Volumetric property of glycine, L-serine, L-alanine and L-proline in aqueous
solutions of 1-phenylpiperazinium tetrafluoroborate

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Abstract

The densities of aqueous solutions of glycine, L-serine, L-alanine, L-proline with the ionic liquid (IL), 1-phenylpiperazinium tetrafluoroborate ([Phpi][BF₄]) at the IL concentrations of (0.025, 0.055 and 0.100) mol·kg⁻¹ have been measured at the temperatures of (298.15, 303.15 and 308.15) K. On the basis of the experimental results, the apparent molar volume (V_{Φ}), standard partial molar volume (V_{Φ}^0), transfer partial molar volume ($\Delta_{tr}V_{\Phi}^0$) and hydration number (n_H) have been calculated. The hydrophilic-hydrophilic, hydrophobic-hydrophilic and hydrophobic-hydrophobic interactions are involved in the studied systems of {[Phpi][BF₄] + amino acids + H₂O}. These volumetric parameters can help to understand the mixing effects and other complex biological processes between amino acids and ionic liquid aqueous solution.

Keywords: ionic liquid; amino acid; apparent molar volume; standard partial molar volume; transfer partial molar volume; hydration number

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1. Introduction

Salt solutions have great influences on the structures and properties of the protein, *e.g.*, the solubility of proteins, denaturation, secondary structure and enzyme activity [1–3], and these influences can be destructive or protective for proteins [4–6]. In the past decades, ionic liquids (ILs) came out as novel abstraction media in the form of aqueous two phase system (ATPS) for abstracting biological macromolecules, including protein and polysaccharide [7–14]. The determination of the physicochemical properties of IL solutions containing amino acids can be helpful to understand the interactions between ILs and biological macromolecules [15–27]. Thus, the investigations on the volumetric properties of various amino acids with organic molecules or salts aqueous solutions have been carried out [28–30].

Volumetric studies can provide unique information in terms of ligand-binding properties, the folding/unfolding character and conformational stability of a protein [31–32]. Among the important thermodynamic parameters of the protein, standard partial molar volume is often used to discuss the hydration process, the stability of protein configuration and the interactions between protein and IL [33–38]. Usmani *et al.* [39] studied the interactions in the (L-alanine/L-threonine + aqueous glucose/aqueous sucrose) systems. The standard partial molar volumes (V_{Φ}^0) and transfer partial molar volume ($\Delta_{tr}V_{\Phi}^0$) of L-alanine and L-threonine in the 1 mol·L⁻¹ sucrose solution are higher than those in the 1 mol·L⁻¹ glucose solution, and it is ascribed to the stronger ionic-hydrophilic and hydrophilic-hydrophilic interactions between zwitterions and –OH groups of sucrose than those with the –OH groups of glucose. Fang *et al.* [40] determined the apparent molar volumes (V_{Φ}) of glycine, L-alanine, L-arginine and L-phenylalanine in mixed aqueous solutions of 1-ethyl-3-methylimidazolium bromide ([EMIm]Br). Other volumetric parameters including V_{Φ}^0 , transfer partial molar volume ($\Delta_{tr}V_{\Phi}^0$), and hydration numbers (n_H) were also obtained. The $\Delta_{tr}V_{\Phi}^0$ values are negative for the glycine, L-alanine, and L-phenylalanine solutions, while positive for the L-arginine solution. In addition, the hydration numbers decrease with the increase of [EMIm]Br concentration and temperature. Wang *et al.* [41] investigated the interactions of amino acids with

aqueous solutions of hydroxypropyl- β -cyclodextrin (HP- β -CD) at different temperatures. The density and viscosity for 0.01 mol·kg⁻¹ aqueous solutions of HP- β -CD with the presence of glycine, L-alanine, L-valine and L-phenylalanine at different temperatures were measured. V_{Φ} , V_{Φ}^0 , S_v , ΔV_{Φ}^0 , Φ_E^0 , n_H , the Falkenhagen coefficient and Jones-Dole coefficient were also calculated. The results indicate the existence of strong interactions between HP- β -CD and amino acids.

In this paper, we measured the densities of aqueous solutions of glycine, L-serine, L-alanine and L-proline with ionic liquid, 1-phenylpiperazinium tetrafluoroborate ([Phpi][BF₄]), at the IL molality of 0.025, 0.055, and 0.100 mol·kg⁻¹ and at the temperatures of (298.15, 303.15 and 308.15) K. The values of V_{Φ} , V_{Φ}^0 , $\Delta_{tr}V_{\Phi}^0$, and hydration number (n_H) are also calculated. The interactions in the ternary systems of ([Phpi][BF₄] + amino acids + H₂O) are discussed based on these volumetric parameters.

2. Experimental

2.1. Chemicals

Glycine (mass fraction >0.99), L-serine (>0.99), L-alanine (>0.99) and L-proline (>0.99) were obtained from Aladdin Industrial Inc. (Shanghai, China), these reagents were used with recrystallization and drying under vacuum. 1-Phenylpiperazine (>0.99) and tetrafluoroboric acid (0.495–0.505 aqueous solution) were purchased from Aldrich. These chemicals were used without further purification. The detailed information of the materials is listed in table 1.

