REVIEW

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Ionic liquid-induced aggregate formation and their applications

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Abstract

In the last two decades, researchers have extensively studied highly stable and ordered supramolecular assembly formation using oppositely charged surfactants. Thereafter, surface-active ionic liquids (SAILs), a special class of room temperature ionic liquids (RTILs), replace the surfactants to form various supramolecular aggregates. Therefore, in the last decade, the building blocks of the supramolecular aggregates (micelle, mixed micelle, and vesicular assemblies) have changed from oppositely charged surfactant/surfactant pair to surfactant/SAIL and SAIL/SAIL pair. It is also found that various biomolecules can also interact with SAILs to construct biologically important supramolecular assemblies. The very latest addition to this combination of ion pairs is the dye molecules having a long hydrophobic chain part along with a hydrophilic ionic head group. Thus, dye/surfactant or dye/SAIL pair also produces different assemblies through electrostatic, hydrophobic, and π-π stacking interactions. Vesicles are one of the important self-assemblies which mimic cellular membranes, and thus have biological application as a drug carrier. Moreover, vesicles can act as a suitable microreactor for nanoparticle synthesis.

Keywords Surfactant·RTIL · SAIL · Biomolecules · Dye molecules · Supramolecular assembly

Introduction

In the year 1999, Thomas Welton first published a review on the topic room temperature ionic liquid (RTIL) (Welton 1999). However, ionic liquids (ILs) are not new; some of them are known for many years. One of the earliest well-known RTIL is ethylammonium nitrate (EAN), ([EtNH$_3$][NO$_3$]) which has its melting pointat 12 °C, reported in 1914 by Paul Walden (1914). However, Rây and Sen have worked with different alkylammonium nitrate salts in 1911 (Rây and Sen 1911). Since then, a significant number of literature is available in this area. EAN is a colorless, odorless protic ionic liquid (PIL) and can form three-dimensional hydrogen bonding networks very similar to that of water. The ethyl chain of PIL, EAN, is sufficient to form a self-assembled structure, and thus, EAN shows nanoscale heterogeneity unlike water. Atkin et al. have demonstrated that the nitrate ion of EAN strongly interacts with the ammonium groups via electrostatic as well as hydrogen bonding interaction whereas the cationic alkyl groups are aggregated together due to the solvophobic interactions (Atkin and Warr 2008). Russina et al. have shown that in the mixture of amphiphilic molecules methanol and EAN, a wide distribution of clusters exist in the region ($0.10 \leq \chi_{EAN} \leq 0.15$) and EAN molecules retain their bulk-sponge-like morphology. This microheterogeneous mixture can influence the solute's motion and shows some interesting results in comparison with other PIL-cosolvent mixtures (Russina et al. 2014, 2015; Kundu et al. 2016). Though there are some reviews available with the phrase "ionic liquid(s)" in the title, this review mainly focuses on the aggregation phenomena induced or improved by ILs (Welton 1999; Pârvulescu and Hardacre 2007; Hallett and Welton 2011; Kuchlyan et al. 2016).

Background

In the last two decades, surfactant-based self-assemblies have been investigated with a great interest due to the wide variety of application of their nanostructures (Kaler et al. 1989; Kaler et al. 1992; Tondre and Caillet 2001). In 1989, Kaler et al. have reported that, when the catanionic single-tailed surfactants are taken at the right mixing ratio, they can

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Fig. 1 Confocal fluorescent images of single catanionic vesicles immobilized on a positive glass surface obtained by objective scanning at 20 °C. The image size is **a** 80 μm × 80 μm and **b** 30 μm × 30 μm. Adapted with permission from (J. Phys. Chem. B 2010, 114, 15506-15511). Copyright (2010) American Chemical Society
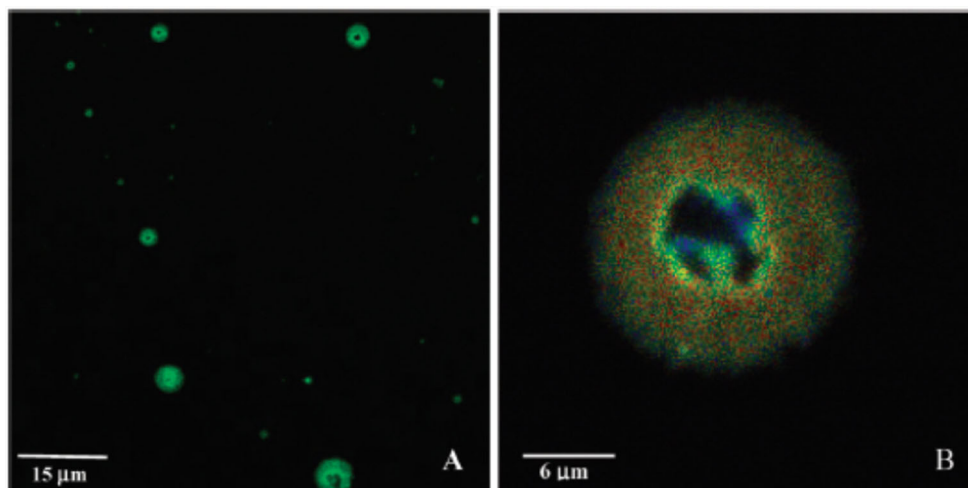
spontaneously form thermodynamically stable vesicles in aqueous solution through ion-pairing. Since then, the catanionic surfactant assemblies in aqueous solution have become a fascinating arena of investigation to understand the vital phenomenon in surfactant sciences, particularly for mixed surfactants in solution. The mixing ratio between the ionic amphiphilic surfactants can modify the charge of the aggregates as well the spontaneous curvature (i.e., packing parameter of surfactants) and gives rise to a broad range of aggregates such as micelles, mixed micelles (ribbons, disks, spheres, and elongated micelles), unilamellar or multilamellar vesicles, planar lamellar phases, etc. The morphology obtained from the self-aggregation of the surfactant molecules depend on the hydrophobic, electrostatic, and steric interactions between head groups and alkyl part of the surfactant molecules.

Surfactant/surfactant assembly

Commercially available, single-tailed anionic surfactant sodium dodecylbenzenesulfonate (SDBS) and cationic surfactant cetyl trimethylammonium tosylate (CTAT) spontaneously forms single-walled vesicles of controlled size. This vesicle formation is the result of the anion-cation surfactant pair formation which subsequently acts as a double-tailed zwitterionic surfactant (Kaler et al. 1989, 1992). Bhattacharyya group has performed confocal imaging for catanionic vesicle comprised of the anionic surfactant sodium dodecyl sulfate (SDS) and cationic surfactant dodecyltrimethyl ammonium bromide

(DTAB) (Dey et al. 2010). Confocal images of single fluorescent vesicles are recorded for a period of 40 min at 10-min intervals. It is found that the vesicles remain in the same position during this period which confirms that vesicles are immobilized on the positively charged glass surface and remain fixed during the experiment, shown in Fig. 1.

