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Mutual Coexistence Curve Measurement of Aqueous Biphasic Systems Composed of [bmim][BF$_4$] and Glycine, L-Serine, and L-Proline, Respectively

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It was found for the first time that glycine, L-serine, and L-proline can form aqueous biphasic systems (ABS) with a hydrophilic ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]). The related mutual coexistence curve data are reported.

Introduction

Ionic liquids are unique solvents composed entirely of ions with melting points below 373.15 K. Due to their special properties, ionic liquids have been used as an important solvent and reaction media in catalysis,[1−5] separations,[6−10] biology,[11] and so on. Among all the applications above, its potential use in separation and extraction is one of the most significant. It is well-known that hydrophobic ionic liquids can be used to extract organics[6−7] and inorganics[8] from the aqueous phase. Another benign environmental separation system composed of supercritical carbon dioxide fluid and ionic liquids has been studied to open insight into the separation of organics from ionic liquid phases,[12,13] although there may be a concern about the polarity of the extracted organic.[14] Recently, an interesting separation system containing hydrophilic ionic liquids, the aqueous biphasic system (ABS) of [bmim][Cl]/K$_3$PO$_4$, was reported[15] which can be used to recycle ionic liquids and separate short-chain alcohols from the aqueous phase. In fact, we also have observed a similar phenomenon during the preparation of [bmim][BF$_4$] where a high concentration of NaCl solution can make [bmim][BF$_4$] salt out to form a new phase. Undoubtedly, this kind of ABS is of significance due to its potential application in fine-tuning separation, and the problem of ion exchange exists between salt and ionic liquid which can result in a different ionic liquid forming. Amino acids are well-known as kinds of inner salts which may preclude ion exchange. In this paper, the authors investigated the ABS formed by an ionic liquid and glycine, L-serine, and L-proline.

Experimental Section

Glycine (99 %), L-serine (99.5 %), L-proline (99 %), NaBF$_4$, and butylchloride were analytical grade produced by the Beijing Chemical Reagent Plant. *N*-Methylimidazole (98 %) was provided by the Linhai Kaile Chemical Factory and was distilled under a vacuum at 393.15 K. [bmim][BF$_4$] was prepared as reported.[16] All aqueous solutions were prepared with deionized water. The constant temperature water bath was controlled by a special temperature controller prepared in our laboratory, and the temperature was determined by accurate mercury thermometers with a precision of ± 0.1 K. Each experiment was done in duplicate, and the results agreed well within 0.5 %.

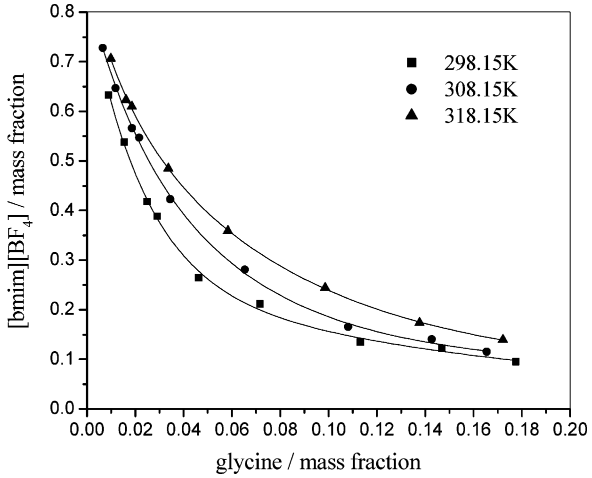

Figure 1. Mutual coexistence curve for the aqueous biphasic systems of [bmim]BF$_4$/glycine.

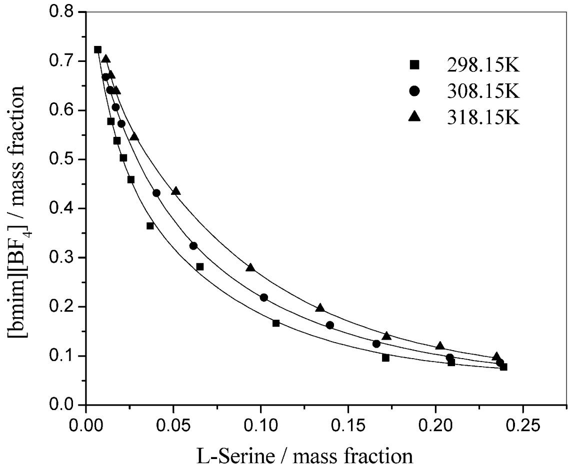

Figure 2. Mutual coexistence curve for the aqueous biphasic systems of [bmim][BF$_4$]/L-serine.

Results and Discussion

Several amino acids such as glycine, L-serine, and L-proline were investigated to determine if they could form ABS with the hydrophilic ionic liquid [bmim][BF$_4$]. As a result, it was found that glycine, L-serine, and L-proline all can salt out this ionic liquid. Different from the ABS K$_3$PO$_4$/[bmim][Cl],[15] the

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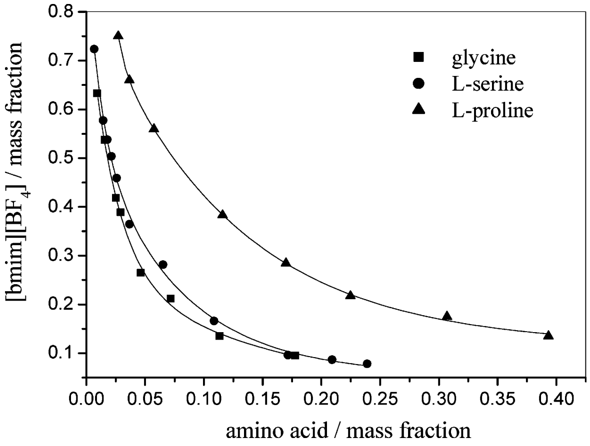

Figure 3. Mutual coexistence curve for the aqueous biphasic systems of [bmim][BF$_4$]/amino acids at 298.15 K.

