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Phase behaviour and vesicle formation in catanionic mixtures of Na oleate and alkyl trimethyl ammonium bromide and its salt-free version

Ekramun Nabi^{1,3} • M. Drechsler² • Michael Gradzielski³

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Abstract We have investigated catanionic mixtures of the anionic surfactant sodium oleate with various alkyltrimethyl ammonium bromides of different alkyl chain length between octyl and tetradecyl. Around equimolar mixing vesicles are formed but only for a chain length of decyl and longer. For shorter chains and with increasing asymmetry of the mixing ratio, the vesicle phase disappears and instead wormlike micelles are formed, which leads to a viscoelastic behaviour of the samples. The vesicle systems are often also viscoelastic, if they contain densely packed multi-lamellar vesicles but this depends also on their salt content, as for instance the salt-free decyl system forms unilamellar vesicles of low viscosity. It is observed that the most well-defined vesicles (unilamellar) occur upon admixing the intermediate cationic surfactant with the dodecyl chain, which then results in low viscous solutions. In general, by appropriately choosing the mixing ratio, the length of the alkyl chain and also the ionic strength of the solution can tune the structure and the properties of these catanionic surfactant mixtures over a wide range in a systematic fashion.

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Michael Gradzielski Michael.Gradzielski@TU-Berlin.de

- ¹ Lehrstuhl für Physikalische Chemie I, Universität Bayreuth, D-95440 Bayreuth, Germany
- ² Bayreuther Institut für Makromolekülforschung (BIMF), Laboratory for Soft Matter Electron Microscopy, Universität Bayreuth, D-95440 Bayreuth, Germany
- ³ Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, D-10623 Berlin, Germany

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Introduction

Mixtures of cationic and anionic surfactants, i. e. catanionics, may form viscoelastic solutions [1-3] but more frequently they either form precipitates [4, 5], lead to spontaneous formation of vesicles [6-10] or even to the formation of highly ordered lamellar phases or well-defined polyhedra [11, 12]. Whether at a given temperature vesicles are formed or precipitates, depends mainly on the stability of the crystalline arrangements in the precipitates. Typically, precipitation becomes more important with increasing chain length of the surfactants [5, 13] as that enhances their tendency for crystallisation. In principle, the phenomenon of precipitation is directly related to the Krafft phenomenon [14], and for catanionics is nothing other than the formation of a surfactant salt, where the counterion is the oppositely charged surfactant. Whether in the catanionic solution mixture vesicles or wormlike micelles are formed basically depends on the packing parameter that is achieved in such a strongly synergistic system.

Vesicles, and in particular unilamellar vesicles, as they are frequently formed in catanionic surfactant mixtures [7-9, 15], are interesting systems for potential applications in drug delivery or cosmetic formulations [15-19]. However, for such purposes, the process of precipitation is an unwanted effect. Therefore, it is interesting to study catanionic surfactant systems where precipitation does not take place. Accordingly, one has to look for surfactant pairs where the tendency for crystallisation is suppressed. In general, this can be achieved by having surfactants that are branched or contain double bonds in their alkyl chain (as for instance is the case for phospholipids of organisms and animals that have to live in an environment of low temperature [20]).

For our investigations on such surfactant systems with a low tendency for precipitation, we chose sodium oleate (NaOl), which is a classical soap molecule that has been studied intensely before [21, 22]. It forms slightly elongated micelles [22, 23] in solution for concentrations well above the cmc, and its Krafft point is significantly lower compared to the corresponding saturated alkyl chain [24], i.e. sodium stearate (Krafft point: 79 °C [24]). Together with its corresponding acid, oleic acid or for addition of medium-chain alcohols such as octanol, sodium oleate has been shown to form small unilamellar vesicles spontaneously [25-28], and vesicles have also been observed in mixtures of sodium oleate and oleyldimethylamine oxide [29]. Similarly, oleic acid can act as such a cosurfactant, and it is automatically formed at lower pH and therefore one observes a pH-induced micelle-tovesicle transformation for the sodium oleate system [30, 31].

In our study, we employed Na oleate in combination with various alkyltrimethyl ammonium bromides or hydroxides with straight alkyl chains of the cationic surfactant from 8 to 14 carbon atoms, in order to explore the effect of a systematic variation of the chain length. Similar systems had been studied before, but not in a systematic fashion. For instance for short chain alkyltrimethyl ammonium bromides such as C₆ and C₈, it has been shown that long rod-like micelles are formed thereby yielding viscoelastic solutions for a surfactant concentration of 3 wt% [1]. A recent investigation of 3 wt% mixtures of Na oleate/OTAMBr (octyltrimethyl ammonium bromide) by means of cryogenic transmission electron microscopy (cryo-TEM) showed that the viscosity peak observed for a 70/30 Na oleate/OTMABr mixture is due to micellar growth of rod-like micelles that at the viscosity peak are very elongated and branched [32]. Similarly for the case of adding cetyltrimethylammonium bromide (CTAB) to sodium oleate, the formation of elongated micelles and viscoelastic systems has been observed, where upon increasing the total surfactant concentration a transition from linear to branched micelles has been deduced [33]. For the longer chain C_{10} and C_{12} alkyltrimethyl ammonium bromides at a constant concentration of 3 wt%, an extended two-phase region has been observed that has not been studied in much detail but was concluded to contain surfactant bilayers in the form of vesicles [1]. However, this comparative work [1] focused mainly on the formation and properties of viscoelastic systems of wormlike micelles.

