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Partitioning behavior of amino acids in aqueous two-phase systems formed by imidazolium ionic liquid and dipotassium hydrogen phosphate

Yuanchao Pei, Zhiyong Li, Li Liu, Jianji Wang*

School of Chemical and Environmental Sciences, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang, Henan 453007, China

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ABSTRACT

Partition coefficients of amino acids, including glycine, alanine, 2-aminobutyric acid, valine, leucine, threonine, methinoine, tryptophan and tyrosine, in [$C_n$mim]Br (n = 4, 6, 8) + K_2HPO_4 aqueous two-phase systems (ATPSs) have been determined, and the relative hydrophobicity of the equilibrium phases in the ionic liquids-based aqueous two-phase systems has been characterized by the Gibbs energies of transfer for methylene group from the bottom salt-rich phase to the top ionic liquid-rich phase. Based on these results, factors affecting the partitioning behavior of the amino acids have been investigated. It is shown that partition coefficients of the amino acids increase with the increase of hydrophobicity of the amino acids and the ionic liquids, solution pH value, tie-line length of the ATPSs and temperature of the systems. The possible driving forces and the thermodynamic parameters for the partitioning of amino acids in the ionic liquids-based ATPSs have also been discussed.

1. Introduction

As a new kind of solvent, ionic liquids (ILs) have a variety of unique properties, such as negligible vapor pressure, non-flammability, high thermal and chemical stability, tunable chemical structures and physical properties, and strong solubilization power [1–5]. This makes them as a potential replacement for volatile organic solvents used in chemical synthesis, biocatalytic transformation, electrochemistry, and analytical and separation processes [4,6–8]. It has been reported that aqueous ILs can form aqueous two-phase systems (ATPSs) in the presence of inorganic salts above a certain concentration [9]. In the recent years, these ILs-based ATPSs have received much attention as 'greener' media to extract/separate biomolecules, drugs and radiological isotopes [10–18].

Amino acids are very important bioproducts. The partitioning studies of such biomolecules in ATPSs not only represent realistic alternatives to traditional recovery methods, but also have the potential to be used as a rapid and simple method to characterize the protein surface, because the partitioning of protein depends on its surface properties. During the past years, there has been some reports concerning the extraction of amino acids using ILs-based ATPSs [13,14,19]. However, extraction of amino acids using ILs-based ATPSs is only limited to aromatic amino acids, no attempt has been made to study the partitioning of aliphatic amino acids and to explore the structure–performance relationship for the partitioning of amino acids as well.

In the present work, partition coefficients of nine amino acids with different chemical structure (see Table 1), including glycine, alanine, 2-aminobutyric acid, valine, leucine, threonine, methinoine, tryptophan and tyrosine in 1-alkyl-3-methylimidazolium bromide [$C_n$mim]Br (n = 4, 6, 8) + K_2HPO_4 ATPSs have been reported. Among the amino acids studied, glycine, alanine, 2-aminobutyric acid, valine and leucine are aliphatic amino acids, and carbon atom number in their alkyl chain increases from 0 to 4. Thus their partition coefficients can be used to evaluate the relative hydrophobicity between the phases of the ILs-based ATPSs by calculating the transfer Gibbs energies of methylene between the phases. Threonine and methinoine are also aliphatic amino acids, they are selected to examine the effect of polar groups —OH and CH_3S— in the alkyl chain on their partitioning behavior. Tryptophan and tyrosine are aromatic amino acids, they are combined with the other amino acids to correlate hydrophobicity and partition coefficients of the amino acids. In addition, the effect of alkyl chain length of the ILs, solution pH, composition of the ATPSs, relative hydrophobicity between the phases of the ILs-based ATPSs and temperature of the systems have been also studied on the partition coefficients of representative amino acids. It is believed that the information obtained here is useful for the understanding of the partition behavior of amino acids in ILs-based ATPSs.

* Corresponding author. Tel.: +86 373 332 5805.
E-mail addresses: Jwang@henannu.edu.cn, jwang1955@126.com (J. Wang).

