

# Aggregation in Systems of Ionic Liquids

Jianji Wang and Huiyong Wang

**Abstract** Material preparation in ionic liquids and environmental pollution control by ionic liquids are often closely dependent on the aggregation behavior of ionic liquids in solution. Therefore, understanding the aggregation behavior of ionic liquids in solution is very important from both fundamental and applied aspects. In this chapter, our aim is to provide a summary of our current state of knowledge of the aggregation of ionic liquids in solutions modulated by alkyl chain length, cationic structure, and anionic type of ionic liquids, and by addition of inorganic salts, organic solvents, and surfactants. The possible mechanism for the effect of these factors on the aggregation behavior of ionic liquids has been analyzed, and the potential applications of ionic liquids aggregation in membrane separation of ionic liquids wastewater, controlled drug release, breakage of oil/water emulsions, and selective separation of protein (BSA) from aqueous saccharides has also been illustrated. In addition, the challenges in this field have been addressed and some suggestions are made for future work.

**Keywords** Ionic liquids • Aggregation in solution • Aggregate microstructure • Potential applications

## 1 Introduction

### 1.1 Ionic Liquids

Room temperature ionic liquids (ILs) are a special class of molten salts composed of organic cations and inorganic or organic anions, melting at temperatures below

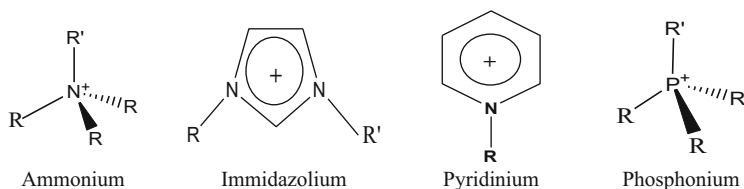
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**Fig. 1** Cationic structures of ILs commonly used

373 K. Usually, the most used cations include alkylimidazolium  $[\text{RR}'\text{IM}]^+$ , alkylpyridinium  $[\text{RPy}]^+$ , tetraalkylammonium  $[\text{NR}_4]^+$ , and tetraalkylphosphonium  $[\text{PR}_4]^+$  (see Fig. 1). Anions consist of chloride  $\text{Cl}^-$ , bromide  $\text{Br}^-$ , iodide  $\text{I}^-$ , hexafluorophosphate  $[\text{PF}_6]^-$ , tetrafluoroborate  $[\text{BF}_4]^-$ , nitrate  $[\text{NO}_3]^-$ , methane sulfonate (mesylate)  $[\text{CH}_3\text{SO}_3]^-$ , trifluoromethane sulfonate (triflate)  $[\text{CF}_3\text{SO}_3]^-$ , bis-(trifluoromethanesulfonyl)amide  $[\text{Tf}_2\text{N}]^-$ , among others [1]. The number of potential ion combinations available reputedly equates to  $10^{12}$ .

Compared with the traditional volatile organic compounds (VOCs), ILs have many unique physical and chemical properties. These properties can be summarized as follows [1]: (1) immeasurable vapor pressure and nonflammability under normal conditions; (2) thermal decomposition temperatures higher than  $300^\circ\text{C}$ , and a large liquid range from  $-200$  to  $300^\circ\text{C}$ ; (3) excellent dissolution performance for organic, inorganic, and polymer materials; (4) wide electrochemical window of  $2 \sim 5$  V; and (5) designable structures and properties for various practical applications.

Among these properties, negligible vapor pressure avoids atmospheric pollution and enhances their recycling, which are the main reason why ionic liquids are often called “green solvents.” However, recent studies have shown that some ionic liquids have a wide range of toxicity and, as a result, the use of the term “green solvents” has been questioned [2, 3].

Even so, the above properties have made ILs applicable to myriads of applications that include chemical synthesis [4], biocatalytic transformations [5, 6], electrochemistry [7, 8], and analytical and separation science [9, 10]. In addition, the opportunity of cation modification and anion selection as well as the enormous number of possible combinations allows us to fulfill technological demands, and provides novel task-specific media for the chemical and biochemical industries [11, 12].

In their applications, ILs exhibit many unique properties and much abnormal behavior. For example, ILs have the ability to dissolve inorganic compounds; at the same time, they can also dissolve organic and polymeric materials over a wide temperature range. It seems likely that the old rule of thumb that “like dissolves like” is not valid for ionic liquids. When  $\text{CO}_2$  is added to ILs, the electric conductivity of the systems increases, although  $\text{CO}_2$  is a nonpolar compound [13]. Ionic liquids dissolve very large amounts of  $\text{CO}_2$ , while the solubility of neat ionic liquids in supercritical  $\text{CO}_2$  is very low [14]. Ionic liquids can be used as stationary phases in gas-liquid chromatography, but they show “dual-nature” behavior: they are

capable of separating polar compounds as if they were polar stationary phases and can also separate nonpolar compounds as if they were nonpolar stationary phases [15]. These unique properties are ascribed not only to the nature of cations and anions but also to the interaction of ionic liquids with other components and the microstructure of ionic liquids in the systems. Therefore, aggregation of ionic liquids in solutions has been the focus of much research [16–19].

## ***1.2 Significance of Ionic Liquids Aggregation***

Many applications of ILs would be closely related to their aggregate formation. It may be expected from the amphiphilicity of ILs that interfacial phenomena play a major role in the behavior of such IL-containing systems. For example, the transfer of a compound through an interface is an important part of the extraction process which is controlled by molecules adsorbed at the interface. The presence of IL aggregates could reduce the efficiency of these processes because of partial extraction of the product into micelles. The formation of aggregation structure may also have consequences in a number of areas including synthesis and purification of bulk ILs, material preparation, environmental pollution control, formation of dispersed or phase-separated systems, distribution of ILs in the environment [12, 20], among others.

The transport and distribution of ILs through soil is also mainly dependent on their aggregation. The size and structure of an aggregate would affect the transport parameters of ILs. It was shown that ILs were adsorbed onto soils initially with electrostatic interaction with clay surface [21], and the aggregates of ILs can also be adsorbed onto mineral surfaces to form hemi-micelles on the surface. The aggregates have the ability to dissolve highly lipophilic substances and promote their distribution as part of a colloid-facilitated transport. This would influence the chemical fate of ILs and eventual possibilities of soils remediation.

Aggregation behavior is obviously very important for the future use and environmental fate analysis of ILs. Also, the knowledge of the aggregation behavior of ILs plays a vital part in understanding how these ionic compounds participate as components in a complex system. Therefore, in this chapter we will analyze and summarize the state-of-the-art on the studies of the formation, microstructure and possible applications of ILs aggregation in solutions in order to provide a better understanding of the progress in this field.

**Table 1** Critical aggregation concentration (mM) of 1-alkyl-3-methyl-imidazolium chloride ([C<sub>n</sub>mim]Cl), 1-alkyl-3-methyl-imidazolium bromide ([C<sub>n</sub>mim] Br), N-alkyl-N-methylpyrrolidinium bromide(C<sub>n</sub>MPB) and 1-alkylpyridiniumbromides (C<sub>n</sub>PyrBr) as a function of alkyl chain length (n<sub>c</sub>) determined by various methods at 298 K

n <sub>c</sub>	[C <sub>n</sub> mim]Cl		[C <sub>n</sub> mim]Br		C <sub>n</sub> PyrBr		C <sub>n</sub> MPB	
	Surface conductivity	fluorescence	other method	Surface conductivity tension	Surface conductivity	fluorescence	other method	Surface conductivity tension
2				2,500[26]	1,900[26]		N(SANS) [26]	
4	N[22] <sup>a</sup>	N[22] <sup>a</sup>		800[26]	900[26]		N(SANS) [26]	
					N[27] <sup>a</sup>		2,579(NMR) [32] <sup>b</sup>	
6	900[19]	N[19] <sup>a</sup>		600[26]	400[26]		600(SANS) [26]	
N[27] <sup>a</sup>				470[28]	770[31] <sup>b</sup>		800(volume) [31] <sup>b</sup>	
							797(NMR) [32] <sup>b</sup>	
8	220[22]	234[22]	200(NMR) [19]	150[26]	150[26]	190[31] <sup>b</sup>	160(SANS) [26]	184(NMR) [38]
100[16]		90[16]	263(ITC) [36]	121[28]	160[31] <sup>b</sup>	130[39]	180(volume) [31] <sup>b</sup>	
220[19]		200[36]		170[38]	169[38]		141(NMR) [32] <sup>b</sup>	
							177(NMR) [38]	
9				40[26]	30[26]			
					74[18]			
10	59.9[22]	53.8[22]	45[19]	20[28]	40[27]	46[31] <sup>b</sup>	39(SANS) [26]	45(NMR) [38]
55[19]		60[23]	66(ITC) [36]	29.3[29]	41[18]	25[39]	42(volume) [31] <sup>b</sup>	
10[23]		40.47[24]		33[38]	32.9[29]		31(NMR) [32] <sup>b</sup>	
39.9[24]		62[36]			39[31] <sup>b</sup>		39(NMR) [38]	
					42[38]			
12	15[19]	20[23]	7[19]	13(NMR) [19]	4.3[28]	10[31] <sup>b</sup>	12(volume) [31] <sup>b</sup>	13.5 [37]
13.17[24]		13.47[24]		13.8(ITC) [19]	10.9[29]	8.5[29]	11(NMR) [32] <sup>b</sup>	13.5 [37]
9.68[37]		14[36]			9.68[37]	9.5[30]	9.56(ITC) [37]	
					9.0[38]	9[31] <sup>b</sup>	8.0(NMR) [38]	
						10[38]		
14	3.4[22]	3.15[22]	3[19]	4(NMR) [19]	2.69[37]	2.5[18]	2.52(ITC) [37]	3.30[37]
4[19]		3.68[24]		3.3(ITC) [36]	1.9[38]	2.6[30]	1.4(NMR) [38]	3.30[37]
2.98[24]		3.8[36]						
2.69[37]								

16	1.3[22] 0.88[25] 0.87[24] 0.51[37]	1.14[22] 0.86[24]	0.51[37] 0.8[28] 0.61[18] 0.65[30]	0.64(ITC) [37]	0.860[37] 0.856[37]
18	0.4[22]	0.45[22]			

<sup>a</sup>No critical micelle concentration was detected

<sup>b</sup>mmol/kg

## 2 Aggregation of Ionic Liquids in Aqueous Solutions

### 2.1 Formation of Ionic Liquids Aggregates

Many research publications suggest that ILs form aggregates in aqueous solutions. It should be noted that different terminologies have been used in the literature for the aggregate/micelle formation of ionic liquids. The reason may lie in the fact that, sometimes, aggregates of ionic liquids could be formed, but the attractive interaction between the alkyl chains was not strong enough to form micelles, especially for ILs with shorter alkyl chains. Therefore, the terms “aggregate” and “critical aggregation concentration (CAC)” have been frequently used in this book.

A significant amount of research has been published on the determination of CAC of ILs in aqueous solution. The data available in the literature [16–39] are collected in Tables 1 and 2. It can be seen that the results from different laboratories are not always consistent. The main reason is that a large variety of experimental techniques, including conductivity, surface tension, molar volume, fluorescence quenching, small angle neutron scattering, isothermal titration calorimetry (ITC), nuclear magnetic resonance (NMR), sound speed, turbidity, etc., has been used to determine the CAC values. However, not all methodologies have been carried out with the same care and rigor, and therefore some uncertainties exist in the results of a number of ILs.

Aggregation behavior of 1-butyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_4\text{mim}][\text{BF}_4]$ ) and 1-methyl-3-octylimidazolium chloride and iodide ( $[\text{C}_8\text{mim}]\text{Cl}$  and  $[\text{C}_8\text{mim}]\text{I}$ ) in aqueous solution has been investigated by Bowers et al. with surface tension, conductivity, and small angle neutron scattering (SANS) measurements [16]. The results showed that these ILs act as short chain cationic surfactants in aqueous solution and form aggregates above their CAC values. The conductivity data for  $[\text{C}_8\text{mim}]\text{Cl}$  and  $[\text{C}_8\text{mim}]\text{I}$  indicated the possible presence of aggregates at concentrations below the CACs. From analysis of the SANS data, the  $[\text{C}_4\text{mim}][\text{BF}_4]$  system was found to be best modeled as a dispersion of polydisperse spherical aggregates, whereas  $[\text{C}_8\text{mim}]\text{I}$  can be modeled as a system of regularly sized near-spherical charged micelles at concentrations above their critical aggregation concentration. A solution of  $[\text{C}_8\text{mim}]\text{Cl}$  displays weak long-range ordering of possibly disklike particles, culminating in the formation of structures with distinct long-range order at higher concentrations.

Miskolczy et al. [17] investigated the aggregation of 1-butyl-3-methylimidazolium octyl-sulfate ( $[\text{C}_4\text{mim}][\text{OctSO}_4]$ ) and  $[\text{C}_8\text{mim}]\text{Cl}$  in aqueous solutions by conductivity, turbidity, and 2-hydroxy-substituted Nile Red solvatochromic probe measurements.  $[\text{C}_4\text{mim}][\text{OctSO}_4]$  was found to form micelles above 0.031 M which were within one's expectation, because a long-chained anion such as the octyl-sulfate has previously been shown to form micelles in its own right. On the other hand,  $[\text{C}_8\text{mim}]\text{Cl}$  produced inhomogeneous solution of larger aggregates. As a continuation of research, these authors investigated the association of 1-alkyl-3-methyl-imidazolium bromide ( $[\text{C}_n\text{mim}]\text{Br}$ ) ionic liquids in aqueous solution at

**Table 2** Comparison of critical aggregate concentration (mM) of ionic liquids determined by various methods at 298 K

IL	Surface tension	Conductivity	Fluorescence	Other method
[C <sub>4</sub> mim][BF <sub>4</sub> ]	800[16]	820[16] 729[39]	960[31] <sup>a</sup>	800 (SANS) [16] 710 (volume) [31] <sup>a</sup> 705 (speed of sound) [39]
[C <sub>4</sub> mim][OctSO <sub>4</sub> ]	40.5[16]	31[17]	31[17]	
[C <sub>8</sub> mim]I	100[16]	150[16]		
[C <sub>8</sub> mim][BF <sub>4</sub> ]		28[39]		25 (speed of sound) [39]
[C <sub>10</sub> mim][NTf <sub>2</sub> ]	N[19]	N[22]		
[C <sub>10</sub> mim][PF <sub>6</sub> ]		N[19]		
[C <sub>12</sub> mim][BF <sub>4</sub> ]	9.2[29]	7.6[29]		
[C <sub>16</sub> mim][BF <sub>4</sub> ]	1.37[25] <sup>b</sup>			

<sup>a</sup>mmol/kg<sup>b</sup>At 313 K

298 K by conductivity measurements [18]. A similar study was conducted by Sirieix-Plénet and coworkers [27]. They examined the properties of mixtures of 1-decyl-3-methylimidazolium bromide ([C<sub>10</sub>mim]Br) with water by conductimetry and electromotive forces (EMF) measurements with bromide- or cationic surfactant-selective electrodes. It was shown that, at low concentrations, this ionic liquid behaves like a classical cationic amphiphile. As the concentration of [C<sub>10</sub>mim]Br increased above the CAC, the association between the cationic aggregate and its counterion was enhanced.

