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ORIGINAL CONTRIBUTION

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Adsorption, association and precipitation in hexadecyltrimethylammonium bromide/sodium dodecyl sulfate mixtures

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Abstract The phase equilibria of surfactant aqueous mixtures, hexadecyltrimethylammonium bromide and sodium dodecyl sulfate, have been studied by polarizing microscopy, quasielastic light scattering, conductivity, potentiometric, electrophoretic, and surface tension measurements. Adsorption at the air/solution interface, association and precipitation in bulk solution strongly depended on the molar ratio and the concentration of surfactants. Catanionic vesicles coexisted with crystalline catanionic salts in a broad concentration range. The relative proportions of crystallites and vesicles varied according to the concentration and the molar ratio of the surfactants. The solid crystalline phase was progressively converted to catanionic vesicles with increasing surfactant molar ratio. At the highest excess of one of the surfactants transition from catanionic vesicles to mixed micelles occurred. The formation and stability of different phases are discussed in terms of surfactant molecular packing constraints and electrostatic interactions in the headgroup region. Surfactant tail-length asymmetry and the change of electrostatic interactions in the headgroup region from attractive to repulsive are governing factors for the transition from planar to curved bilayers.

Key words Catanionic surfactant – hexadecyltrimethylammonium bromide – mixed micelles – mixed monolayer – sodium dodecyl sulfate – vesicles

Introduction

The properties of systems containing oppositely charged surfactants have been the subject of extensive experimental and theoretical investigations [1–23]. Competition between various molecular interactions (van der Waals, hydrophobic, electrostatic, hydration forces, etc.) may result in a variety of microstructures, catanionic surfactant salts, mixed micelles, catanionic vesicles, etc. A catanionic surfactant is an amphiphilic compound that contains amphiphilic cations and amphiphilic anions in an equimolar ratio, while a catanionic vesicle is a vesicle that contains amphiphilic cations and amphiphilic anions. Recently, a growing body of literature has confirmed the potential of such investigations in many applicable aspects (design of efficient detergents, microemulsions for tertiary oil recovery, drug carrier systems, etc.).

Spontaneous vesicle formation has rarely been observed in single-tailed chain systems without adequate chemical or mechanical treatment [23–25], but in cationic/anionic surfactant mixtures spontaneous formation of vesicles is frequently observed. Recently, we have described the phase transition from the planar to the curved lamellar phase and the formation of catanionic vesicles in symmetric mixtures of a cationic and anionic surfactant [5, 26]. The physical forces driving this phase transition are mostly of electrostatic origin. It was found that with increasing mole fraction of one of the surfactants the phase transition proceeds in several stages. In the first stage the surfactant in excess is incorporated into a planar bilayer of the catanionic salt. This leads to curving of planar lamellae and finally to the formation of a closed lamellar structure, i.e. vesicles. At this stage coexistence of the catanionic crystalline phase and vesicles was usually observed. At the highest excess of one of the surfactants only mixed micelles existed.

The present article deals with the properties of the monolayer at the air/solution interface, phase behavior and solution microstructures in asymmetric mixtures of a cationic and anionic surfactant, hexadecyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (NaDS). The sequence of aggregate structures (planar bilayers–vesicles–micelles) formed by shifting the composition of mixtures from the equimolar range may, at least in part, be explained by both electrostatic interactions in the head-group region and by chain packing considerations for the asymmetric hydrophobic tails in the bilayer.

Experimental

Materials and methods

NaDS, especially pure, obtained from BDH Chemical Ltd. was recrystallized from ethanol. CTAB was purchased from Merck and recrystallized several times from acetone. The purity of the surfactants was tested by surface tension measurements. Systems were prepared with a constant anionic and an increasing cationic surfactant concentration and vice versa; the cationic surfactant was always added to the anionic surfactant. They were equilibrated 1 day before the measurement was performed. All experiments were carried out at 303 K in order to approach experimental conditions above the Krafft points of both NaDS and CTAB. The Krafft point of CTAB is 297 K (determined by measuring the change of specific conductivity of a 0.1% solution with temperature). The surface tension measurements were performed with an interfacial tensiometer (K8, Krüss, Hamburg).

Solution microstructures were investigated using a combination of quasielastic light scattering (QELS) and light microscopy. A Brookhaven Bi-200SM goniometer, a BI-2030AT correlator and a 300 mV Ar Lexel laser were used for light-scattering measurements. A Leitz Orthoplan microscope was equipped with photographic apparatus in a bright field and a polarizing mode and phase contrast. The liquid crystalline phases were identified by comparison of textures with photomicrographs from the literature [27].

Electrophoretic experiments (Pen Kem, Bedford Hills) were applied to determine the charge and electrophoretic mobility of the particles. The activities of Na^+ and Br^- ions were determined with the corresponding ion-selective electrode and an Orion Research Inc. digital pH/mV meter as was previously described [28]. Conductivity measurements were carried out with a conductometer (conductivity meter MA 5964, Iskra, Kranj).

Interpretation of data

The adsorption of a single surfactant at the air/solution interface was determined from the slope of the surface tension γ, versus ln c_{CTAB} or versus ln c_{NaDS} with the concentration of the other surfactant being constant. In the absence of electrolyte the maximum surface excess of CTAB, $\Gamma_{\max}$ (CTAB) or NaDS, $\Gamma_{\max}$ (NaDS), surfactant, respectively, is calculated [29] by the following equations.

$$\Gamma_{\max}(\mathrm{CTAB}) = -1/2RT(\mathrm{d}\gamma/\mathrm{dln}\ c_{\mathrm{CTAB}}) \tag{1}$$

and

$$\Gamma_{\max}(\mathrm{NaDS}) = -1/2RT(\mathrm{d}\gamma/\mathrm{dln}\ c_{\mathrm{NaDS}}) \tag{2}$$

where c denotes concentration, R is the gas constant and T is the absolute temperature. The minimum area occupied by a surfactant molecule adsorbed at the air/solution interface, $A_{\min}$, (nm^2), when $\Gamma_{\max}$ is expressed in units of moles per centimeter squared is

$$A_{\min} = 10^{14}/\Gamma_{\max}N_{\mathrm{A}}\ , \tag{3}$$

where N_{A} is Avogadro's number.

