

Electromotive Force Studies in the System Sodium Dodecylsulfate – Water – n-Alcohol

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Electromotive force studies in water-rich solutions of sodium dodecylsulfate at 298.2 K as a function of added n-pentanol or n-hexanol have been performed. The measurements were executed at several different surfactant molalities both below and above the critical micelle concentration (c.m.c.). The alcohols show various effects on the cell potential, depending primarily on the molalities of both the surfactant and the alcohol. The results clearly show that the alcohols lower the c.m.c. and that the micelles formed in alcohol containing solutions bind counter-ions. Values for the c.m.c. in alcohol containing solutions have been determined from measured potentials.

The self-aggregation of ionic surfactants to micelles and the different interactions at the micellar surface have been thoroughly investigated during the past few years. One of the reasons for this is that the attractive forces acting between the hydrocarbon chains in micelles are of the same kind as the forces keeping together biological membranes.¹ The opposing forces at the micellar surface are of electrostatic character and binding of counter-ions to the micellar surface weakens these opposing forces and makes it possible for micelles to form. It is therefore of great importance to study the association of counter-ions to micelles under various circumstances.

Some potentiometric measurements of counter-ion activity as a function of the concentration of hydrocarbons or alcohols in micellar systems have been reported.^{2–12} These measurements are difficult to perform with satisfying accuracy, moreover, the additives may have an unpredictable effect on the electrodes. Some authors^{2,3} have determined, along with the activity, the conduc-

tivity of the surfactant solutions.

The most systematic study has been made by Lawrence and Pearson.⁴ They investigated the effect of several homologous alcohols on a solution containing 2% sodium dodecylsulfate. Our aim is to investigate the effects of these same alcohols on solutions with varying sodium dodecylsulfate molality.

EXPERIMENTAL

Chemicals. Sodium dodecylsulfate, SDS, was used as supplied by BDH Ltd. Due to its high purity ($\geq 99\%$) no purification was necessary.¹³ The n-pentanol, C₅OH, (E. Merck AG, *p.a.* quality) and n-hexanol, C₆OH, (Fluka AG, *puriss.* quality) were used as such. Sodium chloride was used as supplied by E. Merck AG (*p.a.* quality). The water was distilled and passed through an ion exchange resin immediately before use. Its conductivity was $0.5 \mu\text{S cm}^{-1}$.

Measurements of the electromotive force. The measurements were performed as titrations in such a way that the alcohols were added to an SDS solution, with the aid of a microburette. The electrodes were not removed from the test solution during titration. The SDS solutions were always fresh, prepared by weighing. The measuring cell was immersed in a water bath at 298.15 ± 0.05 K. The changes in the sodium ion activity were observed with a sodium responsive glass electrode manufactured by Electronic Instruments Ltd., Type GEA 33. The reference electrode was a double junction electrode manufactured by Orion, Model 90–02, with $3 \text{ mol dm}^{-3} \text{ NH}_4\text{NO}_3$ as bridge solution. KCl could not be used because potassium dodecylsulfate is almost insoluble. Other types of reference electrodes such as ordinary calomel

electrodes with a porous pin or an agar bridge were found unsuitable.

Measurements of the critical micelle concentration. The change in the c.m.c. of the surfactant solution upon addition of pentanol was also measured by the fluorescence method. The fluorescence probe was anilino-naphthalene sulfonate. The method has been described elsewhere.¹⁴ The spectrophotometer used was a Perkin-Elmer MPF 3 Fluorescence Spectrophotometer.

RESULTS AND DISCUSSION

Nernst's equation for our cell reads as eqn. (1), where E is the measured potential and E_j^\ominus is a term containing both the standard potential of the cell and the liquid junction potential. The symbol k_E stands for the Nernstian slope; we used the theoretical value. The counter-ion activity is denoted by a_{Na^+} .

$$E = E_j^\ominus - k_E \log a_{\text{Na}^+} \quad (1)$$

The cell potential E was measured as a function of the SDS molality in order to determine the c.m.c. in pure aqueous solutions (m_c^*) and the degree of counter-ion dissociation from the micelles (α). To convert E to a_{Na^+} it was assumed that the activity coefficient of the sodium ion in dilute solutions below c.m.c. equals the mean activity coefficient in a NaCl solution of same ionic strength.

