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PROPERTIES OF LIQUID FOOD COMPONENTS IN
AQUEOUS SOLUTION AND THEIR BEHAVIOR
DURING FREEZE DRYING

by

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A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
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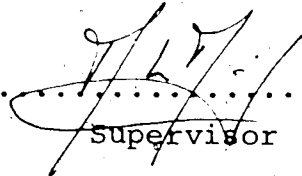OF DOCTOR OF PHILOSOPHY

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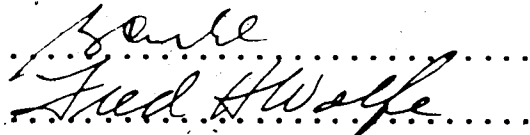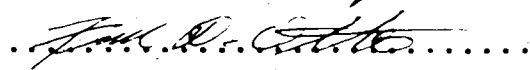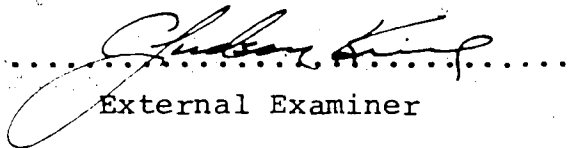
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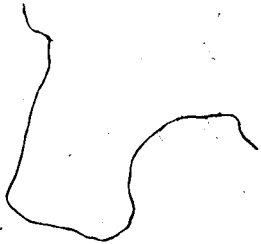External Examiner

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iv

ABSTRACT

Some physical properties of liquid food components in model aqueous solutions were investigated. Diffusion coefficients of a sugar (sucrose), an amino acid (glycine) and a polyfunctional alcohol (glycol) were measured at 25°C by using the schlieren optical system of a preparative ultracentrifuge. The schlieren optical system was modified by the incorporation of a 35 mm single lens reflex camera. The diffusion coefficients, obtained from a 10 min experiment, were well within 2% of values found in existing literature and had an intrinsic precision of better than 2%. The technique was found to be sensitive enough to monitor the variation of diffusion coefficients with small changes in solute concentration and temperature.

The solubilities of the sparingly soluble essential oil components, piperitone, pulegone and carvone, were determined in aqueous solutions containing dissolved sucrose, glucose or sodium chloride. All dissolved solids were found to reduce the solubility of the essential oil components. Studies conducted at 10, 20 and 30°C showed that the solubilities of piperitone and pulegone increased with a decrease in temperature,

whereas carvone exhibited a solubility minimum close to 20°C. Calculated enthalpies, free energies and entropies were compatible with the current theories of dilute aqueous solutions.

The retentions of terpenic essential oil components (piperitone, pulegone and carvone) and non-terpenic essential oil components (eugenol and m-anisaldehyde) were measured during freeze drying of model aqueous solutions. Model solutions contained sucrose, glucose, sodium chloride and gum arabic which are all common food components. Retention of the essential oil components was found to be dependent on; solids con-centration, solids composition, sample thickness, initial volatile content, the presence of additional volatiles, freezing rate and solution pH.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

I. Measurement of Diffusion Coefficients of Low Molecular

    Weight Compounds in Aqueous Solution Using an Ultra-

    centrifugal Technique

A. INTRODUCTION

         For many years quantitative diffusion measure-

ments have greatly added to the knowledge of molecular

weight and characteristic properties of proteins and other

macromolecules of biological interest. In addition diffu-

sion studies have become increasingly important in other

areas; extraction, absorption, distillation and ion ex-

change (Holmes, 1960). Correlation of mass-transfer coef-

ficients requires a knowledge of diffusion coefficients.

For example, the diffusion phenomenon has been success-

fully applied to various food processing techniques in an

attempt to explain the mass-transfer characteristics of

food components during processing. The degree of volatile

retention in spray drying (Rulkens and Thijssen, 1972b),

air drying (Menting et al., 1970b) and freeze drying

(Thijssen, 1972b and King and Chandrasekaran, 1973) has

been explained in terms of diffusion theories.

         Diffusion may be defined as the process whereby

concentration differences in a solution spontaneously

decrease until the solution finally becomes homogeneous.

Diffusion occurs because molecules in a solution are in constant motion, this continual wandering being a direct consequence of their thermal energy. The term diffusion is applied only to the macroscopic flow of solution components due to concentration differences, whereas the random movements of individual molecules through the solution, which occur after the solution has reached macroscopic homogeneity, are not referred to as diffusion.

Fick's first law, as denoted by Equation (1) for

$$J_1 = -D\left(\frac{\partial c_1}{\partial x}\right)$$ (1)

one dimensional transport of solute, defines the diffusion coefficient, D, in terms of flux of solute, J ($kgm^{-2}s^{-1}$), and its concentration gradient. A straightforward calculation of D is not possible since only concentration gradients may be measured directly whereas flow of solute is not susceptible to direct measurement. Most methods for determining D utilize integrated forms of Fick's second law, Equation (2), or Equation (3) if D varies appreciably with concentration.

$$\frac{\partial c_i}{\partial t} = D\,\frac{\partial^2 c_i}{\partial x_i^2}$$ (2)

$$\frac{\partial ci}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial ci}{\partial xi}\right) \qquad (3)$$

B. LITERATURE REVIEW

This section will deal mainly with techniques used to determine diffusion coefficients in binary liquid systems of non-electrolytes. Diffusion in electrolytic solutions has been reviewed by Harned (1947). Miller (1959) and Gosting (1956) have reviewed diffusion in three component systems. In his review article Gosting (1956) also presents an excellent review of binary diffusion.

Diffusion measurements may be classified into three main types. The first type to be considered include techniques where diffusion occurs in a quasi-stationary state and it is possible to measure the diffusion rate and concentration gradient. The second type includes techniques where a given initial concentration distribution at a starting time is known and the concentration distribution at the end of the experiment is determined. In the third type the concentration distribution is determined continuously or at intervals throughout the experiment.

1) Quasi-Stationary Diffusion Measurements

Techniques falling into this category offer the closest approach to a direct determination of flow where J_1 is computed from the measurement of concentration changes produced in two homogeneous solutions. Since experimental techniques employing solution of Fick's first law offer the easiest approach to measuring diffusion coefficients, a considerable amount of effort has been expended to develop and improve a suitable apparatus. Northrop and Anson (1929) successfully introduced the diaphragm cell technique. In this apparatus diffusion takes place through a porous diaphragm of sintered glass connecting two cells in which the respective liquid concentrations are kept uniform. The diaphragm may be considered to approximate a large number of small parallel tubes. Since the diaphragm has a greatly reduced cross-section, the lessened interfacial area between the two liquids eliminates errors due to thermal or mechanical disturbances. The diaphragm cell technique, as it is most often used today, is based largely on the model designed by Stokes (1950). The Stokes diaphragm cell is illustrated in Figure 1. The diaphragm exhibits an effective cross-section, A, and a path length, l, to the diffusing liquid. In a typical experiment the compartments are

filled with solutions c^1 and c^{11} in such a manner that all the air is forced out of the pores of the diaphragm. Filling the cell with the test solutions requires a strict sequential procedure. Diffusion is allowed to take place until the concentration differences in the compartments are appreciable after which time the cell contents are sampled and diffusion coefficients calculated. D values are evaluated using Equation (4), where c^1 and c^{11} are uniform

$$\ln \left(\frac{c^1 - c^{11}}{c^1 - c^{11}}\right) \begin{matrix} f \\ i \end{matrix} = -\left[\left(\frac{1}{V^1} + \frac{1}{V^{11}}\right) \frac{A}{1}\right] Dt \qquad (4)$$

concentrations on each side of the diaphragm, i and f refer to the initial and final states respectively and t is the time. The cell constant, β, is often evaluated in terms of cell geometry.

$$\beta = \left[(1/V^1) + (1/V^{11})\right] (A/1)$$

β must be determined by calibrating the cell with a material of known diffusion coefficient, for example, urea (Bremer and Cussler, 1970) or potassium chloride (Wedlake and Dullien 1974).

Equation (4), when applied to the evaluation of D, yields an integral or average diffusion coefficient. If

the differential diffusion coefficient can be considered
a linear function of concentration over the concentration
range under study and if equal volumes are used on both
sides of the diaphragm, the measured integral coefficient
is equal to the true differential coefficient for the
mean concentrations. However, for systems where D is a
function of solute concentration, the conversion of
measured integral coefficients into differential coef-
ficients is done mathematically as outlined by Gordon
(1945). Often it is desirable to convert integral coef-
ficients into differential coefficients since the latter
are more useful as they represent a point condition. Thus
they may be used to compare data among different investi-
gators, whereas integral coefficients obtained by different
experimental techniques can be compared only qualitatively.

In experiments using the diaphragm cell it is
necessary to completely purge the pores of the diaphragm
of air or vapor. Entrapment of a gas may seriously alter
the effective cross-section for diffusion. There appears
to be some uncertainty of the effect that stirring speed
has on the experimentally derived diffusion coefficients.
As an example, Leffler and Cullinan (1970) state that
the cell factor β varied by as much as 12% with stirring
speed whereas Ghai and Dullien (1974) state that the stirring

speed does not influence measured diffusivities to any

great extent. Equation (4) requires that the logarithm

of the ratio of concentration differences be used to cal-

culate D. With small differences in initial concentration,

extreme precision is required to reduce the subsequent

error in D to a tolerable value because of the multiplying

effects of the mathematical treatment. Holmes et al. (1962)

studied the diffusion of toluene in various solvents and

found that the precision of toluene determinations (as

measured spectrophotometrically) was ±1.0%. However, the

corresponding error in the diffusion coefficient was ±6%.

Many variations of the original Stokes cell

have appeared in the literature. Bremer and Cussler (1970)

designed a cell whereby a polarimeter was used to monitor

optically active solutes undergoing diffusion. Calus and

Tyn (1973) modified the Stokes cell by incorporating

third compartment to accommodate solution expansion occurring

at elevated temperatures. Sanni and Hutchison (1973) also

designed a cell to work at high temperatures, however,

expansion was allowed for by the incorporation of a U-tube

containing mercury. Hayduk and Ioakimidis (1976) con-

structed an apparatus having all the essentials of a dia-

phragm cell. Their cell was comprised of a cylindrical

Teflon disk containing 252 drilled holes each fitted with

a precision stainless steel capillary 2 cm long and 1 mm
inside diameter. These authors report that their cell
has the advantages of requiring no prior calibration
and diffusivities could be measured in relatively short
times.

In gen al diffusion coefficients obtained by
the diaphragm cell technique are considered to be accu-
rate to approximately 1%. This technique, however, re-
quires a lengthy time period for significant changes in
concentration to occur within the cell components (Holmes
et al., 1962). Lees and Sarram (1971) have shown that
the diaphragm cell technique may be used close to con-
ditions of infinite dilution as revealed by their study
of water diffusivities in organic liquids.

2) Unsteady-State Diffusion Measurements with Analysis
   at the End of Experime Only

Capillary cells fall within this category. In
the open-ended capillary technique a capillary, which is
closed at the bottom and open at the top, is filled with
a solution of known concentration. The open en is
immersed in a well stirred solvent. Since the volume of
the capillary is small compared to that of the solvent, the
concentration at the top of the capillary is maintained

close to zero throughout the experiment. At the end of
an experiment the diffusion coefficient can be determined
by measuring the total amount of material which has passed
out of the capillary.

For self-diffusion measurements, particularly
when using radioactive materials, the capillary cell has
the economic and experimental advantages of requiring
only small amounts of diffusing solution (Wang, 1952).
With non-radioactive compounds very exacting methods of
analysis are required whereas with radioactive materials
the isotopic concentration can be determined by adapting
the standard techniques for radiation measurement.

Despite diffusion times of up to several days,
the capillary technique can provide diffusion coefficients
to an accuracy of about 1%. Adamson and Irani (1958)
showed, using labelled sucrose, that the diffusion coef-
ficients measured by the diaphragm cell technique and
the capillary technique agreed within the limits of
experimental error.

3) Unsteady-State Diffusion   ..surements with Continuous
    or Intermittent Analysis

The most desirable method of conducting a
diffusion experiment is to use a suitable means of physical

analysis to determine the concentration distribution as
a function of time at any desired cross-section of a
diffusion cell. Methods for observing concentration
changes as diffusion proceeds are then limited only by
the accuracy of the analytical method. Although many
methods of analysis may be used, for example, electrical
capacitance, surface tension, velocity of sound, calibrated
floats, absorption of light; only radioactive measurements
and refractive index measurements are in common use today.

As with other diffusion techniques, the avail-
ability of radioactive isotopes facilitates the measure-
ments of self-diffusion coefficients. Using isotopes
emitting beta particles, Walker (1950) determined concen-
tration gradients during diffusion by measuring the ac-
tivity through a small slit surrounding the diffusion
cell. This method is subject to the inaccuracy intro-
duced by a finite slit width and is limited to use with
pure beta emitters. This technique, however, allows the
utilization of experimental methods that are not feasible
with ordinary analytical techniques. One technique that
has been used is to continuously measure the amount of
material present in a thin layer at the end of a diffusion
cell. This is possible if the penetration of the emitted
particles is sufficiently small so that only the surface

layer contributes to the observed radioactivity. Beta
particles from sulfur-35 and carbon-14 satisfy this con-
dition.

For systems with a suitable difference in re-
fractive index between the two components the measurement
of changes in refractive index as diffusion proceeds in
a properly designed cell is currently the most reliable
way to determine a liquid diffusion coefficient. With
most optical techniques the experimental diffusion cell is
such that a uniform denser solution is placed beneath a
uniform solution of lower density. At the start of the
experiment the interface between the two solutions is
made as sharp as possible.

Diffusion cells for studying free diffusion
must have optically flat, parallel windows and must also
be capable of forming a very sharp initial boundary
between the two solutions. The Tiselius electrophoresis
cell with only slight modification has been found to be
the most satisfactory. Kahn and Polson (1947) described
a simple capillary sharpening procedure which produced
a very sharp initial boundary when adopted to the Tiselius
cell. Figure 2 shows the Kahn-Polson cell in which a
fine stainless steel capillary produces a sharp boundary
between the two solutions. Schachman (1957) thoroughly

discusses the procedures for filling the cell and sub-

sequent boundary formation. Although various other

boundary sharpening techniques have recently been devel-

oped (Staker and Dunlop, 1973), the diffusion cells used

at the present time essentially retain the original

Tiselius design.

There are several main methods by which diffu-

sion may be studied using refractive index measurements.

These include the schlieren method, the Gouy interference

method, the Rayleigh interference method and the Jamin

interference method.

English and Dole (1950) measured the diffusion

coefficients of sucrose in supersaturated solutions using

the schlieren method in conjunction with the Tiselius-

type of diffusion cell. The authors found that the

schlieren patterns obtained were extremely difficult to

interpret. They found that the analysis of the schlieren

photographs in different ways gave diffusion coefficients

which varied by as much as 12%. Due to difficulties such

as these the schlieren method has been largely replaced

by interferometric methods. The theory of the schlieren

phenomenon is explained well by Gosting (1956) and is

elegantly presented in a Beckman publication (1964).

The Gouy interference method owes much of its

success to the efforts of Gosting and co-workers. Studies

by these investigators on aqueous solutions of urea

(Gosting and Akeley, 1952), glycoamide (Dunlop and Gosting,

1953) and sucrose (Gosting and Morris, 1949 and Akeley

and Gosting, 1953) have shown that the Gouy technique is

capable of yielding diffusion coefficients accurate to

0.1%. In these experiments which were of approximately

four hours duration, diffusion temperatures were constant

at ±0.002°C. Sucrose diffusion coefficients obtained by

Ellerton and Dunlop (1967) using the Gouy method varied

by no more than 0.1% from values previously obtained by

Gosting. The theory of the Gouy interferometric technique

is discussed by Gosting (1956).

The Rayleigh interference method, the theory of

which is also dealt with by Gosting (1956), has been re-

ported to give diffusion coefficients comparable in accu-

racy to those obtained by the Gouy interferometric method.

Thompson and Oncley (1961) calculated a D value for gly-

cine at 25°C with $\bar{c}$ = 0.6101 g/dl from results they ob-

tained at 20°C. Their value of 1.0490 x 10^{-5} cm^2/s

compared well with the results of Lyons and Thomas (1950)

who obtained a D value of 1.0470 x 10^{-5} cm^2/s using the

Gouy method at the same concentration and at 25°C. Glycine

diffusion coefficients in water were also measured by

Creeth (1955) using both the Rayleigh and Gouy inter-
ferometric techniques which yielded respective values of
$1.0451 \times 10^{-5} cm^2/s$ and $1.0458 \times 10^{-5} cm^2/s$.

Chatterjee (1964) using Jamin interference optics
found that the diffusion coefficients of sucrose deviated
from the values of Gosting and Morris (1949) (Gouy
technique) by approximately 0.04%.

There is little doubt that the diffusion coef-
ficients obtained by the various interferometric tech-
niques are by far the most accurate. In many cases
diffusion coefficients obtained by interferometric
techniques in conjunction with the Tiselius-type diffusion
cell are considered as absolute. Inspection of the lit-
erature shows that when a new technique for measuring
diffusion coefficients is developed or when an older
technique is modified, the diffusion coefficients ob-
tained are invariably compared to those obtained from
interferometric techniques (Pepela et al., 1970). Diffu-
sion coefficients obtained by interferometric techniques
are considered as differential coefficients since the
concentration differences employed may be small $(10^{-5} g/ml)$.

Recently Chandrasekhar and Hoelscher (1975)
reported a study of unsteady-state diffusion of glycerol,
glycol and n-butanol in water using the schlieren technique.

Boundary formation was achieved in an analytical ultra-centrifuge using a valve-type synthetic boundary cell. Even though the ultracentrifuge has been used for many years to study the diffusion and sedimentation properties of macromolecular species in aqueous solution, the report of Chandrasekhar and Hoelscher (1975) was the first in which the ultracentrifugal technique had been used to investigate the diffusion properties of small molecules in aqueous solution.

Le Maguer et al. (1976) have recently reported measuring diffusion coefficients of small molecules using a preparative ultracentrifuge. The schlieren optical accessory of the ultracentrifuge was converted to 35 mm slr photography (Smyrl et al., 1977).

C. EXPERIMENTAL

1) Chemicals

Diffusing materials included sucrose, glycol and glycine. All were reagent grade and were used as received from the J.T. Baker Chemical Company. All solutions were prepared with distilled-deionized water.

2) Equipment

A Beckman Model L2-65B Preparative Ultracentrifuge (Spinco Division, Beckman Instruments, Inc., Palo Alto, California) was used in the diffusion experiments. The preparative ultracentrifuge was equipped with a schlieren optical accessory (Spinco Division, Beckman

Instruments, Inc., Palo Alto, California) and is described by Griffith and Gropper (1969).

The optical column of the schlieren accessory was modified in such a manner that the photographs of the schlieren image could be recorded by a 35 mm single lens reflex camera rather than the Polaroid camera which was standard with the schlieren accessory. This was accomplished by removing the Polaroid camera from the column and attaching the 35 mm slr camera mount which is depicted in Figure 3. The optical tower of the schlieren attachment for the L2-65B Preparative Ultracentrifuge is represented by A. The tower attachment, B, is mounted on the tower with the existing facilities for the standard Polaroid attachment. The outer edge of B is threaded such that D, the camera adaptor, can screw onto and over B. A double convex lens, C, with a focal length of 20 cm is positioned between B and D. The outerside of B and the inner surface of D are tapered to accomodate the curvature of the double convex lens, C. The camera mount, E, is able to slide horizontally on the barrel of D. The right hand section of the camera mount is threaded to accept a Miranda 35 mm single lens reflex camera body. The camera mount can be securely fastened to D with the tightening nut on the camera mount. During an experiment

in which the schlieren patterns are monitored with time, the light source which is located in the base of the tower is kept illuminated at all times. One preliminary run is required to ascertain the correct camera shutter speed for the light sensitivity of the 35 mm film used. Generally it was found that a shutter speed of 1/8 s was suitable when Tri-X film (400 ASA) was used. To maximize the image sharpness as viewed through the camera viewer, the camera mount was moved horizontally along the barrel of D (Figure 3) and then secured tightly onto D with the tightening nut. Once the correct shutter speed and camera position had been determined no further adjustments were required unless a film of different ASA was used. Following a schlieren pattern with time consisted simply of advancing the film and taking photographs at the desired times.

The diffusion cell was a double sector capillary synthetic boundary cell with a polished Epon centerpiece and quartz windows (Spinco Division, Beckman Instruments, Inc., Palo Alto, California). An Analytical-D rotor (Spinco Division, Beckman Instruments, Inc., Palo Alto, California) was used to house the diffusion cell during the diffusion runs.

A Labline Environmental Chamber (Labline Inc.)

was used to equilibrate the rotor, cell and solutions at the required temperatures. Chamber temperatures are accurate to ±0.2°C. Magnification of schlieren images on 35 mm negatives was accomplished with a Kodak Ektagraphic Slide Projector, Model AF (Kodak).

3) Methods

Sucrose and glycine were prepared on a weight-by-volume basis whereas the glycol solutic   ᵊre pre-pared on a weight-by-weight basis. All sol   were used on the same day of preparation to avoid ffec s of microbial growth. After cell assembly, the   hand sector of the cell was completely filled with the ᵢₑs dense solution. The right hand sector was flushed twice with the more dense solution and was then filled with the more dense solution such that the top of the meniscus just reached the lower capillary (0.15 ml). For all aqueous solutions used in this study, the density was found to increase with increasing solute concentration. To avoid possible leakage from one sector to another, through either the top or bottom capillary, the cell was kept in a horizontal position until the time of the diffusion run. For runs at 25°C the chamber of the preparative ultracentrifuge was prewarmed with a goose-

18

necked lamp. This step was necessary since the Model L2-65B was not equipt with a chamber heating system and the surrounding laboratory temperature was usually less than 25°C. For diffusion runs at 25°C, the rotor, cell, and solutions were equilibrated for at least 1 h at 25°C. For runs below room temperature the chamber was precooled using the refrigeration unit of the L2-65B, and the rotor, cell and solutions were precooled to the desired temperature in the Labline Environmental Chamber. After the rotor containing the cell was placed on the driveshaft of the centrifuge the chamber door was closed and the chamber was evacuated. When the chamber pressure had reached 200 μ the rotor was accelerated to the desired final revolutions per minute. As the rotor begins to accelerate the less dense solution in the left sector flows through the lower capillary of the diffusion cell and layers onto the more dense solution in the right sector. The less dense solution was layered onto the more dense solution to maintain gravitational stability (Gosting and Fujita, 1957).

Photography of the schlieren patterns in a diffusion run was initiated after the position of the air-liquid interface in the right sector had stabilized. The time intervals between successive photographs depended

on the diffusion rate of the particular compound being
studied. For example, during sucrose diffusion runs, 1
min time intervals between successive photographs were
found to be suitable. For glycol studies a time interval
of 30 s was used. In all diffusion runs photographs
were taken until the peak height had decreased to approx-
imately 50% of the height of the first photograph. The
angle of inclination of the schlieren diaphragm θ was
selected so that an optimum in peak height and peak
sharpness was obtained.

After a diffusion experiment, the film was
removed from the camera and developed according to speci-
fications outlined by the manufacturer of the film. The
35 mm negatives were mounted in 35 mm glass slide mounts.
Glass slide mounts were necessary to prevent any bulging
of the negative. The Kodak slide projector was then
used to project the schlieren images onto a vertical
gradient such that the peak height was magnified by a
factor of approximately 40X. The projector was adjusted
so that the base line of the vertical gradient bisected
the baseline of the schlieren image. The projected
schlieren image was horizontally shifted so that the
schlieren peak maximum coincided with X=0 on the vertical
gradient. Once the schlieren peak was properly aligned

on the vertical gradient, the height of the peak was
measured at 5 mm intervals (X=0, ±5, ..., ±35 mm).
Peak heights were measured from the middle of the base
line to a point corresponding to one half the vertical
thickness of the peak image at each value of X. The
reference lines arising from the counterbalance in the
Analytical-D rotor were used to calculate the magnifi-
cation factor β. A value of β was determined from each
photograph in the diffusion experiment and an average
value of β was used to calculate the diffusion coefficient
for that particular run.

Diffusion coefficients were calculated using a
linear regression involving Equation (5). The derivation

$$\ln(y^1 t^{\frac{1}{2}}) = \ln\left(\frac{\alpha \Delta c}{2\sqrt{\pi D}}\right) - \frac{x^1{}^2}{\beta^2 4Dt} \qquad (5)$$

and notation of Equation (5) are outlined in Appendix A1.
Appendix A2 describes the computer program used to cal-
culate the diffusion coefficient. Since fifteen values
of y^1 and x^1 were obtained from each photograph and
since at least five photographs were taken during the
diffusion run, the resulting D value was calculated
from a linear regression involving at least 75 points.

Zero time corrections (Longsworth, 1947) were determined using the method outlined by Chervenka (1969). The zero time corrections were incorporated into all calculated diffusion coefficients.

All diffusion experiments were conducted in triplicate.

D. RESULTS

The diffusion coefficient of sucrose was determined as a function of average sucrose concentration. In these experiments, conducted at 25.3°C, the average sucrose concentration, $\bar{c}((c_1+c_2)/2)$, was systematically varied from values of 1.000g/100ml to 7.000g/100ml. The concentration difference, $\Delta c(c_1-c_2)$, was kept constant at 2.000g/100ml. Δc values of this magnitude were chosen because previous investigators (Gosting and Morris, 1949 and Chatterjee, 1964) had shown that the diffusion coefficients of sucrose are independent of Δc values in this range. Moreover, Gosting and Morris (1949) state that the variation of the refractive index with concentration is linear over the concentration range studied in this work. Hence these experiments are considered to yield the differential diffusion coefficient corresponding to the mean concentration.

Figure 4 shows a plot of the experimentally determined sucrose diffusion coefficients as a function of $\bar{c}$, □ . The least square line relating D with $\bar{c}$ is given by Equation (6). The least squares analysis

$$D = 5.32(1-0.0138\bar{c}) \times 10^{-10} \qquad (6)$$

yielded a correlation coefficient of -0.993 indicating an excellent linear relationship between D and $\bar{c}$. The interferometrically obtained results of Gosting and Morris (1949) at a slightly lower temperature of 24.95±0.005°C are also included in Figure (4), O. The least-square line relating D to $\bar{c}$ as applied to the data of Gosting and Morris (1949) is given by Equation (7). The least-square analysis as applied to the data

$$D = 5.226(1-0.0148\bar{c}) \times 10^{-10} \qquad (7)$$

obtained with the ultracentrifugal technique and the absolute data of Gosting and Morris (1949) show that the slopes are within 5% of each other. The slope of the D vs. $\bar{c}$ plot may be considered as a criterion for assessing the sensitivity of D to $\bar{c}$. Thus it appears that the ultracentrifugal technique is sufficiently sensitive to

monitor the variation of the diffusio coefficient with small changes in the average concentration of the diffusing molecule.

From Equations (6) and (7), the values of the diffusion coeffi it at infinite dilution, D^0, are $5.32 \times 10^{-10} m^2/s$ and $5.226 \times 10^{-10} m^2/s$ respectively. The slightly higher D^0 value from the ultracentrifugal technique over that obtained using Gouy interferometry is expected because of different experimental temperatures. Using the well known Stokes-Einstein relationship, as depicted in Equation (8), and available viscosity data

$$D_0 N_0/T = D_0^1 N_0^1/T^1 \qquad (8)$$

for water (Handbook of Chemistry and Physics, 1969), the value of D^0 from the ultracentrifugal technique becomes $5.27 \times 10^{-10} m^2/s$ at 24.95°C. This represents a 1% deviation from the absolute value of Gosting and Morris (1949). The D^0 obtained by the ultracentrifugal technique also compares well with the results of Chatterjee (1964) who measured a D^0 value of $5.224 \times 10^{-10} m^2/s$ using the Jamin interferometric technique.

Table 1 shows the diffusion coefficients of sucrose at 25.0°C as a function of final rpm setting on

the ultracentrifuge. In these experiments $\bar{c}$ and Δc were kept constant at 1.000g/100ml and 2.000g/100ml respectively. The Dav values listed in the third column of table 1 show that the diffusion coefficients are independent of rpm over the range studied. Calculation of an overall average diffusion coefficient Davo, yields a value of $5.19 \pm 0.05 \times 10^{-10} m^2/s$ whereas Gosting and Morris (1949) found a value of $5.148 \times 10^{-10} m^2/s$ at $24.95 \pm 0.005°C$ with $\bar{c} = 1.011g/100ml$ and $\Delta c = 1.5016g/100ml$. Table 1 also serves to point out that the experimentally determined diffusion coefficients are precise to approximately 1% (as measured by the relative standard deviation).

Table 2 illustrates the variation of sucrose diffusion coefficients with temperature where $\bar{c}$ and Δc have been kept constant at 1.000g/100ml and 2.000g/100ml respectively. Again the results of Gosting and Morris (1949) are included for comparative purposes. Dlit values for T=2.6 and 14.8°C have been calculated from the respective data of Gosting and Morris (1949) at 1.00 and 24.95°C, hence they should be considered as approximate. Again the precision of the experimentally determined diffusion coefficients is good in all cases. A plot of ln(Dexp) vs. 1/T(°K) (Glasstone et al., 1941)

follows the expected linear relationship as evidenced in
Figure 5, and thus would permit determination of activation
energies of diffusion. Thus the ultracentrifugal
technique of determining diffusion coefficients appears
useful in temperature related investigations.

The ultracentrifugal technique was extended to
the study of ethylene glycol in water. Diffusion coef-
ficients were determined at 25.0°C using several $\bar{c}$
values as shown in Table 3. The least square line
relating Dexp and $\bar{c}$ renders a D° value of $1.14 \times 10^{-9} m^2/s$
which compares well with D° = $1.16 \times 10^{-9} m^2/s$ as obtained by
Garner and Marchant (1961) who used the interferometric
technique. A least squares analysis of the data pre-
sented by Byers and King (1966) yields a D° value of
$1.17 \times 10^{-9} m^2/s$. However, inspection of Figure 6, which
includes data from this study, □ , and data presented by
Byers and King (1966), O, shows that the diffusion
coefficients obtained by the ultracentrifugal technique
are consistently below the values of Byers and King
(1966) who used the diaphragm cell technique. Moreover,
the plots representing the different data appear to
diverge towards increasing ethylene glycol concentrations.

The diffusion coefficients of glycine in water
at 25.0°C ($\bar{c}$ = 0.5995g/100ml and Δc = 1.990g/100ml) was

found to be $1.02 \pm 0.01 \times 10^{-9} m^2/s$. This result compares favorably with Thompson and Oncley's (1961) value of $1.049 \times 10^{-9} m^2/s$ at $25.00°C$. Creeth (1955) obtained values of $1.0451 \times 10^{-9} m^2/s$ and $1.0458 \times 10^{-9} m^2/s$ using the Rayleigh and Gouy techniques.

E. DISCUSSION

1) Importance of an Initially Sharp Boundary

Diffusion coefficients, obtained by the ultra-centrifugal technique, have been determined using Equation (5) which is essentially an integrated form of Fick's second law (Equation (2)). When Fick's second law is integrated, the following initial and boundary conditions are required. c_1 and c_2 represent initial

$t=0$		$t>0$	
$c=c_1$	$(x<0)$	$c \to c_1$	$(x \to -\infty)$
$c=c_2$	$(x>0)$	$c \to c_2$	$(x \to \infty)$

solute concentrations on each side of the boundary which is located at x. Longsworth (1945) showed that integration of Equation (2) yields the following relation.

$$\frac{\partial c}{\partial x} = \frac{\Delta c}{2\sqrt{\pi D t}} e^{-x^2/4Dt} \qquad (9)$$

In a two component system where the refractive index, n, is a linear function of the solute concentration, n may be substituted into Equation (9) to give Equation (10).

$$\frac{\partial n}{\partial x} = \frac{\Delta n}{2\sqrt{\pi D t}} e^{-x^2/4Dt} \qquad (10)$$

The schlieren optical system of the preparative ultracentrifuge used in this study records the variation of $\partial n/\partial x$ with x in the diffusion cell.

Figure 7 illustrates a theoretical diffusion process in which solutions of concentration c_1 and c_2 have been brought together to form a perfectly sharp interface at t=0 and at a position x=0 in the diffusion cell. The first vertical set of diagrams represents the concentration profile curves with concentration increasing along the vertical axis and distance within the diffusion cell represented by the horizontal axis. To the right are the corresponding concentration gradient curves as would be produced by the schlieren optical system. These schlieren curves are recorded by the 35 mm

camera and it is from these curves that x^1 and y^1 are measured.

Assuming a very sharp interface at $t=0$, the concentration profile curve takes the form of a step curve with the concentration to the left of x being c_1 and the concentration to the right of x equalling c_2. Under these conditions the requirements for integration of Fick's second law are fully satisfied. At times greater than $t=o$ there will be a net flux of solute molecules from the region of higher concentration, c_2, to the region of lower concentration c_1. This net flux of the solute molecules is the diffusion process. The molecules of solute closest to the interface in the c_2 region (x>0) will be the first to cross the interface into the c_1 region. Therefore the solute concentration to the right of x will decrease near x and correspondingly the solute concentration in the c_1 area (x<0) very near to x will increase. The resulting concentration profile diagram from the initial diffusion is represented by the $t=100$ s case. The boundary region between c_1 and c_2 in this case is very narrow, that is, the concentration varies by a large amount over a short distance along x. Thus the resulting concentration gradient curve is sharp and narrow. As time passes the width of the boundary

increases and the rate of change of concentration with x diminishes. Consequently the corresponding concentration gradient curves broaden and decrease in intensity as shown in the t=200 s and t=300 s cases. A time will be reached when the concentrations of the solute at the cell extremities begins to vary. When this happens the diffusion experiment has reached a stage of restricted diffusion and the calculation of diffusion coefficients according to Equation (5) is no longer valid. At t=∞ the solution is homogeneous.

Figure 8 shows the actual schlieren peaks as recorded on 35 mm film. These photographs represent a sucrose diffusion experiment at 25°C ($\bar{c}$ = 1.000g/100ml and Δc = 2.000g/100ml). The peak height is seen to decrease with time and the peak width increases with increasing time. This peak behavior is in accordance with the previously discussed theoretical diffusion experiment.

Figure 9 (a, b, c and d) illustrates how the photographically obtained schlieren image is influenced by the bar angle (θ) setting of the schlieren optical system. These photographs were recorded within seconds of each other hence they represent the concentration gradient curve at the same time. Comparison of Figure 9a

($\theta=75°$) and Figure 9b ($\theta=80°$) show that as the bar angle

is increased the schlieren image becomes sharper but

the peak height decreases. At bar angles of 60° and

50°, as shown in Figures 9c and 9d respectively, the peak

height is greatly enlarged but clarity and sharpness are

sacrificed. Therefore the choice of which bar angle is

used in an experiment is based upon which bar angle

will give the highest degree of precision when y^1

values are measured. The precision of measured y^1

values will be a function of both image height and sharp-

ness.

The mathematical derivation of Equation (5), as

discussed previously, is based on the assumption that

at t=0 a perfectly sharp interface is present between

the two solutions. Therefore it is essential that the

boundary between the two solutions be as sharp as

possible and it is this requirement that has prompted

much research towards better boundary formation tech-

niques especially with the interferometric-Tiselius

cell methods.

Currently there are several centerpieces avail-

able which can accomplish boundary formation between two

solutions in an ultracentrifuge. The valve-type

synthetic boundary cell and the double sector capillary

synthetic boundary cell are illustrated in Figure 10.
Both devices operate on the principle that the less dense
solution is layered on top of the more dense solution
under the influence of a gravitational field. Chandrasekhar
and Hoelscher (1975) used the valve-type synthetic boun-
dary cell in their ultracentrifugal determinations of
the diffusion coefficients of n-butanol, glycerol and
ethylene glycol. The valve-type cell contains a small
rubber valve which is compressed as the rotor speed in-
creases. When the valve is fully compressed the less
dense solution present in the cup is allowed to drain
into the wedge-shaped sector containing the more dense
solution. Earlier work in this laboratory with s type
of cell revealed that a considerable amount of   lence
occurred at the interface of the two solutions as boundary
formation was taking place. This turbulence was moni-
tored by photographing the schlieren image as the liquid
from the cup was being layered onto the liquid in the
sector. Figure 11 (a, b and c) shows successive photo-
graphs taken during boundary formation in the valve-
type cell. It is obvious that considerable mixing occurs
as the schlieren peaks exhibit definite irregularities
which are most evident at the base of the peaks. Figure
11d illustrates the resultant peak after boundary for-

mation has ceased. The peak appears to be far from symmetrical as would be expected if the diffusion were to commence from an initially sharp interface. This turbulence during boundary formation probably results from the momentum acquired by the less dense solution as it falls from the cup to the layer of more dense solution already present in the body of the cell. The result is a distorted schlieren peak and apparently erroneous diffusion coefficients (Huang and Winnick, 1976).

In this study the double sector capillary synthetic boundary cell (Figure 10) was used as the diffusion cell. With this type of cell the less dense solution flows from the full sector to the sector partially filled with the more dense solution. Figure 12 illustrates the mechanism of boundary formation in this cell. As the rotor gains speed the less dense solution is forced through the lower capillary onto the more dense solution. Since the surface of the more dense solution is level with the lower capillary, boundary formation is achieved without the less dense solution having to fall through any appreciable distance before contacting the more dense solution. The less dense solution will flow into the opposite sector until the levels in both sectors are equal. The upper capillary serves the purpose of

allowing the air in the sector being filled to flow into the sector being emptied. An additional feature of the double sector capillary synthetic boundary cell is that as the less dense solution enters the lower sector it sweeps over the interface and thus sharpens the boundary.

Boundary formation with the double sector capillary synthetic boundary cell was investigated photographically. Figure 13 (a to g) shows the schlieren images recorded at 15 s intervals starting from the time of rotor acceleration. It is evident that none of the irregularities, which were observed in photographs of boundary formation with the valve-type cell, are present in Figure 13. The resultant schlieren peaks appear very symmetrical as shown in Figure 13h. Analysis of enlarged schlieren peaks reveal that they do indeed approach the shape of a Gaussian curve. Further evidence of sharp boundary formation lies in the fact that the calculated zero time corrections, Δt, are invariably in the order of a few seconds.

2) Calculation of the Diffusion Coefficient

Neurath (1942) has described several standard methods to calculate diffusion coefficients from schlieren photographs of diffusing systems. The maximum ordinate

method involves dividing the maximum ordinate, h max,
by e to give the ordinate of the inflection points, $h\mu$.
The diffusion coefficient is calculated by the relation,
$D = \mu^2/2t$ where μ is one half the distance between the
inflection points. Thus the diffusion coefficient is
based on a single peak measurement from a single photo-
graph. In the method of successive analysis the diffusion
curve is divided into a series of vertical and horizontal
chords and the diffusion coefficient is calculated from
a pair of successive values of x_i and y_i. Thus the
diffusion coefficient is calculated from two height
measurements on a sinc photograph.

The frequently used maximum height-area method
of calculating diffusion coefficients was used by
Chandrasekhar and Hoelscher (1975) and English and Dole
(1950). This type of analysis involves a plot of
$(h_i max)^2$ vs. $1/t_i$ from which the diffusion coefficient is
calculated from the slope. A knowledge of the peak area
is also required. Such plots appear to yield excellent
linear relationships. However, as pointed out by
English and Dole (1950), there is uncertainty in the
absolute magnitude of the diffusion coefficient because
considerable personal latitude exists in estimating
both peak height and peak area. Since peak height

determinations are limited to an accuracy of about 1%
(Gosting, 1956), the diffusion coefficients calculated
by the technique cannot be expected to give results
with a precision better than 4% (the maximum height-area
method involves the square of the peak height and the
square of the peak area).

When Equation (5) is used to determine diffusion
coefficients from schlieren peaks, the only error involved
is that incurred in measuring the peak height, y^1, at
various values of x^1. Use of Equation (5) also avoids
the necessity of determining the peak area (which includes
a $(h^1max)^2$ term) thus eliminating any uncertainty in the
diffusion coefficient arising from this quantity. Since
peak heights, y^1, are measured at fifteen values of x^1
on each peak and since at least five peaks are recorded
duri a diffusion experiment, the resulting diffusion
coefficient is based on at least 75 y^1 values. Diffusion
coefficients calculated by the maximum height-area
method are typically based on a plot consisting of five
to ten points. Figure 14 illustrates a plot of Equation (5)
for glycine at 25.0°C.

3) Adaptation of the Schlieren Optical System to 35 mm Photography

Conversion of the schlieren optical attachment of the Beckman Model L2-65B Preparative Ultracentrifuge to 35 mm photography offers several advantages to the measurement of diffusion coefficients of small molecules. With the Polaroid attachment which is standard with the schlieren accessory, the time of exposure of the film to the light is regulated by switching the light source on and off. When double sector cells are used, a period of up to 10 s exposure time may be required when the Polaroid-type of film is used (Beckman, 1969). Exposure times of this duration do not yield sharp photographic images of a rapidly changing schlieren pattern. The height of a schlieren peak may decrease by five percent in such a 10 s time period as has been evidenced in the diffusion of small molecules. However, when a high speed film is used with the 35 mm adaptation, very short exposure times are required and very sharp images are recorded.

Generally, measurements on the photographic images of optical patterns formed in an ultracentrifuge are performed with an optical microcomparator (Chervenka, 1969) or analogously on tracings of the optical pattern made under an enlarger. According to Schachman (1957)

the measurement of schlieren patterns which have been
enlarged by a factor of five is comparable to using a
microcomparator. Since very clear and sharp images are
obtained with the 35 mm system, magnification to 40X yields
high clarity enlargements. Hence the magnitude of relative
error on image measurements is minimized.

The 35 mm adaptation offers several other ad-
vantages not attainable with the standard polaroid
attachment. The ability of the apparatus to take pictures
at intervals of several seconds is essential when mea-
suring diffusion coefficients of small molecules since
they diffuse very rapidly. The investigation of boundary
formation in the valve-type and double sector capillary
synthetic boundary cells would not have been possible
with the Polaroid camera. The adaptation to 35 mm slr
photography offers the convenience of being able to
simultaneously observe and record schlieren images. Such
a feature as constant viewing is useful, for example, to
insure that schlieren peaks are not recorded when the
point of restricted diffusion is reached. With the
unmodified system, if further viewing is desired once the
Polaroid camera is installed, the camera must be removed
and replaced with the viewing apparatus. Because of the
fact that high clarity enlargements may be produced,

the 35 mm adaptation lends itself to the study of phenomena occurring in a very narrow range about the interface. In sucrose diffusion experiments, it has been determined that the actual physical size of the concentration gradient is less than 1.5 mm.

Figure 15 summarizes the comparison between diffusion coefficients obtained by using interference optics (ordinate) and diffusion coefficients arising from the other methods (abscissa). The closeness of the ultracentrifugally determined diffusion coefficients to the 45 degree line asserts their validity and reflects the substantial improvement in the accuracy of the ultracentrifugal technique compared to previous work with an analytical ultracentrifuge (Chandrasekhar and Hoelscher, 1975). The dashed lines in Figure 15 represent the limits of the 5% deviation interval. It must be emphasized at this point that the ultracentrifugal technique involves an experiment of less than 10 min duration whereas interferometric or diaphragm cell techniques involve times of hours or even days.

4) Possible Extensions of the Ultracentrifugal Technique

It is conceivable that this ultracentrifugal technique could be extended to yield diffusion coefficients

of increased accuracy and precision. The Beckman Model E

Analytical Ultracentrifuge has a much better temperature

control (±0.05°C) than the Model L2-65B used in this

study and would allow for diffusion studies at elevated

temperatures. In addition the Model E is equipt with a

Rayleigh interference optical system. Besides yielding

more accurate diffusion coefficients, the Rayleigh system

would permit diffusion studies at concentration levels

well below those possible with the schlieren optical

system.

II. Retention of Essential Oil Components During Freeze

Drying of Aqueous Solutions

A. INTRODUCTION

Freeze drying may be defined as a low temperature dehydration process. At low partial pressures of water and at low temperature, the water is removed from the frozen product by sublimation. The key to the success of freeze drying in producing high quality products such as instant coffee, fruit juices and instant tea (Flink, 1975a) lies both in the removal of water by sublimation as well as by the low temperatures employed. Since the material undergoing dehydration by the freeze drying technique is normally in a frozen or rigid state, the matrix remaining after the disappearance of the ice crystals essentially remains intact. Thus the freeze-dried products rehydrate completely and quickly. Spillage losses during processing which may occur as a result of frothing or bubbling are eliminated since a free liquid phase is not present. Redistribution of soluble components by capillary flow is limited due to the absence of a free liquid phase. In a freeze drying sample, the transition zone separating the fully hydrated frozen product and the dry layer is very sharp, hence the

41

time is short where any portion of the product is kept in an intermediate moisture state where undesirable degradative reactions might occur. As pointed out by King (1971), the lower temperatures employed will cause the dehydration rate to decrease. However, at lower temperatures the rate of undesirable degradative reactions, such as non-enzymatic browning, is decreased to a much greater extent. Low temperatures also provide a favorable environment for biological molecules such as proteins.

This study is concerned with the retention of terpenic (carvone, piperitone and pulegone) and non-terpenic (eugenol and m-anisaldehyde) essential oil components in model aqueous systems during freeze drying. The essential oil components used in this investigation are commonly found in many food systems. Table 4 has been prepared from the review of Hall and Oser (1965). The amounts listed as "average maximum parts per million" are not tolerance limits and are often exceeded in use. The dissolved solids used in preparing the model systems include sucrose, glucose, gum arabic and sodium chloride which are all common food components.

