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Complexes of Ionic Liquids with Poly(ethylene glycol)s

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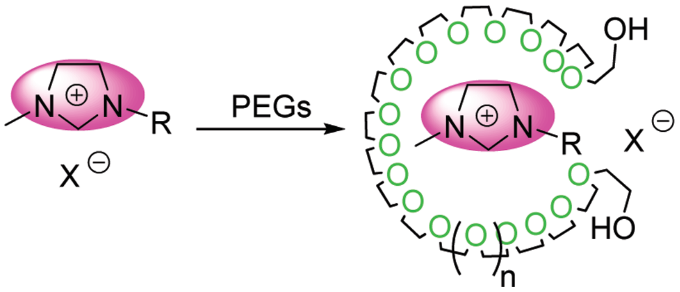

The self-assembly behavior of ionic liquids with acyclic polyethers was studied. The cations of 1-alkyl-3-methylimidazolium salts and 1-alkylpyridinium salts could form complexes at a ratio of 1:1 with poly(ethylene glycol)-800 (PEG800) and poly(propylene glycol)-1000 (PPG1000) in which the chain length was suitable to wrap around the cations. On the basis of the investigation by NMR, mass spectrometry, UV−vis spectroscopy, and TG analysis, the formation and characteristics of the novel complexes were discussed.

Introduction

Ionic liquids (ILs) nowadays are very fascinating for a growing number of scientists and engineers due to their unique properties as "green" materials: low melting point, nonflammability, negligible vapor pressure, a wide electrochemical window, and extraordinary tunability.[1] These characteristics of ILs promoted them to being used in a wide range of applications, from catalysis,[2] synthesis,[3] separations,[4] electrochemistry,[5] polymers,[6] to magnetic or nanostructured materials.[7,8] For their eventual success in technological applications, the extensive studies of ILs were ongoing to provide the insights into the molecular factors that determined their properties.[9] Recently it

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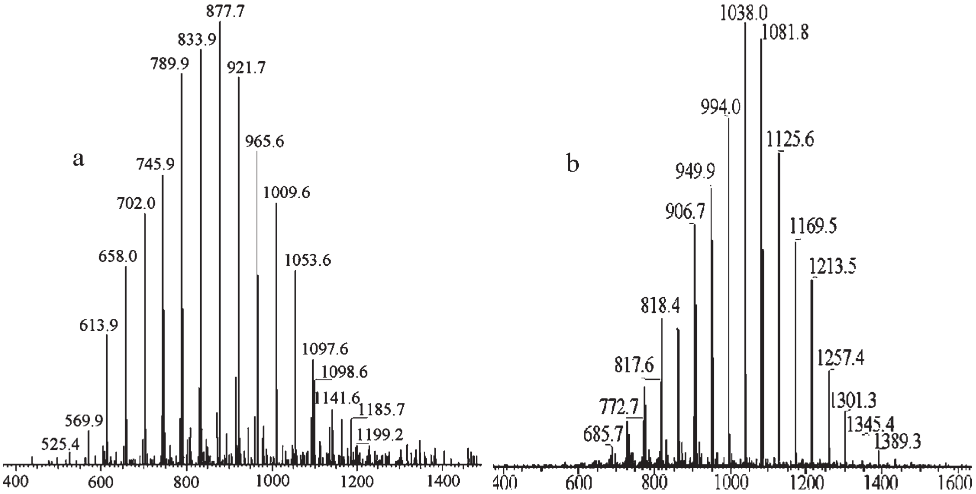

FIGURE 1. ESI mass spectra of the PEG800 (a) and PEG800/[C_4mim]BF_4 (b).

was found that ILs could be encapsulated as novel guests for cucurbit[6]uril in water.[10] The interesting self-assemble capability of ILs provides a challenging terrain for chemists and opens a new application.

