In a subsequent paper, the critical point condition will be discussed and the results of the first two papers illustrated with real systems, that is, the spinoidal and critical points of pure components and mixtures will be determined using typical equations of state.

NOTATION

$\underline{A}$ = total Helmholtz free energy
$\mathcal{G}_{ijk}$ = determinant defined in Equation (10)
$\mathcal{D}_k$ = determinant defined in Equation (9)
$\underline{G}$ = total Gibbs free energy
$\underline{H}$ = total enthalpy
$\mathcal{L}_j$ = determinant defined in Equation (25)
N_j = moles of j
P = pressure
R = gas constant
$\underline{S}$ = total entropy
$\underline{T}$ = temperature
$\underline{U}$ = total energy
$\underline{V}$ = total volume
x_j = extensive independent variable
$y^{(k)}$ = kth order Legendre transform
Z_k = extensive parameter defined in Equation (8)

Greek Letters

μ_j = chemical potential of j
ξ_j = intensive independent variable that is the conjugate coordinate of x_j

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Charged Membrane Ultrafiltration of Inorganic Ions in Single and Multi-Salt Systems

An experimental study of the ultrafiltration of several ionic inorganic solutes, using a negatively-charged membrane, is detailed. Both single salt and multi-salt systems are investigated in a continuous flow, thin channel unit, with an average transmembrane pressure difference of 2.76×10^5 N/m^2 and a channel Reynolds number of 2800. The solute rejection is predictable to some extent in terms of Donnan ion exclusion theory, and the water flux is dictated by the combined effects of osmotic pressure and membrane-cation interaction.

In the single salt experiments, the anion rejections can be related to the inlet (feed) concentration by power functions of the form: rejection $= 1 - K\,C_i^a$, in which $0 < a < 1.0$. The power a is 0.4 for chloride salts, 0.25 for monovalent oxyanion salts, and 0.1 for divalent oxyanion salts, but a is independent of the cation present (Na^+, Ca^{2+}, or La^{3+}). The constant K is generally a function of both the anion (except in the case of SO_4^{2-}, HPO_4^{2-}, and CrO_4^{2-}) and the cation, being determined by such factors as ion charge density and membrane-cation interaction. The membrane resistance to water flux is found to depend on cation charge and cation radius. For systems containing two or more salts, the presence of a divalent anion decreases the rejection of the monovalent anion. For multi-salt systems, a rejection of Ca^{2+} plus Mg^{2+} of 0.82 and a water flux of 12.9×10^{-4} cm/s (27.2 gal/ft^2-day) are achieved at a transmembrane pressure difference of 4.10×10^5 N/m^2 (4.1 atm), indicating that the process has considerable potential for industrial water softening.

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SCOPE

Ultrafiltration is a pressure-activated membrane process and is generally carried out at low pressures of about 10^5 to 10^6 N/m^2. Ultrafiltration with conventional uncharged anisotropic membranes has been used primarily for the separation of modest molecular weight organic solutes, organic macromolecules, and colloids from aqueous solution. In a recent article, Porter and Nelson (1972) have reviewed applications of conventional ultrafiltration in the chemical, food processing, pharmaceutical, and medical industries.

The solute rejection characteristics of a membrane depend both on the pore size distribution and on the nature of the membrane (whether charged or uncharged). The charged ultrafiltration (anisotropic) membrane is a recent development in separation technology and has been used by Bhattacharyya et al. (1974) for the removal of several inorganic ions present in laundry wastes. High pressure reverse osmosis is conventionally used to remove inorganic ions from water, whereas the present work will show that adequate rejections of inorganic ions and high water flux can be obtained at low pressure using a charged ultrafiltration membrane. Such membranes reject low molecular weight inorganic electrolytes because of the well-known Donnan exclusion mechanism. The use of charged polymeric membranes is reported only for the high pressure reverse osmosis process (LaConti et al., 1972; Yasuda et al., 1971; Kimura, 1971). Recently LaConti et al. (1972) investigated cation exchange, reverse osmosis membranes (sulfonated polyphenylene oxide) to treat brackish water, caustic feeds, secondary sewage, and synthetic wash water; the desired water permeability and solute rejection were obtained by controlling the ion exchange capacity of the sulfonated polymer.

Low pressure, charged membrane ultrafiltration is particularly promising for the removal of ionic solutes (for example, toxic, heavy metal ions) from a dilute waste stream or for water treatment where complete demineralization is not necessary. For ultrafiltration of inorganic ions by a charged membrane, the concentration polarization model must include osmotic pressure effects. The polarization model used in the case of reverse osmosis is equally applicable here although solvent and solute transport mechanisms through the membrane are quite different (Lonsdale, 1972). Severe concentration polarization may cause membrane-solute interaction with a subsequent change in the intrinsic properties of the membrane.

The objective of this study is to determine the extent of separation of ionic inorganic solutes from aqueous solutions by a charged (containing fixed, negatively-charged groups) ultrafiltration membrane. The investigation is carried out at a channel velocity sufficient to eliminate concentration polarization. The study of single salt systems includes a series of mono- and divalent oxyanion salts of sodium, and of the sulfate and chloride salts of mono-, di-, and trivalent cations. The results are discussed in terms of Donnan theory and membrane-solute interactions. For systems containing a mixture of two solutes (sodium salts), the effects of the presence of divalent anions on the rejection of a monovalent anion are established. Finally, the potential application to water softening is addressed; three types of synthetic natural waters (multi-salt systems) which contain predominately carbonate hardness or noncarbonate hardness are ultrafiltered.

