Regular Article

Thermodynamic Study of the Ternary Electrolyte (1-Butyl-3-methylimidazolium chloride + sodium chloride + Water) System Using Potentiometric Measurements

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In this paper, the thermodynamic properties of the aqueous mixed electrolyte system containing 1-butyl-3-methylimidazolium chloride ([BMIm]Cl) and NaCl are reported based on the potentiometric method. The potentiometric measurements were performed on the galvanic cells without liquid junction of the type:Ag-AgCl [BMIm]Cl (m_1), NaCl(m_2), H$_2$O │ IL-ISE, over total ionic strengths from 0.0025 to 2.000 mol kg^{-1} for different series of salt molal ratios r (r = $m_{[BMIm]Cl}/m_{NaCl}$ = 0.2, 1.0, 2.5, 5.0) and pure [BMIm]Cl in aqeous system at T = 298.2 K. The PVC based [BMIm]-selective electrode (IL-ISE) and Ag-AgCl electrode used in this work were prepared in our laboratory. The experimental results were analyzed with the Harned rule and Pitzer model. The Harned coefficients and the Pitzer mixing interaction parameters ($\theta_{[BMIm]Na}$, $\psi_{[BMIm]NaCl}$) were evaluated under investigation system. The results show the under-studied system obeys the Harned rule. Furthermore, the obtained parameters by the Pitzer model were used to calculate the values of the mean activity coefficients of NaCl, the osmotic coefficients, the solvent activity, and the excess Gibbs free energies for the whole series of the studied mixed electrolyte systems.

Keywords: Activity coefficient, Potentiometric measurements, [BMIm]Cl, NaCl, Pitzer model

INTRODUCTION

Study of the thermodynamic properties of aqueous mixed electrolyte solutions are of the great interest because of their importance in areas such as chemistry, biology, process engineering, desalination and atmospheric processes [1]. In addition, one of the most important types of organic salts is ionic liquids (ILs), which are liquids at or near room temperature in their pure state. They have been widely used in a number of fields in both academia and industry and exhibit many advantages such as a low melting point (<373 K), a wide liquid range, suitable viscosity, thermal stability, the ability to dissolve a variety of materials, good heat transfer properties and high conductivity [2,3]. The key property is that the vapor pressure of ionic liquids is negligibly small [4].Their physical properties are tunable by wise selection of cation, anion and substituents [3]. Besides,

ILs have been suggested as green and benign replacements for traditional volatile organic solvents. Aqueous solutions of ILs have been used in many processes such as synthesis, catalysis, separations, and extractive processes involving ILs on an industrial scale [2,3].

To measure the thermodynamic properties in the mixed electrolyte solutions, the most common methods involve the isopiestic vapour pressure [5,6], hygrometric method [7,8] and emf techniques [9-11]. Among the various methods, potentiometric method has the rapidity and relative simplicity to generate experimental data in comparison with the other fore going techniques.

In the last decades, a series of ion-interaction models for electrolyte solution have been proposed to predict activity coefficient of each solute and osmotic coefficient of the aqueous systems. One of the most famous and useful models was proposed by Pitzer [12].

In this article, the results related to the thermodynamic properties of the ternary solutions of 1-butyl-3-methyl-

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imidazolium chloride ([BMIm]Cl) and NaCl in water using the potentiometric method are reported at $T = 298.2$ K. This paper is the continuation of the research on ternary and quaternary electrolyte solutions [13-15].The potentiometric measurements reported in this work were carried out on a galvanic cell containing a solvent polymeric (PVC) IL-ISE and Ag-AgCl electrodes over the ionic strength ranging from (0.0025 to 2.000) mol kg^{-1}. To modify the molality of the mixed electrolyte in the experimental cell, different series of the salt molal ratio r (r = $m_{[BMIm]Cl}/m_{NaCl}$ = 0.2, 1.0, 2.5, 5.0) and pure [BMIm]Cl in aqueous system were used in a standard addition technique. The activity coefficients data were interpreted based on the Harned rule and Pitzer model. The unknown Pitzer mixing interaction parameters were evaluated for the mixed electrolyte system. This obtained parameters ($\theta_{[BMIm]Na}$, $\psi_{[BMIm]NaCl}$) were used to calculate the values of the mean activity coefficient of NaCl, osmotic coefficient, solvent activity, and excess Gibbs free energy for the whole series of the studied mixed electrolyte system.