CH₃

H₃C   CH₃
piperitone

CH₃

H₃C   CH₃
pulegone

CH₃   O

H₃C   CH₃
carvone

OH
O-CH₃
H
H-C-C=CH₂
H
eugenol

CHO

OCH₃
m-anisaldehyde
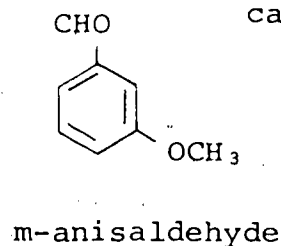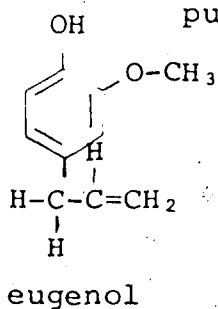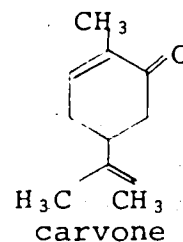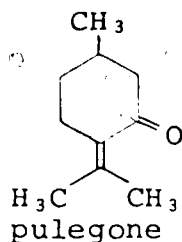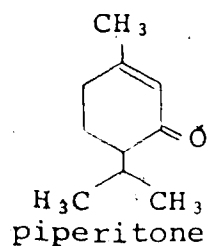
B. LITERATURE REVIEW

Many excellent review articles dealing with
various aspects of freeze drying are available. King
(1970).has reviewed many of the fundamental areas of
the process and discusses possible degradative reac-
tions which may take place in the dried product. The
publication of the lectures from the "International
Course on Freeze Drying and Advanced Food Technology"
held in Bürgenstock, Switzerland in June 1973 provides
an excellent review of many areas of freeze drying
(Goldblith et al., 1975).

Since the present study deals with the
retention of volatile flavoring compounds in aqueous
solutions during freeze drying, the literature review
will first of all be concerned with the freezing and

subsequent drying of aqueous solutions. The retention

of volatile organic compounds, as influenced by

various freeze drying parameters, will then be discussed.

1) Freezing of Aqueous Solutions

The behavior of a solution during freezing

depends to a large extent on the composition of the

dissolved solute. Several studies have shown that,

for example, salt solutions freeze very differently

than carbohydrate containing solutions. Using a macro-

scopic observation technique, Ito (1970a, b) has shown

that solutions of sodium chloride, potassium chloride

and sodium hydroxide form well defined eutectics. Ito

(1970a, b) attributed the formation of densely opaque

spots in the freezing salt solution to the formation of

the eutectic structure. The temperatur at which these

macroscopic changes occurred was the eutectic temperature,

T_e, and these eutectic points were confirmed by electrical

resistance measurements. However, for solutions con-

taining glucose, sucrose, lactose and other sugars no

or very little macroscopic change in appearance was

observable. Electrical resistance measurements also

failed to produce evidence of any type of eutectic

transition.

During the freezing of aqueous solutions, an

increased separation of pure ice occurs with decreasing

temperature and the remaining solution is thereby con-

centrated. The concentration of the residual solution

changes according to the ideal relationship between the

equilibrium freezing curve and the concentration. Hence

the concentration of the residual solution may accurately

be expressed as a function of temperature. The prin-

ciples governing this phenomenon are explained by

Heiss and Schachinger (1951).

According to Bellows and King (1973), when

solutions are cooled to very low temperatures, nucleation

of solutes other than ice and salts is very difficult

since the latter solidify completely at the eutectic

point. Food liquids such as juices or extracts contain

dissolved solutes (carbohydrates) which are not able

to solidify at the eutectic point. Figure 16 illustrates

the phase diagram for the sucrose-water system. If

equilibrium prevails for both sugar and water, the

sucrose-water system would solidify completely at -13°C,

the eutectic temperature. However in practice these

solutions do not form any crystallized sugar and thus

do not solidify completely at temperatures well below

-13°C. Instead the observed behavior follows the exten-

sion of the ice-equilibrium curve which represents

equal chemical potential between ice and water remaining

dissolved in the concentrated solution. Thus the

initial liquid separates into two equilibrium phases

consisting of solid pure ice and a region of concen-

trated solutes. This concentrated region has been

labelled the concentrated amorphous solution, CAS,

since it has no long range ordered structure. Figure 17

diagramatically illustrates the two equilibrium phases

in the frozen product. In reality the actual structure

is much less regular than that presented in Figure 17.

Within the volume occupied by the CAS,

Massaldi and King (1974a) have shown that a concentration

polarization phenomenon occurs near the face of the

growing crystal. Ice crystals form very selectively,

rejecting dissolved solutes and suspended matter away

from the growing crystal structure. These rejected

substances must diffuse away from the crystal surface or

else they will accumulate near the surface of the ice

crystal. However, under conditions of low temperature

and elevated concentrations which are prevalent during

freezing, diffusion of the rejected substances away

from the ice is hindered. Dissolved solute or sus-

pended matter concentrations will consequently attain

levels higher at the outer extremeties of the CAS

region than concentration levels in the interior portion

of the CAS. The concentration polarization is depicted

in Figure 18. The solute concentration at the ice

surface corresponds to equilibrium with the ice at the

prevailing temperature, therefore for a low enough

diffusivity this phenomenon will stop ice crystal

growth. The polarization theory finds support from ob-

servations that show there is a limiting initial

dissolved solids content above which no ice-crystal

formation will occur at all.

Studies on the physical nature of the CAS net-

work have been carried out by Bellows and King (1973)

and as will be discussed later, the fluidity of the

CAS is of primary importance. Viscosity measurements of

sugar solutions at temperatures and concentrations

approaching those expected of the CAS have shown that

the CAS is highly viscous and can be considered rigid

below a critical temperature.

Several studies have shown that during the

freezing of aqueous solutions, an impermeable film may

be formed on the outer surface of the product. Ito

(1970b) reported that during the freezing of a 10%

ε-amino caproic acid solution, a shell is produced on

the surface which has a solute concentration approximately 5X that of the bulk. Quast and Karel (1968) found that during the freezing of liquid extracts a concentrated region of solute developed at the free surface and attributed this to the concentration of carbohydrates. The same behavior has been noted during freezing of whole egg concentration where the lipid and protein fractions concentrate the surface (Flink and Fosbol, as reported by Flink 1975a). Ito (1970b) and Bellows and King (1973) have attributed this phenomenon to the concentrated solutes region being pushed upward through the growing ice crystals as freezing proceeds. Thus the solute is more concentrated in the surface layer than in the bulk and in the highly concentrated layer, nucleation and crystal growth will be minimized as discussed previously. Flink (1975a) has outlined several methods for preventing or eliminating this surface layer formation as it has a detrimental influence on the subsequent drying process.

In many liquid foods a second liquid phase may be present before freezing or may be formed during the freezing process. Often this immiscible phase may be a flavoring substance such as d-limonene (Massaldi and King, 1974b, c). In the case of d-limonene, the compound

is initially present at levels which exceed the sol-
ubility limit in aqueous solution. Massaldi an King
(1974a) speculate that the components of the second
phase may be distributed in three ways during freezing;
volatile droplets present at the CAS-ice interface,
volatile droplets embedded in the CAS and volatile
molecules homogeneously dissolved in the CAS. Further-
more Massaldi and King (1974a) postulate that volatiles
which are in homogeneous solution prior to freezing
remain in solution within the CAS and do not develop
into droplets under conditions of low temperature and
high concentrations within the CAS. The authors suggest
that the volatile components undergo a similar con-
centration polarization as dissolved solids and for
exactly the same reason (Figure 19).

Flink et al. (1973), using microscopic tech-
niques, have studied aqueous solutions of maltodextrin
and hexanol during freezing. In contrast to the view
of Massaldi and King (1974a), these authors suggest
that during the freezing process, the hexanol (volatile)
solubility limit is exceeded as evidenced by the appear-
ance of many droplets. The droplets are then entrapped
in the interstitial solute matrix of maltodextrin. Of
particular interest is the fact that hexanol droplet

formation occurs over a wide range of initial volatile
concentrations. The appearance of liquid droplets of
alcohols in freeze-dried aqueous maltodextrin solutions
was related to the solubility of the volatile alcohols
(Flink and C-jl-Hansen, 1972). Massaldi and King
(1974a) photographed sucrose solutions containing the
insoluble compounds n-hexyl acetate and d-limonene and
concluded that drop size increases with increasing
amounts of the volatiles in excess of their saturation
concentration.

The morphological structure of the frozen
product is strongly influenced by the rate at which the
solution is frozen. Thijssen and Rulkens (1969) have
shown that a decrease in freezing rate results in an
increase of the width of the ice region and correspondingly
results in an increase in the thickness of the CAS regions
as represented in Figure 17.

2) Drying of Frozen Aqueous Solutions

The drying of a frozen aqueous solution may be
considered as a two stage process. The first step in-
volves the removal of pure ice from the frozen material
by sublimation. The second step is the removal of
water from the CAS region by evaporation. The drying

process is governed mainly by the mass transfer of water vapor which in turn is regulated by the heat provided to the ice within the frozen sample. The balance between heat and mass transfer determines the drying rate. The parameters influencing these transfers have been reviewed by King (1970), Karel (1975) and Rothmayr (1975). In general it has been shown that the properties of the dry layer have an important influence on heat and mass transfer. The freezing rate also has an ultimate effect on drying due to its influence in regulating pore size and the resulting loss of water vapor.

The drying rate and the quality of the product are influenced by the structure of the frozen product. Ideally during the removal of water, the structure of the product is retained if proper conditions are maintained throughout the drying process. However, if structural changes do occur during drying, vapor transfer from the sample may be retarded. Depending on the nature of the frozen product, i.e. eutectic forming or non-eutectic forming, different theories have been advanced to describe structural changes which could occur during drying.

For solutions of sodium chloride and potassium

chloride which form well defined eutectics during freezing, the shaded portions of Figure 17 would represent the eutectic mixture. During sublimation, ice in the eutectic mixture would sublime soon after passage of the ice front, leaving behind a matrix of dry crystalline solute. Collapse, or loss of structural integrity of the frozen sample, will occur at the collapse temperature, Tc. When the frozen zone temperature exceeds T_c the rigid eutectic mixture would redissolve to a liquid. This liquid, under the influence of surface tension and gravitational forces, would flow and seal the open pores left by the sublimed ice. This collapse phenomenon, termed the eutectic melting theory of collapse, may be envisioned as a series of   sive steps as illustrated in Figure 20. For eutectic forming solutes Ito (1970b) has demonstrated that the collapse temperature, $T_{c'}$ is equivalent to T_e. As Figure 20 illustrates, the pores through which water vapor must flow away from the ice front are blocked. Consequently collapse results in a lower drying rate.

Ito (1970a) and Bellows and King (1973) have discussed collapse in drying systems which do not form a eutectic. The latter authors have labelled such collapse "the amorphous viscosity theory of collapse". In this case the shaded portion of Figure 17 represents the CAS region.

After passage of the ice front collapse occurs i is interstitial concentrate does not remain sufficiently rigid to maintain its structural integrity. If rigidity is not maintained the concentrate region will develop liquid tendancies and flow, thereby closing the pores above the ice front. Again Figure 20 represents the progressive steps of collapse. Sealing of the pores causes puffing and splattering as water vapor bursts through this liquid barrier which separates the region of elevated water partial pressure immediately above the ice front from the region of lower vapor partial pressure as determined by the condenser temperature of the freeze drier. Since collapse reduces the permeability of the dry layer to the flow of vapor, the drying rate will decrease. As a result, the requirements for the heat of sublimation will decrease causing the temperature of the frozen zone to rise. Consequently the fluidity of the residual concentrate increases and accentuates the tendancy toward collapse. The vital factor determining whether collapse occurs or not is the viscosity of the concentrate, which in turn is a function of both concentrate temperature and concentrate composition. Bellows and King (1973) have calculated that during a normal freeze drying experiment collapse occurs when the viscosity of the concentrate falls

within the range of 10^7-10^{10} cP. Viscosity measurements
and collapse studies by these workers supported the
calculated limits of collapse viscosity. Swinnen et al.
(1976), however, found that collapse occurs when the
critical viscosi⋅ ne ⋅s situated between 10^5 and 10^7
cP.

In addi⋅ ⋅ Swinnen et al. (1976) have correla-
ted the temperatures at which collapse occurs with the
devitrification temperature. The devitrification tem-
perature is defined as the temperature at which the CAS
molecules acquire sufficient mobility to pass from the
amorphous to the crystalline state. Ito (1971) and
MacKenzie (1975) had reported similar correlations.

Bellows and King (1973) have discussed the
effects that parameters such as solute composition,
solute concentration, the presence or absence of a sur-
face layer and the type of heat transfer geometry have
on collapse temperature.

As discussed previously, solute migration
during freezing produces a layer of high solids content
on the surface of the frozen product. Such a surface
layer may block the vacant pores remaining after the ice
has sublimed. Consequently the drying rate will be
decreased and to prevent collapse, lower drying tem-

peratures are required.

Microscopic investigations of the freeze-drying process have recently come into prominence. MacKenzie (1965) studied the possible paths followed by water vapor during dehydration. Flink et al. (1973) have photographed freeze-dried maltodextrin solutions. Gejl-Hansen and Flink (1976) have applied optical and electron microscopic techniques to the study of structures of various freeze-dried foods.

At this point it is appropriate to mention that structured foods can be dried at much higher temperatures than liquid systems owing to the fact that the structure of the food gives support to the frozen fluid part.

3) Volatile Retention During Freeze Drying: Freeze Drying Parameters

The concentration of volatile flavoring compounds in a rehydrated freeze-dried food should be very close to their concentration prior to freeze drying if the product is to be organoleptically acceptable. Due to their low concentrations in aqueous solutions nearly all flavoring components, even the high boiling ones, are much more volatile than water. With elevated volatilities such volatiles would be lost in an evaporation

process (Rulkens and Thijssen, 1972b). Chandrasekaran
and King (1971) showed that the retention of volatile
compounds, during the freeze drying of fruit juices,
was independent of their relative volatility. Similarly
Flink and Karel (1970a, 1970b) and Karel and Flink
(1973) were not able to find any direct correlation
between the volatility and the degree of retention of
volatile compounds during freeze drying. However,
Voilley et al. (1973), Saravocos and Moyer (1968) and
Chalmers and Watts (1972) reported that in their studies
the degree of volatile retention was influenced by the
volatility of the volatile compound.

Many studies have been directed towards
determining the influence that different parameters have
on the level of volatile retention.

a. Solids Composition

The degree of volatile retention in freeze-
dried liquid systems is strongly influenced by the nature
of dissolved solids and, in some cases, by the presence
of suspended solid material.

Saravocos and Moyer (1968) found that ethyl
acetate, ethyl butyrate, methyl anthranilate and acetic
acid in food gels were retained to different extents

depending on the material from which the gel is made.
Low methoxy pectin retained less of the flavoring com-
pound than pectin and cellulose exhibited a better
retention capacity than gelatin or starch.

Flink and Karel (1970a, b) have determined
the retention values of several volatile compounds with
a variety of mono-, di- and polysaccharides which were
freeze dried under identical conditions. The ability to
retain volatiles decreased in the order; disaccharide,
monosaccharide, polysaccharide. The retention of
sodium chloride, a salt, was found to be less than one
tenth that of the polysaccharide, dextran-10. Similar
trends were noticed by Sugisawa et al. (1973) for the
retention of n-propanol in freeze-dried solutions
containing mono- and disaccharides.

Studies on the retention of 2-propanol in
aqueous suspensions of cellulose and starch (Chirife and
Karel, 1973a) revealed starch gave much higher retentions
than cellulose even at identical initial solids content.

Chirife and Karel (1974b) demonstrated that the
protein, pepsin, gave a significantly higher retention
of 2-propanol than did bovine serum albumin even though
both proteins were present initially at a 20wt% con-
centration.

Studies on binary systems at a fixed total
solids concentration have yielded variable results
(Ofcarcik and Burns, 1974). For some carbohydrate
mixtures (lactose-glucose), the retention of pyruvic
acid improved in a synergistic manner while in other
mixtures no effects were noticed.

Massaldi and King (1974b) proved that the
presence of colloidal matter (cloud) influenced the
retention of d-limonene during the freeze drying of
orange juice.

b. Dissolved Solids Content

In the first quantitative analysis of volatile
retention during freeze drying, Rey and Bastien (1962)
found that the retention of acetone was enhanced as
successive amounts of glucose were added to an Earle-
salt solution.

Saravocos and Moyer (1968) studied the reten-
tion of ethyl acetate, ethyl butyrate, methyl anthranilate
and acetic acid in model food gels and found that the
degree of volatile retention increased with the addition
of glucose and sucrose prior to freeze drying.

In freeze drying slabs of malto-dextrin, the
retention of methanol, propanol and n-pentanol was found

to approach 100% at initial malto-dextrin concentrations of 60wt%. At reduced malto-dextrin levels, the retention was much lower (Thijssen, 1972b).

Similar results were reported from volatile retention studies on orange juice (Sauvageot et al., 1969). An increase in the dry matter content resulted in increased retentions for myrcene, limonene and pinene. However, in the same experiments ethanol exhibited the opposite behavior.

A higher initial solids content has also been found to give substantially better retention of volatile flavor species in apple juice (Chandrasekaran and King, 1971). In this study ethyl acetate, n-hexanol and n-hexyl acetate were chosen as representative apple volatiles.

Flink and Karel (1970b) demonstrated that in model solutions containing glucose and acetone, acetone retention after freeze drying decreased as the initial glucose concentration decreased.

Chirife et al. (1973) have found similar results in the polyvinylpyrollidone-n-propanol system where PVP has been used as a water soluble polymer which partially simulates a protein in solution. At low solids concentration (below 10-20wt%), increases in the

solids concentration significantly elevated the degree of n-propanol retention.

Chirife and Karel (1973a) showed that increasing the amount of suspended starch and cellulose had a beneficial effect on the retention of 2-propanol, but the increase was much more pronounced with starch.

Chirife and Karel (1974b) noted similar behavior as protein concentrations were increased in aqueous solutions of pepsin and bovine serum albumin.

Using a mixture of four carbohydrate gums, up to a dissolved content of 3wt%, Kayaert et al. (1975) obtained a linear relationship between the retention of acetone and n-propanol and the initial gum concentration.

Rulkens and Thijssen (1972a) concluded, on the basis of retention experiments using methanol, n-propanol and n-pentanol in aqueous mixtures of malto-dextrin, that retention increases with increasing dissolved solids content up to a critical value above which no further increase in volatile retention could be obtained.

Sugisawa et al. (1973) have shown that n-propanol retention in glucose, maltose and sucrose solutions reaches a maximum at about 40 to 50wt% sugar. Increased retention with initial sugar concentrations above this value do not occur.

Ofcarcik and Burns (1974) reported that an increase in sucrose, glucose and lactose concentrations in model aqueous systems and Bermuda onion juice resulted in increased carbonyl (expressed as pyruvic acid) retention. A leveling off of carbonyl retention occurred at approximately 5wt% carbohydrate.

Natural volatile components in mushroom extracts were retained to a very high degree even at relatively low initial solids content (Bartholomai et al., 1975).

This observed increase in volatile retention as the dissolved solids content of the solution increases, forms the basis for preconcentrating liquid foods prior to freeze drying. Thijssen (1970) discusses the different processes available for concentrating liquid foods containing volatile flavoring compounds.

c. Initial Volatile Concentration

Most re ts describing studies on the effect of initial volatile concentration on retention come from Flink and/or Karel and co-workers (Flink and Karel, 1970b, Kayaert et al., 1975, Chirife et al., 1973, Chirife and Karel, 1973a and Chirife and Karel, 1974b). All of these studies have indicated that an increase in

the initial volatile concentration, at constant
dissolved solids, results in a decrease in the percentage
of volatile retained.

Such findings are supported by the work of
Bartholomai et al. (1975) who monitored benzaldehyde
retention as a function of its initial concentration.

The results of Berry and Froscher (1969)
appear somewhat inconclusive since there was no evidence
of any relationship between initial volatile content
and percent retention in freeze-dried orange juice.

Voilley et al. (197), however, observed the
opposite behavior. When they increased the n-alcohol
concentration in a synthetic solution composed of sugars
(glucose, sucrose and fructose), citric acid, calcium
chloride, pectins and albumins, the percent retention
increased.

Massaldi and King (1974a) showed that initial
volatile concentration in freeze-dried liquid systems
was very important especially when the initial volatile
content exceeded the solubility limit of the volatile in
the aqueous solution. In the region of the solubility
limit a sharp drop in retention was noted and beyond the
solubility limit an asymptotic level of retention was
observed.

d.   Heat Treatment of the Drying Sample

An increase in the ice front temperature and
an increase in the heating plate temperature will cause
respective improvements in mass transfer and heat
transfer within the drying sample. Better heat and
mass transfer on the drying sample obviously will in-
crease drying rate. By calculation Thijssen (1972a)
has predicted that higher volatile retention should
result from more rapid drying. Rulkens and Thijssen
(1972a) proved this experimentally maintaining the
ice front at a constant temperature while heating
through the frozen layer and controlling the rate of
drying by manipulation of the chamber pressure. As an
example, drying at chamber pressures giving a doubling
of the drying rate at an ice front temperature of -20°C
resulted in an increase in 1-propanol retention from
65% (slow drying) to 85% (rapid drying). It should be
noted that maintaining the ice front temperature at
-20°C by heating through the dry layer gave similar
volatile retentions as heating through the frozen
layer, when the samples were dried at equal rates.
Both Thijssen (1972a) and Voilley et al. (1973) have
shown that as the ice front temperature decreases,
volatile retention increases. In addition decreasing

the chamber pressure results in lower ice front tem-
peratures. In the absence of collapse volatile losses
with higher ice front temperatures h... .... en attributed
to a decrease of the solids matrix co.. ....ration as
some of the ice crystals melt. 1... temperature of the
ice front is also influenced, to some extent, by the
rate at which the sample was frozen. It has been shown
previously that pore size will increase with a decreasing
freezing rate. An increase in pore diameter reduces
the vapor pressure drop over the dry porous matrix and
thus reduces the ice front temperature at a constant
platen temperature and chamber pressure; thus causing
an increase in volatile retention.

Collapse during freeze drying as discussed
previously, is a phenomenon in which the matrix under-
goes structural degradation due to the onset of
viscous flow. If temperature conditions in the drying
matrix are such that collapse occurs, substantial amounts
of volatile are lost as has been verified by Bellows
and King (1973) and Swinnen et al. (1976).

e. Freezing Rate

The rate at which a volatile containing liquid
solution freezes has been shown to have a pronounced

effect on the level of volatile retention. It ha

been shown that the constitution of the frozen prou

is directly related to the rate of freezing. Ettrup

Petersen et al. (1973) have systematically investigated

seven freezing treatments on coffee extract and found

that slower freezing treatments generally produce a

higher level of volatile retention than a fast freezing

treatment. However, samples of uniform thickness which

were dried very slowly had less retention than samples

dried slowly. Flink and Labuzza (1972) have shown

that volatile retention in maltose solutions was 8 to

10 times greater in slowly frozen samples than in

quickly frozen samples, whereas the freezing rate was

not found to be as critical in dextrin solution.

n-Propanol retention in quickly frozen samples of

polyvinylpyrrolidone was similarly own to be less

than in slowly frozen samples when all other freeze-

drying parameters remained invariant (Chirife and Karel,

1973b). This trend was also found by Massaldi and

King (1974a) with sucrose solutions.

f. Sample Dimensions

Chirife et al. (1973) have shown that as the

thickness of the freeze dried sample increased, the

degree of volatile retention decreased. Thijssen (1972c) reported similar results for volatile retention in layers of granules. Rulkens and Thijssen (1972a) have shown that for any layer thickness there exists an optimal granule size at which volatile retention is maximum. Ettrup Petersen et al. (1973) showed that in freeze-dried coffee granules, thicker drying samples exhibited higher retentions than thinner samples. These authors postulated that the thicker samples would freeze more slowly than thin ones, and result in a higher level of volatile retention as would be expected with a decreased freezing rate. Flink and Karel (1970b) observed that varying the surface arc while maintaining a constant sample thickness   ) effect on volatile retention.

Very high retentions can be obtai   during freeze drying if the following conditions are satisfied; (i) high initial dissolved solids content; (ii) low freezing rate; (iii) low ice front temperature; (iv) high drying rate; (v) low initial volatile concentration; (vi) thin layer of sample The preceding list should be considered as a generalization since in many cases, results contrary to those expected have been reported.

3.2.3 Mechanisms of Retention

Several theories have been advanced to explain why the various process parameters influence volatile retention during freeze drying.

a. Microregion Theory

Flink and Karel (1970a, b) have adopted the microregion theory to explain the retention of volatiles during freeze drying of liquid systems. The microregion theory is based on the fact that as ice crystals grow in the freezing sample, volatiles and dissolved solutes are excluded from the pure ice. During freezing, solute molecules will interact with each other by hydrogen bonding, thus producing a structure which will act as a cage to entrap homogeneously dissolved volatiles which are present in an immiscible phase. As water is removed during drying, interaction between solute molecules increases since the extent of water-solute interactions will decrease. Below a certain moisture content the degree of association between solute molecules will be very high and literally prevent movement of the trapped volatile.

Karel and co-workers have devised numerous

experiments to give support to the microregion theory.
Flink and Karel (1970a) have shown by layering exper-
iments that volatile retention principly occurs only
in the layer which contained the volatile initially.
Furthermore the volatile was homogeneously retained
throughout the whole sample when the volatile was
initially homogeneous within the sample. Volatile
loss during rehumidification experiments was attributed
to the degree of disruption of hydrogen bonds in the
amorphous freeze-dried cake (Flink and Karel, 1972 and
Chirife and Karel, 1973). Rehumidification thus leads
to the partial destruction of the cage structure which
traps the volatile. Total destruction of the micro-
region comes only with total dissolution of the freeze-
dried cake. Flink and Karel (1972) and Chirife and
Karel (1974a) demonstrated that thermal energy also
disrupted the structure of the microregion as evidenced
by volatile loss at elevated temperatures.

Retention of volatiles and subsequent micro-
region disruption studies have been carried out with
numerous systems; polyvinylpyrrolidone (Chirife et al.,
1973), cellulose and starch suspensions (Chirife and
Karel, 1974b), maltose (Chirife and Karel, 1974b) and
mushroom extracts (Bartholomai et al., 1975). In all

systems the results were considered compatible with the microregion theory. In addition the investigators were able to correlate the retention influence of the various process parameters with the microregion theory.

2.3.2 Adsorption

Adsorption of volatiles on the dried matrix, as the volatile passes through the capillaries of the dry layer, has been considered to account for the high degree of volatile retention during freeze drying. Rey and Bastien (1962) attributed the high degree of acetone retention in glucose-containing systems to the adsorption of acetone onto glucose. Boskovic and Issenberg (1969) and Issenberg et al. (1968) have studied the adsorption and desorption of organic volatiles on food components.

Maier (1969, 1970, 1971, 1972) and Gray and Roberts (1970) studied the binding of various volatile organic compounds to food and food components and found strong interactions between specific substrates and some adsorbates. Lee et al. (1975) found that stable anhydrous α-lactose had a high capacity for adsorbing alcohols, esters and ketones.

Maier (1972) observed that sorption of ketones

usually required the presence of water to allow ketone

penetration into polymeric aggregates or the presence

of fat in which the ketones apparently dissolved. In

the absence of water there was some sorption of acetone

on zein, starch and pectin. The adsorption was

irrev sible. Infrared measurements confirmed that

adsorption was due to (ketone) C=O---H-O (polymer)

hydrogen bonding.

Chirife and Karel (1973b) showed that the

adsorption phenomena could contribute significantly

to the total amount of n-propanol retained in freeze-

dried polyvinylpyrrolidone solutions. Hydrogen bond

formation between the carbonyl moiety of the poly-

vinylpyrrolidone and the hydroxyl group of the alcohol

was considered to be the main mode of interaction.

Infrared studies by Strassmair et al. (1971) demon-

strated that this type of hydrogen bond formation was

plausible in the polyvinylpyrrolidone-n-propanol

system. However it should be emphasized that Chirife

and Karel (1973b) considered the amount of volatile

retained by microregion entrapment far exceeded the

amount retained by adsorption.

d.   Diffusion Theory

When a liquid layer is cooled ice crystals
grow perpendicularly to the cooled surface causing
ice and solute fractions to be separated within the
frozen product as depicted in Figure 17. As sublimation
proceeds vacant spaces or pores remain. These pores
separate the eutectic solids or CAS region. The volatiles
are initially distributed throughout the solutes phase.
As the sublimation front retreats from the sample
surface, water within the CAS will diffuse into the
vacant pores. The water content in the matrix, during
this period of secondary drying will decrease with in-
creasing distance from the ice front. Since the ice
crystals are impermeable to volatiles, the volatiles
can only escape from the matrix at or above the ice
front by the process of diffusion.

Thijssen and Rulkens (1969) have presented a
semi-quanitative diffusion analysis of volatile loss
during freeze drying. This interpretation of volatile
loss has been made using a binary analysis to calculate
diffusion coefficients (Menting et al., 1970a) and to
predict rates of loss during drying (Menting et al.,
1970a, b). Earlier work by Menting and Hoogstad (1967a, b)
showed that the movement of a volatile organic species

through a highly concentrated carbohydrate matrix is severely rest... ed. In fact at very low moisture contents, the ca..hyd...te matrix was considered to be impermeable to th... low of volatile but not to the flow of water. Explanations for this volatile impermeability come from the studies of Menting et al. (1970a) who showed that the diffusion coefficient of acetone in an aqueous malto-dextrin solution is substantially less than the diffusion coefficient of water in the same solution. On the basis of a binary diffusion model they proved that as the moisture content of the malto-dextrin solution decreased, the diffusion coefficients of volatile (acetone) and water decreased. Furthermore the decrease in the diffusion coefficient of volatile was much greater than the decrease in the diffusion coefficient of water. In coffee extract at approximately 95% dissolved solids, the ratio Dacetone to Dwater was close to 10^{-4} (Thijssen, 1972b). This illustrates that at very low water concentrations, as would prevail in the CAS, the system can be considered as being permeable to water only. The selective diffusivity is also strongly dependent on temperature. Temperature studies, again by Thijssen (1972b), have shown for example that at 25°C

for a ratio of Dacetone:Dwater of 0.01 the water content in a malto-dextrin solution would have to be approximately 10wt%, whereas at -30°C the water content would have to be 40wt% to give a similar Dacetone:Dwater value. This difference in diffusivity of volatile (as typified so far by acetone) and water forms the basis for the selective diffusion theory explaining volatile retention during freeze drying.

Chandrasekaran and King (1972b) and King and Chandrasekaran (1973) have extended the analysis of volatile loss during drying to a three component diffusion model as opposed to Thijssen's binary model. In the ternary model, the authors employed multi-component diffusion coefficients which they had previously measured in aqueous systems of volatile and sugar (Chandrasekaran and King, 1972a). Flux equations for volatile and water during drying were solved and suggested that, because of the sugar-water composition gradient formed during drying, the transport of volatile components would create a local accumulation of volatile species. This predicted local accumulation of volatile was verified experimentally by the sectioning of samples. Although the authors conceded that the previous binary diffusion analysis was useful

in a qualitative manner, the ternary diffusion model gave
a much better quantitative explanation of observed
volatile loss and concentration profiles. In addition
the ternary analysis provided a better explanation for
the effect of various processing conditions on volatile
loss.

King (1970) has shown that the influence
which different processing parameters may have on volatile
loss can be qualitatively related to increasing or
decreasing values of the Fourier group, Dt/L^2, as applied
to individual regions within the CAS.

C. EXPERIMENTAL

1) Chemicals

Dissolved solids or substrates were sucrose
(Baker), d-glucose (Fisher), sodium chloride (MCB) and
gum arabic (Sigma) and were used without further
purification. Carvone (K and K), piperitone (CN),
pulegone (Fluka), eugenol (ICN) and m-anisaldehyde (ICN)
were found to be at least 90% pure by gas chromato-
graphic analysis and were used without further purifi-
cation. Ethanol (Canlab) and octanol (Baker) were
used as received. Buffering salts were obtained from

Fisher. Potassium chromate (Fisher) lithium chloride
(Fisher) and sodium dichromate (Baker) were used to
prepare relative humidity chambers. Distilled water
was used to prepare all solutions.

2) Equipment

A Model 42, RePP Sublimator (The VirTis Co.,
Inc.) was used to freeze dry the samples. This subli-
mator was equipt with a Hyvac 45 vacuum pump with a
capacity of 15 ft^3/min and an ultimate dry chamber
vacuum of 5 microns. Condenser and tray temperatures
could not be independently regulated since the cooling
of one automatically eliminated cooling of the other.
Pressure measurements were made with a McLeod guage.

Ultraviolet absorption measurements were
conducted on a Unicam SP1800 Ultraviolet Spectrophoto-
meter which was equipt with a deuterium lamp for
ultraviolet analysis. The instrument was operated on
the fixed wave length mode using a band width of 1.2 mm
and a slit width of 0.4 mm. Quartz cells (Canlab) were
used for both reference and sample.

pH measurements were carried out with a Fisher
Model 230 pH/ion Meter (Fisher). Certified buffer
solutions (Fisher) were used to calibrate the pH meter.

A Virtronics temperature recorder (The VirTis Co., Inc.), in conjunction with a thermistor was used to monitor sample temperatures during freeze drying.

All glassware was Pyrex and was cleaned either with an alcoholic potassium hydroxide solution or a chromic acid solution. Prior to use all glassware was rinsed thoroughly with distilled water.

3) Sample Preparation

Aqueous solutions of the substrate were prepared on a weight percent basis. Volatile concentrations are expressed on a volumetric basis (ppm). Volatile containing solutions were prepared by one of two possible ways. Individual samples were prepared by injecting the desired volume of volatile, using a 10 μl Hamilton syringe, into a known volume of solution in a 50 ml Erlenmeyer flask. After the volatile was added to the matrix containing solution, it was necessary to vigourously shake the Erlenmeyer flask for at least several minutes to effect solubilization of the volatile as indicated by absence of an organic phase. Such a mixing procedure was required even for volatiles well below their solubility limit in the solution. Numerous analyses have shown that this technique of volatile

addition is reproducible to ±1.5%. When volatile-containing solutions were made in this manner, four samples were prepared, three for freeze drying and one as a reference which was stored at 4°C. Bulk samples containing volatiles were prepared by introducing weighed quantities of volatile into volumetric flasks and filling to the mark with the appropriate solution. The volumetric concentrations were then calculated using density data for the volatile.

When necessary solutions were stored in stoppered flasks at 4°C. To avoid possible interactions between the volatile and the stopper, the stoppers were enclosed in aluminum foil. All bulk solutions were prepared on a regular basis to minimize possible effects of microbial growth.

4) <u>Freeze Drying</u>

Prior to freezing, the samples (normally 5.0 ml) were weighed. The samples were frozen on the shelf of the freeze-drying apparatus. Before placing the samples in the freeze-drying apparatus, the shelf temperature was lowered to -40°C. When the shelf temperature had reached -40°C, the samples were quickly placed on the shelf and allowed to freeze. Since each

sample was prepared in triplicate each member of the triplicate was placed on a different shelf within the freeze drier. The sample temperatures were monitored by a reference sample containing the thermistor. This reference sample was the last sample to be placed in the freeze drier. When the reference temperature had reached -35°C (after approximately 1 h) the shelf cooling was switched off and the condenser cooling was switched on. At a condenser temperature of -40°C, the drying chamber was sealed and the vacuum pump was activated. The condenser temperature for all runs was -70°C. The samples were allowed to dry for 48 h without the input of any heat. After drying the samples were removed from the shelves of the freeze-drying apparatus and stoppered immediately.

5) Volatile Analysis

Immediately after freeze drying, the samples were weighed and rehydrated to their original weight. Volatile content was determined spectrophotometrically. Using pipets and volumetric flasks, the rehydrated samples were diluted with water such that the resulting volatile concentration gave an absorbance detectable by the ultraviolet spectrophotometer. The fourth member of

reference, which was kept stoppered at 4°C, was diluted in exactly the same fashion. The percent retention was calculated as a ratio of the absorbance of the rehydrated freeze-dried samples to the absorbance of the reference. Standard deviations were calculated on the basis of triplicate measurements. It should be noted here that the reference absorbance used in calculating the percent retention was not the absorbance of a single reference but generally the average of five or six reference samples.

In cases where samples contained volatile in excess of its solubility, both the freeze-dried samples and the reference sample were diluted to such an extent that all the volatile was homogeneously dissolved and then the dilutions for spectrophotometric analysis were performed.

All experiments were carried out with a view to minimize all variables during the study of a certain parameter during freeze drying. Data relating to any particular parameter was obtained from a single freeze-drying experiment and thus the comparison of results from different freeze-drying runs was avoided.

D.   RESULTS

1)   General Observations

The samples were dried for a period of 48 h. A temperature profile during freezing and drying over the 48 h period is shown in Figure 21. After drying the final sample temperature in all cases was between -3 and -5°C. Experiments conducted with no samples in the freeze drier showed that shelf temperatures decreased to -3 to -5°C due to the cooling effect of the condensers (-70°C) which are in close proximity to the shelves. Upon evacuation the chamber pressure decreased to between 20 and 50 microns after 15 min and at the end of all freeze-drying runs, the chamber pressure was invariably close to 10 microns.

In freeze-dried solutions of 10% sucrose, 10% glucose, 1% gum arabic and 5% sodium-chloride it was found that the residual moisture content was approximately 1 to 2% after 20 h. By expressing the fractional water retention as a function of drying time, it is possible to obtain an estimate of the drying rate of each solution. Table 5 illustrates the calculated drying rates for the solutions as expressed in the relation,

$$y = mx + b$$

where $y=\%$ moisture remaining (wet basis) after a certain time represented by x. Values of m denote the drying rate (% water lost per hour on a wet basis) up to drying times of 12 h. Inspection of m values, tabulated in Table 5, illustrate that the dr_ _g r_ _s of the four types of solutions employed are quit   _eing between 5 and 6%/h.

All solutions appeared to freeze dry well as there was no evidence of structural collapse. Upon rehydration the samples appeared to "melt" as the cake structure disintegrated with the addition of water. With the exception of freeze-dried glucose samples, the cakes retained their structural integrity for several hours when exposed to the atmosphere. Freeze-dried glucose samples. however, immediately took on a semi-liquid appearance.

2) Volatile Retention

a. Drying Time

Retention of carvone as a function of drying time has been studied in 10% sucrose, 10% glucose, 5% sodium chloride and 1% gum arabic. Carvone, initially

at 500 ppm, was lost at a greater rate during the first part of the drying period when the water content of the sample was appreciable. At very low moisture contents (1 to 2%) carvone loss ceased and the percent retention remained constant even for extended periods of time under a vacuum of 10 microns. As a typical example, carvone retention as a function of drying time in 1% gum arabic is shown in Figure 22. In this Figure the vertical bars represent the standard deviation calculated on the basis of triplicates. Figure 22 also includes the moisture retention as a function of drying time. The retention of carvone in the other solutions was quite similar, differing only in the degree of retention after 48 h.

b. Sample Dimensions

Experiments were carried out to investigate the effect of sample geometry on carvone retention in 10% sucrose and 1% gum arabic solutions. Layer thickness studies were performed in beakers ranging in size from 10 to 125 ml. The layer thickness of the sample was varied by adding 5.0 ml of solution to each beaker, thus keeping the volume of sample constant for all thicknesses. Figure 23 illustrates that at a constant

initial volume of sample, carvone (500 ppm) retention

increases as the layer thickness increases and the

retention appear to level off at a layer thickness

of approximately 3 mm.

Figure 24 shows that surface area of the

freeze-drying sample has very little influence on the

retention of carvone (ppm) in either 10% sucrose or

1% gum arabic. In these experiments the sample thick-

ness was kept constant at 7 mm

c. Dissolved Solids Content

Figures 25, 26 and 27 illustrate the beneficial

effect that increasing initial sucrose content has on

the respective retention of carvone (500 ppm), m-

anisaldehyde (500 ppm) and eugenol (500 ppm). Previous

solubility studies have shown that at 500 ppm concen-

trations all of the volatiles are well below their

solubility limit in the sucrose solutions. In each

case the volatile retention increases in a linear

fashion with increasing initial sucrose content. In

addition at initial sucrose contents of between 20%

and 25% the retention of the volatiles appears to level

off. Freeze drying of sucrose solutions at initial

concentrations of 30% or greater was unsuccessful since

the samples appeared to melt while drying. Because the shelf cooling of the freeze-drying apparatus could not be operated independently of the condenser cooling, this problem of melting could not be overcome.

Figure 28 reveals an increase in volatile retention with increasing gum arabic content. In each case the volatile retention increases linearly with increasing initial gum arabic. Figure 28 shows that the retentions of carvone and m-anisaldehyde are very similar at the same initial gum arabic concentrations. However, Figure 28 also illustrates that at a given initial gum arabic content the retention of eugenol is at least 20% greater than the retention of carvone or m-anisaldehyde. The degree of retention of eugenol in gum arabic appears to level out at an initial concentration of 4%.

Data on the retention of carvone, m-anisaldehyde and eugenol in glucose solutions, are presented in Table 6. In each case the volatile was present initially at 500 ppm. Inspection of Table 6 points out several interesting features. As the initial glucose content increases from 3 to 7wt%, the volatile retention increases substantially. Above 7% initial glucose the retention of the volatiles appears to stabilize. This is in

sharp contrast to the sucrose case where stabilization of retention values occurred at approximately 25%. Although the glucose solutions, ranging from 3 to 15%, appeared to freeze dry well, the standard deviations tabulated in Table 6 often approach 10% of the mean value determined from the three samples. Solutions containing glucose initially above 15% could not be freeze dried successfully under the experimental conditions used because melting of the sample occurred.

Table 7 illustrates that an increased initial sodium chloride content causes an increase in the retention levels of carvone and m-anisaldehyde. The percent retention for both of these volatiles is seen to be much lower in sodium chloride solutions than in sucrose, glucose or gum arabic solutions. Data for the retention of eugenol in sodium chloride were not obtained because the absorbances of the rehydrated sodium chloride solutions were greater than the absorbances of the reference samples.

d.   Nature of the Volatile Species

Inspection of Figures 25, 26 and 27 indicate

that the respective retentions of carvone, m-anisaldehyde

and eugenol in sucrose solutions are very similar.

Each volatile has a retention level of 30 to 40% at 5%

sucrose and the retention increases in a fairly

linear manner to approximately 90% at 25% sucrose in

all cases. Carvone and m-anisaldehyde have similar

retentions in all gum arabic solutions as evidenced

in Figure 28, however, the eugenol retention in the

gum arabic solutions is significantly higher than carvone

or m-anisaldehyde. Table 6 shows that m-anisaldehyde

and eugenol appear to have a slightly higher retention

level than carvone in glucose solutions. Carvone

retention in sodium chloride solutions is substantially

below that of m-anisaldehyde as evidenced in Table 7.

The terpenic essential oil components,

carvone, pulegone and piperitone, all have the same

basic hydrocarbon skeleton and differ only in the

position of the carbonyl group and/or the position of

the double bond. Due to their similar structures and

very similar molecular weights, retention experiments

were conducted in 10% sucrose, 10% glucose, 5% sodium

chloride and 1% gum arabic. At an initial volatile

concentration of 500 ppm, the three volatiles were retained to very similar extents as evidenced in Figure 29. Piperitone in 10% sucrose exhibits a 10% higher retention than carvone or pulegone.

e. Initial Volatile Concentration

Figures 30 through 34 illustrate the respective retention of carvone, pulegone, eugenol, piperitone and m-anisaldehyde as a function of initial volatile concentration in a 10% sucrose solution. In these figures percent retention is plotted against the parameter, n, which represents the ratio of initial volatile concentration to the volatile solubility in 10% sucrose as measured at 10°C. For all volatiles n ranged from approximately 0.2 to 1.4. Figures 30 through 34 invariably show that volatile retention decreases with increasing values of n. For values of n<1, the volatile retentions appear to decrease in a regular fashion. Carvone and pulegone, the least soluble of the volatiles, exhibit a sharp decrease in retention at n values close to 1 and the retention level appears to level out when n>1 (Figures 30 and 31). A similar trend is revealed in Figure 32 which illustrates eugenol retention as a function of n. However,

it can be seen that the dip in the curve at n values close to 1 is not as pronounced as in the carvone and pulegone cases. For n>1, the eugenol retention appears to stabilize. m-Anisaldehyde and piperitone, the most soluble of the volatiles, do not exhibit this pronounced decrease in retention at n values near 1 as evidenced in Figures 33 and 34. The respective solubilities of m-anisaldehyde and piperitone in 10% sucrose at °C are 2690 and 2820 ppm. A definite inflection point is observed for m-anisaldehyde at n near 1 as, once again, the retention level appears to stabilize for n>1 (Figure 33). Figure 34 illustrates that the curve relating piperitone retention to n decreases in a regular fashion with no inflection points discernable.

Figures 35, 36 and 37 depict the respective retentions of carvone, pulegone and piperitone as a function of n in 1% gum arabic solutions. In all cases a steady decrease of volatile retention is observed as n is increased to values greater than 1.

f. Freezing Rate

Table 8 illustrates the retention of carvone and piperitone in various solutions as a function of the sample freezing rate. Fast freezing was accom-

plished by immersing the samples in liquid nitrogen
for a period of 3 min prior to loading n the shelf of
the freeze dryer at -40°C. Slow freezing was performed
by placing the samples on the shelf of the freeze
dryer which was previously cooled to -40°C. In all
samples, with the exception of sodium chloride, it is
apparent that the fast freezing treatment gave higher
retentions of carvone and piperitone during freeze
drying.

g. Influence of Added Volatile

        The retentions of carvone, eugenol and m-
anisaldehyde in 10% sucrose was studied when another
volatile compound was present in the freeze-dried
solution. Ethanol was used as an infinitely water
soluble volatile. Table 9 shows that the retentions
of carvone, eugenol and m-anisaldehyde are independent
of the initial ethanol concentrations within the
range studied. Octanol was chosen as a relatively in-
soluble volatile (approximately 590 ppm in water).
It is evidenced that increasing the initial octanol
concentration has the overall effect of reducing the
reten on level of carvone, eugenol and m-anisaldehyde
in 10% sucrose as shown in Table 10. More specifically

carvone and eugenol retentions decrease in a steady

manner, whereas the m-anisaldehyde results appear some-

what erratic, although the trend to decreasing

retentions with increasing octanol is evident.

h.   pH of Freeze-Dried Solutions

Retention values of carvone and eugenol in 10%

sucrose as a function of initial solution pH are

depicted in Figure 38. The pH values of Figure 38

are those of the aqueous sample containing sucrose

and volatile i.e. the pH of the solution immediately

before freeze drying. It is evident that both carvone

and eugenol retention values reach a minimum near

neutrality and attain very high values at the upper

and lower ends of the pH scale. As evidenced in

Figure 39 both piperitone and pulegone retentions

exhibit exactly the same behavior, with a varying pH

in 10%   se. In these experiments water was treated

with h;   loric acid or sodium hydroxide to produce

aqueous solutions from which the 10% sucrose solution

was prepared. The volatile was then added to give

volatile concentrations of 500 ppm. The pH values of

the solutions at various stages of preparation and after

freeze drying are given in Table 11. It is evident

that the pH values at various stages are generally
quite constant although in some cases variation is
observed. The greatest variation is seen to occur in
the highest pH values of the rehydrated freeze-dried
samples. For each of the four volatiles, the highest
pH value decreases approximately 1.5 pH unit from the
pH values measured at previous stages of the experiment.

