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Effect of temperature on ion exchange equilibrium between AMX membrane and binary systems of $\mathrm{Cl^-}$, $\mathrm{NO_3^-}$ and $\mathrm{SO_4^{2-}}$ ions

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ABSTRACT

The effect of the temperature variation on ion exchange equilibrium between an anion exchange membrane and solutions of electrolytes containing the most dominant anions of natural waters ($\mathrm{Cl^-}$, $\mathrm{NO_3^-}$ and $\mathrm{SO_4^{2-}}$) was studied. All experiments were carried out at 0.3 mol $\mathrm{l^{-1}}$. AMX membrane experimented in this work is a commercial product provided by TOKUYAMA SODA. Humidity percentage and ion exchange capacity were determined. Ionic exchange isotherms for the binary systems $\left(\mathrm{Cl^-/NO_3^-}\right)$, $\left(\mathrm{Cl^-/SO_4^{2-}}\right)$ and $\left(\mathrm{NO_3^-\,/\,SO_4^{2-}}\right)$ were established at different temperatures from 283 to 313 K. At 283 and 298 K, the affinity order was: $\mathrm{Cl^- > NO_3^- > SO_4^{2-}}$. This order was $\mathrm{NO_3^- > Cl^- > SO_4^{2-}}$ at 313 K. Selectivity coefficients $\mathrm{K_i^j}$ and thermodynamic equilibrium constants $\mathrm{K_i^{oj}}$ calculated for uni-univalent and uni-bivalent ions exchange reaction system increase with increasing temperature. Thermodynamic parameters such as standard free enthalpy change, standard enthalpy change, and standard entropy change were calculated. Ion exchange equilibrium at temperatures 283, 298 and 313 K of studied binary systems are found to be endothermic processes. Standard deviations calculated for ion exchange selectivity coefficient and thermodynamic equilibrium constant were lower than 5% at studied temperatures.

Keywords: Ion exchange membrane; Selectivity coefficient; Isotherms; Binary system; Influence of temperature; Thermodynamics

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1. Introduction

Ion exchange membranes are receiving considerable attention and are successfully applied for desalination of sea and brackish water and for treating industrial effluents [1–3]. They are the efficient tools for the concentration or separation of food and pharmaceutical products containing ionic species as well as the manufacture of basic chemical products [4]. The advantages of membrane technology compared to other physical and chemical processes mainly reside in the continuity of operations, the facility of their control and the respect for the environment.

Mixtures of ions can be separated without any auxiliary reagents using ion-exchange methods based on the dependence of ion-exchanger selectivity upon temperature, concentration, etc. Extensive work was done by previous researchers [5–9] to study the concentration and temperature effect in ion exchange equilibrium between resin and uni-univalent and uni-bivalent ion systems.

The influence of temperature on the equilibrium properties of ion exchange resins was studied in the pioneering works of many researchers [10] mainly using newly discovered resins with the strongly acidic sulfonic and strongly basic active groups synthesized from functionalized copolymer of styrene and divinylbenzene. It was shown that the selectivity of cation exchange resin usually decreased insignificantly with temperature in the case of

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exchange of the equally charged cations, and increased in case of exchange of monovalent and divalent cations.

Valverde et al. [11], had studied the equilibrium ion-exchange isotherms of (H^+/Cu^{2+}), (H^+/Zn^{2+}) and (H^+/Cd^{2+}) on a strong acid resin, Amberlite IR-120 at 283 and 303 K in order to assess the possibility of using ion exchange to eliminate heavy metal ions from industrial aqueous liquid streams. They showed that the affinity of the resin for the metal ions increases with increasing temperature. This result was confirmed by the studies of Lee et al. [12] for the same systems using the same resin.

Lokhande and Singare [13], had studied ion exchange equilibrium in $\left(Cl^-/SO_4^{2-}\right)$ system using strongly basic anion exchanger Amberlite IRA-400. It was shown that the equilibrium constant increase from 20 at 30°C to 31 at 41°C.

