Role of the surfactant headgroup on the counterion specificity in the micelle-to-vesicle transition through salt addition

Nina Vlachy [a],[*], Markus Drechsler [b], Jean-Marc Verbavatz [c], Didier Touraud [a], Werner Kunz [a]

[a] *Institute of Physical and Theoretical Chemistry, University of Regensburg, D-93040 Regensburg, Germany*
[b] *Institute of Macromolecular Chemistry, University of Bayreuth, D-95440 Bayreuth, Germany*
[c] *DBCM/SBCe, C.E. de Saclay, F-91191 Gif sur Yvette, France*

Abstract

A transition from micelles to vesicles is reported when salts are added to a catanionic micellar solution composed of sodium dodecylcarboxylate (SL) and dodecyltrimethylammonium bromide (DTAB), with an excess of SL. The counterion binding and increase in aggregate size was monitored by mass spectrometry, rheology and dynamic light scattering measurements, whereas the vesicles were characterized by freeze-fracture and cryo-transmission microscopy experiments. The effect of counterions on the formation of vesicles was studied and compared to a previously studied catanionic system with a sulfate head group, SDS/DTAB. As in the latter case, no anion specificity was found, while large differences in the hydrodynamic radii of the formed objects were observed, when the cation of the added salt was varied. A classification of the cations could be made according to their ability to increase the measured hydrodynamic radii. It is observed that, if the sulfate headgroup of the anionic surfactant is replaced by a carboxylic group, the order of the ions is reversed, i.e. it follows the reversed Hofmeister series. Different morphologies are observed as the ionic strength of the system is increased. The aggregates are analogous to those found in the SDS/DTAB system.
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1. Introduction

The investigation of specific ion effects has engaged researchers for decades. Despite that, ion properties and their interactions with other molecules are still not understood in detail, and we are far away from being able to predict their behavior. A mayor difficulty in the study of salts presents the fact that many phenomena involve the action of both the cations and anions of the electrolyte.

Molecular self-assembly in surfactant systems is largely dependent on the number of water molecules surrounding the headgroups. When ions are added to a solution, they dehydrate the surfactant headgroups [1,2]. This causes a decrease in the value a (effective area per molecule at the interface) and consequently an increase of the structural packing parameter P, which may result in the formation of vesicles. The effect of salts on a charged system can differ much depending on their kosmotropic or chaotropic character. It is well known that small ions of high charge density (e.g., sulfate, carboxylate, sodium) are strongly hydrated (kosmotropes) whereas large monovalent ions of low charge density (e.g., iodide, potassium) are weakly hydrated (chaotropes) [3,4]. Each salt is therefore expected to have an individual influence on vesicle formation, whether it tends to adsorb at the interface between micelle and water or remains strongly hydrated in the bulk.

Collins' concept of "matching water affinities" provides us with a simple model of specific ion–ion interactions. From various experimental results (for an extensive review see Ref. [5]) he concluded that the dominant specific forces on ions of the same valency in water are short-range forces of chemical nature and that "the long range electrostatic forces generated by simple ions in water are weak relative to the strength of water–water interactions." Therefore, contact ion-pair formation is actually dominated by hydration–dehydration. A good agreement was also found with recent calculations of water pairing, where ex-

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[*] Corresponding author. Fax: +49 0 941 943 45 32.
E-mail address: Nina.Vlachy@chemie.uni-regensburg.de (N. Vlachy).

plicit water molecules were modeled [6]. It is challenging to see if this simple concept holds also for specific ion–headgroup interactions.

A salt induced micelle-to-vesicle transition was studied previously in a catanionic system composed of sodium dodecyl sulfate (SDS) and dodecyl trimethylammonium bromide (DTAB) with an excess of SDS [7]. Large cation specificity was found, following the Hofmeister series. In the present paper this study is extended to another catanionic system in order to elucidate the fact that not the types of the ion alone, but rather the specific cation–surfactant interactions shape the surface behavior. The sulfate headgroup of the anionic surfactant in the catanionic mixture was therefore replaced by a carboxylate. In this way, the system resembles more to a biological membrane than a system containing SDS; it had been determined that cellular membranes consist of roughly 2 to 5% of free long-chain carboxylic acids, whereas the trimethylammonium group resembles the choline group that is often present in membranes [8,9]. The effect of different anions and cations on the micellar solutions was studied by phase diagrams, rheology, dynamic light scattering and mass spectrometry, whereas the vesicles were characterized by freeze-fracture and cryo-TEM imaging. The mechanism of micelle-to-vesicle transition is investigated and compared to the one found in SDS/DTAB systems.

