Purification of Ionic Liquids: Sweeping Solvents by Nitrogen

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Room-temperature ionic liquids (ILs) which are regarded as environmentally benign solvents are widely used in many research areas. However, the purity of ILs influences the properties of ILs and further applications. The remains of water and organic solvents in ILs not only reduce the purity of ILs but also influence the physicochemical properties and even the results of reactions performed in ILs. In this work, we found a new method, sweeping solvents by N_2, to remove quickly the volatile impurity in ILs at mild conditions. The effecting factors of the new method and the comparison with the traditional method have been investigated, and it was found that temperature and N_2 flow rate influence the time for removing volatile impurities from four types of ILs. The new method can easily remove the IL's impurities, including water, ethanol, methanol, acetonitrile, ethyl acetate, and acetone, to a mass fraction as low as 10^{-3}, and the time decreases greatly to just a few hours, even less than 0.5 h. Furthermore, the mechanism of sweeping solvents by blowing N_2 has been investigated.

Introduction

Room-temperature ionic liquids (ILs), low-temperature molten salts, are regarded as environmentally benign solvents and have been widely investigated for their many unique properties, including extremely low vapor pressure, tunable structure, high thermal and chemical stability, and excellent solvent power for organic and inorganic compounds. Therefore, they have a wide variety of engineering applications in many research areas, such as reactions[1,2] and gas separations.[3−6] However, due to the use of large amounts of solvents in synthesis processes of ILs, solvent impurities cannot be avoided. Those solvent impurities mainly are water and organic solvents,[7,8] such as acetonitrile, methanol, ethanol, benzene, ethyl acetate, dichloromethane, and 1,1,1-trichloroethane. Furthermore, normally ILs are hygroscopic. Both hydrophilic ILs and hydrophobic ILs have the property to absorb water. The remains of water and organic solvents not only reduce the purity of ILs but also influence the physicochemical properties of ILs. For example, the presence of water can change the conductivity, the viscosity, and the density of ILs.[9,10] Moreover, the presence of water can make the catalysts in ILs inactive and influence the resultants.[11]

The traditional method to remove water and organic solvents is to heat ILs under vacuum. Particularly, the reduction of water commonly needs (12 to 48) h under pressures of (133 to 665) Pa at (60 to 120) °C. This method has some disadvantages in the purification of ILs. For instance, the time of this process is at least 12 h. Sometimes, to obtain a low content of water, the time may need 24 h or even more. The long-term thermal stability of ILs has been investigated by Wooster et al.[12] They found that degradation occurs when the temperature is held at an elevated level for a longer period (about 10 h). After the drying procedure, the ILs which are referred to as "dried" ILs may still contain some water.[13] Some types of ILs are hydrophilic, with strong hydrogen bonds between ILs and water, and this method can with difficulty decrease the water content to a low value. During the dehydrating process, the vacuum and the heat of ILs need much energy because of the long period of treatment.

In this work, we presented a new method, sweeping solvents by nitrogen, to remove water and volatile organic solvents from ILs. By this method, the impurity of ILs can be removed in a few hours, and even water in hydrophilic ILs can be removed to very low content, less than 0.0010 mass fraction. The short time of purification of ILs can save much energy and avoid the degradation of ILs. In our work, the new method can also be used to know the interaction power of solvents with ILs to choose the solvents before synthesis and purification of ILs, and the mechanism of this method is explained.

Experimental Section

Materials. N_2 with a volume fraction purity of 0.9995 was supplied from Beijing Haipu Gases. 1,1,3,3-Tetramethylguanidine was purchased from Baigui Chemical Company (Shijiazhuang, China), which was distilled before use. Monoethanolamine was purchased from Tianjin Fuchen Chemical Company (Tianjin, China). Lactic acid was from Shanghai Jingchun Reagent Plant (Shanghai, China). Acetic acid, methanol, ethanol, acetone, and ethyl acetate were from Beijing Chemical Plants (Beijing, China). Acetonitrile was from Tianjin Xihua Special Regent Plant (Tianjin, China). 1-Butyl-3-methyl imidazolium tetrafluoroborate ([Bmim][BF_4]) was from Henan Lihua Pharmaceutical Co., Ltd. (Henan, China) and had a mass fraction purity of 0.99. All of the reagents and solvents were analytical reagents. 1,1,3,3-Tetramethylguanidinium lactate ([TMG]L) was synthesized and characterized following the procedures reported in the literature.[4,14] Monoethanolamine lactate ([MEA]L) and monoethanolamine acetate ([MEA]Ac) were synthesized and characterized following the procedure reported by Yuan et al.[15]