Ion exchange processes in systems containing Cl^-, NO_3^- and SO_4^{2-} anions have been studied in a number of works in the connection with the problem of water purification from nitrates [14–19]. Most of researchers account that the most suitable resins for selective removal of nitrates from natural waters are strong base resins on styrene–divinylbenzene matrix with tetraalkylammonium groups.

The aim of the present work is to study the influence of temperature on ion exchange between the AMX membrane and the binary systems $\left(Cl^-/NO_3^-\right)$, $\left(Cl^-/SO_4^{2-}\right)$ and $\left(NO_3^-/SO_4^{2-}\right)$. The affinity order and the values of the selectivity coefficients at different temperatures will be determined. All experiments were maintained at constant concentration of 0.3 mol l^{-1}. The thermodynamic parameters such as standard free enthalpy change, standard enthalpy change, and standard entropy change were calculated.

Ions analyses were performed by ionic chromatography, coupled to a conductimetric detector.

2. Experimental procedure

2.1. Ionic chromatography

The analyses of nitrate, chloride, and sulphate ions were carried out by ion chromatography using a Metrohm 761 compact IC with conductivity detector and chemical suppression, 4.6 × 250 mm Metrosep A Supp 1 (6.1005.300), an eluent of 3 mmol l^{-1} sodium carbonate at 1 ml min^{-1}, an injection volume of 20 µl , and a pression from 8 to 9 MPa.

2.2. Membrane characteristics

The anion exchange membrane studied was the AMX membrane produced by TOKUYAMA SODA. The base polymer of this membrane is styrene and divinylbenzene, and the ionic fixed sites are quaternary ammonium groups, so the membrane is a strong anion exchanger.

The membrane characteristics were determined in our laboratory by measuring the humidity percentage and the ion exchange capacity. The methodology has already been described in previous papers [20,21].

Before experiments the membrane was acid-conditioned with 0.1 mol l^{-1} HNO_3 and HCl several times to remove impurity from the membrane and to convert the exchange sites to the desired ionic form [22].

2.3. Ion exchange equilibrium

In order to obtain the ion exchange equilibrium of $\left(Cl^-/NO_3^-\right)$, $\left(Cl^-/SO_4^{2-}\right)$ and $\left(NO_3^-/SO_4^{2-}\right)$ systems at desired temperatures 283, 298 and 313 K, different samples of the AMX membrane (5 × 5 cm^2) in A^{z_a-} form were immersed in the solution with two exchanging anions $\left(A^{z_a-} \text{ and } B^{z_b-}\right)$ in a certain proportions. All experiments were carried at constant concentration 0.3 mol l^{-1}. The solution and membrane were maintained at a fixed temperature under vigorous stirring, until equilibrium was achieved. At the end of equilibrium, the concentration of ionic species in the solution was determined by ion chromatography. The membrane phase composition was determined by the following equations:

$$m \cdot C_E + V \cdot \left[A^{z_a-}\right]_0 = V \cdot \left[A^{z_a-}\right]_s + m \cdot \left[A^{z_a-}\right]_m \qquad (1)$$

$$V \cdot [B^{z_b-}]_0 = V \cdot [B^{z_b-}]_s + m \cdot [B^{z_b-}]_m \qquad (2)$$

where $[i]_s$ is the concentration of the ionic species in solution, $[i]_m$ is the solute concentration in the membrane, C_E is the ion exchange capacity of the membrane, V and m are the volume of solution and the mass of the dry ion exchange membrane, respectively.

The equivalent ionic fractions in the solution phase, $X_s(i)$, and in the membrane, $X_m(i)$, for a binary system can be introduced as:

$$X_s(i) = \frac{z_i[i]_s}{C_T} \qquad X_m(i) = \frac{z_i[i]_m}{C_E} \qquad (3)$$

where z_i is the valence of the ionic specie i and C_T is the total concentration.

