Thermodynamic Properties of the Mixed Electrolyte System: The Ternary NH_4Br + NaBr + H_2O System[†]

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The thermodynamic properties of NH_4Br salt in the ternary NH_4Br (m_1) + NaBr (m_2) + H_2O mixed electrolyte system are reported in this work. A galvanic cell containing a solvent polymeric (PVC) ammonium ion-selective membrane electrode (ISE) and an Ag/AgBr electrode was employed for collecting the potentiometric data with a series of mixed salt solutions, at similar constant ionic strengths, and each was characterized by a fixed salt molal ratio r (where $r = m_1(NH_4Br)/m_2(NaBr) = 1$, 10, 50, and 100, respectively). Pitzer semiempirical ion-interaction theory for mixed salts was used for modeling the nonideal behavior of the system, over the ionic strength ranging from (0.01 to 5) $mol\cdot kg^{-1}$, at 298 K, where the mean activity and osmotic coefficients, solvent activities, and excess Gibbs free energies were determined for this ternary electrolyte system. The impact of the magnitude of the potentiometric selectivity coefficient (K_{12}^{Pot}) of the NH_4^+ ISE, as a limiting factor, on the results is evaluated.

Introduction

Aqueous mixed electrolyte solutions are implicated in many industrial and environmental processes, such as desalination, chemical separation, marine chemistry, geology, and environment. Determination of the thermodynamic properties of electrolytes in aqueous solutions is needed for understanding the nature of various ionic interactions and for handling of the involved processes.[1−3] Although solvent activity methods such as the time-consuming isopiestic method are widely used for this purpose, a more recent development of the ion-selective electrodes (ISEs) offers an attractive alternative method for the determination of the activity coefficients in electrolyte systems. In this context, we have, for many years, used in our laboratory pH-glass membrane[4] and, particularly, solvent polymeric membrane ISE for the determination of mean activity coefficients of NH_4Cl in mixed (ROH + H_2O) solvents and in several mixed electrolyte systems (see refs and and references therein). We report also in this work the results of the exploitation of a solvent polymeric membrane electrode for measurements on the ternary NH_4Br + NaBr + H_2O system. Using a galvanic cell containing a solvent polymeric (PVC) NH_4^+ ISE and Ag/AgBr electrodes, the activity coefficients for NH_4Br were determined, at similar ionic strengths, in different series of mixed electrolyte systems, each characterized by a defined molal ratio ($r = m_1(NH_4Br)/m_2(NaBr) = 100$, 50, 10, and 1), at 298 K. Pitzer semiempirical ion-interaction theory was used for modeling the thermodynamic properties of the investigated ternary system over the total molality, ranging from 0.01 $mol\cdot kg^{-1}$ up to about 5 $mol\cdot kg^{-1}$. Finally, the thermodynamic properties such as solvent osmotic coefficients, solvent activities, and excess Gibbs free energies were determined for this ternary electrolyte system. The impact of the magnitude of the potentiometric selectivity of the ISE membrane (K_{12}^{Pot}) on the potentiometric measurement was analyzed.

Experimental

Reagents. High molecular poly(vinyl chloride) (PVC), a mixture of nonactin (72 %) and monactin (28%) as an ionophore (CAS-RN: 6833-84-7 and 7182-54-9, respectivly), and bis(2-ethylhexyl)sebacate, all of Selectophore grade (Fluka, Switzerland), were used as ingredients for the preparation of solvent polymeric NH_4^+ ISE. All primary stock solutions were, first, prepared by mass using doubly distilled water and by potentiometric titration using $AgNO_3$ standard solution. Prior to use, the analytical grade NH_4Br and NaBr salts (with mass fractions > 99.5 % and > 99 %, respectively) from Fluka were dried overnight in an oven (at 110 °C).

Potentiometric Measurement. NH_4^+ selective membranes were prepared and evaluated as previously reported (see refs 5 and 6 and references therein). The ISE membranes had the following composition (mass fraction): 1.05 % ionophore, 0.5 % potassium tetrakis(4-chlorophenyl)borate, 67.07 % bis(2-ethylhexyl)sebacate, and 31.88 % PVC. The electrodes were each time back-filled with NH_4Br internal filling solution, and an Ag/AgBr wire was used as internal reference electrodes. The Ag/AgBr wire electrodes were prepared essentially as described elsewhere by electrolysis.[7] From the preliminary experimental tests performed with different concentrations of internal electrolyte filling solution, the best results were those obtained with 0.1 M NH_4Br electrolyte. The fabricated electrodes were, initially, conditioned for 48 h in 0.001 $mol\cdot L^{-1}$ NH_4Br aqueous electrolyte solution and then calibrated using NH_4Br standard solutions. The experimental cell potentials were recorded using a Metrohm ion-meter (model 619) with high input impedance (> 1 TΩ) connected, via a Topward multimeter equipped with a GPIB interface (Bus option, model 1304, Taiwan, Korea), to a personal computer (Samsung, 386/32 MHzprocessor) for data acquisition and processing. A laboratory written Basic program was used for data acquisition. Using this automated data acquisition setup, the uncertainties of the potentiometric mesurement and the obtained mean activity coefficient were ± 0.05 mV, and $\pm 5\cdot 10^{-4}$, respectively. All measurements were performed under stirring conditions, and the temperature was