Apparatus and Procedures. The traditional method used in this experiment was to heat ILs containing solvents under vacuum (less than 665 Pa) at 70 °C in a vacuum oven, and ILs

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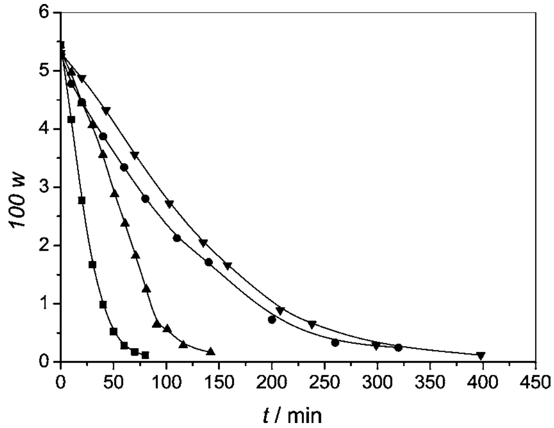

Figure 1. Mass fraction of water (w) in different ILs as a function of time with 100 mL·min^{-1} of sweeping N_2 at 70 °C: ■, [BMIM]BF_4; ●, [TMG]L; ▲, [MEA]L; ▼, [MEA]Ac.

are loaded in a test tube with an inner diameter of 12 mm and a length of 200 mm. The sweeping method was carried out at an ambient pressure using N_2 gas as the sweeping gas at certain temperatures. It consisted mainly of a cylinder containing N_2 gas, a test tube with an inner diameter of 12 mm and a length of 200 mm, a constant temperature oil bath, and a rotometer.

In a typical experiment of the sweeping method, the N_2 gas was bubbled through an amount of IL (about 5 g with about 0.05 mass fraction of water or organic solvents) loaded in the test tube. The test tube was almost totally immersed into the oil bath, which temperatures were maintained within ± 1 °C. The flow rate of N_2 was controlled by a rotometer and calibrated by a soap film fluid meter.

After a given time, two methods were used to measure the mass fraction of water and organic solvents in ILs. The mass fraction of water in ILs was determined by Karl Fischer titration (ZDJ-400S, Multifunctional titrator, Beijing Xianqu Weifeng Company, Beijing, China). The expanded uncertainty of water mass fraction is ± 6.4 % at the mass fraction of water $= 10^{-3}$. The mass fractions of organic solvents in ILs were determined by the mass difference of the test tube via an electrical balance (BS224S, Sartorius) with an accuracy of ± 0.0001 g. The expanded uncertainty of organic solvent mass fraction in ILs is ± 4.2 % at organic solvent mass fraction $= 10^{-3}$.

Results and Discussion

Sweeping Water from Different Types of ILs. In this study, four types of hydrophilic ILs, [BMIM]BF_4, [TMG]L, [MEA]L, and [MEA]Ac, with about 0.05 mass fraction of water, were prepared. The mass fractions of water in ILs as a function of time are shown in Figure 1 with 100 mL·min^{-1} of N_2 as the sweeping gas at 70 °C. The mass fraction of water decreases from 0.05 to about 0.001 in a few hours. Taking [BMIM]BF_4, for example, the water mass fraction reduces from 0.055 to 0.0011 in only 80 min.

The time consumed in this process is much shorter than that in the traditional method. Table 1 shows the comparison of the traditional method with this sweeping method. It indicates that, using the traditional method in the drying procedure of [BMIM]BF_4, the time is more than 1440 min (24 h). For some types of ILs, such as [TMG]L and [MEA]L, there are strong hydrogen bonds between water and ILs. Thus, the residual water in these ILs is very high, and the water content decreases slowly. At entry 7 in Table 1, for the traditional method, after 2880 min (48 h), the water mass fraction in [TMG]L only can decrease from 0.053 to 0.019, while, using the sweeping method, the water mass fraction in [TMG]L can be decreased from 0.053 to 0.0025 in 320 min as shown at entry 9 in Table 1.