The results of pH influence on carvone
retention in 5% sodium chloride are tabulated in Table 12.
pH appears to have only a slight influence on the degree
of retention of the volatile.

Carvone (500 ppm) retention in 10% glucose
as a function of pH is shown in Figure 40, O. Once
again carvone retention is lowest near pH 7 with
increasing levels of retention at higher and lower pH
values. Figure 40 also illustrates eugenol (500 ppm)
retention, in 10% glucose with varying pH. The
retention of eugenol increases on the basic side of
neutrality, however at the low pH value of 2.7, the
retention is slightly lower than observed retentions
in the neutral pH range. The pH values at various
stages of the experiment were similar but, as was the
case with sucrose, a significant decrease was ob-
served for the highest pH value of the rehydrated

... ...

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and ... ...
... ...
exhibit ... ...
Figures 42 and 43 illustrate ... trends ... ...
temperature ... respectively in ... ... lag
frond. The retention in solutions where the pH has
been adjusted by hydrochloric acid ... ... hydroxide
are ... by the ... ... The ... values of the ...
arabic solutions at different stages of the experiment
are given in Table 16. Gum arabic was found to ...
exhibit a strong buffering action since when added to
water or water adjusted to pH 9 with sodium hydroxide,
a resultant pH very close to 5 was ... readily obtained.
Acid solutions, initially at pH 3, became slightly
more basic as the pH increased to approximately 4 when
gum arabic was added. Highly basic solutions (pH 10 -
11) were less affected by the addition of gum arabic.
The most basic pH values recorded after freeze drying
decreased by 1 to 1.5 pH unit from observed values
prior to freeze drying. This phenomenon was ... ...
previously with sucrose and glucose.

Gum arabic solutions of pH 6.9 and 9.1 were

prepared by adding gum arabic to water buffered to these pH values. Buffering solutions were chosen to investigate volatile retention in 1% gum arabic in the pH range 5 to 9 because the addition of dilute sodium hydroxide, in an attempt to raise the pH above 5, would have altered the gum arabic concentration. The pH profile of the buffered solutions was found to be constant throughout all stages of solution preparation except a slight decrease of 0.2 pH unit was measured for the rehydrated samples initially at H 9.1. Figures 42 and 43 include the respective retentions of piperitone and pulegone at pH values of 6.8 and 9.1 and are denoted by the symbol V. Thus it appears that volatile retention in gum arabic solutions increases steadily with increasing pH for pH values greater than 5.

i. Layering Experiments

To investigate the possibility that adsorption might play a role in the retention of volatiles, the distri ... of the retained volatiles in 10% sucrose and 1% gum arabi was studied using carvo: s a representati atile. These experiments were conducted by freezing a layer of solution containing no volatile

on top of a previously frozen solution containing carvone
(500 ppm). For 10% sucrose a percentage retention level
of 58.1±0.6 was observed when the layering was performed
with no mechanical separation between the two layers.
When the layers were separated by placing a screen
between the two layers and the upper and lower layers
were analyzed individually, a total retention (sum of
retention in upper (3.3±0.5) and lower (53.6±0.3)
layer) of approximately 57% was obtained. Thus it
appears that approximately 5% of the volatile is
retained in the upper layer.

Similar experiments with gum arabic revealed
an overall increase in retention as a non-volatile
containing 1% gum arabic solution was layered on a
frozen gum arabic solution containing carvone.
Analyses of the upper and lower layers after freeze
drying yielded a total percentage retention of 32.7±0.6
(sum of retention in upper (4.5±0.2) and lower (28.2±0.7).
The percent retained in a single carvone containing
layer was found to be 26.8±2.7.

j. Rehumidification

Freeze-dried samples of 10% sucrose containing
carvone were exposed to atmospheres of different

relative humidity (Wink and Sears, 1950) for extended

periods of time. The carvone content was monitored at

various times up to 80 h. Figure 44 illustrates

carvone retention (expressed as the ratio of carvone

content after a certain time to the initial carvone

content) as a function of time for each of the three

relative humidities. It is evident that the final

carvone content is strongly dependent on the relative

humidity. The freeze-dried sucrose cakes retained

their structure at 11.1% relative humidity after 80 h

and were very easily and quickly rehydrated. At

relative humidities of 50.8 and 86.5% the cakes showed

obvious signs of disintegration and these samples were

not quickly rehydrated.

k. Extension of Volatile Retention Studies to Systems

    of Lower Volatile Concentration

        To investigate the possibility of using the

ultraviolet spectrophotometric method of analysis to

monitor very low volatile concentrations (i.e. less

than 500 ppm as was most generally used), 10% sucrose

solutions containing carvone and piperitone at 10, 25

and 50 ppm were freeze dried and analyzed for volatile.

Although no retentions were calculated, the absorbances

of the rehydrated freeze-dried samples, as tabulated in
Table 14, are substantial and could be used in deter-
mining retention values at such reduced volatile
concentrations.

It was found that when analyzing solutions
containing sucrose in relatively large amounts (10%),
the sucrose solution had to be used in the reference
cell of the ultraviolet spectrophotometer. In such
cases the use of water as a reference was found to
cause errors of 7 to 10% in the absorbance reading
of the volatile.

E. DISCUSSION

The high degree of volatile retention during
the freeze drying of aqueous solutions has been attri-
buted to adsorption, microregion formation or selective
diffusion. At the present time adsorption is considered
to play only a minor role in contributing to the overall
retention of volatile flavoring compounds during
freeze drying. The work of Chirife and Karel (1973b)
has shown that only a small portion of the retained
volatile may be accounted for by adsorption while the
bulk of the volatile is retained by some other
mechanism. Layering experiments with the essential

oil component carvone as used in this study also indicates that only a small fraction of the volatile retained may be attributed to adsorption.

Microregion entrapment, as favored by Karel and Flink and co-workers, or selective diffusion, as supported by King and Thijssen and co-workers, are considered to be the only plausible mechanisms which explain volatile retention at the present time. Both the microregion theory and the selective diffusion theory have been successfully applied to freeze-dried systems. In the opinion of several authors (King and Massaldi, 1974 and Flink, 1975b), these two proposed mechanisms describe the same phenomena from two different approaches, namely mathematical or macroscopic vs. morphological or microscopic viewpoints.

Figures 25, 26 and 27 show that the respective retentions of the essential oil components carvone, m-anisaldehyde and eugenol significantly increase as the initial content of the dissolved sucrose increases. In addition these Figures show that the volatile retention appears to level out at an initial sucrose content of between 20 and 25%. Bellows and King (1973) have investigated the collapse phenomena associated with freeze-drying sucrose solutions. The authors reported

that the collapse temperatures of sucrose samples

varied slightly with initial sucrose content, with a

25% sucrose sample having a collapse temperature of -24°C.

As noted in the Experimental section, the samples were

cooled to -35°C, a temperature well below the sucrose

collapse temperature. As shown in Figure 21, the sample

temperatures remained well below the collapse temperature

for a considerable length of time during drying. Thus

it was concluded that the sucrose solutions freeze dried

well i.e. without collapse. Additional proof that the

sucrose solutions freeze dried without collapse was found

in the ability of the freeze-dried product to be

quickly and completely rehydrated.

Bellows and King (1973) and Ito (1970a) showed

that the collapse temperature of a freeze-drying sample

increased as the average molecular weight of the

dissolved solids increased. This fact in conjunction

with the excellent rehydration characteristics of the

freeze-dried gum arabic solutions suggested that the

gum arabic solutions freeze dried well. As indicated

in Figure 28 gum arabic possess an enormous ability to

retain volatile during freeze drying. Comparison of

Figure 28 with Figures 25, 26 or 27 shows that a 1%

gum arabic solution retains a significantly greater

proportion of volatile than a 5% sucrose solution.
The ability of gum arabic to "lock in" or "encapsulate"
flavoring compounds is very well known and has been
used to great advantage in spray-drying operations
(Glicksman, 1969). Kayaert et al. (1975) showed that
a mixture of four carbohydrate gums gave very high
retentions of acetone and n-propanol at low initial gum
concentrations of 3%. Thus it appears that the gums, in
contrast to other macromolecular species, give a higher
volatile retention than the simpler sugars. Chirife and
Karel (1973a) have shown that the degree of volatile
retention in solutions containing a macromolecular species
(starch, cellulose and dextran 10) is generally much lower
than for solutions containing either a mono or disaccharide.
Thus ability of gum arabic to retain volatiles to such
a high degree is likely due to its ability to form a
crosslinked network. Thus the viscosity of the CAS
regions in frozen gum arabic solutions would be greater
than the viscosity of sucrose CAS regions at the same
temperature. Since the diffusion coefficient of the
volatile within the CAS is dependent upon the viscosity
of the CAS, it follows that volatile retention in the
gum arabic solutions will be greater than retention
values for sucrose solutions.

As evidenced in Table 6, increased initial glucose results in increased volatile retention. However, the observed increase in volatile retention in the glucose samples appears less regular than that found previously with sucrose or gum arabic. Table 6 also illustrated that the calculated standard deviations often approach 10% of the mean retention value. Bellows and King (1973) and Ito (1970a) found that the collapse temperatures of freeze-drying glucose solutions were very close to -40°C. Thus it is probably true that the glucose solutions, especially the more concentrated samples, collapsed during freeze drying. Bellows and King (1973) and Swinnen et al. (1976) have shown that volatile retention decreases with the onset of collapse during freeze drying. The data for carvone and m-anisaldehyde presented in Table 6 indicate that collapse occurred in the more concentrated glucose solution (10 and 15%) since the retention values should be significantly higher as would be the case if collapse had not occurred.

On the basis of the results of Ito (1970a) it was assumed that the sodium chloride solutions freeze dried well. Ito (1970a) found that sodium chloride solutions undergo collapse at -22°C, well above the temperatures used in this study. Table 7 illustrates

that dissolved salts as well as carbohydrates may retain

carvone and eugenol to an appreciable extent. Retention

values of eugenol in sodium chloride solutions were not

obtained since it was suspected that sodium chloride and

eugenol reacted chemically. The ultraviolet characteris-

tics of sodium chloride and eugenol solutions were very

different from those of eugenol in pure water.

The increase in volatile retention with in-

creasing dissolved solids content may be a consequence

of more hydrogen bonding (microregion theory) or reduced

Dt/L^2 values for the volatile. However in the sodium

chloride system, where significant volatile retentions

are observed, the microregion entrapment mechanism

would appear to be inoperative since sodium chloride can

form no hydrogen bonds. Thus it appears that the selec-

tive diffusion theory would offer the most probable

explanation for volatile retention in this case. How-

ever, it should be pointed out that the selective diffus-

ivity of water at low moisture concentrations has been

verified only on non-crystalline hydrophilic organic

systems and not in an inorganic system such as one con-

taining sodium chloride.

The retentions of pulegone and piperitone as

influenced by the initial dissolved solids content were

not determined. Since carvone, pulegone and piperitone

have similar molecular weights, the same carbon skelton

and the same functional groups, it was expected that these

three compounds would exhibit very similar retentions.

Figure.29 does indeed show that these three terpenic

compounds do have similar retentions in sucrose, glucose,

sodium chloride and gum arabic solutions. On the basis

of the selective diffusion theory, the degree of volatile

retention may be qualitatively related to the value of the

diffusion coefficient of the volatile within the CAS.

Due to the similarities in molecular weight, structure and

functional groups, the diffusion coefficients of carvone,

pulegone and piperitone would be expected to be very

similar. Figures 25 through 28 and Tables 6 and 7

generally show that volatile retention decreases in the

order; eugenol > m-anisaldehyde > carvone. Because these

three compounds vary in molecular weight, shape and

chemical structure it is expected that they would exhibit

different diffusion characteristics and consequently

different levels of volatile retention. It is conceivable

that within the CAS regions, the volatiles might interact

with the ssolved solids. Eugenol, for example,

contains a hydroxyl group which might enter into hydrogen

bonding with one of the many hydroxyl groups present in

the dissolved solute. m-Anisaldehyde and carvone might similarly interact with the dissolved solid through their carbonyl groups.

Inspection of Figures 25, 26 and 27 reveals that when retention curves are extrapolated to 0% sucrose, the plot will not pass through the origin but rather intersects the ordinate at retention values greater than zero. Retention experiments with carvone dissolved in water showed, that in the absence of dissolved solids, the volatile retention was zero. Therefore it appears that the effect of dissolved solids is most pronounced at very low dissolved solids content (0 to 5%). Figures 25, 26 and 27 indicate that for carvone, m-anisaldehyde and eugenol respectively, the volatile retention due to the first 5% dissolved solids approaches 35%. No other portion of these retention curves exhibits such a marked influence on volatile retention over a range of 5% dissolved solids. A similar situation is found with freeze-dried gum arabic solutions as evidenced in Figure 28. In this case, with carvone as an example, the retention increases from zero without any dissolved solids to approximately 40% at 1% initial gum arabic concentration so once again the marked influence of initially

low dissolved solids is evident.

Figure 24 illustrates that at a constant layer thickness the degree of carvone retention is independent of the sample area in freeze-dried sucrose and gum arabic solutions. This result is compatable both with the microregion and selective diffusion theories in that the area of the sample would not be expected to influence the nature of the CAS regions formed during freezing. Being of equal thicknesses all samples would freeze at the same rate hence in all cases the thickness of pure ice regions and the thickness of the CAS regions would be similar. Flink and Karel (1970b) found similar results for glucose and dextran-10. Figure 23 illustrates carvone retention in 10% sucrose and 1% gum arabic as a function of sample thickness. In both cases the sample retention increases with sample thickness until a thickness of approximately 8 mm is reached. At greater thicknesses the carvone retention appears to become independent of the sample thickness. This trend of increasing volatile retention with increased sample thickness was also observed by Ettrup Petersen et al. (1973) in samples of freeze-dried coffee. These findings of increased volatile retention with increased sample thickness appear to conflict

with the results of several investigators (Flink and Karel, 1970b and Bartholomai et al., 1975) who have found that volatile retention increases as sample thickness decreases. An explanation for greater volatile retention in thin samples is based on the fact that in thin samples rapid drying and steep moisture gradients would decrease the time during which the moisture content would remain at levels high enough to permit volatile escape. However, as pointed out by Ettrup Petersen et al. (1973) most literature regarding the effect of sample thickness on volatile retention considers primarily the dehydration phase of freeze drying. The authors postulate that the higher volatile retentions found with thicker samples is due to the different freezing rates of the thin and thick samples. The thick samples freeze more slowly than the thin ones and hence exhibit a greater volatile retention. This explanation of increased volatile retention with increased sample thickness, as proposed by Ettrup Petersen et al. (1973), would appear to explain the results presented in Figure 23 in a satisfactory manner.

Retentions of carvone, pulegone, eugenol, m-anisaldehyde and piperitone as a function of initial volatile concentration are shown in Figures 29 to 34

respectively. The initial volatile content as recorded on the abscissa is represented by the ratio of initial volatile concentration (ppm) to the saturation concentration (ppm) of the volatile in 10% sucrose solutions. This ratio is symbolized by n. The respective solubilities of the above volatiles in 10% sucrose solution were found to be 1560, 1490, 2052, 2690 and 2820 ppm at 10°C. All volatiles appear to exhibit a steady decrease in retention as n approaches a value of 1. Figures 29 and 30 respectively illustrate that the carvone and pulegone retention curves exhibit a sharp dip to lower retention values at n values very near 1. Both carvone and pulegone were shown to have very similar solubilities in 10% sucrose solutions. The retention values of carvone and pulegone appear to level off for n>1. Of the compounds investigated, eugenol has an intermediate solubility of 2052 ppm in 10% sucrose. Figure 31 illustrates that the dip in the retention curve at near 1 is very much less pronounced than that of carvone or pulegone. Again when initial eugenol content exceeds the solubility limit (n>1), the eugenol retention appears to level off. The retention curve for m-anisaldehyde, as shown in Figure 33, exhibits no deflection whatsoever at the

solubility limit however the retention levels for

m-anisaldehyde appear to become more constant when the

solubility limit is exceeded. The retention of piperitone

as a function of its initial concentration is shown in

Figure 34. It is evident that piperitone retention

decreases steadily with increasing values of n.

Massaldi and King (1974a) have studied the

retention of d-limonene and n-hexyl acetate as a function

of initial volatile concentration and obtained retention

curves very similar to those illustrated in Figures 29

and 30. In addition these workers were able to cal-

culate theoretical retention curves for 25% and 10%

sucrose solutions which predicted experimental results

quite well especially for n-hexyl acetate in 25%

sucrose. In the calculation of the theoretical model,

Massaldi and King (1974a) assumed that the retentions

of volatile initially present below the saturation

limit would be constant because these volatiles would

be homogeneously dissolved. Figures 29 to 34 show

that the retention in solutions where the volatile con-

tent is initially below saturation are not constant

and decrease with increasing initial volatile content.

This decrease in volatile retention at initial

volatile contents below saturation may be attributed

to the solubility limit of the vola le being exceeded during the freezing process and thus giving rise to pure droplets of volatile. If these droplets are in close proximity to the vapor phase after sublimation of the ice they will be totally lost through evaporation when exposed to the vacuum. According to Massaldi and King (1974a) the droplets entrapped within the CAS and not in contact with the vapor phase will be largely retained as will that portion of the volatile which remains homogeneously dissolved within the CAS.

Although the retention studies of Massaldi and King (1974a) were directed more to emulsified systems rather than toward unsaturated systems (n<1) several favorable comparisons may be made with this work. In both studies volatile retention appears to become constant as the initial volatile content exceeds the solubility limit. It has been previously shown (Figures 20 to 34) that as the solubility of the volatile decreases, more pronounced inflections of the retention curve occur at n values near 1. Massaldi and King (1973) have shown that the solubilities of n-hexyl acetate and d-limonene are respecti
509 ppm and 13.8 ppm in water at 25°C. Thus it would be expected that more pronounced inflections wou

occur in retention curves for these compounds than those
obtained in this work. The curves presented by Massaldi
and King (1974a) appear to verify this prediction to a
certain extent.

Microscopic observations by Flink and
Gejl-Hansen (1972) indicate that the solubility charac-
teristics of volatile compounds are a very important
factor in determining volatile retention during freeze
drying. Photographs of freeze-dried malto-dextrin
solutions revealed droplets of 1-butanol and diacetyl.
On the basis of solubility data reported by Flink and
Gejl-Hansen (1972), it is expected that droplets of
1-butanol and diacetyl were formed during the freezing
of the malto-dextrin solutions since the initial
volatile concentrations used by these workers suggest
that the volatile containing solution was homogeneous
prior to freeze drying. Droplets of the relatively
insoluble volatile hexanal were also observed however
the source of these droplets is somewhat uncertain.
These authors report that the hexanal containing
solutions prepared prior to freeze drying appeared
homogeneous and further state that these highly insoluble
compounds such as hexanal are present in the initial
solution as small drops. If the droplets present in

the freeze-dried malto-dextrin originated from a
homogeneous solution, their formation could be attri-
buted to the solubility limit being exceeded during
freezing. However if the initial solution was in fact
a suspension then the droplets present in the freeze-
dried malto-dextrin could be identified with the
droplets originally present. Obviously a precise
knowledge of the solubility characteristics of these
slightly soluble compounds would be useful in clarifying
this ambiguity. A knowledge of the solubility parameters
of hexanol in malto-dextrin solutions would similarly
facilitate an interpretation of the microscopic
studies of Flink et al. (1973). However, retention and
microscopic data presented by Flink and Gejl-Hansen (1972)
do point out that the degree of retention of highly
insoluble volatiles is much lower than that of very
soluble compounds and therefore confirms the prediction
of Massaldi and King (1974a) that droplets near the
gas pores will be lost during the drying stage and
droplets embedded within the carbohydrate matrix will
be largely retained.

Many studies have shown that the degree of
volatile retention during freeze drying is greatly
affected by the rate at which the liquid sample is

frozen (Flink and Labuza, 1972 and Chirife and

Karel, 1974b). It has generally been found, that the

degree of volatile retention is significantly reduced

as the freezing rate of the sample increases. The

data presented in Table 8 appear to contradict previous

finding since in all cases, with the exception of

sodium chloride, the retentions of carvone and piperitone

increase with an increased freezing rate. The increased

retention with greater freezing rates are most apparent

in the sucrose and glucose solutions. Most previous

studies directed toward the influence of freezing rate

on volatile retention have been carried out using

infinitely water soluble volatiles. Massaldi and King

(1974a) have determined that the retention of emulsified

d-limonene in 25% sucrose solutions decreases as the

sampl. freezes more quickly. A possible explanation

for the results of Table 8 is offered by Thijssen (1972c).

During freezing, which is in fact a freeze concentration

of dissolved solids and volatiles, the sparingly

soluble volatiles become supersaturated and segregate

in the form of dispersed droplets. This droplet for-

mation has been observed by Flink and Gejl-Hansen

(1972). Because these droplets will be preferentially

formed at or near the ice crystals, the droplets will

come into direct contact with the open gas pores after the sublimation front is passed. As stated by Massaldi and King (1974a) these droplets will evaporate completely. Therefore if there are volatiles present which will become supersaturated during freezing, the size of the droplets and consequently the probability of an open contact with the ice crystals will increase with a decrease in freezing rate. For these systems a decrease in the freezing rate therefore will result in a lower volatile retention. The combined results of Flink and Gejl-Hansen (1972), Massaldi and King (1974a) and this work appear to lend support to the prediction of Thijssen (1972c).

Massaldi and King (1974a) have suggested that the presence of an immiscible liquid phase, in a product that is to be freeze dried, may adversely effect the retention of important flavoring volatiles. An immiscible phase would extract useful volatile components from the aqueous mixture and thus the useful volatiles would be more susceptible to loss during the drying stage. The results presented in Table 10 indicate that the presence of immiscible octanol does indeed cause a marked decrease in the retentions of carvone, eugenol and m-anisaldehyde. The solutions with initial octanol

concentrations of 600 ppm and 800 ppm were non-homogeneous

since the solubility limit of octanol in the 10%

sucrose solution was exceeded. It is apparent that in-

creasing amounts of initial octanol above the solu-

bility limit cause increased losses of volatile. It

is also apparent that octanol, initially present at

levels below the solubility limit, decreases the reten-

tion of the volatiles under consideration. In all

probability this homogeneously dissolved octanol

separates as pure liquid as the solution is cooled and

then extracts the other volatiles in much the same

manner as the initially immiscible octanol. Table 10

also suggests that the different volatiles (carvone,

eugenol and m-anisaldehyde) are extracted to different

extents by the octanol since the decrease in retention

is not the same in all cases. King and Massaldi

(1974) have discussed the implications of having an

immiscible phase present in a liquid food that is to be

freeze dried. Table 9 illustrates that the retentions

of carvone, eugenol and m-anisaldehyde are not affected

by the presence of varying amounts of ethanol which is

an infinitely water soluble volatile.

Figures 38 and 39 illustrate that retention of

the essential oil components in 10% sucrose is very

dependent on the solution pH as measured prior to freeze drying. The four volatiles represented in Figures 38 and 39 all have very similar retention curves which exhibit a minimum at pH values close to neutrality and increase toward the extreme ends of the pH scale. Inspection of the literature shows that the effect of pH on volatile retention has not been previously studied to any great extent. Chalmers and Watts (1972) have investigated the effect of pH at the start of freeze drying on the recoveries of several organic acids of biological interest. These freeze-drying studies, which were conducted without any dissolved solids, indicated that the different acids were retained to different extents depending on the values of their heats of vaporization or sublimation. No general trends could be found relating retention with increasing pH values. Voilley et al. (1973) noted in their alcohol retention studies that the pH of the solution prior to freeze drying was 2.3. The complex model solutions employed by these investigators contained citric acid which would account for the low pH values measured.

The effect that pH has on retention, as revealed in Figures 38 and 39, could be related to several factors. In the first place it is possible that

the pH could alter the chemical nature of the volatile.
Secondly it is possible that the pH may influence the
characteristics of the dissolved solids. In addition
the observed trends may be due to a combination of both
of the above possibilities.

To check the first possibility the solubility
of carvone in water and 10% sucrose was measured as a
function of pH. The results of this stu   conducted
at room temperature, showed that the car n   olubility
in water and 10% sucrose was constant in t   p   range
2.7 to 11.0. These findings suggest that th chemical
nature of the carvone molecule remains intact throughout
the pH range studied. It was suggested (Fouron, 19 7
that the carvone may react with base at high pH values
according to the following reaction scheme.
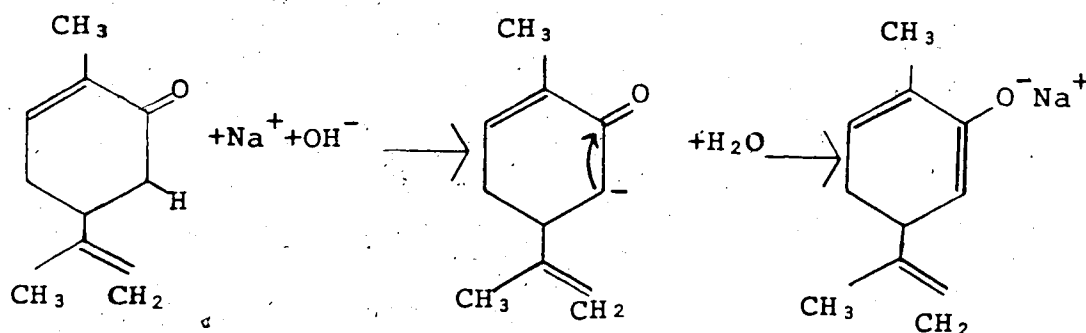
If such a reaction were to take place the
solubility of the carvone would be significantly in-
creased because the reaction product would have the
structure of a salt and therefore enhanced water solu-
bility. Additional proof that the carvone remains
intact at all pH values is found in the ultraviolet
characteristics of the solutions. Carvone dissolved on
water exhibited a maximum absorption at 241.5 mm. All
solutions in which the pH was adjusted gave maximum
absorptions at exactly the same wavelength. If the
above reaction was to occur, the ultraviolet absorption
properties of the salt would be entirely different from
that of unreacted carvone because the ultraviolet
absorption of carvone at 241.5 mm is due to electronic
transitions involving the double bond within the six-
membered ring and the carbonyl moiety. One could
intuitively predict, on the basis of the results of
Figures 38 and 39, that pH does not influence the
nature of the volatile compound. It is unlikely that
pH would affect eugenol (a non-terpenic essential oil
component) and carvone, piperitone and pulegone (terpenic
essential oil components) in exactly the same way since
these compounds have very different chemical structures.
Thus it appears that the influence pH has on retention

does not result from changes arising in the volatile.

It is well known that the sucrose molecule may break down in acidic or basic solution (Honig, 1953). In acidic solutions sucrose may be hydrolyzed to glucose and fructose. The rate of this hydrolysis reaction increases with a decrease in pH and increases with temperature. Stadler (1932) has correlated sucrose hydrolysis data over the range 50-120°C and 4.6-7.2 pH. Using Stadler's data a rough calculation has shown that at 20°C and pH 3.0 approximately 0.031% of the sucrose would be inverted in one hour. When sucrose solutions were prepared at low pH values, the solutions were immediately freeze dried and were not subjected to any high temperature. Thus it may be concluded that under the experimental conditions employed, sucrose hydrolysis would not take place and the sucrose molecules in solution retain their characteristic structure. Under alkaline conditions sucrose undergoes decomposition with the formation of furfural, methylglyoxol, acetone, lactic acid, trioxcglutaric acid, acetic acid, formic acid and several other acids which have not yet been characterized (Yudkin et al., 1971). This decomposition is accompanied by the formation of unknown mixtures of substances in very small quantities but of very intense

brown color. Generally however alkaline decomposition
of sucrose requires very high temperatures. Honig (1953)
cites as an example that in a solution of sucrose with
lime of pH 12 the sugar loss in 1 h of boiling under
normal pressure was found to be 0.5%. Since the
conditions which the alkaline sucrose solutions were
subjected to in this work were much less severe, it is
unlikely that any appreciable amounts of sucrose would
decompose. Table 11 points out that the pH values of
the different solutions remain practically constant
throughout the freeze-drying experiment. However it is
evident that the pH values of the rehydrated freeze-
dried samples are approximately 2 pH units below the
values recorded before freeze drying for the most basic
samples. It has been mentioned previously that sucrose
decomposition is accompanied by the formation of a
variety of acids which would have the effect of lowering
the solution pH. The rehydrated samples were perfectly
clear and showed no discoloration as would be expected
if decomposition had occurred. The reason for this
decrease in pH for the basic samples after freeze
drying remains to be explained. In light of the
mild conditions employed in these retention studies
it is believed that the sucrose remains unaltered at

all pH levels and does not degrade to form products
which may modify retention values.

Hydrogen bonding between sucrose molecules
in solution could conceivably be altered by the presence
of excess protons or hydroxyl groups. If an increased
degree of hydrogen bonding was to take place at high
and low pH values, the results of Figures 38 and 39
could be explained by the microregion theory and the
selective diffusion theory. According to the microregion
theory if hydrogen bonding between sucrose molecules
were to be enhanced, more microregions would be formed
and increased volatile retention would be expected.
On the basis of the selective diffusion theory an
increase in hydrogen bonding would have the effect of
increasing the viscosity within the CAS region. Since
the diffusion coefficients of the volatiles within the
CAS would decrease as the viscosity within the CAS
increases, volatile retention would increase. Viscosity
measurement of 10% sucrose solutions at room temperature
showed that the pH had negligible effect on viscosity
over the pH range 2.7 to 11.0.

At this point in time the increased retention
of volatiles at low and high pH values remains unexplained.
It has been shown that the parameters of volatile solu-

bility and solution viscosity are not changed by pH
at room temperature. It must be remembered, however,
that the freezing of a solution is a concentration process.
As water separates as pure ice, the remaining solution
will be concentrated in dissolved solids, volatile and
protons or hydroxyl ions. Thus the chemical composition
of the CAS is far removed from that of the initial
solution in which the solubility and viscosity were
tested as a function of pH.
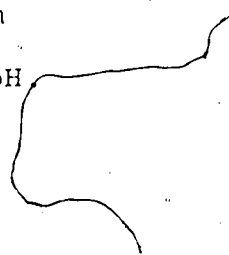
Figure 40 illustrates that carvone retention
in 10% glucose is similar to the results obtained in
sucrose solutions as pH is varied. The carvone reten-
tion curve exhibits a minimum near neutrality and in-
creases at high and low pH values. Figure 40 also
illustrates that eugenol retention in 10% glucose is
constant over the pH range 3 to 7 and then rises as the
solution becomes more basic.

Volatile retention in gum arabic solutions
of different pH values indicate trends similar to those
found with sucrose and glucose as evidenced in Figure 41.
Gum arabic is a polysaccharide of molecular weight
240,000-300,000 and contains D-galactose, L-arabinose,
L-rhamnose and D-glucuronic acid groups (Furia, 1968).
The presence of the D-glucuronic acid residues accounts

for the resultant pH of the solutions being very close to pH 5. It is clearly indicated in Figures 42 and 43 that piperitone and pulegone show behavior similar to that of eugenol and carvone. Figures 42 and 43 also point out that for pH values greater than 5, the degree of volatile retention increases in a steady manner as the pH of the solution is raised.

The chemistry of gum arabic is fairly well documented (Glicksman, 1962). As in the case of sucrose and glucose, there is no indication why retention should increase at high and low pH values in gum arabic solutions. Studies at room temperature have shown that the viscosity of gum arabic solutions is a maximum at pH 6 to 7 (Glicksman, 1969) where volatile retention is close to its minimum value. Studies on systems which approximate conditions found within the CAS would undoubtedly be helpful in determining the effect that pH has on retention in these carbohydrate systems.

In contrast to the dissolved carbohydrate systems, it is apparent that initial pH has little influence on volatile retention in salt solutions. Table 12 illustrates that carvone retention in sodium chloride is practically independent of the solution pH These results together with the results of the car-

bohydrate-containing systems would suggest that the influence pH exerts on volatile retention is important only for systems where hydrogen bonding is possible.

Figure 22 illustrates that the volatile containing freeze-dried product is very stable even when subjected to a vacuum for long periods of time. Chirife and Karel (1974a) have shown that freeze-dried maltose solutions containing 1-propanol are stable under vacuum at elevated temperatures. These authors have also demonstrated that volatile loss from the freeze-dried matrix is dependent to a large extent on the water activity of the surrounding atmosphere. Figure 44 points out that carvone retention in a freeze-dried sucrose matrix is critically dependent on the moisture content as well. Volatile retention in rehumidified freeze-dried samples has been discussed by Chirife and Karel (1974a) and King and Massaldi (1974). King and Massaldi (1974) developed a diffusion based mechanism to explain the loss of volatiles in rehumidified freeze-dried samples. These authors pointed out that the loss of volatiles may be a function of the thickness of the CAS regions within the freeze-dried samples. The thinner regions lose the volatile more quickly during rehumidification whereas the volatile is kept for a longer period of time within the thicker regions.

F. CONCLUSIONS

The retentions of piperitone, pulegone and carvone (terpenic essential oil components) and eugenol and m-anisaldehyde (non-terpenic essential oil components) were studied during the freeze drying of model solutions. Sucrose, glucose, sodium chloride and gum arabic were used as dissolved solids. The retention level of these sparingly soluble volatiles was enhanced by:

1. an increase in sample thickness

2. an increase in initial dissolved solids content

3. a reduced initial volatile content

4. an increase in the freezing rate

5. acidic or basic conditions

6. the absence of additional sparingly soluble volatiles

It is apparent that the behavior of the sparingly soluble essential oil components parallels that of infinitely soluble volatiles to some extent. However, as shown by experiments on the freezing rate and sample thickness, differences do exist as the two classes of volatile exhibit different retention characteristics. Because liquid food concentrates contain both soluble and relatively insoluble flavoring components, processing conditions must be regulated to give maximum retention of

the different types of volatile. The organoleptic
quality of a rehydrated freeze-dried food is directly
related to the concentrations of the volatile flavoring
compounds.

Massaldi and King (1974a) have warned that the
practice of adding flavoring components to a food con-
centrate before freeze drying may not be advantageous.
The results using octanol as an additional volatile
show that the presence of an additional sparingly
soluble volatile adversely effects the degree of volatile
retention.

The fact that the solution pH tremendously
influences the degree of volatile retention is very
interesting. The implications of these findings are
at once recognizable. If a liquid food could be
successfully acidified, the retentions of the volatile
flavoring compounds would be increased, hence the quality
of the rehydrated product would more closely match that
of the original liquid food.

In most cases, the degree of volatile retention
can be rationalized on the basis of the selective
diffusion theory or the microregion concept. Volatile
retention by the adsorption mechanism is seen to play only
a minor role.

III.   Solution Properties of Terpenic Essential Oil
Components

A.   INTRODUCTION

Recent studies, involving the retention of
flavoring organic compounds during the freeze drying of
aqueous solutions, have shown that the degree of solubil-
ity of the flavoring compound has a pronounced effect on
volatile retention (Flink and Gejl-Hansen, 1972,
Flink et al., 1973 and Massaldi and King, 1974a).

Solubility data for many of the important
sparingly soluble flavoring compounds is scarce. The
essential oil components, both terpenic and non-terpenic,
remain relatively unexplored even though these compounds
are commonly used in the preparation of non-alcoholic
beverages, ice creams and ices (Hall and Oser, 1968).
Thus an investigation was initiated to determine the
solubility parameters of pulegone, piperitone and
carvone in sucrose, glucose and sodium chloride solutions
of varying solids concentration. The solubility studies
were carried out at temperatures of 10, 20 and 30°C with
a view to exploring some thermodynamic properties of the
saturated solutions.

B.   LITERATURE REVIEW

1.   Techniques for Determining the Solubility of Liquids
     in Liquids

Since solubility measurements in liquid-liquid systems do not require experimentation of any great complexity, the variety of experimental designs is not large. Classical techniques such as the volume method and the cloud point method, as reviewed by Zimmerman (1951), are very useful in the determination of mutual solubilities of various organic compound-water mixtures (Hill, 1923, Hill and Malisoff, 1926 and Ginnings and Baum, 1937).

At the present time instrumental methods are most widely used as analytical tools in the determination of mutual solubilities of liquids. Gas-liquid chromatography has proven to be very suitable for solubility studies. McAuliffe (1966) obtained solubility values of paraffins, cycloparaffins, olefins, acetylene, cycloolefins and aromatic hydrocarbons in water using the glc technique. Buttery et al. (1969) used glc to determine the solubilities of alkanals, alkan-2-ones and methyl alkanoates. The technique employed in these two studies consisted basically of saturating water with

the desired organic compound and then letting the two

phases separate. The saturated aqueous phase was

analyzed by glc and saturation concentrations were

determined by comparison with standard solutions. Sutton

and Calder (1975) modified the approach somewhat by

extracting the hydrocarbon dissolved in water with a

non-interfering organic solvent. Massaldi and King (1973)

determined aqueous solubilities of n-hexyl acetate,

n-butylbenzene and d-limonene using a head-space type of

analysis. The head-space technique had the advantage

of not requiring phase separation of saturated solutions.

In general solubility measurements by glc offer several

distinct advantages. Impurities are of no significance

if their peaks do not interfere with the measurement of

the desired hydrocarbon peak. In addition very high

sensitivities are attainable especially with flame

ionization detectors.

Spectrophotometric techniques have proven

useful in the determination of solubilities of various

aromatic hydrocarbons in water. In particular ultra-

violet spectrophotometry has been very useful in monitoring

unsaturated compounds. Andrews and Keefer (1950)

investigated the solubilities of substituted benzenes

in water and aqueous silver nitrate at 25°C. Samples

of the saturated solution were extracted with hexane and

the resultant hexane solutions were analyzed spectro-

photometrically. Bohon and Claussen (1951) used both

a non-extractive and a n-heptane extractive procedure

to study the solubility of substituted benzenes in water.

Wauchope and Getzen (1972) employed the ultraviolet

method in a temperature study of the solubilities of solid

aromatic hydrocarbons in water. The ultraviolet technique

suffers from the disadvantage of being suitable only

to those compounds which exhibit strong absorptions

within the ultraviolet region of the spectrum.

A non-instrumental method worthy of mention

is that developed by Sobotka and Kahn (1931). This

technique involves the dispersion of a water-insoluble

dye (Sudan IV) into large amounts of water or aqueous

solution and adding the organic compound in small increments

using a microburet. When the aqueous sample is saturated

with the organic compound, the excess organic appears

as immiscible red liquid droplets as the excess organic

dissolves the dye. This technique still finds application

at the present time as evidenced by the work of Sada et al.

(1975) who studied the solubilities of toluene in aqueous

salt solutions.

2. Properties of Dilute Aqueous Solutions

Aqueous solutions, which are saturated with a
sparingly soluble compound, may be considered as being
infinitely dilute. Thus solubility values of relatively
insoluble compounds allow for the evaluation of thermo-
dynamic parameters for solutions at infinite dilution.

Rowlinson (1969) has segregated nonelectrolytes
into two classes. Typically aqueous solutes are those
which exhibit in aqueous solution such anomalous thermo-
dynamic properties as found only in aqueous systems.
Typically aqueous solutes are subdivided into two classes,
apolar solutes and mixed solutes. Apolar solutes, as
the name suggests, contain no polar groups and
include pure hydrocarbons and the inert gases.   ed
solutes are those which contain a large apolar region
and a polar group. Alcohols, ketones, amines and
ethers are examples of species which would be included
within the mixed category. Typically nonaqueous solutes
are those which have aqueous sc ition properties similar
to those of normal nonaqueous solutions. Glucose, sucrose
and other sugars are prime examples of typically non-
aqueous solutes.

Dilute aqueous solutions of typically aqueous
solutes have received a great deal of attention within

the past few years. Thermodynamic data obtained from
solubility studies or calorimetric experimentation has
shown that water is a unique solvent in that it exhibits
properties not found in any other solvent. All of the
typically aqueous solutes such as the inert gases
(Alexander, 1959), hydrocarbons (Nemathy and Scheraga,
1962), alcohols (Franks and Reid, 1973), cyclic ethers
(Cabani et al., 1971a), amines (Franks and Watson, 1969)
and ketones (Gross et al., 1939) were found to possess
very highly negative partial molar entropies of hydration,
ΔS_h, (h subscript refers to the process, pure solute
(ideal vapor)→solute (solution) whereas s subscript
refers to the process, pure solute (liquid)→solute
(solution)). In addition the aqueous solubilities of
most typically aqueous solutes were found to decrease
with increasing temperature. The molar heat capacities
of such solutions are also large and positive.

Various theories have been advanced to account
for the unusual properties exhibited by aqueous solutions
of typically aqueous solutes. The starting point for the
most advanced and sophisticated water theories is the
"iceberg" model which was proposed by Frank and Evans
(1945). This iceberg model supposes that pure water
is a mixture of distinguishable molecular species which

are in a state of equilibrium. $(H_2O)b$ is termed bulky

$$(H_2O)b \rightleftharpoons (H_2O)d$$

water and it is a species which is extensively hydrogen
bonded with predominantly four fold coordination (as in
ice) and therefore possesses a low density. $(H_2O)d$
is termed dense water as it contains nonbonded OH groups
such that the O-O distances are shorter than the normally
accepted hydrogen bond lengths and therefore possesses
a higher density. Frank and Evans (1945) labelled the
ordered water structures, $(H_2O)b$, as "icebergs" since
the properties of $(H_2O)b$ have been identified with those
of ice. The presence of an apolar solute or the apolar
region of a mixed solute in water is believed to shift
the above equilibrium to the left i.e. toward the more
structured form of water. Thus the number of icebergs
in reases when a typically aqueous solute is placed in
water. This equilibrium shift to the more ordered
water structure accounts for highly negative ΔS values
as typically aqueous solutes are dissolved in water.
Highly negative entropies are a sign of ordering or loss
of randomness within a system, with the $(H_2O)d$ species
being the less ordered form of water. Solubilization of

an apolar solute or a mixed solute occurs when the solute
molecules occupy a cavity or partial cavity within the
$(H_2O)b$ cluster. The ability of the guest molecule to
occupy a cavity within the $(H_2O)b$ host is dependent upon
the size of the guest molecule and it has been shown
that there exists an optimum molecular diameter for
maximum solubility (Franks and Reid, 1973).

Many solutes, which may be considered as typically
aqueous, exhibit decreasing solubilities in water with an
increase in temperature. Compounds such as ketones
(Gross et al., 1939), butyl alcohol (De Santis et al.,
1976), butane (Rice et al., 1976), ethyl ether and isoamyl
alcohol (Kablukov and Malischeva, 1925), ethyl acetate
(Glasstone and Pound, 1925), isomeric pentanols (Ginnings
and Baum, 1937) and aliphatic ethers (Bennett and
Phillips, 1928) have lower solubilities at higher
temperatures. In a sense the solubility characteristics
of liquid organics appear to parallel the well known
solubility characteristics of gases.

The explanation for this decrease in solubil-
ity with an increase in temperature comes from con-
sidering the effect that elevated temperature has on the
iceberg. According to the iceberg model, the $(H_2O)b$
species acts as a host for the solutes. An increase

in temperature has the effect of decreasing the number of

$(H_2O)b$ species (melt the icebergs!) and thus shifts the

equilibrium in favor of the $(H_2O)d$ species. Thus at

higher temperatures, the number of host clusters is lower

and the solutes are less soluble.

In contrast to the above examples several organic

species do not exhibit an increased solubility with lower

temperatures. Wauchope and Getzen (1972) have shown

that the solubilities of solid aromatic hydrocarbons

increase as the temperature is increased. d-Limonene

was also found to have higher solubilities at higher

temperatures (Massaldi and King, 1973). Bohon and

Claussen (1951) noted that many aromatic hydrocarbons

exhibited a solubility minimum at 18°C and identified

this s   ibility minimum with a heat of solution being

equal to z o.

It is well known that the presence of a dis-

solved solid (ionic or nonionic) in water may signifi-

cantly reduce the solubility of a liquid organic species

(Rice et al., 1976 and Massaldi and King, 1973). Many

authors currently hold the opinion that this salting

out effect is due to the added solute becoming hydrated

in solution so that the molecules of water involved in

the hydration are no longer available for dissolution

of the second substance, thus the solubility of the
second substance is reduced. Many years ago Glasstone
and Pound (1925) questioned this concept and concluded,
on the basis of calculated hydration values, that other
more important factors were operative in the salting out
effect.

The ability of different types of sugars and
salts to reduce the solubility of typically aqueous
solutes in water has been investigated from the view-
point of the iceberg model of water. Ben-Naim
(1965a, 1965b and 1967) has studied the solubilities of
the apolar solute, argon, in aqueous solutions containing
an additional component. In solutions containing methanol,
ethanol, n-propanol and n-butanol, the solubility of
argon was found to be higher than the solubility in
pure water. These alcohols fall within the mixed cate-
gory of solutes and are considered to be solutes which
increase the structural integrity of water. The solu-
bility of argon decreased in aqueous solutions of glucose,
sucrose, glycerol and simple electrolytes. Ben-Naim
concluded that these hydrophilic solutes decreased argon
solubility by decreasing the structural integrity of
water i.e. reduced the number of host $(H_2O)b$ species.
Franks (1973) has criticized Ben-Naim's explanation and

Franks (1973) maintains that molecules of glucose in aqueous solution are surrounded by $(H_2O)b$ species and that glucose is in fact a promoter of water structure. In this case the hydroxyl groups of glucose are accommodated into the structured water. The fact that glucose reduces the solubility of typically aqueous solutes in aqueous solution indicates that the hydration of glucose and argon are incompatible. At the present time the exact mechanism of this salting out effect is still under investigation. Franks and Reid (1973) warn that extreme caution must be exercized when one attempts to explain interactions in ternary systems.

C. EXPERIMENTAL

1. Materials and Chemicals

d-Glucose (Fisher), sucrose (Baker) and sodium chloride (MCB) were used as received. Carvone (K and K), piperitone (ICN), and pulegone (Fluka) were used as received. Analysis by gas chromatography revealed these compounds to be at least 90% pure. All solutions were prepared with distilled water.