Ionic liquid (IL) and room temperature ionic liquid (RTIL)

Room temperature ionic liquids (RTILs) are organic salts composed of an organic cation and either an organic or an inorganic anion and melt at relatively low temperature with a conventional limit of 100 °C unlike the common organic salts, which melt at high temperatures. As the RTILs are composed of sterically mismatched ions, they melt at low temperature and remain as a liquid at the room temperature. Widely studied cationic components of the RTILs are imidazolium, pyridinium, piperidinium, pyrrolidinium, ammonium, and phosphonium derivatives, shown in Scheme 1 while $[BF_4]^-$, $[PF_6]^-$, $CF_3SO_3^-$, and $[(CF_3SO_2)_2N]^-$ are popularly used as anionic components. It is noteworthy that the properties of RTILs highly depend on their constituent ions, and thus, it is possible to prepare a RTIL of the desired property by simply tuning the cationic and anionic constituents. Therefore, RTILs are often called "designer solvent." As a result, they are commonly used in catalysis, electrochemical studies, and other chemical applications (Hallett and Welton 2011; Pârvulescu

Scheme 1 Cationic components of the RTILs

Imidazolium **Pyridinium** **Piperidinium** **Pyrrolidinium** **Ammonium** **Phosphonium**
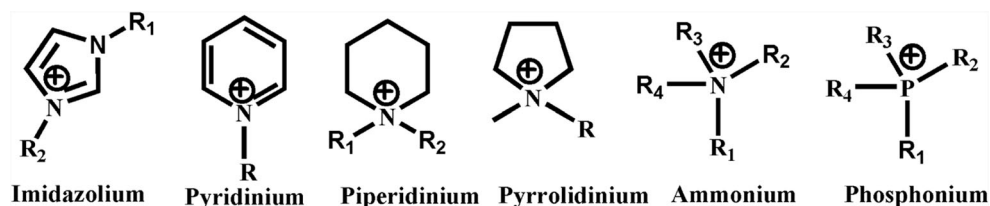
and Hardacre 2007; Bhattacharyya 2010). RTILs also have promising applications in the field of green chemistry due to their thermal and chemical stability (Earle and Seddon 2000). Moreover, RTILs possess unique physical and chemical properties like nonflammability, broad liquidus range, high thermal stability, low volatility, and thus exhibit a wide range of potential applications in industrial processing, chemical synthesis, and energy storage (Banerjee et al. 2013). Recently, researchers are interested in investigating various self-assembly formation using ILs or RTILs. The remarkable solvation ability of ILs facilitates their interactions with classical surfactants. Solvatophobic interactions between the hydrocarbon portion of the conventional surfactant and IL play the crucial role and guide the formation of surfactant micelles in presence of ILs and enhance the solvation characteristics of the (IL + surfactant) system.

Surface active ionic liquids (SAILs)

The ILs are occasionally termed as surface-active ionic liquids (SAILs) as they have combined properties of both conventional surfactants and RTILs. Generally, short chain containing ILs behave like ordinary inorganic salts. On the other hand, long hydrophobic alkyl chain containing ILs show amphiphilic nature, i.e., surface-active properties. Among the 1-alkyl-3-methylimidazolium family of cations, $[C_nmim]^+$, with varying alkyl chain length and different counterions, $[C_nmim]X$ with $n > 8$, $(X = Cl, PF_6, Tf_2N)$ can unambiguously form various aggregates in solution through the electrostatic and hydrophobic contributions of the isolated cation. Very interestingly, $[C_6mim]Cl$ is the transitional ionic liquid, which develops a monolayer at the aqueous solution-air interface but does not show any noticeable self-aggregation in the bulk fluid (Blesic et al. 2007). The structures of various cationic and anionic SAILs are shown in Scheme 2.

SAIL/surfactant assembly

Zheng group has compared the vesicles formed in the aqueous solution of conventional cationic surfactant DTAB and anionic surfactant SDS with the same chain length containing cationic SAIL 1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr) and SDS. C_{12}mimBr/SDS forms vesicular aggregates in aqueous solution due to the combination of both electrostatic and hydrophobic interactions. The oppositely charged head groups, C_{12}mim$^+$ and DS$^-$, forms ion pairs due to the strong electrostatic interaction and the C_{12}mim$^+$-DS$^-$ ion pair forms aggregates which develop into vesicles via hydrophobic interactions. Their study reveals that the variation of charge density and geometric packing of the head groups of the surfactants are the main differences between a conventional surfactant and an
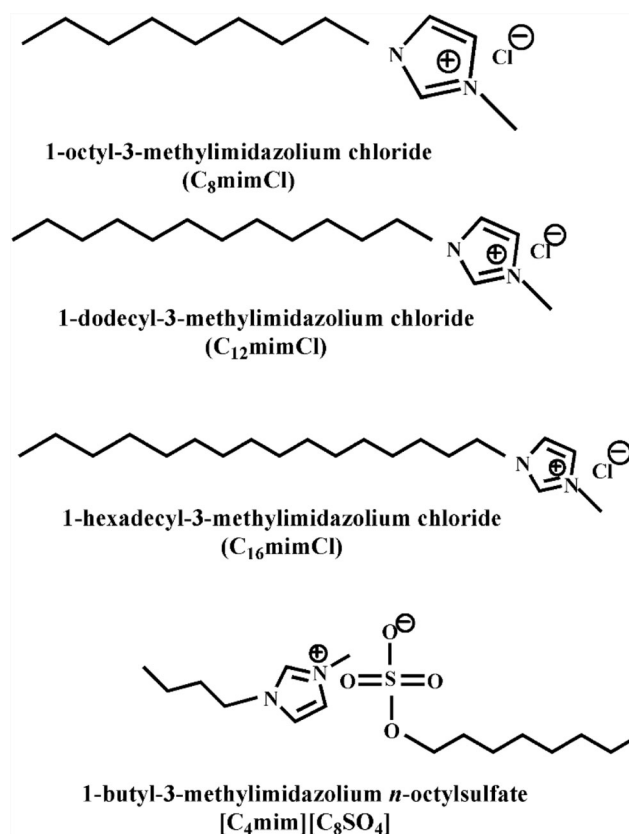
Scheme 2 Structures of different cationic and anionic SAILs

imidazolium cation-based SAIL of same chain length (Yuan et al. 2010; Dutta et al. 2017a). Cationic surfactant cetyl trimethylammonium bromide (CTAB) and anionic SAIL 1-butyl-3-methylimidazolium n-octyl sulfate, $[C_4mim][C_8SO_4]$ can form tiny micelles (~ 3 nm) in aqueous solution (Ghosh et al. 2013). Sarkar and co-workers have investigated the interaction between them and reported that cationic surfactant CTAB and the anionic SAIL $[C_4mim][C_8SO_4]$ can spontaneously form vesicles in aqueous solution. Here, the electrostatic interaction between sulfate and ammonium groups and also
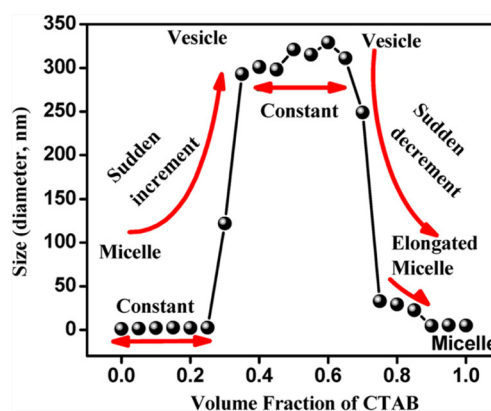

