

# Concentration of Radioactive Liquid Streams by Membrane Processes

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## Synopsis

The possibility of concentrating radioactive effluents by reverse osmosis was investigated. Cellulose acetate membranes of the Loeb-Sourirajan type were used, and their performance was evaluated for CsCl and SrCl<sub>2</sub> solutions in concentrations ranging from millimolar to trace level. The applicability of solution-diffusion and irreversible thermodynamic models for predicting solute separation in the above concentration range has been investigated. Some aspects of the selectivity with reference to trace radionuclides are also reported.

## INTRODUCTION

The use of modified cellulose acetate membranes for reverse osmosis desalination of brackish waters has been studied in recent years both in laboratory and plant scale. Most of these investigations are reported using sodium chloride as the reference system. However, the selectivity of these membranes for radionuclides in trace concentrations with the objective of separating them from various streams generated in nuclear industry has not been widely evaluated. Few investigations on laboratory and pilot plant scales are reported<sup>1-11</sup> for decontamination and concentration of radioactive liquid effluents. Application of reverse osmosis technology for the removal of radioactive constituents contained in aqueous streams has been extensively reviewed, and ion rejection for various dissolved radionuclides has also been tabulated.<sup>12</sup> System decontamination factor calculations were reported for a semibatch RO process.<sup>13</sup> Recently, reverse osmosis has also been included<sup>14</sup> as one of the unit operations for radioactive effluent treatment.

The criteria for the successful application of this technique for radionuclide separation is a requisite degree of selectivity even under low ionic concentrations. Further, the membranes and the modules should be capable of withstanding higher radiations arising from these streams. Detailed investigations were carried out<sup>15</sup> in our laboratory to ascertain membrane stability under radiation environment. The gamma dose on the membrane surface in the case of a typical waste effluent containing <sup>134</sup>Cs was computed for a tubular membrane geometry. The computed dose as well as gamma photon flux at various points in the tube are presented in Table I.

Based on this computation and the safe dose limit evaluated for CA membranes,<sup>15</sup> it is estimated that these membranes could be safely used for a period of 60 days (24 continuous) for a radioactive feed activity of 1 mCi/mL.

This paper deals with laboratory studies, carried out to evaluate the performance of caesium chloride and strontium chloride solutions having concentra-

TABLE I  
Computed Gamma Dose on Membrane Surface

Distance from one end (cm)	Gamma flux photons/(cm <sup>2</sup> /s)	Dose (mrad/h)
50	60.052	0.581
60	60.462	0.585
90	60.465	0.585
120	60.126	0.582
150	51.997	0.503

tions ranging from millimolar down to tracer level. The selectivity aspects of certain alkali and alkaline earth metal ions in low concentrations and also for ruthenium tracers which form the major constituents in a typical effluent from CANDU-type nuclear reactors are also reported. The applicability of solution-diffusion and irreversible thermodynamic models for predicting the solute separation under extremely dilute concentrations is also looked into.

### EXPERIMENTAL

Cellulose acetate membranes prepared in our laboratory as per the Loeb-Sourirajan technique<sup>16</sup> was used in our studies. Reverse osmosis experiments were carried out in a static test cell shown in Figure 1. Inactive feed solutions were prepared from analar grade reagents, and tracer feed solutions were prepared by spiking distilled water with different radioisotopes, i.e., <sup>134</sup>Cs, <sup>85+89</sup>Sr, and <sup>103</sup>Ru. Inactive solutions were analyzed by atomic absorbance spectrophotometry. A few analysis were carried out by conductometry. Radioisotopes were assayed using single channel gamma ray spectrometer equipped with a well type Na I (TI) detector crystal.