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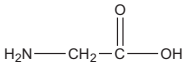
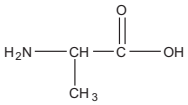
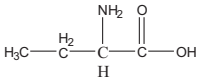
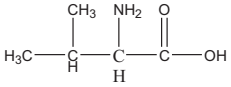
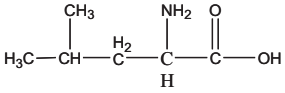
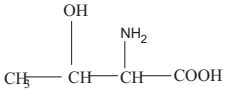
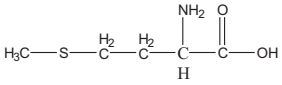
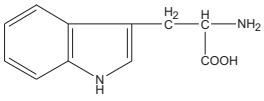
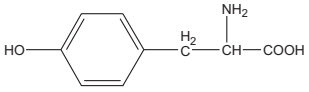
Table 1
Structure, dissociation constants and isoelectric points of the amino acids at 298.15 K.

Amino acid	Structure	pK_1	pK_2	pK_3	pI [20]
Glycine		2.34	9.60		5.97
Alanine		2.34	9.69		6.02
2-Aminobutyric acid		–	–		–
Valine		2.32	9.62		5.96
Leucine		2.36	9.60		6.02
Threonine		2.63	10.43		6.53
Methinoine		2.28	9.21		5.75
Tryptophan		2.38	9.39		5.89
Tyrosine		2.20	9.11	10.07	5.66

2. Experimental

2.1. Materials

Commercially available N-methylimidazolium (Linhai Kaile Chemical Company, Zhejiang Province, China) and a series of alkyl halides (Aladdin-reagent Company, Shanghai, China) were distilled twice before use. Glycine (>99%), alanine(>99%), 2-aminobutyric acid (>99%), valine (>99%), leucine (>99%), threonine (>99%), methinoine (>99%), tryptophan (>99%), tyrosine (>99%) and $K_2HPO_4{\cdot}3H_2O$ (>99%) were purchased from Aladdin-reagent Company and used without further purification. All other reagents were of commercially available analytical grade and used as received. Doubly distilled deionized water was used throughout the experiments.

2.2. Synthesis of the ILs

1-Alkyl-3-methylimidazolium bromide, [$C_n$mim]Br (n = 4, 6, 8), were prepared and purified by using the procedure described in literature [21,22]. Briefly, the reaction of 1-methylimidazole and any alkyl bromide (such as butyl bromide, hexyl bromide and octyl bromide) was refluxed in ethylacetate for 36 h at 343 K with continuous magnetic stirring. The residual solvent was then removed by rotary evaporation, and the resulting products were dried under vacuum for 24 h. ^{1}H NMR spectra data of these ILs were determined by using an AV-400 Bruker spectrometer, and they are found to be in good agreement with those reported in literature [22].

2.3. Determination of the phase diagram

Phase diagram data are useful for the design of aqueous two-phase extraction process and for the development of thermodynamic models from which the partitioning of amino acids can be predicted. For the ILs/K_2HPO_4 aqueous two-phase systems, their binodal curves were determined by a cloud-point method [9], and the results were reported in a previous paper [23]. It is shown that the phase-forming ability of the ILs follows the order: [C_6mim]Br > [C_8mim]Br > [C_4mim]Br, this anomalous alkyl chain dependence is likely to be resulted from the micelle formation of [C_8mim]Br in aqueous salt solutions.

The tie lines, which describe the concentrations of ILs and salt in the two phases, were measured with the procedure outlined in literature [24]. The tie line length (*TLL*) of the ILs-based ATPSs can be calculated by the equation:

$$TLL = [(w_1^t - w_1^b)^2 + (w_2^t - w_2^b)^2]^{0.5} \quad (1)$$

where w_1^t, w_1^b, w_2^t and w_2^b are the equilibrium mass fractions of the IL (1) and salt (2) in the top (t) and bottom (b) phases.

Table 2
Partition coefficients of the amino acids in [C_4mim]Br + K_2HPO_4 ATPSs at 298.15 K.

TLL	Partition coefficient (*K*)								
	Glycine	Alanine	2-Aminobutyric acid	Valine	Threonine	Leucine	Methinoine	Tyrosine	Tryptophan
0.3220	0.40	0.70	0.68	0.95	0.53	3.71	6.65	2.75	3.34
0.4926	0.29	0.63	0.96	2.33	0.78	5.62	11.3	6.51	9.24
0.6107	0.27	0.53	1.25	3.02	0.93	7.93	12.7	8.35	12.6
0.6414	0.24	0.56	1.48	5.12	1.13	18.5	24.8	19.6	22.0
0.6939	0.23	0.64	2.15	7.71	1.35	23.2	25.5	33.3	29.3