Table 1. Comparison of the Traditional Method with the Sweeping Method in the Removal of Water from Two Types of ILs[a]

entry	IL	T/°C	100 w(B)	100 w(A)	100 R	t/min	method
1	[BMIM]BF_4	70	5.6	0.45	92	360	traditional
2	[BMIM]BF_4	70	5.6	0.16	97	720	traditional
3	[BMIM]BF_4	70	5.6	0.12	98	1440	traditional
4	[TMG]L	70	5.3	4.4	16	360	traditional
5	[TMG]L	70	5.3	3.8	29	720	traditional
6	[TMG]L	70	5.3	2.9	45	1440	traditional
7	[TMG]L	70	5.3	1.9	65	2880	traditional
8	[BMIM]BF_4	70	5.5	0.11	98	80	sweeping
9	[TMG]L	70	5.3	0.25	95	320	sweeping

[a] w(B), the mass fraction of water in IL before purification; w(A), the mass fraction of water in IL after purification; R, removal efficiency of water.

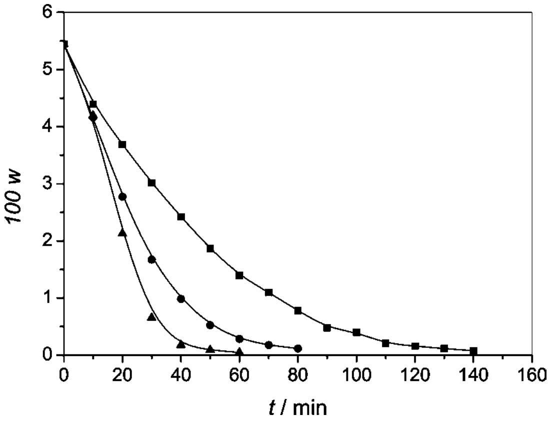

Figure 2. Mass fraction of water (w) in [BMIM]BF_4 as a function of time with 100 mL·min^{-1} of sweeping N_2 at different temperatures: ■, 50 °C; ●, 70 °C; ▲, 90 °C.

The results suggest that this new method can save much time and energy compared with the traditional one in the synthesis and purification of ILs, and it can make ILs, which are referred to as "dried" ILs after the traditional drying procedure, be really dried.

Effect of Temperatures and N_2 Flow Rates on Sweeping Water from [BMIM]BF_4. Temperature has an influence on the removal rate of water from ILs by the traditional vacuum treatment. Therefore, in this work, the effect of temperature on sweeping process was investigated. Figure 2 shows the mass fraction of water in [BMIM]BF_4 as a function of time with 100 mL·min^{-1} of sweeping N_2 at temperatures of (50, 70, and 90) °C. Figure 2 indicates that the increase of temperatures can make the water mass fraction of [BMIM]BF_4 decrease quickly. For instance, when the temperatures increase from (50 to 90) °C, the time of this dehydration process is from (140 to 60) min with the water mass fraction of ILs decreasing from 0.055 to less than 0.0010.

Although an increase of the temperatures of this drying process can save much time of drying ILs, some types of ILs are not suitable to heat under high temperatures, because of the low decomposition temperatures of these ILs. So the other effecting factor of this new method, N_2 flow rates, was studied. The flow rates were changed from (50 to 150) mL·min^{-1} at 70 °C, and the results are shown in Figure 3. From Figure 3, it can be seen that, as flow rates increase, the mass fraction of water can also decrease quickly at the same temperature. For example, when the flow rate of nitrogen was set at 50 mL·min^{-1}, the time of this process was 140 min with the water