2.2. Synthesis of [Phpi][BF₄]

Tetrafluoroboric acid (0.1 mol) was added dropwise to the 1-phenylpiperazine aqueous solution (0.1 mol) that was cooled in an ice-water bath under the protection of nitrogen gas. After 6 h of vigorous stirring, the solvent was removed under vacuum. The brown solid was recrystallized with 1-butanol and water, and it was further dried by freeze-drier (Peking Sihuan Scientific Instrument, LGJ-10, China). The obtained product, [Phpi][BF₄], was stored in a pure nitrogen atmosphere [42].

¹H and ¹³C NMR characterizations of [Phpi][BF₄] were recorded on an Avance III, Bruker 400Hz spectrometer with D₂O as solvent. The spectra are presented in the

Supporting Information (figures S1 and S2). The chemical shifts of [Phpi][BF₄] are: δ_H 6.98-7.33 (m, 5H, hydrogen atoms on the benzene ring), 3.33-3.32 (m, 8H, N-(CH₂-C)₂-N⁺ and N-(C-CH₂)₂-N⁺); δ_c 43.00 (N-(C-CH₂)₂-N⁺), 46.95 (N-(CH₂-C)₂-N), 117.79, 122.65 and 129.65 (carbon atoms on the benzene ring). The water content in [Phpi][BF₄] was determined via a Karl-Fischer titration on a coulometer (Mettler Toledo, C20, Switzerland), and it was lower than 0.0001 mass fraction. The purity of [Phpi][BF₄] is higher than 0.99 mass fraction.

The thermostability of IL was determined by TGA (DSC1, Mettler Toledo) and the data can be found in the Supporting Information (figure S3).

2.3. Apparatus and procedure

All solutions were prepared with ultra pure water with resistivity $\geq 18.2 \text{ M}\Omega \cdot \text{cm}$ and supplied by ultra-pure water meter (Milipore, France). The weights of the materials were determined on a Mettler Toledo AL204 balance with a precision of 0.0001g. The standard uncertainty of molality is $u(m) = 0.01m$.

The densities (ρ) of all solutions at the temperature (T) of $T = (298.15, 303.15 \text{ and } 308.15) \text{ K}$ and atmospheric pressure $p = 0.1 \text{ MPa}$ were measured using the Anton Paar DMA55 (Austria) density meter. The standard uncertainties of temperature and pressure is $u(T) = 0.01 \text{ K}$ and $u(p) = 2000 \text{ Pa}$. The density meter was calibrated by dry air and ultra-pure water before measurements, and the standard uncertainty of density is $u(\rho) = 2 \times 10^{-4} \text{ g} \cdot \text{cm}^{-3}$.

3. Results and discussion

3.1. Apparent molar volume

The densities of solutions containing amino acids and ([Phpi][BF₄]) as a function of the IL concentration at different temperatures are listed in tables 2, 3 and 4, respectively. The apparent molar volumes (V_ϕ) of glycine, L-serine, L-alanine and L-proline in aqueous solutions of [Phpi][BF₄] have been calculated based on the following equation [40].

$$V_\phi = \frac{M}{\rho} - \frac{1000(\phi - \rho_0)}{m\rho_0\rho} \quad (1)$$

where M and m are the molar mass and molality of amino acid in ([Phpi][BF₄] +

H₂O) solutions, respectively, and ρ and ρ_0 are the densities of the ([Phpi][BF₄] + amino acids + H₂O) and ([Phpi][BF₄] + H₂O) solutions, respectively. The calculated results are also listed in tables 2, 3 and 4.

The V_Φ values of four kinds of amino acids increase when the temperature and molality of amino acid are elevated. The apparent molar volumes of four amino acids follow the order. L-proline > L-serine $\approx$ L-alanine > glycine. The apparent molar volumes increase with the increase of the size of alkyl chain for four amino acids, and the positive apparent molar volumes indicate the strong solute-solvent interactions [41].

3.2. Standard Apparent Molar Volume

The V_Φ^0 value is calculated using the following equation [40].

$$V_\phi = V_\phi^0 + B_v m \quad (2)$$

where V_Φ^0 stands for the partial molar volume [39], which by definition is free from interactions between solutes and reveals the solute-solvent interactions, and B_v represents the liner regression slope parameter in the model and provides information about solute-solute interactions. The V_Φ^0 values of glycine, L-serine, L-alanine, L-proline are listed in table 5.

The V_Φ^0 value increases generally with temperature, carbon atom number, as well as the size of alkyl group of amino acids and the increase of the molality of [Phpi][BF₄]. The V_Φ^0 values follow the order. L-proline > L-serine $\approx$ L-alanine > glycine. The V_Φ^0 of L-alanine appears to be larger than that of L-serine because of the structure-enhancing behaviour of alkyl group. In fact, the V_Φ^0 value of L-alanine is very close to that of L-serine, which can be ascribed to the hydrophilic –OH group of L-serine, making L-serine act as a structure breaker [43]. Thus, the increase of V_Φ^0 originating from the increase of group size is slightly offsetted by the structure-breaking effect of the –OH group in L-serine. All of the V_Φ^0 values are positive for four amino acids at studied temperatures, which indicate that strong solute-solvent interactions exist in these systems [44]. Meanwhile, the V_Φ^0 values of four amino acids increase with the rising temperature in aqueous [Phpi][BF₄] solution.

