

Catanionic and Chain-packing Effects on Surfactant Self-Assembly in the Ionic Liquid Ethylammonium Nitrate

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ABSTRACT

Hypothesis

Micelle formation, particularly the formation of compact, globular micelles in the high ionic strength environment of an ionic liquid, seems to be at odds with the principle of opposing forces and the concept of the surfactant packing parameter. Here we examine how interactions between polar head-groups, with solvent ions, and chain packing affect self-assembly structure in ionic liquids.

Experiments

The self-assembly of pure cationic and anionic surfactants, their catanionic mixtures, and the effect of the cosurfactant tetradecanol in the ionic liquid ethylammonium nitrate (EAN) is investigated by small-angle neutron scattering (SANS).

Findings

The critical micelle concentrations of cationic surfactants are much higher and micelles much smaller in EAN than in water, whereas anionic micelles are less dramatically affected. Catanionic surfactant mixtures form small micelles in EAN at all compositions, unlike their counterparts in water which form vesicle dispersions or precipitates near 1:1 mole ratios. This contrasts with the behavior of cationic surfactants when mixed with double-chained analogs or alkanol cosurfactants, which induce micelle growth and shape transitions to rod-like and bilayer aggregates through chain packing effects similar to aqueous systems. This enables the aggregate morphology in the ionic liquid to be controlled through the composition of the surfactant mixtures.

Keywords: catanionic surfactant; ionic liquid; mixed micelle; cosurfactant; neutron scattering

Introduction

Ionic liquids (ILs) – salts that melt at low temperatures – have been the subject of investigation as substitutes for molecular solvents due to their low vapour pressures,[1, 2] combined with their efficacy as solvents for a wide range of organic and inorganic solutes. Many ILs promote the self-assembly of both ionic and nonionic surfactants into micelles, microemulsions, and a variety of lyotropic liquid crystals.[3-10] These self-assembly structures and formulations have shown potential for a diverse range of applications including synthesis of mesoporous solids,[11, 12] polymer particles[13] and membranes[14], inorganic nanoparticles,[15] drug delivery,[16] and solvent extraction.[2]

The first IL shown to support surfactant self-assembly was ethylammonium nitrate (EAN), which has a dense, three-dimensional H-bond network reminiscent of water, making it an ideal candidate to exhibit a solvophobic effect, and for examining surfactant self-assembly.[17-19]

Ionic surfactants form similar micelles in EAN as they do in water, albeit with higher critical micelle concentrations (CMCs) and lower aggregation numbers.[6-8, 10, 20-23] This itself is contrary to expectations, as in water the high ionic strength leads to lower CMCs and larger, less-curved micelles.[24-26] In EAN the high CMC is attributed to a weaker solvophobicity in comparison to water,[3, 5, 6, 27] but the very existence of compact globular micelles of ionic surfactants in EAN and other ILs remains anomalous. In a conventional view of micelle shape based on the surfactant packing parameter,[28] high ionic strengths should decrease the head group area by screening head-group repulsions[29] so that cylindrical micelles or even bilayers would result. Also surprising is the observation that micellization of cationic surfactants depends on the identity of the counterion,[6] even in the presence of swamping amounts (~12 M) of nitrate from EAN. This prompts us to ask what surfactant packing constraints determine the micelle structures in ILs?

In water, strong electrostatic attractions between anionic and cationic surfactants causes a synergistic, catanionic effect which significantly lowers the CMC and leads to the formation of vesicles.[30-

34] Close binding of oppositely charged headgroups produces a pseudo double-tailed surfactant with reduced head group area,[31] which increases the surfactant packing parameter such that planar structures are formed, even if spherical micelles are present in solutions of the individual surfactants.[28, 35] Fine-tuning of self-assembly structures can be achieved by altering the type and ratio of ionic surfactants, temperature, and electrolyte concentration.[32, 36-39] Bulk equimolar mixtures of cationic and anionic surfactants often yield a precipitate,[31, 32, 40] but when one of the surfactants is in excess, a slight charge accumulates on the cationic vesicles resulting in electrostatic stabilization of a vesicle dispersion.[31, 36, 38] Typically, addition of salt destabilizes cationic vesicles. This is attributed to the salt screening intra- or inter-vesicle electrostatics leading to the formation of planar lamellar sheets,[32] which may then collapse. Added salt can bind to the surface of the vesicle resulting in the aggregate composition shifting away from 1:1 and towards that of the bulk, so that mixtures containing an excess of cationic or anionic surfactant form micelles.[41-45]

Vesicle formation through the cationic effect has also been reported in several nonaqueous molecular solvents,[46] but not in ILs. Phospholipids form vesicles in EAN and other protic ILs,[47] as do conventional double-chained cationic surfactants such as didodecyldimethylammonium bromide (DDAB) in EAN.[3-10]

In this work we examine the self-assembly structures formed by a range of ionic surfactants and their mixtures in EAN by small-angle neutron scattering (SANS). We investigate the structure in mixed systems, comparing head-group interactions in cationic mixtures with the effects of chain packing in mixtures with tetradecanol and a double-chained surfactant, in order to understand and control the factors that determine self-assembly structures in EAN. Achieving control over aggregate morphology is an important step in bringing self-assemblies in ILs closer to potential applications.