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kept constant at 298 K (± 0.1 K) using a thermostatic system (Julabo M12) coupled to a double-wall container enabling the circulation of thermostatted water. The primary concentrated mixed electrolyte solutions were prepared by weighing the salts using a Metler electronic balance (± 0.05 mg). The molality of the electrolyte in the galvanic cell was varied step by step by a standard addition method,[8] adding each time an appropriate volume of a primary concentrated standard electrolyte solution, having the same mole ratio as that previously utilized in the galvanic cell. The standard addition steps were performed using appropriate Hamilton syringes, with uncertainties within ± 1 % of nominal volumes (as indicated by the manufacturer).

Method

Ion-Interaction Model. The semiempirical Pitzer ion-interaction theory was successfully used for modeling various highly concentrated pure and mixed electrolyte systems.[3,9–11] In this theory, the nonideal behavior of the electrolyte system is conveniently described by the related activity and osmotic coefficients or excess Gibbs free energies. For a single $M_{\nu+}X_{\nu-}$ electrolyte (e.g., NH_4Br) and for a (1:1) mixture of NH_4Br and NaBr electrolyte, the corresponding Pitzer equations are written, respectively, as

$$\ln \gamma_{\pm} = |z_+ z_-| f^{\gamma} + m\left(\frac{2v_+ v_-}{v}\right)B^{\gamma} + m^2\left(\frac{2(v_+ v_-)^{3/2}}{v}\right)C^{\gamma} \quad (1)$$

$$\begin{aligned}\ln \gamma_{\pm \mathrm{NH_4Br}} = {} & f^{\gamma} + \mathrm{I}\{B^{\gamma}_{\mathrm{NH_4Br}} + y_2(B^{\phi}_{\mathrm{NaBr}} - B^{\phi}_{\mathrm{NH_4Br}} + \\ & \theta_{\mathrm{NH_4Na}})\} + \\ & I^2\left\{\left(\frac{3}{2}C^{\phi}_{\mathrm{NH_4Br}}\right) + y_2\left(C^{\phi}_{\mathrm{NaBr}} - C^{\phi}_{\mathrm{NH_4Br}} + \frac{\psi_{\mathrm{NH_4NaBr}}}{2}\right) + \right. \\ & \left. y_2(1 - y_2)\frac{\psi_{\mathrm{NH_4NaBr}}}{2}\right\} \end{aligned} \quad (2)$$

where

$$f^{\gamma} = -A_{\phi}\left[\frac{\sqrt{I/m^0}}{1 + b\sqrt{I/m^0}} + \frac{2}{b}\ln(1 + b\sqrt{I/m^0})\right] \quad (3)$$

$$B^{\gamma} = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2(I/m^0)}\left[1 - e^{-\alpha\sqrt{I/m^0}}\left(1 + \alpha\sqrt{I/m^0} - (1/2)\alpha^2(I/m^0)\right)\right] \quad (4)$$

$$C^{\gamma} = (3/2)C^{\phi} \quad (5)$$

$\gamma_{\pm}$ is the molality-scale mean ionic activity coefficient of the electrolyte $M_{\nu+}X_{\nu-}$; Z is the charge number of the ion; $v = v_+ + v_-$ is the number of ions dissociated in one unit electrolyte formula; m is the molality of the electrolyte ($\mathrm{kg \cdot mol^{-1}}$); I is the ionic strength on a molality scale; $\beta^{(0)}$ ($\mathrm{kg \cdot mol^{-1}}$), $\beta^{(1)}$ ($\mathrm{kg \cdot mol^{-1}}$), and C^{ϕ} $(\mathrm{kg \cdot mol^{-1}})^{1/2}$are the parameters of the Pitzer equations; $b = 1.2$ $(\mathrm{kg \cdot mol^{-1}})^{1/2}$; and $\alpha = 2$ $(\mathrm{kg \cdot mol^{-1}})^{1/2}$. In addition, $\theta_{\mathrm{NH_4Na}}$ and $\psi_{\mathrm{NH_4NaBr}}$ represent the ionic interaction parameters for the mixed salt system. The Debye–Hückel coefficient for the osmotic coefficient (A_{ϕ}) is defined as

$$A_j = \frac{1}{3}(2\pi N_A \rho_A)^{1/2}\left(\frac{e}{4\pi\varepsilon_o DkT}\right)^{3/2} \quad (6)$$

where the constants ε_o, k, N_A, D, and ρ_A are vacuum permittivity, Boltzmann constant, Avogadro constant, dielectric constant, and density of the mixed solvent, respectively. For water, its value is 0.39145 $(\mathrm{kg \cdot mol^{-1}})^{1/2}$ at 298 K.