1. Sodium ion activities in pure aqueous SDS solutions. In Fig. 1 the activity, a_{Na^+} , is plotted versus the SDS molality. The curve shows an obvious break at $8.1 \times 10^{-3} \text{ mol kg}^{-1}$ which is accepted as the c.m.c. in aqueous solutions (m_c^*), corresponding

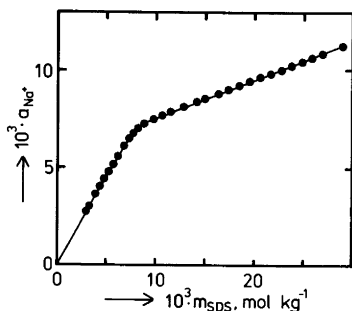


Fig. 1. Sodium ion activity, a_{Na^+} , in pure SDS solutions as a function of the SDS molality at 298.2 K.

well with our fluorescence measurements and with data in the literature.^{13,15-18}

The slope of the curve decreases above c.m.c. because of the association of counter-ions to the micelles. The sodium ion activity above c.m.c. is given by eqn. (2), where γ_{Na^+} is the activity coefficient of free counter-ions, m^\ominus is 1 mol kg^{-1} and α is the degree of counter-ion dissociation of the micelles. Derivation of this formula, while assuming a constant γ_{Na^+} , gives eqn. (3).

$$a_{\text{Na}^+} = \frac{\gamma_{\text{Na}^+}}{m^\ominus} (m_c^* + \alpha(m_{\text{SDS}} - m_c^*)) \quad (2)$$

$$\alpha = \frac{m^\ominus}{\gamma_{\text{Na}^+}} \frac{d a_{\text{Na}^+}}{d m_{\text{SDS}}} \quad (3)$$

For $m_{\text{SDS}} > 10.3 \times 10^{-3} \text{ mol kg}^{-1}$ the slope, $da_{\text{Na}^+}/dm_{\text{SDS}}$, of the curve in Fig. 1, is equal to $0.192 \text{ kg mol}^{-1}$. Assuming $\gamma_{\text{Na}^+} = 0.900$ (which is the extrapolated activity coefficient at m_c^* gives $\alpha = 0.213$, in good agreement with the literature.¹⁶⁻¹⁹

2. Behaviour of cell potentials as alcohol is added. The results of alcohol addition to solutions containing various amounts of SDS, are plotted as ΔE versus the alcohol molality in Figs. 2-5. ΔE is defined as $\Delta E = E^* - E$ where E^* and E are the

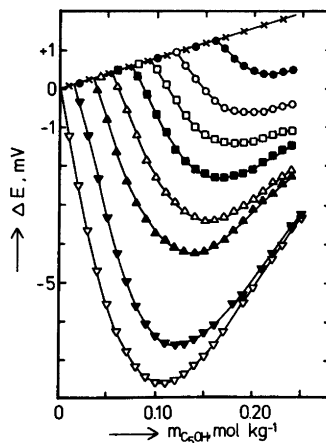


Fig. 2. Influence of pentanol on cell potential at 298.2 K in a NaCl solution with $m_{\text{NaCl}} = 0.020 \text{ mol kg}^{-1}$ (\times) and following SDS solutions: m_{SDS}/m_c^* - 0.137 (\bullet); 0.214 (\circ); 0.300 (\square); 0.380 (\blacksquare); 0.480 (\triangle); 0.600 (\blacktriangle); 0.788 (\blacktriangledown); 1.004 (∇). $m_c^* = 8.1 \times 10^{-3} \text{ mol kg}^{-1}$.

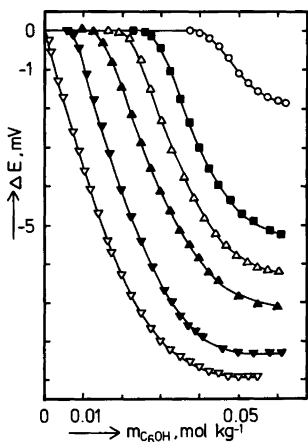


Fig. 3. Influence of hexanol on cell potential at 298.2 K in SDS solutions, with the same molalities as in Fig. 2.

measured cell potentials in alcohol free and alcohol containing solutions, respectively. We have also measured the influence of pentanol on E in one NaCl solution, these data are in Fig. 2. The influence of hexanol on E in NaCl solutions was too small to be detected. The alcohols will lower the dielectric constant of the medium thus influencing both E_j^\ominus and γ_{Na^+} .

