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The Surface Activity of Tetrabutylammonium Halides in the Aqueous Solutions

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The surface activity of the tetrabutylammonium halides at the air/aqueous solution interface or at the hexane/aqueous solution interface has been studied. The surface or interfacial tension *versus* the concentration curves of the electrolytes are markedly dependent on the kind of their counter-ions, just as with these electrolytes in aqueous solutions. The surface activity of tetrabutylammonium iodide is fairly strong; it approximately corresponds to that of the surface-active straight-chain electrolyte with an octyl group. From the thermodynamic parameters of the adsorption of tetrabutylammonium iodide, it is found that the standard free energy of adsorption becomes negative as a result of the large positive values of the standard entropy of adsorption, irrespective of the positive values of the standard enthalpy change. This suggests that the adsorption is a "hydrophobic" effect; that is, the "icebergs" around the nonpolar groups of the electrolyte return to the original water by the process of the transfer of the hydrophobic ions from the aqueous solution to the surface phase.

Frank and Evans(1) proposed, concerning the decrease in entropy in the process of dissolving a hydrocarbon in water, the idea that the water molecules form frozen patches or microscopic "icebergs" around nonpolar molecules of the hydrocarbon. Many peculiar properties shown by the aqueous solutions of the tetraalkylammonium salts have also been interpreted in terms of the "icebergs" formation around the alkyl groups of the cations. More recent studies of the effect of the water structure on the behavior of the tetraalkylammonium salts in aqueous solutions have been carried out by Diamond,(2) Lindenbaum and Boyd,(3) and Wen and Saito.(4) The object of this paper is to consider the relation of the surface-active properties to the bulk properties of the tetrabutylammonium salts.

Experimental

The tetrabutylammonium halides used in this work were obtained from the Tokyo Kasei Kogyo Co., and were recrystallized from suitable solvents, *i. e.*, an ethanol-ether mixture for chloride salt, ethyl acetate for bromide salt, and an ethanol - ethyl acetate mixture for iodide salt. The partially-substituted butylammonium salts were prepared by the reaction of the amine with dry hydrogen chloride gas in benzene, as has been described elsewhere.(5) Hexane was shaken with concentrated sulfuric acid, thoroughly washed with water, dried over calcium chloride, and then distilled. It was further purified by passage through an alumina column. Water was obtained by redistillation from an alkaline permanganate solution.

Surface and interfacial tensions measurements were made by the drop-volume method using a micrometer syringe. The drop was formed rapidly to a size about 3/4 of its final volume, and suspended for 2 min; the rest was then formed slowly until the drop broke away. It was found to exhibit no slow surface-ageing phenomenon. Density measurements were made by an Ostwald pycnometer with a 5 m*l* capacity. Surface and interfacial tensions were calculated on the basis of the correction method of Harkins and Brown.(6) The apparatus was calibrated with solutions of butyric acid of known surface tensions.

Results and Discussion

The Surface Activity of Aqueous Solutions of Partially-substituted Butyl and Tetrabutylammonium Chlorides. To elucidate the effect of the number of the substituted butyl groups, the surface activity of butyl-, dibutyl-, tributyl- and tetrabutylammonium chlorides at the air/aqueous solution and at the hexane/aqueous solution interface were measured; the results for the former case are illustrated in Fig. 1 as an example. It may be noticed from this figure that the surface activities for tributyl- and tetrabutylammonium salts are of similar values, even though the surface activity of the alkyl-substituted ammonium salts is expected to increase generally with the number of substituted alkyl groups. In aqueous solutions tetrabutylammonium salt was expected to behave

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

2) R. M. Diamond, *J. Phys. Chem.*, **67**, 2513 (1963).

3) S. Lindenbaum and G. E. Boyd, *ibid.*, **68**, 911 (1964).

4) W. Y. Wen and S. Saito, *ibid.*, **68**, 2639 (1964).

5) K. Tamaki, *Kolloid-Z.*, **170**, 113 (1960).

6) W. D. Harkins and F. E. Brown, *J. Am. Chem. Soc.*, **41**, 499 (1919).

