Density and Surface Tension of Amino Acid Ionic Liquid 1-Alkyl-3-methylimidazolium Glutamate

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An amino acid ionic liquid (AAIL) [C_3mim][Glu] (1-propyl-3-methylimidazolium glutamate) was prepared by the neutralization method and characterized by ^{1}H NMR spectroscopy and DSC trace. Since the AAIL has a strong hydrogen bonding ability, the water content $(8.41 \pm 0.01)\cdot10^{-3}$ mass fraction in the IL is difficult to remove by a common method, so trace water becomes the most problematic impurity. To eliminate the effect of the impurity water, the standard addition method (SAM) was applied to the measurement of densities and surface tensions for [C_3mim][Glu] in the temperature range of (318.15 to 343.15 ± 0.05) K and (318.15 to 338.15 ± 0.05) K, respectively. Since per methylene ($-CH_2-$) group in the alkyl chains of the imidazolium-based ionic liquids has almost the same chemical environment, using semiempirical methods we may predict physicochemical properties of 1-alkyl-3-methylimidazolium glutamate [$C_n$mim][Glu] (n = 1, 2, 3, 4, 5, 6): the molecular volume, V_m, the standard molar entropy, S^0, the parachor, P, the surface tension, γ, and the molar enthalpy of vaporization, $\Delta_l^g H_m^0$. In terms of the interstice model, the thermal expansion coefficient, α, was $3.28\cdot10^{-4}$ K^{-1}, which was in good agreement with experimental α for [C_3mim][Glu], $(4.35 \pm 0.03)\cdot10^{-4}$ K^{-1}.

Introduction

Since Kou et al.[1] and Fukumoto et al.[2,3] succeeded in synthesizing amino acid ionic liquids (AAILs) from natural amino acids, AAILs have attracted considerable attention from industry and the academic community as a new generation "greener ionic liquid".[1–6] Since AAILs have a strong hydrogen bonding ability that is useful for dissolved biomaterials, such as DNA, cellulose, and other carbohydrates, they can be expected to find application in all of the biological, medical, and pharmaceutical sciences.

Recently, there is a developing trend in the literature toward estimation of physicochemical properties for ILs, which is to be commended because it provides valuable insight into the origins of the behavior of ILs.[7] As a continuation of our previous investigation,[8,9] this paper reports that a new amino acid ionic liquid [C_3mim][Glu] (1-propyl-3-methylimidazolium glutamate) was prepared by the neutralization method according to Fukumoto[3] and characterized by ^{1}H NMR spectroscopy and DSC trace. The densities and surface tensions of [C_3mim][Glu] were measured at (318.15 to 343.15 ± 0.05) K and (318.15 to 338.15 ± 0.05) K, respectively. Since trace water is a problematic impurity in the AAIL, the standard addition method (SAM) was applied in these measurements.[10–12] Since per methylene ($-CH_2-$) group in the alkyl chains of the imidazolium-based ionic liquids has almost the same chemical environment, we may use semiempirical methods for predicting physicochemical properties of 1-alkyl-3- methylimidazolium glutamate [$C_n$mim]-[Glu] (n = 1, 2, 3, 4, 5, 6): the molecular volume, V_m, the standard molar entropy, S^0, the parachor, P, the surface tension, γ, the molar enthalpy of vaporization, $\Delta_l^g H_m^0$, and the thermal expansion coefficients, α.

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Experimental Section

Chemicals. Deionized water was distilled in a quartz still, and its conductance was $(0.8 \text{ to } 1.2)\cdot10^{-4}$ S·m^{-1}. Glutamic acid was recrystallized twice[11] and was dried in the pressure of (1.0 ± 0.1) kPa. 1-Methylimidazole AR grade reagent was obtained from ACROS and was vacuum distilled in the pressure of (1.0 ± 0.1) kPa prior to use. Bromopropane, ethyl acetate, and acetonitrile obtained from Beijing Chemicals Co. were AR grade reagent and were distilled before use. Anion-exchange resin (type 717) was purchased from Shanghai Chemical Reagent Co. Ltd. and activated by the regular method before use.

