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ZIF-8-porous ionic liquids for the extraction of 2,2,3,3-tetrafluoro-1-propanol and water mixture†

Zenghui Wang,[a] Pingping Zhao, ⭐[ab] Jimin Wu,[a] Jun Gao,[a] Lianzheng Zhang[a] and Dongmei Xu*[a]

The design of stable ionic liquids (ILs) has become crucial for efficient liquid–liquid extraction (LLE) of alcohol and water. Porous ionic liquids (PILs), as a special class of ILs, have attracted attention by virtue of their unique porous structure and IL characteristics. In this research, a series of zeolitic imidazolate framework-8 based porous ionic liquids (ZIF-8-PILs) were synthesized by simply mixing a solution of zeolitic imidazolate framework-8 (ZIF-8) and rationally designed ILs. The introduction of ZIF-8 resulted in a unique liquid porous structure and molecular sieve for ZIF-8-PILs. The improved extraction properties endowed ZIF-8/[Bpy][NTf$_2$] with more efficiency for the separation of 2,2,3,3-tetrafluoro-1-propanol (TFP) and water with 88.1% TFP extraction rate and steady reuse. The excellent extraction performance of ZIF-8-PILs is discussed in relation to their textural property and unique intermolecular interaction.

1. Introduction

2,2,3,3-Tetrafluoro-1-propanol (TFP, $C_3H_4F_4O$), as a valuable fluoride alcohol, has been extensively applied in industry.[1–3] Especially, TFP is adopted as a solvent and cleaning reagent due to the high solubility and gasification speed as well as the low toxicity, but it is inevitable that it forms aqueous solutions with different TFP contents. Owing to the pollution and cost,[4] the recycling of TFP from wastewater is profound and extraordinary. Meanwhile, TFP tends to form an azeotropic mixture with water at 365.7 K,[5,6] so the distillation operation is not a worthwhile method to obtain highly purified TFP. Liquid–liquid extraction (LLE) is considered to be an extremely important industrial process for separating azeotropic mixtures.[7] At present, feasible works have been investigated for the systems involving fluoride alcohol by LLE,[8,9] but only a few works have been reported due to the absence of an appropriate extracting solvent.[10,11] In this context, task-specific design of new efficient solvent systems play a crucial role in TFP extraction from aqueous solution.

Ionic liquids (ILs) have been used in the alcohol–water separation system due to their wide liquid range, relatively low melting point, good solvation performance, excellent thermal stability and other characteristics.[12] More importantly, the structure of ILs can be task-specifically designed at the molecular level according to the characteristics of the system. Therefore, IL systems are considered to be promising environmentally friendly green solvents for the separation of alcohol–water.[12,13] Very recently, we have prepared a series of ILs for obtaining pure TFP by separation from aqueous solution by LLE.[14,15] However, conventional ILs, even hydrophobic 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF$_6$]) and 1-decyl-3-methylimidazolium bis(trifluoromethane)sulfonamide ([Dmim][NTf$_2$]), usually have certain solubility in water. Therefore, it is difficult to use these ILs as effective extractants to gain high separation efficiency in fluoroalcohol–water azeotropic systems.

Porous ionic liquids (PILs), as Type III porous liquids, recently have been successfully developed and recognized as a promising new type of porous materials.[16] It refers to a porous frame material uniformly dispersed in ILs, where ILs are held out of the pore structure frame. Such porous materials combine the classic characteristics of porous solids, such as permanent multistage pores and molecular sieving, with the tunable structure and good solubility of ILs. As a result, PILs attract great attention due to their unique and fascinating physico-chemical properties and provide unique possibilities for storage and adsorption, homogeneous catalysis and separation fields.[16–21] However, so far, only a few successful examples of PILs have been reported,[19–21] and they have not been used in liquid–liquid extraction separations.

It is worth noting that zeolitic imidazolate framework-8 (ZIF-8), a kind of metal organic porous framework, has been used as a novel adsorption material for many chemical separation with the advantages of enhanced stability and improved molecular

[a] College of Chemical and Biological Engineering, Shandong University of Science and Technology, Qingdao 266590, China. E-mail: zhaopingping@sdust.edu.cn, xudongmei@sdust.edu.cn

[b] Shandong Key Laboratory of Biochemical Analysis, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China. E-mail: zhaopingping@sdust.edu.cn