In contrast, our perspective was to determine in detail the tendency for vesicle formation of Na oleate as a function of the chain length of the admixed cationic surfactant in a systematic fashion. By doing so, we explore how vesicle size and polydispersity are related to the molecular composition of the catanionic surfactant pair. The aim then is to find optimised conditions for given applications by variation of size and polydispersity, i.e. systematic relations between the ability for vesicle formation and the chain length of the cationic surfactant. For that purpose in our experiments, we varied the mixing ratio of Na oleate and cationic surfactant and the total concentration in order to see how the composition of the surfactant system affects the behaviour of the corresponding mixtures. Finally for the case of the decyl system, we also addressed the question of the effect of salt being present in the mixtures, by studying the corresponding salt-free system. It might be noted that for our systems, we did not observed a dependence of the structural properties on the preparation path and also no ageing (except for the precipitation range, where precipitation may require some time to occur). This indicates that the vesicles here form not only spontaneously but also seem quickly to achieve a final equilibrium state, as seen previously for related catanionic surfactant mixtures [10].

Materials and methods

Materials

Sodium oleate (Na oleate, cmc=0.9 mM [34]) was prepared by pH-titration of oleic acid (Fluka, technical quality), according to the method of Flockhart and Graham [35] in aqueous solution. Titration was performed in an enclosed environment, so that atmospheric CO₂ could not become absorbed into the solution (this is important as the equivalence point of the titration is in the basic region, see Fig. S1).

Octyl trimethyl ammonium bromide (OTMABr, cmc= 257 mM [34]), decyl trimethyl ammonium bromide (DeTMABr, cmc=64.6 mM [34]), dodecyl trimethyl ammonium bromide (DTMABr, cmc=16.0 mM [34]) and tetradecyl trimethyl ammonium bromide (TTMABr, cmc=3.6 mM [34]) were purchased from Fluka with purity \geq 98 % (TTMABr: \geq 99 %) and used without further purification or treatment. D₂O in 99.9 % isotopic purity was obtained from Eurisotop (Gif-sur-Yvette, France). For all experiments not employing D₂O, deionised water was used.

Decyl trimethyl ammonium hydroxide (DeTMAOH) was obtained from DeTMABr by passing it through a basic ion exchange column. Its cmc was determined by means of the surface tension method to be 69.3 mM (where our own measurement for the employed DeTMABr yielded 57.2 mM, i.e. a value somewhat lower than the literature value of 64.6 mM [34]). It is interesting to note that the surface tension curves for DeTMABr and DeTMAOH differ significantly in their appearance; as for the DeTMAOH, a pronounced minimum is observed at the cmc which is not present for DeTMABr (see Fig. S2 in the supplementary information). This peculiar behaviour has not been accounted for yet, but we confirmed that it is not due to contamination of the DeTMAOH by DeTMABr (which could be the case due to the ion exchange performed), by deliberately adding DeTMABr to the obtained DeTMAOH and measuring the corresponding surface tension curves.

Methods

For the study of the phase behaviour, the respective stock solutions of cationic or anionic aqueous surfactant solutions were mixed in the appropriate amount and subsequently homogenised by using a vortex mixer and placed in a thermostat at 25 °C. The next day, the samples were homogenised again and kept afterwards in the thermostat at 25 °C for 1 week. During this time, samples were completely at rest in order to achieve equilibrium conditions.

Conductivity measurements were performed with a microprocessor conductivity meter LF 197i. It has a thermal sensor connected to the cell, so the device is capable of measuring conductivity and temperature (accuracy ± 0.1 °C) of the solution simultaneously. A standard-conductivity cell TetraCon 325 with a cell constant 0.475 cm⁻¹ (± 1.5 %) was used. The instrument was calibrated regularly by means of aqueous KCl standard solutions. The conductivity for every system was measured at 25.0 °C after 1 week of equilibration at this temperature. During the measurements, the solutions were at rest. For the case of biphasic samples, they were shaken and homogenised and then directly measured before separating again.

Surface tension measurements were performed by a Lauda tensiometer TE 1C (Du Noüy ring method) equipped with a thermo-controller. Before each measurement, calibration was done using the standard ring and the samples were measured repeatedly for more than three cycles. The deviation from the accepted result was set below 0.2 mN/m in every cycle of measurement.

For cryo-transmission electron microscopy studies, a sample droplet of 2 µl was put on a bare copper grid (600 mesh, thin bar, Science Services, Muenchen). Subsequently, most of the liquid was removed with blotting paper leaving a thin film stretched over the holes. The specimens were instantly shock frozen by rapid immersion into liquid ethane cooled to approximately 90 K by liquid nitrogen in a temperaturecontrolled freezing unit (Zeiss Cryobox, Carl Zeiss Microscopy GmbH, Jena, Germany). The temperature was monitored and kept constant in the chamber during all the sample preparation steps. The specimen was inserted into a cryotransfer holder (CT3500, Gatan, Muenchen, Germany) and transferred to a Zeiss/LEO EM922 Omega EFTEM (Zeiss Microscopy GmbH, Jena, Germany). Examinations were carried out at temperatures around 90 K. The TEM was operated at an acceleration voltage of 200 kV. Zero-loss filtered images $(\Delta E=0 \text{ eV})$ were taken under reduced dose conditions $(100-1000 \text{ e/nm}^2)$. All images were registered digitally by a bottom-mounted CCD camera system (Ultrascan 1000,

Gatan, Muenchen, Germany) combined and processed with a digital imaging processing system (Digital Micrograph GMS 1.5, Gatan, Muenchen, Germany).

