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Preparation of microcapsules containing ionic liquids with a new solvent extraction system

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ABSTRACT

Ionic liquids have recently attracted much attention as newly developed green solvents, but their high viscosity greatly limits their application. Immobilizing these ionic liquids using microencapsulation may solve this problem. In this study, a new extraction system for preparing microcapsules was developed in which a mixture of poly(dimethylsiloxane) and *n*-butyl acetate was used as the continuous phase, and polyacrylonitrile and ionic liquids were dissolved in *N*,*N*-dimethylformamide for the dispersed phase. The emulsion was prepared using a microfluidic device. The solidification of droplets was realized by extracting *N*,*N*-dimethylformamide from the dispersed phase to the continuous phase. Three different ionic liquids, [BMIM][PF6], [BMIM][BF4] and [HMIM][BF4], were successfully encapsulated with the average diameter of the microcapsules in the range of 200–350 μm. The properties of microcapsules – the surface structure, the loading ratio and the mean diameter – could be controlled by changing the operating conditions such as phase composition and the flow rate of two phases.

1. Introduction

Ionic liquids (ILs) are fluids at room temperature and are composed entirely of ions, typically large organic cations and small inorganic anions. The thermodynamic characteristics of ILs are very different from those of conventional media, they possess negligible volatility, are non-flammable, thermally and chemically stable, and exist as liquids over a wide temperature/pressure range [1]. These unique traits make ILs suitable as solvents alternative to traditional volatile organic compounds in different research areas such as separations [2–7], catalytic reactions [8,9], electrochemistry [10,11], and combined reaction/separation processes [12].

Although the high viscosity of ILs greatly impedes fluid flow and mass transfer, these negative effects can easily be avoided by immobilizing ILs via microencapsulation. The small size and huge total interfacial area of microcapsules are essential for overcoming the difficulties in phase mixing and phase separation caused by high viscosity. Yang et al. [13] encapsulated [BMIM][PF6] in polysulfone (PsF) by a solvent evaporation method. The microcapsules were monodispersity and had spherical morphology, but the encapsulation capacity for the ionic liquid was only 30.8%. There was significant loss of ILs during preparation because of their solubility in the continuous phase. Gong et al. [14,15] used poly(dimethylsiloxane) (PDMS) as the continuous phase in a solvent evaporation process. Polar compounds or macromolecular compounds were encapsulated with negligible loss in the preparation process. But, the evaporation temperature was very high and the process required a long period of time for microcapsule solidification.

Up to now, various methods have been used for microcapsule preparation including polymerization [16,17], solvent evaporation [18–21], solvent extraction [22–25], coacervation [26]. Solvent extraction is one of the

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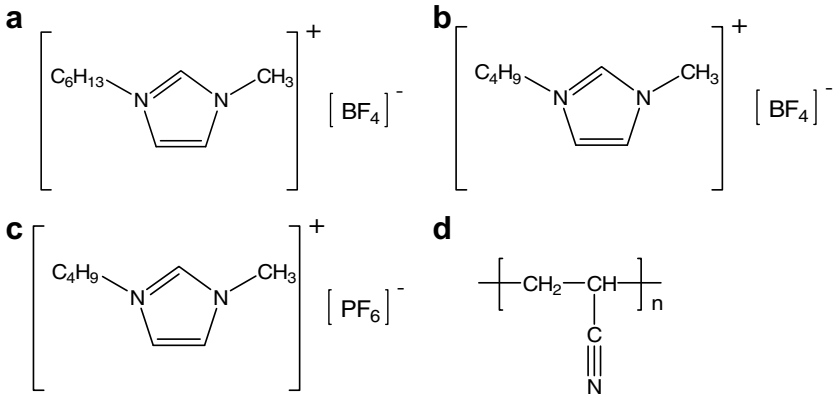

Fig. 1. Structural formulas. (a) [HMIM][BF4]; (b) [BMIM][BF4]; (c) [BMIM][PF6]; and (d) PAN.

