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Ammonium based zwitterions showing both LCST- and UCST-type phase transitions with water in a very narrow temperature range

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Through the study to analyse the required factors for zwitterion(ZI)-type ionic liquids to show LCST-type phase transition with water, we have found ammonium based ZIs having adequate hydrophilicity showed both LCST- and UCST-type phase transition in a very narrow range of temperature after mixing with water.

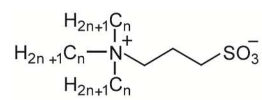
Compared with volatile organic solvents, ionic liquids (ILs) have been recognised as environmentally benign materials due to their unique properties such as negligible vapour pressure, flame retardancy, thermal stability and hydrophilicity.[1,2] Their most attractive character is the designability of their physico-chemical properties through the structural design of both cations and anions. Considering wide variety of hydrophilicity of the component ions, it is comprehensible that some ILs provide liquid-liquid biphasic systems after adding water.[3] IL/water biphasic systems are generally characterised by their stable phase separation state against external stimuli. These static biphasic systems are useful for separation, reaction, and other many processes.

On the other hand, there are some IL/water mixtures showing dynamic phase transition by outer stimuli. There are mainly two types of thermoresponsive phase transition as upper critical solution temperature (UCST)- and lower critical solution temperature (LCST)-type phase transition. In UCST-type phase transition, miscibility of two liquids increases upon heating. Most of adequate hydrophobic ILs exhibit this type of phase transition with water.[4] Oppositely, LCST-type phase transition is seen when miscibility of two liquids increases upon cooling. This LCST-type phase transition is ordinarily observed in aqueous solutions containing some non-ionic polymers.[5] There are only a few examples of the IL/water mixture showing LCST-type phase transition. We have previously elucidated the required factors for IL/water mixture to show LCST-type phase transition, and ILs having more hydrophilicity than the threshold value underwent LCST-type phase transition after adding water.[6] Phase transition temperature of LCST-type IL/water mixture depended on the hydrophilicity of component ions of the ILs. However there is a limitation to linearly change the phase transition temperature by only the design of ions.

One of excellent strategy to finely control the physicochemical properties is the mixing of different ILs. Numerous IL mixtures have been examined to develop designer properties of ILs such as thermo-physical properties,[7] conductivity,[8] and phase behaviour with water.[9] There are excellent reviews on the characteristics of these IL mixtures.[10] As previously reported, one of the disadvantageous points of IL mixture is the formation of undesired ion pairs which may detracted solution properties such as melting point and viscosity.

One of way to suppress ion exchange in the IL mixtures is the use of zwitterions (ZIs) in which both cation and anion are tethered by covalent bond. The ion pairs of ZI should be kept even in the homogeneous mixtures of IL and the ZI.[11] This is quite effective to avoid formation of unexpected ion pairs having unfavourable properties. Here we have investigated required factors for ZIs to show temperature driven phase transition after mixing them with water.

A series of ammonium-based ZIs (Scheme 1) were synthesised according to the method mentioned in the previous report.[12] The structure and purity of the synthesised ZIs were confirmed by ^{1}H NMR and elemental analysis (see ESI). The thermal properties of ZIs were evaluated by DSC and TG/DTA methods (Table S1) First, we have studied the phase behaviour of the prepared ZI after adding certain amount of water. N_{555}C3S, a ZI with relatively shorter alkyl chain length, is hydrophilic and forms homogeneous solution with water. Against this, N_{666}C3S was hydrophobic and insoluble in water. Furthermore, phase of both mixtures (10-60 water molecules



Scheme 1 Structure of ammonium-based zwitterions used in this study

Table 1 Phase behaviour of N_{555}C3S/N_{666}C3S/water mixtures (0 - 70°C)