The diffusion coefficient ( $D_{2m}$ ) was determined,<sup>17</sup> using a suitably designed diffusion cell (Fig. 2), by measuring the concentration changes with the time of the diffusing electrolyte under different concentration gradients. Using eq. (1),  $D_{2m}$  was calculated from the plot of  $\log[(C_f - C_t)/(C_f - C_0)]$  vs time:

$$(C_f - C_t)/(C_f - C_0) = 8/\pi^2 \exp(-\pi^2 D_{2m} t/\lambda^2) \quad (1)$$

The distribution coefficient ( $K_2$ ) was determined by equilibrating a sample of membrane with the solution of interest, removing the sample, and quickly

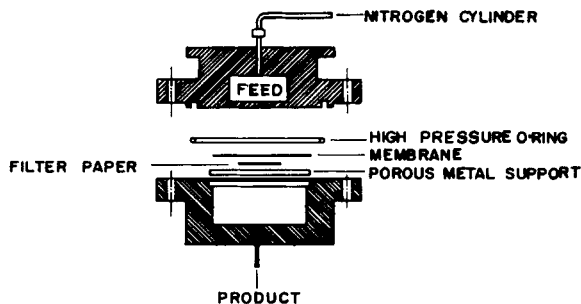


Fig. 1. Reverse osmosis test cell.

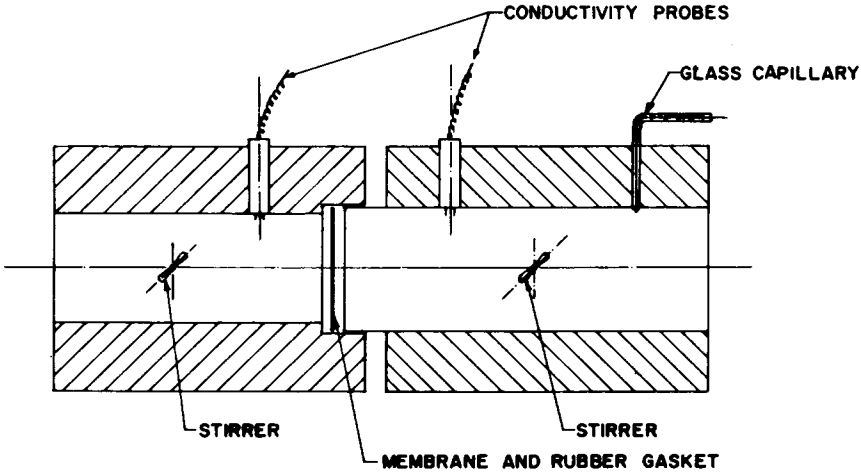


Fig. 2. Diffusion cell.

washing it before immersing it in distilled water in which solute desorption was followed by change in conductivity. The distribution coefficient was then computed from the solute concentration in the film relative to that in solution with which it was initially equilibrated.

Salt permeability ( $\omega$ ) measurements were made in the laboratory test cell used for diffusion measurements. The concentration of the permeating electrolyte was monitored with the help of the conductance electrodes. The solute flux  $J_s$  and its corresponding osmotic gradient  $\Delta\pi$  gave the salt permeability.