Using regular solution theory and the standard-state surface tension method [30–32] the composition of the mixed monolayer, the surface activity coefficient of the components (f_{CTAB} and f_{NaDS}) and the monolayer interaction parameter, β_{mon}, were determined. The value of the standard surface tension is arbitrarily chosen to be in the region where the complete monolayer is formed, but corresponding to concentrations sufficiently below the critical micelle concentration (cmc). This method requires only one set of data for thermodynamic parameter calculations. The molar fraction of NaDS in the mixed monolayer (X_{NaDS}) was estimated from solution molar concentrations of the individual surfactants NaDS (c_{NaDS}) and CTAB (c_{CTAB}) and their mixture ($c_{\mathrm{CTAB+NaDS}}$), required to obtain the same value of the surface tension in all three cases. The basic equation is

$$1 = \frac{(X_{\mathrm{NaDS}})^2 \ln(\alpha_{\mathrm{NaDS}} c_{\mathrm{CTAB+NaDS}}) c_{\mathrm{NaDS}} X_{\mathrm{NaDS}})}{(1 - X_{\mathrm{NaDS}})^2 \ln[(1 - \alpha_{\mathrm{NaDS}}) c_{\mathrm{CTAB+NaDS}}/(1 - X_{\mathrm{NaDS}}) c_{\mathrm{CTAB}}]}\ , \tag{4}$$

where α_{NaDS} is the mole fraction of NaDS in solution. The iterative solution of the above equation gives X_{NaDS}. The surface molecular interaction parameter (β_{mon}) and the surface activity coefficients for NaDS

(f_{NaDS}) and CTAB (f_{CTAB}) in the mixed monolayer are calculated according to the following equations:

$$\beta_{\mathrm{mon}} = \frac{\ln(\alpha_{\mathrm{NaDS}} c_{\mathrm{CTAB+NaDS}} / c_{\mathrm{NaDS}} X_{\mathrm{NaDS}})}{(1 - X_{\mathrm{NaDS}})^2} \quad , \tag{5}$$

$$f_{\mathrm{NaDS}} = \exp \beta_{\mathrm{mon}} (1 - X_{\mathrm{NaDS}})^2 \tag{6}$$

and

$$f_{\mathrm{CTAB}} = \exp \beta_{\mathrm{mon}} (X_{\mathrm{NaDS}})^2 \quad . \tag{7}$$

Regular solution theory attributes all nonideality in mixing to the heat of mixing, represented by an interaction parameter. Theoretically, the excess enthalpy of mixing (ΔH_{E}) is equal to the excess free energy of mixing (ΔG_{E})

$$\Delta G_{\mathrm{E}} = \Delta H_{\mathrm{E}} = \beta_{\mathrm{mon}} X_{\mathrm{NaDS}} X_{\mathrm{CTAB}} RT \quad , \tag{8}$$

where X_{NaDS} and X_{CTAB} are the mole fractions of the two surfactants in the mixed monolayer, R is the gas constant and T is the absolute temperature.

The parameters for mixed micelles, mole fraction of NaDS in mixed micelles (x_{NaDS}), corresponding activity coefficients and the molecular interaction parameter (β_{mic}) are calculated using Eqs. (4)–(7). In the calculations the cmc's of the individual surfactants and their mixture at a mole fraction α, were used instead of c_{NaDS}, c_{CTAB} and $c_{\mathrm{CTAB+NaDS}}$ [32].

The precipitation/solubility boundary was determined visually (light microscopy). The boundary was taken as the maximum concentration of reactants that did not result in the solid phase formation. The monomer-catanionic surfactant salt equilibrium is

$$\mathrm{C_{16}H_{33}N(CH_3)_3Br + C_{12}H_{25}SO_4Na} \leftrightarrow \mathrm{C_{16}H_{33}N(CH_3)_3SO_4C_{12}H_{25} + Na^+ + Br^-} \quad , \tag{9}$$

where $\mathrm{C_{16}H_{33}N(CH_3)_3SO_4C_{12}H_{25}}$ denotes hexadecyltrimtehylammonium dodecyl sulfate (CTADS).

The aggregation properties of CTAB/NaDS mixtures have been characterized through the cmc and counterion binding (results are presented as the apparent degree of counterion dissociation, α, from the micelle/solution interface) deduced from specific conductivity and potentiometric measurements [28]. To a first approximation α was taken as the ratio of the slope above and below breaks in curves of conductivity κ, versus c and concentration of free counterions (counterions not bound to the mixed micelle) versus the total concentration of surfactant in excess, respectively.

Light-scattering measurements yield information about sizes and polydispersities of the particle populations. The measured autocorrelation functions were analyzed by two-component analysis [33].

Results

Adsorption at the air/water interface

The surface adsorption studies showed that there exists a strong synergism between cationic and anionic surfactants due to electrostatic interactions between oppositely charged headgroups of surfactant molecules [10, 34, 35]. The surface activity of oppositely charged surfactant mixtures is generally greater than that which would be expected for other types of mixtures. This synergistic

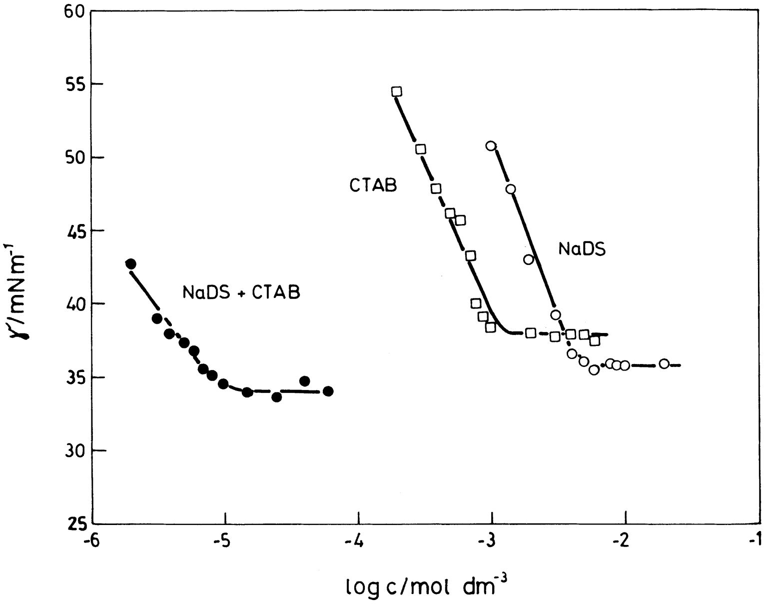


Fig. 1 Surface tension, γ, vs concentration, c, [total surfactant concentrations for single hexadecyltrimethylammonium bromide, *CTAB*, (□), single sodium dodecyl sulfate, *NaDS*, (○) and their equimolar mixture (●)]. The temperature is 303 K and the aging time is 1 day

effect has also been demonstrated in CTAB/NaDS equimolar mixtures.