3. Results and discussion

3.1. Humidity percentage and ion exchange capacity

Humidity percentage and ion exchange capacity values for the AMX membrane in Cl^-, NO_3^- and SO_4^{2-} form are given in Table 1.

Table 1
Humidity percentage and ion exchange capacity of AMX membrane

Ionic form	τ (%)	C_E (meq . g^{-1})	Ionic radius r_i (Å)
Cl	27.4	1.5	1.81
NO_3^-	24.8	1.5	1.89
SO_4^{2-}	22.8	1.5	2.40

Humidity percentage varies with the ionic form of the membrane. The obtained result can be interpreted by the fact that the humidity percentage of ion exchange membrane depends on a number of different parameters such as the membrane matrix, the nature of the counter-ions, their charge and their size [23,24]. It can be shown that the humidity percentage increases with the decreasing of the ionic radius of the counter-ion given in Table 1, small counter-ion will absorb more molecule of water.

The results shown in Table 1 confirm that the ion exchange capacity is independent for the nature of the counter-ion [26].

3.2. Effect of temperature on ion exchange equilibrium

The fitted isotherms at different temperatures (283, 298 and 313 K) and for the studied binary systems were plotted in Figs. 1–3 in order to study the effect of temperature on ion exchange equilibrium.

These isotherms make possible the determination of the affinity order of the AMX membrane. Affinity for nitrate over chloride, sulphate over chloride and sulphate over nitrate increases with increasing temperature.

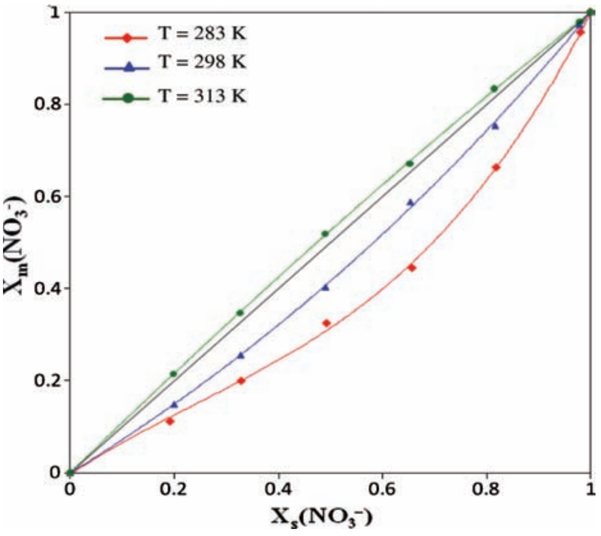

Fig. 1. Ion exchange isotherms for the system $\left(Cl^-/NO_3^-\right)$, $C_0 = 0.3$ mol·L^{-1}.

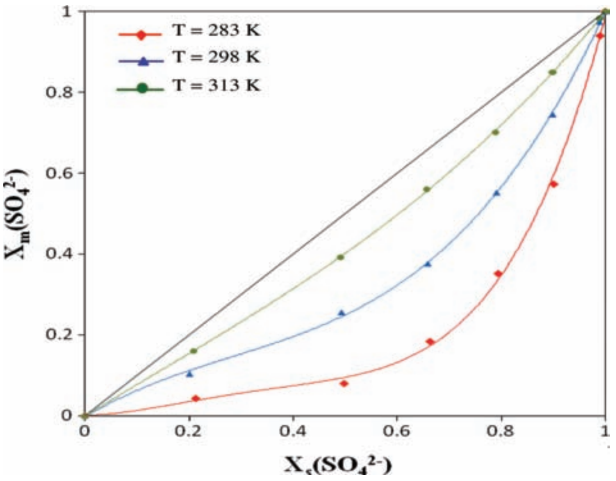

Fig. 2. Ion exchange isotherms for the system $\left(Cl^-/SO_4^{2-}\right)$, $C_0 = 0.3$ mol·L^{-1}.