CONCLUSIONS AND SIGNIFICANCE

An experimental investigation of the charged (fixed negatively-charged groups) membrane ultrafiltration of several ionic inorganic solutes, in single and in multi-salt systems, is presented. All ultrafiltration experiments were conducted in a continuous flow, thin channel unit, using commercially (Millipore PSAL) available, noncellulosic membranes. Use of a 167 cm/s channel velocity (Reynolds number = 2800) at an average transmembrane pressure difference of 2.76×10^5 N/m^2 was sufficient to eliminate concentration polarization. The average membrane resistance (R_m) in the absence of any solute was 3.33×10^8 N/m^2/cm/s. The solute rejection (R^*) was predictable to some extent in terms of Donnan ion exclusion theory, and the water flux (J_w) was dictated by the combined effects of osmotic pressure and pore swelling (or shrinkage) due to membrane-cation interaction.

For all of the single salt experiments, the ultrafiltrate concentrations of the various anions, and thus the salt rejections, could be related to inlet anion concentration by simple power functions:

Na^+ salts of SO_4^{2-}, HPO_4^{2-}, or CrO_4^{-2}:

$$R^* = 1 - 0.042\, C_i^{0.10}$$

Na^+ salts of HCO_3^-, $H_2PO_4^-$, or $HCrO_4^-$:

$$R^* = 1 - K_1\, C_i^{0.25}$$

Na^+, Ca^{2+}, Mg^{2+}, or La^{3+} salts of SO_4^{2-}:

$$R^* = 1 - K_2\, C_i^{0.10}$$

Na^+, Ca^{2+}, Mg^{2+}, or La^{3+} salts of Cl^-:

$$R^* = 1 - K_3\, C_i^{0.40}$$

For the monovalent oxyanions, K_1 for $HCrO_4^-$ was 0.73, compared to values of 0.10 and 0.19 for $H_2PO_4^-$ and HCO_3^-, respectively. The poor rejection of $HCrO_4^-$ was probably produced by its low charge density. For both chloride and sulfate salts, the charge of the cation did not influence the power on C_i, and the rejection of SO_4^{2-} was consistently better than that of Cl^-. For sulfate salts, K_2 for Na^+ was 0.042, and for Ca^{2+} or Mg^{2+} or La^{3+}, K_2 was 0.065. For chloride salts, K_3 was 0.33, 0.24, and 0.13 for Na^+, for Ca^{2+} or Mg^{2+}, and for La^{3+}, respectively. In the case of $LaCl_3$, the highly charged La^{3+} interacted with membrane fixed sites and resulted in membrane charge reversal.

For single salt systems containing SO_4^{2-} or Cl^-, J_w decreased with an increase in C_i because of an increase in osmotic pressure. The membrane resistance R_m was found to depend on cation charge and cation radius (z^2/r). The highly hydrated Na^+ caused membrane swelling, whereas La^{3+} caused membrane pore shrinkage due to electrostatic crosslinking.

For systems containing two salts ($NaHCO_3$-Na_2SO_4, or $NaHCO_3$-Na_2HPO_4), the presence of divalent anions decreased the rejection of the monovalent HCO_3^- ion. The three multi-salt solutions studied contained Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-}, HCO_3^-, and Cl^-. When the molar concentration of SO_4^{2-} was twice that of HCO_3^-, the rejection of HCO_3^- was only 0.26 compared to 0.90 in the single salt system, and the rejections of divalent cations were 0.83. For the multi-salt system containing HCO_3^- at six times the SO_4^{2-} concentration, the rejection of HCO_3^- was 0.64 and the rejections of cations were approximately 0.76. The multi-salt solution containing high chloride concentration gave poor rejection of Cl^- ($R^* = 0.10$) but quite high rejection of divalent Ca^{2+} ($R^* = 0.79$). In all three multi-salt systems, the rejection of SO_4^{2-} was greater than 0.89, and total hardness rejection was greater than 0.76.

In applications in which the complete demineralization

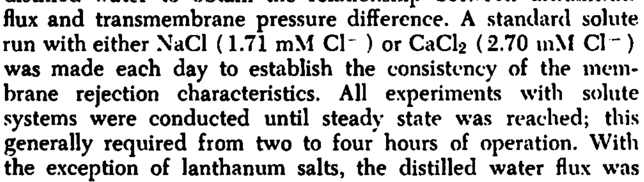
of a water is not necessary, low pressure ultrafiltration with a charged membrane would be an attractive softening process. For example, 82% of the hardness was removed from a Missouri River type water (high noncarbonate hardness) at an average water flux, $J_w = 12.9 \times 10^4$ cm/s (27.2 gal/ft^2-day). Another application of the work would be the removal of toxic ionic solutes from dilute wastewaters; in particular, the removal efficiency (rejection) would increase with a decrease in the feed solute concentration. For a water containing CrO_4^{2-}, 97% of the chromium was removed at 0.1 mM (5 mg/l Cr) concentration.

