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Osmotic and Activity Coefficient of 1-Ethyl-3-methylimidazolium Bromide in Aqueous Solutions of Potassium Dihydrogen Phosphate, Dipotassium Hydrogen Phosphate, and Tripotassium Phosphate at $T = 298.15$ K

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Vapor−liquid equilibrium data (water activity, vapor pressure, osmotic coefficient, and activity coefficient) of the mixed electrolyte aqueous solution, 1-ethyl-3-methylimidazolium bromide, [Emim][Br], + tripotassium phosphate, [Emim][Br], + dipotassium hydrogen phosphate, [Emim][Br], + potassium dihydrogen phosphate, and their corresponding binary aqueous solutions have been measured by the isopiestic method at temperature 298.15 K. The osmotic coefficients for binary aqueous solutions were correlated to the Pitzer and modified Pitzer models. From these data, the corresponding mean molal activity coefficients, $\gamma_{\pm}$, have been calculated. The activity coefficients of mixed electrolytes were calculated by Scatchard's neutral-electrolyte method. The activity results were also satisfactorily fitted to the semiempirical equation.

Introduction

Presently, ionic liquids (ILs) are being used as separation agents in phase equilibria {(vapor + liquid) equilibria, (liquid + liquid) equilibria} with very promising results.[1−5] Experimental data for phase equilibria of systems involving ILs are necessary to obtain information about the influence of the structure of the ILs on its physical and solvent properties. This information is important for developing predictive models. (Vapor + liquid) equilibria (VLE) data[4,5] permit checking the potential of models that are applied for the description of the real behavior of systems with ionic liquids. For the prediction of the VLE behavior, the activity and osmotic coefficients are of great interest.

In this study, experimental data on the vapor−liquid equilibria of binary aqueous solutions of 1-ethyl-3-methylimidazolium bromide, [Emim][Br], tripotassium phosphate, K_3PO_4, dipotassium hydrogen phosphate, K_2HPO_4, and potassium dihydrogen phosphate, KH_2PO_4, and ternary [Emim][Br] + K_3PO_4 + H_2O, [Emim][Br] + K_2HPO_4 + H_2O, and [Emim][Br] + KH_2PO_4 + H_2O solutions are investigated through the isopiestic method at $T = 298.15$ K. Vapor−liquid equilibrium data are required for these ternary systems since they form biphasic systems which may be used for separation of biomolecules.[3] The Pitzer and modified Pitzer equations[6,7] are applied to correlate the osmotic coefficient results for the investigated binary solutions. Both of the Pitzer and modified Pitzer models are capable of reproducing satisfactorily the experimental osmotic coefficients. The parameters obtained with these models were adopted to calculate the mean molal activity coefficients. For calculation of activity coefficients of the studied mixed electrolyte solutions, Scatchard's[8] neutral-electrolyte method is applied.

Experimental Section

Materials. All the chemicals were obtained from Merck. Sodium chloride with minimum mass fraction purity 0.995 was dried in an electrical oven at about 110 °C for 24 h prior to use. The tripotassium phosphate trihydrate (K_3PO_4, $3H_2O$) and [Emim][Br] with mass fraction purity > 0.98, anhydrous dipotassium hydrogen phosphate (K_2HPO_4), and anhydrous potassium dihydrogen phosphate (KH_2PO_4) with mass fraction purity > 0.99 were used without further purification. The water content in the IL was determined using a microprocessor based automatic Karl Fischer Titrator. The mass fraction of water for [Emim][Br] was $w = 0.0029$. The water content in the IL and tripotassium phosphate was taken into account during the preparation of the aqueous solutions.

(Vapor + Liquid) Equilibrium Measurements. In this study, the isopiestic method is used to obtain the activity of water in aqueous ([Emim][Br] + salt) solutions. It is based on the phenomenon that different solutions, when connected through the vapor space, approach equilibrium by transferring solvent mass by distillation. Equilibrium has been established once the temperature and pressure are uniform throughout the system, provided that no concentration gradients exist in the liquid phase. At equilibrium, the chemical potentials of the solvent in each of the solutions in the closed system are identical. Equality of

Table 1. Isopiestic Equilibrium Molalities, Osmotic Coefficients, Water Activities, and Vapor Pressures of [Emim][Br] in Water at $T = 298.15$ K

m_{IL} / $(mol \cdot kg^{-1})$	m_{NaCl} / $(mol \cdot kg^{-1})$	ϕ	a_w	p / (kPa)	$\gamma_{\pm}{}^{a}$	$\gamma_{\pm}{}^{b}$
0.5514	0.4841	0.811	0.9840	3.124	0.515	0.520
0.6588	0.5697	0.801	0.9812	3.115	0.494	0.498
0.6883	0.5934	0.799	0.9804	3.113	0.488	0.492
0.7764	0.6649	0.795	0.9780	3.105	0.474	0.477
0.9367	0.7907	0.787	0.9738	3.092	0.451	0.455
1.0405	0.8738	0.786	0.9710	3.083	0.439	0.442
1.9432	1.5336	0.763	0.9591	3.010	0.374	0.375
2.3076	1.7842	0.757	0.9585	2.981	0.358	0.359
2.5419	1.9505	0.759	0.9329	2.962	0.350	0.351
3.1886	2.3957	0.763	0.9161	2.908	0.333	0.335
4.3588	3.2063	0.786	0.8839	2.806	0.317	0.319
5.4096	3.9633	0.821	0.8521	2.705	0.312	0.315
7.1696	5.2229	0.883	0.7960	2.527	0.321	0.322

[a] Obtained by using the Pitzer model (eq 5). [b] Obtained by using the modified Pitzer model (eq 7).

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Table 2. Isopiestic Equilibrium Molalities, Osmotic Coefficients, Water Activities, and Vapor Pressures of K_3PO_4, K_2HPO_4, and KH_2PO_4 in Water at $T = 298.15$ K