EXPERIMENTAL

Apparatus and Reagents

All of the potentiometric measurements were made using a digital multimeter (Martini instruments Mi180) with resolution of 0.1 mV. The output of the multimeter was connected to a personal computer by the RS232 connector for data acquisition. The Mi 5200 software together with Microsoft Excel (Office 2007) software were used for data acquisition and calculations. The solutions were continuously stirred using a magnetic stirrer (Delta Model HM-101) at a slow constant rate to avoid concentration gradients in the test solutions. A Model GFL circulation water bath was used to control the temperature of the test solution at $T = 298.2 \pm 0.1$ K. Dibutyl phthalate (DBP), potassium tetrakis(p-chlorophenyl) borate (KT$_P$ClPB), high molar mass poly(vinyl chloride) (PVC), tetrahydrofuran (THF), 1-butyl-3-methylimidazolium chloride ([BMIm]Cl), sodium chloride (NaCl) and all other reagents used were purchased from chemical companies in Table 1 and all of them were of analytical reagent grade. Salt solutions were prepared gravimetrically by the use of a balance with a resolution of 0.1 mg. All primary stock solutions were prepared by mass using double-distilled water. The stock solution of the mixed electrolyte was prepared from 1-butyl-3-methylimidazolium chloride and sodium chloride by adding weighed amounts of solid using an analytical balance (Sartorius GMBH 2842) with a resolution of 0.1 mg, and double-distilled water with specific conductance less than 2.0×10^{-4} S m^{-1}.

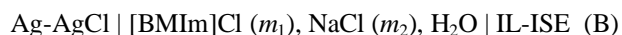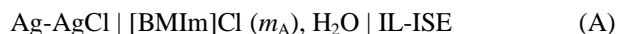## Preparation of Electrodes and Data Acquisition

The N,N´-(4,4´-ethylene biphenyl) bis(2-hydroxy-5-(4-methylphenylazo)benzylidene imine was used as an ionophore [16]. The general procedure used to prepare the PVC membrane for 1-butyl-3-methylimidazolium was to mix thoroughly optimized amounts of 32 mg of powdered PVC, 60 mg of plasticizer DBP and 5.1 mg of additive KT$_P$ClPB in 1.8 cm^3 of dry freshly distilled THF. To this solution, 2.9 mg of N,N´-(4,4´-ethylene biphenyl) bis(2-hydroxy-5-(4-methylphenylazo) benzylidene imine as an ionophore was added and mixed very well. The resulting clear mixture was transferred into a glass dish of 2 cm

Table 1. The Company and Purity Value of Compounds Used

Chemical used	Company	Mass fraction purity
Sodium chloride	Merck	>0.995
1-Butyl-3-methylimidazolium chloride	Kimia Exir	0.98
Tetrahydrofuran (THF)	Merck	>0.99
Dibutyl phthalate	Merck	>0.99
Potassium tetrakis(p-chlorophenyl) borate	Fluka	>0.98
Poly(vinyl chloride)	BDH Laboratory	0.996

diameter. The solvent was evaporated at the room temperature. After 2 h, the polymer membrane was easily removed from the plate. Then, the transparent PVC membrane was taken up from the plate and attached to the end of a glass tube with a diameter of 1 cm and height of 5 cm by means of PVC-THF viscose solution. The made electrode was initially conditioned for 48 h in 0.01 mol dm^{-3} [BMIm]Cl internal filling solution. The Ag-AgCl electrodes were used as both internal reference electrodes and chloride selective electrode. These electrodes were prepared essentially as described elsewhere by electrolysis [17]. Both the IL-ISE and Ag-AgCl electrodes were calibrated against a saturated calomel reference electrode before using in a 10^{-4}-1 mol dm^{-3} concentration range of pure solution of [BMIm]Cl, and showed a good Nernst slope (s) and linear relation (R^2).

The activity coefficients for [BMIm]Cl in the ternary system ([BMIm]Cl + NaCl + H$_2$O) were determined from the emf measurements using the following galvanic cells:

Ag-AgCl | [BMIm]Cl (m_A), H$_2$O | IL-ISE   (A)

Ag-AgCl | [BMIm]Cl (m_1), NaCl (m_2), H$_2$O | IL-ISE   (B)

Ag-AgCl | NaCl (m_B), H$_2$O | IL-ISE   (C)

Here m_A and m_B are the molalities of [BMIm]Cl and NaCl as single salt in aqueous solution, respectively. The m_1 and m_2 were the molalities of [BMIm]Cl and NaCl in the mixture, respectively. The emf measurements of the galvanic cell (B) were made using standard addition procedure. For this purpose, the concentrated mixed electrolyte solutions were added into the cell (B) containing a proportion volume of double-distilled water. The standard addition steps were carried out using proper burette and suitable Hamilton syringes (CH-7402 Bonaduz). In each series and for each standard addition step, data collection was performed every 10 s interval and during 10 (for concentrated solutions) to 20 min (for dilute solutions) using a multimeter (Martini instruments Mi 180) connected to the personal computer. As usual, all measurements were performed under stirring conditions and the temperature was kept constant at 298.2 K, employing a double-wall container enabling the circulation of thermostated water from a Model GFL circulation.

