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Reverse Osmosis Performance of Cellulose Acetate Membranes in the Separation of Zinc from Dilute Solutions *

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Abstract

Cellulose acetate membranes have been characterized in terms of pure water permeability, solute transport parameter, mass transfer coefficient, and percent solute separation with a reference system of aqueous sodium chloride solution. These membranes were used in the determination of reverse osmosis characteristics such as product rates and solute separation of zinc salt solutions. The importance of the chemical species present in solution and its effect on the degree of separation of the zinc salt has been illustrated. Correlation between the percent solute separation and the equilibrium constant for the formation of ion-pairs in solution has been established.

INTRODUCTION

The principles of reverse osmosis, the physicochemical criteria for the separation of metal ions, and the conditions governing the stability of membranes in the reverse osmosis treatment of metal-bearing waste solutions have been reviewed recently (*1*). The performance of cellulose acetate membranes in the reverse osmosis separation of metal ions contained in a sample of acid mine-water has been studied (*2*). Studies on the low-pressure

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reverse osmosis treatment of dilute uranium solutions using cellulose acetate membranes have been reported (*3*). The results obtained in our laboratory, with respect to low-pressure reverse osmosis treatment of heavy metal-bearing effluents, are encouraging in that both pure product water and the heavy metals could be recovered at the same time.

There are many possible sources of pollution in mining and the subsequent processing of metals from ores. Some of the sources of pollution are pit water from mining operations, contaminated water from the weathering of tailings, and liquid effluents arising from purification and subsequent chemical operations. The liquid effluents from treatment plants, in particular the raffinate or barren liquor discharged after the recovery and purification of the metals from the leach liquors, have to be free from toxic metal contaminants before discharge to rivers or streams. The composition of the barren solutions depends on the type of process used, such as leaching followed by ion exchange or solvent extraction or an electrolytic method of purification. In any case the barren solution contains significant amounts of metal ions of interest, and these solutions should be treated from the point of view of recovery of both metal values and product water which can be used in recycle operations.

Recently Parsons (*4*) has proposed a complete flow sheet for the recovery of the valuable constituents (Zn, Cu, Pb) from the complex Zn-Pb-Cu sulfide deposits found in New Brunswick, Canada. Briefly the proposed scheme involves chlorination of the ore followed by oxidizing roasting and leaching to obtain zinc chloride solutions. The zinc can be recovered by electrolytic means and the spent electrolyte can be recycled to the leaching stage. Effluents containing a significant amount of zinc along with associated metallic impurities are encountered at some stage in the circuit. Hence the solution should be treated to recover the zinc and also to produce water of suitable quality for recycling to the leaching stage. This can be achieved by treatment of the barren solutions by reverse osmosis.

One of the most promising methods for desalinization and concentration of aqueous salt solutions and their purification is reverse osmosis, which does not involve any phase transformation of the liquid. Low expenditure of energy, simplicity of the processing technology, and the operation of the process at ambient temperatures are some of the attractive features of the reverse osmosis process. The high capital investment and the membrane compaction problems make the reverse osmosis process at high pressures prohibitive. The reverse osmosis treatment of metal-ion-bearing effluents at low pressures ($\sim$300 psig) is attractive and can result in the recovery of metal ions and the production of water that can be used for recycling. For these reasons a detailed study of the reverse osmosis behavior of zinc salt solution under a variety of conditions was undertaken.

EXPERIMENTAL

Nonflow-Type Apparatus

The static cell and the schematic diagram of the nonflow-type experimental setup are the same as reported earlier (*3*). The static cell was made of stainless steel and consisted of two detachable parts. The membrane rested on a stainless steel porous plate embedded in the lower part of the cell. The product solution permeating through the membrane was withdrawn at atmospheric pressure from an outlet provided in the lower part of the cell. The top part of the cell contained the feed solution under pressure in contact with the membrane. The two parts of the cell were fitted and sealed by the use of rubber O-rings. The effective area of the membrane surface in the cell was 14.4 cm^2. Pressurization was achieved by compressed nitrogen gas from a gas cylinder. During the course of the experiment the feed solution was stirred by a magnetic stirrer fitted in the cell about 0.64 cm above the membrane, and this eliminated the concentration polarization. Cellulose acetate membranes obtained from Osmonics Inc. were used.