2. Equipment

Saturated solutions were prepared in a Labline Environmental Chamber (Labline, Inc.) and temperatures are accurate to ±0.2°C. A Vortex-Genie (Scientific Industries, Springfield, Mass.) was used to mix the aqueous solution with the added organic species. Separation of the saturated aqueous layer from excess organic was accomplished on a Janetzki T5 Centrifuge (Heinz Janetzki Kg.) which was equipt with a fixed angle rotor. Ultraviolet absorption measurements were conducted on a Unicam SP1800 Ultraviolet Spectrophotometer (Pye Unicam). The instrument was operated on the fixed wavelength mode using a band width of 1.2 mm and a slit width of 0.4 mm. Quartz cells (Canlab) were used for reference and sample during ultraviolet analysis.

3. Preparation of Standard Curves

Standard solutions of the organic species in water were prepared so that the range of absorbances for the standard solutions fell between 0.4 and 1.4. It has been found that absorbances falling within this range are the most reliable for double beam spectrophotometers (Willard et al., 1965). The standard curves for carvone (Figure 45), pulegone (Figure 46) a iperi-

tone (Figure 47) illustrate that the Beer-Lambert Law is valid for absorbances between 0 and 1.2. Values of log ε, the extinction coefficient, were calculated from the slope of the standard curve and are tabulated in Table 15 together with previously measured values of log ε in ethanolic solution.

4. Preparation of Saturated Solutions and Solubility Determinations

All saturated solutions were prepared in a Labline Environmental Chamber (±0.2°C). Conical 12 ml centrifuge tubes with screw tops were filled with 8.0 ml of aqueous solution. Approximately 0.1 ml of the organic species was added. The contents of the centrifuge tubes were mixed on the vortex mixer for 8 min. After mixing the tubes were centrifuged for as long as was required to effect separation between excess organic and the aqueous phase. In some cases centrifugation times of several hours was required. The centrifugation was carried out at the temperature at which the saturation was performed. When centrifugation was completed, as evidenced by a totally clear aqueous phase, a 1 ml graduated pipet with a teflon extension was used to remove aliquots from the aqueous phase. To insure that

none of the less dense organic phase entered the pipet,
a gentle blowing action was applied as the teflon tip
passed through the organic layer. After the 1 ml
aliquot had been withdrawn from the centrifuge tube,
the teflon tips were removed and the contents of the pipet
were emptied into a suitable volumetric flask and diluted
with water. The absorbance of the diluted saturated
solution was measured and the concentration of the organic
species was determined from the previously obtained
standard curves.

Various tests were performed to insure that
the above technique produced saturated solutions. Eugenol
was chosen as the test component because it was observed
that during the preparation of the standard solutions
eugenol required the longest times and most vigorous
shaking for dissolution in water. For example in the
preparation of standard eugenol solutions, vigorous
shaking for at least 15 min was required to dissolve
0.05 g of eugenol in 500 ml water (1/20 th saturation
concentration). At room temperature saturated solutions
of eugenol in 30% glucose were prep.   by vortex
mixing for 3, 5, 7 and 9 min. 1 ml aliquots were with-
drawn after centrifugation and suitably diluted. The
respective measured absorbances were 0.378, 0.384, 0.377

and 0.378. Thus it was concluded that the 30% glucose
solution was saturated with eugenol within 3 min of
vortex mixing. It was also shown that the concentration
of the organic species in the aqueous phase did not
increase with increased contact time between the aqueous
phase and the excess organic. For example, at 10°C
the solubility of pulegone in 40% glucose was found to be
0.655±0.008 g/l immediately after vortexing. The
saturated pulegone samples were allowed to stand for 48 h
at 10°C in contact with excess pulegone and then remixed.
The pulegone concentration after this period was found
to be 0.659±0.007 g/l. In a similar test, the saturation
concentration of piperitone, after vortexing a 15%
sodium chloride solution at 10°C was 0.677±0.011 g/l.
After six days the concentration was found to be
0.675±0.005 g/l. Hence on the basis of these tests it
was concluded that the aqueous solutions were saturated
with the organic species during vortex mixing.

5. Evaluation of Thermodynamic Parameters

a) Activity Coefficients

The activity coefficients, γ, for piperitone,
pulegone and carvone in aqueous solution were calculated

according to Henry's Law which is depicted in Equations 1

$$p = p°\gamma X \quad \text{(1a)}$$

$$p = \frac{p°X}{Xs} \quad \text{(1b)}$$

where p is the partial pressure of solute above the solution, X is the mole fraction of solute in solution, p° is the vapor pressure of the pure solute and Xs is the solubility of the solute in the aqueous solution expressed as a mole fraction. At saturation, p equals p° (X=Xs) and thus γ is defined by the term 1/Xs. p° values (Pa) for piperitone, pulegone and carvone were determined at 10, 20 and 30°C from existing vapor pressure data (Handbook of Chemistry and Physics, 1969).

b) Partial Molar Free Energies

Partial molar free energies of hydration, ΔGh, were derived by Equation 2. As outlined in Appendix 4

$$\Delta Gh = RT \ln \frac{p}{Xs} \quad \text{(2)}$$

ΔGh is the defined as the difference in chemical potential between the solute at infinite dilution in aqueous solution and the solute as an ideal vapor. The subscript h

refers to the process, solute (ideal vapor) → solute
(solution).

Partial molar free energies of solution, ΔGs,
were derived using Equation 3 with a knowledge of ΔGh
(Cabani et al., 1971b). The subscript s refers to the

$$\Delta Gh = \Delta Gs + RT\ln p° \qquad (3)$$

process, solute (pure liquid) → solute (solution). $p°$
values are defined in terms of Pascals.

c) Partial Molar Enthalpies

Partial molar enthalpies of solution, ΔHs, were
obtained from plots involving Equation   which is derived
in Appendix 5. ΔHs is defined as the enthalpy difference

$$\frac{\partial \ln \gamma}{\partial \frac{1}{T}} = \frac{\Delta Hs}{R} \qquad (4)$$

between the solute in saturated aqueous solution and
pure liquid solute.

Partial molar enthalpies of hydration, ΔHh,
were determined using Equation 5 with a knowledge of ΔHs

values (Franks et al., 1970).   ΔHv values (latent hea⁺ of

$$\Delta Hs = \Delta Hh + \Delta Hv \qquad (5)$$

vaporization) for piperitone, pulegone and carvone
were calculated at 10, 20 and 30°C using the Watson
correlation (Reid and Sherwood, 1966) and ΔHvb values were
obtained using the Reidel empirical method (Reid and
Sherwood, 1966).

Partial molar entropies of hydration and solution
ΔSh and ΔSs respectively, were calculated from Equation 6
(Wall, 1965).

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

D.   RESULTS

Solubility data for piperitone in aqueous
solutions of sucrose,   .ucose and sodium chloride is
given in Table 16. Generally the solubilities, expressed
as g/l solution, are precise to ±1% as expressed in terms
of the relative standard deviation. Two main trends
are evident in Table 16. Firstly, the solubility of
piperitone in the aqueous solutions decreases as temper-

ature increases. Secondly, the solubility of piperitone invariably decreases as dissolved solid content increases. It is apparent that the ability of the dissolved solid to decrease the piperitone solubility follows the order, sodium chloride > glucose > sucrose. Table 16 shows that for each of the dissolved solids at 0 wt% a solubility value is given. Since solubilities for the different dissolved solids were carried out at different times, a water solubility test was carried out with each dissolved solid to insure that factors involving instrumentation and technique remained invariant.

Solubility data for pulegone is tabulated in Table 17. Although the solubility of pulegone was found to be close to one half the value obtained for piperitone, the solubilities, as influenced by temperature and dissolved solids content, followed trends similar to piperitone.

Carvone solubility, as shown in Table 18, was found to reach a minimum value between 10 and 30°C as evidenced by the lowest solubility value at 20°C. Table 18 also illustrates that carvone solubility decreases as the dissolved solid content increases.

Tables 19, 20 and 21 illustrate calculated activity coefficients, γ, for piperitone, pulegone

and carvone respectively. Figures 48, 49 and 50 depict ln γ as a function of dissolved solids content expressed as wt%. Generally for the compounds piperitone and pulegone, γ tends toward higher values with an increase in temperature at any dissolved solids content. At a constant temperature γ for pulegone (Figure 49) and piperitone (Figure 48) are seen to increase with increasing dissolved sodium chloride and glucose contents. γ values for pulegone and piperitone in sucrose solutions do not appear to follow the same trends found in the glucose and sodium chloride solutions. At 10°C both pulegone and piperitone γ values show a definite increase with dissolved sucrose content, whereas at 20°C the γ for both compounds appears to be independent of sucrose content. At 30°C γ for piperitone decreases slightly with increased sucrose whereas pulegone shows a more pronounced decrease between 40 and 50% sucrose.

As shown in Figure 50, the effect of the different dissolved solids on the γ for carvone is quite similar to that previously found for pulegone or piperitone. Once again sodium chloride content has the greatest influence on γ, followed next by glucose and sucrose.

Tables 22 through 30 show the calculated

thermodynamic values for piperitone, pulegone and carvone

in aqueous solutions containing sucrose, glucose or

sodium chloride. Several trends are at once evident.

ΔHh and ΔHs values for piperitone (Table 22), pulegone

(Table 25) and carvone (Table 28) generally become more

positive with increasing temperature at a constant

dissolved solids content. At a constant temperature

ΔHh and ΔHs appear to become more positive with increasing

dissolved solids content in most cases. However, ΔHh and

ΔHs for the sodium chloride solutions appear very

erratic. Since ΔHs values were calculated from a plot

of $\ln \gamma$ vs. $1/T$, the experimental errors incurred in

the measurement of γ will be greatly magnified, hence

the ΔHs values will inherently have a high degree of

uncertainty. In addition, ΔHh values will be approximate

because of the empirical expressions used to calculate

ΔHv. Thus any discussion of ΔHs or ΔHh must be restricted

to general trends.

ΔGh and ΔGs values for piperitone (Table 23),

pulegone (Table 26) and carvone (Table 29) invariably

increase with increasing temperature at a constant

dissolved solids content. In all three cases values of

ΔGh and ΔGs appear to be relatively independent of dissolved

sucrose or glucose. Increased sodium chloride concen-

trations, however, are seen to increase ΔG_h and ΔG_s values at constant temperature.

ΔS_h and ΔS_s values for piperitone (Table 24), pulegone (Table 27) and carvone (Table 30) generally become more positive with increasing temperature at constant dissolved solids content however it is evident that exceptions do exist. Since ΔS_h and ΔS_s values were obtained from a differentiation procedure involving γ, the experimental errors incurred in the determination of γ will be magnified, hence some erratic behavior in the entropy terms is expected.

F. DISCUSSION

The iceberg model of water solutions was invoked by Frank and Evans (1945) to explain the unusual thermodynamic properties of aqueous solutions, especially those involving enthalpies and entropies. Values of ΔHs (the heat associated with the transfer of one mole of solute as a pure liquid to an aqueous solution at infinite dilution) are preferably derived by calorimetric techniques. The use of a calorimetric technique obviates the use of γ to find ΔHs and thus errors in γ are not magnified in the computation process. ΔHh is the preferred thermodynamic parameter used by most authors (Franks and Watson, 1969) and is related to ΔHs by ΔHv, the latent heat of vaporization. ΔHh reflects total solute-solvent interactions because solute-solute interactions in the vapor state are considered negligible (the vapor is considered an ideal gas). ΔHs values, on the other hand, reflect the difference between solute-solute and solute-solvent interactions because the pure liquid solute is chosen as the standard state. Owing to the complexity of the solute-solute interactions in the pure liquid state, the hydration parameters are preferred since solute-solute interactions need not be considered.

Figure 51 illustrates the curves relating γ
and T used for the evaluation of ΔHs for piperitone, pule-
gone and carvone in pure water. Values of ΔHs are
derived at any temperature by computing the slope of
the curve at that temperature. Values of ΔHh, tabulated
in Tables 22, 25 and 28 for piperitone, pulegone and
carvone respectively show that the process of trans-
ferring one mole of solute from the ideal vapor to a
solution at infinite dilution (mole fraction of solute
at saturation is approximately 10^{-4}) is an exothermic
process i.e. heat is evolved. The overall magnitude of
ΔHh is determined from the contributions of two mechan-
isms. A positive heat (endothermic) corresponds to the
heat required to form a cavity for the solute molecule
to occupy. A negative heat (exothermic) results from
the formation of a more ice-like water structure i.e.
icebergs. Obviously the formation of a more ordered
form of water is the main contribution to ΔHh. It is
interesting to note that the ΔHh values for cyclic
ethers (Cabani et al., 1971b and Franks et al., 1970)
dialkylamines (Franks and Watson, 1969) and the three
compounds of this study all fall within the range
-50000 to -70000 Jmole^{-1}.

Tables 22, 25 and 28 indicate that the respective

]48

ΔHh values for piperitone, pulegone and carvone become
less negative with an increase in temperature. Several
previous studies have shown similar results. Gross
et al. (1939) noted that ΔHh for many aliphatic ketones
became less negative with increased temperatures in the
range 0 to 50°C. ΔHh for cyclic ethers (Franks et al.,
1970) and dialkylamines (Franks and Watson, 1969) were
found to exhibit exactly the same tendency in pure
water. Again the model of the iceberg may be used to
rationalize the less negative ΔHh values at higher
temperatures. More positive ΔHh values indicate that
at higher temperatures the heat capacities, ΔCp, are her.
A larger value of ΔCp at higher temperatures is a direct
consequence of the "meltir   greater number of
iceberg species at the higher temperature.

Figure 51 and Tab.e ? illustrate that at a
temperature very near 20°C, ΔHs for carvone has a value of
zero. When ΔHs=0, the negative heat due to increased order-
ing in water exactly balances the positive heat of cavity
formation. Figure 51 shows that the pulegone and piper-
itone curves are quickly approaching a maximum similar
to that shown by carvone. According to Bohon and Claussen
(1951) the temperature at which ΔHs=0 corresponds to
the point of minimum solubility of the solute in water.

Tables 22, 25 and 28 indicate that the presence of dissolved solids has the general effect of making the ΔHh values more positive at constant temperature. These results lend support to the theory of Ben-Naim (1965a, 1965b and 1967) who has defined glucose, sucrose and ionic salts as water structure breakers. More positive ΔHh values with increasing dissolved solids content indicates that there are less $(H_2O)b$ species formed hence the contribution of the negative heat (due to the formation of ice-like water) is much less.

ΔGh values for piperitone (Table 23), pulegone (Table 26) and carvone (Table 29) in water appear to be very similar in magnitude. In addition, at a constant temperature, ΔGh, appear to be practically constant in water and aqueous solutions of sucrose and glucose. Only increasing concentrations of sodium chloride appear to have any significant effect on ΔGh. In most cases the values ΔGh are seen to increase with an increase in temperature (at constant dissolved solids content). Similar observations were made for aliphatic ketones (Gross et al. 1939). As shown in Tables 23, 26 and 29, values of ΔGs are invariably lower than ΔGh. The relative magnitude of ΔGh and ΔGs are determined by the units of $p°$ in the expression $\Delta Gh = \Delta Gs + RT\ln p°$.

In this study, p° was expressed in terms of Pascals hence the RTlnp° term is always positive. Cabani et al. (1971a) expressed p° values in terms of atmospheres, hence the calculated ΔCh values were less than ΔGs values.

The partial molar entropies of hydration and solution, ΔSh and ΔS respectively are of considerable interest since these values reflect the degree of ordering or structure within the solution. ΔSh values for piperitone (Table 24), pulegone (Table 27) and carvone (Table 28) in water are seen to be highly negative. Such highly negative values of ΔSh point out that the solubilization of piperitone, pulegone or carvone brings about a less random or more ordered state within the solution i.e. formation of a greater number of $(H_2O)b$ species. It is also evident that values of ΔSh generally appear to become less negative as dissolved solids content increases at a constant temperature. This effect of increasing dissolved solids to reduce the order within the solution again lends support to the theory of Ben-Naim (1965a, 1965b and 1967) who considers such dissolved solids as structure breakers.

The solubility data presented in Tables 16, 17 and 18 show that the solubilities of the essential oil components are quite low and explains why such compounds
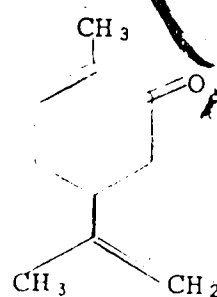
have generally been considered as insoluble. It is
remarkable that the three compounds, piperitone, pulegone
and carvone, which are very similar in structure, should
have different solubilities. In particular piperitone
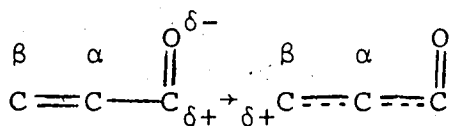solubility is twice that of carvone or pulegone. A
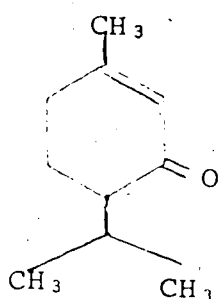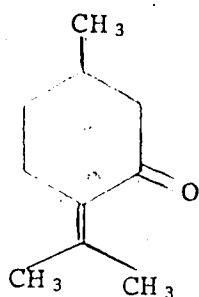
piperitone   pulegone   carvone

possible explanation for the higher solubility of
piperitone over that of pulegone may be found by con-
sideration of the electronic structures in a method
analogous to that of Palit (1947). According to
Palit (1947) the doubly-bound oxygen in the carbonyl
group shows an electromeric effect in that it serves as
a sink for electrons, C=O. Thus the electron density
on the carbonyl carbon atom is reduced and this
carbon atom acquires a partial positive charge. In
saturated ketones or aldehydes, the loss of electrons
from the carbonyl carbon may be partially replenished
by a flux of electron density from neighbouring C-H bonds.

As the electron density is decreased in the C-H bond, this bond will become polarized with the hydrogen atom becoming slightly positive in character, $C-H^{\delta+}$. It is the degree of polarization of C-H linkages which determines the solubility of aldehydes or ketones as the partially positive hydrogen atoms are able to interact with water by hydrogen bonding. It is well known that the C-H linkages on methyl groups are especially susceptible to this type of polarization as evidenced by the infinite solubility of acetone (CH_3COCH_3) and acetaldehyde (CH_3CHO). A similar, but different situation would prevail for the α, β unsaturated ketones. In this case the π electrons of the double bond would serve as the main electron source for the electron deficient carbonyl carbon atom. As a result the β carbon

$$\overset{\beta}{C}=\overset{\alpha}{C}-\overset{O^{\delta-}}{\underset{\delta+}{\overset{||}{C}}}\quad\overset{+}{\underset{\delta+}{}}\overset{\beta}{C}\cdots\overset{\alpha}{C}\cdots\overset{O}{\overset{||}{C}}$$

would acquire a partial positive charge since the electron density between the α and β carbon atoms has been diminished. In the case of piperitone and pulegone, the following intermediate structures may be envisioned.
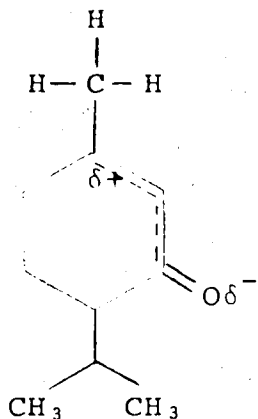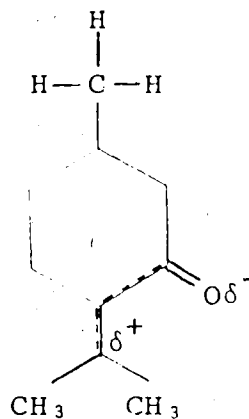
piperitone   pulegone

In both cases the carbon atom, β to the carbonyl carbon,
has acquired a partial positive charge. In piperitone
this partially positive β carbon is adjacent to a
methyl group and a CH_2 group within the ring whereas in
pulegone the β carbon is adjacent to two methyl groups.
At this point the excellent electron releasing abilities
of the methyl groups come into play. In piperitone
electron density from the lone methyl group will act
as an electron source to replenish negative charge on
the β carbon thus inducing a polarized C-H bond.
Similarly in pulegone, the two methyl groups will act
as an electron source for the β carbon, but in this

case the polarization of the C-H bonds will be signi-

ficantly less than the polarization of the C-H bonds

in piperitone due to the fact that each methyl group of

pulegone will donate only a fraction of the total

negative charge to the β carbon. As stated previously

the presence of strongly polarized C-H bonds in a methyl

group is of the utmost importance in determining the

solubility of an aldehyde or ketone in water. Moreover,

it is probably true that the presence of one methyl

group in which the C-H bonds are strongly polarized

confers greater solubility than that of two methyl

groups in which the C-H bonds are less strongly polarized

as in piperitone and pulegone respectively. Solubility

studies on aliphatic ketones (Gross et al., 1939) give

qualitative support to these arguements. The solubilities

of methyl n-propyl ketone and methyl isobutyl ketone

were found to be 0.630 and 0.166 moles per 1000 g of

water. As indicated by their structures, a rough analogy
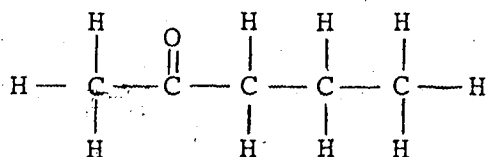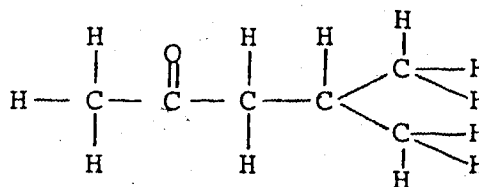
Methyl n-propyl ketone   Methyl isobutyl ketone

can be made between the structures of piperitone and methyl n-propyl ketone, and pulegone and methyl isobutyl ketone.

An alternate more thermodynamically based explanation for the observed solubilities of piperitone, pulegone and carvone is derived from considering the iceberg model of water. The guest molecule or solute occupies a cavity or partial cavity within the $(H_2O)b$ cluster. The ability of the guest molecule to occupy a cavity is dependent on the size of the guest molecule and it has been shown that there exists an optimum molecular diameter for maximum solubility (Franks, 1973). If it can be assumed, that in piperitone, pulegone and carvone, the carbonyl-water interactions are similar (the carbonyl has two proton acceptor sites) then the difference in the solubilities of these compounds may be due to the difference in the molecular diameter of the molecules. It is evident that pulegone and carvone will have different diameters than piperitone since the former compounds both possess unsaturated isopropyl groups outside of the six-membered ring whereas piperitone does not. The presence of this unsaturated isopropyl group may render the molecular structure incompatible with the structure of the cavity, hence carvone and pulegone

exhibit lower water solubilities. Piperitone, on the other hand, may not be sterically hindered to such a great extent so as to prevent inclusion into a water cavity.

Piperitone (Table 16) and pulegone (Table 17) display decreased solubilities in water with higher temperatures. This behavior, as discussed previously, is followed by very many liquid organic compounds in aqueous solution. An explanation for a decreased solubility with an increase in temperature can be found, once again, by considering the iceberg model of water. The $(H_2O)b$ species, which exists in equilibrium ⊥th $(H_2O)d$, has many characteristics that have been likened to ice. An increase in temperature has the effect of decreasing the number of $(H_2O)b$ species, i.e. decrease the number of host species for the solute. Thus the consequence is lower solubilities at higher temperatures.

Of the three compounds studied, carvone is unique in that it exhibits a solubility minimum between 10 and 30°C as seen in Table 18. Bohon and Claussen (1951) noted a similar solubility minimum for aromatic hydrocarbons in water. Bohon and Claussen (1951) correlated this solubility minimum with the temperature at which the heat of solution became equal to zero.

Figure 51 shows that ΔH_s values for piperitone and pulegone will similarly equal zero at a temperature slightly higher than 30°C.

The activity coefficients, γ, for piperitone, pulegone and carvone in saturated aqueous solutions are tabulated in Table 19, 20 and 21 respectively. γ values were derived on the basis that at saturation, the vapor pressure of the dissolved solute approachs that of the pure solute (ps=p°) hence γ is equivalent to $1/X_s$. On the basis of the low mole fraction (approximately 10^{-4}) of the volatile solute in the saturated solution, and from the work of Nawar (1971), it was assumed that the term γX_s was close to unity in all aqueous solutions.

γ values for piperitone (Table 19), pulegone (Table 20) and carvone (Table 21) are represented graphically as a function of dissolved solids content in Figures 48, 49 and 50 respectively. The high values of γ for the three compounds in water reflect the fact that these solute molecules are not comfortable within their aqueous environment due to unfavorable interactions between the large apolar segment of the solute molecule and the very polar water molecules. Figure 48 and 49 illustrate that increased sodium chloride and glucose contents result in increased values of γ for piperitone.

and pulegone. It is apparent that sodium chloride has
by far the greatest influence on γ. Bomben et al. (1972),
using the data of Glasstone and Pound (1925), showed that
γ for ethyl acetate was also extremely sensitive to
sodium chloride concentrations. The addition of inor-
ganic salts to increase the vapor pressure of volatile
components in dilute aqueous solution is often applied
in headspace aroma analysis (Nelson and Hoff, 1968).
The effect of the salt is to reduce the solubility of
the volatile solute in the aqueous solution and thus
increase the amount of volatile solute in the vapor
above the solution. Nawar (1966) reported that added
glucose also had the ability to increase the vapor
pressure of dilute volatile solutes but the increase in
the headspace concentration of the volatile was signifi-
cantly less than when inorganic salts were added.

Inspection of Figures 48, 49 and 50 illustrate
that the influence of increased sucrose contents is
variable. Piperitone (Figure 48) and pulegone (Figure
49) exhibits slightly increased values of γ with
increasing sucrose content at 10°C. At 20°C γ for
piperitone and pulegone appear to be relatively inde-
pendent of dissolved sucrose. At 30°C γ for these
compounds appears to decrease slightly. Massaldi and

King (1973) and Chandrasekaran and King (1971) have
shown that sucrose in solution increases the γ of
highly oxygenated volatiles at 20°C whereas non-
oxygenated volatiles show a decrease in γ with increasing
sucrose concentrations. The ability of dissolved sucrose
to selectively differentiate between different species
of volatile solutes partly explains the work
Wientjes (1968) who found that when sugars were added
to synthetic strawberry mixtures, some of the volatile
components were forced out of the aqueous solution more
than others.

Figures 48 and 49 illustrate that temperature
as well as dissolved solids has an effect on γ. For the
compounds piperitone and pulegone, γ is seen to invari-
ably increase with increasing temperature. Bomben
et al. (1972) described a similar trend for ethyl
acetate. Owing to the solubility minimum exhibited by
carvone (Table 16) near 20°C, γ for carvone will attain
a maximum value near 20°C and decrease at higher and
lower temperatures. Massaldi and King (1973) noted that
γ for d-limonene and n-butyl benzene decreased with
increasing temperature and probably suggests that in
the temperature range 0 to 25°C, Massaldi and King (1973)
were working on the high temperature side of the minimum
in d-limonene and n-butylbenzene solubility.

F.   CONCLUSIONS

The solubility studies of pipe   one, pulegone
and carvone in water and aqueous s   tions of sucrose,
glucose and sodium chloride have provided a great deal
of valuable information regarding the behavior of
volatile flavoring compounds in dilute aqueous solution.

Enthalpies, entropies and free energies, which
were calculated from solubility data at 10, 20 and 30°C,
appear to be in good agreement with the iceberg model of
water as proposed by Frank and Evans (1945). This study
shows that the solution behavior of dilute volatile
components can be successfully described in terms of
thermodynamic parameters and it is expected that the use
of such thermodynamic quantities will help to clarify the
nature of volatile solvent interactions in other systems.

Of particular interest to the processor is the
fact that the solubility of many sparingly soluble
compounds increases with a decrease in temperature.
This phenomena at once becomes relevant in processes
employing low temperatures, e.g. freeze drying.   n the
basis of the studies by Ben-Naim (1969a) it appears
possible to increase the solubility of a sparingly soluble
volatile by incorporating additional structure making
volatiles.

Table 1. Diffusion Coefficients of Sucrose at 25°C (m²/s x 10¹⁰);

$\bar{c}$ = 1.000g/100ml, Δc = 2.000g/100ml

Run	Dexp	Dav	Davo	Dlit[d]	Deviation(%)
1[a]	5.16				
2[a]	5.17	5.20±0.06[a]			
3[a]	5.27				
4[b]	5.20				
5[b]	5.24	5.20±0.04[b]	5.19±0.05	5.148±0.005	0.8
6[b]	5.16				
7[c]	5.20				
8[c]	5.10	5.15±0.005[c]			
9[c]	5.15				

a) 5,000 rpm
b) 15,000 rpm
c) 10,000 rpm
d) Diffusion coefficient of sucrose; $\bar{c}$ = 1.011g/100ml,
   Δc = 1.5016g/100ml and T = 24.95°C (Gosting and Morris, 1949)

Table 2. Variation of Sucrose Diffusion Coefficients

$(m^2/s \times 10^{10})$ with Temperature; $\bar{c} = 1.000g/100ml$,

$\Delta c = 2.000g/100ml$

Temperature(°C)	Dexp	Dlit	Deviation(%)
25.0	5.19±0.05	5.148	+0.8
14.8	3.80±0.06	3.866	.7
2.6	2.54±0.02	2.53	-0.4

Table 3. Diffusion Coefficients (m²/s x 10⁹) of Ethylene
Glycol at 25.0°C

$\bar{c}^a$	Δc^a	$\bar{D}_{exp}$	D^0_{exp}	$D^0_{lit.}$	Deviation (%)
0.7507	1.5003	1.13±0.04			
10.2068	2.0031	1.02±0.01	1.14	1.16, 1.17	1.7
25.0109	1.9625	0.83±0.01			

a) wt%

Table 4.   Concentration a of Essential Oil Components in

Various Foods

Flavoring Substances	Beverages	Ice Cream	Candy	Baked Goods	Other
m-anisaldehyde	6.3	5.6	14.0	16.0	chewing gum-30
carvone	850	120	180	110	-
eugenol	1.4	3.1	32	33	chewing gum-500 meats-2,000
piperitone	11	18	-	-	-
pulegone	8.0	32	17	25	-

a) ppm(by volume)

Table 5.   Regression Coefficients of Weightloss Curves

Solution	b	m	Correlation Coefficient
Sucrose(10%)	103.0	-6.2	-0.991
Glucose(10%)	100.7	-5.9	-1.000
Sodium Chloride(5%)	104.1	-5.8	-0.992
Gum Arabic(1%)	96.6	-5.0	-0.999

Table 5. Retention of Carvone, m-Anisaldehyde and Eugenol
as a Function of Initial Glucose Content

Wt% Glucose

		Retention(%)	
	Carvone[a]	m-Anisaldehyde[a]	Eugenol[a]
3	52 ±3.2	57.8±5.3	43.0±7.6
5	60.7±2.4	61.6±5.1	57.4±4.9
7	69.1±1.0	73.2±3.3	56.8±3.7
10	66.3±3.7	77.3±3.1	76.9±
15	66.8±3.9	76.9±4.8	83.2±2.8

a) Initial volatile content, 500 ppm

Table 7. Retention of Carvone and m-Anisaldehyde as a
          Function of Initial Sodium Chloride Content

Wt% Sodium Chloride	Retention(%)	
	Carvone[a]	m-Anisaldehyde[b]
3	4.1±0.9	13.7±0.9
5	7.8±0.8	23.5±1.6
7.5	13.4±1.6	31.4±2.1
10	18.0±1.4	36.3±1.5

a) Initial carvone content, 300 ppm
b) Initial m-anisaldehyde content, 500 ppm

Table 8. Retention of Carvone and Piperitone as a Function of Freezing Rate

Volatile[a]	Solution	Volatile Retention(%)	
		Fast Freezing	Slow Freezing
carvone	10% sucrose	79.9±1.1	54.7±2.2
piperitone	10% sucrose	88.1±0.5	65.9±4.2
carvone	10% glucose	84.9±0.6	78.1±8.4
carvone	1% gum arabic	37.0±0.9	36.2±0.3
carvone	5% sodium chloride	10.8±0.8	12.9±1.2

a) Initial volatile content, 500 ppm

Table 9. Retention of Carvone, Eugenol and m-Anisaldehyde as a

Function of Initial Ethanol Concentration in 10% Sucrose

Initial Ethanol Concentration	Volatile Retention(%)		
(ppm)	Carvone[a]	Eugenol[a]	m-Anisaldehyde[a]
0	53.0±1.3	58.3±1.4	56.8±1.1
300	54.4±2.8	59.3±2.4	56.2±2.2
600	53.9±2.2	61.7±1.2	58.3±0.6
900	52.5±4.6	58.9±2.4	57.6±1.3
1200	54.6±2.9	60.1±2.0	56.7±1.5

a) Initial volatile content, 500 ppm

Table 10. Retention of Carvone, Eugenol and m-Anisaldehyde as a Function of Initial Octanol Concentration in 10% Sucrose

Initial Octanol Concentration (ppm)	Volatile Retention (%)		
	Carvone[a]	Eugenol[a]	m-Anisaldehyde[a]
0	53.0±1.3	58.3±1.4	56.8±1.1
200	43.5±4.3	54.7±2.0	46.3±3.1
400	42.5±3.1	47.3±1.0	51.7±0.7
600	41.0±2.9	42.5±1.0	53.9±0.9
800	34.3±2.1	41.2±1.6	48.9±0.6

a) Initial volatile content, 500 ppm

Table 11. pH Values of 10% Sucrose Solutions at Various Stages of Sample

Preparation and after Freeze Drying

Volatile[a]	pH 10% Sucrose Solution	pH After Volatile Added	pH of Rehydrated Freeze Dried Sample
carvone	2.9,5.5,7.0,8.5,10.3	3.0,4.8,7.0,7.4,10.0	not recorded
eugenol	2.9,5.5,7.0,8.5,10.3	2.9,5.5,6.6,7.3,9.8	2.8,6.0,7.1,7.6,8.1
piperitone	2.9,5.3,6.7,7.5,10.2	2.9,5.3,6.9,7.3,10.2	2.9,5.5,7.0,7.3,8.5
pulegone	2.9,5.3,6.7,7.5,10.2	2.9,4.8,6.1,6.9,10.0	2.9,5.5,6.7,7.1,8.4

a) Initial volatile content, 500 ppm

Table 12. Retention of Carvone in 5% Sodium Chloride

as a Function of Initial pH

Initial pH	Volatile Retention(%) Carvone[a]
2.8	12.8±0.8
6.0	11.7±1.4
7.2	14.6±1.4
8.6	14.3±1.7
11.0	15.4±2.6

a) Initial volatile content, 500 ppm

Table 13. pH Values of 1% Gum Arabic Solutions at Various Stages of Solution Preparation and after Freeze Drying

Volatile[a]	pH before gum arabic added	pH after gum arabic added	pH after volatile added	pH of rehydrated samples
carvone	3.0,5.5,7.0,7.4,10.6	4.0,4.9,5.0,5.1,10.9	4.2,4.9,5.0,5.1,9.4	not recorded
eugenol	3.0,5.5,7.0,7.4,10.6	4.0,4.9,5.0,5.1,10.9	4.0,5.0,5.0,5.2,9.8	4.0,4.9,5.0,5.2,8.2
piperitone	2.8,5.0,7.0,8.0,11.0	3.9,4.9,5.0,5.2,10.7	3.9,4.9,5.0,5.5,9.6	4.0,5.0,5.2,5.3,8.3
pulegone	2.8,5.0,7.0,8.0,11.0	3.9,4.9,5.0,5.2,10.7	3.9,4.9,5.0,5.1,9.2	4.0,5.0,5.2,8.3

a) Initial volatile content, 500 ppm

Table 14. Absorbance of Reh<u>drated 10% Sucrose Samples at</u>
Low Initial Volatile Concentrations

Volatile	Initial volatile concentration (ppm)	Dilution factor prior to U.V.	Absorbance
Carvone	50	1:5	0.577
	25	2:5	0.621
	10	none	0.784
Piperitone	50	1:5	0.780
	25	2:5	0.822
	10	none	1.049

Table 15. Extinction Coefficients of Carvone, Pulegone and Piperitone in Water and Aqueous Solution

Solute	λmax (nm)	logε	
		H_2O	EtOH
Carvone	241.5	3.92	3.93
Pulegone	263.0	3.80	3.91
Piperitone	242.5	4.03	4.11

Table 16. Solubilities of Piperitone in Aqueous Solutions of Sucrose, Glucose and Sodium Chloride at 10, 20 and 30°C

| Dissolved Solid | wt% | Solubility (g/l) | | |
		10°C	20°C	30°C
Sucrose	0	3.00	2.52	2.36
	10	2.82	2.40	2.34
	20	2.60	2.24	2.10
	30	2.34	2.07	1.96
	40	2.05	1.87	1.81
	50	1.71	1.65	1.64
Glucose	0	2.99	2.56	2.35
	8	2.33	2.27	2.17
	16	2.09	2.00	1.94
	24	1.87	1.74	1.70
	32	1.55	1.50	1.46
	40	1.30	1.28	1.26
Sodium Chloride	0	3.02	2.52	2.37
	4	1.99	1.67	1.57
	8	1.31	1.11	1.03
	12	0.88	0.76	0.68
	16	0.58	0.51	0.44
	20	0.31	0.27	0.23

Table 17. Solubilities of Pulegone in Aqueous
Solutions of Sucrose, Glucose and Sodium
Chloride at 10, 20 and 30°

Dissolved Solid	wt%	Solubility (g/l)		
		10°C		30°C
Sucrose	0	1.62	1.38	1.22
	10	1.49	1.29	1.15
	20	1.36	1.19	1.04
	30	1.21	1.08	0.92
	40	1.04	0.97	0.82
	50	0.87	0.85	0.77
Glucose	0	1.60	1.37	1.26
	8	1.38	1.24	1.13
	16	1.17	1.10	1.01
	24	0.99	0.94	0.88
	32	0.82	0.79	0.76
	40	0.66	0.66	0.63
Sodium Chloride	0	1.62	1.38	1.28
	4	1.06	0.87	0.82
	8	0.68	0.55	0.52
	12	0.43	0.37	0.33
	16	0.27	0.25	0.21
	20	0.14	0.13	0.13

Table 18. Solubilities of Carvone in Aqueous

Solutions of Sucrose, Glucose and Sodium

Chloride at 10., 20 and 30°C

Dissolved Solid	wt%	Solubility (g/l)		
		10°C	20°C	30°C
Sucrose	0	1.66	1.50	1.60
	10	1.57	1.47	1.54
	20	1.46	1.40	1.47
	30	1.34	1.31	1.38
	40	1.20	1.22	1.29
	50	1.05	1.12	1.18
Glucose	0	1.70	1.55	1.62
	10	1.40	1.38	1.42
	20	1.19	1.21	1.27
	30	0.99	1.04	1.15
	40	0.78	0.87	1.04
	50	0.63	0.70	0.93
Sodium Chloride	0	1.73	1.57	1.61
	4	1.18	1.10	1.15
	8	0.80	0.73	0.77
	12	0.54	0.50	0.49
	16	0.36	0.38	0.29
	20	0.21	0.20	0.18

Table 19. Activity Coefficients of Piperitone in

Saturated Aqueous Solutions at 10, 20 and 30°C

Dissolved Solid	wt%	Activity Coefficients		
		10°C	20°C	30°C
Sucrose	0	2811	3341	3559
	10	2815	3312	3537
	20	2846	3296	3508
	30	2911	3292	3467
	40	3021	3297	3405
	50	3204	3313	3312
Glucose	0	2818	3280	3571
	8	3472	3547	3703
	16	3677	3845	3941
	24	3885	4179	4272
	32	4405	4551	4660
	40	4887	4966	5010
Sodium Chloride	0	2797	3339	3551
	4	4300	5114	5434
	8	6599	7760	8369
	12	9977	11515	12817
	16	15263	17319	20112
	20	28778	33033	39239

Table 20. Activity Coefficients of Pulegone in Saturated Aqueous Solutions at 10, 20 and 30°C

Dissolved Solid	wt%	Activity Coefficient		
		10°C	20°C	30°C
Sucrose	0	5225	6110	6924
	10	5328	6148	6861
	20	5472	6227	7107
	30	5667	6310	7434
	40	5935	6373	7545
	50	6322	6408	7104
Glucose	0	5264	6165	6696
	8	5860	6496	7119
	16	6562	7016	7623
	24	7393	7735	8239
	32	8384	8632	9017
	40	9569	9598	10049
Sodium Chloride	0	5211	6114	6589
	4	8047	9869	10378
	8	12688	15648	16651
	12	20259	23562	26551
	16	33211	34924	41651
	20	64524	68829	69840

Table 21. Activity Coefficients of Carvone in Saturated Aqueous Solutions at 10, 20 and 30°C

Dissolved Solid	wt%	Activity Coefficient		
		10°C	20°C	30°C
Sucrose	0	5013	5563	5196
	10	5004	5322	5069
	20	5013	5223	4953
	30	5039	5126	4839
	40	5082	4979	4720
	50	5143	4827	4582
Glucose	0	4910	5385	5138
	10	5618	5723	5533
	20	6210	6124	5805
	30	6961	6613	5950
	40	8055	7231	6000
	50	8974	8068	6020
Sodium Chloride	0	4806	5286	5157
	4	7169	7659	7330
	8	10731	11744	11025
	12	15996	17163	17697
	16	24233	23003	30079
	20	42627	43325	48533

Table 22. Partial Molar Heats of Hydration, ΔHh, and Partial Molar Heats of Solution, ΔHs, for Piperitone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C)					
		10		20		30	
		$-\Delta Hh$ Jmole^{-1}	$-\Delta Hs$ Jmole^{-1}	$-\Delta Hh$ Jmole^{-1}	$-\Delta Hs$ Jmole^{-1}	$-\Delta Hh$ Jmole^{-1}	$-\Delta Hs$ Jmole^{-1}
Sucrose	0	76731	16051	68145	−7991	61169	−1548
	10	75534	14854	67923	−7769	61726	−2105
	20	73956	13276	67287	−7133	61843	−2222
	30	71823	11143	66114	−5960	61438	−1817
	40	68808	8128	64206	−4052	60415	794
	50	64306	3626	61199	−1045	58602	−1018
Glucose	0	73555	12875	68355	8200	64084	4464
	8	61183	503	62557	2403	63543	3922
	16	64482	3802	62551	2397	60895	1274
	24	67642	6963	63336	3182	59780	159
	32	63229	2549	62134	1980	61146	1525
	40	62035	1354	61017	863	60090	470
Sodium Chloride	0	77278	16598	68207	7905	60843	1222
	4	76920	16240	68059	8059	60863	1242
	8	75065	14385	68294	8140	62769	3148
	12	71710	11030	68974	8820	66675	7055
	16	68073	7393	70138	9983	71674	12054
	20	68366	7686	71411	11257	73732	14111

Table 23. Partial Molar Free Energies of Hydration, ΔGh, and Partial Molar Free Energies of Solution, ΔGs, for Piperitone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C)					
		10		20		30	
		ΔGh Jmole⁻¹	ΔGs Jmole⁻¹	ΔGh Jmole⁻¹	ΔGs Jmole⁻¹	ΔGh Jmole⁻¹	ΔGs Jmole⁻¹
Sucrose	0	23228	18695	26285	19776	29096	20611
	10	23231	18699	26264	19755	29080	20595
	20	23257	18725	26252	19744	29059	20574
	30	23310	18777	26249	19740	29029	20544
	40	23398	18865	26253	19745	28984	20499
	50	23536	19003	26265	19756	28914	20429
Glucose	0	23234	18701	26240	19731	29104	20619
	8	23725	19192	26431	19922	29195	20710
	16	23860	19328	26628	20119	29353	20868
	24	23990	19457	26831	20322	29556	21071
	32	24286	19753	27039	20530	29775	21290
	40	24530	19997	27251	20742	29958	21473
Sodium Chloride	0	23217	18684	26284	19775	29090	20605
	4	24229	19696	27323	20814	30162	21677
	8	25237	20704	28339	21831	31251	22766
	12	26210	21677	29301	22793	32325	23840
	16	27211	22678	30296	23787	33461	24976
	20	28704	24171	31870	25361	35145	26660

Table 24. Partial Molar Entropies of Hydration, ΔS_h, and Partial Molar Entropies of Solution, ΔS_s, for Piperitone Saturated Aqueous Solutions

| Dissolved Solid | wt% | Temperature (°C) | | | | | |
| | | 10 | | 20 | | 30 | |
		$-\Delta S_h$ Jmole^{-1}°K^{-1}	$-\Delta S_s$ Jmole^{-1}°K^{-1}	$-\Delta S_h$ Jmole^{-1}°K^{-1}	$-\Delta S_s$ Jmole^{-1}°K^{-1}	$-\Delta S_h$ Jmole^{-1}°K^{-1}	$-\Delta S_s$ Jmole^{-1}°K^{-1}
Sucrose	0	353	123	322	95	298	73
	10	349	119	321	94	300	75
	20	343	113	319	92	300	75
	30	336	106	315	88	298	74
	40	326	95	309	81	295	70
	50	310	80	298	71	289	64
Glucose	0	342	112	323	95	307	83
	8	300	70	304	76	306	81
	16	312	82	304	77	298	73
	24	324	93	308	80	295	70
	32	309	79	304	77	300	75
	40	306	75	301	74	300	75
Sodium Chloride	0	355	125	322	95	297	72
	4	357	127	325	98	300	76
	8	354	124	330	102	310	86
	12	346	116	335	108	327	102
	16	337	106	343	115	347	122
	20	343	113	353	125	359	135

Table 25. Partial Molar Enthalpies of Hydration, ΔHh, and Partial Molar Enthalpies of Solution, ΔHs, for Pulegône Saturated Aqueous Solutions

Dissolved solid	wt%	Temperature (°C)					
		16		20		30	
		$-\Delta Hh$ Jmole⁻¹	$-\Delta Hs$ Jmole⁻¹	$-\Delta Hh$ Jmole⁻¹	$-\Delta Hs$ Jmole⁻¹	$-\Delta Hh$ Jmole⁻¹	$-\Delta Hs$ Jmole⁻¹
Sucrose	0	71113	11702	68836	9954	66901	8557
	10	70294	10883	67801	8919	65693	7349
	20	67850	8439	68266	9385	68484	10141
	30	64167	4756	68851	9969	72480	14137
	40	60010	598	67903	9022	74099	15755
	50	56531	-2881	63445	4564	68858	10514
Glucose	0	73052	13641	67178	8296	62368	4024
	8	66709	7297	65808	6927	64974	6631
	16	63159	3748	64323	5441	65139	6795
	24	61644	2232	62840	3958	63682	5338
	32	60729	1317	61550	2668	62091	3748
	40	57796	1615	60820	1939	61474	4780
Sodium Chloride	0	73597	14185	66923	8042	57580	3131
	4	79401	19989	67337	8455	58662	-764
	8	79518	20107	67991	9109	66474	319
	12	70750	11338	68437	9555	75491	8130
	16	57437	-1975	67534	8652	57958	17147
	20	65797	-6385	61504	2622		386

