Characterization of the L_1 Phase of the System Sodium Dodecylsulfate-Hexanol-Water

Sune Backlund[a], Jarle Bakken[b], Anne Marit Blokhus[b], Harald Høiland[b] and Inger Vikholm[a]

[a]Department of Physical Chemistry, Åbo Akademi, SF-20500 Åbo, Finland
[b]Department of Chemistry, University of Bergen, N-5014 Bergen, Norway

Backlund, Sune, Bakken, Jarle, Blokhus, Anne Marit, Høiland, Harald and Vikholm, Inger, 1986. Characterization of the L_1 Phase of the System Sodium Dodecylsulfate-Hexanol-Water. – Acta Chem. Scand. A 40: 241–246

Viscosity, conductivity, density, ultrasonic velocity, and quasielastic light scattering measurements have been used to characterize aqueous solutions of hexanol and sodium dodecylsulfate, i.e., the L_1 phase of the system. At low surfactant contents, conductivity and ultrasound measurements showed that a change in the solubilization pattern took place as hexanol was added. Above a certain content, hexanol was solubilized not only in the palisade layer, but also in the interior of the micelles, thus producing swollen micelles. Quasielastic light scattering indicated that this swelling was modest in terms of an increased micellar volume, and this was confirmed by viscosity measurements; the viscosity remained practically constant as hexanol was added. At higher surfactant contents, the relative viscosities and the activation energy for viscous flow increased sharply above a certain hexanol content. This suggests a shape transition from spherical to larger rod- or disc-like micelles at these hexanol-sodium dodecylsulfate contents.
The L_1 phase of the system sodium dodecylsulfate – hexanol – water at 298.15 K has thus been divided into 4 structurally different regions; one of monomeric species (below the c.m.c.), one of spherical micelles, one of swollen spherical micelles, and one of rod- or disc-like micelles.

It is well known that micelles are capable of solubilizing added organic compounds, as illustrated in 3-component phase diagrams. Over a period of several decades, Ekwall and coworkers investigated phase equilibria in such 3-component systems. Their data have later been reviewed.[1]

We have previously studied the solubilization of alcohols in aqueous sodium dodecylsulfate (NaDDS).[2-4] Closer inspection of the isotropic aqueous phase, the L_1 phase, of the system water-hexanol-NaDDS has shown that, at low NaDDS contents, the solubilization ratio is as high as 5, i.e. 5 molecules of hexanol per NaDDS molecule in solution. Geometric calculations show that a maximum of 2.5 alcohol molecules can be accomodated at the micellar surface of tetradecyltrimethylammonium bromide micelles.[5]

This should be approximately correct for NaDDS micelles as well, suggesting that a large proportion of hexanol must be solubilized in the micellar interior,[6,7] producing swollen micelles. On the other hand, Stilbs[8] has demonstrated by self-diffusion studies that solubilized short chain 1-alcohols cause breakdown of NaDDS micelles when large amounts of alcohol are added and suggests highly disordered structures. However, for the hexanol system, only one solution has been studied.

The solubility of hexanol in aqueous NaDDS decreases abruptly at a NaDDS content of about 0.05 mol kg^{-1}.[4] A similar effect has been observed for 1-pentanol, 1-hexanol and 1-heptanol in various surfactants.[2,5,9,10] It has been explained in terms of a change in the solubilization mechanism, i.e. a transition from spherical swollen micelles to micelles where the alcohol is solubilized only in the palisade layer of the micelles. These

---

Dedicated to Professor Per Ekwall on his 90th Birthday.

micelles grow to become anisodiametric, rod- or disc-like, as the surfactant content increases.[5]

So far, the results indicate that the L_1 phase of the water-hexanol-NaDDS system can be divided into several structurally different regions. No systematic study of structural transitions within the L_1 phase has been carried out; in most cases, measurements have been performed at one NaDDS concentration only, generally in the vicinity of the c.m.c. In this work, the L_1 phase has been studied over a large range of NaDDS concentrations and by several experimental techniques, all in order to elucidate the structural transitions of the solubilized NaDDS micelles.

Experimental

Sodium dodecylsulfate (NaDDS) was supplied by BDH, "specially pure" grade, and 1-hexanol by Fluka, puriss grade. NaDDS was dried in an evacuated desiccator at 50 °C. Both compounds were used without further purification. Water was distilled twice immediately before use. All solutions were made by weight.