The rheological measurements were done with a Haake RS600 with a cone-plate system and a Haake RS300 with a double-gap cylindrical system. These two different shear geometries were used depending on the viscosity of the solutions: RS600 was employed for highly viscous fluids or gels and RS300 for low viscous liquids. During the measurement, the temperature was controlled to an accuracy of ± 0.1 °C by a thermo-controller (Haake TC81) for RS600 and by an ethylene glycol circulator with an accuracy of ± 0.5 °C for RS300. The measurements were operated by the software Haake RheoWin Job Manager, and the measured data were analysed by Haake RheoWin Data manager.

The dynamic light scattering (DLS) measurements were done by means of an ALV DLS/SLS SP 5022F compact goniometer system with an ALV 5000/E correlator. A He-Ne laser of 632.8 nm wavelength served as light source, and samples were typically measured at 90° scattering angle. Prior to the light scattering experiments, the sample solutions were filtered using Millipore Nylon filters with a pore size of 450 nm. During the measurements, the temperature was kept constant at 25 ± 0.2 °C by means of a thermostated water circulator.

Small-angle neutron scattering (SANS) experiments were performed at the instrument PACE of the Laboratoire Léon Brillouin using neutrons of a wavelength of 0.6 nm and sample-to-detector distances of 1 and 4 m, as well as with a wavelength of 1.2 nm and a sample-to-detector distance of 4 m, thereby covering a q-range of 0.005–0.32 Å⁻¹. The raw data were afterwards corrected for the sample transmission, cuvette background, and then put onto absolute scale by comparison with the scattering from a 1 mm water sample by using standard routines [36].

Results and discussion

Mixtures of Na oleate and alkyltrimethly ammonium bromide

Phase behaviour-macroscopic observation

The phase behaviour of the catanionic systems based on Na oleate as anionic surfactant and the various alkyl trimethyl ammonium bromides as cationic surfactants was explored by visual inspection in the concentration range from 10 mM (for TTABr: 5 mM) up to a total surfactant concentration of 200 mM (in steps of 25, 10 or 5 mM—as found to be appropriate), and covering all mixing ratios of cationic and anionic surfactant.

The simplest phase behaviour is observed for the ternary system Na oleate/octyltrimethyl ammonium bromide (OTMABr)/water. Here, all samples are clear, transparent and single phase within the studied concentration range of 10 to 200 mM total concentration. The most noticeable point for this system is that no phase separation or precipitate formation is observed, as it is otherwise typically found for catanionic systems [15]. However, although the pure anionic and cationic samples have almost water-like viscosity, the viscosity of samples with concentration ≥50 mM and for compositions around equimolar mixing is increasing significantly with increasing total concentration as similarly observed before [1]. Yet, in that study, only micelles were observed, and no vesicle formation was observed for 3 wt% total surfactant concentration. For higher concentrations, we observed that these samples exhibit viscoelastic properties. This is in good agreement with these former observations by Kaler et al. where an increase by about six orders of magnitude was reported for about equimolar mixing at 3 wt% total concentration [1]. However, our observations confirm that in this system, no vesicular structures are formed (as they would normally already lead to a substantial increase of turbidity).

A very different and much more complex phase behaviour is observed for the Na oleate/DeTMABr system for which the partial phase diagram is given in Fig. 1. Of course, the pure anionic and cationic solutions form visually transparent and isotropic micellar L_1 -phases. Upon gradually increasing the amount of contained DeTMABr in the mixture, one finds for a total concentration higher than 20 mM that the isotropic L_1 phase becomes transformed into a two-phase region composed of a clear L_1 -phase and a much more turbid and bluish vesicle phase (L_v). Around equimolar mixing ratio, a pure isotropic vesicle phase is then present, which is characterized by its bluish appearance. Upon increasing the content of anionic surfactant, the same behaviour is observed again, i.e. passing through a two-phase region before entering the micellar L₁-phase of the anionic Na oleate solution again. The passing through a two-phase region clearly indicates that the transition from micellar to vesicle solution is a first-order phase transition. Such a behaviour has been observed for a variety of catanionic [9, 15, 37-39] or zwitanionic [40, 41] surfactant mixtures before. The main difference to the majority of phase diagrams reported so far is that even at equimolar mixing ratio, no precipitate formation is observed, a finding that has to be attributed to the presence of the oleate that suppresses crystal formation. However, the phase diagram is clearly asymmetric with a pronounced extension of the two-phase region towards the DeTMABr side, which can be explained by the fact of the large difference between the chain lengths of the two surfactants and the corresponding largely different cmc (factor of 70). It is also interesting to note that vesicle formation is observed well below the cmc of the pure DeTMABr (indicated in Fig. 1 by the dotted line). Obviously, the tendency for formation of mixed aggregates is very much enhanced due to the presence of the oppositely charged surfactant and the correspondingly pronouncedly synergistic mixing.

For the case of the Na oleate/DTMABr system, the phase diagram (Fig. 2) looks already much more symmetric, as might be expected due to the more similar cmc's. Here, an extended vesicle phase is observed with its centre shifted to-wards the side of the anionic surfactant and again showing no precipitate formation. It is interesting to note that the lowest concentration required for the formation of the pure vesicle phase with 40 mM is somewhat higher than for the case of the DeTMABr system. The compositional width of the vesicle phase is similar as in the case of DeTMABr.

