The pH Change with Concentration of Aqueous Solutions of Metal Dodecyl Sulfates

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Lawrence and McDonald[1] reported that the critical micelle concentration (CMC) of aqueous solutions of sodium dodecyl sulfate (SDS) could be determined by pH measurements, showing that the pH vs. concentration curve of SDS solution has a kink point at the CMC. We have made experiments on the concentration dependence of the pH of aqueous solutions of some metal dodecyl sulfates and obtained a result different from theirs for SDS. For some metal dodecyl sulfates, however, for example copper and nickel salts, we have found that the kink point appears in the pH vs. concentration curve at the CMC of each dodecyl sulfate solution.

SDS used in the present experiment was prepared from fractionally distilled pure dodecyl alcohol. It was recrystallized several times from butanol solution and washed with ether for 60 hr. Finally the sample was recrystallized from aqueous solution. Copper dodecyl sulfate tetrahydrate (CuDS) and nickel dodecyl sulfate hexahydrate (NiDS) were prepared from SDS by the method of Lottermoser and Püschel[2]. They were recrystallized several times from aqueous solution. The purity of these samples were confirmed by elementary analysis and surface tension measurements. The pH measurements were performed with a glass electrode pH meter at 25°C. Special precautions were not taken for eliminating carbon dioxide from the solution investigated in order to compare the result with that of Lawrence and McDonald. We suppose, in any way, that the effect of carbon dioxide is not so serious for the solution of anionic detergents as for cationic ones.

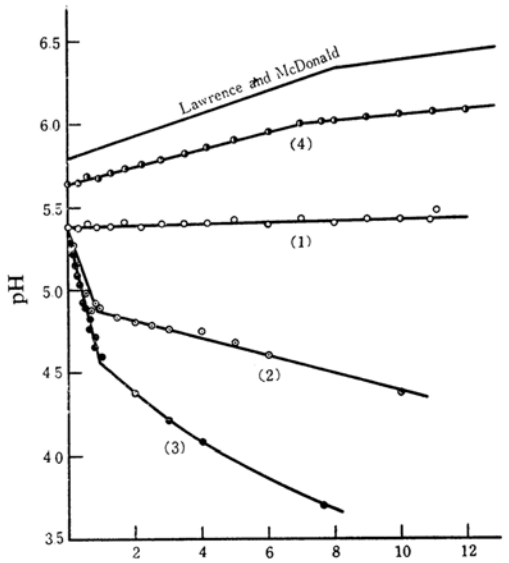

Fig. 1. The pH vs. concentration curves for aqueous solutions of metal dodecyl sulfates.
(1) SDS, (2) CuDS, (3) NiDS, (4) SDS+NaOH ($1:1\times10^{-4}$)

The result is shown in Fig. 1. It is evident that the pH vs. concentration curve for SDS (curve 1) shows no kink point at the CMC ($6\sim8\times10^{-3}$ mol./l.), while the curve for CuDS (curve 2) and for NiDS (curve 3) shows a clear kink at the CMC (both 1×10^{-3} mol./l.[3]). The Lawrence and McDonald's curve for SDS is shown in Fig. 1 for comparison with ours. The difference is remarkable. We do not completely understand the origin of this difference at the present stage, but one reason is supposed to exist in the purity of the sample. We investigated the effect of alkali added to the SDS solution on the pH vs. concentration curve and found that small amounts of alkali

1) A. S. C. Lawrence and M. P. McDonald, Abstract of the 2nd International Congress of Surface Activity, I, 385 (1957).

2) A. Lottermoser and F. Püschel, *Kolloid-Z.*, **63**, 175 (1933).

3) S. Miyamoto, This Bulletin, **33**, 375 (1960); I. Satake and R. Matuura, to be published.

caused an appearance of a kink at the CMC of the SDS solution. The curve 4 in Fig. 1 represents this effect. In this case the mole ratio of SDS to sodium hydroxide in the solution was 1 to 1×10^{-4}. It may be inferred that SDS used by Lawrence and McDonald contained alkali as an impurity.

The kink at the CMC of CuDS and NiDS solutions comes undoubtedly from hydrolysis of these detergents. The details of the discussion will be reported in connection with the surface activity of metal dodecyl sulfates in a near future.

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