PROCEDURE

All the reverse osmosis experiments were carried out at the laboratory temperature (23 to 25°C). The cellulose acetate membranes were pressurized with pure water at 400 psig for about 2 hr before subsequent use in reverse osmosis experiments at operating pressures of 100 to 300 psig. In every experiment the pure water permeation rate, the membrane permeated product rate per given area of membrane surface, and the solute separation (f) were determined at preset operating conditions. Aqueous feed solutions containing sodium chloride at a concentration of 1500 mg/l were used to obtain data on membrane specifications and to specify the mass transfer coefficient on the high-pressure side of the membrane. The concentrations of sodium chloride in the feed and the product solutions were determined by specific resistance measurements. The feed and the product solutions containing zinc salt were analyzed by atomic absorption spectrophotometry at a wavelength of 2139 Å. The product rate data reported are corrected with respect to the viscosity and the temperature

(25°C). The product rates are accurate to within 3%. As reported before (*2*), low metal ion concentrations are involved in the experiments and hence the solute separation (f) data were obtained from the relation:

$$f = \frac{\text{solute concentration in feed} - \text{solute concentration in product}}{\text{solute concentration in feed}}$$

RESULTS AND DISCUSSION

Membrane Specifications

Reverse osmosis membranes can be specified in terms of parameters such as the pure water permeability constant, A, and the solute transport parameter, D_{AM}/K_σ, at a particular value of operating pressure. The product rate (flux) and the solute separation obtainable with a membrane so specified are functions of the mass transfer coefficient, k, on the high-pressure side of the membrane, which is governed by the feed flow rate and the feed concentration used in the experiment. A computer program (*5*) using experimental data on pure water permeation rate, membrane permeated product rate, and solute separation at preset operating conditions for the aqueous sodium chloride feed solution containing 1500 mg/l salt was used in the calculation of A, D_{AM}/K_σ, and k. The data given in Table 1 on the values of A and D_{AM}/K_σ for sodium chloride at 300 psig specify the membranes used in the present studies. The feed flow conditions used in all the experiments carried out in the present studies are specified in terms of the corresponding value of k obtained with the reference sodium chloride solution system containing 1500 mg/l salt. In order to compare the relative performance of the membranes for feed solutions for which physicochemical data such as osmotic pressure and other relevant data

TABLE 1

Membrane Specification Data[a]

Film no.	$A \times 10^6$ g-mole H_2O ($cm^{-2}sec^{-1}atm^{-1}$)	D_{AM}/K_σ for NaCl (10^5 cm/sec)	Feed concentration, 1500 mg/l NaCl; $k = 14.72 \times 10^{-4}$ cm/sec	
			Solute separation (%)	Product rate (g/hr)
1	2.57	11.64	80.26	29.78
1	2.60	11.50	81.07	30.44

[a] Film area 14.4 cm^2; pressure 300 psig.

are not readily available, it is useful to provide such specifications for membranes in terms of easily obtainable parameters for a convenient and well-studied reference feed solution system such as sodium chloride solution. The data presented in Table 1 show the high productivity of the cellulose acetate membranes at low operating pressures (100 to 300 psig).

Solute Transport Parameter

Solute transport parameter values were obtained using the experimentally obtained data on product rates (PR) and solute separation from

$$D_{AM}/K_\sigma = \frac{PR}{3600sd}\frac{1-f}{f}\left(\exp\frac{PR}{3600kd}\right)^{-1}$$

where s is the effective membrane area and d is the density of the solution. The values of k were obtained by using

$$k = k_{\text{ref}}\left[\frac{D_{AB}}{D_{AB\,\text{ref}}}\right]^{2/3}$$

where k_{ref} is the mass transfer coefficient for the reference system of 1500 ppm of aqueous sodium chloride solution (14.72×10^{-4} cm/sec) and $(D_{AB})_{\text{ref}}$ and D_{AB} represent the diffusivity of sodium chloride and the zinc salt, respectively.