In comparison, the phase diagram for the Na oleate/ TTMABr (Fig. 3) now looks much more complicated than



Fig. 1 Phase diagram of the ternary system Na-oleate/DeTMABr/water at 25 °C (L_1 isotropic micellar phase, L_v bluish isotropic vesicle phase, and 2 Φ 2-phase region of L_1/L_v ; cmc of pure DeTMABr is indicated for the different mixing ratios)



Fig. 2 Phase diagram for the ternary system of Na-oleate/DTMABr/ water at 25 °C (L_1 isotropic micellar phase, L_v bluish isotropic vesicle phase, and 2Φ : 2-phase region of L_1/L_v ; cmc of pure DTMABr is indicated for the different mixing ratios)



Fig. 3 Phase diagram for the ternary system of Na-oleate/TTMABr/ water at 25 °C (L_1 isotropic micellar phase, L_v bluish isotropic vesicle phase (either positively or negatively charged), *P* precipitation, and 2Φ 2phase region of L_1/L_v ; cmc of pure TTMABr is indicated for the different mixing ratios)

for the shorter chain counterparts. Again, one finds vesicle formation upon admixing similar amounts of oppositely charged surfactant, and the phase diagram is rather symmetric. Compared to the shorter chain cationic surfactants, the vesicle phase is broader with respect to the mixing ratios and extends to a lower total surfactant concentration of 18 mM. However, in addition, one observes the formation of a precipitate (here denoted as P), which splits the vesicle region into a lobe rich of anionic surfactant (L_{v}) and one rich in cationic surfactant (L_{v+}) . Apparently, the longer chain cationic surfactant is responsible for the formation of a precipitate, and such behaviour is typical for catanionic surfactant mixtures [15, 41]. The formation of cationic or anionic vesicles is due to the fact that the residual charge remaining on the vesicles for nonequimolar mixing is effectively stabilising the dispersed vesicles.

Accordingly, we find a very systematic change of the phase behaviour upon admixing alkyl trimethyl ammonium bromides of different alkyl chain length to Na oleate. While for the octyl chain, apparently, only micellar solutions are formed; formation of vesicles takes place for all longer chain cationic surfactants. This has to be due to the packing parameter p [42]:

$$p = \frac{v_s}{a_s \cdot l_s} \tag{1}$$

where the packing parameter is determined by the volume v_s of the hydrophobic part of the surfactant, its head group area a_s and the length l_s of the stretched hydrophobic chain. Accordingly, the packing parameter p increases systematically with increasing chain length of the cationic surfactant. It is interesting to note that in all cases, we observe coexistence regions for vesicles and rod-like micelles. However, for the decyl and dodecyl chain, no precipitate formation is observed, which only occurs for the case of the tetradecyl surfactant.

Evidently, only here the alkyl chain of the cationic surfactant is sufficiently long to allow for effective crystal formation at room temperature.

Electric conductivity

A first indication of the structural changes that take place in these mixtures is possible by means of measurements of electric conductivity. These results at 100 mM total concentration as a function of composition are displayed in Fig. 4 for the various catanionic surfactant mixtures. Obviously, the conductivity of pure cationic solutions increases significantly with decreasing alkyl chain length in agreement with the increasing cmc (which should be close to the concentration of monomerically dispersed surfactant under these conditions).

For OTMABr, a continuous and linear decrease with increasing content of Na oleate is observed, in agreement with the observed phase behaviour where a continuous L_1 -phase is seen. At x(NaOl), the high conductivity arises from the monomerically dissolved OTMABr and with increasing Na oleate content the OTMABr becomes incorporated into micelles, which explains the reduced conductivity. For the other cationic surfactants, the admixture to the Na oleate leads to a steady increase in conductivity until around $x_{NaOA} = 0.8$. This increase can be explained by the counterions released upon surfactant pairing (they contribute more strongly to the conductivity then the more bulky surfactant ions). At higher content of cationic surfactant, a reduced increase of the electric conductivity is observed (evidenced by a bump in the curves of Fig. 4) that can be explained by vesicle formation. Here, the released counterions become partly enclosed within the



Fig. 4 Specific electric conductivity κ at 25 °C as a function of the mole fraction of Na oleate (x(NaOl)) for mixtures of 100 mM total concentration and for various cationic surfactants (\square : OTMABr, \bigcirc : DeTMABr, Λ : DTMABr, ∇ : TTMABr). The samples in the 2 Φ -region (indicated by *dashed lines*) or precipitate regime were measured after homogenising them prior to the measurements

interior of the vesicles and hence can no longer contribute to the electric conductivity. Accordingly, the measurement of conductivity allows for a very easy determination of the occurrence of vesicles by the relative reduction of conductivity that would otherwise be expected (and even allows in principle for estimating the vesicle size [43]). The qualitatively different behaviour of the OTMABr system at low content of Na oleate is simply due to the fact that here no micelles are present for the pure cationic system, and accordingly a release of counterions by admixing Na oleate cannot take place. Therefore, one only observes a continuous decrease of conductivity with increasing content of Na oleate.

