Colloid Polym Sci 276:92–95 (1998)

SHORT COMMUNICATION

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Evaporation and aggregation in aqueous monododecyltrimethylammonium *n*-dodecanephosphonate solutions

Received: 23 June 1997
Accepted: 13 August 1997

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Abstract Electrobalance evaporation rate measurements were used to measure solute weights in the aqueous catanionic system monododecyltrimethylammonium-*n*-dodecanephosphonate. At very low concentration premicelles composed of ion pairs between 3.6 and 7 were found, which increased with concentration. Above the cmc the aggregates increased in size with concentration much more rapidly. Aggregates had 54 ion pairs at the higher studied concentration (6×10^{-3} mol dm^{-3}). This value agrees with literature data of other similar systems. Since the system is probably polydisperse and the evaporation rate method gives number average weights, the true aggregation numbers are probably higher than those found. In this system the cmc did not indicate the starting point of aggregation, but a change in the aggregates structure and growing regime.

Key words Catanionic surfactants – evaporation rate – electrobalance – premicelles – dodecyltrimethylammonium *n*-dodecanephosphonates – micelles

Introduction

Evaporation is an active research field. It has been investigated in pure liquids [1], microemulsions [2, 3], and through insoluble surfactant monolayers [4–9]. Recently, computer simulations were made [10–15]. The evaporation through insoluble surfactant monolayers depends on the structure of the adsorbed layer. The evaporation through soluble surfactant monolayers was studied in our group [16, 17]. In these studies, it was found that the evaporation rate through soluble surfactant monolayers depended on bulk water activity. No dependence on the state of the adsorbed monolayer was found. In principle, this finding enables us to study the colligative properties of surfactant solutions in bulk by evaporation measurements.

Interactions occurring between oppositely charged large organic ions are important in many technical areas: analytical separations, solubilization, medicine formulation and design, etc. From this point of view, the study of the aggregates formed and the influence of the polar head characteristics in the formation of these aggregates are of interest. We studied the aqueous system of the catanionic surfactant mono-dodecyltrimethylammonium *n*-dodecanephosphonate, because this system is weakly ionized [18]. Thus, the colligative properties of the system are mainly related to the aggregation of the monomers.

Experimental

The synthesis of *n*-dodecanephosphonic acid and the preparation of dodecyltrimethylammonium hydroxide were described elsewhere [19, 20]. The preparation of the catanionic system was also described in another work [18].

The evaporation rate measurements were performed in a CAHN 1000 electrobalance, operating in a register range

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of 100 mg and an output potential of 10 mV. The pressure was 101.325 kPa. The samples were measured at 293.2 K, thermostatted at $\pm$ 0.1 K with water circulation. Known volumes of the solutions were poured into Pyrex cylindrical containers with a 2.9 cm internal diameter. To avoid secondary Archimedes effects, a compensator container was hung on the other arm of the electrobalance. The thermocouple (Fe-constantan) was in contact with the solution through a thin glass sheath.

Data interpretation

Evaporation rate data of a volatile liquid fit of the equation [17]:

$$v\ (\mathrm{kg\,m^{-2}\,s^{-1}}) = v_o - K\sqrt{t}\ , \tag{1}$$

where t is the time in seconds and v_o the initial rate of evaporation. McCoy [21], using a mass transfer model of Ly et al. [8], found the following relation for the evaporation through the air/water interface:

$$Q_w = 2\sqrt{D_s t/\pi}\ (p^*/RT - c_i)\ , \tag{2}$$

where Q_w is in $\mathrm{mol\,m^{-2}\,s^{-1}}$, D_s the water diffusivity in air ($= 3\times10^{-5}\,\mathrm{m^2\,s^{-1}}$) [21], p^* the vapor pressure of water at the temperature of the experiment, and c_i the initial concentration of water in the gaseous phase. By comparison of Eqs. (1) and (2) it may be seen that

$$K\ (\mathrm{kg\,m^{-2}\,s^{-3/2}}) = 2M_w\sqrt{D_s/\pi}\ (p^*/RT - c_i)\ , \tag{3}$$

where M_w is the molar mass of water. The value of c_i depends on the experimental conditions, and it was determined by measurements on pure water. We found $K = 1.63\times10^{-7}\,\mathrm{kg\,m^{-2}\,s^{-3/2}}$ for pure water at 298.2 K. With $p^* = 3.166$ kPa, we found $c_i = 1.265\times10^{-3}\,\mathrm{mol\,dm^{-3}}$ in the experimental conditions. Since we found that the state of the soluble surfactant-adsorbed monolayer did not affect the evaportion rate of water, we treated the solution/air interface as if it were a pure water/air interface. This enabled us to study the evaporation rate of the solutions as a purely colligative effect. From Eq. (3) the water vapor pressure of solutions may be derived

