Studies on Volumetric Properties of Concentrated Aqueous Amino Acid Ionic Liquid [C_3mim][Glu]

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A new amino acid ionic liquid, [C_3mim][Glu] (1-methyl-3-propylimidazolium glutamic acid salt), was prepared by a neutralization method and characterized by ^{1}H NMR and TA. Using an Anton Paar model DMA 4500 oscillating U-tube densitometer, the densities of aqueous [C_3mim][Glu] were measured over mole fraction of IL from 0.039 to 0.543 in the temperature range of T = (283.15 to 338.15) K at intervals of 5 K. Values of the apparent molar volumes of aqueous [C_3mim][Glu] were calculated and were treated by Pitzer−Simonson (PS) equation, Pitzer−Simonson−Clegg (PSC) equation, and the simplified PSC equation. In comparison with the values of PS and the simplified PSC parameters, the PSC parameters have a smaller standard deviation. Obviously, when the number of parameters augments, the fitting accuracy increases.

Introduction

Recently, amino acid ionic liquids (AAILs) have become one of the most rapidly growing new research areas of ionic liquids (ILs) and have attracted considerable attention from industry and the academic community because they are derived from natural ions and are heralded as new "natural ILs" or "bio-ILs"[1−8] that can be expected to find application in the biological, medical, and pharmaceutical sciences. Because there is a strong hydrogen bonding ability between AAIL and water, aqueous AAILs in a wide range of compositions provide an ideal opportunity for the chemistry of electrolyte solutions.[9,10]

Pitzer and coworkers have successfully treated electrolyte solutions of limited concentration by semiempirical equations based on a virial series plus a Debye−Hückel limiting term derived from rigorous statistical mechanics.[9] However, any virial expansion becomes unsatisfactory at sufficiently high concentration so that an alternative mole-fraction-based model has been developed by Pitzer and Simonson.[11] Then, Clegg and Pitzer[12,13]extended the model by introducing composition-dependent terms into the Debye−Hückel expression and an additional short-range parameter for the interaction between the solvent and a single anion and cation in highly concentrated solutions. As a continuation of our previous investigation,[14−16] this Article reports on the densities of aqueous 1-methyl-3-propylimidazolium glutamic acid salt [C_3mim][Glu] over the mole fraction from 0.039 to 0.543 measured using an Anton Paar model DMA 4500 oscillating U-tube densitometer in the temperature range of T = (283.15 to 338.15) K at intervals of 5 K. The values of the apparent molar volumes for the aqueous [C_3mim][Glu] were calculated and treated by the Pitzer−Simonson (PS) equation, the Pitzer−Simonson−Clegg (PSC) equation, and the simplified PSC equation.

Experimental Section

Chemicals. Deionized water was distilled in a quartz still, and its conductance was $(0.8 - 1.2)\cdot 10^{-4}$ S·m^{-1}. Glutamic acid was recrystallized twice from water/ethanol mixed solvent and was dried under reduced pressure. *N*-Methylimidazole AR grade reagent was vacuum distilled prior to use. Bromopropane (AR grade reagent) was distilled before use. Ethyl acetate and acetonitrile were distilled and then stored over molecular sieves in tightly sealed glass bottles. Anion-exchange resin (type 717) was purchased from Shanghai Chemical Reagent and activated by the regular method before use.

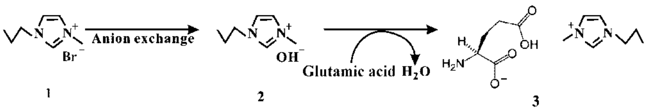

Figure 1. Preparation of AAIL [C_3mim][Glu] by the neutralization method: 1, [C_3mim][Br]; 2, [C_3mim][OH]; 3, [C_3mim][Glu].