METHOD

Potentiometric Measurements

The values of the experimental mean activity coefficients for [BMIm]Cl in the mixture were obtained from the emf measurements using the galvanic cells (A, B and C). At first, the emf of cell (A) was measured to calibrate the electrode pair composing the cell (A), and furthermore to obtain its experimental standard potential and the slope of the Nernst response. Then, the emf measurements of the galvanic cell (B) were made by using standard addition procedure to give the experimental mean activity coefficients of [BMIm]Cl at different ionic strengths in the mixed electrolyte solutions. The experimental mean activity coefficients of [BMIm]Cl in mixture can be calculated from the following equation:

$$E_B = E' + k\lg\left[(m_1+m_2)m_1\gamma^2_{\pm[BM\,Im]Cl} + K^{pot}_{[BM\,Im]Na}(m_1+m_2)m_2\gamma^2_{NaCl}\right]$$
(1)

In the above equation, E´ is the standard potential, $k = (\ln10)RT/F$ represents Nernst slope and $K^{Pot}_{[BM\,Im]Na}$ denotes the selectivity coefficient of IL-ISE electrode for sodium ions illustrating the interfering effect of sodium ions on the response of IL-ISE electrode.

Finally, the emf of the galvanic cell (C) was determined to get the selectivity coefficient of [BMIm]$^+$ and Na$^+$ ions ($K_{[BMIm]Na}$). To this aim, the emf response of IL-ISE electrode was measured by varying concentration of NaCl from 1.0 × 10^{-3} to 1.0 mol kg^{-1}. The selectivity coefficient was calculated according to the equation:

$$E_C = E'_C + k\lg\left(K_{[BM\,Im]Na}m_B^2\gamma^2_{\pm[BM\,Im]Cl}\right)$$
(2)

The value of $K_{[BMIm]Na}$ was found to be less than 1.0×10^{-2}. Therefore, the selectivity coefficient is so small that the second term on the right of Eq. (1) can be neglected. Consequently, we will get the simplified form of Eq. (1):

$$E_B = E' + k\lg\left[(m_1+m_2)m_1\gamma^2_{\pm[BM\,Im]Cl}\right] = E^\circ + s\lg\left(\gamma_{\pm[BM\,Im]Cl}I\right)$$
(3)

Therefore, the mean activity coefficients of [BMIm]Cl in

the aqueous mixture can be determined according to the Eq. (3).

Pitzer Model

The Pitzer ion interaction model was used for the experimental data correlation and calculation of thermodynamic properties of the mixed electrolyte solutions [18,19]. According to the Pitzer model, the mean molal activity coefficient, $\gamma_{\pm}$, for [BMIm]Cl in the aqueous mixed electrolyte solution, [(1-y)[BMIm]Cl + y NaCl] is written as:

$$\ln \gamma_{\pm[BM\,Im]Cl} = \ln \gamma^{\circ}_{\pm[BM\,Im]Cl} +$$
$$yI\left[\left(B^{\phi}_{NaCl} - B^{\phi}_{[BM\,Im]Cl}\right) + I\left(C^{\phi}_{NaCl} - C^{\phi}_{[BM\,Im]Cl}\right)\right] + yI\left[\theta + \left(1 + \frac{y}{2}\right)I\psi\right]$$

(4)

$$\ln\gamma^{\circ}_{\pm[BM\,Im]Cl} = f^{\gamma} + B^{\gamma}_{[BM\,Im]Cl}I + \frac{3}{2}C^{\phi}_{[BM\,Im]Cl}I^{2}$$ (5)

Where

$$f^{\gamma} = -A_{\phi}\left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b}\ln\left(1 + b\sqrt{I}\right)\right]$$ (6)

$$B^{\phi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\exp\left(-\alpha_{1}\sqrt{I}\right)$$ (7)

$$B^{\gamma}_{MX} = B + B^{\phi} = 2\beta^{(0)}_{MX} + \left(2\beta^{(1)}_{MX}/\alpha^{2}I\right)\left[1 - \left(1 + \alpha\sqrt{I} - \frac{\alpha^{2}I}{2}\right)\exp\left(-\alpha\sqrt{I}\right)\right]$$

(8)

In these equations, A_{φ} denotes the Debye-Huckel parameter for the osmotic function with value of 0.3915 kg$^{1/2}$ mol$^{-1/2}$ for an aqueous solution at $T = 298.2$ K [18]. I and y are the total ionic strength on a molality scale and ionic strength fraction, respectively. The MX stands for [BMIm]Cl and NaCl in mixture Solutions; $\beta^{(0)}$, $\beta^{(1)}$ and C^{φ} symbolize the parameters of Pitzer equation for single salt electrolyte

solution, which were taken from the literature [2,18] and are presented in Table 2. θ and ψ indicate the unknown mixing interaction parameters which should be determined. The other symbols have their usual meaning [18].