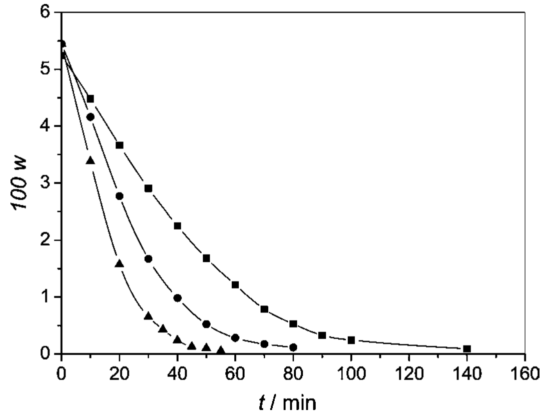

Figure 3. Mass fraction of water (*w*) in [BMIM]BF_4 with different fluxes of N_2 at 70 °C: ■, 50 mL·min^{-1} of N_2; ●, 100 mL·min^{-1} of N_2; ▲, 150 mL·min^{-1} of N_2.

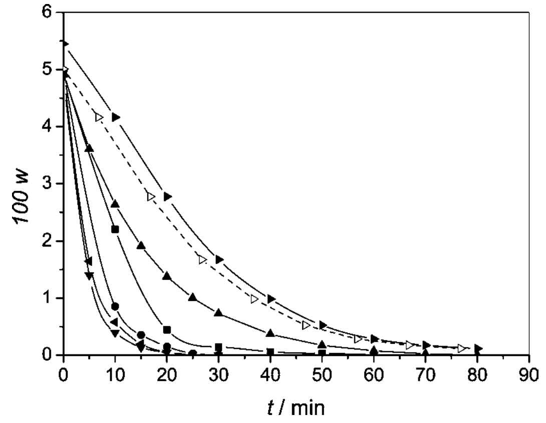

Figure 4. Mass fraction of different kinds of solvents (*w*) in [BMIM]BF_4 with 100 mL·min^{-1} of N_2 at 70 °C: ■, ethanol; ●, methanol; ▲, acetonitrile; ▼, ethyl acetate; solid left-pointing triangle, acetone; solid right-pointing triangle, water; open right-pointing triangle, water (the initial water content is set as 0.05 close to the other solvent's content by interpolation for comparison).

mass fraction in the IL from 0.052 to less than 0.0010. However, when the flow rate of nitrogen was set at 150 mL·min^{-1}, the time was just 55 min with the same water mass fraction changes. The time is much shorter than that at 50 mL·min^{-1}.

As shown in Figures 2 and 3, both temperature and flow rate of sweeping gas have great influence on the removal efficiency of water in ILs. The higher temperature and the higher flow rate, the shorter the sweeping time for purifying ILs. The short time can reduce the degradation of ILs and save energy.

Sweeping Organic Solvents from [BMIM]BF_4. From Figures 1 to 3, it can be seen that this sweeping method can reduce the water mass fraction of ILs in a short time. However, after the synthesis, not only water exists in ILs, but also the organic solvents exist. These organic solvents mainly contain ethanol, methanol, acetonitrile, ethyl acetate, and so on. In Figure 4, five kinds of organic solvents in [BMIM]BF_4 were studied to remove with the sweeping method and to compare the strength between the IL and the different kinds of solvents.

Figure 4 indicates that these five kinds of volatile organic solvents in [BMIM]BF_4 can be blown out by sweeping gas at 70 °C in just a few hours. The mass fraction of organic solvents in [BMIM]BF_4 can decrease from about 0.05 to nearly zero. For example, with 0.050 mass fraction of ethanol in [BMIM]BF_4, the ethanol can be almost removed in 60 min to less than 0.0001 mass fraction.

Although all of these five volatile organic solvents and water can be removed by sweeping gas in a few hours, the time of each solvent has a few differences. Figure 4 shows that the removal rates of organic solvents are different. For example, with 0.049 mass fraction of acetonitrile in [BMIM]BF_4, the purification time is 80 min. But when 0.050 mass fraction of acetone is present in the IL, the time of sweeping is 30 min. The increase order of sweeping time is ethyl acetate, acetone, methanol, ethanol, acetonitrile, and water. This may be due to the polarity and dipole moment of these solvents. ILs are molten salts and composed of cations and anions. As a result, the polarity of ILs is strong. ILs have strong force with the polarity solvents. Because of this reason, these kinds of solvents, such as water, acetonitrile, are hard to be desorbed from ILs. However, the weak polarity solvents, such as ethyl acetate and acetone, can be easily blown out from ILs.