$$p^*/RT = \frac{K\sqrt{\pi/D_s}}{2\,M_w} + c_i\ . \tag{4}$$

The average molar mass of the solute species M_{sol} was found with

$$M_{sol} = \frac{w_{surf}M_w}{w_w(1 - p^*/p_o^*)}\ , \tag{5}$$

where w_{surf} and w_w are the weights of surfactant and water in the solution, and p_o^* the vapor pressure of pure water. The aggregation number n was found by

$$n = M_{sol}/M_{surf}\ , \tag{6}$$

where M_{surf} is the molar mass of the surfactant species, taken as the catanionic surfactant dimer DTA.HDP ($M_{surf} = 477.744\,\mathrm{g\,mol^{-1}}$). Thus, this aggregation number is given in DTA.HDP units. The number of sufactant ions ($DTA^+ + HDP^-$) is twice the value of n.

Results

Figure 1 shows an example of the change in weight of one of the samples with time. Figure 2 shows the values of v_o and K found as a function of the catanionic surfactant concentration ($C_T = [DTA^+] + [HDP^-]$). In Fig. 3 the average aggregation number of aggregates were plotted vs. total concentration. The critical micelle concentration (cmc) of this system was measured by several methods and

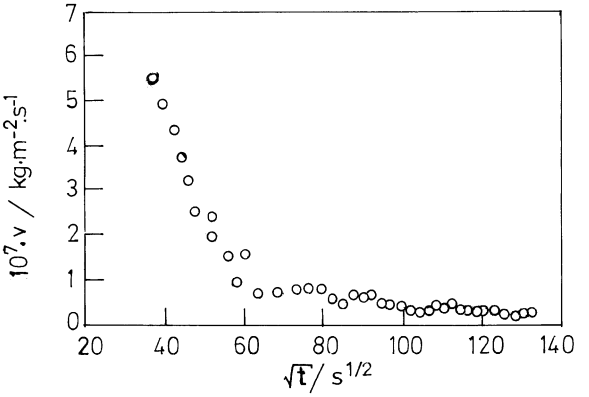

Fig. 1 Evaporation rate of water vs. time square root, DTA.HDP $8.08\times10^{-4}\,\mathrm{mol\,dm^{-3}}$

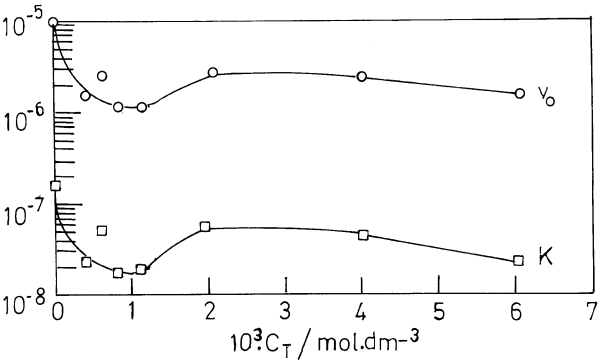

Fig. 2 Values of v_o and K of Eq. (1), vs. surfactant concentration (on a monomer basis)

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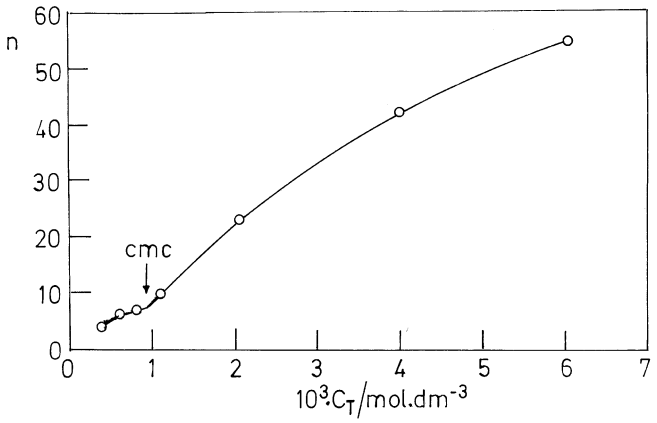

Fig. 3 Average aggregation number vs. surfactant concentration (on a monomer basis)

it is 8×10^{-4} mol dm^{-3}, and the aggregates are weakly ionized [18].