Materials and Methods

EAN was prepared by reacting equimolar amounts of nitric acid (Ajax Finechem, 70%) with ethylamine (Sigma-Aldrich, 70%) to produce an aqueous solution, as previously described.[23] Excess water was removed by rotary evaporation followed by freeze-drying. Karl Fischer titration was used to ensure water removal to below 1 wt% and nuclear magnetic resonance (NMR) was used to confirm EAN formation, which was stored under dry conditions. Deuterated d_3 -EAN ($C_2H_5ND_3NO_3$) for SANS was made by repeated washing with D_2O , followed by extensive drying, as above. Successful exchange was confirmed by NMR.

Tetradecylpyridinium chloride (TDPCl) and tetradecylpyridinium bromide (TDPBr) were synthesized as previously described.[48] Dodecylpyridinium chloride (DDPCl), hexadecylpyridinium chloride (HDPCl), octadecylpyridinium chloride (ODPCl) and didodecyldimethylammonium bromide (DDAB) were obtained from Aldrich and used as received. Tetradecanol (Fluka, 95%) sodium dodecylbenzenesulfonate (SDBS) (Tokyo Chemical Industry, 95%), and sodium dodecylsulfate (SDS) (Sigma Aldrich, 98%) were used as received. The chemical structures of all compounds are shown in Figure 1.

Isothermal penetration experiments were performed as previously described[5, 49, 50] to examine lyotropic phase formation over a wide range of concentrations. Briefly, a small amount of surfactant, approximately 40 μm thick, was placed between a microscope slide and a coverslip. A drop of EAN was placed on the outer edge of the coverslip and was drawn in by capillary action. This creates a concentration gradient from pure EAN to pure surfactant. Polarising optical microscopy was used to identify phases formed across this concentration gradient based on optical signatures.[51] The microscope stage is accurate to ± 0.1 $^{\circ}C$ and was heated from room temperature to 353 K to examine phase changes with temperature.

Small-angle X-ray scattering (SAXS) was performed on an Anton-Paar SAXSess with point collimation using 1 mm quartz capillary cells at 25 °C.

Samples for SANS were prepared by mixing stock solutions of the pure components in d_3 -EAN, maintaining a constant total surfactant concentration of 190 mM with the ratio of the component surfactants varying as follows: 1:0, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 0:1. The following combinations of surfactants were examined at 25 °C TDPCl + SDBS, TDPCl + DDAB, TDPBr + SDBS, HDPCl + SDBS. Tetradecanol/TDPCl and SDS/TDPCl mixtures, which were insoluble at room temperature, were examined at 55 °C, well above their melting temperature.

Small-angle neutron scattering was performed on the above samples on the V4 instrument at HZB as described previously.[52] Sample-to-detector distances of 1 m, 4 m and 15.75 m were used with 6 Å neutrons for a combined q range of 0.003 - 0.4 Å⁻¹. Raw scattering patterns were reduced, radially averaged, and placed on an absolute scale using BerSANS,[53] and was analysed using SASView (Version 4.2.1, see <http://www.sasview.org/> for more information) to determine the best fit parameters and model structures for each data set. SASView fits include weighting for statistical uncertainty in the data. SANS data, including errors and models of best fit are shown in the Supplementary Information. Each scattering pattern was analysed using the standard models for homogenous spheres,[54] ellipsoids,[55] and cylinders,[55] yielding the dimensions, aggregation number, and CMC of each mixture of surfactants using the following equations.

$$V_{\text{Agg}} = I(0) / (S(0)\phi\Delta\text{SLD}^2) \quad (1)$$

Where V_{Agg} is the volume of the aggregates, $I(0)$ and $S(0)$ are the intensity and structure factor at $q = 0$ (where $S(0)$ was calculated from a hard sphere model, for details see the Supplementary Information), ϕ is the volume fraction of aggregates determined by a model of best fit and ΔSLD is the difference between the scattering length density of the surfactant and the solvent.[54, 56-58] From the

best-fit to an ellipsoid (or other shape), V_{agg} can also be calculated from the radii of curvature by $V_{agg} = 4\pi R_1 R_2 R_3 / 3$ (1'). V_{agg} was then used to calculate the aggregation number, N_{agg} :

$$N_{agg} = V_{agg} / v_{mol} \quad (2)$$

where v_{mol} is the average volume of a single surfactant molecule (where here as well as in all the following the counterions are not considered). For the purposes of these equations the molecular volume was based on just the tail component of the surfactants, using the equation described by Tanford:[59] $v_{mol} = x(27.4 + 26.9(n_C - 1)) \text{ \AA}^3$, where x is the number of chains and n_C is the number of carbons in the chain. In the case of mixtures the molecular volume was taken to be the average volume of each component, weighted for the molar composition of each surfactant mixture. The CMC was calculated from:

$$CMC = C_{Tot} - \phi / V_{mol} \quad (3)$$

Where C_{Tot} is the total concentration of the surfactant in the sample (always 190 mM), ϕ the volume fraction of aggregates and V_{mol} the molar volume of the surfactant.