As we know, when ILs are synthesized and purified, many kinds of organic solvents could be used. It is important for users to choose the proper solvents. Figure 4 shows that the interaction forces between solvents and ILs are different, which hints the order of the polarity of these solvents. The figure also suggests a way to choose solvents that can be easily removed during the processes of synthesis and purification of ILs.

Mechanism of the Sweeping Process. From these data and figures we can conclude that the sweeping method is an efficient way to remove solvents from ILs. In Figure 5, a mechanism for the new sweeping method is proposed and compared with the traditional method. When the mixture of IL and solvent is heated to a certain temperature, there is a saturation steam of solvent on the surface of IL. The saturation pressure is connected with the mole ratio of solvent to IL, which obeys Henry's law.

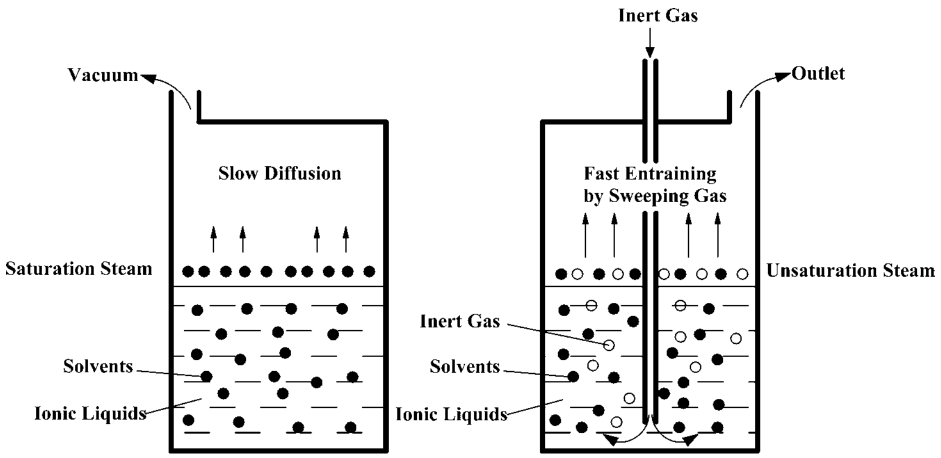

Figure 5. Mechanism of the traditional method and the sweeping method in the removal of solvents from ILs.

In the traditional method to remove solvent, when the pressure of the system is vacuumed to a low value, the difference of solvent contents between the surface and the system drives the diffusion. However, this force is not strong enough, and the diffusion is very slow, which costs much time. While using the sweeping method, the saturation steam in the surface of ILs is diluted by the blowing gas, and the vapor−liquid equilibrium of the solvent on the surface is broken greatly and continuously. The reduction of the solvent's vapor pressure makes more and more solvent molecules in ILs vaporized into the upper vapor phase through the IL surface. The moving inert gas entrains quickly away the solvent in the vapor phase, and this driving force is much stronger than the diffusion. Moreover, the stir of the liquid mixture by the moving inert gas can also enhance the evaporation of solvents from the ILs. In the sweeping method, when the temperature increases, the evaporation pressure of the solvent becomes higher. This makes the removal rate fast. When the gas flow rate increases, the vapor pressure of the solvent in steam through IL and on the IL surface is farther from the saturation value, and then the mass transfer force is larger, which also speeds the rate of solvent removal from ILs and shortens the purification time.

Conclusions

In this work, we proposed a new sweeping method to efficiently purify ILs. This new method was compared with the traditional method. It shows that the new method can be used to remove water and volatile organic solvents in just a few hours, even much less than 0.5 h, and can make the water mass fraction of hydrophilic ILs to about 0.0010. It is found that the increase of temperature and the N_2 flow rates can speed the purification process. The sweeping method can supply a new way to find the interaction force between solvents and IL, which may help to choose solvents for synthesis and purification of ILs. A possible mechanism for the new method has been proposed.

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