Fig. 2 shows how pentanol influences the cell potential in several SDS solutions with SDS molalities below and at m_c^* . At low pentanol molalities the SDS solutions behave as the NaCl solution

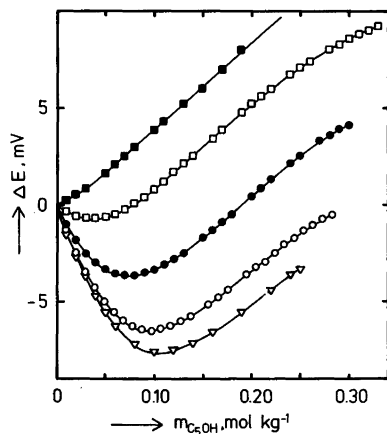


Fig. 4. Influence of pentanol on cell potential at 298.2 K in following SDS solutions: $m_{SDS}/m_c^* = 1.004$ (∇); 1.200 (\circ); 1.640 (\bullet); 2.746 (\square); 5.105 (\blacksquare).

upon addition of pentanol, but at a definite pentanol molality ΔE reaches a maximum value whereafter it decreases, reaching a minimum, only to rise again. The explanation to these curves may be as follows:

At first the solution behaves as an *ordinary electrolyte solution*, while the pentanol is dissolved in water. At a definite pentanol molality ΔE decreases, which indicates *formation of micelles with bound counter-ions*. This formation of micelles is analogous to the well-known effect called 'c.m.c.-lowering'.^{20,21} At the maximum of the curves, the pentanol molality has reached a point where the SDS molality corresponds to the c.m.c. in a solution containing exactly this amount of pentanol (m_c). One can therefore put m_c at this pentanol molality equal to m_{SDS} . The values for m_c determined in such a way have been plotted vs. the pentanol molality in Fig. 6. As can be seen, a plot of $\ln m_c$ against m_{C_5OH} yields a straight line, corresponding well to our fluorescence data and rather well to the data of Hayase and Hayano,²¹ determined by conductivity measurements.

The positive slope of the curves at higher pentanol molalities cannot solely be a result of the effect of pentanol on E_j^\ominus , there must also be some *liberation of sodium ions from the micelles* as pentanol is incorporated into the micelles. The solubility limit of pentanol in an NaCl solution is about 0.24 mol kg^{-1} , which corresponds to the solubility in the SDS solutions in Fig. 2. Hence, only a small portion of the pentanol will be incorporated in the micelles.

Fig. 3 shows how hexanol influences the cell potential in several solutions with SDS molalities

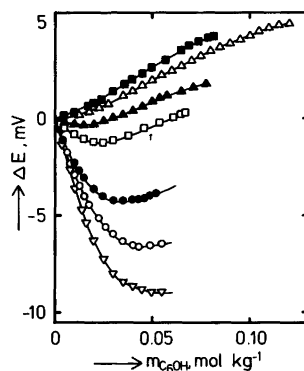


Fig. 5. Influence of hexanol on cell potential at 298.2 K in SDS solutions: $m_{SDS}/m_c^* = 3.670$ (\blacktriangle); 7.500 (\triangle). Other symbols as in Fig. 4.

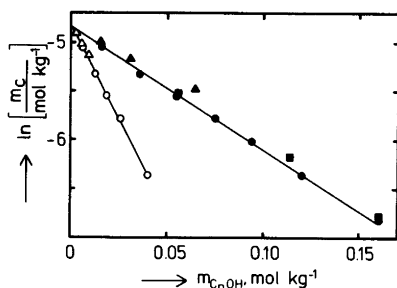


Fig. 6. The logarithm of the critical micelle concentration as a function of the alcohol molality at 298.2 K. Pentanol (●); hexanol (○); data from Ref. 21 (▲ and △); fluorescence measurements (■).

below and at m_c^* . The influence on E_j^\ominus was too small to be detected. These curves give the c.m.c. in hexanol containing solutions (m_c) and these values are plotted in Fig. 6. The interpretation of the curves in Fig. 3 is quite similar to the interpretation of the pentanol curves in Fig. 2. The solubility of hexanol²² in water is about $0.061 \text{ mol kg}^{-1}$, so most of the alcohol is evidently dissolved in the bulk water.

Fig. 4 shows the influence of pentanol and Fig. 5 the influence of hexanol on the cell potential in solutions with SDS molalities above $8.1 \times 10^{-3} \text{ mol kg}^{-1}$. At low molalities the alcohols induce micelle formation, but at higher alcohol molalities sodium ions are liberated from the micelles. The solubility of alcohols increases with increasing SDS molality because of the solubilizing power of the micelles. At SDS molalities above $41.4 \times 10^{-3} \text{ mol kg}^{-1}$ the plots are nearly straight lines with immediate rise, monotonously up to the solubility limit.

CONCLUSIONS

Electromotive force measurements in surfactant solutions containing alcohol are an effective means to determine the critical micelle concentration as a function of alcohol molality and to investigate the effect of alcohol on counter-ion association to micelles containing alcohol.

Summarizing:

- (i) The studied alcohols induce formation of micelles with some bound counter-ions.
- (ii) Solubilization of the alcohols into micelles liberates counter-ions from the micelles.

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