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The influence of a thermoresponsive polymer on the microdynamic phase transition mechanisms of distinctly structured thermoresponsive ionic liquids†

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The study of a ternary solution involving a thermoresponsive polymer, a thermoresponsive ionic liquid (IL), and a solvent will not only help with interpreting their distinct phase transition behavior, but also promote the development of novel thermoresponsive systems. In this paper, we investigate the influence of a conventional thermoresponsive polymer, poly(2-isopropyl-2-oxazoline) (PIPOZ), on the phase transition behavior of two thermoresponsive ILs ([P\textsubscript{4,4,4,6}][MC\textsubscript{3}S], [P\textsubscript{4,4,4,4}][SSI]) with different structures. Although the addition of PIPOZ reduces the transition temperatures of both ILs, our analyses demonstrate that there exists a large difference in the microdynamic phase transition mechanisms between [P\textsubscript{4,4,4,6}][MC\textsubscript{3}S]/PIPOZ and [P\textsubscript{4,4,4,4}][SSI]/PIPOZ aqueous solutions. Both PIPOZ and [P\textsubscript{4,4,4,4}][SSI] experience unexpectedly an unusual over-hydration process before a two-step phase transition of the mixture solution, which can be explained by the presence of a new kind of intermolecular bridging hydrogen bond (IL–water–polymer), whereas only PIPOZ undergoes dehydration around the transition temperature of the [P\textsubscript{4,4,4,6}][SSI]/PIPOZ aqueous solution. Further spectral analyses reveal that both [P\textsubscript{4,4,4,6}][MC\textsubscript{3}S] and PIPOZ engage in the phase separation of the ternary solution jointly, whereas PIPOZ takes part in the phase transition of [P\textsubscript{4,4,4,4}][SSI]/PIPOZ solution more independently.

1. Introduction

Ionic liquids (ILs) are a class of low temperature molten salts (melting points usually below 100 °C), which consist of an organic cation with large asymmetry and an organic or inorganic anion with easy designability. Since the first IL, ethylammonium nitrate, discovered by Walden in 1914 with a low melting point of 12 °C, researchers have increasingly focused on developing ILs with distinctive molecular structures as well as exploring their potential applications. Alteration of the types of cations and anions tends to produce variations in melting point,1 density,2 water miscibility,3 and viscosity.4 Therefore, it’s no wonder that the number of kinds of ILs can potentially reach approximately 1 million and the binary mixtures, ~1 billion, estimated by Seddon.5 Generally, ILs are characterized by their wide range of miscibility, solubility, excellent thermal and chemical stability, good electrical conductivity and negligible vapor pressure, and these outstanding properties have shown huge potential in various fields, such as electrochemistry,6–8 extraction,9–11 bioscience,12–14 catalysis,15–17 analysis,18,19 and organic synthesis.20–22

In recent years, combining the inherent characteristics of conventional ILs and the unique thermosensitivity, thermoresponsive ILs are drawing more and more attention, and in particular the LCST-type ones, whose homogeneous IL/solvent mixture solutions exhibit phase separation around the lower critical solution temperature (LCST), have been used in a lot of high-end applications.21–26 Until now, there have been plenty of reports relating to the phase transition behavior of LCST-type ILs in their mixtures, or that of thermosensitive poly(ionic liquid)s (PILs) that are derived from LCST-type ILs.27–29 For instance, Ohno and co-workers first found that some kinds of anionic-type ILs (tetrabutylphosphonium 4-vinylbenzenesulfonate, [P\textsubscript{4,4,4,4}][SS], and tributylhexylphosphonium 3-sulfopropylmethacrylate, [P\textsubscript{4,4,4,6}][MC\textsubscript{3}S]) can exhibit LCST-type phase transitions in water, and they also prepared a sequence of thermoresponsive PILs via polymerizing LCST-type IL monomers in water or organic solvents.30,31 Later, Yuan’s group synthesized a new set of cationic-type ILs (tributyl-4-vinylbenzylphosphonium allanesulfonate, TVBP-CxS) and their PILs (poly(TVBP-CxS)) with tunable LCST-type
phase transition behavior. Recently, another kind of cationic LCST-type PIL (poly[(tri-n-alkyl(vinylbenzyl) phosphonium chloride), poly[[P_{n}vinyl][Cl]] has been obtained by Ohno et al. who also investigated the salting-out effect on the water absorption/desorption behavior of the corresponding PILs. Despite the existing relevant studies on the phase behavior of polymer–IL binary systems or polymer–IL–water ternary systems that mainly involve ILs or polymers with no thermosensitivity, little is known about the interplay between thermo-responsive ILs and thermo-responsive polymers in a cosolvent, not to mention the probable changes of microdynamic phase transition mechanisms in these integrating systems. The study of the phase transition behavior of thermo-responsive ILs and thermo-responsive polymers in a cosolvent will be helpful to both elucidate their distinct phase transition mechanisms and to develop novel thermo-responsive systems for more practical applications, as they may either co-precipitate with the temperature change resulting in only one phase transition or precipitate separately with a two-step phase separation. Our group previously examined the LCST-type phase transition behavior of a thermo-responsive IL, [P_{4,4,4,6}][MC3S], in the presence of two different kinds of thermo-responsive polymers, poly(N-isopropylacrylamide) (PNIPAM) and poly(N-vinylcaprolactam)(PVCL). We found that, due to the formation of strong intra- or intermolecular C=O–H–N hydrogen bonds, PNIPAM decreases the LCST of [P_{4,4,4,6}][MC3S], whereas in the case of PVCL without the formation of such hydrogen bonds, the LCST of [P_{4,4,4,6}][MC3S] is increased. These preliminary results have shown us that the interactions between thermo-responsive ILs and polymers are very complicated, and closely depend on the structures of both ILs and polymers as well as their distinct phase transition behavior. Therefore, in view of the structural diversity of ILs, it is also in great demand to investigate the structural effect of the IL on the phase transition behavior of IL–polymer–solvent ternary solutions. In this paper, taking [P_{4,4,4,6}][MC3S] and [P_{4,4,4,6}][SS] as examples of thermo-responsive ILs, and poly(2-isopropyl-2-oxazolines) (PIPOZ) as an example of a thermo-responsive polymer, we will try to reveal the structural effect of the IL by comparing the phase transition behavior of the two different IL–polymer–water solutions. ILs, [P_{4,4,4,6}][MC3S] and [P_{4,4,4,6}][SS], are chosen as their LCST-type phase transitions have been mostly studied, and their chemical structures are similar but with much difference in the anion type (Fig. 1). PIPOZ is isomeric in the repeat unit to that of PNIPAM, but has exhibited a few advantages superior to