Table 1. Mutual Coexistence Curve Data for the Aqueous Biphasic Systems of [bmim]BF$_4$/Glycine

T/K	glycine	[bmim][BF$_4$]	glycine	[bmim][BF$_4$]
298.15 ± 0.01	0.0090	0.6328	0.0717	0.2118
	0.0156	0.5375	0.1132	0.1350
	0.0250	0.4182	0.1469	0.1223
	0.0291	0.3886	0.1776	0.0951
	0.0462	0.2648		
308.15 ± 0.01	0.0066	0.7275	0.0654	0.2808
	0.0119	0.6466	0.1081	0.1655
	0.0187	0.5658	0.1472	0.1401
	0.0216	0.5468	0.1655	0.1154
	0.0345	0.4228		
318.15 ± 0.01	0.0099	0.7059	0.0583	0.3590
	0.0162	0.6231	0.0986	0.2439
	0.0186	0.6098	0.1377	0.1738
	0.0337	0.4848	0.1722	0.1392

Table 2. Mutual Coexistence Curve Data for the Aqueous Biphasic Systems of [bmim][BF$_4$]/L-Serine

T/K	L-serine	[bmim][BF$_4$]	L-serine	[bmim][BF$_4$]
298.15 ± 0.01	0.0067	0.7235	0.0653	0.2815
	0.0143	0.5771	0.1088	0.1662
	0.0178	0.5380	0.1716	0.0959
	0.0214	0.5035	0.2092	0.0865
	0.0258	0.4592	0.2391	0.0779
	0.0368	0.3645		
308.15 ± 0.01	0.0112	0.6675	0.1019	0.2187
	0.0138	0.6410	0.1396	0.1624
	0.0170	0.6063	0.1663	0.1243
	0.0203	0.5727	0.2082	0.0965
	0.0403	0.4316	0.2370	0.0861
	0.0615	0.3240		
318.15 ± 0.01	0.0114	0.7030	0.0941	0.2783
	0.0142	0.6708	0.1340	0.1961
	0.0172	0.6388	0.1720	0.1383
	0.0276	0.5446	0.2026	0.1188
	0.0515	0.4339	0.2350	0.0972

upper phase is the glycine-rich phase, and the lower phase is the [bmim][BF$_4$]-rich phase.

The mutual coexistence curves were determined by the cloud-point method. Figures 1 and 2 show the coexistence curves of [bmim][BF$_4$]/glycine and [bmim][BF$_4$]/L-serine at (298.15, 308.15, and 318.15) K, respectively. It was found that the ABS is more easily formed at lower temperatures which may be due to the decreased miscibility between the [bmim][BF$_4$]-rich phase and the amino acid-rich phase with temperature. This can be demonstrated by the fact that the system, at the cloud point, can become transparent when the temperature is increased. The ABSs of three amino acids at 298.15 K are compared in Figure 3. It shows that their tendency to form an ABS with [bmim][BF$_4$] is in the order of glycine > L-serine > L-proline. Tables 1 to 3 show the detailed data of their mutual coexistence curves.

Table 3. Mutual Coexistence Curve Data for the Aqueous Biphasic Systems of [bmim][BF$_4$]/Amino Acids at 298.15 K

	x	*y*	*x*	*y*
glycine	0.0090	0.6328	0.0462	0.2648
	0.0156	0.5375	0.0717	0.2118
	0.0250	0.4182	0.1132	0.1350
	0.0291	0.3886	0.1776	0.0951
L-serine	0.0067	0.7235	0.0653	0.2815
	0.0143	0.5771	0.1088	0.1662
	0.0178	0.5380	0.1716	0.0959
	0.0214	0.5035	0.2092	0.0865
	0.0258	0.4592	0.2391	0.0779
	0.0368	0.3645		
L-proline	0.0270	0.7500	0.1699	0.2842
	0.0366	0.6599	0.2248	0.2173
	0.0575	0.5595	0.3070	0.1750
	0.1159	0.3832	0.3933	0.1349

To find out if all hydrophilic ionic liquids can form an ABS with the above amino acids, another two hydrophilic ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF$_4$]) and 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), were investigated. They failed to form an ABS with these amino acids no matter how the ratio between the ionic liquid and amino acids was adjusted. On the contrary, amino acids seemed to salt out from the transparent phase when both ionic liquids were added, which may be explained by the fact that the above two hydrophilic ionic liquids have a stronger hydration ability.

Conclusion

In summary, the hydrophilic ionic liquid [bmim][BF$_4$] can form aqueous biphasic systems with amino acids such as glycine, L-serine, and L-proline. It was found that this kind of ABS, composed of [bmim][BF$_4$] and amino acids, is more easily formed at lower temperature. Their tendency to form ABS is glycine > L-serine > L-proline.

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