2.4. Extraction of the amino acids

A given amount of IL, $K_2HPO_4{\cdot}3H_2O$ and aqueous amino acid solution was added into a graduated glass tube. The volume of the glass tube was calibrated before use. The mixture was diluted by the addition of a given volume of water, and then shaken vigorously for 30 min to attain equilibrium by a thermostated oscillator (Jinghong Instrument Factory, Shanghai, China), and temperature of the system was controlled at 298.15 ± 0.05 K with a DC-2006 low temperature thermostat. The phase separation quickly occurred after cessation of the shaking process. Then, a XYJ-802 centrifuge (Jiangsu Medical Instrument Factory, Jiangsu, China) operated at 4000 rpm was used to run for a period of 5 min in each test to ensure a complete phase separation. After the volume of the top and bottom phases was recorded, the samples were collected from the both phases for analysis. To avoid interference from the phase components, the samples were diluted and analyzed against the blanks containing the same phase components but without amino acid. The concentrations of glycine, alanine, 2-aminobutyric acid, valine, leucine, threonine and methinoine were determined by ninhydrine method [25], and that of tryptophan and tyrosine in both phases were determined by measuring the absorbance at 281 nm using a Shanghai 752N UV–vis spectrophotometer. At least three samples were quantified for each aqueous phase, and the relative uncertainty of the experimental results for the amino acid concentration is about 3%. Partition coefficient of an amino acid, *K*, is defined here as the ratio of the concentration of amino acid in the IL-rich and salt-rich phases, and can be described by:

$$K = \frac{C_t}{C_b} \quad (2)$$

where C_t and C_b are equilibrium concentrations of the partitioned amino acid in the top IL-rich phase and the bottom salt-rich phase, respectively.

3. Results and discussion

3.1. Structural effect of amino acids and ILs on the partitioning of amino acids

The partition coefficients of glycine, alanine, 2-aminobutyric acid, valine, leucine, threonine, methinoine, tryptophan and tyrosine in [C_4mim]Br + K_2HPO_4 ATPSs determined at 298.15 K are given in Table 2, and in the extraction experiment, the pH of [C_4mim]Br + K_2HPO_4 ATPSs was in the range of 9.3–9.4. It can be seen that partition coefficients of the amino acids at a given composition of the ATPSs exhibit following features: (i) aromatic amino acids > aliphatic amino acids, except methinoine in which a CH_3S— group is present in its alkyl chain; (ii) in aromatic amino acids, tryptophan > tyrosine; (iii) in aliphatic amino acids, methinoine > leucine > valine > 2-aminobutyric acid > threonine > alanine > glycine. From chemical structure of the amino acids shown in Table 1, it is clear that compared with tyrosine, tryptophan has an additional hydrophobic pyrrole ring and a missing hydrophilic —OH group; in aliphatic amino acids, there are more hydrophobic —CH_2 group in the side chain of amino acids from glycine, alanine, 2-aminobutyric acid, valine to leucine; and compared with 2-aminobutyric acid, threonine has an additional hydrophilic —OH group, while methinoine has an additional hydrophobic —SCH_3 group. Thus it seems appropriate to state that hydrophobic groups of the amino acids increase but hydrophilic groups decrease the partition coefficients of the amino acids at the same composition of the ATPSs. According to the hydrophobicity scale, defined as the Gibbs energy change when amino acid transfers from water to ethanol phases [26], hydrophobicity of the amino acids follows the order: tryptophan (14.28 kJ mol^{-1}) > tyrosine (9.66 kJ mol^{-1}) > leucine (7.56 kJ mol^{-1}) > valine (6.30 kJ mol^{-1}) > methionine (5.46 kJ mol^{-1}) > alanine (2.10 kJ mol^{-1}) > threonine (1.68 kJ mol^{-1}) > glycine (0 kJ mol^{-1}). Compared with the partition coefficients included in Table 2, it is evident that partition coefficients increase with increasing the hydrophobicity of amino acids. Based on these results, it can be deduced that hydrophobic interactions might be one of the main driving forces in the uptake of amino acids by the IL-based ATPSs. Similar conclusion has been given for the extraction of amino acids by polymer-based ATPSs [27,28].