![Fig. 1](image-url) Chemical structures of [P_{4,4,4,6}][MC3S], [P_{4,4,4,6}][SS] and PIPOZ.

2. Experimental section

2.1 Materials

[P_{4,4,4,6}][SS] and [P_{4,4,4,6}][MC3S] (purity: ~95 mol% and ~91 mol%) were synthesized according to the literature. POZOZ (M_n = 14 400 g mol⁻¹, PDI = 1.16) was synthesized via cationic ring-opening polymerization of 2-isopropyl-2-oxazoline (TCI Co. Ltd) with methyl p-toluene sulfonate (TCI Co. Ltd) as the initiator, according to the literature. D_2O was used as received without further purification.

2.2 Instruments and measurements

Calorimetric measurements of both [P_{4,4,4,6}][MC3S]/PIPOZ and [P_{4,4,4,6}][SS]/PIPOZ aqueous solutions (total concentration, 24% (w/v, g ml⁻¹)) with different weight ratios of IL/PIPOZ (24%/0%, 20%/4%, 16%/8%, 12%/12%, 8%/16%, 4%/20%, 0%/24%) were conducted on a Mettler-Toledo differential scanning calorimeter (DSC) from 5 to 70 °C with a heating rate of 10 °C min⁻¹. Optical micrographs were obtained on a DM2500P polarizing microscope attached to a Linkam THMS600 temperature control console (heating rate, 0.5 °C min⁻¹).

Temperature-variable 1H NMR spectra of [P_{4,4,4,6}][MC3S]/PIPOZ and [P_{4,4,4,6}][SS]/PIPOZ in D_2O (IL/PIPOZ = 20%/4%) were recorded on a Varian Mercury plus (400 MHz) spectrometer with an increment of 1 °C. Prior to FT-IR experiments, both [P_{4,4,4,6}][MC3S]/PIPOZ and [P_{4,4,4,6}][SS]/PIPOZ in D_2O (IL/PIPOZ = 20%/4%) were placed at 4 °C for a week to make them dissolve adequately. Then, the samples were sealed between two ZnS tablets. Temperature-dependent FT-IR measurements were carried out on a Nicolet Nexus 6700 spectrometer. A resolution of 4 cm⁻¹ and 32 scans were chosen to get a desirable signal-to-noise ratio. Temperature was adjusted by an electronic cell holder at a rate of 0.5 °C min⁻¹ with an increment of 1 °C. After collection of all spectra, the software OMNIC, ver. 8.0, was applied for baseline correction.

The temperature-dependent FT-IR spectra of different chemical groups at certain wavenumber ranges were selected to conduct the PCMW analysis by using the software 2D Shige, ver. 1.3 (© Shigeki Morita, Kwansei Gakuin University, Japan, 2004–2005) with an appropriate window size (2n + 1 = 11). Then, the software Origin, ver. 8.0, was utilized to plot the contour maps with warm colors (red and yellow) representing positive intensities and cool colors (blue) representing the negative ones.

