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Ionic Liquids

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Reversible Hydrophobic–Hydrophilic Transition of Ionic Liquids Driven by Carbon Dioxide**

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Abstract: *Ionic liquids (ILs) with a reversible hydrophobic–hydrophilic transition were developed, and they exhibited unique phase behavior with H_2O: monophase in the presence of CO_2, but biphase upon removal of CO_2 at room temperature and atmospheric pressure. Thus, coupling of reaction, separation, and recovery steps in sustainable chemical processes could be realized by a reversible liquid–liquid phase transition of such IL-H_2O mixtures. Spectroscopic investigations and DFT calculations showed that the mechanism behind hydrophobic–hydrophilic transition involved reversible reaction of CO_2 with anion of the ILs and formation of hydrophilic ammonium salts. These unique IL-H_2O systems were successfully utilized for facile one-step synthesis of Au porous films by bubbling CO_2 under ambient conditions. The Au porous films and the ILs were then separated simultaneously from aqueous solutions by bubbling N_2, and recovered ILs could be directly reused in the next process.*

A large number of chemical processes involving reactions and separations are carried out in solution. However, reaction, product separation, and solvent recovery are often considered as separated unit operations, and different solvents are always used. This significantly adds to the economic cost and environmental impact of the process. To achieve chemical processes that are both economically competitive and environmentally friendly, the solvents must simultaneously address reaction efficiency, product separation, and recyclability. Herein, we designed and developed a class of green, simple, and recyclable solvents based on a hydrophobic–hydrophilic transition of ionic liquids (ILs) to couple reaction, separation, and recovery steps in a sustainable chemical process at room temperature and atmospheric pressure.

CO_2 is nontoxic, benign, inexpensive, and easily removable, thus it is preferred as the trigger for process switching. Jessop et al. carried out pioneering work in switching polarity,[1] hydrophility,[2] ionic strength,[3] and viscosity[4] of the solvents by using CO_2. These switchable solvents contain a nitrogenous base in the form of amidine, guanidine, or amine molecules,[5] and some of them have very little volatility. It is important to find that these switchable solvents have a number of applications in organic reactions,[3c] extraction,[2c,d,3a,e] and emulsions.[2a] Recently, ILs have attracted growing interest as "green" solvents to replace volatile organic solvents in chemical reactions[6] and material synthesis,[7] owing to their extremely low vapor pressure, wide liquid temperature range, non-flammability, and tunable structures and properties.[8] Nevertheless, efficient coupling of reaction, separation, and recyclability in conventional ILs remains a major challenge. Unlike the ordinary solvents, their very high boiling point often precludes recovery of ILs by distillation under ambient conditions. Also, their very strong solubilization capacity makes it extremely difficult to separate the products and to reuse the ILs. The groups of Leitner and of Cheng[9] found that supercritical carbon dioxide ($ScCO_2$)/IL systems could be used to realize the coupling of reaction, separation, and recyclability by varying the pressure of CO_2. Although this IL/$ScCO_2$ system was greener and effective, a specialized apparatus and a high amount of energy were needed owing to high process pressure, which weakened the widespread use of the IL/$ScCO_2$ system. Ohno et al.[10] recently developed an IL, tetrabutylphosphonium N-trifluoromethanesulfonyleucine, 40 wt % of which was completely miscible with 60 wt % of water at 20 °C in the absence of CO_2, but they were partially miscible in the presence of CO_2. However, there have not been any reports of switchable hydrophilic solvents (including ILs) being utilized as media for chemical syntheses to date,[11] and the system created by Ohno et al. is also not used for product separation and IL recovery probably because the mutual solubility of the IL and water is not small in the partially miscible two phases. Thus, it is highly necessary to explore more simple, inexpensive, recyclable, and environmentally benign ILs to solve the problems for the coupling of reaction, separation and recovery processes.