The effect of alkyl chain length of the ILs on the partition coefficients of tryptophan in [$C_n$mim]Br (n = 4, 6, 8) + K_2HPO_4 ATPSs was given in Table 3, together with those reported in other systems [29–31]. The results show that partition coefficients of tryptophan in ILs-based ATPSs are substantially higher than in the usual polymer/polysaccharide [29] and polymer/inorganic salts [30] ATPSs. In addition, the magnitudes of tryptophan partition coefficients in [$C_n$mim]Br (n = 4, 6, 8) + K_2HPO_4 ATPSs are higher than those reported in the water-immiscible ILs biphase systems [31]. In traditional PEG-salt ATPSs, partition coefficients of amino acids increase with the increase of PEG molecular weight. Considering the fact that the bigger the PEG molecular weight, the more hydrophobicity the PEG-rich phase [32], the increased partition coefficients of amino acids may be resulted from the hydrophobic interaction of amino acids with PEG macromolecules. In the present work, partition coefficients of tryptophan in [$C_n$mim]Br (n = 4, 6, 8) + K_2HPO_4 ATPSs follow the order: [C_8mim]Br > [C_6mim]Br > [C_4mim]Br. It is known that hydrophobicity of the ILs increase with increasing alkyl chain length of the ILs [33]. Therefore, hydrophobic interaction between tryptophan and the ILs is also suggested to account for the partition coefficient order of tryptophan observed in different

Table 3
Partition coefficients of tryptophan in different two-phase systems.

System	Partition coefficient
[C_4mim]Br + K_2HPO_4 [a]	8.74
[C_6mim]Br + K_2HPO_4 [a]	11.2
[C_8mim]Br + K_2HPO_4 [a]	15.4
PEG8000/ben-dextran [29]	0.93
PEG6000/$MgSO_4$ [30]	≈2.4–4
[C_8mim]BF_4 [b] [31]	3.81

[a] The test concentration of tryptophan was 1.0 mg ml^{-1}, and 1.0 g IL, 0.8 g $K_2HPO_4{\cdot}3H_2O$ and 1.30 ml H_2O were added for the ATPSs formation.
[b] The test pH = 2.30.

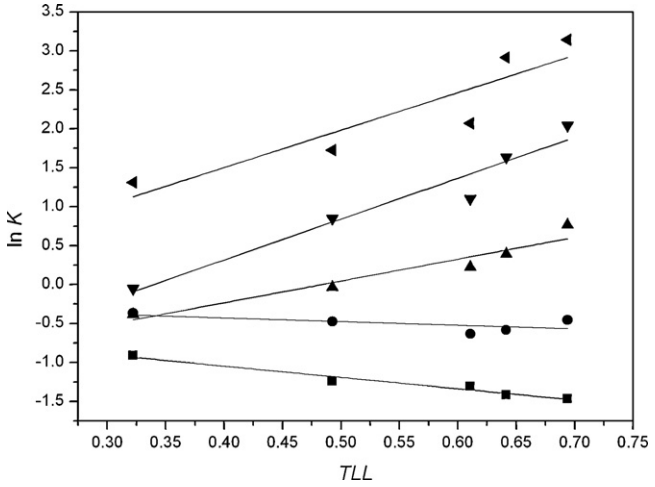


Fig. 1. Effect of *TLL* on the ln *K* of amino acids at 298.15 K: ◄, leucine; ▼, valine; ▲, 2-aminobutyric acid; ●, alanine; ■, glycine.

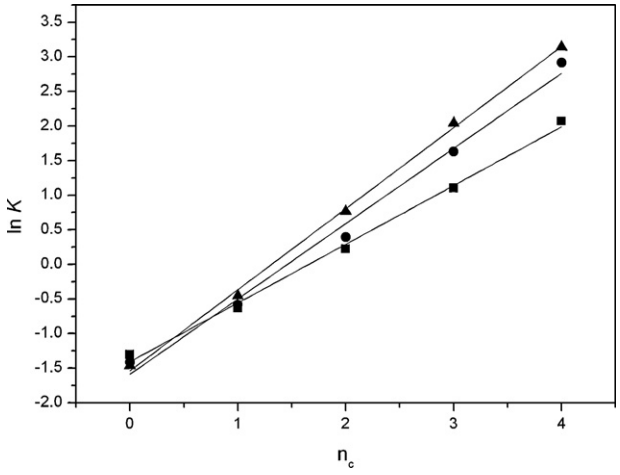


Fig. 2. Variation of partition coefficients at 298.15 K with alkyl chain length of the amino acids at given *TLLs*: ■, *TLL* = 0.6107; ●, *TLL* = 0.6414; ▲, *TLL* = 0.6939.

