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The Effect of Medium Chain Length Alcohols on the Micellar Properties of Sodium Dodecyl Sulfate in Sodium Chloride Solutions

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The effect of medium chain length alcohols on the micellar size and shape of sodium dodecyl sulfate in electrolyte solutions has been investigated by means of small angle neutron scattering (SANS), dynamic light scattering (DLS), and viscosity measurements. The surfactant content was kept constant throughout, at 0.04 *m*, and the alcohols used were 1-butanol, 1-pentanol, and 1-hexanol. The data from the various techniques are qualitatively in agreement. The SANS data generally fit a model for prolate ellipsoids with varying ratios of the major to minor axis. Addition of butanol first leads to a decrease in micellar size, the major to minor axis ratio decreases from about 6 to less than 2. However, as the butanol concentration exceeds 0.5 *m*, the micelles starts to grow again. The same can be seen from the diffusion coefficient as measured by DLS. Addition of pentanol or hexanol do not bring about this minimum in micellar size. The minor axis decreases and the major axis increases as these alcohols are added. Thus these alcohols make the prolate ellipsoidal micelles grow continuously towards large rod-like structures. The viscosity data are less detailed, but confirm the general trend upon alcohol addition.

INTRODUCTION

The size and structure of ionic micelles in the presence of additives have been extensively studied during the last decades (1–10). The wide attention given to these systems is a result of their importance and their complicated aggregation behavior. For most aqueous ionic surfactant solutions just above the critical micelle concentration (cmc), the micelles are regarded as spherical in shape (4, 8). Addition of neutral salt and alcohol may affect the micellar structure. This effect depends on the types of surfactants used, their concentration, the salt content, and the alcohol (1–7).

Addition of neutral salt decreases the electrostatic interactions between monomers in the micelle and can bring about structural changes towards larger rod- or disc-like aggregates (9–13). It will also affect the distribution coefficient of any added alcohol between the micelles and the surrounding water, giving rise to increased solubilization of the alcohol (14).

Several authors have shown that short and medium chain length alcohols may lead to a decrease in the micellar size (6, 7, 15–17). On the other hand, addition of medium to long chain alcohols increases the aggregation number producing larger alcohol-surfactant mixed micelles (2–6, 18–22). These changes in micellar size are often explained in terms of differences in the solubilization mechanism of the alcohols. The principal location of alcohol molecules in aqueous micellar solution depends on the solubilizate itself. While short chain length alcohols mainly affect the micelles through their effect on the solvent (22–24), the medium chain length alcohols (butanol to hexanol) have distribution coefficients in the range 0.3 to 0.9 giving rise to mixed alcohol-surfactant aggregates (1–7, 15, 16, 18–30).

At high alcohol contents it has been proposed that the medium chain length alcohols are solubilized in the micellar interior as well as in the palisade layer, thus producing large alcohol swollen aggregates (3–5, 16, 18–21). The measured changes in the micellar size or structure upon addition of medium chain length alcohols are not entirely consistent, suggesting that to a certain extent the conclusions depend upon the measuring technique used (12, 16, 18, 25, 31). On the other hand, data from the various workers are difficult to compare directly due to the many variables of the system. The results refer to different surfactant systems at different concentrations and with different additives.

In order to look more closely at the effect of alcohols on the structure of micelles we have chosen to compare results from two scattering techniques, dynamic light scattering (DLS) and small angle neutron scattering (SANS) plus viscosity measurements, all performed on the same systems. Here we have used a constant 0.04 *m* aqueous solution of sodium dodecyl sulfate and added 1-butanol, 1-pentanol, or 1-hexanol. In order to screen the charge of the micelles, important for the interpretation of the DLS data, the experiments have been conducted with a constant amount of added NaCl.

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EXPERIMENTAL

Materials. Sodium dodecyl sulfate (SDS) was obtained from BDH "Specially pure." It was dried in an evaccuated desiccator at 50°C before use. Sodium chloride was obtained from Merck "Pro analysi" reagent grade. It was dried at 120°C. The alcohols, 1-butanol, 1-pentanol, and 1-hexanol were from Fluka "Puriss grade." They were used without further purification. The SANS experiments required D_2O instead of water.