Table 26. Partial Molar Free Energies, ΔG_h, and Partial Molar Free Energies of Solution, ΔG_s, for Pulegone Saturated Aqueous Solutions

Temperature (°C)

Dissolved Solid	wt%	10 — ΔG_h Jmole⁻¹	10 — ΔG_s Jmole⁻¹	20 — ΔG_h Jmole⁻¹	20 — ΔG_s Jmole⁻¹	30 — ΔG_h Jmole⁻¹	30 — ΔG_s Jmole⁻¹
Sucrose	0	20795	20155	24681	21248	28445	22288
	10	20841	20201	24696	21263	28422	22265
	20	20904	20263	24727	21294	28511	22354
	30	20986	20345	24759	21327	28625	22467
	40	21095	20455	24783	21351	28662	22505
	50	21244	20603	24797	21364	28510	22353
Glucose	0	20813	20172	24703	21270	28361	22203
	8	20425	19146	24830	21397	28516	22358
	16	20691	19481	25018	21584	28688	22530
	24	20972	19784	25255	21823	28884	22726
	32	21268	20089	25523	22090	29111	22954
	40	21579	20458	25781	22449	29384	23227
Sodium Chloride	0	20789	20148	24682		28320	22163
	4	21812	21172	25849	22416	29466	23308
	8	22884	21434	26973	23540	30657	24500
	12	23985	22718	27970	24538	31833	25676
	16	25149	24160	28930	25497	32968	26810
	20	26712	25475	30583	27150	34271	28113

Table 27. Partial Molar Entropies of Hydration, ΔSh, and Partial Molar Entropies of Solution, ΔSs, for Pulegone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C)					
		10		20		30	
		$-\Delta Sh$ $Jmole^{-1}{}^{\circ}K^{-1}$	$-\Delta Ss$ $Jmole^{-1}{}^{\circ}K^{-1}$	$-\Delta Sh$ $Jmole^{-1}{}^{\circ}K^{-1}$	$-\Delta Ss$ $Jmole^{-1}{}^{\circ}K^{-1}$	$-\Delta Sh$ $Jmole^{-1}{}^{\circ}K^{-1}$	$-\Delta Ss$ $Jmole^{-1}{}^{\circ}K$
Sucrose	0	325	113	319	106	315	102
	10	322	110	316	103	310	98
	20	313	101	317	105	320	107
	30	301	89	319	107	334	121
	40	286	74	316	104	339	126
	50	275	63	301	88	321	108
Glucose	0	332	119	313	101	299	87
	8	310	98	309	97	308	96
	16	298	86	305	92	310	97
	24	294	82	301	88	305	93
	32	292	80	297	85	301	88
	40	283	71	295	83	305	92
Sodium Chloride	0	333	121	313	100	296	83
	4	357	145	318	105	287	74
	8	362	150	324	111	295	82
	12	335	123	329	116	324	112
	16	292	80	329	117	358	145
	20	327	115	314	102	304	92

Table 28. Partial Molar Enthalpies of Hydration, ΔHh, and Partial Molar Enthalpies of Solution, ΔHs, for Carvone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C)					
		10		20		30	
		$-\Delta H_h$ Jmole^{-1}	$-\Delta H_s$ Jmole^{-1}	$-\Delta H_h$ Jmole^{-1}	$-\Delta H_s$ Jmole^{-1}	$-\Delta H_h$ Jmole^{-1}	$-\Delta H_s$ Jmole^{-1}
Sucrose	0	74637	14155	60501	543	49090	-10338
	10	69227	8745	59949	-9	52420	-7007
	20	67163	6681	59123	-835	52584	-6843
	30	64759	4277	58190	-1768	52827	-6601
	40	60530	48	57171	-2787	54373	-5054
	50	55815	4667	55867	-4091	55797	-3631
Glucose	0	72460	11978	60983	1025	51697	-7731
	10	63910	3429	59191	-768	55306	-4122
	20	61226	744	57372	-2587	54178	-5249
	30	59369	-1113	54103	-5856	49781	-9647
	40	56654	-3828	49070	-10888	42896	-16531
	50	61297	815	44853	-15105	31597	-27831
Sodium Chloride	0	71830	11348	61947	2016	53984	-5444
	4	69500	9019	60285	327	52806	-6621
	8	72930	12448	60270	311	50037	-9391
	12	66826	6344	63410	3451	60566	1138
	16	43531	-16951	69074	9115	89379	29952
	20	57456	3026	65024	5066	70961	11534

Table 29. Partial Molar Free Energies of Hydration, ΔGh, and Partial Molar

Free Energies of Solution, ΔGs, for Carvone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C)					
		10		20		30	
		ΔGh Jmole⁻¹	ΔGs Jmole⁻¹	ΔGh Jmole⁻¹	ΔGs Jmole⁻¹	ΔGh Jmole⁻¹	ΔGs Jmole⁻¹
Sucrose	0	23516	20057	26601	21019	29260	21564
	10	23511	20052	26493	20911	29198	21502
	20	23516	20057	26447	20865	29139	21444
	30	23528	20069	26401	20820	29081	21385
	40	23548	20089	26331	20749	29018	21322
	50	23576	20117	26255	20673	28943	21247
Glucose	0	23467	20009	26512	20940	29231	21536
	10	23784	20325	26670	21088	29418	21723
	20	24020	20561	26835	21254	29539	21844
	30	24288	20830	27022	21441	299??	21906
	40	24632	21174	27240	21658	2?622	21927
	50	24886	21428	27507	21925	29???	21935
Sodium Chloride	0	23416	19958	26476	20895	29??11	21545
	4	24358	20899	27380	21799	30127	22432
	8	25307	21849	28422	22841	31156	23460
	12	26247	22789	29347	23765	32349	24653
	16	27255	23767	30061	24479	33686	25990
	20	28555	25096	31604	26022	34891	27196

Table 30. Partial Molar Entropies of Hydration, ΔSh, and Partial Molar Entropies of Solution, ΔSs, for Carvone Saturated Aqueous Solutions

Dissolved Solid	wt%	Temperature (°C)					
		10		20		30	
		$-\Delta S_h$ Jmole^{-1}°K^{-1}	$-\Delta S_s$ Jmole^{-1}°K^{-1}	$-\Delta S_h$ Jmole^{-1}°K^{-1}	$-\Delta S_s$ Jmole^{-1}°K^{-1}	$-\Delta S_h$ Jmole^{-1}°K^{-1}	$-\Delta S_s$ Jmole^{-1}°K^{-1}
Sucrose	0	397	121	297	74	258	37
	10	328	102	295	71	269	48
	20	320	94	292	68	270	48
	30	312	86	289	65	270	49
	40	297	71	285	61	275	54
	50	280	55	280	57	280	58
Glucose	0	339	113	299	75	267	46
	10	310	84	293	69	280	58
	20	301	75	287	64	276	55
	30	295	70	277	53	262	40
	40	287	61	260	37	239	18
	50	304	79	247	23	202	-19.4
Sodium Chloride	0	336	111	302	78	275	53
	4	332	106	299	76	274	52
	8	347	121	303	79	268	46
	12	329	103	316	93	307	85
	16	250	-24	338	115	410	185
	20	304	78	329	106	350	128
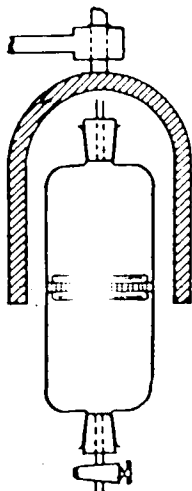
Figure 1. The Stokes diaphragm cell.
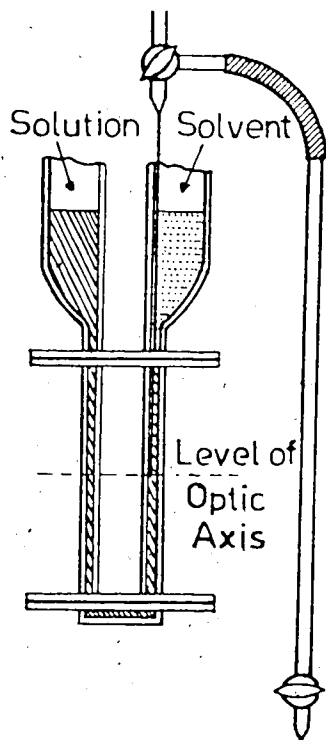
Figure 2. The Kahn and Polson boundary sharpening
technique as applied to a Tiselius electro-
phoresis cell used for diffusion measurements.
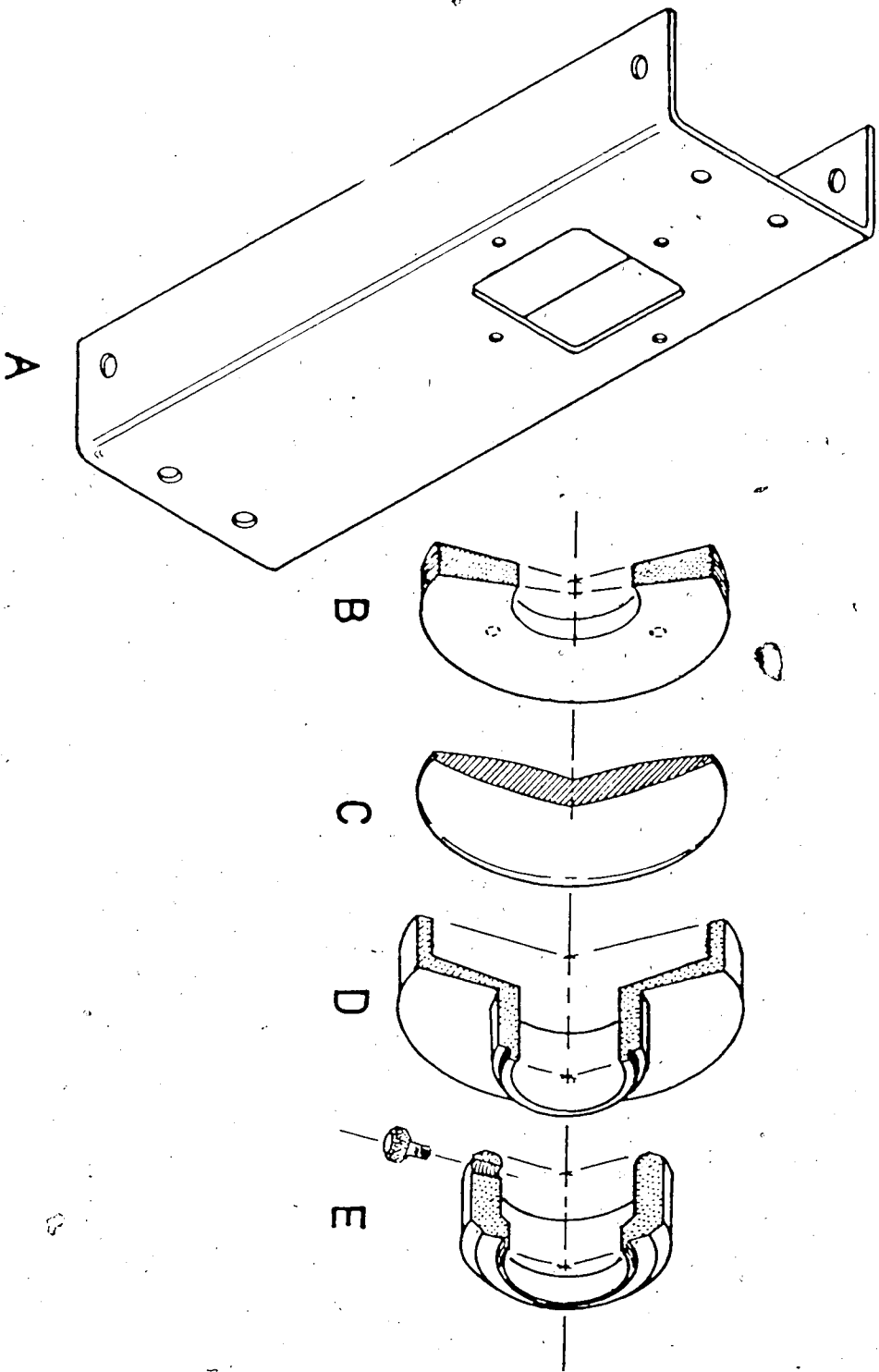
Figure 3. Adaptation of the 35 mm camera to the optical column of the schlieren accessory.
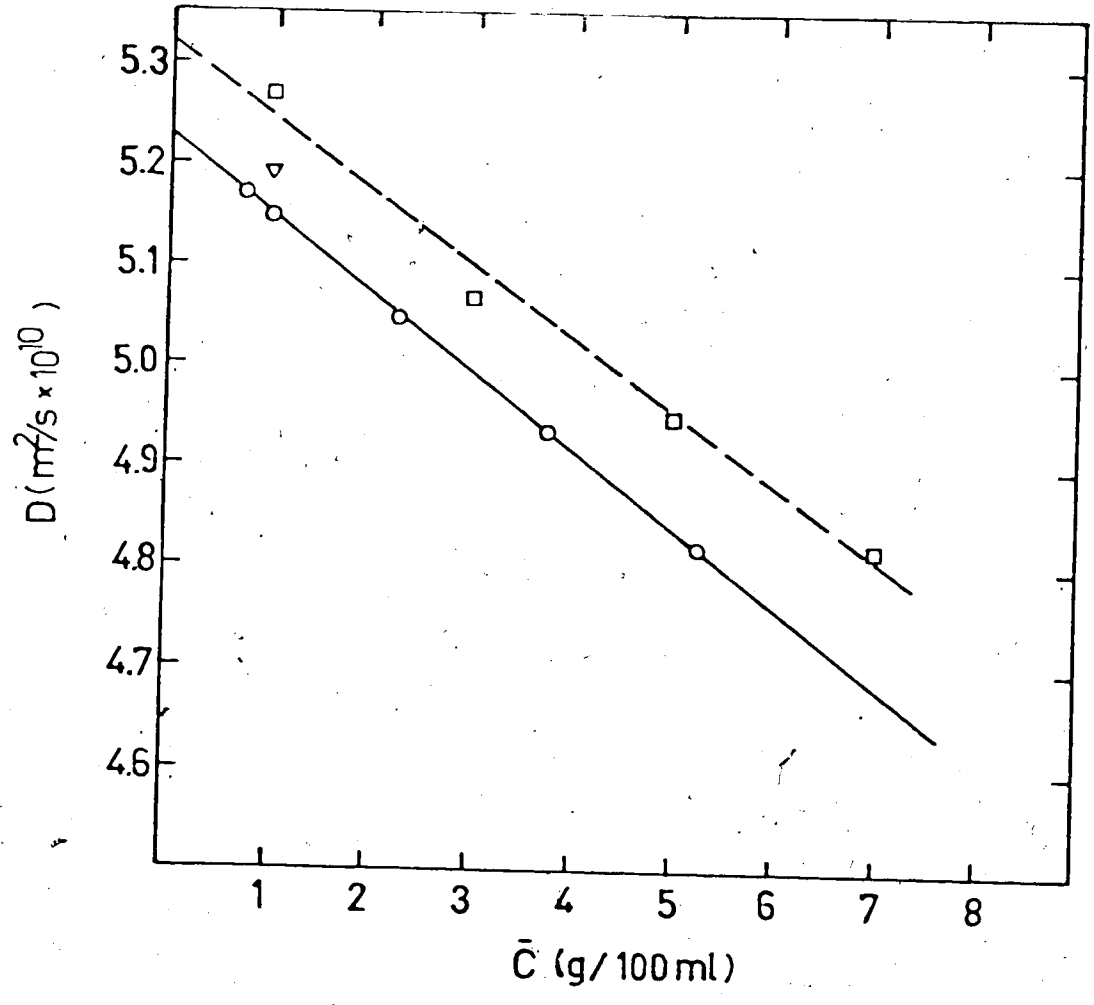
Figure 4. D as a function of the average sucrose concentration. □ , this work at 25.3°C; O, Gosting and Morris (1949) at 24.95°C; ∇, this work at 25.0°C; ____, best fit of data at 25.3°C.
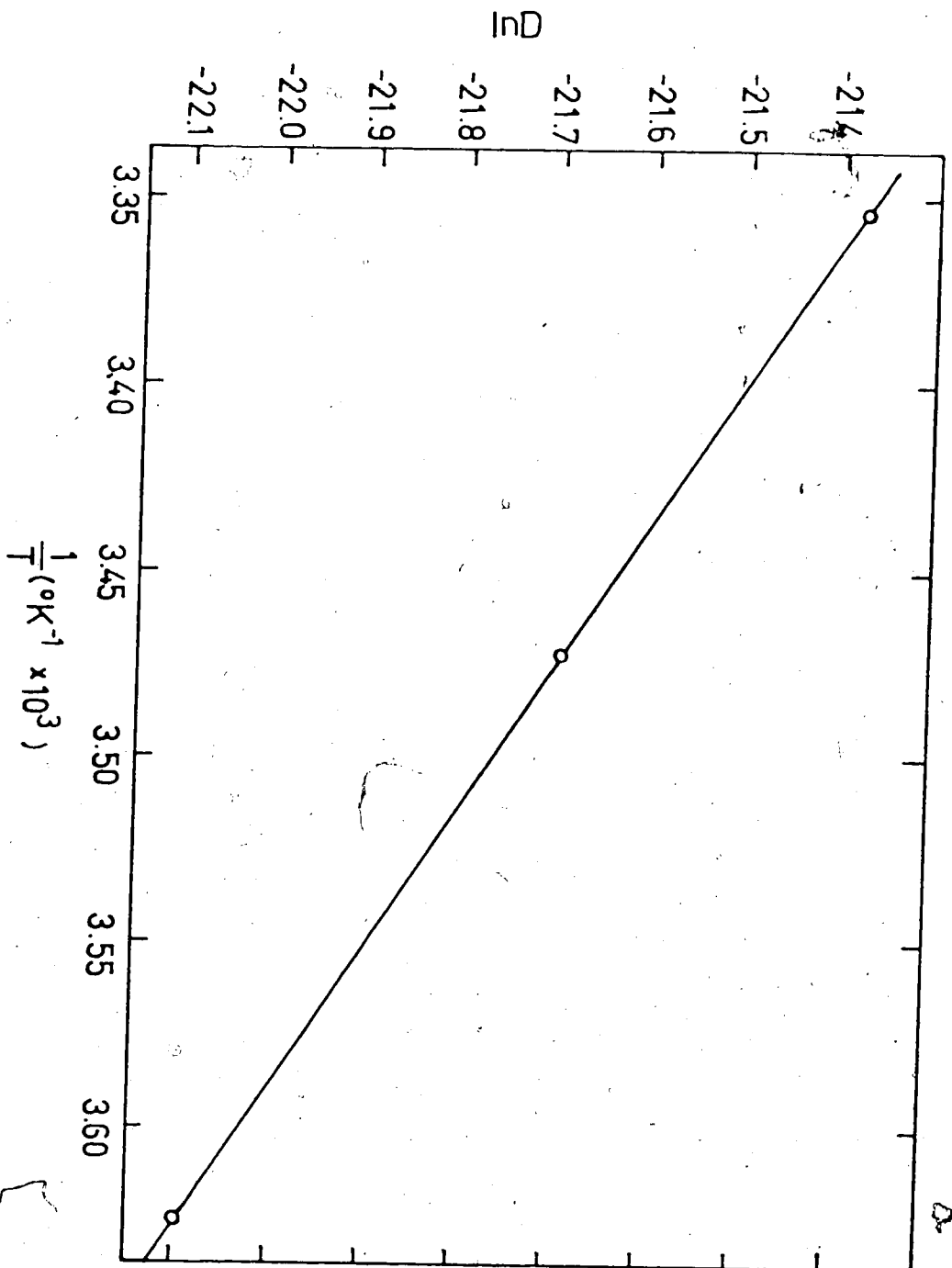
Figure 5. Arrhenius type plot of D and T.
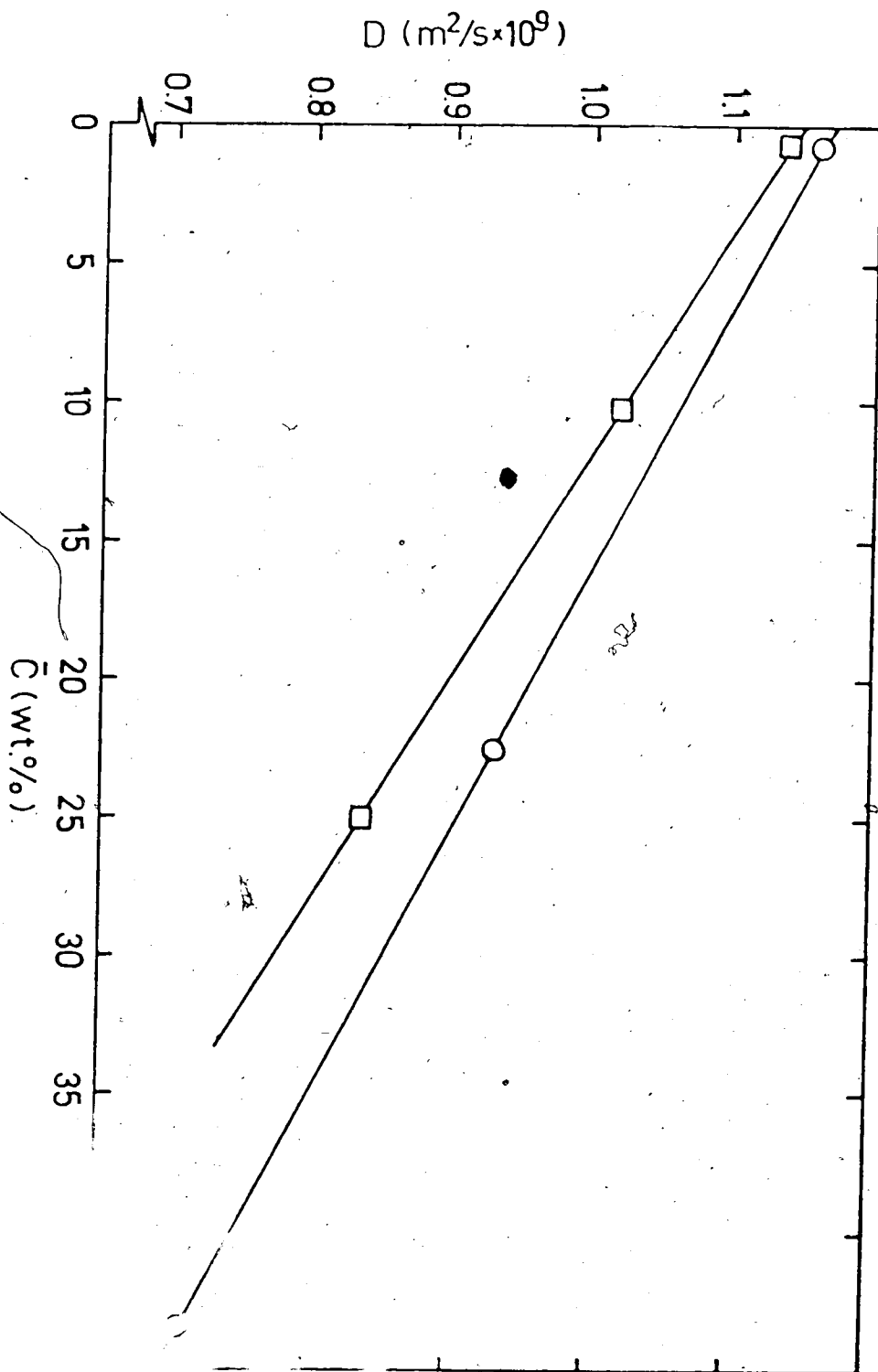
Figure 6. D as a function of average ethylene glycol concentration. □, this work; O, Byers and King (1966).

Concetration
Profile Curve

Concentration
Gradient Curve
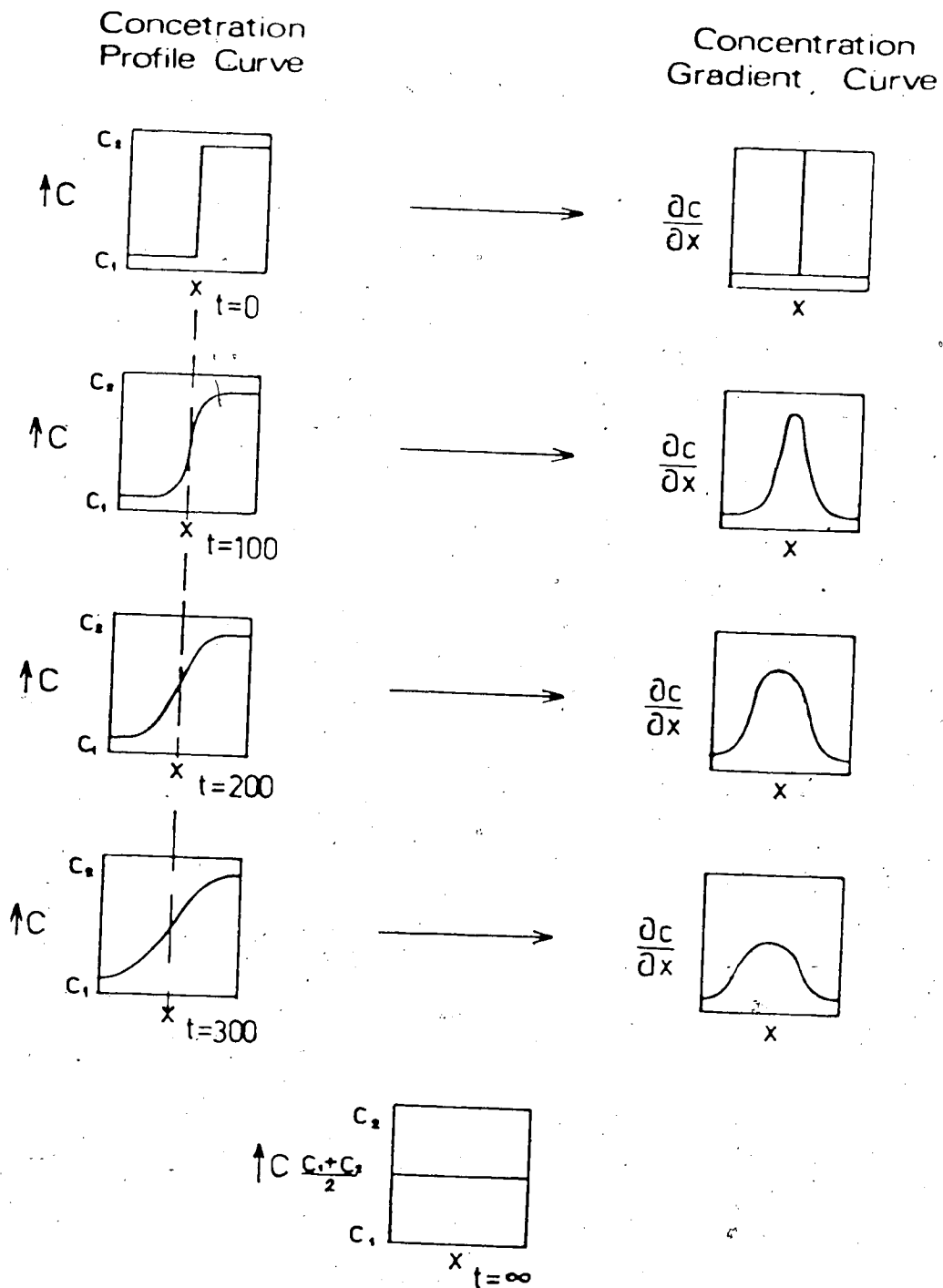
Figure 7. Theoretical diffusion experiment showing con-
centration curves and concentration gradient
curves as a function of time.
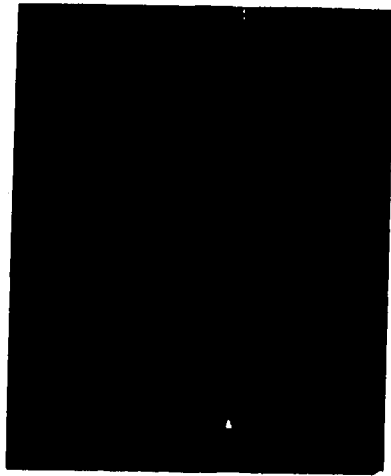
$\theta = 180s$

$\theta = 240s$
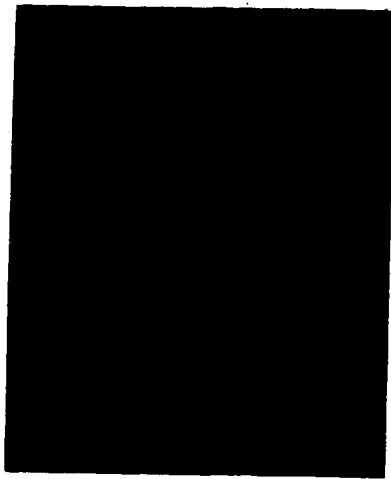
$\theta = 300s$

$\theta = 360s$

Figure 8. Decrease of the photographically recorded schlieren image and time.

a. = 75°

b. = 80°

c. θ = 60°

d. θ = 50°

Figure 9.   Influence of the schlieren bar angle on the photo-
graphic images.
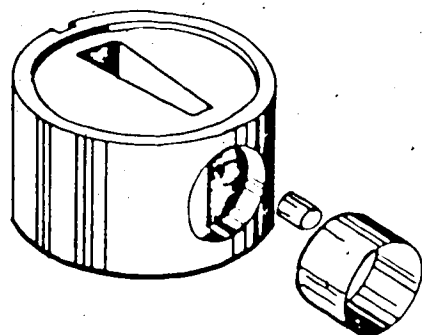
Valve-type synthetic boundary cell
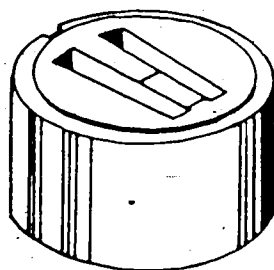
Double sector capillary synthetic
boundary cell

Figure 10. Centerpieces for achieving boundary
formation in an ultracentrifuge.
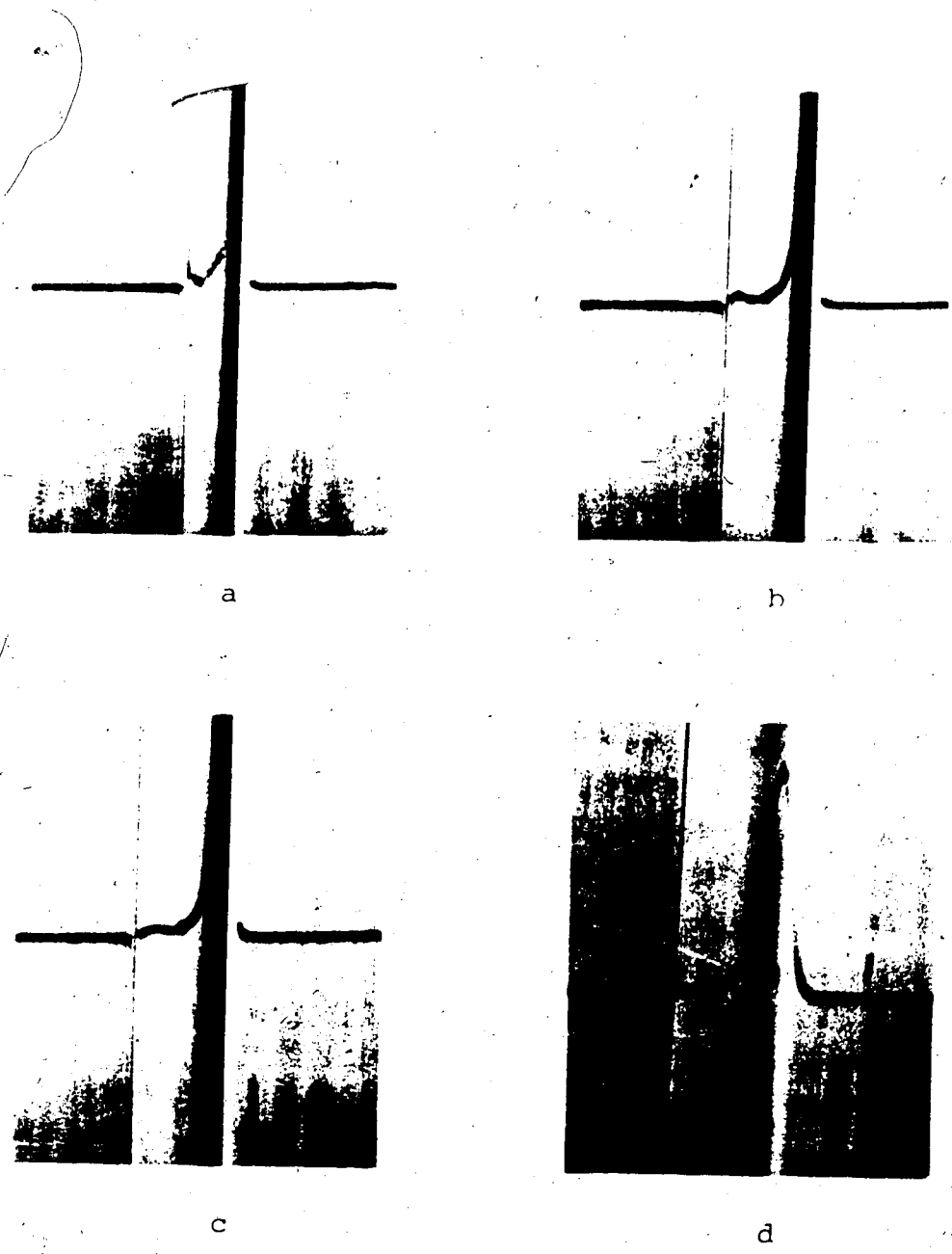
Figure 11. Boundary formation in the valve-type synthetic
boundary cell as monitored photographically.

Gravitational Field in the Ultracentrifuge

Less dense solution

More dense solution

t = 0
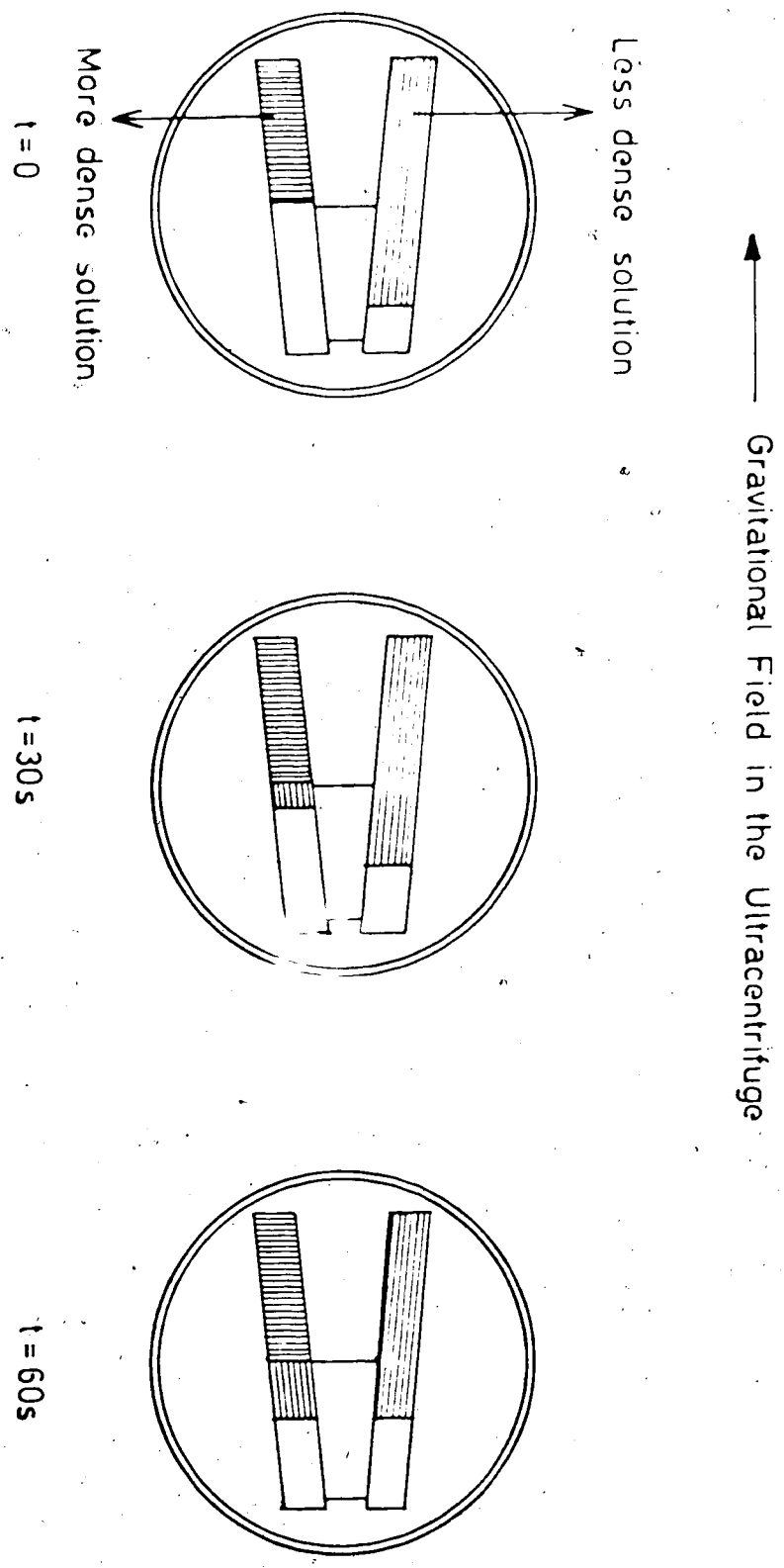
t = 30s

t = 60s

Figure 12. Mechanism of boundary formation in the double sector capillary synthetic boundary cell.

a. $\therefore$ = 15s

b. Ω = 30s

c. ϑ = 45s
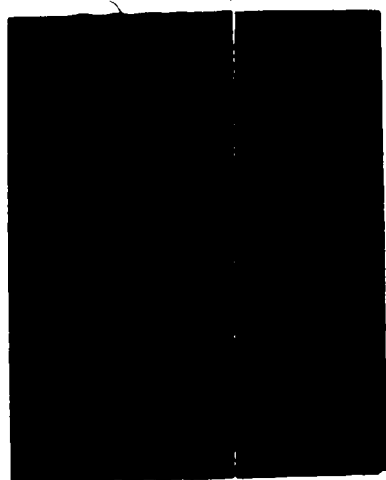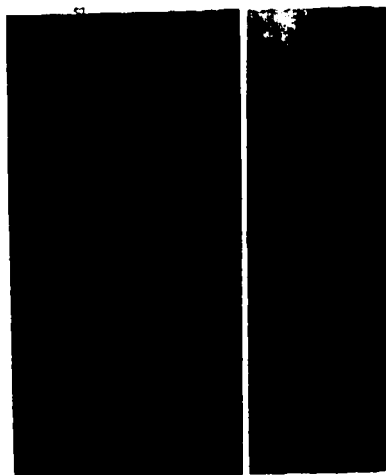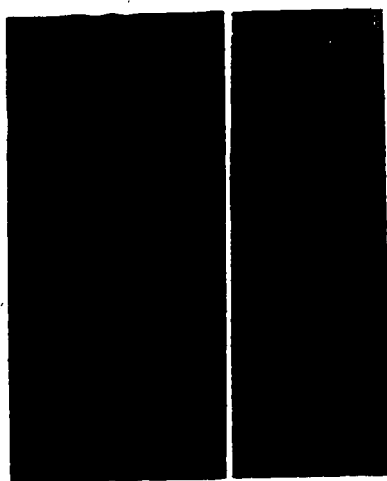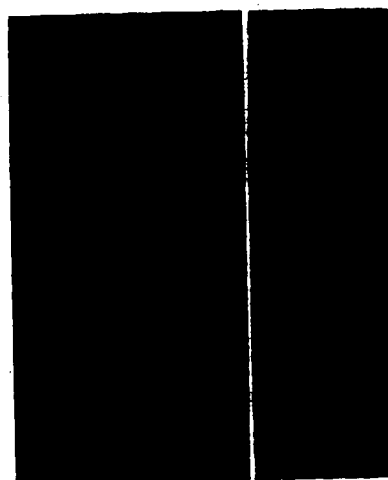
d. Ω = 60s

Figure 13. Boundary formation in the double sector capillary

synthetic boundary cell as monitored photographi-

cally.

e.   θ = 75s

f. θ = 90s

g.   θ = 105s
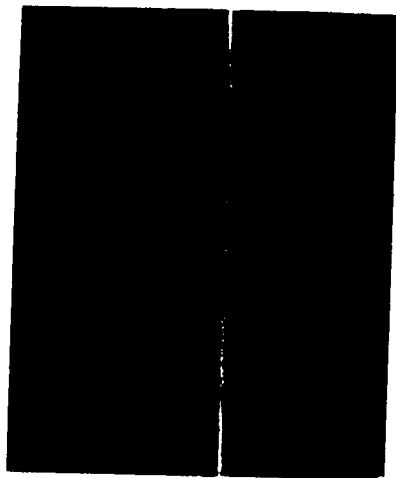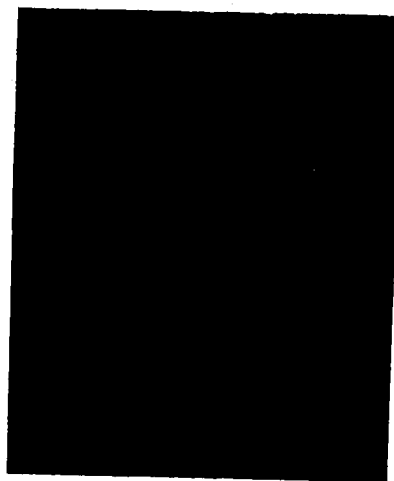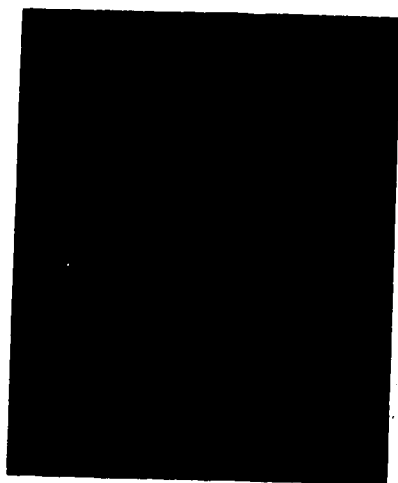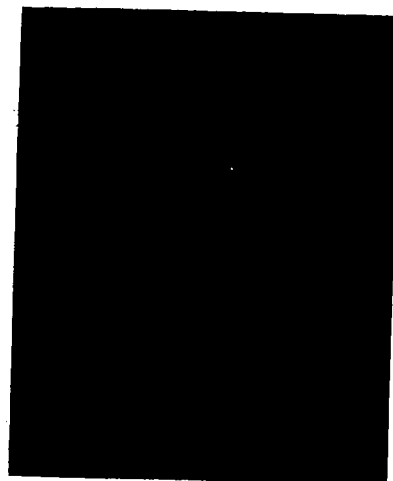
h.   θ = 180s