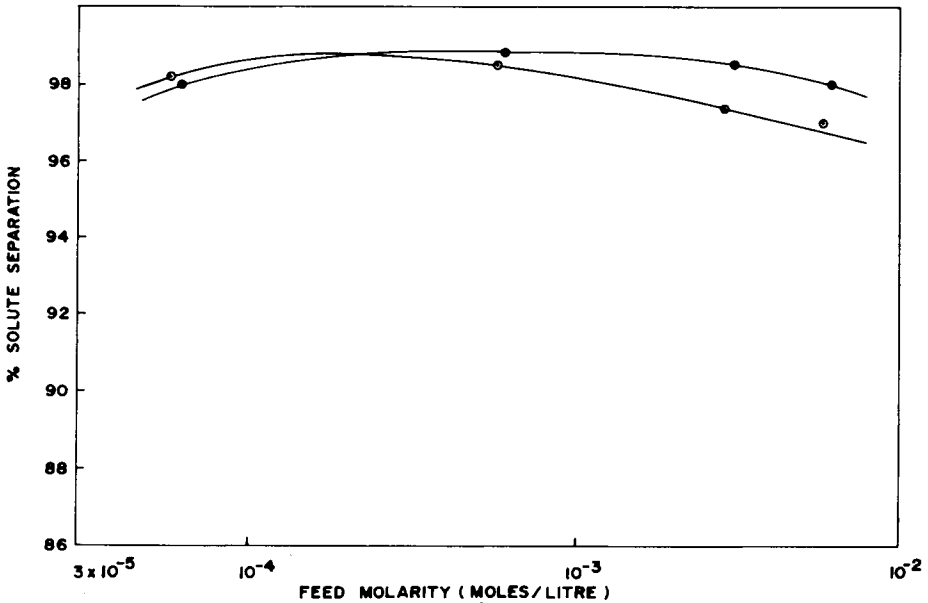


Fig. 3. (⊙) Caesium chloride; (⊗) strontium chloride;  $\Delta P = 40 \text{ kg/cm}^2$ ; average water flux =  $696 \text{ L}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ .

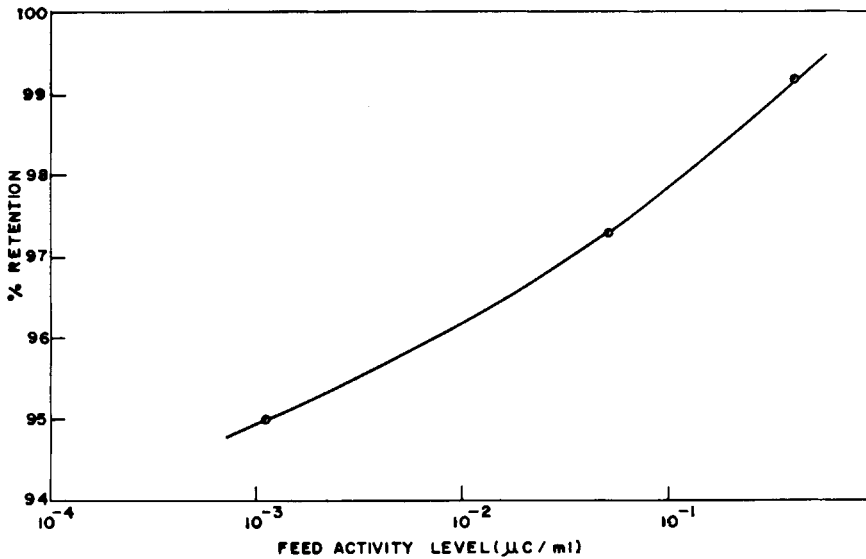


Fig. 4. % Retention vs. feed activity level:  $\Delta P = 40 \text{ kg/cm}^2$ ; average water flux =  $696 \text{ L}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ .

## RESULTS AND DISCUSSION

Performance data for caesium chloride and strontium chloride of millimolar to micromolar concentrations are shown in Figure 3. Similar studies were carried out for tracer feed solutions containing  $^{134}\text{Cs}$  in the activity range of  $10^{-3} \mu\text{Ci/mL}$  to  $10^{-1} \mu\text{Ci/mL}$ , and the results are shown in the Figure 4. It is found that with the increase in solute concentration from tracer level to millimolar the % solute separation increases gradually and reaches a maximum around  $10^{-4}M$  and declines subsequently.

It may be noted that in desalination operations where decimolar to molar solute concentrations are employed, the % solute separation is reported to decline with increase in feed salinity. It is apparent therefore that there is a distinct change in performance for the two regions of feed salinity above and below  $10^{-4}M$ . In

TABLE II  
Prediction of  $J_s$  from the Solution-Diffusion Model<sup>a</sup>

Feed	Concn (M)	$D_{2m}$ ( $\text{cm}^2/\text{s}$ ) ( $\times 10^9$ )	$K_2$ ( $\frac{\text{g/cc memb}}{\text{g/cc soln}}$ )	Computed $J_s$ ( $\text{mol}/\text{cm}^2\cdot\text{s}$ )
CsCl	$5.94 \times 10^{-3}$	8.76	2.08	$5.41 \times 10^{-9}$
	$2.97 \times 10^{-3}$	7.95	0.78	$9.87 \times 10^{-10}$
	$5.94 \times 10^{-4}$	4.51	0.62	$1.45 \times 10^{-11}$
	$5.94 \times 10^{-5}$	5.63	3.91	$6.94 \times 10^{-11}$
SrCl <sub>2</sub>	$6.31 \times 10^{-3}$	4.51	0.91	$1.21 \times 10^{-9}$
	$3.15 \times 10^{-3}$	2.60	0.61	$2.33 \times 10^{-10}$
	$6.31 \times 10^{-4}$	1.63	0.56	$2.88 \times 10^{-11}$
	$6.31 \times 10^{-5}$	3.01	2.92	$2.59 \times 10^{-11}$