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1nj01053k
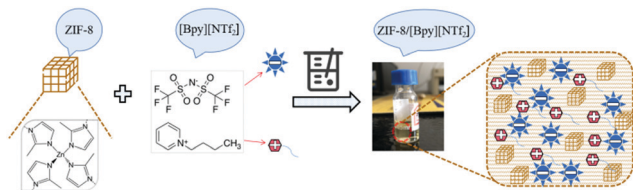
Fig. 1 The synthesis of ZIF-8-PILs (ZIF-8/[Bpy][NTf$_2$]).

sieving.[22,23] Actually, as a thermally and chemically stable porous framework material, ZIF-8 has been adopted as the porous host of PILs, which can cause significant improvements in gas separation.[18,19] Taking account of the good alcohol-water separation performance and tunable structure of ILs as well as the improved molecular sieving of ZIF-8, we think that it is rational to try a ZIF-8-PIL solvent system for obtaining pure TFP by separation from aqueous solution, which has not been reported yet. Herein, we report a series of ZIF-8-PILs that can be synthesized by a simple mixture of ZIF-8 and specially designed ILs (Fig. 1 illustrates the formation of ZIF-8/[Bpy][NTf$_2$] porous ionic liquids). The resulting PILs were fairly stable over reasonably long periods of time, and no accumulation was observed. They were used as the extractants to separate TFP aqueous solutions by LLE, showing an improved separation performance and good recyclability. A possible extraction mechanism for getting TFP from the aqueous solution by ZIF-8-PILs is proposed.

2. Experimental

2.1. Materials and methods

All chemicals were commercially available and used without further purification. The reagents were AR grade. The purity of TFP was checked by gas chromatography (GC, SP6890). The deionized water was prepared in our laboratory using an ultra-pure water machine (CSR-1D, Beijing Aisitaike Technology Development Co., Ltd.).

X-Ray diffraction (XRD) patterns were collected on a Bruker D8 Advance powder diffractometer using a Ni-filtered Cu Kα radiation source at 40 kV and 200 mA in the 2 range of 5°–50° at a scan rate of 2° min^{-1}. Thermogravimetric (TG) analysis was implemented using a STA409 instrument in dry air at a heating rate of 10 °C min^{-1}. A Hitachi S-4800 field-emission scanning electron microscope was used to obtain the scanning electron microscopy (SEM) images. Elemental analyses were performed on a CHN elemental analyzer (FlashEA 1112). A Thermo Elemental X7 ICP-MS equipped with a laser unit Thermo New Wave UP/213 was used for the Zn element analyses in ZIF-8.

2.2. Preparation of extractant

2.2.1. The preparation of ZIF-8 nanocrystals.
The preparation of ZIF-8 nanocrystals was carried out based on previous literatures.[20,24] Typically, Zn(NO$_3$)$_2$·6H$_2$O (0.738 g, 2.48 mmol) and 2-methylimidazole (1.643 g, 19.99 mmol) were dissolved in methanol (100 ml) at 323.15 K for 1 h with stirring at 500 rpm. The formed precipitate was washed with methanol three times

and collected by centrifugation (10 000 rpm, 5 min), and then dried in vacuum at 343.15 K for 1 h to give ZIF-8 nanocrystals.

2.2.2. Synthesis of the ionic liquids.
The IL N-butylpyridinium bromide ([Bpy]Br) was prepared according to a previous literature.[19] Pyridine (1.5820 g, 20 mmol) and 1-bromobutane (2.7404 g, 20 mmol) were added to 40 ml ethanol, and the mixture was refluxed under vigorous stirring at 343.15 K for 12 h. Then, the ethanol was removed by a rotary evaporator at 333.15 K, followed by washing with acetone (3 × 30 ml) and vacuum drying at 353.15 K for 12 h to give white solid N-butylpyridinium bromide ([Bpy]Br). Then, with a 1:1 molar ratio of IL [Bpy]Br (1.0806 g, 5 mmol) and bis(trifluoromethane)sulfonimide lithium Li[NTf$_2$] (1.4355 g, 5 mmol), the 10 ml acetonitrile solution of [Bpy]Br was drop-wise added into 10 ml acetonitrile solution of Li[NTf$_2$] under vigorous stirring at room temperature for 24 h. The acetonitrile was removed by a rotary evaporator at 333.15 K, followed by washing with methylene chloride (3 × 50 ml), and dried to obtain colorless transparent IL N-butylpyridinium bis(trifluoromethane)sulfonimide ([Bpy][NTf$_2$]). ^{1}H NMR (500 MHz, D^6-DMSO, TMS); δ0.91 (t, 3 H), 1.33 (m, 2 H), 1.92 (m, 2 H), 4.60 (t, J = 7.4 Hz, 2 H), 8.15 (m, 2 H), 8.59 (m, 1 H), 9.08 (m, 2 H). (Fig. S1, ESI†).