SANS measurements. The small angle neutron scattering experiments were carried out at room temperature at Risø National Laboratory, Denmark. The neutron wavelength was 0.60 nm and the sample to detector distance was 1 and 3 m, which correspond to a q range from 0.001 to 0.025 nm. The scattering from the cuvette and the instrumental background was subtracted from the data. The data were normalized with respect to normal water, and were finally radially integrated.

All the normalized and radially integrated data sets were fitted to the intraparticle structure factor for various geometric models, spheres, rods, prolate ellipsoids, and oblate ellipsoids as previously described (32).

DLS measurements. The light source for the dynamic light scattering experiments was a 2-watt argon ion laser from Spectra Fysics operating at a wavelength of 488 nm. The rest of the optical system was from Malvern. The scattered light was collected at an angle of 90° by a photomultiplier cathode, type RF 313. The time dependent correlation function was derived by using a digital correlator (Malvern K-7023), and the data were fitted to a single exponential equation to obtain the average self diffusion coefficient. The normalized variance, associated to the correlation function, as described by Pusey (33), was calculated. This is the so called polydispersity factor. The measurements were carried out at (25.00 ± 0.01)°C. The solvents used were 0.1 to 0.4 m NaCl. This provides a sufficiently high ionic strength so that intermicellar electrostatic interactions could be neglected when calculating the diffusion coefficients. The solutions were made dust-free by ultrafiltration through 0.1-μm filters and by centrifugation for 1 h at 8000 rpm in the scattering cell.

Viscosity measurements. The viscosity measurements were carried out at (25.00 ± 0.01)°C by using an Ubbelohde capillary viscometer.

RESULTS

With no alcohol added the SANS data showed that 0.04 m SDS in an aqueous solution with 0.4 m NaCl added, fitted a model of prolate ellipsoids with a major to minor axial ratio of about 4.

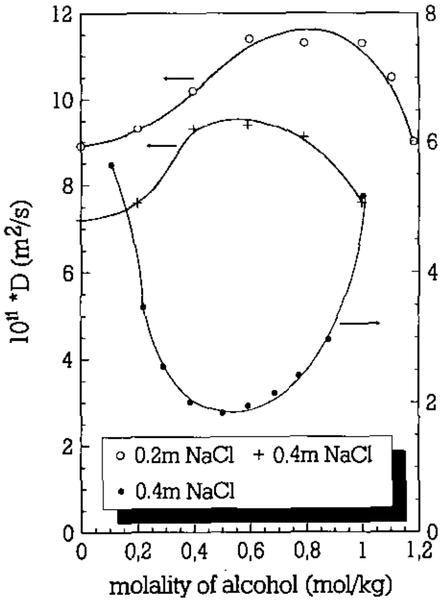

FIG. 1. Left side: The diffusion coefficient from light scattering, D, plotted against the molality of butanol at various molality of added NaCl. Right side: The major to minor axial ratio of the micelles plotted against the molality of added butanol.

Figure 1 shows what happens when butanol is added to this solution. The diffusion coefficient of the SDS micelles, as measured by light scattering, increases with increasing amount of butanol up to about 0.5 m. If more butanol is added, the diffusion coefficient starts decreasing. This suggests that the micelles first decrease in size as a result of butanol addition and then starts growing after a certain amount has been added. The polydispersity factor was below 0.1 in the entire range of butanol addition, suggesting fairly monodisperse micelles. The same general trend is found when the amount of neutral salt is reduced to 0.2 m, but the maximum occurs at a slightly higher butanol content. The SANS data on the same system containing 0.4 m NaCl were best fitted to a model for prolate ellipsoids. The ratio between the major and minor axis of the ellipsoid is plotted in Fig. 1, also as a function of the butanol added. The major to minor axis ratio of the prolate micelles first decreases as butanol is added, reach a minimum, and then increases as even more butanol is added. This minimum coincide with the maximum on the curve of the diffusion coefficient.