3. Results and discussion

3.1 Calorimetric measurements

In order to figure out the difference in the phase transition behavior of [P_{4,4,4,6}][MC3S]/PIPOZ and [P_{4,4,4,6}][SS]/PIPOZ aqueous solutions, differential scanning calorimetric (DSC) measurements were carried out. As shown in Fig. 2a and b, DSC heating curves of both [P_{4,4,4,6}][MC3S]/PIPOZ and [P_{4,4,4,6}][SS]/PIPOZ samples

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with different weight ratios present distinct phase transition temperatures and enthalpic peak changes. Either pure [P4,4,4,4][SS] or [P4,4,4,4][MC3S] aqueous solution (24% (w/v)) exhibits a broad and asymmetric enthalpic peak around the LCST (36.5 °C, 32 °C) indicating a gradual phase transition, whereas the phase separation of pure PIPOZ aqueous solution (24% (w/v)) occurs at 38 °C with a much bigger and more symmetric enthalpic peak than pure ILs.

The variation tendencies of the phase transition temperatures of [P4,4,4,6][MC3S]/PIPOZ and [P4,4,4,4][SS]/PIPOZ samples with different ratios turn out to be a little similar to each other. When 4% (w/v) PIPOZ is added to 20% (w/v) IL, the LCST of the mixture solution appears to decrease sharply from 36.5 to 26.5 °C or from 32 to 28.5 °C. Then, surprisingly, the transition temperatures increase gradually with the weight percentage of PIPOZ increasing from 4% to 24% and that of IL decreasing from 20% to 0%. The same tendencies of transition temperature variation can also be obtained by turbidity measurements in Fig. S1 (ESI†). Additionally, the enthalpic peaks become bigger and more symmetric, and the shape and height of those peaks get closer to that of the pure PIPOZ solution. Herein, we speculate that PIPOZ may dominate the phase transition process of [P4,4,4,4][SS]/PIPOZ and [P4,4,4,6][MC3S]/PIPOZ aqueous solutions, especially when the concentration of PIPOZ is relatively high. With regard to the LCSTs of IL/PIPOZ solutions, which are always lower than that of the pure PIPOZ solution, we attribute this phenomenon to the Hofmeister salting-out effect, i.e., a polymer is less soluble at high salt concentrations, which in the case of LCST-type polymers, lowers the LCST.45–48

Despite the small difference between the two systems in DSC results, we are still able to get an overview. Compared to [P4,4,4,6][MC3S]/PIPOZ, [P4,4,4,4][SS]/PIPOZ samples present higher transition temperatures and bigger enthalpic peaks during heating, which are more similar to the pure PIPOZ solution. This reveals that PIPOZ contributes more to the phase separation process of [P4,4,4,4][SS]/PIPOZ than that of [P4,4,4,6][MC3S]/PIPOZ. In other words, [P4,4,4,6][MC3S] plays a more important role in the dehydration process of the [P4,4,4,6][MC3S]/PIPOZ system than [P4,4,4,4][SS] does in the dehydration of [P4,4,4,4][SS]/PIPOZ, and it is assumed that the dehydration process of [P4,4,4,4][MC3S]/PIPOZ is accomplished with the joint collaboration of [P4,4,4,6][MC3S] and PIPOZ. This may be because the different IL–PIPOZ interactions from distinctly structured ILs lead to different hydration environments around ILs. To further investigate this structural effect, IL20%/PIPOZ4% samples with the lowest LCSTs were chosen to carry out the following measurements.

3.2 Optical microscopy

With the purpose of visually observing the LCST-type phase separation behavior of the two ternary systems, optical microscopy was utilized. Fig. 3 presents the optical micrographs of [P4,4,4,6][MC3S]/PIPOZ and [P4,4,4,4][SS]/PIPOZ solutions during heating (15–40 °C), as well as those of pure PIPOZ and ILs for comparison. For both pure IL solutions, when the temperature rises to the LCST, the horizon gets blurry gradually because of the occurrence of phase transition. A mass of globous and homogeneous droplets form, which represent the appearance of liquid–liquid phase separation (LLPS)—a common phenomenon that can be observed in various thermoresponsive polymer systems including PIPOZ.43,49,50 The difference of droplet morphology in the two pure IL solutions above the LCST can be explained by the existence of C–O in [P4,4,4,6][MC3S] with a larger affinity to water than the more hydrophilic benzene ring of [P4,4,4,4][SS]; this makes the [P4,4,4,6][MC3S]-rich droplets tend to merge into bigger ones, whereas the [P4,4,4,4][SS] droplets remain uniform and stable in size. Nevertheless, the variations in the morphologies of droplets of [P4,4,4,6][MC3S]/PIPOZ and [P4,4,4,4][SS]/PIPOZ solutions are somewhat different during the whole heating process. At the initial heating stage, the droplets of [P4,4,4,6][MC3S]/PIPOZ are spherical and uniform similar to the case of pure PIPOZ solution, whereas the aggregates of [P4,4,4,4][SS]/PIPOZ are fragmented and indiscernible and cannot be regarded as droplets. Later, with the temperature increasing, the droplets in [P4,4,4,6][MC3S]/PIPOZ gather into bigger ones with a cobblestone-like shape, whereas the aggregates in [P4,4,4,4][SS]/PIPOZ remain almost unchanged. This phenomenon indicates that there may exist some kind of interaction between [P4,4,4,6][MC3S] and PIPOZ resulting in the unusual morphology of the droplets, which do not exist in pure PIPOZ and [P4,4,4,6][MC3S] aqueous solutions.40,43 For [P4,4,4,4][SS]/PIPOZ, there is no tendency to merge together for adjacent droplets indicating that the solutes exist stably and independently in
both dense and dilute phases. To clarify the details of the difference in the mechanisms of these two IL-involved ternary systems, temperature-variable $^1$H NMR and FT-IR spectroscopic investigations were performed.