The diffusivity values of the solutes of interest were calculated using the Nernst equation:

$$D_{AB} = \frac{\left(\frac{1}{z_+} + \frac{1}{z_-}\right)RT}{\left(\frac{1}{\lambda_+} + \frac{1}{\lambda_-}\right)F^2}$$

where z_+ and z_- are the valencies of the cation and anion, respectively, R is the gas constant (8.314 J °K^{-1} mole^{-1}), T is the absolute temperature, λ_+ and λ_- are the limiting ionic conductances (ohm^{-1} cm^2 equiv^{-1}), and F is the Faraday.

The data on D_{AM}/K_σ together with solute separation and product rates are given in Table 2.

Separation of Different Zinc Salts

Figures 1 and 2 illustrate the effect of pressure (100 to 300 psig) on the degree of solute separation and the product rates for zinc nitrate, zinc

TABLE 2

Data on Solute Transport Parameters[a]

Salt	Solute separation	Product rate (g/hr)	k (cm/sec)	D_{AM}/K_σ (cm/sec)
$Zn(NO_3)_2$	0.9219	28.71	12.29×10^{-4}	4.69×10^{-5}
$ZnCl_2$	0.9323	30.20	12.52×10^{-4}	4.23×10^{-5}
$ZnSO_4$	0.9683	30.41	9.71×10^{-4}	1.92×10^{-5}

[a] Film area 14.4 cm^2; pressure 300 psig.

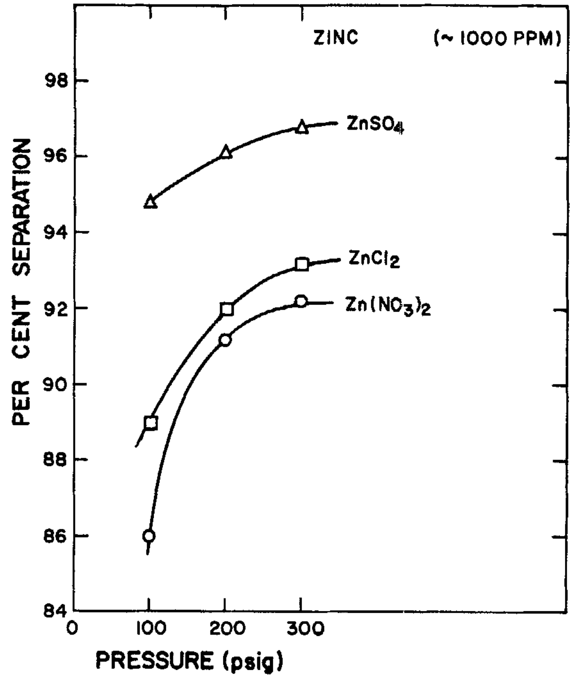

FIG. 1. Separation of zinc salts (~1000 ppm) as a function of pressure.

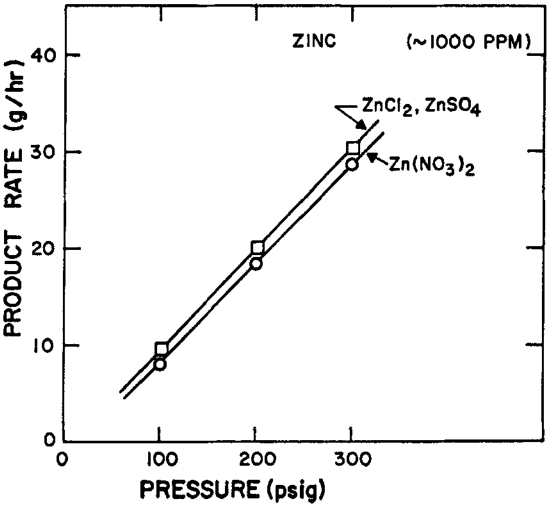

FIG. 2. Product rate as a function of pressure at ~1000 ppm.