<sup>a</sup> Skin thickness of the membrane assumed as  $0.2 \mu$ .

TABLE III  
Prediction of  $J_s$  from Irreversible Thermodynamic Model

Feed	Concn (M)	$\omega$ (mol/dyn-s)	$\Delta\pi$ (dyn/cm <sup>2</sup> )	$\sigma$	$\bar{C}_s$ (mol/cm <sup>3</sup> ) ( $\times 10^2$ )	$J_w$ (cm/s)( $\times 10^3$ )	$\omega\Delta\pi$ (mol/cm <sup>2</sup> -s)	$(1-\sigma)\bar{C}_s J_w$ (mol/cm <sup>2</sup> -s)	$J_s$ (mol/cm <sup>2</sup> -s)
CsCl	$5.939 \times 10^{-3}$	$1.056 \times 10^{-18}$	$2.963 \times 10^8$	0.97	1.221	1.133	$3.129 \times 10^{-10}$	$4.14 \times 10^{-10}$	$7.269 \times 10^{-10}$
	$2.969 \times 10^{-3}$	$1.616 \times 10^{-18}$	$1.48 \times 10^8$	0.974	0.228	1.133	$2.392 \times 10^{-10}$	$6.71 \times 10^{-11}$	$3.063 \times 10^{-10}$
	$5.939 \times 10^{-4}$	$1.102 \times 10^{-18}$	$2.962 \times 10^7$	0.985	0.036	1.117	$3.264 \times 10^{-11}$	$6.93 \times 10^{-12}$	$3.867 \times 10^{-11}$
SrCl <sub>2</sub>	$5.939 \times 10^{-5}$	$7.37 \times 10^{-17}$	$2.962 \times 10^6$	0.982	0.108	1.116	$2.182 \times 10^{-10}$	$2.16 \times 10^{-11}$	$2.398 \times 10^{-10}$
	$6.808 \times 10^{-3}$	$6.024 \times 10^{-19}$	$4.718 \times 10^8$	0.980	0.567	1.167	$2.842 \times 10^{-10}$	$1.32 \times 10^{-10}$	$4.164 \times 10^{-10}$
	$3.154 \times 10^{-3}$	$1.271 \times 10^{-18}$	$2.359 \times 10^8$	0.986	0.186	1.167	$2.998 \times 10^{-10}$	$3.04 \times 10^{-11}$	$3.802 \times 10^{-10}$
	$6.308 \times 10^{-4}$	$1.351 \times 10^{-18}$	$4.89 \times 10^7$	0.938	0.178	1.117	$6.606 \times 10^{-11}$	$2.37 \times 10^{-11}$	$8.976 \times 10^{-11}$
	$6.308 \times 10^{-5}$	$7.01 \times 10^{-18}$	$4.89 \times 10^6$	0.929	0.085	1.125	$3.427 \times 10^{-11}$	$6.72 \times 10^{-11}$	$1.05 \times 10^{-10}$