Figure 13 (cont'd). Boundary formation in the double sector
capillary synthetic boundary cell as
monitored photographically.
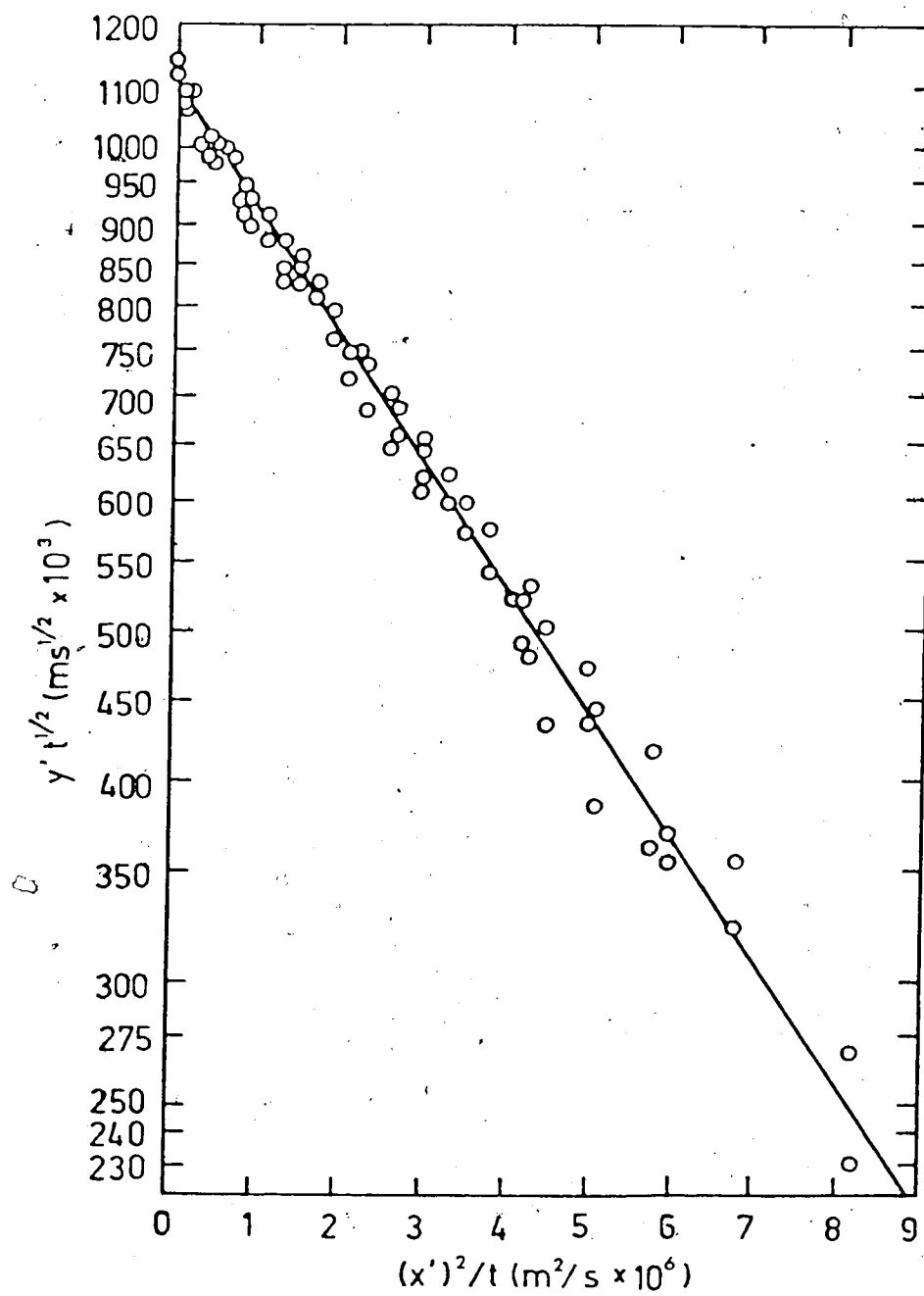
Figure 14. Plot of Equation 5 for glycine at 25.0°.
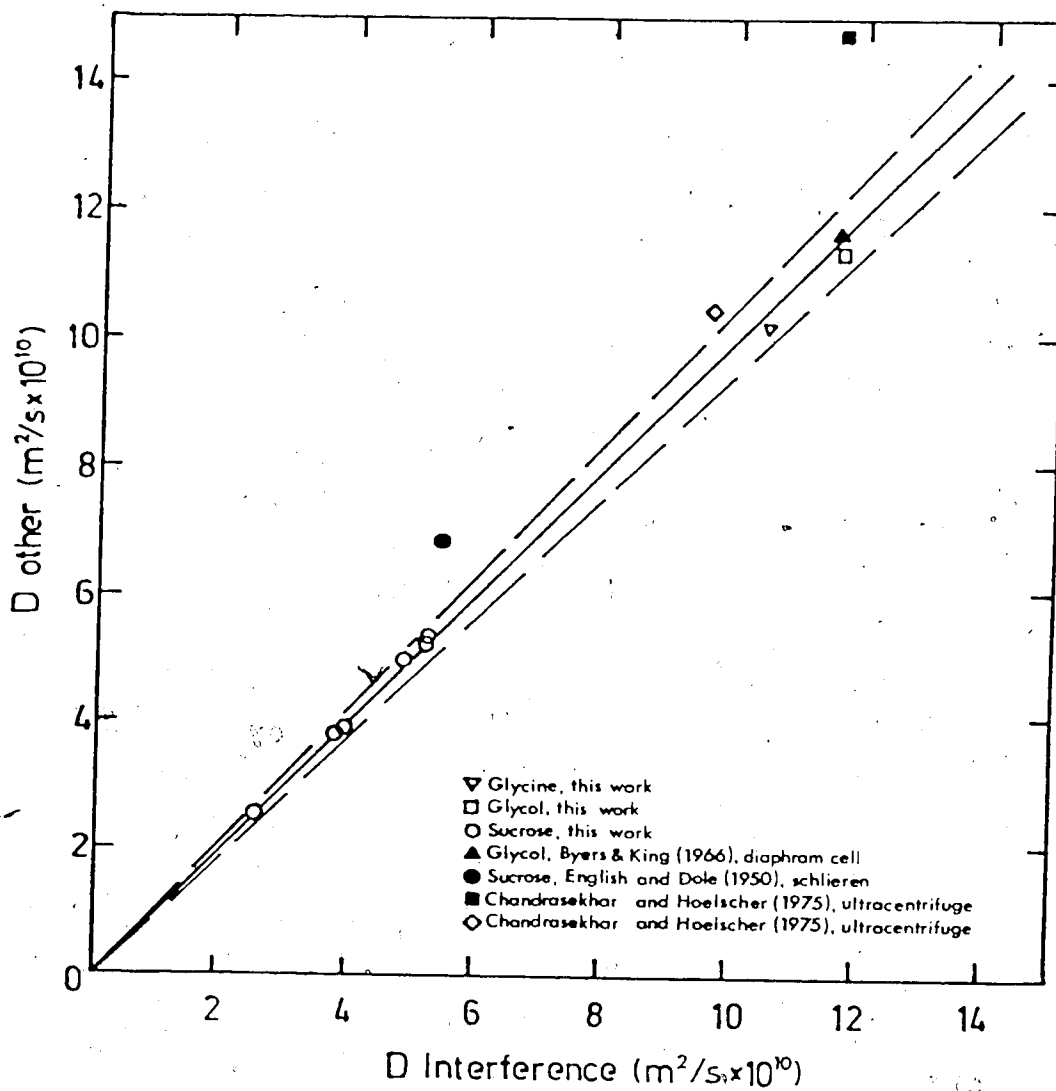
Figure 15. Dinterference <u>vs</u>. Dother.
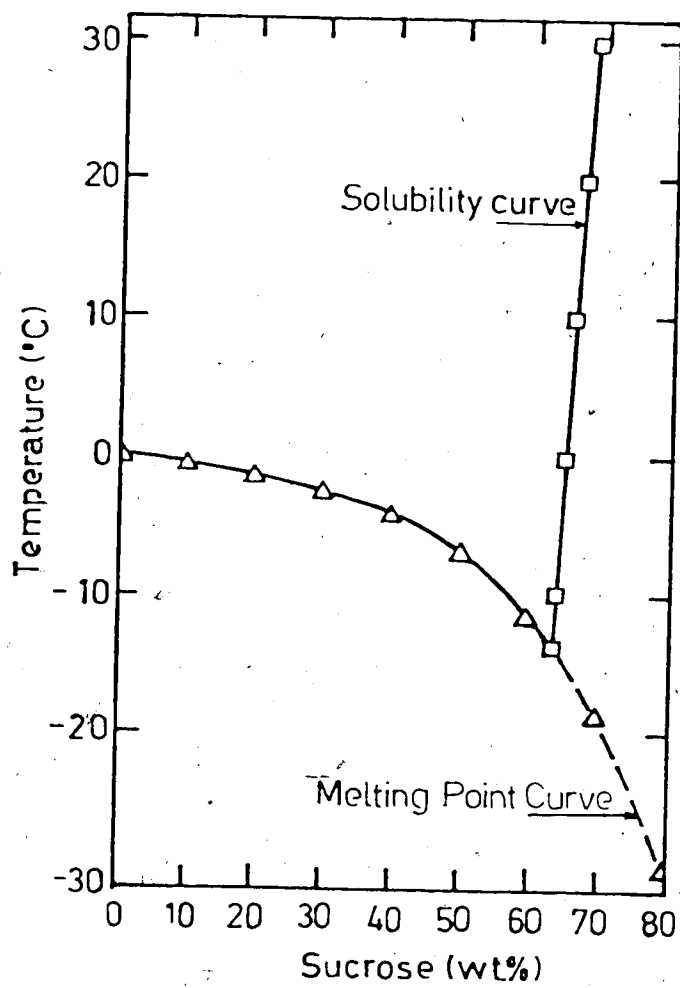
Figure 16. Sucrose-water phase diagram.

Pure Ice

Concentrated
Amorphous Solution
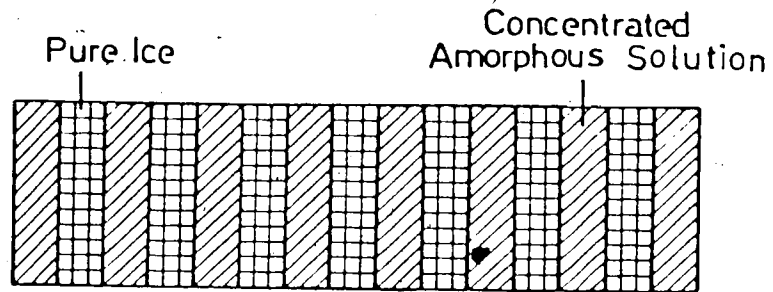
Figure 17. Cross section of a frozen solution.

ICE   CAS

C_i

C_B
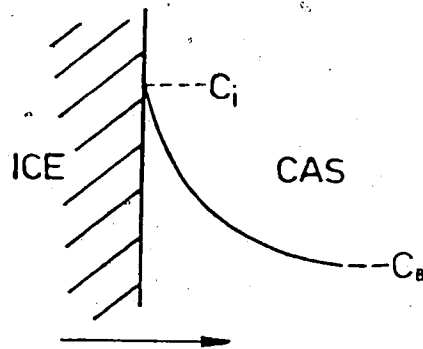
Figure 18. Concentration polarization effect of dissolved solids in the CAS during freezing (C_i, interface concentration; C_b, bulk concentration).
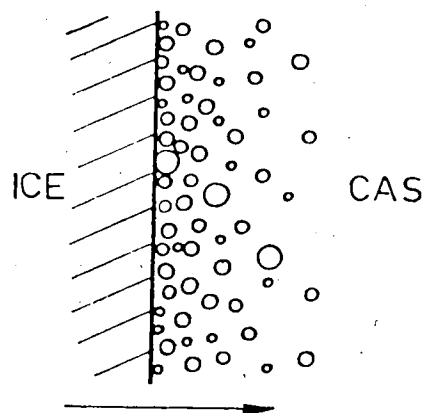
Figure 19.   Concentration polarization of volatile above
             the solubility limit during freezing.
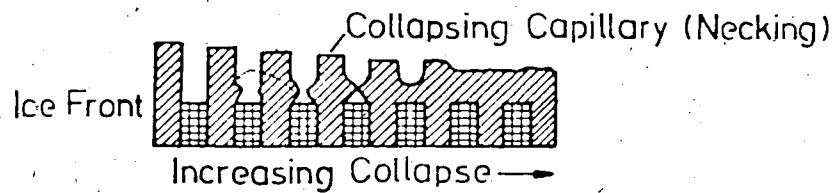
Figure 20.   Progressive stages of collapse.
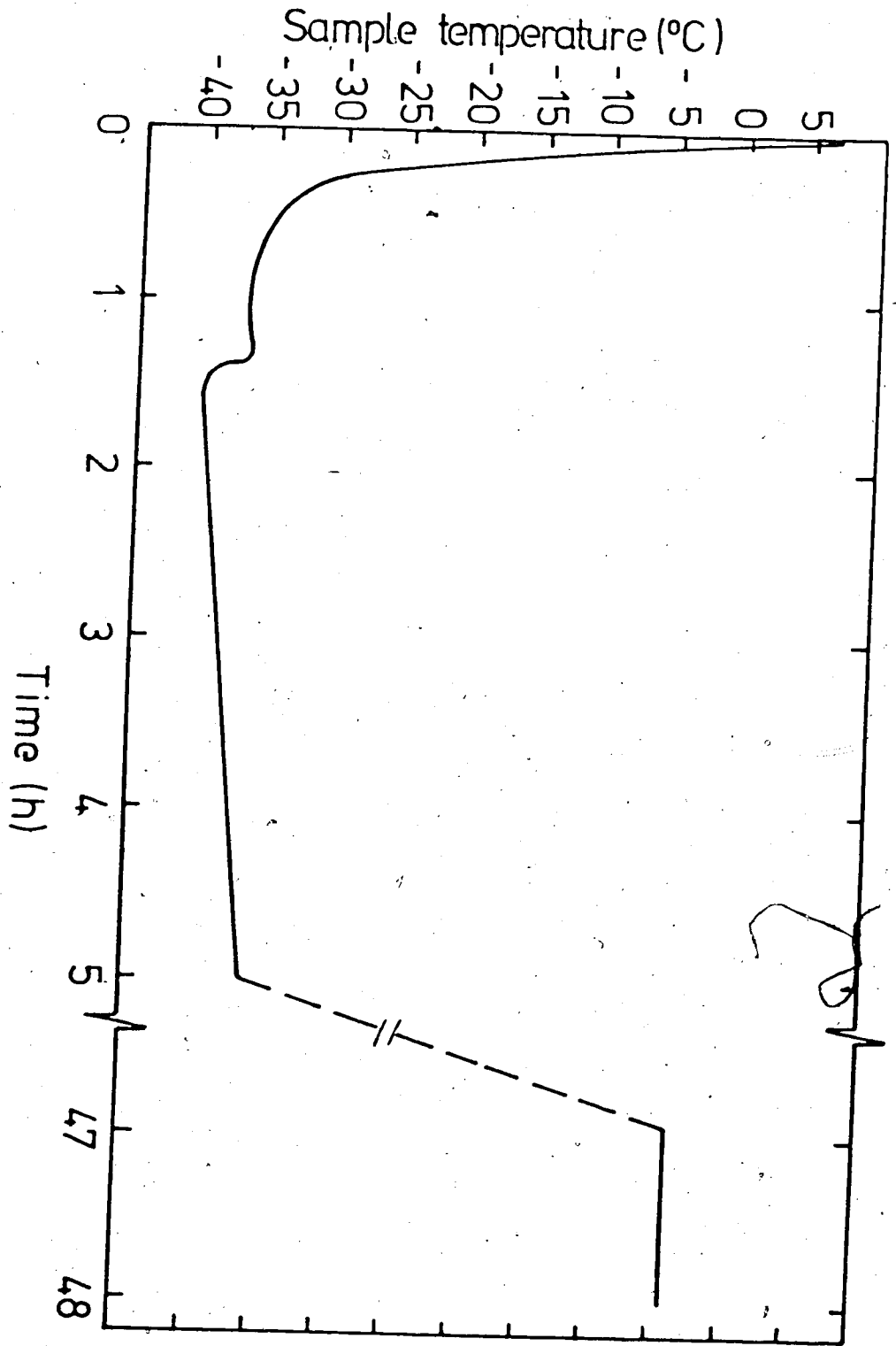
Figure 21. Temperature history of 20% sucrose sample during freezing and drying.
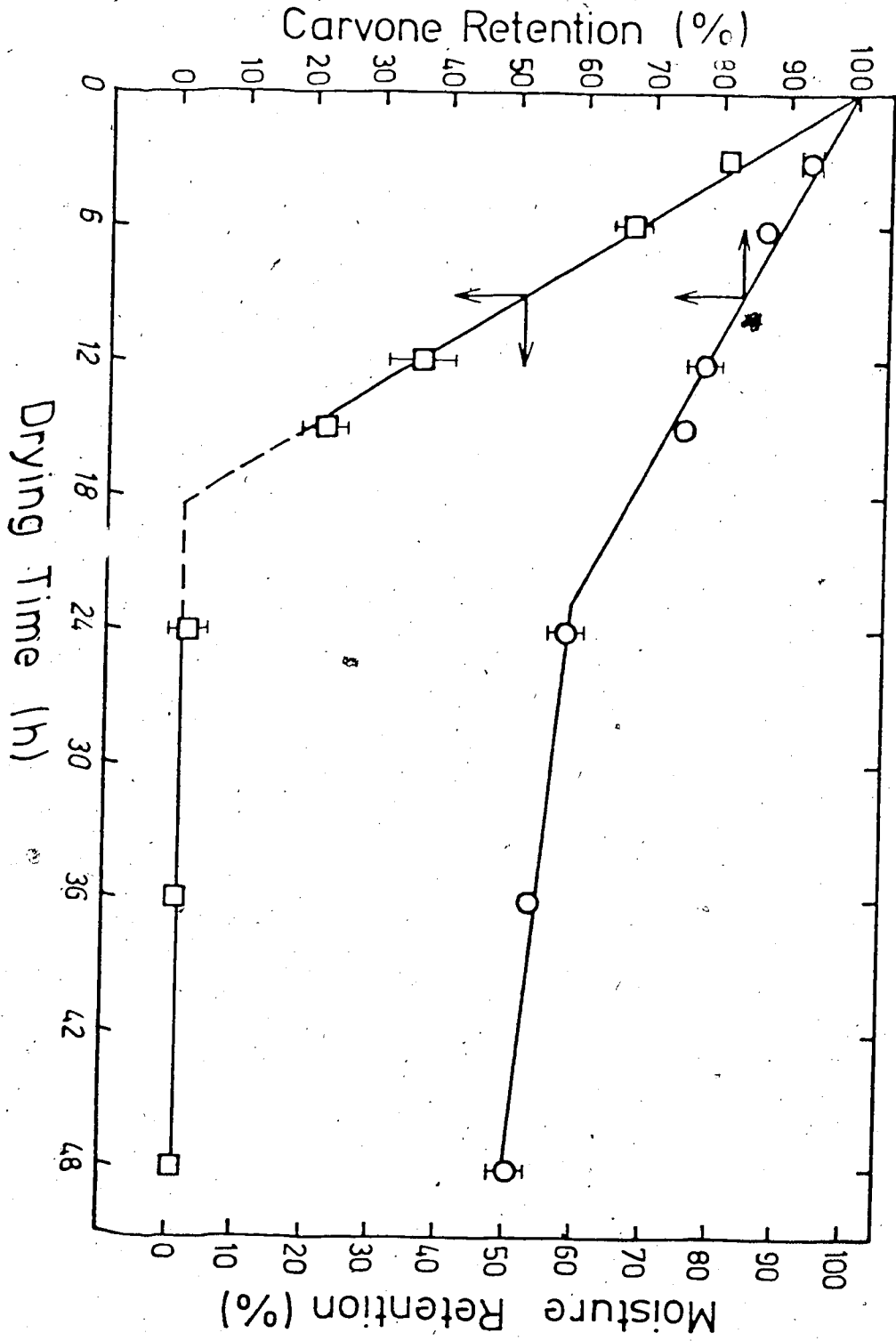
Figure 22. Carvone and moisture retention in gum arabic (1%) as a function of drying time.
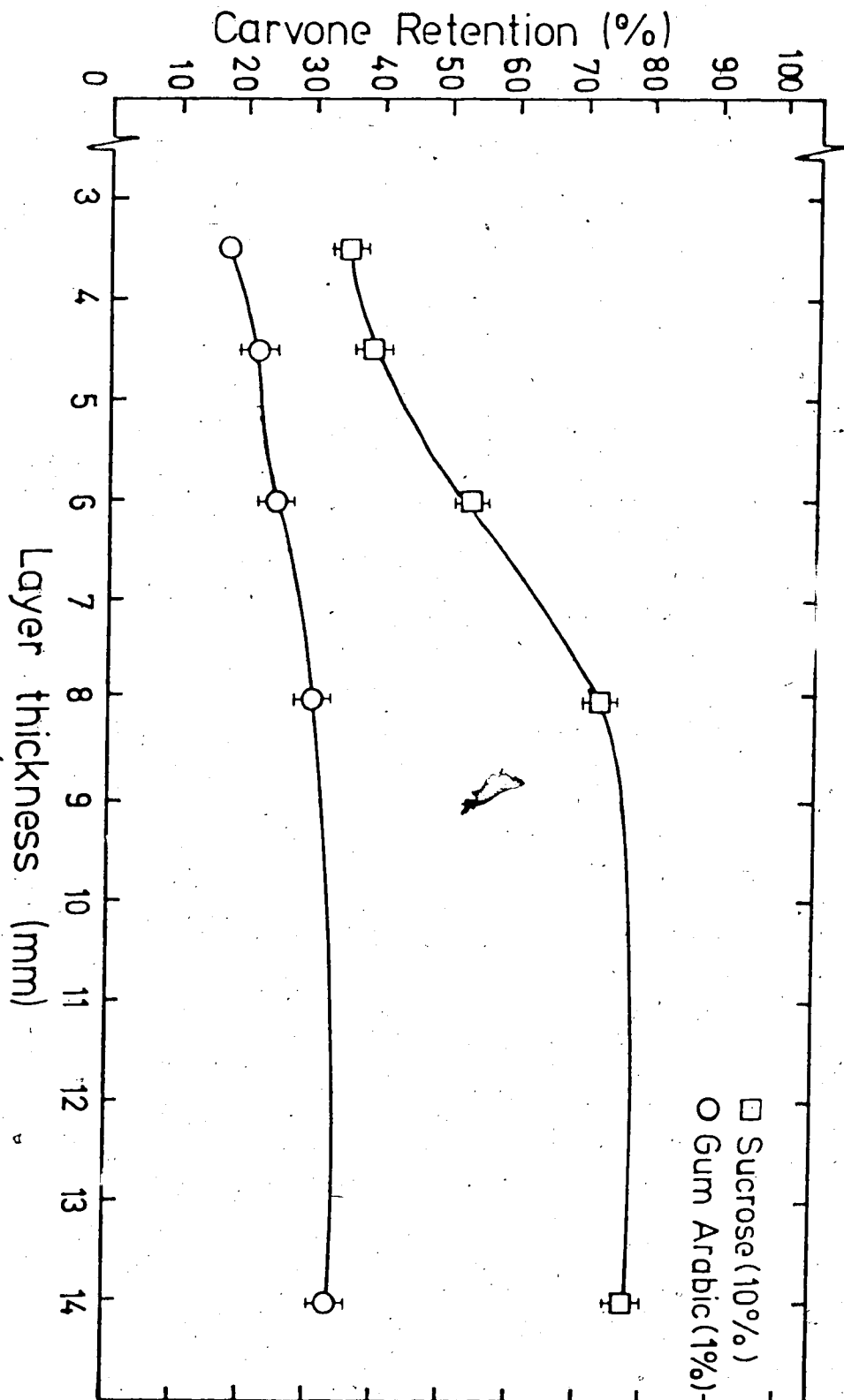
Figure 23. Influence of layer thickness on retention of carvone in sucrose (10%) and gum arabic (1%) at constant sample volume.
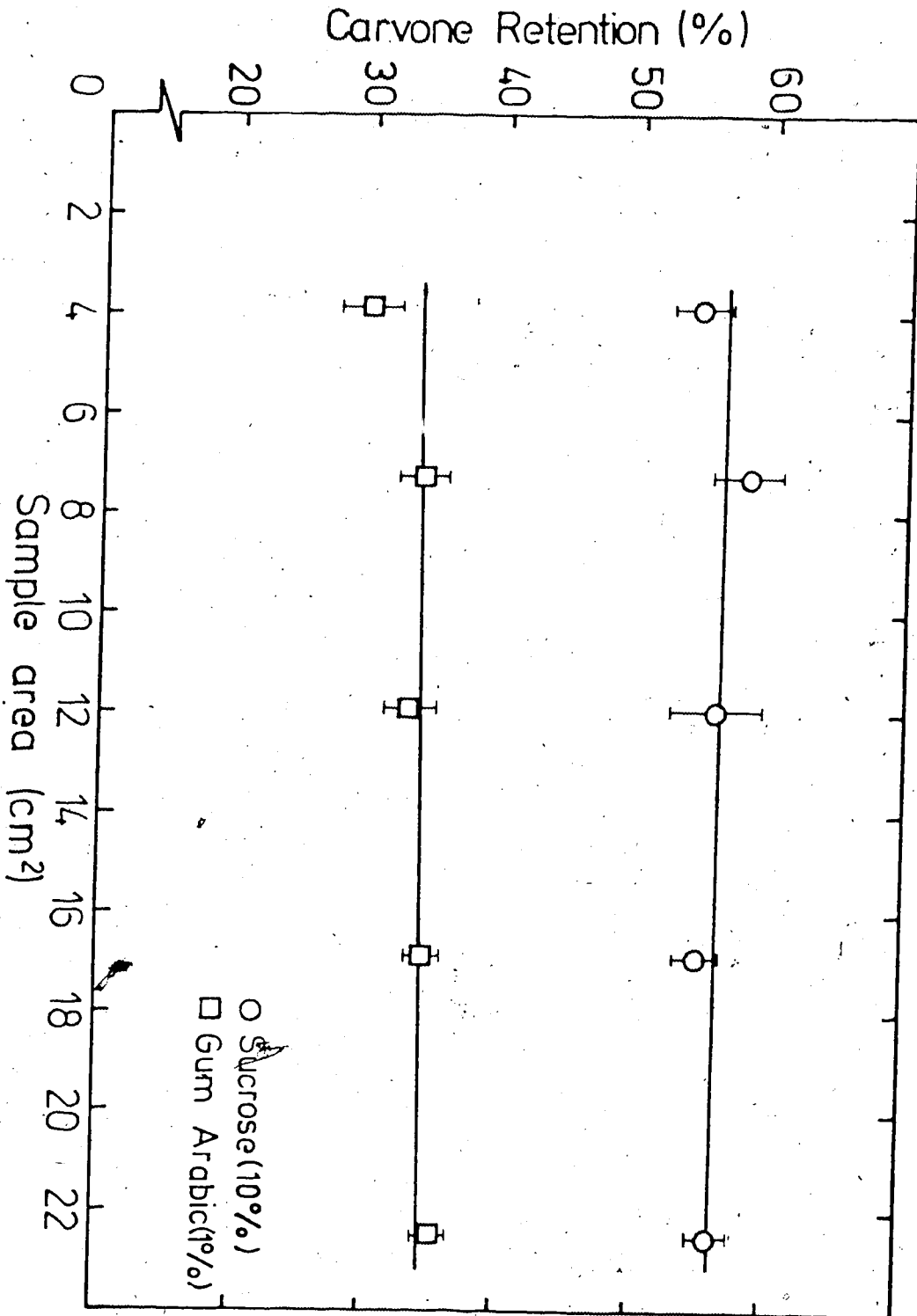
Figure 24. Retention of carvone as a function of surface area in sucrose (10%) and gum arabic (1%) at constant sample thickness.
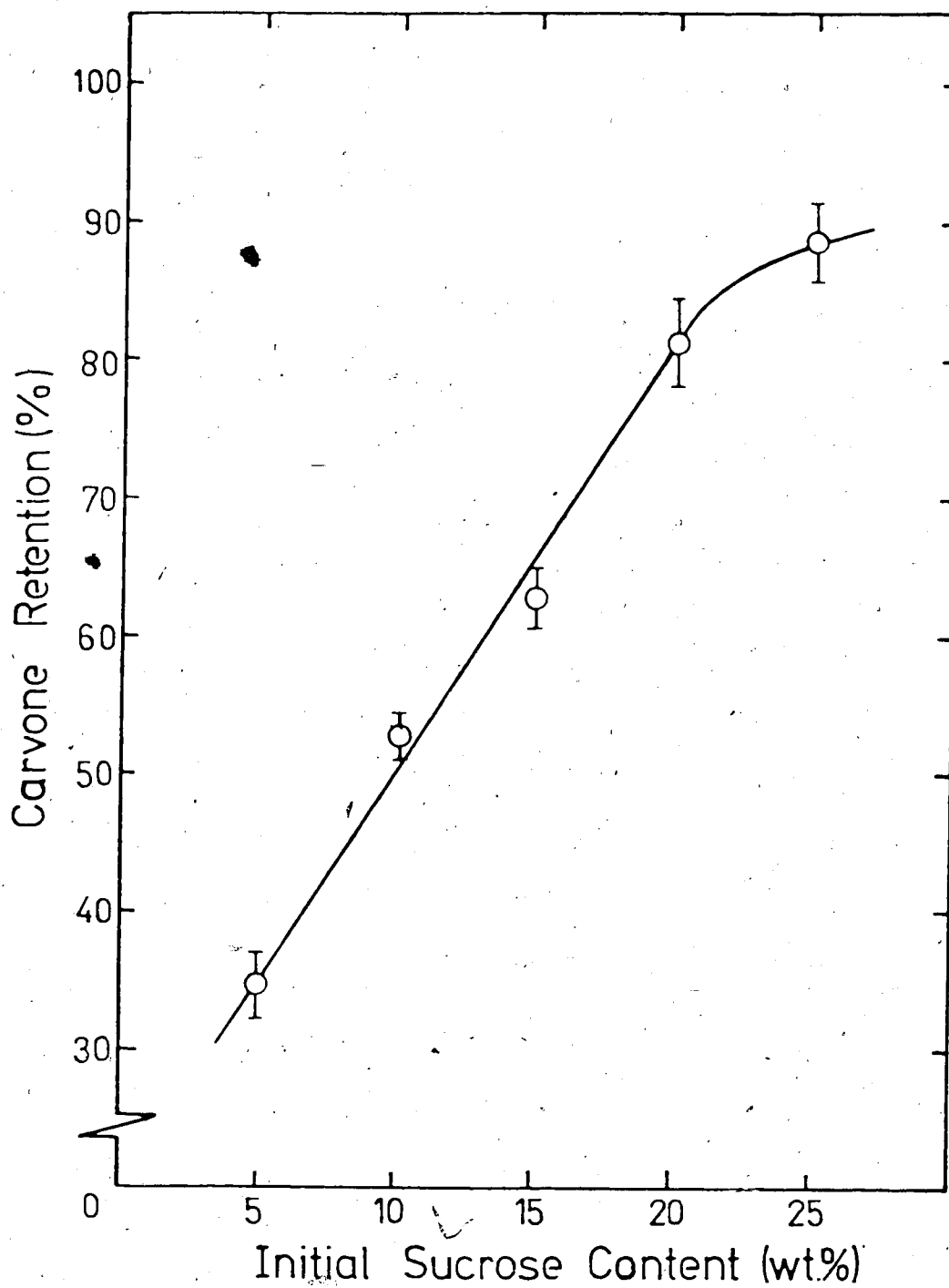
Figure 25. Retention of carvone as a function of initial sucrose content.
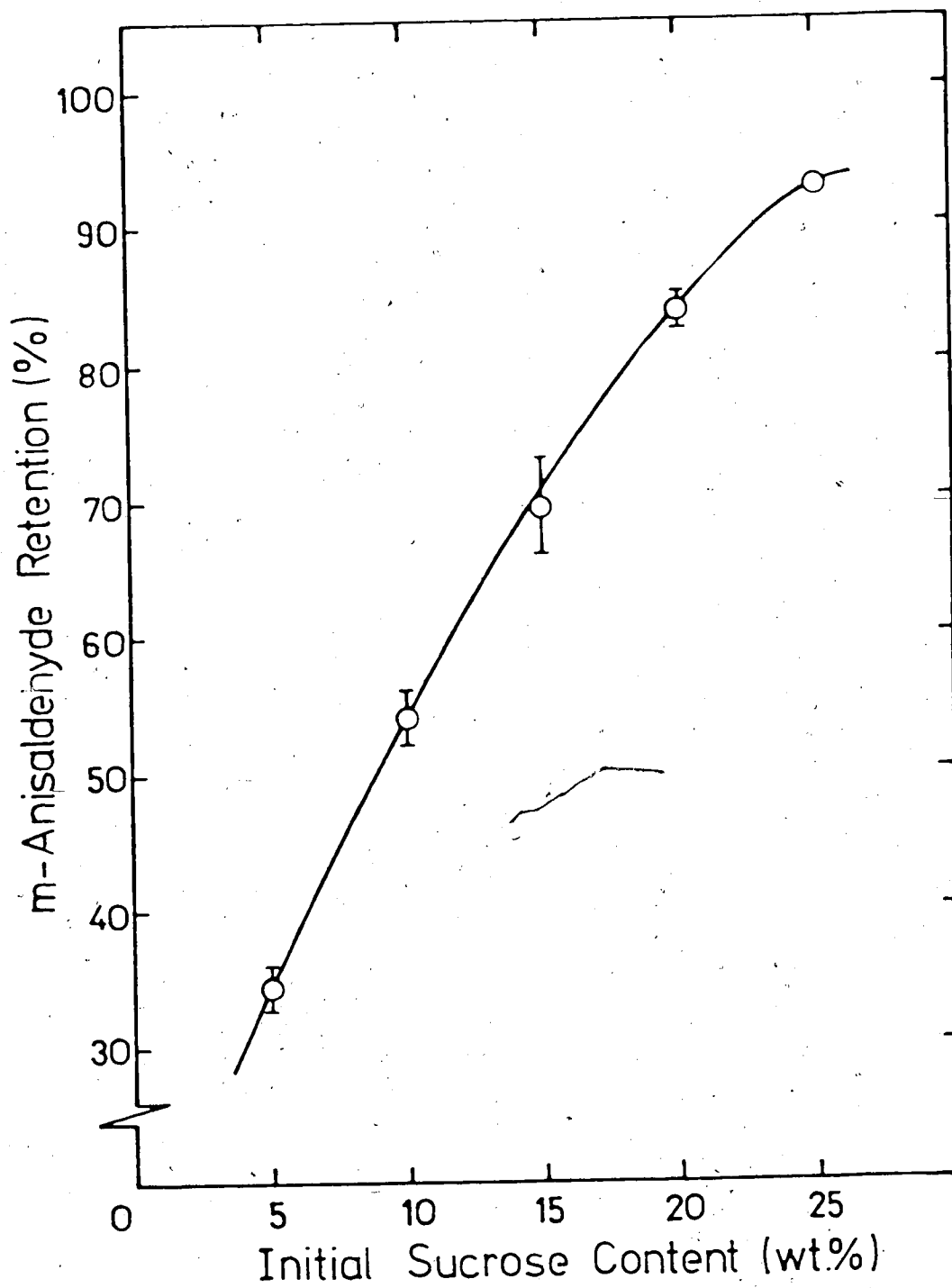
Figure 26. Retention of m-anisaldehyde as a function of initial sucrose content.
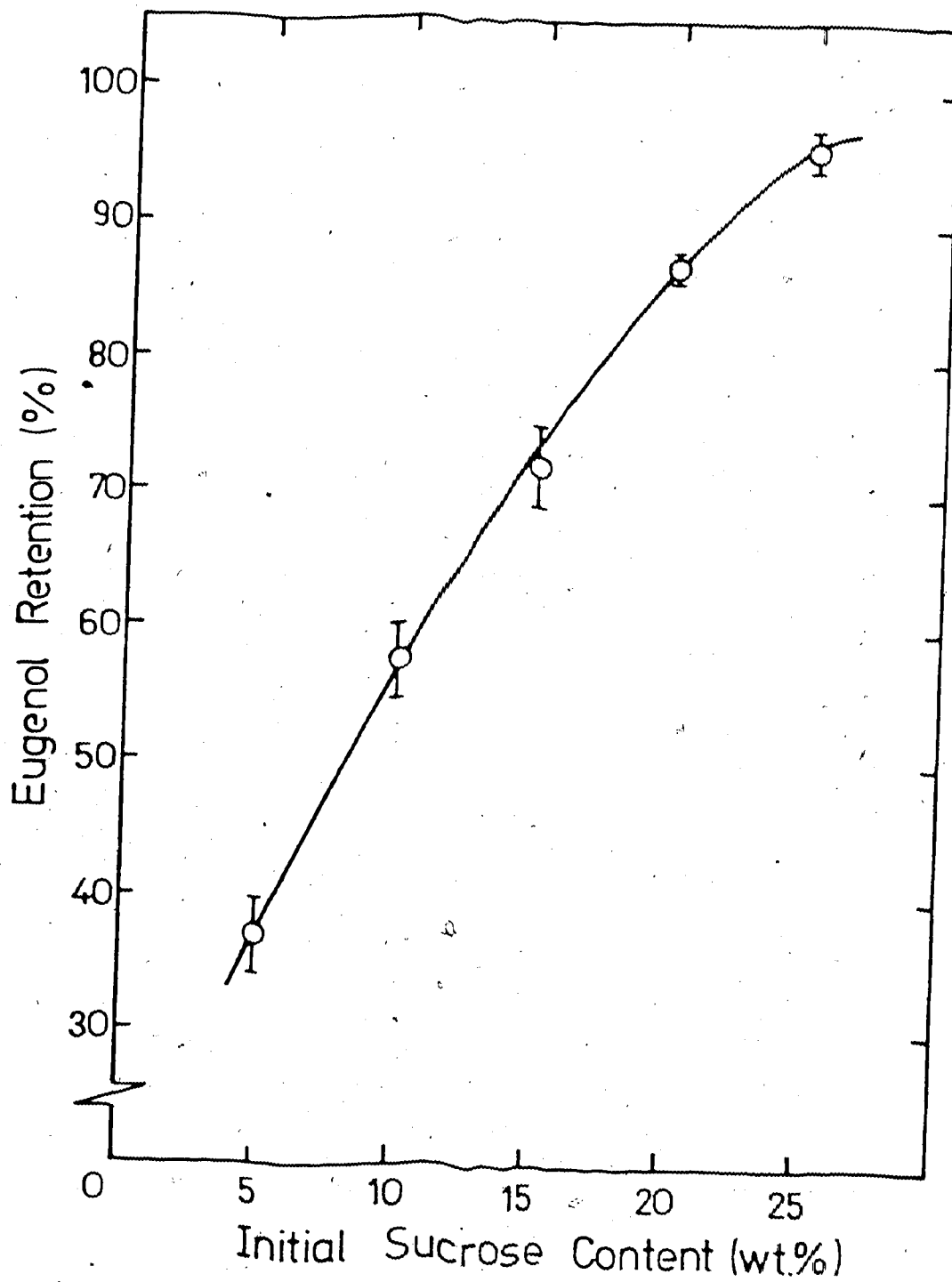
Figure 27. Retention of eugenol as a function of initial sucrose content.
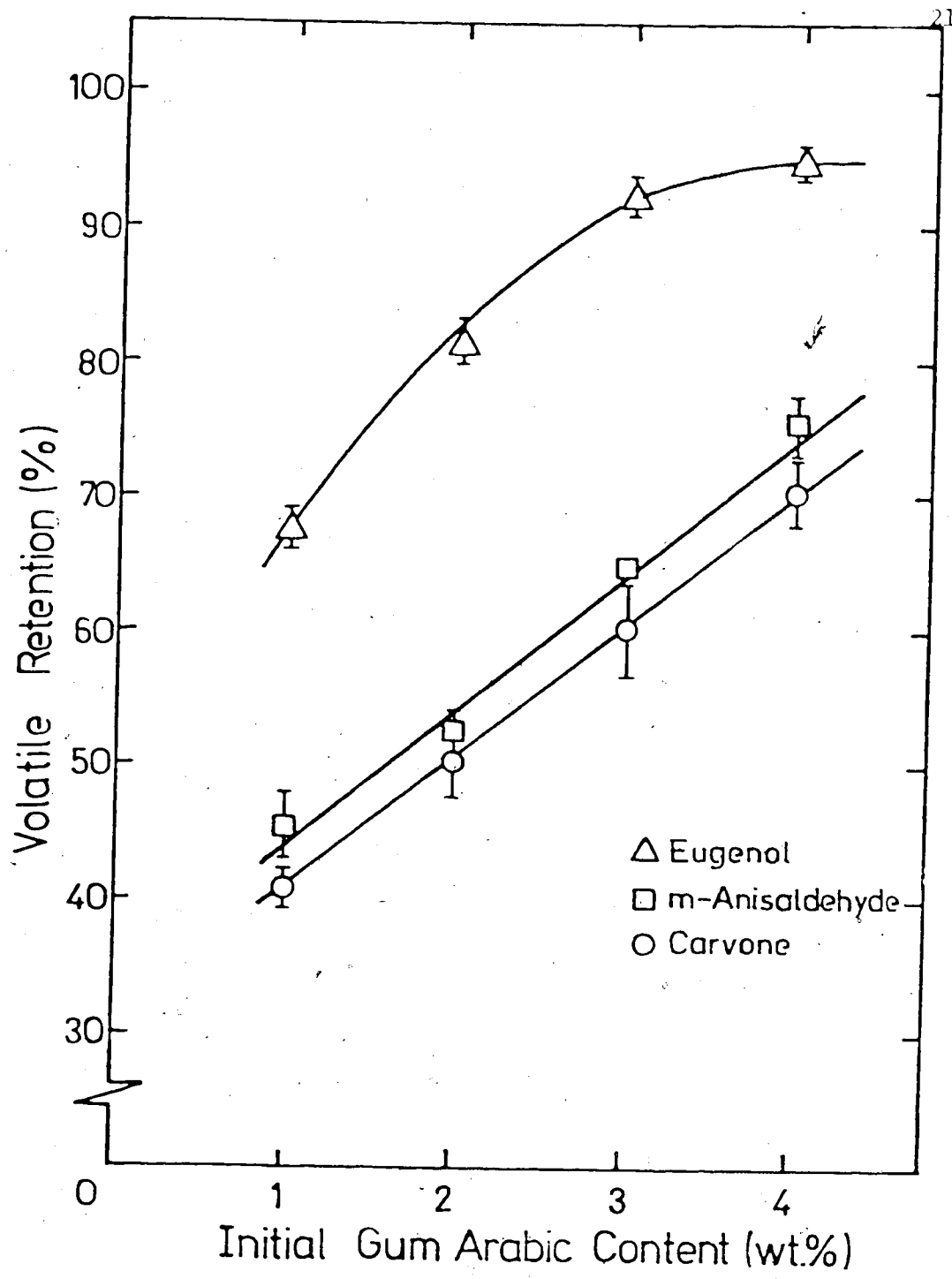
Figure 28. Retention of carvone, m-anisaldehyde and eugenol as a function of initial gum arabic content.
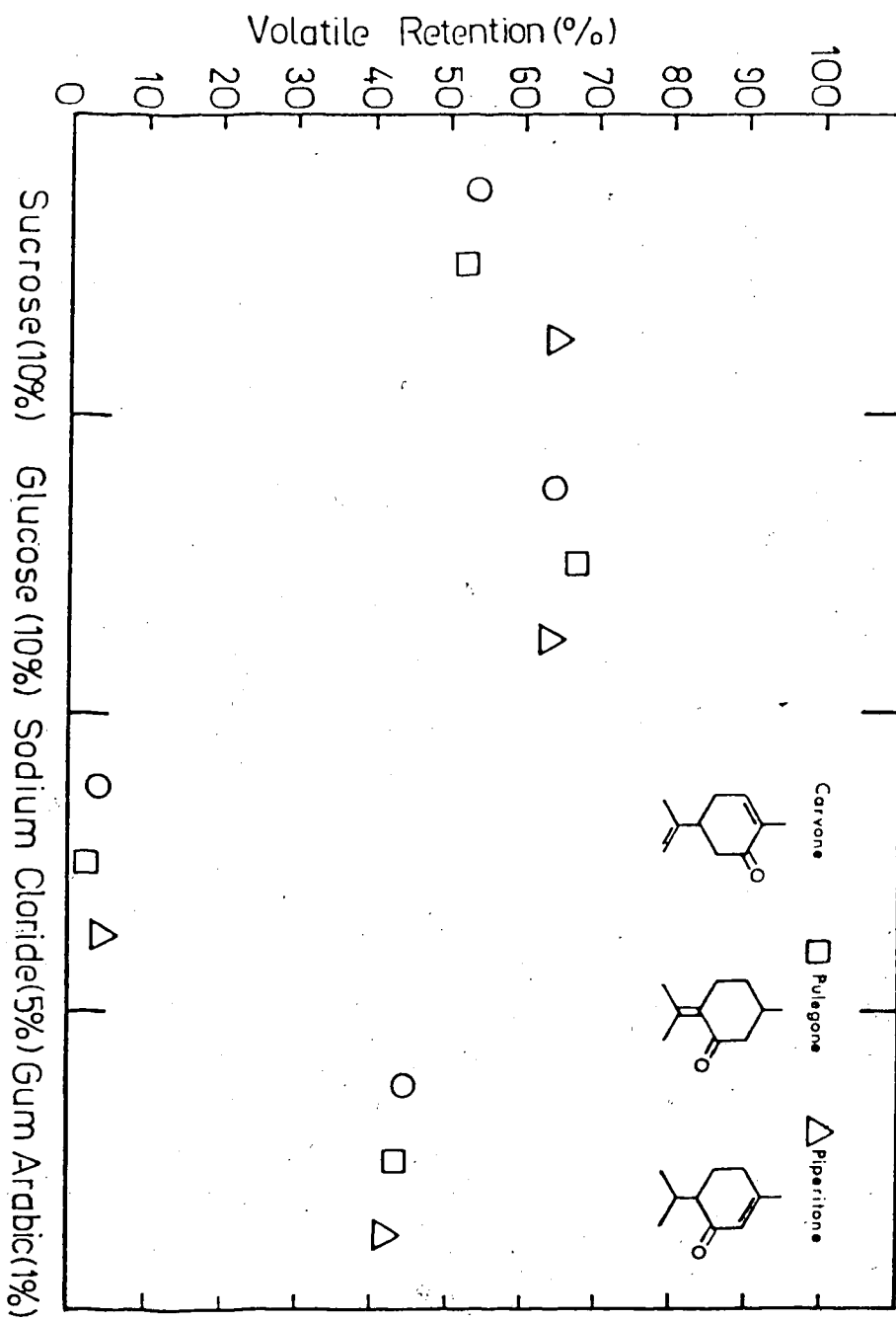
Figure 29. Retention of carvone, pulegone and piperitone in sucrose, glucose, sodium chloride and gum arabic solutions.
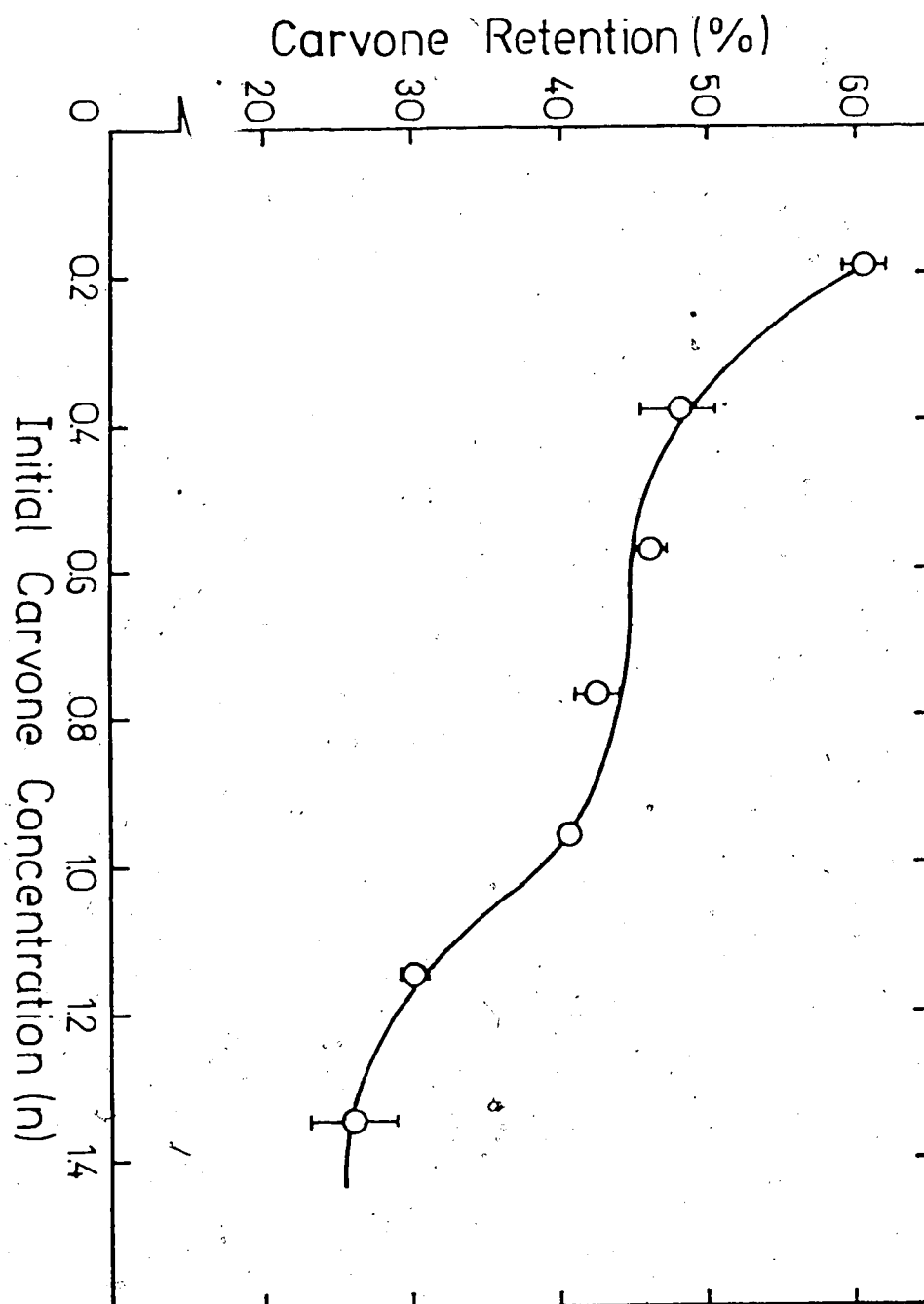
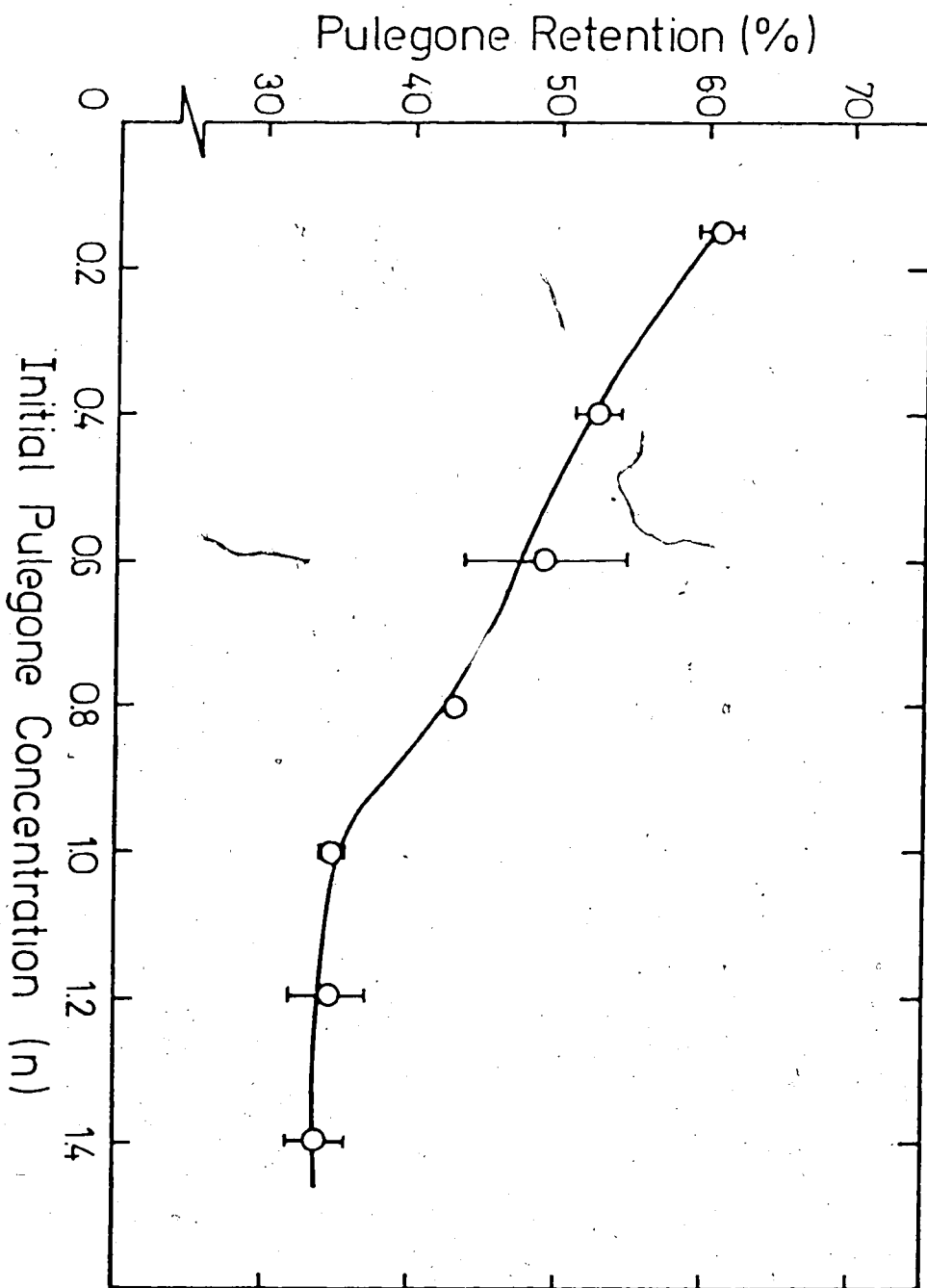Figure 30. Carvone retention as a function of initial carvone concentration in 10% sucrose.

