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$NH_4Cl + NH_4NO_3 + H_2O$ Ternary Mixed Electrolyte System: Thermodynamic Modeling Based on Potentiometric Measurements

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This work reports the results of the thermodynamic modeling of NH_4Cl salt in the ternary NH_4Cl (m_1) + NH_4NO_3 (m_2) + H_2O mixed electrolyte system based on potentiometric measurements. The electrochemical measurements were performed, at similar constant ionic strengths, in different series of mixed salt solutions, each characterized by a fixed salt molal ratio r (where $r = m_1/m_2 = 0.05$, 1, 5, 10, and m_1, m_2 are the molalities of NH_4Cl and NH_4NO_3, respectively). The galvanic cell used for collecting the potentiometric data consisted of a solvent polymeric (PVC) NH_4^+ selective membrane electrode (NH_4^+ ISE) and an Ag/AgCl electrode. Pitzer ion-interaction equations for mixed salts were used for modeling the nonideal behavior of the system, over the ionic strength ranging from 0.01 mol·kg^{-1} up to about 6 mol·kg^{-1}, at 298.15 K. On the basis of the obtained Pitzer ion-interaction parameters, the osmotic coefficients, solvent activities, and excess Gibbs free energies were also determined for these investigated ternary electrolyte systems.

1. Introduction

The study of aqueous electrolyte, and particularly of mixed salt electrolyte, systems at high concentrations is important both theoretically and experimentally.[1,2] Knowledge of the thermodynamic properties of various electrolyte systems is required for understanding the nature of various ionic interactions in electrolyte mixtures and for the investigation of the problems such as phase equilibria and separation technique. Moreover, electrolyte systems are involved in many chemical industries, geochemistry, marine chemistry, and atmospheric sciences, and in various application processes such as extraction techniques, desalination, or various environmental processes. This work reports the results of exploitation of a solvent polymeric membrane electrode for the thermodynamic modeling of an aqueous mixture of 1:1 salts with a common cation. Recently, we have used in our laboratory pH-glass membranes[3] 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 4 to 5 and refs therein). The mixed electrolyte system investigated in this work concerns the ternary NH_4Cl + NH_4NO_3 + H_2O system, for which the activity coefficients for NH_4Cl were first determined at similar ionic strengths in different series of mixed electrolyte systems, each characterized by a defined molal ratio ($r = m_1/m_2 = 0.05$, 1, 5, 10). The measurements were performed at 298.15 K, using a galvanic cell containing a solvent polymeric (PVC) NH_4^+ ISE and Ag/AgCl electrodes. Subsequently, the 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·kg^{-1} up to about 6 mol·kg^{-1}. As a result, the thermodynamic properties such as solvent osmotic coefficients, solvent activities, and excess Gibbs free energies were determined for this ternary electrolyte system.

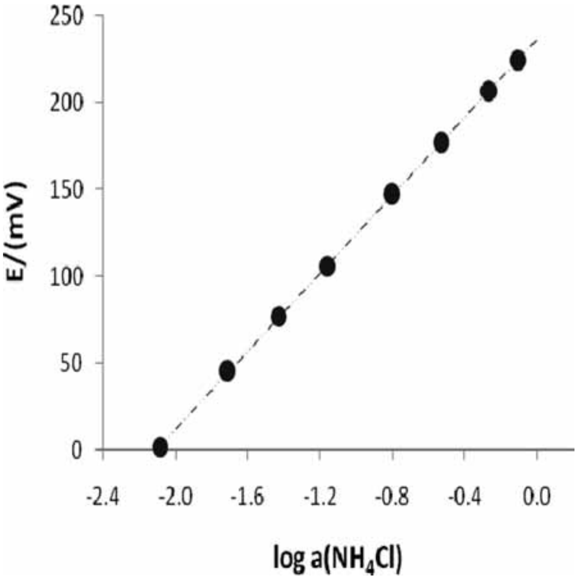

Figure 1. Cell potential versus logarithm of NH_4Cl activity in pure aqueous NH_4Cl solution at 298.15 K.

2. Experimental

2.1. Reagents. High molecular poly(vinyl chloride) (PVC), a mixture of nonactin (72 %) and monactin (28 %) as ionophore, and bis(2-ethylhexyl)sebacate were used as ingredients for the preparation of solvent polymeric NH_4^+ ISE. The membrane reagents were Selectophore grade compounds (Fluka, Switzerland), which were used as received. All primary stock solutions were, first, prepared by weight using doubly distilled water and by potentiometric titration using $AgNO_3$ standard solution. Prior to use, the analytical grade NH_4Cl and NH_4NO_3 salts (both with mass % > 99.5) from Fluka were dried overnight in an oven (at 110 °C).

