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The Effect of Urea on the First and Second CMC's of Aqueous Solutions of Sodium and Lithium Dodecyl Sulfates

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Synopsis. The effect of urea on the 1st and 2nd CMC's of aqueous solutions of sodium and lithium dodecyl sulfates was investigated by the measuments of electric conductivity. The results were discussed in terms of the breaking effect of urea on the water structure not only around the hydrocarbon chains, but also around the counter ions of these surfactants.

In our previous papers, the micelle structure in the aqueous solutions of sodium dodecyl sulfate (NaDS) was investigated mainly in the concentration region above the 1st critical micelle concentration (CMC) through systematic studies including measurements of the electric conductivity,[1] density, viscosity,[2] light-scattering,[3] and depolarization of fluorescence.[4] It was revealed by these studies that there exists a 2nd CMC, where a change in the micelle structure takes place. Furthermore, in order to investigate the effect of the counter ions on the 2nd CMC, conductivity measurements were carried out in solutions of potassium (KDS) and lithium (LiDS) dodecyl sulfates in addition to NaDS.[5] It was revealed that, at the 2nd CMC, there occurs an increased counter-ion binding with the micelle.

It is well known that urea disrupts the water structure.[6] Several workers have used dissolved urea as a probe for investigating the contribution of structural changes in water to micelle formation.[7-9] In this study, conductivity measurements were carried out over a wide concentration range of NaDS and LiDS solutions in the presence of urea. The results were discussed by taking into account the effect of urea on the water structure, not only around the hydrocarbon chains, but also around the counter ions of these surfactants.

Experimental

The NaDS and LiDS used in this study were the same as those described in our previous paper.[5] Urea obtained from the Wako Pure Chemical Co. was recrystallized from 65 vol% aqueous etanol below 40°C.[10] The conductivity was measured in the manner described in a previous work.[1]

Results and Discussion

The results of the conductivity measurements in the neighborhood of the 1st CMC are shown in Fig. 1, where the specific conductivity (κ) is plotted againt the concentration of NaDS solutions containing various amounts of urea. The 1st CMC of a NaDS solution rises with an increase in the concentration of urea, as has been observed by other workers.[7-9] In recent investigations, the micelle formation has been discussed in terms of a change in the water structure according to Frank and Evan's theory;[11] the formation of the so-called iceberg structure around the hydrocarbon chains of surfactant molecules brings about a loss of entropy at their dissolution. The increase in CMC values in the presence of urea may be ascribed to a drop in the standard chemical potential of the surfactant in the monomeric state due to the breaking effect of urea on the iceberg structure, without any corresponding large change in the micellar state.

The ratio of the CMC in the presence of urea to the CMC in the absence of urea, CMC/CMC(0), is plotted against the concentration of urea in Fig. 2, where the results for the NaDS solution are compared with those for the LiDS solution. These results agree fairly well with those obtained by Schick,[9] who gives no explanation for the difference in CMC/CMC(0) between the NaDS solution and the LiDS solution. The effect of urea on the two hydrated counter ions, Li^+ and Na^+, needs to be discussed.

Bower and Robinson[12] revealed, by means of the isopiestic vapor pressure method, that the activity coefficient of NaCl is decreased by the addition of urea. The Na^+ ion is a structure-former, as is well known, and has a structural-orienting influence on neighboring water molecules.[11,13] The decrease in the activity coefficient of NaCl by urea may result from an increased electrostatic interaction between Na^+ and Cl^- due to a diminished hydration of Na^+. That is, urea disrupts the water structure in the vicinity of Na^+. This effect of urea may facilitate the adsorption of Na^+ as a counter ion on the micelle surface. The results shown in Fig. 2 may include the effect of urea on the counter ion, which lowers the 1st CMC, in addition to that on the hydrocarbon chain, which raises the 1st CMC. The Li^+ ion, which is more strongly hydrated in the absence of urea (than Na^+), may be more effective on the lowering of the 1st CMC in the presence of urea than Na^+. Thus, the increment in CMC/CMC(0) for LiDS solutions is less than that for NaDS solutions, as is shown in Fig. 2.

The conductivity measurements over a wide concentration range of NaDS solutions are shown in Fig. 3, where the results in the presence of urea are compared with those in the absence of urea. There occurs a break point corresponding to the 2nd CMC, in addition to that at the 1st CMC, as revealed by the conductivity measurements in our previous papers.[1,5] Moreover, the specific conductivity *vs.* concentration curve bends toward the concentration axis at the 2nd CMC in the presence of urea, while it breaks upward in the absence of urea, as was also observed in our previous work.[1,5] The conductivity behavior of the NaDS solutions at the 2nd CMC can be made clear in Fig. 4(a), which shows the deviation of the specific conductivity from the extrapolation of the linear plot of the specific conduc-

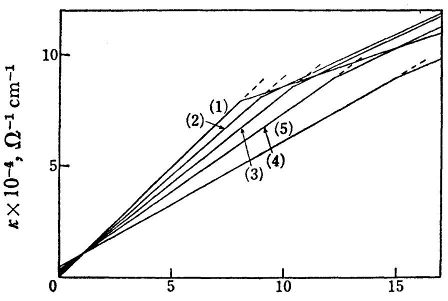

Fig. 1. Specific conductivities of NaDS solutions in the presence of urea in the neighborhood of the 1st CMC; concentration of urea: (1) 0 M, (2) 2 M, (3) 4 M, (4) 6 M, (5) 8 M.

