A thermally reversible vesicle to micelle transition driven by a surface solid–fluid transition

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This study presents evidence for a vesicle to worm-like micelle transition in solutions of a new surfactant cetyltrimethylammonium hydroxynaphthalenecarboxylate (CTAHNC) driven by a possible coulombic solid–fluid transition on the micellar surface.

In this report we present the experimental results on solutions of a new surfactant CTAHNC. Earlier we reported[1] the observation of strong viscoelasticity in solutions of cetyltrimethylammonium bromide (CTAB) on addition of sodium 3-hydroxynaphthalene-2-carboxylate (SHNC). This mixed system had very different properties from that of well studied CTAB + sodium salicylate (SS) solutions[2] and this led us to investigate the single surfactant CTAHNC which is a salt of CTAB and SHNC in the absence of NaBr.

Turbid dispersions of CTAHNC were prepared in water in various concentrations by heating to *ca.* 90 °C for homogenization and cooling to room temperature. For solutions $>3\%$ (m/m) CTAHNC concentration birefringence was observed and it was concluded that these solutions consisted of lamellar dispersions on the basis of polarized microscopic observations of spherulettes. These solutions became clear on heating to well defined temperatures and the transition from turbid to clear solutions was reversible. Of particular importance was the observation that these turbid solutions, on heating to optical clarity, became highly viscous and strongly viscoelastic. Fig. 1(*a*) shows the intensity of the light scattered by a 0.6% m/v optically isotropic solutions of CTAHNC at an angle of 90° and also the viscosity [Fig. 1(*c*)] as a function of temperature. Since these viscoelastic solutions are non-Newtonian fluids, rheometric studies were carried out using a Rheometrics Fluid Spectrometer RFS II at various shear rates, and Fig. 1(*c*) shows the viscosity at a shear rate of $0.1\ s^{-1}$. It can be seen that the viscosity increases by two orders of magnitude as the solution became clear.

We suspected the possibility of vescile formation in the turbid solutions and a 0.6% m/v solution at room temperature was viewed using a JEOL Cryo-SEM instrument and the freeze-fracture technique was employed to confirm the presence of vesicles (diameter $\approx 5\ \mu m$). We also attempted to deposit platinum on these vesicles by precipitating Pt in solutions containing vesicles. The platinum-deposited samples were also viewed under the electron microscope at room temperature.

On heating to clarity, these solutions became strongly viscoelastic and we suspected the formation of giant worm-like micelles. We performed NMR experiments using 300 MHz FT NMR Varian spectrometer equipped with a variable temperature probe.

Fig. 2 shows the temperature dependence of the ^1H NMR spectrum of CTAHNC in the range 30–75 °C. Fig. 2(*a*) shows the HNC^- region and 2(*b*) the CTA^+ region. It is clearly seen that the spectrum of the HNC^- region at 30 °C covers a wide chemical shift range and is solid-like. On heating only *part* of the spectrum narrows down, in spite of increase in viscosity, indicating asymmetric hindered rotation of only some of the groups in the molecule. Such effects are known in CTAB–SS systems and have been ascribed to axial rotation of SS on the micellar surface[3] which indicates the *non-isotropic* fluid nature of the surface of micelle in this class of system. Presumably the presence of the naphthalene ring in CTAHNC pushes the system towards a more solid-like surface. Only at 75 °C does the spectrum start to show signs indicating comparatively free movement of the HNC^-. The CTA^+ spectrum changes smoothly (in comparison to HNC^-) from extremely broad lines, indicating the possibility of solid-type packing at room temperature, to a standard type of narrower lines characteristic of worm-like micelles. This seems to suggest that we have a transition from solid-like micelles to fluid micelles. This view is further supported by the fluorescence anisotropy of the HNC^- ion shown in Fig. 1(*b*); variation of this occurs in the *same* temperature range as the vesicle to worm-like micelle transition during which the mobility of the HNC^- group increases drastically. The fluorescence anisotropy of freely rotating HNC^- ions at room temperature in a solution in the absence of CTAB is shown [point ○ in Fig. 1(*b*)]. It is evident that only above 60 °C does the mobility of the ion on the CTAB micelle surface approach that of the free ion. This strongly suggests the possibility that the melting of the ionic surface of vesicle, covered by CTA^+HNC^- pairs, drives the vesicle–micelle transition. It can be seen intuitively that a *bound* CTA^+HNC^- pair with effectively two hydrophobic portions acts like a *lipid* and has a tendency to form vesicles while each of the ions containing single chains act like detergents, with a tendency to form micelles, therefore one should naturally expect a transition from a vesicle to micelle on heating. This analogy with lipid–detergent mixtures, investigated in the literature,[4] suggests that vesicle-to-micelle transitions should also be induced by detergent additives to CTAHNC solutions at room temperature. This has been confirmed by addition of Triton X-100, SHNC and CTAB. These arguments and evidences suggest the emergence of a new and interesting point of view that the coulomb correlations between the two ions within the two-dimensional surface, which can be modelled quantitatively,[5] could lead to changes in the bend elastic constants of the surface and induce supramolecular transitions.[6] Preliminary calculations performed seem to support this point of view.[7] Electric birefringence and small-angle neutron scattering performed on this system also indicate a vesicle-to-micelle transition[8] and details will be published separately. This point of view is also consistent with the reported observation of vesicles in mixed anionic–cationic surfactants[9] and also rationalizes the several observations of double peaks in zero-shear viscosity in a number of systems.[2,10]

