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Tunable LCST-type phase behavior of [FeCl₄]⁻-based ionic liquids in water

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In this work, 16 kinds of $[FeCl_4]^-$ -based magnetic ionic liquids (ILs) with different cation structures have been designed and synthesized, and their structures are characterized by IR and Raman spectroscopy. Then the lower critical solution temperature (LCST)-type phase behavior of these magnetic ILs in water is investigated as a function of concentration. It is shown that cation structure, alkyl chain length and molar ratio of FeCl₃/chloride IL have a significant influence on the LCST of the mixtures. The phase separation temperature can be tuned efficiently by these factors. Meanwhile, the LCST-type phase separation process is also investigated by dynamic light scattering. The results support the mechanism that the hydrogen bonds of the [FeCl₄]⁻ anion with water have been gradually disrupted to form ILs aggregates with increasing temperature. In addition, the stability of the ILs in water is also examined in some details. These LCST-type phase separation systems may have potential applications in extraction and separation techniques at room temperature.

magnetic ionic liquids, IR and Raman spectroscopy, lower critical solution temperature, tunable phase separation

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1 Introduction

Ionic liquids (ILs) are entirely composed of ions as the name implies, and they melt at the temperatures below 100 °C [1,2]. Their extraordinary high ion density results in the negligible vapor pressure under ordinary conditions. Such a remarkable property makes it possible for ILs to be alternatives of volatile organic solvents used in many areas of synthetic, separation and electrochemical applications. The most important feature of ILs is their structural designability. In general, cations are mainly responsible for the tune of melting point and for the amphiphilic property of ILs, and the selection of anions can readily tailor the liquid

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properties such as polarity, viscosity and miscibility with molecular solvents. Such component ions allow for the fine tuning of liquid properties of the resulting functional ILs by the chemical modification of both cation and anion.

In recent years, functional ILs have attracted great interest especially those which are responsive to pH [3], temperature [4], CO_2 [5], light [6] and magnet [7]. Among these external stimulus responsive ILs, magnetic ILs exhibit potential applications in catalytic, separation, electrochemistry, magnetic hydraulics in engineering, gas absorption and microemulsion owing to their paramagnetic nature [8–14].

Lower critical solution temperature (LCST) phase behavior is a not-so-common, entropy driven phenomenon where the miscibility of two liquids increases upon cooling. Usually, LCST-type phase separation is observed for some

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non-ionic polymers with water [15,16]. For ILs, it is shown that most of them exhibit upper critical solution temperature (UCST)-type phase separation with water [17], only a few ILs-water mixtures show LCST-type phase separation. In this context, Ohno and co-workers [18-25] reported excellent results on LCST-type phase separation of some functional ILs. For example, in 2007 they synthesized a series of functional amino acids ILs with tri-n-butyloctylphosphonium [P4448] and tetra-n-butylphosphonium [P4444] as cations, and N-trifluoromethanesulfonyl amino acid methyl ester as anion. These ILs were found to exhibit LCST-type phase separation with water. The effect of water content and component-ion structure on the phase-separation temperature of IL/water mixtures was investigated [18]. After that, they also synthesized other LCST-type ILs based on [P₄₄₄₄] cation, and the LCST-type phase behavior of these ILs in water was studied in detail [19-25]. In addition, Xie and Taubert [26] investigated the thermomorphic behavior of $[C_4 mim][FeCl_4]$ and $[C_{12} mim][FeCl_4]$ in water, and the LCST phase behavior for the mixtures of magnetic ILs with water was reported for the first time.

In this work, 16 kinds of [FeCl₄]⁻based magnetic ILs were prepared with different cation structures, such as imidazoliumcations, cholinium cations, quaternary ammonium cations and quaternary phosphonium cations, and different alkyl chain lengths. Chemical structures for the synthesized magnetic ILs are shown in Figure 1. These ILs were characterized by means of IR, Raman spectroscopy and differential scanning calorimetry (DSC), and then used to study the LCST-type phase separation behavior in water. The modulation of the phase separation temperature of the mixtures by cationic structure, alkyl chain length and molar ratio of FeCl₃/chloride IL was examined, and the results were discussed from the hydrogen bond between the ILs anion and water and the change in hydrophobicity of cations of the ILs.