IL-based ATPSs. This result supports the above observation that hydrophobic interaction was one of the main driving forces for the partition of amino acids. This is similar to the results obtained form our previous work for the proteins partition in ILs-based ATPSs [23].

The effect of the composition of ATPSs has been investigated on the partition coefficients of amino acids. *TLL* is a useful parameter for characterizing the system composition. As the *TLL* increases, the top- and bottom- phases show increasing difference in compositions [15]. In other words, the chaotropic and kosmotropic components are enriched in this case, and the top phase becomes more chaotropic and the bottom phase becomes more kosmotropic. As an example, natural logarithm of partition coefficients (ln *K*) of leucine, valine, 2-aminobutyric acid, alanine and glycine was shown in Fig. 1 as a function of the *TLL* of [C_4mim]Br + K_2HPO_4 ATPS. As can be seen, ln *K* values of leucine, valine and 2-aminobutyric acid increase, but those of glycine and alanine decrease in a nearly linear fashion with increasing *TLL* of the ATPSs. This behavior may be interpreted by taking into account the relative hydrophobicity of these amino acids. Because hydrophobicity of the IL-rich phase increases with the increase of *TLL* values, partition coefficients of the longer alkyl chain amino acids should increase with increasing *TLLs*. Glycine and alanine have shorter alkyl chain, their hydrophobicity is weaker than other amino acids investigated, leading to their unfavorable partitioning in the IL-rich phase. This result was similar to that of amino acids in polymer-salt ATPSs [34].

At the same time, it is clear from Fig. 1 that at any given *TLL*, the more hydrophobic amino acids have greater partition coefficients. This is resulted from the increased kosmotropicity of the bottom phase which increases the preference of chaotropic solutes for the top phase [35]. It is also noticeable, however, that the resolution between hydrophobic solutes increases with increasing *TLL*, indicating that the partition coefficients for more hydrophobic amino acids increase with increasing *TLL* at a greater rate than those for less hydrophobic solutes. Therefore, changing *TLL* is one of the important ways to regulate the partition behavior of amino acids in ATPSs.

3.2. The Gibbs energies of transfer for a methylene group ΔG_{CH_2}

Here, values of ΔG_{CH_2} could be calculated from the partitioning data of a series of amino acids according to the procedure described in literature [36]. For this purpose, the ln *K* values of glycine, alanine, 2-aminobutyric acid, valine and leucine between the phases of [C_4mim]Br + K_2HPO_4 ATPSs were determined at five different *TLLs*. As an example, Fig. 2 shows the relationship between ln *K* values and carbon atom number n_c in the alkyl chain of the partitioned amino acids at some given *TLLs*. It is clearly indicated that ln *K* values increase linearly with the increase of n_c, and each linear relationship can be described by the equation:

$$\ln K = C + En_c \quad (3)$$

where the intercept *C* is a constant related to the hydration properties of the phases, and the slope *E* can be used to calculate ΔG_{CH_2} values by the equation [37]:

$$\Delta G_{CH_2} = -RTE \quad (4)$$

where *R* is the gas constant, and *T* is the thermodynamic temperature. Values of ΔG_{CH_2} provide a measure for the relative hydrophobicity of the bottom phase to the top phase at a particular *TLL*, and the relationship between ΔG_{CH_2} and *TLL* are shown in Fig. 3. It can be seen that the values of ΔG_{CH_2} are negative, indicating that transfer of methylene group is favorable from the bottom phase to the top phase, and the IL-rich phase is more hydrophobic than the salt-rich phase. At the same time, ΔG_{CH_2} value is a measure of cavity formation for an additional methylene group in the equilibrium phases of ATPSs [38]. The decrease in the ΔG_{CH_2} with *TLL* implies that as the concentration of kosmotropic salt increases, the kosmotropic phase becomes more structured (harder to form a cavity) and the top phase becomes more chaotropic. This leads to a more destructured phase, thus allowing for easier cavity formation and amino acid transfer. The tunability of these systems is apparent