Fig. 2 Variation of size (diameter) of $[C_4mim][C_8SO_4]$/CTAB solution at different volume fraction values. Adapted with permission from (Langmuir 2013, 29, 10066-10076). Copyright (2013) American Chemical Society

Fig. 3 DLS intensity versus size distribution histograms of **a** [C$_4$mim][C$_8$SO$_4$] micelles, **b** mixed micelles ($\chi_{C_{12}mimCl}$ = 0.15), **c** mixed micelles ($\chi_{C_{12}mimCl}$ = 0.25), and **d** mixed SAILs that form vesicles ($\chi_{C_{12}mimCl}$ = 0.50). Adapted with permission from (Chemphyschem 2014, 15, 3544-3553)
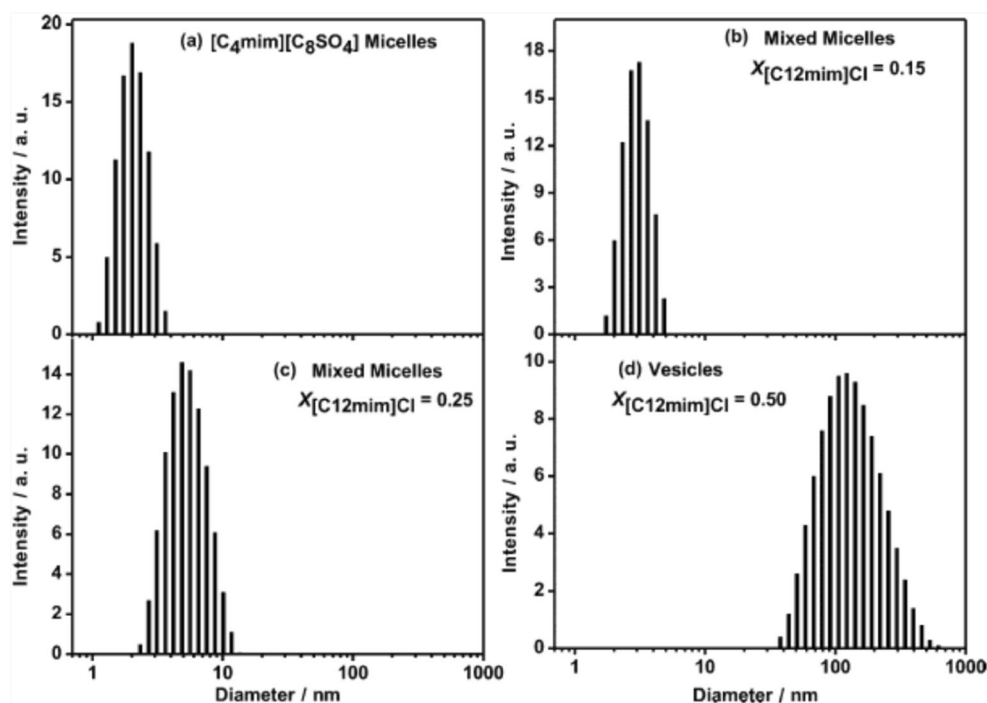
the hydrophobic interaction of alkyl chains of CTAB and [C$_4$mim][C$_8$SO$_4$] are the governing forces for the formation of vesicles. It is found that mixing in different volume ratios of [C$_4$mim][C$_8$SO$_4$] and CTAB can form stable micelles and vesicles. With increase in the volume fraction of CTAB, size of the aggregates increases and reaches a maximum in the range 0.4–0.6 volume fraction of CTAB and then again decreases as shown in Fig. 2.

Similarly, cationic imidazolium-based surfactant, 1-alkyl-3-methylimidazolium chloride (C$_n$mimCl; n = 12, 16) displays micelle-vesicle-micelle transition in presence of anionic surfactant, SDBS at different mole fraction of C$_n$mimCl. This study focuses on the impact of chain length of imidazolium-based SAILs in the micellar or vesicular aggregate formation. Very interestingly, it is found that at χ_{C_nmimCl} = 0.80, SDBS-C$_{12}$mimCl solution mixture mainly exists as vesicles whereas SDBS-C$_{16}$mimCl solution mixture forms mixed micelles. This report dictates that the incorporation efficiency of C$_{16}$mimCl in

SDBS micelle is higher than C$_{12}$mimCl due to the presence of relatively longer alkyl chain which results in stronger hydrophobic interaction. The main governing force behind the formation of these stable vesicles are the synergistic interaction between the cationic imidazolium moieties with the anionic sulfate group of surfactant and also the hydrophobic interaction between alkyl parts of the concerned pairs (Dutta et al. 2017a).

SAIL/SAIL assembly

Two oppositely charged SAILs, anionic ([C$_4$mim][C$_8$SO$_4$]) and cationic C$_{12}$mimCl, can also exhibit spontaneous micelle-to-vesicle transition at different mole fractions of the counterions (Mandal et al. 2014a). The head groups of SAILs show significantly stronger hydrogen-bonding interactions to the anionic counterparts due to the presence of acidic imidazolium hydrogen atoms. Therefore, the mixed SAIL

Fig. 4 TEM images of unilamellar vesicles of C$_{16}$mimCl-vitamin E (**a**, **b**). Adapted with permission from (J. Colloid Interface Sci. 2017, 501, 202-214)
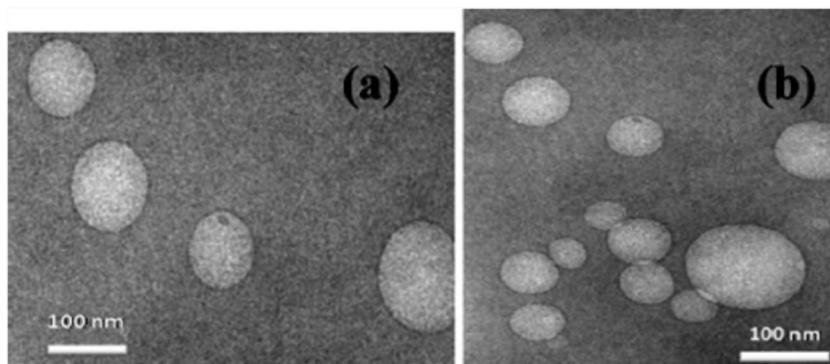
system ([C₄mim][C₈SO₄]/[C₁₂mim]Cl) exhibit considerably higher extent of synergistic interactions compared to the Na[C₈SO₄]/[C₁₂mim]Cl system or the mixtures of conventional catanionic surfactant mixtures. The dynamic light scattering (DLS) measurement reveals the micelle to vesicle transition and is shown in Fig. 3.