2.2. Solvent Polymeric NH_4^+ Selective Membrane Electrode and Potentiometric Measurement. NH_4^+-selective membranes were prepared and evaluated as previously reported (see

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Table 1. Cell Potentiometric Data and the Resulting Experimental Mean Activity Coefficient for NH_4Cl versus Electrolyte Molality and Ionic Strength, in the Investigated Mixed $NH_4Cl + NH_4NO_3$ Electrolyte Systems, for Various Molal Salt Ratios ($r = m_1/m_2 = 0.05, 1, 5, 10$), at 298.15 K

$m_1(NH_4Cl)$ / $mol \cdot kg^{-1}$	$m_2(NH_4NO_3)$ / $mol \cdot kg^{-1}$	$\gamma_1(\pm)$	E / mV	$m_1(NH_4Cl)$ / $mol \cdot kg^{-1}$	$m_2(NH_4NO_3)$ / $mol \cdot kg^{-1}$	$\gamma_1(\pm)$	E / mV
	$r = m_1/m_2 = 10$				$r = m_1/m_2 = 1$		
0.0091	0.0009	0.9007	−1.0	0.0050	0.0050	0.9003	−8.0
0.0227	0.0023	0.8560	45.0	0.0125	0.0125	0.8551	35.0
0.0455	0.0045	0.8139	76.0	0.0251	0.0251	0.8125	66.0
0.0909	0.0091	0.7658	108.0	0.0501	0.0501	0.7635	93.0
0.2273	0.0227	0.6968	150.1	0.1252	0.1252	0.6922	133.2
0.4545	0.0455	0.6448	181.3	0.2505	0.2505	0.6375	162.2
0.9091	0.0909	0.5983	212.6	0.5010	0.5010	0.5865	191.0
1.3636	0.1364	0.5761	231.3	0.7515	0.7515	0.5603	208.1
1.8182	0.1818	0.5638	244.8	1.0020	1.0020	0.5442	220.3
2.2727	0.2273	0.5567	255.5	1.2525	1.2525	0.5334	229.9
2.7273	0.2727	0.5527	264.4	1.5030	1.5030	0.5258	237.8
3.1818	0.3182	0.5507	272.0	1.7535	1.7535	0.5201	244.6
3.6364	0.3636	0.5498	278.7	2.0040	2.0040	0.5157	250.5
4.0909	0.4091	0.5496	284.7	2.2545	2.2545	0.5121	255.8
4.5455	0.4545	0.5498	290.0	2.5050	2.5050	0.5089	260.5
5.0000	0.5000	0.5500	294.9	2.7555	2.7555	0.5058	264.7
5.4545	0.5455	0.5502	299.3	3.0060	3.0060	0.5027	268.6
				3.2565	3.2565	0.4995	272.1
				3.4333	3.4333	0.4971	274.7
	$r = m_1/m_2 = 5$				$r = m_1/m_2 = 0.05$		
0.0083	0.0017	0.9007	2.0	0.0005	0.0098	0.8989	−75.0
0.0208	0.0042	0.8560	45.0	0.0012	0.0244	0.8531	−38.0
0.0417	0.0083	0.8139	77.0	0.0024	0.0488	0.8096	−7.0
0.0833	0.0167	0.7658	106.0	0.0049	0.0976	0.7593	21.0
0.2083	0.0417	0.6968	146.9	0.0122	0.2441	0.6856	55.0
0.4167	0.0833	0.6448	176.8	0.0244	0.4884	0.6279	82.7
0.8333	0.1667	0.5983	206.9	0.0489	0.9778	0.5724	109.0
1.2500	0.2500	0.5761	224.7	0.0734	1.4681	0.5425	124.3
1.6667	0.3333	0.5638	237.6	0.0980	1.9595	0.5231	135.1
2.0833	0.4167	0.5567	247.8	0.1226	2.4517	0.5094	143.5
2.5000	0.5000	0.5527	256.2	0.1473	2.9450	0.4991	150.5
2.9167	0.5833	0.5507	263.5	0.1720	3.4393	0.4909	156.3
3.3333	0.6667	0.5498	269.9	0.1967	3.9345	0.4843	161.5
3.7500	0.7500	0.5496	275.5	0.2215	4.4307	0.4786	166.0
4.1667	0.8333	0.5498	280.6	0.2464	4.9279	0.4735	170.1
4.5833	0.9167	0.5500	285.2	0.2713	5.4261	0.4688	173.9
5.0000	1.0000	0.5502	289.4				

refs 4 to 5 and refs therein). The used ISE membranes had the following composition (mass %): 1.05 % ionophore, 0.5 % potassium tetrakis(4-chlorophenyl)borate, 67.07 % bis(2-ethylhexyl)sebacate, and 31.88 % PVC. The electrodes were back-filled each time with NH_4Cl internal filling solution, and Ag/AgCl wire was used as internal reference electrodes. The Ag/AgCl wire electrodes were prepared essentially as described elsewhere by electrolysis.[6] From the preliminary experimental tests performed with different concentrations of internal electrolyte filling solution, the best results were those obtained with 0.25 M NH_4Cl electrolyte. The fabricated electrodes were, initially, conditioned for 48 h in 0.001 M NH_4Cl aqueous electrolyte solution and then calibrated using NH_4Cl standard solutions. Both NH_4^+ and Ag/AgCl electrodes were conditioned overnight in the appropriate mixed electrolyte system before each series of measurements.