The other two ILs with varying carbon chains, N-ethyl-pyridinium bis(trifluoromethane)sulfonimide ([Epy][NTf$_2$]) and N-hexylpyridinium bis(trifluoromethane)sulfonimide ([Hpy][NTf$_2$]), were prepared accordingly. The analogues of ILs, N-ethyl-methylimidazole bis(trifluoromethane)sulfonimide ([Emim][NTf$_2$]), N-butylmethylimidazole bis(trifluoromethane)sulfonamide ([Bmim]-[NTf$_2$]) and N-hexylmethylimidazole bis(trifluoromethane)-sulfonimide ([Hmim][NTf$_2$]) were prepared following a similar process using the corresponding IL precursors. Moreover, the synthesis scheme of [Bpy][NTf$_2$] and various counterparts is illustrated in Scheme S1 (ESI†).

2.2.3. Synthesis of ZIF-8-PILs.
The ZIF-8-PILs were synthesized according to the literature with minor changes.[19,20] The synthesis of ZIF-8/[Bpy][NTf$_2$] is shown here as an example. In a 10 ml round-bottom flask, ZIF-8 powder (2 mg) was added to 0.75 g [Bpy][NTf$_2$], and then the mixture was ultrasonically treated for 2 h at room temperature to obtain homogeneous ZIF-8/[Bpy][NTf$_2$]. The resulting solution was vacuum-dried at 353.15 K overnight for further use. The other ZIF-8-PILs used in this work were synthesized by similar procedures with consistent mass ratios of ZIF-8 to ILs.

2.3. Extraction experiment

The standard solution of TFP and water mixture was selected based on the azeotrope composition of 72.5/27.5 (TFP/water by weight) at 365.7 K and atmospheric pressure.[14,15] The LLE experiments were performed as follows: a suitable amount of TFP and water standard solution and ZIF-8-PILs were blended in a customized thermostatic glass container with a magnetic stirrer for 10 min. Then, the stirring was ceased and the mixture was motionless for some time at the same temperature. The typical extraction temperature and time were 298.15 K and 10 min, respectively. During the settlement process, external interference was avoided until the phase equilibrium state was reached.

After that, the two layers were presented clearly and each phase was analyzed accurately by a gas chromatography (GC, SP-6890) instrument equipped with a thermal conductivity detector (TCD). The detailed analysis conditions are listed in Table S1 (ESI†). All samples were tested at least three times, and the average was considered as the final result. The TFP extraction rate was calculated by eqn (1).

$$R = \left[\frac{C_0 - C_f}{C_0} \right] \times 100\% \qquad (1)$$

where C_0 is the concentration of TFP in the standard solution of (TFP + water), and C_f refers to the concentration of TFP in the upper phase after the extraction.

Extraction time, extraction temperature, mass ratio of extractant to (TFP + water) and ZIF-8 content in ZIF-8-PILs were changed to investigate the influences of the conditions. In order to test the extraction recyclability of ZIF-8-PILs, the extractant was separated by a separating process and dried in vacuum at 373.15 K for 24 h. The recovered extractant was charged into the next run for a reuse.

3. Results and discussion

3.1. Extractant characterization

The XRD pattern of ZIF-8 (Fig. S2, ESI†) displayed strong diffractions at $7°$, $10°$, $12°$ and $18°$, similar to the pattern simulated by known structural data, which suggested a high-purity crystal structure. Table S2 (ESI†) shows the CHNS and ICP elemental analysis results of ZIF-8. It could be seen that the element mass percentages in the prepared ZIF-8 sample were almost consistent with the calculated values. The ratio between N and Zn was approximately 4, pointing to a formula of $Zn(C_4H_5N_2)_2$, a coordination composed of one Zn and two imidazole rings. Fig. S3 (ESI†) shows the adsorption–desorption isotherms of ZIF-8, which exhibited a combination of type I and type IV adsorption isotherms. The high N_2 adsorption capacity at very low relative pressure revealed the microporous property of ZIF-8. The small hysteresis loop at high relative pressure indicated the existence of ZIF-8 intergranular large accumulated pores. Based on the desorption branch of the isotherms, ZIF-8 showed a rather high BET surface area of 1228 $m^2 g^{-1}$. The implication of these results was that ZIF-8 could be a good porous frame of PILs. The SEM image in Fig. S4(A) (ESI†) illustrated the regular morphology of ZIF-8 nanoparticles, which were hexagonal blocks with uniform particle size. Based on the SEM image of ZIF-8/[Bpy][NTf$_2$] (Fig. S4(B), ESI†), ZIF-8 nanoparticles had low polymerization and distinct edge, and the elemental mapping images disclosed homogeneous dispersions of Zn across the image area. It indicated that ZIF-8 probably has a high and stable dispersion energy in [Bpy][NTf$_2$]. Fig. S5 (ESI†) shows the TGA curves of ZIF-8/[Bpy][NTf$_2$] and [Bpy][NTf$_2$]. It could be seen from the measured data that the sharp decomposition temperatures of [Bpy][NTf$_2$] and ZIF-8/[Bpy][NTf$_2$] both began at 365 °C, suggesting an excellent thermal stability.