2 Experimental

2.1 Materials

N,*N*-dimethylethanolamine (DMEA) (99%), *N*-methyldiethanolamine (MDEA) (99%), methyl trioctylammonium chloride ([$N_{8,8,8,1}$]Cl) (97%), (tri-*n*-butyl)-*n*-tetradecylphosphonium chloride ([$P_{4,4,14}$]Cl) (97%), anhydrous FeCl₃ (99%) and FeCl₃·6H₂O (99%) were purchased from Aladdin (China). 1-Methylimidazole (99%), allyl chloride (98%), 1-chlorobutane (99%), 1-chlorodecane (95%), 1-chlorododecane (99%), 1-chlorotetradecane (98%) and 1-ethyl-3-methylimidazolium chloride (96%) were acquired from J&K Chemicals (China). All chemicals were used as received without any further purification.



Figure 1 Chemical structures for cations of the ILs investigated in this work.

2.2 Synthesis of the ILs

All the $[FeCl_4]^-$ -based ILs were synthesized according to the procedures described in the literatures [27,28]. These ILs are readily obtained by mixing equal molar iron trihalide with corresponding cationic chloride ILs [29]. The mixtures were stirred at room temperature, and a two-phase mixture consisting of a brown liquid and a water layer was formed after a few minutes. The crude product was obtained after removal of the top water layer, and was then washed with an excess of deionized water to remove un-reacted FeCl₃ from the final product. Thus obtained magnetic ILs were dried under vacuum at 70 °C for 48 h.

2.3 Characterization of the ILs

The final obtained ILs were characterized by IR, Raman spectroscopy and DSC. Because of the magnetism of these ILs, the synthesized precursors ILs (chloride ILs), instead of these magnetic ILs, were characterized by ¹H NMR (Bruker, AV-400). FTIR and Raman spectra of the magnetic ILs were recorded by using a Thermo Nicolet FTIR Nexus 470 spectroscopy (USA) with an instrument resolution of 2 cm⁻¹. The spectra measurements were performed at room temperature. The glass transition temperature (T_g) and the melting point (T_m) of the ILs were measured by means of a differential scanning calorimeter (Netzsch DSC 204F-1, Germany).

2.4 Phase separation temperature measurements of the IL/water mixture

The phase separation temperature (T_c) of the IL/water mixture was determined based on the visual detection of the turbidity of the mixture according to the reported procedures [30,31]. Briefly, a given concentration of IL/water mixture was gravimetrically prepared using an analytical high precision balance with an uncertainty of ± 0.0001 g. The IL/water mixture was then placed in a glass tube. In each separate experimental run, the glass tube was immersed in a thermostatic water bath with an accuracy of ± 0.05 °C. The mixture was heated or cooled at an interval of 0.1 °C, and the mixture was maintained at least 5 min at each temperature. The process was continued until the phase transition was observed (turbidity-to-transparency with cooling or transparency-to-turbidity with heating). Such obtained phase separation temperature datum was then confirmed by at least quintic cooling-heating cycles. The final uncertainty in the phase separation temperature was estimated to be smaller than 0.3 °C.

2.5 Droplet size measurements

The size and size distribution of the IL/water mixture were measured by dynamic light scattering (DLS) technique using a Malvern Zetasizer Nano-90 light scattering instrument (Malvern Instrument Ltd., UK). The scattering angle was set at 90°. After the samples were equilibrated for 24 h, the samples were filtered through a 0.45 μ m Millopore filter to remove the dust or any contaminants.

3 Results and discussion

3.1 Characterization of the ILs and their stability in water

The $T_{\rm g}$ and $T_{\rm m}$ of the prepared ILs are listed in Table 1. It

Table 1 The glass transition temperature (T_g) and the melting point (T_m) of the ILs