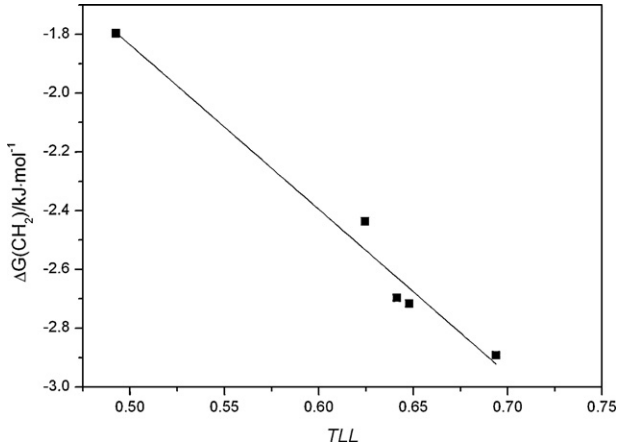


Fig. 3. Linear plot between ΔG_{CH_2} and *TLLs* for [C_4mim]Br + K_2HPO_4 ATPSs at 298.15 K.

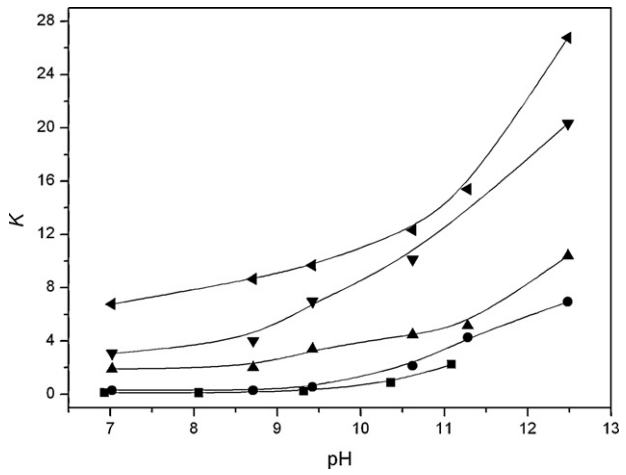


Fig. 4. Effect of pH values on the partition coefficients of the amino acids in the ATPSs of $[C_4mim]Br + K_2HPO_4$: ■, glycine; ●, alanine; ▲, valine; ▼, tyrosine; ◀, tryptophan.

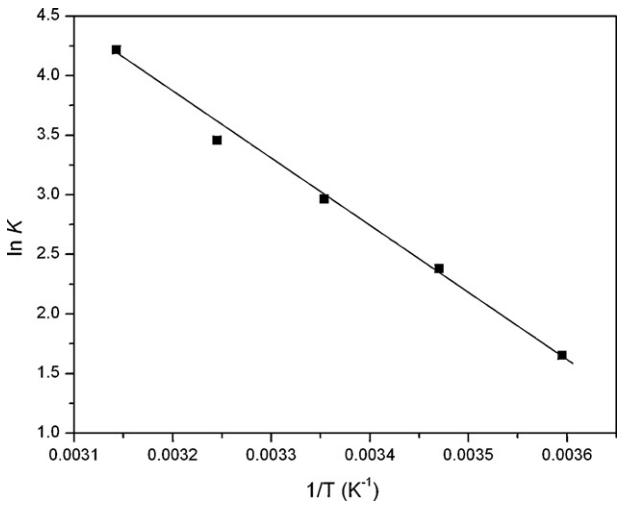


Fig. 5. Effect of temperature on the ln K of leucine in $[C_4mim]Br + K_2HPO_4$ ATPSs at pH 9.3 (0.6 g IL + 0.8 g $K_2HPO_4 \cdot 3H_2O$ + 1.3 ml H_2O). The tested concentration of leucine was 1.0 mg ml^{-1}.

from the fact that the ΔG_{CH_2} values can be modulated simply by changing the composition of the phases in ATPSs.

3.3. Effect of pH on the partitioning of amino acids

It is known that pH is a crucial parameter to influence the partitioning of solutes in ILs-based ATPSs. Because IL-phosphate systems cannot form aqueous two phases at pH below 6.0, attempt has been made to determine partition coefficients of glycine, alanine, valine, tyrosine and tryptophan in the pH range from 7.0 to 13.0, and the results are shown in Fig. 4. It can be seen that partition coefficients of the amino acids generally increase with the increase of pH values. Amino acids are amphoteric substances and exist as anions, cations, or neutral molecules depending on their isoelectric points and solution pH. They exist as cations when pH is lower than their isoelectric points and exist as anions when pH is higher than their isoelectric points. At the isoelectric point, both functional groups are charged but the molecule as a whole carries no net charge. It is known from Table 1 that isoelectric points of the studied amino acids are around 6.0 in aqueous solutions, and these amino acids will be negatively charged in the range of pH > 7.0. Therefore, it is deduced that electrostatic interactions between anionic amino acids and imidazolium cations of the ILs play an important role in determining the pH dependence of partition coefficients of amino acids in the ATPSs. The partition coefficients of amino acids may be modulated by the electrostatic interactions.