In this work, a novel class of ILs with a reversible hydrophobic–hydrophilic transition was developed through carefully design of the chemical structures of cations and anions. Interestingly, this type of ILs exhibited unique phase behavior with water: their miscibility with water was very small (their solubility in water was as low as 0.06–0.90 % at 20 °C; see the Supporting Information, Table S1), but they were completely miscible with water in the presence of CO_2 at room temperature and atmospheric pressure. Thus the liquid–

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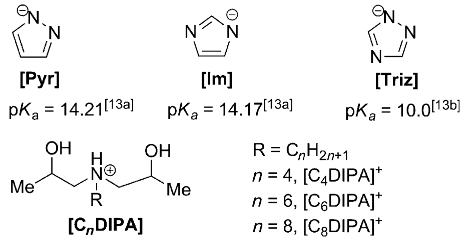
liquid phase transition of the mixtures of such ILs with water was reversible from two phases to homogeneous phase and then to two phases again by alternatively bubbling and removal of CO_2. Importantly, hydrophobic–hydrophilic transitions of these ILs were observed in a wide range of IL content and reaction temperature, and the ILs could be easily recovered and reused owing to their strong hydrophobicity. This dramatic phase transition opens up opportunities to couple reaction, separation, and recovery processes in reaction engineering. The mechanism of the hydrophobic–hydrophilic transition was investigated in detail. In particular, these unique IL–water mixtures were used for facile and efficient synthesis of Au nanochain-built 3D netlike porous films. By bubbling and removal of CO_2, preparation, and separation of the Au porous films as well as recovery of the ILs were successfully achieved.

A series of these ILs were synthesized by the acid–base neutralization[12] between ammonium hydroxide and azole-based weak proton donors (Scheme 1) in a solution (see the Experimental Section in the Supporting Information). The ammonium cations used here were hydroxy-functionalized diisopropanolamine (DIPA) with different alkyl chain lengths. Considering the influence of the reactivity of the anions towards CO_2, three kinds of weak proton donors such as pyrazole (Pyr), imidazole (Im), and trizole (Triz) with different pK_a values (range from 14.21 to 10.0 in water) were chosen. The chemical structures of these ILs were confirmed by NMR and IR spectroscopy (see the Supporting Information). Thermal gravimetric analysis (TGA) revealed that stability of the ILs significantly increased with the increase of the alkyl chain length of their cations (Supporting Information, Table S2). Furthermore, glass transition temperatures (T_g) of the studied ILs ranged from −73 to −62 °C and increased with the decrease of pK_a values of the corresponding weak proton donors (Supporting Information, Table S2).



Scheme 1. Chemical structures of the anions and the cations of the studied ILs, and their pK_a values in water.[13]

$[C_4DIPA][Im]$ was used as a representative example to investigate the hydrophobic–hydrophilic transition of the ILs. It was found that when $[C_4DIPA][Im]$ and water were mixed in a glass vessel, the reversible phase transition of the mixture of $[C_4DIPA][Im]$ and water were observed upon alternately bubbling and removal of CO_2 (Figure 1). At the initial state (in the absence of CO_2), the upper phase was $[C_4DIPA][Im]$, while the lower phase was water, implying that $[C_4DIPA][Im]$ was strongly hydrophobic (Figure 1 a). Then, bubbling of CO_2 through the mixture of $[C_4DIPA][Im]$ and water caused the two phases to merge and a homogeneous phase was formed after a few minutes at room temperature and atmospheric pressure. This suggests that $[C_4DIPA][Im]$ changed from hydrophobic to hydrophilic and was completely dissolved in water (Figure 1 b). The possible reason for this phase transition is that $[C_4DIPA][Im]$ reacted with CO_2 in aqueous solution, and the hydrophilic products were formed. Importantly, this homogeneous aqueous IL solution could be readily transformed back into two phases by bubbling N_2 (or air) at room temperature or at 65 °C for a more rapid reversion. The water solubility in the recovered ILs was determined at 20 °C and the results are shown in the Supporting Information, Table S3. Furthermore, the anionic structure and the alkyl chain length of the cations were found to have a great effect on the time of bubbling CO_2 for the formation of homogenous systems. As shown in the Supporting Information, Table S4, the time of bubbling CO_2 through the mixtures of the ILs and water decreased with the decrease of alkyl chain length and pK_a values of the corresponding weak proton donors. Furthermore, we found that the hydrophobic–hydrophilic transitions of these ILs were observed in a wide range of IL content and reaction temperature. For example, the hydrophobic–hydrophilic transition of $[C_4DIPA][Im]$ could be realized in the IL content range of 10–55 wt % at 20 °C, and in the temperature range of 10–50 °C at 20 wt % IL content.