### 3.3 Temperature-variable $^1$H NMR analysis

Conventional $^1$H NMR spectra of $[\text{P}_4,\text{t}_{4,4,6}]\text{[MC3S]}_{20\%}/\text{PIPOZ}_{4\%}$ and $[\text{P}_4,\text{t}_{4,4,4}]\text{[SS]}_{20\%}/\text{PIPOZ}_{4\%}$ in D$_2$O are shown in Fig. S3 in the ESI,† and the assignments of the protons in different groups were made based on previous reports.40,41,43 According to Fig. S3 (ESI†), we define $H_{\text{top}}$ and $H_{\text{s}}$ as the characteristic peaks of PIPOZ, which can be clearly distinguished from the majority of the peaks of ILs. Capturing the changes of the protons situated in various chemical environments with a temperature increase is one of the most effective methods of studying the phase separation behavior of thermo-responsive polymers, from which we can easily detect the changes in different components in the solution during phase transition.51

![Fig. 3](image)

Fig. 3 Optical micrographs of $[\text{P}_4,\text{t}_{4,4,6}]\text{[MC3S]}_{20\%}/\text{PIPOZ}_{4\%}$, $[\text{P}_4,\text{t}_{4,4,4}]\text{[SS]}_{20\%}/\text{PIPOZ}_{4\%}$, pure PIPOZ$_{4\%}$, $[\text{P}_4,\text{t}_{4,4,6}]\text{[MC3S]}_{20\%}$ and $[\text{P}_4,\text{t}_{4,4,4}]\text{[SS]}_{20\%}$ solutions (heating rate, 0.5 °C min$^{-1}$) in the heating process from 15 °C to 40 °C.

The temperature-dependent $^1$H NMR spectra of $[\text{P}_4,\text{t}_{4,4,6}]\text{[MC3S]}_{20\%}/\text{PIPOZ}_{4\%}$ and $[\text{P}_4,\text{t}_{4,4,4}]\text{[SS]}_{20\%}/\text{PIPOZ}_{4\%}$ in D$_2$O are presented in Fig. 4. It can be seen that almost all peaks corresponding to each solute move to a lower field (or a higher chemical shift) in the whole temperature range except the HDO peak from the deuterated solvent. The peak shift is also accompanied by an apparent intensity decrease, and the peaks for PIPOZ even totally disappear in the final heating stage. This phenomenon shows that the solutes carrying those protons become gradually insoluble during phase transition.

To depict the degree of phase transition quantitatively, we introduced the phase separation fraction $p$ to illustrate the degree of dehydration as well as the phase transition quantitatively.52 The mathematical expression of $p$ is defined as:

$$p = 1 - \frac{I}{I_0}$$

### Fig. 4

Normalized temperature-variable $^1$H NMR spectra of (a) $[\text{P}_4,\text{t}_{4,4,6}]\text{[MC3S]}_{20\%}/\text{PIPOZ}_{4\%}$ and (b) $[\text{P}_4,\text{t}_{4,4,4}]\text{[SS]}_{20\%}/\text{PIPOZ}_{4\%}$ in D$_2$O. (c) and (d) show the temperature-dependent variation of phase separation fraction $p$ for different protons in ILs and PIPOZ.

![Fig. 4](image)
where \( I_0 \) is the integral intensity of the selected characteristic peak before phase transition and \( I \) is the integral intensity of the peak at a specified temperature in the heating process. We chose the integral intensity at the initial temperature (15 °C) as \( I_0 \) for the reference. In addition, \( H_{o,p} \) and \( H_{d,p} \) in PIPOZ, \( H_{o,d} \) and \( H_{d,d} \) in [P4,4,4,4][MC3S], and \( H_{o,d} \) and \( H_{d,d} \) in [P4,4,4,4][SS] were selected for tracking the phase transition of ILs and PIPOZ. Temperature-dependent variations of the phase separation fraction \( p \) of the other proton peaks of the ILs are the same as the selected ones, as listed in the ESL.