Principle of Potentiometric Measurements. The potentiometric measurements were performed using the following three galvanic cells containing a solvent polymeric PVC NH_4^+ ISE and an Ag/AgBr electrode

$$\mathrm{Ag|AgBr|NH_4Br}(m_1),\ \mathrm{H_2O|NH_4^+\ ISE} \quad (\mathrm{A})$$

$$\mathrm{Ag|AgBr|NaBr}(m_2),\ \mathrm{H_2O|NH_4^+\ ISE} \quad (\mathrm{B})$$

$$\mathrm{Ag|AgBr|NH_4Br}(m_1), \mathrm{NaBr}(m_2), \mathrm{H_2O|NH_4^+\ ISE} \quad (\mathrm{C})$$

As shown below, cell A was used for the measurement of the slope s and the cell constant potential E', and cell B was used for the measurement of the potentiometric selectivity coefficient K_{12}^{Pot} of the NH_4^+ ISE toward the Na^+ interfering ions. Finally, the galvanic cell C was used for the determination of the mean activity coefficients for NH_4Br in the aqueous mixed (NH_4Br + NaBr) electrolyte at 298 K. Effectively, for this mixed electrolyte system, the cell potential can be expressed by

$$E_C = E' + s\log[a_1 + K_{12}^{\mathrm{Pot}} a_2] \quad (7)$$

$$a_1 = m_1(m_1 + m_2)\gamma_{\pm,1}^2 \quad (8)$$

$$a_2 = m_2(m_1 + m_2)\gamma_{\pm,2}^2 \quad (9)$$

In eq 7, K_{12}^{Pot} represents the potentiometric selectivity coefficient of the NH_4^+ ISE toward the Na^+ interfering ions. For the determination of the experimental mean activity coefficient values in mixed salt solutions, it is first necessary to evaluate the value of the potentiometric selectivity coefficient K_{12}^{Pot}. Accordingly, the following procedure was used for the evaluation of K_{12}^{Pot}. In pure solution of interfering NaBr salt, the potentiometric response of the galvanic cell B could be rearranged as

$$K_{12}^{\mathrm{Pot}} = \left(\frac{1}{a_2}\right)10^{(E_B - E')/s} \quad (10)$$

Therefore, using pure standard NH_4Br solutions and the above-mentioned regressed slope s and intercept values E', the potentiometric selectivity coefficient of the NH_4^+ ISE toward the Na^+ interfering ions could be determined. On the other hand, for the aqueous mixed NH_4Br + NaBr salt solutions, the cell potential of C can be expressed by

$$E_C = E' + s\log\left[a_1\left(1 + K_{12}^{\mathrm{Pot}}\frac{a_2}{a_1}\right)\right] \quad (11)$$

If, in the used concentration range for all series of electrolyte solutions, the interfering effect of Na^+ on the response of the NH_4^+ ISE would be negligible, the the second term in the parenthesis of the above equation ($K_{12}^{\mathrm{Pot}}a_2/a_1$) could practically be ignored, and eq 11 is simplified to the Nernst relation

$$E_C = E' + s\log a_1 \quad (12)$$

As a result, the mean activity coefficient values for $NH_4Br(m_1)$ could be calculated, for all studied series of the ternary systems, as a function of molality by

$$\gamma_{\pm} = \frac{1}{\sqrt{m_1(m_1 + m_2)}}10^{(E_C - E')/2s} \quad (13)$$

Determination of Mixed Ion-Interaction Parameters (θ_{NH_4Na},ψ_{NH_4NaBr}). The Pitzer graphical method was used for the determination of the mixed ionic interaction parameters ($\theta_{\mathrm{NH_4Na}}$,$\psi_{\mathrm{NH_4NaBr}}$) for the studied ternary system.[3,10] According to this method

$$\left(\frac{1}{m_{\mathrm{Na}}}\right)\Delta \ln \gamma_{\pm \mathrm{NH_4Br}} = \theta_{\mathrm{NH_4Na}} + \frac{1}{2}(m_{\mathrm{NH_4}} + m_{\mathrm{Br}})\psi_{\mathrm{NH_4NaBr}} \quad (14)$$

