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The Surface Activity of Tetra-*n*-alkylammonium Halides in Aqueous Solutions. The Effect of Hydrophobic Hydration

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Surface tensions are reported for aqueous solutions of a series of homologous tetra-*n*-alkylammonium chlorides, bromides, and iodides (R_4NX) at 25 °C, and the experimental results are discussed with particular reference to the bulk properties of these salts in water. It is found that Me_4NX salts are surface inactive in aqueous solutions and that they may be classified as simple salts. On the other hand, it is found that Et_4NX and higher homologous salts are surface active in aqueous solutions and that the surface activity increases with the number of carbon atoms in the alkyl chains; thus, they are hydrophobic structure-makers in the water phase. The surface tensions for aqueous solutions of Me_4NX salts are only slightly dependent on the kind of counter-ion, such as Cl^-, Br^-, and I^-. In the cases of Et_4NX, Pr_4NX, and Bu_4NX salts, the effectiveness of the anions for the same cation on the surface activity increases progressively in this order: $I^- > Br^- > Cl^-$.

The physical properties of aqueous solutions of tetra-*n*-alkylammonium salts have been studied by many investigators in terms of the structural changes in liquid water caused by the salts.$^{1-3)}$ In a previous paper,$^{4)}$ the surface active properties of tetra-*n*-butylammonium halides in aqueous solutions were discussed with emphasis on the solution behavior of these salts in water. This paper will be concerned with the surface activity of a homologous series of tetra-*n*-alkylammonium chlorides, bromides, and iodides (R_4NX) in aqueous solutions.

Experimental

Pr_4NCl was from Wako Pure Chemical Industries, Ltd., and Pen_4NBr was from Eastman Kodak Co. The other organic chemicals were from Tokyo Kasei Kogyo Co. All the salts were recrystallized from suitable solvents: methanol for Me_4NBr, distilled water for Me_4NI, ethanol for Et_4NI, ethyl acetate for Bu_4NBr and Pen_4NBr, ethanol–diethyl ether mixtures for Pr_4NCl and Bu_4NCl, and ethanol–ethyl acetate mixtures for the other salts. Water was triply distilled.

The surface tensions were measured at 25±0.1 °C by means of the drop-volume method described in a previous paper.$^{4)}$ Some of the data were checked by the Wilhelmy plate method using a surface tension apparatus, Model ST-1, of Shimadzu Seisakusho Ltd. No surface-ageing phenomenon was observed in this work. With R_4NI salts and Pen_4NBr, measurements were carried out to the solubility limit.

In this work, the solutions were made by weight, and the molar concentration, C, was deduced from the molal concentration, m, and the measured densities. The change in surface tension denoted by $\Delta\sigma$ is defined as; $\sigma_0 - \sigma$, where σ_0 and σ are the surface tension of pure water and solution respectively.

Results and Discussion

The Surface Tensions versus *Concentration Curves for R_4NBr.* Figure 1 shows the surface tensions of aqueous solutions of R_4NBr salts as a function of the molal concentration. It may be seen that Me_4NBr slightly raises the surface tension of pure water, whereas Et_4NBr and higher homologous salts reduce the surface tension of pure water, and that the surface activity increases progressively with the number of carbon atoms in the alkyl groups. These facts are reasonably compatible with the results$^{5)}$ on the surface tensions at 0 °C for the aqueous solutions of Me_4NCl, Et_4NCl, and Pr_4NCl.

