Liquid–liquid extraction of caprolactam from water using room temperature ionic liquids

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ABSTRACT

In this paper, investigations have been carried out to determine the suitability of imidazolium-based ionic liquids (ILs), 1-alky-3-methylimidazolium hexafluorophosphate $[C_nmim][PF_6]$ (n = 4, 6, 8), 1-hexyl-3-methylimidazolium tetrafluoroborate $[C_6mim][BF_4]$ and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_4mim][NTf_2]$, in replacing toxic organic solvents for liquid–liquid extraction of caprolactam from aqueous solution. The results show that distribution ratio of caprolactam is influenced significantly by the chemical structures of the ILs. The anion/cation effects are the main structural factors ruling the distribution ratio. The results also show that the distribution ratios are much higher for caprolactam into selected ILs than into benzene or toluene. New experimental data for the partitioning of caprolactam between water and the ionic liquid at 303.05 K, 313.05 K, 322.95 K, 332.95 K, 342.95 K, 352.95 K, and 362.95 K have been reported, respectively. It is expected that these ILs are promising for caprolactam recovery from aqueous media. The NRTL model has been employed to correlate the experimental data.

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1. Introduction

Liquid–liquid extraction is a useful separation method in analytical science and in chemical industry. Generally speaking, partitioning of a solute between two immiscible phases which are usually an organic solvent and an aqueous solution is employed in traditional solvent extraction. The organic solvents used are usually volatile, toxic and flammable. Therefore, establishing more effective and cleaner extraction solvents are desired for the development of new separation processes.

Caprolactam is one of the most important industrial chemicals. It is mainly used to manufacture nylon 6 and resins. The production of caprolactam will discharge a large quantity of wastewater containing low concentration caprolactam and some ammonium sulfate [1]. This causes both a reduction in economic profit and an increase in the Chemical Oxygen Demand (COD) of the wastewater [2]. Therefore, it is necessary to deal with this wastewater. Until now, most researchers applied benzene as the extractant to treat wastewater containing caprolactam [1,3–5]. As well known, benzene is recognized as a human leukemogen [6]. Toluene is considered as a good alternative for benzene [7]. Many other extractants with less toxicity have been tested in recent years, such as ethers [8], esters [8], alcohols [9,10] and ketones [8,11]. But these

traditional solvents are usually toxic, flammable and volatile. So it is important to find a new solvent which is green and kind to environment and human being, and also has high extraction efficiency to replace the traditional solvents.

ILs are, as their name implied, liquid ionic media composed of organic cations and inorganic or organic anions, which always remain liquid at the temperature below 100 °C. The unique properties of ILs, such as negligible vapor pressure, good thermal stability, tunable viscosity and miscibility with water or organic solvents, as well as good extractability for various organic compounds and metal ions, make it possible for ILs to be used in separation [12]. ILs have been used in chromatographic methods [13–17], and electrochemical applications [18]. In recent years, application of ILs in liquid–liquid extraction instead of traditional organic solvent, for example, extracting heavy metal ions [19–26], aromatic hydrocarbons [24,27,28], organic acids [29], amino acids [30,31], S-compounds in diesel oil [32–34], organic compounds in plants [35,36], and organics in water [37–39] has received increasing attention.

In this work, imidazolium based ionic liquids $[C_4mim][PF_6]$, $[C_6mim][PF_6]$, $[C_8mim][PF_6]$, $[C_4mim][NTf_2]$ and $[C_6mim][BF_4]$ have been used at 303.05 K, 313.05 K, 322.95 K, 332.95 K, 342.95 K, 352.95 K, and 362.95 K, for the first time, to remove caprolactam from aqueous solutions. Effect of structure of ILs and concentration of ammonium sulfate solution has been investigated. A model has been developed to correlate the obtained experimental data.

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Table 1
ILs studied and correspondent abbreviations.

