Lamellar to Hexagonal Columnar Liquid Crystalline Phase Transition in a Catanionic Surfactant Mixture: Dodecylammonium Chloride/Sodium Bis(2-ethylhexyl) Sulfosuccinate

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(a) Adsorption at the air/solution interface from catanionic mixtures

The regular solution theory has been proven to be remarkably successful in modeling the nonideal behavior of mixed surfactant systems. According to this theory and the standard state surface tension method, the mixed monolayer composition, the surface activity coefficients of the components, the monolayer interaction parameter and the excess free energy of mixing were calculated.[1-5] In the mixture, DDACl was denoted as Surfactant 1, whereas AOT was denoted as Surfactant 2. The value of standard surface tension was chosen arbitrarily as if being situated in the region within which a complete monolayer was formed but corresponding to the concentrations sufficiently below the cmc. This method required only one set of data for thermodynamic parameter calculations.

The molar fraction of the cationic surfactant in the mixed monolayer (X_{DDACl}) was estimated from the solution molar concentrations of DDACl (C_{DDACl}), AOT (C_{AOT}) and their mixture ($C_{1,2}$) required to obtain the same value of surface tension in all three cases. The basic equation is

$$1 = [(X_{DDACl})^2 \ln (\alpha_{DDACl} C_{1,2}) / C_{DDACl} X_{DDACl})] / (1-X_{DDACl})^2 \ln [(1-\alpha_{DDACl}) C_{1,2}/(1-X_{DDACl}) C_2], \qquad (1)$$

where α_{DDACl} is the molar fraction of DDACl in solution. The iterative solution of the above equation gives X_{DDACl}. The surface molecular interaction parameter (β_{mon}) and the surface activity coefficients for the cationic surfactant, (f_{DDACl}) and AOT (f_{AOT}), in the mixed monolayer are calculated according to the following equations:

$$\beta_{mon} = \ln [(\alpha_{DDACl} C_{1,2}) / C_{DDACl} X_{DDACl})] / (1 - X_{DDACl})^2, \qquad (2)$$

$$f_1 = \exp \beta_{mon} (1 - X_{DDACl})^2 \qquad (3)$$

and

$$f_2 = \exp \beta_{mon} (X_{DDACl})^2. \qquad (4)$$

The regular solution theory attributes all nonideality in mixing to the heat of mixing, which is represented by an interaction parameter. When parameter β is negative, the interaction is attractive; however, when it is positive, the interaction is repulsive. Theoretically, the excess free energy of mixing (ΔG_{mix}) is equal to the excess enthalpy of mixing (ΔH_{mix}):

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} = \beta \, X_{\text{DDACl}} X_{\text{AOT}} \, RT. \tag{5}$$

According to the regular solution theory, the deviation of experimentally obtained mixed micelle cmc value (cmc^*) from that calculated by assuming ideal mixing can be represented by the molecular interaction parameter in the mixed micelle (β_{mic}). The parameters for mixed micelles, molar fraction of surfactants 1 and 2 in the mixed micelle (x_{DDACl} and x_{AOT}), the corresponding activity coefficients (f_{DDACl} and f_{AOT}) and β_{mic} are calculated using Equations 1-5. These parameters were determined using the cmc of individual surfactants ($\text{cmc}_{\text{DDACl}}$ and cmc_{AOT}) and of their mixture (cmc^*) at the molar fraction of surfactant 1 (α_{AOT}) in a mixture instead of C_{DDACl}, C_{AOT} and $C_{1,2}$.

References

1. D. N. Rubingh, Mixed Micelle Solutions in *Solution Chemistry of Surfactants*, ed. K. Mittal, Plenum Press, New York, 1979, pp. 337-354.

2. P. M. Holland, D. M. Rubingh, *J. Phys. Chem.*, 1983, **87**, 1984-1990.

3. P. M. Holland, *Colloid Surf.*, 1986, **19**, 171-183.

4. M. J. Rosen, *Am. Chem. Soc. Sym. Ser.*, 1986, **311**, 144-162.

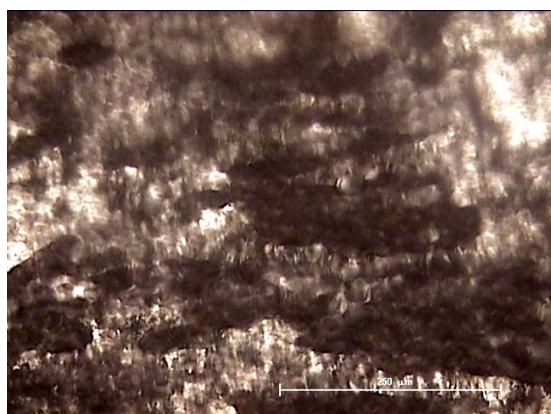5. C. M. Nguyen, J. F. Scamehorn, *J. Colloid Interface Sci.*, 1988, **123**, 238-248.