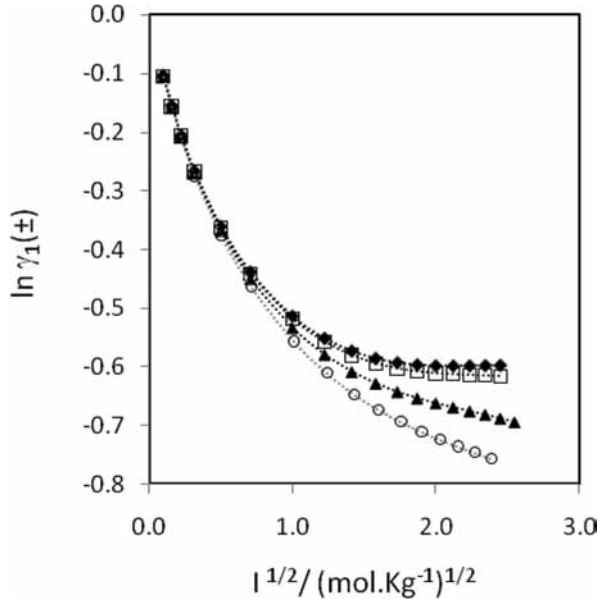

Figure 2. Natural logarithm of NH_4Cl mean activity coefficient versus square root of ionic strength for the ternary $NH_4Cl + NH_4NO_3 + H_2O$ electrolyte systems, for various molal salt ratios ($r = m_1/m_2 = 10, 5, 1,$ and 0.05), at 298.15 K. ♦, $r = 10$; □, $r = 5$; +, ▲, $r = 1$; ○, $r = 0.05$.

Table 2. Values of Pitzer Mixed Ion-Interaction Parameters ($\theta_{ClNO_3}, \psi_{ClNO_3NH_4}$) in the Investigated Ternary Electrolyte Systems, Determined According to the Pitzer Graphical Method, For Various Molal Salt Ratios ($r = m_1/m_2 = 0.05, 1, 5, 10$), at 298.15 K

r	θ_{ClNO3} / $(mol \cdot kg^{-1})^{-1}$	$\Psi_{ClNO3,NH4}$ / $(mol \cdot kg^{-1})^{-2}$
10	0.0245	−0.0036
5	0.0324	−0.0042
1	0.0191	−0.0025
Mean	0.0253	−0.0034
SD	0.0067	0.0009
0.05	0.0035	−0.0008

The experimental cell potential data were recorded using a PC automated potentiometric data acquisition setup, a thermostatic system coupled to a double-wall container enabling the circulation of thermostatted water from a bath, as explained elsewhere (see refs 4 to 5 and refs therein).

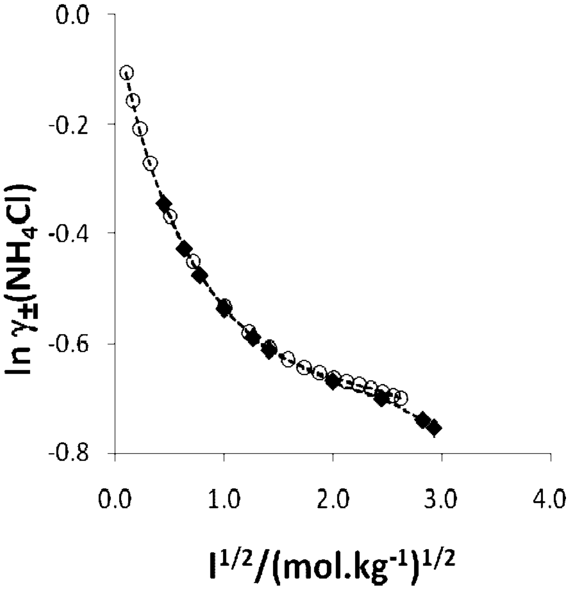

Figure 3. Plot of the value of osmotic coefficients (ϕ) versus square root of ionic strength, for various molal salt ratios ($r = m_1/m_2 = 0.05$, 1, 5, and 10) at 298.15 K. ♦, $r = 10$; □, $r = 5$; +, ▲, $r = 1$; ○, $r = 0.05$.

The molality of electrolyte in the galvanic cell was varied step by step by a standard addition method,[7] adding an appropriate volume of a primary concentrated standard electrolyte solution each time, having the same mole ratio as that previously utilized in the galvanic cell. The standard addition steps were performed using appropriate Hamilton syringes, with accuracies within ± 1 % of nominal volumes and with precisions within 1 % (as indicated by the manufacturer).