EXPERIMENT

A schematic diagram of the experimental unit is shown in Figure 1. The ultrafiltration cell was constructed of clear Lucite and the feed channel (high pressure side) length, width, and height were 39.6 cm, 1.27 cm, and 0.079 cm, respectively. The effective membrane area was 50.3 cm^2. A typical ultrafiltration run was initiated by pumping the inlet stream from the feed tank into the high pressure side of the membrane cell. The feed stream temperature was maintained at 25 ± 0.5°C. The pressure and the flow rate were controlled by regulating the needle valves and by adjusting the pump speed control. Most experiments were conducted at an average transmembrane pressure difference, $\Delta p = 2.76 \times 10^5$ N/m^2 and at an average channel velocity $U = 167$ cm/s. The reported Δp is p inlet $- 0.5\ \Delta p$ loss. At $U = 167$ cm/s, Δp loss (channel pressure drop) was 0.28×10^5 N/m^2.

All ultrafiltration experiments were conducted with Millipore PSAL (noncellulosic skin on cellulosic backing) membranes containing sulfate functional groups. A total of five membranes was used, all from the same lot in order to enhance reproducibility. Initially, each membrane was calibrated with distilled water to obtain the relationship between ultrafiltrate flux and transmembrane pressure difference. A standard solute run with either NaCl (1.71 mM Cl^-) or $CaCl_2$ (2.70 mM Cl^-) was made each day to establish the consistency of the membrane rejection characteristics. All experiments with solute systems were conducted until steady state was reached; this generally required from two to four hours of operation. With the exception of lanthanum salts, the distilled water flux was the same before and after each run with the solute systems.

The distilled water had a conductivity of 5 μmho/cm at 25°C. The following Analytical Reagent Grade salts were used: NaCl, Na_2SO_4, $NaHCO_3$, NaH_2PO_4, Na_2HPO_4, $Na_2Cr_2O_7 \cdot 2H_2O$, $CaCl_2 \cdot 2H_2O$, $CaSO_4 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 7H_2O$, $LaCl_3 \cdot 6H_2O$, $La_2(SO_4)_3 \cdot 8H_2O$. Most systems with single solutes were analyzed by conductivity measurements. Phosphate and chromate concentrations were determined by the vanadomolybdophosphoric acid colorimetric method and by the diphenylcarbazide method, respectively (Anon., 1971). Bicarbonate was always measured by a Beckman Model 915 Carbon Analyzer. For systems containing two or more solutes, the sulfate concentration was measured by the turbidimetric method, and chloride by the argentometric method (Anon., 1971). Total hardness and calcium were each analyzed by the EDTA titrimetric method, and magnesium was calculated by difference (Anon., 1971).



(1) Feed Solution Tank
(2) Valve (on-off)
(3) Gear Pump With Speed Control
(4) Flowmeter (inlet flow)
(5) Pressure Gauge (inlet)
(6) Thin Channel Ultrafiltration Cell
(7) Pressure Gauge (concentrate flow)
(8) Needle Valve (fine control)
(9) Flowmeter (concentrate flow)
(10) Needle Valve (coarse control)
(11) Pressure Gauge (ultrafiltrate)
(12) Flowmeter (ultrafiltrate)
(13) Needle Valve (fine control)

Fig. 1. Schematic diagram of experimental apparatus.

MEMBRANE REJECTION

The removal of solutes by ultrafiltration can be defined in terms of a rejection parameter R^*

$$R^* = 1 - \frac{J_s}{J_w C_i} = 1 - \frac{C_f}{C_i} \tag{1}$$

in which C_f is the concentration of a particular solute (or ion) in the ultrafiltrate, C_i is the concentration of the same solute (or ion) in the inlet (feed) stream, J_s is the solute flux, and J_w is the water flux. Charged membranes reject ionic solutes because of the phenomenon of Donnan exclusion (Helfferich, 1962). For a membrane containing fixed negative groups, the effect of Donnan potential is to repel anions (coions) from the membrane, and because of the electroneutrality requirement, the solute itself is rejected. Solute rejection by a negatively-charged membrane depends on the charge density (related to effective radius and valency) of the anion, on the extent of interaction of fixed membrane charge sites with the cation and possible resultant swelling (or shrinkage) of the membrane, and on the feed solute concentration. Anions of high valency (or charge density) and cations of low valency are rejected best. Cations of high valency and small effective radius interact with fixed negative groups in the membrane and may cause electrostatic cross-linking. The quantitative effect of specific cations on the rejection of a common anion is difficult to predict when membrane swelling (or shrinkage) occurs; Donnan potential and hence solute rejection are inversely proportional to the degree of swelling. Solute rejection by the Donnan mechanism is unavoidably decreased by an increase in the feed solute concentration because of the increased tendency of the ions to eliminate concentration differences by diffusion. Finally, it should be recognized that the overall flux of an ion through the membrane is the sum of fluxes due to convection, diffusion, and electrical potential. Simons and Kedem (1973) and Dresner (1972) have developed models for solute flux computations in the case of reverse osmosis, involving no membrane-solute interaction.