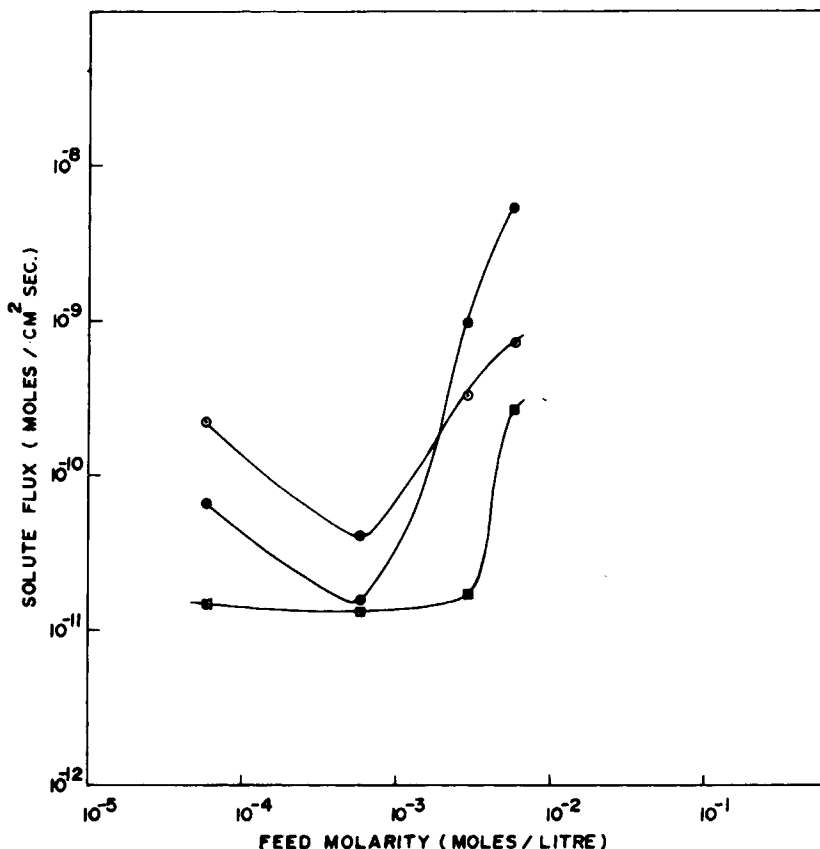


Fig. 5. Comparison of observed and calculated solute flux in the case of caesium chloride: (⊗) solution-diffusion model; (⊙) irreversible thermodynamic model; (⊠) observed.

order to explain the experimental results the transport behavior of the membrane as explained by solution-diffusion mechanism<sup>18</sup> as well as irreversible thermodynamic mechanism<sup>19</sup> are considered.

### Prediction of Salt Flux Using Transport Equations

The solution-diffusion model describes the transport of solvent and solute species as solution in the membrane substance and diffusion through the membrane material. This approach restricts the coupling of diffusive flows of the solution components within the membrane. The two flux equations derived using Fick's law are given in their final form<sup>18</sup>:

$$J_w = -D_{1m}C_{1m}V_1(\Delta P - \Delta\pi)/\lambda \quad (2)$$

$$J_s = -D_{2m}K_2\Delta C_2/\lambda \quad (3)$$

Equation (3) predicts decreasing solute flux with decrease in effective concentration gradient which holds good as long as  $D_{2m}$  and  $K_2$  remain independent of mean feed concentration. The  $D_{2m}$  and  $K_2$  values determined for caesium chloride and strontium chloride solutes under identical concentrations from