$$\Delta \ln \gamma_{\pm \mathrm{NH_4Br}} = (\ln \gamma_{\pm \mathrm{NH_4Br}})_{\mathrm{exptl}} - (\ln \gamma_{\pm \mathrm{NH_4Br}})_{\mathrm{calcd}} \quad (15)$$

where $(\ln \gamma_{\pm \mathrm{NH_4Br}})_{\mathrm{calcd}}$ is calculated with $\psi_{\mathrm{NH_4NaBr}} = 0$ and $\theta_{\mathrm{NH_4Na}} = 0$. Accordingly, the two and three particle mixed ion-interaction parameters $\theta_{\mathrm{NH_4Na}}$ and $\psi_{\mathrm{NH_4NaBr}}$ could be determined from the slope and intercept of the linear portion of the regression plot of the $(1/m_{\mathrm{Na}})\Delta \ln \gamma_{\pm \mathrm{NH_4Br}}$ versus 1/2 $(m_{\mathrm{NH_4}} + m_{\mathrm{Br}})$ values.

Determination of Osmotic Coefficients, Solvent Activities, and Excess Gibbs Free Energies. Using the obtained Pitzer ion-interaction parameters and the following equations for aqueous mixed salt electrolyte systems,[3,9−11] the values of osmotic coefficients (ϕ), excess Gibbs free energies (G^{E}), and water activities (a_{w}) were determined for all series of investigated mixed electrolyte solutions

$$\phi - 1 = z^2 f^{\phi} + I\{(1-y_2)B^{\phi}_{\mathrm{NH_4Br}} + y_2 B^{\phi}_{\mathrm{NaBr}} + y_2(1-y_2)\theta_{\mathrm{NH_4Na}}\} + I^2\{(1-y_2)C^{\phi}_{\mathrm{NH_4Br}} + y_2 C^{\phi}_{\mathrm{NaBr}} + y_2(1-y_2)\psi_{\mathrm{NH_4NaBr}}\} \quad (16)$$

$$G^{\mathrm{E}} = RT\sum_i \upsilon_i m_i(1 - \phi + \ln \gamma_i) \quad (17)$$

$$a_{\mathrm{w}} = \exp[(-M_{\mathrm{w}}/1000)(\sum_i m_i)\phi] \quad (18)$$

In the above equations, M_{w} is the molecular mass of water and $\sum_i m_i$ is the sum of the molality of all solute species.

Results and Discussions

As a preliminary step, using cell A, the response quality of the fabricated $\mathrm{NH_4^+}$ ISE versus Ag/AgBr electrode was evaluated in pure solutions of $\mathrm{NH_4Br}$. The reported Pitzer parameter values[11] for aqueous pure $\mathrm{NH_4Br}$ ($\beta^{(0)} = 0.0624$, $\beta^{(1)} = 0.1947$, and $C^{\phi} = -0.00436$) were used for the calculation of electrode slope s and intercept E'. Then, the potentiometric selectivity coefficient of the $\mathrm{NH_4^+}$ ISE toward the $\mathrm{Na^+}$ interfering ions was determined in pure NaBr solutions, using the reported Pitzer parameter values.[12] The resulting potentiometric selectivity coefficient value was found to be $K_{12}^{\mathrm{Pot}} = 2.3 \cdot 10^{-3}$. Figure 1 shows a resulting typical linear Nernstian plot with a regressed slope value of $2s = 117.74$ mV/(per decade molal change), and an intercept of $E' = 140.56$ mV ($R^2 = 0.99994$), respectively. Similarly, Pitzer parameter values for aqueous pure $\mathrm{NH_4Br}$ were as well determined in this work and were then used for further calcultions as reported below. The obtained values ($\beta^{(0)} = 0.06187$, $\beta^{(1)} = 0.19765$, and $C^{\phi} = -0.00425$, with σ(rms) = 0.038) compared well with the available literature values (see above),[11] giving also the same regressed electrode slope and intercept values in aqueous pure $\mathrm{NH_4Br}$ solutions. Table 1 shows the corresponding potentiometric data and natural logarithm of the mean activity coefficients for pure $\mathrm{NH_4Br}$ as a function of electrolyte molality at 298 K.

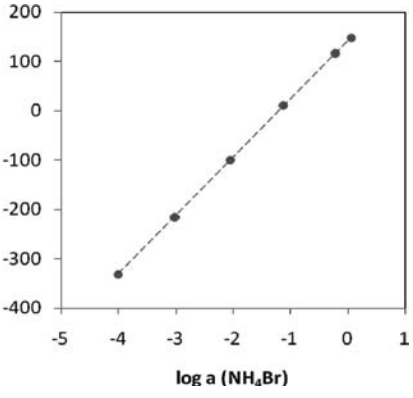

Figure 1. Cell potential versus logarithm of $\mathrm{NH_4Br}$ activity in pure aqueous $\mathrm{NH_4Br}$ solution at 298 K.