m_S $(mol \cdot kg^{-1})$	m_{NaCl} $(mol \cdot kg^{-1})$	ϕ	a_w	p (kPa)	$\gamma_{\pm}{}^{a}$	$\gamma_{\pm}{}^{b}$
$K_3PO_4 + H_2O$						
0.4308	0.6443	0.694	0.9787	3.107	0.203	0.184
0.5142	0.7698	0.698	0.9745	3.094	0.192	0.174
0.6347	0.9534	0.705	0.9683	3.074	0.181	0.165
0.7575	1.1334	0.708	0.9621	3.054	0.173	0.158
0.8132	1.2249	0.716	0.9589	3.044	0.171	0.156
1.0023	1.5429	0.744	0.9477	3.009	0.166	0.151
1.0119	1.5579	0.745	0.9471	3.007	0.165	0.151
1.2412	1.9517	0.778	0.9328	2.961	0.164	0.148
1.6947	2.8165	0.866	0.8996	2.856	0.169	0.153
1.8303	3.0836	0.893	0.8889	2.822	0.171	0.156
$K_2HPO_4 + H_2O$						
0.6496	0.7441	0.711	0.9753	3.096	0.278	0.271
0.7592	0.8577	0.704	0.9715	3.084	0.263	0.257
1.1118	1.2106	0.690	0.9594	3.046	0.231	0.226
1.2506	1.3533	0.690	0.9544	3.030	0.222	0.217
1.6042	1.6994	0.689	0.9420	2.991	0.205	0.201
1.7119	1.8147	0.694	0.9379	2.978	0.202	0.198
1.9646	2.0610	0.696	0.9287	2.948	0.195	0.191
2.1627	2.2818	0.709	0.9204	2.922	0.192	0.187
$KH_2PO_4 + H_2O$						
0.6269	0.5418	0.800	0.9821	3.118	0.518	0.532
0.9843	0.7849	0.744	0.9740	3.092	0.445	0.455
1.1131	0.8700	0.731	0.9711	3.083	0.425	0.434
1.2275	0.9377	0.717	0.9688	3.076	0.409	0.417
1.2705	0.9666	0.715	0.9678	3.073	0.403	0.411
1.5077	1.1093	0.696	0.9629	3.057	0.376	0.383
1.7071	1.2218	0.680	0.9590	3.045	0.357	0.364

[a] Obtained by using the Pitzer model (eq 5). [b] Obtained by using the modified Pitzer model (eq 7).

the solvent chemical potential implies the equality of the solvent activity. Since the solvent activity is known for one or more standard solutions, it will be known for each solution within the isopiestic system. The isopiestic apparatus used in this work was similar to the one used by Ochs et al.[9] This apparatus consisted of a seven-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions; one flask contained the pure [Emim][Br] solution; one flask contained the pure potassium phosphate solution; two flasks contained ([Emim][Br] + potassium phosphate) solutions; and the central flask was used as a water reservoir. For binary systems, this apparatus consisted of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions; two flasks contained the pure [Emim][Br] solution; and the central flask was used as a water reservoir. The apparatus was held in a constant-temperature bath for at least 120 h for equilibrium. During the equilibration process, the manifold was removed at least once a day, and the samples were agitated. After the third day, the samples were not agitated, but left in the bath to approach their final equilibrium conditions. The temperature was controlled to within ± 0.05 K by a Heto temperature controller (Hetotherm PF, Heto Laboratory Equipment, Denmark). After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance (Shimadzu, 321-34553, Shimadzu Co., Japan) with a precision of $\pm 1 \cdot 10^{-4}$ g. From the mass of each flask after equilibrium and the initial mass of salt and IL, the mass fraction of each solution was calculated. The water activity for the standard aqueous NaCl solutions at different concentrations had been calculated from the correlation of Colin et al.[10] It was assumed that the equilibrium condition was reached when the differences between the mass fractions of two standard solutions were less than 1 %. In all cases, averages of the mass fractions of two standard solutions are reported. The accuracy of the method depends upon the standard solutions, sample mixing during the equilibrium period, temperature stability, and the time allowed for the equilibrium process. The uncertainty in the measurement of solvent activity was estimated to be $\pm 2 \cdot 10^{-4}$.

Results and Discussion

In this work, the isopiestic measurements at $T = 298.15$ K were carried out for [Emim][Br] + $K_3PO_4 + H_2O$, [Emim][Br] + $K_2HPO_4 + H_2O$, and [Emim][Br] + $KH_2PO_4 + H_2O$ solutions and their corresponding binary solutions to study the vapor−liquid equilibria behavior of these systems. For the understanding of interactions in liquids, the activity or osmotic coefficients of the different components are of great interest. They are the most relevant thermodynamics reference data, and they are often the starting point of any modeling.[11−13] At isopiestic equilibrium,

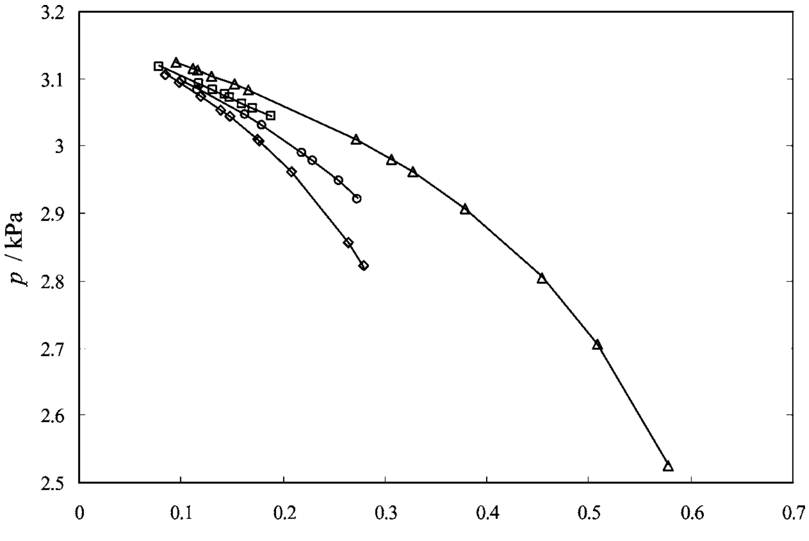

Figure 1. Plot of vapor pressure of water vapor of the binary systems against mass fraction of salt or IL, w, at $T = 298.15$ K: △, IL + H_2O; □, $KH_2PO_4 + H_2O$; ○, $K_2HPO_4 + H_2O$; ◇, $K_3PO_4 + H_2O$; —, modified Pitzer model.