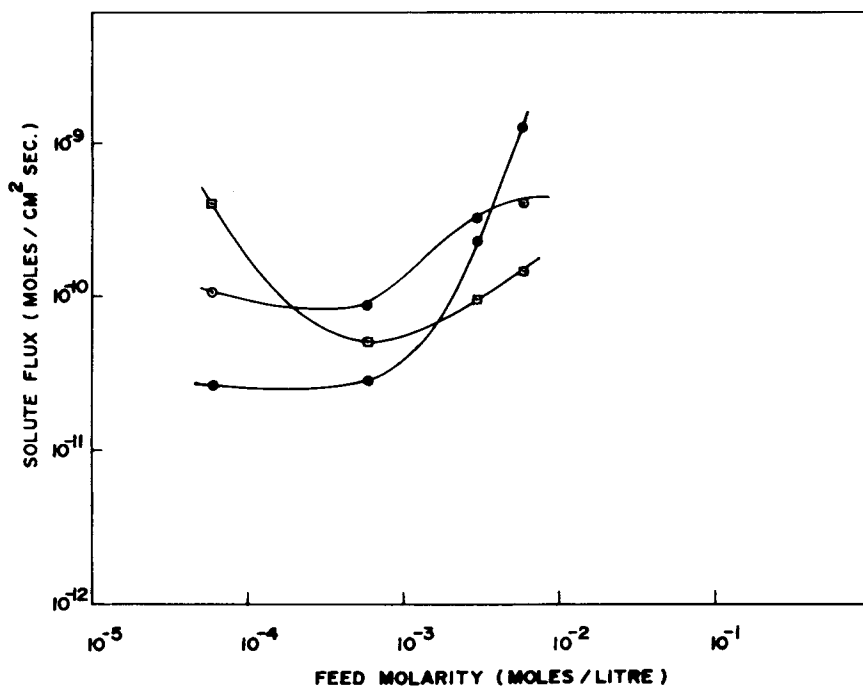


Fig. 6. Comparison of observed and calculated solute flux in the case of strontium chloride: (⊗) solution-diffusion model; (○) irreversible thermodynamic model; (□) observed.

millimolar to micromolar, along with  $J_s$  values calculated using eq. (3) are shown in Table II.

It can be seen from Table II that both  $D_{2m}$  and  $K_2$  values continuously decrease up to a particular concentration, i.e.,  $10^{-4}$  mol/L, and then increase as the concentration decreases from millimolar to micromolar. Accordingly, the  $J_s$  values go through a minimum around that concentration. This compares well with our reported experimental maxima in solute separation (Fig. 2). It is reported<sup>20</sup> that at higher concentrations the salt diffuses through a nearly neutral membrane where as at lower feed concentrations (around  $10^{-2}$  mol/L) the action of the fixed charges of the membrane<sup>21</sup> (3.4–5.0 meq/g wet membrane) on the mobility of the salt ions in the membrane appears. When external feed concentration becomes comparable to this fixed charges of membrane, a Donnan equilibrium will exist between the solution and membrane phases. Because of this Donnan equilibrium,  $K_2$  becomes independent of feed concentration. This is evident from the near constancy in  $K_2$  values in the middle region. But at still lower concentrations, this equilibrium may be drastically disturbed to effect enhanced solute concentration in the membrane phase due to reduced coulombic repulsion of the counterion.

At concentrations in the millimolar range, it is reported that<sup>22</sup> diffusivity of the electrolyte in solution decreases due to electrophoretic drag and deviation from unity of the activity factor. The diffusion coefficient  $D_{2m}$  of a solute in the membrane phase is governed by the diffusion coefficient of its counterion. The effect of fixed charges in the membrane on the mobility of the counterion and co-ions is significant. The fixed charges increasingly retard the movement

TABLE IV  
Selectivity Coefficients and Solute Separation for a Few Inorganic Ions and Radio Tracers

Salt ion	$T_A^R$	% SR	Radio tracers	$T_A^R$	% SR
$\text{Li}^+$	0.765	95.41	$^{134}\text{Cs}$	1.000	95.0
$\text{Na}^+$	1.000	94.00	$^{85+89}\text{Sr}$	0.960	96.2
$\text{K}^+$	1.105	93.37	$^{103}\text{Ru}$	0.520	97.4

of the counterions with decreasing concentration by ion pair formation. At still lower concentrations the reported decline in effective charge concentration on the membrane might improve the salt mobility. An estimate of the  $D_{2m}$  values reported<sup>23</sup> for lithium chloride in the concentration range of  $10^{-1}$ – $10^{-4}$  mol/L shows a similar minimum at the more or less identical concentration range.