2. Experimental

2.1. Materials

The surfactants, sodium dodecanoate (SL; Sigma, Germany; grade: 99–100%) and dodecyltrimethylammonium bromide (DTAB; Merck, Germany; assay >99%) were used as received. All sodium and chloride salts used in the experiments were supplied by Merck, Germany. They were also used as received without further purification. Millipore water was used as solvent in all cases.

2.2. Phase diagrams

Surfactant stock solutions were prepared by dissolving weighed amounts of dried substances in Millipore water. The solutions were then left for 24 h to equilibrate at 25 °C. The catanionic solutions were prepared by mixing the surfactant stock solutions to obtain a fixed anionic/cationic surfactant mass ratio of 60/40 (this corresponds to a molar ratio of approximately 2/1). The starting ratio was determined from phase diagrams (Fig. S1, supporting information). The total surfactant concentration was kept at 1 wt% at all times. Salts were added to the micellar solution at increasing concentrations up to 50 mM. The solutions were then stirred and left to equilibrate for a day at 25 °C before making measurements.

2.3. Rheology

Rheological experiments were performed on a Bohlin CVO 120HR rheometer (Bohlin Instruments GmbH). A cone-and-plate geometry of 4/40 (4° angle with 40 mm diameter) was used. All measurements were performed at 25 °C.

2.4. Dynamic light scattering (DLS) measurements

Particle size analysis was performed using a Zetasizer 3000 PCS (Malvern Instruments Ltd., England), equipped with a 5 mW helium neon laser with a wavelength output of 633 nm. The scattering angle was 90° and the intensity autocorrelation functions were analyzed using the CONTIN software. The polydispersity as detected by the CONTIN fitting procedure is reported in Fig. S2, supporting information. All measurements were performed at 25 °C.

2.5. Electrospray mass spectrometry (ES-MS)

Cation affinities for the vesicular interface/carboxylate group were determined by electrospray mass spectrometry. ES-MS was carried out using a Thermoquest Finnigan TSQ 7000 (San Jose, CA, USA) with a triple stage quadrupole mass spectrometer. The solutions were sprayed through a stainless steel capillary held at 4 kV, generating multiply charged ions. Data were collected using the Xcalibur software. The surfactant concentration was kept 1 wt% and the concentration of the various chloride salts was 15 mM in all cases.

2.6. Cryo-transmission electron microscopy (Cryo-TEM)

Specimens for cryo-TEM were prepared as described before [7]; samples were examined with a Zeiss EM922 EF transmission electron microscope (Zeiss NTS mbH, Oberkochen, Germany).

2.7. Freeze-fracture electron microscopy

Samples used for cryo-fracture were prepared as described previously [7]. Freeze-fracture was performed in a BAF 060 (Balzers, Switzerland) apparatus at −130 °C under a vacuum of 10^{-7} Torrs. Metallic replicas were obtained by Pt and carbon shadowing of fracture surfaces. The replica were examined and photographed with a Philips CM 12 transmission electron microscope.

3. Results

The addition of salts to the SL/DTAB catanionic mixture at a certain ratio of the surfactants induces an easily observable aggregation, due to a formation of a bluish color or turbidity. Salts were added to samples from all parts of the phase diagram, however homogeneous vesicular systems upon salt addition were observed only at a certain anionic/cationic surfactant ratio (see phase diagram, Fig. S1, supporting information). For this reason, the starting solution was taken from the micellar region of the phase diagram, a little way from the equimolarity line, with an excess of the anionic species (with a mass ratio of 60/40). This system is similar to a previously studied system SDS/DTAB [7], where also an excess amount of the anionic
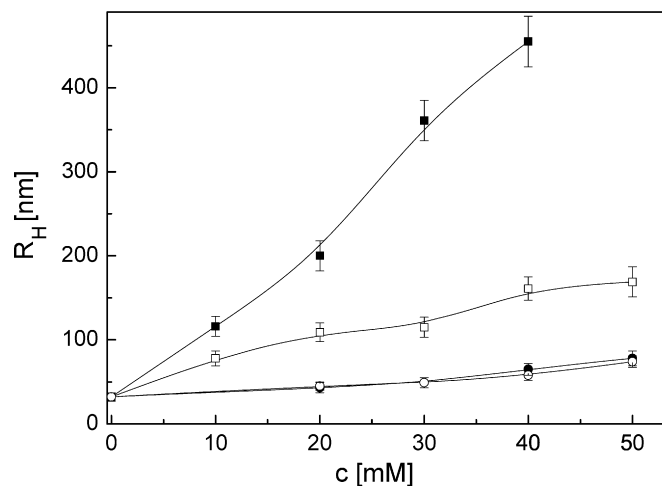
Fig. 1. The effect of various cations/chloride salts on the growth of the hydrodynamic radii R_H of the catanionic aggregates in SL/DTAB systems: LiCl (■), NaCl (□), KCl (●), CsCl (○).