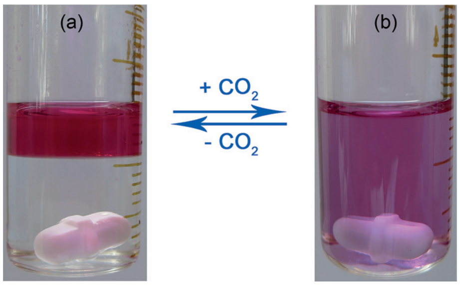


Figure 1. Photographs a) before and b) after bubbling CO_2 through the mixture of $[C_4DIPA][Im]$ (0.004 mol) and H_2O (2.0 g) at 20 °C for 30 min. The IL phase was colored by Nile red.

To gain a deep insight into the mechanism of hydrophobic–hydrophilic transition of the ILs, ^{13}C NMR spectra were determined and used to confirm the hydrophilic products generated by the reaction of the ILs with CO_2 in aqueous solution. As an example, ^{13}C NMR spectra of $[C_4DIPA][Im]$ before and after the reaction with CO_2 in aqueous solution were shown in Figure 2. The signal at 161.8 ppm was ascribed to the carbon atoms of the carbonate and bicarbonate anions, which exchanged rapidly on the NMR timescale by proton scrambling, but the bicarbonate anion was predominant.[2d,14] Furthermore, the two nitrogen atoms in $[Im]^-$ anion are equivalent, thus it may be expected that unsymmetrical monocarbamate $[ImCO_2]^-$ and symmetrical biscarbamate $[Im(CO_2)_2]^-$ can be formed at the same time.[15] Therefore, a couple of low-field resonances was identified to be the carbonyl group of the monocarbamate $[ImCO_2]^-$ (165.8 ppm) and biscarbamate $[Im(CO_2)_2]^-$ (165.9 ppm) (Supporting Information, Table S5).[15] The strong signal at 122.8 ppm was mainly assigned to the Im molecule, and the small shoulder at 122.7 ppm indicated the

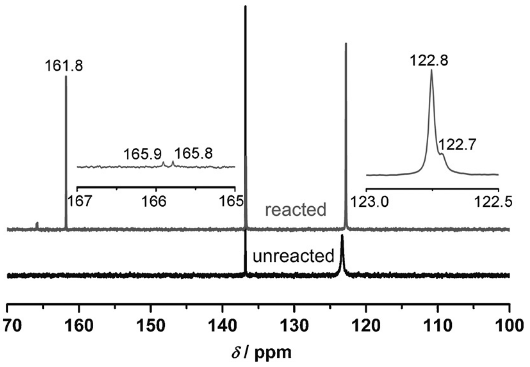
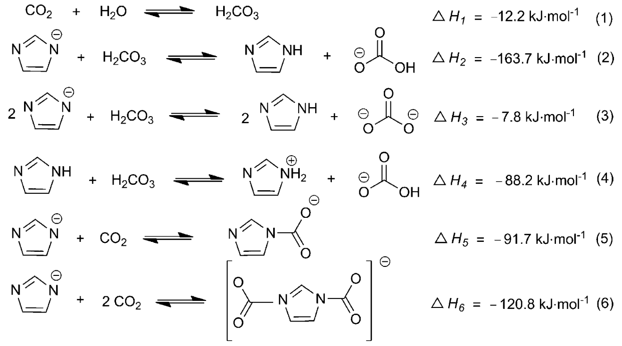


Figure 2. ^{13}C NMR spectra of fresh [C_4DIPA][Im] and [C_4DIPA][Im] in the mixture of [C_4DIPA][Im] with D_2O after bubbling CO_2.

formation of the unsymmetrical monocarbamate. As two carbon atoms of the Im ring in monocarbamate are not equivalent, one of their chemical shifts was observed at 122.7 ppm, while the other was buried in the signal at 122.8 ppm. Furthermore, a direct reaction of neat [C_4DIPA][Im] with CO_2 generated mono- and biscarbamates, and the corresponding signals were observed in the ^{13}C NMR spectrum (Supporting Information, Figure S1), which is in agreement with the result mentioned above. Similar results were also found for the other ILs such as [C_4DIPA][Pyr] and [C_4DIPA][Triz] (see the Supporting Information). Therefore, based on the observed products, the possible mechanism of hydrophobic–hydrophilic transition of the ILs could be proposed, as described in Scheme 2. The mechanism involves the reaction between CO_2 and the anions of the ILs in aqueous solution and the formation of hydrophilic products, including bicarbonate, carbonate, and carbamate. First, the carbonic acid (H_2CO_3) was formed as described in Equation (1), and then [Im] anion reacted with H_2CO_3 to form neutral Im molecules, bicarbonate and carbonate anions, as given in Equations (2) and (3), respectively. Meanwhile, the generated Im molecules reacted with H_2CO_3 to form bicarbonate anion (Equation (4)), and the [Im] anion reacted with CO_2 to form monocarbamate and biscarbamate anions (Equations (5) and (6), respectively).