Typical γ versus log c curves for NaDS, CTAB and their mixed solutions at an equimolar ratio are shown in Fig. 1. It can be seen that a much lower concentration for the equimolar mixture than that for the cationic or anionic surfactant alone is required to reach a constant surface tension value. The break point between a steeply descending and fairly constant branch of a γ versus log c curve for a mixed solution corresponds to the precipitation of the catanionic surfactant, CTADS.

By applying regular solution theory, the composition of the mixed monolayer, the surface activity coefficients, the molecular interaction parameter and the change of standard mixing enthalpy for equimolar mixtures were calculated using a surface tension value of 40 mN m^{-1} as the standard state. The results presented in Table 1 show almost equimolar monolayer formation with activity coefficient values much less than unity indicating a large deviation from ideality. The formation of an equimolar adsorption film is in accord with the literature data [10, 34]. According to its definition, a negative β_{mon} value is related to attractive molecular interactions in the mixed monolayer. The relatively high negative value of β_{mon} indicates a strong attractive interaction between adsorbed CTA^{+} and DS^{-} ions.

The maximum surface excess concentrations of each surfactant and their equimolar mixtures obtained from the premicellar slope of the surface tension-concentration curve are presented in Table 2. The smaller Γ_{max} and consequently higher A_{min} for a single NaDS molecule compared with those for a single CTAB molecule are due to the smaller surface activity of NaDS. The addition of an oppositely charged surfactant increased Γ_{max}, i.e. packing at the air/water interface was enhanced.

Changes in the surface tension with surfactant concentration in the series of mixtures with constant NaDS and varying CTAB concentrations and vice versa were used for determination of the premicellar slope. Addition of a small quantity of an oppositely charged surfactant shifts the premicellar slope of mixtures towards higher values. The changes in Γ_{max} of CTAB or NaDS are presented in Fig. 2. Both curves, Γ_{max} (CTAB) and Γ_{max} (NaDS) versus concentration revealed that the addition of an oppositely charged surfactant enhanced the maximum concentration which CTAB or NaDS can attain at the air/solution interface.

The maximum adsorption of either surfactant in a mixed adsorption film is influenced by the effective headgroup area of each single surfactant and by the interaction between them at the interface. The increase of Γ_{max} and the decrease of A_{min} are the results of strong electrostatic attraction between oppositely charged headgroups. Each component occupies a greater area per molecule due to electrostatic repulsion, while the presence of oppositely charged surfactants reduces the repulsion between headgroups and the area per molecule decreases.

Bulk properties: association and precipitation

The solution properties of CTAB/NaDS mixtures exhibited complex phase behavior over the entire concentration range. Figure 3 shows the precipitation/solubility boundary and the decrease of the cmc of both CTAB and NaDS with the addition of an oppositely charged surfactant. Inside the precipitation region a phase transition from turbid to isotropic was observed when one of the surfactants was continuously added to the equimolar mixtures.

The phase separation process was observed above the molar ratio of surfactants ≥0.01. Examination of samples from the turbid region by light microscopy showed heterogeneous mixtures of irregularly shaped crystals (Fig. 4a) and slightly anisotropic spherical and ellipsoidal structures (Fig. 4b, c). Under polarized light the appearance of spherulites with Maltese crosses was observed. The crystalline phase was identified as the catanionic surfactant salt, CTADS [36]. Microscopic examination revealed the presence of vesicles, but no further information could be obtained regarding vesicular morphology, i.e. whether vesicles are unilamellar or multilamellar. The fraction of the solid crystalline phase decreases as the sample composition deviates from the equimolar line.

Two cross-sections were examined by microelectrophoretic and QELS measurements; with a constant c(CTAB) $= 1 \times 10^{-4}$ mol dm^{-3} and varying c(NaDS) or with a constant c(NaDS) $= 1 \times 10^{-4}$ mol dm^{-3} and varying c(CTAB). The results of microelectrophoretic measurements are illustrated in Fig. 5. The ζ potential varied in relation to the surfactant concentration and the molar ratio. The reversal of particle charge almost coincided with equimolar mixtures. The particles were

Table 1 Surface mole fraction of sodium dodecyl sulfate (NaDS) in a mixed monolayer, X_{NaDS}, activity coefficients of NaDS, f_{NaDS}, and of hexadecyltrimethylammonium bromide (CTAB), f_{CTAB}, the monolayer interaction parameter, β_{mon}, and the excess enthalpy of mixing, ΔH_{E}, in a CTAB/NaDS equimolar mixture at the standard surface tension $\gamma = 40.0$ mN m^{-1}. Temperature is 303 K

X_{NaDS}	f_{NaDS}	f_{CTAB}	β_{mon}	ΔH_{E}/kJ mol^{-1}
0.48	0.001	0.003	−25.2	−15.8

Table 2 Maximum surface excess, Γ_{max}, at the air/solution interface of single surfactants, CTAB and NaDS, and their equimolar mixture. Temperature is 303 K and the aging time is 1 day

System	$\Gamma_{max} \times 10^6$/mol m^{-2}
CTAB	2.48
NaDS	2.10
CTAB + NaDS	2.80

positively charged in the mixtures with CTAB in excess and vice versa. The charge of the particles and the ζ potential depended on the relative amounts of each surfactant. Microelectrophoretic measurements confirmed a surfactant molar ratio-induced change in the vesicle composition. This difference in composition resulted in changes of surface charge density and the degree of the counterion dissociation.