Water transport through charged ultrafiltration membranes follows a viscous flow mechanism. The water flux can be related to the effective transmembrane pressure difference:

$$J_w = \frac{\Delta p - \Delta\pi}{R_m} \tag{2}$$

in which R_m is the resistance of the membrane and $\Delta\pi$ is the osmotic pressure difference. The membranes used in this study had an average R_m of 3.33×10^8 N/m^2/cm/s, in the absence of solutes. It should be noted that the value of R_m may depend (compared to solute free water) on the valency and effective radii of cations in the solution. The osmotic pressure can be computed from the Van't Hoff equation, in the absence of concentration polarization:

$$\Delta\pi = (i\,C_i\,R\,T)(R^*) \tag{3}$$

RESULTS AND DISCUSSION

All ultrafiltration experiments were conducted with Millipore PSAL charged membranes which contained fixed sulfate groups. Most experiments were performed at $\Delta p = 2.76 \times 10^5$ N/m² and at an average channel velocity = 167 cm/s. This velocity, corresponding to a Reynolds number of 2800, essentially eliminated concentration polarization: for example, a series of variable-channel-velocity experiments (with Reynolds numbers from 1400 to 4200) was carried out both with a single-salt system and a multi-salt system; results showed no change in water flux or rejection with the decrease in the Reynolds number to 1400.

Sodium Salts of Oxyanions

An extensive initial set of single salt experiments was run with the sodium salts of

SO_4^{2-} (pH 8.6)	HCO_3^- (pH 8.0)
HPO_4^{2-} (pH 8.6)	$H_2PO_4^-$ (pH 5.5)
CrO_4^{2-} (pH 9.0)	$HCrO_4^-$ (pH 4.8)

over the concentration range 0.10 to 16 mM (1.0×10^{-4} to 1.6×10^{-2} M). Results in terms of the ultrafiltrate concentration of each oxyanion are presented in Figure 2. For the three divalent oxyanions a single correlation gave a good fit, $C_f = 0.042\ C_i^{1.10}$, indicating that the membrane rejection

$$R^* = 1 - \frac{0.042\ C_i^{1.10}}{C_i} = 1 - 0.042\ C_i^{0.10} \qquad (4)$$

was a rather weak function of concentration. The fact that the rejection did decrease with an increase in concentration is in agreement with Donnan theory. The percent average deviation of calculated values of C_f from experimental values was 17% for 12 points, omitting one point with an anomolously high error. The average deviation is defined as

$$\sum_n |C_{f\,\text{experimental}} - C_{f\,\text{calculated}}|/C_{f\,\text{experimental}}$$

with the summation taken for the $n = 12$ points.

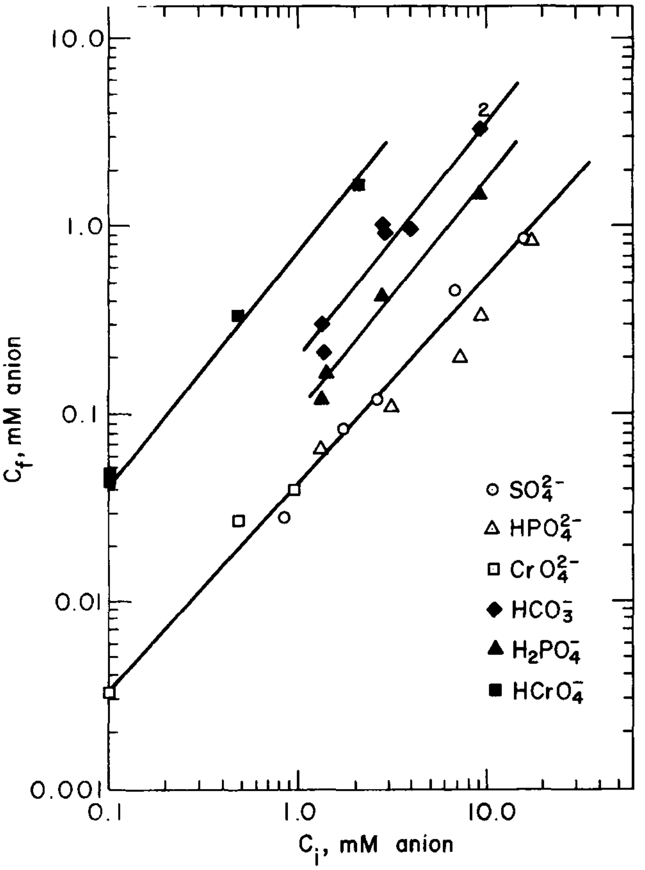


Fig. 2. Ultrafiltrate concentration vs. inlet (feed stream) concentration for sodium salts of mono- and divalent oxyanions.

Table 1. Rejection of a Monovalent Anion in the Presence of a Divalent Anion
$\Delta p = 2.76 \times 10^5$ N/m², $U = 167$ cm/s

Feed concentration, mM anion			Rejection		
$NaHCO_3$	Na_2SO_4	$NaHPO_4$	HCO_3^-	SO_4^{2-}	HPO_4^{2-}
10.6	0	0	0.62	—	—
0	3.0	0	—	0.95	—
10.6	3.0	0	0.40	0.94	—
8.2	0	0	0.65	—	—
0	0	2.6	—	—	0.96
8.2	0	2.6	0.49	—	0.94

The monovalent oxyanions were not rejected by the membrane as well as the divalent species, in agreement with Donnan theory. The ultrafiltrate concentration, and thus the rejection, were stronger functions of concentration although the same function gave a good fit for all three monovalent species,

$$C_f = K_1\ C_i^{1.25}; \quad R^* = 1 - K_1\ C_i^{0.25} \qquad (5)$$

The intercepts, K_1 (ultrafiltrate concentration at unit inlet concentration) and the percent average deviations of calculated versus experimental values were