It can be explained by the size of primary and secondary solvation layers around the zwitterions moieties of amino acids. In other words, solvent molecules from the secondary solution layer of amino acids zwitterions release into the bulky solvent at higher temperatures, leading to the volume expansion of the solution with the increase of the temperature [45].

The interaction modes in these ternary systems can be classified as follows. (a) hydrophilic-hydrophilic interactions between the charged head group of amino acids and charged ionic moieties of IL. The interactions between the zwitterions head group ($-\text{OH}$ and $-\text{NH}_2$) of each amino acid and $[\text{Phpi}][\text{BF}_4]$ aqueous solution mainly belong to hydrophilic-hydrophilic interactions, which leads to the reduction of the electrostriction of water molecules and increase the V_ϕ^0 value. Whereas the V_ϕ^0 value decreases due to the disruption of the hydration of $-\text{OH}$ and $-\text{NH}_2$ groups [45]; (b) hydrophobic-hydrophilic interactions between ions of ionic liquid ($[\text{Phpi}]^-$ and $[\text{BF}_4]^+$) and hydrophobic side chain of amino acids. (c) hydrophobic-hydrophobic interactions between the side chain of L-alanine, L-proline and the benzene ring of IL.

3.3. Transfer partial molar volume ($\Delta_{\text{tr}}V_\phi^0$)

Standard partial molar properties provide information regarding solute and solvent interactions without taking the effect of solute and solute interactions into account [41], and the transfer partial molar volume ($\Delta_{\text{tr}}V_\phi^0$) of amino acids are calculated from standard partial molar volume. The value of $\Delta_{\text{tr}}V_\phi^0$ is related to the volume increase or decrease of corresponding amino acids in transferring from pure water to the $[\text{Phpi}][\text{BF}_4]$ solutions. According to previous experiment results [39], the positive or negative $\Delta_{\text{tr}}V_\phi^0$ value stands for the volume increase or decrease of related amino acids in transporting from pure water to aqueous ionic liquids solutions. The $\Delta_{\text{tr}}V_\phi^0$ values of glycine, L-serine, L-alanine and L-proline from water to aqueous solution of $[\text{Phpi}][\text{BF}_4]$ are calculated based on the following relationship.

$$\Delta_{\text{tr}}V_\phi^0 = V_\phi^0(\text{in aqueous } [\text{Phpi}][\text{BF}_4] \text{ solution}) - V_\phi^0(\text{in pure water}) \quad (3)$$

The calculated values of $\Delta_{\text{tr}}V_\phi^0$ are summarized in table 5, and the $\Delta_{\text{tr}}V_\phi^0$ values are negative for glycine, L-serine, L-alanine, L-proline within the temperature range

of the present study, while the $\Delta_{tr}V_{\Phi}^0$ values are positive for glycine at the [Phpi][BF₄] molality of 0.1 mol·kg⁻¹. In addition, the $\Delta_{tr}V_{\Phi}^0$ value of each amino acid increases with the increasing [Phpi][BF₄] concentration, and the $\Delta_{tr}V_{\Phi}^0$ value of L-serine and L-alanine decline in the IL molality of 0.055 mol·kg⁻¹, but increase at 0.1 mol·kg⁻¹. At the same time, temperature always arose with the decrease of $\Delta_{tr}V_{\Phi}^0$ value in the ternary system. However, the values of $\Delta_{tr}V_{\Phi}^0$ of glycine and L-alanine become less negative with increasing molality and more negative with increasing temperature. The expansion or shrinkage effects of the interactions in these ternary systems can be explained by co-sphere overlap model [45]. The hydrophilic-hydrophilic interaction can release some water molecules back to their original position, which can lead to a positive $\Delta_{tr}V_{\Phi}^0$ value [40]. Therefore the observed negative value of $\Delta_{tr}V_{\Phi}^0$ in table 5 is due to the stronger hydrophobic-hydrophobic and hydrophilic-hydrophobic interactions compared with hydrophilic-hydrophilic interaction mentioned above. The small positive $\Delta_{tr}V_{\Phi}^0$ value of glycine in 0.100 mol·kg⁻¹ [Phpi][BF₄] solution shows that the hydrophilic-hydrophilic interaction is more stronger than hydrophobic-hydrophobic and hydrophilic-hydrophobic interactions. Moreover, the small negative values of $\Delta_{tr}V_{\Phi}^0$ of glycine and L-serine indicate that there is a balance among all these interactions. As shown in table 5, the $\Delta_{tr}V_{\Phi}^0$ values of L-alanine are more negative than those of L-serine. For L-serine, the hydrophilic-hydrophilic interactions exist between ionic moieties of IL and the hydrophilic groups of amino acids. For L-alanine, the hydrophilic-hydrophilic interactions exist between the head groups (NH₃⁺, COO⁻) and [Phpi][BF₄], and the hydrophobic-hydrophilic interactions exist between the methyl group and [Phpi][BF₄]. The smallest negative $\Delta_{tr}V_{\Phi}^0$ value is observed for L-proline, which is dominated by hydrophilic-hydrophobic and hydrophobic-hydrophobic interactions [46]. However, the negative values of $\Delta_{tr}V_{\Phi}^0$ in four kinds of amino acids indicate that the hydrophilic-hydrophobic and hydrophobic-hydrophobic interactions are the predominant interactions. Hydrophobic-hydrophobic interaction can be enhanced by the interaction between side chain of amino acid and the benzene ring in [Phpi][BF₄]. Nevertheless, the interaction mechanism between amino acids and IL solution should be complex, and it

significantly depends on the type of amino acid and the ionic moieties of IL.