chloride, and zinc sulfate solutions containing 1000 ppm of zinc. Similarly Figs. 3 and 4 depict the effect of pressure on the percent solute separation and the product rates for the three zinc salts containing 500 ppm of zinc. The product rates in the case of zinc chloride and zinc sulfate for 1000 ppm zinc feed solution (Fig. 2) were identical while the observed product rates for zinc nitrate solution were slightly lower. In the case of feed solutions containing 500 ppm zinc the product rates were identical for all three zinc salts. In general, product rates increased linearly with operating pressures and decreased slightly with increase in feed concentrations; these observations are similar to those reported for many other solution systems (*6*). From Figs. 1 and 3 it is obvious that the solute separation levels off at a pressure of 300 psig. At a given operating pressure the separation of zinc nitrate was less than of zinc chloride which in turn was less than of zinc sulfate. This trend holds true at all the feed concentrations used in the present studies (100, 500, and 1000 ppm Zn). Solute separation as a function of pressure with two component mixtures such as zinc nitrate and zinc sulfate and zinc chloride and zinc sulfate (ratio of 1: 1) was studied. The solute separation obtained in the case of zinc chloride and zinc sulfate mixtures was greater than in the case of zinc nitrate and zinc sulfate mixtures. The observed solute separation of the zinc salts [$ZnSO_4 > ZnCl_2 > Zn(NO_3)_2$] can be attributed to the concentration of ion-paired species

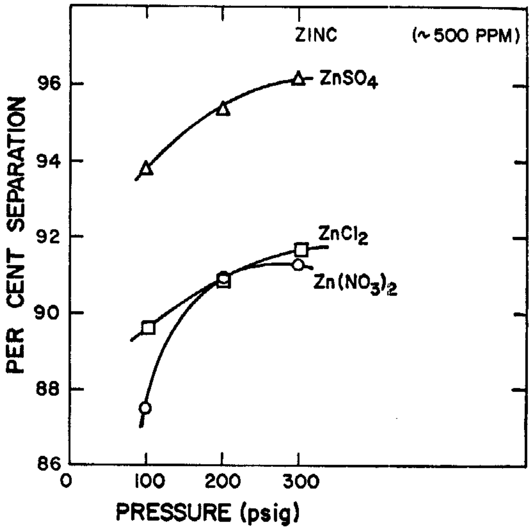

FIG. 3. Separation of zinc salts (~500 ppm) as a function of pressure.

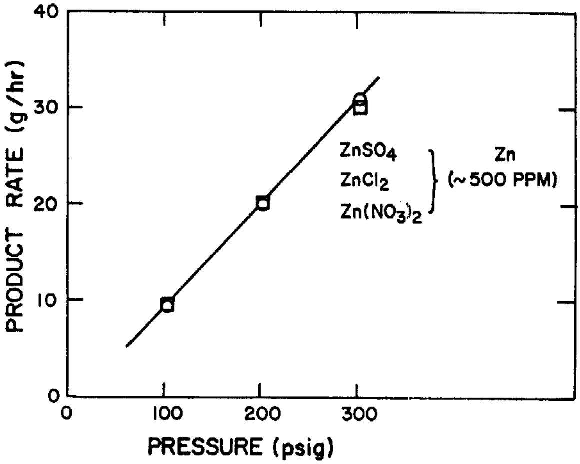

FIG. 4. Product rates for zinc salts as a function of pressure at ~500 ppm.

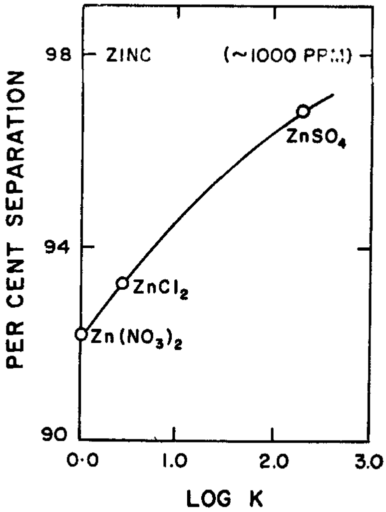

FIG. 5. Separation of zinc as a function of ion-pair equilibrium constants at 300 psig.

present in the solutions. The ease with which ion-pairing occurs in the zinc salt solution is in the order $ZnSO_4 > ZnCl_2 > Zn(NO_3)_2$, and this order is in keeping with the order of solute separation.