Species	K_1	Percent deviation
$H_2PO_4^-$	0.10	14
HCO_3^-	0.19	18
$HCrO_4^-$	0.73	12

The low rejection of acid chromate was due to its low charge density: $HCrO_4^-$ has an effective ionic radius (r) of 1.72 Å (Cobble, 1953) compared to values of 1.26 and 1.37 Å for HCO_3^- and $H_2PO_4^-$, respectively. The charge density is commonly related to a parameter such as z^2/r. The value of z^2/r for $HCrO_4^-$ is 0.58 Å^{-1} compared to values of 0.79 and 0.73 for HCO_3^- and $H_2PO_4^-$, respectively. In the cases of the divalent oxyanions, the values of z^2/r were much larger (1.9 − 2.7 Å^{-1}) and differences would not be expected to have as significant an effect on the relative rejections.

Bhattacharyya et al. (1974) reported very high rejections ($R^* = 0.99$) of the highly charged polyphosphate anion ($HP_3O_{10}^{4-}$) using a similar membrane. The rejections of sodium salts of $HP_3O_{10}^{4-} > HPO_4^{2-} > H_2PO_4^-$ are in agreement with the Donnan ion exclusion mechanism.

An additional series of experiments was run with the inlet solutions containing sodium salts both of a monovalent anion and of a divalent anion. The results are given in Table 1. In both cases the presence of the divalent anion significantly decreased the rejection of HCO_3^-, while the presence of HCO_3^- only produced a slight decrease in the rejection of the divalent anion, making the comparison with the single salt systems.

Salts of Chloride and of Sulfate

For an additional series of single salt experiments, Figure 3 relates the ultrafiltrate concentration to the inlet concentration for sodium, calcium, magnesium, and lanthanum salts of sulfate and of chloride, over the inlet concentration range 0.35 to 16 mM. Again, power functions gave an excellent fit for both chloride and sulfate with each cation.

First looking at the sulfate experiments, the rejection of SO_4^{2-} with multivalent cations as the counterions was poorer (higher ultrafiltrate concentration) than in the presence of sodium in accordance with Donnan theory. For calcium, magnesium, and lanthanum,

$$C_f = 0.065\, C_i^{1.10}; \quad R^* = 1 - 0.065\, C_i^{0.10} \qquad (6)$$

The rejection of $La_2(SO_4)_3$ may have been increased by La^{3+}-membrane interaction, as is discussed.
The percent average deviation of the values of C_f calculated with Equation (6) from experimental values was 8%, for the 7 points. Recall that Equation (4) applies to Na_2SO_4, for comparison with Equation (6).

For chloride, three conclusions can be drawn: first, the rejection was consistently poorer than with sulfate, in accordance with Donnan theory; divalent sulfate was more strongly repulsed by the negatively-charged membrane sites. Second, the ultrafiltrate concentration was a much stronger function of the inlet anion concentration than in the case of any of the oxyanions. This would be a process limitation particularly when high water recovery is needed. Third, the rejection of chloride in the presence of sodium was poorer than in the presence of either calcium or magnesium (which consistently behaved quite similarly) which in turn was poorer than the rejection in the presence of lanthanum. The equations for chloride are

$$C_f = K_3\, C_i^{1.40}; \quad R^* = 1 - K_3\, C_i^{0.40} \qquad (7)$$

Cation	K_3	Percent deviation
Na^+	0.33	9
Ca^{2+}, Mg^{2+}	0.24	9
La^{3+}	0.13	12

The rejection of $LaCl_3$ was considerably higher than that of NaCl. The highly charged La^{3+} interacted with the membrane fixed sites, resulting in membrane charge reversal, and the rejection of $LaCl_3$ was due to cation exclusion. Such a type of interaction has been reported by Rosenberg et al. (1957). Charge reversal was validated by a reduction in the rejection of NaCl, after the membrane was exposed to a $LaCl_3$ solution. This interaction probably contributed largely to the lack of agreement with Donnan theory exhibited by the chloride salts.

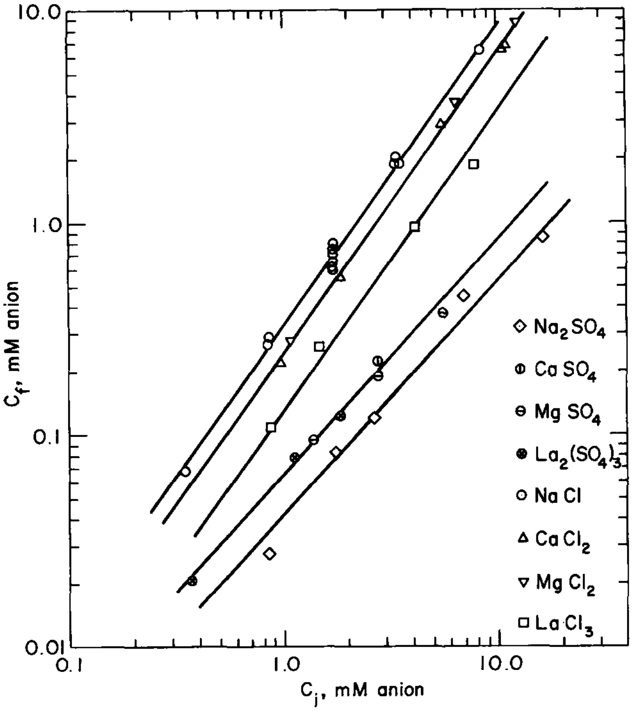


Fig. 3. Ultrafiltrate concentration vs. inlet (feed stream) concentration for chloride and for sulfate salts with cations of different valences.