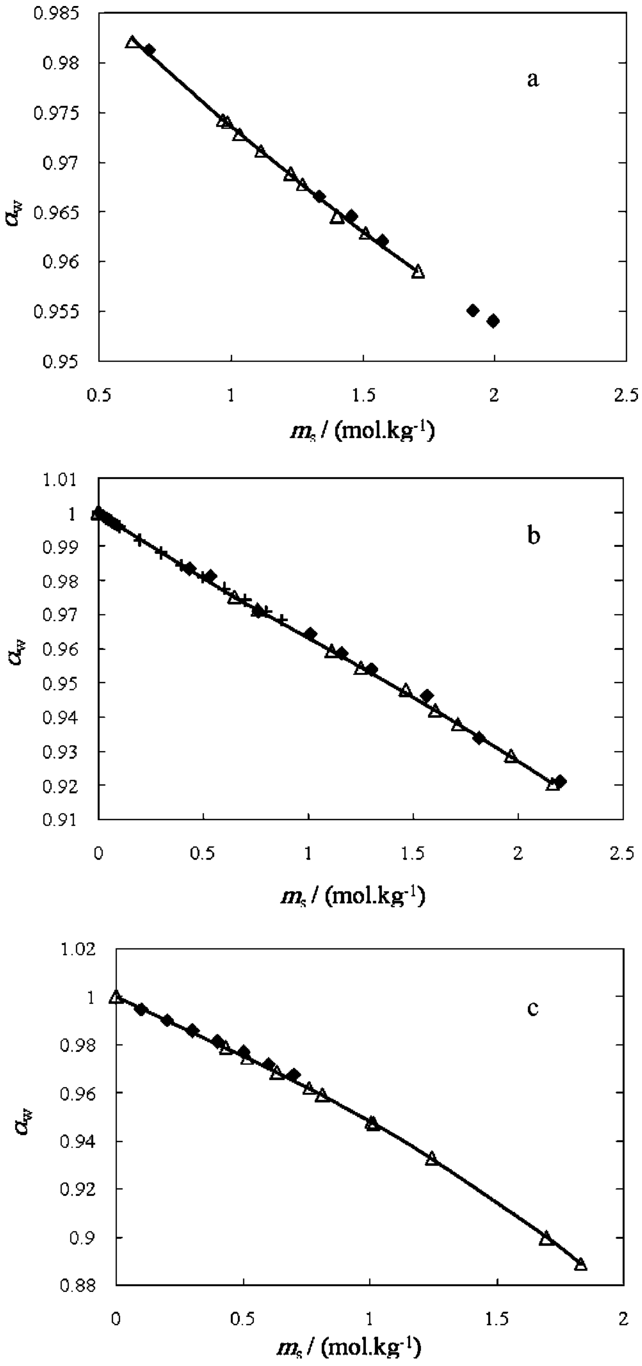

Figure 2. Plot of water activity a_w of the phosphate salt solution against molality of salt at $T = 298.15$ K: (a) $KH_2PO_4 + H_2O$ system, △, this work; ♦, ref 18; (b) $K_2HPO_4 + H_2O$ system, △, this work; ♦, ref 18; +, ref 19; (c) $K_3PO_4 + H_2O$ system, △, this work; ♦, ref 14; —, Pitzer model.

the activity of the solvent in the reference and sample solutions must be the same. Therefore, the isopiestic equilibrium molalities with reference standard solutions of NaCl in water as reported in Tables 1 and 2 enabled the calculation of the osmotic coefficient, ϕ, of the solutions of [Emim][Br], K_3PO_4, K_2HPO_4, and KH_2PO_4 in water from[14]

$$\phi = \frac{\nu_R \phi_R m_R}{\nu m} \tag{1}$$

where ν_R and ν are the sum of stoichiometric numbers of the anion and cation in the reference solution and the solution of salts, respectively; m is the molality of the salt solution; m_R is the molality of the reference standard in isopiestic equilibrium with this solution; and ϕ_R is the osmotic coefficient of the isopiestic reference standard, calculated at m_R. The necessary ϕ_R values at any m_R were calculated from the correlation given by Colin et al.[10] From the calculated osmotic coefficient data, the activity of water in salt solutions and the vapor pressure of these solutions were determined at isopiestic equilibrium molalities, with the help of the following relations[14]

Table 3. Parameters of Pitzer and Modified Pitzer Equations for the Studied Binary Systems

	Pitzer equation (eq 4)			
system	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	$\sigma(\phi)$
[Emim][Br] + H_2O	−0.01039	−0.24406	0.00423	0.0027
$K_3PO_4 + H_2O$	0.31062	5.92108	−0.02312	0.0029
$K_2HPO_4 + H_2O$	0.05660	1.32492	0.00138	0.0017
$KH_2PO_4 + H_2O$	−0.18125	0.40920	0.04772	0.0013
	modified Pitzer equation (eq 6)			
	b_{MX}	B_{MX}	C_{MX}	$\sigma(\phi)$
[Emim][Br] + H_2O	0.58138	0.02825	0.00089	0.0023
$K_3PO_4 + H_2O$	2.86649	0.03050	0.00603	0.0024
$K_2HPO_4 + H_2O$	2.26662	−0.04373	0.00515	0.0015
$KH_2PO_4 + H_2O$	3.25979	−0.21347	0.02459	0.0013

$$\phi = -\frac{\ln a_W}{\nu m M_W} \tag{2}$$

$$\ln a_W = \ln\left(\frac{p}{p_W^0}\right) + \frac{(B - V_W^0)(p - p_W^0)}{RT} \tag{3}$$

where a_W is the activity of water; M_W is the molar mass of the water; and B is the second virial coefficient of water vapor. V_W^0 is the molar volume, and p and p_W^0 are the vapor pressure of solutions and pure water, respectively. The second virial coefficient of water vapor was calculated using the equation provided by Rard and Platford.[15] Molar volume of liquid water was calculated using the density of water at different temperatures.[16] The vapor pressure of pure water was calculated using the equation of state of Saul and Wagner.[17] After the establishment of isopiestic equilibrium, water activities were calculated using eq 2. The values of p for studied systems were calculated using eq 3. The results are collected in Tables 1 and 2.

In Figure 1, the experimental vapor pressure and calculated values obtained using the modified Pitzer model for aqueous binary solutions are plotted against mass fraction of IL or salt. As can be seen from Figure 1, at the same solute mass fraction, vapor pressure depression for the investigated salt solutions increases by increasing the charge of the anion ($K_3PO_4 > K_2HPO_4 > KH_2PO_4$). This is because the vapor pressure depression is a collegative property; by increasing the number of moles of ions in salt solutions, the depression of vapor pressure is increased. In IL solution, vapor pressure depression is less than KH_2PO_4, and the presence of ion pairing in aqueous IL solution may be the main reason for this phenomenon. In Figures 2a, 2b, and 2c, respectively, comparisons of the experimental water activity data for the $K_3PO_4 + H_2O$, $KH_2PO_4 + H_2O$, and $K_2HPO_4 + H_2O$ systems measured in this work with those taken from refs 14, 18, and 19 have been made at $T = 298.15$ K. Figures 2a to 2c show that our data are in good agreement with those given in refs 14, 18, and 19 for all of these phosphate solutions.

