Thermochimica Acta 394 (2002) 31–37

thermochimica
acta

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A calorimetric study of the gel-to-liquid crystal transition in catanionic surfactant vesicles

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Received 4 November 2001; received in revised form 28 January 2002; accepted 2 March 2002

Abstract

Dilute solutions of catanionic vesicles formed by the mixed single-chained (sodium dodecylsulphate, SDS) and double-chained (didodecyldimethylammonium bromide, DDAB) surfactants have been investigated by differential scanning calorimetry. It is for the first time reported a gel-to-liquid crystal phase transition temperature, T_m, in this type of mixed vesicles. The SDS-rich vesicles (at $X_{SDS} = 0.71$) show a concentration-dependent T_m in the range 9–16 °C. Addition of salt is seen to have an effect on T_m similar to that observed with increasing surfactant concentration, both inducing a decrease in T_m. These results differ from those obtained for neat DDAB vesicles. The observed effects in the two types of vesicles are rationalised in terms of headgroup electrostatic interactions which may have influence on the chain packing and phase transition temperature.

Keywords: Catanionic surfactant; Vesicle; Phase transition; Gel phase; Liquid crystalline phase; Electric double-layer forces

1. Introduction

Double-chained surfactants such as dialkyl quaternary ammonium salts and phospholipids have the required packing properties to self-organise in water into structures based on a bilayer arrangement of molecules [1–3]. Thus, when dispersed in water they usually form a lamellar liquid crystalline phase (*lc phase*) over a certain range of concentration and above a certain characteristic temperature, T_m, the main transition temperature. In the presence of excess solvent, a lamellar dispersion (a two-phase region) is formed where the bilayers can be found as polydisperse discrete aggregates, vesicles, also displaying T_m [4–6].

The phase transition at T_m occurs between the so-called *gel phase* and the lamellar lc phase [3]. In the latter, usually denoted as the L_α phase, the chains are in a liquidlike state with considerable conformational disorder, i.e. there is a high ratio of gauche-trans chain conformers. Upon cooling, the gel phase eventually forms where the chains in the bilayer are in a quasi-crystalline state (i.e. fully extended in *all-trans* conformation) and experience much slower dynamic motions (rotation, lateral diffusion). Different structures are possible for the gel phase, depending on the relative mismatch between the hydrated headgroup area and the cross-section of the “frozen”

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PII: S0040-6031(02)00235-6

chains. If the area per surfactant headgroup is comparable to that of the hydrocarbon cross-section area, in principle a simple "lamellar" gel phase (L_β) is formed. In cases of higher mismatch, tilted ($L_{\beta'}$), rippled ($P_{\beta'}$) or interdigitated gel structures may form.

These thermally induced phase transitions between bilayer states have been well studied for single lipids or mixtures of lipids in water, especially by means of differential scanning calorimetry [7–10] and X-ray diffraction [11–13] techniques. For some lipids, below the main gel-to-lc transition temperature, T_m, a gel–gel phase transition may occur, typically involving much lower enthalpy changes. T_m is shown to be dependent on factors such as the headgroup structure, hydrocarbon chain length of the lipid, pH and ion binding ([5] and references therein). Bilayer thermotropic transitions have been also extensively investigated for lipid–cholesterol mixtures and also mixtures of lipid vesicles with drugs, proteins and polymers ([6] and references therein).

A class of surfactant systems which yield vesicles in a state of thermodynamic equilibrium is that of the catanionic surfactants, based on mixtures of cationic and anionic amphiphiles [14–19]. For these systems, equimolar mixing normally leads to precipitation, but once charge is added to the mixture by excess ionic surfactant, narrow solution regions of stabilised vesicles appear. In this work, the goal has been to investigate the possible presence of a characteristic gel-to-lc transition in these mixed "synthetic" vesicles, and also any dependence of the transition temperature on chemical parameters, such as composition and salt. The system investigated here consists of vesicles formed by sodium dodecylsulphate (SDS) and didodecyldimethylammonium bromide (DDAB). Phase diagrams of the SDS–DDAB–water mixture and properties of the catanionic vesicles therein found have been reported in previous works [17,19–22]. In the catanionic vesicle, surfactant–ion pairs are formed (due to headgroup electrostatic attractions) and coexist with the excess ionic surfactant. Addition of salt or changes in bilayer composition directly affect these interactions. Consequently, the chain organisation in the bilayer may suffer changes with possible consequences for the phase transition, which is principally located at the chain level.