component (SDS) was needed (mass ratio 70/30) to obtain similar structures.

The catanionic solutions were first studied by dynamic light scattering. DLS showed a pronounced increase in the hydrodynamic radius of the particles in accordance with visual observations. While the sodium salts where the anionic part was varied assisted the micelle-to-vesicle transition to the same extent (the curves overlap—cf. Fig. S3, supporting information), the variation of the cationic part of the salt results in strong differences in the hydrodynamic radii (see Fig. 1), similarly to the previously studied SDS containing catanionic system [7]. However, if the sulfate headgroup of the anionic surfactant is replaced by a carboxylic group, the order in which the ions assist the formation of vesicles is reversed. Salts containing small highly charged and highly hydrated cations (such as LiCl) more efficiently induce vesicle/aggregate formation than big cations having a smaller charge density (for instance CsCl).

Cation affinities for the vesicular interface/carboxylate group were determined by electrospray ionization mass spectrometry. Although in this method the ionization process takes place in the gas phase, the chemical nature of surfactant monomers and simple ions is the same in the liquid and in the gas phase. Therefore, the preferential ion-surfactant interactions can easily be noted [10,11]. Results show that most of the mass signals (peaks) remain unchanged independently of the nature of the added salts. A typical ES-MS spectrum of the complete m/z region (m and z are the mass and charge of an ion, respectively) is shown in supporting information (cf. Fig. S4). Fig. 2 represents the anion fragmentation patterns upon the addition of various salts: for better visibility only a part of the m/z region is presented. A closer look reveals that the position of the peak representing the binding of sodium ions to the carboxylate $(2A^- + Na^+)^-$ remains unchanged. Also the size of the peak is comparable in all spectra with the exception of spectrum (A). When LiCl is added, two same-sized peaks appear, one representing the binding of sodium, the other of lithium ions to the carboxylate anion. This suggests that Li$^+$ is able to come closer to the vesicular surface, replacing a part of the

sodium ions at the interface. The exactly opposite is observed in the case of CsCl (Fig. 2D). The latter suggests a very small occurrence of cesium ions at the vesicle interface (very small $(2A^- + Cs^+)^-$ peak). A general ordering of the cations can be determined from the ES-MS spectra, with lithium showing the greatest affinity for the anionic group and the other cations following: Li$^+$ > Na$^+$ > K$^+$ > Cs$^+$.

Results from rheology experiments performed on catanionic solutions with various salts show that the viscosity decreases with applied strain rate (Fig. S5, supporting information). This behavior is common for solutions containing large non-spherical molecules, which tumble at random under low shear, but align themselves in the direction of increasing shear and produce less resistance as the shear rate is increased [2]. This behavior points to the presence of rod-like micelles in the solutions, which is confirmed also by microscopy (see ahead). No change in the rheological behavior of the samples is observed however as the nature of the salt is varied. Probably, the change in the overall concentration of elongated micelles present in the solution is too low for such detection to be possible with our equipment.

Homogeneous samples exhibiting a bluish color typical for solutions containing vesicles were further investigated by Cryo-TEM. The images show a highly polydisperse sample. Fig. 3A shows the presence of long ribbon-like micelles unravelling and forming sheets. This effect was observed also in the SDS/DTAB system. It seems that the addition of salts produces a similar effect in both systems. Fig. 3B shows many half-closed and some already fully-closed vesicles.