Cryogenic transmission electron microscopy

The presence of vesicles in the intermediate mixing regime is most clearly documented by means of cryogenic transmission electron microscopy (cryo-TEM) experiments, which show, for the case of DeTMABr (Fig. 5), a mixture of unilamellar and multi-lamellar vesicles with sizes from 60 nm of up to 1 µm (it should be noted that the upper limited is difficult to image as for larger vesicles it will not be possible to be contained within the thin film of the cryo-TEM preparation). However, it is apparent that the vesicles are very polydisperse with the majority having diameters in the range of 80-200 nm. It is also visible that most unilamellar vesicles are again encapsulated by closed bilayers, i.e. one has multi-lamellar vesicles with multiple cores. Accordingly, the bilayer system here does not show well-defined structures but is rather varied with respect to its morphology. From Fig. 5, it is also apparent that the vesicles present here are rather densely packed due to their relatively large average size, which also explains the substantial drop of conductivity (see Fig. 4) and the corresponding large increase in viscosity (Fig. 6), as here one has almost no free counterions and a densely packed system.



Fig. 5 Cryo-TEM micrograph of vitrified specimen of the catanionic mixture of NaOA: DeTMABr=1:1 at 100 mM total concentration



Fig. 6 Zero-shear viscosity η_0 as a function of the mole fraction of Naoleate in catanionic mixtures at 100 mM total concentration and 25 °C for various alkyltrimethyl ammonium bromides. (\square : OTMABr; \bigcirc : DeTMABr; \bigwedge : DTMABr; \bigvee : TTMABr; samples in the vesicle phase are denoted with full symbols)

Rheology

The viscosity in the mixtures of Na oleate and the various alkyl trimethyl ammonium bromide changes drastically as a function of the composition of the mixture-except for the case of DTMABr. In Fig. 6, the zero-shear viscosity as a function of the content of the anionic Na oleate for a total concentration of 100 mM surfactant is shown for the cationic surfactants of different alkyl chain lengths. In general, one finds that the viscosity increases pronouncedly (by more than three orders of magnitude) around equimolar mixing ratios. It is interesting to note that this increase occurs similarly for the system that remains in the L₁-phase (OTMABr) and for the others where around equimolarity vesicle phases are formed. Apparently, the viscosity behaves similar for the case of large entangled wormlike micelles or for the one of densely packed vesicles (Fig. 5). In contrast, for the case of DTMABr, the viscosity remains always low, independent of the mixing ratio of cationic and anionic surfactant, and the solutions show simple Newtonian flow behaviour. It might be pointed out that already in the previous work by Raghavan et al. [1], only a much smaller viscosity increase had been observed for the DTMABr system. This is a very intriguing observation and an explanation is that here, relatively small unilamellar vesicles are formed that do not lead to a high effective volume fraction of vesicles, and in the region before their formation in the phase diagram also no elongated micelles are formed (as observed in the case of OTMABr). Therefore, no pronounced increase in viscosity takes place, while for DeTMABr (see Fig. 5) and TTABr, large and multi-lamellar systems are formed that posses a high effective volume fraction and are densely packed.

Further rheological investigations showed a pronounced shear thinning for the viscous samples of the OTMABr/Na Ol system (Fig. 7a) as it is typically observed for wormlike micelles [44–46]. For high shear rates, the viscosity then becomes basically reduced to that of the solvent. This decrease of the apparent viscosity appears at lower shear rates; the higher the zero-shear viscosity of the given system, which is the case for about equimolar mixing.

For these cases of pronounced shear thinning, the viscosity curves were analysed by means of the cross-equation [47]:

$$\eta = \frac{\eta_0 - \eta_\infty}{1 + (\dot{\gamma} \cdot \tau)^m} + \eta_\infty \tag{2}$$

where η_0 and η_∞ are the viscosities in the low and high shear rate limit, respectively, $\dot{\gamma}$ the shear rate, τ a characteristic time (the inverse of the shear rate at which the viscosity drops half the value between η_0 and η_∞) and *m* a parameter that describes the cooperativity of the shear thinning effect. Of course, the



Fig. 7 Shear viscosity η as a function of the shear rate for catanionic mixtures at 100 mM total concentration at 25 °C for various mixing ratios of **a** NaOl/OTMABr; x(OTMABr)=0.8 (\square), 0.6 (\bigcirc), 0.5 (\bigwedge), 0.4 (\heartsuit), 0.2 (\diamondsuit) and **b** NaOl/DeTMABr; x(DeTMABr)=0.9 (\square), 0.8 (\bigcirc), 0.6 (\bigwedge), 0.5 (\heartsuit), 0.4 (\diamondsuit), 0.2 (\checkmark), 0.1 (\triangleright)

cross-equation can only be applied to viscosity curves where the plateaus at high and low shear rates are reached. In addition, for all cases with a low shear rate plateau, we also deduced from visual inspection of the viscosity curves the zeroshear viscosity and the critical shear rate $\dot{\gamma}_{cr}$ at which the viscosity starts to be reduced.

For the case of mixtures with DeTMABr, pronounced shear thinning is only observed for the 5:5 mixture while for the other mixing ratios, an extended viscosity plateau is observed, indicating Newtonian flow behaviour (Fig. 7b). Only at very high shear rates of above 1000 s^{-1} some shear thinning is observed, but these values have to be taken with some precaution since at such high shear rates, the measurements are not really very reliable.

