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Desalination 221 (2008) 448–454

DESALINATION

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Ion exchange equilibrium between ion exchange membrane and electrolyte solutions

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Received 4 January 2007; accepted 13 January 2007

Abstract

The ion exchange equilibrium between an ion exchange membrane and solutions of different electrolytes was studied. The matrix of the ion exchange membrane used consists of a vinyl polychloride network reinforced by a polyester screen; with quaternary and tertiary ammonium as functional groups. The data, provided by manufacturer, were completed by the experimental determinations of humidity percentage and ion exchange capacity.

This paper focuses on the study of exchange reaction between an anion exchange membrane and selected binary and ternary electrolyte solutions. Experimental data are reported for the ion exchange equilibrium of the binary system Cl^-/NO_3^-, Cl^-/SO_4^{2-}, NO_3^-/SO_4^{2-} and the ternary system $Cl^- - NO_3^- - SO_4^{2-}$. The ion exchange isotherms were established and affinity order of ions was given. The prediction of the ternary system based only on the binary data was consistent with the experimental data obtained for this system. Selectivity coefficients $K_{Cl^-}^{NO_3^-}$, $K_{2Cl^-}^{SO_4^{2-}}$, $K_{2NO_3^-}^{SO_4^{2-}}$ were determined at ionic strength 0.1 M.

Ion analyses were performed by ion chromatography, coupled to a conductimetric detector.

Keywords: Anion membrane; Binary system; Ternary system; Isotherms; Selectivity coefficients; Thermodynamic constants; Prediction

1. Introduction

Membrane separation is becoming more attractive in water treatment. Particularly, the ion exchange membranes are found to be efficient for hemodialysis and electrodialysis.

They are more and more used to improve water quality in different fields such as agriculture, medical care and water supplying [1–7].

Many attempts were proposed for ternary exchange equilibrium: Smith et al. [8] had used

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Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

doi:10.1016/j.desal.0000.00.000

exchange equilibrium constants and activity coefficients correlations in order to predict ternary systems using binary data and Wilson model [9].

Their graphic representation showed a good correspondence between predicted and experimental results. Pieroni and Dranoff [10] proved that graphic representation of $H^+/Na^+/Ca^{2+}$ ternary system can be realized using only the data base of each binary couples. In fact, this result confirmed the previous work of Dranoff and Lapidus [11] which suggested that it would be possible to predict ternary equilibrium from binary data alone.

Zuyi and Heimei [12] had also studied $SO_4^{2-}-NO_3^--Cl^-$ ternary system prediction from binary data. It is shown that this approach is easy for practice.

The majority of the ion exchange equilibrium between an ion exchange membrane and solutions were limited for binary systems study. Jonquiéres et al. [13] studied EtBE/EtOH/AcL 1250 MDI-AP ternary system from binary data. Their prediction showed an important difference between experimental and predicted results attributed to tertiary effects.

In this way, our study will concern ion exchange equilibrium between anionic membrane and the following binary and ternary electrolyte solutions: Cl^-/NO_3^-, Cl^-/SO_4^{2-}, NO_3^-/SO_4^{2-} and $Cl^-/NO_3^-/SO_4^{2-}$.

2. Materials and methods

2.1. Ionic chromatography

Anions were determined by ionic chromatography using a Metrohm 761 compact IC with conductivity detector and chemical suppression. The feed solutions were prepared from reagent grade chemicals and pure water.

2.2. Membrane characteristics

Binary and ternary ion-exchange equilibrium data were obtained for the RHONE POULENC RPA membrane. The matrix of the ion exchange membrane studies consists of a vinyl polychloride network reinforced by a polyester screen, with quaternary and tertiary ammonium as functional groups [14]. The manufacture data were completed by the determination of the humidity percentage and the ion exchange capacity of the membrane.

2.2.1. The humidity percentage

Each membrane sample (5×6 cm) under specific ionic form was immersed during four hours of agitation in known ionic solution.

At the equilibrium, the membrane was rapidly dried (m_h is the humid membrane mass) and put under emptiness with $MgSO_4$ during 24 h until obtaining a constant mass (m_s is the dried membrane mass).

The humidity percentage τ was calculated by the following equation:

$$\tau = 100 \times \frac{(m_h - m_s)}{m_h}$$

2.2.2. The ion exchange capacity

Experience were done on pieces of membrane (5×6 cm) in ion A^- (NO_3^-, Cl^-) form immersed in 1 M solution of B^- (NO_3^-, Cl^-). At equilibrium, the quantity n of A^- leached in solution linked to the dried mass m of the membrane had to the ion exchange capacity C_E:

$$C_E = \frac{n}{m}$$

2.3. Isotherm establishment

Membrane sample in Cl^- form were immersed in different solution of binary mixtures ($Cl^- - NO_3^-$), ($Cl^- - SO_4^{2-}$) and ($NO_3^- - SO_4^{2-}$) with variable concentration of each anion the total concentration of each solution was kept constant at 0.1 M and at 0.05 M.