Table 4. Water Activity and Vapor Pressure for the $[Emim][Br]_{(IL)} + K_3PO_{4(s)} + H_2O_{(w)}$, $[Emim][Br]_{(IL)} + K_2HPO_{4(s)} + H_2O_{(w)}$, and $[Emim][Br]_{(IL)} + KH_2PO_{4(s)} + H_2O_{(w)}$ Systems for Different Mass Fraction, *w*, at $T = 298.15$ K

w_{IL}	w_s	w_{NaCl}	a_w	p/(kPa)	w_{IL}	w_s	w_{NaCl}	a_w	p/(kPa)
				$[Emim][Br] + K_3PO_4 + H_2O$					
0.1264	0.0000				0.0940	0.0850			
0.0832	0.0187	0.0363	0.9787	3.107	0.0000	0.1754			
0.0704	0.0261				0.2752	0.0000			
0.0000	0.0838				0.1446	0.0538	0.0834	0.9471	3.007
0.1471	0.0000				0.0788	0.0984			
0.0925	0.0245	0.0430	0.9745	3.094	0.0000	0.1768			
0.0614	0.0434				0.3268	0.0000			
0.0000	0.0984				0.1957	0.0512	0.1024	0.9328	2.961
0.1809	0.0000				0.0988	0.1110			
0.1134	0.0277	0.0528	0.9683	3.074	0.0000	0.2085			
0.0508	0.0678				0.3939	0.0000			
0.0000	0.1187				0.2464	0.0574	0.1300	0.9098	2.888
0.2136	0.0000				0.1187	0.1349			
0.1184	0.0393	0.0621	0.9621	3.054	0.0000	0.2469			
0.0657	0.0744				0.4176	0.0000			
0.0000	0.1385				0.2564	0.0642	0.1413	0.8996	2.856
0.2281	0.0000				0.1173	0.1508			
0.1277	0.0411	0.0668	0.9589	3.044	0.0000	0.2646			
0.0664	0.0807				0.4427	0.0000			
0.0000	0.1472				0.2654	0.0726	0.1527	0.8889	2.822
0.2736	0.0000				0.1546	0.1392			
0.1557	0.0470	0.0827	0.9477	3.009	0.0000	0.2798			
				$[Emim][Br] + K_2HPO_4 + H_2O$					
0.1449	0.0000				0.0882	0.1013			
0.0955	0.0223	0.0417	0.9753	3.097	0.0000	0.2032			
0.0420	0.0583				0.2956	0.0000			
0.0000	0.1017				0.1714	0.0535	0.0903	0.9420	2.991
0.1658	0.0000				0.0824	0.1190			
0.0919	0.0344	0.0477	0.9715	3.084	0.0000	0.2184			
0.0569	0.0581				0.3106	0.0000			
0.0000	0.1168				0.1798	0.0583	0.0959	0.9379	2.978
0.2245	0.0000				0.0921	0.1193			
0.1302	0.0411	0.0661	0.9594	3.046	0.0000	0.2297			
0.0608	0.0913				0.3417	0.0000			
0.0000	0.1622				0.1967	0.0633	0.1075	0.9287	2.948
0.2471	0.0000				0.0898	0.1423			
0.1357	0.0496	0.0733	0.9544	3.030	0.0000	0.2550			
0.0699	0.0972				0.3655	0.0000			
0.0000	0.1789				0.2040	0.0723	0.1177	0.9204	2.922
0.2778	0.0000				0.1100	0.1409			
0.1457	0.0599	0.0822	0.9480	3.010	0.0000	0.2736			
				$[Emim][Br] + KH_2PO_4 + H_2O$					
0.1058	0.0000				0.1888	0.0000			
0.0722	0.0190	0.0307	0.9821	3.118	0.1171	0.0387	0.0535	0.9678	3.073
0.0388	0.0424				0.0501	0.0812			
0.0000	0.0786				0.0000	0.1484			
0.1523	0.0000				0.1992	0.0000			
0.0922	0.0332	0.0439	0.9740	3.092	0.1217	0.0419	0.0585	0.9645	3.062
0.0517	0.0639				0.0705	0.0802			
0.0000	0.1181				0.0000	0.1603			
0.1671	0.0000				0.2073	0.0000			
0.1010	0.0362	0.0484	0.9711	3.083	0.1329	0.0392	0.0609	0.9629	3.057
0.0464	0.0788				0.0648	0.0919			
0.0000	0.1316				0.0000	0.1702			
0.1788	0.0000				0.2258	0.0000			
0.1032	0.0407	0.0520	0.9688	3.076	0.1374	0.0473	0.0666	0.9590	3.045
0.0558	0.0792				0.0780	0.0932			
0.0000	0.1431				0.0000	0.1885			

The Pitzer model which has been used for the correlation of osmotic coefficient and activity coefficient has the following form for a binary electrolyte solution

$$\phi - 1 = -A^{\phi}|Z_M Z_X|\frac{I^{1/2}}{(1 + bI^{1/2})} + 2\left(\frac{\nu_M \nu_X}{\nu}\right) \cdot [\beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha I^{1/2})]m + \frac{2(\nu_M \nu_X)^{3/2}}{\nu} m^2 C_{MX}^{\phi} \quad (4)$$

and

$$\ln \gamma_{\pm} = -A^{\phi}\frac{I^{1/2}}{1 + bI^{1/2}} + \left(\frac{2}{b}\right)\ln(1 + bI^{1/2}) + m\left[2\beta^{(0)} + 2\beta^{(1)}\left[\frac{1 - \exp(-\alpha I^{1/2})(1 + \alpha I^{1/2} - 1/2\alpha^2 I)}{\alpha^2 I}\right]\right] + m^2 1.5C^{\phi} \quad (5)$$

In these equations, $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, and C_{MX}^{ϕ} are Pitzer's ion-interaction parameters obtained by fitting of experimental osmotic coefficient data; α and b are adjustable parameters; and I is the ionic strength on the molality basis. ν_M, ν_X, Z_M, and Z_X are the stoichiometric numbers and charges of cation and anion, respectively. For adjustable parameters, the values $\alpha = 2.0\ \mathrm{kg}^{1/2}\cdot\mathrm{mol}^{1/2}$ and $b = 1.2\ \mathrm{kg}^{1/2}\cdot\mathrm{mol}^{1/2}$ were used. Table 3 summarizes the parameters