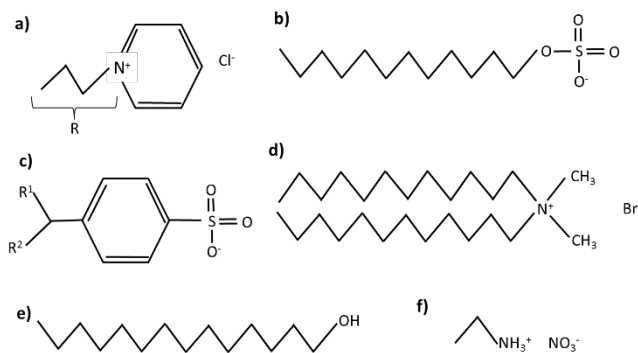


Figure 1. Compounds used in this work; a) alkylpyridinium chloride/bromide, $R = C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, or $C_{18}H_{37}$, b) sodium dodecylsulfate c) sodium dodecylbenzenesulfonate, $R^1 + R^2 = C_{12}H_{25}$, d) didodecyltrimethylammonium bromide, e) tetradecanol, f) ethylammonium nitrate.

Results and Discussion

Single Component Systems

Polarizing Optical Microscopy. Most of the cationic surfactants examined formed only hexagonal phases during isothermal penetration experiments, as shown in Table 1. A clear effect of alkyl chain length on phase formation of cationic surfactants is seen. DDPCl formed no lyotropic phases at room temperature. Increasing the tail length to TDPCl resulted in hexagonal phase formation at room temperature. Subsequent increases to the tail length caused an increase in the minimum temperature at which solid surfactant was swollen by solvent and formed a hexagonal phase (*i.e.* penetration temperature or chain-melting temperature). These observations are consistent with previous reports that HDPBr forms a hexagonal phase in EAN above 50 wt% and 30 °C,[22] and that ODPBr in EAN forms a hexagonal phase above 49 °C.[60] These trends in the phase behaviour of the cationic surfactants parallels previous reports for nonionic, poly(oxyethylene) n-alkyl ethers in EAN,[5] where the minimum alkyl chain length for lyotropic phases was C₁₄, and the penetration temperature increased with alkyl chain length, as it does in water.[61] DDAB has been reported previously to form a lamellar phase and vesicle dispersions in EAN.[3]

Changing the counterion from chloride to bromide stabilises the crystal and increases the transition temperature, but does not change the types of phase formed. This reveals stronger association of bromide with the surfactant aggregates, as is also reflected in the CMCs of cationic surfactant micelles in EAN.[6]

In contrast to the cationic surfactants, the anionic surfactants were not swollen by EAN and formed no lyotropic phases. SDS remained as insoluble crystals, whilst SDBS maintained its non-swelling lamellar structure (L_{β}) up to the maximum temperature of the microscope warming stage (55 °C). See Figure S1 for example microscope images.

Table 1. Minimum penetration temperature and lyotropic phase formed by isothermal penetration of surfactants by EAN between 23 and 55 °C.

	Temperature (°C)	Phases Observed
DDPCl	< 25	solution
TDPCl	< 25	hexagonal
TDPBr	< 25	hexagonal
HDPCl	32	hexagonal
HDPBr	37	hexagonal
ODPBr	43	hexagonal
DDAB		lamellar[3]
SDS	Up to 55	crystals
SDBS	Up to 55	non-swelling lamellar

Small-Angle Neutron Scattering. Figure 2 shows SANS patterns for 190 mM solutions of each surfactant in d_3 -EAN, together with best model fits to monodisperse micelle shapes. A structure factor was included in the modeling of both HDPCl and TDPBr to parameterise the correlation peak, but was not required for other systems. Note that the markedly higher intensity of TDPBr compared to TDPCl is not due to it forming larger micelles, but instead to a lower CMC (Table 2). DDPCl, which is below its expected CMC in EAN, exhibited no scattering above background (See Figure S2). Although many shorter alkanols are miscible with protic ILs,[62] tetradecanol is insoluble in EAN at 190 mM, and likewise evinces no structure. Key parameters from the fits are summarized in Table 2. In all cases, micelles are spherical or slightly eccentric ellipsoids. Aggregation numbers derived from both the forward scattering (Eq. 1) and geometric model fits (Eq. 1') are generally in good agreement.

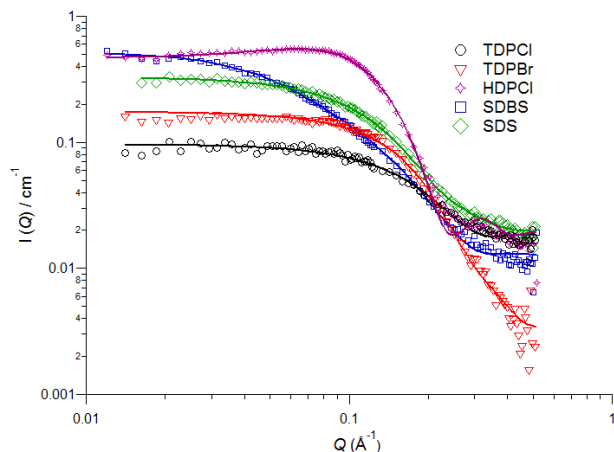


Figure 2. SANS data and fits for each of the pure surfactants at a total concentration of 190 mM in d_3 -EAN ($T = 25\text{ }^\circ\text{C}$). See Supplementary Information for complete set of fitting parameters.

Table 2. Solution parameters of pure surfactant systems from fitting to SANS patterns ($T = 25\text{ }^\circ\text{C}$).