Preparation of AAIL [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 the literature.[13,14] The structure of [C_3mim]Br was confirmed by ^{1}H NMR spectroscopy (Varian XL-300), and the spectrum is in good agreement with the literature (see Figure A in Supporting Information).[13,14] 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 used immediately after preparation. The aqueous hydroxide was added dropwise to a slightly excess glutamic acid aqueous solution. The mixture was stirred under cooling for 12 h, and 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. Filtrate was evaporated to remove solvents. The product of [C_3mim][Glu] was dried in vacuo for 2 days at 80 °C. Taking a small amount of the product to dissolve in water, and then

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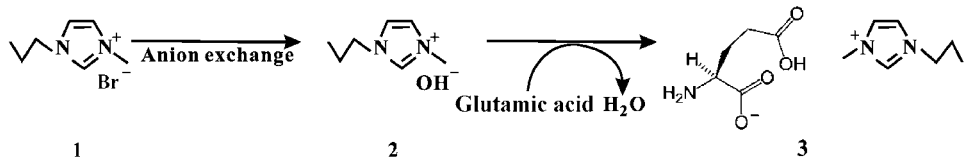

Figure 1. Preparation of AAIL [C_3mim][Glu] by the neutralization method. 1, [C_3mim][Br]; 2, [C_3mim][OH]; 3, [C_3mim][Glu].

Table 1. Values of Density, ρ (g·cm^{-3}), of [C_3mim][Glu] Containing Various Amount of Water at Different Temperatures[a]

	ρ (g·cm^{-3})							
10^3w (H_2O)	0 ± 0.02[b]	8.41 ± 0.01	10.02 ± 0.02	11.26 ± 0.02	12.81 ± 0.02	14.04 ± 0.02	10^4s(g·cm^{-3})	r
298.15	1.2292 ± 0.0004							
318.15	1.2186 ± 0.0004	1.2048 ± 0.0002	1.2020 ± 0.0002	1.2003 ± 0.0002	1.1974 ± 0.0001	1.1956 ± 0.0002	1.7	−0.99
323.15	1.2159 ± 0.0004	1.2022 ± 0.0002	1.1993 ± 0.0001	1.1976 ± 0.0002	1.1947 ± 0.0002	1.1930 ± 0.0001	2.0	−0.99
328.15	1.2132 ± 0.0004	1.1995 ± 0.0001	1.1967 ± 0.0002	1.1950 ± 0.0001	1.1920 ± 0.0002	1.1904 ± 0.0002	2.3	−0.99
333.15	1.2106 ± 0.0004	1.1969 ± 0.0002	1.1940 ± 0.0001	1.1923 ± 0.0002	1.1894 ± 0.0002	1.1877 ± 0.0002	2.0	−0.99
338.15	1.2082 ± 0.0004	1.1943 ± 0.0002	1.1914 ± 0.0001	1.1896 ± 0.0002	1.1867 ± 0.0001	1.1850 ± 0.0002	1.9	−0.99
343.15	1.2053 ± 0.0003	1.1916 ± 0.0001	1.1887 ± 0.0001	1.1870 ± 0.0002	1.1841 ± 0.0002	1.1824 ± 0.0001	2.0	−0.99

[a] w(H_2O) is water content. r is correlation coefficient, and s is standard deviation. [b] The extrapolated values for 0 mass fraction of water in [C_3mim][Glu].

Table 2. Values of Surface Tension, γ (mJ·m^{-2}), of [C_3mim][Glu] Containing Various Amounts of Water at Different Temperatures[a]

	γ (mJ·m^{-2})							
10^3w (H_2O)	0 ± 0.02[b]	8.90 ± 0.02	12.00 ± 0.02	15.10 ± 0.02	19.20 ± 0.02	22.20 ± 0.02	s (mJ·m^{-2})	r
298.15	60.8 ± 0.3							
318.15	54.7 ± 0.3	55.2 ± 0.2	55.4 ± 0.2	55.5 ± 0.2	55.7 ± 0.2	56.0 ± 0.2	0.06	0.98
323.15	53.2 ± 0.2	53.8 ± 0.1	54.0 ± 0.2	54.2 ± 0.2	54.4 ± 0.1	54.7 ± 0.2	0.04	0.99
328.15	51.8 ± 0.2	52.5 ± 0.2	52.6 ± 0.1	52.8 ± 0.2	53.1 ± 0.1	53.4 ± 0.2	0.07	0.99
333.15	50.1 ± 0.3	50.7 ± 0.2	51.2 ± 0.2	51.4 ± 0.1	51.7 ± 0.2	51.9 ± 0.2	0.10	0.98
338.15	48.7 ± 0.3	49.4 ± 0.2	49.9 ± 0.1	50.2 ± 0.2	50.4 ± 0.2	50.7 ± 0.1	0.11	0.98