Sample number (*i*)	N_{555}C3S : N_{666}C3S (mol:mol)	Number of water molecules per ZI (n)					
		10	15	20	25	30	35
1	0.44 : 0.56	homogeneous solution	biphasic system	biphasic system	biphasic system	biphasic system	biphasic system
2	0.50 : 0.50	homogeneous solution	homogeneous solution	biphasic system	biphasic system	biphasic system	biphasic system
3	0.56 : 0.44	homogeneous solution s	homogeneous solution	UCST[*1] (6 °C) / LCST[*2] (28 °C)	biphasic system	biphasic system	biphasic system
4	0.60 : 0.40	homogeneous solution	homogeneous solution	homogeneous solution	UCST[*1] (7 °C) / LCST[*2] (32 °C)	biphasic system	biphasic system
5	0.64 : 0.36	homogeneous solution	homogeneous solution	homogeneous solution	homogeneous solution	UCST[*1] (10 °C) / LCST[*2] (36 °C)	biphasic system
6	0.67 : 0.33	homogeneous solution	homogeneous solution	homogeneous solution	homogeneous solution	homogeneous solution	UCST[*1] (17 °C) / LCST[*2] (41 °C)

[*1] Upper critical solution temperature, [*2] Lower critical solution temperature

per ZI) did not change at temperatures from 0 to 70°C.

It is known that phase behaviour of IL/water mixtures is greatly affected by the hydrophilicity of ILs.[2,13] Recently we have reported that total hydrophilicity of component ions was important factor for designing IL/water mixture to show LCST-type phase transition, and ILs having more hydrophilicity than the threshold underwent LCST-type phase transition after adding water.[6] Since total hydrophilicity of component ions in the major factor to affect the phase behaviour of the IL/water mixtures, not only changing the hydrophilicity of component ions but also mixing ILs having different hydrophilicity was effective to control the temperature-driven phase transition of IL/water mixtures.[6] Here we have examined the effect of mixing ratio of these ZIs to successively change the total hydrophilicity of the ZI mixtures. Table 1 shows the effects of mixing ratio of different ZIs and that of ZI and water on the phase behaviour of N_{555}C3S/N_{666}C3S/water mixtures. When N_{555}C3S and C_{666}C3S were mixed equimolarly (sample number **2** in Table 1), the mixture containing 15 water molecules per ZI underwent homogeneous solution, but those with more than 20 water molecules per ZI formed biphasic system. Hereafter, the ZI/water mixtures were abbreviated as ***i***/water$_n$, where ***i*** and n indicate the sample number (see Table 1) and number of water molecules per ZI, respectively. All **2**/water mixtures were found to show static phase behaviour, i.e., phases were stable against temperature change from 0 to 70 °C. Slight decrease in the hydrophilicity of the IL/water mixture should lead the phase separation under less amount of water. For example, **1**/water$_{15}$ mixtures formed biphasic system due to increasing molar ratio of more hydrophobic N_{666}C3S as compared with **2**/water$_{15}$ mixtures.

On the other hand, increase in the total hydrophilicity of the ZI mixture by increasing mole fraction of N_{555}C3S induced shift of the required amount of water to show phase separation to larger value. Results in Table 1 clearly show this tendency. Throughout these experiments, ZI mixtures with relatively more hydrophilic properties were found to show dynamic phase change under the condition in between for homogeneous mixture and for biphasic system. As we have reported previously that LCST-type phase transition was found between homogeneous mixture and biphasic system by successively changing the hydrophilicity.[6] Interestingly, the present ZI/water mixed systems, not only LCST-type phase change but also UCST-type phase change were observed as shown in Table 1. For instance, **3**/water$_{20}$ showed LCST- and UCST-type phase transitions with phase transition temperatures of 28 and 6°C, respectability. These unique phase transitions were shown in only a small range, because phase behaviour of **3**/water$_{15}$ and **3**/water$_{25}$ did not show such dynamic phase change upon heating or cooling. When molar ratio of N_{555}C3S was increased, larger number of water molecules per ZI was needed to show temperature-driven phase transition.

To examine the two types of temperature-driven phase transition in detail, we have investigated the effect of number of water molecules per ZI in **4**/water$_n$ and **6**/water$_n$ on the phase transition temperature. Phase transition temperatures of **4**/water$_{23}$ were 38°C (LCST) and 2°C (UCST) respectively. Subsequently an LCST was found to decrease with increasing number of water molecules per ZI (Fig. 1, closed circles), and a UCST was found to increase with increasing it (Fig. 1, closed squares). Both LCST- and UCST-type phase transitions of the analysed ZI/water mixtures underwent in a very narrow temperature range. While phase transition temperature of **6**/water$_n$ mixture followed a similar trend to that of **4**/water$_n$ mixture (Fig. 1, ○ and □). Especially, **6**/water$_n$ mixtures had higher phase transition temperature than **4**/water$_n$ mixtures. These results clearly show that the phase transition temperature of the prepared mixtures is controllable by the mixing ratio of ZI and water.