Surfactant	Model	CMC (mM)	N_{agg} (eq. 1)	N_{agg} (eq. 1')	$R_1(\text{\AA})$	$R_2(\text{\AA})$
TDPCI	Sphere	163	27	21	13	-
TDPBr	Oblate Ellipsoid	131	22	20	8	16
HDPCI	Sphere	109	60	58	18	-
SDBS	Prolate Ellipsoid	134	104	105	57	12
SDS	Oblate Ellipsoid	114	41	39	7	20

Critical micelle concentrations of all surfactants are substantially higher in EAN than in water, consistent with previous studies.[1, 10] Significantly, there is also a difference between CMCs of cationic and anionic surfactants in EAN *versus* water; The CMC of SDS of 114 mM in EAN is 15 times higher than the 8.2 mM in water, whereas that of TDPBr (131 mM) in EAN is 50 times higher than in water (2.9 mM).[63] We have also previously reported the CMC of the nonionic surfactant $C_{14}E_4$ to be several hundred times larger in EAN than in water.[64]

Insight into the origin of these differences can be gleaned from the phase separation approximation. Here the free energy of micellization is parameterised into a solvophobic component of transferring the alkyl chain from EAN into the micelle core (ΔG_{chain}^o), the interfacial free energy ($\Delta G_{interface}^o$) which arises from the interfacial tension between the micelle core and EAN solvent, γ , and favours minimizing micelle surface area, and the effect of head group repulsion mediated by any counterions present ($\Delta G_{head-group}^o$) as[59, 65, 66]:

$$\Delta G_{mic}^o = RT \ln(CMC) = \Delta G_{chain}^o + \Delta G_{interface}^o + \Delta G_{head-group}^o \quad (4)$$

The differences in CMCs correspond to a 6.5 kJ mol⁻¹ smaller free energy of formation of SDS micelles in EAN than in water, compared to 10 kJ mol⁻¹ for TDPBr, and 15 kJ mol⁻¹ lower free energy of micellization for C₁₄E₄. This indicates that for aggregation in EAN the type of head group has a much larger effect than in water, where thermodynamics of assembly is largely dominated by the hydrophobic alkyl chain.

The solvophobic contribution to the free energy, whether determined from the solubilities of non-polar gases[10], the partitioning of nonionic surfactants,[67] or the alkyl-chain length dependence of the CMC,[10, 68] has been consistently found in EAN to be 50-60% of the value for water, and is independent of head group type. Here also increasing alkyl chain length from C₁₄ to C₁₆ lowers the CMC in EAN by about a factor of 3, which corresponds to an incremental free energy of transfer from EAN into the micelle core per -CH₂- of 1.6 kJ mol⁻¹, or about half the corresponding value in water.

Although the surface tension of EAN is much lower than that of water, the surface tensions of ionic and nonionic surfactants above their CMCs also differ only slightly,[10, 64] which means that differences in the interfacial contribution to the free energy of micellization are small. As this contribution also arises from interactions between alkyl tails and the solvent, but at the interface,[59] this is not surprising. This leaves only $\Delta G_{head-group}^o$ as a potential culprit for the marked differences in the CMCs of cationic *versus* anionic surfactants.

TDPBr forms oblate ellipsoids with principle radii of 8 Å and 16 Å, and an aggregation number of 20 – 22 in EAN above its CMC of 130 mM. These results are consistent within error with the values obtained by Evans *et al.* who reported a CMC of 100 mM, a hydrodynamic radius of 14 ± 3 Å, a hydrocarbon core radius of 11.8 Å, and an aggregation number at the CMC of 17 for TDPBr in EAN.[23] These micelle aggregation numbers and radii are much smaller than those of TDPBr in aqueous solution,[69] and the radii are also smaller than the length of a fully-extended tetradecyl chain (19 Å).[70] This is similar to the behavior seen for dodecyltrimethylammonium surfactants in EAN.[6]

SDS was also best fit by oblate ellipsoidal micelles. The SDS aggregation number of 40 in EAN is about double that of TDPBr, and very close to values reported in water at 55 °C.[71, 72] The much lower aggregation numbers of alkyipyridinium micelles in EAN compared to SDS suggests the amphiphilic ethylammonium cation, the *co-ion*, is incorporated into mixed micelles with the cationic surfactants. The presence of the ammonium cation would increase the average area per surfactant molecule, thus decreasing the packing parameter, and favour globular micelles in EAN.[23, 73, 74] In contrast, ethylammonium is the *counterion* for dodecylsulfate, so its binding screens head group repulsions; This will favour micellization and also head-group area, hence increasing packing parameter, so aggregation numbers are higher than for the TDPBr. For the same reason, SDBS forms prolate micelles, but with slightly larger aggregation numbers than in water.[75] As SDBS is a commercial mixture comprising benzenesulfonate substituted at various points along the dodecyl chain,[76] its packing geometry is less clearly defined than true single component systems.

TDPCl has a higher CMC than TDPBr and forms spherical micelles in EAN, which qualitatively corresponds to the known behaviour of the more weakly-binding chloride ion in aqueous solutions, and also parallels that of dodecyltrimethylammonium bromide and chloride in EAN.[6]

The SANS pattern of HDPCl also shows an interaction peak that is well-described by hard-sphere interactions. The best-fit sphere radius of 18 Å is larger than TDPCl, but still smaller than expected

for a fully extended hexadecyl chain. Aggregation numbers, calculated from both $I(0)/S(0)$ and micelle volume, are likewise larger than the tetradecyl analogue. As with the tetradecyl salts, HDPCl aggregation numbers are also larger than found by Evans *et al.* for HDPBr at its CMC.[23]