Figure 2 shows what happens when pentanol or hexanol is added to the same SDS system. The SANS data again fit prolate ellipsoids. For both alcohols the major to minor axial ratio increases as alcohol is added making the micelles more and more rod-like. Hexanol is the more efficient of the two and at the solubility limit, the minor axis is about 1.6 nm while the major axis is about 11 times as large.

Spherical SDS micelles have a radius of about 2.5 nm (9). The minor axis of the prolate ellipsoidal micelles in 0.4 m NaCl as measured by SANS, is significantly lower, Fig. 3. Addition of hexanol has only a marginal effect on the minor

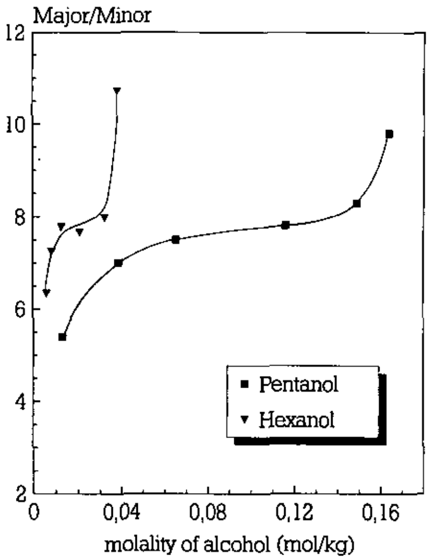

FIG. 2. The major to minor axial ratio of the micelles, major/minor, plotted against the molality of added alcohol. The sodium chloride content is 0.4 mol/kg.

axis, whereas addition of propanol and butanol further decreases the minor axis. For butanol the minor axis first exhibit a small decrease as the total micellar size decreases. However, above approximately 0.5 *m* butanol added, the minor axis decreases significantly whereas the micellar size increases, suggesting that for this system rod-like aggregates are formed with a minor radius significantly less than that of a spherical micelle. The viscosity data, Fig. 4, are less detailed. The viscosity values certainly suggest large micellar aggregates, and there is a general increase in the viscosity as butanol is added. There also appears to be a change in the slope at a butanol concentration of about 0.5 *m*, where the other two techniques

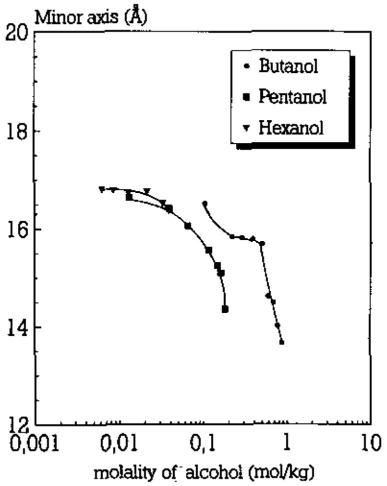

FIG. 3. The minor axis of the micelles plotted against the molality of alcohol. The sodium chloride content is 0.4 mol/kg.

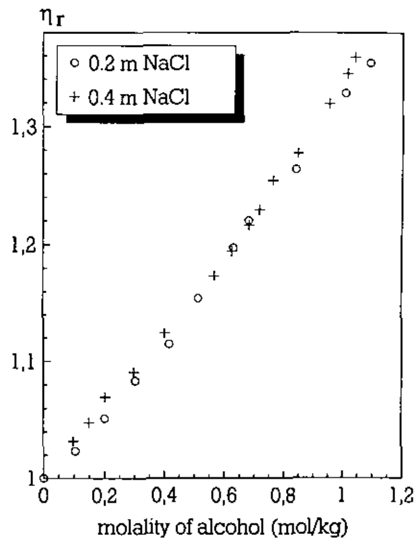

FIG. 4. The relative viscosity (aqueous micellar sodium dodecyl sulfate solution containing butanol against the micellar solution without added alcohol), η_r, plotted against the molality of butanol at various contents of added sodium chloride.

suggest that the micelles start to grow as a consequence of further butanol addition.