Interfacial tension, fluorescence, and <sup>1</sup>H NMR measurements were used by Blesic et al. [19] to monitor the aggregation behavior of ionic liquids with 1-alkyl-3-methyl-imidazolium cations [C<sub>n</sub>mim]<sup>+</sup> (*n* = 2–14) and different counterions, Cl<sup>−</sup>, [PF<sub>6</sub>]<sup>−</sup> and bis(trifluoromethylsulfonyl)imide anion ([NTf<sub>2</sub>]<sup>−</sup>) in aqueous solutions. It was found that [C<sub>6</sub>mim]Cl showed no noticeable aggregation in water, and aggregates formation was detected for the ILs possessing at least eight carbon atoms in an imidazolium cation with Cl anion. When the Cl<sup>−</sup> anion in [C<sub>10</sub>mim]Cl was replaced by [NTf<sub>2</sub>]<sup>−</sup> or [PF<sub>6</sub>]<sup>−</sup>, no micelle formation was observed, because the low solubility of these ILs induced phase separation before their bulk aggregation.

Goodchild et al. [26] used conductivity, surface tension, and SANS to investigate the surface, phase, and aggregation behavior of 1-alkyl-3-methyl-imidazolium bromides in water. Aggregation for the ILs with alkyl chain length greater than six carbon atoms was observed, and their CACs were reported.

An investigation on the aggregation of [C<sub>4</sub>mim][PF<sub>6</sub>], [C<sub>10</sub>mim]Cl, [C<sub>12</sub>mim]Cl and 1-butyl-3-methylimidazolium methylsulfate; [C<sub>4</sub>mim][CH<sub>3</sub>SO<sub>4</sub>] in aqueous solutions was completed by Modaressi et al. [23]. The methods used were electrical conductivity, density, and surface tension. The authors found that the ILs with a butyl chain do not favor an aggregate self-assembly.

Inoue et al. [30] used conductivity technology to study the aggregation behavior of long-chain imidazolium ionic liquids of 1-alkyl-3-methylimidazolium bromides

**Table 3** Aggregation numbers ( $N_{\text{agg}}$ ) of  $[\text{C}_n\text{mim}]\text{Br}$  in aqueous solutions at 298 K

$n_c$	$N_{\text{agg}}$	Method	$\text{C}_n\text{TAB}$
8	22[26]	SANS	
	53[31]	Fluorescence quenching	
	22[31]	Molecular geometry	
	25[32]	NMR	
9	45[18]	Fluorescence quenching	
10	40[26]	SANS	
	42[18]	Fluorescence quenching	
	40[24]	Fluorescence quenching	
	48[24]	Molecular geometry	
	35[31]	Fluorescence quenching	
	33[31]	Molecular geometry	
	27[32]	NMR	
12	44[18]	Fluorescence quenching	55[33]
	43[30]	Electrical conductivity	
	58[24]	Fluorescence quenching	
	67[24]	Molecular geometry	
	44[31]	Fluorescence quenching	
	49[31]	Molecular geometry	
	46[32]	NMR	
14	59[18]	Fluorescence quenching	70[33]
	61[30]	Electrical conductivity	
	79[24]	Fluorescence quenching	
	89[24]	Molecular geometry	
16	66[18]	Fluorescence quenching	89[33]
	76[30]	Electrical conductivity	
	99[24]	Fluorescence quenching	
	114[24]	Molecular geometry	

**Table 4** Aggregation numbers ( $N_{\text{agg}}$ ) of  $[\text{C}_n\text{mim}]\text{Cl}$  in aqueous solutions at 298 K

$n_c$	$N_{\text{agg}}$	Method	$\text{C}_n\text{TAB}$
8			
9			
10	23[36]	Electrical conductivity	
12	37[36]	Electrical conductivity	55[33]
14	46[36]	Electrical conductivity	70[33]
16			89[33]

with  $\text{C}_{12}$ – $\text{C}_{16}$  alkyl chains in water. Based on the mixed electrolyte model of micellar solution, the aggregation number and the degree of counterion binding,  $\beta$ , were estimated. The results clearly demonstrate that the general behavior of aggregation of long-chain imidazolium ILs is analogous to the case of traditional surfactants. However, the CAC values of these ILs are lower by about 30 % compared to those of the typical cationic surfactants  $\text{C}_n\text{TAB}$  with the same hydrocarbon chain, and their aggregation number (Tables 3 and 4) is 10–15 times smaller



than those of the  $C_n$ TAB surfactants. This may be attributed to the difference in the head group size.

Jungnickel et al. [22] reported a study on the aggregates formation of a homologous series of 1-alkyl-3-methylimidazolium derivatives with alkyl chain lengths  $n = 4-18$ . The CACs of these ILs were reproducibly determined by conductivity and surface tension. From these data, the degree of ionization and the standard Gibbs energy of aggregation were calculated as a function of alkyl chain length of the imidazolium cations. A significant correlation between retention times in reversed phase gradient high performance liquid chromatography (HPLC) and the CACs of the ILs was observed. It was also shown that the CACs were directly related to the lipophilicity of cations of the ionic liquids.

Wang et al. [31, 32] studied the aggregation behavior of  $[C_n\text{mim}]\text{Br}$  ( $n = 4, 6, 8, 10, 12$ ) and  $[C_4\text{mim}][\text{BF}_4]$  in aqueous solutions by conductivity, volume, fluorescence probe, and NMR technologies. The critical aggregation concentrations of the ionic liquids, the ionization degree of the aggregates, and the standard Gibbs energy of aggregation were obtained. It was shown that no aggregation occurs for  $[C_4\text{mim}]\text{Br}$  in aqueous solutions,  $[C_6\text{mim}]\text{Br}$  and  $[C_4\text{mim}][\text{BF}_4]$  form weak aggregates above the critical aggregation concentration, while the aggregation of  $[C_8\text{mim}]\text{Br}$ ,  $[C_{10}\text{mim}]\text{Br}$ , and  $[C_{12}\text{mim}]\text{Br}$  is strong enough to form micelles above their CACs. The alkyl chain length of a cation can then be tailored to switch the aggregation behavior of ILs in aqueous solutions.

The adsorption and aggregation behavior of a chiral long-chain ionic liquid, *S*-3-hexadecyl-1-(1-hydroxy-propan-2-yl)-imidazolium bromide ( $[C_{16}\text{hpim}]\text{Br}$ ) in aqueous solution were described by Li et al. [34]. The CAC value obtained for this IL is similar to 1-cetyl-3-methylimidazolium bromide ( $[C_{16}\text{mim}]\text{Br}$ ), but lower than the conventional ionic surfactants, demonstrating that long-chain imidazolium ILs have superior capability for the formation of aggregates. The maximum surface excess concentration of  $[C_{16}\text{hpim}]\text{Br}$  is lower than  $[C_{16}\text{mim}]\text{Br}$  due to the larger head group size of  $[C_{16}\text{hpim}]\text{Br}$ . This relatively large headgroup size of  $[C_{16}\text{hpim}]\text{Br}$  and higher electrostatic repulsion between these headgroups also result in a looser packing of the resulting aggregates. Thus, a higher micropolarity and smaller aggregation number are observed compared with the conventional cationic surfactants with the same length of hydrophobic chain.

Zhang et al. [35] reported the results on the aggregation of 1-alkyl-3-methylimidazolium-based ionic liquids ( $[C_n\text{mim}]\text{Br}$ ,  $n = 8, 10, 12$ , and 16) in aqueous solutions using UV spectrum, electrical conductivity, and resonance light scattering. This investigation reveals the aggregation differences between the surface active  $[C_n\text{mim}]\text{Br}$  and the traditional surfactants. Hydrogen bonds were suggested to play a dominant role in the aggregation of ILs in addition to coulombic and hydrophobic interactions. Compared with the traditional cationic surfactants, these ILs display a stronger aggregation due to the formation of the hydrogen bonded network. Such hydrogen bonded network also results in the loose arrangements of imidazolium rings in the subaggregates of  $[C_n\text{mim}]\text{Br}$  ( $n < 10$ ).

Eighteen mono- and di-cationic imidazolium bromide ILs were investigated by Baltazar et al. [28]. Surface tension measurements were used to determine the CAC

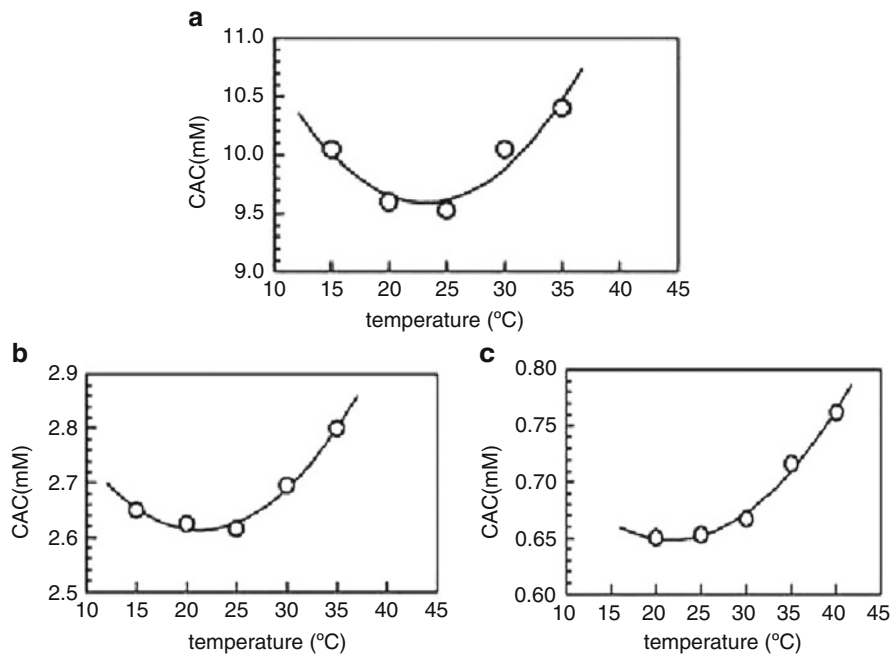
values of these ILs, and a correlation between the substituted alkyl chain length and the CAC values was reported. A comparison of the mono-cationic and di-cationic imidazolium ILs indicates that the mono-cationic imidazolium ILs generally have higher CACs than the di-cationic imidazolium ILs. The CAC values for different classes of di-cationic ionic liquids were found to decrease with increasing length of the linkage chain connecting the two imidazolium rings, and also to depend on the nature of the free alkyl side chain.

### 3 Thermodynamics of Aggregates Formation

Thermodynamic analysis on the aggregation behavior of ILs by using Gibbs energy, enthalpy and entropy of aggregate formation, is important for a deeper understanding of the driving forces and some molecular details involved in the aggregation processes [36]. The effect of the structure of ILs, in particular the alkyl chain length of the cations, can be reflected by thermodynamic parameters. Often these thermodynamic properties can be derived from measurements of the variation of the critical aggregation concentration of ILs with temperature by applying the mixed electrolyte model and phase separation model reported in the literatures [30, 40].

Using electrical conductivity methods [30, 40], CAC values of imidazolium ILs with alkyl chains length  $n = C_{12}-C_{16}$  in aqueous solutions were determined at different temperatures. It is known that, for aqueous solutions of conventional ionic surfactant, the critical micelle concentration first decreases to a certain point and then increases with increasing temperature, which creates a U-shape dependence with a minimum temperature ( $T_{\min}$ ) close to room temperature [41–44]. It can be seen from Fig. 2 that the curves of CACs vs temperature for ionic liquids have a similar shape. The effect of temperature on the CACs of surfactants in aqueous solution is usually a result of two opposing factors. It may be assumed that similar behavior could be observed in the case of aqueous IL solutions. First, when the temperature increases, the degree of hydration of the ionic imidazolium head domain decreases, leading to the increase of hydrophobicity of cations of the ionic liquids. This favors the aggregation process, and aggregation can take place at a lower concentration. On the other hand, with the increase of temperature, the structured water around the hydrophobic domain would be partially broken. This is unfavorable to the aggregation, as the low entropy of the structured water is a key driving force for the self-association process [45, 46]. Thus it is possible for us to assume that at lower temperatures the first effect is predominant, and after passing  $T_{\min}$  the second effect becomes evident. Values of  $T_{\min}$  depend on the hydrophobicity of the alkyl chain and the counterions. More hydrophobic amphiphiles have lower  $T_{\min}$  values [47].

The mixed electrolyte model [30] and phase separation model [40] have been used to estimate the thermodynamic parameters for the formation of ILs aggregates.



**Fig. 2** Plots of CAC against temperature for the ILs: (a) [C<sub>12</sub>mim]Br; (b) [C<sub>14</sub>mim]Br; (c) [C<sub>16</sub>mim]Br (Reprinted from [30])

The standard Gibbs energy of aggregation ( $\Delta G_m^0$ ) can be calculated from the following equation:

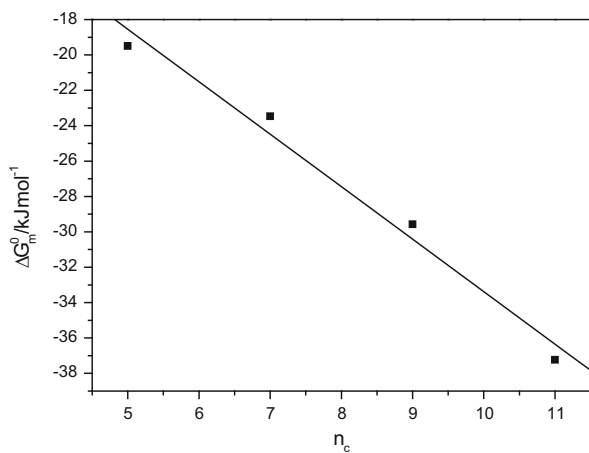
$$\Delta G_m^0 = (2 - \alpha)RT \ln \chi_{CAC} \quad (1)$$

where  $\chi_{CAC}$  is the critical aggregation concentration expressed in mole fraction scale and  $\alpha$  is the ionization degree of the aggregates. The standard enthalpy of aggregation ( $\Delta H_m^0$ ) can be derived from the  $\Delta G_m^0$  values as a function of temperature by applying the Gibbs–Helmholtz equation:

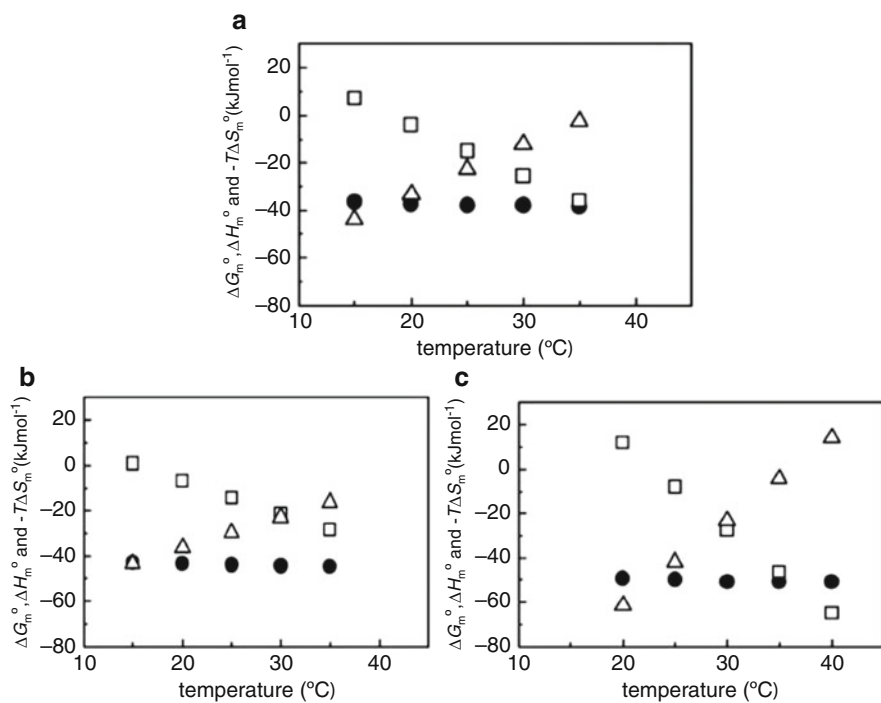
$$\Delta H_m^0 = \left[ \frac{\partial(\Delta G_m^0/T)}{\partial(1/T)} \right] \quad (2)$$

and the standard entropy of aggregation  $\Delta S_m^0$  can be obtained from

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \quad (3)$$



**Fig. 3** Linear plot between  $\Delta G_m^0$  of  $[\text{C}_n\text{mim}]\text{Br}$  at 298.15 K and the number of carbons in the alkyl chains (Reprinted from [31])



**Fig. 4** Variation of the thermodynamic parameters for the micelle formation of ILs with temperature: (a)  $[\text{C}_{12}\text{mim}]\text{Br}$ ; (b)  $[\text{C}_{14}\text{mim}]\text{Br}$ ; (c)  $[\text{C}_{16}\text{mim}]\text{Br}$ . Symbols: circles  $\Delta G_m^0$ , squares  $\Delta H_m^0$ , triangles  $T\Delta S_m^0$  (Reprinted from [30])

Figure 3 shows the standard Gibbs energy of aggregation of imidazolium ILs at 298.15 K as a function of the alkyl chain length of cations. This figure provides the following information: (1) the Gibbs energy change was found to be negative, implying as expected that aggregation of ionic liquids occurs spontaneously once the CAC is reached; (2) the longer the alkyl chain of ILs, the more negative the standard Gibbs energy of aggregation, indicating that the aggregation comes more easily with the increase of the alkyl chain length of ILs; (3) the aggregation is driven by alkyl chain-ion inductive and hydrocarbon-hydrocarbon interactions [31].

Figure 4 shows the thermodynamic parameters thus obtained for aggregate formation of long-chain imidazolium ILs as a function of temperature. As can be seen, first,  $\Delta H_m^0$  decreases with the increase in temperature, and then it changes its sign from positive to negative at 20–25°C. This means that the aggregate formation process is endothermic at lower temperature and exothermic at higher temperature, and this is the origin of the appearance of a minimum in CAC at 20–25°C. Second,  $-T\Delta S_m^0$  increases with the increase in temperature, and intersects with  $\Delta H_m^0$  at 25–30°C. This indicates that the entropy term ( $-T\Delta S_m^0$ ) plays a dominant role in negative  $\Delta G_m^0$  below the crossing temperature, while the contribution from an enthalpy term becomes dominant above this temperature. In other words, the process for aggregate formation of long-chain imidazolium ILs is driven by entropy at lower temperature, while driven by enthalpy at higher temperature.

Zhao et al. [48] also investigated the aggregation behavior of the ionic liquid *N*-alkyl-*N*-methylpyrrolidinium bromide ( $C_n$ MPB,  $n = 12, 14$  and  $16$ ) in aqueous solutions by surface tension, electrical conductivity, and static luminescence quenching measurements. The critical aggregation concentrations at different temperatures and a series of thermodynamic parameters ( $\Delta G_m^0$ ,  $\Delta H_m^0$ , and  $\Delta S_m^0$ ) for the ILs aggregation were evaluated from electrical conductivity measurements in the temperature range 25–45°C. Their thermodynamic parameters also show that the aggregate formation is an entropy-driven process at low temperature and an enthalpy-driven process at high temperature.

Because the enthalpy and entropy parameters have been derived indirectly from measurements of the variation of the critical aggregation concentration with temperature, these parameters have an intrinsic large uncertainty. Nowadays, more and more studies show that calorimetry is the most sensitive technique for the direct and precise measurements of the thermodynamic properties involving ILs aggregation [36, 37].

The thermodynamic parameters for the aggregation of  $[C_n\text{mim}]\text{Cl}$  ( $n = 8, 10, 12$ , and  $14$ ) in aqueous solution have been reported by Bai et al. [36] using isothermal titration calorimetry and conductivity. It was shown that the increase in alkyl chain length of the ILs causes a decrease in all thermodynamic parameters,  $\Delta G_m^0$ ,  $\Delta H_m^0$ , and  $T\Delta S_m^0$ . The large negative values of the Gibbs energy are primarily due to an entropic contribution, an effect common in aggregation processes driven by hydrophobicity. Nevertheless, the percentage of the Gibbs energy change that is due to the enthalpic term increases with increasing alkyl chain length. Further it was

found that the aggregation process was mainly driven by entropy, as is common in aggregation processes induced by hydrophobicity.

Geng et al. [37] also used isothermal titration microcalorimetry and surface tension measurements to study the aggregation of three long-chain imidazolium ionic liquids, [C<sub>12</sub>mim]Br, [C<sub>14</sub>mim]Br, and [C<sub>16</sub>mim]Br, in aqueous solutions. It was found that the process of aggregation is also driven by entropy. An enthalpy–entropy compensation study reveals the effect of alkyl chain length on the aggregation: the longer the alkyl chain, the easier it is to form aggregates. Their results showed that [C<sub>14</sub>mim]Br and [C<sub>16</sub>mim]Br act as ideal surfactants in the aggregation process because there are no aggregate–aggregate interactions, whereas [C<sub>12</sub>mim]Br does not behave ideally because of aggregate–aggregate interactions in the high concentration solutions.

### 3.1 Effect of Cationic Structure on the Aggregation of Ionic Liquids

With the possibility of fine-tuning hydrophobicity of ILs by changing the alkyl chain length, the type of headgroup, and the nature of the anions, one can modulate the structure of these aggregates. This leads to the modification of some major characteristics such as the critical aggregate concentration, the average aggregation number ( $N_{\text{agg}}$ ), and the physicochemical properties in the aggregation processes of ionic liquids. Therefore, a number of research projects have been focused on the effect of cationic structure on the self-aggregation of ILs in aqueous solutions.

For a homologous series of linear single-chain amphiphiles, the CACs follow the empirical Stauff-Klevens rule [49], which suggests a logarithmic relationship between CAC and the number of carbon atoms in the alkyl chain as shown in the following equation:

$$\log(\text{CAC}) = A - Bn_c \quad (4)$$

where  $A$  and  $B$  are constants for a given homologous series at a given temperature, and  $n_c$  is the number of carbon atoms in the alkyl chain. The constant  $A$  changes with the nature of the hydrophilic groups, while  $B$  is a constant which measures the effect of each additional methylene group on the CAC. It can be seen from Table 5 that the  $B$  value is approximately 0.5, 0.28–0.30, and 0.25 for nonionic amphiphiles, paraffin chain salts with a single ionic head group, and divalent ionic surfactants, respectively [50]. For different homologues, the  $A$  values are considerably variable, whereas  $B$  is close to  $\log 2$ , which indicates that addition of each  $-\text{CH}_2$  group to a hydrocarbon chain reduces the CAC of these compounds by about a factor of 2. Based on this rule, the CAC values can be estimated for surfactants with various chain lengths [51].

**Table 5** Values of *A* and *B* from Stauff-Klevens equation for various surfactants and ILs

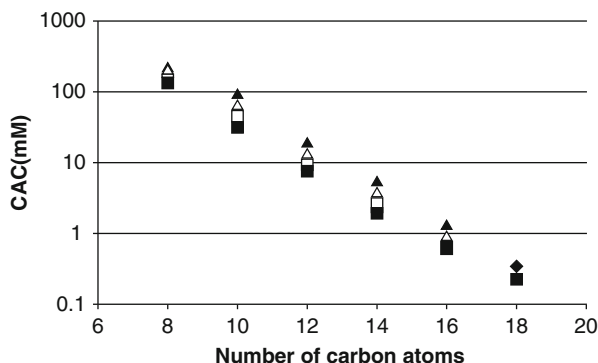
Compound	T/K	<i>A</i>	<i>B</i>
Typical surfactant [49]			
Na carboxylates	293	2.41	0.341
K carboxylates	298	1.92	0.290
K carboxylates	318	2.03	0.292
Alkane sulfonates	313	1.59	0.294
Alkane sulfonates	323	1.63	0.294
Alkyl sulfates	318	1.42	0.295
Alkylammonium chlorides	298	1.25	0.265
Alkylammonium chlorides	318	1.79	0.296
Alkyltrioxyethylene glycol monoether	298	2.32	0.554
Alkydimethylamine oxide	300	3.3	0.5
Alkyltrimethylammonium bromides	333	1.77	0.292
Ionic liquid			
Alkyl-methyl-imidazolium bromides [28]	298	0.29	4.29
Alkyl-methyl-imidazolium bromides [18]	298	0.30	4.6
Alkyl-methyl-imidazolium bromides [31]	298	0.325	1.845
Alkyl-methyl-imidazolium bromides [46]	298	0.32	1.78
Alkyl-methyl-imidazolium chlorides [19]	298	0.29	4.7
Alkyl-methyl-imidazolium chlorides [22]	298	0.28	4.51
Alkyl-butyl-imidazolium bromides[28]	298	0.34	4.41
Alkyl-bis-butyl-imidazolium bromides [28]	298	0.16	3.77
<i>N</i> -alkyl- <i>N</i> -Methylpyrrolidinium bromides [28]	298	0.30	4.72
1-alkylpyridinium bromides [46]	298	0.31	1.71

It is known that CAC values of single alkyl chain amphiphiles decrease with addition of  $-\text{CH}_2$  groups to the alkyl chain, resulting from elongation of the hydrophobic part of the surfactant molecules, which favors aggregate formation. The CAC is also dependent on the relative sizes of their hydrophilic and hydrophobic domains. A larger hydrophobic domain would result in a lower CAC, and a more hydrophilic domain area would result in a higher CAC [50].

As far as ILs are concerned, the results indicate that elongation of the alkyl chain decreases the CAC values of ILs as shown in Table 1. This implies that an increase of hydrophobic alkyl chain of the cations favors the formation of ionic liquid aggregates as has been shown above for surfactants. For homologous series of ILs, the linear relationship described by Eq. 4 has been proved to be valid. The *B* value is comparable to that established for ionic surfactants, such as alkylpyridinium bromides, alkyltrimethylammonium chlorides, alkylpyridinium chlorides, and alkyltrimethylammonium bromides.

The introduction of the second alkyl substituent on the imidazolium cations may also play a dominant role in CAC values of ionic liquids. For example, the lower CAC values have been observed for the ILs with butyl substituents instead of methyl in the imidazolium ring [28].

**Fig. 5** CAC dependence on the number of carbon atoms in alkyl chains of some ILs and cationic surfactants at 298 K: (filled diamonds)  $[C_n\text{mim}]\text{Cl}$ ; (open squares)  $[C_n\text{mim}]\text{Br}$ ; (filled triangles)  $C_n\text{TAC}$ ; ( $\Delta$ )  $C_n\text{TAB}$  and (filled squares) SAS (Reprinted from [52])



In order to compare the critical aggregation properties of ILs with some typical cationic surfactants, the CAC values of trimethylammonium chloride ( $C_n\text{TACl}$ ), bromide ( $C_n\text{TAB}$ ), and sodium alkyl sulfate (SAS) were collected. It is shown that the CAC values of  $[C_n\text{mim}]\text{Br}$  ionic liquids lay between those of  $C_n\text{TAB}$  and SAS containing the same number of carbon atoms in the alkyl moiety. An analogical relationship was found for  $[C_n\text{mim}]\text{Cl}$ ,  $C_n\text{TACl}$  and SAS, as shown in Fig. 5. This might be ascribed to the special structure of the imidazolium head group which allows the possible formation of a hydrogen bond with water, but the same is not true for the head group of  $C_n\text{TAB}$ . This may also be the result of interactions between anion and aromatic ring in imidazolium derivatives which did not occur in the case of typical surfactants.

The influence of the type of ring in the cations on the aggregation behavior was also investigated. The underlying reason for this effect is very complex because head groups have two opposing effects: (1) repulsive interaction related with electrostatic repulsion, hydration and steric hindrance and (2) attraction interaction arising from a need to minimize hydrocarbon-water contacts. The stronger hydrophobicity of the cations favors the aggregation of the ILs in aqueous solutions, and the stronger binding strength of the cation with a given anion can decrease the repulsive interaction between the head groups and then the CAC values. In contrast, the bigger steric hindrance of the cations causes an increase in the CAC values of the ILs. For example, Wang et al. [53] reported that the CAC values of 1-octyl-methylimidazolium bromide ( $[C_8\text{mim}]\text{Br}$ ), 1-octyl-4-methylpyridinium bromide (4 m- $[C_8\text{pyr}]\text{Br}$ ), and 1-methyl-1-octylpyrrolidinium ( $[C_8\text{mpyr}]\text{Br}$ ) increase in the order 4 m- $[C_8\text{pyr}]\text{Br} < [C_8\text{mim}]\text{Br} < [C_8\text{mpyr}]\text{Br}$ . This indicates that the ability of the cations to form aggregates follows the order  $[C_8\text{mpyr}]^+ < [C_8\text{mim}]^+ < 4\text{ m-}[C_8\text{pyr}]^+$ . It was reported that there was an increase in hydrophobic tendency for the cations in the order  $[C_n\text{mim}]^+ < [C_n\text{mpyr}]^+ < [C_n\text{mpyr}]^+$  [54]. On the basis of this observation, the CAC values of the investigated ILs should increase in the order  $[C_8\text{mpyr}]\text{Br} < 4\text{ m-}[C_8\text{pyr}]\text{Br} < [C_8\text{mim}]\text{Br}$ . Obviously, the experimental result is not the case. However, the order of van der Waals volumes of the cations was found to be  $[C_4\text{mpyr}]^+ (167 \text{ \AA}^3) > [C_4\text{mim}]^+ (150 \text{ \AA}^3) > [C_4\text{pyr}]^+ (144 \text{ \AA}^3)$  [55], and the qualitative order of  $[C_4\text{mim}]^+ > [C_4\text{pyr}]^+ > [C_4\text{mpyr}]^+$  has



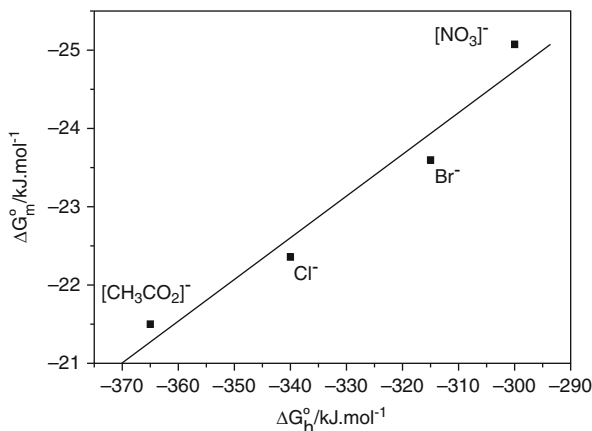
been observed for the intrinsic binding strength of the cations with  $\text{Br}^-$  [56]. From this information it seems likely that the aggregation is controlled mainly by the balance among the factors of hydrophobicity of the cations, binding strength of the cations with a given anion, and the steric repulsion between the cations. The aggregates of  $[\text{C}_8\text{mpyrr}]\text{Br}$  were formed unfavorably due to probably its biggest van der Waals volume, that is, the biggest steric hindrance and the weakest interaction with  $\text{Br}^-$ . On the other hand, it is clear that the difference in steric hindrance between  $[\text{C}_8\text{mim}]^+$  and 4 m- $[\text{C}_8\text{pyr}]^+$  is small. Therefore, compared with  $[\text{C}_8\text{mim}]^+$ , the stronger aggregation of 4 m- $[\text{C}_8\text{pyr}]^+$  is driven by its stronger hydrophobicity.