Preparation of Amino Acid Ionic Liquids [C_3mim][Glu]. According to Fukumoto,[3] [C_3mim][Glu] was prepared by a neutralization method. (Figure 1 is the scheme.) First, [C_3mim]Br was synthesized according to literature.[17] The structure of [C_3mim]Br was confirmed by ^{1}H NMR spectroscopy (Varian XL-300), and the spectrum of ^{1}H NMR, which is in good agreement with the literature,[3] is listed in the Supporting Information (Figure A). Then, aqueous 1-methyl-3-propylimidazolium hydroxide ([C_3mim][OH] was prepared from [C_3mim]Br using anion-exchange resin in a 100 cm column. However, [C_3mim][OH] is not particularly stable, and it should be immediately used after preparation. The hydroxide aqueous solution was added dropwise to a slight excess of glutamic acid in aqueous solution. The mixture was stirred under cooling for 12 h. Then water was evaporated under reduced pressure. To this reaction mixture was added the mixed solvent (volumetric ratio: acetonitrile/methanol 9:1) under vigorous stirring, and the mixture was then filtered to remove excess glutamic acid. The filtrate was evaporated to remove solvents. The product of [C_3mim][Glu] was dried in vacuo for 2 days at 80 °C. When a small amount of the product was dissolved in water and aqueous silver nitrate was dripped, no white deposition appeared. The water content (w_2) of the product, determined by a Karl Fischer

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Table 1. Values of Densities of [C_3mim][Glu] and Aqueous Solutions at T = (283.15 to 338.15) K

	$\rho/(\mathrm{g \cdot cm^{-3}})$					
x_{IL}	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15
0.0390	1.09040	1.08842	1.08611	1.08372	1.08122	1.07864
0.0455	1.10076	1.09839	1.09592	1.09338	1.09077	1.08806
0.0497	1.10690	1.10445	1.10192	1.09930	1.09664	1.09389
0.0683	1.12912	1.12636	1.12356	1.12071	1.11781	1.11486
0.0783	1.13904	1.13621	1.13331	1.13035	1.12736	1.12433
0.0894	1.14770	1.14479	1.14180	1.13878	1.13572	1.13263
0.0975	1.15337	1.15037	1.14734	1.14430	1.14118	1.13807
0.1235	1.16978	1.16660	1.16335	1.16015	1.15696	1.15381
0.1451	1.17822	1.17507	1.17201	1.16885	1.16564	1.16249
0.1925	1.19185	1.18867	1.18547	1.18221	1.17890	1.17573
0.2390	1.20176	1.19815	1.19483	1.19161	1.18836	1.18505
0.2888	1.20810	1.20486	1.20146	1.19783	1.19459	1.19136
0.3294	1.21185	1.20849	1.20508	1.20185	1.19855	1.19530
0.3767	1.21500	1.21168	1.20849	1.20525	1.20191	1.19871
0.4265	1.21860	1.21472	1.21193	1.20967	1.20645	1.20315
0.4713	1.22069	1.21733	1.21390	1.21064	1.20732	1.20395
0.5112	1.22172	1.21847	1.21518	1.21178	1.20842	1.20515
0.5427	1.22307	1.22026	1.21693	1.21392	1.21064	1.20734
	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 328.15	T/K = 333.15	T/K = 338.15
0.0390	1.07597	1.07322	1.07037	1.06743	1.06443	1.06136
0.0455	1.08527	1.08241	1.07946	1.07644	1.07332	1.07011
0.0497	1.09107	1.08819	1.08524	1.08222	1.07913	1.07598
0.0683	1.11185	1.10880	1.10570	1.10255	1.09936	1.09610
0.0783	1.12125	1.11814	1.11498	1.11178	1.10854	1.10526
0.0894	1.12950	1.12634	1.12314	1.11990	1.11663	1.11331
0.0975	1.13491	1.13171	1.12849	1.12524	1.12194	1.11860
0.1235	1.15057	1.14732	1.14403	1.14073	1.13740	1.13405
0.1451	1.15924	1.15599	1.15270	1.14940	1.14606	1.14271
0.1925	1.17252	1.16927	1.16600	1.16268	1.15935	1.15598
0.2390	1.18178	1.17848	1.17527	1.17200	1.16859	1.16530
0.2888	1.18810	1.18482	1.18151	1.17821	1.17499	1.17172
0.3294	1.19209	1.18884	1.18558	1.18229	1.17898	1.17577
0.3767	1.19542	1.19217	1.18894	1.18567	1.18234	1.17904
0.4265	1.19974	1.19617	1.19288	1.18964	1.18635	1.18309
0.4713	1.20057	1.19703	1.19363	1.19041	1.18718	1.18394
0.5112	1.20178	1.19821	1.19479	1.19155	1.18822	1.18493
0.5427	1.20393	1.20061	1.19722	1.19366	1.19035	1.18707

moisture titrator (ZSD-2 type), was less than 0.84 mass %. The analysis by ^{1}H NMR resulted in a spectrum (Figure B of the Supporting Information) that was in good agreement with the literature[3] in addition to methylene and a little water. The thermal decomposition temperature of the IL, T_d was about 483 K, and was determined by thermogravimetric analysis using a TA Instruments (SDT) model Q600 thermogravimetric analyzer. (See Figure C of the Supporting Information.)