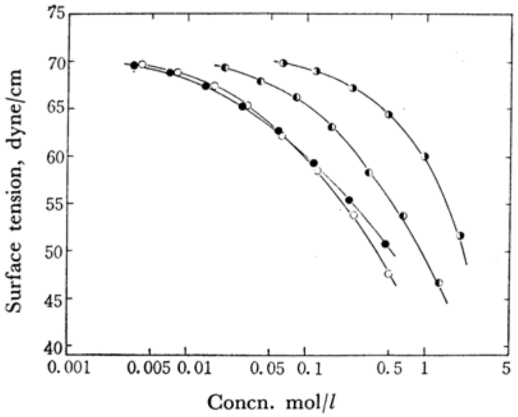

Fig. 1. Surface tension *vs.* concentration curves at 30°C.
◑, butyl-; ◐, dibutyl-; ○, tributyl-; ●, tetrabutylammonium chloride

in a more hydrophobic manner than tributylammonium salt; however, one more butyl group in the former salt does not actually serve to drive the molecule from the aqueous phase to the interface, probably because at the interface it is difficult for all the butyl groups of tetrabutylammonium salt to extricate themselves completely from the aqueous phase because of the symmetrical structure of the molecule. The results of the interfacial tension at the hexane/aqueous solution interface *versus* the concentration curves also show a marked resemblance with those at the air/aqueous solutions interface.

The Effect of Counter-ions. Figures 2 and 3 indicate the surface or interfacial tension *versus* the concentration curves for tetrabutylammonium chloride, tetrabutylammonium bromide and tetrabutylammonium iodide at the air/aqueous solution interface and at the hexane/aqueous solution interface respectively. It will be seen that the surface activity increases progressively in this order; iodide salt>bromide salt>chloride salt. In fact, the ability of iodide salt to lower the surface or interfacial tension approximately corresponds to that of the straight-chain electrolyte with an octyl group.

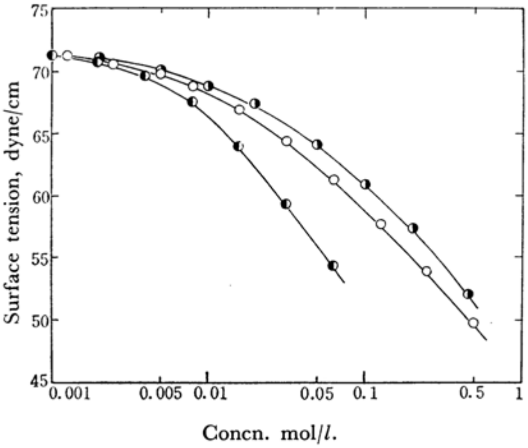

Fig. 2. Surface tension *vs.* concentration curves of tetrabutylammonium halides at 25°C.
◑ chloride salt; ○, bromide salt; ◐, iodide salt

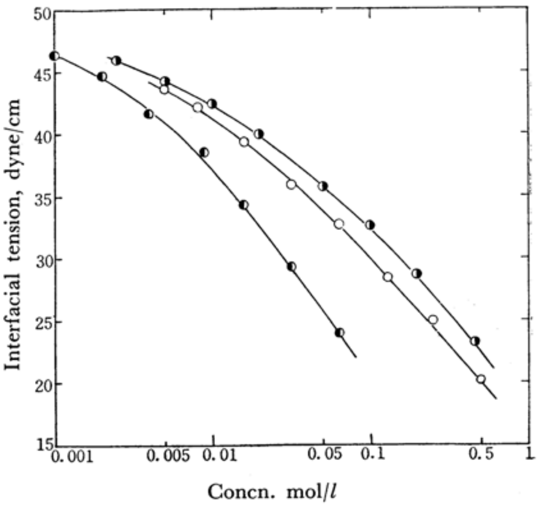

Fig. 3. Interfacial tension *vs.* concentration curves of tetrabutylammonium halides at 25°C.
◑, chloride salt; ○, bromide salt; ◐, iodide salt.

In order to explain this difference in the surface activity for tetrabutylammonium salts with different counter-ions, it is of importance to understand the effect of counter-ions on the behavior of these salts in the aqueous phase. Diamond[2] has proposed, with regard to the behavior of the tetra-alkylammonium salts in aqueous solutions, a "water structure-enforced ion-pairing" mechanism, which means that the strong cohesion of the water structure is compelled to form an association between the large, poorly-hydrated cations and anions in order to minimize the disturbance to itself. Diamond[2] has found that with the iodide salt the tendency toward ion-pairing was most pronounced, while with the chloride salt the formation of the ion-pairing was of least importance as a result of the most hydrated nature of the chloride ion; with the bromide salt the ion-pairing was intermediate.