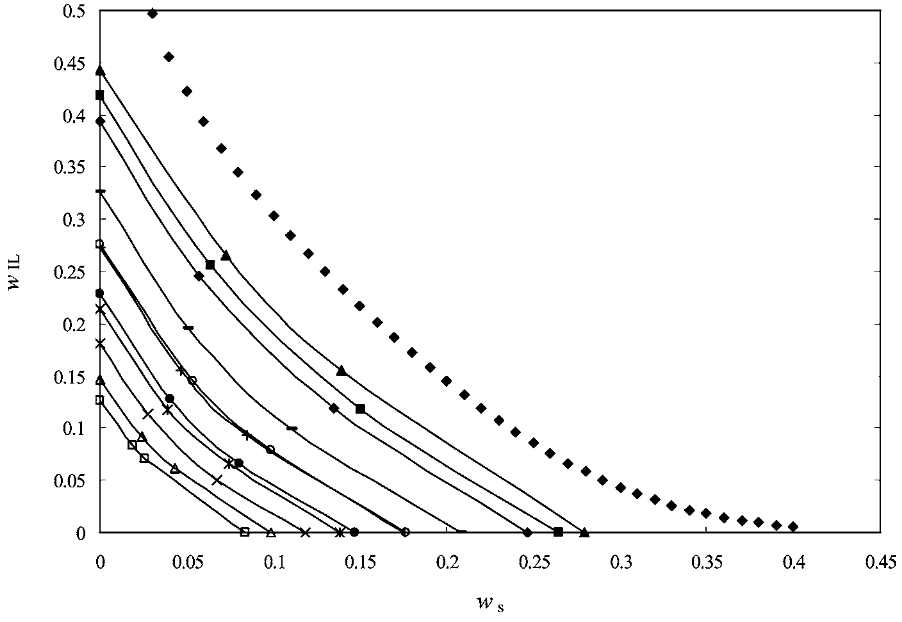

Figure 3. Constant water activity curves for the [Emim][Br](IL) + K_3PO_4(s) + H_2O(w) system at T = 298.15 K: □, 0.9787; △, 0.9745; ×, 0.9683; *, 0.9621; ●, 0.9589; +, 0.9477; ○, 0.9471; −, 0.9328; ♦, 0.9098; ■, 0.8996; ▲, 0.8889; ♦, binodal curve taken from ref 3.

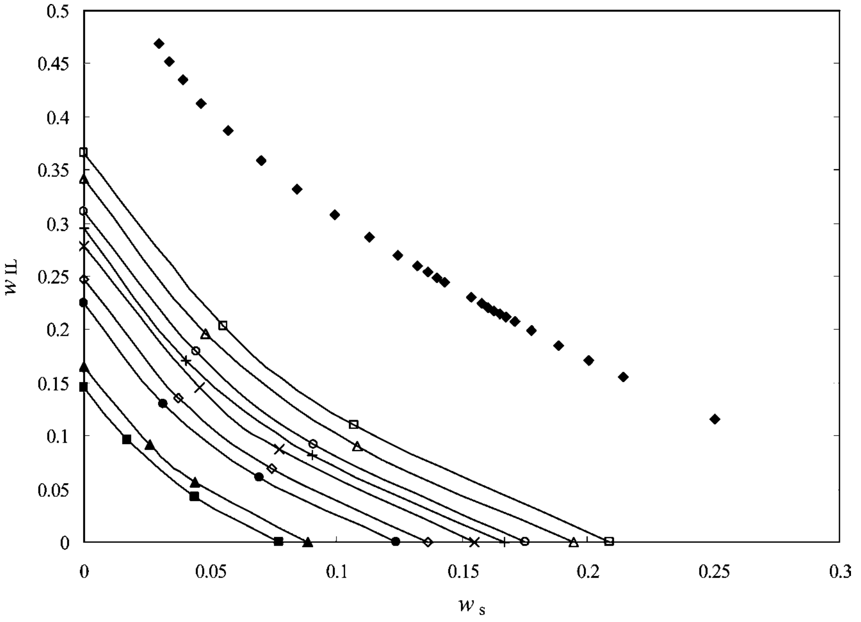

Figure 4. Constant water activity curves for the [Emim][Br](IL) + K_2HPO_4(s) + H_2O(w) system at T = 298.15 K: ■, 0.9753; ▲, 0.9715; ●, 0.9594; ◇, 0.9544; ×, 0.9480; +, 0.9420; ○, 0.9379; △, 0.9287; □, 0.9204; ♦, binodal curve obtained in this work.

obtained from fitting of the experimental osmotic coefficient data to eq 4.

The modified Pitzer model[7] has the following form for a binary electrolyte solution

$$\phi - 1 = \frac{-A^{\phi}I^{1/2}|Z_{M}Z_{X}|}{(1 + b_{MX}I^{1/2})} + 2\left(\frac{\nu_{M}\nu_{X}}{\nu}\right)mB_{MX} + \frac{4(\nu_{M}\nu_{X})^{3/2}}{\nu}|Z_{M}Z_{X}|^{1/2}m^{2}C_{MX} \quad (6)$$

In eq 6, b_{MX}, B_{MX}, and C_{MX} are three characteristic parameters which are obtained from fitting of osmotic coefficient data. These parameters are also given in Table 3. On the basis of the standard deviation values reported in Table 3, we conclude that a better quality of fitting is obtained with the modified Pitzer model.

The mean molal activity coefficients, $\gamma_{\pm}$, for the modified Pitzer model were calculated by[7]

$$\ln \gamma_{\pm} = -A^{\phi}\left[\frac{I^{1/2}}{1 + b_{MX}I^{1/2}} + \frac{2}{b_{MX}}\ln(1 + b_{MX}I^{1/2})\right]|Z_{M}Z_{X}| + 4\left(\frac{\nu_{M}\nu_{X}}{\nu}\right)mB_{MX} + \frac{6(\nu_{M}\nu_{X})^{3/2}}{\nu}|Z_{M}Z_{X}|^{1/2}m^{2}C_{MX} \quad (7)$$

The calculated values of $\gamma_{\pm}$ are also given in Tables 1 and 2.

Table 4 reports the water activities and vapor pressures of the ternary [Emim][Br] + K_3PO_4 + H_2O, [Emim][Br] +