SAIL/biomolecules assembly

SAILs have drawn a significant interest in the field of chemistry and biology and can form various supramolecular aggregates in presence of various biomolecules. Cholesterol is an indispensable structural and functional constituent of animal cell membranes and controls the membrane fluidity and permeability. Cationic SAIL, C₁₆mimCl, forms micellar aggregate in aqueous medium and transforms into stable unilamellar vesicles upon increasing concentration of cholesterol (Mandal et al. 2014b). Vitamin E (tocopherols) is an essential vitamin for humans and a well-known fat-soluble antioxidant. Since vitamin E is soluble in lipid, it can directly affect the physical properties of lipid membranes. The effect of vitamin E on the morphology and phase behavior of cationic SAIL, C₁₆mimCl, is studied with the help of transmission electron microscopic technique, shown in Fig. 4. Therefore, vitamin E induces the C₁₆mimCl micellar aggregates to convert into unilamellar vesicular assembly (Roy et al. 2017).

Anionic DNA nucleotide adenosine-5′-monophosphate disodium (AMP) also forms supramolecular assembly. It is reported that the micellar aggregates of imidazolium-containing SAILs, C₁₂mimCl and [C₄mim][C₈SO₄], can transform into larger micellar assemblies interacting with anionic DNA nucleotide AMP (Roy et al. 2016a). Interestingly, the micellar aggregates of C₁₆mimCl convert to vesicular assembly with increase in the concentration of organic additive 5-methyl salicylic acid (5-ms). The C₁₆mimCl-5-mS aggregates slow down the dynamics of hydrophobic fluorophore compared to the C₁₆mimCl micelle whereas the totally opposite trend is found for the hydrophilic fluorophore. The C₁₆mimCl-5-mS containing vesicles can be transformed into micelles again upon increment of temperature and turbidity study confirms this, shown in Fig. 5 (Roy et al. 2016b).

Turbidity measurement reveals that nonionic surfactant sorbitan stearate (Span 60) can form vesicular aggregates when added to the micellar aggregate of C₁₆mimCl (Fig. 6). Sugar molecule trehalose can significantly enhance the size of the formed vesicular aggregates (Roy et al. 2016c).

It is reported that when the biomolecules (e.g., proteins, enzymes, and DNA) are combined with ILs, their structural and chemical utility significantly enhances. Biomolecule-friendly ILs are also designed which dissolves the biolmolecules with minimum alteration of structure (Sivapragasam et al. 2016). Coulombic interaction plays the dominant role for the
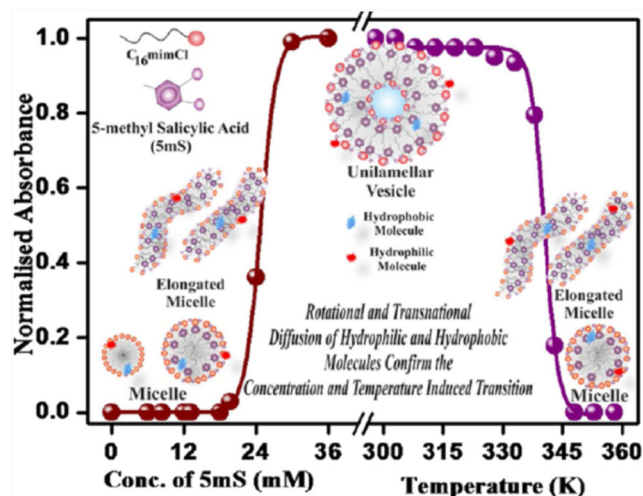

Fig. 5 Change in the turbidity of C₁₆mimCl-5-mS aggregates with change in the concentration of 5-mS and the temperature of the system. Adapted with permission from (Langmuir 2016, 32, 7127-7137). Copyright (2016) American Chemical Society

combination of ILs with biomolecules whereas the impact of hydrogen bond, steric effect, dispersion interactions also cannot be ruled out (Benedetto and Ballone 2016). Very recently, interactions between various imidazolium salts with bilayer membranes have been studied by Galla and co-workers. It is observed that long-chain containing salts can efficiently intercalate bilayers without disintegration, whereas shorter alkyl components disintegrate and lyse the bilayers (Drücker et al. 2017).

SAIL/dye assembly

After the replacement of the conventional surfactants by the SAILs to form the self-assemblies, researchers have further
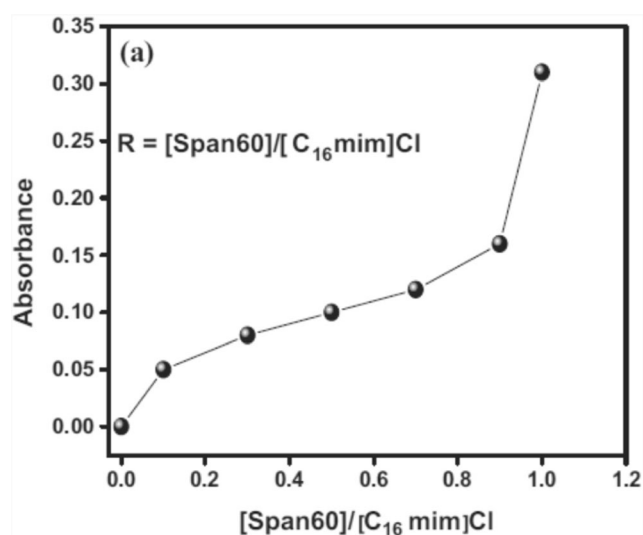

Fig. 6 Variation of turbidity of [Span 60]/[C₁₆mim]Cl at a fixed concentration of [C₁₆mim]Cl (0.02 M) with varying concentration of span60. Adapted with permission from (Chem. Phys. Lett. 2016, 665, 14-21)

Fig. 7 SEM (**a**, **b**) and CLSM (**c** (bright field), **d** (dark field)) images of giant vesicles formed by 0.5 mmol L^{-1} AO/ 0.5 mmol L^{-1} C$_{14}$mimBr. Adapted with permission from (Langmuir 2016, 32, 9548-9556). Copyright (2016) American Chemical Society