Measurement of Density. All aqueous solutions to be measured were freshly prepared by mass with allowance of air buoyancy. The uncertainty in the molal fraction of all ran solutions was within ± 0.02 %. The densities of aqueous [C_3mim][Glu] were measured from molar fraction 0.039 to 0.543 using an Anton Parr model DMA 4500 oscillating U-tube densitometer and are provided with an automatic viscosity correction in the temperature range of T = (283.15 to 338.15) K at intervals of 5 K. The temperature in the cell was regulated to ± 0.01 K with solid thermostat. The apparatus was calibrated once a day with dry air and freshly degassed pure water and gave an uncertainty of ± 0.00002 $\mathrm{g \cdot cm^{-3}}$.

Results and Discussion

Density and the Apparent Molar Volume of Aqueous Solution of [C_3mim][Glu]. The measured values of the densities of aqueous solution are listed in Table 1. Each value in Table 1 is an average of three determinations. As an example, Figure 2 is a plot of values of density against mole fraction, x_{IL}, at 283.15 K, 298.15 K, and 323.15 K. The apparent molar volumes, V_ϕ, are given by[18]

$$V_\phi = [1000(\rho_0 - \rho) + mM_2\rho_0]/m\rho\rho_0 \tag{1}$$

where ρ_0 and ρ are the density of pure water and aqueous [C_3mim][Glu], respectively, m is molality, which was obtained from x_{IL}, and M_2 is the molar mass of [C_3mim][Glu]. The

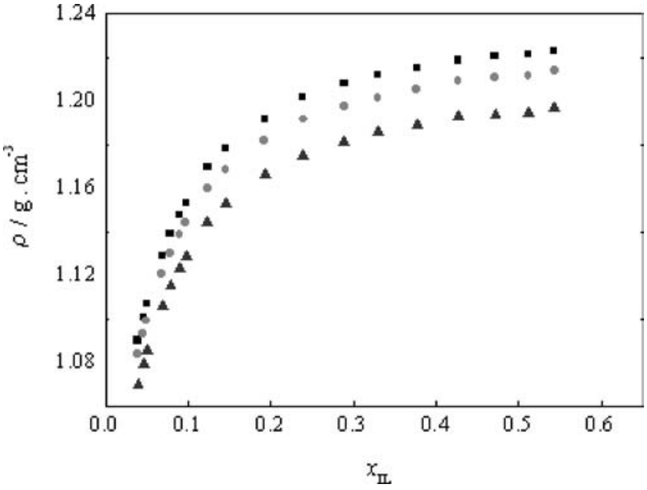

Figure 2. Plot of values of density, ρ, of aqueous [C_3mim][Glu] against mole fraction, x_{IL}: ■, T/K = 283.15; ●, T/K = 298.15; ▲, T/K = 323.15.

Table 2. Values of Apparent Molar Volume, V_ϕ, of [C$_3$mim][Glu] Solutions at T= (283.15 to 338.15) K