The variable relations between \( p \) and temperature for the two IL-involved ternary systems in D2O are presented in Fig. 4c and d. For [P4,4,4,4][MC3S]/PIPOZ, the addition of PIPOZ has a significant effect on the phase transition behavior of the IL and coordination of the phase transition between PIPOZ and [P4,4,4,4][MC3S] can be observed through the whole heating process. Both [P4,4,4,4][MC3S] and PIPOZ undergo unusual over-hydration before the first dehydration. Furthermore, they all experience a two-step phase transition process, which has never been reported before. At the initial heating stage, all \( p \) values decrease from zero gradually, corresponding to the better water solubility of the two solutes. When the temperature rises to 27 °C, the \( p \) value curves reach the lowest point \( p_{\text{min}} \), indicating the largest degree of hydration. Then, [P4,4,4,4][MC3S] and PIPOZ start to dehydrate synchronously, which corresponds to an obvious ascent in their \( p \) value curves. This is also in accordance with the above-mentioned DSC results as well as optical microscopy observation. This result provides evidence for the speculation that the [P4,4,4,4][MC3S] and PIPOZ components complete the macroscopic phase transition of the IL/PIPOZ solution cooperatively. Due to the Hofmeister salting-out effect, the IL as a unique kind of salt decreases the LCST of PIPOZ. Additionally, it is assumed that the intermolecular interaction between [P4,4,4,4][MC3S] and PIPOZ may be strengthened with the temperature rising before 27 °C, which promotes the consistency of their dehydration behavior. After the first dehydration process with a narrow temperature range (ca. 3 °C), the \( p \) values of PIPOZ reach 0.3 and then remain unchanged for a while, whereas the curves of [P4,4,4,4][MC3S] reach a plateau close to zero indicating a hydrophilic/hydrophobic balance between the cations and anions of the IL. Around 34 °C, both [P4,4,4,4][MC3S] and PIPOZ dehydrate drastically, and especially for [P4,4,4,4][MC3S], the change in \( p \) value becomes bigger than that in the first stage of dehydration. The remarkable PIPOZ-dominated temperature responsiveness in the first dehydration process (27 °C) covers the IL-dominated phase transition phenomenon in the second dehydration process (34 °C), which may account for the observation that only one exothermic peak was observed in each DSC curve. However, the \( p_{\text{max}} \) of [P4,4,4,4][MC3S] is just around 0.25, which is only half that of the pure IL solution.\(^{40}\) It can be concluded that the addition of PIPOZ not only weakens the dehydration degree of the IL, but also slightly reduces the LCST of the IL compared with pure [P4,4,4,4][MC3S] solution (36 °C) at the same concentration (20% (w/v)).

In contrast, the case of [P4,4,4,4][SS]/PIPOZ is quite different. As shown in Fig. 4d, the addition of PIPOZ to the [P4,4,4,4][SS] solution results in a two-step dehydration process for PIPOZ, whereas the curves of [P4,4,4,4][SS] present only one phase transition, from which we can obtain the same LCST as the pure IL solution (36 °C). In addition, without showing any fluctuations like [P4,4,4,4][MC3S], the \( p \) values of [P4,4,4,4][SS] remain unchanged at zero before dehydration and the \( p_{\text{max}} \) is 0.5, which is also close to the result of the pure [P4,4,4,4][SS] solution previously reported.\(^{41}\) This reveals that the phase transition of [P4,4,4,4][SS] is relatively independent in the mixture solution. The phase transition temperature (28 °C) presented in the first step of the dehydration process of PIPOZ is in good accordance with the DSC result, which can be explained by the Hofmeister salting-out effect on PIPOZ as well, whereas at higher temperatures, PIPOZ is less affected by the salting-out effect showing a phase transition temperature of 36 °C, similar to pure PIPOZ. The above results combined with DSC and microscopy observations indicate that PIPOZ dominates the phase separation of the [P4,4,4,4][SS]/PIPOZ solution to some extent.

Furthermore, the final dehydration degree of PIPOZ in both mixture systems is almost double that of the ILs, which reveals that the dehydration of PIPOZ is much more complete than that of the thermoresponsive ILs. However, it is difficult to trace the changes of chemical groups without protons during the heating process by using \(^1\)H NMR. Thus, to solve this issue, temperature-variable FT-IR spectroscopy was employed.

### 3.4 Conventional IR analysis

Temperature-dependent FT-IR spectroscopy was used to investigate the variations of C–O groups of ILs and PIPOZ during phase transition owing to its good sensitivity to slight conformational changes. It should be pointed out that we used D2O instead of H2O as the solvent to avoid the overlap of the (O–H) peak of H2O at about 1640 cm\(^{-1}\) with \( \nu(C=O) \) peaks. There are two kinds of discernible C–O groups in the ternary systems. One is the ester group of [P4,4,4,4][MC3S], which is located in the range of 1740–1670 cm\(^{-1}\), and the other is the amide group of PIPOZ (1670–1550 cm\(^{-1}\)). As shown in Fig. 5a and b, with temperature rising, all C–O stretching bands shift to higher wavenumbers, which indicates the occurrence of the dehydration process, and similar changes can be observed in other thermosensitive polymers and ionic liquids.\(^{39,53}\) According to Fig. 5a, the change of ester groups is much smaller than that of amide groups, which reflects the much more remarkable change of the water environment around PIPOZ chains. For the amide C–O of PIPOZ in the IL-involved ternary systems, it is noted that there mainly exist two strong bands at 1605 and 1631 cm\(^{-1}\), which largely differs from the case of pure PIPOZ solution (Fig. 5c).