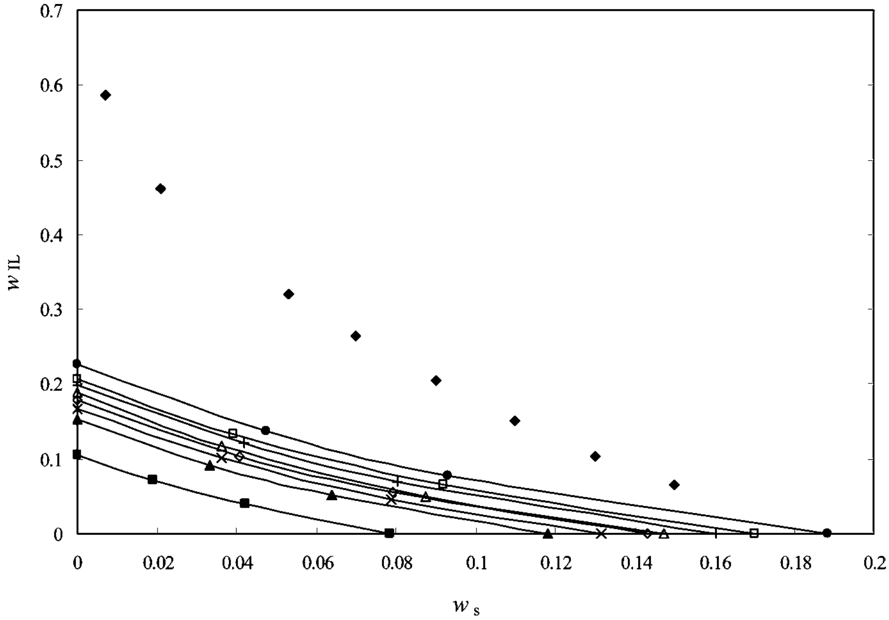

Figure 5. Constant water activity curves for the [Emim][Br](IL) + KH_2PO_4(s) + H_2O(w) system at T = 298.15 K: ■, 0.9821; ▲, 0.9740; ×, 0.9711; ◇, 0.9688; △, 0.9678; +, 0.9645; □, 0.9629; ●, 0.9590; ♦, binodal curve obtained in this work.

Table 5. Vapor Pressure Depression for Several [Emim][Br](IL) + Salt(s) + H_2O(w) Solutions Along with Those for the Corresponding Binary Solutions at T = 298.15 K

		$(p^0 - p)$/kPa		
w_S	w_{IL}	[Emim][Br](IL) + K_3PO_4(s) + H_2O(w)	[Emim][Br](IL) + H_2O(w)	K_3PO_4(s) + H_2O(w)
0.081	0.178	0.353 (0.260[a])	0.0726	0.2654
0.070	0.168	0.319 (0.239)	0.0642	0.2564
0.062	0.158	0.287 (0.220)	0.0574	0.2464
0.045	0.090	0.166 (0.136)	0.0470	0.1557
0.037	0.067	0.121 (0.103)	0.0393	0.1184

		$(p^0 - p)$/kPa		
w_S	w_{IL}	[Emim][Br](IL) + K_2HPO_4(s) + H_2O(w)	[Emim][Br](IL) + H_2O(w)	K_2HPO_4(s) + H_2O(w)
0.055	0.108	0.197 (0.163)	0.0583	0.1798
0.054	0.085	0.165 (0.140)	0.0599	0.1457
0.037	0.074	0.129 (0.111)	0.0411	0.1302
0.030	0.051	0.091 (0.081)	0.0344	0.0919

		$(p^0 - p)$/kPa		
w_{IL}	w_S	[Emim][Br](IL) + KH_2PO_4(s) + H_2O(w)	[Emim][Br](IL) + H_2O(w)	KH_2PO_4(s) + H_2O(w)
0.040	0.078	0.130 (0.119)	0.0473	0.1374
0.035	0.069	0.113 (0.104)	0.0419	0.1217
0.034	0.058	0.099 (0.091)	0.0407	0.1032
0.033	0.022	0.057 (0.054)	0.0424	0.0388

[a] Sum of vapor pressure depression for the corresponding binary solution.

Table 6. Parameters of Equation 11 for the Studied Systems

system	b_{01}	b_{02}	b_{03}	$\sigma(\phi)$	$\sigma(a)$
[Emim][Br] + K_3PO_4 + H_2O	0.37200	−0.02635	0.00192	0.0060	0.0004
[Emim][Br] + K_2HPO_4 + H_2O	0.31452	0.05215	−0.01758	0.0159	0.0008
[Emim][Br] + KH_2PO_4 + H_2O	0.70349	−0.75342	0.31575	0.0193	0.0006

K_2HPO4 + H_2O, and [Emim][Br] + KH_2PO_4 + H_2O systems at T = 298.15 K. The lines of constant water activity or vapor pressure of [Emim][Br] + salt + H_2O systems at T = 298.15 K are plotted in Figures 3 to 5. As can be seen in Table 4, in fact four points on each line in Figures 3 to 5 have a constant water activity or chemical potential, and thus these points are in equilibrium. The line with the lowest water activity must be in the neighborhood of the binodal curve where this system splits into two phases. In Table 5, vapor pressure depression for several [Emim][Br] + salt + H_2O solutions along with those for corresponding binary solutions is given at T = 298.15 K. This table shows that the vapor pressure depression for the ternary aqueous [Emim][Br] + salt system is more than the sum of those for the corresponding binary solutions. In the aqueous solutions, ions of IL are hydrated strongly with several water molecules. Such binding will result in a reduction in the free water content and consequently in an increase in effective concentration of the salt. Similarly, ionic species in the aqueous phosphate salt solutions are hydrated, and this hydration will result in an increase in the effective concentration of the IL. Thus, it can be expected that the vapor pressure depression for an aqueous [Emim][Br] + salt system will be more than the sum of those for corresponding binary solutions. The same trend has been observed for aqueous sodium tungstate + poly(ethylene glycol) solutions by Sadeghi et al.[20]

For the correlation or prediction of osmotic coefficients of studied ternary systems, it is not feasible to use the Pitzer[21] or modified Pitzer[22] models for mixed-electrolyte solutions since the investigated systems belong to the mixed-electrolyte solutions without common ions and the corresponding common ion systems are unknown. Therefore, in this work we decided to use a general equation for correlation of osmotic coefficient and calculation of the activity coefficients for mixed-electrolyte solutions, proposed by Scatchard.[8] The ionic strength fraction, y, of [Emim][Br] is given by

$$y = \frac{I_{IL}}{I_{IL} + I_S} \tag{8}$$

where I_{IL} and I_S refer to the ionic strength on the molality basis of [Emim][Br] and each of K_3PO_4, K_2HPO_4, and KH_2PO_4. The total ionic strength, I, of mixed solution was calculated by