The unknown Pitzer mixing interaction parameters ($\theta_{[BMIm]Na}$, $\psi_{[BMIm]NaCl}$) were evaluated by the graphical procedure recommended by Pitzer. This procedure defines the quantity of $\Delta\ln\gamma_{\pm}$ as the difference between the measured mean activity coefficients for the mixture ($\ln\gamma_{exp}$) and that calculated ($\ln\gamma_{calc}$) on the basis of $\theta = \psi = 0$ from Eq. (4). Then, this equation is simplified and rearranged to yield:

$$\frac{1}{m_{Na}}\Delta\ln\gamma_{\pm[BM\,Im]Cl} = \theta + \frac{1}{2}\left(m_{[BM\,Im]} + m_{Cl}\right)\psi$$ (9)

So, a plot of the left side of the Eq. (9) *vs.* $1/2(m_{[BMIm]}+m_{Cl})$ should give θ as the intercept and ψ as the slope. Firstly, from the measurements on the ternary solutions, the mixing ionic parameters were determined, then, these parameters were used to calculate the thermodynamic properties such as osmotic coefficients, activity coefficients in the mixture, and the excess Gibbs free energy for the systems under investigation as a function of total ionic strength.

Harned Rule

In relation to the electrolytic system studied, the Harned rule [20] can be simplified to the following equation:

$$\ln\gamma_{\pm[BM\,Im]Cl} = \ln\gamma^{\circ}_{\pm[BM\,Im]Cl} - \alpha_{12}yI = \ln\gamma^{\circ}_{\pm[BM\,Im]Cl} - \alpha_{12}m_{2}$$ (10)

where α_{12} represents the Harned interaction coefficient, y is the ionic strength fraction of NaCl in the solutions and $\gamma_{\pm[BMIm]Cl}$ is the mean activity coefficients of [BMIm]Cl in the mixed solutions at the same total ionic strength, which corresponding values can be determined by potentiometric measurements using cell (B). The results, listed in Table 3 and shown in Fig. 1, indicate that at constant ionic strength

Table 2. Pitzer Parameter Values $\beta^{(0)}$, $\beta^{(1)}$ and C^{φ} for Single Electrolyte of [BMIm]Cl and NaCl

Electrolyte	T (K)	B$^{(0)}$ (kg mol^{-1})	B$^{(1)}$ (kg mol^{-1})	C$^{\varphi}$ (kg^2 mol^{-2})	Ref.
[BMIm]Cl	298.2	0.04733	-1.20989	-0.01159	[2]
NaCl	298.2	0.0765	0.2664	0.00127	[18]

Table 3. The Parameter Values of Harned Equation at T = 298.2 K

I	α_{12}	R^2
1.2000	-0.3896	0.9556
1.4000	-0.3678	0.9775
1.6000	-0.3145	0.9735
1.8000	-0.2424	0.9815
2.0000	-0.2095	0.9672
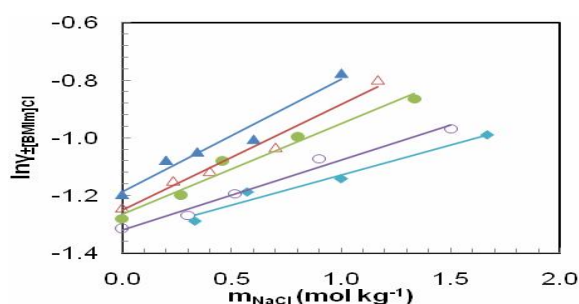
Fig. 1. Plot of $\ln\gamma_{\pm[BMIm]Cl}$ against m_{NaCl} at constant total ionic strengths (I = 1.2;▲, I = 1.4; △, I = 1.6;●, I = 1.8; ○, and ♦I = 2).
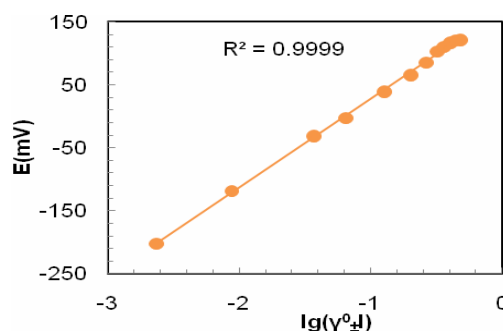
Fig. 2. The plot of cell (A) emf *vs.* $\lg(\gamma I)$ for calibration of IL-ISE and Ag-AgCl electrode pair at 298.2 K.

the relationship between $\ln\gamma_{\pm[BMIm]Cl}$ and y is linear, so it is concluded that the Harned rule can be applied to describe the above system very well.

RESULTS AND DISCUSSION

The Calibration of Electrode Pair of IL-ISE and Ag-AgCl

In order to check the response of the electrodes, before performing each series of experiments, the emf of the cell (A) was measured in standard [BMIm]Cl solutions with concentration range from 0.0001 to 1.0000 mol kg^{-1}.

The measured potentials were plotted against the $\lg(\gamma^0_{\pm}I)$ to check the linear correlation coefficient (R^2). The degree of the linear correlation coefficient ($R^2 = 0.9999$) in Fig. 2 indicates that the obtained results are in consistent with the literature data [2]. Figure 2 also illustrates that the electrode pair is well suited for our measurements.