3.4. Hydration number

The number of water molecules (n_H) hydrated to the amino acid can be obtained from standard partial molar volume (V_ϕ^0) from the following equation [47].

$$n_H = \frac{V_\phi^0(\text{elect})}{V_e^0 - V_b^0} \quad (4)$$

where V_e^0 is the molar volume of electrostrictive water and V_b^0 is the molar volume of bulk water, respectively. According to the report by Millero *et al.* [47], this model assumes that water molecules can be taken from the bulk phase into the region near the amino acid. Furthermore, the volume is decreased by $(V_e^0 - V_b^0)$, whose value is $-3.3 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 298.15 K and $-4.0 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 308.15 K. The electrostriction partial molar volume $V_\phi^0(\text{elect})$ can be expressed as follow.

$$V_\phi^0(\text{elect}) = V_\phi^0(\text{int}) - V_\phi^0(\text{cryst}) \quad (5)$$

where $V_\phi^0(\text{int})$ is the intrinsic partial molar volume. $V_\phi^0(\text{int})$ can be calculated according to the equation.

$$V_\phi^0(\text{int}) = \frac{0.7}{0.634} V_\phi^0(\text{cryst}) \quad (6)$$

where 0.7 and 0.634 stand for the packing density for molecules in organic crystals and random packing sphere, respectively. The $V_\phi^0(\text{cryst})$ is obtained from the investigation of dry amino acids by Berlin *et al.* [48].

According to table 6, it shows that the n_H values of amino acids decrease when the concentration of [Phpi][BF₄] aqueous solution or the temperature increases. It is also found that the hydration effect is stronger in pure water than that in the [Phpi][BF₄] solution. The hydration number of the amino acid (*e.g.* L-serine) reduces significantly when the temperature increases [40]. The enhancement of electrostriction around the zwitterion end group of amino acids leads to a larger value of hydration number [41]. The results also confirm that the [Phpi][BF₄] has dehydration effect in these systems. Density functional theory calculations have also been performed for the ternary systems formed by ionic liquid, amino acids and water molecules, and the optimized structures ($\text{\AA}$) of these complexes are shown in figure 1. The computational details

can be found in supporting information. The calculations showed that these complexes are generated via multiple hydrogen bond interactions between ionic liquid, amino acids and water molecules.

4. Conclusions

The partial molar volumes (V_{Φ}) of glycine, L-serine, L-alanine, L-proline in aqueous solution of ionic liquid (IL), 1-phenylpiperazinium tetrafluoroborate ([Phpi][BF₄]), have been obtained from density data at 298.15, 303.15, and 308.15 K, and the other parameters including standard partial molar volume (V_{Φ}^0), transparent partial molar volume ($\Delta_{tr}V_{\Phi}^0$) and hydration number (n_H) were also calculated. The results showed that the $\Delta_{tr}V_{\Phi}^0$ values are negative for four kinds of amino acids, except for glycine in 0.1 mol·kg⁻¹ [Phpi][BF₄] solution. The $\Delta_{tr}V_{\Phi}^0$ value of each amino acid increases along with the increase of the [Phpi][BF₄] concentration, while decreases with the rising temperature. The value of n_H declines when the concentration of [Phpi][BF₄] solution or temperature increases. It turns out that [Phpi][BF₄] interacts strongly with four kinds of amino acids. The present results show that hydrophilic-hydrophobic and hydrophobic-hydrophobic interactions between IL and amino acids play the dominant roles in these (IL + amino acids + water) systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