Samples of higher ionic strength (35 mM) were analyzed also by FF-TEM. The advantage of this technique is that it enables us a more detailed view of the membrane surface. Fig. 4 shows the presence of individual unilamellar vesicles with completely smooth membranes.

4. Discussion

4.1. Influence of salt on the aggregation behavior of surfactants

The geometry of aggregates in colloidal systems is attributed to the packing of the amphiphilic molecules. The packing parameter is dependent on the length and volume of the hydrophobic tail and the size of the hydrophobic head of the surfactant molecule. These factors are often expressed in a packing parameter $P = v/(l_{max}a)$, where v and l_{max} are the volume and length of the hydrophobic part, respectively, and a the area per molecule at the interface. If the hydrocarbon part of the surfactant is kept constant and only the headgroup is varied, then the difference in the aggregation behavior can be attributed solely to the properties of the polar headgroup. Because a describes the effective headgroup size, which in the case of ionic surfactants is largely determined by repulsive electrostatic forces, and not the ionic radius, the change of morphology in surfactant systems is largely dependent on the number of water molecules surrounding the headgroups. It has been observed by chemical trapping method [12] that in association colloids, the changes in
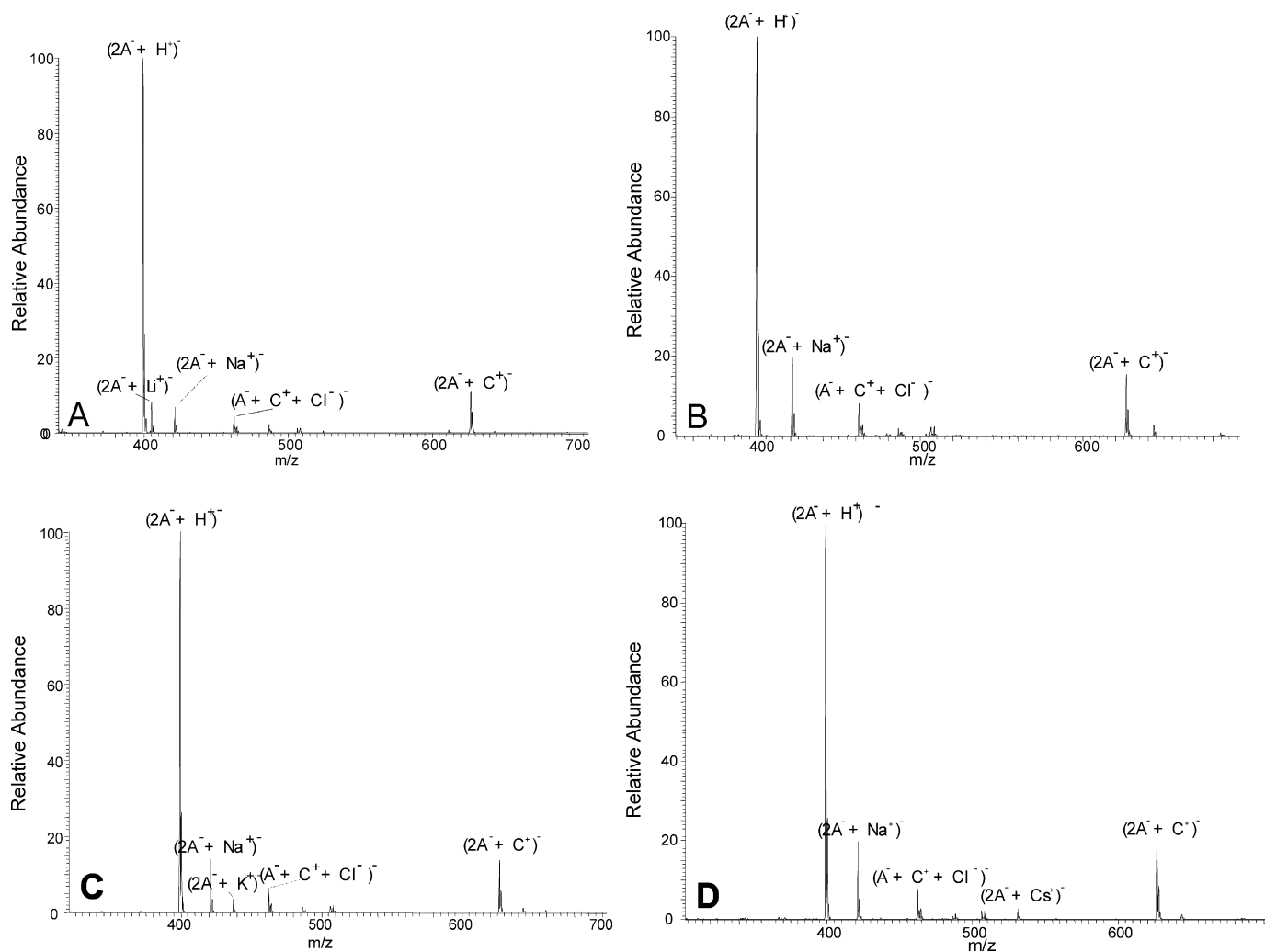
Fig. 2. Ion binding as determined by ES-MS: addition of 15 mM of (A) LiCl, (B) NaCl, (C) KCl and (D) CsCl to a SL/DTAB micellar solution. A^-: dodecylcarboxylate anion (199 Da); C^+: dodecyltrimethylammonium cation (228 Da).
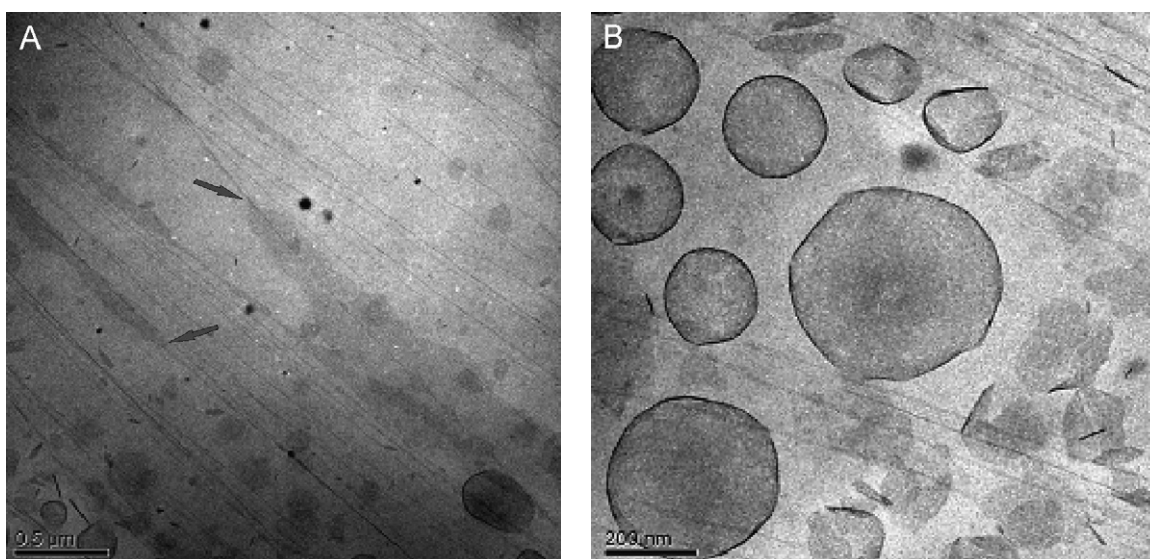

