAME

2 = AMN ---------- The group-interaction parameters as reported by
                   Gmehling  et al. (1982)

FILE NO. & NAME          DATA                  VARIABLES        COMPONENTS

3 = FVDATA
                          2,1.0D0               ---NCOMP, B
                          1.0D0,18.015D0  ---C(1), VM(1)        1 = Water
                          1.0D0,177.6D0   ---C(2), VM(2)        2 = Glucose

FILE NO. & NAME          DATA           VARIABLES        COMPONENTS

4 = GCODE
                          1         ----------NSYSTM
                          2    5   ----------NC, NG
                          0         ----------NGC(1,1)
                          0         ----------NGC(2,1)
                          0         ----------NGC(3,1)   J = 1 = Water
                         17        ----------NGC(4,1)
                          0         ----------NGC(5,1)
                          2         ----------NGC(1,2)
                          3         ----------NGC(2,2)
                         15        ----------NGC(3,2)   J = 2 = Glucose
                          0         ----------NGC(4,2)
                         21        ----------NGC(5,2)

FILE NO. & NAME          DATA           VARIABLES        COMPONENTS

5 = NEW
                          0        -----------NU(1,1)
                          0        -----------NU(2,1)
                          0        -----------NU(3,1)   J = 1 = Water
                          1        -----------NU(4,1)
                          0        -----------NU(5,1)
                          1        -----------NU(1,2)
                          4        -----------NU(2,2)
                          5        -----------NU(3,2)   J = 1 = Glucose
                          0        -----------NU(4,2)
                          1        -----------NU(5,2)
```

FILE NO. & NAME	DATA	VARIABLES	COMPONENTS
6 = NEWCR			
	0.0D0	---------CRNU(1,1)	
	0.0D0	---------CRNU(2,1)	
	0.0D0	---------CRNU(3,1)	J = 1 = Water
	1.0D0	---------CRNU(4,1)	
	0.0D0	---------CRNU(5,1)	
	1.0D0	---------CRNU(1,2)	
	4.0D0	---------CRNU(2,2)	
	5.0D0	---------CRNU(3,2)	~~J = 1 = Gl~~ucose
	0.0D0	---------CRNU(4,2)	
	1.0D0	---------CRNU(5,2)	

FILE NO. & NAME	DATA	VARIABLES	COMPONENTS
7 = TMOLEF			
	1	-----NT	
	298.16D0	-----T	
	5	-----NXCSET	
	1.0000000D+00	-----XC(1,1)	
	0.0000000D+00	-----XC(1,2)	
	9.9900182D-01	-----XC(2,1)	
	9.9817735D-04	-----XC(2,2)	J = 1 = Water
	9.9482074D-01	-----XC(3,1)	J = 2 = Glucose
	5.1792617D-03	-----XC(3,2)	
	9.8912857D-01	-----XC(4,1)	
	1.0871435D-02	-----XC(4,2)	
	9.8284332D-01	-----XC(5,1)	
	1.7156680D-02	-----XC(5,2)	

FILE NO. & NAME	DATA	VARIABLES
8 = GCV		
	2,3,15,17,21	-----------NSG(I)
	1,1,5,7,10	----------NPG(I)

9.2 FREEZE

This program computes the freezing temperature of aqueous mixtures. A detailed description of the program is given below:

```
C**************************************************************
C
C    PROGRAM  :  FREEZE
C
C    PURPOSE  : To compute freezing point of solutions for a
C               given composition.
C
C    METHOD   : This program computes the FREEZING TEMPERATURE
C               of a solution solution by using the  "UNIFAC-FV"
C               IMSL  subroutine "ZSCNT"
C
C               In UNIFAC-FV  the activity of the components is
C               calculated by computing the activity coefficients
C               in non-electrolyte liquid mixtures using mole
C               fractions of components, and then multiplying
C               activity coefficient with the mole fractions.
C
C               In "ZSCNT" the freezing temperature for a particular
C               water activity is found out by solving the non-linear
C               equation which relates the Aw to freezing temptrature
C               by the following equation :.
C
C                   ln(Aw) = 528.72(1.0/T) + 4.5821n(T) - 27.641
C
C               The roots of this equation is found by an iterative
C               approach and compared with the starting temperature.
C               If the two do not match the calculation is repeated
C               with the new temperature obtained by the iterative
C               approach
C
C    TO RUN :  Use the following run file
C
C                 $R BROU:BIG T=2S 1=RKQK 2=AMN 3=FREEV 4=GCODE
C                    5=NEW 6=NEWCR 7=TMOLEF 8=GCV 11=GC-OUT1 12=GC-OUT2
C                    PAR=GC-FREEZ.O+*IMSLDPLIB
C                 $ENDFILE
C
C
C    PROGRAMED BY : Gour Choudhury
C
C**************************************************************
C
C Declare real and integer variables
C
      REAL*8    RK(90), QK(90), A(90,90), T(90), B, C(90), VM(90),
     &          GLUNFV(200,90), ACTVTY(200,90)
      INTEGER   NRQ
```