Table 1. Cell Potentiometric Data and the Resulting ln $\gamma_{(\pm)}$ for Pure $\mathrm{NH_4Br}$ versus Electrolyte Molality at 298 K

m/mol·kg^{-1}	ln $\gamma_{(\pm)}$	E/(mV)
0.010	−0.1043	−106.3
0.025	−0.1547	−61.7
0.050	−0.2042	−28.6
0.100	−0.2637	4.0
0.250	−0.3541	46.5
0.500	−0.4255	78.5
1.000	−0.4895	110.8
1.500	−0.5177	130.3
1.926	−0.5295	142.5
2.500	−0.5359	155.6
3.000	−0.5365	165.0
3.500	−0.5346	173.0
4.000	−0.5316	180.0
4.500	−0.5282	186.3
5.000	−0.5252	191.8

On the basis of the evaluated K_{12}^{Pot} value, the interfering effect of $\mathrm{Na^+}$ on the response of the $\mathrm{NH_4^+}$ ISE was considered negligible. Consequently, as mentioned above, the second term $(K_{12}^{\mathrm{Pot}}(a_2/a_1))$ in the parentheses of eq 11 was dropped, and the Nernst equation (eq 13) was used for the determination of the $\mathrm{NH_4Br}$ mean activity coefficients for all series of electrolyte solutions (with $r = m_1/m_2 = 100$, 50, 10, and 1). Table 2 shows the cell potentiometric data and the resulting experimental mean activity coefficients for $\mathrm{NH_4Br}$ versus electrolyte molality, for the investigated ternary systems at 298 K. Figure 2 shows also the trend of natural logarithm of $\mathrm{NH_4Br}$ mean activity coefficient versus square root of ionic strength, for these electrolyte systems at 298 K. To check the impact of the ignored second term $(K_{12}^{\mathrm{Pot}}(a_2/a_1)$ in eq 11) on the results, its value was evaluated in the corresponding concentration range for the whole studied series of ternary electrolyte systems. Table 3 shows the range of variability of the magnitude of this term $(K_{12}^{\mathrm{Pot}}(a_2/a_1))$ for each series of solutions and its influence (Δ log a_1) on the determined log a_1 values. As can be seen, the magnitude of this term increases as the molal ratio (r) decreases; however, the calculation confirms that for the series of solutions with $r = m_1/m_2 = 100$, 50, and 10 the corresponding logarithm of the mean activity coefficients could conveniently be determined, up to their fourth decimal places, by the Nernst equation.

According to the Pitzer graphical method, the value of the two and three particle mixed ionic interaction parameters $(\theta_{\mathrm{NH_4Na}}, \psi_{\mathrm{NH_4NaBr}})$ was also determined from the slope and intercept of the linear portion of the regression plot of $(1/m_{\mathrm{Na}})\Delta$ ln $\gamma_{\pm \mathrm{NH_4Br}}$ versus $1/2(m_{\mathrm{NH_4}} + m_{\mathrm{Br}})$. Effectively, the resulting individual value of these interaction parameters for each series of mixed electrolyte solutions ($r = m_1/m_2 = 100$, 50, 10, and 1), along with their resulting mean values (± SD), are presented in Table 4. As can be seen from the reported data (Table 4) for the series of solutions with $r = m_1/m_2 = 1$, the corresponding value of interaction parameters $(\theta_{\mathrm{NH_4Na}}, \psi_{\mathrm{NH_4NaBr}})$ is significantly different from the resulting mean values calculated of the remaining series of solutions ($r = m_1/m_2 = 100$, 50, and 10). Therefore, the value of $\theta_{\mathrm{NH_4Na}}, \psi_{\mathrm{NH_4NaBr}}$ parameters for the series of solutions with $r = m_1/m_2 = 1$ were excluded in the evaluation of the final mean values. Finally, based on the obtained Pitzer

Table 2. Cell Potentiometric Data and the Resulting Experimental Mean Activity Coefficients for $NH_4Br(m_1)$ versus Electrolyte Molality, in the Investigated Mixed $NH_4Br(m_1)$ + $NaBr(m_2)$ Electrolyte Systems, for Various Molal Salt Ratios ($r = m_1/m_2$ = 100, 50, 10, and 1), at 298 K