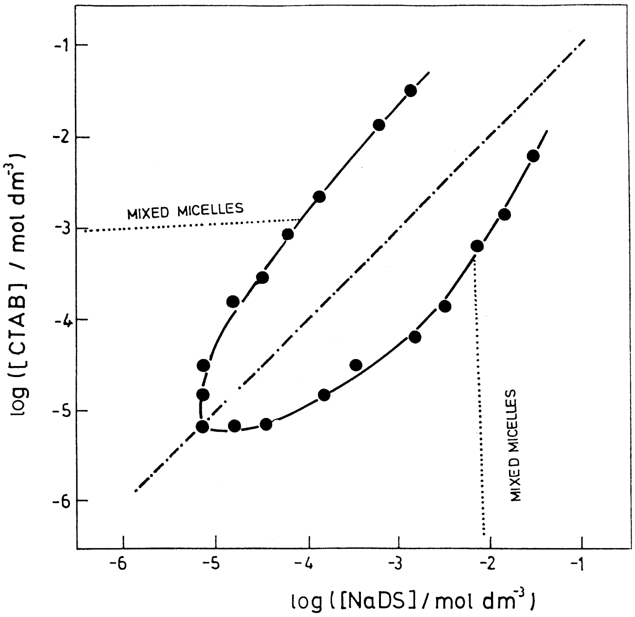


Fig. 3 Phase boundaries observed in NaDS and CTAB mixtures. The *solid line* corresponds to the clear/turbid boundary; *dotted lines* correspond to the change of the cmc of the surfactant in excess. The equimolar line is denoted as *dashed line*. The temperature is 303 K and the aging time is 1 day

QELS measurements showed a bimodal particle size distribution for the system from the turbid region. Table 3 provides representative examples of how turbid systems were analyzed by two-component analysis. Two different cross-sections corresponding to the constant concentration of one surfactant with increasing concentration of the other are shown. At the equimolar concentration the polydispersity, V, is high ($V >$ 100%) because of two separate populations: vesicles (d_1 = 620 nm) and crystalline particles (d_2 = 8000 nm). On both cross-sections, polydispersities of particle populations increased up to the equimolar range and then decreased with the increase in concentration of one of the surfactants. Mixtures with high excess of either cationic or anionic surfactant appeared to contain vesicles only. The mean hydrodynamic diameter of vesicles and the mean crystallite size changed in a similar way. Vesicles, characterized by relatively large diameters (ranging from 200 to 700 nm), coexisted with a smaller population of crystallites (ranging from 4000 to 9500 nm). NaDS-rich vesicles (overall negative charge) were somewhat smaller than CTAB-rich vesicles (overall positive charge). The method cannot give the exact size of the largest particles, i.e. crystallites. At high excess of either CTAB or NaDS, the number of crystallites was so low (≤1) that it was impossible to resolve them in the number distribution. The relative proportions (by weight) of the two species vary in relation to the surfactant molar ratio. The fraction of vesicles increased gradually as mixtures shifted from the equimolar range, while the fraction of crystallite decreased suggesting that crystallites are being progressively converted to vesicles.

The mean hydrodynamic diameters of vesicles for both cross-sections are shown in Fig. 6. The apparent

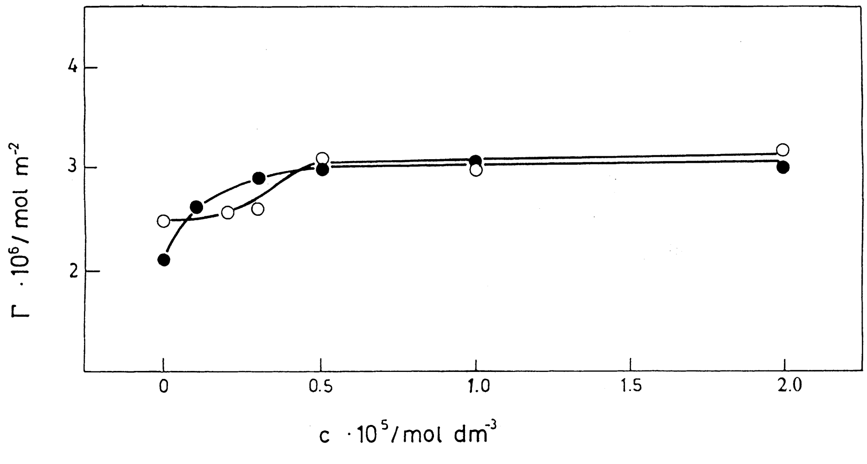


Fig. 2 Surface excess concentration, Γ_{max}, at the air/solution interfaces vs c in mixtures with constant c(NaDS) and increasing c(CTAB) (○), or constant c(CTAB) and increasing c(NaDS) (●). The temperature is 303 K and the aging time is 1 day