The solution densities were measured by a Paar densitometer, the viscosities by Ostwald viscosimeters. All the solutions where Newtonian. The ultrasound measurements were carried out by the "sing-around" technique as previously described.[11] The electrical conductivities were also measured as previously described.[10] Quasielastic light scattering experiments were carried out by using a Spectraphysics argon laser (488 nm) connected to a Malvern K7033 correlator system. The temperature was kept within ±0.01 K as measured by a Hewlett-Packard quartz thermometer.

Results and discussion

First, a brief recapitulation of the binary system water-NaDDS. At 298.2 K, the relative viscosity, η/η H_2O, of this system increases slowly and almost linearly with the NaDDS molality up to 1.1 m. As NaDDS molality exceeds 1.1 m, the relative viscosity increases sharply, indicating a transition from spherical micelles to larger aggregates, rod- or disc-like micelles. Small X-ray diffraction measurements confirm this transition.[12] A similar increase in the relative viscosity has been observed by Ekwall et al.[13] in the binary system water-hexadecyltrimethylammonium brom-
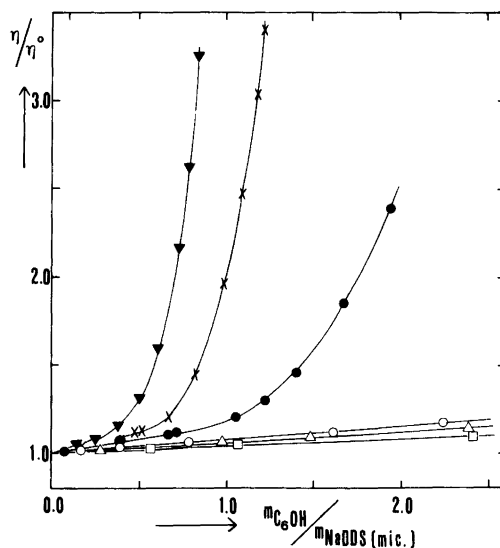

Fig. 1. The relative viscosity, $\eta/\eta°$, of NaDDS solutions as functions of added hexanol at 298.2 K. $\eta°$ is the viscosity of 0.05 (□); 0.074 (△); 0.10 (○); 0.20 (●); 0.30 (×) and 0.40 m NaDDS (▼). The micellar surfactant content has been calculated as $m_{NaDDS\,(mic)} = m_{NaDDS}^{tot} - m_c$, the total surfactant molality minus the molality at the critical micelle concentration.

ide. It should be noted that this transition point is not an analogue to "the second critical concentration" of NaDDS which has been determined to be 0.065 M at 298.2 K.[14]

Turning to the ternary system water-hexanol-NaDDS, Fig. 1 shows the relative viscosities of six NaDDS solutions as a function of the solubilization ratio. The c.m.c. values required were taken from the literature.[15] The curves show that at low NaDDS contents, less than 0.12 m, the relative viscosities increase only marginally as hexanol is added. This can be interpreted in terms of a small increase in the micellar volume as hexanol becomes solubilized,[16] or possibly just micelle-micelle interactions. The main point is that the viscosity does not increase sharply above a certain solubilization ratio, i.e., no large anisodiametric micelles are indicated.

At NaDDS contents above 0.12 m, the relative viscosities do increase sharply above a certain solubilization ratio. The higher the NaDDS content, the less hexanol is needed to bring about this increase in viscosity. These viscosity curves

Fig. 2. The activation energy for viscous flow, E_a, as a function of NaDDS molality for different water-hexanol mixtures, H_2O (▲); 0.00 (△); 0.10 (○); 0.15 (×); 0.20 (◇); 0.25 (●) and 0.30 m C_6OH (□).
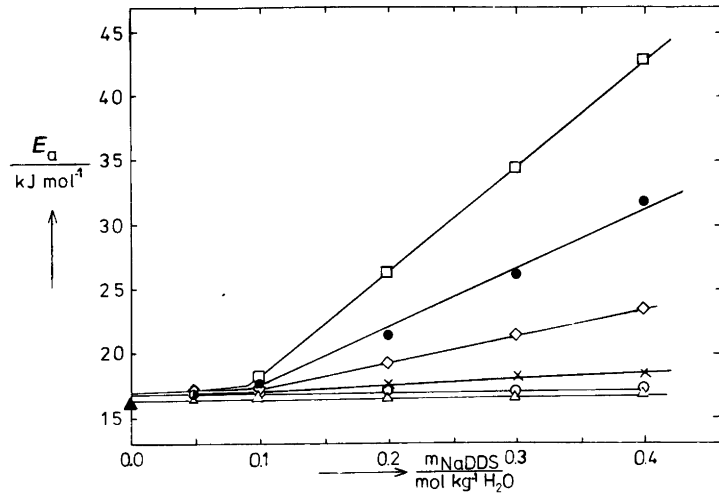
are similar to that observed for the binary water-NaDDS system and must be interpreted likewise: a transition from spherical to large rod- or disc-like micelles. The data show that hexanol promotes the transition. This is not surprising, since the addition of nonelectrolytes like alcohols generally makes micelles grow.[16-21]