f	ature ILs, their glass transition temperature varies from
1	about -100 to -65 °C with the change of cation structure
t	and alkyl chain length. This suggests great advantages as
e	solvent and reaction medium at low temperature. These ILs
у	were further characterized by IR and Raman spectra. As an
	example, the IR and Raman spectra of $[C_2mim][FeCl_4]$ and
n	[C ₆ DMEA][FeCl ₄] are shown in Figure 2(a) and (b), respec-
e	tively. It can be seen from Figure 2(a) that in the IR spec-
S	trum of [C ₂ mim][FeCl ₄], the characteristic frequency bands
	at ~3149 and ~3116 cm^{-1} can be assigned to the stretching
	modes of C-H bond of the imidazolium ring. The bands at
	~2961 and ~2932 cm ⁻¹ belong to aliphatic C-H vibrations
	of the imidazolium ring. The peak at ~1590 cm^{-1} is $-\text{C}=\text{N}-$
e	stretching vibration of the ring. Similarly, in the IR spec-
-	trum of [C ₆ DMEA][FeCl ₄], the characteristic frequency
t	bands at ~3280 cm ⁻¹ can be assigned to the stretching vibra-
S	tion of -OH group on the cation. The bands at ~2955,
e	~2928 and ~2865 cm ⁻¹ are assigned to aliphatic C-H vibra-
5	tions of the cholinium cation. The above analysis indicates
	that cationic structures of the prepared ILs are in good
	agreement with those shown in Figure 1.

should be noted that the melting point was not revealed for all ILs. It can be seen that these ILs are really room temper-

According to the previous report [32], $[FeCl_4]^-$ and $[Fe_2Cl_7]^-$ are the main anion in the Fe-based ILs. The $[FeCl_4]^-$ anion is present in the ILs where the ratio of FeCl₃/chloride IL is less than or equal to 1:1, while the $[Fe_2Cl_7]^-$ anion is only present in the ILs when the ratio of FeCl₃/chloride IL is higher than 1:1. Here, Raman spectra

ILs	$T_{\rm m}$ (°C)	$T_{\rm g}$ (°C)	ILs	$T_{\rm m}$ (°C)	$T_{\rm g}$ (°C)
[Amim][FeCl ₄]	— ^{a)}	-100	[C14mim][FeCl4]	33	-86
[bbim][FeCl4]	-	-87	[C ₄ DMEA][FeCl ₄]	-	-84
[C ₂ mim][FeCl ₄]	18	-65	[C ₆ DMEA][FeCl ₄]	-	-76
[C ₄ mim][FeCl ₄]	-	-84	[C ₈ DMEA][FeCl ₄]	-	-80
[C ₆ mim][FeCl ₄]	-	-82	[C ₄ MDEA][FeCl ₄]	-	-74
[C ₈ mim][FeCl ₄]	-	-81	[C ₆ MDEA][FeCl ₄]	-	-65
[C10mim][FeCl4]	-	-77	[P _{4,4,4,14}][FeCl ₄]	-	-82
[C ₁₂ mim][FeCl ₄]	18	-65	[N _{8,8,8,1}][FeCl ₄]	-	-94

a) Not detected.



Figure 2 IR (a) and Raman (b) spectra of [C₂mim][FeCl₄] and [C₆DMEA][FeCl₄] ionic liquids at room temperature.

were used to examine what is the right anion in the prepared ILs. As an example, Figure 2(b) shows the Raman spectra of $[C_2mim][FeCl_4]$ and $[C_6DMEA][FeCl_4]$. It can be seen that a strong single peak appears at ~330 cm⁻¹, which could be assigned to the symmetric stretching vibrations of Fe–Cl bond in $[FeCl_4]^-$. The symmetry vibrations of $[Fe_2Cl_7]^-$ anion should be located at ~360 cm⁻¹ [33]. Thus, it can be confirmed that the synthesized ILs contain the same $[FeCl_4]^-$ anions.

In addition, it was reported that hydrolysis of [FeCl₄]⁻ anions is inevitable when contacting with water [34]. However, in our experiment, pH value for the equilibrated aqueous phase was around 1.0, and no obvious precipitation was observed during the reversible circulation of heating and cooling around the phase separation temperature. After phase separation, the aqueous and ILs phases were also transparent even at higher temperatures (say 70 °C). Furthermore, the phase stability of IL/water mixture was also examined at room temperature. It was shown that no precipitation was observed in IL/water mixture during 6 months. This result implies that the two-phase mixture is stable and the magnetic ILs do not hydrolyze significantly at such a low pH value. The same conclusion has been obtained by Xie and Taubert [26]. In order to examine the stability of these ILs after phase separation with water, IR and Raman spectroscopy was also determined for both the fresh ILs and the ILs recovered from phase equilibrium measurements. It was found that there are no differences in the IR and Raman spectra from fingerprint area (400-1300 cm⁻¹) to characteristic frequency area (1300-4000 cm⁻¹) for such ILs. These results indicate that these ILs are quite stable after phase separation with water, and the hydrolysis of the ILs is negligible in the concentration and temperature range studied.