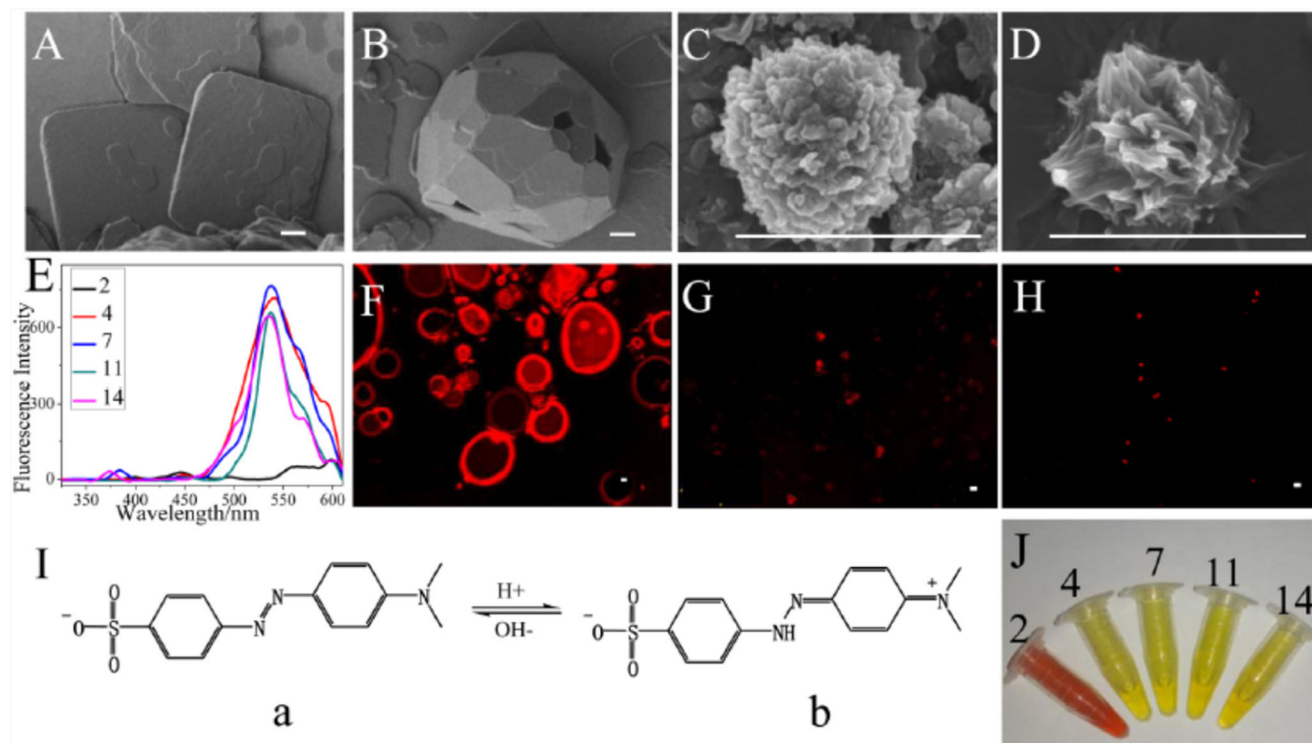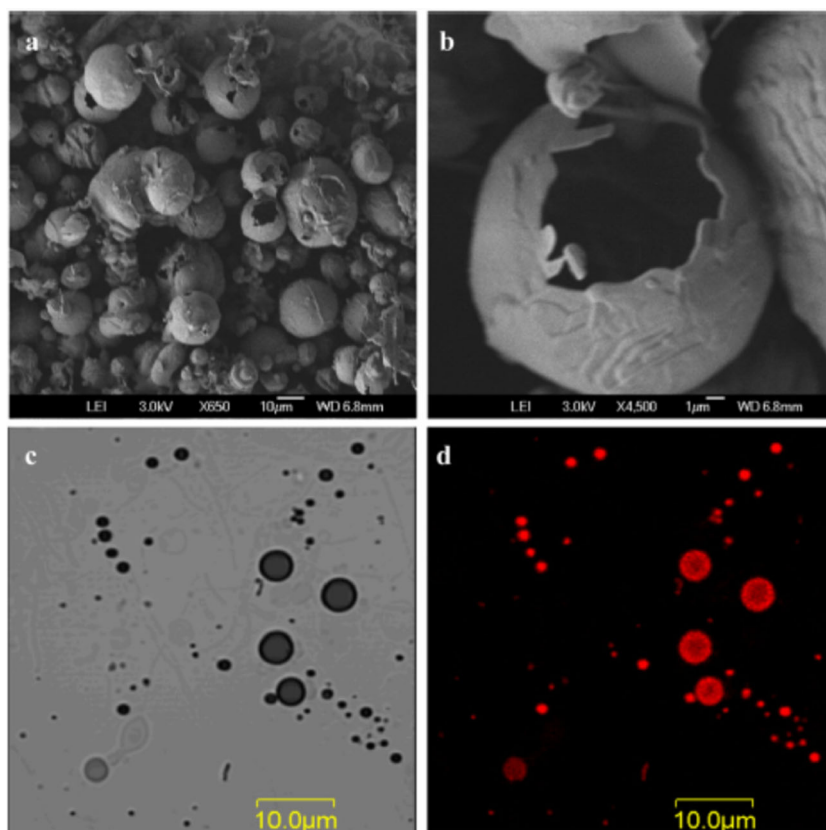**Fig. 8** SEM images of 0.5 mmol L^{-1} MO/C$_{14}$mimBr at different pHs: **a** pH = 2; **b** pH = 4; **c** pH = 11; **d** pH = 14. **e** Fluorescence spectra of 0.5 mmol L^{-1} MO/C$_{14}$mimBr at different pHs. CLSM images of 0.5 mmol L^{-1} MO/C$_{14}$mimBr at different pHs: **f** pH = 4; **g** pH = 11; **h** pH = 14. **i** pH-dependent mechanism of the MO molecule. **j** The digital photo of solutions at different pHs (scale bar = 2 μm). Adapted with permission from (J. Phys. Chem. C 2016, 120, 27533-27540). Copyright (2016) American Chemical Society