Blesic et al. [57] found that 1-dodecyl-3-methylpyridinium bromide ( $[\text{C}_{12}\text{mpy}]\text{Br}$ ) and 1-methyl-1-dodecylpiperidinium bromide ( $[\text{C}_{12}\text{mpip}]\text{Br}$ ) have almost the same CAC values in water. Probably, in the case of  $[\text{C}_{12}\text{mpip}]\text{Br}$ , the two effects compensate each other. On the one hand, the higher hydrophobicity of the  $[\text{C}_{12}\text{mpip}]^+$  cation and stronger bound anion,  $\text{Br}^-$ , in comparison with the  $[\text{C}_{12}\text{mpy}]^+$  cation, where the positive charge is delocalized, would give a lower CAC. On the other hand, because these two cations have a different geometry and volume, we can expect that, compared with the boat and/or chair structures of a cyclic six-membered ring of a planar aromatic molecule, the more space-demanding  $[\text{C}_{12}\text{mpip}]^+$  cation has a higher CAC because of the steric hindrance effect.

In the case of gemini ILs, the CAC values depend on the length of the alkyl linkage chain connecting the two cations, and on the length of the free alkyl substituents on three positions of the imidazolium head group. Increasing the lengths of the linking chains results in a linear decrease of the CACs. Analogically elongation of the free alkyl chain causes the same effect [28]. The partitioning behavior of such gemini IL aggregates in water is comparable to mono cationic aggregates, and it has been found that the size of the alkyl chain influences the partitioning of nonpolar solvents inside the aggregates. However, gemini ILs were found to have a lower portioning to nonpolar solvents. It was theorized that the gemini IL aggregates, even though they have a lower CAC, form less well defined aggregates [58].

The degree of ionization ( $\alpha$ ) is also an important characteristic parameter for ILs aggregation in water. The degree of ionization is the fraction of charges of amphiphile ions in the aggregates neutralized by aggregate-bound counterions. Monomer amphiphiles are entirely dissociated in solution, but in their aggregates they are partially associated with the counterions. The degree of ionization of the aggregate was calculated from the ratio of the slopes of the two linear fragments of the experimental conductivity curves [59]. A lower  $\alpha$  value indicates a better packed aggregate. Usually, slightly decreased  $\alpha$  values are observed for conventional ionic surfactants with elongation of the alkyl chain. A similar trend is also found for ILs [28].

**Fig. 6** Linear plot of the standard Gibbs energy of aggregation of the ILs ( $\Delta G_m^0$ ) vs the Gibbs energy of hydration of the anions ( $\Delta G_h^0$ ) (Reprinted from [53])



### 3.2 Effect of Anionic Type on the Aggregation of Ionic Liquids

For the ionic liquids of imidazolium salts, the nature of their anions determines the water solubility of ionic liquids and cation–anion interactions. Consequently, the aggregation of ILs in water is also affected by the nature of ILs anions. The role of anions in the aggregation of imidazolium ILs in water has been systemically studied by us [53]. It is found that, for a given  $[\text{C}_8\text{mim}]^+$  cation, there is a pronounced effect of the anions on the values of CAC and  $\alpha$  of the ILs. These values increase in the sequence:  $[\text{CF}_3\text{COO}]^- < [\text{NO}_3]^- < \text{Br}^- < \text{Cl}^- < [\text{CH}_3\text{COO}]^-$ . In other words, the ability of these anions to promote aggregation of the ILs follows the order  $[\text{CF}_3\text{COO}]^- > [\text{NO}_3]^- > \text{Br}^- > \text{Cl}^- > [\text{CH}_3\text{COO}]^-$ . This anionic effect correlates well with the Hofmeister series of the anions for cationic surfactants [60]. In general, the formation of IL aggregates in water is dictated by a balance between the repulsive headgroup interactions and the attractive forces arising from a need to minimize the exposure of the hydrophobic core to water. The anions act by altering both of these forces. Adsorption of the anions onto the surface of aggregates can reduce the repulsive headgroup interactions, thereby lowering the CAC values of the ILs. So the position of an anion in this series is considered to depend on its hydrated radius/polarizability, hydrophobicity, and bulkiness of the anions. A decreased hydration radius of the anions is usually accompanied by an increased polarizability. A high polarizability should enhance the binding of the anions at the aggregates surface and decrease the electrostatic repulsion between the head groups of the ILs, thus increasing the tendency towards aggregation and lowering both values of  $\alpha$  and CAC. However, no formation of the aggregates was detected for the ILs with  $[\text{CF}_3\text{SO}_3]^-$  and  $[\text{ClO}_4]^-$  as anions, because the systems broken down into two phases before any bulk aggregation occurred. This ascribed to the much weaker hydration of the anions and then low solubility of the ILs in aqueous solutions. Rebelo et al. [19] also found that, when the  $\text{Cl}^-$  anion in

[C<sub>10</sub>mim]Cl was replaced by [NTf<sub>2</sub>]<sup>−</sup> or [PF<sub>6</sub>]<sup>−</sup> anion, no micelle formation was detected because the low water solubility of these ILs induced phase separation before their bulk aggregation.

The anions also markedly affect the standard Gibbs energy of aggregation of ILs, and the effect follows the Hofmeister series. The ILs with the larger anions show the stronger effect, while those with smaller hydrophilic anions, which have higher values of hydration Gibbs energy, are only weakly incorporated in the aggregation phases. It can be seen from Fig. 6 that the  $\Delta G_m^0$  values correlate reasonably well with Gibbs energies of hydration of the anions [61], indicating that the Hofmeister series is strongly related to the nature of the hydration shell of the anions. Interaction of anions with cationic moiety of the headgroup of these ILs is stronger for readily dehydrated ions than for those with tight hydration shells. The decreased values of  $\Delta G_m^0$  indicate that the aggregation becomes much easier with increasing hydrophobicities of the anions. One possible explanation is that the increased hydrophobicity enhanced anionic penetration of the interface and the electrostatic interactions with the ILs headgroup accordingly decreased the repulsive headgroup interactions. These results are similar to those reported by Bunton et al. [62] for the interactions between cetyltrialkylammonium bromides and methyl naphthalene 2-sulfonate.

Aggregation number is a major parameter for the structure of IL aggregates. It was found that the average aggregation number generally increases with increasing hydrophobicity of the anions, indicating that the growth of aggregates is favored by the increased hydrophobicity. This result was similar to the counterionic effect of some typical surfactants [63]. Thus, it is appropriate to conclude that the anions with stronger hydrophobicity can bind the cations more strongly and reduce the repulsive interaction between head groups, and thus enhance the growth of the aggregates.

### 3.3 Effect of Added Salts on the Aggregation of Ionic Liquids

Aggregation behavior of ILs could be easily modulated by the addition of inorganic salts. It is well known that for typical ionic surfactants, the addition of an electrolyte reduces the repulsion between charged groups at the surface of the micelle by the screening effect. This phenomenon can be observed in the case of the CAC lowering. For ionic compounds this effect is more significant than for nonionic ones because the interaction is stronger in the case of the former. Presence of salts usually influences water structure and then hydration of the head groups, leading to salting-in and salting-out effects. When the monomers are salted-out by an electrolyte, the CAC would be reduced, and if the monomers are salted-in, the reverse takes place [60, 64]. For nonionic surfactants, the influence of salts is weaker but nevertheless significant.

The effect of salts on the formation of IL aggregates depends on the nature of anions and cations of the salts and the ionic liquids. For example, the addition of

NaCl, Na<sub>2</sub>SO<sub>4</sub>, and tetrabutylammonium bromide to aqueous IL solutions was investigated by Blesic et al. [19]. All these electrolytes diminish the CACs of the ILs; moreover, addition of the short chain IL of [C<sub>2</sub>mim]Cl into aqueous solution of the long-chain IL of [C<sub>10</sub>mim]Cl also causes the same effect. In this case, the short chain IL behaves as a simple electrolyte throughout the interaction with Stern layer of the micelle, and screens the ionic charge of that surface [19]. Zheng et al. [29, 65] studied the effect of sodium halides (NaCl, NaBr, and NaI) on the aggregation behavior of [C<sub>n</sub>mim]Br ( $n = 10, 12, 16$ ) in water. It was found that the addition of salts significantly decreases the CACs of the ILs, and the anion dependence of the salt effect is analogous to the case of conventional ionic surfactants:  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ . It is known that the hydration of these anions decreases in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ , suggesting that the anion being less hydrated is more effective in neutralizing the charges on the micelle surface. The influence of NaCl and Na<sub>2</sub>SO<sub>4</sub> on the surface chemical and aggregation characteristics of ionic liquids [C<sub>8</sub>mim]Cl, [C<sub>8</sub>mim]Br, and [C<sub>8</sub>mim]I in water was monitored through surface tension and small angle neutron scattering measurements [66]. It was shown that the addition of salts also drastically decreased the CAC values and increased the area per adsorbed IL molecule. The co-ions of salts modify the surface of ILs and prefer to form aggregates through various interactions such as charge neutralization, specific interactions, and dehydration.

In recent work we systematically investigated the influence of 15 kinds of salts on the aggregation behavior of [C<sub>10</sub>mim]Br in aqueous solutions by conductivity, fluorescence, and dynamic light scattering [67]. It was shown that NaCl, NaBr, NaI, CH<sub>3</sub>CO<sub>2</sub>Na, NaSCN, NaNO<sub>3</sub>, NaBrO<sub>3</sub>, NaClO<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>COONa, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>, and Na<sub>3</sub>CH<sub>5</sub>O<sub>7</sub> have salting-out effects on the aggregation of [C<sub>10</sub>mim]Br and, at a given salt concentration, the effect of anions of the added salts on the CAC value of the IL increases in the sequence  $\text{SCN}^- < \text{I}^- < \text{C}_6\text{H}_5\text{COO}^- < \text{ClO}_3^- < \text{NO}_3^-$ ,  $\text{C}_4\text{H}_4\text{O}_6^{2-} < \text{C}_6\text{H}_5\text{O}_7^{3-} < \text{Br}^- < \text{SO}_4^{2-} < \text{CO}_3^{2-} < \text{Cl}^- < \text{BrO}_3^- < \text{CH}_3\text{COO}^-$ . This specific effect correlates well with the Hofmeister series of the anions, and can be explained by the hydrophobicity of these anions. For a given salt, the logarithm of CAC values of the IL decreases linearly with increasing concentration of the salt, which can be described by the empirical equation of salt effect for the conventional surfactants:

$$\log(\text{CAC}/\text{CAC}_0) = a - km_s \quad (5)$$

where CAC and CAC<sub>0</sub> are the critical aggregation concentrations with and without salt,  $m_s$  is molality of the added salt, and  $a$  and  $k$  are adjusted parameters.

The effect of the added salts on the degree of anions binding at the aggregates surface, the standard Gibbs energy of aggregation, and the aggregation number of [C<sub>10</sub>mim]Br also basically follow the Hofmeister series of the anions. Values in the degree of anion binding and aggregation number of the IL increase with increasing salt concentrations to a different extent for a given salt. It was also found that the size of aggregates increases with increasing hydrophobicity of anions of the salts.

The results suggest that hydrophobicity of the anions plays an important role in the salt effect on the aggregation of  $[C_{10}mim]Br$  in aqueous solutions. The possible reason is that the stronger hydrophobicity of anions enhances their binding on the aggregate surface and decreases the electrostatic repulsion between the ionic head groups of the IL, thus promoting the IL aggregation, increasing the aggregation number, and lowering the CAC value of the ionic liquid.

However,  $FeBr_3$  and  $AlBr_3$  were found to have salting-in effects on the aggregation of  $[C_{10}mim]Br$  in aqueous solutions. The possible reason is that tetrahedral complex  $FeBr_4^-$  (or  $AlBr_4^-$ ) was formed from  $Br^-$  and  $FeBr_3$  (or  $AlBr_3$ ) in aqueous solutions.  $FeBr_4^-$  and  $AlBr_4^-$  anions have larger radius and less charge density compared with  $Br^-$ . They cannot decrease effectively the electrostatic repulsion between the ionic head groups of the IL, but can interact with the hydrophobic moiety of the cation of the IL, thus decreasing the tendency of the IL aggregation and then increasing its CAC.

Based on the binding mechanisms of anions on the aggregates surface of cetyltrimethylammonium bromide (CTAB) [68] and cetyltrimethylammonium chloride (CTAC) [69],  $SCN^-$ ,  $I^-$ ,  $ClO_3^-$ ,  $NO_3^-$ ,  $C_4H_4O_6^{2-}$ ,  $C_6H_5O_7^{3-}$ ,  $Br^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$ ,  $Cl^-$ ,  $BrO_3^-$ , and  $CH_3COO^-$  can be considered to be adsorbed on the surface of the aggregates due to their weak or moderate association with the IL cation, whereas the aromatic anions, like  $C_6H_5COO^-$ , penetrate inside the aggregates with their hydrophilic groups staying in the IL head group region and the hydrophobic groups partially embedded into the hydrophobic core of the aggregates.

### 3.4 *Effect of Organic Additives on the Aggregation of Ionic Liquids*

Studies on the influence of organic solvents on the aggregation behavior of ILs are of great importance, not only in the field of colloid and interface science but also in the development of potential chromatographic applications of IL aggregates. Micellar liquid chromatography (MLC) is a chromatographic technique using surfactants in the mobile phase at concentrations above the CAC [70–72]. Most applications of MLC require the utilization of hybrid micellar mobile phases which contain surfactants at concentrations above the CAC and form ternary systems upon addition of organic solvents [71, 73, 74]. Few traditional surfactant systems have successfully been used in MLC [72, 75]. In this sense, it is important to understand the effect of organic solvents in aqueous solutions on the ILs aggregates when intending to expand the applicability of MLC with these designer surfactants.

It was reported that a few organic compounds can influence the CACs and other properties of micellar solutions. The presence of a small amount of surface active organic impurities may create a characteristic minimum in the area of CAC in the curves of surface tension against concentration. These impurities are usually

present in commercial materials and originate from the synthesis of surfactants. Such minima were also observed in the commercial ILs. The impurities may be adsorbed onto the interface at concentrations below CAC and then solubilized in the aggregates at concentrations above the CAC. Generally, CAC values may be affected by the compounds which can be incorporated in the outer region of the aggregates.