Abbreviation	Ionic liquid
[C₄mim][PF₆]	1-Butyl-3-methylimidazolium hexafluorophosphate
[C₆mim][PF₆]	1-Hexyl-3-methylimidazolium hexafluorophosphate
[C₈mim][PF₆]	1-Octyl-3-methylimidazolium hexafluorophosphate
[C₄mim][NTf₂]	1-Butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide
[C₆mim][BF₄]	1-Hexyl-3-methylimidazolium tetrafluoroborate

2. Experimental

2.1. Materials

The ILs employed in this work were purchased from Lanzhou Greenchem ILS, LICP with mass fraction purities >99%. The abbreviations used for the ILs are listed in Table 1 and the structures of their constituting ions are represented in Fig. 1. The caprolactam (>99 wt.%) was purchased from J&K chemical Co., Ltd. Its chemical structure is represented in Fig. 2. The ammonium sulfate ((NH₄)₂-SO₄) was purchased from Sinopharm Chemical Reagent Co., Ltd. The aqueous solutions were prepared with deionized water. All chemicals were used as received without any further purification.

2.2. Extraction experimental

Caprolactam aqueous solutions were prepared by directly dissolving the chemicals into deionized water. The caprolactam mass fraction in the initial aqueous solution was in the range from (0 to 30) mass%, and the concentration of ammonium sulfate aqueous solution was in the range from 0.05 to 0.3 g/mL which were both based on the actual industrial situation of waste water [9]. 2 mL caprolactam aqueous solution were added into 2 mL different ILs and then the mixture were vigorously vibrated. The effects of different anions, cations and temperatures were systematically studied in this work. The phase separation occurred quickly after cessation of vibrating process.

Before and after each extraction, the concentration of caprolactam in the aqueous solution was determined with a high performance liquid chromatography (HPLC). HPLC experiments were performed on a Waters 600CONTROLLER system equipped with a UV detector. The mobile phase was methanol:water (35:65, v/v) at a flow-rate of 1 mL/min, the UV detector was set at 240 nm, and the separation temperature was 22 °C. An aliquot of 5 μL of the aqueous solution was injected into the HPLC system. The concentration of caprolactam in the ionic liquid phase was determined by material balance.

The distribution ratio of caprolactam, *D*, was determined as the ratio of the mole fraction of caprolactam in the ionic liquid phase and in the aqueous solution phase after extraction, according to the following equation:

$$D = \frac{[\text{Caprolactam}]_{IL}}{[\text{Caprolactam}]_{aq}} \tag{1}$$
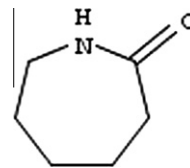
Fig. 2. Chemical structure of caprolactam.
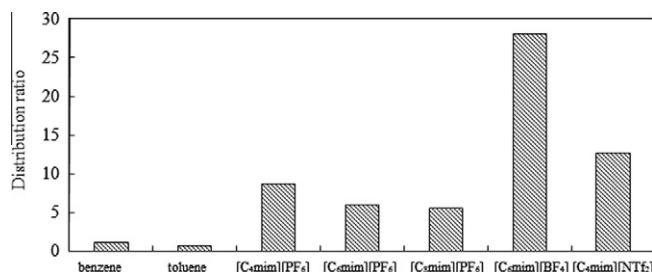
Fig. 3. Distribution ratio of the caprolactam into different solvents.

3. Results and discussion

3.1. Effect of the chemical structure of the ILs

The influence of variation in 1-alkyl group of [Cₙmim][PF₆], [C₄mim][NTf₂] and [C₆mim][BF₄] on extraction of caprolactam was investigated and also the distribution ratios of ILs were compared with the distribution ratios of benzene and toluene at 303.05 K. As can be seen from Fig. 3, distribution ratios of the caprolactam into ILs are much higher than those into benzene and toluene under the same condition, especially when [C₆mim][BF₄] was used. For example, the distribution ratio value of caprolactam into [C₆mim][BF₄] is 28.1 at the same time the distribution ratio value of caprolactam into benzene is 1.07 [4]. Fig. 4 shows the chromatograms of caprolactam determination when different ILs were used. There is no interference for the analysis of caprolactam when [C₆mim][BF₄] or [C₄mim][PF₆] exists. The retention time is 5.372, 4.394, and 4.087 min for caprolactam, [C₆mim][BF₄] and [C₄mim][PF₆], respectively.