Fig. 9 FLIM images of the aggregates formed at **a** 20 mM MC 540/20 mM C$_8$mimCl, **b** 10 mM MC 540/10 mM C$_8$mimCl, **c** 5 mM MC 540/5 mM C$_8$mimCl, **d** 2 mM MC 540/ 2 mM C$_8$mimCl, and **e** 1 mM MC 540/1 mM C$_8$mimCl. Adapted with permission from (Langmuir 2017, 33, 9811-9821). Copyright (2017) American Chemical Society.
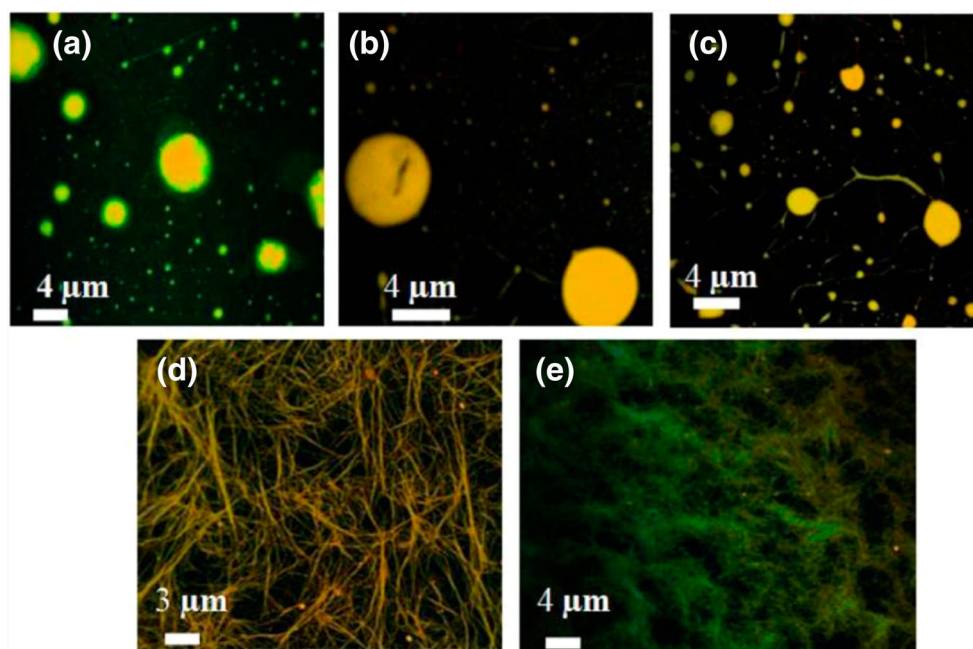
attempted to modify the building blocks of the aggregates. It is noteworthy to mention that dye molecules also can be a suitable candidate to form different assemblies with suitable surfactants or SAILs through ionic self assembly (ISA) strategy as the dye molecules have extended π-conjugation, regular shape, and various optical applications. Faul and Antonietti have studied dye-surfactant assemblies using a series of azo dyes with varying surfactant molecules (Faul and Antonietti 2002; Zakrevskyy et al. 2006; Faul 2014). The Yuan group has demonstrated that anionic dye Acid Orange II (AO) can form giant vesicles (1–10 μm) in presence of oppositely charged cationic SAIL 1-tetradecyl-3-methylimidazolium bromide (C$_{14}$mimBr) via ISA strategy (Shen et al. 2016b). Moreover, this is the first report of giant vesicle preparation using ISA strategy. This giant vesicle can retain the original vesicular morphology during the solvent evaporation and exhibits solid-like properties at low concentration, shown in Fig. 7. The electrostatic force of attraction, hydrophobic effect, and

π-π stacking interactions play the dominant role in this self-assembly process.

This prepared vesicular system can successfully load carbon quantum dots (CQDs) inside the assembly and also can exhibit its controlled release action. Another important application of these giant vesicles is their use as microreactor to synthesize Ag nanoparticles of ~ 5–10 nm size by the reduction of Ag$^+$ in the presence of ascorbic acid (Shen et al. 2016b). Similar to the previous study, a solid-like giant vesicle is prepared using ISA strategy employing cationic SAIL 1-tetradecyl-3-methylimidazolium bromide (C$_{14}$mimBr) and anionic dye methyl orange (MO) (Shen et al. 2016a). This synthesized giant vesicles show luminescent property due to the breakdown of intermolecular π-π stacking interaction of MO, which achieves the transformation from the aggregation-caused quenching (ACQ) process to aggregation-induced emission (AIE) by noncovalent interaction. The giant vesicular complex formed due to the interaction between MO and

Fig. 10 TEM microscopic images of vesicles formed by **a** [CTA][AOT] and **b** [BHD][AOT] ILs in water at 298 K. Adapted with permission from (J. Phys. Chem. B 2013, 117, 3927-3934). Copyright (2013) American Chemical Society
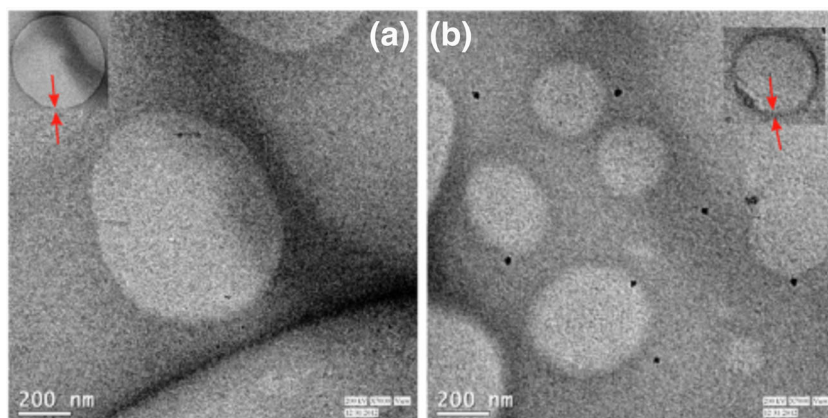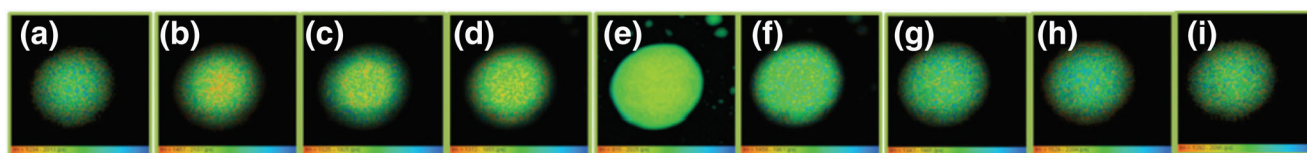
Fig. 11 FLIM Z stack recording of [C$_{16}$mim][AOT], excitation at 488 nm, emission above 495 nm. Z step width ± 5 μm; "e" is the optimum position. FLIM data format 256 × 256 pixels. Reproduced from Phys. Chem. Chem. Phys. 2016, 18, 14520-14530 with permission from the PCCP Owner Societies

C$_{14}$mimBr can exhibit pH-responsive properties and abundant thermic phase behavior. Different fluorescent structures (chrysanthemum, giant vesicle, polyhedron, peony-like structure) are attained when pH ≥ 4, whereas a nonfluorescent structure (microflake) is obtained when pH = 2, and this is due to the change of MO configuration, depicted in Fig. 8.