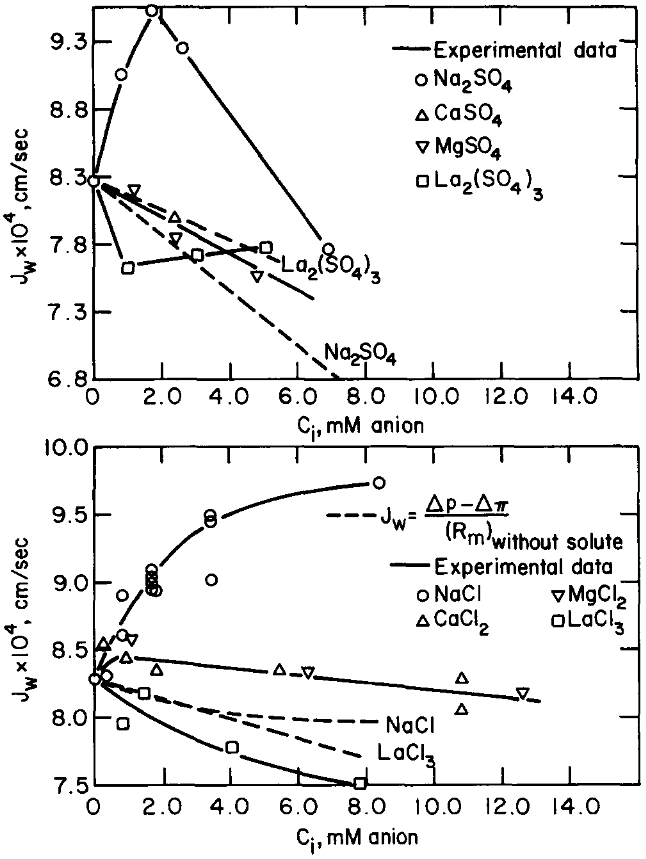


Fig. 4. Dependence of water flux on the anion concentration in inlet (feed) stream for both sulfate salts and chloride salts.

Figure 4 shows the effect of feed concentration on the ultrafiltrate flux for the same SO_4^{2-} (top figure) and Cl^- (bottom figure) salts as in Figure 3. For a fixed Δp and in the absence of membrane swelling, J_w should decrease with an increase in C_i because of an increase in $\Delta\pi$. The dotted lines show the calculated J_w obtained from Equations (2) and (3), $J_w \propto (\Delta p - \Delta\pi)$, for the case of a constant (in absence of solute) $R_m = 3.33 \times 10^5$ N/m^2/cm/s. For Ca and Mg salts, the dotted lines (not plotted) fell in between those for the Na and La salts. Both Na_2SO_4 and NaCl produced membrane swelling: a maximum increase in J_w of about 17% (compared to $C_i = 0$) occurred. With all salts except NaCl, the percent decrease of water flux with C_i was in qualitative agreement with the drop in effective $\Delta p - \Delta\pi$ (with Na_2SO_4 one experimental value of $J_w = 5.89 \times 10^{-4}$ for $C_i = 16.0$ mM is not shown in the figure). With NaCl at high concentration, $\Delta\pi$ was negligible (note dotted NaCl line) because of poor solute rejection, and hence J_w did not decrease with C_i.

Figure 5 shows the dependence of membrane resistance R_m on cation z^2/r at a constant $C_i = 1.1$ mM. An ordinate value of 1.0 indicates no membrane-solute interaction. The highly-hydrated, monovalent Na^+ caused membrane swelling whereas the highly charged La^{3+} caused electrostatic cross-linking and resultant membrane pore shrinkage. Swelling of the membrane (such as with Na^+ salts) would cause a lowering of the membrane charge density and thus of the Donnan potential. This would adversely affect the rejection of anions, particularly of the monovalent type. The rejection of NaCl < $CaCl_2$ [Equation (7)] is in accordance with the swelling behavior. With trivalent La^{3+}, a permanent flux decrease was observed. and the La^{3+}-membrane interaction produced the rejection of $LaCl_3$ > $CaCl_2$. Similar behavior with multivalent cations was also observed by LaConti et al. (1972) and Kimura (1971), using charged reverse osmosis membranes.

The data from Figure 3 (single salts) may be utilized to estimate the possible extent of separation of sulfate from chloride in the presence of sodium or of calcium and magnesium or of lanthanum. The ratio of the rejections is related to the total inlet anion concentration in Figure 6. The ratio of the rejections increases with solution concentration and decreases with cation charge. For example, for a solution 2.0 mM in sulfate and 6.0 mM in chloride with sodium as the counterion (C_i = 8.0 mM), the ratio of the rejections of sulfate to chloride would be about four. According to Table 1 which shows that the rejection of a monovalent oxyanion was decreased by the presence of a divalent oxyanion, Figure 6 probably gives fairly conservative estimates of the possible extent of separation. It should be stressed that Figure 6 is based on single salt data and that when applied to a solution containing a sulfate salt and a chloride salt, it gives only an approximate (and conservative) estimate of the extent of separation.