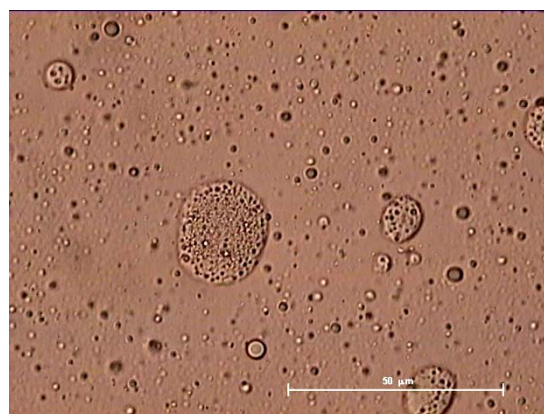**(b) Additional POM images of catanionic surfactant aggregates**
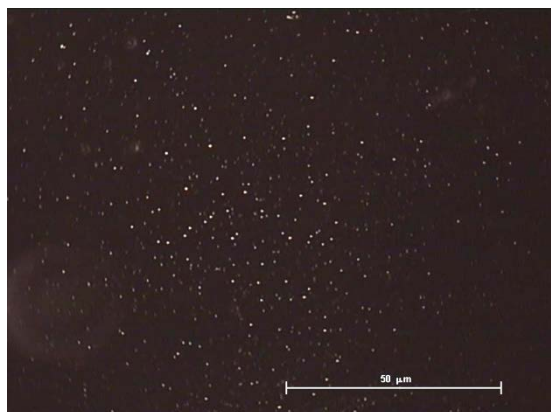
(a) c_{AOT} =0.01 mol dm^{-3} (α_{DDACl} = 0.67)
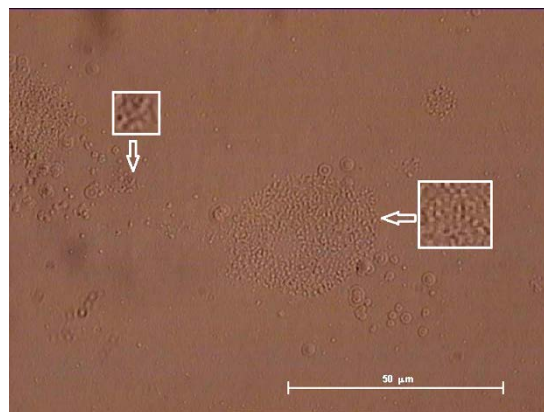
(b) c_{AOT} =0.03 mol dm^{-3} (α_{DDACl} = 0.40)

c_{AOT} =0.03 mol dm^{-3} (α_{DDACl} = 0.40)
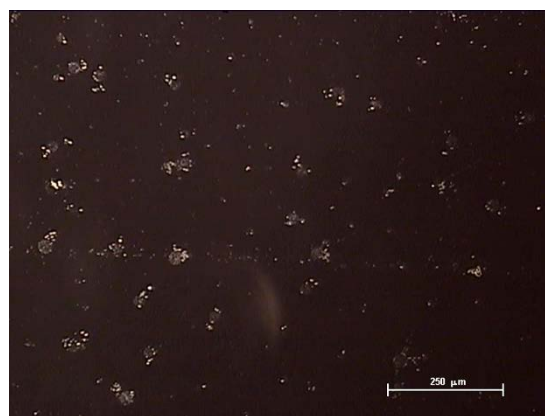
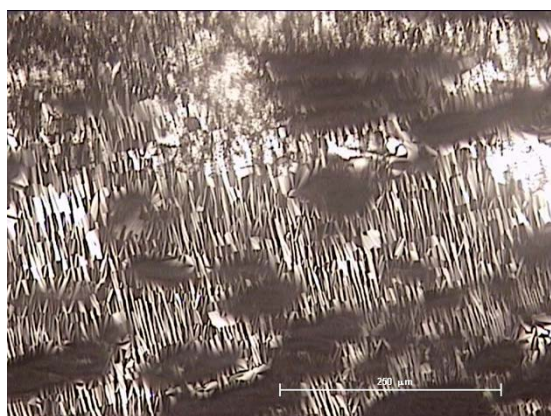

c_{AOT} =0.05 mol dm^{-3} (α_{DDACl} = 0.29)