Scheme 2. The mechanism proposed for the hydrophobic–hydrophilic transition of [C_4DIPA][Im] in the presence of CO_2 and the enthalpies for the reactions calculated at B3LYP/6-31++G(d,p) level.

Furthermore, the reversibility of the process was confirmed by monitoring ^{13}C NMR spectroscopy. Heating the homogeneous solution of [C_4DIPA][Im]–H_2O–CO_2 in a graduated cylinder at 65 °C for 30 min with N_2 bubbling caused a phase split. ^{13}C NMR spectrum showed that the signals at 161.8, 165.8, and 165.9 ppm in the IL phase disappeared (Supporting Information, Figure S2), suggesting that the reaction between the anion of the IL and CO_2 in aqueous solution was completely reversible at 65 °C.[2d] Consequently, the CO_2-driven hydrophobic–hydrophilic transition of the ILs was resulted from reversible reaction of CO_2 with the anions of the ILs, which triggered reversible liquid–liquid phase changes of the mixtures of the IL and water between two phases and a single phase.

As further evidence of the proposed reaction mechanism, we calculated the reaction energetics of [C_4DIPA][Im] with CO_2 in aqueous solution according to Scheme 2 at B3LYP/6-31++G(d,p) level. The reaction enthalpies of [Im]–H_2CO_3, 2[Im]–H_2CO_3, Im–H_2CO_3, [Im]–CO_2, and [Im]–2 CO_2 were −163.7, −7.8, −88.2, −91.7, and −120.8 kJ mol^{-1} (Scheme 2), respectively. Among these complexes, the reaction enthalpy of [Im]–H_2CO_3 exhibited a very negative value (−163.7 kJ mol^{-1}), revealing the significantly stronger interaction of [Im] with H_2CO_3 than that of [Im] with CO_2. Therefore, the anion [Im] is easier to react with H_2CO_3 to generate bicarbonate anion and Im molecule (Scheme 2; Equation (2)). Furthermore, the reaction between H_2CO_3 and the generated Im, via Equations (2) and (3), was favorable for the formation of bicarbonate (Scheme 2; Equation (4)). Therefore, bicarbonate and carbonate displayed a much stronger resonance than carbamate (Figure 2). The mole percentage of Im molecules was determined quantitatively by means of ^{13}C NMR spectroscopy according to the method described by Mani et al.[14] It was found that about 98 mol % of Im molecules were formed (see the Supporting Information) although a tiny fraction of the generated Im molecules might react with H_2CO_3 to form [ImH]$^+$. The reaction enthalpies of [Im]–CO_2 and [Im]–2 CO_2 complexes were nearly equal in value, thus the resonances of mono- and biscarbamate were almost the same (Figure 2). Consequently, DFT calculations are in good agreement with the suggested reaction mechanism, which involves the reactions between CO_2 and the anions of the ILs in aqueous solution and the formation of hydrophilic ammonium salts including bicarbonate, carbonate, and carbamate.

To explain the effect of CO_2 on the hydrophobic–hydrophilic transition of the ILs in aqueous solution, the interaction between the [Im] anion and water and that between the cation and the anion of [C_4DIPA][Im] were also investigated at B3LYP/6-31++G(d,p) level. The calculated interaction enthalpies of the corresponding complexes were found to decrease in the order: [Im]–H_2CO_3 (−163.7 kJ mol^{-1}) > [Im]–[C_4DIPA] (−114.9 kJ mol^{-1}) > [Im]–H_2O (−69.0 kJ mol^{-1}). This result suggests that the interaction in the [Im]–[C_4DIPA] complex was much stronger than that in the [Im]–H_2O complex but much weaker than that in the [Im]–H_2CO_3 complex. Consequently, although these ILs are hydrophobic, they can transform from hydrophobic to hydrophilic in the presence of CO_2.