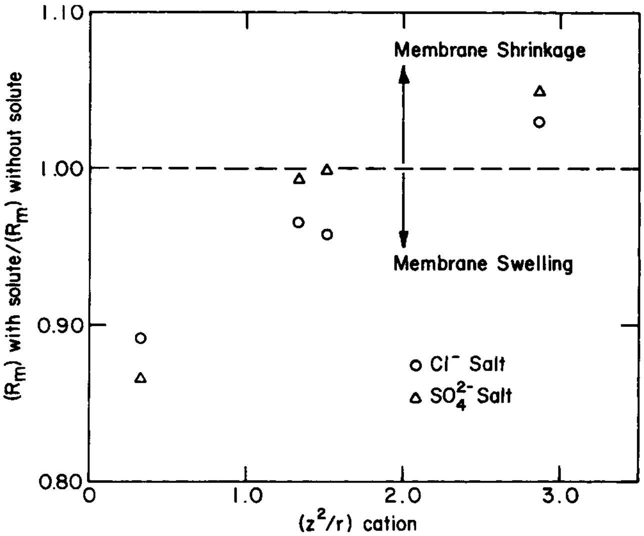


Fig. 5. Dependence of membrane resistance on cation charge density.

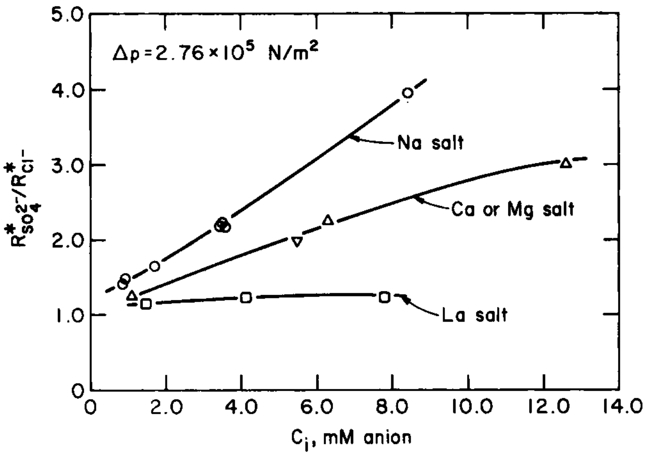


Fig. 6. Dependence of relative sulfate ion and chloride ion rejections on the solute (anion) concentration in inlet (feed) stream.

TABLE 2. COMPOSITIONS OF THREE SYNTHETIC WATERS AND THE REJECTIONS OF INDIVIDUAL IONS
$\Delta p = 2.76 \times 10^5$ N/m², $U = 167$ cm/s

	Feed composition mg/l as ion	Rejection
Total hardness	250 (as $CaCO_3$)	0.83
Ca^{2+}	72 (1.8 mM)	0.83
Mg^{2+}	17 (0.70 mM)	0.82
Na^+	30 (1.3 mM)	—
SO_4^{2-}	230 (2.4 mM)	0.93
HCO_3^-	82 (1.3 mM)	0.26
Cl^-	10 (0.28 mM)	—
Total hardness	171 (as $CaCO_3$)	0.76
Ca^{2+}	38 (0.95 mM)	0.75
Mg^{2+}	18 (0.74 mM)	0.77
Na^+	30 (1.3 mM)	—
HCO_3^-	152 (2.5 mM)	0.64
SO_4^{2-}	39 (0.41 mM)	0.90+
Cl^-	30 (0.84 mM)	—
Total hardness	200 (as $CaCO_3$)	0.79
Ca^{2+}	80 (2.0 mM)	0.79
Na^+	500 (21.7 mM)	—
SO_4^{2-}	150 (1.6 mM)	0.89
HCO_3^-	18 (0.30 mM)	—
Cl^-	780 (22.0 mM)	0.10

Multi-Salt Systems

Table 2 lists the feed composition of the three systems that were studied and the rejections (both cations and anions) which were observed. The pH of each system was 7.0 to 8.2. It should be noted that to maintain electroneutrality in the ultrafiltrate $\Sigma[C_i(1 - R^*)z]$ must be equal for both cations and anions. (For the single salt systems, although the rejection values were reported in terms of anions, R^* of cation must always equal R^* of anion).

The first system shown in Table 2 had both divalent and monovalent oxyanions present and the molar concentration of SO_4^{2-} was about twice that of HCO_3^-. The rejection of SO_4^{2-} was greater than 0.90, similar to the single salt system; however, HCO_3^- rejection was 0.26, compared to R^* of 0.90 at the same bicarbonate concentration in the single salt system. If either Ca^{2+} or Mg^{2+} were present in a single-salt (with SO_4^{2-} as anions) system, R^* of Ca^{2+} or Mg^{2+} would have been 0.93 [Equation (6)] instead of 0.83. The lower rejection was primarily due to the presence of monovalent HCO_3^-. The second system shown in Table 2 had a HCO_3^- concentration six times that of SO_4^{2-}. The rejection of HCO_3^- in this system was higher than the previous system, and, as expected, the rejection of cations ($R^* \approx 0.76$) was somewhat poorer because R^* for HCO_3^- was less than R^* for SO_4^{2-}. The third system was similar to the first system but contained a high chloride concentration. Rejections of both Ca^{2+} and SO_4^{2-} were slightly lower than that in the first system; Cl^- rejection was only 0.10. The charged ultrafiltration membrane would remove divalent (or multivalent) cations from water, but NaCl removal would be too low for the membrane to be used in desalination.