The distribution ratios of the ILs for caprolactam follow the order: [C₆mim][BF₄] > [C₄mim][PF₆] > [C₆mim][PF₆] > [C₈mim][PF₆] under the same condition. This remarkable difference in distribution ratio implies that the anion of the ionic liquid plays a key role in the extraction of caprolactam. Quantum chemical calculations [40] indicate that the effective negative charge in the [BF₄]⁻ anion is much stronger than that in the [PF₆]⁻ anion. So, compared with [PF₆]⁻ anion, strength of hydrogen-bonding between [BF₄]⁻ and the caprolactam should be much stronger, suggesting higher distribution ratio accordingly [30,41]. Also because of the strong hydrogen-bonding between [BF₄]⁻ and water, a partially miscible phenomenon which was bad for extraction would be observed
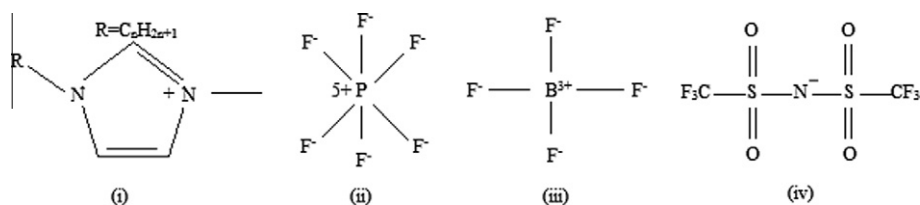

Fig. 1. Chemical structure of the anions and cations composing the ILs studied: (i) [Cnmim]⁺; (ii) [PF₆]⁻; (iii) [BF₄]⁻; (iv) [NTf₂]⁻.
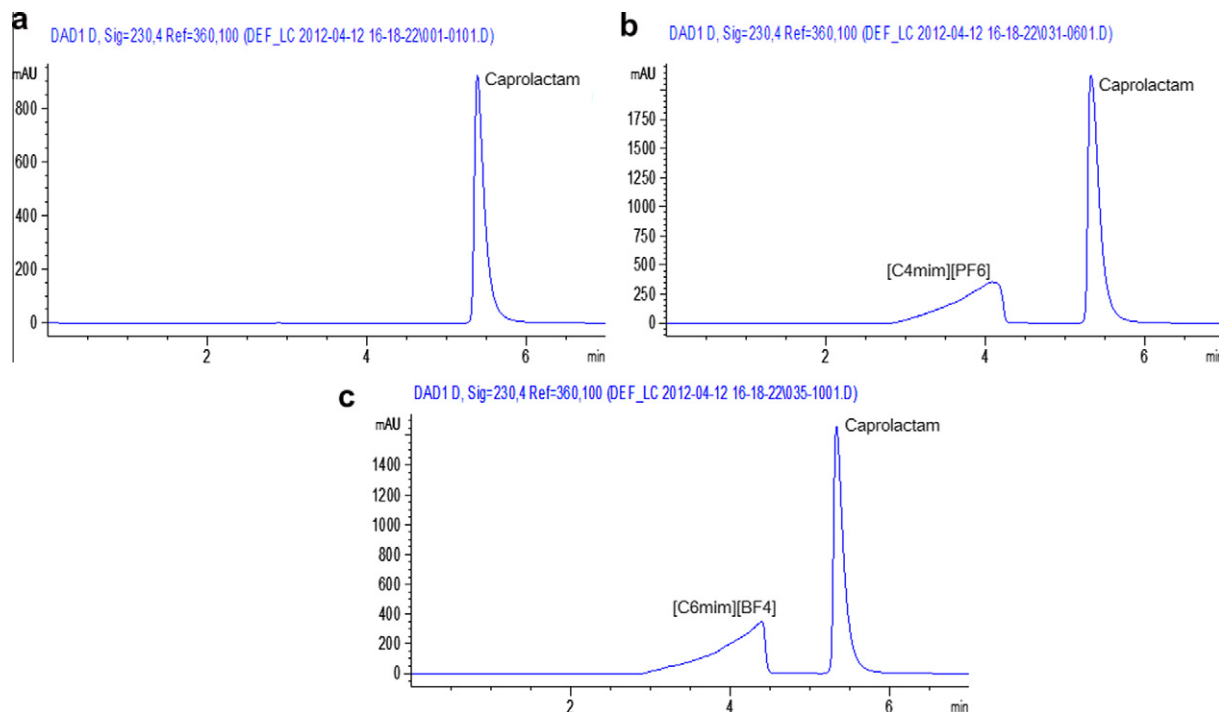
Fig. 4. Chromatograms of caprolactam solution (a), extracts of sample by [C$_4$mim][PF$_6$] (b), extracts of sample by [C$_6$mim][BF$_4$] (c).