[a] w(H_2O) is water content. r is correlation coefficient, and s is standard deviation. [b] The extrapolated values for 0 mass fraction of water in [C_3mim][Glu].

dripping aqueous silver nitrate, any deposition did not appear. The water content (w_2) of the product, determined by a Karl Fischer moisture titrator (ZSD-2 type), was (8.41 ± 0.01)·10^{-3} mass fraction. Analysis by ^{1}H NMR resulted in a spectrum (see Figure B in Supporting Information) in good agreement with the literature[3] except for a methylene (−CH_2−) group in the imidazole side chain. The thermal decomposition temperature of the IL, T_d = (483 ± 1) K, was determined by thermogravimetric analysis using a TA Instruments (SDT) model Q600 thermogravimetric analyzer (see Figure C in Supporting Information). Differential scanning calorimetric (DSC) measurements show that IL [C_3mim][Glu] has no melting point, but a glass transition temperature (T_g) is (−18.8 ± 0.1) °C (see Figure D in Supporting Information).

Measurement of Density and Surface Tension for AAIL [C_3mim][Glu]. Since the AAIL [C_3mim][Glu] has a strong hydrogen bonding ability, the small amounts of water in the AAIL are difficult to be removed by a common method so that trace water becomes the most problematic impurity. To eliminate the effect of the impurity water, the SAM was applied to the measurement of densities and surface tensions.[11,12] According to SAM, a series of samples of water-contained [C_3mim][Glu] were prepared.

The densities of degassed water (boiling and cooling) were measured by a Westphal balance (PZ-A-5 type produced by Shanghai Scientific Instrument Co.) in the temperature range of (318.15 to 343.15) K and were in good agreement with the literature[15] within experimental error of ± 0.0002 g·cm^{-3}. Then, the densities of the samples were measured in the same temperature range. The sample was placed in a cell with a jacket and was thermostatted at each temperature with an accuracy of ± 0.05 K.

Using the tensiometer of the forced bubble method (DPAW type produced by Sang Li Electronic Co.) which was thermostatted at each temperature with an accuracy of ± 0.05 K, the surface tension of water was measured in the temperature range of (318.15 to 338.15) K and was in good agreement with the literature[15] within experimental error ± 0.1 mJ·m^{-2}. Then the surface tension of AAIL samples was measured by the same method in the same temperature range.

Results and Discussion

Values of Density and Surface Tension for the Samples. The values of density and surface tension for the samples of [C_3mim][Glu] containing various contents of water were listed in Table 1 and Table 2, respectively. Each value in the tables is the average of triple measurements. According to SAM, the values of density and surface tension at given temperatures were plotted against the water content, w, of samples, so that the good straight lines were obtained and the intercepts were the values of density and surface tension of AAIL [C_3mim][Glu] without water, respectively. Figures 2 and 3 are the plots of density and surface tension against w at different temperature, respectively. The correlation coefficients, r, of all linear regressions are larger than 0.98, and the standard deviation, s, is within experimental error. These facts show that the standard addition method is suitable for AAIL [C_3mim][Glu].

The values of surface tension of the AAIL without water obtained from SAM vs T were fitted with a correlation coefficient of 0.9998, standard deviation s = 0.07 mJ·m^{-2}, so that the value of surface tension (γ = (60.8 ± 0.3) mJ·m^{-2}) at 298.15 K was obtained by using linear extrapolation.

Volumetric Properties of [$C_n$mim][Glu]. The values of ln ρ of [C_3mim][Glu] without water against T were fitted by the

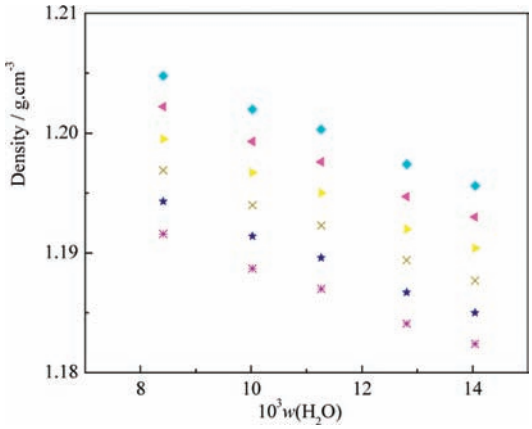

Figure 2. Plot of density vs water content, w, in [C_3mim][Glu]. ♦, 318.15 K; triangle pointing left, 323.15 K; triangle pointing right, 328.15 K; ×, 333.15 K; ★, 338.15 K; *, 343.15 K.