3.2. Influences of extraction conditions

For the purpose of a high TFP extraction efficiency, influences of the extraction temperature and extraction time were investigated with a mass ratio of 2 [ZIF-8/[Bpy][NTf$_2$]: (TFP + water)], which are shown in Fig. 2. The results proved that both were significant extraction parameters, which influenced the extraction performance of ZIF-8/[Bpy][NTf$_2$]. As shown in Fig. 2(a), the viscosity of ZIF-8/[Bpy][NTf$_2$] decreased and the solubility increased as the temperature increased, making it easier for TFP to be separated from its aqueous solution, and eventually the extraction efficiency gradually increased. Furthermore, the low viscosity was beneficial to increase the mass transfer rate, which was the other key factor of the extraction efficiency increase. However, considering the actual situation of industrial production and the idea of energy conservation, 25 °C was selected as the optimal extraction temperature with a relatively satisfying TFP extraction efficiency. Fig. 2(b) shows that the length of the extraction time had only a little influence on the extraction efficiency. The extraction could reach equilibrium in 10 min, which was supposed to arise from the strong electrostatic interaction and hydrogen bonding between ZIF-8/[Bpy][NTf$_2$] and TFP.[14,15] Therefore, 10 min was used as the optimal extraction time.

In addition, ZIF-8/[Bpy][NTf$_2$] and [Bpy][NTf$_2$] were surveyed separately for the extraction of TFP and water, and the results are shown in Fig. 3. Whatever kind of extractant was used, the increase in the mass ratio of extractant to (TFP + water) from 0 to 3 led to a remarkable increase in the TFP extraction efficiency. It showed that [Bpy][NTf$_2$] could separate TFP from
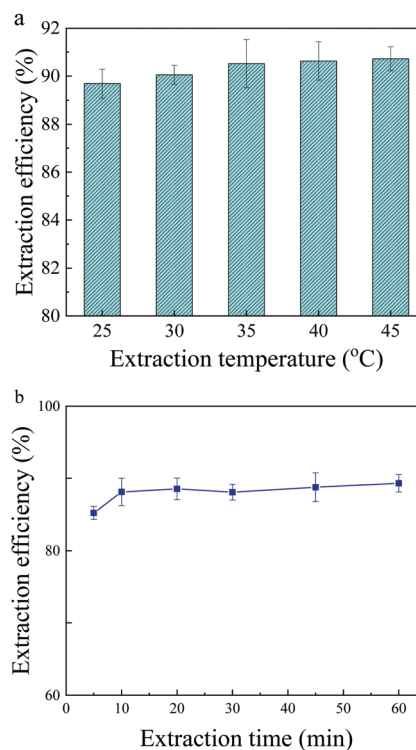

Fig. 2 Influence of (a) extraction temperature and (b) extraction time on the extraction of TFP and water.

the aqueous solution by LLE, consistent with the proposal that ionic liquids are excellent extractants for the separation of water–ethanol mixture.[25–27] Further analysis also demonstrated that ZIF-8/[Bpy][NTf$_2$] maintained the excellent extraction property of ionic liquids. It was of interest to note that when the mass ratio of the extractant to (TFP + water) increased above 0.25, ZIF-8/[Bpy][NTf$_2$] caused a higher TFP extraction efficiency than [Bpy][NTf$_2$]. It verified that ZIF-8 had some effects on the improvement of TFP extraction efficiency, which were supposed to arise from a combination of the stable porous architecture of ZIF-8/[Bpy][NTf$_2$] and the strong intermolecular interaction among [Bpy][NTf$_2$], ZIF-8 and TFP.[14,15] The maximum rate of 92.3% could be obtained at the mass ratio of 3.0. However, considering the economics of extraction, the mass ratio of 2.0 was verified as the optimum condition in this study.

