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ULTRAFILTRATION OF SALTED ACID WHEY

BY

AKHILESH GAUTAM

A THESIS SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF **MASTER OF SCIENCE**

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DEPARTMENT OF AGRICULTURAL, FOOD, and NUTRITIONAL SCIENCE

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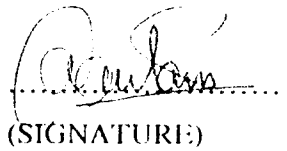

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **ULTRAFILTRATION OF SALTED ACID WHEY** submitted by **AKHILESH GAUTAM** in partial fulfilment of the requirements for the degree of **MASTER OF SCIENCE in FOOD ENGINEERING.**

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Dr. J. Leonard

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Dr. M. Micko

Date:.....

"KARMANNEY WADHIKARASTE MA FALESHU KADA CHANHA"

ACTION IS THY DUTY
REWARD IS NOT
THY CONCERN

To my loving parents Dr. Jai Krishna and Mrs. Meenakshi
and beloved wife Shalini

for their loving support
and understanding

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ABSTRACT

Ultrafiltration (UF) of salted acid whey with two different salt types (NaCl and $CaCl_2$) at various concentrations (0-15%) and pH levels was performed on a bench-top laboratory size unit using an inorganic tubular membrane. The membrane was a 0.44 m long section of commercial Carbosep, with a filtration area of 8.1 X 10^{-3} m^2 and molecular weight cut-off of 20,000 Dalton.

The permeate flux first increased with increase in salt concentration and then decreased with further addition of salts. At pH 4.5 and 5.7, the maximum flux was observed at 6% NaCl concentration, with the flux at pH 5.7 being twice as high as at pH 4.5. Similarly, addition of up to 6% $CaCl_2$ resulted in dramatic increase in flux rate. However, with $CaCl_2$ the flux at pH 5.7 was slightly lower than at pH 4.5. With both salts and pH 3.0, minimum flux was noted at 3% salt concentration and maximum at 0%.

In an attempt to confirm that proteins were the main cause of observed maxima and minima in the flux rates, UF of whey protein concentrate (WPC), β-lactoglobulin (β-lg), α-lactalbumin (α-la) solutions, and protein-free acid whey permeate was also performed. The flux patterns with salt concentration in the UF of protein solutions (WPC, β-lg, and α-la) were similar to that observed for acid whey. However, flux continuously decreased with increasing salt concentrations during UF of protein-free acid whey permeate.

By examining the water flux values through pre-soaked membrane in whey at various salt concentrations (0-15%) at pH 3.0 and 4.5 it was found that proteins became tightly adsorbed on membranes. Further investigation by measuring optical density of whey at various salt concentrations enabled to postulate that changes in both ionic concentration and pH probably caused dissociation and conformational changes in protein, leading to the observed effect on permeate flux.

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CHAPTER 1

INTRODUCTION

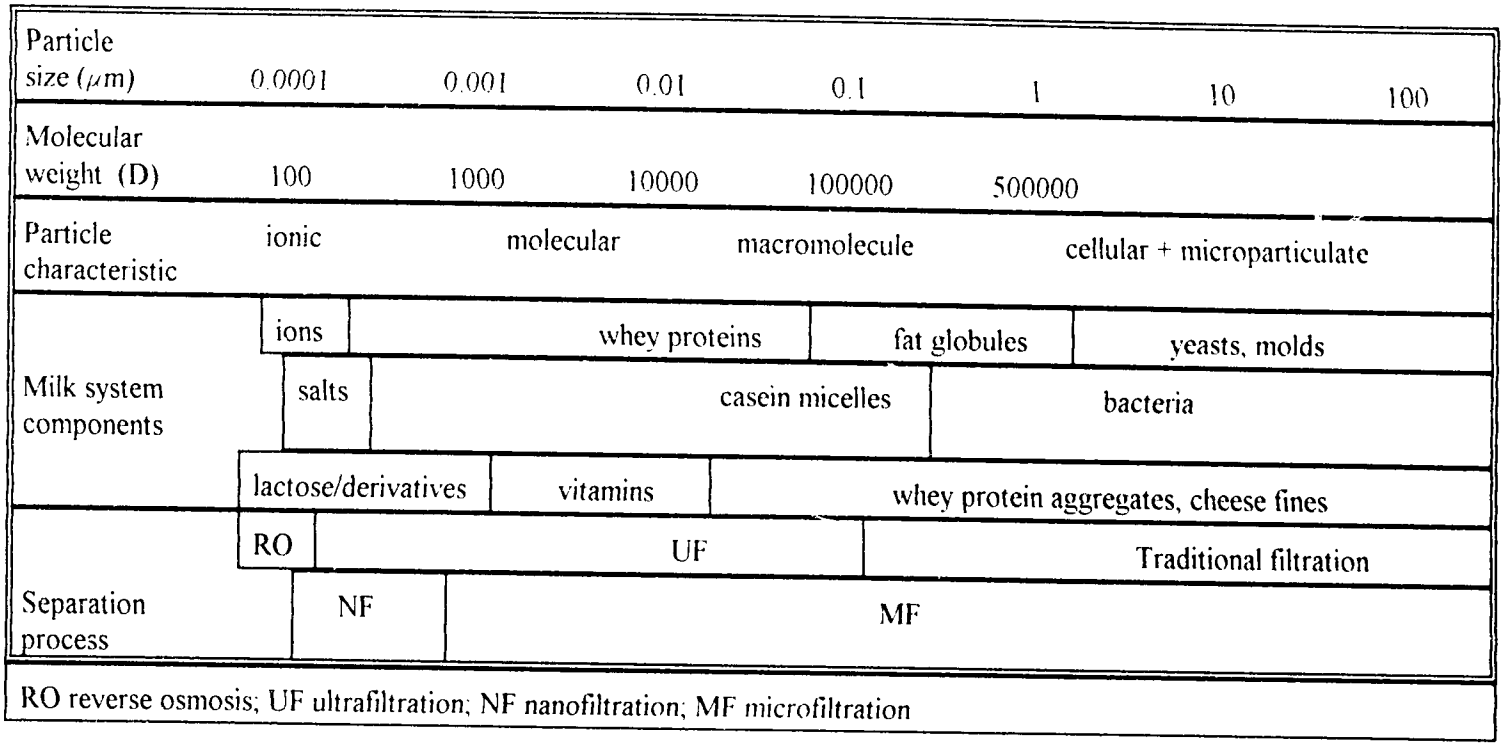
Ancient papyrus rolls suggest that centuries ago the Egyptians used a type of ceramic clay mesh for the clarification of wine (Gelman, 1965). These ceramic filters might be considered to be the first membranes used in food processing. Membranes for large-scale commercial processes were not developed until the invention of asymmetric membranes in the late 1950's (Merin, 1979). With these type of membranes, the high fluxes across the membrane that are essential for commercial applications became possible.

There is an increasing tendency to develop specific membranes for particular separation problems. Selection of the appropriate membrane is the key step during process development, and frequently specific membrane preparation or modification is involved (Lonsdale, 1982). A rough classification of membrane processes can be made based on the molecular size of the product to be separated, as shown in Fig. 1. (Jelen, 1991a).

The food industry has accepted and developed membrane processing extensively. Uses range from the production of dried-egg white proteins to sterilization of milk to production of quark. Table 1 lists some membrane processes used in food processing.

Salted whey, with a NaCl content of 5-10%, is a by-product in the manufacture of Domiati cheese, the most popular soft cheese variety in Egypt. In this type of cheese, NaCl is normally added in variable quantities to milk before renneting, depending on the season and whether the cheese will be consumed fresh or after pickling (Abd El Salam et al., 1976). The addition of NaCl has several effects on the colloidal system of milk that would affect the composition and the properties of the resultant whey (Abd El Salam, 1987). Salted whey is also obtained as whey drippings from pressing hard cheeses, such as cheddar. One way to utilize this whey is through a combination of ultrafiltration and nanofiltration for the recovery of whey proteins.

Fig. 1. Spectrum of application of membrane separation processes in the dairy industry



Adapted from Jelen, 1991a.

Table 1.

Examples of membrane operations in food processing

Process and/or application	Typical product	Membrane process	Industry
Cold sterilization	beer, wine, milk	MF	dairy, beverage
Clarification	wine, beer, fruit juices	MF, UF	beverage
Drying, thickening	proteins (whey), fruit juices	UF, RO (often combined)	potato, dairy
Dealcoholization	beer, wine	UF	beverage
Fractionation	proteins (egg, whey, blood), carbohydrates	UF	dairy, meat, egg, sugar
Product recovery	lactic acid, citric acid, rennet	UF, ED	biotechnology
Product improvement	aromas, flavours	RO	beverage
Desalination	soft water, potable water, desalted cheese whey	RO, ED, NF	beverage, dairy

ED, electrodialysis; MF, microfiltration; NF, nanofiltration; RO, reverse osmosis; UF, ultrafiltration

Adapted from Cuperus and Nijhuis, 1993.

Ultrafiltration (UF) is a well-established technique for concentrating dilute protein solutions and separating proteins from low molecular weight components. An important industrial application of this technique is the purification and concentration of biological macromolecules such as vaccines, whey proteins, and plasma proteins (Palecek et al., 1990).

Many commercial membrane processes involve the filtration of protein solutions in the presence of electrolytes, e.g., the exchange of buffers in the downstream processing of proteins or enzymes, and the sterile filtration of therapeutic proteins (Palecek and Zydney, 1993). One of the critical factors determining the total effectiveness of these membrane processes is the decline in permeate (filtrate) flux that typically occurs during filtration due to a phenomenon that is often referred to as membrane fouling (Hayes et al., 1974; Lee et al., 1976; Cheryan, 1986; Bennasar and Tarodo, 1987).

Several previous studies have explained that membrane fouling can be affected dramatically by pH, salt concentration, and electrolyte composition of the protein solution (Hayes et al., 1974; Hiddink et al., 1981; Fane et al., 1983a, b). Although these studies have provided some insight into the effects of the solution environment on flux decline during protein filtration, there is no complete understanding of the underlying phenomena that determine the effects of electrolyte composition on the filtration behavior of proteins with different physico-chemical characteristics.

Previous study in our laboratory indicated that there was an effect of NaCl on the permeate flux during UF of whey (Hewedy et al., 1992). The literature also suggests that flux during UF decreases with increase in viscosity of the feed (De Fillipi, 1977; Porter, 1983). This study was an attempt to verify the relationship between flux and salt concentrations during UF of salted acid whey and to determine the causes for the observed behaviour.

1.1 Objectives

The general objective of this study was to confirm and explain the effect of electrolytes and pH on permeate flux during ultrafiltration of salted acid whey.

Particular objectives were:

1) To verify the relationship between flux and electrolyte composition in ultrafiltration of salted acid whey.

2) To elucidate the causes of the observed phenomena by studying the effect of NaCl on the permeate flux during ultrafiltration of protein-free acid whey permeate, whey protein concentrate, β-lactoglobulin and α-lactalbumin solutions.

3) To further investigate the effect of salt on whey permeate flux by means of independent experiments to identify specific protein-membrane and/or protein-salt interactions.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Processing

Membrane processing is a general and widely applicable technique for separation, concentration, or fractionation of substances in solution. Ultrafiltration (UF), microfiltration (MF), and nanofiltration (NF) involve separation mechanisms through porous membranes, while reverse osmosis (RO) make use of tight dense membranes. UF and MF membranes separate on the basis of a sieving mechanism. The particle dimensions in relation to the pore size distribution of the membrane determines whether or not a particle can pass through the membrane (Mulder, 1991). RO is able to separate species that have comparable molecular sizes, such as sodium chloride and water. In such cases, affinity between the membrane and target component is important. Differences in diffusion coefficients of the components across the membrane also causes separation (Cheryan, 1986). The way in which NF works is not entirely clear. Possibly both size exclusion and solution-diffusion mechanisms play a role (Jelen, 1991b). A brief history of the developments of membrane processing is presented in the following paragraphs. The information is taken from Lonsdale (1982), Gelman (1965), Dutka (1981), and Lloyd (1985).

2.1.1 Historical developments

In 1748, Abbe Nollet observed that water diffuses from a dilute solution to a more concentrated one when separated by a semipermeable membrane. This phenomenon was called osmosis. The first synthetic membrane, apparently made of nitrocellulose, was developed by Fick in 1865 (Porter, 1983). Two years later, Traube prepared artificial membranes while, in 1877, Pfeffer reported the successful manufacture of membranes by precipitating copper ferrocyanide in the pores of porcelain. In 1907, Bechhold

developed methods for controlling the pore size of membranes. Bechhold was the first to suggest the use of air pressure for improving permeation rates, and also developed methods to determine pore diameters using air pressure and surface tension measurements. He is credited with coining the term "ultrafiltration" (Kesting, 1971; Porter, 1983; Zeman, 1987).

Membrane filters became commercially available in 1927 from the Sartorius company in Germany. Later, Elford developed methods for sterilizing membrane filters by using ultra-violet radiation (Lonsdale, 1982).

Until 1945, membrane filters were used primarily for removal of microorganisms and particles from liquid and gaseous streams. In 1957, the United States Public Health Service officially adopted membrane filtration for drinking water analysis. Simultaneously with these developments in MF membranes, there was considerable interest in developing membranes for RO applications (Dutka, 1981).

In the early 1950's Sourirajan reported some success in obtaining fresh water from sea water using commercially-available homogeneous membranes. From 1958 to 1960, Sourirajan, now with Sidney Loeb, attempted to modify commercial cellulose acetate membranes by heating them under water. Heating contracted the pores, which increased the rejection of salt and resulted in a much higher flux. This heating or annealing process created a phenomenon known as anisotropy or asymmetry in the ultrastructure of the membrane. That is, the behavior of the membrane was different depending on which side of the membrane faced the feed solution. This concurred with an observation made over 100 years ago with natural membranes (Dutka, 1981).

With the advances in membrane technology, the potential applications for filtration technologies widened. Today, ultrafiltration and its twin, microfiltration, have penetrated into food, drug and chemical industries as an efficient, low-energy, and economic separation processes for liquid systems (Cuperus and Nijhuis, 1993).

2.1.2 Polymers used in membrane manufacture

Various polymers and other materials are used for the manufacture of permselective membranes. Lloyd and Meluch (1985) have listed over ninety different homopolymers, copolymers and blends, of which most of them have become obsolete. Cellulose acetate (CA) was used until late 70's (Lloyd, 1985). These membranes had some advantages and several disadvantages, including low working temperature and pH ranges, poor resistance to chlorine, and susceptibility to microbial attack. CA is also reported to undergo creep or compaction phenomenon to a greater extent than other materials (Keller, 1976; Merin, 1979; Cheryan, 1986). Polyamide membranes were no improvement over the cellulose acetate membranes (Merin, 1979). In fact, they were worse in some respects, especially in regards to free chlorine tolerance (Deanin, 1972).

For these reasons, polysulfone have largely replaced CA and polyamide in UF systems because of their better thermal and chemical stability (Lee, 1977).

Polysulfone: Polysulfone membranes are characterized by diphenyl sulfone repeating units. Fig. 2 shows a possible empirical structure, as suggested by Leslie et al. (1974) and Kai et al. (1985). The $-SO_2$ group in the polymeric sulfone is quite stable because of the electronic attraction of resonating electrons between adjacent aromatic groups. The oxygen molecules projecting from this group each have two pairs of unshared electrons to permit strong hydrogen bonding of solute or solvent molecules. Repeating phenylene rings create both steric hinderance to rotation within the molecule and electronic attraction of resonating electron systems between adjacent molecules. Both effects contribute to a high degree of molecular immobility, producing high rigidity, strength, creep resistance, and dimensional stability. Phenylether and phenylsulfone groups have high thermal and oxidative stability, producing long term high-temperature stability during use (Deanin, 1972). Polysulfone flat sheet membranes introduced by De Danske Sukkerfabrikker (DDS) withstand the full pH range and temperatures up to 100°C (Glover et al., 1978). The main limitation of polysulfone membranes is that they must be used under relatively low pressure (Merin, 1979).