The peaks located at different wavenumbers for the amide groups of PIPOZ stand for different hydrogen bonding forms between the C–O of PIPOZ and water molecules; one is the weak bridging hydrogen bond of C–O ⋅⋅⋅ O–D⋅⋅⋅ O–C (1631 cm\(^{-1}\)), and the other is C–O ⋅⋅⋅ D2O from hydrated C–O (1605 cm\(^{-1}\)). Comparing the FT-IR spectra of IL/PIPOZ and pure PIPOZ, it is clear that the introduction of PIPOZ to the IL solution leads to a change in the peak shape of the amide C–O groups belonging to PIPOZ (Fig. 5c and d). To be specific, the peak at 1631 cm\(^{-1}\)
ternary systems before the occurrence of phase separation. In hydrogen bonds has already appeared in both IL-involved IL/PIPOZ at 1670–1550 cm\(^{-1}\)/C\(_{0}\)PIPOZ. As the temperature increases to 40°C in the transition ranges of C\(_{Q1}\), the peak at 1631 cm\(^{-1}\)/C\(_{0}\)PIPOZ, and the peak at 1605 cm\(^{-1}\)/C\(_{0}\)PIPOZ, which represents the C=O–D–O–D–O=–C intermolecular hydrogen bonds has already appeared in both IL-involved ternary systems before the occurrence of phase separation. In particular for [P\(_{4,4,4,6}\)][MC3S]/PIPOZ, it can be observed that the band at 1631 cm\(^{-1}\) is stronger than the band for C=O ·· D\(_2\)O at 1605 cm\(^{-1}\) at 15°C, which proves the speculation obtained from \(^1\)H NMR that there may exist a new kind of intermolecular hydrogen bond (IL ·· D\(_2\)O ·· PIPOZ) between [P\(_{4,4,4,6}\)][MC3S] and PIPOZ. As the temperature increases to 40°C, the peak shape of IL/PIPOZ at 1670–1550 cm\(^{-1}\) becomes similar to that of pure PIPOZ, and the peak at 1631 cm\(^{-1}\) is almost the only one that can be seen. In other words, the number of intermolecular hydrogen bonds increases along with a decrease of hydrated C=O bands during heating. This shows that the breaking of hydrogen bonds from hydrated C=O promotes the formation of more intermolecular hydrogen bonds (C=O ·· D–O–D–O=–C) as the PIPOZ backbones collapse.

As for [P\(_{4,4,4,6}\)][SS]/PIPOZ, the change in peak shape resembles that of pure PIPOZ, and there exist three peaks corresponding to three kinds of amide C=O group of PIPOZ with different water environments. The peak at 1581 cm\(^{-1}\) originates from fully hydrated C=O bonds (C=O ·· 2D\(_2\)O), which [P\(_{4,4,4,6}\)][MC3S]/PIPOZ does not have. The other two peaks are located at the same wavenumbers as [P\(_{4,4,4,6}\)][MC3S]/PIPOZ. However, compared to the peak at 1605 cm\(^{-1}\), the peak at 1631 cm\(^{-1}\) is not as strong as that in [P\(_{4,4,4,6}\)][MC3S]/PIPOZ at 15°C but becomes predominant at 40°C, which indicates that the phase transition of [P\(_{4,4,4,6}\)][SS] has no effect on that of PIPOZ, and the phase separation behavior of the two components is relatively independent.

3.5 Perturbation correlation moving window (PCMW)

In order to determine the exact phase transition temperatures and transition ranges of C=O groups in these two kinds of IL-involved ternary systems, the PCMW method generated from temperature-variable FT-IR spectra was applied. PCMW is a newly developed analytical technology in recent years, whose fundamental principles date back to the conventional moving window proposed by Thomas.\(^{54}\) Later, in 2006, this method was further improved by Morita and Ozaki\(^{55}\) and the external perturbation variable was introduced into the correlation equation to make it usable in many more application fields. PCMW can be very helpful to determine the transition points as the conventional moving window does, and it can also monitor the complex spectral variations along the perturbation direction, which appears to be difficult using other conventional determination methods. PCMW synchronous spectra are able to provide information regarding accurate phase transition temperature points, whereas asynchronous spectra help us to confirm the phase transition temperature ranges by using the strongest signal intensities at specific wavenumbers.