References

- [1] D.C. Parr, G.R. Hedwig, A.W. Hakin, *J. Chem. Eng. Data* 54 (2009) 606–612.
- [2] Q. Yuan, Z.F. Li, B.H. Wang, *J. Chem. Thermodyn.* 38 (2006) 20–33.
- [3] H.L. Friedman, C.V. Krishnan, F. Franks, In *comprehensive treatise on water and aqueous solutions*; Plenum Press: New York, 1973.
- [4] Z.J. Tan, F.F. Li, X.L. Xu, *Separ. Purif. Tech.* 98 (2012) 150–157.
- [5] H. Passos, M.P. Trindate, T.S.M. Vaz, L.P.D. Costa, M.G. Freire, *Separ. Purif. Tech.* 108 (2013) 174–180.
- [6] A.F.M. Claudio, M.G. Freire, C.S.R. Freire, A.J.D. Silvestre, J.A.P. Coutinho, *Separ. Purif. Tech.* 75 (2010) 39–47.
- [7] Q. Zeng, Y.Z. Wang, N. Li, X. Huang, X.Q. Ding, X. Lin, S.Y. Huang, X.J. Liu, *Talanta* 116 (2013) 409–416.
- [8] M.T.Z. Moattar, S. Hamzehzadeh, *Fluid Phase Equilib.* 304 (2011) 110–120.
- [9] J. Han, Y. Wang, C. Chen, W.B. Kang, Y. Liu, K.K. Xu, L. Ni, *J. Mol. Liq.* 193 (2014) 23–28.
- [10] M.Y. Shao, X.L. Zhang, N. Li, J.Y. Shi, H.J. Zhang, Z.B. Wang, H.Q. Zhang, A.M. Yu, Y. Yu, *J. Chromatogr. B.* 961 (2014) 5–12.
- [11] T. Matos, H.O. Johansson, J.A. Queiroz, L. Bulow, *Separ. Purif. Tech.* 122 (2014) 144–148.
- [12] P. Weschayanwivat, O. Kunanupap, J.F. Scamehorn, *Chemosphere* 72 (2008) 1043–1048.
- [13] A. Muller, A. Gorak, *Separ. Purif. Tech.* 97 (2012) 130–136.
- [14] M.R. Helfrich, E.M. Kouedi, M.R. Etherton, C.D. Keating, *Langmuir* 21 (2005) 8478–8486.
- [15] S. Afrin, Riyazuddeen, *J. Chem. Eng. Data* 55 (2010) 2643–2648.
- [16] J.A. Siddique, S. Shama, S. Naqvi, *J. Chem. Eng. Data* 55 (2010) 2930–2934.
- [17] C.L. Liu, L. Zhou, L. Ma, *J. Chem. Eng. Data* 55 (2010) 4509–4513.
- [18] N.V. Sastry, P.H. Valand, P.M. Macwan, *J. Chem. Thermodyn.* 49 (2012) 14–23.

- [19] A. Pal, N. Chuanhan, J. Chem. Eng. Data 56 (2011) 1687–1694.
- [20] Riyazuddeen, M.A. Usmani, J. Chem. Eng. Data 56 (2011) 3504–3509.
- [21] T.S. Banipal, J. Kaur, P.K. Banipal, A.K. Sood, J. Chem. Eng. Data 56 (2011) 2751–2760.
- [22] T.S. Banipal, J. Kaur, P.K. Banipal, J. Chem. Thermodyn. 48 (2012) 181–189.
- [23] Riyazuddeen, U. Gazal, J. Chem. Eng. Data 57 (2012) 7–13.
- [24] H. Kumar, K. Kaur, J. Chem. Thermodyn. 53 (2012) 86–92.
- [25] J.A. Siddique, S. Naqvi, Int. J. Thermophys. 33 (2012) 47–57.
- [26] Z.N. Yan, Q. Zhang, W.W. Li, J.J. Wang, J. Chem. Eng. Data 55 (2010) 3560–3566.
- [27] Z.N. Yan, X.M. Sun, W.W. Li, Y. Li, J. Chem. Thermodyn. 43 (2011) 1468–1474.
- [28] N.V. Sastry, P.H. Valand, P.M. Macwan, J. Chem. Eng. Data 56 (2011) 627–637.
- [29] M.S. Santosh, D.K. Bhat, A.S. Bhatt, J. Chem. Eng. Data 56 (2011) 768–782.
- [30] Riyazuddeen, U. Gazal, J. Chem. Eng. Data 57 (2012) 1468–1473.
- [31] A.A. Zamyatnin, Biophys. Bioeng. 13 (1984) 145–165.
- [32] T.V. Chalikian, R. Annu, Biophys. Biomol. Struct. 32 (2003) 207–235.
- [33] M. Natarajan, R.K. Wadi, H.C. Gaur, J. Chem. Eng. Data 35(1990) 87–93.
- [34] R. Bhat, J.C. Ahluwalia, J. Phys. Chem. 89 (1985) 1099–1105.
- [35] R.K. Wadi, R.K. Goyal, J. Solution. Chem. 21 (1992) 163–170.
- [36] R.K. Wadi, R.K. Goyal, J. Chem. Eng. Data 37 (1992) 377–386.
- [37] T.S. Banipal, G. Sehgal, Thermochim. Acta 262 (1995) 175–183.
- [38] T.S. Banipal, S. Gagandeep, S.L. Bhajan, J. Solution Chem. 30 (2001) 657–670.
- [39] Riyazuddeen, M.A. Usmani, Thermochim. Acta 527 (2012) 112–117.
- [40] S. Fang, D.H. Ren, J. Chem. Eng. Data 58 (2013) 845–850.
- [41] X. Wang, G.Q. Li, Y.H. Guo, Q. Zheng, W.J. Fang, P.F. Bian, L.J. Zhang, J. Chem. Thermodyn. 78 (2014) 128–133.
- [42] X.X. Lu, Q. Cao, J. Yu, Q.F. Lei, H.J. Xie, W.J. Fang, J. Phys. Chem. B. 119 (2015) 11798–11806.
- [43] N. Meena, R.K. Wadi, H.C. Gaur, J. Chem. Eng. Data 35 (1990) 87–93.
- [44] D.P. Kharakoz, J. Phys. Chem. 95 (1991) 5634–5642.