The data are summarized in Table 1 and show that at high shear rate always water viscosity is approached. For the OTMABr system, the values of the characteristic time τ become smaller in a similar fashion as the zero-shear viscosity η_0 of the samples. In comparison, for the most viscous systems with DeTMABr and TTMABr, not only η_0 becomes consistently higher but the increase of τ is even more pronounced. This means that with increasing chain length of the cationic surfactant, the shear thinning sets in earlier, which could be interpreted such that here stiffer rod-like micelles are formed. These then are correspondingly more easily oriented, and this leads to the observed shear thinning. An even more pronounced shear thinning is found for the vesicular samples, as seen for instance to the case of the TTMABr system (Fig. S3b). This is an indication that here the vesicles must be densely packed (in agreement with the cryo-TEM given in Fig. 5) and for such a situation, one often observes a shear thinning behaviour which is described by a power law according to $\eta \tilde{\gamma}^{m}$, where the exponent is typically in the range of 0.7-0.8 [48, 49]. In addition, some of the shear rate-dependent changes of viscosity can also be related to the change of the vesicle morphology, for instance by ripping off outer shells of multi-lamellar vesicles due to the shear forces [50].

Dynamic light scattering

In order to gain further insight into the structural and dynamical behaviour of these systems, dynamic light scattering

 Table 1
 Parameters of the fit of the cross-equation (Eq. 1) to the rheological data

	η_0 [Pas]	η_{∞} [Pas]	τ[s]	m	γ_{cr}
x(OTMABr)=0.4	1.43	0.0094	0.085	1.32	4.7
x(OTMABr)=0.5	0.243	-	0.008	1.41	34.5
x(OTMABr)=0.6	0.043	_	0.0024	0.77	214
x(DeTMABr)=0.5	2.26	_	107	0.63	0.03
x(TTMABr)=0.6	46.9	_	698	0.63	0.02
x(TTMABr)=0.3	0.78	_	24	0.72	8.5

(DLS) measurements were performed. In Fig. 8, intensity autocorrelation functions are given for mixtures of Na oleate with DeTMABr and TTMABr for various mixing ratios. It is apparent that the relaxation process becomes much slower with increasing content of the cationic surfactant, being almost two orders of magnitude slower for the ~equimolar mixtures compared to the pure Na oleate micelles, where one observes a hydrodynamic radius of 1.54 nm. This means that the structural units in the mixtures are correspondingly larger than simple micelles of the pure surfactant solutions. At the same time, the relaxation remains monomodal, i.e. we do not observe two different types of aggregates here.

From these data, we determined with a cumulant fit the hydrodynamic radius $R_{\rm h}$ for the different samples, and the data are collected in Fig. 9. It is evident already that within the L₁phase, some increase of $R_{\rm h}$ occurs that can be attributed to the formation of rod-like micelles. However, the much bigger sizes are seen then upon the formation of vesicles. It might be noted that the values of $R_{\rm h}$ here do not really reflect the actual size of the vesicles, as for instance seen for the 1:1 mixture of Na oleate and DeTMABr (x(NaOl)=0.5), $R_{\rm h}$ is only 38 nm but in Fig. 5 for the twice as concentrated sample vesicles of several 100 nm are seen. This discrepancy is due to the fact that in DLS, one sees collective diffusion, but for such a densely packed vesicle system the collective diffusion is no longer directly related to an individual particle size and accordingly the 38 nm obtained here do not really indicate a structural size of the vesicles present. It might be added that the polydispersity indices obtained from the cumulant fit are always in the range of 0.2-0.25, indicating that here rather polydisperse systems are present.

In summary, it can be stated that cryo-TEM, rheology, DLS and electric conductivity yield a consistent picture that confirms and details the structural phase behaviour given in Figs. 1, 2 and 3. The pure surfactants form spherical micelles by themselves but upon admixture of the oppositely charged surfactant elongation of the micelles is observed that can then quickly lead to the formation of viscoelastic networks of wormlike micelles. Around equimolar mixing then the preferred curvature approaches zero and therefore vesicles are formed, which is clearly indicated by a substantial further size



Fig. 9 Hydrodynamic radius R_h from DLS at 25 °C for a constant total surfactant concentration of 50 mM as a function of the mol fraction of Na oleate x(NaOl) for mixtures with DeTMABr (\square), DTMABr (\bigcirc), and TTMABr (\triangle) (samples in the vesicle phases are given as full symbols)

increase seen in DLS and the dip in conductivity. For sufficiently high total concentration (in our cases already for concentrations of \sim 50 mM), these vesicles are densely packed and therefore form viscoelastic solutions with pronounced shear thinning.

Salt-free system oleic acid/DeTAOH

In a next step and in order to extend our investigation with respect to the impact of the electrostatic interactions, we then also investigated the salt-free system as it is obtained by directly combining oleic acid with decyl trimethylammonium hydroxide (DeTAOH). It has been observed before that salt-free catanionic systems often behave quite differently compared to the corresponding ones with the counterions [51–53], and for our system of Na oleate/DeTMABr, we had seen before that one forms densely packed larger multi-lamellar vesicles around equimolar mixing (see, e.g. Fig. 5).