The temperature dependence of the viscosity is usually expressed by an Arrhenius type of equation

$$\eta = A \ e^{E_a/R \ T};$$ (1)

E_a is the activation energy for viscous flow. This can be determined by plotting ln η versus $1/T$. Straight lines were observed in all cases, and the resulting activation energies have been plotted versus the NaDDS molality in Fig. 2. At low NaDDS contents, the activation energy does not change with addition of hexanol. Moreover its value is close to 17 kJ mol⁻¹, which is equal to the activation energy for the viscous flow of water and a normal value for aqueous solutions of spherocolloids.[13,22] For NaDDS molalities above 0.1 m and hexanol contents above 0.15 m, the ac-
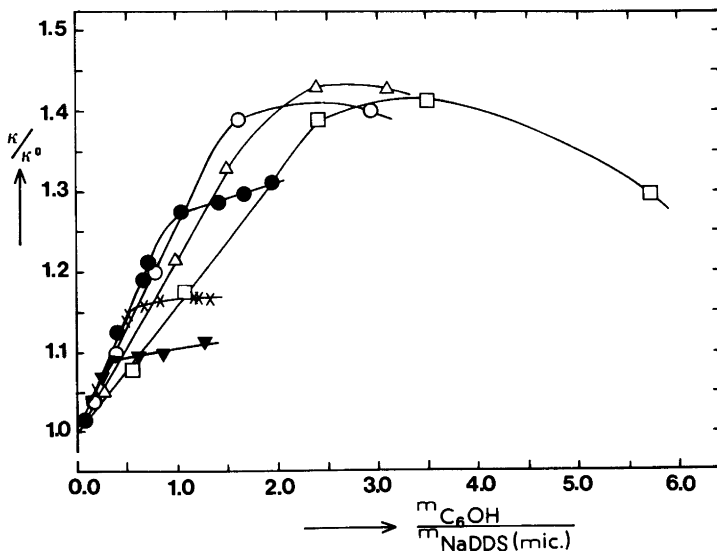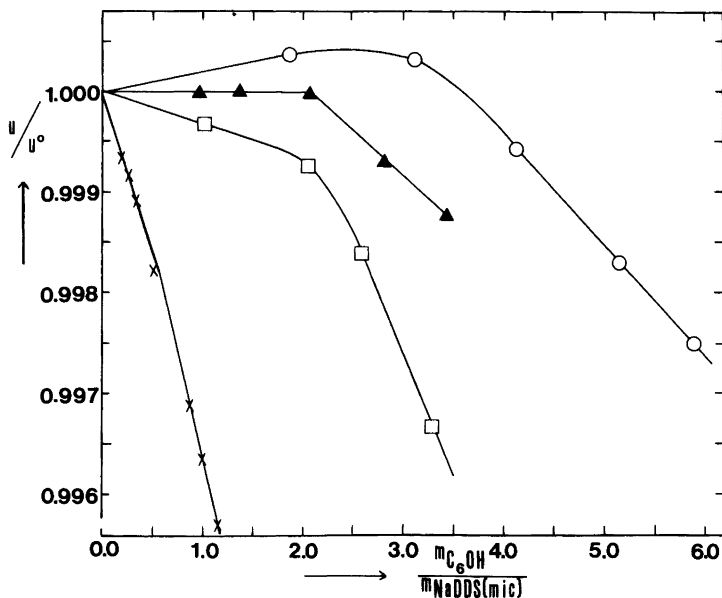

Fig. 3. The relative conductivity, $\varkappa/\varkappa°$, of NaDDS solutions as a function of added hexanol at 298.2 K. $\varkappa°$ is the conductivity of the pure NaDDS solutions with the same symbols as in Fig. 1.

243

Fig. 4. The relative speed of sound, u/u^0, of NaDDS solutions as a function of added hexanol at 298.2 K. u^0 is the speed of sound of 0.05 (○); 0.074 (▲); 0.10 (□) and 0.302 m NaDDS (×).

tivation energy suddenly starts increasing, suggesting that a micellar shape transition has taken place.