Does the self-assemble of ILs widely exist? We anticipate that the ether compounds, such as crown ethers and acyclic polyethers, are suitable for exploring the physicochemical property of ILs because they have the ability to form complexes with metal salts and organic salts by ion−dipole interaction.[11,12] On the basis of the structural difference between ILs and metal salts, poly(ethylene glycol)s (PEGs) as acyclic polyethers that have flexible polyethylene oxide chains and broad applications in biotechnology and medicine were chosen.[13] In this article, we would like to report our new laboratory work that ILs, for example, 1-alkyl-3-methylimidazolium salts ([$C_n$mim]X) and 1-alkylpyridinium salts ([$C_n$py]X), could form complexes with PEGs. More importantly, this complexes of PEG-ILs could not only have potential applications in chemosensors, catalysis,[14] supramolecular materials,[15] and the ILs recycle,[16] but also stimulate the interactional research of ILs with biopolymers, polypeptides, and proteins.[12a]

Results and Discussion

To assess the complex formation ability of [$C_n$mim]X (n = 0−14, X = BF_4, PF_6, Cl, Br, HSO_4, H_2PO_4, Tf, NTf_2), [C_4mim]BF_4 and PEGs which had different molecular weights were dissolved in methanol as samples of the initial study. In the qualitative research, we found electrospray ionization mass spectrometry (ESI-MS) was an available examination method to give the direct evidence supporting the presence of the presumed PEG-ILs complexes. As Figure 1 shows, in the positive ion mode ESI mass spectra of PEG-800, the normally distributed ion peaks were easily identified at a m/z ratio in agreement with the calculated values $[HO(C_2H_4O)_nH + Na^+]$ (n = 13−24). When the mixture of [C_4mim]BF_4 with PEG-800 was tested, the signals move up to the higher mass region in Figure1b and an ∼116 Da shift was observed from the signals in Figure 1a, respectively. For example, an ∼116 Da shift from the signal at m/z 877.7 in Figure.1a gave rise to m/z 994.0 in Figure.1b. Therefore, the signals in the higher mass region in Figure.1b could be assigned to ions of [PEG800 + (C_4mim)-BF_4]$^+$, which demonstrated that the stable host−guest complexes of 1-butyl-3-methylimidazolium cation ([C_4mim]$^+$) with PEG800 were formed at a ratio of 1:1. Furthermore, the same phenomenon was found in PEG1000 which have similar polyethylene oxide chains. PEG200, PEG400, PEG600, PEG1500, and PEG2000 which have shorter or longer chains could not wrap [C_4mim]$^+$ at the same conditions (Supporting Information). As structurally related polymers, poly(propylene glycol)s (PPGs) were embodied with the same binding regularity and only PPG1000 could form 1:1 complexes with [C_4mim]BF_4 (Figure2).

The self-assembly behavior of different ILs with PEG800 was also studied in the ESI mass spectra. When the alkyl chains at the 1-position of the imidazolium were changed

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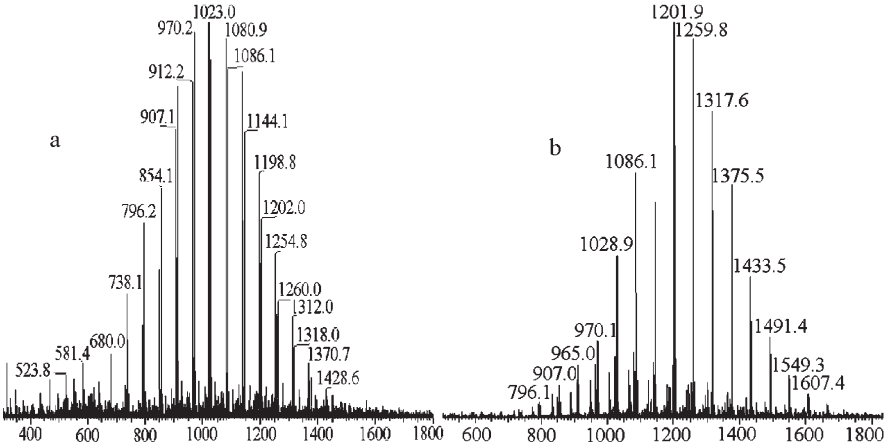

FIGURE 2. ESI mass spectra of the PPG1000 (a) and PPG1000/[C_4mim]BF_4 (b).