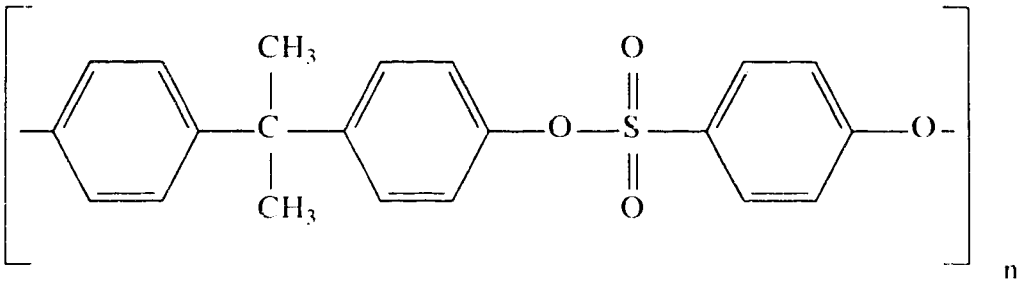


Figure 2. Structure of polysulphone (Adapted from Leslie, et al., 1974)

Mineral or ceramic membranes: Ceramic membranes are used principally in MF and UF applications (0.02 to 2.0 μm and 0.001 to 0.02 μm, respectively) Most of the ceramic membranes have a composite structure, consisting of two or more layers. The porosity of each layer consists of a well-controlled size range to provide the desired separation selectivity. The extremely uniform ultrafine pore size of the inner layer is produced by the "Sol-gel" method, one of the most advanced ceramic manufacturing technologies (Chan and Brownstein, 1991). Sol-gel is a general description of a process that converts a solution to a gelatinous substance, followed by low-temperature drying to transform the "gel" to a ceramic. A typical example is the "carbon tubes" presently available from Gaston County Ultrafiltration Systems, North Carolina, USA and formerly available from Societe de Fabrication d'Elements Catalytiques (SFEC), Bollene, France. Zirconium oxide is a commonly used solute for ceramic membranes. Some other ceramics such as silicon, alumina and titania are also used (Hsieh, 1985).

The use of ceramic membranes represents a relatively new technology which has aroused much interest in membrane processing applications. Their thermal capabilities permit their use at temperatures above 100°C, making them suitable for operations that require steam cleaning. Their resistance to chemicals makes them immune to a wide variety of solvents, acids, alkalies, and detergents. Their excellent structural integrity enables them to withstand high pressures, which allows them to be used for high throughput processes by means of high pressure or back flushing (Chan and Brownstein, 1991). Although these performance characteristics are highly attractive to many processing industries, ceramic membranes have not been used extensively outside of France because of their high costs.

2.1.3 Mechanisms of ultrafiltration

Membrane separation processes are used to separate substances of molecular size less than 10 μm and can concentrate or fractionate the retained materials. These processes are based on the principle of selective permeability of one or more components

of an aqueous mixture through a membrane (Jelen, 1991a), referred to as permselectivity.

UF is a pressure-driven membrane process that can be used for the separation and concentration of substances having molecular weights between 10^3-10^6 Dalton. By convention, UF is distinguished from RO in that UF does not retain species for which bulk solution osmotic pressure is significant and is distinguished from MF in that UF exhibit retention for soluble macromolecules (Matsura, 1994).

UF is usually applied to aqueous streams which may contain soluble macromolecules, colloids, salts, and sugars. It is used to concentrate and fractionate, often simultaneously. Basically, UF is regarded as a molecular sieve process in which the membrane has extremely fine continuous channels through the filtration layer. The following two performance parameters are very important for the effectiveness of UF:

- permeation rate (flux)
- retention of macromolecules

Permeate is the material that passes through the membrane. Retentate is the material remaining on the upstream side of the membrane. Flux (J), the amount of permeate per unit area per unit time, is a measure of membrane productivity. Various models to predict permeate flux are discussed in section 2.1.4 of this manuscript. Retention (R), also called rejection or reflection, is defined as (Zeman, 1987):

$$R = 1 - \frac{P_c}{F_c} \qquad (1)$$

where P_c is solute concentration in the permeate and F_c is solute concentration in the feed.

Most UF membranes retain macromolecules by sieving, although some other types have been said to act as diffusion barriers (Glover et al., 1978). UF membranes can be made from a much wider range of polymers than RO membranes, since a sieving mechanism does not require the membrane polymer be intrinsically water absorbent. However, to avoid the need for wetting agents, the membrane polymer should be wetted

by water (Glover et al., 1978). With a sieving mechanism, macromolecules smaller than the pore size may be retained to some extent because molecules will impinge on the edge of the pore.

For most UF membranes the retention of microsolutes increases with pressure, while the retention of macrosolutes varies only a little. The reason for the latter is obvious, since molecules with diameters greater than the pore diameter will be 100% retained by sieving at any applied pressure. One possible reason for the former is a consequence of pores being closed by the applied pressure, a phenomenon called membrane compaction. The overall effect is that for any particular membrane, the separation mechanisms tend towards sieving as molecular weight increases (Glover et al., 1978).

2.1.4 Permeate flux

There have been several attempts to model flux as a function of system operating parameters and physical properties. The major problem appears to be an inability to precisely model the phenomenon occurring near the membrane surface. Belfort and Kleinstrueneur (1989) have presented several approaches to the mathematical modelling of fluid flow and solute distribution. Models for predicting flux in UF systems generally take the engineering mass-transfer approach since, invariably, it is the concentration polarization layer (discussed later in this section) and not the membrane itself that limits the flux (Blatt et al., 1970; Cheryan 1977).

It is generally believed that the description of fluid flow through microporous membranes can be given by the Hagen-Poiseuille law. However, it is not a good model for membranes. The model relates pressure drop, viscosity, density, and channel dimension (such as diameter of a tube) to flow rate. One form of the model useful in UF processing of an "ideal solution", e.g., uniformly distributed evenly sized pores in

membranes, no fouling or concentration polarization is given as follows (Cheryan, 1986; Hobman, 1992):

$$J = \frac{\epsilon r^2 \Delta P}{8 \mu \Delta x} \tag{2}$$

where J is flux in units of volume/unit area/time, r is the channel radius, ΔP is the applied transmembrane pressure, μ is the viscosity of the liquid permeating the membrane, Δx is the length of the channel, and ϵ is the surface porosity of the membrane.

Equation 2 shows a linear relationship between the flux J and cross membrane pressure ΔP, and an inverse proportionality of J to the viscosity μ; however, in practice, substantial deviations from this theoretical relationship occur. In UF of protein containing liquids, no increase of permeate flux is observed beyond a critical pressure (Jelen, 1979). Membrane compaction is an important factor contributing to the reduction in permeate flux below that predicted by Eq. (2) (Tarnawski and Jelen, 1986). In reality UF membranes do not have perfect pores, and factors such as variations in pore size distribution, shape, and tortuosity will affect the relationship expressed by Eq. (2). In addition, rejection of a solute by a membrane is not based on size alone, and some interaction with the membrane often occurs, especially if the membrane possesses a significant charge (Lonsdale, 1972). For a membrane-protein system, J is generally given as follows (Cheryan, 1986):

$$J = A \frac{\Delta P - \Delta \pi}{\mu} \tag{3}$$

where A is defined as a membrane permeability coefficient, and $\Delta \pi$ is the transmembrane osmotic pressure of the rejected solutes against which the driving force ΔP is applied.

However, the osmotic pressure of macromolecules retained is negligible due to their large molecular weights, although Goldsmith (1971) has suggested that osmotic pressure may be significant during concentration.

Another model, known as the resistance model, which is essentially the filtration equation, is given as follows (Hobman, 1992):

$$J = \frac{\Delta P}{R_m + R_p} \tag{4}$$

where R_m is the intrinsic membrane resistance determined using pure water as the feed, and R_p is the resistance owing to the gel polarization layer.

Equation 4 was found to be applicable over a limited range of operating conditions such as low protein concentrations and low pressures, particularly for noncellulosic anisotropic membranes (Baker et al., 1972; Blatt et al., 1970; Cheryan and Schlesser, 1978). At higher pressures and high protein concentrations, the flux typically becomes independent of pressure and this has been shown to be the result of a build-up of rejected protein molecules on the membrane surface (Kozinski and Lightfoot 1972)

One of the simplest and most widely used theories for modelling permeate flux in pressure-independent, mass-transfer-controlled systems is the film theory (Blatt et al., 1970; De Fillipi and Goldsmith, 1970; Porter, 1972). The model is represented schematically in Fig. 3, where concentration polarization is described to a first approximation by simple film theory. As the solution is ultrafiltered, solute is brought to the membrane surface by convective transport at a rate J_S, thus,

$$J_S = JC_B \tag{5}$$

where J is the permeate flux and C_B is the concentration of solute in the bulk of the

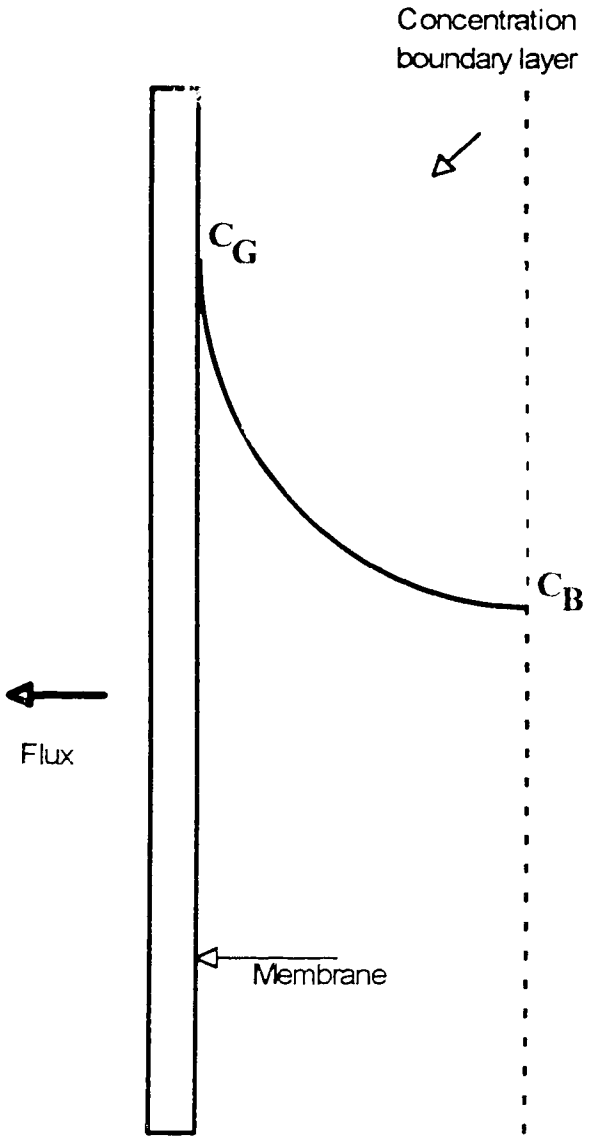


Figure 3. Schematic of concentration polarization and the concentration profile during ultrafiltration.

solution. The resulting concentration gradient causes solute to be transported back into the bulk of the solution due to diffusional effects within the fluid above the membrane. Neglecting axial concentration gradients, the rate of back-transport of solute will be given by:

$$J_s = D\frac{dc}{dx} \tag{6}$$

where D is a diffusion coefficient and dc/dx is the concentration gradient over a differential element in the boundary layer. Initially, the rate of convective transport is greater than the back transport rate, thus concentration in the boundary layer increases and so, dc/dx increases until steady state is reached. At this state, due to restricted mobility of solute molecules, a "close packed" configuration is obtained, denoted as C_G (Michaels et al., 1971). The two mechanisms (convective transport rate and back transport rate) balance each other and at a steady state, Eq. (5) and (6) can be equated, integrated and written as follows:

$$J = K \ln\frac{C_G}{C_B} \tag{7}$$

where K is a mass transfer coefficient. K has the same units as flux and is equal to D/δ where δ is the thickness of the boundary layer over which the concentration gradient exists.

The above model implies that the final UF flux is controlled by the rate at which solute is transferred back from the membrane surface into the bulk fluid. Since in most operations the values of C_G and C_B depend on the properties of the feed and cannot be manipulated directly, efforts to improve permeate flux usually focus on enhancing K as much as possible by adjusting operating parameters. As mentioned frequently in the literature, any attempt to increase flux without providing a compensating mechanism to increase rate of back-transport will be self-defeating (Hiddink et al., 1980; Bennasar and

Tarodo, 1987; Colman and Mitchell, 1991; Belmar-Beiny et al., 1993). This explains why increasing transmembrane pressure has little effect on flux in the totally polarized regime. The increasing driving force merely results in a thicker or denser solute layer, and flux rates are again governed by Eq. (7).

A number of qualitative relationships correlating the mass transfer coefficient to physical properties and operating parameters have been developed. For all thin-channel configurations of interest, the basic equation is (Porter, 1972; Goldsmith, 1971):

$$Sh \quad A\ (Re)^{\alpha}\ (Sc)^{\beta} \tag{8}$$

where,

Sh = Sherwood Number = $K\ d_H / D$

Re = Reynolds Number = $d_H\ V\ \rho / \mu$

Sc = Schmidt Number = $\mu / (\rho\ D)$

d_h = equivalent hydraulic diameter

V = average fluid velocity

μ = viscosity of fluid

ρ = density of fluid.

Values of α and β vary with the system geometry and operating conditions (Porter, 1972; Henry, 1971).

2.1.5 Factors affecting flux: operating parameters

In addition to pressure, as previously discussed, three other operating parameters affect flux during UF. They are as follows:

Feed concentration: Generally, increasing the concentration of feed increases the viscosity, which in turn will result in lower fluxes.

Temperature: In general, higher temperatures will lead to higher flux in both the pressure-controlled and mass transfer-controlled regimes. This relationship is based on the assumption that there is no fouling of the membrane due to precipitation of insoluble salts at higher temperatures (De Fillipi, 1977; Porter, 1983). As temperature increases, the diffusivity increases and viscosity decreases. Therefore, temperature control can significantly affect the efficiency of UF operations.

Flow Rate and Turbulence: Turbulence, whether produced by stirring or pumping of the fluid, has a major effect on the mass-transfer-controlled region. Agitation and mixing of the fluid near the membrane surface "sweeps" away the accumulated solute, thus reducing the thickness of the boundary layer and increasing the flux (deFillipi, 1977; Porter, 1979).

2.1.6 Membrane fouling

Flux during membrane processing of a solution or suspension is usually much lower than pure water flux for the following reasons:

- change in membrane properties
- change in feed solution properties
- concentration polarization
- membrane fouling

Fouling can be described as a condition in which a membrane undergoes plugging or coating by some component(s) in the feed stream in such a way that the flux through the membrane is reduced. Furthermore, the foulant is not in dynamic equilibrium with the stream being ultrafiltered (Eykamp, 1978). Depending on the system, flux may decline in one or more stages due to membrane fouling. The decline in flux is usually rapid in the first few minutes, followed by a more gradual decline (Kuo and Cheryan, 1980). The general consensus appears to be that membrane fouling is due to the deposition of submicron particles on the membrane surface and/or crystallization and precipitation of smaller solutes on the surface and within the pores of the membrane itself (Lim et al, 1971; Hayes et al., 1974; Lee, 1977; Merson and Ginnette, 1972; Nisbet et al., 1981; Tong et al., 1988).

During the UF of dairy liquids, fouling is caused mainly by milk proteins which may:

1) form a gel layer on the membrane;
2) be adsorbed on the membrane (Tong et al., 1988); and
3) plug membrane pores (Taddei et al., 1989).