3.3. Extraction mechanism

On the basis of the above experiments, we deduced that the effected TFP extraction efficiency probably stemmed from several factors. First, the ZIF-8 material in PILs possessed a multistage pore structure, high specific microporous surface area characteristics and a large micropore volume, which could make huge improvements on the physical adsorption of PILs, so that could affect the extraction efficiency of TFP. Second, the combination of strong electrostatic interaction among ZIF-8, [Bpy][NTf$_2$] and TFP was one of the biggest factors in reaching an excellent extraction efficiency.

To verify the above speculation, ZIF-8 content in ZIF-8/[Bpy][NTf$_2$] was also surveyed and displayed in Fig. 4. The TFP extraction efficiency slightly rose with the changing of ZIF-8 content in ZIF-8/[Bpy][NTf$_2$], where a maximum extraction efficiency of 89.5% was achieved. Actually, the content of ZIF-8 was so little in ZIF-8/[Bpy][NTf$_2$], and a higher ZIF-8 content caused serious aggregation of nanoparticles in the practical experiment. Therefore, the adsorption capacity of ZIF-8 played little part in the extractive separation of TFP.

To get a deeper insight into the extraction mechanism of the ZIF-8-PILs, different ZIF-8-PILs were prepared; the extraction performances are listed in Table 1. It can be seen that all extraction rates were reduced with the decrease in the mass ratio
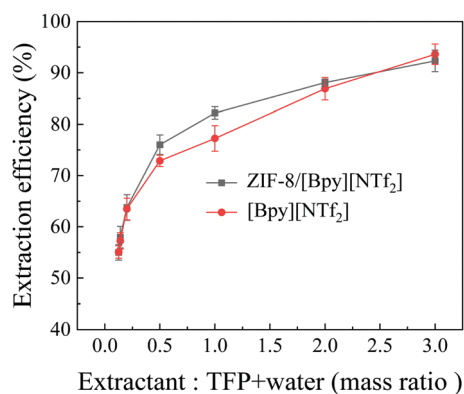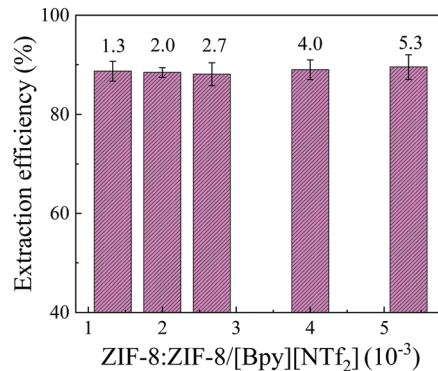

Fig. 4   Influence of ZIF-8 content in 10 min at 25 °C and at the mass ratio of 2.0 (ZIF-8/[Bpy][NTf$_2$]: (TFP + water)) for the extraction of TFP and water.

of ZIF-8-PILs to (TFP + water). This suggested that the ZIF-8-PIL content played an important role during the extraction process, which was consistent with the results of previous reports.[14,15,25,28]

Table 1 displays the extraction results over various functionalized pyridine and imidazole ZIF-8-PILs for comparison. It was observed that increasing the length of the carbon chain in cations could improve the efficiency of TFP extraction (entries 1–3). This could be attributed to the increase of acting force between anions and cations as well as the improvement of the electrostatic attraction between TFP molecules and cations. In addition, this was most likely due to the fact that ionic liquids with longer alkyl chains were more hydrophobic,[29–31] which was preserved in ZIF-8-PILs and functioned as excellent hydrophobic interaction. Furthermore, the extraction efficiency of imidazolyl-PILs was slightly lower than that of pyridinyl-PILs (entries 1–6). It could be seen from the structures of imidazole and pyridine that the nitrogen atoms in pyridine had some enhancement in the polarity of ILs. When pyridinyl-PILs interacted with TFP, the stronger polarization generated some effect on the extraction efficiency.

In addition, ZIF-8/[Hmim][NTf$_2$] still exhibited a lower TFP extraction rate as compared to ZIF-8/[Emim][NTf$_2$] and ZIF-8/[Bmim][NTf$_2$] (entries 4–6). It was most likely that the introduction

Fig. 3   Influence of ZIF-8/[Bpy][NTf$_2$] and [Bpy][NTf$_2$] in 10 min at 25 °C for the extraction of TFP and water.