3. Method

3.1. Ion-Interaction Model. The Pitzer ion-interaction model was found to be successful in modeling various high concentrated pure and mixed electrolyte systems.[2,8–10] In this model, 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 and for a (1:1) mixture of MX and MY electrolytes, the corresponding Pitzer equations are written, respectively, as

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

$$\ln \gamma_{\pm NH_4Cl} = f^\gamma + I\{B^\gamma_{NH_4Cl} + y_2(B^\phi_{NH_4NO_3} - B^\phi_{NH_4Cl} + \theta_{ClNO_3})\} + I^2\left\{\left(\frac{3}{2}C^\phi_{NH_4Cl}\right) + y_2\left(C^\phi_{NH_4NO_3} - C^\phi_{NH_4Cl} + \frac{\psi_{ClNO_3NH_4}}{2}\right) + y_2(1-y_2)\frac{\psi_{ClNO_3NH_4}}{2}\right\} \quad (2)$$

where

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

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

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

$$B^\phi = \beta^{(0)} + \beta^{(1)}e^{-\alpha\sqrt{I/m^0}} \quad (6)$$

$\gamma_\pm$ 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 ($mol \cdot kg^{-1}$); I is the ionic strength on a molality scale; $\beta^{(0)}$ ($kg \cdot mol^{-1}$), $\beta^{(1)}$ ($kg \cdot mol^{-1}$), and C^ϕ $(kg \cdot mol^{-1})^{1/2}$are the parameters of the Pitzer equations; $b = 1.2\ kg^{1/2} \cdot mol^{-1/2}$; and $\alpha = 2\ kg^{1/2} \cdot mol^{-1/2}$. In addition, y_2 is the ionic strength fraction of NH_4NO_3 ($y_2 = I_{NH4NO3}/I_{NH4Cl} + I_{NH4NO3}$), and θ_{ClNO_3} and $\psi_{ClNO_3NH_4}$ represent the ionic interaction parameters for the mixed salt system. The Debye–Hückel coefficient for the osmotic coefficient (A_ϕ) is defined as

$$A_\phi = \frac{1}{3}(2\pi N_A\rho_A)^{1/2}\left(\frac{e^2}{4\pi\varepsilon_o DkT}\right)^{3/2} \quad (7)$$

where the constants e, ε_o, k, N_A, D, T, and ρ_A are electron charge, vacuum permittivity, Boltzmann constant, Avogadro constant, temperature, dielectric constant, and density of the solvent, respectively. For water, its value is 0.39145 $(kg \cdot mol^{-1})^{1/2}$ at 298.15 K.

3.2. 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/AgCl electrode

$$Ag|AgCl|NH_4Cl(m_1),\ H_2O|NH_4^+\ ISE \quad (A)$$

$$Ag|AgCl|NH_4NO_3(m_2),\ H_2O|NH_4^+\ ISE \quad (B)$$

$$Ag|AgCl|NH_4Cl(m_1), NH_4NO_3(m_2),\ H_2O|NH_4^+\ ISE \quad (C)$$

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 Ag/AgCl electrode. Finally, the galvanic cell (C) was used for the determination of the mean activity coefficients for NH_4Cl in the aqueous mixed (NH_4Cl + NH_4NO_3) electrolyte (at 298.15 K). Effectively, for this mixed electrolyte system, the cell potential can be expressed by

$$E_{(C)} = E' + s\log[a_1 + K_{12}^{Pot}a_2)] \quad (8)$$

$$a_1 = m_1(m_1+m_2)\gamma^2_{\pm,1} \quad (9)$$

$$a_2 = m_2(m_1+m_2)\gamma^2_{\pm,2} \quad (10)$$

where K_{12}^{Pot} represents the potentiometric selectivity coefficient of the Ag/AgCl electrode (Cl^- ISE) toward the NO_3^- interfering ions. For the determination of the experimental mean activity coefficient values in mixed salt solutions, it is first necessary to know 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 NH_4NO_3 salt, the potentiometric response of the galvanic cell (B) could be expressed by

$$E_{(B)} = E' + s\log(K_{12}^{pot}a_2) \quad (11)$$

or

$$K_{12}^{Pot} = \left(\frac{1}{a_2}\right)10^{[(E_{(B)}-E')/s]} \quad (12)$$

Therefore, using pure standard NH_4NO_3 solutions and the above-mentioned regressed slope (s) and intercept values (E'), the potentiometric selectivity coefficient of the Ag/AgCl

Table 3. Calculated Solvent Osmotic Coefficients, Excess Gibbs Free Energies, and Solvent Activities, in the Ternary ($NH_4Cl + NH_4NO_3 + H_2O$) Electrolyte Systems, for Various Molal Salt Ratios ($r = m_1/m_2 = 0.05, 1, 5, 10$), at 298.15 K