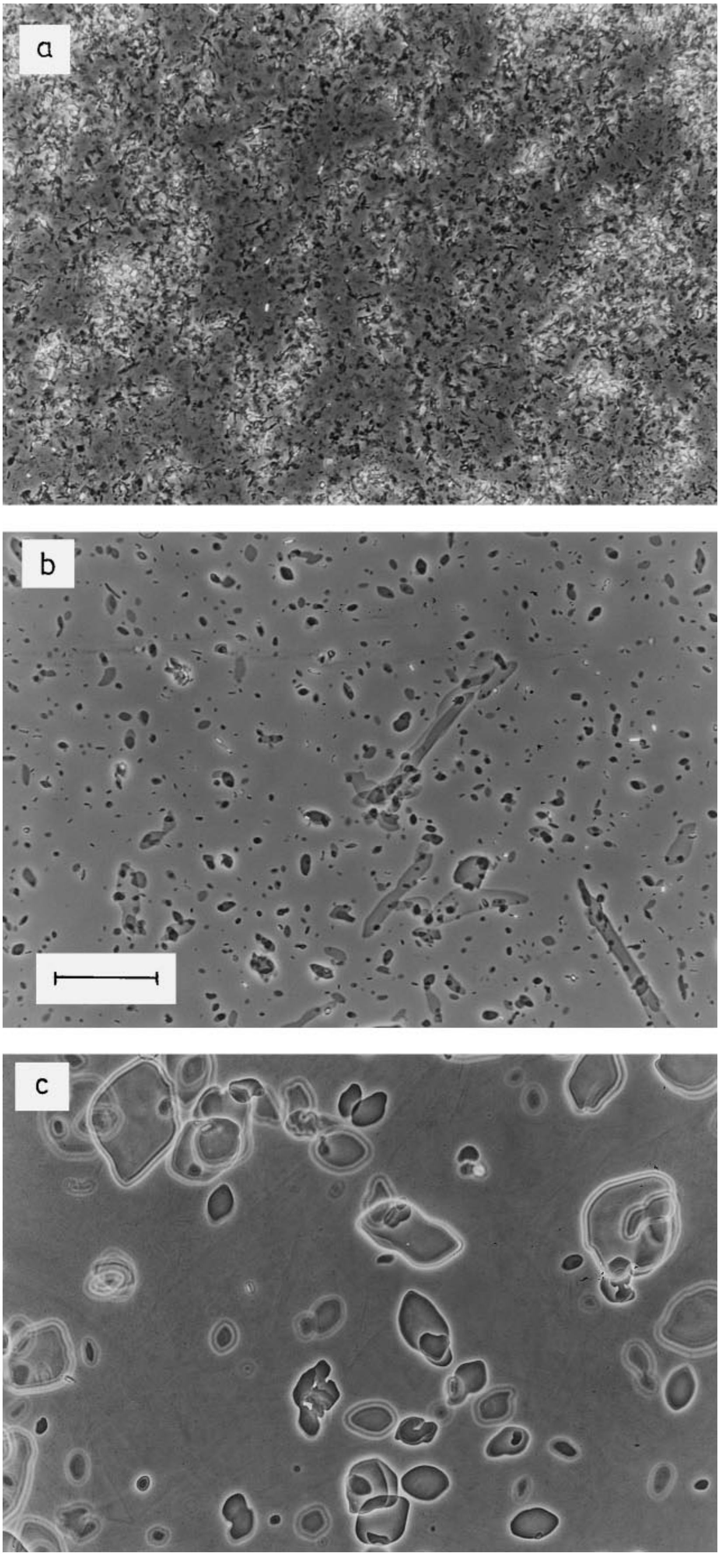
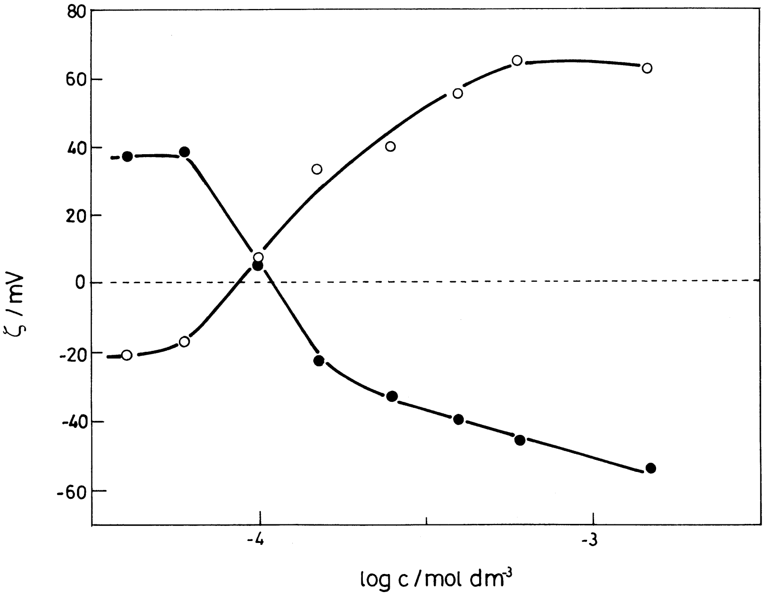


Fig. 4 Microphotographs of **a** crystalline hexadecyltrimethylammonium dodecyl sulfate (CTADS) formed from an equimolar mixture [$c(\mathrm{CTAB}) = c(\mathrm{NaDS}) = 0.025\ \mathrm{mol\ dm^{-3}}$], **b** vesicles from a mixture with $c(\mathrm{CTAB}) = 0.015\ \mathrm{mol\ dm^{-3}}$ and $c(\mathrm{NaDS}) = 0.025\ \mathrm{mol\ dm^{-3}}$, and **c** vesicles from a mixture $c(\mathrm{CTAB}) = 0.025\ \mathrm{mol\ dm^{-3}}$ and $c(\mathrm{NaDS}) = 0.015\ \mathrm{mol\ dm^{-3}}$. The temperature is 303 K and the aging time is 1 day. The bar represents 100 nm

Fig. 5 Zeta potential (ζ) vs *c* in CTAB/NaDS mixtures with increasing CTAB concentration and constant c(NaDS) = 1×10^{-4} mol dm^{-3} (○), and with increasing NaDS concentration and constant c(CTAB) = 1×10^{-4} mol dm^{-3} (●). The temperature is 303 K and the aging time is 1 day



vesicular size changed with mixture composition. The mean vesicle size is highest at the equimolar ratio and decreases on either side of the equimolar line. Microelectrophoretic results revealed that vesicles are positively and negatively charged, respectively. Similar general changes in the apparent sizes were also observed with larger particles, i.e. crystallites (Fig. 7).