$$I = I_{IL} + I_S \tag{9}$$

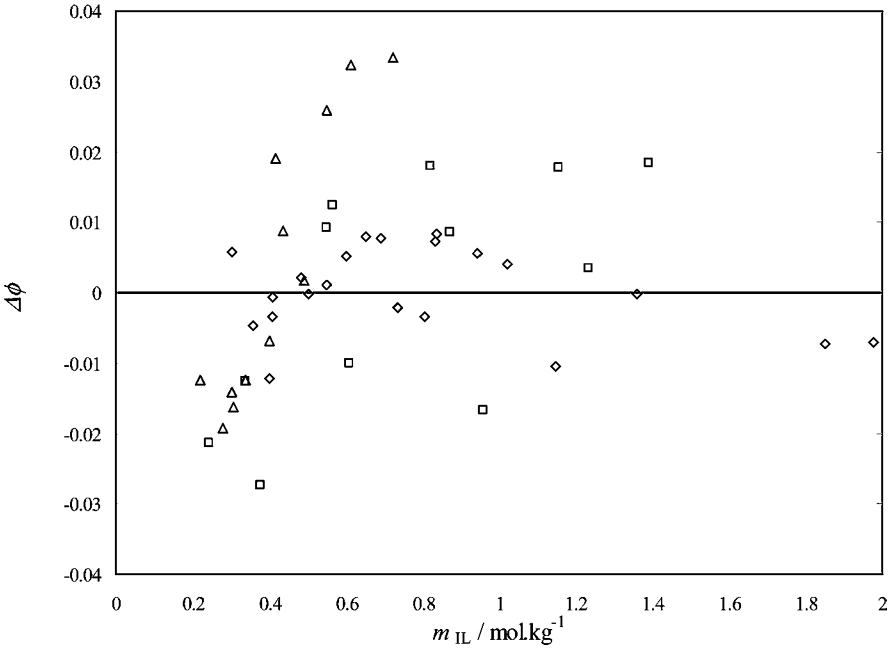

Figure 6. Deviations $\Delta\phi = \phi_{(\mathrm{expt})} - \phi_{(\mathrm{calc})}$ of experimental osmotic coefficients $\phi_{(\mathrm{expt})}$ at $T = 298.15$ K from values $\phi_{(\mathrm{calc})}$ obtained using the Scatchard method (eq 11) as a function of molality of [Emim][Br], m_{IL}, for the systems: ◇, [Emim][Br](IL) + K_3PO_4(s) + H_2O(w); □, [Emim][Br](IL) + K_2HPO_4(s) + H_2O(w); △, [Emim][Br](IL) + KH_2PO_4(s) + H_2O(w).

Table 7. Activity Coefficient $\gamma_\pm$ of [Emim][Br] and KH_2PO_4 for [Emim][Br] + KH_2PO_4 + H_2O Systems at $T = 298.15$ K by Schatchard's Equation at Different Ionic Strength Fraction *y* of [Emim][Br]

	I/mol·kg^{-1}				
y	0.5	0.75	1	1.25	1.5
			$\gamma_\pm$ ([Emim][Br])		
0.2	0.841	0.820	0.804	0.793	0.790
0.4	0.736	0.700	0.672	0.652	0.641
0.6	0.656	0.611	0.578	0.555	0.540
			$\gamma_\pm$ (KH_2PO_4)		
0.2	0.620	0.562	0.521	0.495	0.487
0.4	0.641	0.600	0.580	0.587	0.636
0.6	0.646	0.631	0.648	0.719	0.890

Table 8. Activity Coefficient $\gamma_\pm$ of [Emim][Br] and K_2HPO_4 for [Emim][Br] + K_2HPO_4 + H_2O Systems at $T = 298.15$ K by Schatchard's Equation at Different Ionic Strength Fraction *y* of [Emim][Br]

	I/mol·kg^{-1}					
y	0.5	1	1.5	2	2.5	3
			$\gamma_\pm$ ([Emim][Br])			
0.2	0.801	0.782	0.785	0.799	0.817	0.835
0.4	0.713	0.663	0.643	0.634	0.630	0.628
0.6	0.644	0.577	0.543	0.522	0.508	0.497
			$\gamma_\pm$ (K_2HPO_4)			
0.2	0.447	0.389	0.364	0.351	0.340	0.329
0.4	0.468	0.429	0.425	0.431	0.436	0.432
0.6	0.483	0.469	0.493	0.527	0.554	0.560

The osmotic coefficient, ϕ, of the mixed-electrolyte solutions is given by

$$\phi = \frac{\nu_R m_R \phi_R}{\sum_i m_i} \qquad (10)$$

which is valid only at isopiestic equilibrium. ν_R is the number of ions formed at the total dissociation of one molecule of the reference solute, NaCl. The Scatchard neutral-electrolyte method[8] gives for the osmotic coefficient

Table 9. Activity Coefficient $\gamma_\pm$ of [Emim][Br] and K_3PO_4 for [Emim][Br] + K_3PO_4 + H_2O Systems at $T = 298.15$ K by Schatchard's Equation at Different Ionic Strength Fraction *y* of [Emim][Br]

	I/mol·kg^{-1}						
y	0.5	1	1.5	2	2.5	3	3.5
				$\gamma_\pm$ ([Emim][Br])			
0.2	0.799	0.781	0.783	0.794	0.811	0.831	0.854
0.4	0.711	0.661	0.639	0.628	0.624	0.624	0.628
0.6	0.642	0.575	0.539	0.518	0.504	0.495	0.490
				$\gamma_\pm$ (K_3PO_4)			
0.2	0.346	0.292	0.269	0.258	0.253	0.251	0.252
0.4	0.372	0.330	0.321	0.325	0.337	0.354	0.376
0.6	0.400	0.375	0.388	0.419	0.465	0.525	0.601

$$(1 + 3y)\phi = 4y\phi^*_{\mathrm{IL}} + (1 - y)\phi^*_{\mathrm{S}} + 2y(1 - y)\cdot \left\{b_{01}\left(\frac{I}{m^0}\right) + b_{02}\left(\frac{I}{m^0}\right)^2 + b_{03}\left(\frac{I}{m^0}\right)^3\right\} \qquad (11)$$

where ϕ^*_{IL} and ϕ^*_{S} are the osmotic coefficients of pure [Emim][Br] and each of K_3PO_4, K_2HPO_4, and KH_2PO_4 solutions of the same ionic strength as the total ionic strength of the mixed-salt solution; and m^0 is a standard molality taken here as 1 mol·kg^{-1}. The parameters determined by the least-squares method are reported in Table 6 along with the standard deviation for the fit. To show the differences between the experimental and calculated osmotic coefficient in a better manner, the values for $\phi - \phi_{\mathrm{calcd}}$ are plotted against the molality of IL as shown in Figure 6. In preparing these figures, the unrestrictive parameters of Table 6 were used. Activity coefficients according to Scatchard's method,[8] given in Tables 7 to 9, at round total ionic strength were calculated by the equations

