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The Surface Activity of *N*,*N*′-Polymethylenebis(trialkylammonium) Dibromides in Aqueous Solutions

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Synopsis. The surface tensions are reported for aqueous solutions of four series of homologous *N*,*N*′-polymethylenebis(trialkylammonium) dibromides $[(C_mH_{2m+1})_3N(CH_2)_nN(C_mH_{2m+1})_3]Br_2$ (m=1—4) at 25 °C. The experimental results are discussed with emphasis on the behavior of these salts in water. It is generally recognized that the structure-breaking solutes are surface inactive in aqueous solutions, whereas hydrophobic structure-making solutes are surface active in aqueous solutions. The critical micelle concentration for $[(C_4H_9)_3N(CH_2)_{12}N(C_4H_9)_3]Br_2$ is estimated to be 0.07 mol dm^{-3}.

The surface active properties of aqueous solutions of tetraalkylammonium salts have been studied with particular reference to the bulk properties of these salts in water.[1,2] This paper is concerned with the surface activity of four homologous series of amphiphilic electrolytes: *N*,*N*′-Polymethylenebis(trimethylammonium) dibromides (to be abbreviated as MeC_nMe), *N*,*N*′-polymethylenebis(triethylammonium) dibromides (to be abbreviated as EtC_nEt), *N*,*N*′-polymethylenebis(tripropylammonium) dibromides (to be abbreviated as PrC_nPr), and *N*,*N*′-polymethylenebis(tributylammonium) dibromides (to be abbreviated as BuC_nBu). Solution properties for some of these salts in water, such as the temperature dependence of the viscosity *B* coefficients[3,4] or the temperature dependence of the heats of solution,[5,6] have also been reported in previous papers.

Experimental

EtC_2Et is prepared by the reaction of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine with ethyl bromide in ethanol. The other samples were prepared by refluxing the α,ω-dibromoalkanes with an excess of the respective trialkylamines in ethanol or acetonitrile.[7,8] $PrC_{12}Pr$, BuC_8Bu, $BuC_{10}Bu$, and $BuC_{12}Bu$ were fairly difficult to obtain as solid samples; they were precipitated from each reaction mixture by means of the repeated extraction of the unreacted or impure materials with dry ethyl acetate or butyl acetate at −20 °C. All the samples were dried in vacuo at room temperature for several days and then analyzed for bromide ion by means of argentometric titration. The salts were found to have a purity greater than 99.5%. Water was triply distilled.

Surface tension measurements were made by the drop-volume method using a micrometer syringe. Densities were measured using a vibrating-tube densitometer (twin-type SS-D-200 of the Shibayama Scientific Co., Ltd.). The electric conductivities were measured with an LCR meter (AG-4301B, of the Ando Electric Co., Ltd.) at a frequency of 1000 Hz.

Results and Discussion.

The Surface Tension versus Concentration Curves. The surface tensions (γ) versus concentration (c) curves for MeC_nMe, EtC_nEt, PrC_nPr, and BuC_nBu are shown in Figs. 1, 2, 3, and 4. Menger and Wrenn[9] reported the surface active properties of aqueous solutions for MeC_4Me, MeC_8Me, $MeC_{12}Me$, BuC_4Bu, BuC_8Bu, and $BuC_{12}Bu$. In general, the surface activity obtained in this study on these salts are found to be less surface active than that reported by Menger and Wrenn.[9] The reason is connected to the samples used. In this work, the samples were carefully purified by recrystallization from suitable solvents.

Figure 1 indicates that MeC_3Me, MeC_4Me, MeC_5Me, and MeC_6Me raise the surface tension of pure water. The MeC_nMe salts with n>7 reduce the surface tension of water and the extent of surface activity increases with

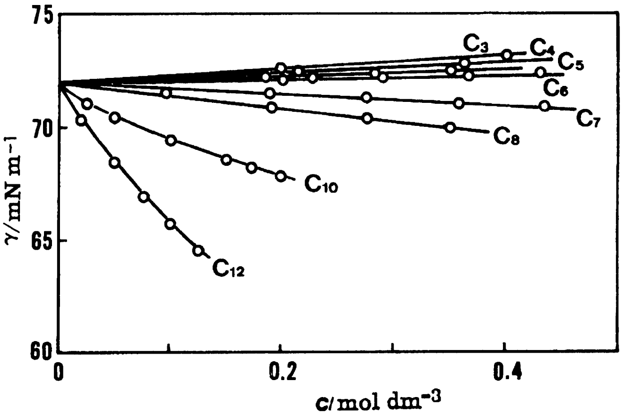

Fig. 1. Plots of γ against c for MeC_nMe.