Table 1
The humidity percentage (%)

Humidity percentage (%)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Average
Ionic form NO_3^-	39.58	35.67	36.12	37.56	36.81	37.14
Ionic form Cl^-	38.58	38.88	39.28	39.37	39.03	39.02

Table 2
The anion exchange capacity of the membrane

Exchange capacity (méq g^{-1})	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Average
Ionic form (NO_3^-)	1.60	1.56	1.68	1.51	1.67	1.60
Ionic form (Cl^-)	1.54	1.53	1.62	1.60	1.65	1.58

At the equilibrium, the ionic species in solution were determined using ionic chromatography and the ionic fractions designated X_s and X_m were calculated.
Where $X_s(i)$ is the ionic fraction of ion i in solution and $X_m(i)$ is the ionic fraction of ion i in membrane.

3. Results and discussion

Table 1 presents humidity percentage for five samples of the same membrane in Cl^- and NO_3^- form. It can be observed that the fluctuation of the humidity percentage was slight for the two ionic forms. This result confirms the previous work of Pollet [15] given for different membrane types (RPA, SELEMION, PERMION and NEPTON).

Table 2 presents the anion exchange capacity C_E of the used membrane for the two ionic forms.

Binary isotherms of ion exchange were established in the case of the couples NO_3^-/Cl^-, SO_4^{2-}/Cl^-, SO_4^{2-}/NO_3^-, and represented in Figs. 1, 2 and 3 respectively. For three figures the values of correlation coefficient were rather close to unity.

Fig. 1 shows that the used membrane has more affinity for nitrate than chloride for the two concentrations.

The same membrane has more affinity for sulphate than chloride for the two concentrations as given in Fig. 2.

Fig. 3 shows that for 0.1 M total concentration, the membrane has more affinity for nitrate than sulphate and for 0.05 M total concentration the affinity is inversed.

These isotherms make possible the determination of the membrane affinity order of these ions. The affinity order depends on the total concentration in the solution. Indeed, Fig. 4

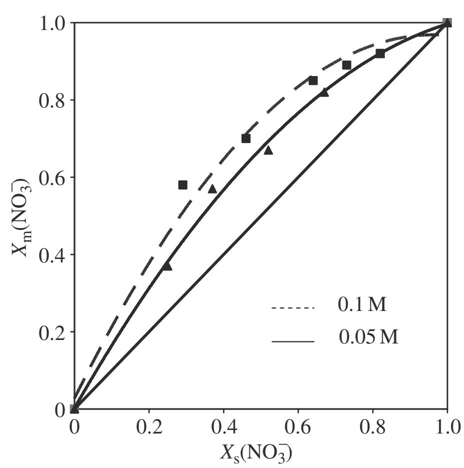

Fig. 1. The ion-exchange isotherm of Cl^-/NO_3^-.

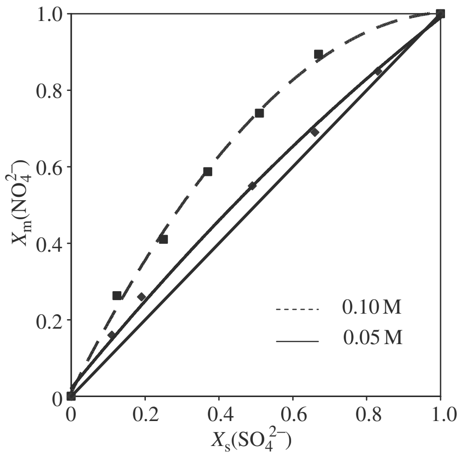

Fig. 2. The ion-exchange isotherm of SO_4^{2-}/Cl^-.

shows for a 0.05 M concentration, the affinity order is: $SO_4^{2-} \rangle NO_3^- \rangle Cl^-$.