Another interesting feature is that partition coefficients of the amino acids decrease in the order: tryptophan > tyrosine > valine > alanine > glycine at the selected pH range. This is consistent with hydrophobicity of these amino acids.

3.4. Partitioning thermodynamics of the amino acids in ATPSs

Previously, Coutinho and co-workers [39] reported that temperature significantly influences the partition coefficients of tryptophan in PEG-salt ATPSs. Here, leucine was used as a representative amino acid to evaluate the temperature effect on the partition behavior of amino acids. As a result, partition coefficient of leucine in $[C_4mim]Br + K_2HPO_4$ ATPSs was determined at 278.15, 288.15, 298.15, 308.15 and 318.15 K, and the results were displayed in Fig. 5. Obviously, the ln K values of leucine decrease linearly with increasing $1/T$ of the system. From a thermodynamic perspective, the partitioning of leucine can be regarded as a transfer process of the amino acid from the salt-rich bottom phase to the IL-rich top phase. At a given temperature, the change in Gibbs energy (ΔG_T°), enthalpic (ΔH_T°) and entropy (ΔS_T°) of such a transfer process can be calculated from the partition data through the equations [40]:

$$\Delta G_T^\circ = -RT \ln K \quad (5)$$

$$\ln K = \frac{-\Delta H_T^\circ}{RT} + \frac{\Delta S_T^\circ}{R} \quad (6)$$

where T and R have the usual meanings. It is clear that values of ΔH_T° and ΔS_T° can be directly obtained from the slope and intercept of the linear equation (6) between ln K and $1/T$. The ΔG_T°, ΔH_T° and ΔS_T° values obtained by linear least-square analysis are listed in Table 4 for the transfer of leucine from K_2HPO_4-rich phase to the $[C_4mim]Br$-rich phase. It can be seen that values of ΔG_T° are negative whereas those of ΔH_T° and ΔS_T° are positive, and $T\,\Delta S_T^\circ$ is always greater than ΔH_T° in value. This indicates that partition of the amino acid is controlled by entropy changes.

Table 4
The transfer thermodynamic properties of leucine from K_2HPO_4-rich phase to the $[C_4mim]Br$-rich phase at pH 9.3.

T	K	ΔG_T° (kJ mol^{-1})	$T\Delta S_T^\circ$ (kJ mol^{-1})	ΔH_T° (kJ mol^{-1})
278.15	5.21	−3.82	49.5	45.6
288.15	10.8	−5.70	51.3	
298.15	19.4	−7.35	53.0	
308.15	31.7	−8.85	54.8	
318.15	67.9	−11.2	56.6	

4. Conclusions

In this article, the partition behavior of glycine, alanine, 2-aminobutyric acid, valine, leucine, threonine, methinoine, tryptophan, tyrosine in $[C_nmim]Br$ (n = 4, 6, 8) + K_2HPO_4 ATPSs have been investigated. From the above discussion, it can be concluded that partition coefficients of the amino acids increase with increasing hydrophobicity of both the amino acids and the ionic liquids, pH values of solution, *TLL* values of the ATPSs and temperature of the systems. Hydrophobicity of the amino acids and the ionic liquids is the main factor affecting the partitioning of amino acids in ATPSs. Amino acids with a more hydrophobic nature prefer the relatively hydrophobic IL-rich phase, as characterized by the Gibbs energies of transfer of a methylene group between the conjugated phases. The pH effect on the partition coefficients of the amino acids could be ascribed to the change of electrostatic interactions between anionic amino acid and imidazolium cations of the ILs.

From a thermodynamic viewpoint, partition of the amino acids is controlled by entropy changes. These results may provide new information for the structure–performance relationship of the partitioning of amino acids and some proteins whose surface residues contain these amino acids in IL-based ATPSs. They are also expected to be useful for the design of novel ILs-based ATPSs.

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