The phase behaviour of the salt-free system as obtained from visual inspection of the samples as a function of the mixing ratio and of the total concentration is depicted in Fig. 10. Only for the solution rich in DeTAOH, a micellar phase (L_1) is observed as

Fig. 8 Intensity autocorrelation functions $g^{(2)}(\tau)$ at 25 °C measured at 90° for a constant total surfactant concentration of 50 mM for various mixtures of Na oleate and **a** DeTMABr; x(DeTMABr)=0 (\square), 0.3 (\bigcirc), 0.5 (\bigwedge) and **b** TTMABr; x(TTMABr)=0 (\square), 0.4 (\bigtriangledown), 0.6 (\bigwedge), 0.8 (\bigcirc)





Fig. 10 Phase diagram for the ternary system oleic acid (OA)/ decyltrimethyl ammonium hydroxide (DeTAOH)/water constructed by plotting the total concentration of two surfactant solutions as a function of mole fraction of DeTAOH in the mixture

oleic acid is not water-soluble. The other monophasic region is observed for almost equimolar mixing ratios in a rather narrow range of mole fractions of DeTAOH 0.43-0.57 (which is tilted towards lower content of DeTAOH for higher total concentrations). Here, a bluish solution is observed that we assigned to be a vesicle phase (L_v) but it is low viscous and thereby differs substantially from the NaOl/DeTMABr system where the solutions are viscoelastic at the same total concentration. The tilt in the phase diagram at higher total concentration is presumably due to the fact that the vesicles formed at higher concentrations can incorporate into their amphiphilic bilayer increasing amounts of oleic acid, which functions here as cosurfactant that stabilizes the vesicles-as similarly observed for medium-chain alcohols as cosurfactants [26, 27, 54]. It is separated from the L_1 -phase by a large 2Φ -region, in which a thin turbid layer is floating atop of an isotropic solution.

However, it is interesting to note that vesicle formation is limited to an upper total concentration of 90 mM, which is in striking contrast to the mixture of the corresponding surfactant salts where a homogeneous vesicle phase is still observed at much higher concentration. This may be attributed to the stronger electrostatic interactions as here no screening salt is present. It is also interesting to note that the vesicle phase becomes somewhat less turbid at the upper limit of the vesicle phase, which could arise from the formation of smaller and more ordered vesicles. The phase boundary towards lower concentrations is not shown, but it is around 5 mM, and here one simply reaches the cmc of the DeTMAOH and without micelle formation even small amounts of oleic acid are no longer soluble.

DLS measurements in the Ly-phase show objects of a size of 50-60 nm hydrodynamic radius, increasing in size with increasing total surfactant concentration (see Fig. S5). Such large aggregates indicate the presence of vesicles. This turbid phase contains exclusively unilamellar vesicles with diameters in the range of 100-200 nm as was confirmed by cryo-TEM experiments (Fig. 11). In addition, especially for the 50 mM sample, also some much smaller vesicles are seen. These vesicles are rather polydisperse but always unilamellar, which indicates that here, one has an energetic stabilization of a given curvature in this surfactant mixture. This is apparently quite different to the case of the salt-containing system depicted in Fig. 5 where much larger multi-lamellar vesicles are observed. It is interesting to note that these unilamellar vesicles guite often seem to have perforated membranes. This might indicate a tendency for local demixing but is so far still a rather unclear effect. However, similarly perforated vesicles have been observed in catanionic surfactant mixtures [55], especially in the vicinity to forming wormlike micelles [56], but similar structures have also been observed for liposomes [57].

The cryo-TEM results could be used further to determine the size distribution of the vesicles in this system and which is shown in Fig. 12 for the 1:1 mixture and total concentrations of 25 and 50 mM. For the case of having energetic stabilization and thermodynamic equilibrium, that distribution of the number of vesicles should be directly related to the bending elasticity of the amphiphilic bilayer via [58]:

$$f_{\rm n} = \left\{ f_0 \cdot \exp\left[-\frac{8 \cdot \pi \cdot K}{k \cdot T} \cdot (1 - R_0 / R)^2 \right] \right\}^{R^2 / R_0^2} \tag{3}$$

Fig. 11 Cryo-TEM micrographs from samples of DeTMAOH and oleic acid with a mixing ratio of 1:1 for **a** 25 mM total concentration and **b** 50 mM total concentration. The *size bar* at the bottom of the images corresponds to 100 and 200 nm for (**a**) and (**b**), respectively



Fig. 12 Histogram of the number averaged vesicle size distribution for the system DeTMAOH/oleic acid system for 1:1 mixing for a a total concentration of 25 mM and **b** a total concentration of 50 mM (obtained by measuring the size of 1000-1500 vesicles)-and curves fitted according to Eq. 3

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where R_0 is the optimum radius and K is the effective bending constant, given as $K = \kappa + \overline{\kappa}/2$, with κ being the mean bending modulus and $\overline{\kappa}$ being the saddle-splay modulus. This formula was then used to fit our experimental data and quite good agreement can be obtained, as seen in Fig. 12. From the fit, one can deduce a value of 55 ± 5 nm for R_0 and 0.25 ± 0.03 kT for K for the 25 mM sample and valued of 60 ± 5 nm for R_0 and 0.17 ± 0.02 kT for K for the 50 mM sample. This means that in cryo-TEM, one sees a similar increase in size with total concentration as observed by DLS (Fig. S4). Furthermore, similar values for K have been observed for other comparable vesicle systems, e.g. 0.7 kT for CTAB/sodium perfluorooctanoate vesicles [58] (where this rather high value may be attributed to the stiffness of the perfluoroalkane chain) or 0.15 kT for CTAT/SDBS [59]. Accordingly, one may conclude that in the DeTMABr/OA system, the vesicles are energetically stabilized.

Finally, this structural picture could be corroborated by additional SANS measurements on samples of different total concentration and for various mixing ratios within the vesicle phase. They show over most of the q-range a rather monotonous decrease with a power law of q^{-2} (Fig. S5) as expected for extended bilayers. From the slope, we could determine the bilayer thickness to be ~ 2.8 nm, irrespective of the mixing ratio and total concentration. This value is in good agreement with the added total length of the decyl plus oleyl chain and indicates that there is effectively an interdigitation of the chains taking place in the bilayer.