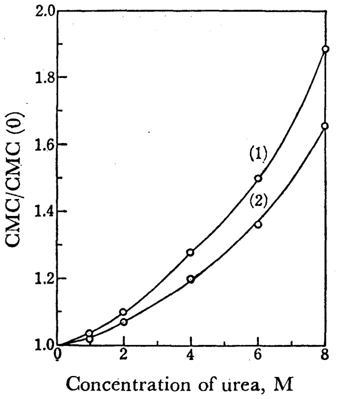

Fig. 2. CMC/CMC (0) of surfactant solutions; (1) NaDS, (2) LiDS.

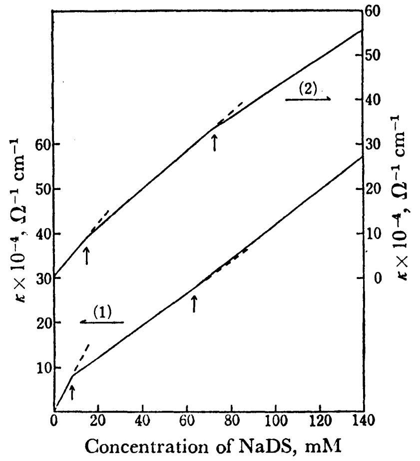

Fig. 3. Specific conductivities of NaDS solutions; (1) no additive, (2) 8 M urea. The arrows in the figure indicate the 1st and 2nd CMC's.

tivity *vs.* concentration below the 2nd CMC in Fig. 3 to a higher concentration, $\Delta\kappa$; $\Delta\kappa$ is negative, at least in the concentration range of urea studied. Furthermore, $\Delta\kappa$ increases and, at the same time, the 2nd CMC as well as the 1st CMC rises, with an increase in the concentration of urea. The effect of urea on the conductivity behavior above the 2nd CMC of LiDS solutions is similar to that in NaDS solutions, as is shown in Fig. 4(b).

It was suggested in our previous studies$^{1-5)}$ that a change in the micelle structure at the 2nd CMC leads to an increase in the counter-ion binding with the micelle to compensate for the increment in the electrostatic energy resulting from the closer aggregation of hydrophilic parts of the amphipathic ions, of which the micelle is composed, above the 2nd CMC than below the 2nd CMC. As has been mentioned above, the disruption of the water structure by urea brings about a diminished hydration of the alkali metal counter ions of dodecyl sulfate. Under these circumstances, some counter ions in the bulk may be adsorbed additionally on the micelle surface at the 2nd CMC. As can be seen in Figs. 4 (a) and 4 (b), the lowering of the slopes of the straight lines above the 2nd CMC may be ascribed at least partly to a decrease in the counter-ion concentration in the bulk. Furthermore, the increase in the 2nd CMC with the concentration of urea (see Figs. 4 (a) and 4 (b)) may be caused primarily by the change in the standard chemical potentials of the surfactant in the monomeric state, as well as in the micellar state between 1st and 2nd CMC, relative to the corresponding change in the micellar state above the 2nd CMC.

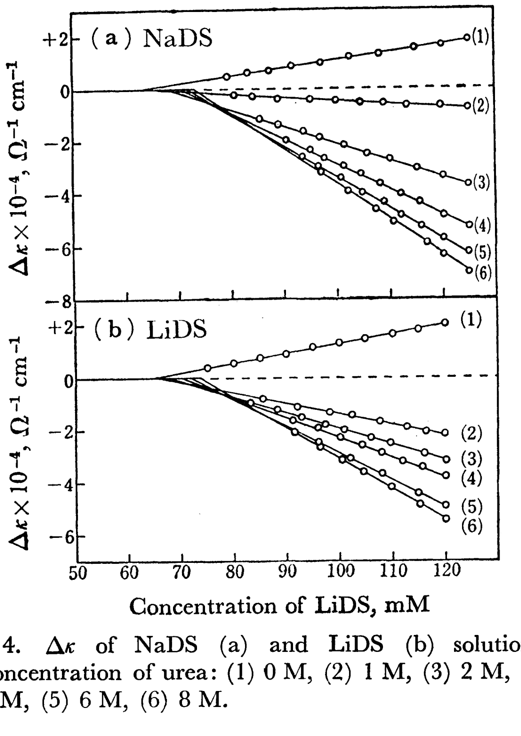

Fig. 4. $\Delta\kappa$ of NaDS (a) and LiDS (b) solutions; concentration of urea: (1) 0 M, (2) 1 M, (3) 2 M, (4) 4 M, (5) 6 M, (6) 8 M.

References

1) M. Miura and M. Kodama, *Bull. Chem. Soc. Jpn.*, **45**, 428 (1972).

2) M. Kodama and M. Miura, *Bull. Chem. Soc. Jpn.*, **45**, 2265 (1972).

3) M. Kodama, U. Kubota, and M. Miura, *Bull. Chem. Soc. Jpn.*, **45**, 2953 (1972).

4) Y. Kubota, M. Kodama, and M. Miura, *Bull. Chem. Soc. Jpn.*, **46**, 100 (1973).

5) M. Kodama, *J. Sci. Hiroshima Univ.*, Ser. A, **37**, 53 (1973).

6) J. A. Rupley, *J. Phys. Chem.*, **68**, 2002 (1964).

7) P. Mukerjee and A. Ray, *J. Phys. Chem.*, **67**,190 (1963).

8) W. Bruning and A. Holtzer, *J. Am. Chem. Soc.*, **83**, 4865 (1961).

9) M. J. Schick, *J. Phys. Chem.*, **68**, 3585 (1964).

10) M. Miura and A. Murakami, *J. Sci. Hiroshima Univ., Ser. A*, **18**, 403 (1955).

11) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

12) V. E. Bower and R. A. Robinson, *J. Phys. Chem.*, **67**, 1524 (1963).

13) H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).