In summary we conclude that in solutions of mixtures of cationic–anionic surfactants, one has situations where the head-group regions are solid-like and the resulting supramolecular

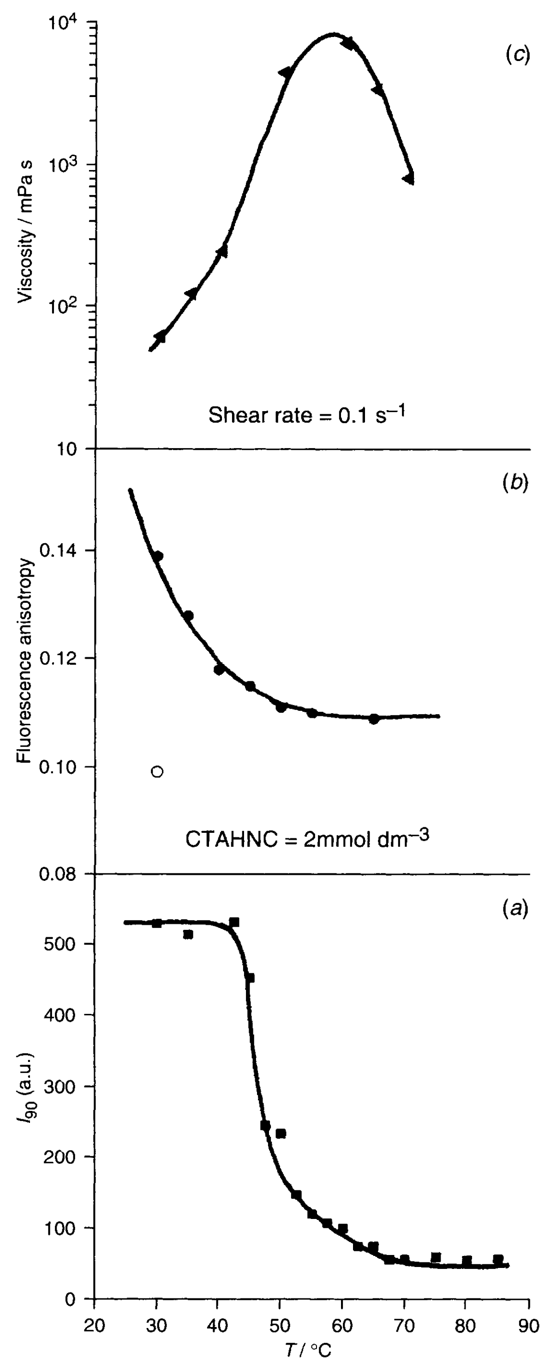

Fig. 1 Scattered light intensity (*a*) and viscosity (*c*) of CTAHNC dilute solutions investigated as a function of temperature showing the vesicle (low temperature) to worm-like micelle transition and its relation to the mobility of the HNC$^-$ ion, indicated by fluorescence anisotropy (*b*), on the vesicle surface. Note that only above 60 °C does the mobility of the HNC$^-$ ion approaches that of the free ion (○) at room temperature.

structure is a vesicle while on heating this solid-like region melts giving rise to worm-like micelles. The solid-like region can also be melted by adding an excess of anions or cations which produce increases in viscosity. It appears that by controlling the degree of crystallinity one can control the character of the supramolecular structure and clearly shows a potential for the design of other types of structures.

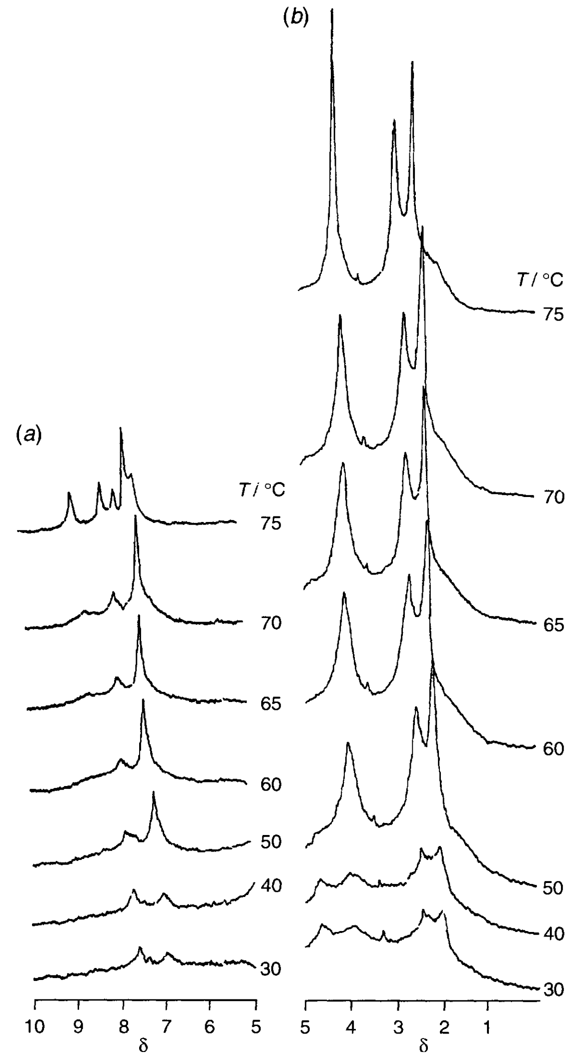

Fig. 2 Temperature dependence of FT NMR spectra of HNC$^-$ (*a*) and CTA$^+$ (*b*). Note that the room-temp. spectra are very wide indicative of the solid-like spectra.

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