It was also observed in this study, with regard to the tendency of the tetrabutylammonium halides to dissolve in water, that the chloride salt was very hygroscopic, while the iodide salt was least hygroscopic and it could not be dissolved above the concentration of 0.1 M at room temperature; the bromide salt exhibited an intermediate property.

The situation that the tetrabutylammonium ions show a tendency to be rejected from the aqueous phase as a result of the strong cohesive force between water-water bonding should have a reasonable relation with the adsorption of these large, hydrophobic cations at the interface in contact with their aqueous solutions. In general, however, if the alkyl groups in the molecules are the same, the electrolyte exhibits a weaker surface activity than the nonelectrolyte, because the electrical repulsive potential of the ionized surface containing the adsorbed surface-active ions tends to repel the further ions from the surface.7) However, this repulsive force should be reduced if more counter-ions are combined with the surface-active ions at the surface.

In view of the behavior of the tetraalkylammonium salts in the aqueous phase, the counter-ion binding at the interface may also be considered to increase in this order; iodide ion$>$bromide ion$>$ chloride ion. This increasing tendency for the tetrabutylammonium ion to be adsorbed at the ionized surface gives rise to a loweing of the surface or interfacial tension in this order; iodide salt$>$ bromide salt$>$chloride salt. It must be pointed out that, for the long-chain alkylammonium and alkylpyridinium halides, the same relation generally holds for the surface activity with their counter-ions; however, the surface activity of the tetraalkylammonium salts is markedly sensitive to variation in their counter-ions.

Lindenbaum and Boyd3) suggested that the tetrabutylammonium bromide aggregates to form micelles at higher concentrations; they reported the value of 0.039 M as the critical micelle concentration of the electrolyte as determined from the spectral change method by the addition of the 2, 6-dichloroindophenol dye to the aqueous solutions. However, on the basis of the surface or interfacial tension *versus* the concentration curves shown in Figs. 2 and 3, there is no such distinct break point as often appears in typical surface-active electrolytes.

The Thermodynamic Parameters of the Adsorption of Tetrabutylammonium Iodide. The thermodynamic parameters of the adsorption of a solute from its aqueous solution to the interface can be obtained from the experimental results of the surface pressure *versus* the concentration curves in lower surface pressure ranges. The standard free energy of adsorption of a solute from its solution to the interface, ΔF°, has been defined by two different conventions. The standard states of unit concentration, say 1 M, in both the bulk and the surface phase have been adopted in the literature.9-12) In using this convention one must choose an appropriate value as the thickness of the surface phase, so that the calculated value of the standard free energy of adsorption comes to be more or less ambiguous. Another standard state, recently adopted by Betts and Pethica,13) as well as by Spaull and Nearn,14) is referred to at 1 M for the bulk phase and at a surface pressure of 1 dyne/cm for the surface phase. In this paper, we adopted this latter convention.

The standard free energy of the adsorption, ΔF°, is written as;

$$\Delta F^\circ = -\boldsymbol{R}T\ln(\pi/C)_0 \tag{1}$$

where π is the surface pressure; C, the concentration, and $(\pi/C)_0 = \lim_{C\to 0}(\pi/C)$. When π does not vary linearly with C, $(\pi/C)_0$ can be obtained from the intercept of the (π/C) - C relation with the ordinate. The standard entropy of adsorption ΔS° may then be obtained from the relation;

$$\Delta S^\circ = -\partial\Delta F^\circ/\partial T \tag{2}$$

and the standard enthalpy of adsorption, ΔH°, may be calculated from the relation;

$$\Delta H^\circ = \Delta F^\circ + T\Delta S^\circ \tag{3}$$

Figures 4 and 5 show the results of the surface pressure *versus* the concentration curves of tetrabutylammonium iodide at 15, 25 and 35°C at the air/aqueous solution and at the hexane/aqueous