Addition of alcohol to a surfactant solution influences the electrical conductivity of the solution. [19,21] Fig. 3 shows the relative conductivities of NaDDS solutions as a function of the solubilization ratio. For higher NaDDS molalities, 0.2–0.4 m, the relative conductivities first increase linearly and become practically constant above a certain hexanol content, corresponding to the hexanol content at which the relative viscosities start increasing. It thus seems that the shape transition from spherical to rod- or disc-like micelles can be observed by conductivity measurements as well. When hexanol is solubilized by the micelles, the surface charge density decreases, and associated counterions are then released.[3,15,19,23,24] The conductivity of the system increases and Fig. 3 shows that this increase is equal at all NaDDS contents on a relative scale as long as the hexanol content is below the transition point from spherical to rod- or disc-like micelles. The fraction of dissociated counterions is apparently constant for a constant ratio of hexanol to NaDDS.

The conductivities of the solutions containing less than 0.1 m NaDDS are in good agreement with the results of Lawrence and Pearson[24] and

Tominaga et al.[19] Fig. 3 shows that the relative conductivities of low content NaDDS solutions, below 0.1 m, also increase with the solubilization ratio due to released counterions as before. However, the curves differ from those at higher NaDDS contents. At low solubilization ratios, the curves do not match as before, and at high hexanol contents, the relative conductivities no longer remain constant, but start decreasing. The maximum is found at a solubilization ratio of 2.5 to 3.5, depending upon the NaDDS molality. The decreasing conductivities compare well with addition of alkane to NaDDS micelles. For instance, addition of octane to NaDDS micelles leads to a decrease in the relative conductivity at all octane contents.[25] Octane is expected to be solubilized only in the interior of the micelles. In comparison, decreasing relative conductivities as hexanol is added, suggest that hexanol now becomes solubilized in the micellar interior as well. The maxima of the conductivity curves of the system NaDDS-hexanol-water are not well defined, but they can still be used to determine a "critical" concentration after which added hexanol becomes solubilized in the micellar interior.

Fig. 4 shows a plot of the relative ultrasonic velocity (relative to the NaDDS solution without added hexanol) versus the solubilization ratio. One observes a distinct change in the slope. This
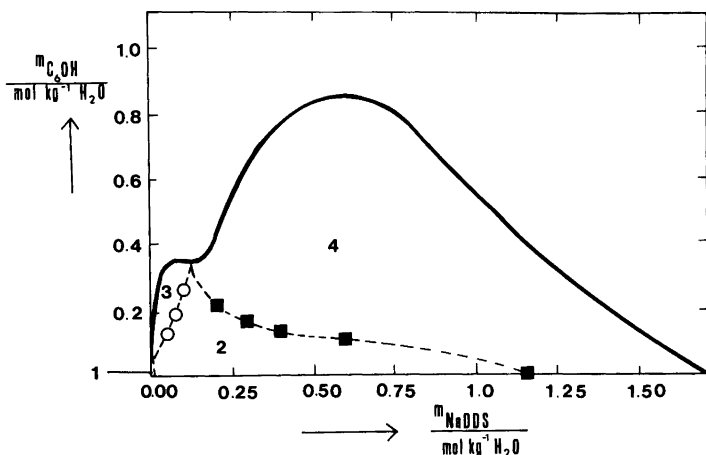
Fig. 5. Various regions in the L_1 phase of the water-hexanol-sodium dodecylsulfate system at 298.2 K: No micelles in region 1. Ordinary spherical micelles in region 2. Spherical swollen micelles in region 3 and large rod- or disc-like micelles in region 4. Conductivity and ultrasound measurements (O). Viscosity and conductivity measurements (■).

sudden change in the slope must be connected with changes in the solubilization process. It occurs at solubilization ratios that correspond to the maxima in the conductivity plots. After the break, the slope is more negative. It means that the partial molar compressibility of the hexanol has increased, just as one would expect for an alcohol in alkane compared to an alcohol in aqueous surroundings.[26] A combination of solubility data, conductivities and ultrasonic velocities show that at low contents, hexanol is mainly located in the palisade and at higher contents also in the interior of the micelles. It should also be noted that at a NaDDS content of 0.3 m, no distinct changes in the slope of the ultrasonic velocity versus the solubilization ratio can be observed, but at these NaDDS contents, the solubilization ratio never exceeds 1.5.

Quasielastic light scattering has been used to check the micellar size as hexanol becomes solubilized in the micellar interior. Since no salt has been added to this system, the micelle-micelle interactions are not screened and care must be exercised when interpreting the data. However, the results show no significant changes in the diffusion coefficient of the micelles before and after the point where alcohol becomes solubilized in the interior, and hence no significant increase in micellar radius. It thus appears that if the micelles swell as a result of solubilization, this swelling is modest in terms of an increased micellar volume. The polydispersity of these mixed micelles appears to be larger than for pure NaDDS micelles.