Catanionic Surfactant Mixtures Figure 3 shows SANS patterns for binary mixtures of TDPCl and SDBS at a total surfactant concentration of 190 mM. Full data sets for all catanionic mixtures, together with best fits and corresponding fit parameters, are provided in the Supplementary Information (Figures S3-S6, Tables S1-S4). Unlike catanionic surfactant mixtures in aqueous solutions where vesicles are often observed,[38, 77] (or at least a substantial change of packing parameter leading to the formation of wormlike micelles[78] in all cases SANS reveals the presence of compact micelles in EAN whose morphologies evolve smoothly between those of the pure components. Best-fit micelle shapes are summarized in Table 3, with detailed fit parameters provided in the Supplementary Information. In general, rather small micelles 3-4 nm size are observed with those containing SDBS being somewhat larger, as already the pure SDBS forms somewhat elongated micelles, but this elongation becomes systematically reduced in the mixtures (contrary to the situation in water where upon admixing an oppositely charged surfactant one typically observes further elongation). Apparently the packing parameter does not increase as in water due to synergistic interactions, but remains basically unaffected in EAN.

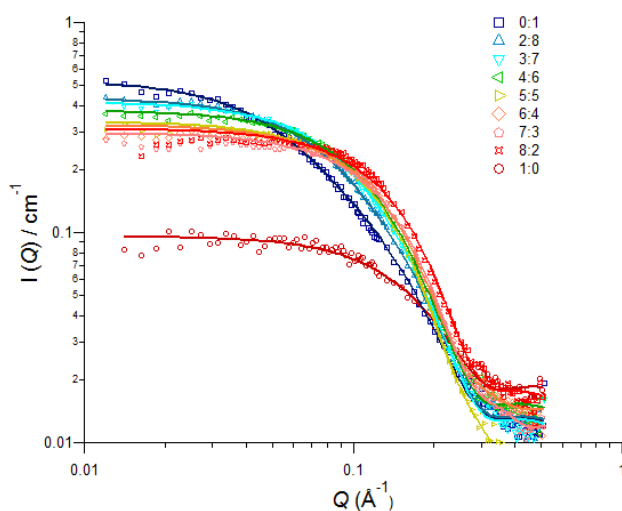


Figure 3. SANS data and fits for the mixing series of TDPCl (1:0, sphere fit) with SDBS (0:1, prolate ellipsoid fit) at a total concentration of 190 mM in EAN ($T = 25\text{ }^{\circ}\text{C}$). See Supplementary Information for fitting parameters.

Table 3. Summary of micelle shapes from models that yielded best fits for each surfactant mixture as a function of composition, represented as mole ratio cationic:anionic at a total surfactant concentration of 190 mM. Where more than one shape is shown it was not possible to discriminate between fits (based on χ^2).

	0:1	2:8	3:7	4:6	5:5	6:4	7:3	8:2	1:0
TDPCl:SDBS	Prolate	Prolate	Prolate	Prolate	Oblate	Oblate	Oblate	Sphere	Sphere
TDPCl:SDS	Oblate	Oblate/ Disk	Oblate/ Disk	Oblate/ Disk	Oblate/ Disk	Oblate/ Disk	Prolate/ Oblate/ Disk	Prolate/ Oblate/ Disk	Sphere
TDPBr:SDBS	Prolate	Prolate	Prolate	Prolate	Oblate	Oblate	Oblate	Oblate	Oblate
HDPCl:SDBS	Prolate	Prolate	Prolate	Oblate	Oblate	Sphere			Sphere
TDPCl:DDAB				Prolate	Prolate	Prolate			Sphere
TDPCl:tetra- decanol		Larger struc- tures		Ob- late/vesi- cle	Prolate			Pro- late/cyl- inder	Sphere

CMCs derived from SANS are shown as a function of the composition of the binary surfactant mixtures in Figure 4, together with predictions of ideal and regular solution theories.[79, 80] No dramatic, synergistic reduction in CMCs like that typically seen in aqueous catanionic mixtures is in evidence in EAN. This is consistent with the best-fits to SANS showing conventional micelles at all compositions.