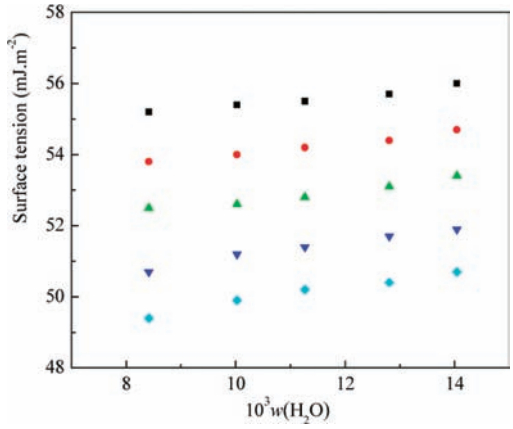

Figure 3. Plot of surface tension vs water content, w, in [C_3mim][Glu]. ■, 318.15 K; ●, 323.15 K; ▲, 328.15 K; ▼, 333.15 K; ♦, 338.15 K.

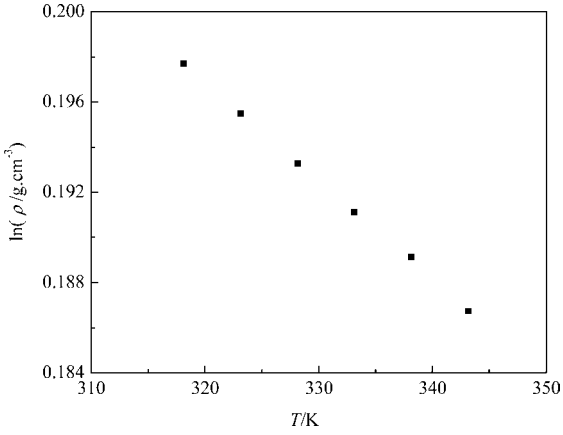

Figure 4. Plot of ln ρ vs T for [C_3mim][Glu].

method of least-squares, and an empirical equation $\ln \rho = 0.3361 - 4.35 \cdot 10^{-4} T$ was obtained (see Figure 4). The correlation coefficient is 0.999, and standard deviation $s = 1.0 \pm 10^{-4}$. The coefficient of thermal expansion of [C_3mim][Glu], α, is defined by the following equation

$$\alpha \equiv (1/V)(\partial V/\partial T)_p = (\partial \ln \rho/\partial T)_p \qquad (1)$$

so that the negative slop of the empirical equation, $\alpha = (4.35 \pm 0.03) \cdot 10^{-4}$ K^{-1}, was an experimental value of thermal expansion of AAIL [C_3mim][Glu] in the experimental temperature range. In eq 1, V is molar volume.

The molecular volume, V_m, of AAIL [C_3mim][Glu] was calculated using the following equation

$$V_m = M/(N \cdot \rho) \qquad (2)$$

where M is molar mass (271.3 g·mol^{-1}); N is the Avogadro constant; and the value of ρ was obtained in terms of the above empirical equation so that $V_m = 0.3666$ nm^3 for [C_3mim][Glu] was obtained.

According to our previous investigation, the contribution to molecular volume per methylene ($-CH_2-$) group is 0.0270 nm^3 in ILs [$C_n$mim][$AlCl_4$] ($n = 1, 2, 3, 4, 5, 6$)[16] and is 0.0278 nm^3 in ILs [$C_n$mim][Ala] ($n = 2, 3, 4, 5, 6$)[6] which agree well with a mean contribution of 0.0275 nm^3 per methylene ($-CH_2-$) group obtained by Glasser[17] from ionic liquids [$C_n$mim][BF_4] and [$C_n$mim][NTf_2]. This fact shows that the methylene ($-CH_2-$) group in the alkyl chains of the imidazolum-based ionic liquids has almost the same chemical environment so that we may use the mean value, 0.0275 nm^3, to predict the volumetric properties of other ILs of the homologue of [$C_n$mim][Glu] ($n = 1, 2, 4, 5, 6$) at 298.15 K. The predicted values are listed in Table 3. From Table 3, it can be seen that the predicted value of the molecular volume of [C_4mim][Glu], $V_m = 0.3941$ nm^3, is close to the corresponding experimental value, 0.3972 nm^3, obtained by Zhang.[18]