In conclusion, the L_1 phase of the water-hexanol-NaDDS system can be divided into 4 structurally different regions. First, there is a small region below the c.m.c. where no micelles are formed. Second, there is a micellar region where the shape is spherical and where hexanol is solubilized, mainly in the palisade. At low NaDDS contents, this transfers to a region of swollen micelles, i.e., micelles where a large proportion of hexanol is solubilized in the micellar interior. The conductivity and ultrasonic measurements clearly register a change in the solubilization pattern at this point. The basic shape of the swollen micelles is probably spherical, but the term swollen may be somewhat misleading. Quasielastic light scattering experiments do not detect any significant increase in the micellar volume, although the polydispersity appears to increase. Third, at higher NaDDS concentrations, one still finds spherical micelles with alcohol solubilized in the palisade. Fourth, adding hexanol leads to a shape transition from these spheres to larger aggregates, which are disc- or rod-like. The solubilization ratio is always less than 2 in this region, suggesting that hexanol is solubilized only in the palisade layer of these large aggregates.

The various regions of the L_1 phase are shown in Fig. 5.

245

References

1. Ekwall, P. In: Brown, G., ed., *Advances in liquid crystals*. Academic Press, New York 1975, vol. 1, p. 1.
2. Kvammen, O., Backlund, S. and Høiland, H. In: Birdi, K. S., ed., *Proceedings 7th Scand. Symp. Surface Chem.* Lyngby, Denmark, 1981, pp. 243–254.
3. Høiland, H., Kvammen, O., Backlund, S. and Rundt, K. In: K. L. Mittal and Lindman, B., eds., *Surfactants in solution*. Plenum Press, New York 1984, vol. 2, pp. 949–962.
4. Høiland, H., Blokhus, A. M., Kvammen, O. and Backlund, S. *J. Colloid Interface Sci. 107* (1985) 576.
5. Lianos, P. and Zana, R. *J. Colloid Interface Sci. 101* (1984) 587.
6. Candau, S. and Zana, R. *J. Colloid Interface Sci. 84* (1981) 206.
7. Hayter, B., Hayoun, M. and Zemb, T. *Colloid Polymer Sci. 262* (1984) 798.
8. Stilbs, P. *J. Colloid Interface Sci. 89* (1982) 547.
9. Vikholm, I., Douhéret, G., Backlund, S. and Høiland, H. *J. Colloid Interface Sci.*, submitted.
10. Blokhus, A. M., Høiland, H. and Backlund, S. *J. Colloid Interface Sci. In press.*
11. Høiland, H. and Vikingstad, E. *J. Chem. Soc. Faraday Trans. 1, 72* (1976) 1441.
12. Reiss-Husson, F. and Luzzati, V. *J. Phys. Chem. 68* (1964) 3504.
13. Ekwall, P., Mandell, L. and Solynom, P. *J. Colloid Interface Sci. 35* (1971) 519.
14. Miura, M. and Kodama, M. *Bull. Chem. Soc. Jpn. 45* (1972) 428.
15. Backlund, S. and Rundt, K. *Acta Chem. Scand. A34* (1980) 433.
16. Passinen, K. and Ekwall, P. *Acta Chem. Scand. 10* (1956) 215.
17. Larsen, J. W., Magid, L. J. and Payton, V. *Tetrahedron Lett. 29* (1973) 2663.
18. Clarke, D. E. and Hall, D. G. *Colloid Polymer Sci. 252* (1974) 153.
19. Tominaga, T., Stem, T. B. and Evans, D. F. *Bull. Chem. Soc. Jpn. 53* (1980) 795.
20. Hirsch, E., Candau, S. and Zana, R. *J. Colloid Interface Sci. 97* (1984) 318.
21. Ljosland, E., Blokhus, A. M., Veggeland, K., Backlund, S. and Høiland, H. *Progr. Colloid Polymer Sci. 70* (1985) 34.
22. Ekwall, P. and Holmberg, P. *Acta Chem. Scand. 19* (1965) 573.
23. Heckmann, K. *Kolloid. Z. 136* (1954) 67.
24. Lawrence, A. S. C. and Pearson, J. T. *Trans. Faraday Soc. 63* (1967) 495.
25. Backlund, S., Blokhus, A. M., Ljosland, E., Høiland, H. and Vikholm, I. *Proc. VI Yugoslav Symp. Surface Active Agents*, Vrnjačka Banja, Yogoslavia, 1985, pp. 147–162.
26. Vikholm, I., Backlund, S., Maldal, T. and Høiland, H. *Finn. Chem. Lett.* (1985) 152.