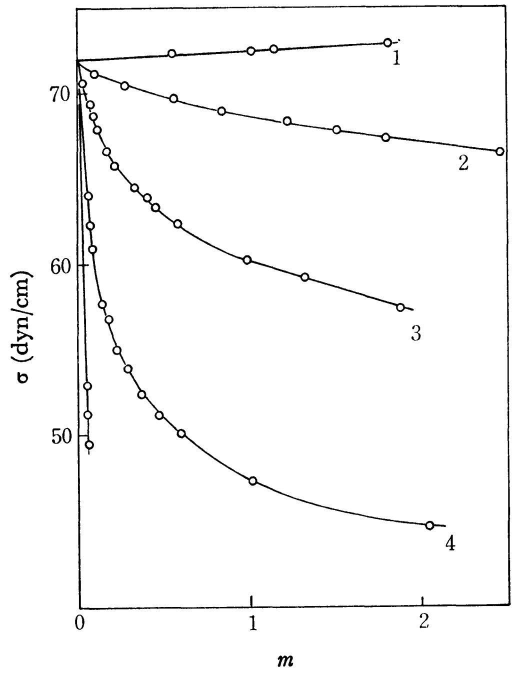

Fig. 1. Surface tension (σ) as a function of molality (m); 1, Me_4NBr; 2, Et_4NBr; 3, Pr_4NBr; 4, Bu_4NBr; 5, Pen_4NBr.

The interaction of simple salts with water may be interpreted in terms of electrostrictive hydration, whereas the interaction of nonpolar organic solutes with water may be interpreted in terms of hydrophobic hydration.$^{6)}$ 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 electrostrictive hydration due to ionic groups.$^{7)}$ The phenomenon that the dissolved substance raises the surface tension of pure water has been observed with a variety of simple salts, whether the constituent ions are electrostrictive structure-makers or -breakers.$^{5)}$ On the other hand, the nonpolar organic solutes, which act as hydrophobic structure-

Table 1. Traube factors (K) for R_4NBr

	$\Delta\sigma=5$ dyn/cm; C (mol/l)	K	$\Delta\sigma=7$ dyn/cm; C (mol/l)	K	$\Delta\sigma=10$ dyn/cm; C (mol/l)	K	$\Delta\sigma=15$ dyn/cm, C (mol/l)	K
Et_4NBr	1.50		2.4		—		—	
		10		8.9				
Pr_4NBr	0.15		0.27		0.55		1.4	
		8.3		8.4		9.1		9.3
Bu_4NBr	0.018		0.032		0.060		0.15	
		9.0		9.7		9.0		9.3
Pen_4NBr	0.0020		0.0033		0.0066		0.016	

makers in water, show the effect of reducing the surface tension of pure water.[8] In view of this relation, the shape of the surface tension-*versus*-concentration curve for an amphiphilic organic salt in aqueous solutions is considered to give a rough criterion of the behavior of the salt in water.[8] In view of the above results, Me_4NBr may be considered to act as a simple salt. With Me_4N^+ ion, the interaction of the ionic part with water will surpass the hydrophobic hydration due to methyl groups. In the cases of Et_4NBr, Pr_4NBr, Bu_4NBr, and Pen_4NBr, conversely, the interaction of alkyl groups with water surpasses the electrostrictive hydration due to the central ionic part; 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.[4] On the basis of this concept, Et_4NBr, Pr_4NBr, Bu_4NBr, and Pen_4NBr are considered to be classifiable as hydrophobic structure-makers in water. In general, these results of classification by the surface tension method are in fairly good agreement with those by other method.[1-3]

In order to compare the strength of the surface activity for these homologous compounds from Et_4NBr to Pen_4NBr inclusive, the Traube factors are obtained using the $\Delta\sigma$ values *versus* the molar concentration curves (not shown). The Traube factor means, in this case, the ratio of the molar concentration of equal $\Delta\sigma$ values when four alkyl chains of a compound are lengthened by every methylene group—*i.e.*, from Et_4NBr to Pr_4NBr, from Pr_4NBr to Bu_4NBr, and from Bu_4NBr to Pen_4NBr. The results are summarized in Table 1. In the case of a homologous series of strong electrolytes with one alkyl chain, such as sodium alkyl sulfates, the surface activity increases by a ratio of about 2 when the chain of an aliphatic compound is lengthened by one methylene group.[9] If we use this relation, the effect of four alkyl groups on the surface activity may be expected to increase by a factor of about 16 ($=2^4$) with an increase of four methylene groups. Therefore, in the case of the surface activity of spherical amphiphilic salts like R_4NBr salts in water, the effect of nonpolar alkyl groups on the surface activity was diminished by about half as compared with that of straight-chain salts.