I / $mol \cdot kg^{-1}$	$\ln \gamma_1$	ϕ	a_w	G^E / $J \cdot mol^{-1}$	I / $mol \cdot kg^{-1}$	$\ln \gamma_1$	ϕ	a_w	G^E / $J \cdot mol^{-1}$
		$r = 10$					$r = 1$		
0.0100	−4.6055	0.9669	0.9997	−6.5	0.0100	−4.6035	0.9658	0.9997	−3.5
0.0250	−3.6890	0.9522	0.9991	−24.5	0.0251	−3.6867	0.9498	0.9991	−13.4
0.0500	−2.9956	0.9386	0.9983	−66.1	0.0501	−2.9937	0.9342	0.9983	−35.9
0.1000	−2.3026	0.9237	0.9967	−175.4	0.1002	−2.3006	0.9159	0.9967	−94.8
0.2500	−1.3863	0.9042	0.9919	−619.5	0.2505	−1.3843	0.8883	0.9920	−333.0
0.5000	−0.6932	0.8923	0.9841	−1569.5	0.5010	−0.6911	0.8664	0.9845	−841.3
1.0000	0.0000	0.8864	0.9686	−3887.3	1.0020	0.0020	0.8451	0.9699	−2084.0
1.5000	0.4055	0.8880	0.9531	−6536.9	1.5030	0.4075	0.8340	0.9558	−3511.4
2.0000	0.6931	0.8924	0.9377	−9406.4	2.0040	0.6951	0.8272	0.9420	−5065.4
2.5000	0.9163	0.8982	0.9223	−12441.6	2.5050	0.9183	0.8228	0.9284	−6718.4
3.0000	1.0986	0.9046	0.9069	−15611.9	3.0060	1.1006	0.8199	0.9150	−8456.0
3.5000	1.2528	0.9111	0.8915	−18899.6	3.5070	1.2548	0.8180	0.9018	−10270.6
4.0000	1.3863	0.9174	0.8761	−22294.2	4.0080	1.3883	0.8168	0.8887	−12159.1
4.5000	1.5041	0.9234	0.8610	−25790.5	4.5090	1.5061	0.8160	0.8758	−14121.5
5.0000	1.6094	0.9288	0.8459	−29387.1	5.0100	1.6114	0.8156	0.8631	−16159.6
5.5000	1.7047	0.9335	0.8311	−33084.0	5.5110	1.7068	0.8153	0.8505	−18276.6
6.0000	1.7918	0.9375	0.8165	−36885.1	6.0120	1.7938	0.8152	0.8381	−20477.6
					6.5130	1.8738	0.8151	0.8259	−22767.4
					6.8666	1.9267	0.8150	0.8174	−24440.4
		$r = 5$					$r = 0.05$		
0.0100	−4.6053	0.9667	0.9997	−5.9	0.0102	−4.5812	0.9647	0.9996	−0.3
0.0250	−3.6887	0.9517	0.9991	−22.4	0.0256	−3.6646	0.9476	0.9991	−1.3
0.0500	−2.9958	0.9378	0.9983	−60.4	0.0512	−2.9713	0.9306	0.9983	−3.5
0.1000	−2.3026	0.9223	0.9967	−160.2	0.1025	−2.2780	0.9098	0.9966	−9.3
0.2500	−1.3863	0.9013	0.9919	−564.8	0.2563	−1.3614	0.8774	0.9919	−32.7
0.5000	−0.6931	0.8877	0.9841	−1430.2	0.5128	−0.6678	0.8501	0.9844	−83.2
1.0000	0.0000	0.8794	0.9688	−3542.5	1.0267	0.0263	0.8220	0.9701	−209.7
1.5000	0.4055	0.8791	0.9536	−5960.2	1.5415	0.4328	0.8057	0.9562	−358.3
2.0000	0.6931	0.8819	0.9384	−8582.5	2.0574	0.7215	0.7945	0.9428	−523.2
2.5000	0.9163	0.8864	0.9233	−11361.3	2.5743	0.9456	0.7860	0.9297	−701.0
3.0000	1.0986	0.8917	0.9081	−14270.1	3.0923	1.1289	0.7793	0.9168	−889.9
3.5000	1.2528	0.8973	0.8930	−17293.8	3.6112	1.2840	0.7738	0.9042	−1088.6
4.0000	1.3863	0.9029	0.8780	−20424.5	4.1312	1.4186	0.7691	0.8918	−1296.4
4.5000	1.5041	0.9083	0.8631	−23659.1	4.6522	1.5373	0.7651	0.8796	−1512.8
5.0000	1.6094	0.9134	0.8483	−26997.5	5.1743	1.6437	0.7616	0.8676	−1737.5
5.5000	1.7047	0.9180	0.8337	−30442.0	5.6974	1.7400	0.7585	0.8558	−1970.5
6.0000	1.7918	0.9221	0.8193	−33997.0					

electrode (Cl^- ISE) toward the NO_3^- interfering ions could be determined.