3.2 Tuning the phase behavior of IL/water mixture by cationic structures of the ILs

In this work, four kinds of cations, including cholinium cation, imidazolium cation, quaternary ammonium cation and quaternary phosphonium cation (Figure 1), were chosen to study the modulation of cations on the phase behavior of the IL/water mixtures. Figure 3 shows the plots of phase separation temperature of these IL/water mixtures as a function of IL concentration. It can be seen that the phase separation temperature of all the mixtures decreased with increasing IL concentration. In other words, the solubility of the ILs in water increased with the decrease of temperature. The IL/water mixture became clear below the phase separation temperature, and turbid above the phase separation temperature. This is the typical feature of LCST-type phase behavior. This process is reversible for the IL/water mixtures upon cooling or heating. It is clear from Figure 3 that in the temperature range investigated, solubility of the ILs in water follows the order: [C₈DMEA][FeCl₄]>[C₄DMEA]- $[FeCl_4] > [C_4mim][FeCl_4] > [P_{44414}][FeCl_4] > [N_{8881}][FeCl_4].$ From the chemical structure of the ILs shown in Figure 1, $[N_{8881}]$ [FeCl₄] and $[P_{44414}]$ [FeCl₄] have more hydrophobic long alkyl chain than [C₈DMEA][FeCl₄], [C₄DMEA] [FeCl₄] and [C₄mim][FeCl₄]. Thus, this result is in accordance with the hydrophilic order of the traditional ILs.

Figure 4 shows the modulation of substitute group in imidazolium cations on the phase behavior of some IL/ water mixture. It was also found that these ILs exhibited LCST-type phase behavior in water. The aqueous solubility of the ILs follows the order: [Amim][FeCl₄]>[C₄mim]-[FeCl₄]>[bbim][FeCl₄] at a given temperature. In comparison with the chemical structure of [bbim]⁺, the methyl group of [C₄mim]⁺ cation was replaced by butyl group. Thus $[bbim]^+$ is more hydrophobic than $[C_4 mim]^+$. In the case of $[C_4 mim][FeCl_4]$ and $[Amim][FeCl_4]$, the butyl group of $[C_4 mim]^+$ cation was replaced by allyl group of $[Amim]^+$. Similarly, $[C_4 mim]^+$ is more hydrophobic than $[Amim]^+$. This result can be used to understand the solubility order of the ILs mentioned above. Therefore, the LCST of these IL/water mixtures can be tuned by cationic hydrophobicity/hydrophilicity.



Figure 3 The modulation of cationic structure on the phase separation temperature of the IL/water mixtures.



Figure 4 The modulation of substitute group in imidazolium cations on the phase separation temperature of the IL/water mixtures.

3.3 Tuning the phase behavior of IL/water mixture by alkyl chain length of the ILs

To examine the effect of alkyl chain length of cations on the temperature-driven phase separation of the IL/water mixtures, imidazolium and cholinium ILs with different alkyl chain lengths were investigated. The phase separation temperature of these IL/water mixture was illustrated in Figures 5 and 6 as a function of the ILs concentration. As can be seen from these figures, solubility of the ILs in water increased with the decrease of temperature. This is also the typical feature of LCST-type phase behavior.