At a very high excess of one of the surfactants, the systems became clear due to mixed micelle formation. The phase boundaries between monomers and mixed micelles were obtained from specific conductivity measurements by determining the shift of the cmc (CTAB) with NaDS addition or the shift of the cmc (NaDS) with CTAB addition, respectively. Mixed micelles were formed only with a high excess of one of the surfactants. For CTAB/NaDS mixed micelles, the cmc decreased in a linear fashion with increasing concentration of a counterpart surfactant (Fig. 3). It can be seen that the dependence of the cmc (NaDS) as a function of c(CTAB) is linear (slope 0.05) which differs from the slope of the cmc (CTAB) as a function of c(NaDS) (slope 0.18). The cmc values show a negative deviation

Table 3 Mean hydrodynamic vesicle diameter, d_1, mean crystallite size, d_2, corresponding relative proportions % by weight of particles for systems **a** with constant concentration of CTAB [c(CTAB) = 1×10^{-4} mol dm^{-3}] and varying NaDS and **b** with constant NaDS [c(NaDS) = 1×10^{-4} mol dm^{-3}], and varying CTAB. *V* indicates the polydispersity of particle populations

a [CTAB]/mol dm^{-3}	d_1/nm	% by weight	d_2/nm	% by weight	*V*/%
2.5×10^{-6}	320 ± 50	≥99	6800 ± 200	≤1	45 ± 3
4.0×10^{-5}	500 ± 50	95 ± 2	7200 ± 250	5 ± 2	74 ± 4
6.0×10^{-5}	550 ± 50	92 ± 5	7500 ± 250	8 ± 5	116 ± 9
1.0×10^{-4}	620 ± 50	90 ± 5	8000 ± 200	10 ± 5	142 ± 12
1.5×10^{-4}	530 ± 60	90 ± 5	7700 ± 250	10 ± 5	134 ± 10
2.5×10^{-4}	470 ± 50	95 ± 3	7000 ± 200	5 ± 2	125 ± 8
4.0×10^{-4}	420 ± 50	97 ± 2	6400 ± 150	3 ± 2	107 ± 5
6.0×10^{-4}	400 ± 50	≥99	5400 ± 150	≤1	96 ± 4
1.5×10^{-3}	280 ± 30	≥99	4500 ± 200	≤1	85 ± 5
1.0×10^{-2}	170 ± 30	≥99	4000 ± 150	≤1	67 ± 3
b [NaDS]/mol dm^{-3}					
2.5×10^{-5}	450 ± 30	≥99	9200 ± 250	≤1	44 ± 3
4.0×10^{-5}	550 ± 50	95 ± 2	8900 ± 250	5 ± 2	76 ± 4
6.0×10^{-5}	580 ± 60	92 ± 5	8500 ± 200	8 ± 5	105 ± 6
1.0×10^{-4}	620 ± 50	90 ± 5	8000 ± 200	10 ± 5	142 ± 8
2.5×10^{-4}	420 ± 50	94 ± 2	7600 ± 250	6 ± 2	113 ± 7
6.0×10^{-4}	300 ± 50	97 ± 2	6500 ± 200	3 ± 2	101 ± 11
1.5×10^{-3}	250 ± 40	≥99	6000 ± 150	≤1	78 ± 7
1.0×10^{-2}	200 ± 30	≥99	4200 ± 150	≤1	59 ± 5

from ideality compared with values calculated from the ideal mixing model, i.e. the formation of mixed micelles is enhanced. The nonideal behavior of surfactants in mixed micelles was evaluated by using the model of Rubingh [32]. It should be noted that the absolute value of β_{mic} was unusually low for CTAB/NaDS surfactant mixtures (about 5) and not constant as predicted by the model. The value of β_{mic} decreased with increasing concentration of either CTAB or NaDS. Despite a possible large error in the calculation of β_{mic} (the accuracy of determination is diminished by high asymmetry in the mixture composition [36]), low and variable β_{mic} values appear to be a consequence of a small quantity of crystalline particles still remaining in the micellar region.

Mixed micelles formed in mixtures with a high CTAB content show a very small increase in α_{Br} values (Table 4) indicating almost no change in the surface charge density with the addition of NaDS. It can be easily observed that the tendency of increasing α values as a function of the concentration of oppositely charged surfactants differs between bromide and sodium counterions; the increase in the α_{Na} value is greater than the increase in the α_{Br} value. This is attributed to either differences in micellar size or differences in interactions between headgroups and counterions [5]. The difference in ionization between NaDS and CTAB pure micelles must somehow relate to the difference in the nature of the interacting species -O-SO_3^- and Na^+ on one side, and $-N^+(CH)_3$ and Br^- on the other. The Br^- and Na^+ ions do not bind in the same way due to their difference in polarizability.

Discussion

Surfactant molecules can form various supramolecular structures in aqueous solution, which are not covalently bonded, but are stabilized by the weaker hydrophobic interactions. It has been demonstrated that the molecular structure of a surfactant molecule, i.e. geometrical factors, primarily determines the most favored structure of surfactant supramolecules [38]. The geometric considerations are based on the packing parameter, given by v/al, where v is the volume of the hydrophobic tail(s), a is the effective area per headgroup, and l is the length of the hydrophobic tail(s). The packing parameter can be expressed in terms of interfacial curvatures and vice versa. It has been demonstrated that aggregates of high curvature are formed by surfactants with low packing parameters, whereas aggregates of lower curvature are formed by surfactants with high packing parameters. When the spontaneous curvature of the surfactant interface is of the order of the surfactant molecule size, micellar aggregates are favored. For small curvatures planar bilayers or vesicles are more stable than micelles [39, 40].

It is assumed [41] that the effective headgroup area at the air/solution interface is the same as on the surfactant aggregate/solution interface. The effective area of the polar headgroup at the air/solution interface in the CTAB/NaDS equimolar mixture is reduced in comparison to that of a single surfactant system due to the formation of ionic pairs between cationic and anionic headgroups. Therefore, a mixture of cationic and anionic surfactants can be considered as a double-tailed surfactant that is easily able to form bilayers in solution.