The irreversible thermodynamic model describes transport through membranes by considering the coupling of flows. The two flux equations in terms of experimentally observable parameters are given as follows<sup>19</sup>:

$$J_w = L_p (\Delta P - \sigma \Delta \pi) \quad (4)$$

$$J_s = \omega \Delta \pi + (1 - \sigma) \bar{C}_s J_w \quad (5)$$

The above equations are modified to give the following expression for solute separation:

$$\frac{J_s}{J_w} = \omega \Delta \pi / J_w + (1 - \sigma) \bar{C}_s \quad (6)$$

For membranes having higher water fluxes the equation becomes

$$\text{SR} \rightarrow \sigma \quad (7)$$

The first and second terms in eq. (5) denote diffusive salt flux and reverse osmotic salt flux arising out of coupling. The  $\omega$  and  $\sigma$  values computed for caesium chloride and strontium chloride under identical concentration ranges from millimolar to micromolar along with  $J_s$  values computed using eq. (5) are shown in Table III. It can be seen from Table III that solute permeability  $\omega$  increases while  $\sigma$  values decreases under extremely dilute solution concentrations. Accordingly, the diffusive salt flux terms and reverse osmotic salt flux terms undergo a minimum at  $\approx 10^{-4}$  molar concentration range. It is reported<sup>23</sup> that  $\sigma$  given in terms of asymptotic salt rejection increases initially with decreasing feed concentration and, subsequently, decreases after passing through a maximum at about 0.005M feed concentration.

The comparison of the observed and calculated  $J_s$  values is shown in Figures 5 and 6. It can be seen from the figure that both solution-diffusion and irreversible thermodynamic models reasonably predict the solute separation behavior under low feed concentration within experimental uncertainty.

### Selectivity of Trace Alkali and Alkaline Earth Cation

The selectivity of trace elements of importance to radioactive effluent treatment has been studied. Generally, rejection of a solute through cellulose acetate membrane increases with increase in ionic charge and decrease ionic radius. The selectivity coefficient, defined<sup>24</sup> as per eq. (8) is used in our studies:



$$T_A^B = (1 - J_B)/(1 - J_A) \quad (8)$$

The  $T$  values of a few alkali metal ions calculated with respect to sodium for CA membranes along with solute separation values are given in Table IV. Similarly  $T$  values for  $^{134}\text{Cs}$ ,  $^{85+89}\text{Sr}$ , and  $^{103}\text{Ru}$  calculated with respect to caesium along with solute separation values are given in Table IV.

It can be seen from Table IV that the  $T$  values of alkali metal ions are closer to unity and those of multivalent ions are smaller than unity. The decrease of selectivity coefficient with increase in charge can be seen in the case of tracer cations also.

## CONCLUSIONS

The possibility of concentrating radioactive effluents by reverse osmosis has been investigated. The increase in % solute separation with increase in feed molarity in extremely dilute concentrations suggests a distinct advantage in radioactive effluent treatment offering reasonable volume reduction. The applicability of solution-diffusion mechanism and irreversible thermodynamic model for predicting the solute separation under low feed concentrations was looked into. The diffusion and distribution coefficients, and the salt permeability values show significant change under low concentrations. At higher feed concentrations, the solute diffuses through a nearly neutral membrane whereas at lower feed concentrations the action of fixed charge concentrations of the membrane play a dominant role. The membranes are found to exhibit distinct selectivity for trace elements, indicating its potential application for sequential separation of desirable cationic species from effluent streams.

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## APPENDIX: NOMENCLATURE

$C_i, C_0$	final and initial concentration of electrolytes in membrane films
$C_t$	concentrations of electrolyte in membrane films in mol/L at time $t$
$D_{2m}$	Diffusion coefficient of electrolyte in the membrane
$t$	time
$\lambda$	membrane thickness
$K_2$	distribution coefficient
$\omega$	solute permeability
$\Delta\pi$	osmotic gradient
$J_s$	solute flux
$J_w$	water permeability
$D_{1m}$	diffusion coefficient of water in the membrane
$C_{1m}$	membrane water content
$V_1$	partial molar volume of water
$\Delta P$	hydrostatic pressure gradient
$\Delta C_2$	concentration gradient of solute across the membrane
$L_p$	hydraulic permeability
$\sigma$	Stavermann's reflection coefficient
$\bar{C}_s$	concentration of solute in the membrane phase
SR	solute separation
$T_A^B$	selectivity coefficient of B with respect to A
$J_B, J_A$	solute flux of B and A, respectively

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