	V_ϕ/(cm^3·mol^{-1})					
x_{IL}	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15
0.0390	211.90	212.83	213.83	214.76	215.66	216.52
0.0455	211.77	212.82	213.81	214.75	215.63	216.50
0.0497	211.72	212.75	213.72	214.65	215.52	216.38
0.0683	212.14	213.11	214.03	214.92	215.77	216.59
0.0783	212.26	213.19	214.08	214.95	215.79	216.60
0.0894	212.73	213.63	214.50	215.35	216.16	216.96
0.0975	213.03	213.92	214.77	215.59	216.40	217.18
0.1235	213.34	214.20	215.04	215.84	216.60	217.34
0.1451	214.20	214.99	215.73	216.48	217.22	217.93
0.1925	215.46	216.19	216.91	217.63	218.35	219.02
0.2390	216.12	216.91	217.62	218.30	218.97	219.65
0.2888	216.93	217.60	218.31	219.05	219.70	220.35
0.3294	217.47	218.15	218.84	219.48	220.14	220.78
0.3767	218.02	218.69	219.31	219.95	220.60	221.22
0.4265	218.30	219.06	219.59	220.02	220.64	221.27
0.4713	218.61	219.25	219.91	220.54	221.17	221.81
0.5112	218.95	219.57	220.19	220.84	221.48	222.10
0.5427	219.06	219.59	220.22	220.79	221.40	222.03
	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 328.15	T/K = 333.15	T/K = 338.15
0.0390	217.35	218.15	218.94	219.71	220.46	221.18
0.0455	217.34	218.15	218.95	219.73	220.51	221.29
0.0497	217.20	217.99	218.76	219.52	220.26	220.99
0.0683	217.39	218.17	218.93	219.68	220.41	221.13
0.0783	217.39	218.16	218.91	219.65	220.37	221.09
0.0894	217.73	218.49	219.23	219.96	220.68	221.39
0.0975	217.95	218.70	219.43	220.15	220.87	221.58
0.1235	218.08	218.80	219.52	220.22	220.91	221.60
0.1451	218.64	219.34	220.04	220.72	221.41	222.08
0.1925	219.69	220.36	221.02	221.69	222.35	223.02
0.2390	220.31	220.98	221.61	222.25	222.92	223.56
0.2888	220.99	221.64	222.29	222.93	223.55	224.18
0.3294	221.40	222.04	222.67	223.30	223.94	224.55
0.3767	221.86	222.48	223.10	223.73	224.37	225.00
0.4265	221.92	222.61	223.24	223.85	224.48	225.10
0.4713	222.46	223.13	223.78	224.40	225.01	225.63
0.5112	222.74	223.42	224.07	224.68	225.32	225.94
0.5427	222.67	223.30	223.94	224.62	225.25	225.87

values of apparent molar volume calculated with eq 1 are listed in Table 2. As an example, Figure 3 is a plot of values of the apparent molar volume, V_ϕ, against mole fraction, x_{IL}, at 283.15 K, 298.15 K, and 323.15 K. From Figure 3, all of the V_ϕ versus x_{IL} curves, at any temperature, present a minimum at $x_{IL} = 0.05$. This is because at $x_{IL} = 0.05$, the distribution of ions in aqueous IL changes from a random pattern at low concentration to one of alternating positive and negative charges at higher concentration.

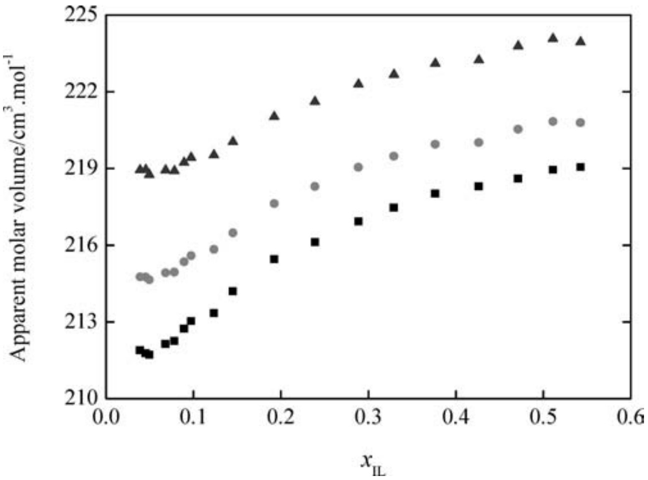

Figure 3. Plot of values of the apparent molar volume, V_ϕ/cm^3·mol^{-1}, of aqueous [C$_3$mim][Glu] against mole fraction, x_{IL}: ■, T/K = 283.15; ●, T/K = 298.15; ▲, T/K = 323.15.