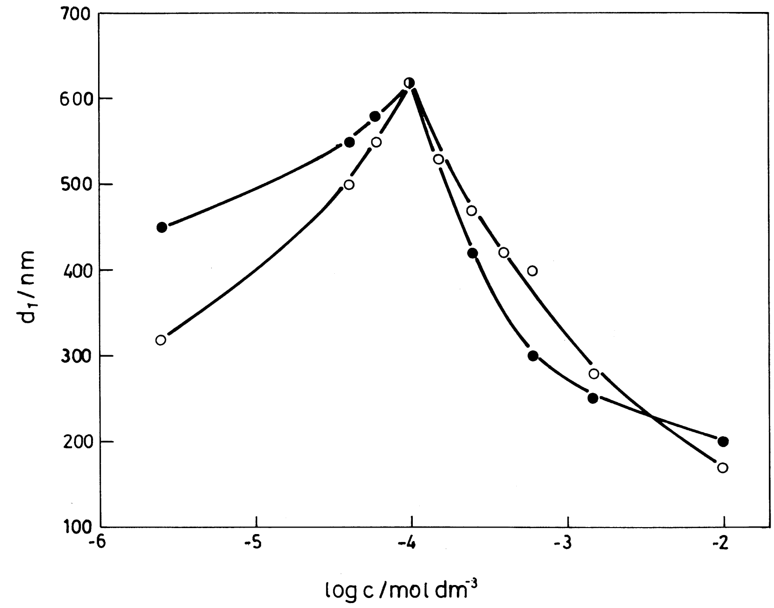


Fig. 6 Mean vesicle hydrodynamic diameter, d_1, vs c for two cross-sections with constant c(CTAB) = 1×10^{-4} mol dm^{-3} (●), or c(NaDS) = 1×10^{-4} mol dm^{-3} (○), respectively. The temperature is 303 K and the aging time is 1 day

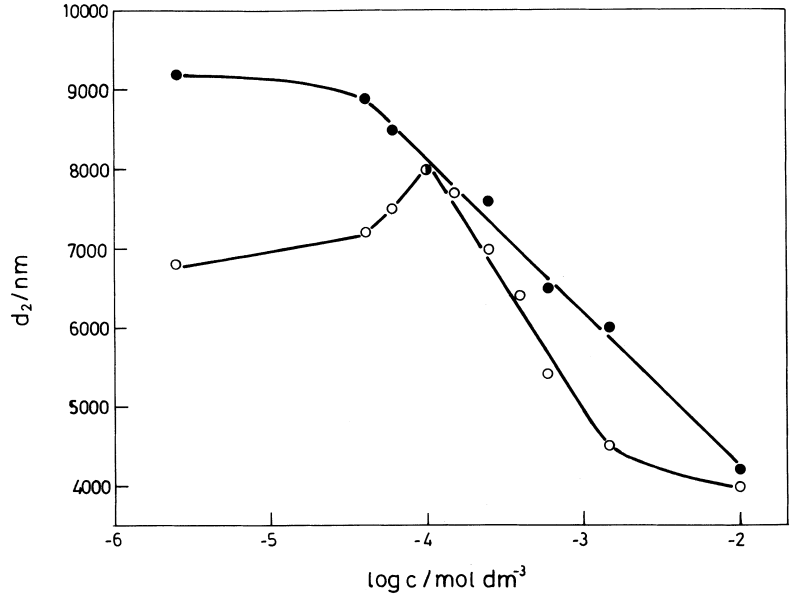


Fig. 7 Mean crystallite size, d_2, vs c for two cross-sections with constant c(CTAB) = 1×10^{-4} mol dm^{-3} (●), or c(NaDS) = 1×10^{-4} mol dm^{-3} (○), respectively. The temperature is 303 K and the aging time is 1 day

Due to very close packing of the oppositely charged headgroups the effective hydrophobic volume will also be larger compared to average volumes of the single surfactants, i.e. the effective size of the headgroup decreases but must accommodate roughly twice the hydrophobic volume. These two effects increase the effective packing parameter and promote the formation of a planar lamellar structure. As the surfactant molar ratio moves away from the equimolar composition, the unpaired surfactants in the bilayer create a surface charge density, i.e. the electrostatic repulsion within the headgroup region grows. These repulsions favor the microstructure that best allows larger effective headgroup areas, such as vesicles and mixed micelles. This is exactly the structural transition that is observed in CTAB/NaDS mixtures.

Table 4 **a** Apparent degree of bromide ion dissociation, α_{Br}, from mixed micelles formed in mixtures with constant c(NaDS) and varying c(CTAB) and **b** apparent degree of sodium ion dissociation, α_{Na}, from mixed micelle formed in mixtures with constant c(CTAB) and varying c(NaDS) calculated from conductivity (I) and potentiometric measurements (II). Temperature is 303 K

System	I		II
a NaDS/mol dm^{-3}		α_{Br}	
0	0.29		0.25
2×10^{-6}	0.29		0.28
3×10^{-6}	0.29		0.28
5×10^{-6}	0.29		0.28
1×10^{-5}	0.30		0.29
2×10^{-5}	0.30		0.30
b CTAB/mol dm^{-3}		α_{Na}	
0	0.40		0.32
2×10^{-6}	0.42		0.42
3×10^{-6}	0.45		0.43
5×10^{-6}	0.45		0.48
1×10^{-5}	0.48		0.46
2×10^{-5}	0.48		0.48

Recently, we have found that in cationic/anionic surfactant mixtures with symmetric alkyl chains a crystalline catanionic surfactant precipitate is formed over a wide range of compositions, while the vesicle phase is formed in a relatively narrow range [3–6]. Vesicles do not form in equimolar mixtures. On the contrary, in mixtures with an asymmetric alkyl chain the vesicle phase is considerably enlarged and vesicles were observed even in equimolar mixtures. This means that the asymmetric alkyl chains cannot pack so efficiently into crystalline lattices as symmetric alkyl chains. When a lamellar structure is composed of surfactants with different chain lengths, the aggregate properties may be treated in terms of a certain mean packing parameter intermediate between those of individual components [38]. The size of a curved structure may thus be increased or decreased by adding an appropriate amount of another component whose packing parameter is larger or smaller. The spacing between adjacent surfactant molecules increases proportionally with the difference in the chain length of the mixed surfactant. Although these changes are very small, they have a very large effect upon aggregate properties. A different chain length results in a looser packing of an aggregate.

Even small deviations from equimolar samples had a dramatic influence on the system due to the electrostatic balance disturbance at the aggregate/solution interface and the packing of hydrophobic tails in the bilayer. In the nonequimolar samples the attractive forces were weaker and less packed supramolecular structures were mainly found. The fraction of the planar and curved lamellar phase was altered by the total surfactant concentration and by the mixing ratio of the two surfactants. The maximum vesicle and crystallite sizes were recorded at equimolar conditions. Vesicles decreased in size with either increase or decrease of the surfactant molar ratio.