Figure 31. Pulegone retention as a function of initial pulegone concentration in 10% sucrose.
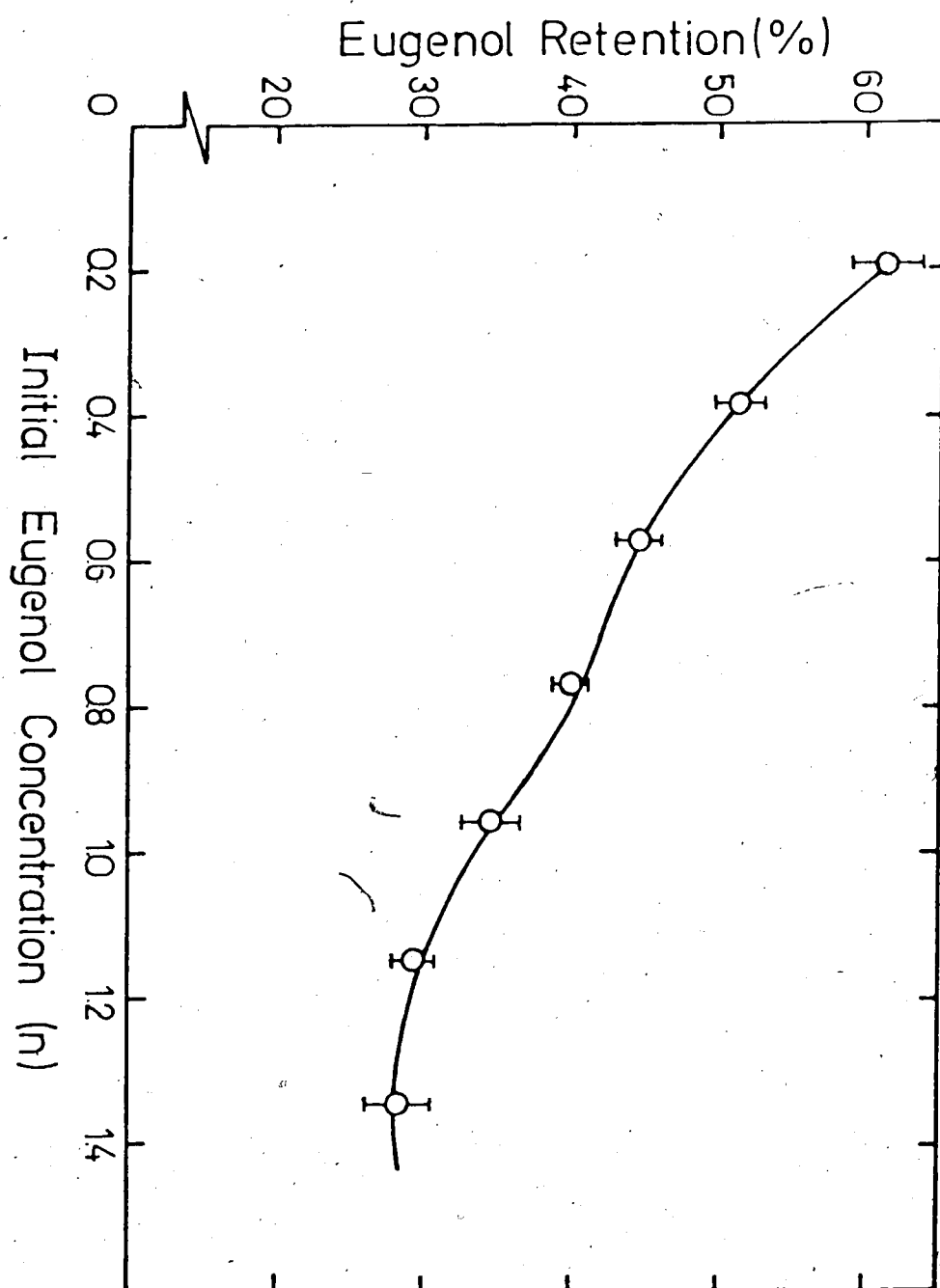
Figure 32. Eugenol retention as a function of initial eugenol concentration in 10% sucrose.
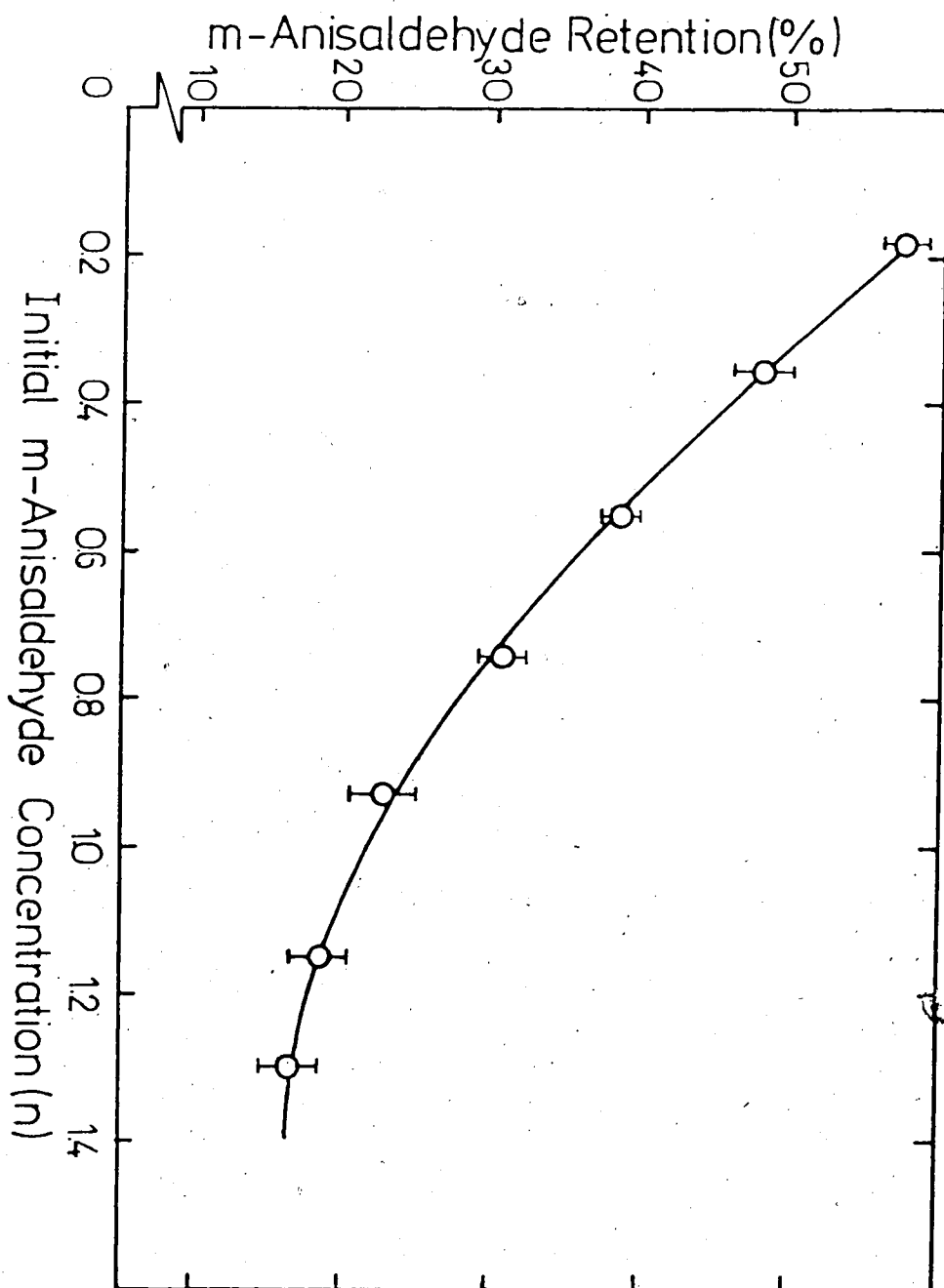
Figure 33. m-Anisaldehyde retention as a function of initial m-anisaldehyde concentration in 10% sucrose.
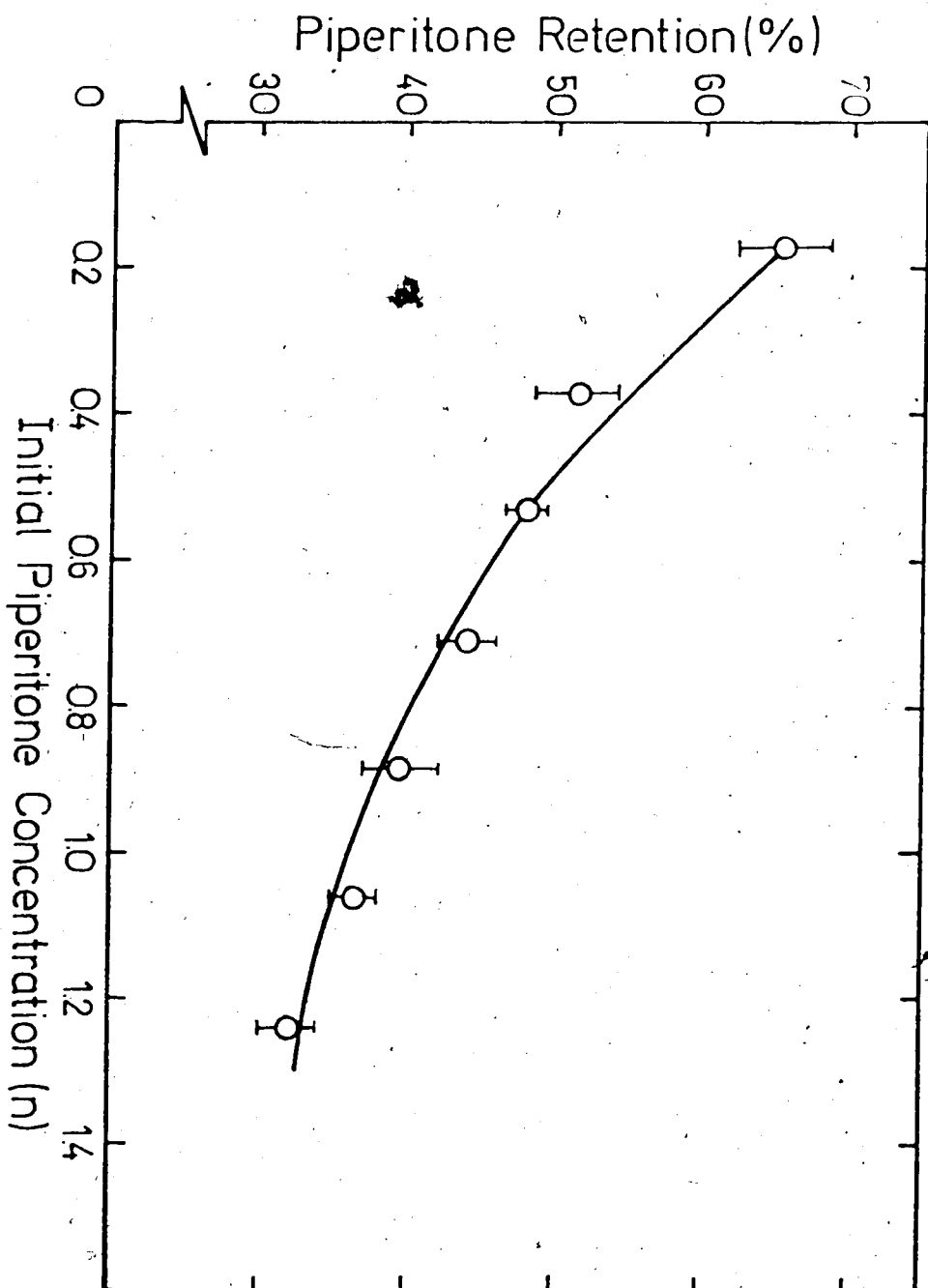
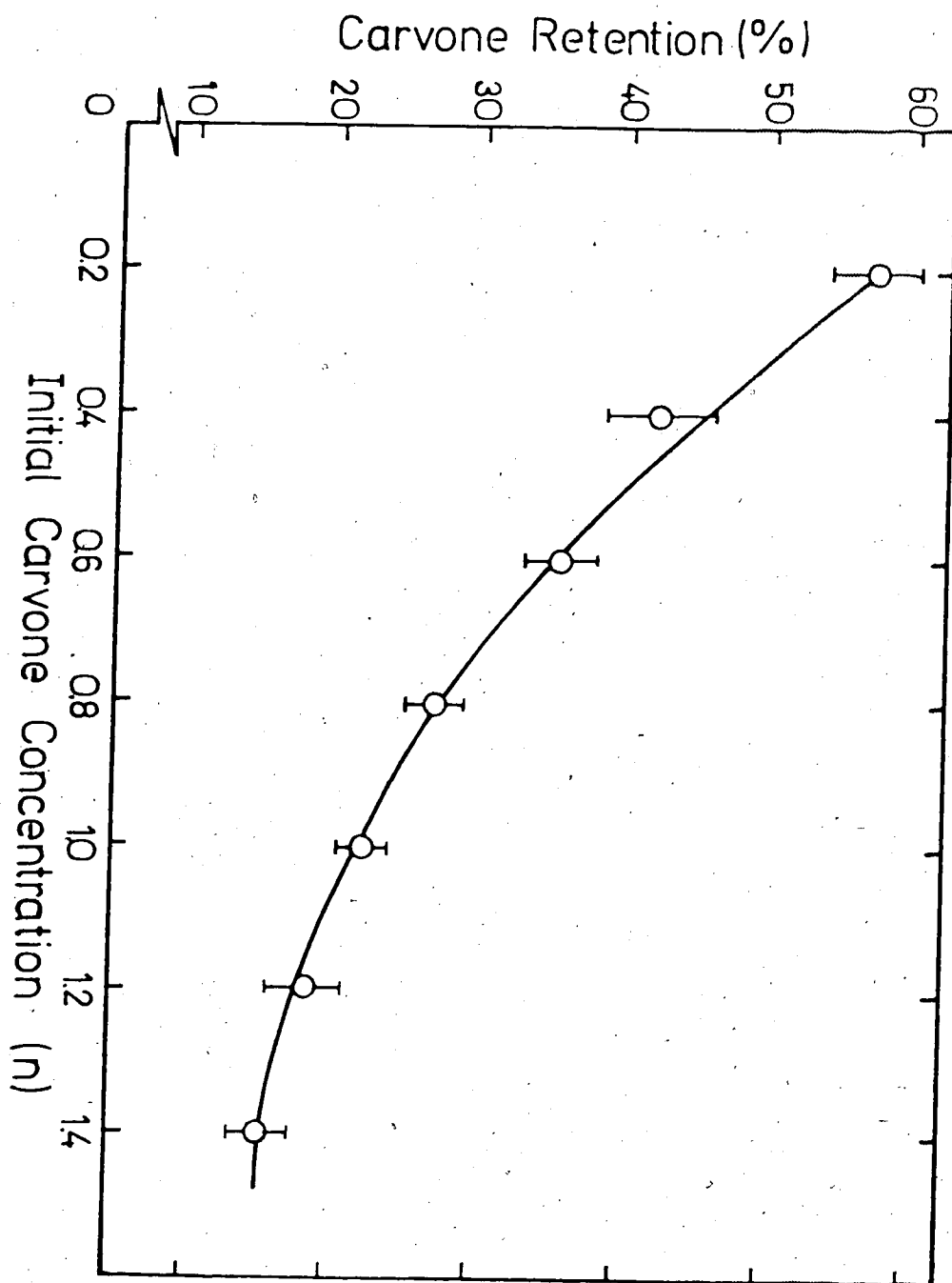Figure 34. Piperitone retention as a function of initial piperitone concentration in 10% sucrose.