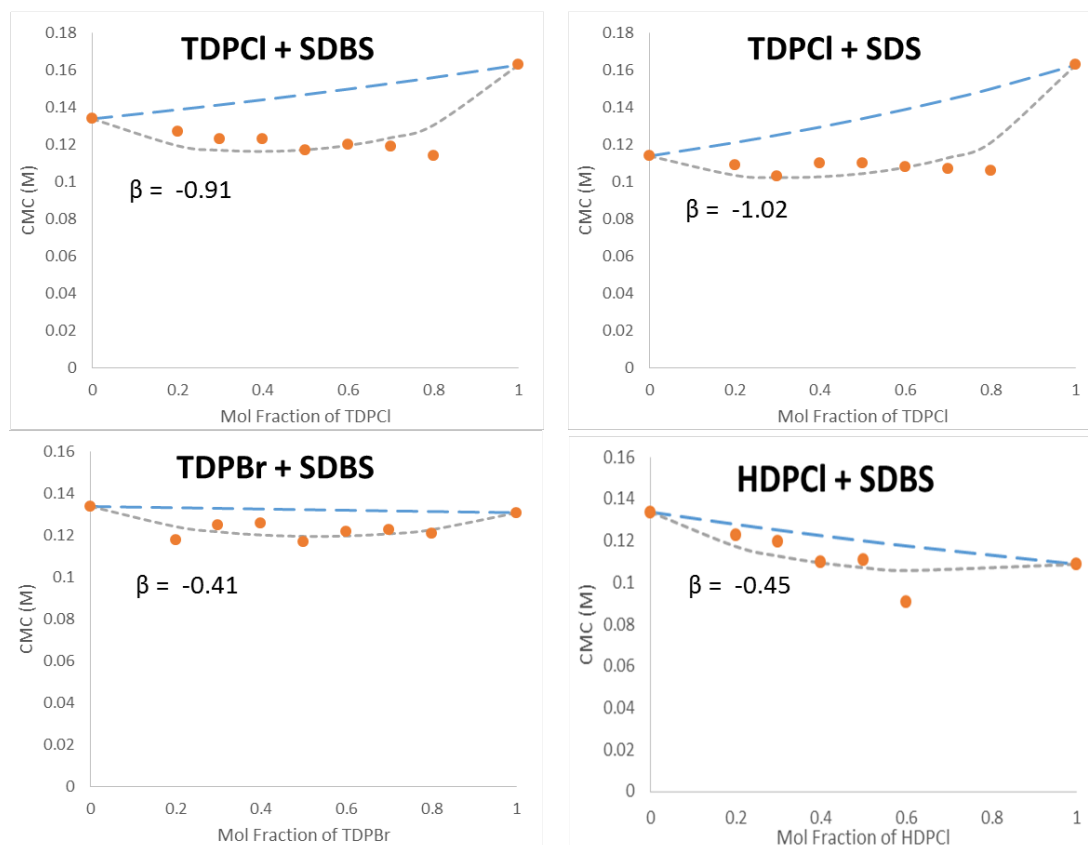


Figure 4. CMCs of cationic surfactant mixtures in EAN across a range of ratios, calculated from the models of best fit. Long dashed lines show predictions of ideal mixing theory and short dashed lines show predictions based on regular solution theory using the average β value for all mixed CMCs. Average β used is shown, with individual best fit β listed in Table S7. Uncertainties in the CMCs is <10% (Eq. 3).

Examined individually, these mixtures show modest synergism (SDBS+TDPCI and SDS+TDPCI), or near-ideal mixing (SDBS+TDPBr and SDBS+HDPCI). In the first two cases, the interaction parameter from regular solution theory, β , averages -1.0 and -0.9, respectively, but the locus of mixed CMCs are not well-described by regular solution theory using any single β value. In the near-ideal cases of SDBS+TDPBr and SDBS+HDPCI, average $\beta = -0.4$ and -0.45 , respectively. These small negative values are comparable to those found for ionic-nonionic surfactant mixtures in water.

Taken together, however, the CMC curves all share a single striking feature; The CMC of the mixture decreases as cationic surfactant content is increased, even if the CMC of the pure cationic is higher

than the anionic. This is also seen in β values calculated at each composition, which become more negative as the mixture is enriched in the cationic component (see Table S7). This supports the asymmetry in the micellization of cationic and anionic surfactants in EAN suggested above due to the amphiphilic character of the ethylammonium cation. In anionic surfactants we propose that the sodium counterion is effectively fully exchanged by ethylammonium, which acts as a cosurfactant or hydro-tropic counterion, and may even over-neutralise the anionic micelle charge due to solvophobic association. In cationic surfactants, there is more conventional competition between the nitrate of the solvent and the chloride or bromide counterions, which gives rise to a counterion dependence of the CMC. This is illustrated schematically in Figure 5.

Increasing cationic surfactant content in anionic micelles leads to ion exchange with ethylammonium and a monotonic decrease in mixed CMC until the positively-charged pyridinium groups are present in sufficiently high concentration to cause chloride or bromide condensation. It is also noteworthy that the effect of chloride or bromide counterion on CMC is only apparent in the pure cationic systems.

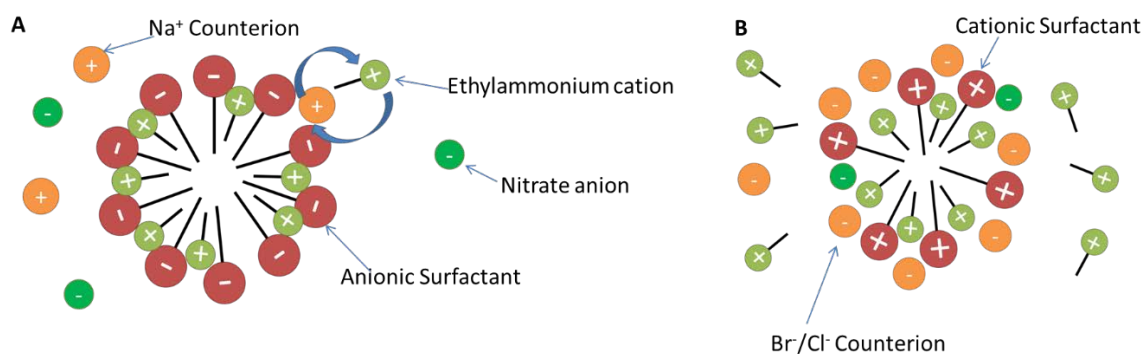


Figure 5. Schematic showing cosurfactant behavior of EAN with ionic surfactants. A) In micelles comprised of the anionic surfactant, the ethylammonium cation replaces the sodium counterion, facilitated by solvophobic association. B) In micelles comprised of cationic surfactant, more conventional competition occurs between the nitrate anion and the Br⁻/Cl⁻ counterion, but the ethylammonium cation remains solvophobically associated with the micelle.