According to Glasser's theory,[17] the standard molar entropy for IL, S^0, is given by

$$S^0(298)/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 1246.5(V_m/\mathrm{nm^3}) + 29.5 \qquad (3)$$

so that values of S^0 for [$C_n$mim][Glu] were predicted and are listed in Table 3. These data imply entropy contribution per methylene group to standard entropy for [$C_n$mim][Glu] of 34.1 J·K^{-1}·mol^{-1}, and this value is in good agreement with the values of 33.9 J·K^{-1}·mol^{-1} for [$C_n$mim][BF_4] and of 35.1 J·K^{-1}·mol^{-1} for [$C_n$mim][NTf_2].[17]

The crystal energy, U_{POT}, may be estimated using the following equation[17]

$$U_{POT}/\mathrm{kJ \cdot mol^{-1}} = 1981.2(\rho/M)^{1/3} + 103.8 \qquad (4)$$

so that $U_{POT} = 432$ kJ·mol^{-1} for [C_3mim][Glu] was obtained, and the value is much less than that of fused salts; for example, $U_{POT} = 613$ kJ·mol^{-1} for fused CsI[15] which is the lowest crystal energy among alkali chlorides. The low crystal energy is the underlying reason for forming ionic liquid at room temperature. The values of the crystal energy for other ILs of the homologue of [$C_n$mim][Glu] ($n = 1, 2, 4, 5, 6$) were estimated using eq 4 and are also listed in Table 3.

Surface Tension of [$C_n$mim][Glu] Predicted by Parachor. Though the parachor, P, is a relatively old concept that relates the surface tension (γ) and density (ρ) of a substance using eq 5, Deetlefs et al.[19] pointed out that it is a remarkably useful tool to predict physicochemical properties of ILs.

$$P = (M\gamma^{1/4})/\rho \qquad (5)$$

Table 3. Values of Molecular Volume, V_m, Standard Molar Entropy, S^0, and Crystal Energy, U_{POT}, of ILs [$C_n$mim][Glu] and [$C_n$mim][Gly] (n = 1, 2, 3, 4, 5, 6) at 298.15 K

ionic liquid	ρ / g·cm^{-3}	V_m / nm^3	S^0 / J·K^{-1}·mol^{-1}	U_{POT} / kJ·mol^{-1}
[C_1mim][Glu]	1.2969 ± 0.0004	0.3116 ± 0.0001	417.9 ± 0.1	450 ± 1
[C_2mim][Glu]	1.2603 ± 0.0004	0.3391 ± 0.0001	452.2 ± 0.1	440 ± 1
[C_3mim][Glu]	1.2292 ± 0.0004	0.3666 ± 0.0001	486.5 ± 0.1	432 ± 1
[C_4mim][Glu]	1.2024 ± 0.0004	0.3941 ± 0.0001	520.8 ± 0.1	424 ± 1
[C_4mim][Glu][a]	1.1967	0.3972	525.0	423
[C_5mim][Glu]	1.1792 ± 0.0004	0.4216 ± 0.0001	555.1 ± 0.1	417 ± 1
[C_6mim][Glu]	1.1587 ± 0.0004	0.4491 ± 0.0001	589.3 ± 0.1	410 ± 1

[a] Zhang, Q.-G. Doctoral Dissertation, Xining, Institute of Salt Lakes, Chinese Academy of Sciences, 2007; p 123.

Table 4. Values of Parachor, Surface Tension, Molar Enthalpy of Vaporization, and Thermal Expansion Coefficient of [$C_n$mim][Glu] (n = 1, 2, 3, 4, 5, 6) at 298.15 K