Pitzer−Simonson Equation. The thermodynamics of electrolyte solutions have been successfully treated using a semiempirical model based on a virial series (in molality) and an extended Debye−Hückel term.[9] However, any virial expansion becomes unsatisfactory at sufficiently high concentration, and for a pure salt, the molality is infinite so that an alternative mole-fraction-based model has been developed by Pitzer and Simonson[11] for electrolytes of symmetrical charge type. For the apparent molar volume, V_ϕ, the PS equation is given by

$$V' = \{V_\phi - V_2^0(\text{ionic-liquid}) - (A_x^V/\text{b}) \ln[(1 + b\, I_x^{1/2})/(1 + bI_x^{0\ 1/2})]\}/2RTx_1 = W_{1,\,\text{MX}}^V + x_2 U_{1,\,\text{MX}}^V \quad (2)$$

where $V^0{}_2$(ionic-liquid) is the molar volume of the IL, MX, and the values were taken from literature.[19] $A_x{}^V$ is the Debye−Hückel parameter on mole fraction, and I_x is the ionic strength on a mole fraction basis given by $I_x = (1/2)\Sigma x_i Z_i{}^2$. PS parameters, $W^V{}_{1,\text{MX}}$ and $U^V{}_{1,\text{MX}}$, are specific to each solute MX and are functions of temperature and pressure, and $x_2 = x_\text{M} + x_\text{X}$ and $x_\text{i} = n_i/(n_1 + 2n_\text{i})$, where i is M or X. V' is the extrapolation function, which can be calculated using experimental data. According to working eq 2, the regressions of extrapolation function V' against x_2 were made using the least-squares program at different temperatures so that the values of $W^V{}_{A,\text{MX}}$, $U^V{}_{A,\text{MX}}$, standard deviation, s, and correlation coefficients, r, of the fits were obtained and are listed in Table 3. Figure 4 is a plot of

Table 3. Values of Pitzer−Simonson Parameters and Pitzer−Simonson−Clegg Parameters

	T/K = 283.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15
Two Parameters (Pitzer−Simonson Equation)						
$W^V \cdot 10^4$	−15.50	−14.05	−12.72	−11.51	−10.41	−9.450
$U^V \cdot 10^3$	3.094	2.915	2.753	2.583	2.479	2.383
$s \cdot 10^5$	7.7	7.2	6.4	6.4	6.1	5.8
r	0.991	0.991	0.992	0.991	0.991	0.991
Three Parameters (Simplified Pitzer−Simonson−Clegg Equation)						
$W^V \cdot 10^4$	−16.65	−15.09	−13.50	−12.10	−10.79	−9.635
$U^V \cdot 10^3$	1.922	1.848	1.961	1.981	2.085	2.194
$V^V \cdot 10^4$	25.95	23.63	17.52	13.31	8.732	4.192
$s \cdot 10^5$	5.3	5.1	5.2	5.8	5.9	5.9
r	0.995	0.996	0.995	0.993	0.992	0.991
Four Parameters (Pitzer−Simonson−Clegg Equation)						
$W^V \cdot 10^4$	−16.36	−14.52	−12.94	−11.60	−10.26	−9.054
$U^V \cdot 10^3$	4.730	7.412	7.421	6.860	7.286	7.909
$V^V \cdot 10^4$	−7.005	−41.66	−46.54	−43.93	−52.31	−62.87
$B^V \cdot 10^{-1}$	−1.077	−2.172	−2.168	−1.971	−2.136	−2.386
$s \cdot 10^5$	5.3	4.7	4.8	5.6	5.7	5.6
r	0.996	0.997	0.996	0.994	0.993	0.993
	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 328.15	T/K = 333.15	T/K = 338.15
Two Parameters (Pitzer−Simonson Equation)						
$W^V \cdot 10^4$	−8.576	−7.788	−7.039	−6.340	−5.593	−4.904
$U^V \cdot 10^3$	2.313	2.267	2.213	2.162	2.112	2.085
$s \cdot 10^5$	5.6	5.7	5.9	6.0	6.3	6.7
r	0.991	0.990	0.990	0.988	0.986	0.985
Three Parameters (Simplified Pitzer−Simonson−Clegg Equation)						
$W^V \cdot 10^4$	−8.560	−7.587	−6.659	−5.794	−4.927	−4.118
$U^V \cdot 10^4$	2.329	2.471	2.601	2.719	2.791	2.887
$V^V \cdot 10^4$	−0.366	−4.538	−8.586	−12.33	−15.03	−17.74
$s \cdot 10^5$	5.8	5.8	5.7	5.6	5.6	5.5
r	0.991	0.991	0.990	0.991	0.990	0.990
Four Parameters (Pitzer−Simonson−Clegg Equation)						
$W^V \cdot 10^4$	−7.950	−6.898	−5.968	−5.174	−4.309	−3.509
$U^V \cdot 10^4$	8.316	9.247	9.388	8.814	8.866	8.863
$V^V \cdot 10^4$	−70.62	−84.04	−88.23	−83.85	−86.31	−87.87
$B^V \cdot 10^{-1}$	−2.540	−2.920	−2.971	−2.709	−2.741	−2.738
$s \cdot 10^5$	5.4	5.1	5.1	5.1	5.1	5.1
r	0.993	0.993	0.993	0.993	0.992	0.992

the values of extrapolation function, V', against mole fraction, x_{IL}.