m_1/mol·kg^{-1}	m_2/mol·kg^{-1}	ln $\gamma_{1(\pm)}$	E/(mV)	m_1/mol·kg^{-1}	m_2/mol·kg^{-1}	ln $\gamma_{1(\pm)}$	E/(mV)
	$r = m_1/m_2 = 100$				$r = m_1/m_2 = 10$		
0.0099	0.0001	−0.1043	−98.3	0.0091	0.0009	−0.1043	−106.4
0.0248	0.0002	−0.1547	−55.1	0.0227	0.0023	−0.1546	−61.4
0.0495	0.0005	−0.2042	−22.9	0.0455	0.0045	−0.2042	−28.8
0.0990	0.0010	−0.2637	9.0	0.0909	0.0091	−0.2636	4.5
0.2475	0.0025	−0.3541	50.1	0.2273	0.0227	−0.3538	46.7
0.4950	0.0050	−0.4254	81.0	0.4546	0.0454	−0.4246	78.5
0.9901	0.0099	−0.4893	112.9	0.9092	0.0908	−0.4874	111.1
1.4851	0.0149	−0.5173	131.4	1.3638	0.1362	−0.5141	130.6
1.9802	0.0198	−0.5302	145.2	1.8184	0.1816	−0.5253	145.3
2.4752	0.0248	−0.5350	156.0	2.2730	0.2270	−0.5283	156.2
2.9702	0.0298	−0.5354	165.2	2.7276	0.2724	−0.5266	165.7
3.4653	0.0347	−0.5332	173.0	3.1822	0.3178	−0.5221	174.3
3.9603	0.0397	−0.5299	179.7	3.6368	0.3632	−0.5162	181.1
4.4553	0.0447	−0.5261	185.8	4.0914	0.4086	−0.5097	187.3
4.9504	0.0496	−0.5227	191.2	4.5460	0.4540	−0.5032	193.3
	$r = m_1/m_2 = 50$				$^a r = m_1/m_2 = 1$		
0.0098	0.0002	−0.1043	−102.8	0.0050	0.0050	−0.1043	−121.8
0.0245	0.0005	−0.1547	−57.8	0.0125	0.0125	−0.1545	−78.1
0.0490	0.0010	−0.2042	−24.5	0.0250	0.0250	−0.2039	−45.8
0.0980	0.0020	−0.2637	7.8	0.0500	0.0500	−0.2630	−13.3
0.2451	0.0049	−0.3541	50.5	0.1250	0.1250	−0.3521	28.0
0.4902	0.0098	−0.4253	82.7	0.2500	0.2500	−0.4208	58.5
0.9804	0.0196	−0.4891	115.2	0.4999	0.5001	−0.4785	91.4
1.4705	0.0295	−0.5169	134.6	0.7499	0.7501	−0.4991	111.1
1.9607	0.0393	−0.5296	149.1	0.9998	1.0002	−0.5033	125.5
2.4509	0.0491	−0.5342	160.9	1.2498	1.2502	−0.4984	137.1
2.9411	0.0589	−0.5343	170.3	1.4998	1.5002	−0.4879	146.9
3.4312	0.0688	−0.5319	178.2	1.7497	1.7503	−0.4737	155.4
3.9214	0.0786	−0.5282	184.9	1.9997	2.0003	−0.4572	162.9
4.4116	0.0884	−0.5241	191.1	2.2497	2.2503	−0.4392	169.6
4.9018	0.0982	−0.5203	196.8	2.4996	2.5004	−0.4204	175.7

[a] Results with $r = 1$ were excluded for the calculation of final θ_{NH_4Na} and Ψ_{NH_4NaBr} (see also Tables 3 and 4).

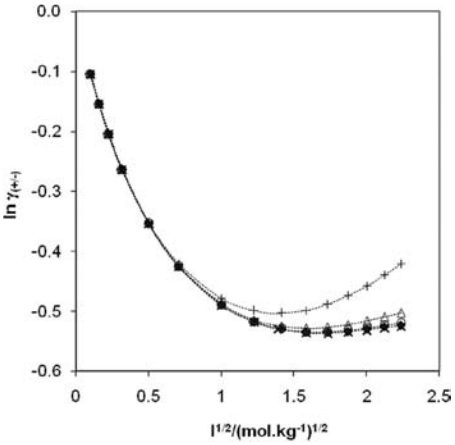

Figure 2. Natural logarithm of NH_4Br mean activity coefficient versus square root of ionic strength for the ternary NH_4Br + NaBr electrolyte systems, for various molal salt ratio ($r = m_1/m_2$ = 100, 50, 10, and 1), at 298 K. ×, pure NH_4Br; ◆, r = 100; ○, r = 50; Δ, r = 10; +, r = 1.

