

A Potentiometric Investigation of Sodium Ion Activity in Micellar Sodium Dodecyl Sulphate Solutions

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Determinations of counter ion binding to micelles by the use of cation-responsive glass electrodes have yielded results which are less reproducible than would be justified by the claimed experimental uncertainties. A renewed investigation of sodium ion activities and the different factors affecting their determination in sodium dodecyl sulphate (SDS) solutions has been made.

In previous investigations the binding of sodium ions to the micelles was estimated from a simple model.^{1,2} Botré *et al.* formally separated the different contributions to the counter ion activity, a_{Na} , in micellar solution above the critical micelle concentration (c.m.c.) in the following way:

$$a_{\text{Na}} = f_1 c_0 + f_2 \alpha (c - c_0)$$

where f_1 = the activity coefficient of Na^+ in the solution surrounding the micelles, f_2 = the activity coefficient of the Na^+ in the ionic atmosphere around the micelles, α = the degree of dissociation of the micelles, c_0 = the c.m.c. and c = the total concentration of surfactant. It is found experimentally that a_{Na} changes linearly with c above the c.m.c., which suggests that f_1 , f_2 , and α are constant. The usual method of calculating an apparent degree of dissociation, α' , is to set f_2 = the activity coefficient of single counter ions at the c.m.c., (f_0). This assumption is probably far from realistic. The activity coefficient of the ions in the ionic atmosphere of a large colloidal ion is probably much lower than in a simple salt solution.

It is therefore proposed that an apparent degree of dissociation should be defined in the following way:

$$\alpha' = f_2 \alpha$$

This quantity will represent the contribution of the micelles in the solution to the total sodium ion activity, without any assumptions being made concerning the nature of the ion-ion interactions which causes the contribution to be of this magnitude. Setting $f_2 = f_0$, ($\alpha' = \alpha f_2 / f_1$) implies a definition of f_2 on an arbitrary scale. f_0 will be quite different for different surfactants. Any abnormal changes in f_1 at low surfactant concentrations (which may be expected for long-chain compounds especially) or with the concentration of neutral salt will be indirectly reflected in α' , variations in which will thus not be exclusively dependent on real changes in the degree of dissociation. α' does not seem to be a suitable quantity for comparing results from different surfactants, or even for the same surfactant at different ionic strengths.

α' , on the other hand, can be determined directly as the slope of the straight line obtained in a plot of a_{Na} against c above c_0 . There is no need to use a correct c_0 , nor a correct f_0 . α' may also be calculated from a combination of the slope and the intercept at $c = c_0$.

Experimental. Materials. The sodium dodecyl sulphate (SDS) was prepared by recrystallizing Merck *p.a.* SDS twice from a hot benzene-ethanol mixture. A plot of the surface tension of this substance as a function of $\log c$ (drop-weight method) showed no minimum below the c.m.c. Subsequent foam fractionation of the SDS caused the absolute value of the surface tension to rise significantly (~ 2 dyn/cm at $c = 0.004$ mol/kg). This could be due to the removal of a trace contamination (dodecanol?).

The water was distilled and passed through an ion exchange resin shortly before measurements. The sodium chloride was Merck *suprapur* quality.

Apparatus. The sodium-responsive glass electrode was an E.I.L. type GEA 33B electrode. The calomel electrode was a Radiometer type K 401 with a porous pin as liquid junction. The silver-silver chloride electrode was prepared by a procedure slightly modified from that of Brown.³ The emf of the cell was partly compensated on a Beckman Research pH-meter, the remaining few millivolts being recorded as a function of time on a Metrohm Labograph E 478 plotter. In this way, all emf values could be extrapolated to zero time after establishing the liquid junction between the

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electrodes. This is necessary because there is a slow precipitation at the junction after it has been formed.

All experiments were carried out in a water bath at $25 \pm 0.05^\circ\text{C}$.

The liquid junction. To check the influence of precipitation at the liquid junction measurements were performed (a) with a four-way stopcock assembly in the bridge, which permitted a fresh junction to be formed immediately before starting to record the emf values, (b) by recording the emf as a function of the time after plunging the calomel electrode with its porous pin into the solution. The calomel electrode was stored in saturated KCl solution between emf readings; prior to immersion, it was carefully washed and lightly wiped with a tissue paper. The electrode was kept in the solution for about 20 sec only. The reproducibility was found to be better with the latter method, and this was used in all subsequent measurements with the calomel electrode. The reproducibility was ± 0.5 mV. No corrections for pH were made (neutral solution).

Any change in the porous pin due to precipitation in the SDS solution was checked by measuring the emf of the calomel electrode against an Ag/AgCl electrode in KCl solution saturated with AgCl. The calomel electrode always returned to its original emf value within 10 min after a prolonged storage in a SDS solution.