2. Experimental section

The ionic surfactants SDS and DDAB of high purity were obtained from BDH, England and Tokyo Kasei, respectively, and used without further purification. The SDS–DDAB vesicle solutions have a composition that can be denoted by the molar fraction of surfactant i in the mixture, $X_i = c_i/(c_i + c_j)$, where c_i and c_j are the molar concentrations of the two surfactants. The solutions were prepared by volume from an SDS micellar solution and diluted DDAB dispersions, carefully homogenised, as described in detail in previous works. For the salt-containing samples, a sodium bromide solution was added to the vesicle solutions with dilution to the desired concentration.

DSC traces were recorded in a high sensitivity calorimeter, MicroCal MC-2 (MicroCal, Northampton, MA), equipped with two twin-cells of 1.2 ml for the reference and sample solutions. The reference thermogram for both cells filled with water was recorded under the same conditions as the sample. The difference between the sample and reference thermograms is proportional to the excess heat capacity, ΔC_p. The transition enthalpy, ΔH_m, was calculated from the area under the peak and the transition temperature was taken as the temperature at the peak maximum. The Origin^{TM} software (v2.9) for data acquisition and analysis was used. For each sample the measurements were repeated twice, showing good reproducibility. The scan rate used was 0.17 K/min for all the investigated solutions.

3. Results

The DSC traces for neat DDAB vesicle solutions were initially recorded and are presented in Fig. 1. To our knowledge, this is the first time that DSC traces are shown for this amphiphile, while the dioctadecyl salt has been extensively reported in the literature. Similar to other double-chained amphiphile vesicles, DDAB vesicles show a characteristic transition temperature, signalling the gel-to-lc phase transition. T_m does not vary with surfactant concentration, remaining within $15.0 \pm 0.2\,^\circ C$ in the range 5–30 mM DDAB. However, when salt is continuously added to a 15 mM DDAB solution, a small increase in T_m is observed; at 50 mM NaBr, $T_m = 16.1\,^\circ C$ (Fig. 2).

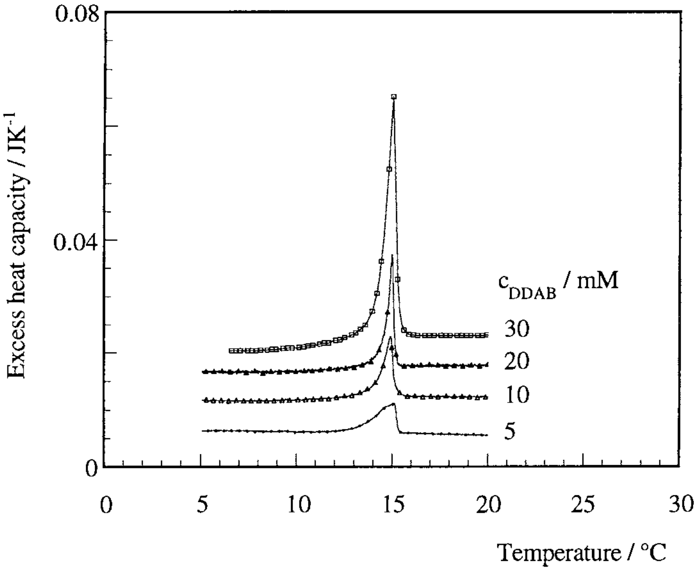

Fig. 1. DSC curves for neat DDAB vesicle solutions, at 5, 10, 20 and 30 mM. Heating rate: 0.17 K/min.

In the mixed system, within the region $X_{SDS} = 0.20$–0.70, a precipitate is observed in equilibrium with a solution. In the region $X_{SDS} = 0.71$–0.75, a bluish single-phase region containing vesicles is formed. A representative DSC trace for an SDS–DDAB vesicle solution at fixed $X_{SDS} = 0.71$ and total concentration, $c_t = 20$ mM, is shown in Fig. 3. Interestingly, these vesicles with excess of single-chained amphiphile, show again a phase transition in the measured temperature interval. Moreover, the main gel-to-lc phase transition peak is preceded very closely by a broad pre-transition peak.