Fig. 3. Cryo-TEM photographs of a SL/DTAB aqueous solution at the mass ratio of 60/40 and a total surfactant concentration of 1 wt% upon the addition of 20 mM of NaCl. The arrows in (A) show the presence of long ribbon-like micelles and the formation of sheets; spherical aggregates can be observed in image (B).
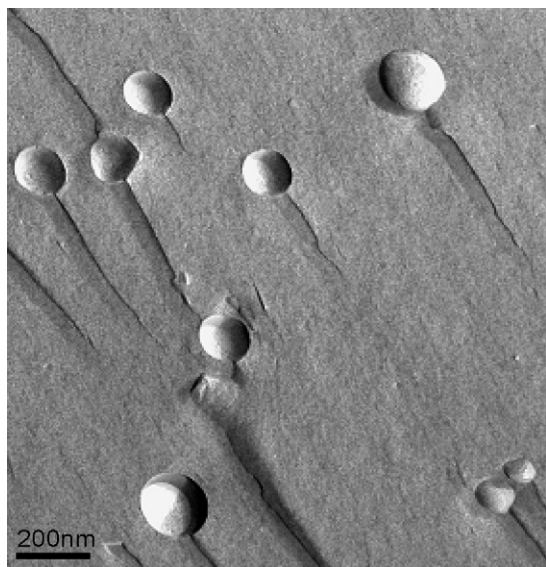
Fig. 4. FF-TEM photographs representing the effect of 35 mM NaCl on the reference SL/DTAB micellar solution.