Table 3. Range of Variability of ($K_{12}^{\mathrm{Pot}}(a_2/a_1)$) Term for All Series of Solutions (with $r = m_1/m_2$ = 100, 50, and 10, and 1) and Its Influence on the Determination of log a_1 Values (Δ log a_1), at 298 K

r	$K_{12}\cdot a_2/a_1$	Δ log a_1
100	$2.3\cdot10^{-5}$ to $2.9\cdot10^{-5}$	$1.0\cdot10^{-5}$ to $1.3\cdot10^{-5}$
50	$4.6\cdot10^{-5}$ to $5.7\cdot10^{-5}$	$2.0\cdot10^{-5}$ to $2.5\cdot10^{-5}$
10	$3.0\cdot10^{-4}$ to $3.8\cdot10^{-4}$	$1.3\cdot10^{-4}$ to $1.7\cdot10^{-4}$
1	$3.0\cdot10^{-3}$ to $4.1\cdot10^{-3}$	$1.3\cdot10^{-3}$ to $1.7\cdot10^{-3}$

Table 4. Values of Pitzer Mixed Ion-Interaction Parameters (θ_{NH_4Na}, Ψ_{NH_4NaBr}) in the Investigated Ternary Electrolyte Systems, Determined According to the Pitzer Graphical Method, For Various Molal Salt Ratios ($r = m_1/m_2$ = 100, 50, 10, 1), at 298 K

r	θ_{NH_4Na}/(mol·kg^{-1})	Ψ_{NH_4NaBr}/(mol^2·kg^{-2})
100	−0.0353	0.0052
50	−0.0316	0.0078
10	−0.0249	0.0061
Mean	**−0.0306**	**0.0063**
SD	**0.0053**	**0.0013**
1	−0.0094	−0.0025

ion-interaction parameters and the series of eqs 16 to 18, the values of osmotic coefficients (ϕ), excess Gibbs free energies (G^E), and water activities (a_w) were, as well, determined for the whole series of investigated mixed electrolyte systems. Table 5 shows the value of these thermodynamic properties as a function of the ionic strength for the investigated mixed electrolyte systems.

Conclusion

In the last decades, the continuous development of different carrier-based solvent polymeric membrane electrodes has led to an attractive and rapid alternative method for the investigation of the thermodynamic properties of electrolytic systems (e.g., see refs 3 to 6). However, the ISE membrane selectivity (K_{12}^{Pot}) could play as a limiting factor on the potentiometric measurements, particularly when it has to be used for the investigation of mixed electrolyte systems. Effectively, this limitation is due to the interfering effect of the secondary ion present in mixed electrolyte systems and proportional to the magnitude of $K_{12}^{\mathrm{Pot}}(a_2/a_1)$, while, it could not be neglected in the $(1 + K_{12}^{\mathrm{Pot}}(a_2/a_1))$ term in eq 11. The obtained results in this work confirm experimentally that the restrictive role of interfering ions on the ISE measurements could, to a certain extent, be counterbal-

Table 5. Calculated Solvent Osmotic Coefficients, Excess Gibbs Free Energies and Solvent Activities, versus Electrolyte Ionic Strength in the Ternary $NH_4Br(m_1) + NaBr(m_2) + H_2O$ Electrolyte Systems, for Various Molal Salt Ratios ($r = m_1/m_2$ = 100, 50, 10, 1), at 298 K

I	a_w	φ	$G^E/J \cdot mol^{-1}$	I	a_w	φ	$G^E/J \cdot mol^{-1}$
$r = 100$				$r = 10$			
0.3162	0.9997	0.9673	−0.1	0.3162	0.9997	0.9671	−1.0
0.3976	0.9991	0.9531	−0.4	0.3976	0.9991	0.9527	−3.7
0.4729	0.9983	0.9403	−1.0	0.4729	0.9983	0.9396	−10
0.5623	0.9967	0.9268	−2.6	0.5623	0.9967	0.9255	−26
0.7071	0.9918	0.9108	−9.1	0.7071	0.9919	0.9085	−88
0.8409	0.9839	0.9037	−22	0.8409	0.9839	0.9003	−214
1.0000	0.9679	0.9059	−51	1.0000	0.9680	0.9014	−491
1.1067	0.9518	0.9142	−80	1.1067	0.9520	0.9096	−770
1.1892	0.9356	0.9244	−109	1.1892	0.9358	0.9205	−1034
1.2574	0.9192	0.9352	−134	1.2574	0.9194	0.9324	−1277
1.3161	0.9028	0.9457	−158	1.3161	0.9029	0.9448	−1495
1.3678	0.8865	0.9556	−178	1.3678	0.8863	0.9571	−1686
1.4142	0.8702	0.9646	−196	1.4142	0.8697	0.9690	−1851
1.4565	0.8541	0.9723	−211	1.4565	0.8530	0.9803	−1989
1.4953	0.8383	0.9788	−222	1.4953	0.8365	0.9909	−2102
$r = 50$				$r = 1$			
0.3162	0.9997	0.9672	−0.2	0.3163	0.9997	0.9662	−4.7
0.3977	0.9991	0.9530	−0.8	0.3976	0.9991	0.9507	−18
0.4729	0.9983	0.9402	−2.0	0.4729	0.9983	0.9360	−47
0.5623	0.9967	0.9266	−5.3	0.5623	0.9967	0.9193	−121
0.7071	0.9918	0.9105	−18.4	0.7071	0.9920	0.8964	−405
0.8409	0.9839	0.9033	−44.7	0.8409	0.9842	0.8816	−960
1.0000	0.9679	0.9054	−103	1.0000	0.9690	0.8742	−2132
1.1067	0.9518	0.9137	−162	1.1067	0.9537	0.8768	−3234
1.1892	0.9356	0.9240	−219	1.1892	0.9383	0.8837	−4200
1.2574	0.9192	0.9350	−271	1.2574	0.9227	0.8932	−5001
1.3161	0.9028	0.9458	−318	1.3161	0.9069	0.9042	−5624
1.3678	0.8864	0.9560	−359	1.3678	0.8909	0.9164	−6068
1.4142	0.8701	0.9654	−394	1.4142	0.8746	0.9294	−6335
1.4565	0.8540	0.9736	−423	1.4565	0.8582	0.9430	−6430
1.4953	0.8381	0.9806	−447	1.4953	0.8416	0.9570	−6364