Pitzer−Simonson−Clegg Equation. Clegg and Pitzer[12,13] extended the PS theory[11] by introducing composition-dependent terms to the Debye−Hückel expression and an additional short-range parameter, $B_{\mathrm{MX}}\, g(x)$, for the interaction between the solvent and a single anion and cation in highly concentrated solutions. According to the PSC theory, the extrapolation working equation is

$$V'' = \{V_\phi - V_2^0(\text{ionic-liquid}) - (A_x^V/b)\ln[(1 + b\, I_x^{1/2})/(1 + bI_x^{0\,1/2})]\}/2RTx_1 = W^V_{1,\,\mathrm{MX}} + x_2U^V_{1,\,\mathrm{MX}} + x_1x_2V^V_{1,\mathrm{MX}} + x_2{}^2B^V_{\mathrm{MX}}\left(2I_x^{1/2}\right) \quad (3)$$

where $V^V{}_{1,\mathrm{MX}}$ and $B^V{}_{\mathrm{MX}}$ are new parameters of the PSC theory. Using the experimental data of V_ϕ for fitting eq 3, the values of the four parameters $W^V{}_{1,\mathrm{MX}}$, $U^V{}_{1,\mathrm{MX}}$, $V^V{}_{\mathrm{A,MX}}$, and $B^V{}_{\mathrm{MX}}$, standard deviation, s, and the correlation coefficients, r, of the fits were obtained at different temperatures, and these values are listed in Table 3. Figure 5 is a plot of the values of V'' for eq 3 against mole fraction, x_{IL}, of the IL. The comparison of Figures 5 and 4 shows that the result of the fitting of the PSC equation is better than that of the PS equation.

Simplified Pitzer−Simonson−Clegg Equation. Zhang et al.[16] point out that the $B^V{}_{\mathrm{MX}}$ parameter is taken directly from Pitzer's molality-based model and may be seen as an ionic-strength-dependent addition to the Debye−Hückel term. However, any data for dilute solution and parameter $B^V{}_{\mathrm{MX}}$ in eq 3 may be neglected so that the PSC equation is reduced to

$$V''' = \{V_\phi - V_2^0(\text{ionic-liquid}) - (A_x^V/b)\ln[(1 + b\, I_x^{1/2})/(1 + bI_x^{0\,1/2})]\}/2RTx_1 = W^V_{1,\,\mathrm{MX}} + x_2U^V_{1,\,\mathrm{MX}} + x_1x_2V^V_{1,\mathrm{MX}} \quad (4)$$

Using the experimental data of V_ϕ for fitting eq 4, the values of three parameters $W^V{}_{1,\mathrm{MX}}$, $U^V{}_{1,\mathrm{MX}}$, and $V^V{}_{1,\mathrm{MX}}$, standard deviation, s, and correlation coefficients, r, of the fits were obtained at different temperatures and are listed in Table 3. Figure 6 is a plot of the values of V''' in eq 4 against mole

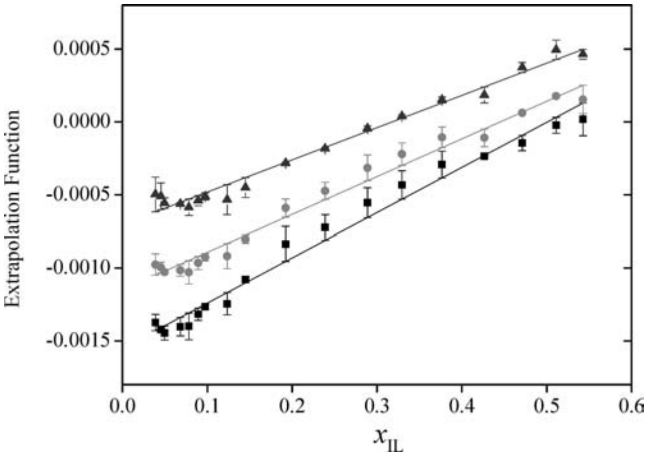

Figure 4. Plot of the values of extrapolation function against mole fraction, x_{IL}, fitting Pitzer−Simonson equation (two parameters). T/K = 283.15: ■, obsd; —, calcd. T/K = 298.15: ●, obsd; —, calcd. T/K = 323.15: ▲, obsd; —, calcd.