Contamination by potassium ions. Potassium ions may influence the measurements not only because the glass electrode is sensitive to them, but also because they are adsorbed at the micellar surface. In order to check whether KCl from the porous pin did diffuse into the solution, 0.001 mol/kg NaCl was added to a number of SDS solutions which were saturated with AgCl. The emf between an Ag/AgCl electrode in these solutions and the calomel electrode was then recorded in a way which was exactly similar to that used in the a_{Na} measurements. The change in Cl^- concentration was never more than 2×10^{-5} mol/kg, and thus seems to be insignificant.

Cell without transference. The NaCl/SDS solutions were also used to measure a_{Na} with an Ag/AgCl electrode in the SDS solution as reference electrode. From this cell, a_{Na} can be estimated if the Debye-Hückel theory is used to estimate a_{Cl} . The error of such a calculation in this concentration range is probably less than 3 %.

Reference solution. To convert emf values to sodium ion activities the electrode system was calibrated in a 0.05 mol/kg NaCl solution with known mean activity.⁴ The sodium ion activity

was calculated assuming that $a_{\text{Na}} + a_{\text{Cl}} = a_{\text{NaCl}}$ (the mean activity of NaCl) in the reference solution, and that the diffusion potential is the same in the reference and sample solutions. All emf readings for the reference solution were performed in the same way as those in the SDS solutions. The performance of the electrode system was checked by measuring the change in the emf with a_{NaCl} in the reference solution. This yielded values which were within 0.5 % of those predicted by the Nernst equation.

Results. The sodium ion activity in SDS solutions were measured by changing the SDS solution after each measurement as well as by changing the SDS concentration by titration, with a maximum of 10 steps in a series. Both methods yielded the same results.

The measured sodium ion activities as a function of the SDS concentration are plotted in Fig. 1. The break in the curve is sharp enough to define the c.m.c. as $(8.1 \pm 0.1) \times 10^{-3}$ mol/kg. Below the c.m.c. there is a significant decrease in activity as compared to NaCl. The activity coefficient for SDS at the c.m.c. is about 0.75 which is 15 % below the value for NaCl at the same concentration. Shedlovsky *et al.*² found $f_0 = 0.81$ at c.m.c. = 0.00755 mol/kg and Botré *et al.*¹ $f_0 = 0.76$ at c.m.c. = 0.00800 mol/kg.

a_{Na} , however, is the same at the break point of the curve in all investigations. The difference in f_0 is probably due to the use of different values for c_0 .

Measurements with the cell without transference (also plotted in Fig. 1) show that the anomalously low sodium ion activity cannot be due to diffusion potentials; the two different methods give results that coincide remarkably well at least up to the c.m.c. Above the c.m.c., the Ag/AgCl electrode cannot be used as a reference because the solubility of AgCl increases. This is seen from the fact that the emf reaches equilibrium much slower at SDS concentrations higher than 0.007–0.008 mol/kg.

The possibility that the activity decrease might be due to a change in the glass electrode potential caused by the adsorption of dodecanol was also examined. Intense foam fractionation (the SDS concentration was determined after the fractionation) did not change the activities.

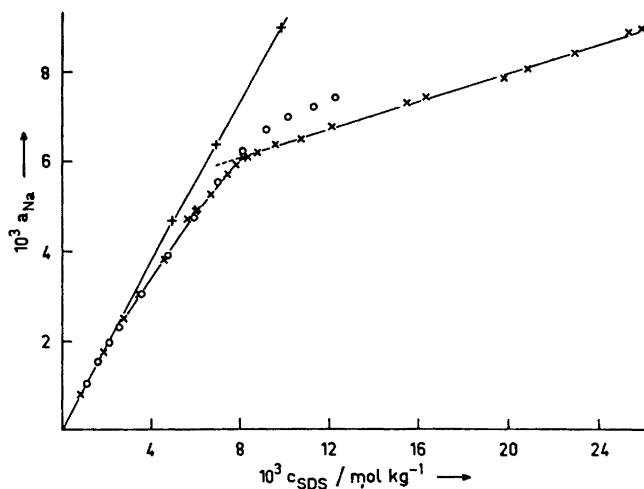


Fig. 1.

The slope of the curve above the c.m.c. and a combination of slope and intercept both yield the same value for α' : 0.151 ± 0.002 . Using the Botré method, α'' becomes 0.202. Shedlovsky *et al.*² found $\alpha'' = 0.22$ and Botré *et al.*⁴ 0.16. In solutions with added NaCl, Feinstein and Rosano⁵ found the value 0.16 for α'' . In their experiments, however, the NaCl/SDS ratio was kept constant, and so there is probably a significant decrease in α'' since the c.m.c. changes with the NaCl concentration.

Okubo *et al.*⁶ found that the single ion activity coefficient of counter ions in aqueous sodium polyacrylate solutions was 0.3, almost independently of polymer concentration over a wide concentration range. If it is assumed that in the present case the micelle can be compared to this macro molecule, *i.e.* $f_2 = 0.3$, the value 0.5 is obtained for α , which is probably closer to the real degree of dissociation than the low values for α'' .

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