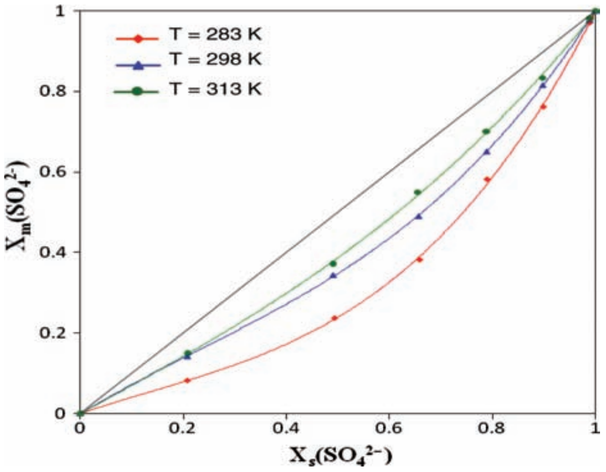

Fig. 3. Ion exchange isotherms for the system $\left(NO_3^-/SO_4^{2-}\right)$, $C_0 = 0.3$ mol·L^{-1}.

This behavior was observed by Valverde et al. [11] and Lee et al. [12]. The order of preference for the anions studied in this investigation at 283 and 298 K is: $Cl^- > NO_3^- > SO_4^{2-}$ and $NO_3^- > Cl^- > SO_4^{2-}$ at 313 K.

The AMX membrane has a greater affinity for chloride than nitrate at 283 and 298 K. This can be explained by comparing the ions ratio Z/r_{ih} for which the order is the following: $Z/r_{ih}\left(Cl^-\right) > Z/r_{ih}\left(NO_3^-\right)$ (Table 2).

Chloride is very strongly preferred by the AMX membrane over sulphate at a temperature range 283–298 K. A similar affinity sequence has been reported previously for Purolite A-520E resin at a total ionic concentration of 0.16 mol l^{-1} [28], as it was observed by Smith and Woodburn [19].

The AMX membrane has more affinity for nitrate than sulphate. In fact Smith and Woodburn [19] found

Table 2
Values of hydrated ion radius [27]

Ions	r_{ih} (Å)	Z/r_{ih}
Cl^-	3.24	0.308
NO_3^-	3.40	0.294

the similar affinity order for Amberlite 400 (quaternary ammonium resin) from 0.2 to 0.6 mol l^{-1} at 295 K. This order $NO_3^- > SO_4^{2-}$ must occur between 0.3 and 0.1 mol l^{-1} since the observed order at 0.05 mol l^{-1} was $SO_4^{2-} > NO_3^-$ [18].

At 313 K, the affinity order was: $NO_3^- > Cl^- > SO_4^{2-}$. Jackson and Bolto [29] found that the affinity sequence for the anion exchange resin IRA 900 was: $NO_3^- > Cl^-$ and $NO_3^- > SO_4^{2-}$ at 293 and 353 K. Since hydrophobic interactions increase with increasing temperature, and since the nitrate selectivity of the anion exchange resins increases with an increase in the hydrophobic nature of the resin, it might have been expected that the nitrate selectivity would increase with temperature [29]. On the other hand, Sata et al. [30] found that, for various anion exchange membranes with different hydrophobicity, the affinity for nitrate over chloride increases with increasing hydrophobicity of anion exchange membranes. A similar finding was obtained by Valverde et al. [11] and Lee et al. [12]. They found by using cationic exchanger Amberlite IR 120 and (H^+/Cu^{2+}), (H^+/Zn^{2+}) and (H^+/Cd^{2+}) binary systems, whose affinity order was $Cu^{2+} > Zn^{2+} > Cd^{2+}$ at 283 K and $Zn^{2+} > Cu^{2+} > Cd^{2+}$ at 303 K.