In Fig. 5 solute separation data for $Zn(NO_3)_2$, $ZnCl_2$, and $ZnSO_4$ are plotted as a function of log K, where K is the equilibrium constant for the formation of the ion-pair:

$$Zn^{2+} + X^{-y} \rightleftarrows Zn^{2+}x^{-y}$$

It is clear from Fig. 5 that the percent solute separation increases with increasing values of the ion-pair equilibrium constant. Thus it is apparent that the chemical species present in solution is of importance in the separation of metal ions by reverse osmosis. The cellulose acetate membranes have proton affinity and, in the case of an ion-pair, both the size and the effective charge may prevent the approach of the ion-pair toward the surface layer of the membrane. As a result the ion-pair is separated better than the hydrated cation. It is appropriate to point out that treatment of a solution containing several anions like SO_4^{2-}, Cl^-, and NO_3^- and a cation like Zn^{2+} by reverse osmosis would result in a separation in keeping with the concentrations of ion-pairs and bare hydrated metal ions.

In order to establish the role of ion-pair species in the solute separation by reverse osmosis, experiments on the separation of zinc chloride and zinc nitrate (1000 ppm Zn) in the presence of added sodium sulfate (0 to 1000 ppm) were carried out. The results obtained in these experiments are illustrated in Figs. 6 and 7. The addition of 250 ppm sodium sulfate to

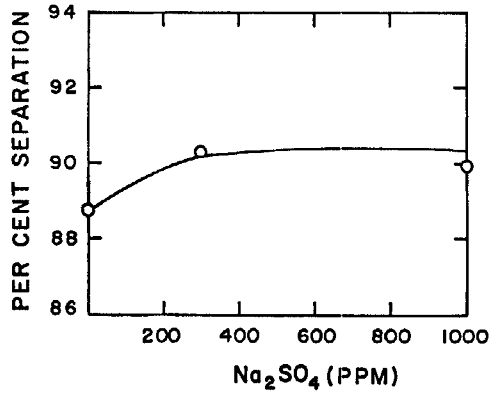

FIG. 6. Effect of Na_2SO_4 on separation of zinc chloride at 300 psig.

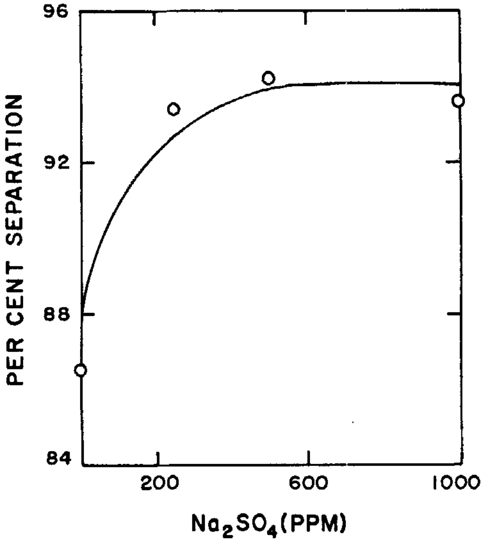

FIG. 7. Effect of Na_2SO_4 on the separation of zinc nitrate at 300 psig.

zinc chloride solution containing 1000 ppm of zinc increased the solute separation from 88.8 to 90.4% (Fig. 6). In the case of zinc nitrate, addition of 250 ppm of sodium sulfate increased the solute separation from 86.5 to 94.2% (Fig. 7). The observed increase in solute separation of zinc in the presence of sodium sulfate can be attributed to the formation of ion-pairs in solution ($Zn^{2+}SO_4^{2-}$) which are separated better than hydrated divalent zinc ions. Ion-pair formation and the resulting increase in solute separation are more pronounced in the case of zinc nitrate than in the case of zinc chloride solution, and this is in keeping with the values of the ion-pair equilibrium constants (Fig. 5). These results have significance in practical situations. In the case of solutions containing metal nitrate or metal chloride, it is possible to increase the solute separation by the addition of sodium sulfate and at the same time obtain high product water recovery by using more porous cellulose acetate membranes. Thus these results are considered significant for practical industrial treatment of barren metallurgical effluents containing trace amounts of metal ions associated with chloride or nitrate anion.