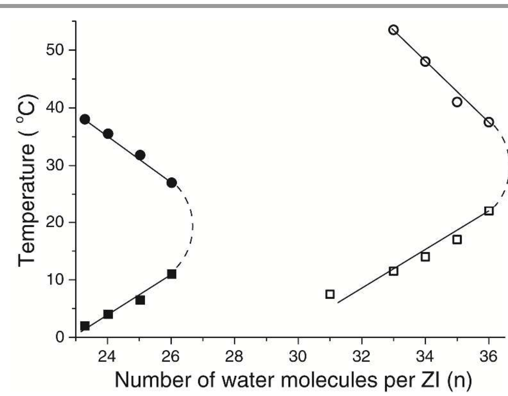


Fig. 1 Phase diagram of **4**/water$_n$ mixture (closed dot) and **6**/water$_n$ mixtures (open dot). Circle plots denote LCST and square plots do UCST.

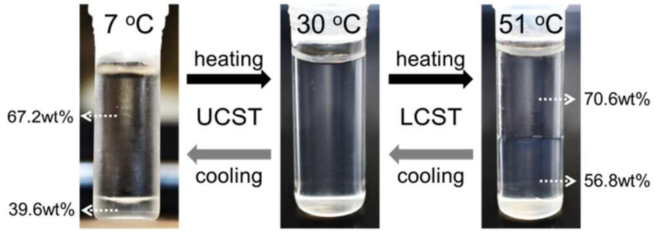


Fig. 2 Visual appearance and water content of **6**/water$_{35}$ mixture before and after phase transitions. It is a homogeneous mixture at 30 °C.

As mentioned above, the mechanism of LCST-type phase transition should not be the same as that of UCST-type phase transition. Water content of each phase is one of important factor to discuss the characteristics of the phases. As seen in Table 1, **6**/water$_{35}$ mixture has two phase transition temperatures at 17 and 41°C. We have previously found that the water content of the phase separated IL phase was dramatically changed at a temperature near the phase transition temperature.[6] The liquid-liquid equilibrium of this mixture was also investigated at 7°C and 51°C those are 10 °C lower or higher than each phase transition temperature. As shown in Fig. 2 (left), **6**/water$_{35}$ mixture formed liquid-liquid biphasic system after UCST-type phase transition, and large water-rich phase floated on the ZI-rich phase. While the volume of water-rich phase was almost the same as that of ZI-rich phase after LCST-type phase transition (Fig. 2, right). These results indicate that distribution of water molecules was different after two different phase transitions. Fig. 2 also shows water content of each phase measured with Karl Fischer titration technique. However similar water content in water-rich phases after both phase transitions was found, ZI-rich phase after LCST-type phase transition contains more water than that after UCST-type phase transition. Water immiscible N_{666}C3S was mainly distributed into ZI-rich phase with small amount of N_{555}C3S because N_{666}C3S was insoluble in water, which makes water content of ZI-rich phase smaller.

It is noteworthy to mention here that ZI/water mixtures provide different water content from IL/water mixture due to their fixed ion pairs. These unique characteristics of ZI/water mixtures would give an interesting and useful interface with water. Recently interface of IL/water mixture have attracted attention as useful for synthesis of inorganic nanostructure[14], template of biopolymer[15], or enzymatic reactions[16]. Since dynamically variable interface could be prepared by temperature-driven phase transition of N_{555}C3S/N_{666}C3S/water mixtures, these mixtures would contribute to many fields of interface science.

Conclusions

In summary, we have found ZI/water biphasic systems to show both LCST-type and UCST-type phase transitions by mixing ZIs having different and appropriate hydrophilicity/hydrophobicity balance. Hydrophilic N_{555}C3S was miscible with water and relatively more hydrophobic N_{666}C3S was immiscible with water. When N_{555}C3S and N_{666}C3S were mixed in suitable molar ratio, the mixture showed both LCST-type and UCST-type phase transitions after mixing with water. Both phase transition temperatures depended on the ratio of ZIs to water molecules. Furthermore, water content of biphasic system composed of N_{555}C3S/N_{666}C3S/water mixture varied dramatically by small temperature change.

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Note and References

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