De Filippi (1977) and Smith and MacBean (1978) indicated that some UF applications involve dissolved or suspended solids that tend to deposit irreversibly on the membrane surface. Taddei et al., (1988) defined fouling as the reduction in transmembrane volumetric flux. They reported that several whey components such as soluble proteins, suspended particles, residual fat and calcium are involved in the fouling of an inorganic membrane during UF of sweet whey. It also appears clear from this study that the membrane selectivity is not an intrinsic value but depends on fouling type, which is closely related to solution composition and operating conditions.

An obvious consequence of fouling is higher cleaning costs (Daufin et al., 1991). In addition, depending on the nature and extent of fouling, restoring the flux may require

powerful cleaning agents which may damage the membrane (Cheryan, 1986; Daufin et al., 1991). Rejection and yields may also be adversely affected. If the build-up of solids on the membrane is significant, it may act as a secondary membrane and change the net sieving and transport properties of the system. Membrane-solute and solute-solute interactions were cited as the major reasons for lower yield and lower protein contents of the retentate when processing extracts of defatted soy flour (Omosaiye and Cheryan, 1979; Nichols and Cheryan, 1981).

2.1.7 Physico-chemical factors affecting fouling

Most components in the feed stream can foul a membrane. Proteins, salts, lipids, and microorganisms have been frequently mentioned in the literature.

Proteins, salts, and pH of the solution: Since proteins are rejected by the membrane, they tend to be highly concentrated at the membrane surface (Hayes et al., 1974; Merin and Cheryan, 1980; Maubois, 1980). Mineral salts also have a profound influence on the fouling of membranes. On one hand, they can interact with the membrane directly or precipitate on the membrane and cause a reduction in flux (Merin and Cheryan, 1980). On the other hand, they contribute to the ionic strength of the solution, which in turn affects the conformation and dispersion of proteins and consequently fouling of the membrane (Fane et al., 1983a, b; Palecek et al., 1990). There is, however, considerable discrepancy regarding the specific effects of electrolyte composition and concentration on the filtrate flux. For example, Fane et al. (1983 a, b) showed that filtrate flux during filtration of bovine serum albumin (BSA) solutions through semipermeable UF membranes was minimal at the protein isoelectric point, i.e., under the condition when protein has no net charge. The flux also decreased with increasing ionic strength (I) for solutions above or below the protein isoelectric point (pI). This behavior was attributed to the effects of solution environment on the extent of protein adsorption within the

membrane pores and/or deposition on the membrane surface.

Bansal et al. (1991) also observed a distinct minimum in flux at the isoelectric point for the filtration of haemoglobin solutions through 0.2 μm microfiltration membranes, although this behavior was attributed to pore blockage effects, coupled with conformational changes in the haemoglobin molecule at alkaline pH. In contrast to the above results, Heinemann et al. (1988) found that the flux during filtration of whey proteins in salt-free solution through 0.2 μm microfiltration membranes decreased monotonically with pH increasing from 3.5 to 8.5, even though the isoelectric point of whey proteins is about pH 5.2. This behavior was attributed to the combined effects of (1) intermolecular electrostatic interactions between adjacent proteins within the deposit that was formed on the upper surface of the membrane, (2) electrostatic interactions between charged proteins and the charged membrane, and (3) protein aggregation in the bulk solution.

Melling and Westmacott (1972) found that penicillinase transmission through a semipermeable microfiltration membrane was at a maximum at pH 6.0 (around the protein pI), with a sharp drop in transmission at higher pH values. The transmission initially increased with increasing ionic strength but then decreased at very high ionic strength. Bil'dyukevich et al. (1989) also found an initial increase in protein transmission at very low ionic strength for the filtration of a variety of proteins through several different types of membranes; the transmission then decreased at higher salt concentrations. The behavior at salt concentrations greater than 0.1 M was more complex. The transmission of trypsin, haemoglobin and lysozyme decreased, while transmission of egg albumin increased with increasing ionic strength.

Direct measurements of the amount of protein deposited during UF showed that BSA deposition was maximal at the pI and increased with increasing ionic strength at all pH values (Fane et al., 1983 b). However, scanning electron micrographs obtained by

Lee and Merson (1976) indicated that deposition of whey proteins on a 0.4 μm microfiltration membrane could be reduced with the addition of NaCl or $CaCl_2$ to the whey solution. The reason for the discrepancy between the two studies is unclear.

Iritani et al. (1991) evaluated the porosity and permeability of the protein deposit formed during dead-end filtration of BSA using a cake-filtration model in which it was implicitly assumed that all the BSA convected to the membrane was actually deposited within the growing protein cake on the upper surface of the membrane. The calculated porosity and permeability of the BSA deposit were minimal at the protein pI and decreased with increasing ionic strength for pH values both above and below the pI. Palecek and Zydney (1993) recently performed a detailed study on the effect of the ionic environment on the properties of BSA deposits that had been formed on the surface of 0.16 μm microfiltration membranes. The permeability of the deposited BSA layers was minimal at the protein pI and decreased with the increasing ionic strength of solutions at pH values both below and above the pI. The permeability was also a function of ion valence, with the dependence on ionic composition and concentration consistent with the effects of electrolytes on the electrostatic repulsion between the charged BSA molecule within the protein deposit.

Lipids and other components Few studies have been performed on the effect of lipids on fouling. Removal of lipids in whey by centrifugation has a beneficial effect on flux (Maubois, 1980). Matthiasson and Sivik (1980) listed several other components that have been reported as fouling agents, from microbial slime and polyhydroxy aromatic compounds to polysaccharides and oil. Watanabe et al. (1979) observed that pectins and other materials similar to cellulose were involved in membrane fouling during RO of orange juice. Low molecular weight sugars have also been reported as foulants (Baker et al., 1972).

2.1.8 Minimizing fouling

There is a tendency in the literature to confuse fouling and concentration polarization. Both phenomena result in lowering of flux. Concentration polarization is a reversible process, which is independent of time. Membrane fouling is an irreversible process whose magnitude depends on the time of operation; the longer the period of operation, the higher the amount of fouling and the lower the flux. Controlling the operating parameters can control or minimize the effect of concentration polarization, but fouling can only be reversed by shutting down the operation and cleaning the membranes (Nisbet et al., 1981; Taddei et al., 1988; Daufin, 1991).

Hayes et al. (1974) presented evidence that casein components and calcium phosphate complexes in HCl-casein whey and cheddar cheese whey cause fouling of UF membranes. They proposed heating the HCl-casein whey at 80°C for 15 sec and then adjusting the pH to an optimum between 5.2 and 5.9 to improve flux. A 100% improvement in flux was observed. They concluded that these heat treatments minimize fouling due to aggregation of a complex of casein and β-lactoglobulin. This treatment also increases the retention of calcium phosphate in the whey protein concentrates and therefore reduces the formation of apatite (complex of calcium and phosphate) deposits on the membrane. However, Taranawaski and Jelen (1986) were not able to confirm the above results.

Lee and Merson (1976) obtained increased UF rates by treating cottage cheese whey with calcium sequestering agents or compounds. Reducing the pH of acid whey to 2.9 enhanced the flux. The change in pH is considered to affect the deposit rather than the composition of the whey (Breslau and Kilcullen, 1976; Glover et al., 1978;). Glover et al. (1978) also reported that turbulence promoters were useful in reducing the fouling of UF systems. Pretreatment and calcium chelation of whey improved the flux in UF of cottage cheese whey (Patocka and Jelen, 1987).

2.2 Whey

Whey is a by-product from cheese or casein manufacture from milk of cows, buffaloes, sheep, goat and other domesticated mammals. The clear yellowish liquid resulting from making soybean curd or soy cheese is sometimes called whey, but this should not be confused with the whey from mammals' milk. Whey has been characterized as the fluid obtained after separating the casein coagulum from the whole milk, cream or skim milk.

Sweet whey results from the manufacture of products that use rennet-type enzymes at pH 5.4-5.8. Acid whey is obtained as a by-product from the manufacture of dairy products in which the casein coagulum is formed by acidification in a pH range of 4.5-5.0. Whey, whether sweet or acid, is a liquid containing lactose, proteins, minerals and traces of fat. Typical compositions of two types of wheys are shown in Table 2 (Coton, 1980; Allum, 1980).

Table 2

Composition of sweet and acid whey

Component	Sweet whey		Acid whey	
	(wt%)	(dry basis)	(wt%)	(dry basis)
Fat	0.5	7.9	0.04	0.6
Protein	0.8	12.6	0.8	12.3
Lactose	4.8	75.6	4.9	75.4
Minerals	0.5	7.9	0.8	12.3
Lactic acid	0.05	0.8	0.4	6.2
Total solids	6.35	-	6.5	-

Whey production in the United States and in the world increases annually. World-wide production of whey was in the order of 130 million tonnes in 1988 (Sorenson, 1988), with cheese production increasing at a rate of 3% per year (Zall, 1992). The United States of America produces 23.8 million tonnes of whey annually (Clark, 1987). Australia and New Zealand contribute about 5.6 million tonnes annually and the EEC contributes 16.8 million tonnes per annum (Zadow, 1987).

At least 50% of the whey produced by the dairy industry is wasted or spread on agricultural land as fertilizer. The remainder is dried or further processed into whey protein concentrates, lactose and other products for use in formulating human food and animal feed products (Jelen and LeMaguer, 1976; Teixeira et al., 1983 a, b; Morr, 1984; Clark, 1987). Whey disposal through sewage treatment plants is not an economic alternative in the United States and most European countries. The U.S. Environmental Protection Agency (EPA) restricts the dumping of whey into rivers and streams. Sewage treatment plants, however are hesitant to process whey because of the huge biological oxygen demand (BOD), about 40,000 ppm (Porter and Michaels, 1971). Furthermore, Potter (1973) considered the disposal of whey as sewage to be an unfortunate loss of money and nutrients.

Most dairy plants that produce large quantities of whey dispose of it by drying or by hauling to other locations for different treatments. The uses of whey in powder or other forms are limited, while whey production is annually increasing (Zall, 1992). The processing of whey by evaporation and spray drying is very expensive because of the initial low solids concentration in whey. In addition, the applied heat may denature the whey proteins, and this compromise their ability to be used as functional ingredients. Examination of the whey problem suggests UF as a method of whey treatment (Kinsella and Whitehead, 1989).

2.2.1 Ultrafiltration of whey

UF appears to be the most effective and attractive technology to process whey, since it has the capability of fractionating the proteins from the unwanted salts, lactic acid and lactose. Membrane processes can reduce the volume of whey and produce whey protein concentrates (WPCs) which are used as human food and animal feed (Hobman, 1992). Lactose and minerals are obtained as permeate. Whey proteins have good solubility at low pH and high nutritional value (Humphries and Marshall, 1974; Kinsella and Whitehead, 1989). UF is one of the best ways to obtain WPC for further use (Muller, 1976; Hobman, 1992).

Whey contains all the milk constituents except milk fat, casein and some small portions of the salt. Serum proteins, as they are also called, present a problem in whey processing with membranes due to membrane fouling and flux decline. However, whey type and whey pretreatments are also responsible for change in flux.

The flux obtained during the UF of acid whey has been reported to be considerably lower than that of sweet whey (Muller et al., 1973). Whey contains a variety of soluble and insoluble components that have the potential to cause fouling of the membranes and reduce flux during ultrafiltration. Fouling during the UF of acid whey is thought to be mainly caused by proteins, while for sweet whey it is predominantly caused by calcium phosphate (Hiddink et al., 1981).

2.2.2 Whey pretreatments

Considerable research has been undertaken to develop methods for pretreating whey as a means of improving flux. The use of microfiltration to remove lipid material and thereby reduce fouling and increase flux has been reported by Merin et al. (1983) and Hanemaajier (1985). Centrifugal clarification to remove fat, casein fines, and microorganisms is now widely practiced commercially.

Calcium ions in whey have been shown to affect UF flux because of their ability to form insoluble complexes with lipid and protein components, and phosphate (Brule et al., 1978). Thus, many pretreatment processes have been examined with the aim of reducing the concentration of calcium ions or improving the solubility of its salts. Flux can also be strongly influenced by the pH of the liquid medium. Changes in pH affect the solubility of calcium phosphate. Precipitation is likely at a pH greater than 5.0. As the pH moves away from the isoelectric point of protein, the electrical charge is increased and the tendency for protein deposition diminished. Breslau and Kilcullen (1976) and Hiddink et al. (1981) observed that, for both acid whey and sweet whey, reduction in pH to 3.0 resulted in marked increase in flux.

Preheating whey to at least 50-55°C and holding prior to UF has been shown by Hiddink et al. (1981) to be effective in increasing the flux. Removal of calcium from whey by demineralization or replacement of calcium ions by sodium ions has been shown to increase flux by as much as two fold (Delaney and Donnelly, 1975; Ennis et al., 1981; Hiddink et al., 1981). Brule et al. (1978) suggested that maximum flux would be attained at approximately 40% calcium removal. Further, addition of calcium sequestering or complexing agents has been found to increase flux (Patocka and Jelen, 1987; Maubois, 1980).

2.2.3 Whey proteins

The protein fraction of whey is 0.6-0.8%. There are two major kinds of whey proteins, β-lactoglobulin (β-lg) and α-lactalbumin (α-la).

The major serum protein is β-lg and it accounts for up to 50% of the non-casein proteins of skim milk. It has a dimer molecular weight of 36,000 Dalton. The dimer exists at pH 5.2, where the two identical chains are held together by monovalent forces. If the pH is lowered or raised from 5.2, there is an increased tendency for dissociation into monomers (McKenzie, 1971). β-lg has well-defined secondary, tertiary and

quaternary structure which are susceptible to denaturation by heat. One sulfhydryl group occurs per monomer. While processing, the integrity of the β-lg molecule must be retained in order to prevent coagulation as a result of irreversible denaturation. In addition, conditions which affect free sulfhydryl groups causing disulphide interchanges with other proteins must be avoided to prevent coagulation (Farrel and Thompson, 1974). It also appears as an octamer form in the native whey system. Its configuration is described in detail by Whitney (1977).

The second major whey protein is α-lactalbumin. Gordon (1971) described α-la as existing in an associated form (low molecular weight polymer such as dimers and trimers) at low pH. Little or no association was observed at pH values in the alkaline to the isoelectric region. Ionic strength and protein concentration influence association and aggregation. The molecular weight of α-la as a monomer is 16,000 Dalton. Acid denaturation may play an important role in the loss of functional properties (Farrel and Thompson, 1974).

Lee and Merson (1976) showed that during UF of cottage cheese whey, fouling could be a series of events initiated by microorganisms and protein complexes, which form a porous matrix on the membrane surface followed by finer grain materials, such as β-lg which filled in the matrix and formed sheets over the membrane. On the other hand, Merin and Cheryan (1980) reported that α-la had the greates. flux depressing effect.

2.2.4 Salted whey

Salted whey is a by-product in the manufacture of Domiati cheese, the most popular soft cheese variety of Egypt. This cheese is made mainly in small factories spread throughout the country but more particularly in the district of Domiat, from which the name is derived (Abd El-Salam et al., 1976). It is a very suitable variety of cheese for manufacture in Egypt because the bacteriological quality of the milk is usually poor

and the addition of salt to fresh milk inhibits bacterial growth to a considerable extent. In the usual method of cheese making, salt (NaCl) is added to milk prior to renneting to a level of 6 to 10% depending on the season and intended storage period (Fahmi and Sharara, 1950). El-Koussy (1966) reported that the best Domiati cheese was made from pasteurized milk containing 7% salt. NaCl has a definite role in determining the chemical, physical and biochemical changes in these cheeses. There is a change in the colloidal system of milk on addition of NaCl (Abd El-Salam, 1987). The by-product of this kind of cheese is salted whey. The composition and properties of whey determine its behavior during processing and its possible use as effluent.