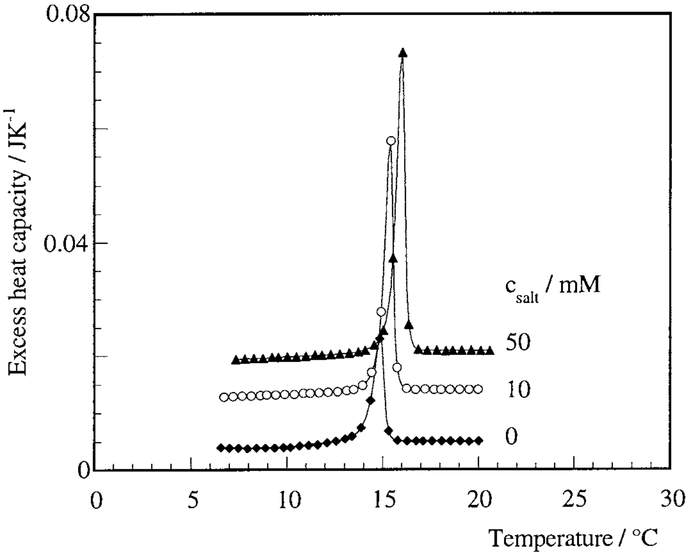

Fig. 2. DSC curves for a 15 mM neat DDAB vesicle solution in the presence of salt (NaBr), at 0, 10 and 50 mM. Heating rate: 0.17 K/min.

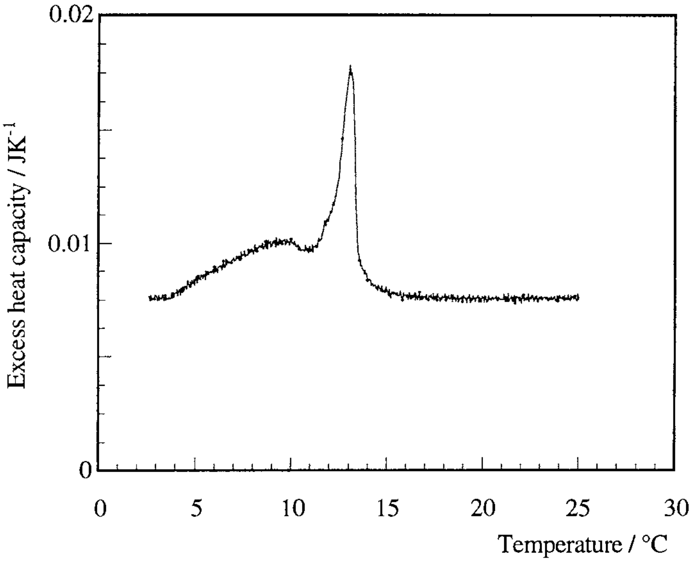

Fig. 3. DSC curve for an SDS–DDAB vesicle solution at total surfactant concentration $c_{\text{SDS}} + c_{\text{DDAB}} = 20\,\text{mM}$ and $X_{\text{SDS}} = 0.71$. Heating rate: 0.17 K/min.

DSC traces for the $c_t = 7.5$–$50\,\text{mM}$ range at fixed $X_{\text{SDS}} = 0.71$, corresponding to a dilution path within the SDS-rich vesicle region, are shown in Fig. 4. The main transition peaks are generally broad and a small broad peak before the main one is visible (more clearly for the lowest concentrations). A fairly significant dependence of T_m with total surfactant concentration is observed in this case: a roughly 6.7-fold dilution results in a variation of +6.5 °C in T_m.