anced by the choice of relatively high molal fraction of mixed electrolyte systems. Effectively, as shown in the reported data, reliable mean activity coefficient values up to 4 decimal significant numbers correspond to the mixed electrolyte systems with molal ratio $r \geq 10$. As a result, the more affected data ($\ln \gamma_{\pm NH_4Br}$) resulting from the experimental cell potential, for the series of electrolyte solutions with $r = m_1/m_2 = 1$, were excluded. Once again, as the two and three particle Pitzer interaction parameter (θ_{NH_4Na},ψ_{NH_4NaBr}) values corresponding to the potentiometric data of the series of solution with $r = m_1/m_2 = 1$ deviate significantly from the resulting mean values of the other series of solutions ($r = m_1/m_2$ = 100, 50, and 10), the corresponding values were as well excluded for further calculations. Finally, the obtained Pitzer two and three particle mixed ionic interaction parameters ($\theta_{NH_4Na} = (-0.0306 \pm 0.0053)\ mol \cdot kg^{-1}$, $\psi_{NH_4NaBr} = (0.0063 \pm 0.0013)\ mol^2 \cdot kg^{-2}$) were used for the evaluation of the other thermodynamic properties, such as the osmotic coefficients ϕ, excess Gibbs free energies G^E, and water activities a_w for the whole series of investigated electrolyte solutions.

Literature Cited

(1) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed.; Reinhold: New York, 1958.

(2) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 5th ed.; Butterworths: London, 1970.

(3) Pitzer, K. S., Ed. *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; CRC Press: Boca Raton, FL, 1991.

(4) Deyhimi, F.; Ebrahimi, A.; Roohi, H.; Koochaki, K. Determination of Activity Coefficients, Osmotic Coefficients, and Excess Gibbs Free Energies of HCl in *N*,*N*-Dimethylformamide-Water Mixed Solvent Systems by Potentiometric Measurements. *J. Chem. Eng. Data* **2004**, *49*, 1185–1188.

(5) Deyhimi, F.; Salamat-Ahangari, R.; Ghalami-Choobar, B. Determination of activity coefficients of NH_4Cl in methanol-water mixed solvents at 25°C by electromotive force measurements. *Phys. Chem. Liq.* **2003**, *41*, 605–611.

(6) Deyhimi, F.; Salamat-Ahangari, R. Potentiometric investigation of the thermodynamic properties of the ternary mixed ($NH_4Cl + CaCl_2 + H_2O$) electrolyte system. *Fluid Phase Equilib.* **2008**, *264*, 113–121.

(7) Bates, R. G. *Determination of pH: Theory and Practice*; John Wiley & Sons: New York, 1964.

(8) Zhang, L.; Lu, X.; Wang, Y.; Shi, J. Determination of Activity Coefficients Using a Flow EMF Method. 1. HCl in Methanol-Water Mixtures at 25, 35 and 45 °C. *J. Solution Chem.* **1993**, *22*, 137–150.

(9) Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **1973**, *77*, 268–277.

(10) Pitzer, K. S.; Kim, J. J. Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes. *J. Am. Chem. Soc.* **1974**, *96*, 5701–5707.

(11) Pitzer, K. S.; Mayorga, G. Thermodynamics of electrolytes. I I. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. *J. Phys. Chem.* **1973**, *77*, 2300–2308.

(12) Kim, H.-T.; Frederick, W., Jr. Evaluation of Pitzer Ion Interaction Parameters of Aqueous Electrolytes at 25 °C. 1. Single Salt Parameters. *J. Chem. Eng. Data* **1988**, *33*, 177–184.

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