Table 1   Comparison of different ZIF-8-PILs for the extraction separation of TFP[a]

Entry	ZIF-8-PILs	Extraction capacity of different mass ratio [ZIF-8-PILs: (TFP + water)]	
		2	0.2
1	ZIF-8/[Epy][NTf$_2$]	84.1	43.1
2	ZIF-8/[Bpy][NTf$_2$]	88.1	63.8
3	ZIF-8/[Hpy][NTf$_2$]	88.0	65.9
4	ZIF-8/[Emim][NTf$_2$]	83.7	46.7
5	ZIF-8/[Bmim][NTf$_2$]	87.5	60.3
6	ZIF-8/[Hmim][NTf$_2$]	79.1	37.9
7	[Emim][NTf$_2$]	76.6	40.3
8	[Bmim][NTf$_2$]	82.1	54.8
9	[Hmim][NTf$_2$]	86.5	57.5

[a] Extraction conditions: the separation of TFP and water at 25 °C and the ZIF-8-PILs mass ratio of 1.3×10^{-3} (ZIF-8: [Bpy][NTf$_2$]) for 10 min.
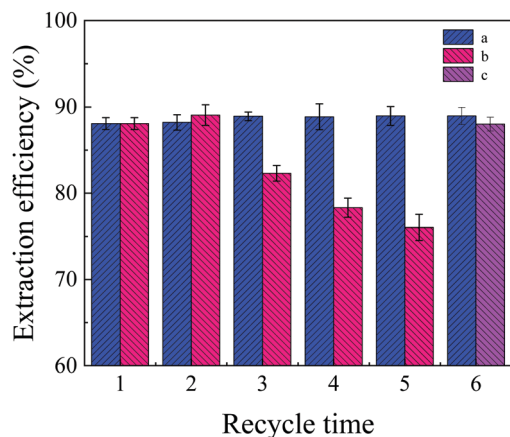
Fig. 5 Extraction recycling of ZIF-8/[Bpy][NTf$_2$] for the extraction separation of TFP and water for 10 min at 25 °C. (a) Recovery and drying, (b) without any further treatment, (c) recovery after the fifth recycle and dried.

of ZIF-8 increased the viscosity of ZIF-8/[Hmim][NTf$_2$] and reduced the extraction efficiency. Based on this speculation, the extraction performances of the corresponding ionic liquids were surveyed under similar extraction conditions (entries 7–9). The results showed that the extraction efficiency improved with the increase of the alkyl chains. These results verified the previous speculation that the pore structure of PILs played an important role in the extraction process. That was to say, the excellent extraction performances of ZIF-8-PILs were closely correlated with their liquid pore and intermolecular interaction.

3.4. Recycling test

To test the repeatability and durability of ZIF-8-PILs, the recycling tests of ZIF-8/[Bpy][NTf$_2$] for the extraction separation of TFP and water were carried out, as shown in Fig. 5. After each cycle, the used ZIF-8/[Bpy][NTf$_2$] was recovered by a separation process. Afterwards, the recovered ZIF-8/[Bpy][NTf$_2$], without any further treatment, was taken directly to next recycle run (Fig. 5(b)). The extraction rate of TFP decreased slowly from 88.1% to 76.0% after five recycle runs. To give an insight into the reasons for the decline in the extraction efficiency, the recovered ZIF-8/[Bpy][NTf$_2$] for the fifth cycle was dried in vacuum at 373.15 K for 24 h, and then reused for the sixth run. As shown in Fig. 5(c), the extraction rate of TFP was nearly back to the first test value. These results indicated that the slow decrease of the extraction efficiency was mainly due to ZIF-8/[Bpy][NTf$_2$] adsorbed and saturated by TFP during the recovery rather than the distortion of the ZIF-8/[Bpy][NTf$_2$] structure. Furthermore, as shown in Fig. 5(a), when ZIF-8/[Bpy][NTf$_2$] from each run was dried and then reused, the extraction rate remained basically unchanged. This suggested that ZIF-8/[Bpy][NTf$_2$] was a reusable extractant for the extraction separation of TFP and water.

4. Conclusions

Porous ionic liquids (ZIF-8-PILs) were synthesized, characterized, and tested for the extraction separation of TFP and water.

The unique liquid porous structure and ionic liquid characteristics enabled ZIF-8/[Bpy][NTf$_2$] to be very efficient in the extraction separation of TFP with a TFP extraction rate of 88%. ZIF-8-PILs also showed a simple preparation, an easy recoverability, and good reusability. The unique liquid pore property and intermolecular interaction were proposed to understand the extraction separation of TFP and water using ZIF-8-PILs. This work may be helpful in the optimization and design of effective functional PILs for the separation of TFP and water.