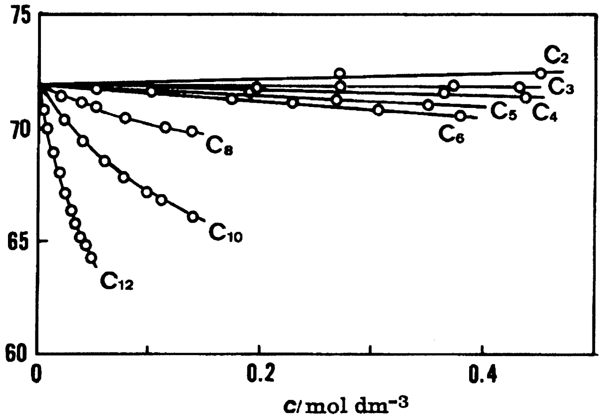

Fig. 2. Plots of γ against c for EtC_nEt.

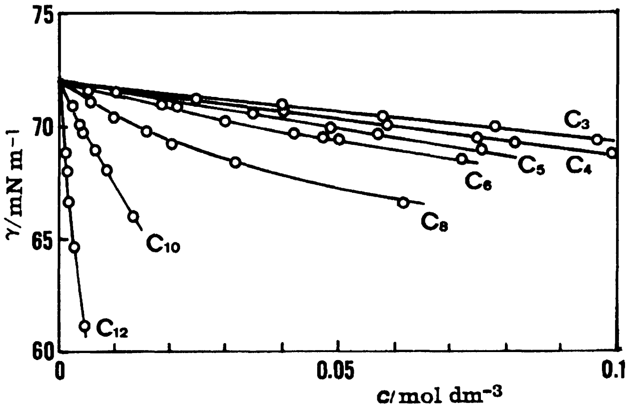

Fig. 3. Plots of γ against c for PrC$_n$Pr.

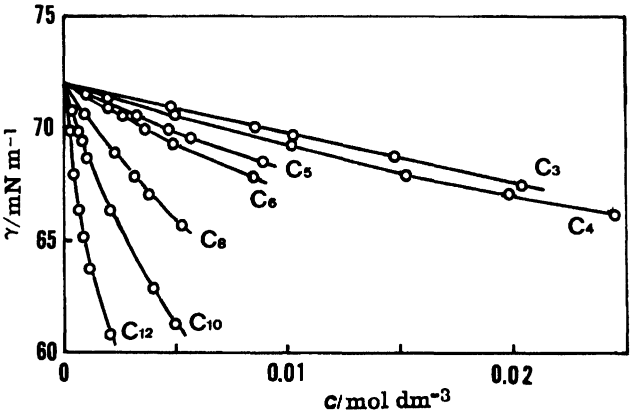

Fig. 4. Plots of γ against c for BuC$_n$Bu.

the number of n.

The behavior of amphiphilic organic ions in water may be generally discussed in terms of the balance of hydrophobic hydration due to nonpolar groups and ionic hydration due to ionic groups. The phenomenon that the dissolved substance raises the surface tension of pure water has been observed with a variety of common salts, whose behavior in water is governed by ionic hydration. On the other hand, the amphiphilic organic solutes, which act as hydrophobic structure-makers in water, show the effect of reducing the surface tension of pure water. In a previous paper,[2] one of us showed that tetramethylammonium bromide, which acts as a structure-breaker, raised the surface tension of water; whereas tetraethyl-, tetrapropyl-, tetrabutyl-, and tetrapentylammonium bromides, which act as structure-makers, exhibited surface active properties in water.

With MeC$_n$Me salts, the temperature dependence of the viscosity B coefficients ($\mathrm{d}B/\mathrm{d}t$),[3] and the change in the heat capacity for dissolution in water (ΔC_p)[5] were reported in previous papers. MeC$_3$Me, MeC$_4$Me, and MeC$_5$Me were classified as hydrophobic structure-breakers. MeC$_6$Me was a borderline salt. MeC$_7$Me and the higher homologs were classified as hydrophobic structure-makers. The classification of the behavior of a salt is somewhat dependent on the experimental method adopted.[3] The results on the surface tensions shown in Fig. 1 corresponds roughly with the general tendency of the befavior of the salts in water. With MeC$_3$Me, MeC$_4$Me, MeC$_5$Me, and MeC$_6$Me salts, the interaction of the ionic parts with water will surpass the hydrophobic interaction due to the polymethylene groups. In the case of MeC$_7$Me and the higher homologs, conversely the interaction of polymethylene groups with water surpass the ionic hydration due to the ionic parts; consequently, the transfer of these salts from the bulk phase to the surface phase is a spontaneous process. Thus, they are surface active in aqueous solutions.

Figure 2 indicates that EtC$_2$Et raises the surface tension of water, whereas EtC$_3$Et slightly reduces the surface tension of water at concentrations above 0.3 mol dm^{-3}. The EtC$_n$Et salts with $n>4$ exhibit surface active property. From the measurement of $\mathrm{d}B/\mathrm{d}t$[4] as well as ΔC_p[6,8] for the EtC$_n$Et salts, it was found that these salts with $n>3$ are all hydrophobic structure-makers; the results of the surface active properties for the EtC$_n$Et salts in this study reasonably correspond to their solution behavior.