The addition of methanol, 1-propanol, 1-butanol, 1-pentanol, and acetonitrile to the aqueous solutions of ILs 1-hexadecyl-3-butylimidazolium bromide and 1,3-didodecylimidazolium bromide was investigated by Pino et al. [76]. Similar to the traditional ionic surfactants, increases in the CAC values have been observed for both ILs when concentration of the organic solvents increases in aqueous solutions, with the largest increase achieved with 1-pentanol, and being more significant for 1,3-didodecylimidazolium bromide. The authors suggest that when organic solvent content increases in water, the dielectric constant of the mixtures is lowered, producing an increase in the electrostatic forces of the ionic head groups in the ILs micelle. At the same time, the interactions between the hydrophobic groups of the ILs are gradually reduced. Both effects justify the higher CAC values observed as the content of organic solvent increases.

Recently we carried out a systematic study [77] on the influence of ethylene glycol, dimethylsulfoxide, diethylene glycol, triethylene glycol, formamide, acetonitrile, methanol, ethanol, 1-propanol, and acetone on the aggregation behavior of [C<sub>12</sub>mim]Br in water. It was found that the critical aggregation concentration, the ionization degree of the aggregates, and the standard Gibbs energy of aggregation of the ionic liquid increase, while its aggregation number and aggregates size decrease with increasing concentration of organic additives in water. These observations were explained through the solvophobic effect of alkyl chain of the ionic liquid for the water-organic solvents. In a simple physical picture, aqueous organic solvents can better dissolve the alkyl chain of the IL than water, resulting in the decrease of aggregation ability of the IL, thus increasing the CAC values and decreasing the aggregation number and the aggregate size of the ionic liquid. Interestingly, a linear relationship between the logarithm of CAC of the IL and the solvophobic parameter ( $S_p$ ) of hydrocarbon in the studied water-organic mixed solvents is found, and this linear relationship can be described by the equation

$$\log(\text{CAC}) = m + n S_p \quad (6)$$

Therefore, we can modulate the aggregation behavior of ILs by choosing the right  $S_p$  value for a particular application.

### 3.5 *Effect of Surfactant on the Aggregation of Ionic Liquids*

Modification of the surfactant CACs may also be completed by the addition of the second surfactant in the way of synergism, which may result in the desired properties and performance. For example, mixtures of ionic and nonionic surfactants are commonly used in many practical applications because the solution behavior of these surfactants can be complementary. Mixed micelles formed are considered to be more versatile than the micelles formed by single surfactant. Examples of such applications are detergency and enhanced oil recovery. As far as more complex systems are concerned, mixtures of ionic and nonionic surfactants and mixtures of surfactants with different alkyl chain lengths or different head group structures have been examined in some detail [78].

To date only the influence of SDS on the aggregation behavior of imidazolium ILs with variable alkyl chain lengths has been evaluated in aqueous solutions [17, 79]. It was shown that with the increase of SDS concentrations, [C<sub>8</sub>mim]Cl can be dissolved in water. This phenomenon can be linked to the formation of mixed micelles. The results obtained indicate the possibility of using ionic liquids to modify the properties of conventional micelles in a controlled way, which is important in many applications. Ionic liquid cosurfactants may play important roles if micelles themselves cannot provide the desired properties, such as surface tension, viscosity, and dispersion stability [17]. It was also observed that short chain ILs increase the CAC values of SDS probably as a result of hindering ion pair formation, whereas in the case of long-chain ILs, synergism was observed as a decreased CAC [19].

## 4 Self-Aggregation of Ionic Liquids in Nonaqueous Solutions

It is well known that, unlike in aqueous solution, the aggregation behavior of traditional surfactants is very complex in nonaqueous solutions. Surfactants also forms micelles in polar organic solvents and invert micelles in nonpolar organic solvents. Sometimes, dimer, triplet, and micelles simultaneously exist in surfactant solutions. Therefore, studies on the aggregation of surfactant in nonaqueous solutions are limited, and the related aggregation behavior is poorly understood. It was reported that polarity, dielectric constant, and other physicochemical properties of the solvents affect the extent and the nature of self-assembly of surfactants in nonaqueous solutions. However, can the ionic liquids form aggregates in nonaqueous solution, and how do the solvent properties affect their aggregation behavior in nonaqueous solvents? Answers to these fundamental questions are not very clear at present.

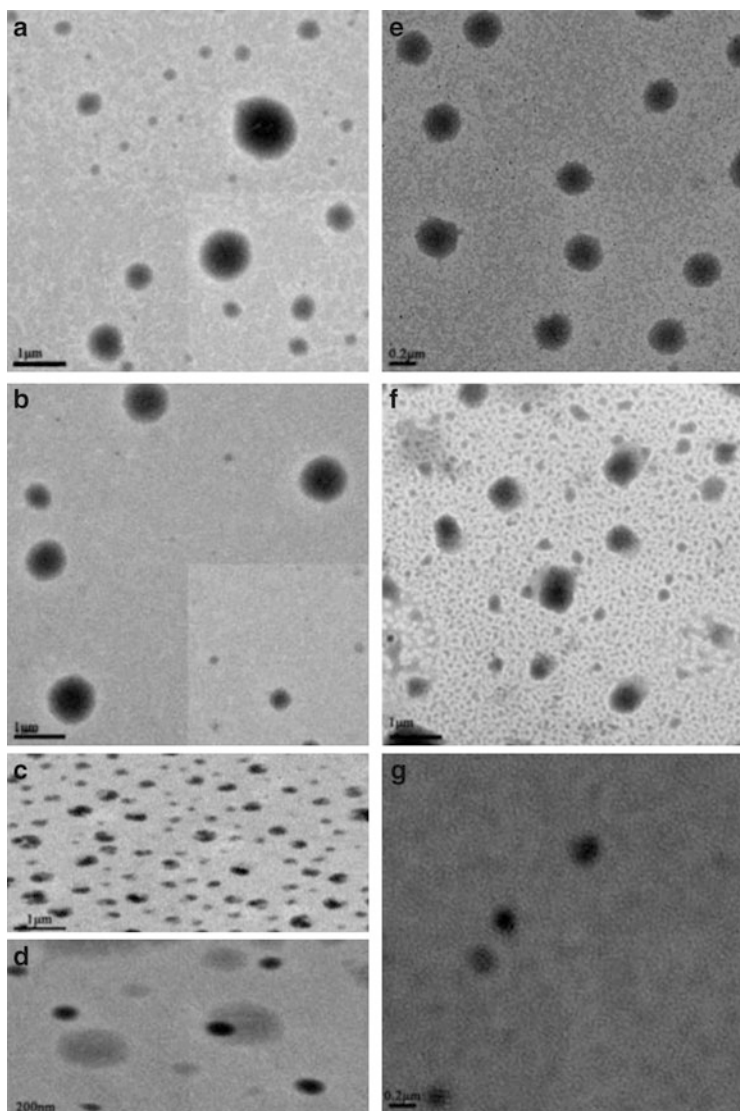
Dorbritz et al. [80] studied the aggregation behavior of [C<sub>4</sub>mim][BF<sub>4</sub>] ionic liquid in methanol, 2-propanol, and ethyl acetate by electrospray ionization mass

spectrometry. They observed the formation of aggregates  $[\text{C}_4\text{mim}]_n[\text{BF}_4]_{n-1}$  and  $[\text{C}_4\text{mim}]_n[\text{BF}_4]_{n+1}$ , and found that with increasing polarity of the solvent and decreasing concentration of the IL, the size of the formed aggregates decreased. Han and his coworkers [81] investigated the aggregation behavior of  $[\text{C}_4\text{mim}][\text{BF}_4]$  and  $[\text{C}_4\text{mim}][\text{PF}_6]$  in some organic solvents by UV-vis spectroscopy and conductivity measurements. It was demonstrated that the aggregation of these ILs depended strongly on the dielectric constant of the solvents. Dupont and coworkers [82] suggested that the ILs with 1,3-dialkylimidazolium as cation and tetrafluoroborate, hexafluorophosphate and tetraphenylborate as anions could form supramolecular aggregates in  $\text{CHCl}_3$ . In our recent work, aggregation behavior of  $[\text{C}_{12}\text{mim}]\text{Br}$  in acetonitrile, ethylene glycol, *N,N*-dimethylformamide, formamide, and dimethylsulfoxide solvents was investigated by conductivity and volume measurements [83]. Solvophobic parameters have been introduced to account for the interaction between alkyl chains of the IL and the solvents. It is shown that solvophobic effects and the hydrogen-bonding interaction between the IL anion and the solvents are the main factors affecting the aggregation of ILs in nonaqueous solvents.

## 5 Microscopic Structure of Ionic Liquids Aggregates

The unique properties and abnormal behavior exhibited in chemical synthesis and material preparation in ionic liquids are closely dependent on the microstructure of ILs in solutions. Thus study of the microstructure of IL aggregates has received increasing attention, and many methods such as small angle neutron scattering (SANS), transmission electron microscopy (TEM), nuclear magnetic resonance (NMR), and molecular dynamics simulations (MD) have been used in this field. In this context, Bowers and coworkers [16] investigated microstructure of the aggregates of  $[\text{C}_8\text{mim}]\text{Cl}$ ,  $[\text{C}_8\text{mim}]\text{I}$ , and  $[\text{C}_4\text{mim}][\text{BF}_4]$  in aqueous solutions by SANS. It was found that the  $[\text{C}_4\text{mim}][\text{BF}_4]$  formed polydisperse spherical aggregates above its CAC,  $[\text{C}_8\text{mim}]\text{I}$  behaved as regularly sized near-spherical charged micelles, while  $[\text{C}_8\text{mim}]\text{Cl}$  displayed weak long-range ordering of possibly disklike particles. In addition, Goodchild et al. [26] also used SANS to study aggregate structure of  $[\text{C}_n\text{mim}]\text{X}$  ( $n = 2, 4, 6, 8, 10$ ;  $\text{X} = \text{Cl}, \text{Br}$ ) in water. It was reported that at the concentration just above the CAC,  $[\text{C}_8\text{mim}]^+$ - and  $[\text{C}_{10}\text{mim}]^+$ -based ILs formed small near-spherical aggregates, which, after initial growth, possess core radii of  $10.5 \pm 0.5 \text{ \AA}$  and  $13.2 \pm 0.5 \text{ \AA}$ , respectively, at the intermediate concentrations. Towards higher concentrations, the aggregates appear to grow, with the aggregates in the  $[\text{C}_{10}\text{mim}]\text{Br}$  system becoming increasingly elongated (prolate) with increasing concentration. No evident aggregates are formed in the systems with  $[\text{C}_2\text{mim}]^+$  and  $[\text{C}_4\text{mim}]^+$ . In the  $[\text{C}_6\text{mim}]^+$  system, it appears that oblate aggregates with radius  $\sim 9 \text{ \AA}$  are formed at the CAC and that the radius increases with increasing concentration of the ionic liquid.

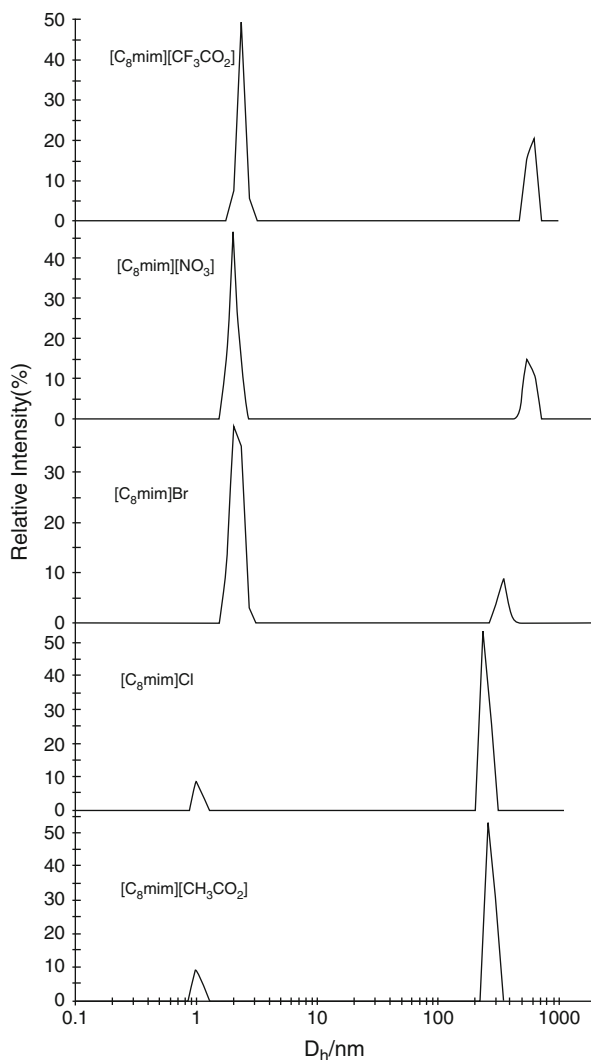




**Fig. 7** TEM images of the aggregates of ILs: (a)  $[\text{C}_8\text{mim}][\text{CF}_3\text{COO}]$ ; (b)  $[\text{C}_8\text{mim}][\text{NO}_3]$ ; (c)  $[\text{C}_8\text{mim}][\text{CH}_3\text{COO}]$ ; (d)  $[\text{C}_8\text{mim}]\text{Br}$ ; (e)  $[\text{C}_8\text{mim}]\text{Cl}$ ; (f)  $[\text{C}_8\text{mpyr}]\text{Br}$ ; (g) 4m- $[\text{C}_8\text{pyr}]\text{Br}$  at the ILs concentration of 0.45 mol/L (Reprinted from [53])

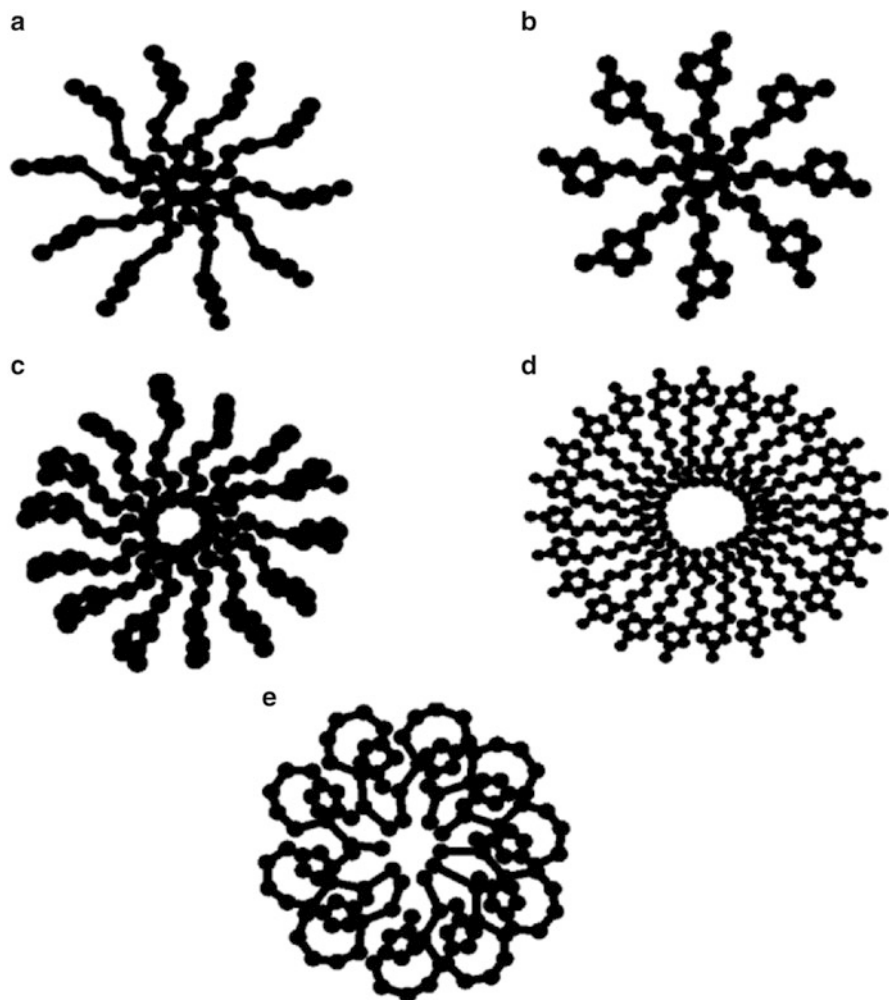
The morphologies and sizes of  $[\text{C}_8\text{mim}]\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{CH}_3\text{COO}$  and  $\text{CF}_3\text{COO}$ ),  $[\text{C}_8\text{mpyr}]\text{Br}$ , and 4 m- $[\text{C}_8\text{pyr}]\text{Br}$  aggregates in water were examined by TEM and dynamic light scattering [53]. The investigated ILs were found to form spherical aggregates (Fig. 7). Structures of the anions and cations have a very weak

**Fig. 8** Size distribution for the aggregates of the ILs from DLS measurements at 0.45 mol/L of  $[\text{C}_8\text{mim}]\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{CH}_3\text{COO}, \text{CF}_3\text{COO}$ ) at 298.15 K (Reprinted from [53])



effect on the morphology, but they do affect the aggregate sizes. The size of the spherical aggregates of the ILs with different anions increased with increasing hydrophobicity of the anions (Fig. 8).