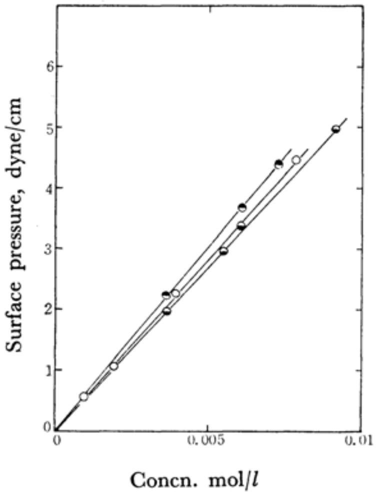

Fig. 4. Surface pressure *vs.* concentration curves of tetrabutylammonium iodide at the air/aqueous solution interface.
◒, 15°C; ○, 25°C; ◓, 35°C

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14) A. J. B. Spaull and M. R. Nearn, *J. Phys. Chem.*, **68**, 2043 (1964).

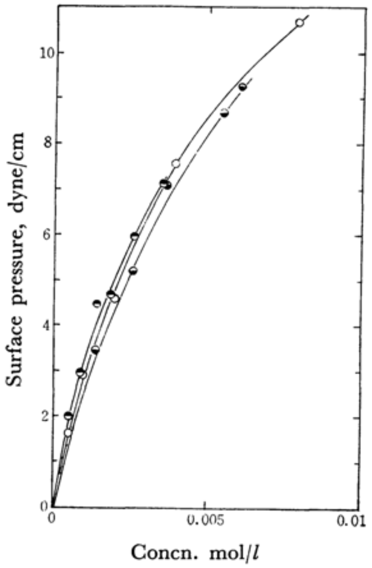

Fig. 5. Surface pressure *vs.* concentration curves of tetrabutylammonium iodide at the hexane/aqueous solution interface.
◒, 15°C; ○, 25°C; ◓, 35°C

TABLE 1. THERMODYNAMIC PARAMETERSAT 25°C

	ΔF° kcal/mol	ΔH° kcal/mol	ΔS° e. u.
Air/Aq. soln. interface	-3.75	$+1.01$	$+16.0$
Hexane/Aq. soln. interface	-4.85	$+1.83$	$+22.4$

tion interfaces respectively. The thermodynamic parameters calculated from these results are listed in Table 1. It is clear that the enthalpy change is positive and that, therefore, the large entropy increment contributes to the negative value of the free energy in both cases. Spaull and Nearn$^{14)}$ also obtained the conclusion that the adsorption of fatty alcohols from the water phase to the air/aqueous solution interface is essentially an entropy process.

In recent years, the entropy increment for the process pertaining to the transfer of nonpolar molecules such as hydrocarbons from the aqueous surroundings to a nonaqueous medium has been interpreted in two different ways. Kauzmann,$^{15)}$ as well as Némethy and Scheraga,$^{16)}$ concluded that the entropy increment caused by the change of the "icebergs" around the nonpolar molecules to the original water is the most characteristic feature in the process. They termed this process a "hydrophobic bond" or "hydrophobic interaction." However, another theory was proposed by Aranow and Witten.$^{17)}$ Their theory implies that at the surface there are three potential minima of the internal rotation about the carbon-carbon bonds, while in the solution the internal rotation is hindered completely; if the number of carbon-carbon bonds is n, the process of the transfer of the solute from the aqueous solution to the interface brings about an increase in the entropy of $n\boldsymbol{R}\ln 3$. However, Aranow and Witten's theory is not applicable to the case of the adsorption of the strong electrolytes, as has been discussed in my previous work.$^{7)}$

From the thermodynamic parameters obtained in this work, it seems best to interpret the adsorption process of large, nonpolar ions from the water phase to the interface in terms of the "hydrophobic interaction." The increase in entropy for the adsorption at the air/aqueous solution interface is higher than that at the hexane/aqueous solution interface; this is probably caused by the hindered movement of the molecules due to the cohesive force between alkyl groups in the former case.

It would be interesting to compare the thermodynamic parameters of adsorption for the bulky symmetrical electrolytes with those for the straight-chain electrolytes. Increments in ΔF° attributed to methyl and methylene groups as well as polar groups are often reported, but not the values of ΔH° and ΔS°. Therefore, for an explicit understanding of the thermodynamics of the adsorption of these surface-active electrolytes, it is imperative to obtain the values of ΔF°, ΔH°, and ΔS° for each constituent of such molecules.

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