Effect of Counter-ions. Figure 2 shows the $\Delta\sigma$ values *versus* the molal concentration curves for Me_4NCl, Me_4NBr, and Me_4NI. Figure 3 also shows the $\Delta\sigma$ values *versus* the logarithms of the molal concentration for Et_4NX and higher homologues. It is found that the surface tensions for R_4NX salts are mainly determined by the chain length; however, there are some specific effects due to the variation in counter-ions.

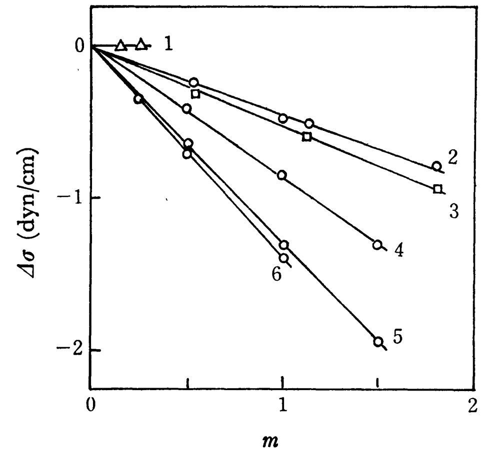

Fig. 2. Change in surface tension ($\Delta\sigma$) as a function of molality (m); 1, Me_4NI; 2, Me_4NBr; 3, Me_4NCl; 4, KI; 5, KBr; 6, KCl.

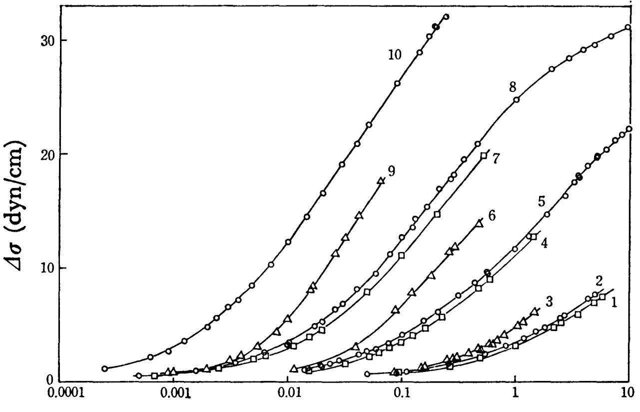

Fig. 3. Change in surface tension ($\Delta\sigma$) as a function of log m; 1, Et_4NCl; 2, Et_4NBr; 3, Et_4NI; 4, Pr_4NCl; 5, Pr_4NBr; 6, Pr_4NI; 7, Bu_4NCl; 8, Bu_4NBr; 9, Bu_4NI; 10, Pen_4NBr.

With Me_4NX salts, the order of raising the surface tension of water is in this order: $Cl^- > Br^- > I^-$. In the case of alkali halides, the same relation has been reported in the literature[5] as well. For comparison, the results[5] for KCl, KBr, and KI are also plotted in Fig. 2. The overall $\Delta\sigma$ values are slightly larger in the case of Me_4NX salts than in the case of alkali halides; this can probably be interpreted in terms of the effect of the slightly hydrophobic nature of the methyl groups. The effects of halide ions on the $\Delta\sigma$ values in the case of Me_4NX salts and in the case of alkali halides are comparable with each other. This fact also supports the above conclusion that Me_4NX salts, where $X=Cl^-$, Br^-, and I^-, can be classified as simple salts. As is evident in Fig. 3, the effect of counter-ions on the surface activity for Et_4NX, Pr_4NX, and Bu_4NX salts is quite remarkable; the order of increasing surface activity is $I^- > Br^- > Cl^-$.

As has been proposed in a previous paper,[8] in the range of low $\Delta\sigma$ values, the $\Delta\sigma$ values are empirically expressed as:

$$\Delta\sigma = AC^{1/2} + BC \qquad (1)$$

where A and B are constants. Equation (1) is found to be applicable up to about 7 dyn/cm in the cases of Et_4NX salts and higher homologues. Equation (1) may be converted to:

$$\Delta\sigma/C^{1/2} = A + BC^{1/2} \qquad (2)$$

Some examples of the plots of data according to Eq. (2) are shown in Fig. 4. The values of the constants, A and B, are obtained as the intercepts and the slopes respectively of such linear plots; the results are summarized in Table 2. Both A and B values are found to be dependent on the chain length as well as on the kind of counter-ion.