ionic liquid	[C_1mim][Glu]	[C_2mim][Glu]	[C_3mim][Glu]	[C_4mim][Glu]	[C_5mim][Glu]	[C_6mim][Glu]
P	554.3 ± 0.9	585.3 ± 0.9	616.3 ± 0.9	647.3 ± 0.9	678.3 ± 0.9	709.3 ± 0.9
γ/mJ·m^{-2}	76.2 ± 0.3	67.6 ± 0.3	60.8 ± 0.3	55.4 ± 0.3	51.0 ± 0.3	47.4 ± 0.3
$\Delta_l^g H_m^0$/kJ·mol^{-1}	238.8 ± 1.1	224.1 ± 1.1	212.6 ± 1.1	203.3 ± 1.1	195.9 ± 1.1	189.8 ± 1.1
$10^4\alpha$/K^{-1}(calcd)	2.75 ± 0.03	3.03 ± 0.03	3.28 ± 0.03	3.51 ± 0.03	3.72 ± 0.03	3.89 ± 0.03
$10^4\alpha$/K^{-1}(exptl)			4.35 ± 0.03	4.13[a]		

[a] Zhang, Q.-G. Doctoral Dissertation, Xining, Institute of Salt Lakes, Chinese Academy of Sciences, 2007; p 123.

where γ and ρ are surface tension and density at 298.15 K and M is molar mass. Using eq 5, the experimental value of parachor, P = 616.3, at 298.15 K for [C_3mim][Glu] was calculated.

Considering the methylene (−CH_2−) group in the alkyl chains of the imidazolum-based ionic liquids has almost the same chemical environment, we have put forward the semiempirical method of predicting P of the ILs[16] that is an experimental value of parachor for a compound of the homologue of ILs plus the contributions of per methylene (−CH_2−) to parachor. In our previous paper, the contributions of per methylene (−CH_2−) to parachor are 31.1 from the homologous series of ILs [$C_n$mim][$AlCl_4$],[16] 31.0 from [$C_n$mim][$GaCl_4$],[20] and 30.9 from [$C_n$mim][$InCl_4$],[21] so that the average is 31.0. For this reason, the values of parachor for the homologue of AAILs [$C_n$mim]-[Glu] can be predicted, and the predicted values for the homologue [$C_n$mim][Glu] (n = 1, 2, 3, 4, 5, 6) are listed in Table 4.

From eq 5 we can seen that the parachor is available as a link between the structure, density, and surface tension, and it may become a tool to estimate surface tension of ILs from its density and vice versa. Therefore, the values of surface tension for ILs [$C_n$mim][Glu] (n = 1, 2, 4, 5, 6) at 298.15 K were estimated using eq 5 and are also listed in Table 4.

According to Kabo's empirical equation[22]

$$\Delta_1^g H_m^0(298\ \mathrm{K}) = 0.01121(\gamma V^{2/3} N^{1/3}) + 2.4\ \mathrm{kJ \cdot mol^{-1}} \quad (6)$$

The molar enthalpy of vaporization, $\Delta_l^g H_m^0$(298 K), of ionic liquids can be estimated. In eq 6, V is molar volume, and its value may be calculated from above V_m; γ is surface tension, and its value has been estimated by parachor; and N is Avogadro's constant. The values of the molar enthalpy of vaporization, $\Delta_l^g H_m^0$(298 K), for [$C_n$mim][Glu] were calculated from eq 6 and are listed in Table 4.

According to the interstice model,[23,24] an expression for calculation of interstice volume, v, was obtained by classical statistical mechanics

$$v = 0.6791(k_b T/\gamma)^{3/2} \quad (7)$$

where k_b is the Boltzmann constant; T is thermodynamic temperature; and γ is surface tension of ILs [$C_n$mim][Glu] (n = 1, 2, 3, 4, 5, 6), which have been estimated above.

The molar volume of ionic liquids, V, consists of the inherent volume, V_i, and total volume of the all interstices; that is

$$V = V_i + 2Nv \quad (8)$$

If the expansion of IL volume only results from the expansion of the interstices when temperature increases, then calculation expression of thermal expansion coefficients, α, was derived from the interstice model

$$\alpha = (1/V)(\partial V/\partial T)_p = 3Nv/VT \quad (9)$$

The values of α(calcd) calculated using eq 9 for ILs [$C_n$mim]-[Glu] and of corresponding experimental value, α(exptl), are listed in Table 4. From Table 4, the magnitude order of α(calcd) is in good agreement with α(exptl) for [C_3mim][Glu] and [C_4mim][Glu] .

Supporting Information Available:

Analysis of [C_3mim]Br by ^{1}H NMR resulting in a spectrum (see Figure A); analysis of the product by ^{1}H NMR; decomposition temperatures; and DSC trace. This material is available free of charge via the Internet at http://pubs.acs.org.

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