In Fig. 5 this order is inversed for the couple SO_4^{2-}/NO_3^- at the concentration 0.1 M. In fact, Smith and Woodburn [16] found that the affinity sequence for Amberlite 400 (quaternary ammonium resin) is $NO_3^- \rangle Cl^- \rangle SO_4^{2-}$ at

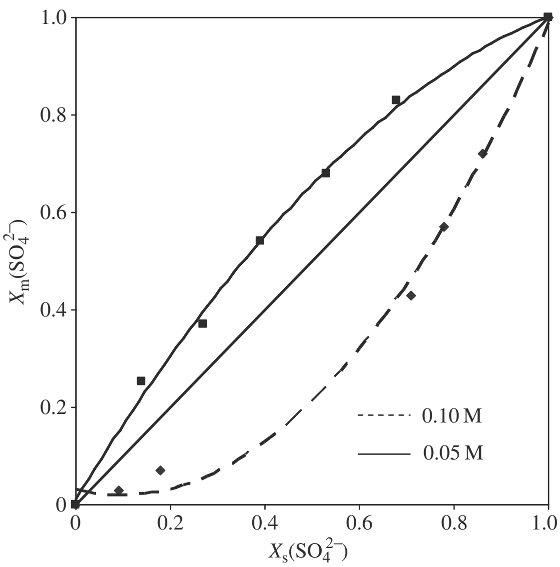

Fig. 3. The ion-exchange isotherm of NO_3^-/SO_4^{2-}.

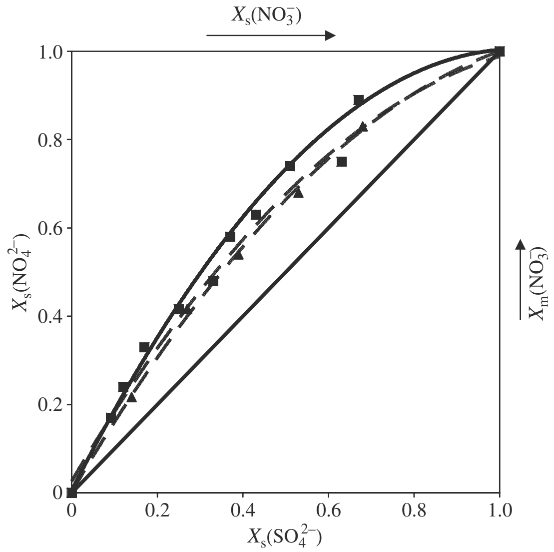

Fig. 4. Equilibrium for the ionic-exchange 0.05 M.

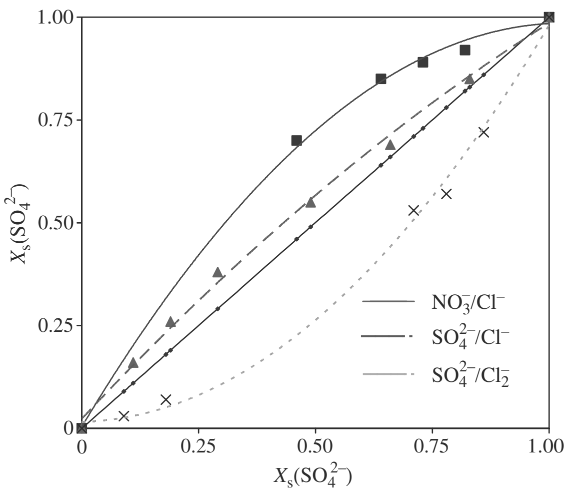

Fig. 5. Equilibrium for the ionic-exchange 0.1 M.

0.2–0.6 mol L^{-1}, Clifford et al. [17] found the affinity sequence for the same type resin to be $SO_4^{2-} \rangle NO_3^-$ at $5 \cdot 10^{-3}$ mol L^{-1}.

For the binary exchange reactions, the equilibrium constants are given below:

Table 3
Equilibrium constant $K_{Cl^-}^{NO_3^-}$ at ionic strength 0.1 M

Sample	$[Cl^-]_s$ mmol L^{-1}	$[NO_3^-]_s$ mmol L^{-1}	$[Cl^-]_m$ mmol g^{-1}	$[NO_3^-]_m$ mmol g^{-1}	$K_{Cl^-}^{NO_3^-}$
1	17.66	82.00	0.15	1.49	2.74
2	26.50	73.00	0.18	1.42	2.80
3	36.80	64.00	0.26	1.33	2.87
4	55.30	46.10	0.38	1.26	3.90
5	67.00	28.02	0.50	1.15	5.49

- $NO^-_{3s} + Cl^-_m \rightleftarrows NO^-_{3m} + Cl^-_s$

$$K_{Cl^-}^{NO_3^-} = \frac{[Cl^-]_s \; [NO_3^-]_m}{[Cl^-]_m \; [NO_3^-]_s}$$

- $2NO^-_{3m} + SO^{2-}_{4s} \rightleftarrows 2NO^-_{3s} + SO^{2-}_{4m}$

$$K_{2NO_3^-}^{SO_4^{2-}} = \frac{[NO_3^-]_S^2 \; [SO_4^{2-}]_m}{[NO_3^-]_m^2 \, [SO_4^{2-}]_S}$$