As shown in Fig. 3, the PrC$_n$Pr salts with $n>3$ are all surface active; the results are related to the fact that the PrC$_n$Pr salts are classified as hydrophobic structure-makers in water from the measurements of $\mathrm{d}B/\mathrm{d}t$.[4]

The surface activity of the BuC$_n$Bu salts studied is fairly strong; especially, BuC$_8$Bu, BuC$_{10}$Bu, and BuC$_{12}$Bu are highly surface active as shown in Fig. 4. These facts also closely correspond to the conclusion from the measurements of $\mathrm{d}B/\mathrm{d}t$[4] that the BuC$_n$Bu salts are highly hydrophobic structure-makers in water.

In the case of the monovalent amphiphilic electrolytes, the surface active properties are generally determined by the balance between ionic hydration and hydrophobic hydration in water. In view of the above results, it was found that the surface active properties for the bolaform electrolytes such as *N,N′*-polymethyl-

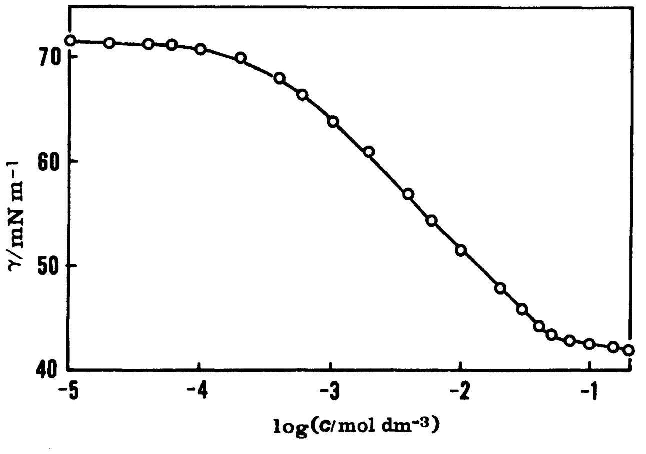

Fig. 5. Plots of γ against $\log c$ for BuC$_{12}$Bu.

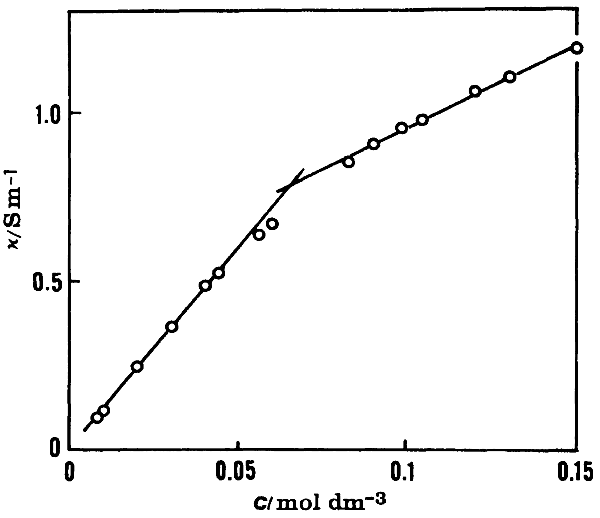

Fig. 6. Electrical conductivity–concentration curve for $BuC_{12}Bu$.

enebis(trialkylammonium) dibromides in water are generally governed by the structural changes in the solvent water upon the dissolution of these amphiphilic electrolytes, although the bolaform electrolytes are expected to be difficult to orientate at the surface.

$BuC_{12}Bu$. $BuC_{12}Bu$ exhibits the most strong surface activity studied in this work. Then the measurements were extended at concentrations up to about 0.2 mol dm^{-3}. The γ–log c curve is shown in Fig. 5. With this salt, Menger and Wrenn[9)] reported the highly surface active values and 0.002—0.004 mol dm^{-3} as the critical micelle concentration. However, in this study the surface activity is not so strong as the results reported by Menger and Wrenn;[9)] there is no such distinct break γ–log c curve as often appears for typical surfactants in the concentration range below 0.01 mol dm^{-3}. The reason probably results from the sample used. In this work, the sample was carefully purified and a white solid (melting point: 85 °C) was obtained. On the other hand, Menger and Wrenn[9)] used the sample as a viscous pale yellow oil. Figure 5 indicates that the surface tensions gradually lower, then the values change slowly at about 0.07 mol dm^{-3}. Perhaps, this concentration is the critical micelle concentration of $BuC_{12}Bu$. For confirmation, the electrical conductivities (κ) of aqueous solutions of $BuC_{12}Bu$ were also measured at 25 °C. The electrical conductivity versus concentration curve is shown in Fig. 6; the critical micelle concentration is estimated to be 0.067 mol dm^{-3} by two limiting linear regions. Yiv and Zana[10)] also measured the electric conductivities for aqueous $BuC_{12}Bu$ solutions up to the concentration of 0.05 mol dm^{-3}. They reported that $BuC_{12}Bu$ did not form micelles up to the concentration of 0.05 mol dm^{-3}.

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