In North America salted whey is obtained as whey drippings from pressing certain hard cheeses like cheddar. Available data on salted whey from Domiati cheese manufacture are relatively incomplete (Abd El-Salam, 1987) and are limited mainly to whey obtained from experimental cheeses with no data on whey obtained from industry. Work by El-Shibiny et al. (1990) suggested that the major whey protein fraction of salted whey was β-lg, followed by α-la, immunoglobulin, and serum albumin. The same was reported by Olling and Van Luin (1988). This means that the addition of salt has no effect on the removal of whey proteins from the cheese milk. The composition of salted whey is similar to other types of whey.

However, literature suggests that whey of different origin behave differently during UF (Tong et al., 1988). Previous studies in our laboratory also indicate an effect of NaCl on permeate flux during UF of whey (Hewedy et al., 1992; Jelen, personal communication). This study is an attempt to confirm and explain the observed phenomena.

CHAPTER 3

MATERIALS, EQUIPMENT AND METHODS

3.1 Preparation of protein solutions for ultrafiltration

3.1.1 Salted acid whey

Cottage cheese whey (acid whey in table 2) was obtained in bulk from the Lucerne dairy plant in Edmonton, Alberta. The whey was stored in 200 L batches at -30°C to maintain a uniform source of raw material. Previous studies had indicated that freezing and thawing have no effect on the physico-chemical properties of whey proteins (Bhargava and Jelen, 1994).

The required amount of whey for each experiment was thawed at 20°C and centrifuged through a centrifugal separator at 10,000 RPM to remove casein fines and other suspended solids. These whey batches were maintained at 4°C for not more than five days before use. Solutions for UF tests were made two hours before each run. The required amount of NaCl or $CaCl_2$ in 3% (w/w) increments was added to the whey (up to 12%), and the pH adjusted using lactic acid and/or sodium hydroxide.

3.1.2 Whey proteins

Whey protein concentrate (WPC): WPC (Alacen 840) used in this study was obtained from New Zealand Milk Products Inc., New Zealand. The typical composition of Alacen 840 as obtained from the manufacturer is presented in Table 3.

Table 3

Composition of WPC Alacen 840*

COMPONENT	% (DRY WT. BASIS)
Protein	79.6
Lactose	8.0
Lipid	6.1
Ash	3.6
Moisture	2.7

* as provided by New Zealand Milk Products Inc., New Zealand

A 0.7% (w/w) aqueous protein solution was prepared by dissolving the WPC powder in distilled water and stirring continuously for two hours at room temperature. Each WPC solution (40 L) was made and stored at 4°C for a maximum of seven days. The required amount of NaCl in 3% (w/w) increment was added to the solution two hours before UF and the pH was adjusted to 4.5 with lactic acid.

Isolated β-Lactoglobulin and α-Lactalbumin: Enriched β-lactoglobulin (β-lg) and α-lactalbumin (α-la) in powder form were obtained from Protose Separations, Toronto, ON. To obtain a 0.7% (w/w) protein solution, the respective proteins were added to distilled water and stirred for two hours at room temperature. Solutions of β-lg and α-la (40 L each) were prepared and stored at 4°C for a maximum of seven days. The required amount of NaCl with an increment of 3% (w/w) was added to the solutions two hours before UF, and the pH was adjusted to 4.5 with lactic acid.

3.1.3 Acid whey permeate

Protein-free acid whey permeate was obtained by UF of acid whey on a S7 module pilot scale UF unit using Carbosep inorganic membranes (SFEC, Bolene, France). The permeate was stored at 4°C, and the required amount of NaCl with an increment of 3% (w/w) was added to the solution as needed.

3.2 Design and construction of the ultrafiltration equipment

A bench-top UF equipment, using an inorganic tubular membrane, was designed and used in this study. The unit was entirely built from standard, stainless steel (SS) Swagelok connectors and 5/8" standard, SS tubing (0.625" OD, 0.545" ID). A detailed layout showing the design of the unit is given in Fig. 4. The connections/attachments were made by using appropriately-sized ferrules. Female connectors (parts No. 6 and 11 in Fig. 4) were machined on a lathe to cut out a 16.4 mm by 2.5 mm section to accommodate the O-rings (Fig. 7). Tube adapter glands (parts No. 4 and 13 in Fig. 4) were also machined to cut out 1.3 mm by 1.0 mm sections from the edges to allow for the required compression on the O-rings (Fig. 5). The Swagelok connectors, valves, SS tubing, and ferules were purchased from Edmonton Valves Ltd., Edmonton, AB. The specifications of the various parts are included in Table. 4.

The UF unit described above was specifically designed to accommodate a variable length membrane. The clearance between the membrane and the inside wall of the tubing was only 1.95 mm. This resulted in a dead volume of only 0.04 x 10^{-3} m^3 for the unit (0.8 x 10^{-3} m^3 including the Teflon tubing and pump) making it possible to operate the equipment with small amounts of whey (about 2 L per run). The unit was also inexpensive, at a cost of about $300 excluding the pump.

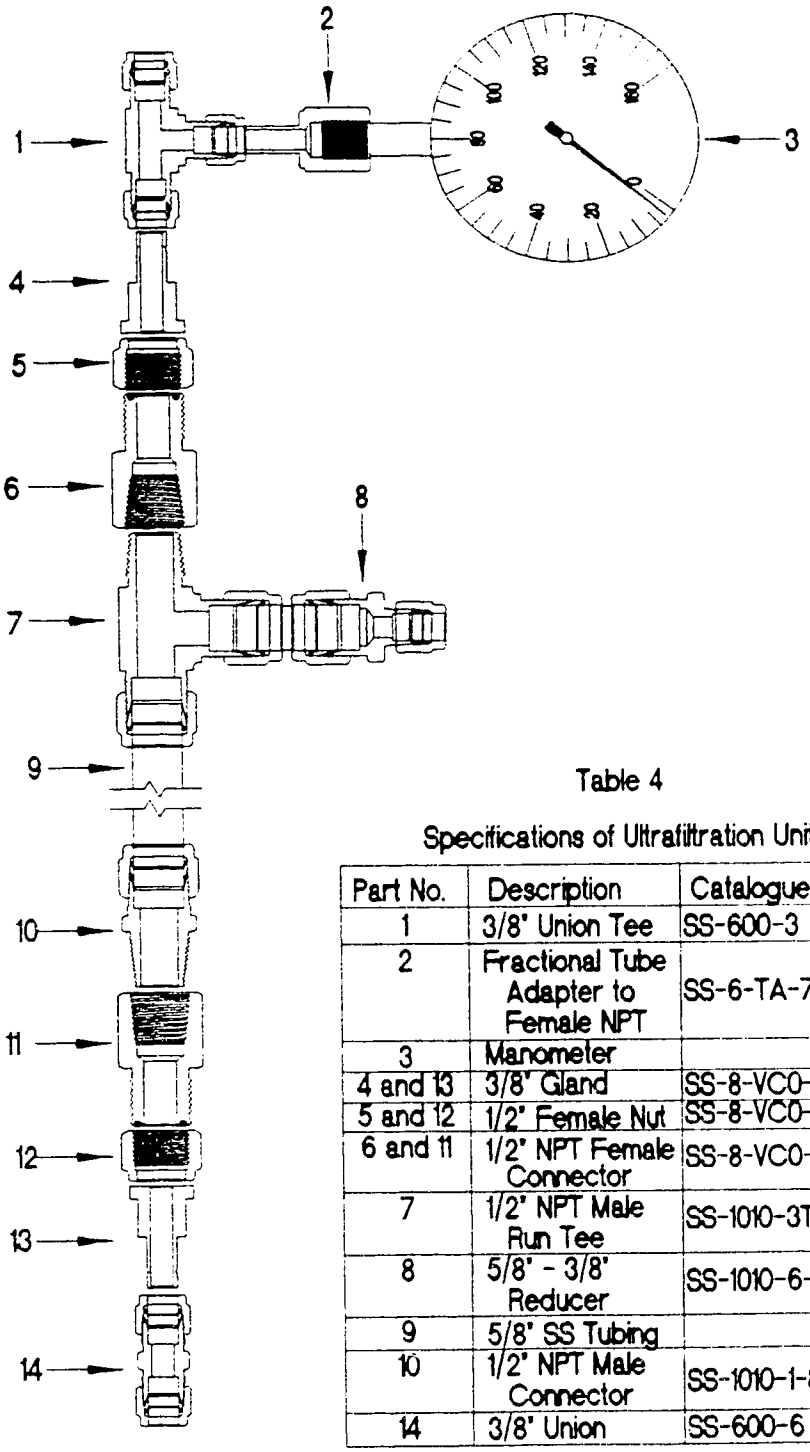


Table 4

Specifications of Ultrafiltration Unit

Part No.	Description	Catalogue No.
1	3/8" Union Tee	SS-600-3
2	Fractional Tube Adapter to Female NPT	SS-6-TA-7-6
3	Manometer	
4 and 13	3/8" Gland	SS-8-VCO-3-6TA
5 and 12	1/2" Female Nut	SS-8-VCO-4
6 and 11	1/2" NPT Female Connector	SS-8-VCO-7-8
7	1/2" NPT Male Run Tee	SS-1010-3TMT
8	5/8" - 3/8" Reducer	SS-1010-6-6
9	5/8" SS Tubing	
10	1/2" NPT Male Connector	SS-1010-1-8
14	3/8" Union	SS-600-6

Figure 4. Layout of the ultrafiltration unit.

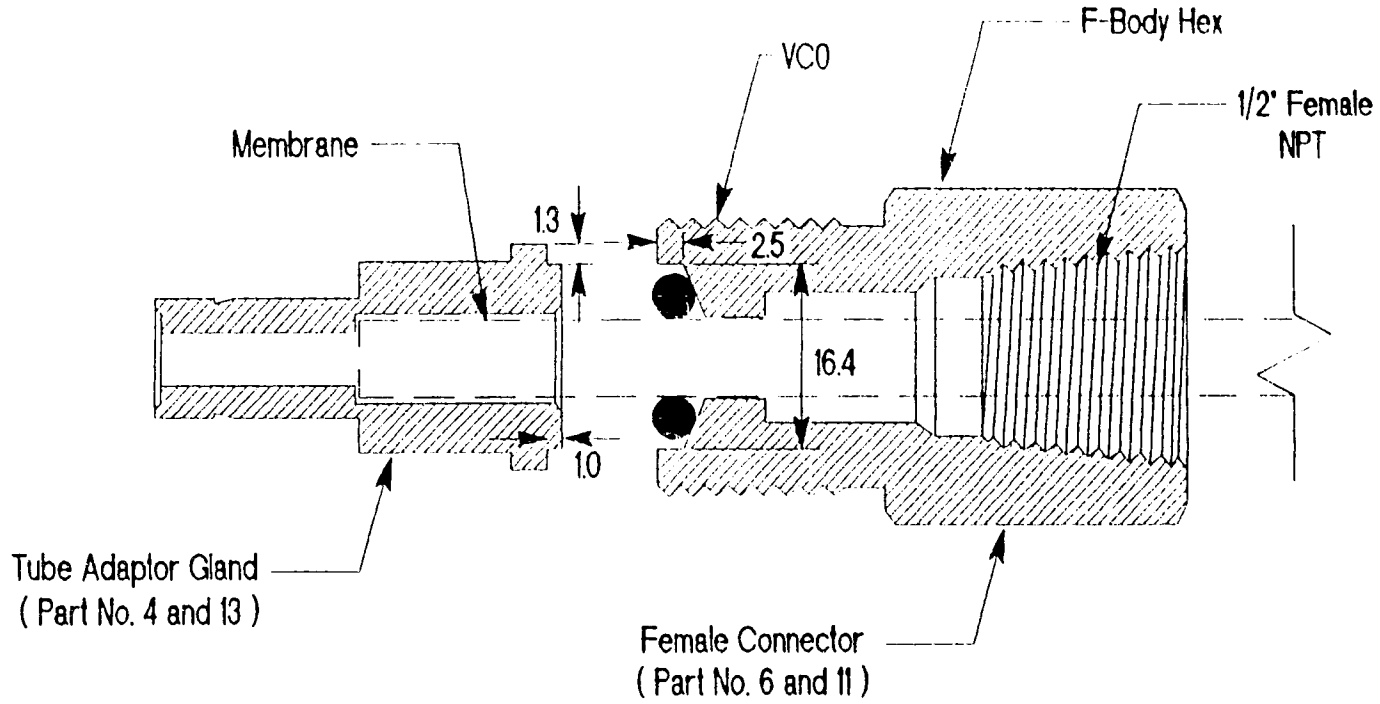


Figure 5. Adapter gland and female connector machined to accomodate the O-rings.
(All dimensions in mm) Drawing not to scale

A magnetically coupled gear pump (Micropump® L-07003-32, Cole Palmer, Anjou, PQ) was used with this equipment. This pump provided a maximum flow rate of 6.6 x 10^{-3} m^3/min. Flow rate could be varied independently of the crossmembrane pressure. The pump could pass air bubbles without losing its prime and was powered by a variable speed motor, (1/3 HP, 90 VDC). The flow rate of the pump was controlled by a SCR speed controller with 20:1 speed range (Cole Palmer, Anjou, PQ). In this study a flow rate of 6 x 10^{-3} m^3/min with 400 kPa crossmembrane pressure was used.

The crossmembrane pressure was regulated by a needle valve located downstream on the retentate side, and it was measured by a manometer attached to the outlet of the unit. Permeate was collected through a 3/8" O.D Teflon tube. Fig. 6 shows the complete experimental setup, and the flow streams are schematically shown in Fig. 7.

3.3 Membrane

An inorganic, porous carbon-type UF membrane, commercially known as Carbosep, was supplied by SFEC, Bolene, France. In this study, a 0.44 m long section of membrane with an effective filtration area of 8.1 by 10^{-3} m^2 was used. However, the area can be easily modified by using different membrane lengths. The membrane consisted of a zirconium oxide porous layer deposited on the inside surface of a tubular microporous carbon support (10.1 mm OD, 5.7 mm ID). The molecular weight cut-off was 20,000 Dalton. The main features of the carbosep ultrafiltration membranes are listed in Table 5.

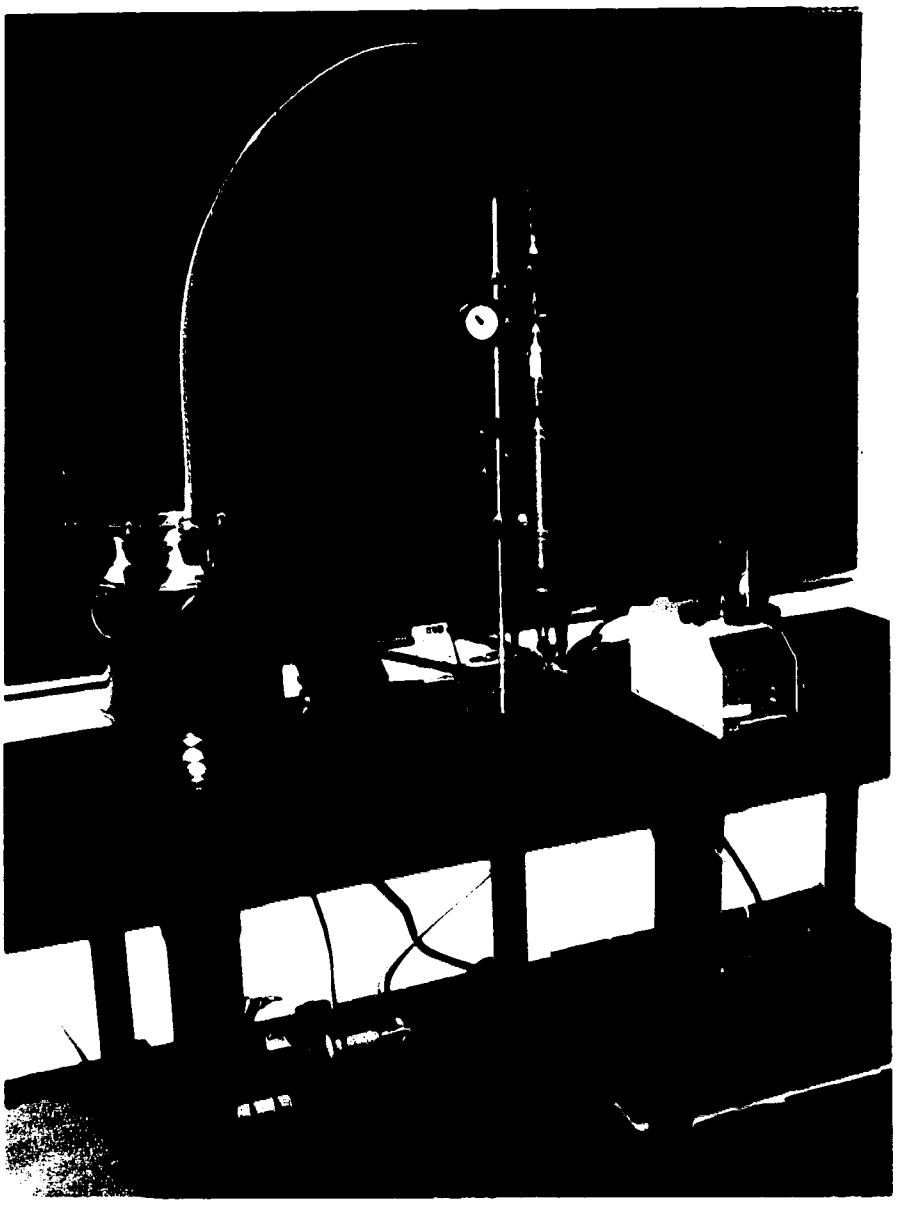


Figure 6. Layout of the equipment.