after extraction when [C$_6$mim][BF$_4$] was used. It is interesting to find out that the distribution ratio of caprolactam into [C$_4$mim][NTf$_2$] is 12.6, while the distribution ratio of caprolactam into [C$_4$mim][PF$_6$] is 8.67. A similar result was found in extracting benzene from cyclohexane [42,43]. [NTf$_2$]$^-$ has a larger anionic radius than [PF$_6$]$^-$, and the interaction strength between the cation and the anion decreased with the increase of the anionic radius [44]. This might induce the loose association between [C$_4$mim]$^+$ and [NTf$_2$]$^-$. So [NTf$_2$]$^-$ may have a stronger hydrogen-bonding with caprolactam which could result in a higher distribution ratio [45].

From the extraction data of the caprolactam into ionic liquids, it is obvious that the distribution ratio of the caprolactam decreased as the length of alkyl substituent on the cation increased. For instance, the distribution ratio of caprolactam is 8.67 into [C$_4$mim][PF$_6$] and 5.45 into [C$_8$mim][PF$_6$], respectively. The longer alkyl chain on the imidazolium ring of the cation of ionic liquid has a screening effect or a steric hindrance effect for the electrostatic attractive interactions of the cationic form of the caprolactam with the ionic liquid [30].

The [BF$_4$]$^-$ may hydrolysis at moderate temperatures[46,47]. Hydrofluoric acid which could erode the extraction equipment might generate during the hydrolytic process [48]. While, [PF$_6$]$^-$ could be assumed stable at different conditions [46,47,49–51]. So, considering both the partially miscible phenomenon and the hydrolysis process, [C$_6$mim][BF$_4$] is not suitable for the extraction process. As [C$_4$mim][NTf$_2$] is much more expensive than [C$_4$mim][PF$_6$], [C$_4$mim][PF$_6$] was selected for the subsequent evaluation.

3.2. Effect of ammonium sulfate concentration

The effect of ammonium sulfate on the extraction distribution ratio of caprolactam into [C4mim][PF6] are shown in Fig. 5. It is clear that, in the presence of ammonium sulfate, the distribution ratio increases with increasing the concentration of ammonium sulfate present in aqueous phase. The ammonium sulfate could increase the ionic strength and enhance the analyte extraction by
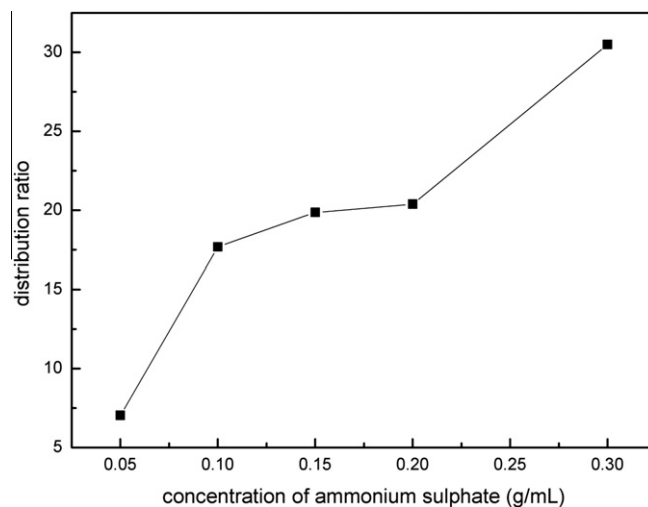