A hydrophobic–hydrophilic transition of the ILs could have potential applications in many fields. As an example, the preparation of Au nanostructures was illustrated in the mixture of [C_4DIPA][Im] and water (see the Experimental Section in the Supporting Information). Figure 3 shows the reaction and separation processes in the preparation of Au nanostructures as well as the recovery process of the IL. It was found that the homogeneous solution system [C_4DIPA][Im]–H_2O–CO_2 (Figure 3a) turned to slight purple (Figure 3b), indicating the formation of Au products. When the CO_2 was removed from the reaction system by bubbling N_2 at 65 °C, the reaction solution gradually changed into three phases: the top phase was recovered [C_4DIPA][Im] and the middle phase was aqueous solution, while the as-synthesized Au products tended to aggregate and deposit in the bottom of the reaction vial (Figure 3c). The corresponding X-ray diffraction (XRD) pattern (Supporting Information, Figure S3) showed that the as-prepared product was indexed to the face-centered cubic structure of Au. From a field-emission scanning electron microscopy (FESEM) image (Supporting Information, Figure S4) of the as-prepared Au product, it can be clearly seen that the Au product possesses 3D netlike structures. These netlike structures consisted of nanochains, which were welded by spherical Au nanoparticles. The porous and netlike Au architectures are promising candidates in catalysis,[16] surface-enhanced Raman scattering sensors,[17] and biomedicine applications.[18] Cai et al.[19] obtained similar Au structures by using laser ablation, which was expensive and sophisticated. Compared with that method, our procedure is very simple and facile for one-step synthesis and separation of Au nanochain-built 3D netlike porous films at room temperature and atmospheric pressure. More importantly, these ILs can be easily recovered by bubbling N_2 and then directly reused for the next process. Even after using three cycles, the as-obtained Au products were examined without a noticeable change in morphology and structure (Supporting Information, Figure S5).

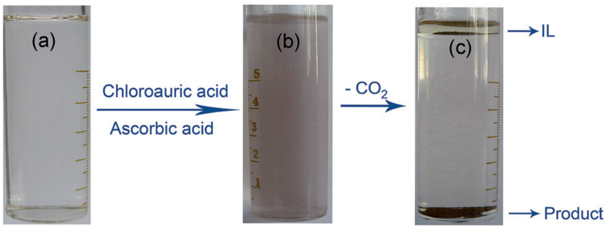


Figure 3. The reaction and separation procedures for the preparation of Au nanostructures in [C_4DIPA][Im]–H_2O–CO_2.

In conclusion, we have prepared a class of novel ILs by simple acid–base neutralization reactions. It is shown that reversible hydrophobic–hydrophilic transition of these ILs is useful to couple the reaction, separation, and recovery processes. As a reversible trigger, CO_2 can be used to switch miscibility of the ILs and water from two phases to homogeneous phase by bubbling of CO_2, and to two phases again by removal of CO_2 at room temperature and atmospheric pressure. Thereby, by using atmospheric pressure CO_2, coupling of the reaction, separation, and recovery processes can be realized in such IL–water mixtures. It has been clearly shown that the hydrophobic–hydrophilic transition of the ILs is a consequence of reversible reaction between CO_2 and the anion of the ILs, leading to the formation of hydrophilic ammonium salts, including bicarbonate, carbonate, and carbamate. Facile and efficient one-step synthesis of Au nanochain-built 3D netlike porous films were successfully achieved in the homogeneous phase systems of IL–H_2O–CO_2. Then the Au porous films and the ILs were separated simultaneously from aqueous solutions by bubbling of N_2. The recovered ILs could be directly reused in the next synthetic process without a noticeable change in morphology and structure of the as-obtained Au products after three cycles. To the best of our knowledge, this is the first example for the coupling of homogeneous chemical reaction, heterogeneous product separation, and solvent recovery (recyclability) by hydrophobic–hydrophilic transition of ILs triggered by CO_2. This finding may open up new paths for the coupling of reaction, separation, and recovery processes to achieve sustainable processing in chemical engineering.

Keywords: carbon dioxide · hydrophobic–hydrophilic transition · ionic liquids · reaction and separation · sustainable chemistry

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