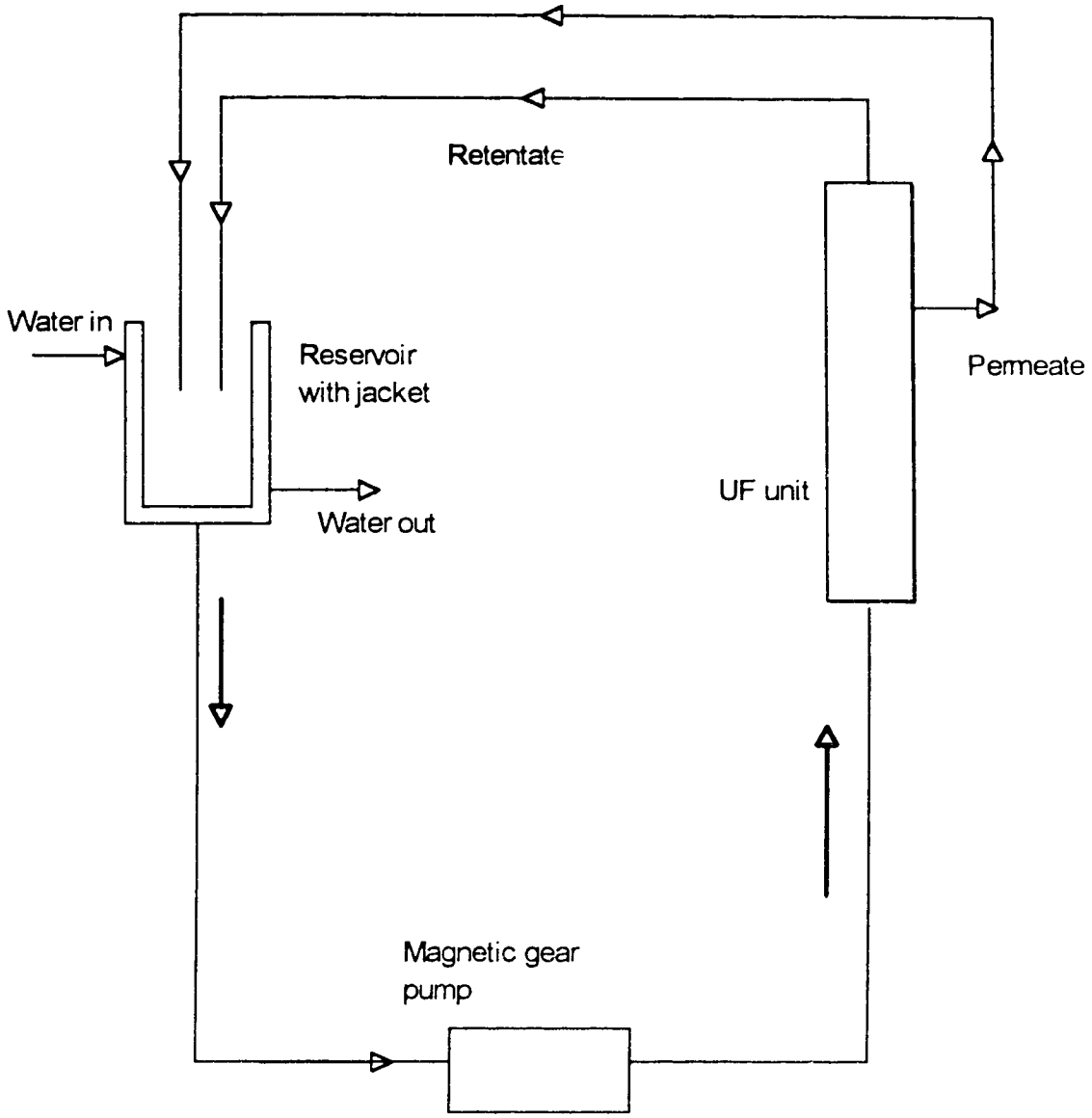


Figure 7. Flow stream schematics

Table 5.

Main features of carbosep ultrafiltration membranes

SPECIFICATION	FEATURES	UNITS
Membrane support	Sintered carbon	
Geometry:		
length	44	mm
outside diameter	10.1	mm
inside diameter	5.7	mm
Mechanical features:		
bursting pressure	60	bar
service pressure	15	bar
crushing force	300	KgF/20mm
Chemical features:		
service pH*	0 to 14	
steam sterilization**	yes	
oxidant sterilization	yes	
Process temperature up to	150	°C
Cut-off capability		
Module M4	20000	Dalton
Module M1	50000	Dalton
Toxicology:		
Approved by the French Higher Council of Hygiene.	Yes	
Approved in West Germany.	Yes	

* At all temperatures between 20 and 90 °C

** Steam at 121°C and 2 bar for 30 minutes

3.4 Cleaning of the UF unit

After each UF test, the UF unit was cleaned in five steps as follows:

1) The unit was rinsed with tap water at 60°C and 300 kPa crossmembrane pressure for 15 minutes (no recycling);
2) a basic solution of 0.1% (w/w) Ultrasil (Klenzade, St. Paul, MN) was recycled for 30 minutes at 75°C and 400 kPa crossmembrane pressure;
3) the unit was rinsed again with tap water at 60°C for 15 minutes at 300 kPa crossmembrane pressure (no recycling);
4) an acid solution (0.2 M nitric acid) was recycled for 15 minutes at 60°C and 300 kPa crossmembrane pressure;
5) the equipment was rinsed with tap water at 60°C and 300 kPa crossmembrane pressure until the water on the permeate side was at neutral pH (no recycling).

To verify that the membrane was fully regenerated, a flux test was performed with tap water at 60°C. A flux of 60-65 g/m^2.min was indicative of complete regeneration, as suggested by the supplier

3.5 Experimental design

3.5.1 Ultrafiltration

Acid whey with two different salt types (NaCl or $CaCl_2$) at various salt concentrations (0-12% w/w in 3% increments) and different pH levels was ultrafiltered to establish a relationship between flux and salt concentration. The pH levels used with NaCl were 3.0, 4.5, and 5.7, while with $CaCl_2$ the pH levels used were 3.0, 4.5, 5.7, and 6.5. In an attempt to elucidate the causes of the effect of salt on permeate flux during UF of acid whey, further UF experiments were carried out at pH 4.5 using protein-free whey, as well as WPC, β-lg, and α-la solutions with 0-15% NaCl. All runs were done in duplicate and randomized.

All experiments were performed at 22°C, 400 kPa crossmembrane pressure, and a flow rate of 6 x 10^{-3} m^3/min. Temperature was maintained constant by circulating water from a water bath to the jacket of the reservoir. Filtration time was limited to 90 minutes. Permeate weight was noted every five minutes, and the permeate was added back to the reservoir.

3.5.2 Protein-membrane interaction

A method adapted from Pouliot (1994) was used to evaluate the adsorption of proteins on the ceramic/mineral membrane. The membrane was first cleaned using the five steps detailed in section 3.4. Water flux at 20°C was measured before and after soaking the membrane in whey with NaCl concentrations ranging from 0-15% at pH 3.0 and 4.5. A comparison of water flux was used to determine the adsorption of protein on the membrane. The full membrane length (0.44 mm) was soaked in 1 L of whey for four hours in random order with respect to salt concentration. The adsorption of proteins in whey with added $CaCl_2$ was evaluated in a similar manner. All experiments were performed in duplicate. Quantitative adsorption of proteins on the membrane was determined by Kjeldhal analysis of whey before and after soaking the membrane in whey at pH 4.5 and various NaCl concentrations.

To determine whether the salts themselves were adsorbed or interacted with the ceramic membrane, the clean membrane was soaked in solutions of NaCl and $CaCl_2$ in distilled water (0-15% w/w in 3% increments). Following soaking of the membranes, the flux of pure water at 20°C was measured.

3.5.3 Spectrophotometric analysis of salted whey

In order to determine whether the salts added to whey had an effect on the state of the whey proteins in solution, a diode array spectrophotometer (Hewlett Packard, model No. 8452-A) was used to measure the light absorbance due to suspended particles in whey at 0-15% NaCl concentrations and pH 3.0 and 4.5. The turbidity of the solutions in the visible range was measured at 650 nm, as this is the wavelength of maximum absorbance of whey proteins (Kato and Nakai, 1980). If absorption measurements are made at the wavelength of an absorption peak, small deviations in the spread of the wavelength will not significantly affect results. However, if the same spread of wavelengths is displaced to a point where the absorbance is changing rapidly with wavelength, the error is greatly increased.

For measurements in the ultra violet (UV) range, samples were first centrifuged at 8650 g for 20 minutes using a Beckman model No. J2-21 centrifuge. The supernatant was collected and analyzed for soluble proteins at 280 nm wavelength using the diode array spectrophotometer. This wavelength was selected to detect changes in aromatic groups of amino acids (i.e., tyrosine, tryptophan, phenylalanine), which are reflective of changes in protein content (Smith et al., 1983).

The above experiments were repeated with $CaCl_2$ at the same salt concentrations and pH values for whey as noted above. The wavelengths used were also the same as indicated for NaCl. All experiments were performed in duplicate.

3.5.4 Other analytical procedures

The protein content of whey was calculated as 6.25 x %N obtained by Kjeldahl analysis. Reagents used were: concentrated sulphuric acid, potassium sulphate, copper sulphate, sodium hydroxide and boric acid (Bradstreet, 1965).

The kinematic viscosity of whey at different salt concentrations was determined using a Cannon-Fenske Routine viscometer No. P701 (State College, PA). The pH of the solutions were measured using a pH meter 150 (Corning, Halstead, England).

CHAPTER 4

RESULTS AND DISCUSSION

A bench-top UF equipment using an inorganic tubular membrane was designed as part of this study. The dead volume of the unit including the Teflon tubing and pump was 0.8 x 10^{-3} m^3, which permitted small experimental batches of solutions to be processed. Excluding the tubing, the dead volume of the unit was only 0.04 x 10^{-3} m^3.

As a starting point for the study, verification experiments were performed to establish the effect of NaCl on the permeate flux during the UF of acid whey as observed by Hewedy et al. (1992). Acid whey was ultrafiltered at various NaCl concentrations (0-12%) and three different pH values (3.0, 4.5, and 5.7), and a relationship between the flux rate and NaCl concentration was established. The permeate flux was found to be maximum or minimum at intermediate salt concentrations, depending on the pH of whey. In an attempt to determine the causes of this effect, UF experiments with protein-free acid whey permeate, and WPC, β-lg, and α-la solutions at various salt concentrations (0-15% NaCl) and pH 4.5 were also performed. Further elucidation of the causes of this phenomenon was attempted by carrying out experiments to establish the protein-membrane and salt-protein interactions.

The average isoelectric point of whey proteins is close to pH 5.2. The above mentioned three pH levels were used because 3.0 was far below the isoelectric point, 4.5 was native pH of whey and 5.7 was closer to the isoelectric point of whey proteins but below the point of calcium precipitation (pH 6.0).

Calcium is a major cause of fouling during UF of whey. To investigate whether the salt-flux effects were ion-specific, $CaCl_2$ was included and tested for its effect on the permeate flux during the UF of acid whey. The pH levels used with $CaCl_2$ were the same as for NaCl with an additional pH of 6.5. At higher pH values, the solubility of calcium salts decreases and insoluble complexes of calcium and phosphate are formed and are responsible for typical fouling of the membrane.

The results in this chapter are presented in graphic form in three main groups, as follows:

(1) effect of salts on flux;

(2) protein-membrane interaction; and

(3) salt-protein interaction;

The graphs represent all the experimentally obtained points and their average values.

4.1 Effect of salts on flux

4.1.1 Effect of NaCl

With the addition of NaCl to whey, the flux first increased reaching a maximum at 6% salt; this was followed by a decrease in flux with further addition of NaCl at both pH 4.5 and 5.7 (Fig. 8). The flux at each salt concentration at pH 5.7 was more than double than at pH 4.5. The pH value was found to affect the flux dramatically, even in the absence of added salt. The flux at 6% NaCl for whey at pH 4.5 was double than at 0%. It has been suggested that increases in viscosity decrease the permeate flux (De Fillipi, 1977; Porter, 1983). However, the observed increase in flux with increasing salt concentration up to 6% is not in agreement with the conventionally held theory. The viscosity of whey at different salt concentration is given in Table 6.