Figure 6A shows the aggregation number of the catanionic mixed micelles, calculated from the intensity at $q = 0$ (equation 1). The aggregation number of all mixtures with SDBS decreases smoothly

from pure anionic to pure cationic surfactant, in agreement with the fact that we do not observe marked synergistic interaction in these surfactant mixtures. Only for the SDS/TDPCI mixture a slight maximum of the aggregation number is seen.

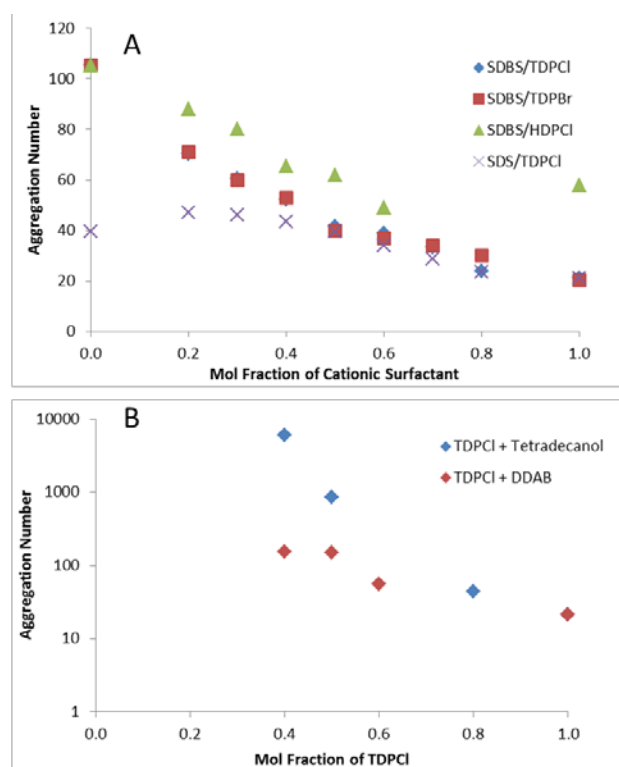


Figure 6. Aggregation number of micelles in EAN across a range of surfactant compositions, calculated using Eq 1'. A) alkylpyridinium halides + SDS/SDBS, B) TDPCI + tetradecanol or DDAB

Controlling Morphology through Alkyl Chain Packing It has long been known that self-assembly structure can also be altered by mixing conventional surfactants with cosurfactants[81] such as aliphatic alcohols or bilayer-forming, double chained surfactants.[82] Whereas the catanionic effect in aqueous solution is primarily due to decreasing the effective area per molecule, a_0 , through electrostatics, chain-packing increases the effective non-polar chain volume, v , with the same net effect of increasing the surfactant packing parameter, v/a_0l_c , and favouring cylindrical or bilayer-based structures over spherical micelles. As chain-packing effects are expected to be insensitive to solvent ionic strength, we have examined the effects of tetradecanol and didodecyldimethylammonium bromide (DDAB) on micelle formation and structure of TDPCI in EAN.

Tetradecanol is insoluble in EAN, and did not form any identifiable structures at 190 mM. Figure 7 shows the scattering data and best model fits for tetradecanol and TDPCl mixtures. As tetradecanol is added to TDPCl at a total concentration of 190 mM, spherical micelles are transformed first to eccentric, polydisperse ellipsoids and then elongated into cylinders with an aspect ratio of 10:1 at 1:1 tetradecanol:TDPCl mole ratio, corresponding to an aggregation number of 860 (see Figure 6B). Upon further increasing the tetradecanol content to 1.5:1, the scattered intensity exhibits a q^{-2} dependence over a wide angular range, consistent with a bilayer-like structure, well described by disklike micelles with a radius of ~ 200 Å and a thickness of ~ 28 Å. This fit to oblate ellipsoidal micelles yields an aspect ratio of approximately 14, indicating that tetradecanol can be incorporated as a cosurfactant into TDPCl micelles in EAN and cause a continuous transformation from spheres \rightarrow cylinders \rightarrow bilayers with continuously decreasing interfacial curvature. Further increasing tetradecanol concentration led to weak and poorly-defined low-angle scattering consistent with the formation of large structures (see Figure S7). We interpret this to be a dilute emulsion which forms as the tetradecanol begins to partition into the interior of the mixed TDPCl/tetradecanol bilayer. In general, tetradecanol behaves here as a cosurfactant in exactly the same way as is typically observed for the addition of medium chain alcohols to surfactants in aqueous solution, where for instance a similar sphere \rightarrow cylinder \rightarrow bilayer transition has been reported for the addition of hexanol to different mixtures of nonionic and cationic surfactant.[83]

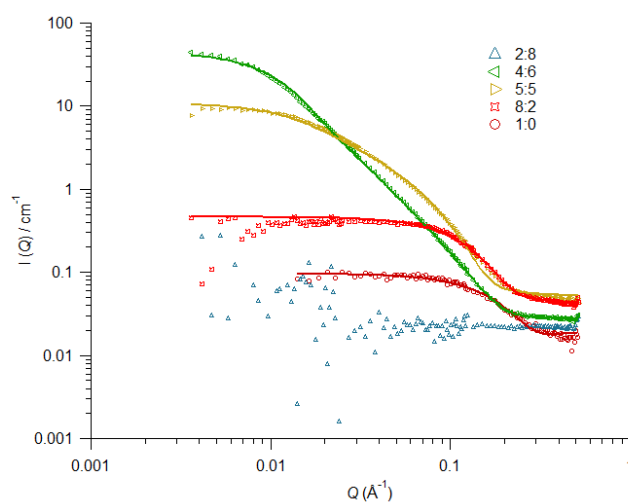


Figure 7. SANS data and fits for the mixing series of TDPCl (1:0, spherical fit) with tetradecanol at a total concentration of 190 mM in EAN ($T = 55\text{ }^{\circ}\text{C}$). See Supplementary Information for fitting parameters.