Fig. 6 shows PCMW synchronous and asynchronous spectra of the [P\(_{4,4,4,6}\)][MC3S]/PIPOZ and [P\(_{4,4,4,6}\)][SS]/PIPOZ aqueous solutions during the phase transition process. For clarity, all the results have been summarized in Fig. 7. For [P\(_{4,4,4,6}\)][MC3S]/PIPOZ, there are two groups of bands in the C=O region of 1740–1560 cm\(^{-1}\) (ester C=O and amide C=O). According to the sequence of transition temperatures of different C=O groups, the temperature responsiveness order during the heating process is listed as follows (“→” means prior to or earlier than): 1716/1643 → 1603 → 1687 → 1632 cm\(^{-1}\), or \(\nu(\text{dehydrated C=O})\) for [P\(_{4,4,4,6}\)][MC3S]/(free C=O) for PIPOZ → \(\nu(\text{C=O} \cdots \text{D}_2\text{O})\) (weak hydration) for PIPOZ → \(\nu(\text{hydrated C=O})\) for [P\(_{4,4,4,6}\)][MC3S] → \(\nu(\text{C=O} \cdots \text{D}_2\text{O} \cdots \text{C}=\text{O})\) for PIPOZ. Obviously, the dehydrated ester C=O for [P\(_{4,4,4,6}\)][MC3S] and the free amide C=O for PIPOZ respond prior to the other kinds of C=O in the sequence. This indicates that the driving force of the phase transition process of the [P\(_{4,4,4,6}\)][MC3S]/PIPOZ mixture solution is the formation of two kinds of dehydrated C=O groups. In addition, although the signal intensity of the ester C=O (1716 cm\(^{-1}\) and 1687 cm\(^{-1}\)) is slightly weaker than that of the
amide C=O, which suggests PIPOZ has a more remarkable effect on the phase transition of the ternary system than IL, we can still draw the conclusion that IL and PIPOZ experience synergistic dehydration during phase transition. This conclusion is in accordance with the results of DSC and temperature-variable ¹H NMR.

In the case of [P₄,₄,₄,₄][SS]/PIPOZ, the response sequence of amide C=O can be described as: 1643 → 1605 → 1581 → 1630 cm⁻¹, or ν₁(free C=O) for PIPOZ → ν₁(C=O···D₂O) (weak hydration) for PIPOZ → ν₁(C=O···2D₂O) (strong hydration) for PIPOZ → ν₁(C=O···D₂O···C=O) for PIPOZ. It is clear that the two kinds of hydrated hydrogen bonds (C=O···D₂O and C=O···2D₂O) respond earlier with their number starting to decrease, and then more and more intermolecular hydrogen bonds (C=O···D₂O···C=O) form resulting in the final response. Notably, there emerges a strong signal intensity at 1581 cm⁻¹ (C=O···2D₂O), which is much weaker in [P₄,₄,₄,₄][MC₃S]/PIPOZ. This reveals that the amide C=O in PIPOZ can achieve strong hydration with more water molecules in the absence of disturbance from the IL, which indirectly indicates that PIPOZ dominates and participates in the phase transition of the [P₄,₄,₄,₄][SS]-involved mixture solution independently.

Proposed phase transition dynamic mechanisms of [P₄,₄,₄,₆][MC₃S]/PIPOZ and [P₄,₄,₄,₄][SS]/PIPOZ aqueous solutions. On the basis of the above analyses, the microdynamic phase transition mechanisms of [P₄,₄,₄,₆][MC₃S]/PIPOZ and [P₄,₄,₄,₄][SS]/PIPOZ become comprehensible, including the different roles of PIPOZ in the phase separation of ternary solutions. A schematic illustration of the mechanisms for the two solutions is presented in Fig. 8.

Generally, regardless of the IL type, the addition of a small amount of PIPOZ into the IL solution decreases the transition temperature due to the Hofmeister salting-out effect as the IL can be regarded as a kind of salt. Herein, in terms of the microscopy variations of different parts of both PIPOZ and ILs during phase transition, the following can be concluded: for the [P₄,₄,₄,₆][MC₃S]/PIPOZ solution, a two-step phase transition phenomenon and the synchronous dehydration of two solutes can be observed during the whole heating process. In contrast to the presence of the rigid and hydrophobic structure of the benzene ring in the anionic moiety of [P₄,₄,₄,₄][SS], there exists a more flexible ester group in [P₄,₄,₄,₆][MC₃S], which is much more easily surrounded by a mass of water molecules resulting in a fully hydrated environment around [P₄,₄,₄,₆][MC₃S]. This may attract the hydrophilic group (amide C=O) of PIPOZ to form a new type of intermolecular hydrogen bond with the IL–D₂O complex. As the temperature rises to 27 °C, the formation of bridging hydrogen bonds between IL and PIPOZ (IL···D₂O···PIPOZ) finishes gradually, which promotes the degree of hydration. After that, due to the connection between [P₄,₄,₄,₆][MC₃S] and PIPOZ via bridging hydrogen bonds, the dehydration of the amide C=O groups of PIPOZ starts to occur, which also forces the ester C=O groups of [P₄,₄,₄,₆][MC₃S] to dehydrate together. As the second dehydration takes place around 34 °C corresponding to the LCST of [P₄,₄,₄,₆][MC₃S], the bridging hydrogel bonds cause the further dehydration of PIPOZ as well. Meanwhile, the number of intermolecular hydrogen bonds (C=O···D···O···D···O=C) of PIPOZ increases. With regard to