Yuet and Blankschtein [18] showed that the free energy of vesicle formation is a sum of several energy contributions: the transfer free energy, the packing free energy, the interfacial free energy, the steric free energy, and the electrostatic free energy. By using the molecular-thermodynamic approach they have studied the role of asymmetry between hydrophobic tails in the formation and stability of vesicles composed of cationic and anionic surfactants. They found that chain packing in the vesicle bilayer has an important effect on the free energy of vesicle formation. A mixed surfactant vesicle can be stabilized energetically in highly asymmetric surfactant mixtures, but when the tail-length asymmetry is small, vesicles are stabilized entropically. Vesicles which are stabilized energetically have a lower free energy of vesiculation than planar bilayers, thus making them more energetically favorable. Surfactant tail-length asymmetry also affects the optimum composition of a vesicle by altering the tail-transfer energy contribution. In highly asymmetric mixtures the optimum vesicle composition reflects a compromise between entropic and energetic factors. With decreasing surfactant tail-length asymmetry, the energetic contribution to the composition distribution is decreased via a reduction in tail-transfer energy [18, 19].

In conclusion, the main factors affecting the transition from a planar to a curved bilayer in asymmetric cationic/anionic surfactant mixtures comprise electrostatic interactions between the surfactant headgroups and chain packing. The effective area per headgroup increases as mixtures shifted from the equimolar range due to the change in the electrostatic interactions from attractive to repulsive. The net effect is a decrease in the packing parameter and the promotion of a curved lamellar structure. When a curved lamellar structure is composed of surfactants with different chain lengths, the spacing between the adjacent surfactant molecules increases proportionally to the difference in the chain length of mixed surfactants.

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References

1. Stellner KL, Amante JC, Scamehorn JF, Harwell JH (1988) J Colloid Interface Sci 123:186
2. Walker SA, Zasadzinski JA (1997) Langmuir 13:5076
3. Tomašić V, Filipović-Vinceković N, Kojić-Prodić B, Kallay N (1991) Colloid Polym Sci 269:1289
4. Filipović-Vinceković N, Škrtić D, Tomašić V (1991) Ber Bunsenges Phys Chem 95:1646
5. Filipović-Vinceković N, Bujan M, Dragčević Đ, Nekić N (1995) Colloid Polym Sci 273:182
6. Bujan M, Vdović N, Filipović-Vinceković N (1996) Colloids Surf A 118:121
7. Kaler EW, Herrington KL, Murthy AK (1992) J Phys Chem 96:6698
8. Jönsson B, Jokela P, Khan A, Lindman B, Sadaghiani A (1991) Langmuir 7:889
9. Marques E, Khan A, Miguel M da G, Lindman B (1993) J Phys Chem 97:4729
10. Dragčević Đ, Bujan M, Grahek Ž, Filipović-Vinceković N (1995) Colloid Polym Sci 273:967
11. Regev O, Khan A (1996) J Colloid Interface Sci 182:95
12. Swanson M, Almgren M, Bergenstahl B, Mukhtar E (1996) J Colloid Interface Sci 178:538
13. Kamenka N, Chorro M, Talmon Y, Zana R (1992) Colloids Surf 67:213
14. Li X, Lin E, Zhao G, Xiao T (1996) J Colloid Interface Sci 184:20
15. Huang JB, Zhao GX (1995) Colloid Polym Sci 273:156
16. Safran S, Pincus P, Andelman D (1990) Science 248:354
17. Fattal DR, Andelman D, Ben-Shaul A (1995) Langmuir 11:1154
18. Yuet PK, Blankschtein D (1996) Langmuir 12:3802
19. Yuet PK, Blankschtein D (1995) Langmuir 12:3819
20. Bergström M, Eriksson JC (1996) Langmuir 12:624
21. Kozlov MM, Andelmann D (1996) Curr Opin Colloid Interface Sci 1:362
22. Yatcilla MT, Herrington KL, Brasher LL, Kaler EW (1996) J Phys Chem 100:5874
23. Kaler EW, Murthy AK, Rodriguez BE, Zasadzinski JA (1989) Science 245:1371
24. Fendler J (1983) Membrane mimetic chemistry. Wiley, New York
25. Gabriel NE, Roberts MF (1984) Biochemistry 23:4011
26. Filipović-Vinceković N, Bujan M, Šmit I, Tušek-Božić Lj, Štefanić I (1998) J Colloid Interface Sci 201:59
27. Demus D, Richter L (1978) Textures of liquid crystals. VEB, Leipzig
28. Filipović-Vinceković N, Škrtić D (1988) Colloid Polym Sci 266:954
29. Rosen MJ (1978) Surfactants and interfacial phenomena. Wiley, New York, p 59
30. Ngyen CM, Scamehorn JF (1988) J Colloid Interface Sci 123:238
31. Rosen MJ (1986) ACS Symp Ser 311:144
32. Rubingh DN (1979) Solution chemistry of surfactants Plenum, New York, p 337
33. Liu CL, Jain UK, Higuchi WI, Mazer NA (1994) J Colloid Interface Sci 162:437
34. Lucassen-Reynders EH, Lucassen J, Giles D (1981) J Colloid Interface Sci 81:50
35. Goralczyk D (1991) Colloids Surf 59:361
36. Tomašić V, Popović S, Tušek-Božić Lj, Pucić I, Filipović-Vinceković N (1997) Ber Bunsenges Phys Chem 101:1942
37. Hoffmann H, Pössnecker G (1994) Langmuir 10:381

38. Israelachvili JN (1985) Intermolecular and surface forces. Academic Press, London
39. Hyde ST (1990) Prog Colloid Polymer Sci 82:236
40. Safran SS (1994) Statistical thermodynamics of surfaces, interfaces and membranes. Addison-Wesley, Reading, Mass, p 238
41. Hoffmann H (1984) Ber Bunsenges Phys Chem 88:1078