Addition of DDAB to TDPCl solutions at 190 mM total concentration shows a similar effect. Figure 8 shows scattering data together with models of best fit. DDAB causes micelles to transform from spheres into prolate ellipsoid or cylinders, also with an aspect ratio near 10:1 at 1:1 DDAB:TDPCl. At still higher DDAB there is again evidence for the presence of larger structures coexisting with micelles, consistent with the reported formation of vesicles by pure DDAB in EAN.[3] This means that here one can tune continuously the aggregate structure by the mixing ratio of the two cationic surfactants (in a similar fashion as observed in water for DDAB addition to dodecyltrimethylammonium bromide [82]). Here it is particularly noteworthy that one can enhance the aggregate size substantially in these mixtures, while typically self-assembly in ILs leads to rather small micellar aggregates.

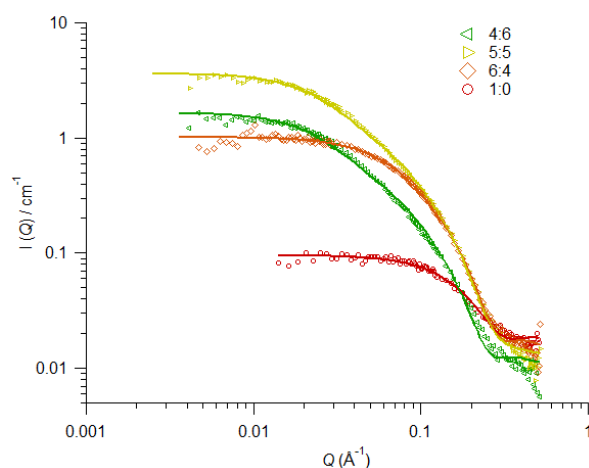


Figure 8. SANS data and fits for the mixing series of TDPCl (1:0, spherical fit) with DDAB (up to 4:6, ellipsoidal fit) at a total concentration of 190 mM in EAN ($T = 25\text{ }^{\circ}\text{C}$). See Supplementary Information for fitting parameters.

Conclusions

This study has shown how the morphology of micelles in the ionic liquid EAN can be controlled by changing the packing constraints of the surfactants through head-group and counterion, and by mixing surfactants and cosurfactants to alter interactions in the core or at the micelle surface.

Micelle formation by ionic surfactants in EAN differs from that in aqueous or electrolyte solutions in many ways.[22, 23, 60] CMCs of both cationic and anionic surfactants are much *higher* in EAN than in water (e.g. 114 mM in EAN vs 8.2 mM in water for SDS; 131 mM in EAN vs 2.9 mM in water for TDPBr). Like aqueous micelles, however, the CMC of cationic, alkylpyridinium surfactants decreases with increasing alkyl chain length. Despite the very high concentration of nitrate ions in EAN, the CMC is also lowered when the chloride counterion is replaced by the more strongly binding bromide (as seen previously for dodecyltrimethylammonium surfactants[6]). The nonpolar ethyl moiety on the cation of EAN causes an asymmetry in the micellization behavior of cationic *versus* anionic surfactants. Cationic surfactants have much higher CMCs and form smaller micelles than anionic surfactants with the same alkyl chain lengths due to the incorporation of ethylammonium as a co- or counter-ion, respectively, which then affects the effective head group area.

Catanionic surfactant mixtures form micelles in EAN at all compositions. Their interaction is only weakly synergistic, but interestingly shows marked ion specificity, being much more pronounced for Cl⁻ compared to Br⁻. Addition of salt to such mixtures has been shown to inhibit the synergistic catanionic effect in aqueous systems.[41, 42] The high ionic strength of EAN along with the association of the ethylammonium cation[10] stabilises small micelles at all cation:anion ratios, and prevents the formation of vesicles seen in aqueous solution.

Changing alkyl chain packing in micelles by incorporation of tetradecanol or DDAB follows aqueous solution behavior more closely. Uptake of both into cationic micelles decreases interfacial curvature and causes a sphere-to-cylinder-to-planar transition. Accordingly, in both cases one is able to tune

the aggregate structure over a wide structural range simply by the composition of the amphiphilic mixture. This is often not so simply the case for self-assembly in ionic liquids and therefore is a finding that extends the application potential of ionic liquids substantially, as aggregation numbers can become enhanced by a factor of more than 100 compared to the small spherical micelles formed by the pure surfactants.

Funding Sources

Australian Research Council; AINSE PGRA (SB);

Acknowledgements

This work was supported by an Australian Research Council Discovery Grant, and UA/DAAD exchange funding. SB thanks AINSE for a PGRA and The University of Sydney for the Joan R. Clark Scholarship. The authors thank Ms Miriam Simon for assistance with the SANS experiments, and thank HZB for the allocation of neutron radiation beamtime.

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