```
C
C Declare common variables
C
        COMMON/ DF1 /VM, C, B
        COMMON/ DFR /TEST
        COMMON/ DU2 /RK, QK, NRQ
        COMMON/ DU6 /A, T
C
C Call DDATA, and DUFV to obtain the UNIFAC AND FREE-VOLUME
C contribution to the activity coefficient of the components.
C
        CALL DDATA
        CALL DUFV  (GLUNFV)
        STOP
        END
C***************************************************************
C
C        Subroutine : DDATA
C
C        Same       : as described in UFACFV
C
C***************************************************************
C
C       Subroutine  : DUFV
C
C       Purpose     : Computes the UNIFAC and FREE-VOLUME contribution
C                     to the activity coefficients of the components
C                     in aqueous solution
C
C***************************************************************
C
        SUBROUTINE DUFV (GLUNFV)
C
C Variables and their dimension for the combinatorial part of
C the activity coefficient
C
        REAL*8   RK(90), QK(90), RC(90), QC(90), RG(90,90), QG(90,90),
     &           CL(90), XC(90,90), THETAC(90), PHIC(90), CLOGC(90),
     &           CRNU(90,90)
C
C Variables and their dimension for the residual part of the
C activity coefficient
C
        REAL*8   XP(90,90), XGM(90,90), XM(90), SUMXP(90), SUMXM,
     &           SUMQXP(90), A(90,90), SHY(90,90), SUMQXM, T(90),
     &           SUMTSP(90,90)
        REAL*8   SUMTSM(90), TEMPP(90), TSPP1(90,90), TSPP(90,90),
     &           TSPM(90), THETAP(90,90), THETAM(90), THETAT, PHIT, XL
        REAL*8   GLOGP(90,90), GLOGM(90), DIFLOG(90,90), RLOGC(90)
C
C Variables and their dimension for the free-volume contribution
C to the activity coefficient of the components
C
        REAL*8   B, C(90), VM(90), LNGFV(200)
C
C Variables and their dimensions for the total activity coefficient
```

```
C
      REAL*8   CLGAMA(90), GLNO(90), GLUNFV(200,90), ACTVTY(200,90)
C
C Variables and their dimension for freezing point computation
C
      REAL*8   X(1), PAR(1), TEST, PCDEV, DABS
C
C Global integer variables and their dimensions
C
      INTEGER NRQ, NGC(90,90), NU(90,90), NPG(90), NSG(90), NXCSET,
     &         NSYSTM, NT, IT, IS, MCOUNT, ICOUNT, LCOUNT
C
C Common variables
C
      COMMON/ DF1 /VM, C, B
      COMMON/ DFR /TEST
      COMMON/ DU1 /NC, NG
      COMMON/ DU2 /RK, QK, NRQ
      COMMON/ DU3 /NU
      COMMON/ DU4 /NGC, NPG, NSG
      COMMON/ DU5 /XC
      COMMON/ DU6 /A, T
      COMMON/ DU7 /NSYSTM, NT, NXCSET, MCOUNT
      COMMON/ DU8 /CRNU
C
C Statement that enables format-free reading of data
C
      LOGICAL *1 FREE(1)/'*'/
C
C Do-loop to calculate activity coefficient for all the
C components in the solution
C
      ICOUNT = 0
      DO 100 I = 1, NSYSTM
C
      MCOUNT = 0
      LCOUNT = 0
      DO 90 IT = 1, NT
      DO 80 IS = 1, NXCSET
      MCOUNT = MCOUNT + 1
C
      CALL DRQLC  (RK, QK, RG, QG, NGC, RC, QC, CL, SUMXP, SUMXM,
     &                  THETAT, PHIT, XL, CRNU, MCOUNT)
      CALL DTPHI  (RC, QC, THETAT, PHIT, THETAC, PHIC, MCOUNT)
      CALL DCOMB  (RC, QC, PHIT, THETAT, CL, XL, CLOGC)
      CALL DGFRP  (SUMXP, SUMXM, QG, XP, XGM, SUMQXP, CRNU, MCOUNT)
      CALL DGFRM  (NSG, XGM, XM, QK, SUMQXM)
      CALL DAFP    (QG, XP, SUMQXP, THETAP)
      CALL DAFM    (NSG, QK, XM, SUMQXM, THETAM)
C
C Repeat the computation of the freezing temperature : Only
C residual calculation need to repeated.
C
   10 CONTINUE
C
      CALL DINPAR (NPG, IT, A, T, SHY)
```