- $2Cl^-_m + SO^{2-}_{4s} \rightleftarrows 2Cl^-_s + SO^{2-}_{4m}$

$$K_{2NO_3^-}^{SO_4^{2-}} = \frac{[Cl^-]_S^2 \; [SO_4^{2-}]_m}{[Cl^-]_m^2 \; [SO_4^{2-}]_S}$$

Indices m and s indicates the species in the liquid and solid phases respectively. The equilibrium constant can be expressed in terms of molar concentrations.

The calculated binary exchange constants were given in Tables 3–5.

The ternary ion-exchange isotherm of $SO_4^{2-}-NO_3^- - Cl^-$ was determined point by point from a series of ion-exchange equilibrium measurements with solutions of different compositions. The graphical representation of experimental data is shown in Fig. 6. The experimental equilibrium composition of the membrane and solution phases corresponds to a total concentration of 0.1 M. There are 24 experimental points for this ternary system.

All the 24 experimental points are divided into four groups. In each group the ratios of the initial equivalent fraction of NO_3^- and Cl^- in mixture solutions were kept at constant values $X_0(Cl^-)/X_0(NO_3^-) = 0.5$, 1, 3 and 9. While the SO_4^{2-} equivalent ionic fractions of the mixture solutions are 0.100, 0.200, 0.500, 0.670, 0.900 and 0.797, respectively.

In Fig. 6 there are 16 experimental points for binary systems. The SO_4^{2-} equivalent fraction of the mixture solutions for binary SO_4^{2-}/Cl^- and SO_4^{2-}/NO_3^- systems are 0.100, 0.200, 0.500, 0.670, 0.900 and 0.797, respectively.

The ratios of the equivalent fraction of Cl^- and NO_3^- in the mixture solutions are also 0.5,

Table 4
Equilibrium constant $K_{2NO_3^-}^{SO_4^{2-}}$ at ionic strength 0.1 M

Sample	$[SO_4^{2-}]_s$ mmol g^{-1}	$[NO_3^-]_s$ mmol g^{-1}	$[SO_4^{2-}]_m$ mmol g^{-1}	$[NO_3^-]_m$ mmol g^{-1}	$K_{2NO_3^-}^{SO_4^{2-}}$
1	86.1	14.4	1.15	0.53	2.51
2	78.9	21.9	0.92	0.69	2.44
3	71.6	29.3	0.71	0.89	2.46
4	18.50	80.95	0.15	1.50	2.50
5	9.40	89.50	0.06	1.59	1.86

Table 5
Equilibrium constant $K_{2Cl^-}^{SO_4^{2-}}$ at ionic strength 0.1 M

Sample	$[SO_4^{2-}]_s$ mmol g^{-1}	$[Cl^-]_s$ mmol g^{-1}	$[SO_4^{2-}]_m$ mmol g^{-1}	$[Cl^-]_m$ mmol g^{-1}	$K_{2Cl^-}^{SO_4^{2-}}$
1	83.6	16.9	1.36	0.23	12.3
2	66.6	33.7	1.11	0.48	11.5
3	49.4	50.5	0.88	0.71	11.56
4	19.90	80.5	0.51	1.24	12.15
5	17.1	85.00	0.29	1.36	6.41

1.3 and 9. The compositions of two phases for binary systems are drawn on the sides of the triangular diagram (Fig. 6); there are 40 experimental points in this figure.

Four straight lines are drawn between the top of the triangle and the points

$X_0(Cl^-)/X_0(NO_3^-) = 0.5$, 1, 3 and 9 for the $Cl^- - NO_3^-$ binary system. It can be seen that all the 24 experimental points for the ternary exchange reaction just fell on or close to these straight lines. It is shown that, because of the presence of the sulphate, the sums (X_m(Cl) + $X_m(NO_3^-)$) were reduced but the ratios of equivalent ionic fractions of Cl^- and NO_3^- in the membrane phase ($X_s(Cl^-) + X_s(NO_3^-)$) are not obviously affected by the sulphate. Another six straight lines were drawn respectively between the points $X_0(SO_4^{2-}) = 0.100$, 0.200, 0.500, 0.670, 0.797 and 0.900 for the $SO_4^{2-} - Cl^-$ binary system. All the 24 experimental points for the ternary system just fell on or close to these straight lines too.