Figure S1. Optical microphotographs of samples prepared with various AOT concentration (c_{AOT}) and at constant DDACl concentration, c_{DDACl} = 0.02 mol dm^{-3}; (a, c) between crossed polarizers, (b, d) by using phase contrast. c_{AOT} and bars are denoted. Enlarged images of flexible tubular vesicles filled with pearls are inserted in Fig. S1b.
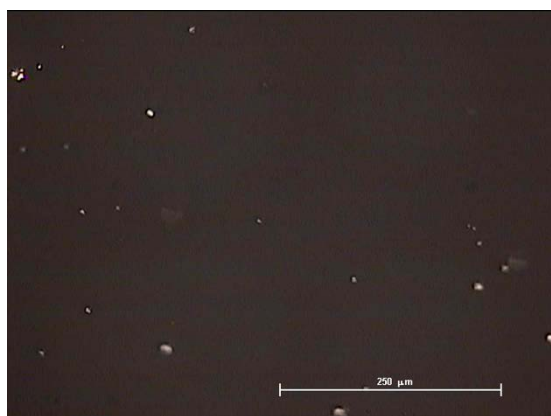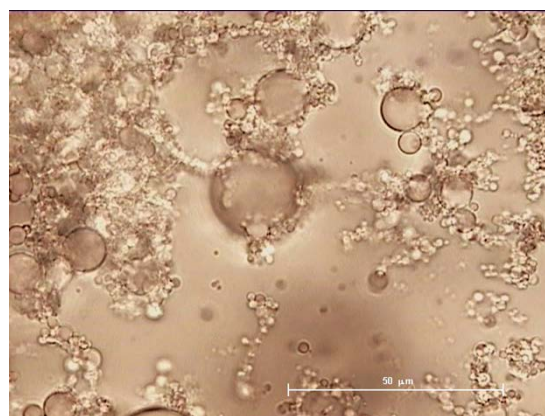
(a) $c_{DDACl} = 0.005$ mol dm^{-3} ($\alpha_{DDACl} = 0.33$)
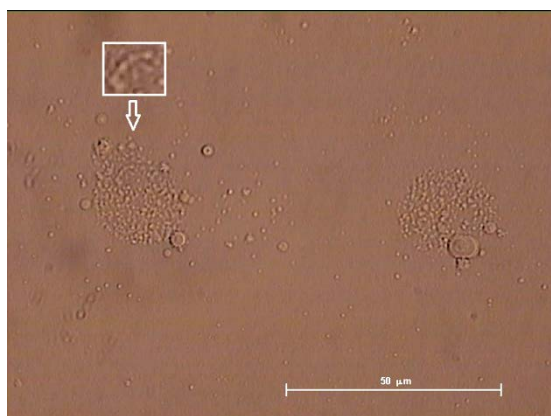

(b) 0.01 mol dm^{-3} ($\alpha_{DDACl} = 0.50$)

(c) $c_{DDACl} = 0.01$ mol dm^{-3} ($\alpha_{DDACl} = 0.50$)

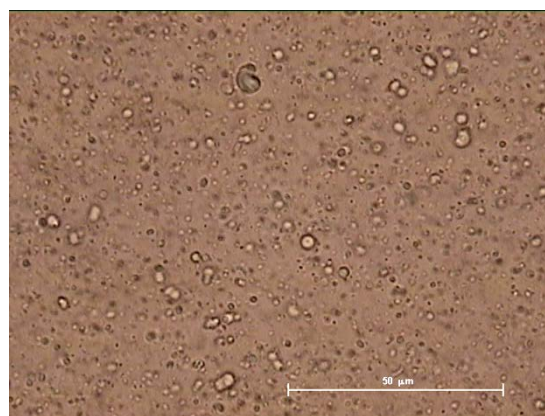

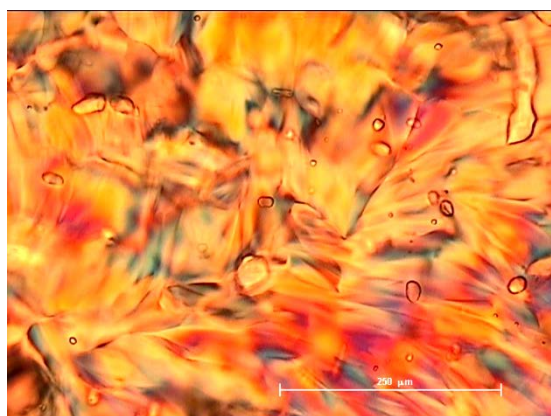(d) $c_{DDACl} = 0.04$ mol dm^{-3} ($\alpha_{DDACl} = 0.80$)

Figure S2. Microphotographs of samples prepared with various DDACl concentration (c_{DDACl}) and at fixed AOT concentration, $c_{AOT} = 0.01$ mol dm^{-3}, (a, b, c) between crossed polarizers and (d) by phase contrast. c_{DDACl} and bars are denoted.