```
      CALL DTSHYP (NPG, THETAP, SHY, TEMPP, SUMTSP)
      CALL DTSHYM (NPG, NSG, SHY, THETAM, SUMTSM)
      CALL DSSUMP (NPG, THETAP, SHY, SUMTSP, TSPP1, TSPP)
      CALL DSSUMM (NPG, NSG, THETAM, SHY, SUMTSM, TSPM)
      CALL DGLNP  (QG, SUMTSP, TSPP, GLOGP)
      CALL DGLNM  (QK, NSG, SUMTSM, TSPM, GLOGM)
      CALL DDLNM  (NSG, GLOGP, GLOGM, DIFLOG)
      CALL DRES   (NSG, CRNU, DIFLOG, RLOGC)
      CALL DFREEV (MCOUNT, RC, LNGFV)
C
C Check for the activity coefficient at infinite dilution when
C mole fraction of a component = 0.0D0
C
      IF (XC(MCOUNT,2) .NE. 0.0D0) GO TO 30
      DO 20 J = 2, NC
         GLN0(J) = CLOGC(J) + RLOGC(J) + LNGFV(J)
   20 CONTINUE
      GO TO 80
C
   30 CLGAMA(1) = CLOGC(1) + RLOGC(1) + LNGFV(1)
      DO 40 K = 2, NC
         CLGAMA(K) =  (CLOGC(K) + RLOGC(K) + LNGFV(K)) - GLN0(K)
   40 CONTINUE
C
      DO 60 L = 1, NC
        GLUNFV(MCOUNT,L) = CLGAMA(L)
   60 CONTINUE
      CALL ACVTY (GLUNFV, ACTVTY)
      X(1) = T(IT)
      PAR(1) = ACTVTY(IS,1)
      WRITE(11,5) X(1), PAR(1)
    5 FORMAT(' ', 2D16.7)
      CALL TEMP(X,PAR)
C
C TEST FOR CONVERGENCE
C
      PCDEV = DABS((T(IT) - X(1)) / T(IT))
      IF (PCDEV .LT. TEST) GO TO  70
      T(IT) = X(1)
      GO TO 10
   70 T(IT) = X(1)
      WRITE(12,75) IS, XC(IS,1), X(1)
   75 FORMAT(9X, I3, 2X, 'X-H20 = ',F9.5,4X,'FREEZING PT. = ',F9.5)
C
   80 CONTINUE
   90 CONTINUE
C
  100 CONTINUE
      RETURN
      END
```

```
C************************************************************
C
C       Subroutines : DRQLC -------- to -------- DFREEV
C
C       Same        : as described in UFACFV
C
C************************************************************
C
C       Subroutine : TEMP
C
C       Purpose     : To compute the freezing temperature of a
C                     solution with known composition whose water
C                     activity has been calculated by using
C                      UNIFAC-FV model.
C
C       Method      :  This procedure uses the IMSL subroutine "ZSCNT"
C                     to find the roots of a non-linear equation by
C                     iterative approach.
C************************************************************
C
        SUBROUTINE TEMP(X, PAR)
C
        INTEGER   N, ITMAX, IER
        REAL*8   WK(22), X(1), PAR(1), FNORM
        EXTERNAL FCN
        N = 1
        NSIG = 5
        ITMAX = 20
        WRITE(11,5) X(1), PAR(1)
    5  FORMAT(' ', 2D16.7)
        CALL ZSCNT(FCN, NSIG, N, ITMAX, PAR, X, FNORM, WK, IER)
        WRITE(12,10) X(1)
   10  FORMAT(' ', 12X, F13.5)
        RETURN
        END
        SUBROUTINE FCN(X, F, N, PAR)
        REAL*8 X(1), F(1), PAR(1), DLOG
        F(1) = 528.72D0 * (1.0D0/X(1)) + 4.582D0*DLOG(X(1)) - 27.641D0
       &          - DLOG(PAR(1))
        RETURN
        END
```

9.3 SLIMIT

This program calculates the solubility limit of components in mixtures. A detailed description of the program is given below:

```
C**********************************************************
C
C    PROGRAM  :  SLIMIT
C
C    PURPOSE  :  To compute solubility of varous solutes at a
C                given temperature using the UNIFAC-FV model.
C
C    METHOD   :  This program computes the solubility of various
C                solutes "UNIFAC-FV" model
C
C                In UNIFAC-FV , the activity of the components is
C                calculated by computing the activity coefficients
C                in non-electrolyte liquid mixtures using mole
C                fractions of components, and then multiplying
C                activity coefficient with the mole fractions.
C
C                This activity is then compared with the activity
C                computed by using the follwing equation :
C
C                        ln(A)s = -(DELTASf / RT) * (Tm - T)
C
C    PROGRAMED BY  :  Gour Choudhury
C
C*************************************************************
C
C Declare real and integer variables
C
C----------------- UNIFAC-FV Variables-------------------C
         REAL*8    A(90,90), RK(90), QK(90), T(90), B, C(90), VM(90),
     &             XC(90,90), CRNU(90,90), DSOL(200)
         INTEGER   NU(90,90), NGC(90,90), NPG(90), NSG(90), NC, NG,
     &             NT, IT, NXCSET, NCOUNT, ICOUNT, NRQ, NCOMP, NCOMPD
C
C ----------------------SLIMIT Variables----------------C
         REAL*8    F, EPS, EPS2, ETA, X(1), TM, DELTAS
         INTEGER   NSIG, N, ITMAX, IER, INDEX
         EXTERNAL  F
C
C Declare common variables
C
         COMMON/ DF1 /VM, C, B
         COMMON/ DS1 /TM, DELTAS, INDEX
         COMMON/ DU1 /NC, NG
         COMMON/ DU2 /RK, QK, NRQ
         COMMON/ DU3 /NU
         COMMON/ DU4 /NGC, NPG, NSG
         COMMON/ DU5 /XC
```

```
      COMMON/ DU6 /A, T
      COMMON/ DU7 /NCOMPD, IT, NT, NXCSET, MCOUNT
      COMMON/ DU8 /CRNU
C
C This statement permits format-free reading of input data
C
      [illegible]AL *1 FREE(1)/'*'/
C
C Call DDATA to read the input data and read other data related to
C subroutine 'ZREAL1'
C
      CALL DDATA
C
      DO 100 IT = 1, NT
        INDEX = 1.0D0
        MCOUNT = IT
        READ (9, FREE) EPS, EPS2, ETA, X(1), TM, DELTAS
        READ (9, FREE) NSIG, ITMAX, N
C
        CALL  ZREAL1 (F, EPS, EPS2, ETA, NSIG, N, X, ITMAX, IER)
        DSOL(IT) = X(1)
        WRITE(11,10) T(IT), DSOL(IT), TM, DELTAS, X(1), ITMAX
   10  FORMAT(' ', 5(3X, F10.5), 3X, I3)
  100 CONTINUE
      STOP
      END
C
C ---------------> External function F(X) -----------------C
      REAL   FUNCTION F(X)
C
C Declare Real, Integer and Common variables
C
C----------------- UNIFAC-FV Variables--------------------C
      REAL*8   A(90,90), RK(90), QK(90), T(90), B, C(90), VM(90),
     $         XC(90,90), CRNU(90,90), GLUNFV(200,90)
      INTEGER  NU(90,90), NGC(90,90), NPG(90), NSG(90), NC, NG,
     &         NT, IT, NXCSET, NCOUNT, ICOUNT, NRQ, NCOMP, NCOMPD
C
C----------------- FUNCTION Variables---------------------C
      REAL*8  X, TM, DELTAS, ATHEOR, GAMMA(200,90)
      INTEGER INDEX, IT
C
      COMMON/ DF1 /VM, C, B
      COMMON/ DS1 /TM, DEBTAS, INDEX
      COMMON/ DU1 /NC, NG
      COMMON/ DU2 /RK, QK, NRQ
      COMMON/ DU3 /NU
      COMMON/ DU4 /NGC, NPG, NSG
      COMMON/ DU5 /XC
      COMMON/ DU6 /A, T
      COMMON/ DU7 /NCOMPD, IT, NT, NXCSET, MCOUNT
      COMMON/ DU8 /CRNU
C
      IF (INDEX .NE. 0) GO TO 20
      XC(IT,2) = X
      XC(IT,1) = 1.0D0 - XC(IT,2)
```

```
      MCOUNT = IT
 20   CALL DUFV  (GLUNFV)
C
      GAMMA(IT,2) = DEXP(GLUNFV(IT,2))
      ATHEOR = DEXP(-(DELTAS/(1.987D0 * T(IT))) * (TM - T(IT)))
      WRITE(12,30) DELTAS, T(IT), TM, ATHEOR
 30   FORMAT(' ', 5X, 3(3X,F10.2), 3X, F10.5)
      F = ATHEOR - (X * GAMMA(IT,2))
      INDEX = 0
      RETURN
      END
C*************************************************************
C
C         Subroutines : DDATA, DUFV and DRQLC --to--DFREEV
C
C         Same        : As described in UFACFV
C
C         Note        : Changes should be made in DUFV so as to
C                       calculate the activity coefficients of
C                       the components in symmetric convention.
C
C*************************************************************
```