On the other hand, for the aqueous mixed $NH_4Cl + NH_4NO_3$ salt solutions, the cell potential (C) can be expressed by

$$E_{(C)} = E' + s \log\left[a_1\left(1 + K_{12}^{\mathrm{Pot}}\frac{a_2}{a_1}\right)\right] \tag{13}$$

If in the used concentration range for all series of electrolyte solutions the interfering effect of NO_3^- on the response of the Ag/AgCl electrode (Cl^- ISE) would be negligible, then the second term in the parenthesis of the above equation ($K_{12}^{\mathrm{Pot}}a_2/a_1$) could practically be ignored, and eq 13 is simplified to the Nernst relation

$$E_{(C)} = E' + s \log a_1 \tag{14}$$

As a result, the mean activity coefficient values for $NH_4Cl(m_1)$ could be calculated, for all studied series of the ternary systems, as a function of molality by

$$\gamma_\pm = \frac{1}{\sqrt{m_1(m_1 + m_2)}} 10^{[(E_{(C)} - E')/2s]} \tag{15}$$

3.3. Determination of Mixed Ion-Interaction Parameters (θ_{ClNO_3}, $\psi_{ClNO_3NH_4}$). For the studied ternary system, the mixed ionic interaction parameters (θ_{ClNO_3},$\psi_{ClNO_3NH_4}$) were determined according to the Pitzer graphical method,[2,9] using the following relations

$$\left(\frac{1}{m_{NO_3}}\right)\Delta \ln \gamma_{\pm NH_4Cl} = \theta_{ClNO_3} + \frac{1}{2}(m_{NH_4} + m_{Cl})\psi_{ClNO_3NH_4} \tag{16}$$

$$\Delta \ln \gamma_{\pm NH_4Cl} = (\ln \gamma_{\pm NH_4Cl})_{\mathrm{exptl}} - (\ln \gamma_{\pm NH_4Cl})_{\mathrm{calcd}} \tag{17}$$

where $(\ln \gamma_{\pm NH_4}Cl)_{\mathrm{calcd}}$ is calculated with $\psi_{ClNO_3NH_4} = 0$, $\theta_{ClNO_3} = 0$. Accordingly, the two and three particle mixed ion-interaction parameters θ_{ClNO_3} and $\psi_{ClNO_3NH_4}$ could be determined from the slope and intercept of the linear portion of regression plot of the $(1/m_{NO_3})\Delta \ln \gamma_{\pm NH_4Cl}$ versus $1/2(m_{NH_4} + m_{Cl})$ values.

3.4. Determination of Osmotic Coefficients, Solvent Activities, and Excess Gibbs Free Energies. 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 using the obtained Pitzer ion-interaction parameters and the eqs 2 and 18 to 20) for aqueous mixed salt electrolyte systems

$$\phi - 1 = z^2 f^\phi + I\{(1 - y_2)B^\phi_{NH_4Cl} + y_2 B^\phi_{NH_4NO_3} + y_2(1 - y_2)\theta_{ClNO_3}\} + I^2\{(1 - y_2)C^\phi_{NH_4Cl} + y_2 C^\phi_{NH_4NO_3} + y_2(1 - y_2)\psi_{ClNO_3NH_4}\} \tag{18}$$

$$G^{E} = RT\sum_{i} v_i m_i(1 - \phi + \ln\ \gamma_i) \qquad (19)$$

$$a_{w} = \exp[(-M_{w}/1000)(\sum_{i} m_i)\phi] \qquad (20)$$

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.

4. Results and Discussion

Using cell A, the response quality of the fabricated NH_4^+ ISE versus Ag/AgCl electrode was evaluated in pure solutions of NH_4Cl. Figure 1 shows the resulting typical linear Nernstian plot, with a regressed slope value of $2s = 112.19$ mV/(per decade molal change) and an intercept of $E' = 236.45$ mV ($R^2 = 0.99995$), respectively. Following the above presented procedures and using the reported Pitzer parameter values ($\beta^{(0)} = 0.05192$, $\beta^{(1)} = 0.19346$, and $C^{\phi} = -0.00298$) for aqueous pure NH_4Cl and NH_4NO_3 solutions,[11] the potentiometric selectivity coefficient of the Ag/AgCl electrode (Cl^- ISE) toward the NO_3^- interfering ions was calculated and was found to be $K_{12}^{\mathrm{Pot}} = 8.2 \cdot 10^{-6}$. Since the interfering effect of NO_3^- on the response of the Ag/AgCl electrode (Cl^- ISE) is negligible, therefore as explained above, in the used concentration range for all series of electrolyte solutions with $r = m_1/m_2 = 10$, 5, 1, and 0.05, the second term ($K_{12}^{\mathrm{Pot}}a_2/a_1$) in the parenthesis of eq 13 was dropped and the Nernst relation (eq 14 or eq 15) was used for the determination of the mean activity coefficients. Table 1 shows the potentiometric cell data and the resulting experimental mean activity coefficients for NH_4Cl versus electrolyte molality and ionic strength, in the investigated mixed $NH_4Cl + NH_4NO_3 + H_2O$ electrolyte systems, at 298.15 K. Figure 2 shows also the natural logarithm of NH_4Cl mean activity coefficient versus square root of ionic strength, for the ternary ($NH_4Cl + NH_4NO_3$) electrolyte systems for various molal salt ratios ($r = m_1/m_2 = 0.05$, 1, 5, and 10), at 298.15 K.