The effect of NaCl at pH 3.0 was opposite to that observed at pH 4.5 and 5.7. The flux initially decreased with addition of up to 3% NaCl; further addition of NaCl led to increased fluxes (Fig. 8). The flux was minimum at 3% NaCl and stayed below the flux of salt-free whey throughout the experimental range. The flux at 3% NaCl was 40% of that observed at 0% NaCl (Fig. 8). However, above 3% salt, the flux

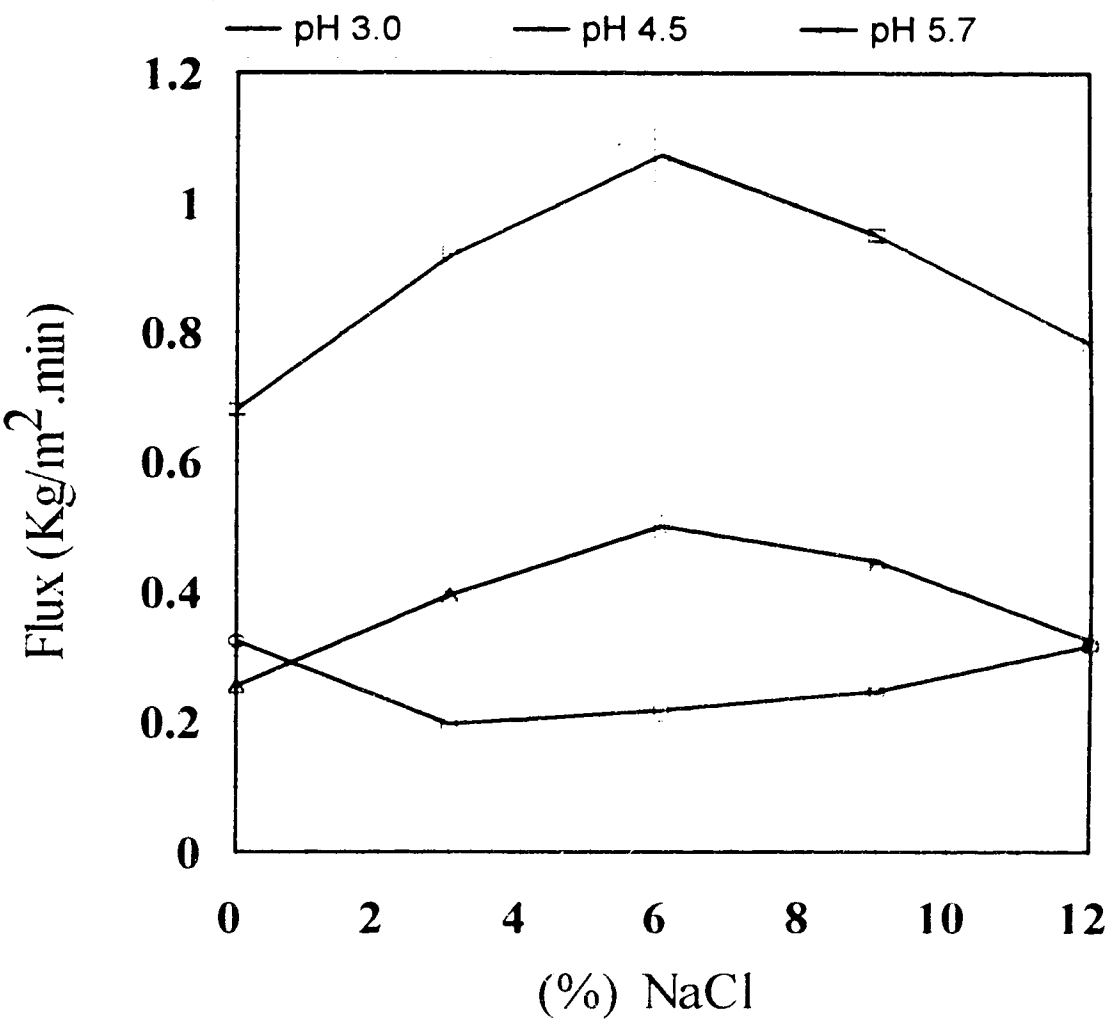


Figure 8. Effect of NaCl on permeate flux at 27.5 minutes in UF of acid whey

Table 6

Kinematic viscosity of whey (pH 4.5) at 22 °C

NaCl CONCENTRATION (%)	VISCOSITY (CENTISTOKES)*
0	1.121±0.002
3	1.177±0.005
6	1.218±0.001
9	1.271±0.002
12	1.309±0.001
15	1.412±0

* average of two measurements

was found to increase despite the increasing viscosity. Although the flux values shown in Fig. 8 correspond to a filtration time of 27.5 minutes (measured from the first emergence of permeate), flux rates were not found to change significantly with filtration times between 5 and 90 minutes (data not shown).

4.1.2 Effect of $CaCl_2$

Fig. 9 illustrates the effect of adding $CaCl_2$ to whey on the permeate flux during UF of acid whey at different pH levels. The flux pattern with changing $CaCl_2$ concentration was similar to that observed for NaCl. At both pH 4.5 and 5.7, the flux initially increased with the addition of $CaCl_2$, reaching a maximum at 6% $CaCl_2$, after which it decreased with further addition of salt. The maximum flux was about 136% higher than the flux at 0% $CaCl_2$. This trend was particularly surprising, since calcium is believed to be the principal foulant during UF of dairy fluids (Muller et al., 1973; Hayes et al., 1974; Hiddink et al., 1981; Patocka and Jelen, 1987). In the present study, the increase in $CaCl_2$ concentration to 6% caused an increase in the flux rate, contrary to both viscosity and calcium flux-depressing effects. However, at pH 6.5, the flux pattern was opposite to that at pH 5.7 and 4.5. The flux first decreased with the addition of salt to 6% $CaCl_2$ and then increased with further addition of $CaCl_2$. Minimum flux observed at 6% salt concentration was 33% lower than the maximum flux at 0% $CaCl_2$ (Fig. 9). The insolubility of calcium salt at pH 6.5 may have been responsible for the flux lowering effect compared to pH 5.7 and 4.5, as suggested by Hayes et al. (1974) and Cheryan (1986). Similarly, at pH 3.0, the flux first decreased with the addition of $CaCl_2$, reaching a minimum at 3% salt concentration and then increased with further addition of salt. The minimum flux observed at 3% $CaCl_2$ was 60% lower than that at 0% $CaCl_2$. In Fig. 9 flux values are reported at 27.5 minutes; however, the patterns remained the same throughout the UF test for 5 to 90 minutes of filtration time.

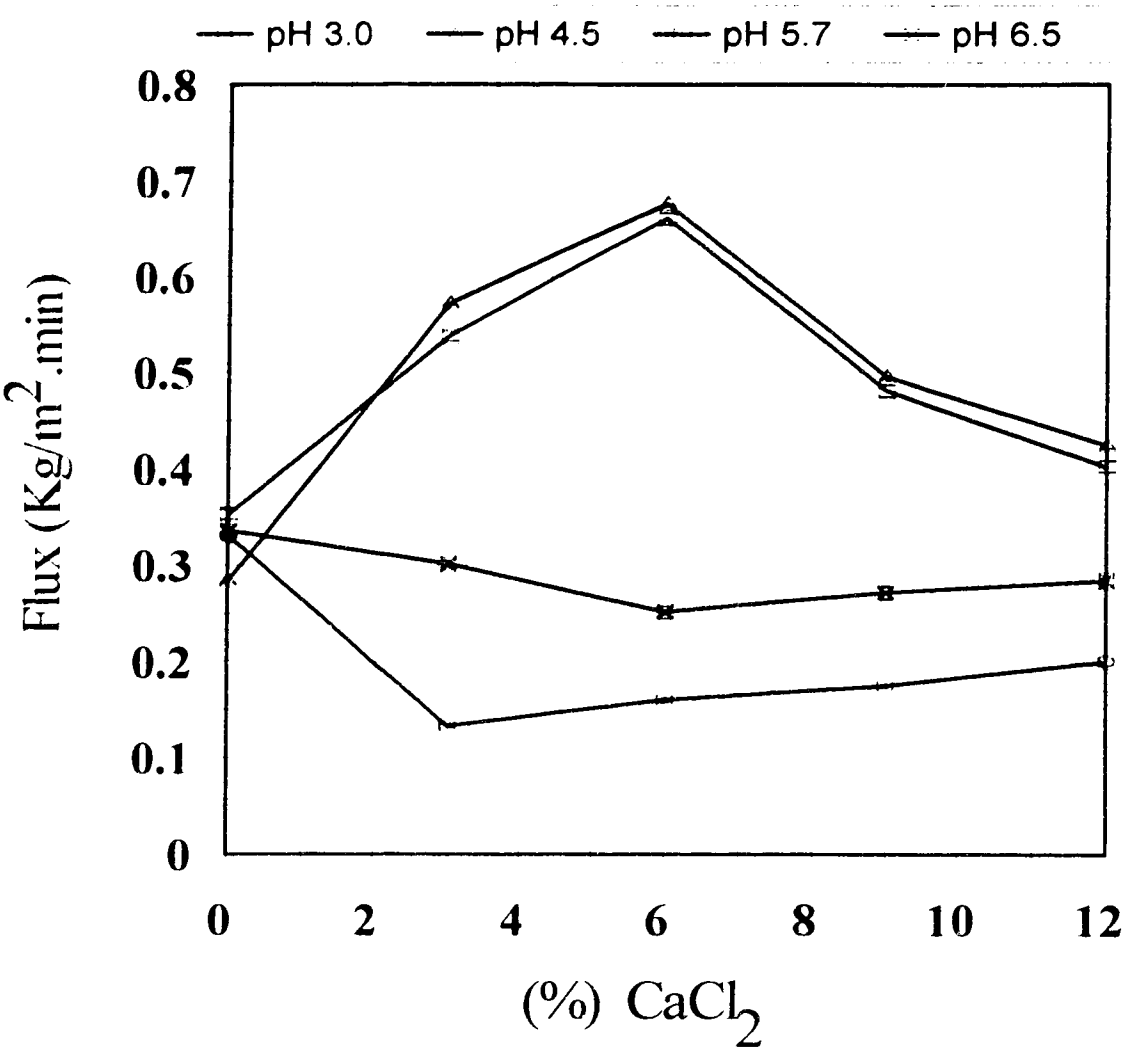


Figure 9. Effect of $CaCl_2$ on permeate flux at 27.5 minutes in UF of acid whey

In an attempt to determine whether the observed effect of salt on the flux was related to any specific whey protein, UF experiments with WPC, β-lg, and α-la solutions were carried out. The protein content and pH of these solutions were 0.7% and 4.5 respectively, which approximate the values found in native acid whey. Flux patterns with changing salt concentration during UF of WPC, β-lg, and α-la solutions were similar to those observed during UF of salted whey (Fig. 10). Generally, flux initially increased with an increase in NaCl concentration and then decreased with further addition of salt for all three kinds of proteins tested. In the case of WPC and β-lg, maximum flux was observed at 3% NaCl, while for α-la flux was maximum at 6% NaCl. As indicated for the processing of whey, the flux rate changed little between 5 and 90 minutes.

To confirm that proteins were the only cause for the observed maxima or minima in the flux rate, protein-free acid whey of different salt concentrations was ultrafiltered. The addition of NaCl to protein free acid whey at pH 4.5 resulted in a continuous decrease in flux (Fig. 11). That is, the flux was highest in the unsalted protein-free acid whey, and decreased in a relatively continuous manner as NaCl concentration increased. This was obviously the standard effect of the increase in viscosity. The fluxes of protein-free whey were much higher than the fluxes of whey protein solutions (Figs. 10 and 11). This was expected as protein-free solution will not contribute to the increased membrane resistance, while protein solution would because of the membrane fouling.

From a comparison of Figs. 8, 10, and 11 it could be concluded that the observed effect of NaCl (i.e., maximal and minimal flux at intermediate salt concentrations) was due to proteins. Furthermore, this effect was not limited to any specific protein. All three kinds of protein tested independently showed similar effect during UF, which was postulated to be due to the protein-membrane interactions.

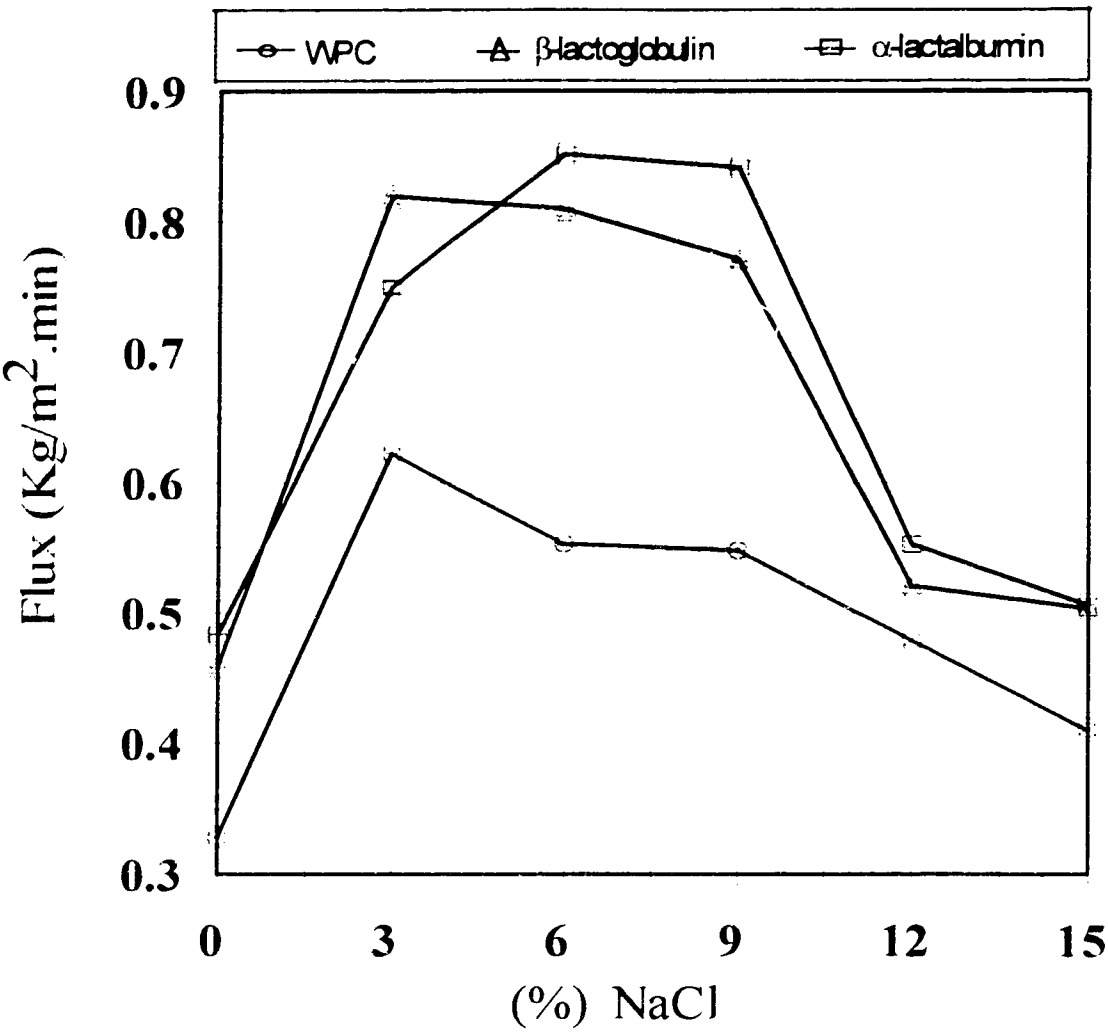


Figure 10. Effect of NaCl on permeate flux at 27.5 minutes in UF of whey protein solutions (pH 4.5, protein concentration 0.7%).

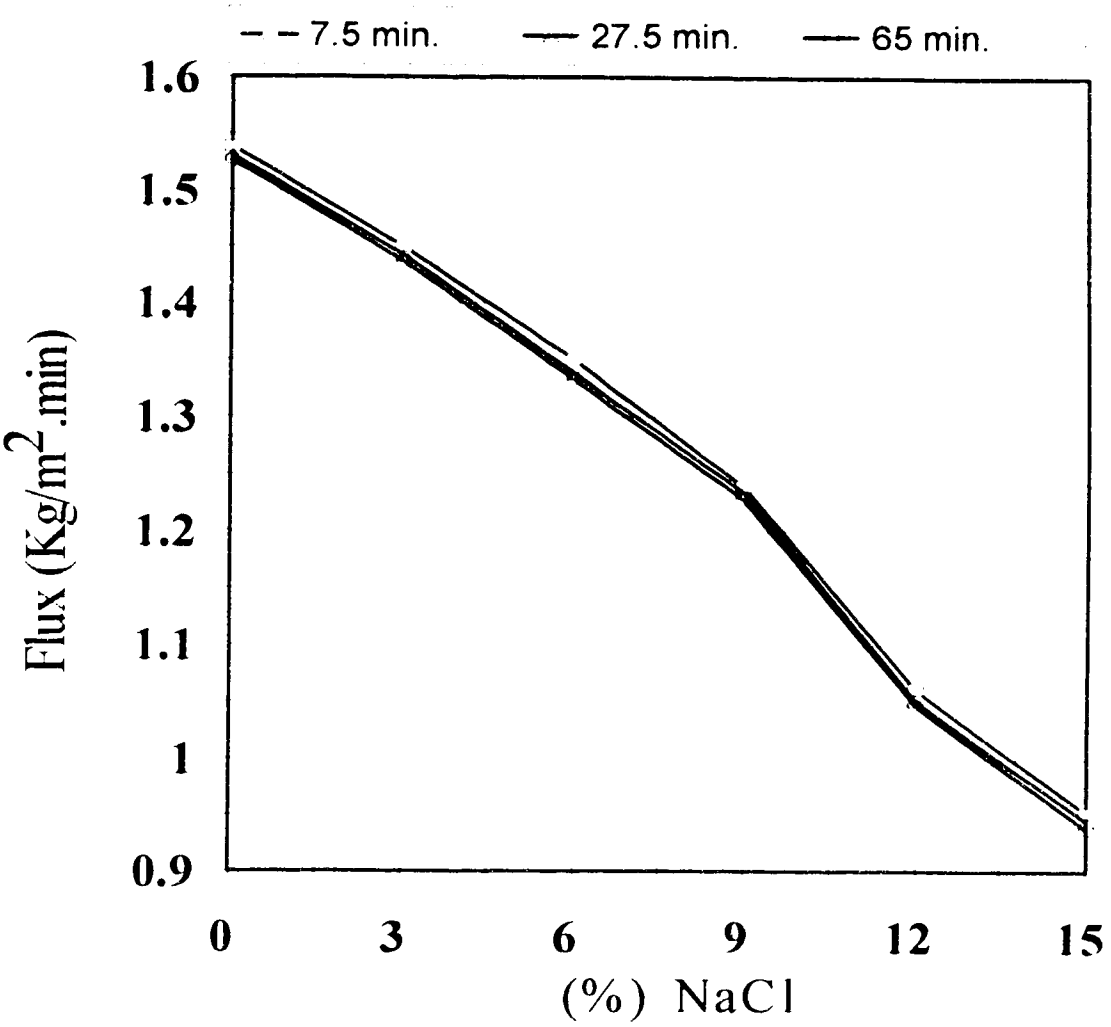


Figure 11. Effect of NaCl concentration on permeate flux during UF of protein-free acid whey permeate (pH 4.5).