Therefore, long chain containing cationic SAILs can successfully construct supramolecular assembly like vesicular aggregates in presence of oppositely charged dye molecules through electrostatic, hydrophobic, and π-π interactions. With this background, Sarkar and co-workers have investigated the interactions using a series of cationic SAILs (C$_n$mimCl, n = 8, 10, 12, 16) and anionic lipophilic dye merocyanine 540 (MC 540) (Dutta et al. 2017b). Very interestingly it is found that among the SAILs, only C$_8$mimCl can exhibit a concentration-controlled vesicle-fibrillar aggregate transition interacting with MC 540. Fluorescence lifetime imaging microscopy (FLIM) technique along with other microscopic techniques reveal that at the higher concentration (10 and

20 mM) of both the building blocks, i.e., MC 540 and C$_8$mimCl, vesicular morphology is present. On the other hand, at lower concentration regime, i.e., 1 and 2 mM, fibrillar morphology prevails whereas at the intermediate concentration (∼ 5 mM) of both the building blocks, both the vesicular as well as fibrillar morphology are observed. The FLIM images at different concentrations are shown in Fig. 9.

This study unveils the synergistic interplay of electrostatic, hydrophobic, and π-π stacking interactions behind the formation of various self-assembly and their concentration-driven structural transition. In this context, it is noteworthy to mention that packing parameter (P) significantly controls these morphological alterations at various concentrations. At the higher concentrations, dye molecules form different higher order aggregates and show either hypsochromic shift (for H-aggregates) or bathochromic shift (for J-aggregates) in the steady state absorption spectra with respect to the monomeric peak. Very interestingly, [C$_n$mim][BF$_4$] (n = 4, 6) can control the J and H aggregation properties of different cyanine dyes
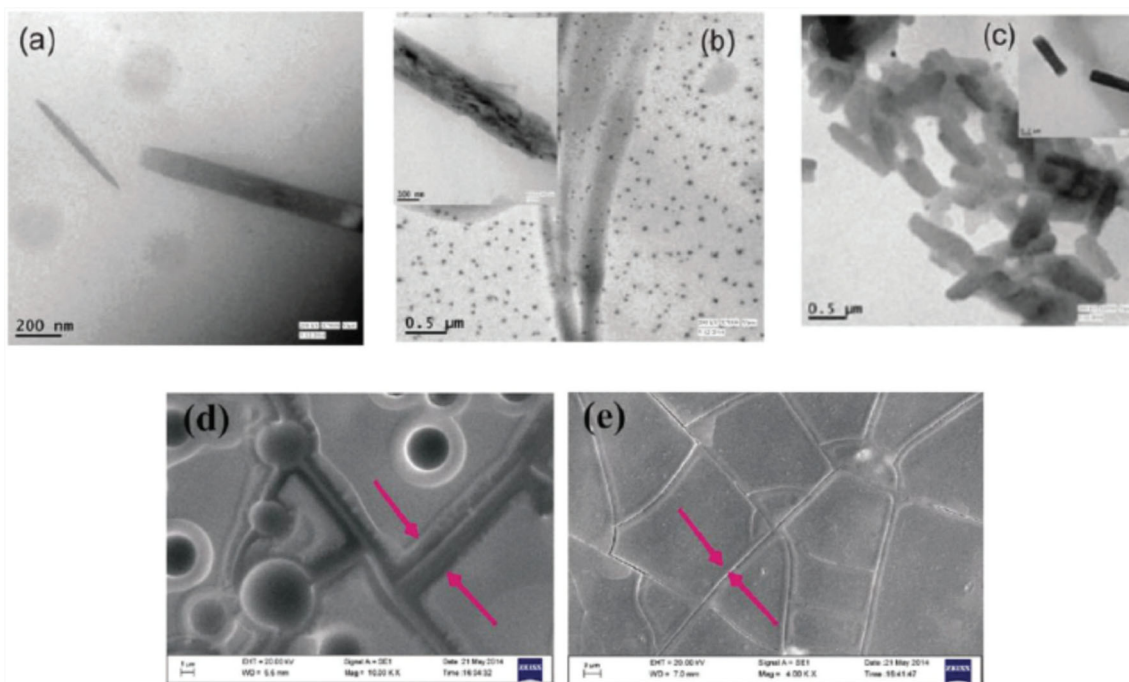
Fig. 12 TEM images of NaDC aggregates in the presence of **a** 1.12 wt% [bmim]-BF$_4$, **b** 1.68 wt% [bmim]-BF$_4$ (the inset shows a single rod-like structure and the scale length of the image is 200 nm), and **c** 11.2 wt% [bmim]-BF$_4$ (the scale length of the inset image is 0.2 mm). The SEM image of 20 mM NaDC **d** in the presence of 1.68 wt% [bmim]-BF$_4$ and **e** in the presence of 5.6 wt% [bmim]-BF$_4$. Reproduced from Phys. Chem. Chem. Phys. 2015, 17, 25216-25227 with permission from the PCCP Owner Societies

Fig. 13 FLIM images of OEA vesicle in the presence of 0.1 M Bmim-BF$_4$ collected in different time scales (time zero indicates the time when the image of the sample is started to record; it does not imply the startin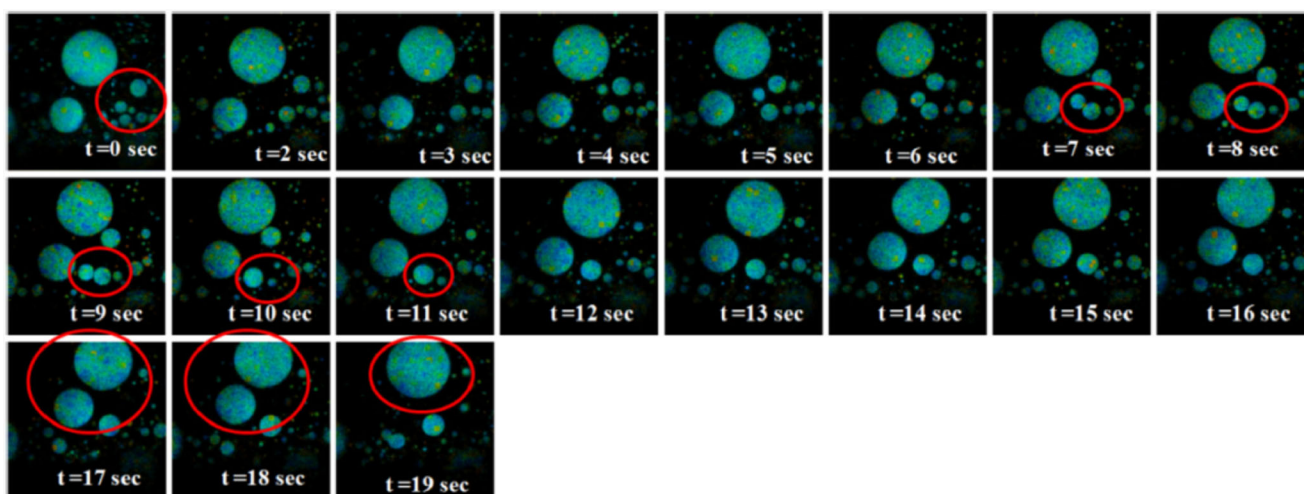g time of the reaction after addition of Bmim-BF$_4$ into the medium). Adapted with permission from (J. Phys. Chem. B 2017, 121, 8162-8170). Copyright (2017) American Chemical Society

(Kumar et al. 2011). The interaction among cationic SAIL 1-decyl-3-methylimidazolium chloride (C$_{10}$mimCl) and three structurally different calixarenes has also been studied in detail (Pandey et al. 2015).