Determination of the Mean Activity Coefficients

The emf measurements of the galvanic cell (B) were performed for determination of the experimental mean activity coefficients of [BMIm]Cl in the mixed electrolyte solutions. To make sure of the accuracy of the determined mean activity coefficients values, the IL-ISE was each time calibrated in standard [BMIm]Cl solutions with concentration range 1-10^{-3} mol kg^{-1} before performing each series of measurements in the mixed electrolyte system. Experimental mean activity coefficients of [BMIm]Cl were determined for various series of salt molal ratio by using the Nernst Eq. (3). The values for the mean ionic activity coefficient of [BMIm]Cl in the mixture over total ionic strengths from 0.0025 to 2.0000 mol kg^{-1} for different series of salt molal ratio r = $m_{[BMIm]Cl}$ /m_{NaCl} with r = 0.2, 1.0, 2.5 and 5.0 and [BMIm]Cl single electrolyte have been illustrated in Table 4 at T = 298.2 K. As well as, Figure 3 shows the experimental activity coefficients of [BMIm]Cl

Table 4. Total Ionic Strengths (I), Molality of [BMIm]Cl ($m_{[BMIm]Cl}$), Experimental Mean Activity Coefficients of [BMIm]Cl ($\gamma_{\pm[BMIm]Cl}$) and emf Data (E/mV) for all of the Investigated Mixed Electrolyte Systems at T = 298.2 K

I^a (mol kg^{-1})	$m_{[BMIm]Cl}{}^a$ (mol kg^{-1})	E^b (mV)	$\pm\gamma_{[BMIm]Cl}{}^c$	I^a (mol kg^{-1})	$m_{[BMIm]Cl}{}^a$ (mol kg^{-1})	E^b (mV)	$\pm\gamma_{[BMIm]Cl}{}^c$
r = pure				r = 5			
0.0025	0.0025	-202.4	0.9401	0.0500	0.0416	-10.8	0.7715
0.0100	0.0100	-118.5	0.8794	0.1000	0.0832	15.1	0.6470
0.0500	0.0500	-31.7	0.7384	0.2500	0.2083	48.2	0.5013
0.1000	0.1000	-3.1	0.6473	0.5000	0.4166	73.5	0.4154
0.2500	0.2500	38.8	0.5079	0.7500	0.6250	85.8	0.3540
0.5000	0.5000	65.3	0.4047	1.0000	0.8334	101.8	0.3655
0.7500	0.7500	85.5	0.3524	1.2000	1.0001	107.4	0.3406
1.0000	1.0000	102.7	0.3204	1.4000	1.1667	111.5	0.3169
1.2000	1.2000	110.6	0.3025	1.6000	1.3333	115.7	0.3015
1.4000	1.4000	116.8	0.2887	1.8000	1.5000	118.1	0.2812
1.6000	1.6000	120.6	0.2777	2.0000	1.5834	122.4	0.2757
1.8000	1.8000	121.5	0.2686				
r = 2.5				r = 1			
0.0500	0.0357	-33.3	0.7631	0.0500	0.0250	-62.9	0.7939
0.1000	0.0715	-3.0	0.6741	0.1000	0.0500	-34.2	0.6636
0.2500	0.1785	31.0	0.5106	0.2500	0.1250	3.1	0.5176
0.5000	0.3573	58.9	0.4312	0.5000	0.2501	34.2	0.4517
0.7500	0.5358	77.2	0.4053	0.7500	0.3751	53.1	0.4224
1.0000	0.7144	87.3	0.3675	1.0000	0.5001	66.4	0.4020
1.2000	0.8573	94.5	0.3506	1.2000	0.6001	71.4	0.3664
1.4000	1.0001	99.1	0.3276	1.4000	0.7001	78.4	0.3559
1.6000	1.1430	108.1	0.3395	1.6000	0.8000	87.9	0.3692
1.8000	1.2858	108.3	0.3029	1.8000	0.9000	90.2	0.3420
2.0000	1.4287	114.3	0.3051	2.0000	1.0000	92.3	0.3196
r = 0.2							
0.0500	0.0083	-105.0	0.7790				
0.1000	0.0167	-71.0	0.7084				
0.2500	0.0417	-31.3	0.5697				
0.5000	0.0833	-1.3	0.4828				
0.7500	0.1250	17.8	0.4504				
1.0000	0.1666	32.2	0.4352				
1.2000	0.2000	45.8	0.4606				
1.4000	0.2333	53.2	0.4497				
1.6000	0.2666	57.1	0.4215				
1.8000	0.2999	57.8	0.3793				
2.0000	0.3333	62.7	0.3721				