![Fig. 7 The phase transition temperatures and temperature ranges of [P₄,₄,₄,₆][MC₃S]/PIPOZ (red) and [P₄,₄,₄,₄][SS]/PIPOZ (black) in D₂O read from PCMW synchronous and asynchronous spectra.](image)

![Proposed phase transition dynamic mechanisms of [P₄,₄,₄,₆][MC₃S]/PIPOZ and [P₄,₄,₄,₄][SS]/PIPOZ aqueous solutions.](image)
[P₄,₄,₄,₄][SS]/PIPOZ solution, the two-step phase transition is distinct from that in [P₄,₄,₄,₆][MC3S]/PIPOZ. Without the bridging hydrogen bonds between [P₄,₄,₄,₄][SS] and PIPOZ, only PIPOZ dehydrates at a reduced LCST of 28 °C due to the Hofmeister salting-out effect of [P₄,₄,₄,₄][SS]. The anion and cation of [P₄,₄,₄,₄][SS] do not dehydrate until the temperature reaches the LCST of the IL (36 °C), when the remaining parts of PIPOZ that are less affected by the Hofmeister effect dehydrate further. In other words, the two thermoresponsive components of the [P₄,₄,₄,₄][SS]/PIPOZ aqueous solution dehydrate more independently.

It is also noted that, in the past few years, aqueous biphasic systems (ABS) consisting of polymers, ILs and water were developed by Rogers, Coutinho, and Pereira, et al.34–36,58 who described a water-rich system combining a polymer such as polyethylene glycol (PEG) and an IL that above certain concentrations leads to an immiscible liquid–liquid region. In ABS, besides IL–water and PEG–water interactions, similar to the case of PIPOZ–IL, PEG–IL interactions could additionally control the phase diagrams, and a “washing-out” effect was also recently proposed to account for the formation of the polymer–IL-based ABS.34–36 Nevertheless, the present PIPOZ–IL–water ternary systems cannot be simply regarded as a polymer–IL-based ABS. First, ABS is characterized by an immiscibility concentration gap in the ternary region, whereas all the binary mixtures are fully miscible at a fixed temperature (type 0 system).36 However, not all the binary mixtures among ILs, PIPOZ and water are fully miscible as featured by the type-0 system: PIPOZ has poor solubility in both [P₄,₄,₄,₆][MC3S] and [P₄,₄,₄,₄][SS]. Moreover, the phase separation of IL/PIPOZ ternary systems can occur at very low concentrations of both IL and PIPOZ (e.g. total concentration, 1% (w/v), Fig. S2, ESI†). Nonetheless, the concentrations of immiscible type-0 systems are much higher. In fact, the phase behaviour of IL/PIPOZ ternary systems is mainly due to the thermoresponsivity of the IL, which is also concentration-dependent, and that of PIPOZ.40,41

4. Conclusion

In this paper, DSC, optical microscopy, temperature-variable ¹H NMR and FT-IR spectroscopy including a PCWM method were applied to study the influence of a LCST-type polymer (PIPOZ) on the phase transition behavior of two different LCST-type ionic liquids ([P₄,₄,₄,₆][MC3S] and [P₄,₄,₄,₄][SS]) with different structures.

Surprisingly, as a consequence of the Hofmeister salting-out effect of ILs, the LCST of the IL-involved solution decreases to 27 °C or 28 °C with the addition of PIPOZ, which largely differs from the case of the PVCL/[P₄,₄,₄,₆][MC3S] solution.19 It is speculated that there is a unique interaction between [P₄,₄,₄,₆][MC3S] and PIPOZ from the observation of cobblestone-like droplets in the phase separation of the [P₄,₄,₄,₆][MC3S]/PIPOZ aqueous solution. Temperature-variable ¹H NMR and FT-IR spectra reveal that during the two-step dehydration, both [P₄,₄,₄,₄][MC3S] and PIPOZ engage in the first dehydration with the connection of bridging hydrogen bonds (IL···D₂O···amide C=O of PIPOZ), whereas PIPOZ dehydrates more independently in the [P₄,₄,₄,₄][SS]/PIPOZ solution. Therefore, it can be concluded that [P₄,₄,₄,₆][MC3S] and PIPOZ play synergistic roles in the whole phase transition of [P₄,₄,₄,₆][MC3S]/PIPOZ solution, whereas PIPOZ dominates the LCST phenomenon of [P₄,₄,₄,₄][SS]/PIPOZ solution. The findings presented here could be helpful to deepen our understanding of the mutual relationship among different LCST-type substances and to develop more advanced stimuli-responsive systems.

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Notes and references