- [45] H.L. Friedman, C.V. Krishnan, *J. Solution Chem.* 2 (1973) 119–140.
- [46] T.S. Banipal, D. Kaur, P.K. Banipal, *J. Chem. Eng. Data* 49 (2004) 1236–1246.
- [47] F.J. Millero, L.S. Antonio, S. Charles, *J. Phys. Chem.* 82 (1978) 784–792.
- [48] E. Berlin, M.J. Pallansch, *J. Phys. Chem.* 72 (1968) 1887–1889.

TABLE 1

Information of chemicals in this work

Chemical name	Source	Purification method	Water content ^a	Final purity ^b	Analytical method
Glycine	Aladdin	recrystallization		>0.990	as stated by the supplier
L-Serine	Aladdin	recrystallization		>0.990	as stated by the supplier
L-Alanine	Aladdin	recrystallization		>0.990	as stated by the supplier
L-Proline	Aladdin	recrystallization		>0.990	as stated by the supplier
1-Phenylpiperazine	Aldrich	none		>0.990	as stated by the supplier
Tetrafluoroboric acid	Aldrich	none		~0.500 aqueous solution	as stated by the supplier
1-Phenylpiperazine tetrafluoroborate ([Phpi][BF ₄])	synthesized	freeze-drying	<0.0001 ^b	>0.990	KF ^a , NMR ^c

^a By Karl-Fischer (KF) titration.^b In mass fraction.^c ¹H and ¹³C nuclear magnetic resonance.

TABLE 2

Density (ρ) and apparent molar volume (V_Φ) of aqueous solutions of IL with amino acids (IL molality = 0.025 mol·kg⁻¹ in water) as a function of amino acid concentration at $T = (298.15, 303.15, \text{ and } 308.15) \text{ K}$ and $p = 0.1 \text{ MPa}^a$

molality ^b / mol·kg ⁻¹	$\rho / \text{g}\cdot\text{cm}^{-3}$			$V_\Phi / \text{cm}^3\cdot\text{mol}^{-1}$		
	$T / \text{K} = 298.15$	303.15	308.15	298.15	303.15	308.15
Glycine + [Phpi][BF ₄] + H ₂ O						
0.0499	1.00038	0.99894	0.99729	41.32	41.64	41.93
0.0999	1.00194	1.00049	0.99882	42.49	42.78	43.06
0.1500	1.00352	1.00205	1.00038	42.72	43.01	43.27
0.2000	1.00505	1.00357	1.00189	43.05	43.34	43.59
0.2499	1.00660	1.00511	1.00341	43.12	43.41	43.66
0.3000	1.00813	1.00663	1.00492	43.23	43.52	43.77
0.3500	1.00963	1.00811	1.00639	43.37	43.66	43.91
0.3999	1.01121	1.00967	1.00795	43.26	43.55	43.78
L-serine + [Phpi][BF ₄] + H ₂ O						
0.0500	1.00104	0.99960	0.99795	58.07	58.39	58.75
0.1000	1.00324	1.00178	1.00011	59.44	59.78	60.12
0.1500	1.00544	1.00396	1.00228	59.73	60.13	60.44
0.2000	1.00760	1.00611	1.00441	60.06	60.40	60.73
0.2499	1.00977	1.00827	1.00655	60.12	60.48	60.80
0.2999	1.01188	1.01036	1.00864	60.35	60.70	61.02
0.3500	1.01397	1.01243	1.01069	60.56	60.90	61.22
0.4000	1.01605	1.01450	1.01275	60.66	61.01	61.32
L-alanine + [Phpi][BF ₄] + H ₂ O						
0.0499	1.00027	0.99883	0.99718	57.57	57.77	58.08
0.0999	1.00172	1.00027	0.99861	58.72	58.95	59.21
0.1499	1.00314	1.00168	1.00002	59.22	59.48	59.70
0.2000	1.00455	1.00308	1.00141	59.53	59.78	60.01

0.2500	1.00591	1.00444	1.00276	59.83	60.08	60.31
0.2999	1.00729	1.00580	1.00411	59.96	60.21	60.44
0.3499	1.00863	1.00714	1.00544	60.14	60.39	60.62
0.4000	1.00999	1.00849	1.00678	60.22	60.47	60.69

L-proline + [Phpi][BF₄] + H₂O

0.0499	1.00054	0.99910	0.99744	78.19	78.53	78.92
0.0999	1.00213	1.00068	0.99901	80.55	80.91	81.28
0.1499	1.00371	1.00224	1.00056	81.34	81.72	82.08
0.1999	1.00525	1.00376	1.00207	81.88	82.26	82.63
0.2499	1.00679	1.00529	1.00358	82.13	82.51	82.90
0.2999	1.00834	1.00686	1.00514	82.25	82.52	82.88
0.3500	1.00988	1.00835	1.00662	82.33	82.67	83.05
0.4000	1.01134	1.00980	1.00806	82.54	82.90	83.25

^a The standard uncertainties are $u(m)=0.01m$ for the molalities (m) of IL and amino acids, $u(\rho) = 2 \times 10^{-4} \text{ g} \cdot \text{cm}^{-3}$, $u(T) = 0.01 \text{ K}$ and $u(p) = 2000 \text{ Pa}$.