[a]The error in ionic strength and molality value was ±0.0001 mol kg^{-1}. [b]The average error in emf value was ±0.3 mV. [c]The average standard deviation in mean activity coefficient value was ±0.0038.
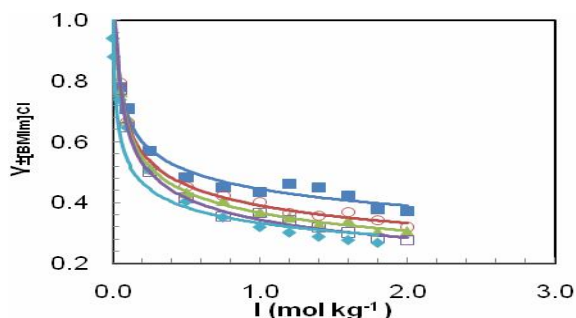
Fig. 3. The values of mean activity coefficients for [BMIm]Cl *vs.* total ionic strength at different molal ratio (r = 0.2; ■, r = 1; ○, r = 2.5 ▲, r = 5; □ and r = pure; ♦) at 298.2 K.

Table 5. Pitzer Mixing Parameters (θ,ψ) Obtained for the ([BMIm]Cl + NaCl + H₂O) Ternary System

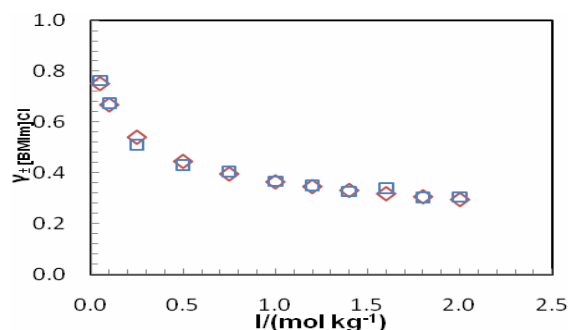| r	θ (kg mol⁻¹)	ψ (kg² mol⁻²)
0.2	0.3446	-0.1237
1.0	0.2564	-0.1109
2.5	0.3699	-0.1668
Mean	0.3236	-0.1338

Fig. 4. The experimental and calculated activity coefficient values *vs.* total ionic strength for r = 2.5 (exp; □, calc; ◊).

against total ionic strength for various series of salt molal ratio. It can be seen that the experimental activity coefficients of [BMIm]Cl is reduced by increasing of total ionic strength at the same [BMIm]Cl molal ratio. In

addition, the experimental activity coefficients of [BMIm]Cl is reduced by increasing of BMIm]Cl molal ratio in the mixture at the same ionic strength.

Determination of the Mixed Ionic Interaction Parameters ($\theta_{[BMIm]Na}$, $\psi_{[BMIm]NaCl}$)

The mixed ionic interaction parameters ($\theta_{[BMIm]Na}$, $\psi_{[BMIm]NaCl}$) were evaluated for the studied ternary system, according to Pitzer graphcal method. The Pitzer mixing parameters were determined from the intercept and slope of the linear regression plot $\frac{1}{m_{Na}}\Delta \ln \gamma \pm [BM\,Im]Cl_{vs.}$ *vs.* $1/2(m_{[BMIm]}+m_{Cl})$. These parameters account for the short-range interactions between two cation and two cation plus anion which are important only at high ionic strengths. The obtained results are presented in Table 5. To evaluate the performance of the Pitzer model used, the correlation between experimental and calculated activity coefficient values of ionic liquid for r = 2.5 was shown in Fig. 4. It can be observed that the experimental and calculated activity coefficient values agree with each other.

Calculation of Thermodynamic Properties by the Pitzer Model

The obtained parameters were used for predicting the thermodynamic properties of the under investigation system by the Pitzer model. The osmotic coefficients (φ), the mean activity coefficients of NaCl, the solvent activity and the excess Gibbs free energy (G^E) were calculated for the whole series of the studied mixed electrolyte system according to following equations:

$$\phi = 1 - \frac{A_\phi \sqrt{I}}{1+b\sqrt{I}} + B^\phi_{[BM\,Im]Cl}I + C^\phi_{[BM\,Im]Cl}I^2 + yI\left[\left(B^\phi_{NaCl} - B^\phi_{[BM\,Im]Cl}\right) + I\left(C^\phi_{NaCl} - C^\phi_{[BM\,Im]Cl}\right)\right] + y(1-y)I(\theta + I\psi)$$

(11)

$$\ln\gamma_{\pm NaCl} = \ln\gamma^\circ_{\pm NaCl} + (1-y)I\left[\left(B^\phi_{NaCl} - B^\phi_{[BM\,Im]Cl}\right) + I\left(C^\phi_{NaCl} - C^\phi_{[BM\,Im]Cl}\right)\right] + (1-y)I\left[\theta + \frac{1}{2}(1+y)I\psi\right]$$

(12)

$$a_W = \exp\left[-\frac{2M\phi\left(m_{[BM\,Im]Cl} + m_{NaCl}\right)}{1000}\right]$$

(13)