Fig. 5. Distribution ratio of caprolactam as a function of ammonium sulfate concentration (303.05 K, used [C$_4$mim][PF$_6$], the initial concentration of caprolactam is 0.01 g/mL).

increasing salting-out power. A higher ionic strength makes lower solubility of the analytes in the aqueous phase and more compounds partition to the ionic liquid phase.

3.3. Experiment data and correlation

Experimental data at 303.05 K, 313.05 K, 322.95 K, 332.95 K, 342.95 K, 352.95 K, and 362.95 K of equilibrium distribution of caprolactam between water and [C$_4$mim][PF$_6$] together with their distribution ratio are presented in Table 2, respectively. It should be pointed out that because of the low mutual solubility of [C$_4$mim][PF$_6$] and water [52], it is assumed that there is very little nearly none water in ionic liquid phase and also there is very little nearly none ionic liquid in water phase. The experimental data show that throughout the studied caprolactam concentration

range the distribution ratio increases as the temperature increases which means the extraction process can be taken under high temperature when ionic liquid is used.

A modeling framework, similar to the one used by Soto et al. [53], has been developed to correlate the experimental data obtained in this study. At equilibrium the activity coefficient, γ, and the composition (mole fraction), x, in the aqueous and ionic liquid phase, respectively, have an equal relationship as

$$x_i^{aq}\gamma_i^{aq} = x_i^{IL}\gamma_i^{IL} \tag{2}$$

The activity coefficients of caprolactam in both water and ionic liquid phases are represented by the NRTL model. The NRTL expression for the activity coefficients in multicomponent systems is given in Eq. (3), and the required interaction parameters are given in Eq. (4) [54,55]:

$$\ln(\gamma_i) = \frac{\sum_j x_{ji}G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}}\left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj}G_{mj}}{\sum_k x_k G_{kj}}\right) \tag{3}$$

Table 2
Equilibrium mole fraction of caprolactam in water and [C₄mim][PF₆] T/K.

T/K	x^{aq}	$x^{IL,exp}$	D	$x^{IL,calc}$	AD
303.05	0.0011	0.0059	5.195	0.0058	0.0001
	0.0053	0.0369	6.915	0.0357	0.0012
	0.0119	0.0554	4.664	0.0784	0.0229
	0.0175	0.1035	5.912	0.1058	0.0023
	0.0253	0.1122	4.439	0.1352	0.023
	0.0304	0.14	4.6	0.1502	0.0102
	0.0396	0.1525	3.854	0.1711	0.0186
313.05	0.0008	0.0096	11.862	0.0096	0.0001
	0.0048	0.0428	8.972	0.0431	0.0003
	0.0092	0.0801	8.663	0.075	0.0051
	0.0166	0.1108	6.667	0.1162	0.0055
	0.0244	0.119	4.88	0.1473	0.0282
	0.0291	0.149	5.113	0.1614	0.0124
	0.0357	0.1768	4.949	0.177	0.0002
322.95	0.0007	0.011	15.887	0.0109	0.0001
	0.0043	0.0478	11.206	0.0453	0.0025
	0.0084	0.0876	10.404	0.0792	0.0084
	0.015	0.124	8.289	0.1209	0.0031
	0.0201	0.1507	7.505	0.1447	0.006
	0.0279	0.1574	5.64	0.171	0.0136
	0.0332	0.1918	5.775	0.1837	0.0081
332.95	0.0007	0.0112	16.83	0.0118	0.0006
	0.0039	0.0513	13.088	0.0471	0.0042
	0.0083	0.0885	10.643	0.0879	0.0006
	0.0129	0.1393	10.759	0.1208	0.0185
	0.018	0.1654	9.212	0.1483	0.0171
	0.0235	0.186	7.931	0.1701	0.0159
	0.0315	0.2015	6.391	0.1913	0.0102
342.95	0.0006	0.0115	17.782	0.0113	0.0002
	0.0039	0.052	13.474	0.0528	0.0008
	0.0084	0.0879	10.505	0.0984	0.0104
	0.0127	0.1411	11.096	0.1311	0.0099
	0.0185	0.1618	8.763	0.1629	0.0011
	0.0243	0.181	7.461	0.1844	0.0034
	0.0288	0.2168	7.531	0.1961	0.0207
352.95	0.0006	0.0119	19.417	0.0119	0
	0.0035	0.0558	16.063	0.0535	0.0023
	0.0079	0.0921	11.656	0.0945	0.0024
	0.0118	0.1475	12.467	0.1364	0.0112
	0.0173	0.17	9.845	0.1692	0.0007
	0.0221	0.1945	8.809	0.1886	0.0058
	0.0286	0.218	7.626	0.2054	0.0126
362.95	0.005	0.0126	22.924	0.0110	0.0015
	0.0034	0.0565	16.611	0.0577	0.0012
	0.0076	0.0945	12.389	0.1101	0.0156
	0.0123	0.1439	11.664	0.1513	0.0074
	0.0172	0.1707	9.953	0.1802	0.0095
	0.0213	0.1992	9.36	0.1967	0.0026
	0.0272	0.2253	8.277	0.2116	0.0136