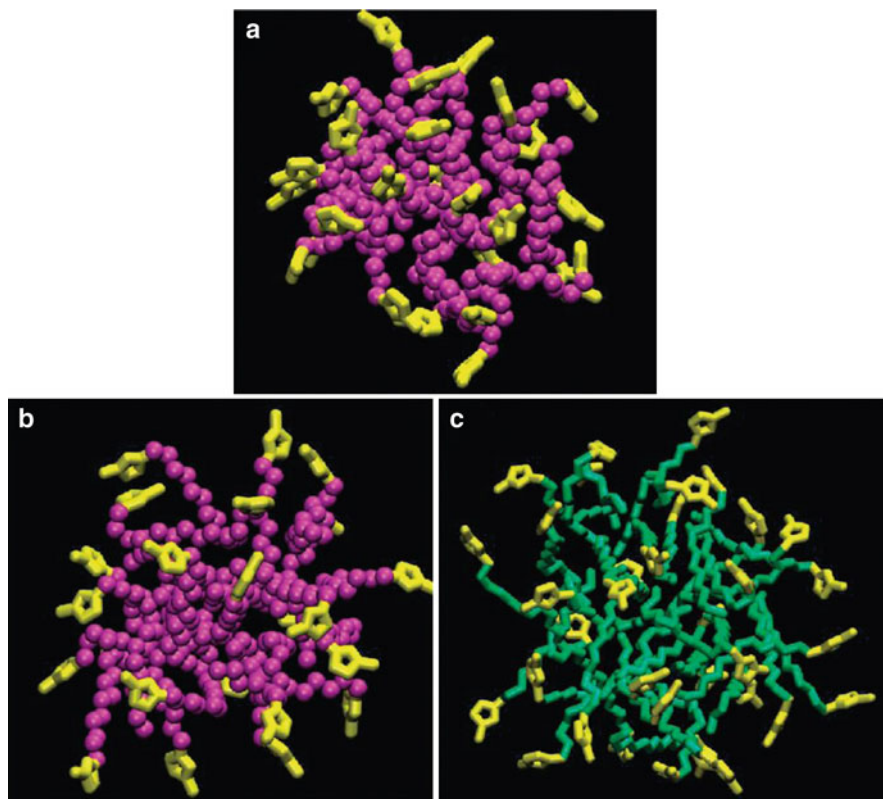
Based on the chemical shift of various protons of  $[\text{C}_4\text{mim}]\text{Cl}$ ,  $[\text{C}_4\text{mim}][\text{BF}_4]$ ,  $[\text{C}_8\text{mim}]\text{Cl}$ , and  $[\text{C}_4\text{mpy}]\text{Cl}$  in water as a function of IL concentrations, the schematic models of aggregates of these ILs were proposed by Singh et al. [84] as shown in Fig. 9. It can be seen that the imidazolium and pyridinium rings of  $[\text{C}_4\text{mim}][\text{BF}_4]$  and  $[\text{C}_4\text{mpy}]\text{Cl}$  are positioned at the aggregate surface in a configuration favorable for ring stacking through  $\Pi$ - $\Pi$  interactions as evidenced by the



**Fig. 9** Schematic models of the aggregates of different ILs: (a)  $[\text{C}_4\text{mim}][\text{BF}_4]$ ; (b)  $[\text{C}_4\text{mim}]\text{Cl}$ ; (c)  $[\text{C}_4\text{mpy}]\text{Cl}$ ; (d)  $[\text{C}_8\text{mim}]\text{Cl}$  (with  $N_{\text{agg}} = 23$ ); (e)  $[\text{C}_8\text{mim}]\text{Cl}$  (with  $N_{\text{agg}} = 10$ ) (Reprinted from [84])

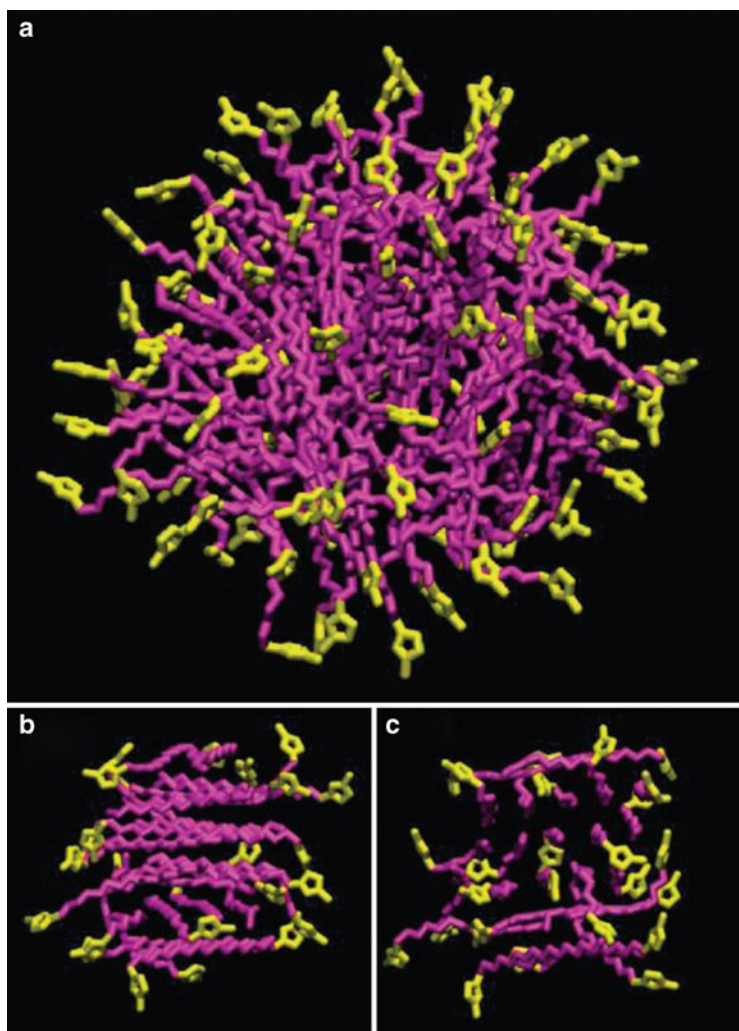
NMR measurements, whereas the imidazolium ring of  $[\text{C}_4\text{mim}]\text{Cl}$  and  $[\text{C}_8\text{mim}]\text{Cl}$  is shown in a configuration not favorable for ring stacking.

The microenvironment of different protons of cations of  $[\text{C}_n\text{mim}]\text{Br}$  ( $n = 4, 6, 8, 10, 12$ ) in the aggregated state was probed by the spin lattice relaxation rate for protons of the ILs [32]. It is suggested that the imidazolium rings of the cation in the aggregates were exposed to water and that the molecular motion of the aggregates is more restricted than that of the monomer of the ILs. The methyl group attached to the imidazolium ring stuck out from the surface of the aggregate into the water.



**Fig. 10** Snapshot of aggregates from various aqueous solutions studied: (a)  $[C_{10}\text{mim}]\text{Br}$ ; (b)  $[C_{12}\text{mim}]\text{Br}$ ; (c)  $[C_{14}\text{mim}]\text{Br}$ . In parts (a) and (b) atoms belonging to the alkyl tail are represented as *magenta* spheres and those belonging to headgroup are shown in *yellow*. In part (c) tail group atoms are shown in *green* and headgroup atoms in *yellow*. Hydrogen atoms of the cations are not shown. Water molecules, anions, and cations not belonging to the shown aggregate are removed for ease of visualization (Reprinted from [86])

The aggregate structures of  $[C_n\text{mim}]\text{Br}$  ( $n = 10, 12, 14, 16$ ) in water were conducted by molecular dynamics simulations [85, 86]. It was found that in all the systems, quasi-spherical polydisperse aggregates were formed by the spontaneous self-assembly of the amphiphilic cations. As shown in Figs. 10 and 11, the alkyl tails of the cations are buried deep inside the aggregates with the polar imidazolium group exposed to exploit the favorable interactions with water. The aggregation numbers steadily increase with the chain length. The hexadecyl aggregates have the most ordered internal structure of the systems studied, and the alkyl chains in these cations show the least number of gauche defects. Anions and water are not found at the core of the aggregates, though water molecules are found to penetrate to some degree. The anions are found to be isotropically distributed throughout the system.



**Fig. 11** Snapshot of aggregates from aqueous  $[C_{16}mim]Br$  solutions: (a) largest aggregate observed; (b, c) another aggregate from different viewing angles. Tail group atoms are shown in *magenta* and headgroup atoms in *yellow*. Hydrogen atoms of the cations are not shown. Water molecules, anions, and cations not belonging to the shown aggregate are removed for ease of visualization (Reprinted from [86])

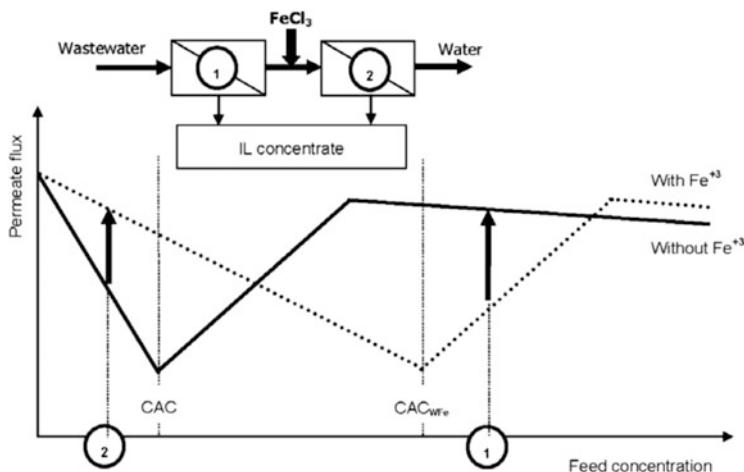


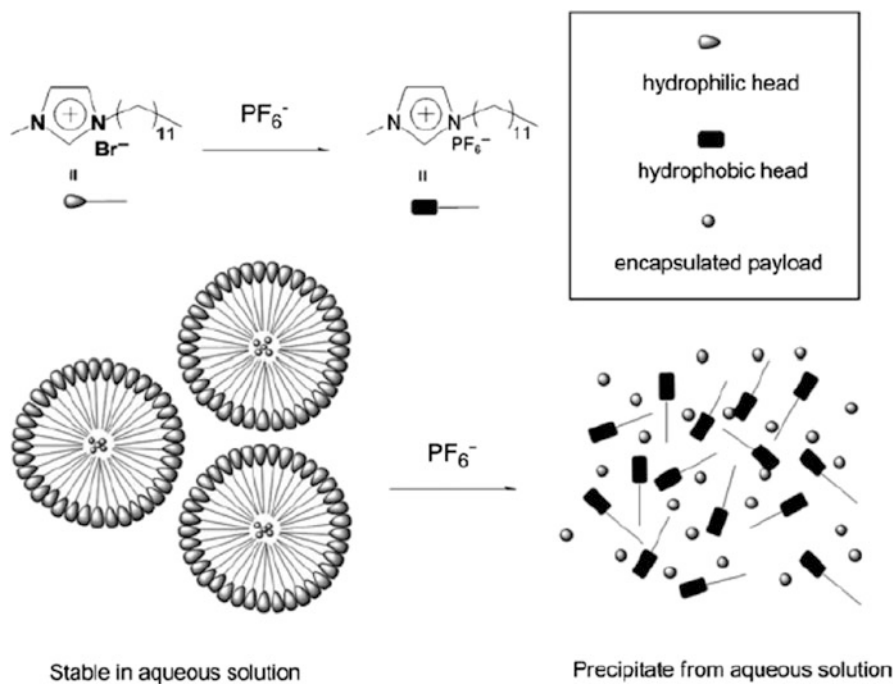
Fig. 12 Permeate flux obtained in a two-stage membrane filtration scheme (Reprinted from [87])

## 6 Application of Ionic Liquids Aggregation

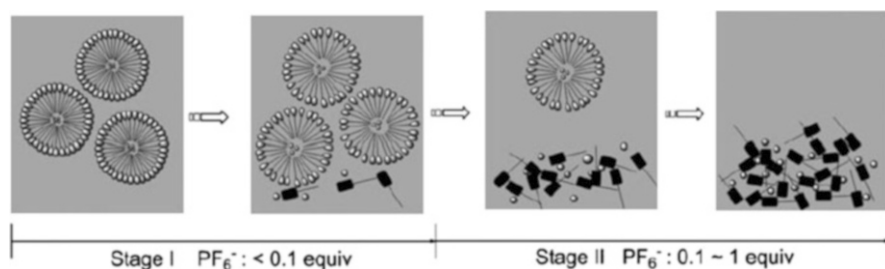
The aggregation behavior of ILs in solutions plays an important role in the application of ILs in material synthesis, biochemicals separation, disposal of ILs wastewater, and others. Herein the role played by ILs can be understood through the following four examples.