For the imidazolium-based ILs, it was also found that solubility of the ILs in water was significantly influenced when the number of carbon atoms in the alkyl chain was increased from 2 to 14. As shown in Figure 5(a), when the number of carbon atoms is below 8, solubility of the ILs in water decreased with the increase of the alkyl chain length at a given temperature: [C₂mim][FeCl₄]>[C₄mim][FeCl₄]> [C₆mim][FeCl₄], which is in agreement with hydrophobicity of the ILs. However, solubility of the ILs in water was found to increase with increasing alkyl chain length at the same temperature when the number of carbon atoms was equal to or greater than 8, as shown in Figure 5(b): $[C_{14}]$ mim][FeCl₄]>[C₁₂mim][FeCl₄]>[C₁₀mim][FeCl₄]>[C₈mim] [FeCl₄]. This order is not in agreement with hydrophilicity of the ILs. The different phase behavior usually implies different solution structures. Indeed, many studies have indicated that long alkyl chain ILs behave like the traditional cationic surfactants. As its concentration was greater than the critical aggregation concentration (CAC), micelle of the IL was formed. Therefore, it is appropriate to state that the higher solubility of long alkyl chain ILs was ascribed to the aggregation of these ILs in water. This result indicates that the LCST phase behavior can be easily modulated by adjusting the alkyl chain length of the ILs.

As far as the cholinium-based ILs are concerned, solubility of the ILs in water was found to increase with increasing alkyl chain length of the IL cations. As shown in Figure 6, the results are similar to what we have observed for long alkyl chain imidazolium-based ILs. It is evident that solubility of the ILs in water follows the trend: $[C_8DMEA]$ - $[FeCl_4]>[C_6DMEA][FeCl_4]>[C_4DMEA][FeCl_4]$, and $[C_4M DEA][FeCl_4]>[C_4DMEA][FeCl_4]$. From the chemical structure of the ILs shown in Figure 1, the methyl group of $[C_4DMEA]^+$ cation was replaced by hydroxyethyl group to form $[C_4MDEA]^+$. Therefore, it seems appropriate to indicate that introduction of an additional –OH group enhances the hydrophilicity of the cation, and thus increasing solubility of the $[C_4MDEA][FeCl_4]$ ionic liquid.

3.4 Tuning the phase behavior of IL/water mixture by molar ratio of FeCl₄/chloride IL

The traditional chloride ILs are usually miscible with water at room temperature, for example, [C₆mim]Cl is completely soluble in water. However, $[C_6 mim][FeCl_4]$ is only partially miscible with water at around room temperature. This result implies that the [FeCl₄]⁻ anion plays the key role in the miscibility of ILs with water. In order to investigate the effect of molar ratio of FeCl₃/chloride IL on the phase behavior of IL/water mixtures, the ILs $[C_6 mim][FeCl_4]_x Cl_{1-x}$ (x=0.36, 0.54, 0.71, 1,0) and [C₆DMEA][FeCl₄]_xCl_{1-x} (x=0.67 and 1.0) were prepared from different molar ratios of FeCl₃/ imidazolium chloride and FeCl₃/cholinium chloride by direct mixing anhydrous FeCl₃ and chloride ILs at respective molar ratio. Then the LCST of these ILs mixtures with water was determined, and the results are shown in Figure 7(a)and (b), respectively. It can be seen that aqueous solubility of these ILs decreased with increasing molar ratio of FeCl₃ to imidazolium chloride or cholinium chloride. When the molar ratio of FeCl₃/[C₆mim]Cl was 1:1, the LCST behavior became strong. However, it became weaker when the molar ratio was below 1:1 due to the fact that the interaction of anion...H2O...anion between the ILs components and water was increasingly weakened by the continuous addition of FeCl₃. In addition, it should be pointed out that during the experimental process, obvious precipitation was



Figure 5 The modulation of alkyl chain length in imidazolium cations on the phase separation temperature of the IL/water mixtures. Carbon atom number (n_c) in the alkyl chain: (a) $n_c < 8$; (b) $n_c > 8$.



Figure 6 The modulation of alkyl chain length in cholinium cations on the phase separation temperature of the IL/water mixtures.

observed as the molar ratio of $FeCl_3/[C_6mim]Cl$ was higher than 1:1. This indicates that significant hydrolysis occurs in the IL/water mixture under this condition.