^b The molality of amino acid is reported per 1 kg of ([Phpi][BF₄] + H₂O) solution.

TABLE 3

The density (ρ) and apparent molar volume (V_Φ) of aqueous solutions of IL with amino acids (IL molality = 0.055 mol·kg⁻¹ in water) as a function of amino acid concentration at $T = (298.15, 303.15, \text{ and } 308.15) \text{ K}$ and $p = 0.1 \text{ MPa}^a$

molality ^b / mol·kg ⁻¹	$\rho / \text{g}\cdot\text{cm}^{-3}$			$V_\Phi / \text{cm}^3\cdot\text{mol}^{-1}$		
	$T / \text{K} = 298.15$	303.15	308.15	298.15	303.15	308.15
Glycine + [Phpi][BF ₄] + H ₂ O						
0.0500	1.00232	1.00085	0.99917	41.56	41.89	42.26
0.1000	1.00384	1.00236	1.00067	43.04	43.34	43.62
0.1499	1.00543	1.00393	1.00223	42.98	43.27	43.55
0.1999	1.00702	1.00550	1.00379	42.96	43.26	43.52
0.2500	1.00860	1.00707	1.00535	42.95	43.23	43.50
0.3000	1.01010	1.00857	1.00683	43.16	43.45	43.70
0.3499	1.01162	1.01007	1.00832	43.25	43.54	43.78
0.4000	1.01314	1.01158	1.00982	43.31	43.60	43.85
L-serine + [Phpi][BF ₄] + H ₂ O						
0.0499	1.00306	1.00158	0.99990	56.81	57.17	57.56
0.0999	1.00523	1.00373	1.00204	59.05	59.42	59.75
0.1499	1.00739	1.00588	1.00417	59.75	60.10	60.43
0.2000	1.00950	1.00798	1.00626	60.30	60.66	60.97
0.2499	1.01166	1.01013	1.00839	60.37	60.71	61.03
0.3000	1.01387	1.01232	1.01057	60.23	60.58	60.89
0.3500	1.01590	1.01433	1.01257	60.59	60.93	61.24
0.4000	1.01802	1.01644	1.01466	60.61	60.95	61.26
L-alanine + [Phpi][BF ₄] + H ₂ O						
0.0500	1.00223	1.00076	0.99908	57.54	57.78	58.07
0.0999	1.00361	1.00213	1.00044	59.34	59.58	59.85
0.1500	1.00508	1.00359	1.00189	59.32	59.59	59.83
0.2000	1.00641	1.00492	1.00322	59.92	60.18	60.41

0.2499	1.00780	1.00629	1.00458	60.04	60.29	60.53
0.3000	1.00920	1.00768	1.00597	60.06	60.31	60.54
0.3500	1.01050	1.00903	1.00705	60.33	60.44	61.39
0.3999	1.01192	1.01038	1.00864	60.22	60.47	60.72

L-proline + [Phpi][BF₄] + H₂O

0.0499	1.00254	1.00106	0.99938	77.20	77.64	77.95
0.0999	1.00413	1.00265	1.00095	80.00	80.38	80.72
0.1499	1.00571	1.00420	1.00250	80.98	81.37	81.72
0.1999	1.00726	1.00574	1.00400	81.52	81.89	82.36
0.2499	1.00883	1.00730	1.00556	81.71	82.08	82.48
0.2999	1.01032	1.00877	1.00702	82.08	82.45	82.83
0.3500	1.01187	1.01031	1.00855	82.13	82.51	82.86
0.3999	1.01334	1.01176	1.00999	82.34	82.71	83.06

^a The standard uncertainties are $u(m)=0.01m$ for the molalities (m) of IL and amino acids, $u(\rho) = 2 \times 10^{-4} \text{ g} \cdot \text{cm}^{-3}$, $u(T) = 0.01 \text{ K}$ and $u(p) = 2000 \text{ Pa}$.

^b The molality of amino acid is reported per 1 kg of ([Phpi][BF₄] + H₂O) solution.

TABLE 4

Density (ρ) and apparent molar volume (V_Φ) of aqueous solutions of IL with amino acids (IL molality = 0.100 mol·kg⁻¹ in water) as a function of amino acid concentration at $T = (298.15, 303.15, \text{ and } 308.15) \text{ K}$ and $p = 0.1 \text{ MPa}^a$