Figure 35. Carvone retention in 1% gum arabic as a function of initial carvone concentration.
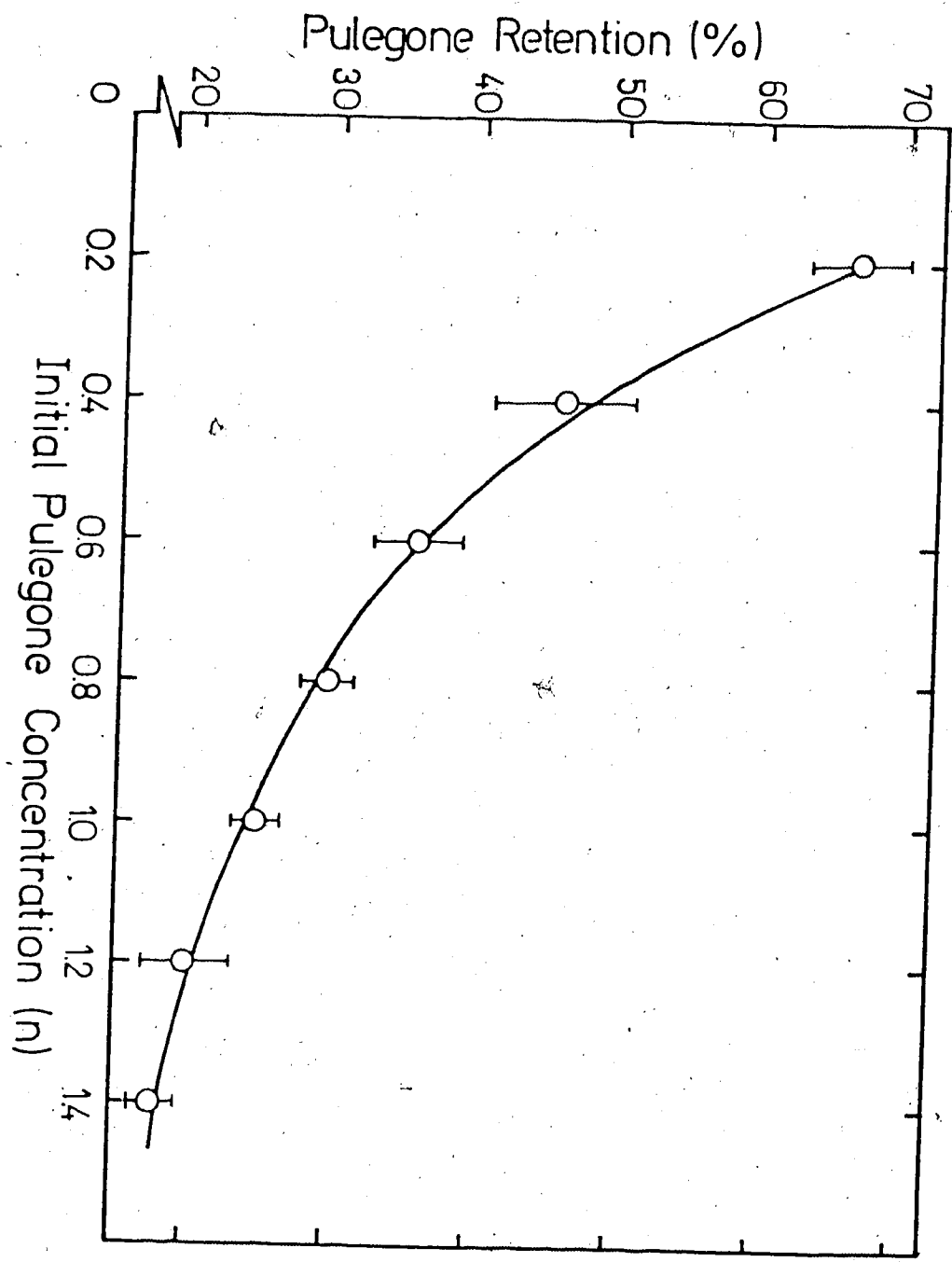
Figure 36. Pulegone retention in 1% gum arabic as a function of initial pulegone concentration.
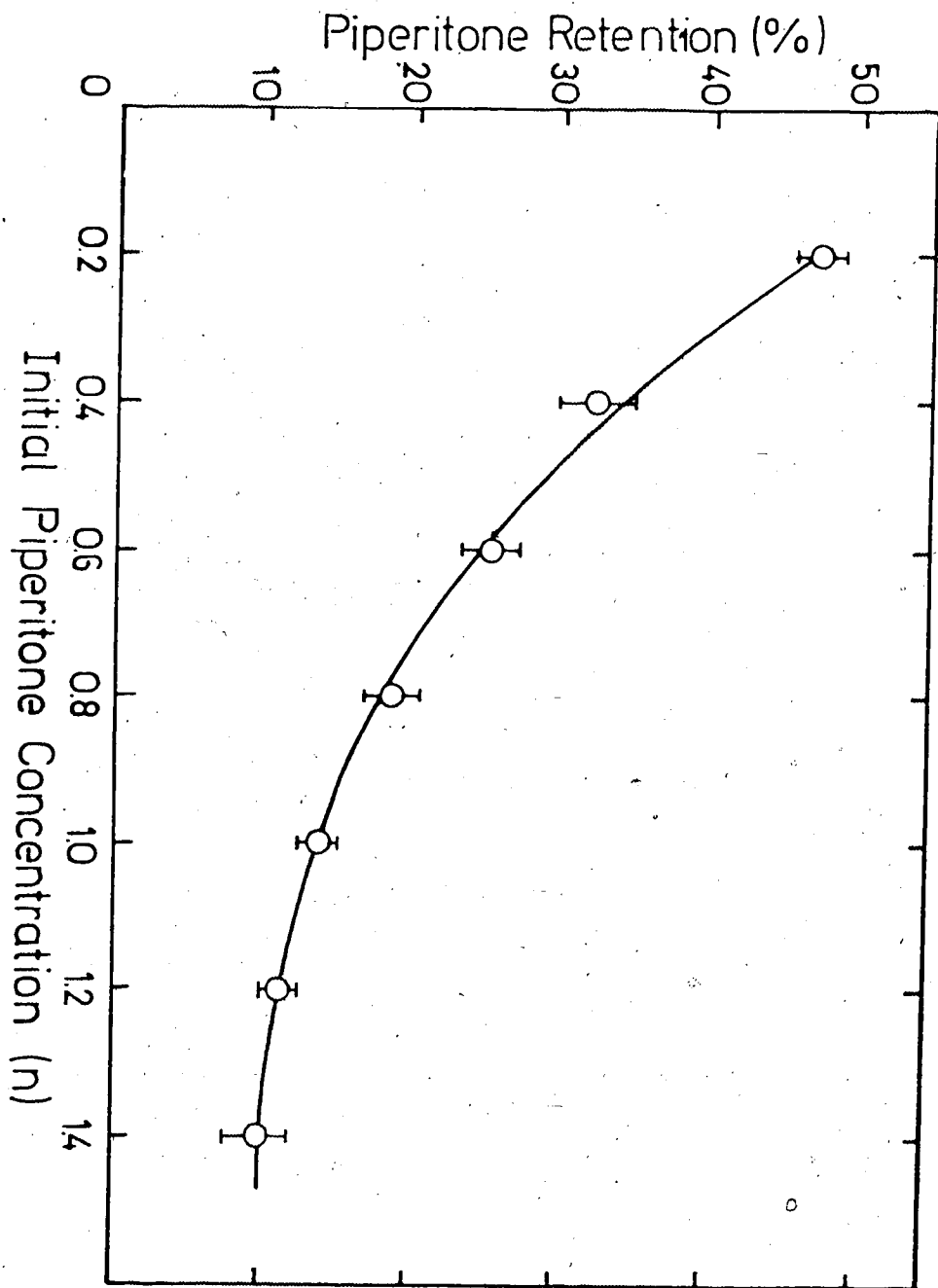
Figure 37. Piperitone retention in 1% gum arabic as a function of initial piperitone concentration.
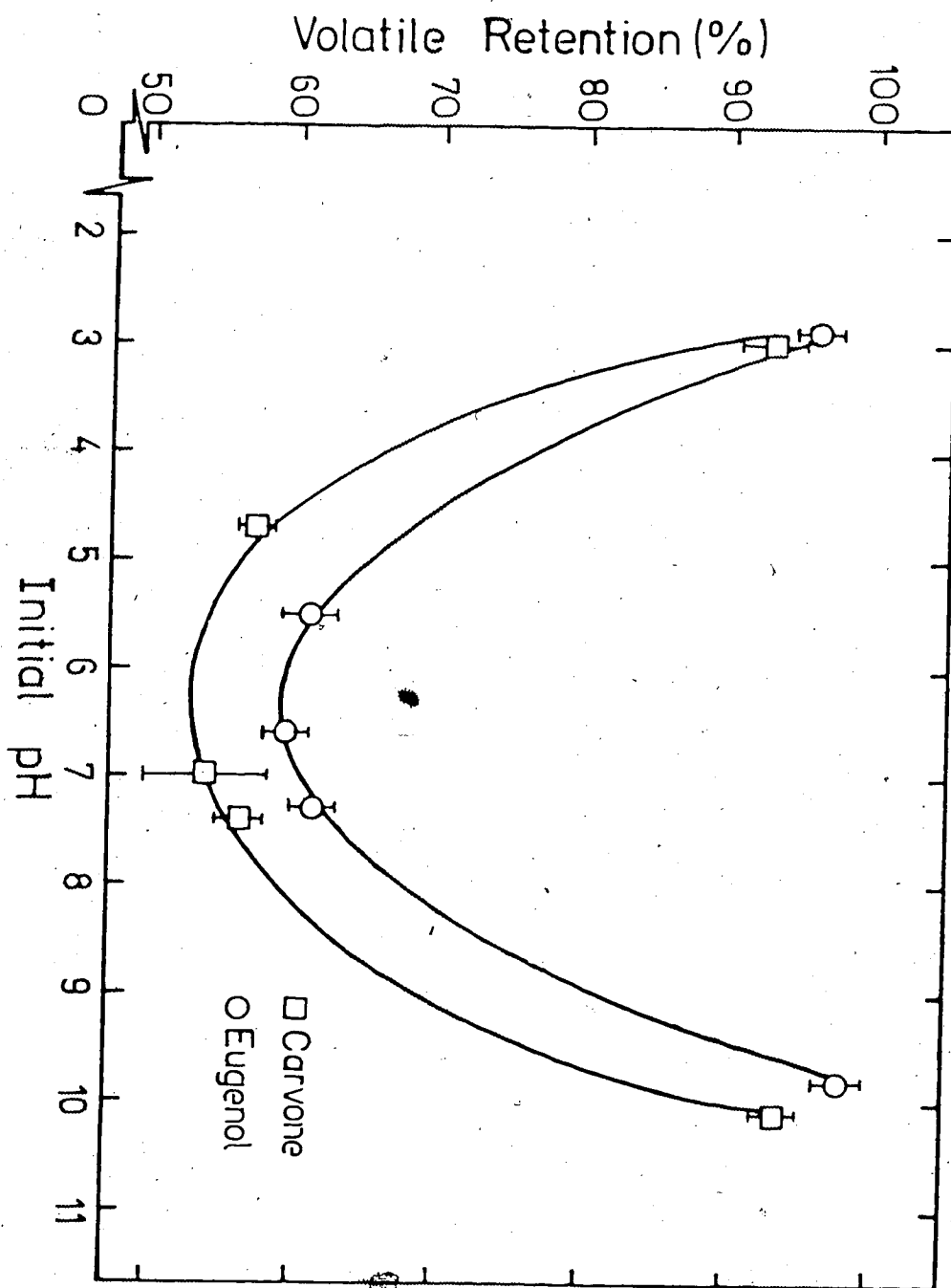
Figure 38. Variation of carvone and eugenol retention in 10% sucrose as a function of initial pH.
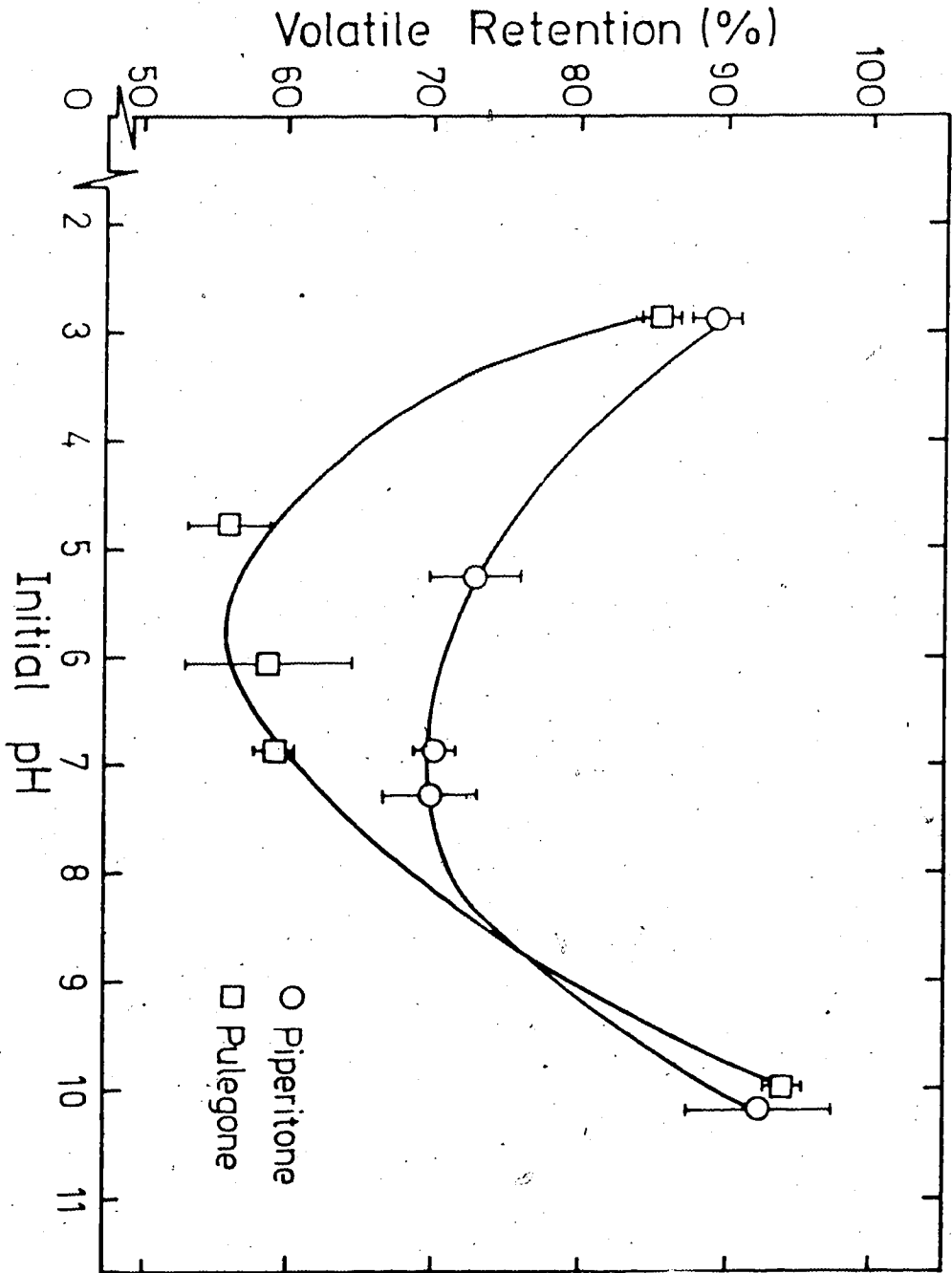
Figure 39. Piperitone and pulegone retention in 10% sucrose as a function of initial pH.
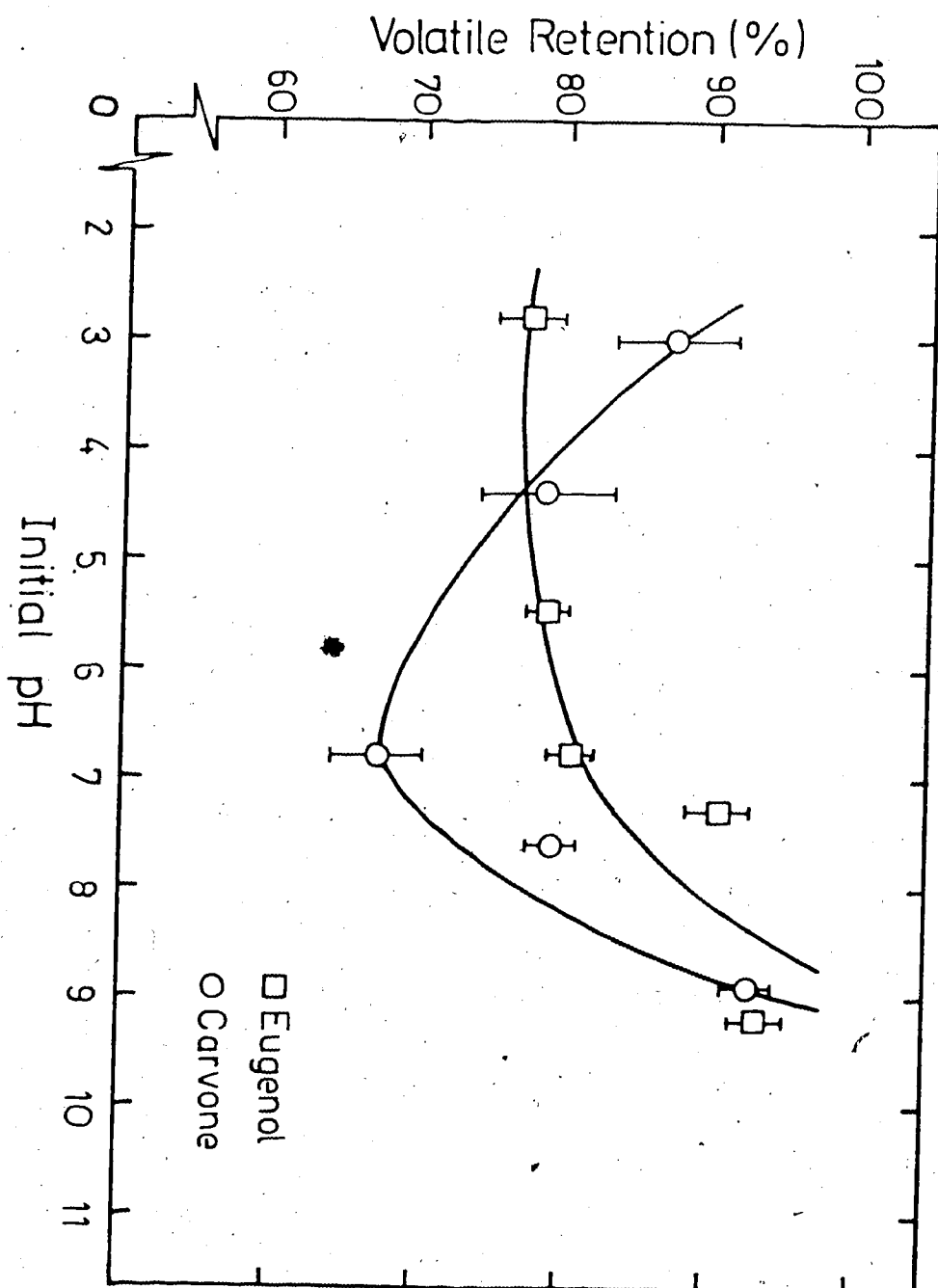
Figure 40. Carvone and eugenol retention in 10% glucose as a function of initial pH.
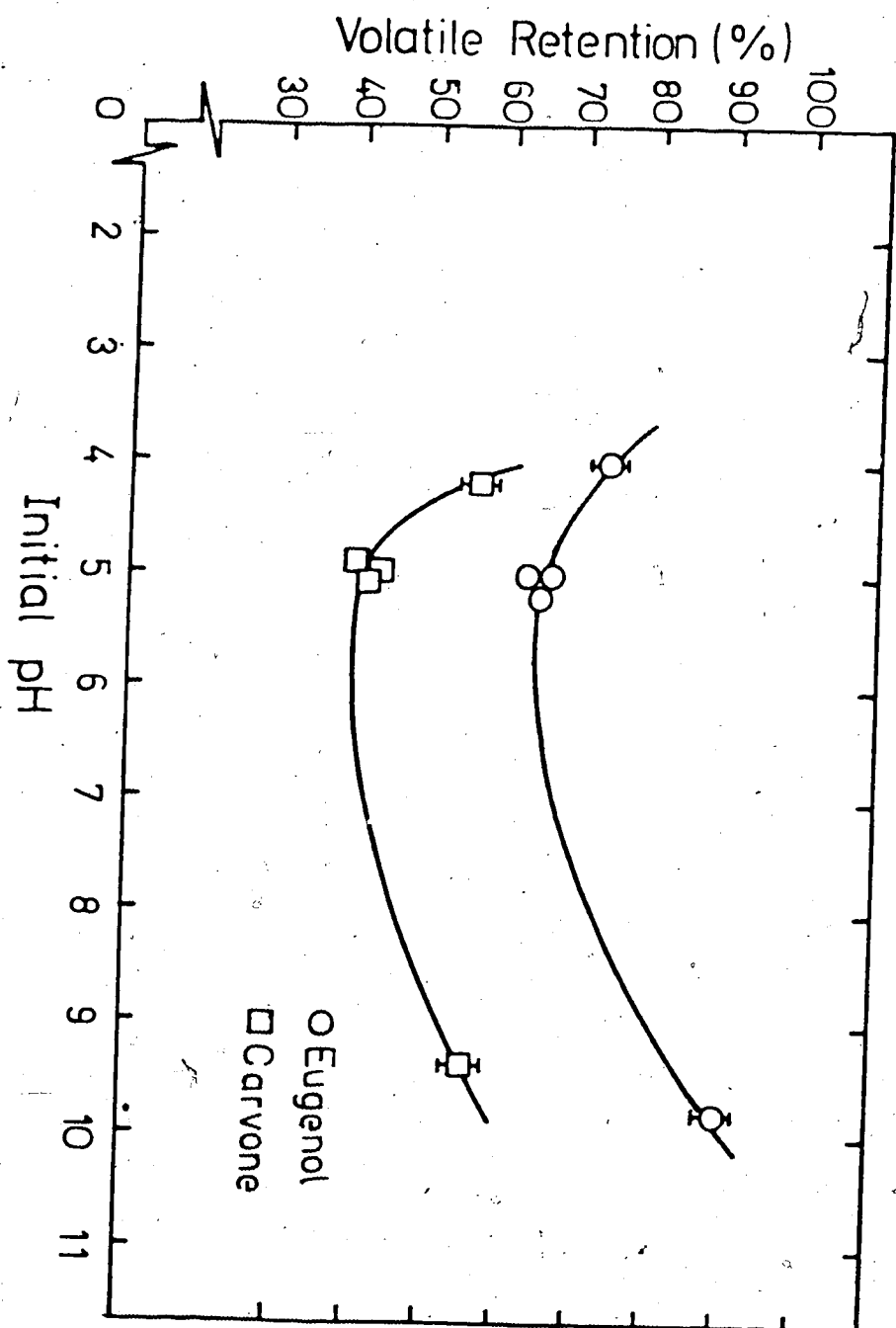
Figure 41. Retention of carvone and eugenol in 1% gum arabic as a function of initial pH.
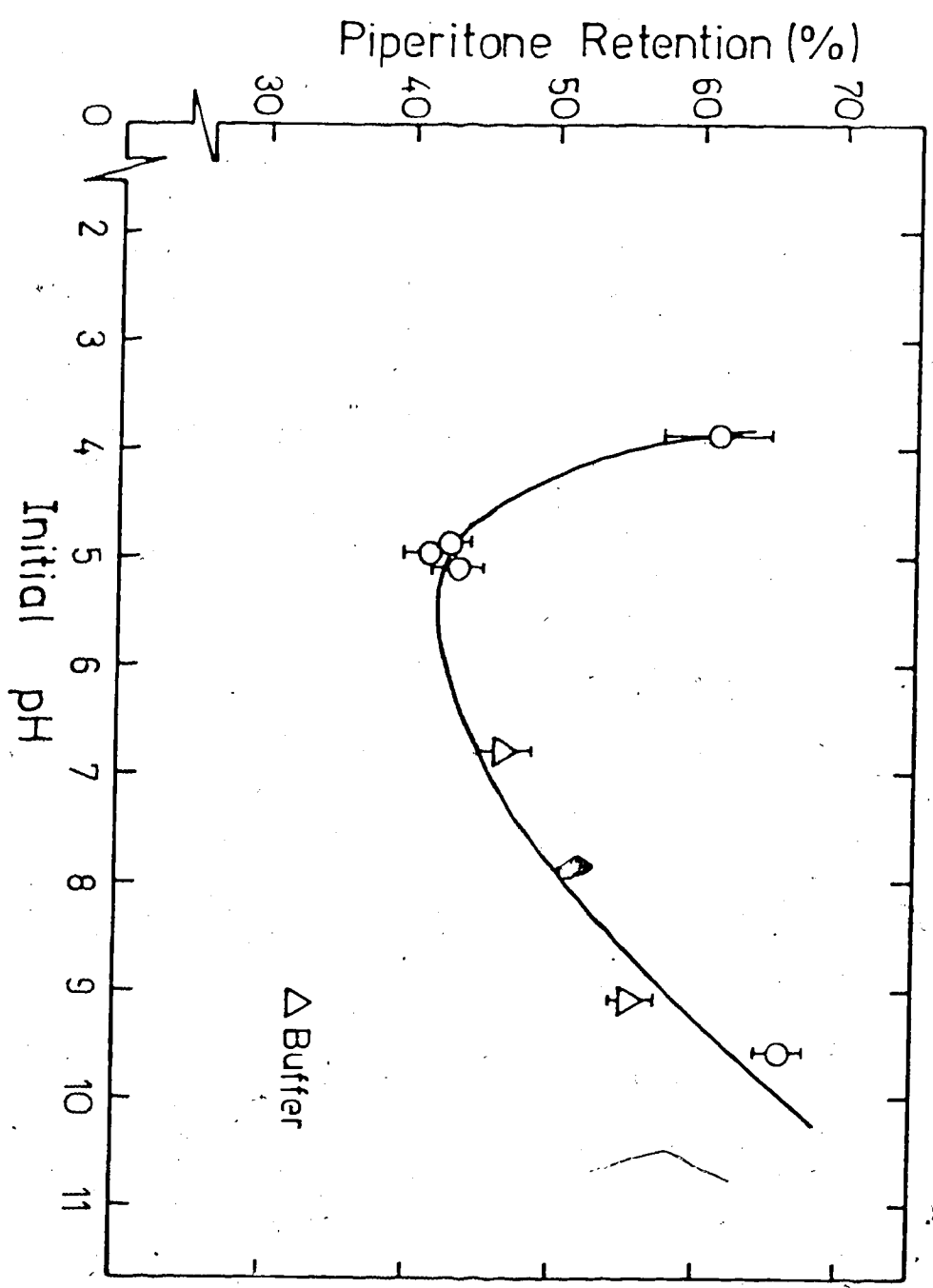
Figure 42. Piperitone retention in 1% gum arabic as a function of initial pH.
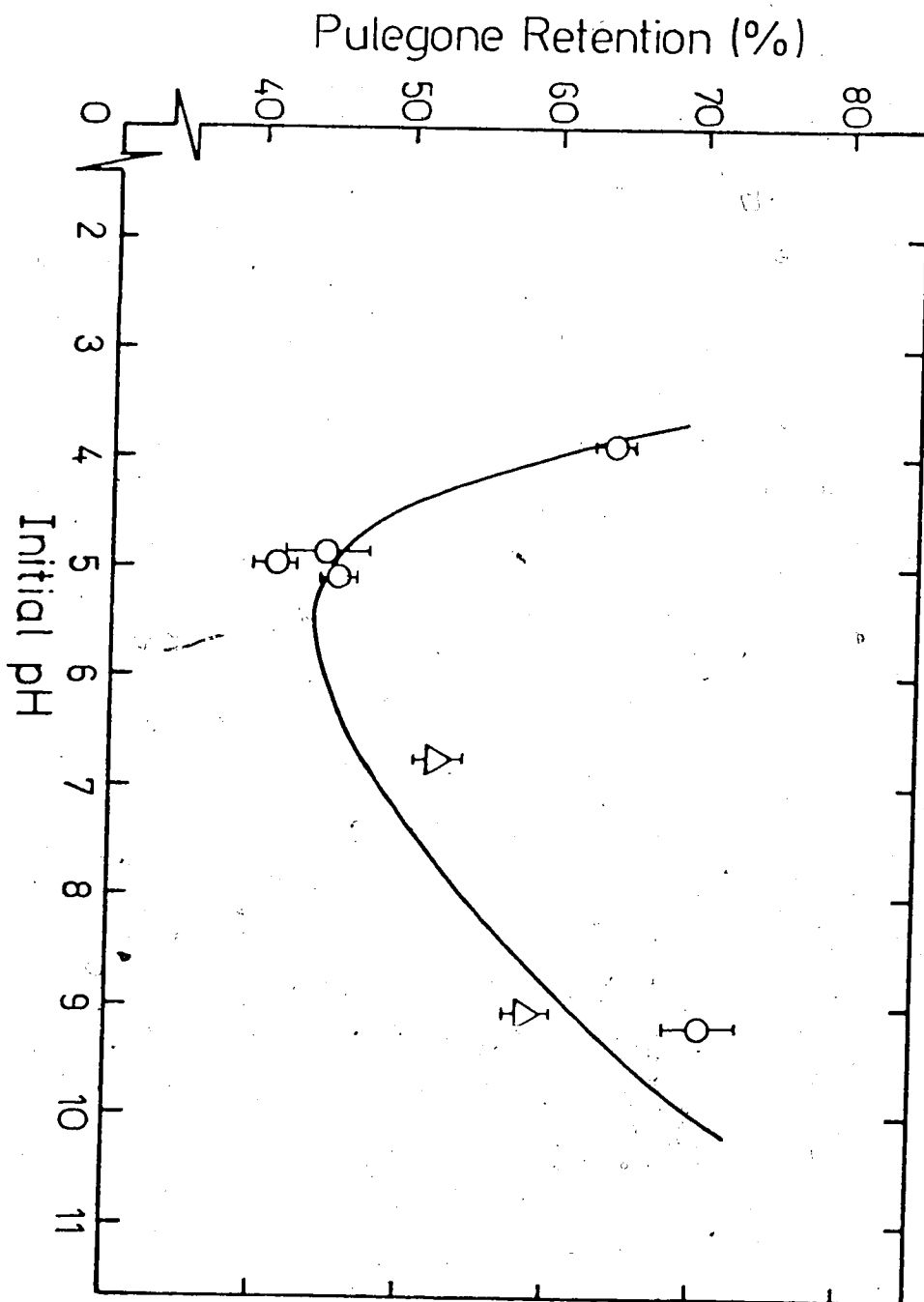
Figure 43. Pulegone retention in 1% gum arabic as a function of initial pH.
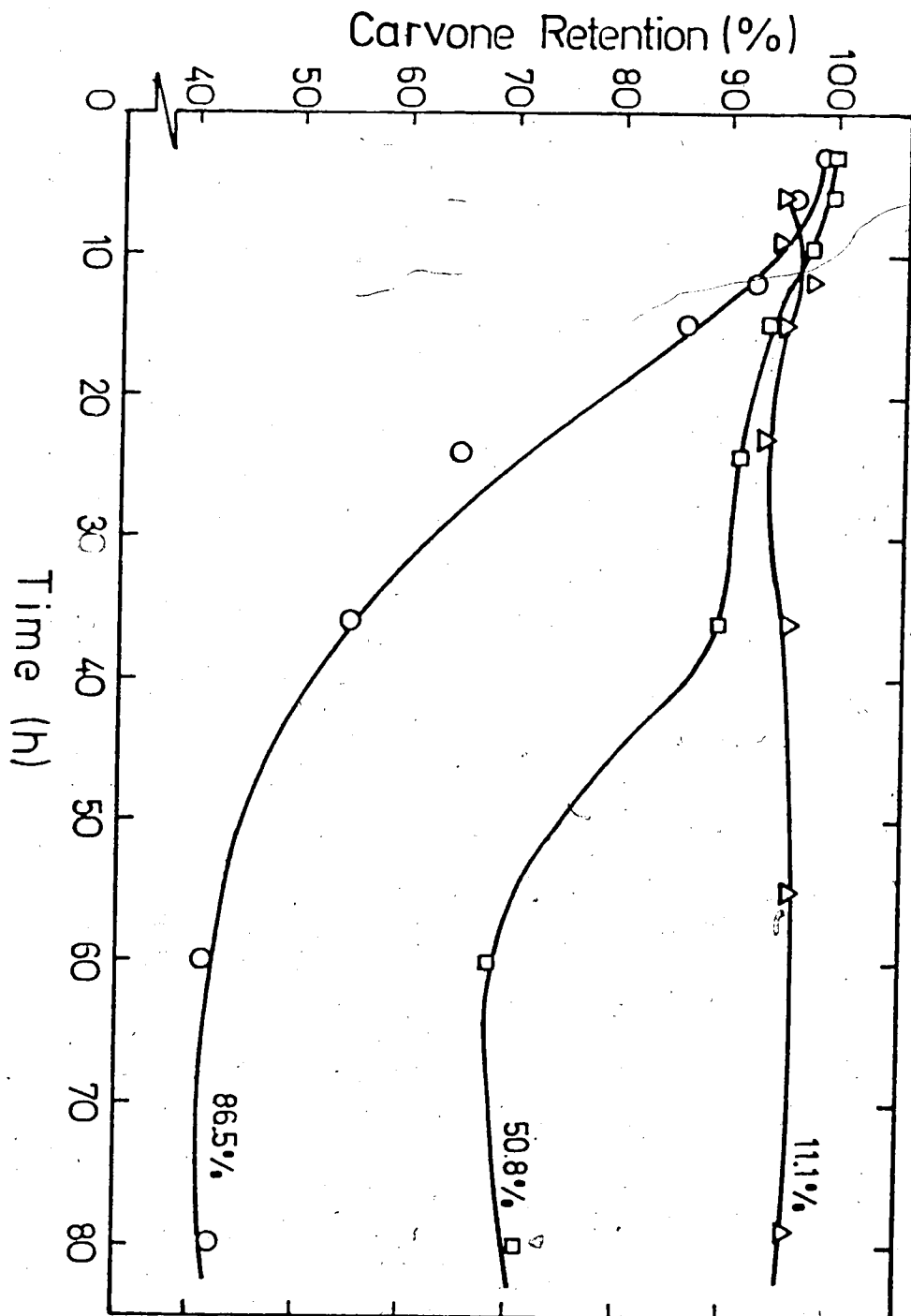
Figure 44. Retention of carvone after rehumidification of freeze-dried sucrose solutions at different relative humidities.
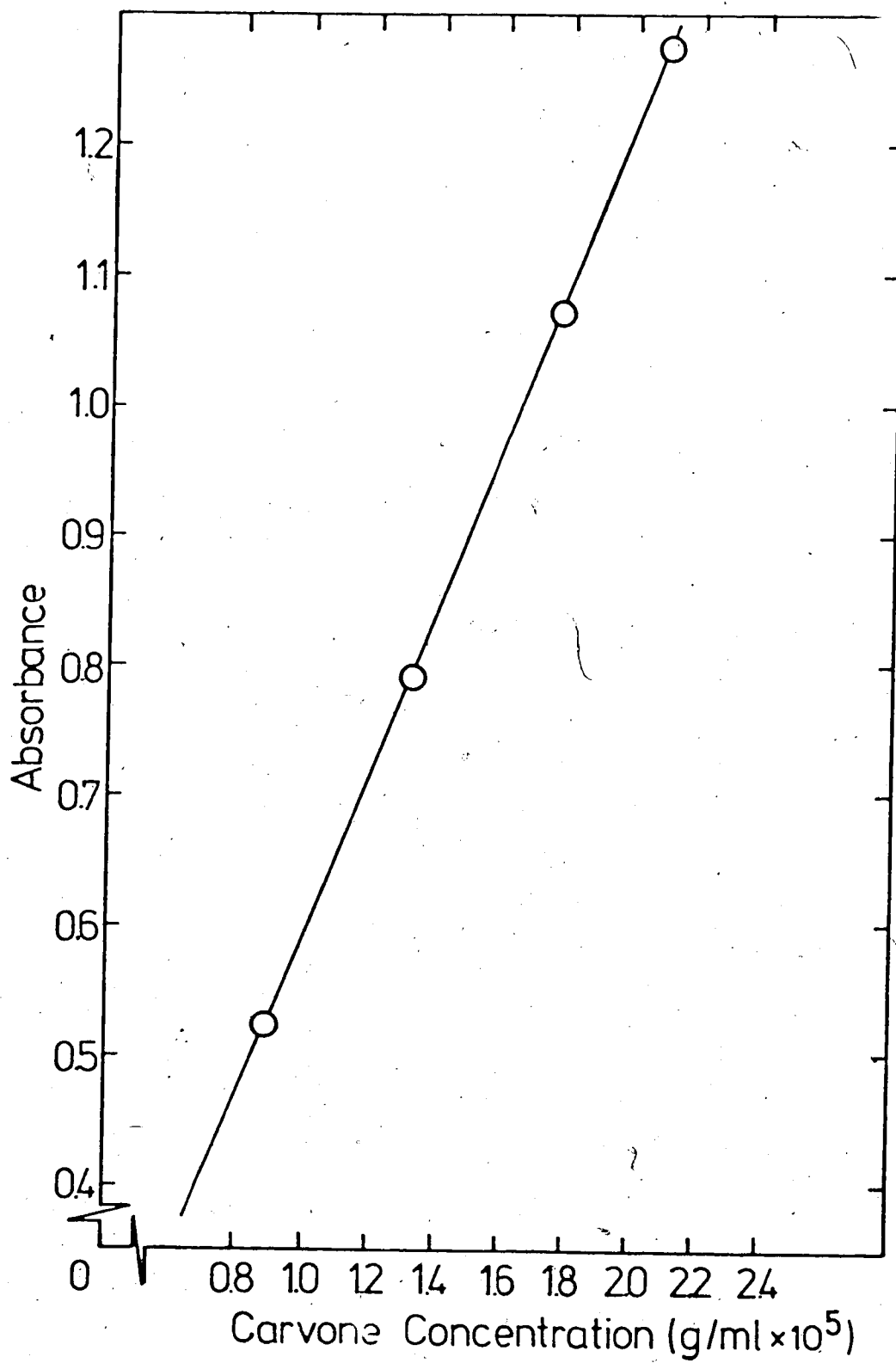
Figure 45. Standard curve for carvone in
water at λ=241.5 nm.
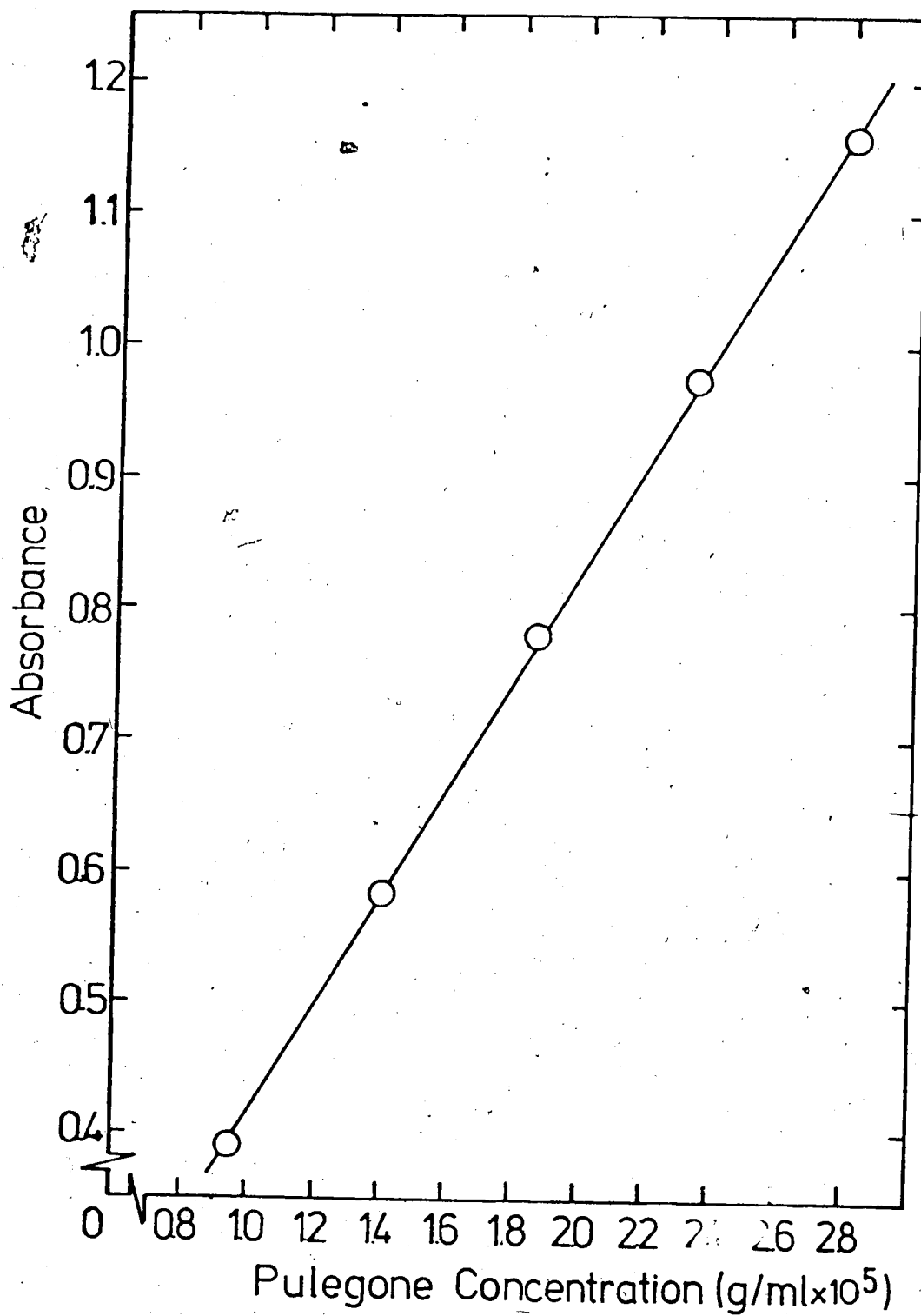
Figure 46. Standard curve for pulegone in water at λ=263.0 nm.
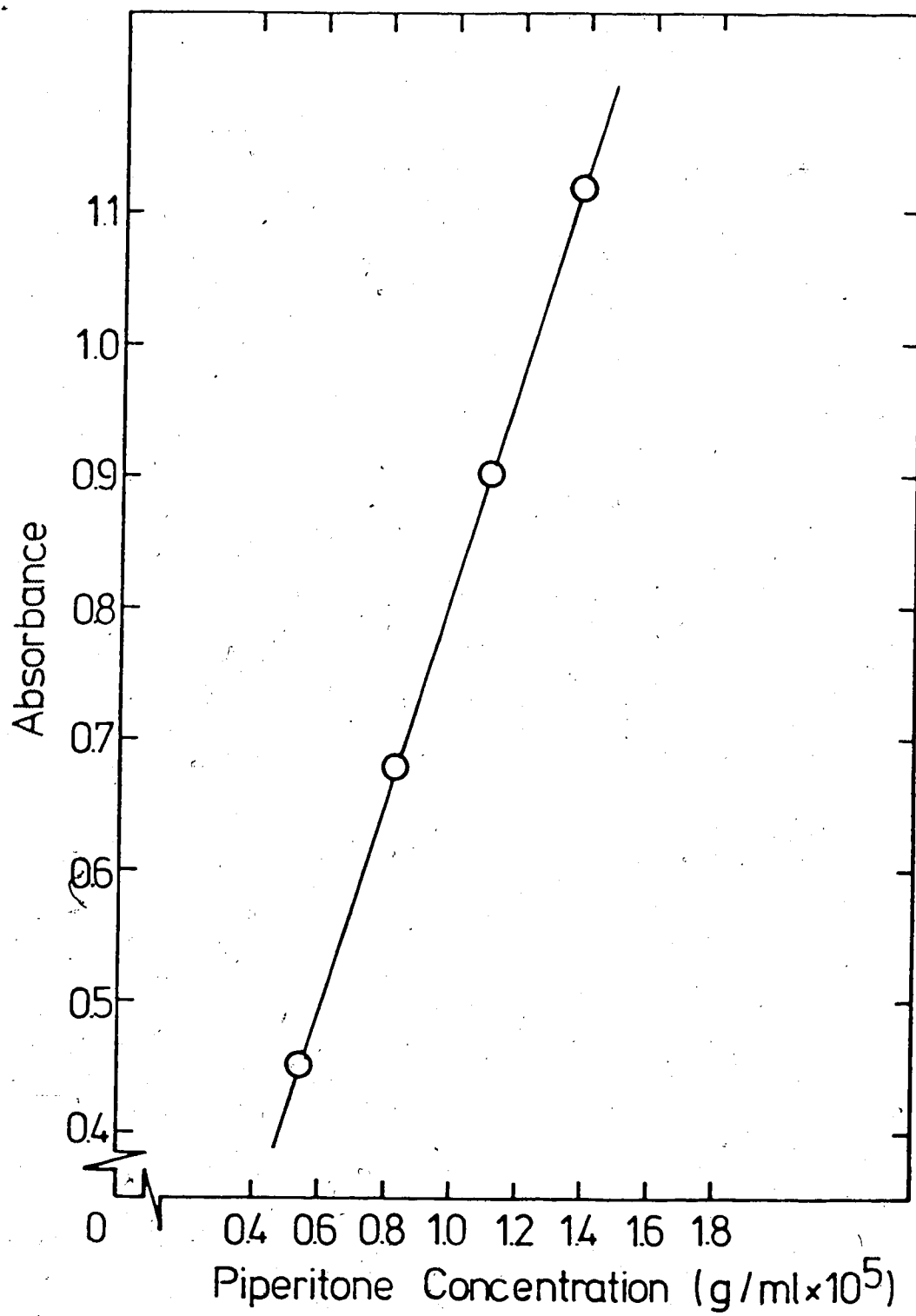
Figure 47. Standard curve for piperitone in
water at λ=242.5 nm.
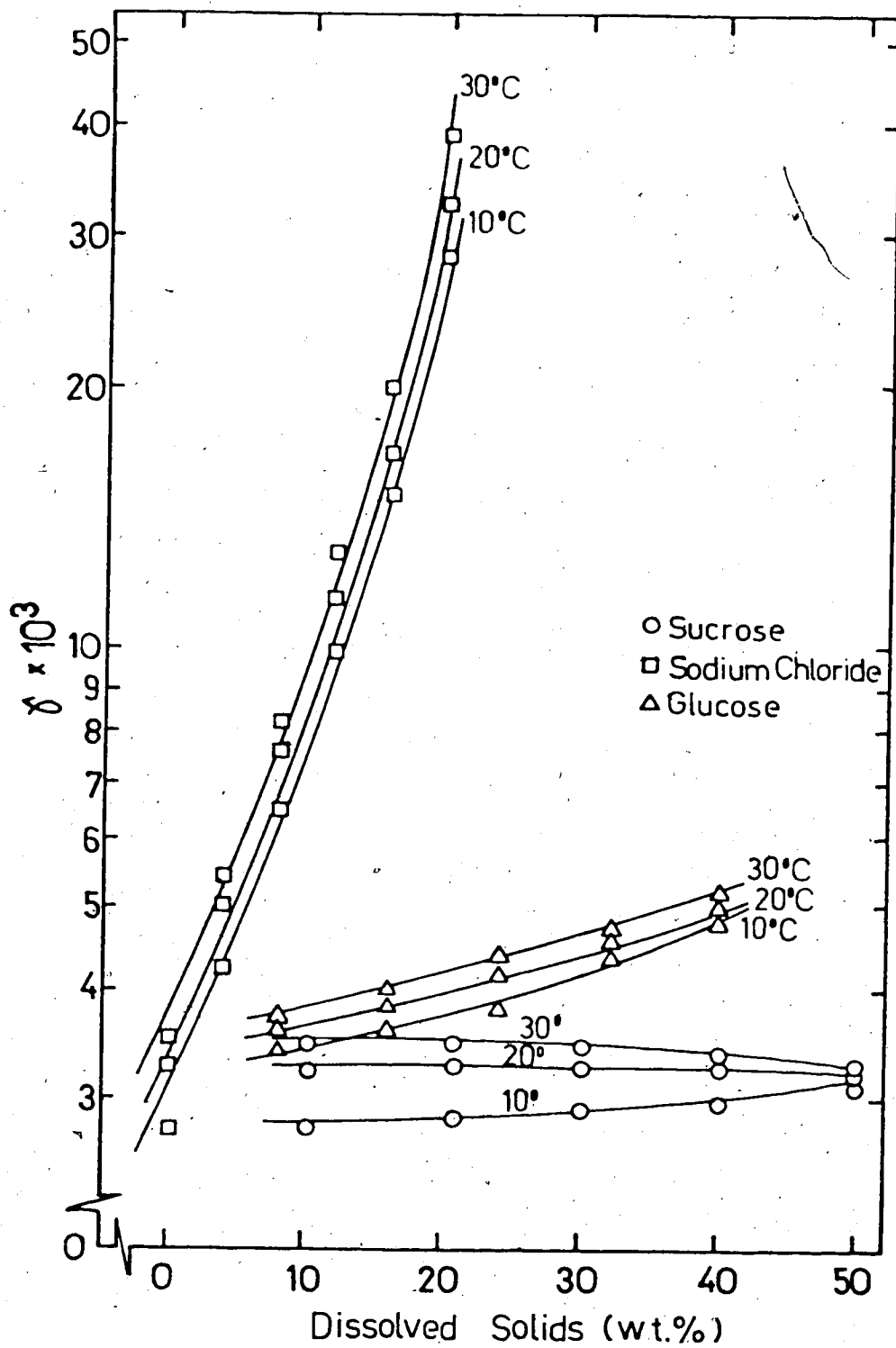
Figure 48. Activity coefficients of piperitone
as a function of temperature and
dissolved solids content.
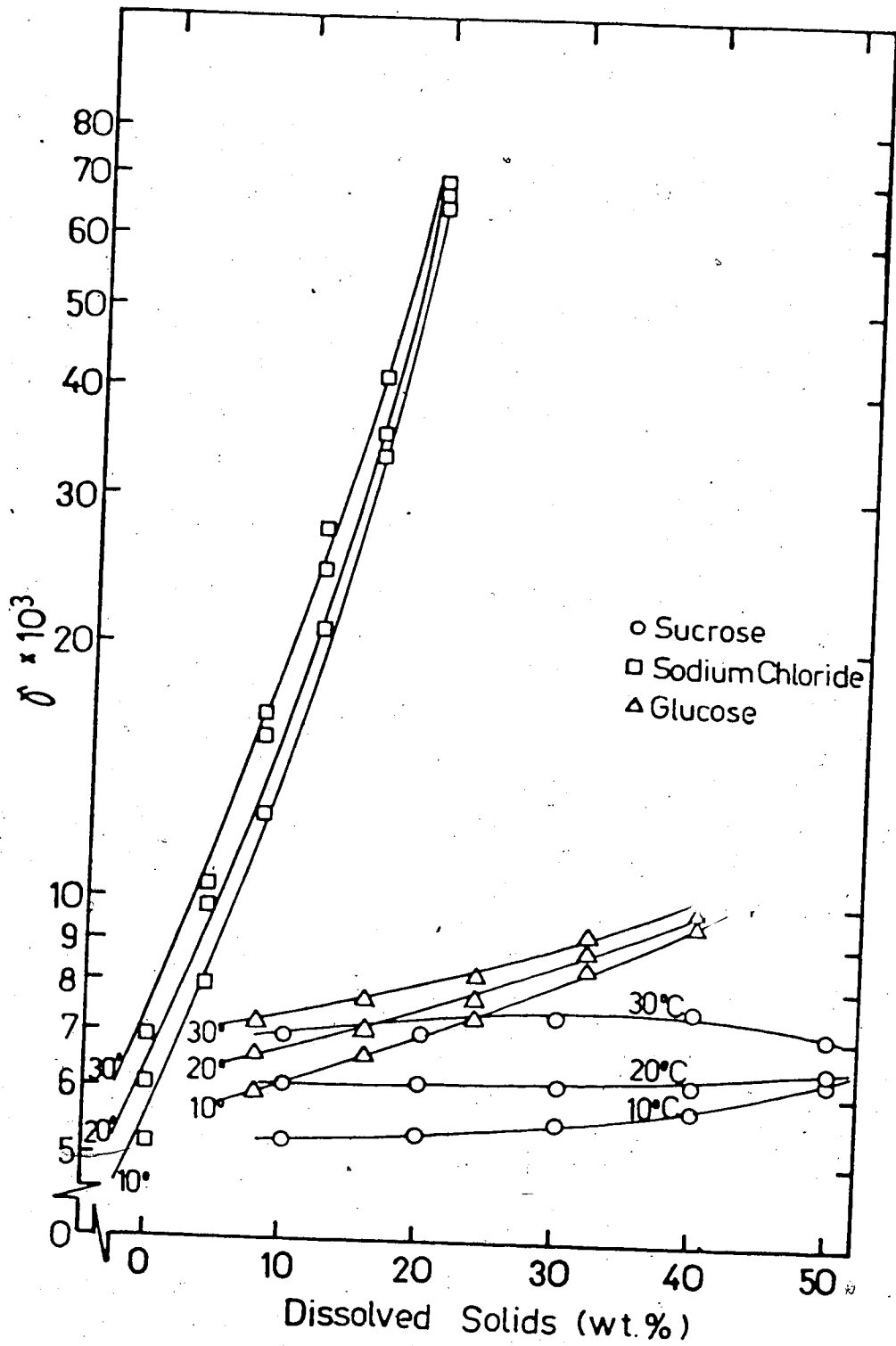
Figure 49. Activity coefficients of pulegone as a function of temperature and dissolved solids content.
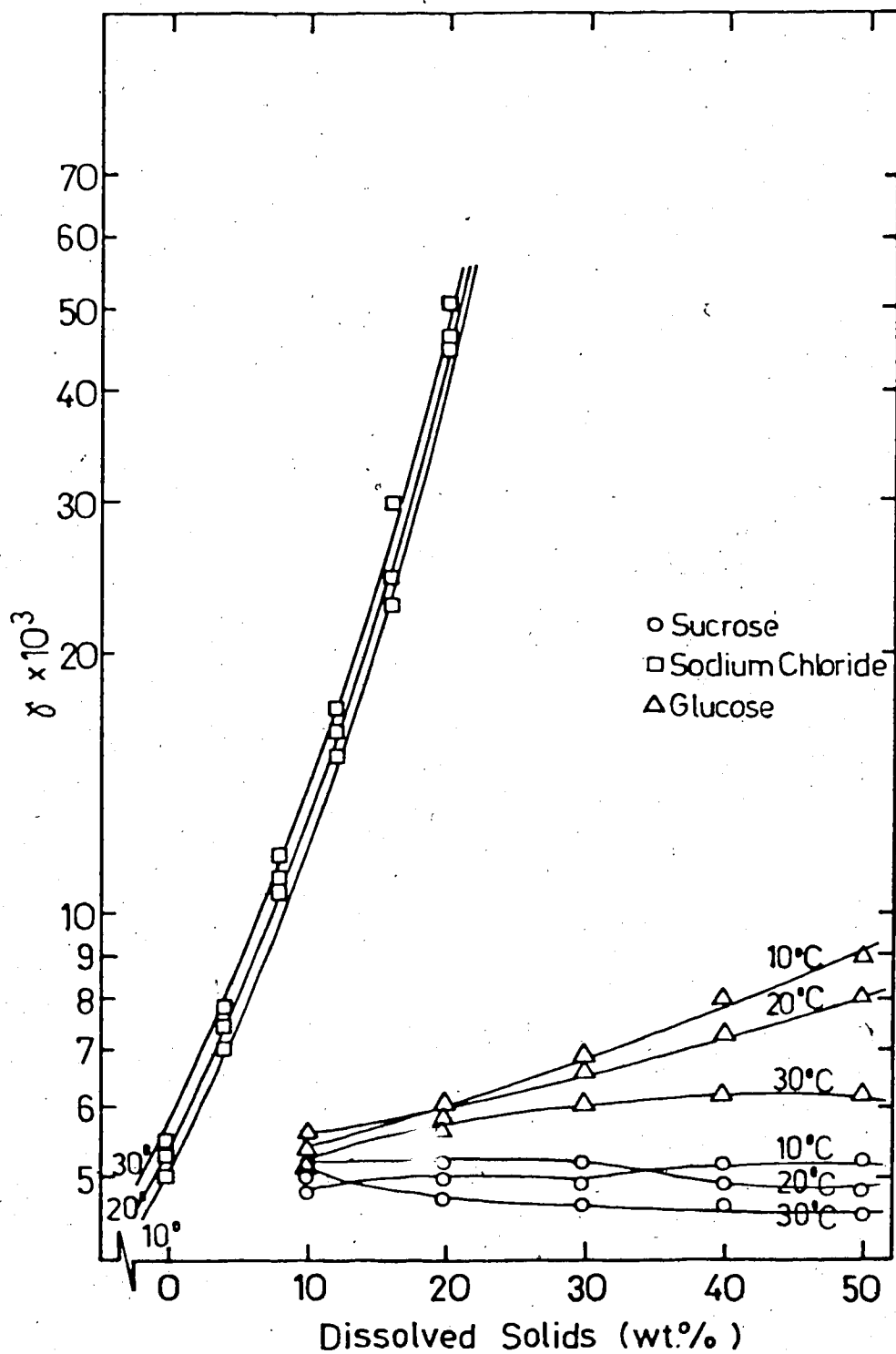
Figure 50. Activity coefficients of carvone as a function of temperature and dissolved solids content.
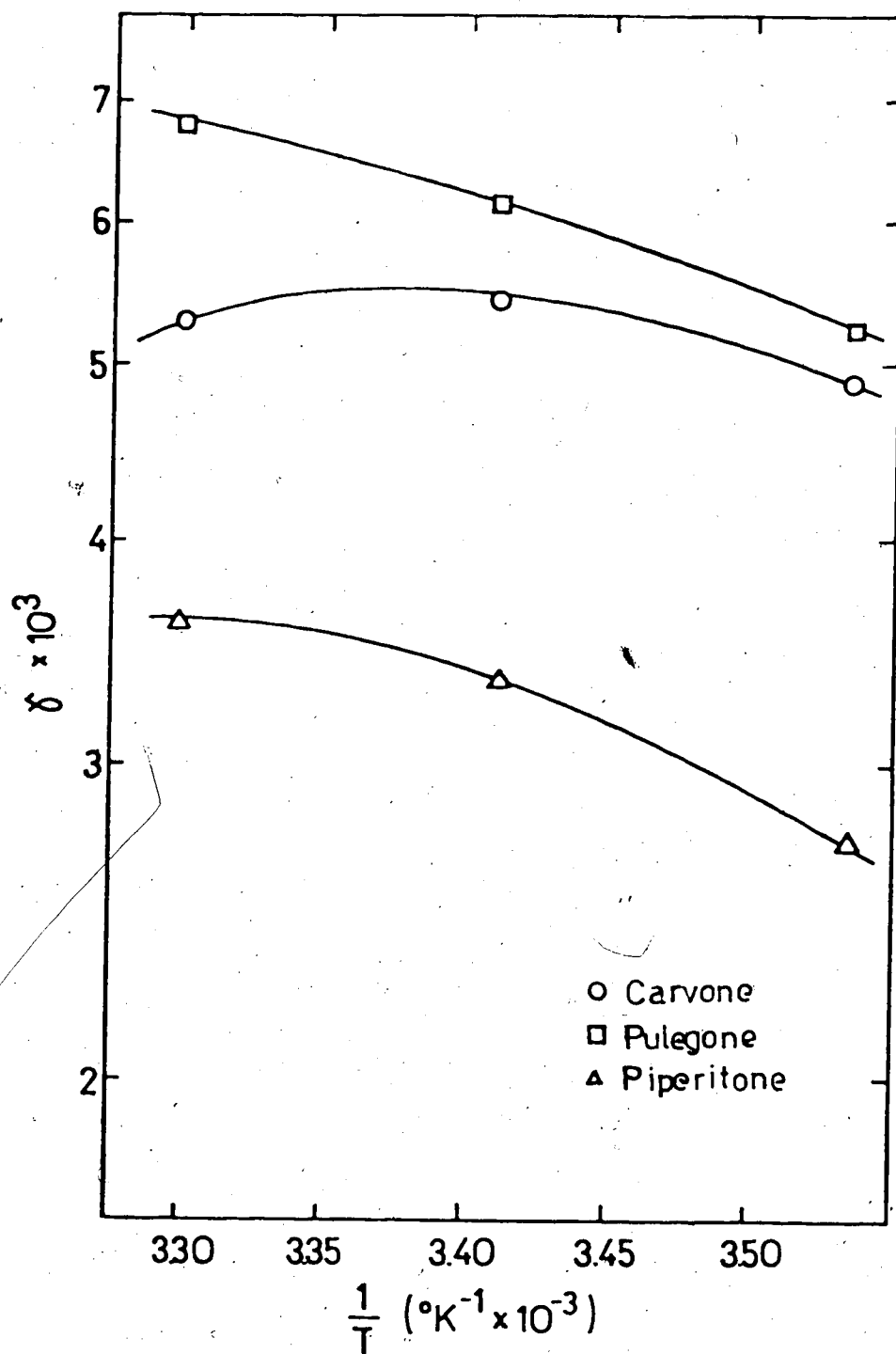
Figure 51. Curves relating γ and T in the determination of ΔHs for piperitone, pulegone and carvone in water.

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V. Appendices

APPENDIX 1   Derivation of Equation(5)

The equation required to calculate the diffusion coefficient for a two-compound system from measurements of the concentration gradient in a free diffusion experiment is given by Longsworth (1945),

$$\frac{\partial c}{\partial x} = \frac{\Delta c}{2\sqrt{\pi D t}} e^{-x^2/4Dt} \qquad (1)$$

where Δc is the concentration difference of the diffusing substance, D is the diffusion coefficient and c is the concentration at a distance x from the interface at time t. The term $\partial c/\partial x$ refers to the actual concentration gradient within the diffusion cell.

The dimensions of the cell are magnified by the lenses of the schlieren optical system. The camera lens magnifies the schlieren curve both in the x and y directions and this magnification by the camera lens is represented by the magnification factor, m_1. The cylindrical lens magnifies the schlieren curve only in the y direction and gives rise to the magnification factor, m_2. Therefore the displacement in the y direction as seen on the film is,

$$Y = La \ \frac{dc}{dx} \ \frac{dn}{dc} \ \frac{m_1 m_2}{\tan\theta} \qquad (2)$$

where L is the distance from the middle of the cell to
the plane of the schlieren analyzer, a is the thickness
of the diffusion cell, dn/dc is the refractive index
increment and θ is the angle of the schlieren analyzer.
The displacement in the y direction is seen to be
influenced by both m_1 and m_2. However the displacement
in the x direction as recorded on film is only a function
of m_1,

$$X = m_1 x \qquad (3)$$

where x again refers to cell dimensions.

Enlargement of the image using the slide
projector introduces an additional magnification factor,
β_1, which is equal for both x and y directions. Therefore
the displacements in the y and x directions as registered
on the projected image are given by Equations (4) and
(5) respectively.

$$y^1 = \beta_1 \ La \ \frac{dc}{dx} \ \frac{dn}{dc} \ \frac{m_1 m_2}{\tan\theta} \qquad (4)$$

$$x^1 = \beta_1 X = m_1 x \beta_1 \qquad (5)$$

The quantities y^1 and x^1 are values measured on the vertical gradient.

Equation (4) may be rearranged to yield Equation (6).

$$\frac{dc}{dx} = \frac{y^1 \tan\theta}{\beta_1 La \; \frac{dn m_1 m_2}{dc}} \qquad (6)$$

Equation (6) relates the concentration gradient in the diffusion cell to the measured quantity y^1.

Substitution of Equation (5) an   nto Equation (1) yields,

$$y^1 = \frac{\alpha \Delta c}{2\sqrt{\pi Dt}} e^{-(x^1)^2/\beta^2 4Dt} \qquad (7)$$

where

$$\alpha = \frac{\beta_1 \; La \; m_1 m_2}{\tan\theta} \; \frac{dn}{d\theta} \qquad (8)$$

$$\beta = \beta_1 m_1 \qquad (9)$$

β is the overall magnification in the x direction and is

obtained from the measurement of the reference lines

in the counterbalance of the Analytical-D rotor.

Rearranging Equation (7) and taking the

natural logarithms yields Equation (10).

$$\ln(y^1 t^{\frac{1}{2}}) = \ln \frac{\alpha \Delta c}{2\sqrt{\pi D}} - \frac{x^{1^2}}{\beta^2 4Dt} \qquad (10)$$

Equation (10) corresponds to Equation (5) of the text.

Since α, Δc, π, D and β are all constants for a par-

ticular diffusion experiment, a plot of $\ln(y^1 t^{\frac{1}{2}})$ vs.

$(x^1)^2/t$ yields a straight line of slope $-1/\beta^2 4D$ and an

intercept of $\ln(\alpha \Delta c/2 \pi D)$ and thus permits a calculation

of D from the slope.

APPENDIX 2   Program for Calculation of D

```
DIMENSION Y(15,8),T(15),YO(15),X(11),Z(200),XT(200)
DIMENSION TO (15)
DATA X/0.,1.,2.,3.,4.,5.,6.,7.,8.,9.,10./
READ(1,100)N
DO 1 1=1,N
READ(1,110)DC,B,C1,C2,DX
READ(1,100)N1
DO 4 M=1,N1
READ(1,120)T(M),(Y(M,J),J=1,8)
N12=N1/2
DO 6 M=1,N12
DO 5 J=1,8
Z(J)=ALOG((Y(2*M-1,J)+Y(2*M,J))/2.SORT(T(2*M-1)))
XT(J)=(X(J)*DX)**2/T(2*M-1)
CALL SLIN1(XT,Z,8,A1,B1,0)
YO(M)=EXP(-B1)*SORT(T(2*M-1)
TO(M)=SORT(T(2*M-1))
YM=1./YO(M)
YM1=Y(2*M-1,1)
TM=T(2*M-1)
WRITE(6,150)TM,YM,YM1
CALL SLIN1(TO,YO,N12,A0,B0,0)
FORMAT(2X,3(E12.5))
DT=B0/A0
WRITE(6,140)DT
FORMAT(10X,'ZERO TIME CORRECTION =',F7.2)
K=0
DO 3 J=1,N1
TC=T(J)+DT
DO 2 L=1,8
IF(Y(J,L).EQ.0.)GO TO 3
K=K+1
Z(K)=ALOG(Y(J,L)*SORT(TC))
XT(K)=(X(L)*DX)**2/TC
CONTINUE
CONTINUE
CALL SLIN1(XT,Z,K,A1,B1,0)
D=-1./(4.*B*B*A1)*I.E-6
ALPHA=2.*SORT(3.14159*D)*EXP(B1)/DC
CAV=(C1+C2)/2.
WRITE(6,130)DC,B,CAV,D,ALPHA
FORMAT(I2)
FORMAT(5E12.5)
FORMAT(12E10.3)
FORMAT(2X,'DC=',F7.4,2X,'MAGNIFICATION=',F7.3,//,2X,'C='
```

```
      F7.4,
     *2X,'DIFFUSION COEFFICIENT =',E12.5,2X,'ALPHA=',E12.5/)
      CONTINUE
      STOP
      END
```

APPENDIX 3   Determination of the Zero Time Corrections

Because the starting boundary may not be per-
fectly sharp, use of the observed times, t^1, may lead
to slightly erroneous values/D. Therefore all values of
t, employed in calculating D are corrected by using the
zero time correction, Δt.

$$t = t^1 + \Delta t$$

The zero time correction is calculated from
a plot of $1/(hmax)^2$ vs. t^1, where hmax is the height
of the schlieren peak at x=0 for the photograph taken
at time t^1. Δt values correspond to the intercept on
the t^1 axis. In all cases Δt has been calculated from
a least squares analysis of $(1/hmax)^2$ and t^1, and the
corrected t^1 values, i.e. t, have been incorporated into
the linear regression from which the diffusion coefficients
are calculated (Equation (5) of text).

APPENDIX 4 Equation for Calculating ΔGh

The chemical potential of a dilute volatile component (i) in aqueous solution is given by the expression,

$$\mu_i^L = \mu_i^* + RT\ln X_i \gamma_i$$

where μ_i^L = chemical potential of the volatile solute in a dilute aqueous solution

μ_i^* = standard chemical potential of the volatile solute in an infinitely dilute reference state

R = gas constant

T = absolute temperature

X_i = mole fraction of the solute in solution

γ_i = activity coefficient of the volatile solute

The chemical potential of the volatile solute in the headspace above the solution is given by the expression,

$$\mu_i^V = \mu_i^O + RT\ln p_i$$

where μ_i^V = chemical potential of volatile solute in the headspace above the solution

μ_i^O = standard chemical potential of volatile solute in the pure gaseous reference state

p_i = vapor pressure of the volatile

At equilibrium, $\mu_i^L = \mu_i^V$, hence

$$\mu_i^* - \mu_i^O - RT\ln\frac{pi}{\gamma_i}$$

Using an infinitely dilute reference state $(\gamma_i=1)$ at saturation $(X_i=X_s)$,

$$\mu_i^* - \mu_i^O = \Delta Gh = RT\ln\frac{pi}{Xs}$$

This Equation corresponds to Equation 2 in t III of the text.

APPENDIX 5   Equation for Calculating ΔHs

The chemical potential for a dilute volatile component (i) in aqueous solution is given by the expression,

$$\mu_i^L = \mu_i^* + RT\ln X_i \gamma_i$$

where
μ_i^L = chemical potential of the volatile component in a dilute aqueous solution

μ_i^* = standard chemical potential of the pure liquid volatile component at a specified temperature and pressure

X_i = mole fraction of the volatile solute in the solution

γ_i = activity coefficient of the volatile solute in the solution

Dividing by T and differentiating with respect to T (P, X = constant)

$$\frac{\partial \frac{\mu_i^L}{T}}{\partial T} = \frac{\partial \frac{\mu_i^*}{T}}{\partial T} + \frac{R\partial \ln X_i}{\partial T} + \frac{R\partial \ln \gamma_i}{\partial T}$$

But

$$\frac{\partial \frac{\mu_i^L}{T}}{\partial T} = \frac{-\bar{H}_i^L}{T^2} \quad \text{and} \quad \frac{\partial \frac{\mu_i^*}{T}}{\partial T} = \frac{-h_i^L}{T^2}$$

Therefore

$$\frac{-\bar{H}_i^L}{T^2} = \frac{-h_i^L}{T^2} + \frac{R\partial \ln \gamma_i}{\partial T}$$

$$\frac{\partial \ln \gamma i}{\partial T} = \frac{hi^L - \bar{H}i^L}{RT^2}$$

This expression may be rearranged to

$$\frac{\partial \ln \gamma i}{\partial \frac{1}{T}} = \frac{\bar{H}i^L - hi^L}{R} = \frac{\Delta Hs}{R}$$

This Equation corresponds to Equation 4 in Part III of the text.