3.3. Effect of temperature on the selectivity coefficients

For the binary ion exchange reaction the selectivity coefficients can be determined at different temperatures according to Eq. (5):

$$Z_bA_m^{z_a-} + Z_aB_s^{z_b-} \;\square\; Z_bA_s^{z_a-} + Z_aB_m^{z_b-} \tag{4}$$

where z_a and z_b are the valences of the ionic species *A* and *B*, respectively, the selectivity coefficient is usually defined as

$$K_A^B = \left(\frac{\left[B^{z_b-}\right]_m}{\left[B^{z_b-}\right]_s}\right)^{z_a} \times \left(\frac{\left[A^{z_a-}\right]_s}{\left[A^{z_a-}\right]_m}\right)^{z_b} \tag{5}$$

Table 3 summarizes the selectivity coefficients, with standard deviations SD (%), at different temperatures for the three studied systems $\left(CI^-/NO_3^-\right)$, $\left(CI^-/SO_4^{2-}\right)$ and $\left(NO_3^- / SO_4^{2-}\right)$.

The selectivity coefficients at 283, 298 and 313 K for chloride, nitrate and sulphate presented in Table 3 show that these coefficients are related to the temperatures and increase with increasing temperature, the reaction products are favored at high temperatures. This is due to the endothermic ion exchange reactions as showed by Pehilvan and Altun [31] and as found in Section 3.5. In addition, according to the Van't Hoff equation selectivity coefficient increases as the temperature increases. This obtained result was found in previous studied with IRA 900 and IRA 400 anion-exchange resins [13,32,33] at different temperatures. The product of selectivity coefficients $\left(K_{CI^-}^{NO_3^-}\right)^2 \cdot K_{2NO_3^-}^{SO_4^{2-}} \cdot K_{SO_4^{2-}}^{2CI^-}$ is close to theoretical value of unity at different studied temperatures, showing the accuracy of our measurements.

3.4. Thermodynamic equilibrium constant

The thermodynamic equilibrium constant for the ion exchange equilibrium given by Eq. (4) is usually defined as:

$$K^{\circ}{}_A^B = \left(\frac{(B)m}{(B)s}\right)^{Z_a} \times \left(\frac{(A)_s}{(A)_m}\right)^{z_b} \tag{6}$$

where $(i)_s$ and $(i)_m$ are the activities of ionic species i in the solution and the membrane, respectively.

The thermodynamic equilibrium constant is related to the selectivity coefficient by:

$$K^{\circ}{}_A^B = K_A^B \times \left(\frac{\gamma_m(B)}{\gamma_s(B)}\right)^{Z_a} \times \left(\frac{\gamma_s(A)}{\gamma_m(A)}\right)^{z_b} \tag{7}$$

Table 3
Effect of temperature on the selectivity coefficients values

Temperatures (K)	$K_{CI^-}^{NO_3^-}$	SD (%)	$K_{2CI^-}^{SO_4^{2-}}$	SD (%)	$K_{2NO_3^-}^{SO_4^{2-}}$	SD (%)	$\left(K_{CI^-}^{NO_3^-}\right)^2 \cdot K_{2NO_3^-}^{SO_4^{2-}} \cdot K_{SO_4{}^{z-}}^{2CI^-}$
283	0.48	3.09	0.03	0.81	0.12	0.81	0.92
298	0.71	2.48	0.11	3.01	0.21	2.19	0.96
313	1.10	3.18	0.29	1.86	0.27	1.16	1.12

where $\gamma_s(i)$ and $\gamma_m(i)$ are the activity coefficients of ion i in the solution and in the membrane, respectively.

The activity coefficients in the solution were determined according to the extended Debye-Hückel model [34,35]:

$$\log \gamma_s(i) = \frac{-Az_i^2\sqrt{I}}{1 + Ba_i\sqrt{I}} + b_i \cdot I \tag{8}$$

where *A* and *B* are the Debye–Hückel constants, I is the ionic strength for aqueous solution, z_i the charge of the ionic species and a_i is the hydrated ionic radius of ion i.