Discussion

Our results showed that the aqueous system DTA.HDP was constituted by aggregates formed by several molecules, even at very low concentration. At concentrations lower than the cmc = 8×10^{-4} mol dm^{-3} (which was determined by several independent methods) [18], these aggregates had between 3.6 and 7 DTA.HDP dimers, or between 7 and 14 monomer molecules. Several authors have postulated the formation of sub-micellar aggregates [22–27], and Despotović et al. confirmed its formation in catanionic systems [28]. In a review on catanionic surfactants, Tomlinson et al. [29] collected formation constants of catanionic ion pairs from literature. The values ranged from 4.17×10^3 to 8.28×10^4 in catanionic systems involving surfactant molecules whose tails were similar to that of the DTA.HDP system. The conclusion is that almost all surfactant molecules are in the form of ion pairs in these systems, even at low concentration. The ion pairs may join to form hydrophobically bound submicelles. The system DTA.HDP also may form hydrogen bonds between $-PO_3H^-$ groups. This interaction was verified in alkanephosphonic acid liquid crystals [30], and it was inferred from the properties of dodecanephosphonic acid micelles [17] and that of the catanionic DTA.HDP micelles [18]. These hydrogen bonds may stabilize the aggregates.

In Fig. 3 it may be seen that the dependence of n on C_T is different below and above the cmc. The increase of n with C_T above the cmc is much higher. At the largest analyzed concentration (6×10^{-3} mol dm^{-3}) we found $n = 54.3$ dimers (108.6 monomers).

Kitakami et al. [31] working on aqueous systems of sodium dodecylsulfate and dodecylamine oxide, found ellipsoidal micelles with axial ratios between 1.3 and 4.5. The largest micelles were in the equimolecular mixture. The largest aggregation number was 195 (on a monomer basis) in systems without added electrolyte. Pilsi et al. [32] analyzed the aqueous system tetradecyldimethylamine oxide–sodium dodecylsulfate by small-angle neutron scattering and found a homogeneous distribution of both monomers in micelles. The cationic surfactant forms rod-like micelles in water, and the anionic surfactant forms spherical micelles. Pilsi et al. found a gradual change in shape from spherical to rod-like micelles when the proportion of cationic surfactant increased in the mixture. The axial ratio in micelles in the equimolecular mixture was 1.99, whose aggregation number was estimated between 100 and 310 (on a monomer basis) depending on the computation method.

Brasher and Kaler [33] found ellipsoidal and rod-like micelles in catanionic systems when the micelle surface charge was reduced by adding electrolyte. Equimolecular catanionic systems are commonly unionized [34]. This is not the situation in the system DTA.HDP, because the *n*-dodecanephosphonic acid has two ionizable protons. The second ionization is weak ($pK_{a,2} = 8.42$) [19], but it is enough to prevent the precipitation of the mixture and to allow micelle formation.

It must be noticed that there is probably a micellar-size distribution, with some oligomers in equilibrium with large polydisperse micelles. Corkill et al. [35] found strong aggregate polydispersity in catanionic systems. Lucassen-Reynders et al. [36] studied the system sodium dodecylsulfate–dodecyltrimethylammonium bromide and found large equimolecular aggregates. It is well known that large micelles are polydisperse. The average micelle size comprises all solute species in solution, including the weak micellar ionization. This means that the true aggregation numbers are probably larger than those found in this work.

In view of the agreement between the aggregation numbers found in the studied system and the scarce literature data in similar catanionic systems, it may be concluded that evaporation rate measurements give a reasonably good estimation of the average micellar weights of the system DTA.HDP.

It may be seen in Fig. 3 that aggregates gradually grow with increase in concentration. Below the cmc, there were oligomers. No free monomers seemed to exist. In this system, the cmc is not the starting point of aggregation, but a structural change between oligomers with a maximum of some 14 monomers, and micelles with more than 20 monomers, having capacity to solubilize water insoluble dyes [18].

Conclusions

- Electrobalance evaporation rate measurements may be used to measure solute weights.
- At very low concentration, the equimolecular system DTA.HDP formed premicelles composed of ion pairs between 3.6 and 7, which increased with concentration.
- Above the cmc the aggregates increase in size with concentration was much more rapid. Aggregates had 54.3 ion pairs at the higher studied concentration (6×10^{-3} mol dm^{-3}). This value agreed with literature data of other similar systems.
- Since the system is probably polydisperse and the evaporation rate method gives number-average weights, the true aggregation numbers are probably higher than those found in this work.
- In this system, the cmc did not indicate the starting point of aggregation, but a change in the aggregates structure and growing regime.

Acknowledgements One of us (RMM) had received a fellowship of the Consejo Nacional de Investiganciones Cientificas y Técnicas de la República Argentina. This work was supported by a grant of the Universidad Nacional del Sur.

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