3.5 The possible mechanism for the LCST phase behavior of IL/water mixture

The [FeCl₄]⁻-based ILs are partially soluble in water at room temperature. The hydrophobicity of these ILs may be ascribed to the nephelauxetic effect of [FeCl₄]⁻ anion [35]. Tang *et al.* [36] suggested that the hydrogen bonding interactions between [FeCl₄]⁻ and water molecules led to the partial solubilization of the [FeCl₄]⁻-based ILs in water. Xie *et al.* [26] and Estager *et al.* [35] proposed a possible explanation for the LCST-type phase behavior of [FeCl₄]⁻based ILs in water by considering cohesive energy of water causing "solvophobic" immiscibility, long-range coulomb forces and competitive hydrogen bonding between cation---anion and anion---H₂O---anion. It is suggested that with the increase of temperature, the [FeCl₄]⁻---H₂O hydrogen

bonds were disrupted gradually. Then, the ILs molecules were aggregated continuously with increasing temperature until the new IL phase was formed above the phase separation temperature.

In order to examine this mechanism, the aggregation of the ILs in aqueous solutions was investigated by means of DLS from the temperature far below the LCST to around the critical point. To this end, the hydrodynamic diameter (d_h) of the ILs in aqueous solutions was measured as a function of temperature at different concentrations. As an example, the hydrodynamic diameters of [C₆DMEA][FeCl₄] and [C₂mim][FeCl₄] are shown in Tables 2 and 3. It is clearly indicated that the d_h values increase with the increase of temperature due to the aggregation of the ILs. Finally, the ILs aggregate into large particles at the temperature above phase separation temperature and form a turbid dispersion. Similar results were observed in other IL/water systems.

Table 2 The diameter (d_h) of [C₆DMEA][FeCl₄] in water at different temperatures

W=47.00%		W=56.34%		W=66.19%	
<i>T</i> (°C)	$d_{\rm h} ({\rm nm})$	<i>T</i> (°C)	$d_{\rm h} ({\rm nm})$	<i>T</i> (°C)	$d_{\rm h}({\rm nm})$
25.0	20.6	23.0	82.4	16.0	254
28.0	23.5	25.0	105	17.0	296
30.0	26.0	26.0	124	18.0	349
31.5	29.5	27.0	156	19.0	370
32.0	31.7	27.3	179	20.0	562
				21.5	938

Table 3 The diameter (d_h) of $[C_2mim][FeCl_4]$ in water at different temperatures

W=24	4.89%	W=29.98%		
<i>T</i> (°C)	$d_{\rm h}$ (nm)	<i>T</i> (°C)	$d_{\rm h}({\rm nm})$	
25.0	137	25.0	163	
28.0	139	28.0	183	
30.0	251	30.0	193	
35.0	290	35.0	228	
40.0	354	40.0	346	
45.0	809	45.0	792	
50.0	988	50.0	867	



Figure 7 The modulation of molar ratio of FeCl₃/chloride ILs on the phase separation temperature of the IL/water mixtures. (a) FeCl₃/[C_6 mim]Cl; (b) FeCl₃/[C_6 DMEA]Cl.

4 Conclusions

In summary, a series of [FeCl₄]⁻-based magnetic ILs with different cationic structures were synthesized and characterized in the present work. The LCST-type liquid-liquid phase separation behavior of these magnetic ILs with water was then investigated in detail. It was shown that the LCST-type phase behavior is essentially determined by the disruption of the hydrogen bonds between the [FeCl₄]⁻ anion and water. When the anion was fixed, the LCST values for the mixtures were affected significantly by cationic structure, alkyl chain length and substitution of hydrophobic and hydrophilic groups. Compared with imidazolium and cholinium based ILs, quaternary ammonium and quaternary phosphonium based ILs have lower solubility in water at a given temperature. For the imidazolium based ILs, their miscibility with water decreases with the increase of alkyl chain length of the cations when the number of carbon atoms in the alkyl chain is smaller than 8, whereas it increases with the increase of alkyl chain length when the number of carbon atoms is equal to or greater than 8 due to the aggregation of these ILs in water. For the cholinium based ILs, solubility increases with the increase of alkyl chain length for the ILs investigated. Meanwhile, the aqueous solubility of these ILs was found to decrease with increasing molar ratio of FeCl₃ to imidazolium chloride or cholinium chloride from 0.36 to 1.0. In addition, it is likely from the DLS results that hydrogen bonds between the ILs and water were disrupted gradually with increasing temperature, and the new phase was formed by the aggregation of the ILs. The above findings may have impact on the design of magnetic ILs and potential applications in extraction and separation techniques at room temperature.

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Conflict of interest The authors declare that they have no conflict of interest.

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