molality ^b / mol·kg ⁻¹	ρ / g·cm ⁻³			V_Φ / cm ³ ·mol ⁻¹		
	T / K = 298.15	303.15	308.15	298.15	303.15	308.15
Glycine + [Phpi][BF ₄] + H ₂ O						
0.0499	1.00512	1.00361	1.00188	43.04	43.35	43.62
0.1000	1.00676	1.00521	1.00348	42.58	43.07	43.32
0.1499	1.00836	1.00681	1.00507	42.63	42.92	43.17
0.2000	1.00989	1.00834	1.00658	42.95	43.24	43.48
0.2499	1.01142	1.00985	1.00809	43.11	43.39	43.64
0.3000	1.01296	1.01138	1.00960	43.19	43.48	43.72
0.3499	1.01447	1.01310	1.01131	43.30	42.93	43.17
0.3999	1.01568	1.01406	1.01225	44.11	44.42	44.69
L-serine + [Phpi][BF ₄] + H ₂ O						
0.0499	1.00585	1.00433	1.00261	58.40	58.74	59.08
0.0999	1.00809	1.00656	1.00482	59.11	59.48	59.80
0.1500	1.01023	1.00868	1.00693	59.95	60.30	60.61
0.1999	1.01238	1.01082	1.00905	60.21	60.57	60.88
0.2500	1.01449	1.01291	1.01113	60.52	60.87	61.16
0.2999	1.01660	1.01500	1.01321	60.66	61.01	61.30
0.3499	1.01873	1.01712	1.01531	60.68	61.02	61.31
0.4000	1.02077	1.01914	1.01733	60.88	61.22	61.51
L-alanine + [Phpi][BF ₄] + H ₂ O						
0.0499	1.00505	1.00354	1.00182	58.46	58.72	58.99
0.1000	1.00649	1.00496	1.00323	59.26	59.52	59.76
0.1499	1.00788	1.00634	1.00461	59.74	60.00	60.22
0.2000	1.00929	1.00775	1.00601	59.82	60.08	60.30

0.2500	1.01070	1.00914	1.00739	59.88	60.14	60.36
0.3000	1.01206	1.01050	1.00874	60.04	60.29	60.51
0.3499	1.01340	1.01183	1.01006	60.17	60.42	60.64
0.3999	1.01478	1.01320	1.01142	60.18	60.43	60.65

L-proline + [Phpi][BF₄] + H₂O

0.0499	1.00531	1.00379	1.00207	79.22	79.61	79.95
0.0999	1.00694	1.00540	1.00366	80.60	81.00	81.35
0.1500	1.00849	1.00694	1.00519	81.50	81.88	82.24
0.1999	1.01004	1.00848	1.00672	81.84	82.24	82.57
0.2499	1.01162	1.01005	1.00827	81.92	82.29	82.65
0.2999	1.01316	1.01156	1.00978	82.07	82.45	82.80
0.3499	1.01465	1.01305	1.01124	82.26	82.63	82.98
0.3999	1.01617	1.01455	1.01274	82.31	82.68	83.03

^a The standard uncertainties are $u(m)=0.01m$ for the molalities (m) of IL and amino acids, $u(\rho) = 2 \times 10^{-4} \text{ g} \cdot \text{cm}^{-3}$, $u(T) = 0.01 \text{ K}$ and $u(p) = 2000 \text{ Pa}$.

^b The molality of amino acid is reported per 1 kg of ([Phpi][BF₄] + H₂O) solution.

TABLE 5

Standard partial molar volume (V_{Φ}^0), and transfer partial molar volume ($\Delta_{tr}V_{\Phi}^0$), of Glycine, L-serine, L-alanine, and L-proline in aqueous solutions of IL at $T = (298.15, 303.15, \text{ and } 308.15) \text{ K}$ and $p = 0.1 \text{ MPa}$

molality /mol·kg ⁻¹	V_{Φ}^0			$\Delta_{tr}V_{\Phi}^0$		
	T / K			T / K		
	298.15	303.15	308.15	298.15	303.15	308.15
Glycine						
0.025	41.77	42.07	42.36	-0.45	-0.52	-0.56
0.055	42.17	42.48	42.81	-0.04	-0.11	-0.11
0.100	42.42	42.89	43.14	0.20	0.30	0.22
L-serine						
0.025	58.50	58.84	59.19	-0.06	-0.35	-0.51
0.055	57.80	58.16	58.53	-0.77	-1.03	-1.17
0.100	58.57	58.93	59.26	0.01	-0.27	-0.44
L-alanine						
0.025	57.89	58.11	58.39	-1.43	-1.57	-1.53
0.055	58.20	58.47	58.64	-1.12	-1.21	-1.28
0.100	58.76	59.02	59.27	-0.57	-0.66	-0.65
L-proline						
0.025	79.13	79.50	79.88	-3.01	-3.12	-3.09
0.055	78.31	78.72	79.08	-3.83	-3.89	-3.89
0.100	79.77	80.16	80.51	-2.38	-2.45	-2.46

TABLE 6

Hydration numbers (n_H) of glycine, L-serine, L-alanine, and L-proline in aqueous solutions of IL at $T = (298.15 \text{ and } 308.15) \text{ K}$ and $p = 0.1 \text{ MPa}$

amino acids	$T = 298.15 \text{ K}$			$T = 308.15 \text{ K}$		
	$m / \text{mol} \cdot \text{kg}^{-1}$					
	$= 0.025^a$	0.055	0.100	0.025	0.055	0.100
Glycine	3.06	2.94	2.86	2.38	2.26	2.18
L-serine	4.50	4.71	4.48	3.54	3.70	3.52
L-alanine	4.20	4.10	3.94	3.34	3.28	3.12
L-proline	4.02	4.27	3.82	3.13	3.33	2.97

^a Molality ($m / \text{mol} \cdot \text{kg}^{-1}$) of [Phpi][BF₄] in water.

FIGURE 1. Optimized structures (Å) of complexes formed by ionic liquid, amino acids and water molecules.

Table of Contents

Ionic Liquid

Glycine

L-alanine

L-serine

L-proline

Amino Acid