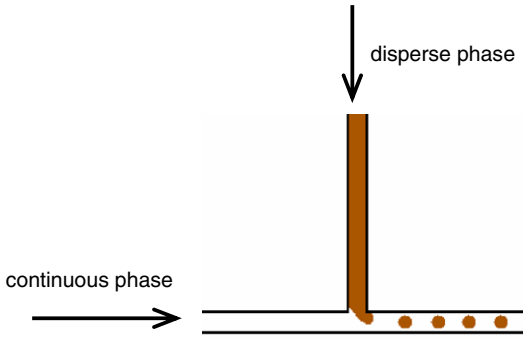

Fig. 2. Microfluidic device.

simplest methods for microcapsule preparation. This method contains a fast solidification process but nevertheless requires a carefully designed working system. In order to apply solvent extraction method for preparing microcapsules containing ILs, a new solvent extraction system was developed. *n*-Butyl acetate (BA) is soluble in both DMF and PDMS but insoluble in ILs, therefore BA was chosen to increase the solubility of DMF in continuous phase. In this new system, polyacrylonitrile (PAN) and ILs were dissolved in *N*,*N*-dimethylformamide (DMF) for the dispersed phase, and a mixture of PDMS and BA was used as the continuous phase. A microfluidic device was used to produce the emulsion and control the microcapsule size and distribution. The prepared microcapsules were evaluated according to the ionic liquid loading ratio, surface morphology and particle size.

2. Experiment

2.1. Reagents

ILs 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF6]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF4]) and 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM][BF4]) were purchased from Henan Lihua Pharmaceutical Co., Ltd. (purity > 99%). PAN (mean molecular weight: 60,000) were purchased from Beijing Trihigh Membrane Technology Co., Ltd. PDMS (viscosity: 100 mPa s) was purchased from Beijing Pinghua Shangmao Co., Ltd. DMF (purity > 99.5%), BA (purity > 99.5%), and petroleum ether (boiling point: 60–90 °C) were purchased from Beijing Xiandai Dongfang Chemical Industry. All the materials were used as received without any further purification. The structural formulas of the ILs and PAN are shown in Fig. 1.

Table 1
Preparation condition and characteristics of microcapsules ($n = 3$)

No.	ILs add in disperse phase	Flow rate of disperse phase, μL/min	Flow rate of continuous phase, mL/min	BA volume concentration in continuous phase	Loading ratio	Mean diameter, μm
1	[HMIM][BF4] 0.300 g	50	2.5	1/6	0.223 ± 0.002	345 ± 2
2	[BMIM][BF4] 0.300 g	50	2.5	1/6	0.234 ± 0.002	330 ± 3
3	[BMIM][PF6] 0.300 g	50	2.5	1/6	0.229 ± 0.002	240 ± 3
4	[BMIM][PF6] 0.300 g	50	2.5	1/7	0.226 ± 0.002	225 ± 2
5	[BMIM][PF6] 0.300 g	50	2.5	1/5	0.229 ± 0.002	235 ± 2
6	[BMIM][PF6] 0.300 g	50	2.5	1/3	0.227 ± 0.002	325 ± 1
7	[BMIM][PF6] 0.300 g	50	0.5	1/6	0.226 ± 0.002	375 ± 1
8	[BMIM][PF6] 0.300 g	50	1.0	1/6	0.231 ± 0.002	300 ± 1
9	[BMIM][PF6] 0.300 g	50	1.5	1/6	0.228 ± 0.002	275 ± 2
11	[BMIM][PF6] 0.300 g	75	2.5	1/6	0.230 ± 0.002	275 ± 1
12	[BMIM][PF6] 0.300 g	100	2.5	1/6	0.223 ± 0.002	365 ± 2
13	[BMIM][PF6] 0.225 g	50	2.5	1/6	0.167 ± 0.002	290 ± 1
14	[BMIM][PF6] 0.450 g	50	2.5	1/6	0.298 ± 0.002	315 ± 2