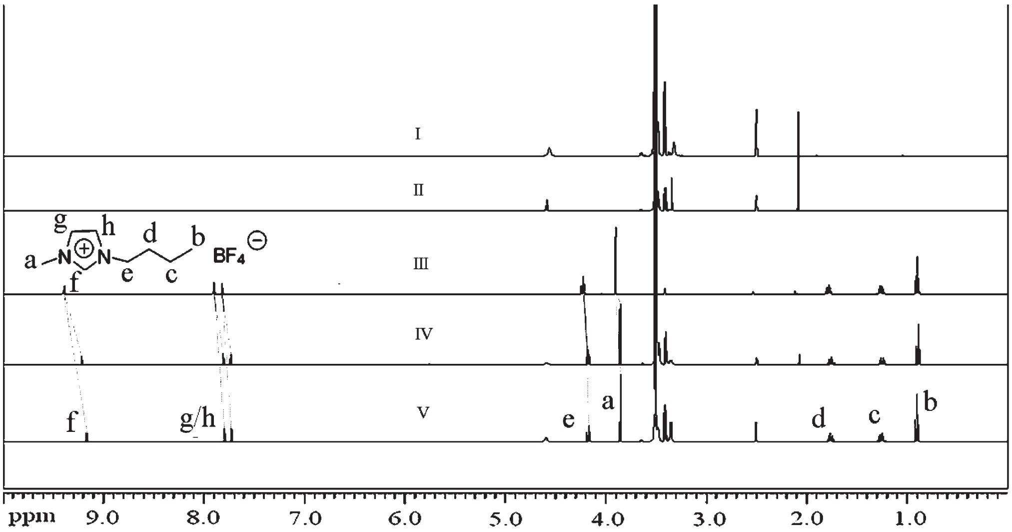

FIGURE 3. Partial ^{1}H NMR spectra of PEG800 (I), PEG1000 (II), [C_4mim]BF_4 (III), PEG800/[C_4mim]BF_4 (IV), and PEG1000/[C_4mim]BF_4 (V).

from H to C14, the complexes were all detected. As was predicted, various anions of imidazolium salts could not affect the complex formation since the anions were dissociating out of the complexes. The same self-assembly appearance was found in another type of ILs, 1-alkylpyridinium tetrafluoroborate ([$C_n$py]BF_4, $n = 2, 4, 8$) with PEG800 (Supporting Information).

To investigate the structure change in the complexation, ^{1}H NMR experiments were performed in DMSO-d_6. As shown in Figure 3, the protons (H_f, H_g, and H_h) on the imidazolium ring were clearly upfield shifted, indicating that they were located within a hole of the coiled PEG800, which gave a shielded environment. However, except for the protons of the alkyl chain related to the imidazolium ring being shift slightly upfield, the other protons of the alkyl chain had no evident changes. The results showed that the alkyl chain was not affected by PEG800 because it was likely out of the hole of PEG800. Obviously, PEG800 wraped around the imidazolium ring, which has the positive electrical property rather than the hydrophobic alkyl chain. By the ion−dipole interaction, the PEG-ILs complexes were the lowest energy structure that had the imidazolium ring of ILs "solvated" by the polymer chain with suitable oxygen atoms as the nearest neighbors.