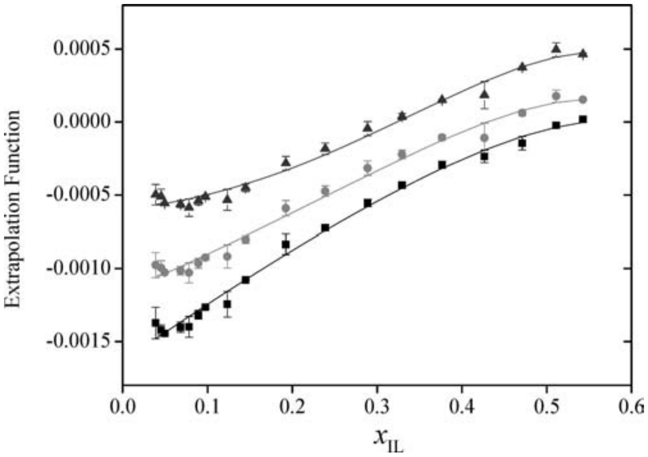

Figure 5. Plot of the values of extrapolation function against mole fraction, x_{IL}, fitting Pitzer−Simonson−Clegg equation (four parameters): T/K = 283.15: ■, obsd; −, calcd. T/K = 298.15: ●, obsd; −, calcd. T/K = 323.15: ▲, obsd; −, calcd.

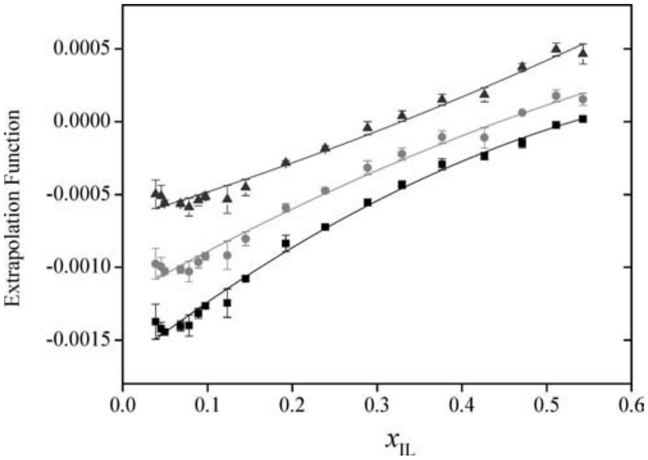

Figure 6. Plot of the values of extrapolation function against mole fraction, x_{IL}, fitting the simplified Pitzer−Simonson−Clegg equation (three parameters): T/K = 283.15: ■, obsd; −, calcd. T/K = 298.15: ●, obsd; −, calcd. T/K = 323.15: ▲, obsd; −, calcd.

fraction, x_{IL}, of IL. From Figure 6, the result of the simplified PSC equation is better than that of PS, but in comparison with Figure 5, it shows that the result of the fitting for four parameters is still better.

Conclusions

A new AAIL, [C$_3$mim][Glu], was synthesized, and the densities of aqueous [C$_3$mim][Glu] were measured over mole fraction of IL from 0.039 to 0.543 in the temperature range of (283.15 to 338.15) K. Values of the apparent molar volumes of aqueous [C$_3$mim][Glu] were calculated and were treated by the PS equation with two parameters, the PSC equation with four parameters, and the simplified PSC equation with three parameters. Obviously, when the number of parameters augments, the fitting accuracy increases.

Supporting Information Available:

Analysis of [C$_3$mim]Br by ^{1}H NMR, the ^{1}H NMR spectrum δ_H of [C$_3$mim]Br, analysis of the product by ^{1}H NMR, ^{1}H NMR spectrum δ_H of IL [C$_3$mim][Glu], and decomposition temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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