The activity coefficients in the membrane phase were calculated using the Wilson equations [36]:

$$\gamma_m(A) = \exp\left[\begin{array}{l} 1 - \text{In}\left(X_m(A) + X_m(B).\Lambda_{AB}\right) \\ -\dfrac{X_m(A)}{X_m(A) + X_m(B).\Lambda_{AB}} \\ -\dfrac{X_m(B).\Lambda_{BA}}{X_m(B) + X_m(A).\Lambda_{BA}} \end{array}\right] \tag{9}$$

$$\gamma_m(B) = \exp\left[\begin{array}{l} 1 - \text{In}\left(X_m(B) + X_m(A).\Lambda_{BA}\right) \\ -\dfrac{X_m(B)}{X_m(B) + X_m(A).\Lambda_{BA}} \\ -\dfrac{X_m(A).\Lambda_{BA}}{X_m(A) + X_m(B).\Lambda_{AB}} \end{array}\right] \tag{10}$$

where Λ_{AB} and Λ_{BA} are the Wilson binary interaction parameters.

The thermodynamic equilibrium constants, at studied temperatures, were calculated starting from relation (7) and the results are represented in Table 4.

The values obtained show that for all temperatures thermodynamic equilibrium constants $K^{\circ B}_{A}\left(I = 0\right)$ are greater than selectivity coefficients $K^{B}_{A}\left(I \neq 0\right)$. The gap appears to be more important at higher temperatures. The influence of ionic strength is more important in ion exchange systems when bivalent ions are involved. This shows that we make significant error by confusing $K^{\circ B}_{A}$ and K^{B}_{A} even with weak ionic strength [21].

3.5. Thermodynamic parameters of ion exchange equilibrium

The standard thermodynamic properties of the binary systems constituted by (Cl^-/NO_3^-), (Cl^-/SO_4^{2-}) and (NO_3^-/SO_4^{2-}) and the AMX membrane could be evaluated from the thermodynamic constant, $K^{\circ B}_{A}$ and the temperature. At the equilibrium at fixed temperature, the standard free enthalpy change ΔG°_T of the ion exchange reaction is given by the following formula:

$$\Delta G^\circ_T = -RT\text{Ln}(K^{\circ B}_{A}) \tag{11}$$

where R is the universal gas constant.

ΔG°_T can be also defined as:

$$\Delta G^\circ_T = \Delta H^\circ_T - T \cdot \Delta S^\circ_T \tag{12}$$

where ΔH°_T and ΔS°_T are the standard enthalpy change and entropy change, respectively.

The combination of Eqs. (11) and (12) gives the following equation which can be used to determine the thermodynamic parameters ΔH°_T and ΔS°_T:

$$\text{Ln}\left(K^{\circ B}_{A}\right) = \left(\frac{\Delta S^\circ_T}{R}\right) - \left(\frac{\Delta H^\circ_T}{R}\right) \cdot \frac{1}{T} \tag{13}$$

According to Eq. (13), $\text{Ln}\left(K^{\circ B}_{A}\right)$ versus 1/T plot should be straight line, as given in Fig. 4, from which the entropy change and the enthalpy of ion exchange process can be obtained.

The various thermodynamic parameters of ΔH°, ΔS° and ΔG° for (Cl^-/NO_3^-), (Cl^-/SO_4^{2-}) and (NO_3^-/SO_4^{2-}) systems at different reaction temperatures (283, 298 and 313 K) are given in Table 5.

Analysis of the data presented in Table 5 indicates that, positive values of standard enthalpy changes (ΔH°)

Table 4
Experimental values of the thermodynamic equilibrium constants, with standard deviation SD (%), for the AMX membrane

	283 K			298 K			313 K		
System A–B	K^{B}_{A}	$K^{\circ B}_{A}$	SD (%)	K^{B}_{A}	$K^{\circ B}_{A}$	SD (%)	K^{B}_{A}	$K^{\circ B}_{A}$	SD (%)
(Cl^-/NO_3^-)	0.48	0.49	2.99	0.71	0.72	2.51	1.10	1.20	3.40
(Cl^-/SO_4^{2-})	0.03	0.05	1.14	0.11	0.24	4.56	0.29	0.80	4.91
(NO_3^-/SO_4^{2-})	0.12	0.31	2.02	0.21	0.67	4.51	0.27	0.94	4.80