The removal of divalent cations (Ca^{2+}, Mg^{2+}) greater than 76% from the waters shown in the above systems indicates potential application of charged membrane ultrafiltration to water softening. The total hardness (generally reported as mg/l $CaCO_3$) of a water may be both carbonate (concentration of Ca^{2+}, Mg^{2+} associated with HCO_3^- ion) and noncarbonate (concentration of Ca^{2+}, Mg^{2+} associated with noncarbonate anions, such as SO_4^{2-}, Cl^-). The first system shown in Table 2 was similar to water in the Missouri River at Kansas City, with noncarbonate hardness 2.7 times the carbonate hardness. The

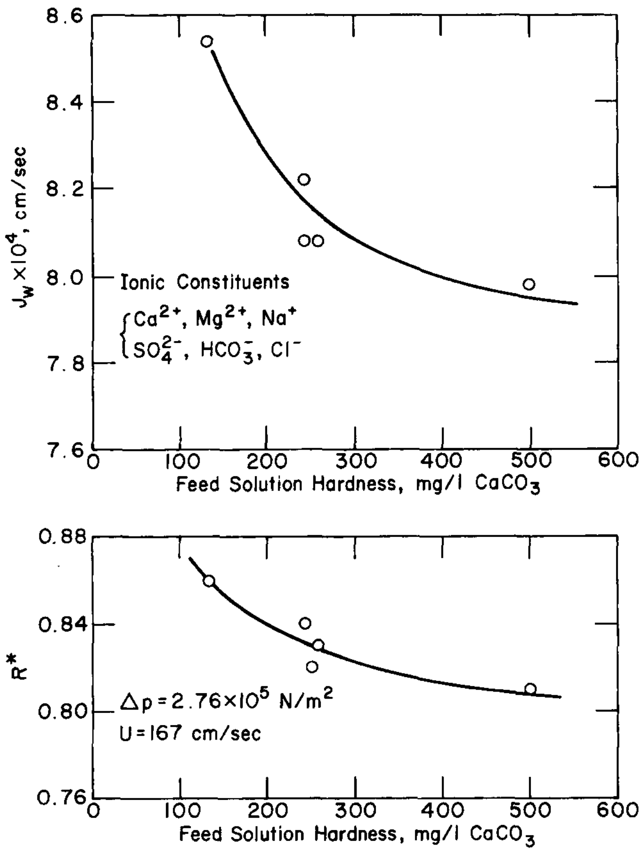


Fig. 7. Dependence of water flux and hardness (divalent cations) rejection of the hardness of inlet stream, for multi-salt system.

composition of the third system was about one-tenth of the ionic concentrations found in well-water at Roswell, New Mexico. The second system contained predominately carbonate hardness. The overall total hardness removal for the three synthetic waters is shown in Table 2; predominance of noncarbonate hardness over carbonate hardness gave a high R^* of 0.83 (total hardness) for the Missouri River-type water.

For membrane process evaluation with reference to water softening, it is necessary to know the effect of feed hardness concentration both on R^* and J_w. Figure 7 was obtained with the first synthetic water (Missouri River type); the different hardness levels were obtained by proportionately changing the concentrations of all species in the water. Rejection (Figure 7 bottom) of total hardness only decreased from 0.86 to 0.81 as the feed hardness was increased from 125 to 500 mg/l $CaCO_3$. The membrane showed no sign of deterioration at the elevated concentrations. At the hardness level of 500 mg/l, the water flux drop (Figure 7 top) was only 7% compared to J_w at $C_i = 0$. The flux drop was produced by a $\Delta\pi$ increase.

Another ultrafiltration experiment with the synthetic Missouri River water was performed at a higher $\Delta p = 4.10 \times 10^5$ N/m^2. A hardness rejection of 0.82 and $J_w = 12.9 \times 10^{-4}$ cm/s (27.2 gal/ft^2-day) were obtained. This would mean a savings of at least one-third in membrane cost compared to that for a system operated at $\Delta p = 2.8 \times 10^5$ N/m^2.

In applications in which the complete demineralization of a water is not necessary, low pressure ultrafiltration with a charged membrane is an attractive process. A membrane softening process not only reduces hardness but also removes all microorganisms and suspended solids from the water.

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NOTATION

C_f = concentration of a solute (or ion) in ultrafiltrate stream, mM
C_i = concentration of a solute (or ion) in inlet stream to ultrafiltration cell, mM
i = ionization factor, Equation (3)
J_s = solute flux, millimoles/cm^2 · s
J_w = water flux, cm^3/cm^2 · s
Δp = average transmembrane pressure difference, N/m^2
r = effective ion radius, Å
R = gas constant
R^* = solute (or ion) rejection, Equation (1)
R_m = resistance of ultrafiltration membrane to water flux, N/m^2/cm/s
T = solution temperature, °K
U = average channel velocity, cm/s
z = ion valence
$\Delta\pi$ = osmotic pressure difference, N/m^2

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