To check the influence of the ignored second term ($K_{12}^{\mathrm{Pot}}a_2/a_1$) in eq 13, its value was estimated in the corresponding concentration range, particularly for the series of electrolyte solutions with $r = m_1/m_2 = 0.05$, in which this term could take its highest value. The calculation shows that in this series ($r = m_1/m_2 = 0.05$) this term lies between $6.9 \cdot 10^{-5} \leq K_{12}^{\mathrm{Pot}}a_2/a_1 \leq 1.6 \cdot 10^{-4}$; as a result, the corresponding logarithm of the mean activity coefficients could only be affected on their fourth decimal places.

The value of the two and three particle mixed ionic interaction parameters ($\theta_{\mathrm{ClNO_3}}$, $\psi_{\mathrm{ClNO_3NH_4}}$) was determined from the slope and intercept of the linear portion of the regression plot of the $(1/m_{\mathrm{NO_3}})\Delta \ln\ \gamma_{\pm \mathrm{NH_4Cl}}$ versus $1/2(m_{\mathrm{NH_4}} + m_{\mathrm{Cl}})$ values, according to the Pitzer graphical method. Effectively, the resulting individual value of these interaction parameters for each series of mixed electrolyte solutions ($r = m_1/m_2 = 10$, 5, 1, and 0.05), along with their resulting mean values (± SD), are presented in Table 2. As can be seen from the data reported in Table 2, for the series of solutions with $r = m_1/m_2 = 0.05$, the corresponding value of interaction parameters ($\theta_{\mathrm{ClNO_3}}$, $\psi_{\mathrm{ClNO_3NH_4}}$) is significantly different from the resulting mean values (± SD), calculated over the remaining series of solutions ($r = m_1/m_2 = 10$, 5, and 1). Therefore, the value of $\theta_{\mathrm{ClNO_3}}$, $\psi_{\mathrm{ClNO_3NH_4}}$ parameters for the series of solutions with $r = m_1/m_2 = 0.05$ were excluded for the evaluation of the final mean values. The resulting two and three particle mixed ionic interaction parameters ($\theta_{\mathrm{ClNO_3}} = 0.0253 \pm 0.0067$ mol·kg^{-1}, $\psi_{\mathrm{ClNO_3NH_4}} = -0.0034 \pm 0.0009$ mol^2·kg^{-2}) compare well (see Figure 3) with those recently reported by El Guendouzi and Errougui[12] from their hygrometric measurements ($\theta_{\mathrm{ClNO_3}} = 0.018$ mol·kg^{-1}, $\psi_{\mathrm{ClNO_3NH_4}} = -0.0023$ mol^2·kg^{-2}). It has to be noted that the slight deviation between these two data sets is mainly due to the different Pitzer parameters for pure aqueous NH_4Cl solution used in this work[11] ($\beta^{(0)} = 0.05192$, $\beta^{(1)} = 0.19346$, and $C^{\phi} = -0.00298$) and those used by El Guendouzi and Errougui[12] ($\beta^{(0)} = 0.0527$, $\beta^{(1)} = 0.2011$, and $C^{\phi} = -0.00306$).

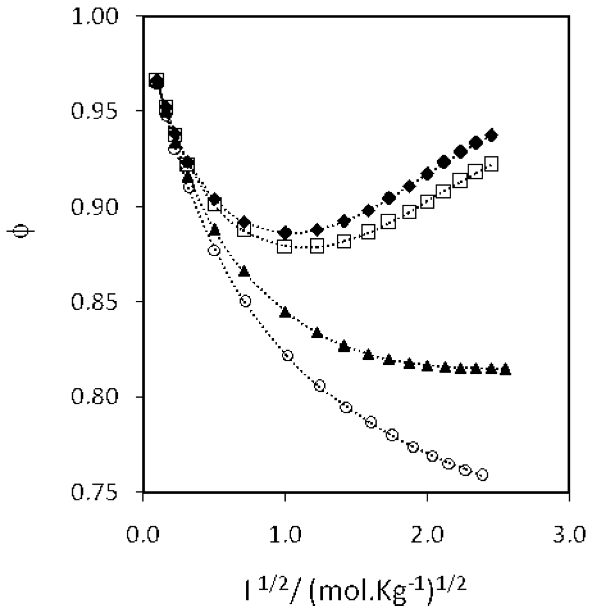

Figure 4. Plot of the value of excess Gibbs free energies (G^E), versus square root of ionic strength, for various molal salt ratios ($r = m_1/m_2 = 0.05$, 1, 5, and 10) at 298.15 K. ♦, $r = 10$; □, $r = 5$; +, ▲, $r = 1$; ○, $r = 0.05$.