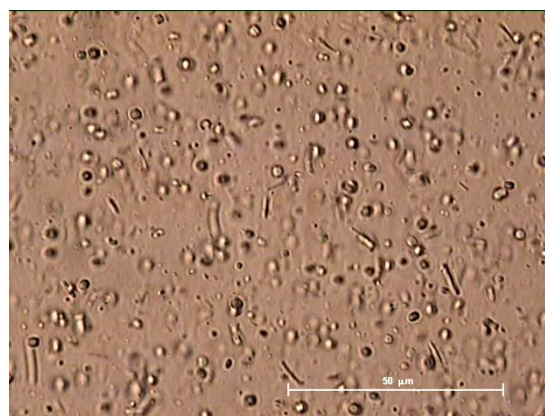(a) $c_{DDACl} = 0.007$ mol dm^{-3} ($\alpha_{DDACl} = 0.19$)

(b) $c_{DDACl} = 0.01$ mol dm^{-3} ($\alpha_{DDACl} = 0.25$)
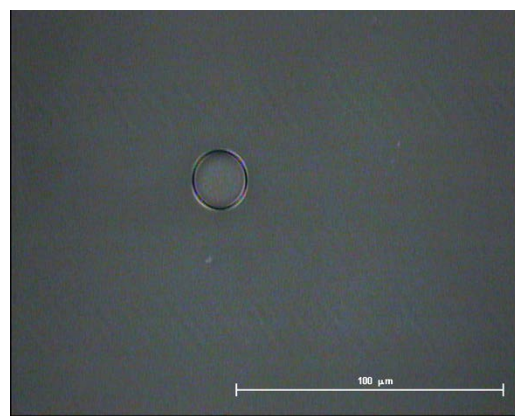
(c) $c_{DDACl} = 0.05$ mol dm^{-3} ($\alpha_{DDACl} = 0.63$)

(d) $c_{DDACl} = 0.07$ mol dm^{-3} ($\alpha_{DDACl} = 0.70$)

Figure S3. Microphotographs of samples prepared with various DDACl concentration (c_{DDACl}) and at fixed AOT concentration, $c_{AOT} = 0.03$ mol dm^{-3} (a, b, d) by using phase contrast and (c) between crossed polarizers. c_{DDACl} and bars are denoted. Enlarged image of flexible tubular vesicles filled with pearls is inserted in Fig. S3a.
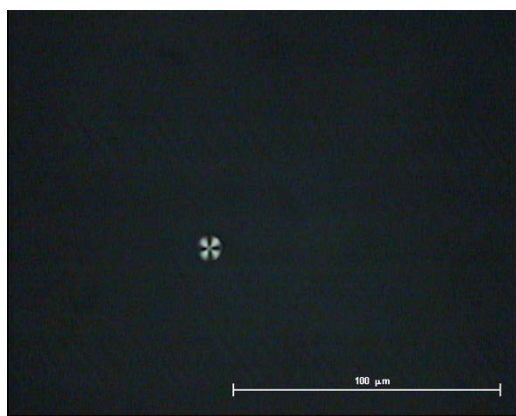
(a) $c_{DDACl} = 0.0003$ mol dm^{-3} ($\alpha_{DDACl} = 0.23$)

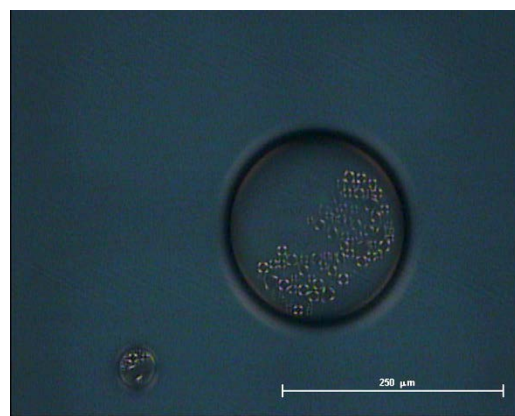(b) $c_{DDACl} = 0.005$ mol dm^{-3} ($\alpha_{DDACl} = 0.63$)

Figure S4. Microphotographs of samples prepared with various DDACl concentration (c_{DDACl}) and at fixed AOT concentration, $c_{AOT} = 0.001$ mol dm^{-3}, between crossed polarizers. c_{DDACl} and bars are denoted.

(a) $c_{AOTl} = 0.0005$ mol dm^{-3} ($\alpha_{DDACl} = 0.67$)

(c) $c_{AOTl} = 0.005$ mol dm^{-3} ($\alpha_{DDACl} = 0.17$)

Figure S5. Microphotographs of samples prepared with various AOT concentration (c_{AOT}) and at fixed DDACl concentration, $c_{DDACl} = 0.001$ mol dm^{-3}, between crossed polarizers. c_{AOT} and bars are denoted.