Table 6. The Calculated Values of Mean Activity Coefficients for NaCl ($\gamma_{\pm NaCl}$), Osmotic Coefficients (φ), Excess Gibbs Free Energy (G^E/RT) and Solvent Activity (a_w) as a Function of Ionic Strength, for the Investigated Mixed Electrolyte Systems at T = 298.2 K

| I (mol kg^{-1})	$\gamma_{\pm NaCl}$	φ	G^E/RT	a_w	I (mol kg^{-1})	$\gamma_{\pm NaCl}$	φ	G^E/RT	a_w
		r = pure					r = 5		
0.0025		0.9789	-0.0002	0.9999	0.0025	0.9499	0.9796	-0.0002	0.9999
0.0100		0.9556	-0.0017	0.9997	0.0100	0.9141	0.9581	-0.0016	0.9997
0.0500		0.8946	-0.0198	0.9984	0.0500	0.8658	0.9050	-0.0145	0.9984
0.1000		0.8506	-0.0571	0.9969	0.1000	0.8536	0.8685	-0.0515	0.9969
0.2500		0.7775	-0.2275	0.9930	0.2500	0.8627	0.8115	-0.2058	0.9927
0.5000		0.7239	-0.6286	0.9871	0.5000	0.9018	0.7746	-0.5240	0.9862
0.7500		0.7022	-1.1179	0.9812	0.7500	0.9436	0.7629	-0.9568	0.9796
1.0000		0.6940	-1.6645	0.9753	1.0000	0.9839	0.7607	-1.2043	0.9730
1.2000		0.6925	-2.1318	0.9705	1.2000	1.0146	0.7616	-1.5760	0.9676
1.4000		0.6932	-2.6197	0.9657	1.4000	1.0436	0.7630	-1.9982	0.9623
1.6000		0.6951	-3.1247	0.9608	1.6000	1.0707	0.7641	-2.4059	0.9569
1.8000		0.6976	-3.6440	0.9558	1.8000	1.0956	0.7642	-2.9028	0.9517
2.0000		0.7000	-4.1758	0.9508	2.0000	1.1180	0.7629	-3.2715	0.9466
		r = 2.5					r = 1		
0.0025	0.9495	0.9801	-0.0002	0.9999	0.0025	0.9486	0.9808	-0.0002	0.9999
0.0100	0.9124	0.9598	-0.0015	0.9997	0.0100	0.9093	0.9626	-0.0014	0.9997
0.0500	0.8591	0.9118	-0.0148	0.9984	0.0500	0.8473	0.9229	-0.0121	0.9983
0.1000	0.8421	0.8802	-0.0422	0.9968	0.1000	0.8219	0.8991	-0.0404	0.9968
0.2500	0.8401	0.8334	-0.1816	0.9925	0.2500	0.8012	0.8676	-0.1538	0.9922
0.5000	0.8649	0.8065	-0.4489	0.9856	0.5000	0.8031	0.8547	-0.3617	0.9847
0.7500	0.8943	0.8006	-0.7164	0.9786	0.7500	0.8142	0.8565	-0.5854	0.9771
1.0000	0.9232	0.8019	-1.0795	0.9715	1.0000	0.8271	0.8624	-0.8260	0.9694
1.2000	0.9451	0.8043	-1.3658	0.9659	1.2000	0.8374	0.8672	-1.0991	0.9632
1.4000	0.9655	0.8064	-1.7179	0.9602	1.4000	0.8472	0.8709	-1.3168	0.9571
1.6000	0.9841	0.8074	-1.8679	0.9546	1.6000	0.8560	0.8728	-1.4362	0.9510
1.8000	1.0008	0.8068	-2.3749	0.9491	1.8000	0.8636	0.8727	-1.7371	0.9450
2.0000	1.0152	0.8041	-2.5907	0.9438	2.0000	0.8698	0.8701	-2.0410	0.9393
		r = 0.2							
0.0025	0.9473	0.9819	-0.0002	0.9999					
0.0100	0.9046	0.9664	-0.0014	0.9997					
0.0500	0.8292	0.9374	-0.0135	0.9983					
0.1000	0.7916	0.9228	-0.0350	0.9967					
0.2500	0.7447	0.9075	-0.1234	0.9919					
0.5000	0.7178	0.9061	-0.3038	0.9838					
0.7500	0.7084	0.9129	-0.4998	0.9757					
1.0000	0.7057	0.9219	-0.7021	0.9674					
1.2000	0.7062	0.9293	-0.8362	0.9606					
1.4000	0.7081	0.9363	-1.0002	0.9539					
1.6000	0.7109	0.9426	-1.1872	0.9472					
1.8000	0.7143	0.9481	-1.4039	0.9404					
2.0000	0.7182	0.9525	-1.5723	0.9337					
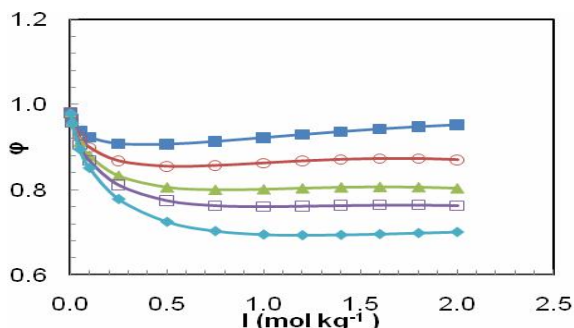
Fig. 5. The osmotic coefficients of solvent against total ionic strength at different molal ratio (r = 0.2; ■, r = 1; O, r = 2.5▲, r = 5; □ and r = pure; ♦) at 298.2 K.
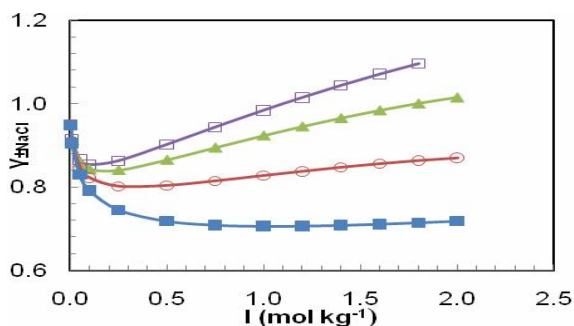