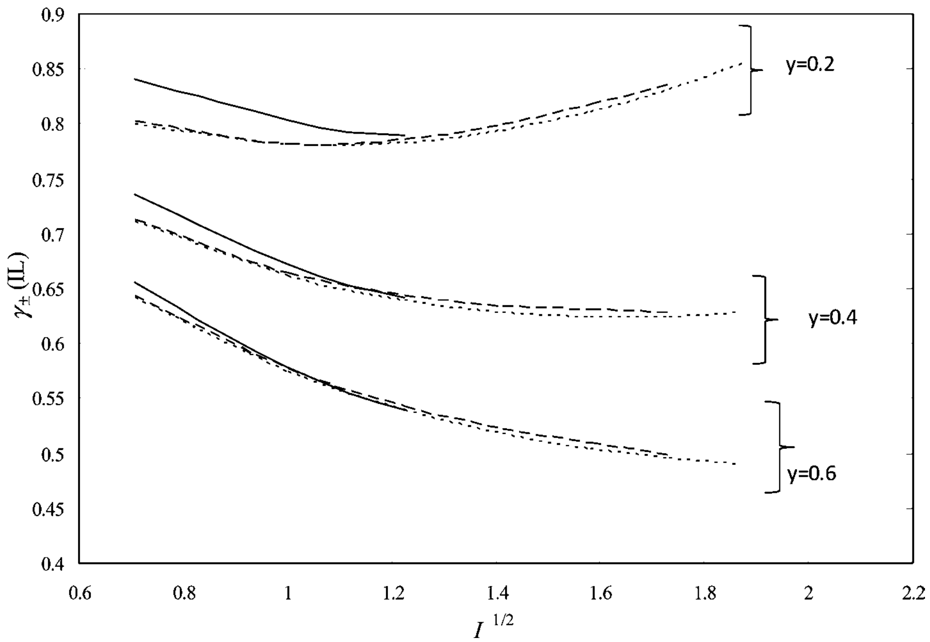

Figure 7. Plot of calculated activity coefficient, $\gamma_{\pm}$, of [Emim][Br] against square root of total ionic strength at constant values of ionic strength fraction (y = 0.2, 0.4, and 0.6) using the Scatchard method (eq 12) for the systems: —, [Emim][Br](IL) + KH_2PO_4(s) + H_2O(w); - - -, [Emim][Br](IL) + K_2HPO_4(s) + H_2O(w); ····, [Emim][Br](IL) + K_3PO_4(s) + H_2O(w).

$$2\ln\{\gamma_{\pm}(\mathrm{IL})\} = 2\ln\{\gamma_{\pm}^{*}(\mathrm{IL})\} + \{1/2(\phi_{\mathrm{S}}^{*} - 1) - 2(\phi_{\mathrm{IL}}^{*} - 1)\}(1 - y) + \left\{b_{01}\left(\frac{I}{m^0}\right) + b_{02}\left(\frac{I}{m^0}\right)^2 + b_{03}\left(\frac{I}{m^0}\right)^3\right\}(1 - y) - \left\{\frac{1}{2}b_{02}\left(\frac{I}{m^0}\right)^2 + \frac{2}{3}b_{03}\left(\frac{I}{m^0}\right)^3\right\}(1 - y)^2 \qquad (12)$$

and

$$\ln\{\gamma_{\pm}(\mathrm{S})\} = \ln\{\gamma_{\pm}^{*}(\mathrm{S})\} + \{4(\phi_{\mathrm{IL}}^{*} - 1) - (\phi_{\mathrm{S}}^{*} - 1)\}y + 2\left\{b_{01}\left(\frac{I}{m^0}\right) + b_{02}\left(\frac{I}{m^0}\right)^2 + b_{03}\left(\frac{I}{m^0}\right)^3\right\}y - 2\left\{\frac{1}{2}b_{02}\left(\frac{I}{m^0}\right)^2 + \frac{2}{3}b_{03}\left(\frac{I}{m^0}\right)\right\}y^2 \qquad (13)$$

where $\gamma_{\pm}$(IL) and $\gamma_{\pm}$(S) are the activity coefficients of pure [Emim][Br] and each of K_3PO_4, K_2HPO_4, and KH_2PO_4 solutions of the same ionic strength as the total ionic strength of the mixed-salt solution. The values of ϕ^* and $\gamma_{\pm}^{*}$ were calculated by the corresponding modified Pitzer equations for the appropriate single electrolyte solution. In Figure 7 the calculated activity coefficients of IL are plotted against the square root of ionic strength at constant values of ionic strength fraction of IL. As can be seen, at the constant ionic strength the values of activity coefficient of IL are decreased by increasing the charge of anion ($K_3PO_4 > K_2HPO_4 > KH_2PO_4$).

The water activity results for the mixed-salt solution are correlated by a semiempirical equation[18]

Table 10. Parameters of Equation 14 for the Studied Systems

system	b_0	b_1	$\sigma(a)$
K_3PO_4 (1) + [Emim][Br] (2) + H_2O	−0.00621	−0.02425	0.0006
K_2HPO_4 (1) + [Emim][Br] (2) + H_2O	−0.00395	−0.01687	0.0004
KH_2PO_4 (1) + [Emim][Br] (2) + H_2O	−0.00057	−0.00944	0.0001

$$a_{12} - a_{\mathrm{W}} = (a_1 - a_{\mathrm{W}}) + (a_2 - a_{\mathrm{W}}) + (m_1m_2)^{1/2}(b_0 + b_1(m_1m_2)^{1/2}) \qquad (14)$$

where a_{12}, a_1, a_2, and a_{W} represent, respectively, the water activity of mixed-salt solution, single-salt 1 and 2 solutions, and pure water ($a_{\mathrm{W}} = 1$). The single-salt water activities a_1 and a_2 are obtained from modified Pitzer osmotic coefficient correlations. The coefficients b_0 and b_1 are empirical parameters, and their values are reported in Table 10 along with the corresponding standard deviations for studied systems. On the basis of standard deviations reported in Table 10 we conclude that the performance of eq 14 is good in the correlation of water activity for the studied ternary systems.

Conclusions

The accurate water activity and osmotic coefficient measurements have been carried out at T = 298.15 K on 1-ethyl-3-methylimidazolium bromide in aqueous tripotassium phosphate, dipotassium hydrogen phosphate, and potassium dihydrogen phosphate solutions. The results show that the vapor pressure depression for a ternary aqueous [Emim][Br] + salt system is more than the sum of those for the corresponding binary solutions. The experimental osmotic coefficient data for the aqueous binary IL or salt solutions were fitted satisfactorily to the Pitzer and modified Pitzer models. The parameters obtained with these models were adopted to calculate the mean molal activity coefficients. Scatchard's neutral-electrolyte method for mixed electrolyte solutions is applied satisfactorily for calculation of activity coefficients. At the constant ionic strength the values of activity coefficient of IL are decreased by increasing the charge of anion ($K_3PO_4 > K_2HPO_4 > KH_2PO_4$).

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