4.2 Protein-membrane interaction

To test the postulated protein-membrane interaction effects, the membrane was immersed in whey at various salt concentrations and pH 3.0 and 4.5. Water fluxes through clean and presoaked membrane were compared as discussed below. The water flux through the membrane pre-soaked in whey at both pH and with both NaCl and $CaCl_2$ was dramatically lower than that observed through the clean membrane (Figs. 12 and 13). This clearly suggests that proteins were adsorbed on the membrane surface during the soaking of the membrane in whey.

The water flux patterns obtained after 1.0 minute of filtering water through the pre-soaked membrane at pH 3.0 or 4.5 and 0-15% concentration of either salt were similar to the flux patterns observed during UF of acid whey at identical pH and salt concentrations (Figs. 8, 9, 12 and 13). At pH 4.5, maximum water flux through the pre-soaked membrane was observed at 6% NaCl concentration, and was 80% higher than that observed with no added salt (Fig. 12). Conversely, at pH 3.0, minimum water flux through the pre-soaked membrane was observed at 3% NaCl concentration; this flux was 37% lower than that observed with no added salt.

Similarly, in the case of $CaCl_2$ treatment, maximum flux was observed when the membrane was soaked in pH 4.5 whey with 6% $CaCl_2$; this flux was 98% higher than that observed when the membrane was soaked in whey with no added $CaCl_2$, as shown in Fig. 13. Soaking the membrane in pH 3.0 whey resulted in the flux being minimum when the $CaCl_2$ content of the whey was 3%. The minimum was approximately 50% of that observed for whey with no salt (Fig. 13).

The effect of soaking the membrane in salted or unsalted whey at various pH values, as discussed above, was most noticeable at 1.0 minute of filtration time. Fluxes measured after 20 minutes of operation were higher than those observed at 1.0 minute at all salt concentrations, but the same pattern persisted (Figs. 14 and 15). The water flux without any added salt increased by 80% after 20 minutes; however, with added salt,

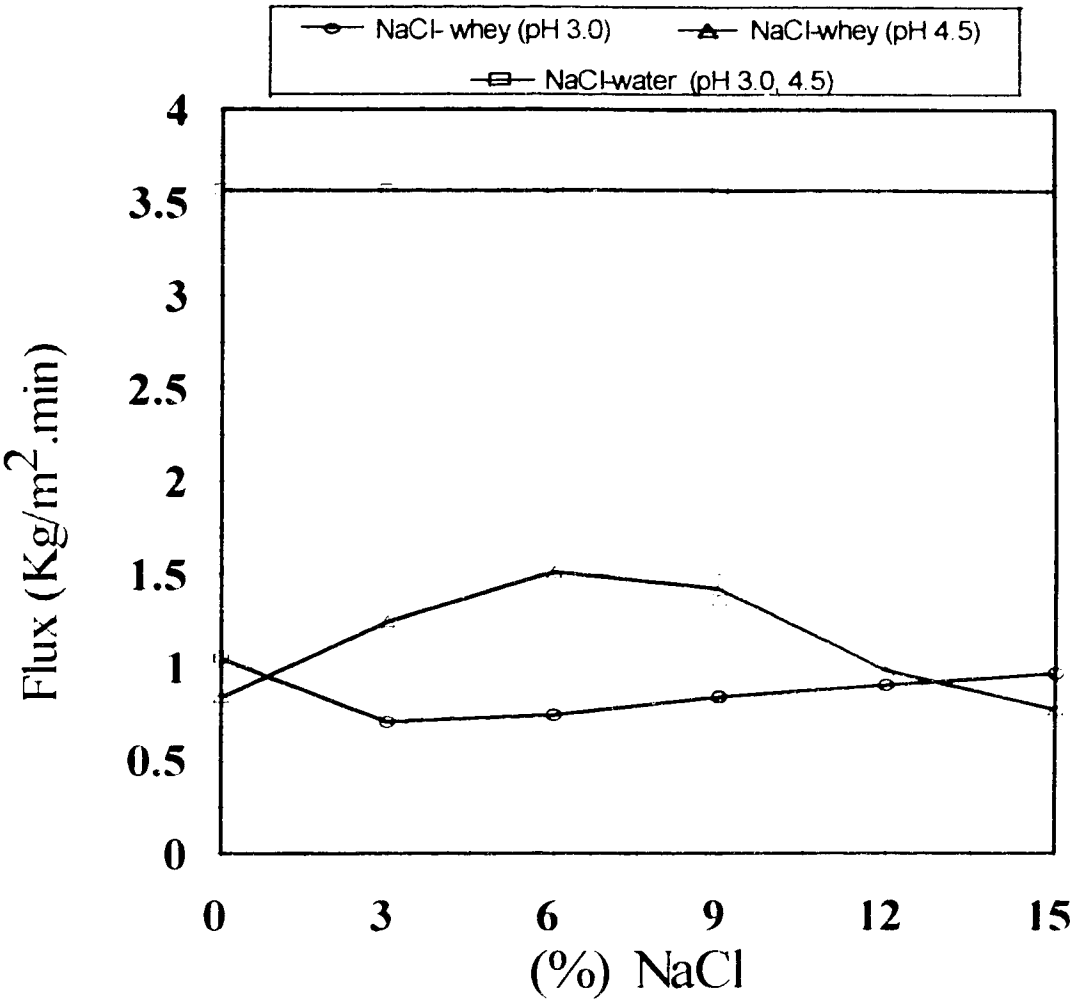


Figure 12. Water flux at 1.0 minute through membrane pre-soaked in NaCl-water and whey solutions

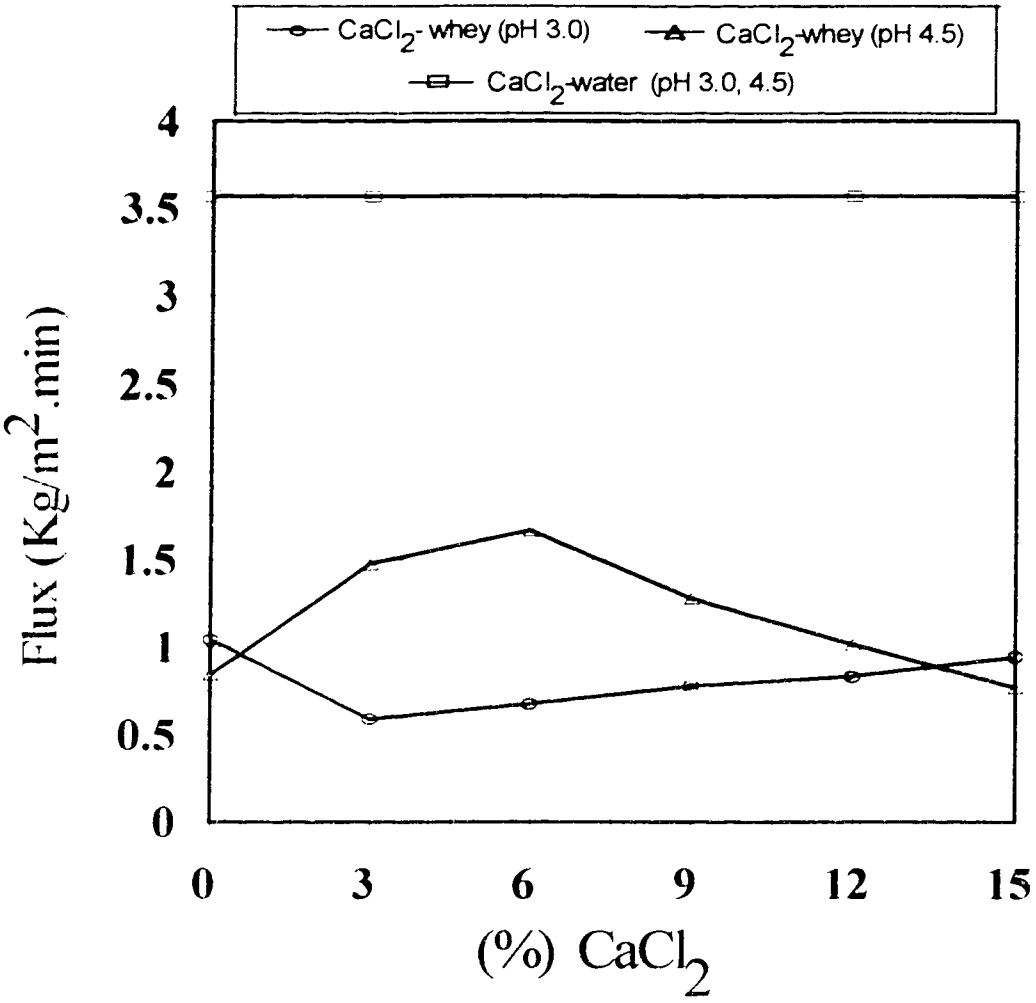


Figure 13. Water flux at 1.0 minute through membrane pre-soaked in $CaCl_2$-water and whey solutions.

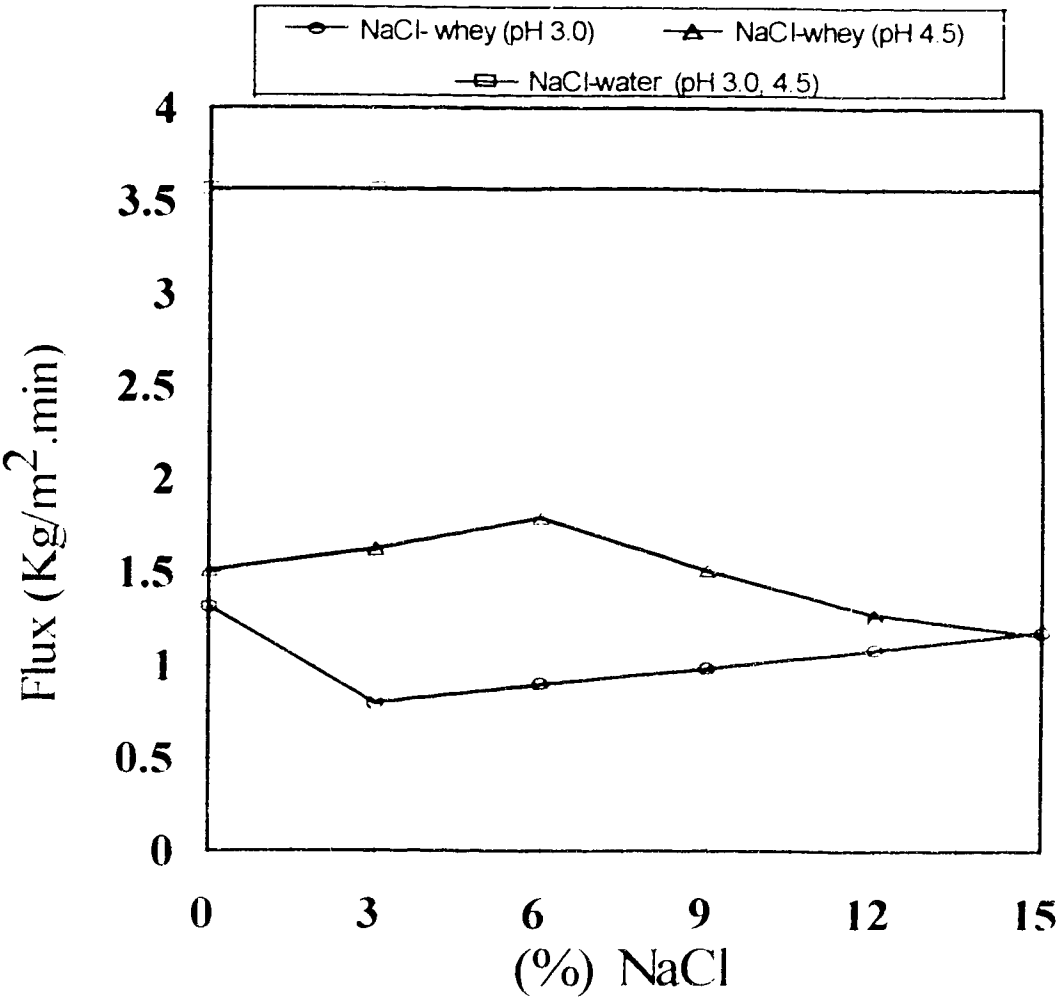


Figure 14. Water flux at 20.0 minute through membrane pre-soaked in NaCl-water and whey solutions

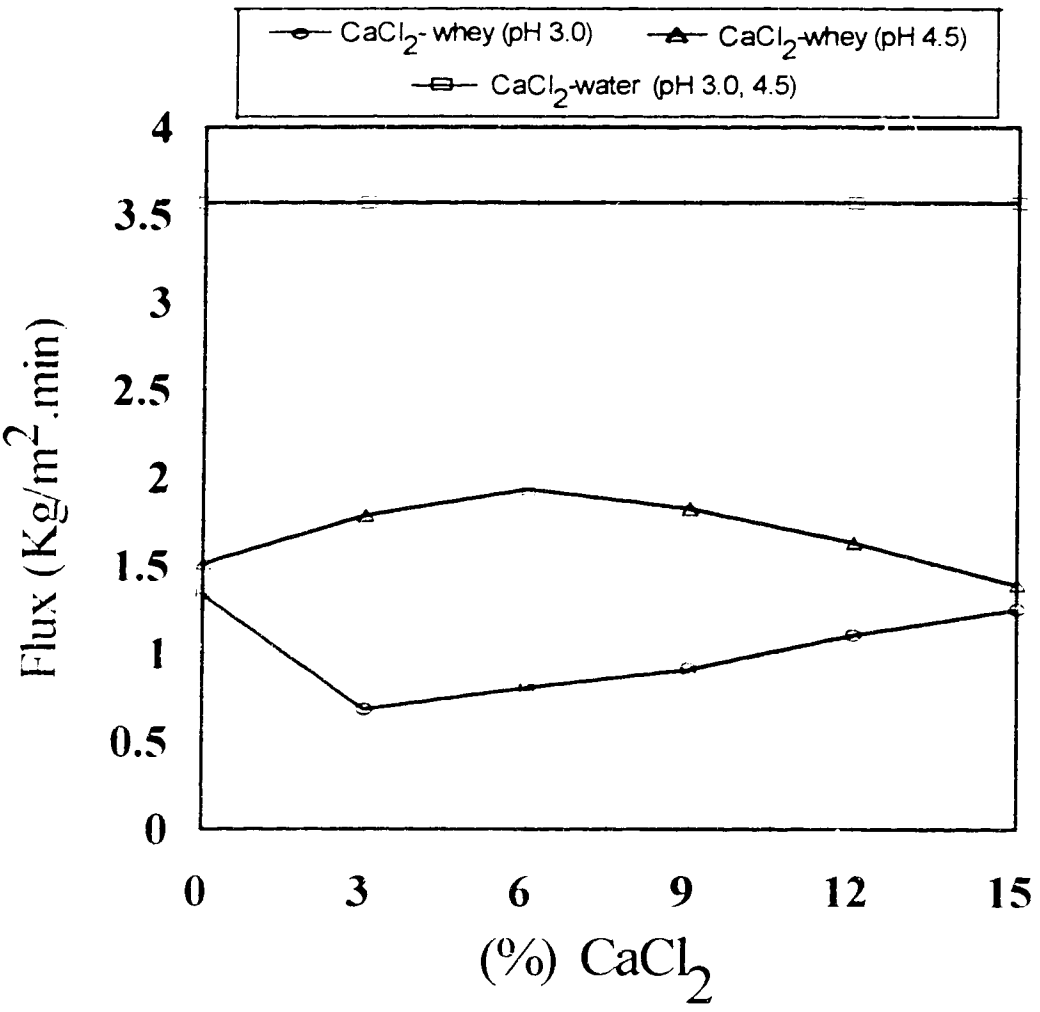


Figure 15. Water flux at 20.0 minute through membrane pre-soaked in $CaCl_2$-water and whey solutions.

the increase ranged from 10% to 44%. The trends were very similar for both salts and pH. This indicates that the interaction between the membrane and the proteins was dependent on the ionic strength of the solution. That is, the proteins are tightly bound, especially in the presence of salt. Most of the proteins appeared to be tightly bound to the membrane, as flux rates after 20 minutes remained much lower than those observed for water through the clean membrane.