Normalized isotherms shown in Fig. 7 are given by:

$$X_m(SO_4^{2-})/\{X_m(SO_4^{2-}) + X_m(Cl^-)\} \text{ v.s.}$$

$$X_s(SO_4^{2-})/\{X_s(SO_4^{2-}) + X_s(Cl^-)\},$$

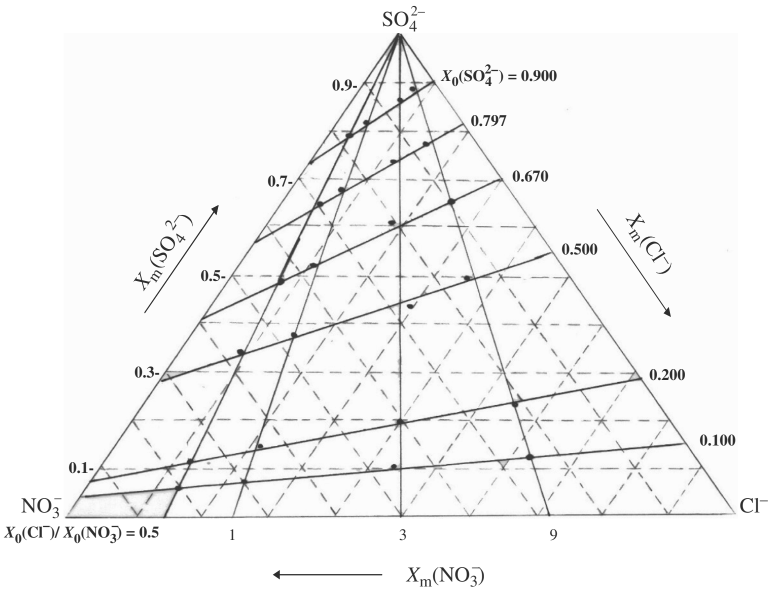

Fig. 6. Graphical representation of experimental data for the ternary system $SO_4^{2-} - NO_3^- - Cl^-$.

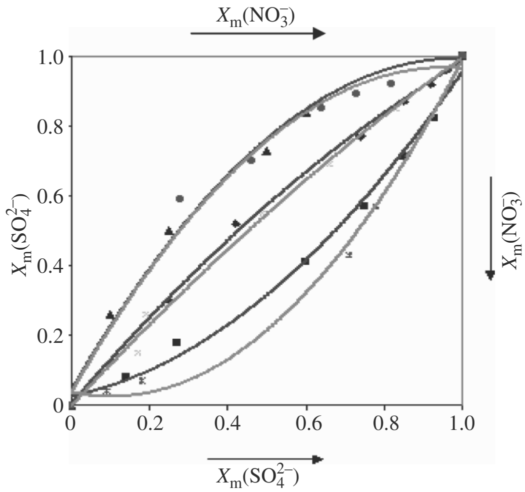

Fig. 7. Normalized equivalent ionic fraction for the ternary exchange system compared with experimental results.

$$X_m(SO_4^{2-})/\{X_m(SO_4^{2-}) + X_m(NO_3^-)\} \text{ v.s.}$$

$$X_s(SO_4^{2-})/\{X_s(SO_4^{2-}) + X_s(NO_3^-),$$

$$X_m(NO_3^-)/\{X_m(NO_3^-) + X_m(Cl^-) \text{ v.s}$$

$$X_s(NO_3^-)/\{X_s(NO_3^-) + X_s(Cl^-)\}.$$

Are shown in Fig. 7. In this figure, the sums of the equivalent ionic fractions of two of the three ions in both solution and membrane phases in the ternary system are normalized to unity. The good agreement between the normalized binary data and the experimental binary isotherms was found in Fig. 7.

4. Conclusion

Ionic exchange equilibrium was studied for the binary system. Isotherm established for these system showed the affinity sequence $SO_4^{2-} \rangle NO_3^- \rangle Cl^-$ for 0.05 M solution and $NO_3^- \rangle SO_4^{2-} \rangle Cl^-$ for 0.1 M solution. Selectivity coefficient $K_{Cl^-}^{NO_3^-}$, $K_{2Cl^-}^{SO_4^{2-}}$, $K_{2NO_3^-}^{SO_4^{2-}}$ were calculated at ionic strength 0.1 M

The prediction of the equilibrium of components in the membrane for the ternary system SO_4^{2-}– NO_3–Cl^- based only on the characteristics of the binaries SO_4^{2-}– NO_3^-, SO_4^{2-}–Cl^-, NO_3^-–Cl^- is consistent with the experimental data.

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