Effect of Zinc Concentration in the Feed on Membrane Performance

The effect of varying the concentration of zinc sulfate on the reverse osmosis characteristics such as product rate (flux rate) and percent solute separation was studied. Experimental data on the product rate and percent solute separation for the feed concentration range of 1000 to 10,000 ppm of zinc sulfate are given in Table 3. These data were obtained using the static cell which gave a mass transfer coefficient value of 14.72×10^{-4} cm/sec for the reference system of 1500 ppm of aqueous NaCl solution. Because divalent salts, such as zinc sulfate, are separated better than monovalent salts, such as sodium chloride, the average pore size on the membrane surface needed to yield a given level of solute separation is higher

TABLE 3

Separation of Zinc Sulfate

$ZnSO_4$ (ppm)	Pressure (psig)	Product rate (g/hr)	Separation (%)
1,000	300	30.41	96.83
3,000	300	26.99	91.81
7,000	300	23.98	90.91
10,000	300	21.09	89.18

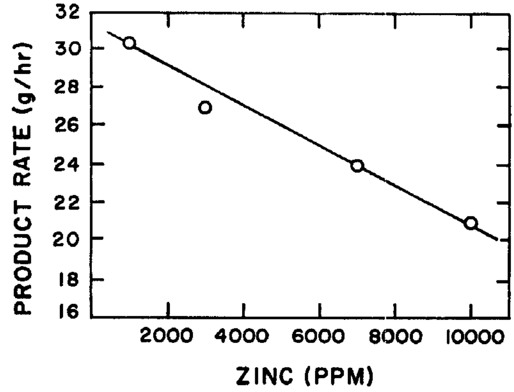

FIG. 8. Effect of zinc concentration on product rate at 300 psig.

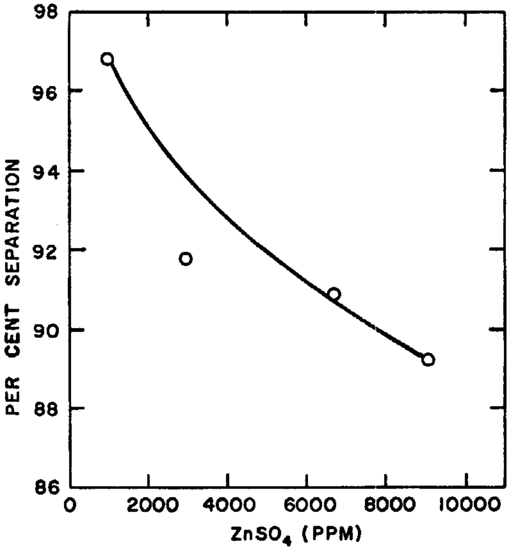

FIG. 9. Separation of zinc as a function of zinc concentration in the feed solution at 300 psig.

for zinc salts than that needed for sodium chloride. Figure 8 shows the effect of the variation of the concentration of zinc sulfate in the feed solution on the product rate. It is clear from this figure that the flux rate drops from 30 to 21 g/hr in going from 1,000 to 10,000 ppm of zinc in the feed solution. The percent zinc separation obtained as a function of the feed concentration is depicted in Fig. 9. In the concentration range of 1,000 to 10,000 ppm of zinc the percent solute separation drops from 97 to 89. From the point of view of obtaining product water for recycle operations, the cellulose acetate membranes used in the present studies are adequate in the sense that a product rate of 21 g/hr at a concentration of 10,000 ppm of zinc and solute separation of 90% can be obtained. Thus cellulose acetate membranes giving 80.7% separation of sodium chloride are adequate for producing product water of suitable quality for recycle operations. It is appropriate at this stage to point out that membranes capable of yielding 90% separation of sodium chloride could be used in treating dilute zinc-bearing effluents to produce product water essentially free from zinc, which can be discharged into streams or rivers, and simultaneously to recover the zinc.

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