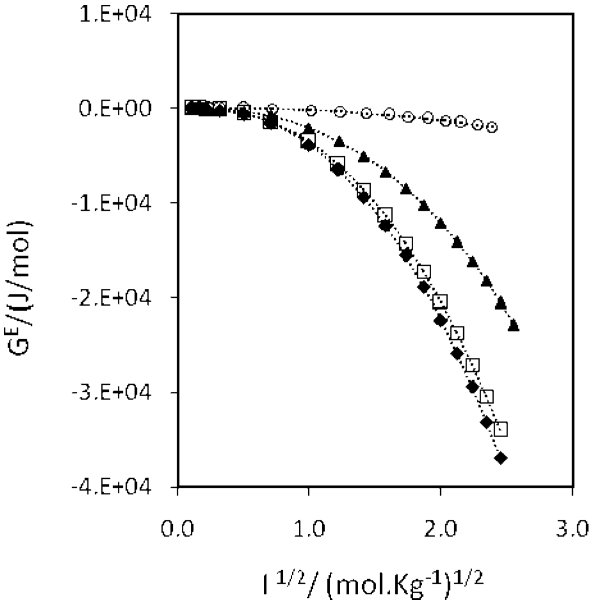

Figure 5. Plot of the value of the natural logarithm of water activities (a_w) versus square root of ionic strength, for various molal salt ratios ($r = m_1/m_2 = 0.05$, 1, 5, and 10) at 298.15 K. ♦, $r = 10$; □, $r = 5$; +, ▲, $r = 1$; ○, $r = 0.05$.

Finally, the value of osmotic coefficients (ϕ), excess Gibbs free energies (G^E), and water activities (a_w) were also determined for the whole series of investigated mixed electrolyte solutions, based on the obtained Pitzer ion-interaction parameters and the series of eqs 18 to 20. Table 3 shows the value of these thermodynamic properties as a function of the ionic strength for the investigated mixed electrolyte systems. Figures 4 to 6

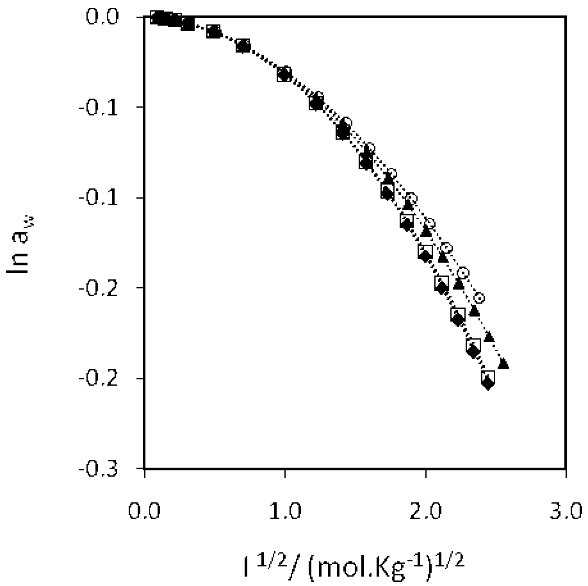

Figure 6. Comparison of the natural logarithm of NH_4Cl mean activity coefficient versus square root of ionic strength for the ternary NH_4Cl + NH_4NO_3 + H_2O electrolyte systems, obtained in this work, with those obtained by the hygrometric method for molal salt ratio $r = m_1/m_2 = 1$ ($y = 0.50$), at 298.15 K. ▲, hygrometric data (see ref 12); ○, potentiometric data (this work).

present also the plot of the value of osmotic coefficients (ϕ), excess Gibbs free energies (G^E), and water activities (a_w) versus the square root of ionic strength for the investigated series of mixed electrolyte solutions, at 298.15 K.

5. Conclusion

The reported results confirm that the potentiometric method using ISEs is as an attractive approach to isopiestic or hygrometric solvent vapor pressure based methods for the thermodynamic investigation of concentrated mixed salt electrolyte systems. Moreover, the potentiometric method presents, comparatively, the advantage of rapidity, efficiency of measurement in the low concentration range, and the particularity of direct detection of the primary ion (e.g., NH_4^+ or Cl^-) in the mixed electrolyte system.

The results have, particularly, shown:

- the impact of the potentiometric selectivity of the ISE and the molal salt ratio ($r = m_1/m_2$) on the determination of the mean activity coefficients of electrolyte for each series of mixed electrolyte solutions.

- the necessity of quantitative evaluation of the interfering effect, in order to obtain appropriate values of the two and three particle mixed ionic interaction parameters (θ_{ClNO_3}, $\psi_{ClNO_3NH_4}$).

- satisfactory comparison between the obtained potentiometric Pitzer two and three particle mixed ionic interaction parameters (θ_{ClNO_3}, $\psi_{ClNO_3NH_4}$) with the published hygrometric method.

- the satisfactoy modeling of the investigated system based on Pitzer ion-interaction theory and potentiometric measurements. Accordingly, in addition to the obtained activity coefficients, the resulting Pitzer two and three particle mixed ionic interaction parameters (θ_{ClNO_3}, $\psi_{ClNO_3NH_4}$) permitted the evaluation of values of osmotic coefficients (ϕ), excess Gibbs free energies (G^E), and water activities (a_w) for the whole series of investigated mixed electrolyte solutions, over the ionic strength ranging from 0.01 mol·kg^{-1} up to about 6 mol·kg^{-1}, at 298.15 K.

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