the balance of forces controlling the aggregate structure are reflected in the changes in interfacial concentrations of water and other components. The ions, when added to a micellar solution, can dehydrate the surfactant headgroups. This causes a decrease in the value a and consequently an increase of the structural packing parameter P. As a consequence, the critical micellar concentration is reduced [13,14] and the aggregate morphology changed [15]. The effects are caused by destruction of the hydration layer of the surfactant, decreased electrostatic repulsions, and an increased counterion binding [14]. Consequently, the surfactant monomers can be packed closer together leading to a bilayer formation.

4.2. Ion-pairing in aqueous solutions

The dissolution of ions brings about changes in solvent structure. Ions have been divided into two classes depending on how they modify the surrounding water molecules: water ordering kosmotropes that hold the first hydration shell tightly, or water disordering chaotropes, that hold water molecules in that shell loosely. The degree and manner, in which the surrounding solvent is modified when two ions are in close proximity, depends specifically on the nature of both ions and the primary forces between them [16]. It has been shown that when both cation and anion are strong water structure formers such as Li^+ and OH^-, or both water structure breakers such as Cs^+ and Br^-, they interact strongly and exhibit a low value of the mean activity coefficient in aqueous solution [15]. However, when a structure-former ionic species is in the presence of a structure-breaker one, the ionic association is less important and the values of the mean activity coefficients are relatively higher [15]. Terms such as "contact" pairs and "solvent-separated" pairs have come into use to distinguish the results of complete and partial depletion of solvent molecules from between two interacting ions. The basic features responsible for the specificities of short-range ionic interactions of ions in general are, in the

case of monoatomic ions, their charge density, their polarizability, and availability of electrons and/or orbitals for covalent contributions (e.g., the binding of iodide to benzene rings [17,18]). The ease with which hydration takes place, depends on the number of ion pairs existent at any instant. These effects are even more pronounced with polyelectrolytes. This is because the effect does not depend only on the individual properties of the participating ionic group and its counterion, but also on the overall charge of the polyion, as well as on the possible cooperating binding sites, which might be located close to the ionic group under consideration. Furthermore, even at high dilution a substantial number of counterions is forced into close proximity to the polyion by the long-range electrostatic forces [19,20], so that there always exist a large number of ion pairs, for which solvation effects should be observable.

Surfactants in solutions form aggregates such as micelles and vesicles by removing their hydrophobic parts from the polar solvent and orienting the polar or charged headgroups to the surface. In this way, these aggregates are much expected to behave as globular polyelectrolytes. One can then expect the same specific ion interactions in surfactant solutions (above the critical micellar concentration) as for polyelectrolyte solutions.

4.3. Conformation of the carboxylate anion

The carboxylate ion has one negative charge delocalized within it, and each oxygen atom has two lone pairs disposed at 120° to the C–H bond in the plane of the carboxyl group. Experimental estimates of carboxylate hydration numbers range from 5 to 7 [21] in agreement with simulations and quantum chemical calculations [22,23]. The geometry of the position of the hydrogen atom in a carboxyl group has been described by Rebek and coworkers [24–27]. They have designed, made, and studied some compounds, in which the carboxylic acid groups, by steric effects caused by the rest of the molecule, are obliged to approach each other in a controlled way. The problem of determining metal cation binding selectivity to a carboxylate group had been addressed by Carrell et al. [28] by analysis of metal cation surroundings of carboxylate groups in crystal structures. Results have shown that alkali metals, which ionize readily, have less specific locations of binding. From alkali metals only Li^+ binds approximately in-plane with the carboxylate group, whereas the other ions (Na^+, K^+, Rb^+, Cs^+) bind greatly out-of-plane. This may account for the strong binding of Li^+ to the carboxylate group. However, only groups that act as isolated ligands were considered; those with neighboring additional metal-binding groups were eliminated. Therefore it is not sure, to what extent these results can be compared to ours.