As the complexes formed, the weakening of the UV−vis absorbance of ILs was also discovered. When the concentration of 1-butylpyridinium tetrafluoroborate ([C_4py]BF_4) remained constant, a mixture of it with a varied molar ratio of PEG800 was detected in tetrahydrofunan. As shown in Figure 4, the absorption intensities of the characteristic absorption of [C_4py]BF_4 were inversely proportional to the addition of PEG800 (curves a−d). The greater change was observed at the valley (238 nm) rather than the peak (260 nm). This indicated that the chromophoric π electron system of the 1-butylpyridinium cation could be influenced by its electrostatic interaction with PEG800. Moreover, it also confirmed the complex formed at a ratio of 1:1 and that the absorption intensity of the characteristic absorption of [C_4py]BF_4 was gradually increased when the PEG800 was sequentially added out of equimolar ratio (curve e and see the Supporting Information).

To study the thermodynamic stability of the PEG-ILs complex, TG investigations were carried out at a heating rate of 5 deg min^{-1} in a nitrogen atmosphere. The mixtures of PEG200, PEG400, and PEG600 with [C_4mim]BF_4 were investigated in contradistinction to the complex of PEG800 and PEG1000 with [C_4mim]BF_4. As shown in Figure 5, the

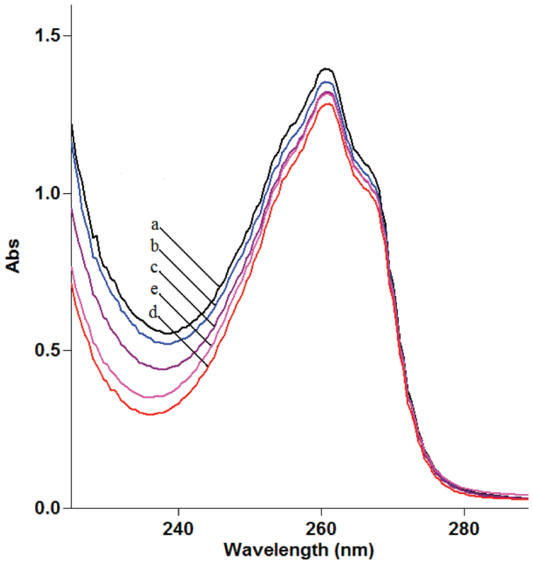

FIGURE 4. UV−vis absorption spectra of [C$_4$py]BF$_4$ (0.4 m mol/L) with different addition of PEG800 in THF. The molar ratio of [C$_4$py]BF$_4$:PEG800: (a) 1:0; (b) 1:0.25; (c) 1:0.5; (d) 1:1; (e) 1:5.

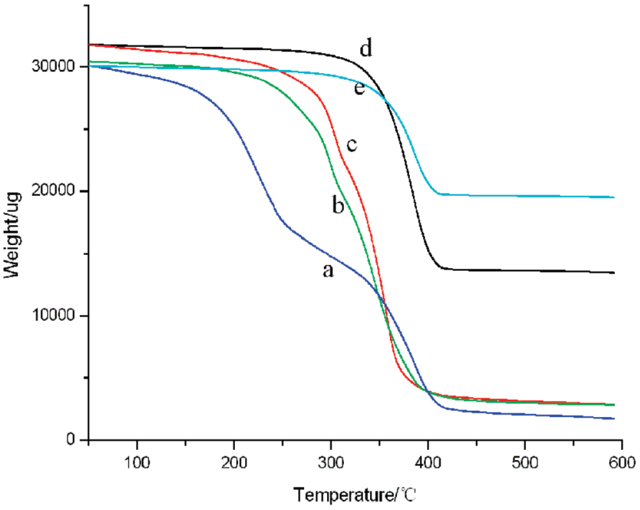

FIGURE 5. TG curves of the mixture of PEGs with ILs [C$_4$mim]BF$_4$: (a) PEG200/[C$_4$mim]BF$_4$; (b) PEG400/[C$_4$mim]BF$_4$; (c) PEG600/[C$_4$mim]BF$_4$; (d) PEG800/[C$_4$mim]BF$_4$; (e) PEG1000/[C$_4$mim]BF$_4$.