Recycling of ILs from water/solutions is an important issue that addresses the economics of ionic liquid use, and also reduces concerns about disposal, biodegradation and toxicity of ionic liquids. Based on the fact that ionic liquids show a similar behavior to that of surfactants in membrane filtration and the aggregation behavior of ILs in water can be controlled and regulated by the addition of inorganic salt, Fernández et al. [87] analyzed the potential of aggregation control to improve the performance of downstream membrane separations by using the system of  $[\text{C}_8\text{mim}]\text{Cl}$  plus iron(III) chloride ( $\text{FeCl}_3$ ). The addition of  $\text{FeCl}_3$  has a significant salt-in effect on the aggregation of  $[\text{C}_8\text{mim}]\text{Cl}$ , and an increase in CAC value of the IL has consequences regarding the design of the corresponding membrane filtration system. A two-stage membrane filtration scheme was proposed and shown in Fig. 12. It can be seen that wastewater with higher ionic liquid concentration is fed to the first stage and at this moment, the IL aggregates are formed due to its lower CAC value, and then high permeate flux is obtained. The retentate stream with low ionic liquid concentration is fed to the second stage after adding  $\text{FeCl}_3$ . In this case, the permeate flux is located at the point indicated by arrow ② in Fig. 12. Obviously, permeate flux after the addition of  $\text{FeCl}_3$  is higher than the original situation without  $\text{FeCl}_3$  in the second stage.

Systems affording controllable formation and breakage of amphiphilic aggregates may be of significant value in the areas such as controlled release,



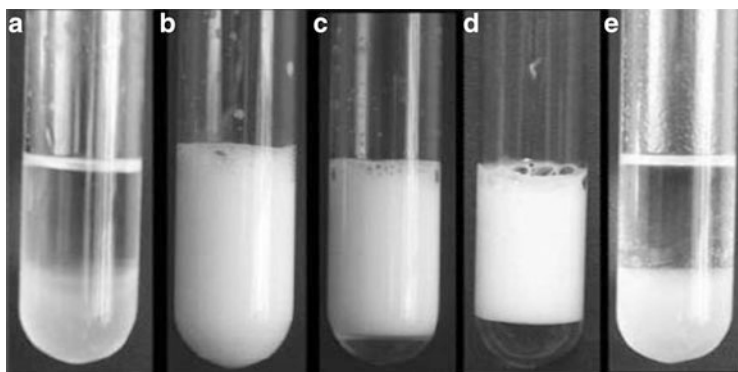
**Fig. 13** Anion exchange to  $[\text{PF}_6]^-$  and resulting micelle collapse (Reprinted from [88])



**Fig. 14** Illustration of the dissociation of micelles and the release of encapsulated payload by adding  $[\text{PF}_6]^-$  (Reprinted from [88])

drug delivery, nanosynthesis, cleaning, and petroleum recovery in oil fields. Niu et al. [88] succeeded in proposing a simple but efficient, rapid, and quantitative ion-responsive micelle system based on counter-anion change of an ionic liquid with  $[\text{C}_{12}\text{mim}]^+$  as cation. As shown in Fig. 13, upon exchange of  $\text{Br}^-$  to  $[\text{PF}_6]^-$ , micelles that  $[\text{C}_{12}\text{mim}]\text{Br}$  formed in aqueous system exhibited progressive, and ultimately complete disaggregation because  $[\text{C}_{12}\text{mim}][\text{PF}_6]$  is insoluble in water. To explore the potential application of this system for controlled release of micellar payloads, different amounts of  $[\text{PF}_6]^-$  were added to Nile-Red-loaded  $[\text{C}_{12}\text{mim}]\text{Br}$





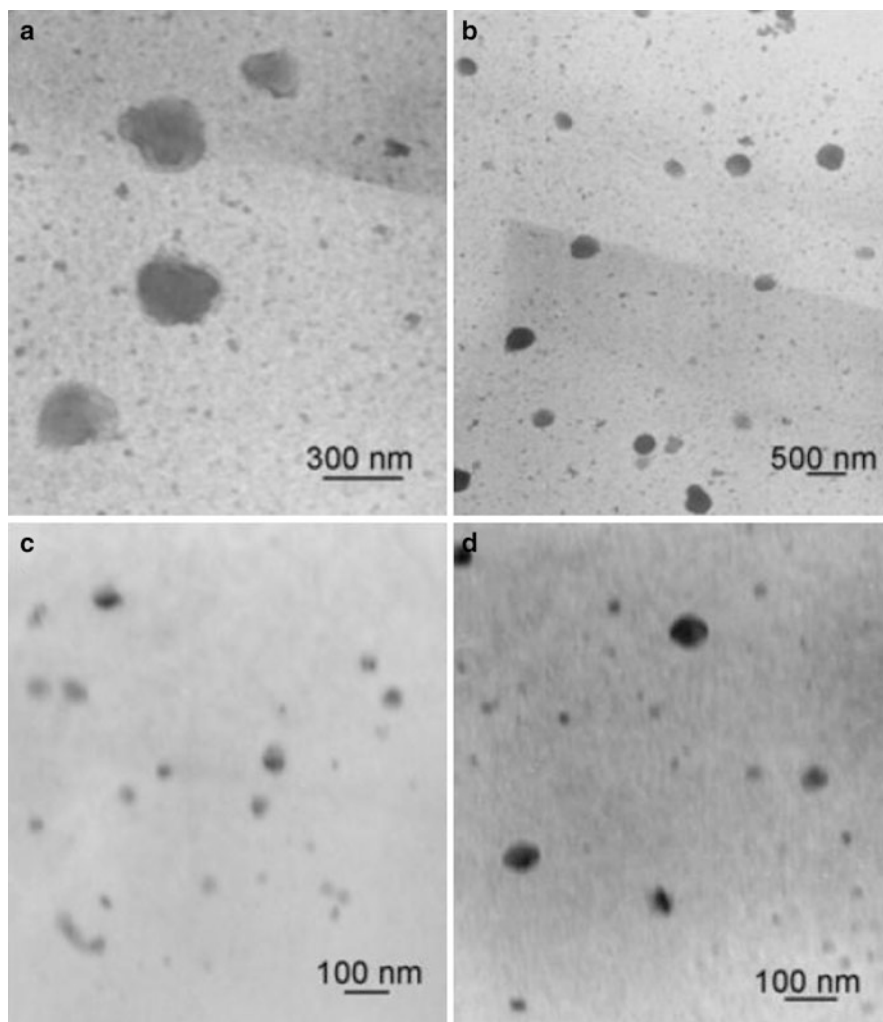
**Fig. 15** The photographs of the oil–water emulsions: (a) 2:1 (v/v) cyclohexane/water mixture; (b) with  $[C_{12}mim]Br$ , shaken 3 min; (c)  $[C_{12}mim]Br$ -induced emulsion after 1 h; (d)  $[C_{12}mim]Br$ -induced emulsion after 50 h; (e) approximately 2 min after adding 1 equiv  $NaPF_6$  to (b) (Reprinted from [88])

micellar solution. It is interesting to note that the controlled release of the hydrophobic dye (Nile-Red) was successfully achieved. Figure 14 shows the procedure of the dissociation of the micelles and the release of the encapsulated payload by adding  $[PF_6]^-$ . It can be seen that when  $\sim 0.1$  equiv of  $[PF_6]^-$  was added, conversion of  $[C_{12}mim]Br$  to  $[C_{12}mim][PF_6]$  (with subsequent extraction from the micelles and desolubilization) caused little overall micelle disruption. In this case (Stage I), the micelles remained metastable and minimal Nile Red was transferred to the aqueous phase from the micelle. However, as the concentration of added  $[PF_6]^-$  was in the range 0.1 to 1 equiv (Stage II), micelle disassociation increased significantly with corresponding release of the encapsulated Nile Red. In this process,  $[C_{12}mim][PF_6]$  was formed and then precipitated.

The applicability of  $[C_{12}mim]Br$  for stabilizing – and  $[C_{12}mim][PF_6]$  for subsequently breaking – oil–water emulsions was also investigated by Niu and coworkers [88]. Towards this end, 95 mg of  $[C_{12}mim]Br$  was added to a vial containing 6 mL of 2:1 (v/v) cyclohexane/water. The mixture was shaken thoroughly and a milk-white emulsion (Fig. 15b) was observed. The resulting emulsion showed little evidence of separation until after  $\sim 1$  h, at which point a clear lower liquid phase began to appear (Fig. 15c). However, after 50 h, the emulsion still occupied  $\sim 80\%$  of the liquid volume (Fig. 15d). In contrast, adding 1 equiv of  $Na[PF_6]$  to a freshly shaken emulsion resulted in complete separation into two liquid layers within 2 min, with  $[C_{12}mim][PF_6]$  precipitating (Fig. 15e). These observations indicate that the ion-exchange/desolubilization mechanism discussed here might have promise for practical industrial emulsion forming/separating applications, including oil transport.

The IL-based aqueous two-phase systems are novel aqueous two-phase systems. 1-Butyl-3-methylimidazolium dicyanamide ( $[C_4mim][N(CN)_2]$ ) +  $K_2HPO_4$





**Fig. 16** TEM images of the aggregates of  $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  ( $2.5 \text{ mol}\cdot\text{L}^{-1}$ ) with and without BSA ( $1.23 \text{ g}\cdot\text{L}^{-1}$ ): (a, b) without BSA; (c, d) with BSA (Reprinted from [89])

aqueous two-phase system has been used by Wang et al. [89] to separate selectively bovine serum albumin (BSA) from aqueous saccharides. It was shown that 82.7–100 % BSA could be enriched into the top IL-rich phase and almost quantitative saccharides (arabinose, glucose, sucrose, raffinose or dextran) were preferentially extracted into the bottom phosphate-rich phase in a single-step extraction. Conductivity, DLS, and TEM studies indicated that the IL aggregates and IL aggregate-protein complexes were formed in the IL-rich phase (Fig. 16). It was suggested that the formation of the IL aggregate-protein complexes is the driving force for the selective separation.

## 7 Summary and Outlook

The above discussion has demonstrated that aggregation of ionic liquids takes place in both aqueous and nonaqueous solutions. Alkyl chain length, cationic structure, and anionic nature of ionic liquids, and addition of inorganic salts, organic solvents, and surfactants were found to have a vital effect on the critical aggregation concentration, the ionization degree of the aggregates, the standard Gibbs energy of aggregation, the aggregation number, and aggregate size. Therefore, the aggregation behaviors of ILs in solutions can be controlled and regulated by altering these factors. At the same time, the possible mechanism for the effect of these factors on the aggregation behavior of ILs in solutions has been analyzed, and the potential application of IL aggregation in the membrane separation of IL wastewater, controlled drug release, breakage of oil/water emulsions, and the selective separation of BSA from aqueous saccharides has been illustrated as well.

In summary, great progress has been made in fundamental and applied aspects on the aggregation behavior of ILs in solutions over the past decade. It can be expected that IL aggregation will find more and more applications in the future. However, research in this field is still in its infancy, and there are a number of issues which require further investigation. In future work, the following studies are suggested:

1. A deeper study should be carried out on the microstructure of IL aggregates. This is a very difficult task, and various experimental methods including macroscopic and microcosmic techniques and molecular simulation are needed. The structural information obtained would be used to establish the relationship between the structure of ionic liquids and their specific performance, which is valuable for the design and application of novel ionic liquids.
2. At present, the aggregation behavior of ionic liquids in nonaqueous and water-organic solutions is poorly understood. In this context, a better understanding of the interactions of alkyl chains of ionic liquids with various classes of organic molecules is essential although solvation of cations and anions of ionic liquids in nonaqueous media is also important.
3. The effect of light, heat, and solution pH on the aggregation behavior of ionic liquids in solutions should be investigated. Based on this knowledge, we can use light, heat, and solution pH to modulate the aggregation behavior of ionic liquids. This is a more advanced concept for the application of ionic liquids. For this purpose, design and synthesis of these functional ionic liquids are necessary.
4. Development of more technically relevant ILs is highly desired, and degradation, toxicity and environmental distribution of ILs aggregates ought to be examined as well.

## References

1. Welton T (1996) Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem Rev* 99:2071–2084
2. Swatloski RP, Holbrey JD, Rogers RD (2003) Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate. *Green Chem* 5:361–363
3. Docherty KM, Kulpa J, Charles F (2005) Toxicity and antimicrobial activity of imidazolium and pyridinium ionic liquids. *Green Chem* 7:185–189
4. Wasserschein P, Welton T (2003) Ionic liquids in syntheses. VCH-Wiley, Weinheim
5. Rantwijk F, Lau RM, Sheldon RA (2003) Biocatalytic transformations in ionic liquids. *Trends Biotechnol* 21:131–138
6. Jain N, Kumar A, Chauhan S, Chauhan SMS (2005) Chemical and biochemical transformations in ionic liquids. *Tetrahedron* 61:1015–1060
7. Buzzeo MC, Evans RG, Compton RG (2004) Non-haloaluminate room-temperature ionic liquids in electrochemistry – a review. *Chemphyschem* 5:1106–1120
8. Endres F, Abedin SZE (2006) Air and water stable ionic liquids in physical chemistry. *Phys Chem Chem Phys* 8:2101–2116
9. Liu J, Jonsson JA, Jing G (2005) Application of ionic liquids in analytical chemistry. *Trends Anal Chem* 24:20–27
10. Zhao H, Xia S, Ma P (2005) Use of ionic liquids as ‘green’ solvents for extractions. *J Chem Technol Biotechnol* 80:1089–1096
11. Seddon KR (2003) Ionic liquids: a taste of the future. *Nat Mater* 2:363–365
12. Visser A, Swaltowski RP, Reichert RM, Mayton R, Sheff S, Wierzbicki A, Davis JH, Rogers RD (2002) Task-specific ionic liquids incorporating novel cations for the coordination and extraction of  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$ : synthesis, characterization, and extraction studies. *Environ Sci Technol* 36:2523–2529
13. Zhang J, Yang C, Hou Z (2003) Effect of dissolved  $\text{CO}_2$  on the conductivity of the ionic liquid [bmim][PF<sub>6</sub>]. *New J Chem* 27:333–336
14. Ianchard LA, Gu Z, Brennecke JF (2001) High-pressure phase behavior of ionic liquid/ $\text{CO}_2$  systems. *J Phys Chem B* 105:2437–2444
15. Armstrong W, Anderson JL (2003) High-stability ionic liquids: a new class of stationary phases for gas chromatography. *Anal Chem* 75:4851–4858
16. Bowers JP, Butts CJ, Martin PC, Vergara-Gutierrez M (2004) Aggregation behaviour of aqueous solutions in ionic liquids. *Langmuir* 20:2191–2198
17. Miskolczy Z, Sebok-Nagy K, Biczok L, Gokturk S (2004) Aggregation and micelle formation of ionic liquids in aqueous solution. *Chem Phys Lett* 400:296–300
18. Vanyur R, Biczok L, Miskolczy Z (2007) Micelle formation of 1-alkyl-3-methylimidazolium bromide ionic liquids in aqueous solution. *Colloids Surf A Physicochem Eng Aspects* 299:256–261
19. Blesic M, Marques MH, Plechkova NV, Seddon KR, Rebelo LPN, Lopes A (2007) Self-aggregation of ionic liquids: micelle formation in aqueous solution. *Green Chem* 9:481–490
20. Huddleston JG, Visser AE, Reichert MW, Willauer HD, Broker GA, Rogers RD (2001) Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem* 3:156–164
21. Stepnowski P, Mroziński W, Nischthäuser J (2007) Adsorption of alkylimidazolium and alkylpyridinium ionic liquids onto natural soils. *Environ Sci Technol* 41:511–516
22. Jungnickel C, Łuczak J, Ranke J, Fernández JF, Müller A, Thöning J (2008) Micelle formation of imidazolium ionic liquids in aqueous solution. *Colloids Surf A Physicochem Eng Aspects* 316:278–284
23. Modaressi A, Sifaoui H, Mielcarz M, Domanska U, Rogalski M (2007) Influence of the molecular structure on the aggregation of imidazolium ionic liquids in aqueous solutions. *Colloids Surf A Physicochem Eng Aspects* 302:181–185