Author contributions

Zenghui Wang: data curation, writing – original draft. Pingping Zhao: writing – review & editing, supervision. Jimin Wu: software, validation, data curation. Jun Gao: writing – review & editing, resources. Lianzheng Zhang: supervision, resources. Dongmei Xu: funding acquisition, supervision.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

References

1 J. K. Kujawski, W. M. Kujawski, H. Sondej, K. Jarzynka, A. Kujawska, M. Bryjak, E. Rynkowska, K. Knozowska and J. Kujawa, Dewatering of 2,2,3,3-tetrafluoropropan-1-ol by hydrophilic pervaporation with poly(vinyl alcohol) based Pervap™ membranes, *Sep. Purif. Technol.*, 2017, **174**, 520–528.

2 M. Abe, Synthesis and applications of surfactants containing fluorine, *Curr. Opin. Colloid Interface Sci.*, 1999, **4**, 354–356.

3 T. Zhao, J. Z. Zheng and G. Sun, Synthesis and applications of vegetable oil-based fluorocarbon water repellent agents on cotton fabrics, *Carbohydr. Polym.*, 2012, **89**, 193–198.

4 Y. Shih, W. N. Putra, Y. H. Huang and J. Tsai, Mineralization and deflourization of 2,2,3,3-tetrafluoro-1-propanol (TFP) by UV/persulfate oxidation and sequential adsorption, *Chemosphere*, 2012, **89**, 1262–1266.

5 Y. Fumihiko and K. Toshiyuki, *Method for recovering fluoroalcohol*. EP 0992476A2, 2000.

6 Q. S. Li, B. Jia, L. P. Wang, M. M. Yan, H. Liu and Y. M. Yu, Liquid-liquid equilibrium for ternary systems of water + 2,2,3,3-tetrafluoro-1-propanol + isopropyl ether/*tert*-butyl methyl ether at 298.2, 308.2 K, *J. Chem. Thermodyn.*, 2018, **124**, 32–37.

7 X. C. Xu, W. Liu, M. Li, Y. Ri and Y. L. Wang, Ternary liquid–liquid equilibrium of azeotropes (ester + alcohol) with

different ionic liquids at T = 298.15 K, *J. Chem. Eng. Data*, 2016, **62**, 532–538.

8 D. M. Xu, L. Z. Zhang, J. Gao, Z. S. Zhang and Z. F. Cui, Measurement and correlation of liquid–liquid equilibrium for the ternary system 2,2,3,3,4,4,5,5-octafluoro-1-pentanol + methanol + water at (298.15, 308.15, and 318.15) K, *Fluid Phase Equilib.*, 2016, **409**, 377–382.

9 J. Gao, L. Z. Zhang, D. M. Xu, Y. Wei, Z. S. Zhang and Z. F. Cui, Liquid–liquid equilibrium for the ternary system 2,2,3,3,4,4,5,5-octafluoro-1-pentanol + ethanol + water at (298.15, 308.15, and 318.15) K, *J. Chem. Eng. Data*, 2015, **60**, 2733–2738.

10 C. Rochester and J. Symonds, Densities of solutions of four fluoroalcohols in water, *J. Fluorine Chem.*, 1974, **4**, 141–148.

11 G. B. Hong, M. J. Lee and H. M. Lin, Liquid–liquid equilibria of ternary mixtures of water + 2-propanol with ethyl acetate, isopropyl acetate, or ethyl caproate, *Fluid Phase Equilib.*, 2002, **202**, 239–252.

12 T. Welton, Room-temperature ionic liquids: solvents for synthesis and catalysis, *Chem. Rev.*, 1999, **99**, 2071–2083.

13 Z. R. Zhang, J. L. Song and B. X. Han, Catalytic transformation of lignocellulose into chemicals and fuel products in ionic liquids, *Chem. Rev.*, 2016, **117**, 6834–6880.

14 B. T. Diao, Z. H. Wang, H. Yang, L. Z. Zhang and Y. L. Wang, Separation of azeotrope 2,2,3,3-tetrafluoro-1-propanol and water by extractive distillation using ionic liquids: vapor-liquid equilibrium measurements and interaction analysis, *J. Mol. Liq.*, 2019, **292**, 111424.

15 X. W. Zhang, Z. J. Wang, K. Wang, J. Reyes-Labarta and Y. L. Wang, Liquid-liquid phase equilibrium and interaction exploration for separation of azeotrope (2,2,3,3-tetrafluoro-1-propanol + water) with two imidazolium-based ionic liquids, *J. Mol. Liq.*, 2019, **300**, 112266.

16 A. Bavykina, A. Cadiau and J. Gascon, Porous liquids based on porous cages, metal organic frameworks and metal organic polyhedra, *Coord. Chem. Rev.*, 2019, **386**, 85–95.