Table 3
Value of the NRTL interaction parameters regressed from the experimental data {caprolactam (1) + water (2) + [C₄mim][PF₆] (3)}.

i–j	a_{ij}	a_{ji}	b_{ij}	b_{ji}
1–2	−2.152	10.757	280.587	−2073.755
1–3	−78.310	104.425	10592.243	−26155.968
2–3	11.306	17.930	−797.698	−2038.955

where

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}), \tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \quad \text{and} \quad \tau_{ii} = 0, G_{ij} = 1, \alpha_{ij}$$
$$= \alpha_{ji} = 0.3 \tag{4}$$

The energy interactions between components i and j are represented by τ_{ij} and the local composition of the system by the non-randomness parameter α_{ij}. Although α can be treated as an adjustable parameter, in this study α is set equal to 0.3 according to the literature [56].

The interaction parameters (a_{ij}, b_{ij}) are determined by fitting the model to the experimental data by minimizing the following objective function:

$$F = \sum_{k=1}^{N}\sum_{i=1}^{3}\left\{\left(x_{i,k}^{IL,\exp} - x_{i,k}^{IL,calc}\right)^2\right\} \tag{5}$$

where N is the number of experimental data, $x_{i,k}^{IL,\exp}$ and $x_{i,k}^{IL,calc}$ are experimental and calculated compositions (in mole fraction) for the component i in ionic liquid phase, respectively.

The interaction parameters obtained from the fitting of the model to the experimental data are presented in Table 3. The calculated mole fraction of caprolactam in ionic liquid phase and the value of absolute deviation (AD = $|x_k^{IL,\exp} - x_k^{IL,calc}|$), are both listed in Table 2.

From Table 2, it can figure out that the maximum value of AD is 0.0282. The average deviation is 0.0076. The small value confirms the good agreement of the experimental data with the NRTL model.

4. Conclusions

In this work, the optimization of the ionic liquid structure for the caprolactam extraction from water was experimentally determined. The effect of the ionic liquid cation and anion structure and concentration of ammonium sulfate solution was also evaluated. The experimental data of equilibrium distribution of caprolactam between water and [C₄mim][PF₆] have been reported at 303.05 K, 313.05 K, 322.95 K, 332.95 K, 342.95 K, 352.95 K, and 362.95 K, respectively. The experimental data have been successfully correlated using NRTL model. Due to the high value of the distribution ratio, [C₄mim][PF₆] seems to be a good choice to act as solvent for caprolactam extraction from water.

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