24. El Seoud OA, Pires PAR, Abdel-Moghny T, Bastos EL (2007) Synthesis and micellar properties of surface-active ionic liquids: 1-alkyl-3-methylimidazolium chlorides. *J Colloid Interface Sci* 313:296–304
25. Thomaier S, Werner K (2007) Aggregates in mixtures of ionic liquids. *J Mol Liq* 130:104–107
26. Goodchild I, Collier L, Millar SL, Prokšs I, Lord JCD, Butts CPB, Bowers J, Webster JRP, Heenan RK (2007) Structural studies of the phase, aggregation and surface behaviour of 1-alkyl-3-methylimidazolium halide + water mixtures. *J Colloid Interface Sci* 307:455–468
27. Sirieix-Plénet J, Gaillon L, Letellier P (2004) Behaviour of a binary solvent mixture constituted by an amphiphilic ionic liquid, 1-decyl-3-methylimidazolium bromide and water: potentiometric and conductimetric studies. *Talanta* 63:979–986
28. Baltazar QQ, Chandawalla J, Sawyer K, Anderson JL (2007) Interfacial and micellar properties of imidazolium-based monocationic and dicationic ionic liquids. *Colloids Surf A Physicochem Eng Aspects* 302:150–156
29. Dong B, Li N, Zheng L, Yu L, Inoue T (2007) Surface adsorption and micelle formation of surface active ionic liquids in aqueous solution. *Langmuir* 23:4178–4182
30. Inoue T, Ebina H, Dong B, Zheng L (2007) Electrical conductivity study on micelle formation of long-chain imidazolium ionic liquids in aqueous solution. *J Colloid Interface Sci* 314:236–241
31. Wang J, Wang H, Zhang S, Zhang H, Zhao Y (2007) Conductivities, volumes, fluorescence, and aggregation behavior of ionic liquids  $[C_4mim][BF_4]$  and  $[C_nmim]Br$  ( $n = 4, 6, 8, 10, 12$ ) in aqueous solutions. *J Phys Chem B* 111:6181–6188
32. Zhao Y, Gao S, Wang J, Tang J (2008) Aggregation of ionic liquids  $[C_nmim]Br$  ( $n = 4, 6, 8, 10, 12$ ) in  $D_2O$ : a NMR study. *J Phys Chem B* 112:2031–2039
33. Lianos P, Zana R (1981) Fluorescence probe studies of the effect of concentration on the state of aggregation of surfactants in aqueous solution. *J Colloid Interface Sci* 84:100–107
34. Li XW, Gao YA, Liu J, Zheng LQ, Chen B, Wu LZ, Tung CH (2010) Aggregation behavior of a chiral long-chain ionic liquid in aqueous solution. *J Colloid Interface Sci* 343:94–101
35. Zhang H, Li K, Liang H, Wang J (2008) Spectroscopic studies of the aggregation of imidazolium-based ionic liquids. *Colloids Surf A Physicochem Eng Aspects* 329:75–81
36. Bai G, Lopes A, Bastos M (2008) Thermodynamics of micellization of alkylimidazolium surfactants in aqueous solution. *J Chem Thermodyn* 40:1509–1516
37. Geng F, Liu J, Zheng L, Yu L, Li Z, Li G, Tung C (2010) Micelle formation of long-chain imidazolium ionic liquids in aqueous solution measured by isothermal titration microcalorimetry. *J Chem Eng Data* 55:147–151
38. Cornellas A, Perez L, Comelles F, Ribosa I, Manresa A, Garcia MT (2011) Self-aggregation and antimicrobial activity of imidazolium and pyridinium based ionic liquids in aqueous solution. *J Colloid Interface Sci* 355:164–171
39. Singh T, Kumar A (2008) Self-aggregation of ionic liquids in aqueous media: a thermodynamic study. *Colloids Surf A Physicochem Eng Aspects* 318:263–268
40. Łuczak J, Hupka J, Thoeming J, Jungnickel C (2007) In: Wilk KA (ed) International scientific conference, surfactants and dispersed systems in theory and practice. PALMA Press, Wrocław/Ksiaz Castle
41. Rodriguez JR, Gonzalez-Perez A, Del Castillo JL, Czapkiewicz J (2005) Thermodynamics of micellization of alkyltrimethylammonium chlorides in aqueous solutions. *J Colloid Interface Sci* 250:438–443
42. Chen L, Shi-Yow L, Chiung-Chang H, En-Ming C (1998) Temperature dependence of critical micelle concentration of polyoxyethylenated non-ionic surfactants. *Colloids Surf A Physicochem Eng Aspects* 135:175–181
43. Mehta SK, Bhasin KK, Chauhan R, Dham S (2005) Effect of temperature on critical micelle concentration and thermodynamic behavior of dodecyltrimethylammonium bromide and dodecyltrimethylammonium chloride in aqueous media. *Colloids Surf A Physicochem Eng Aspects* 255:153–157

44. Muller N (1993) Temperature dependence of critical micelle concentrations and heat capacities of micellization for ionic surfactants. *Langmuir* 9:96–100
45. Richard CR, Wildin JL, Rapp AL, Moyna GM (2007) Hydrogen bonds in ionic liquids revisited: (35/37)Cl NMR studies of deuterium isotope effects in 1-n-butyl-3-methylimidazolium chloride. *J Phys Chem B* 111:11619–11621
46. Stepnowski P, Nichthauser J, Mrozik W, Buszewski B (2006) Usefulness of  $\pi \dots \pi$  aromatic interactions in the selective separation and analysis of imidazolium and pyridinium ionic liquid cations. *Anal Bioanal Chem* 385:1483–1491
47. Gonzalez-Perez A, Ruso JM, Prieto G, Sarmiento F (2004) Self-assembly of sodium heptafluorobutylate in aqueous solution. *Colloids Surf A Physicochem Eng Aspects* 249:41–44
48. Zhao M, Zheng L (2011) Micelle formation by N-alkyl-N-methylpyrrolidinium bromide in aqueous solution. *Phys Chem Chem Phys* 13:1332–1337
49. Klevens HB (1953) Structure and aggregation in dilute solution of surface active agents. *J Am Oil Chem Soc* 30:74–80
50. Huibers PDT, Lobanov VS, Katritzky AR, Shah DO, Karelson M (1997) Prediction of critical micelle concentration using a quantitative structure–property relationship approach. *J Colloid Interface Sci* 187:113–120
51. Baker GA, Pandey S, Pandey S, Baker SN (2004) A new class of cationic surfactants inspired by N-alkyl-N-methyl pyrrolidinium ionic liquids. *Analyst* 12:890–892
52. Luczaka J, Hupkaa J, Thöing J, Jungnickel C (2008) Self-organization of imidazolium ionic liquids in aqueous solution. *Colloids Surf A Physicochem Eng Aspects* 329:125–133
53. Wang H, Wang J, Zhang S, Xuan X (2008) Structural effects of anions and cations on the aggregation behavior of ionic liquids in aqueous solutions. *J Phys Chem B* 112:16682–16689
54. Freire MG, Neves CMSS, Carvalho PJ, Gardas RL, Fernandes AM, Marrucho IM, Santos LMNBF, Coutinho JAP (2007) Mutual solubilities of water and hydrophobic ionic liquids. *J Phys Chem B* 111:13082–13089
55. Tokuda H, Ishii K, Suan MABH, Tauzaki S, Hayamizu K, Watanabe M (2006) Physicochemical properties and structures of room-temperature ionic liquids. 3. Variation of cationic structures. *J Phys Chem B* 110:2833–2839
56. Bini R, Bortolini O, Chiappe C, Pieraccini D, Siciiano T (2007) Development of cation/anion “interaction” scales for ionic liquids through ESI-MS measurements. *J Phys Chem B* 111:598–604
57. Blesic M, Lopes A, Melo E, Petrovski Z, Plechkova NV, Canongia Lopes JN, Seddon KR, Rebelo LPN (2008) On the self-aggregation and fluorescence quenching aptitude of surfactant ionic liquids. *J Phys Chem B* 112:8645–8650
58. Pino V, Baltazar QQ, Anderson JL (2007) Examination of analyte partitioning to monocationic and dicationic imidazolium-based ionic liquid aggregates using solid-phase microextraction-gas chromatography. *J Chromatogr A* 1148:92–99
59. Zana R (1996) Critical micellization concentration of surfactants in aqueous solution and free energy of micellization. *Langmuir* 12:1208–1211
60. Sepúlveda L, Cortés J (1985) Ionization degrees and critical micelle concentrations of hexadecyltrimethylammonium and tetradecyltrimethylammonium micelles with different counterions. *J Phys Chem* 89:5322–5324
61. Marcus Y (1991) Thermodynamics of solvation of ions. Part 5. – Gibbs free energy of hydration at 298.15 K. *J Chem Soc Faraday Trans* 87:2995–2999
62. Bunton CA, Cowell C (1988) The binding of phenols and phenoxide ions to cationic micelles. *J Colloid Interface Sci* 122:154–162
63. Abdel-Rahem R (2008) The influence of hydrophobic counterions on micellar growth of ionic surfactants. *Adv Colloid Interface Sci* 141:24–36
64. Shaw DJ (1992) Introduction to colloid and surface chemistry. Butterworth, Heinemann, Oxford

65. Dong B, Zhao X, Zheng L, Zhang J, Li N, Inoue T (2008) Aggregation behavior of long-chain imidazolium ionic liquids in aqueous solution: micellization and characterization of micelle microenvironment. *Colloids Surf A Physicochem Eng Aspects* 317:666–672
66. Vaghela NM, Sastry NV, Aswal VK (2011) Effect of additives on the surface active and morphological features of 1-octyl-3-methylimidazolium halide aggregates in aqueous media. *Colloids Surf A Physicochem Eng Aspects* 373:101
67. Wang H, Feng Q, Wang J, Zhang H (2010) Salt effect on the aggregation behavior of 1-decyl-3-methylimidazolium bromide in aqueous solutions. *J Phys Chem B* 114:1380–1387
68. Lin Z, Cai JJ, Scriven LE, Davis HT (1994) Spherical-to-wormlike micelle transition in CTAB solutions. *J Phys Chem* 98:5984–5993
69. Magid LJ, Han Z, Warr GG, Cassidy MA, Butler PD, Hamilton WA (1997) The effect of counterion competition for cetyltrimethylammonium micellar surfaces on micellar growth horizons: electrostatics and specific binding. *J Phys Chem B* 101:7919–7927
70. Armstrong DW, Henry SJ (1980) Use of an aqueous micellar mobile phase for separation of phenols and polynuclear aromatic hydrocarbons via HPLC. *J Liq Chromatogr* 3:657–662
71. Berthod A, García-álvarez-Coque C (2000) *Micellar liquid chromatography*. Marcel Dekker, New York
72. Esteve-Romero J, Carda-Broch S, Gil-Agustí M, Capella-Peiró ME, Bose D (2005) Micellar liquid chromatography for the determination of drug materials in pharmaceutical preparations and biological samples. *Trends Anal Chem* 24:75–91
73. Armstrong DW (1985) Micelles in separations: application and theory. *Sep Purif Methods* 14:213–304
74. Thomas DP, Foley JP (2007) Efficiency enhancements in micellar liquid chromatography through selection of stationary phase and alcohol modifier. *J Chromatogr A* 1149:282–293
75. Ruiz-ángel MJ, Torres-Lapasíó JR, García-álvarez-Coque MC (2008) Retention mechanisms for basic drugs in the submicellar and micellar reversed-phase liquid chromatographic modes. *Anal Chem* 80:9705–9713
76. Pino V, Yao C, Anderson JL (2009) Micellization and interfacial behavior of imidazolium-based ionic liquids in organic solvent–water mixtures. *J Colloid Interface Sci* 333:548–556
77. Wang J, Zhang L, Wang H, Wu C (2012) Aggregation behavior modulation of 1-dodecyl-3-methylimidazolium bromide by organic solvents in aqueous solution. *J Phys Chem B* 115:4955–4962
78. Sugihara S, Era Y, Funatsu M, Kunitake T, Lee S, Sasaki Y (1997) Micelle formation of dodecylammonium surfactant with mixed counterions: perfluorocarboxylate and alkanesulfonate ions. *J Colloid Interface Sci* 187:435–442
79. Beyaz A, Oh WS, Reddy VP (2004) Ionic liquids as modulators of the critical micelle concentration of sodium dodecyl sulfate. *Colloids Surf B Biointerfaces* 35:119
80. Dorbritz S, Ruth W, Kragl U (2005) Investigation on aggregate formation of ionic liquids. *Adv Synth Catal* 347:1273–1279
81. Li W, Zhang Z, Zhang J, Han B, Wang B, Hou M, Xie Y (2006) Micropolarity and aggregation behavior in ionic liquid + organic solvent solutions. *Fluid Phase Equilibria* 248:211–216
82. Consorti CS, Suarez PAZ, de Souza RF, Burrow RA, Farrar DH, Lough AJ, Loh W, da Silva HML, Dupont J (2005) Identification of 1,3-dialkylimidazolium salt supramolecular aggregates in solution. *J Phys Chem B* 109:4341–4349
83. Feng Q, Wang H, Zhang S, Wang J (2010) Aggregation behavior of 1-dodecyl-3-methylimidazolium bromide ionic liquid in non-aqueous solvents. *Colloids Surf A Physicochem Eng Aspects* 367:7–11
84. Singh T, Kumar A (2007) Aggregation behavior of ionic liquids in aqueous solutions: effect of alkyl chain length, cations, and anions. *J Phys Chem B* 111:7843–7851
85. Bhargava BL, Klein ML (2009) Molecular dynamics studies of cation aggregation in the room temperature ionic liquid [C<sub>10</sub>mim][Br] in aqueous solution. *J Phys Chem A* 113:1898–1904
86. Bhargava BL, Klein ML (2009) Initial stages of aggregation in aqueous solutions of ionic liquids: molecular dynamics studies. *J Phys Chem B* 113:9499–94505

87. Fernández JF, Waterkamp D, Thöming J (2008) Recovery of ionic liquids from wastewater: aggregation control for intensified membrane filtration. *Desalination* 224:52–56
88. Shen Y, Zhang Y, Kuehner D, Yang G, Yuan F, Niu L (2008) Ion-responsive behavior of ionic-liquid surfactant aggregates with applications in controlled release and emulsification. *Chemphyschem* 9:2198–2202
89. Pei YC, Li ZY, Liu L, Wang JJ, Wang HY (2010) Selective separation of protein and saccharides by ionic liquids aqueous two-phase systems. *Sci China Chem* 53:1554–1560

Structures and Interactions of Ionic Liquids

Zhang, S.; Wang, J.; ZHAO, Q.; Zhou, Q. (Eds.)

2014, VII, 197 p. 115 illus., 19 illus. in color., Hardcover

ISBN: 978-3-642-38618-3