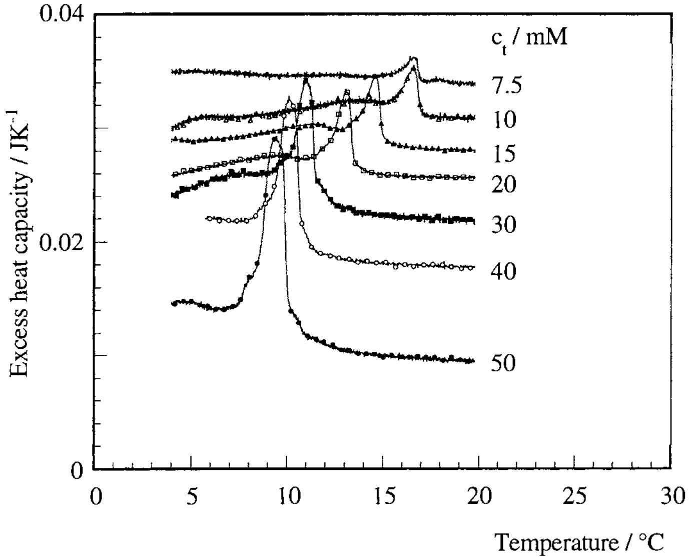

Fig. 4. DSC curves for SDS–DDAB vesicle solutions ($X_{\text{SDS}} = 0.71$) at different total surfactant concentration, $c_{\text{SDS}} + c_{\text{DDAB}} = 7.5$, 10, 15, 20, 30, 40 and 50 mM. Heating rate: 0.17 K/min.

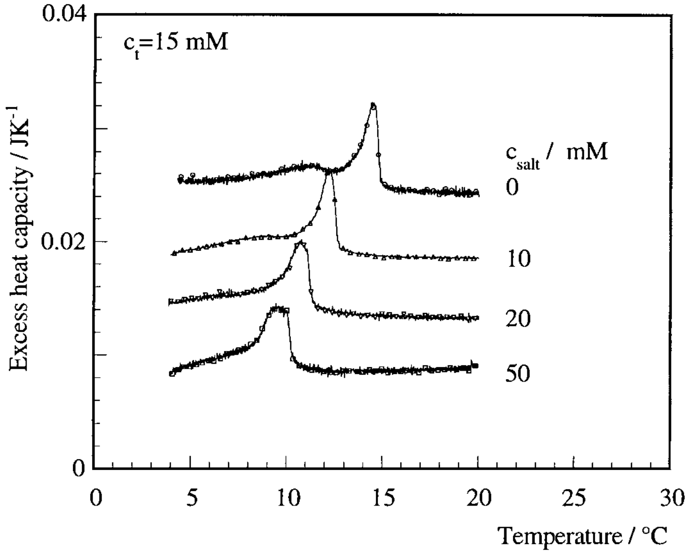

Fig. 5. DSC curves for a 15 mM SDS–DDAB vesicle solution ($X_{\mathrm{SDS}} = 0.71$) in the presence of salt (NaBr), at 0, 10, 20 and 50 mM. Heating rate: 0.17 K/min.

Similar effects to that of dilution are induced by salt addition. When increasing concentrations of NaBr are added to a 15 mM mixed vesicle solution, the main transition peak gradually shifts also to lower temperature (Fig. 5). The peaks appear to become gradually broader as well. A comparative view of the variation of T_m in the different cases reported above is shown in Fig. 6.

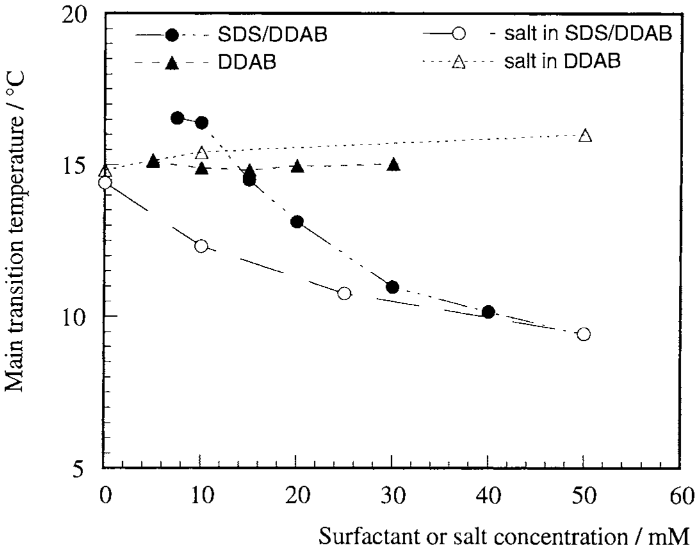

Fig. 6. The effect on T_m, of: (i) surfactant concentration for SDS–DDAB vesicles, $X_{\mathrm{SDS}} = 0.71$ (full circles) and neat DDAB vesicles (full triangles); (ii) added salt concentration for SDS–DDAB vesicles at 15 mM and $X_{\mathrm{SDS}} = 0.71$ (empty circles), and DDAB vesicles at 15 mM (empty triangles). Lines are guides for the eye.