4.4. Counterion selectivity of alkyl carboxylates

As already mentioned, the micelle-to-vesicle transition was studied before in a system with the same cationic surfactant and an excess of an anionic surfactant containing a sulfate headgroup [7]. However, while with the sulfate group the binding increases with the decreasing size of the hydrated alkali metal ions, the order is reversed when the headgroup is exchanged

for a carboxylate. The carboxylate headgroup exhibits water-ordering properties and the addition of an alkyl chain should not change the kosmotropic behavior of the headgroup.

Collins' "Law of Matching Water Affinities" has been employed to explain the specific ion effects in a sulfate containing catanionic system [3–5,7]. From various experimental results Collins concluded that small kosmotropic ions can come close together forming inner sphere ion pairs without intermediate water molecules. The same is supposed to be true for big chaotropic ions, whereas when a kosmotropic ion approaches a chaotropic counterion, the ions should remain separated by at least one water molecule. In the present case the headgroups in excess are alkylcarboxylates. According to Collins' concept, alkylcarboxylates should come in close contact with kosmotropic ions like lithium, making it more possible to form inner-sphere ion pairs, whereas caesium ions remain further away. Therefore it is expected that Li^+ screens more efficiently the negative charge excess on the aggregates than Cs^+, and this is precisely what is observed, cf. Figs. 1 and 2.

The same order of counterion-binding to carboxylate headgroups that was found in our catanionic surfactant system is found in polyelectrolyte solutions [29–32], when measuring the cation affinity to ion-exchange resins [33,34], in studies of membrane potentials [33], of electrophoretic mobility of colloids [35], and of ion-transport phenomena [36]. Our results are also in agreement with measurements of counterion binding to soap micelles [37–40] and long-chain fatty acids [38,41–43]. Recent MD simulations have shown that the carboxylate groups dominate the counterion behaviour even in complex systems such as proteins [44].

Although the Hofmeister series is experimentally known in many fields, its mechanisms remains to be fully elucidated due to a complex interplay of direct and indirect effects of ions on the solute molecule and a combination of effects on the water structure. Morgan et al. [45] proposed that partial dehydration of the competing counterions dominates their exchange at the interface. Counterions, fully hydrated in solution, become partially dehydrated upon association with an exchange site. Thus, the free energy of ion exchange is related to the standard free energies of hydration of the counterions.

4.5. Anion effect and effect of non-ionic additives

All added sodium salts produced a similar increase in the hydrodynamic radii. No specificity was found. This particle increase is mainly due to a decrease of the headgroup repulsions because of electrostatic screening. Due to the fact that the net charge of the system is negative, the anions most likely do not accumulate near the surface, but assist the vesicle formation purely by increasing the ionic strength. The small differences in the observed radius size (Fig. S3, supporting information) are likely due to the differences in the hydration of the anions [4,46]. The addition of non-ionic additives (such as fructose) had no effect on the growth of the micelles, once again showing that dehydration of the headgroups alone is not sufficient to trigger the micelle-to-vesicle transition and confirming that electrostatic interaction is the first order effect.

5. Conclusion

Through the addition of salts a transition from rod-like micelles to vesicles was observed in aqueous solutions composed of DTAB and an excess of SL. Strong cation specificity was found in assisting the vesicle formation, following a reversed Hofmeister series. No anion specificity was observed. The system was compared to a similar one containing alkylsulfate headgroups, showing that the nature of the headgroup of the dominating surfactant in a catanionic system controls the counterion concentration in the vicinity of the aggregates. The ion specificity was explained using Collins' concept of matching water affinities, showing that the alkylcarboxylate has to be regarded as a kosmotrope. The morphologies observed during the micelle-to-vesicle transition are analogous to the ones found in systems containing a sulfate headgoup, hinting at a general mechanism common to catanionic systems. In particular, the intermediate steps in this micelle-to-vesicle transition are the same for both catanionic systems [47].

Supporting information available

Ternary phase diagram of the SL/DTAB system at 25 °C (Fig. S1); polydispersity index upon the addition of alkali salts to the micellar SL/DTAB system (Fig. S2); the effect of various anions the growth of the hydrodynamic radii R_H of the catanionic aggregates in SL/DTAB systems (Fig. S3); ES-MS spectrum of 1 wt% SL/DTAB micellar solution with 15 mM NaCl (Fig. S4); Viscosity as a function of shear rate of 1 wt% SL/DTAB micellar solution upon the addition of chloride salts (Fig. S5).

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