TG trace of PEG200/ILs (curve a) offered some interesting observations, and showed ca. 46% weight loss during the first stage, which was related to PEG200. The second experimental weight loss as observed in the curve could be attributed to the ILs. Furthermore, the phenomena of PEG400/ILs (curve b) and PEG600/ILs (curve c) were similar to that of PEG200/ILs. However, the complexes (curves d and e) showed only one-stage weight loss in inert atmosphere. The TG curves revealed the complex was a stable structure that had favorable thermomechanical properties.

Conclusions

In summary, we have discovered an interesting physicochemical property of 1-alkyl-3-methylimidazolium and 1-alkylpyridinium based ionic liquids, which can form complexes with acyclic polyethers by an ion−dipole interaction. The formation of 1:1 self-assemble complexes provided the stable structure detected by mass spectra, NMR spectra, UV−vis spectra, and TG analysis. Further studies to explore the utility of these complexes are underway.

Experimental Section

Materials. ILs, poly(ethylene glycol)s, and poly(propylene glycol)s were purchased commercially and were used without further purification. The molecular weights of the PEG and PPG were determined by electrospray ionization (ESI) mass spectrometry.

Preparation of the PEG-ILs Complexes. ILs (1.0 mmol) was added to 10 mL of methanol containing PEG (1.0 mmol) and stirred under room temperature for 10 min. The solution was concentrated under vacuum to give the product.

Measurements. Electrospray mass spectrometry analysis was performed with a Finnigan LCQ ion trap mass spectrometer (Finnigan, San Jose, CA). TG was carried out employing a METTLER TG 50 thermobalance, provided with the same TC10A processor. The explored temperature range was room temperature to 600 °C under N$_2$ flow, and the heating rate was 5 deg min^{-1}. ^{1}H NMR spectra were measured with JEOL JMNEX-500 (500 MHz) spectrometers. UV−vis spectra were recorded on a SHIMADZU UV-2550 diode-array spectrophotometer.

Spectroscopic Data. [C$_4$mim]BF$_4$: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.389 (m, 1H), 7.896−7.903 (m, 1H), 7.815−7.822 (m, 1H), 7.214−4.243 (m, 2H), 3.904 (s, 3H), 1.755−1.814 (m, 2H), 1.228−1.302 (m, 2H), 0.888−0.918 (m, 3H).

PEG800/[C$_4$mim]BF$_4$: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.216 (m, 1H), 7.803−7.810 (m, 1H), 7.730−7.737(m, 1H), 4.163−1.191 (m, 2H), 3.859 (s, 3H), 3.462−3.498 (m, 6H), 3.390−3.411 (m, 5H), 3.346−3.364 (m, 2H), 1.730−1.789 (m, 2H), 1.228−1.273 (m, 2H), 0.878−0.903 (m, 3H). ESI-MS [PEG800 + [C$_4$mim]BF$_4$ − BF$_4$]$^+$ found: 905.9, 949.9, 994.0, 1038.0, 1081.8, 1125.6, 1169.5, 1213.5.

PEG1000/[C$_4$mim]BF$_4$: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.169 (m, 1H), 7.793−7.800 (m, 1H), 7.723−7.729 (m, 1H), 4.159−4.188 (m, 2H), 3.857 (s, 3H), 3.484−3.520 (m, 89H), 3.399−3.420 (m, 5H), 3.353 (s, 4H), 1.736−1.795 (m, 2H), 1.222−1.296 (m, 2H), 0.889−0.919 (m, 3H). ESI-MS: [PEG800 + [C$_4$mim]BF$_4$ − BF$_4$]$^+$ found: 1028.9, 1086.1, 1201.9, 1259.8, 1317.6, 1375.5, 1433.5.

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Supporting Information Available: Proton NMR spectra, ESI mass spectra, UV−vis spectra, and TG curves of the mixture of PEGs with ILs. This material is available free of charge via the Internet at http://pubs.acs.org.