The light scattering data of Figs. 5 and 6 show the effect of varying salt concentration as pentanol and hexanol is added to a 0.04 *m* SDS solution. For all systems it is seen that alcohol lowers the diffusion coefficient significantly up to a point after which there is hardly any effect of adding alcohol. The larger the salt content the lower is the lowest value of the diffusion coefficient. For these systems the poly-

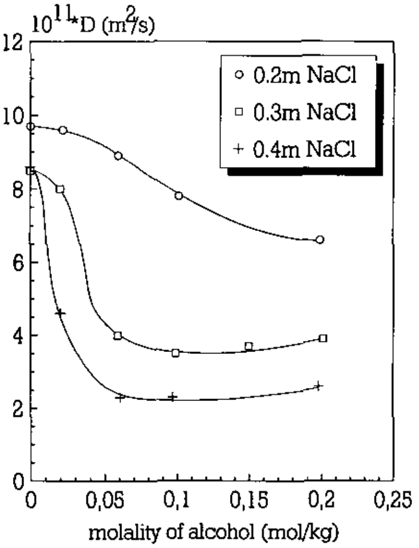

FIG. 5. The diffusion coefficient from light scattering, *D*, plotted against the molality of pentanol at various sodium chloride contents.

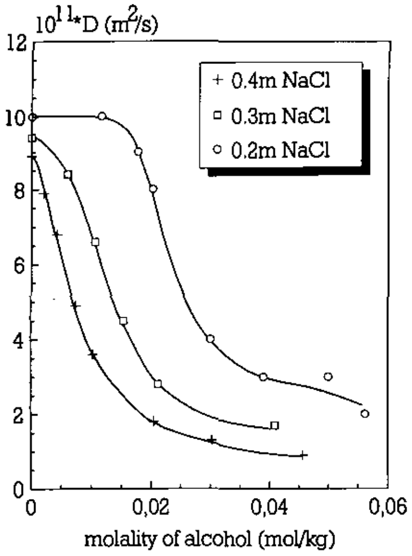

FIG. 6. The diffusion coefficient from light scattering, D, plotted against the molality of hexanol at various sodium chloride contents.

dispersity factor increased as alcohol was added, suggesting a larger size distribution as the micelles grow. The viscosity data on the same systems, Figs. 7 and 8 show similar trends.

DISCUSSION

The observed lowering of the mutual diffusion coefficient of micelles when salt is added, is due to a dominant size increment effect as a result of a decreased micellar surface potential (11, 31). The sphere to rod, or sphere to prolate ellipsoid, transition causes a change in the packing condition as well as in the aggregation number (9–11). Our SANS measurements suggest that prolate ellipsoids with a major to minor axial ratio of about 4 is present for a 0.04 m SDS dissolved in an aqueous solution of 0.4 m NaCl.

The lower alcohol homologues, methanol to propanol, mainly dissolves in the aqueous phase, and leads to a breakdown of the micellar aggregates (15, 33). Butanol is distributed between the aqueous and micellar phases, the distribution coefficient being 0.35 at this SDS concentration in pure water and it is practically independent of the alcohol concentration (34). Even if the distribution coefficient increases as a result of added salt, a major part of the butanol will still be dissolved in the aqueous phase. This seems to be sufficient to start the process seen for the lower homologues, a tendency towards breaking down the micelles. Both scattering techniques first show a decrease in the micellar size as butanol is added. However, as the butanol concentration increases, the number of alcohol molecules per micelle increases. The micellar charge density will decrease accordingly (35). There will be less repulsion between the monomers of the micelle. Apparently this reach a level where the micellar surface is sufficiently modified to bring about micellar growth, as observed for both scattering techniques above a butanol content of 0.5 m.