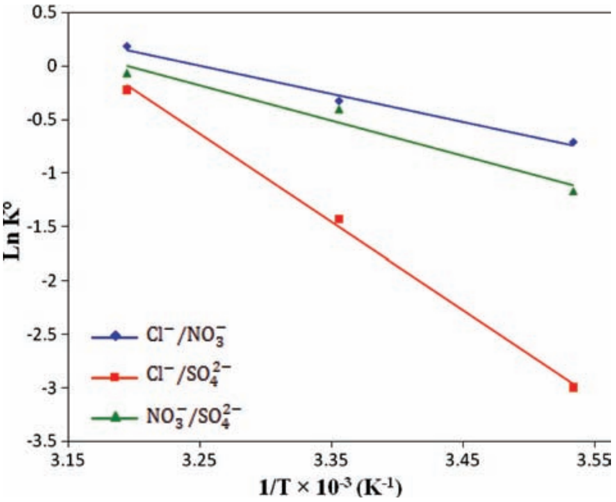

Fig. 4. Ln $\left(K^{\circ B}_{A}\right)$ versus $\frac{1}{T}$ plot for (Cl^-/NO_3^-), (Cl^-/SO_4^{2-}) and (NO_3^-/SO_4^{2-}) exchange systems.

Table 5
Thermodynamic parameters of the binary systems studied

System A–B	T (K)	ΔG°_T (KJ.mol^{-1})	ΔH°_T (KJ.mol^{-1})	ΔS°_T (J.mol^{-1}.K^{-1})
$\left(Cl^-/NO_3^-\right)$	283	1.68	21.91	71.28
	298	0.81		
	313	−0.47		
$\left(Cl^-/SO_3^{2-}\right)$	283	7.04	68.15	216.16
	298	3.53		
	313	0.58		
$\left(NO_3^-/SO_4^{2-}\right)$	283	2.75	27.39	87.46
	298	0.99		
	313	0.16		

were reported for all systems studied. This observation indicates that, the ion exchange between the AMX membrane and the binary system of Cl^-, NO_3^- and SO_4^{2-} is an endothermic process resulted in the equilibrium extent of reaction increase with an increasing with temperature [37]. The standard entropy in this study is found to be positive; it means that the increased randomness appeared on the membrane–solution interface during the ion exchange reaction, this obtained result was found by Mohan et al. [38]. In addition, the standard free enthalpy change ΔG°_T value for all systems studied becomes smaller with increasing temperature, which is an indication that the anion exchange becomes more favorable [39].

4. Conclusion

The effect of the temperature on ion exchange equilibrium was studied for the three binary systems: $\left(Cl^-/NO_3^-\right)$, $\left(Cl^-/SO_4^{2-}\right)$ and $\left(NO_3^-/SO_4^{2-}\right)$ from 283 to 313 K and at constant concentration of 0.3 mol l^{-1}. The affinity order for the AMX membrane was $Cl^- > NO_3^- > SO_4^{2-}$ at 283 and 298 K and $NO_3^- > Cl^- > SO_4^{2-}$ at 313 K. Selectivity coefficients $K_{Cl^-}^{NO_3^-}$, $K_{2Cl^-}^{SO_4^{2-}}$ and $K_{2NO_3^-}^{SO_4^{2-}}$ were determined and increase with increasing temperature. The product of selectivity coefficients $\left(K_{Cl^-}^{NO_3^-}\right)^2 \cdot K_{2NO_3^-}^{SO_4^{2-}} \cdot K_{SO_4^{2-}}^{2Cl^-}$ is close to theoretical value of unity at different studied temperature. Thermodynamic equilibrium constants $K_i^{\circ j}$ and thermodynamic parameters of ion-exchange equilibrium were determined. Furthermore, the exchange process is endothermic, as the positive standard enthalpy indicates.

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