Fig. 7. The values of solvent activity *vs.* total ionic strength at different molal ratio (r = 0.2; ■, r = 1; O, r = 2.5▲, r = 5; □ and r = pure; ♦) at 298.2 K.

Fig. 6. The values of mean activity coefficients for NaCl *vs.* total ionic strength at different molal ratio (r = 5; □, r = 2.5▲, r = 1; O and r = 0.2; ■) at 298.2 K.

Fig. 8. The excess Gibbs energy for mixed electrolyte solution ([BMIm]Cl+NaCl+Water) against total ionic strength at different molal ratio (r = 0.2; ■, r = 1; O, r = 2.5▲, r = 5; □ and r = pure; ♦) at 298.2K.

$$G^E = 2RT\left[m_{[BM\,Im]Cl}\left(1-\phi+\ln\gamma_{\pm[BM\,Im]Cl}\right)+m_{NaCl}\left(1-\phi+\ln\gamma_{\pm NaCl}\right)\right]$$

(14)

The values of these thermodynamic properties are illustrated for different series of salt molal ratio in Table 6. Figure 5 shows the plot of the osmotic coefficient against total ionic strength. It can be seen that the osmotic coefficient is decreased by increasing the salt molal ratios at the same ionic strength. In addition, Figs. 6 to 8 show that the mean activity coefficients of NaCl increase by increasing the salt molal ratios, and solvent activity and the excess Gibbs free energy decreases with an increase of total ionic strength for all of the investigated mixed electrolyte system.
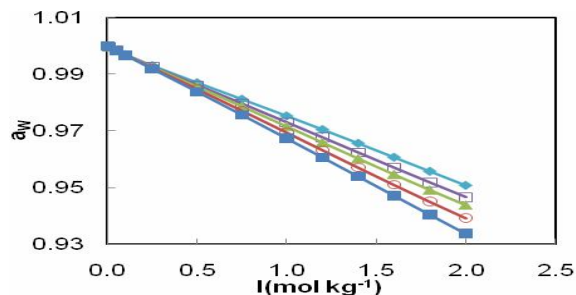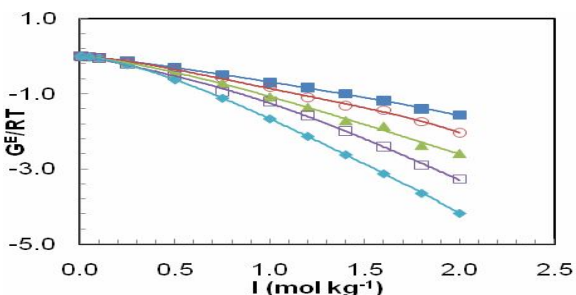
CONCLUSIONS

The thermodynamic study of the ternary mixed electrolyte ([BMIm]Cl+NaCl+Water) system was performed by a potentiometric method using the solvent polymeric ion selective membrane electrodes with an Ag-AgCl electrode at T = 298.2 K. The activity coefficients of [BMIm]Cl in the mixture were determined by the galvanic cells without liquid junction. These measurements were made for different series of salt molal ratios. The experimental results were also analyzed with the Harned rule and Pitzer models. It was found that the Harned rule can be applied to describe the system studied. The pitzer ion-interaction model was used for the experimental results

correlation and calculation of activity coefficients for under investigation system. The mixing Pitzer parameters $\theta_{[BMIm]Na}$, $\psi_{[BMIm]NaCl}$ were determined for this system. The obtained Pitzer parameters were used for the calculation of the other thermodynamic properties such as the osmotic coefficients, the activity coefficients of NaCl, the solvent activity, and the excess Gibbs free energy. It was seen that the Pitzer model can be used to analyze this system successfully.

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