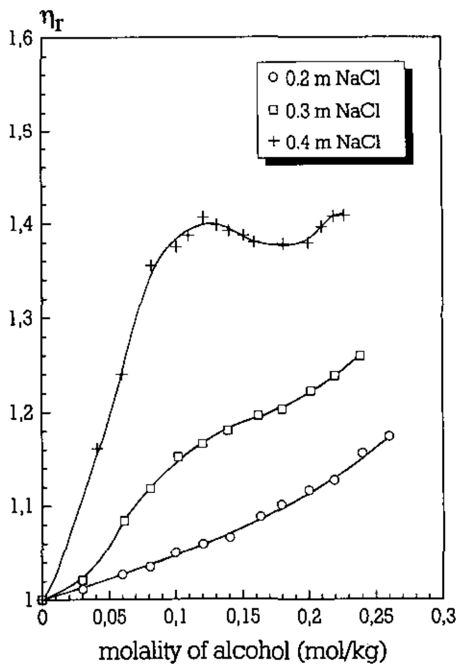

FIG. 7. The relative viscosity (aqueous micellar sodium dodecyl sulfate solution containing pentanol against the micellar solution without added alcohol), η_r, plotted against the molality of pentanol at various sodium chloride contents.

Addition of pentanol up to an alcohol to surfactant mol ratio above one show that this makes the micelles grow to longer rod-like micelles (or rather prolate micelles with de-

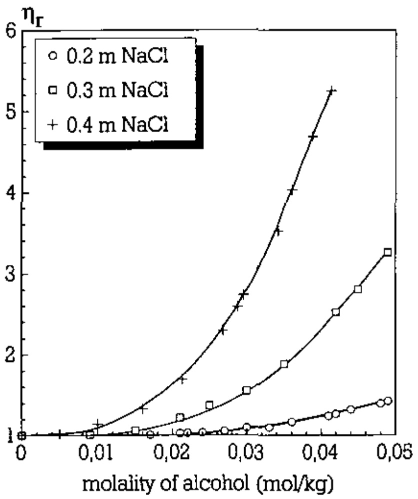

FIG. 8. The relative viscosity (aqueous micellar sodium dodecyl sulfate solution containing hexanol against the micellar solution without added alcohol), η_r, plotted against the molality of hexanol at various sodium chloride contents.

creasing minor and increasing major axis). The distribution coefficient of pentanol in SDS systems is about 0.75, and it is practically independent of the alcohol concentration (34). As for butanol added salt will make it even higher. This means that the major part of the alcohol is solubilized by the micelles. One would thus expect a micellar volume increase due to the solubilized alcohol molecules, but probably more important, a lower micellar charge density, less repulsion between the micellar monomers and thus more favourable condition for increased micellar size. Apparently the amount of pentanol dissolved in the aqueous phase is too small to have any affect on the micellar size. Hexanol has an even higher distribution coefficient, about 0.9, probably higher in salt solutions. Both the larger size of the hexanol molecule and the larger distribution coefficient suggest that hexanol will be more efficient in making the micelle grow, as is indeed observed. The SANS data of Fig. 2 suggest a significant increase in the micellar size when we are close to the solubility limit for pentanol and hexanol. The effect is particularly strong when hexanol is added. This increase in size is not observed in the light scattering experiments and could be an effect of less well controlled temperature of the SANS measurements. The viscosity data are in agreement with this interpretation.

In conclusion the scattering techniques are in agreement with regard to what happens as alcohol is added to micelles in aqueous NaCl solutions. Viscosity measurements are only an indirect method of elucidating micellar size, but the data are in qualitative agreement with the scattering techniques as regards the micellar size. SANS data show that addition of 0.4 *m* sodium chloride makes SDS micelles grow from spheres to prolate ellipsoids (rods) with a major to minor axis ratio of about 4 for a SDS concentration of 0.04 *m*. Addition of alcohols apparently affects micelles in two ways; by their effect on water and by solubilization. For the lower homologues the effect on water is dominant leading to a break-down of the micellar structure. For the higher homologues, starting with pentanol, solubilization outweighs the effect on water, the overall result being increased micellar size. Hexanol is more efficient than pentanol as regards increasing the micellar size. Butanol is intermediate, at first it leads to a reduced micellar size probably due to its effect on water, but as more butanol is solubilized the micelles grow again.

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