Application of the vesicular assemblies

Drug delivery

Sarkar and co-workers have reported that when Na$^+$ ion of NaAOT (sodium 1,4-bis(2-ethylhexyl) sulfosuccinate) is replaced by a long chain containing cation, cetyl trimethylammonium (CTA) and/or benzyl-n-hexadecyldimethylammonium (BHD), it yields waxy solid IL [CTA][AOT] and [BHD][AOT] (Banerjee et al. 2013). Interestingly, these ILs can spontaneously form large unilamellar vesicles (LUVs) in water, depicted in Fig. 10.

New SAILs have been synthesized through the replacement of the Na$^+$ ion of NaAOT by the imidazolium ion containing ILs (C$_n$mimCl, $n = 8$, 12, 16) which produces [C$_n$mim][AOT] (Banerjee et al. 2016). The prepared SAILs are taken in buffer solution of pH 7.4 and subsequent sonication of the sample for 1–2 min produces the corresponding giant vesicles. The lifetime images (Z stack images) of the vesicle formed by [C$_{16}$mim][AOT] SAIL are shown in Fig. 11.

To improve the biocompatibility of the aggregates formed from SAILs, biologically relevant compounds (cholesterol and amino acid L-glycine) have been introduced. A novel class of cholesterol and amino acid (L-glycine) containing SAIL ([Chol-Gly][AOT]) has been synthesized which forms vesicular assembly in water. This amino acid functionalized cholesterol, Chol-Gly, is cationic in nature at low pH. Therefore, this is used to replace Na$^+$ ion of NaAOT by simple ion exchange

mechanism to produce the desired SAIL. Designing of new SAILs from biologically relevant compounds provide more physical insight into the understanding of vesicles. These vesicles can potentially serve as good biomimicking models, and therefore, various processes occurring in biological molecules entrapped in biomembranes can be monitored. These types of aggregates also have the application as suitable drug carriers (Pyne et al. 2017). Giant vesicles have potential biological as well as biomedical application (Banerjee et al. 2016).

Effect of IL/SAILs on various self-assemblies or nanoaggregates

The cyclodextrins (CDs) are formed by bacterial digestion of cellulose. These CDs are natural products and can be classified into α-CD, β-CD, and γ-CDs where the number of glucose units is 6, 7, and 8, respectively. Addition of SAIL C$_{12}$mimCl disrupts the aggregated nanostructures of γ-CDs (cyclodextrins) due to the inclusion complex formation between γ-CD and SAIL whereas relatively shorter hydrophobic alkyl chain containing SAIL, 1-octyl-3-methyl imidazolium chloride (C$_8$mimCl), cannot exhibit such transition and reveals the importance of hydrophobicity of the alkyl chain length of SAILs in inclusion complex formation (Kuchlyan et al. 2014). Kundu et al. have reported that hydrophilic IL, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]-BF$_4$), can influence the aggregation properties of a biological surfactant, sodium deoxycholate (NaDC). At the low concentration of IL, NaDC reorganizes to form an elongated rod-like structure. However, with the further addition of IL, the aggregated network structure gets disintegrated to form small aggregates, shown in Fig. 12 (Kundu et al. 2015).

Popular imidazolium-based hydrophilic IL, BmimBF$_4$, can influence the morphology of protic ionic liquid of fatty acid

(oleate ethyl amine, OEA) based vesicle. OEA vesicle is considered as a model membrane system. In the presence of IL, vesicles exhibit fusion kinetics, and the observation is analyzed using time scan FLIM measurements (Fig. 13). The main reason behind the swelling of the vesicle is the strong electrostatic as well as hydrophobic interaction between the IL cation with the bilayer of vesicle. Cis-trans isomerization process of anionic membrane binding fluorophore Merocyanine 540 (MC 540) is utilized to determine the membrane fluidity. IL-induced perturbation on cell membrane mainly governs the underlying principle of IL cytotoxicity. This study is highly important to design novel biocompatible and nontoxic ILs (Kundu et al. 2017a, b).

Protein aggregation or amyloid fibril formation causes a wide range of neurological disorders to humans such as Parkinson's, Alzheimer's, Prion, Huntington's, and type 2 diabetes diseases. Oligomeric protofibrils are the primary toxic species compared to the mature fibrils and therefore to inhibit or disrupt this protein aggregation in the initial stages itself different approaches have been made by the researchers. Very recently, it is found that SAILs are also efficient members for the inhibition of fibrillar aggregates due to hydrophobic as well as electrostatic reason. Three cationic SAILs (C_8mimCl, C_{12}mimCl, and C_{16}mimCl) have been exploited to study their effect on the bovine serum albumin (BSA) and human serum albumin (HSA) fibrillar aggregates. It is found that the inhibitory efficacy of C_{16}mimCl is considerably greater compared to C_8mimCl and C_{12}mimCl due to the presence of relatively longer hydrocarbon chain (Kundu et al. 2017a, b).

Different microemulsion preparation

Besides the use in the improvement of aggregation behavior of various micellar assemblies, RTILs have been extensively used in various aqueous and nonaqueous microemulsion formation (Eastoe et al. 2005; Kuchlyan et al. 2016).

Concluding remarks The governing forces behind the formation of different SAIL-based self-assemblies are quite well understood. Vesicular assemblies formed by the interactions between the counterions have immense biological as well as biomedical applications.

Overview In the recent past, SAIL-based self-assemblies have been extensively studied over the oppositely charge surfactant-based assemblies due to the certain advantages of SAILs over surfactants. Moreover, dye-SAIL-based assemblies have emerged as a new research area as some benefits are provided by the dye molecules when employed as a building block of self-assemblies.

Compliance with ethical standards

Conflict of interest Rupam Dutta declares that he has no conflict of interest. Sangita Kundu declares that she has no conflict of interest. Nilmoni Sarkar declares that he has no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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