Conclusions

We investigated in a systematic fashion the aggregation behaviour of catanionic surfactant mixtures with oleate as anionic part and alkyltrimethyl ammonium with different chain lengths of octyl, decyl, dodecyl and tetradecyl as cationic part. Such systems in general are known for having a tendency for spontaneous formation of vesicles, but can also form rod-like micelles depending on the final packing parameter achieved in the mixture. In that context, it is interesting to note that such catanionic mixtures have a strong tendency for bilayer formation, but that results typically in the formation of vesicles but not of planar lamellar phases or L₃(sponge) phases [60], that could be an alternative arrangement. For the case of mixing the surfactant salts (Na oleate + alkyltrimethyl ammonium bromide), the tendency for vesicle formation depends strongly on the length of the alkyl chain of the cationic surfactant. For the octyl chain (OTMABr), the added hydrophobic chain is too small to shift the system into a packing parameter regime where vesicle formation is favoured and accordingly only the formation of wormlike micelles takes place, which already at the investigated concentration of 100 mM leads to highly viscoelastic solutions.

In contrast, the longer chain cationic analogues decyl (DeTMABr), dodecyl (DTMABr) and tetradecyl (TTMABr) trimethyl ammonium bromide are forming vesicles around equimolar conditions, where for the TTMABr precipitation occurs at equimolar conditions and the vesicle region becomes split into a cationic and anionic branch. The shorter chain surfactants apparently do not form such stable salts to yield precipitation. The vesicles formed here are multi-lamellar (MLV) with diameters of 200–500 nm at total concentrations of 100 mM and the densely packed vesicles lead to viscoelastic solutions that exhibit pronounced shear thinning. An interesting finding here is that almost no viscosity increase is observed for the DTMABr case, which can be attributed to the fact that here only rather small unilamellar vesicles are formed rather easily, thereby avoiding the formation of a viscoelastic micellar solution. This means that the precise morphology of the vesicles formed depends to a large extent on the length of the cationic surfactant.

The structure and the properties change substantially when going to salt-free systems, i.e. having the oleic acid and the alkyltrimethyl ammonium. As shown for the case of DeTMAOH, exclusively unilamellar vesicles are formed, and here the maximum total surfactant concentration is around 90 mM, and in the whole vesicle regime only low viscous samples are formed. For the chain length dependence, it is interesting to note that both for the TTMABr and the DeTMABr rather large multi-lamellar vesicles are formed, while for the DTMABr with its intermediate chain length smaller more well-defined vesicles are formed, which then

also results in a much lower viscosity, as here no dense packing is achieved.

In summary, it can be concluded that the electrostatic interactions in this system are very important in determining size and lamellarity of the vesicles and thereby also their rheological properties. By systematic variation of the alkyl chain length of the cationic surfactant in the mixture with sodium oleate, one is able to tune both the structure of the formed vesicles and the macroscopic properties of the mixtures. This then allows for a rational design of the vesicle phase in such surfactant systems, which is interesting as they form spontaneously and allow for a simple way of producing such vesicle systems.

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Markus Drechsler was born in Zuerich in 1957. He studied Physics in Freiburg (Germany) from 1977-1985 and received his PhD in 1991 with a thesis on electron energy loss spectroscopic and electron microscopic investigations of the light induced calcium release in bovine photoreceptor cells. From 1991-1995 he worked at the Institute for Biophysics and Radiation Biology of the Albert - Ludwigs University of Freiburg (Germany). He was leading the electron microscopy service group of the collaborative re-

search centre "Structure and Function of Macromolecular Systems" (SFB60) of the Deutsche Forschungsgemeinschaft (DFG). Between 1995 and 1997 he was head of the atomic force microscopy group of the Cardiological Research Laboratory of the Cardiological Clinic of the Medical Faculty Charité at the Humboldt University of Berlin (Germany). From 1997 - 2003 he worked at the Department of Pharmaceutical Technology of the Friedrich - Schiller University of Jena (Germany), where he was head of the electron microscopic service group. In 2002 he was working for 6 months as a visiting scientist at the Physical Institute of the University of Zuerich (Switzerland) in the Biophysics group. In April 2003 he joined the Department of Macromolecular Research (BIMF) at the University of Bayreuth (Germany). His general research interest is the cryo electron microscopical characterisation of colloidal organic systems.



Michael Gradzielski was born in 1962 in Bayreuth, studied chemistry at the Universität Bayreuth, Germany, and also received his PhD there in 1992. In between he stayed in 1985/86 as a Fulbright scholar at the University of Wisconsin – Madison and received a MSc in chemistry from there. After a post-doctoral stay at the Laboratoire de Physique Statistique at the Ecole Normale Superieure, Paris (Prof. D. Langevin), he finished his habilitation for Physical Chemistry at

the Universität Bayreuth in 2000. During all his time after graduation in Bayreuth he enjoyed a fruitful and successful research time together with Prof. Heinz Hoffmann. Since 2004 he is full professor for Physical Chemistry at the Technische Universität Berlin, Germany. His research work is concerned with the investigation of colloidal systems with an emphasis on their structural characterisation and structure-property relations. Particular fields of interest here are sufactants and amphipilic copolymers, micelles, microemulsions, solubilisation, vesicles and properties of nanoparticles.