17 H. Liu, B. Liu, L. C. Lin, G. J. Chen, Y. Q. Wu, J. Wang, X. T. Gao, Y. N. Lv, Y. Pan, X. X. Zhang, X. R. Zhang, L. Y. Yang, C. Y. Sun, B. Smit and W. C. Wang, A hybrid absorption–adsorption method to efficiently capture carbon, *Nat. Commun.*, 2014, **5**, 5147.

18 K. Ballerat-Busserolles, A. R. Lowe, Y. Coulier and J. Coxam, *Thermodynamic approach of CO2 capture, combination of experimental study and modeling*, John Wiley & Sons, Ltd. 2016.

19 W. D. Shan, P. F. Fulvio, L. Y. Kong, J. A. Schott, C. L. Do-Thanh, T. Tian, X. X. Hu, S. M. Mahurin, H. B. Xing and S. Dai, A new class of type III porous liquids: a promising platform for rational adjustment of gas sorption behavior, *ACS Appl. Mater. Interfaces*, 2017, **10**, 32–36.

20 S. J. Liu, J. D. Liu, X. D. Hou, T. T. Xu, J. Tong, J. X. Zhang, B. J. Ye and B. Liu, Porous liquid: a stable ZIF-8 colloid in ionic liquid with permanent porosity, *Langmuir*, 2018, **34**, 3654–3660.

21 G. Margarida Costa, P. Laure, C. Ctirad and P. Agilio, Porous ionic liquids or liquid metal–organic frameworks?, *Angew. Chem.*, 2018, **57**, 11909–11912.

22 T. Virdis, V. Danilov, G. Baron and J. F. M. Denayer, Non-ideality in the adsorption of ethanol/ethyl acetate/water mixtures on ZIF-8 metal organic framework, *Ind. Eng. Chem. Res.*, 2018, **57**, 7040–7047.

23 Y. W. Tang, D. Dubbeldam, X. M. Guo, G. Rothenberg and S. Tanase, Efficient separation of ethanol-methanol and ethanol-water mixtures using ZIF-8 supported on a hierarchical porous mixed-oxide substrate, *ACS Appl. Mater. Interfaces*, 2019, **11**, 21126–21136.

24 C. W. Tsai and E. H. G. Langner, The effect of synthesis temperature on the particle size of nano-ZIF-8, *Microporous Mesoporous Mater.*, 2016, **221**, 8–13.

25 J. Gao, Y. X. Ma, L. Z. Zhang, W. Liu, D. M. Xu, X. C. Xu and Y. L. Wang, Measurement and correlation of phase equilibria for ternary systems of water + (ethanol/1-propanol) + 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide at 298.15 K, *Fluid Phase Equilib.*, 2016, **427**, 340–344.

26 W. Liu, Z. Zhang, Y. S. Ri, X. C. Xu and Y. L. Wang, Liquid-liquid equilibria for ternary mixtures of water + 2-propanol + 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids at 298.15 K, *Fluid Phase Equilib.*, 2016, **412**, 205–210.

27 M. P. Cumplido, A. Cháfer, J. D. L. Torre and H. Poy, Separation of the azeotropic mixture 2-propanol + water employing different imidazolium ionic liquids as solvents, *J. Chem. Thermodyn.*, 2020, **140**, 105889.

28 D. M. Xu, L. Z. Zhang, J. Gao, D. Pratik, L. W. Zhao and Z. F. Cui, Liquid-liquid equilibrium for ternary systems of ethyl acetate/isopropyl acetate + 2,2,3,3-tetrafluoro-1-propanol + water at 298.15, 318.15K, *J. Chem. Thermodyn.*, 2016, **106**, 218–227.

29 Y. Y. Zhang, L. K. Wang, Q. P. Rao, Y. C. Bu, T. R. Xu, X. J. Zhu, J. Zhang, Y. P. Tian and H. P. Zhou, Tuning the hydrophobicity of pyridinium-based probes to realize the mitochondria-targeted photodynamic therapy and mitophagy tracking, *Sens. Actuators, B.*, 2020, **321**, 128460.

30 D. Cao, X. Xu, X. Feng and L. Zhang, Designed multifunctional visual observation of magnetic ionic liquid coupling with microwave-assisted derivatization for determination of bio-genic amines, *Food Chem.*, 2020, **333**, 127518.

31 A. Acharyya and D. DiGiuseppi, B. L. Stinger, R. Schweitzer-Stenner and T. D. Vaden, Structural destabilization of azurin by imidazolium chloride ionic liquids in aqueous solution, *J. Phys. Chem. B*, 2019, **123**, 6933–6945.