A significant observation for these DSC measurements is that the kinetics of complete gel formation in the sample appears to be rather slow (several hours), both for the neat DDAB vesicles and for the mixed SDS–DDAB vesicles. The area of the main endothermic peak was seen to be strongly dependent on the duration of the in situ equilibration time of the sample (kept at ≈3–4 °C) prior to the heating scan. Thus, only preliminary values for the transition enthalpies, ΔH_m, are reported here, since this important kinetic study is being currently undertaken. For the DDAB vesicles, a rough estimate for ΔH_m is of the order of 25 kJ mol^{-1}, whereas for the SDS–DDAB vesicles the value is smaller, around 10 kJ mol^{-1}. The value for DDAB yields a ΔH_m per methylene group (CH_2) around 1.0 kJ mol^{-1}, a value that compares reasonably well with 1.2 kJ (mol CH_2)$^{-1}$ obtained for the $C_{18}C_{18}$ homologue of DDAB [23]. The latter values are somewhat smaller than the 1.9–2.1 kJ (mol CH_2)$^{-1}$ obtained for a series of phospholipids with identical headgroups [6], which seems to indicate a less organised structure for the gel phase in the synthetic surfactants as compared to the lipids.

4. Discussion and final remarks

The catanionic vesicles studied in this work differ from current lipid or cationic surfactant vesicles in a few significant ways. They are formed essentially due to a favourable balance between the cationic–anionic headgroup attractions and the packing of the chains. In the bilayer, the catanionic ion pairs coexist with the excess ionic surfactant. The salt resulting from the counterion release from the surface to the bulk screens to some extent the headgroup interactions. Thus in the vesicle surface the charge-to-charge distance can vary if the electrostatic interactions are in some way changed, say by addition of salt or by direct changes in bilayer composition. The chain packing in the bilayer can also change as a consequence of interfacial changes and thus the relative stability of the gel and lc state of the bilayer.

For the neat DDAB vesicles, dilution does not affect the T_m values. This is reasonably expected, since for such dilute samples the degree of counterion binding ($\beta \approx 0.8$ for bromide) is practically constant with concentration. When salt is added, the electric double-layer repulsions between aggregates are screened (decreased vesicle stability); moreover, and for this case more significantly, the headgroups repulsions in the bilayer interface are screened. Consequently, one can expect a smaller area per molecule and more favourable chain–chain interactions—i.e. a stabilisation of the gel phase with respect to the lc phase. Thus, the observed increase in T_m with salt concentration. It should be noted that similar trends have been reported in the literature for the effect of salt addition on the T_m of negatively charged lipids (cf. [6] and references therein cited).

For the SDS–DDAB vesicles, an interpretation of the observed effects does not appear to be so straightforward. Upon dilution, the composition of the vesicle should not change since the monomeric surfactant concentration is expected to be fairly low (catanionic mixtures show much lower CMC than the individual surfactants [18]). The average vesicle radius has also been shown to remain essentially constant within this range, around 30 nm, so changes in average aggregate curvature cannot account for the observations. However, as discussed above, salt is always present even before direct addition and salt concentration does indeed change with dilution. For example, a $c_t = 50$ mM solution at $X_{SDS} = 0.71$ has $c_{salt} \approx 15$ mM, simply resulting from the surfactant charge neutralisation. The attractions between the cationic–anionic headgroups are probably screened in the presence of salt, in particular as its concentration becomes significant. Upon dilution, less salt in the bulk is present; thus, headgroups attractions can become stronger. Consequently this could explain, at least partially, the increase in T_m associated with the dilution process. The effects of direct addition of salt in T_m are in line with this explanation. As salt is directly added (higher screening), a decrease in T_m is observed.

Further investigation of these dilution/salt effects can be done in the DDAB-rich area of the phase diagram for this mixture, where stable vesicles are also formed [20]. Such measurements are currently being performed. Moreover, we believe that the trends observed here can be probably generalised to other types of mixed cationic–anionic vesicles, including mixtures of two single-tailed amphiphiles. A thorough monitoring of the transition enthalpy values is also needed for the characterisation of the phase transition in catanionic vesicles.

Acknowledgements

Gerd Olofsson and Margarida Bastos are kindly acknowledged for valuable discussions. EFM is grateful to TFR, Sweden and Centro de Investigação em Química (U.P.)-linha 5, F.C.T., Portugal, for financial support.

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