In order to quantitatively support the conclusion that there was adsorption of whey proteins on the membrane during the soaking period, the protein content of whey was determined by Kjeldahl analysis both before and after soaking the membrane. These results are shown in Table 7.

Table 7

Protein concentration in whey (pH 4.5) before and after soaking the membrane.

% NaCl	Protein concentration in whey (%)*		Protein adsorbed on the membrane (%)
	Before soaking the membrane	After soaking the membrane	
0	0.62±0.05	0.53±0.01	0.09
3	0.59±0.03	0.50±0.04	0.09
6	0.55±0.006	0.46±0.01	0.09
9	0.51±0.007	0.42±0.008	0.09
12	0.48±0.02	0.38±0.03	0.1
15	0.43±0.019	0.33±0.06	0.1

* average of two determinations

Taken together, the results in Figs. 12 and 13 and in Table 7 suggest that proteins were adsorbed on the membrane during the soaking period. The adsorption was static in nature and the amount of protein adsorbed was not influenced by the ionic strength of

whey, as is clear from Table 7. However, the nature of the adsorbed layer changed with addition of salt. Proteins were more tightly bound to the membrane in presence of salt than without added salt. The decrease in protein concentration with addition of salt was more pronounced than expected from dilution effects alone (Table 7). There is no explanation for this at the present time. Although the adsorption of whey proteins on the membrane resulted in lower water fluxes, and proteins were more tightly bound to membrane in the presence of salts, this does not explain completely the increase in whey flux observed as salt content increased to 6% or the decrease in flux as salt content was raised above 6%.

Furthermore, the water flux through the membrane soaked in aqueous solutions of NaCl or $CaCl_2$ at concentrations of 0-15% (w/w) was identical to flux values for water through the clean membrane. Thus, the salts themselves did not interact with the membrane and could not cause the observed changes in flux rates. It was therefore necessary to determine the effect of salt type and/or concentration on the state of whey proteins in solution.

4.3 Salt-protein interaction

In order to assess the interaction between NaCl or $CaCl_2$ and whey proteins, the optical density of the solutions at various pH levels and salt concentrations was determined at 650 nm and 280 nm. Absorbance values at 650 nm are a measure of the turbidity of solutions. In the present study turbidity was attributable mainly to whey proteins. As shown in Figs. 16 and 17, as salt concentration increased (for both NaCl and $CaCl_2$), absorbance values at 650 nm decreased, reflecting a decrease in the turbidity of the solutions. This may have been due to the dissociation of whey proteins, especially β-lg, from octamers to dimers or monomers in the presence of salt. The dissociation of whey proteins, which probably resulted in less resistance or increased permeability of the protein layer, may have been responsible for increased flux up to a salt concentration of

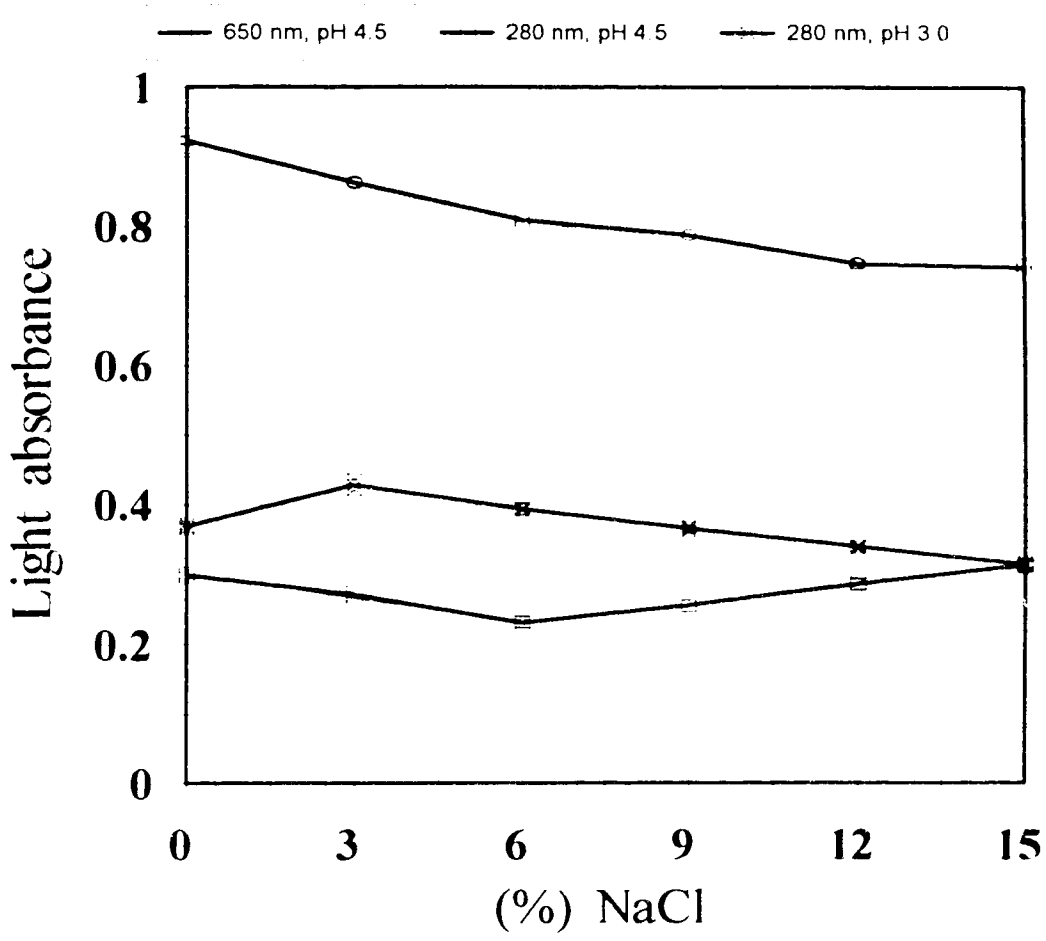


Figure 16. Light absorbance by whey containing varying amounts of NaCl.

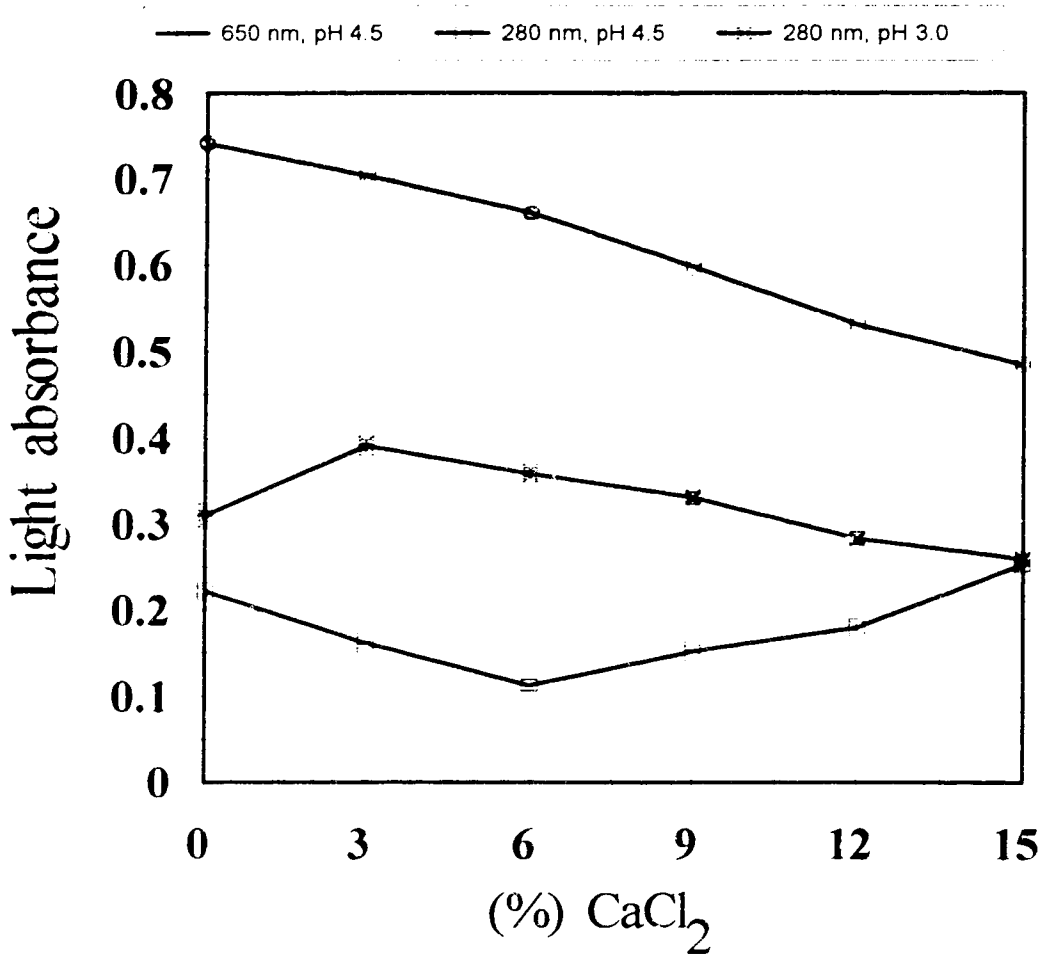


Figure 17. Light absorbance by whey containing varying amounts of $CaCl_2$.

6% during UF of whey at pH 4.5 and 5.7.

The protein-salt interactions in the whey were also estimated by UV analysis. At 280 nm, the aromatic groups of amino acids such as tyrosine, tryptophan, and phenylalanine absorb light (Smith et al., 1983); thus, absorbance at 280 nm can be used as a measure of protein content. As shown in Figs 16 and 17, the light absorbance of pH 4.5 whey at 280 nm decreased with increased concentration of both salts up to 6%. This was a mirror image of the flux pattern observed during UF of whey at identical pH and % salt (Figs. 8 and 9). The decrease in light absorption at 280 nm as the salt concentration increased in the 0 to 6% range may have been due to the dissociation of whey proteins from oligomer to dimers and monomers with increase in ionic strength of the solutions. At salt levels above 6% there may have been more extensive unfolding of the proteins, leading to the exposure of aromatic groups which were previously buried within the protein. This would account for the increase in absorbance at 280 nm at salt levels above 6%. Such conformational changes may have also contributed to increased protein layer resistance, thus leading to decreased whey flux above 6% salt.

For whey acidified to pH 3.0, absorbance values at 280 nm initially increased to a maximum at 3% salt, and decreased with further addition of salt (Figs. 16 and 17). As with whey at pH 4.5, the pattern of UV (280 nm) light absorption was the inverse of the observed flux patterns at identical pH values and salt concentrations (Figs. 8 and 9). As discussed above, the addition of salt may lead to conformational changes in proteins, allowing more aromatic groups to be exposed and absorb light as the protein unfolds at the lower ionic strength, while the reverse may be true above 6% salt. However, there is also an obvious influence of pH on the conformational changes occurring. The maximum and minimum absorbances at 280 nm with respect to salt concentration were dependent on the pH of whey. This was not surprising, as proteins are often very sensitive to changes in pH.

CHAPTER 5

CONCLUSIONS

In this work, an attempt was made to confirm and explain the effect of salt type (NaCl and $CaCl_2$) and salt concentration on the flux observed during the UF of whey and standard whey protein solutions at various pH values. The pH of whey was found to have a significant effect on permeate flux and it also influenced the effect of salt on flux rates. Flux rates generally exhibited a maximum at intermediate salt concentrations (6%) at pH 4.5, which is the native pH of acid whey. A similar flux pattern was observed at pH 5.7, which is close to the isoelectric point of whey proteins. However, the flux patterns were totally opposite at pH far below (pH 3.0) and far above (pH 6.5) the isoelectric point. Although calcium is considered a major foulant during UF of dairy fluids, addition of up to 6% $CaCl_2$ resulted in a dramatic increase in permeate flux at pH 4.5 and 5.7.

During the UF of salted WPC, β-lg, and α-la, fluxes were also maximized at 3% or 6% salt. These results suggested an interaction between salts and proteins, which was confirmed by decreased absorbance of proteins in solution at 650 nm as the salt concentration increased. The decrease in turbidity of the solution at higher salt concentrations was attributed to dissociation of proteins in the presence of salt, resulting in decreased resistance of the protein layer and increased flux rates with increasing salt concentrations. Also, conformational changes of proteins at intermediate salt concentrations (6% or 3%) at pH 4.5, as evidenced by light absorbance of whey at 280 nm, may have been responsible for the increased membrane resistance and decreased flux rates above 6% salt.

Whey proteins appeared to be tightly adsorbed as a static layer on the membrane surface. This effect was enhanced in the presence of salt, resulting in much lower flux rates. Thus, the effect of salt on permeate flux was probably due to conformational changes of proteins in the adsorbed layer.

This study sheds some light on the effect of electrolytes on the permeate flux during ultrafiltration of salted acid whey and its probable causes. It also explain some of the important determinants of UF efficiency. The results presented in this thesis indicate that the presence of moderate levels of salt in whey could enhance UF efficiency. These results could also be used as a guideline by membrane manufacturers in developing new membranes.

Large quantities of salted whey are obtained as by-product of Egyptian Domiati cheese and whey drippings from hard cheeses manufactured in North America. At present few economically attractive and/or cost effective outlets exist for the further utilization of this whey. The results presented in this manuscript suggests that it may be feasible to develop UF processes to allow for the recovery of whey proteins from salted whey sources. As an example whey can be first concentrated by UF and then subjected to nanofiltration (NF) to remove salts. Using these processes (UF and NF) in such a sequence could allow for the efficient recovery of whey proteins while minimizing the volume of whey to be processed by NF. WPC thus obtained could be utilized in other sectors of the food industry.

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