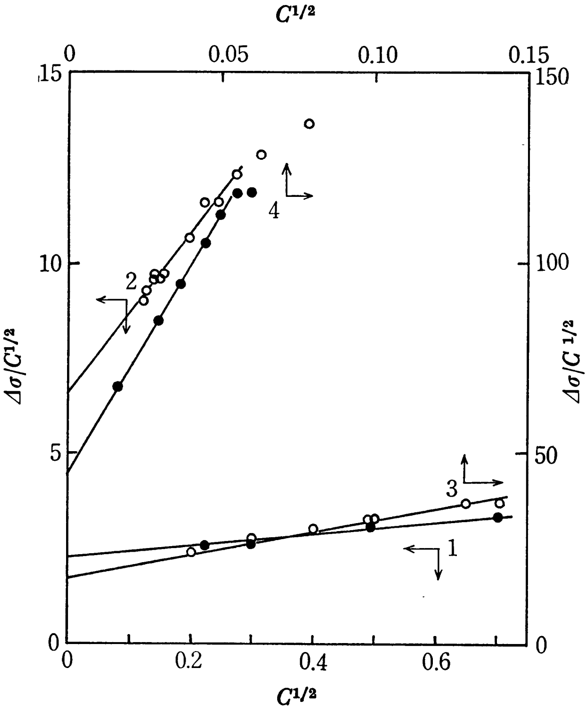

Fig. 4. Plots according to Eq. (2) up to about 7 dyn/cm; 1, Et_4NBr; 2, Pr_4NBr; 3, Bu_4NBr; 4, Pen_4NBr.

Table 2. The constants A and B in Eq. (2)

	A			B		
	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-
Me_4N^+	0	0	0	−0.5	−0.45	≒0
Et_4N^+	2.4	2.3	1.65	1.1	1.5	3.7
Pr_4N^+	6.6	6.4	4.0	13	19	57
Bu_4N^+	19.5	17	9.0	95	160	440
Pen_4N^+	—	44	—	—	1350	—

The B coefficients are considered to be measures of the surface activity of the salts in water.[8] The value of $-RT \ln B$ is the approximate value of the standard free energy of the transfer of an organic electrolyte from the bulk phase to the surface phase, where R is the gas constant, and T, the absolute temperature. In this case, the standard state for the bulk solution is taken as the state where $C=1$, and the standard state for the surface phase is taken as the state of $\Delta\sigma=1$ dyn/cm. The B value depends on both the chain length and the kind of counter-ion; *i.e.*, it increases with the chain length and with the strength of the electrostrictive structure-breaking action of a counter-ion for a given cation.

From the perfect analogy of Eq. (1) with the equations for other properties such as viscosity, conductivity, and activity coefficient of the aqueous solutions of strong electrolytes, it seems that the A coefficient is related to some type of ion-ion interaction. The A coefficient increases with the chain length, while it decreases with the increase in the size of the counter-ions; *i.e.*, it decreases in the order of $I^- < Br^- < Cl^-$ for each combination of R_4NX salts, as is evident in Table 2. This relation was also found in a previous work[8] for *n*-alkylammonium halides. The less the A values, the more ideal the $\Delta\sigma$ values-*versus*-concentration plots become. From these findings, it may be assumed that the A coefficient is related to the ion-ion interaction of organic salts at the adsorbed layer; *i.e.*, the A coefficient is probably a function which increases with the strength of the adsorbability of organic cations and which decreases in the strength of the interaction of the adsorbed organic ions with their counter-ions at the surface phase.

The Values of Adsorption at the Surface. Lindenbaum and Boyd[10] published the ionic mean activity coefficients for Me_4NX, Et_4NX, Pr_4NX, and Bu_4NX salts in water at 25 °C. From the combination of their results[10] with those shown in Fig. 3, the $\Delta\sigma$ values can be plotted as a function of the activity, as shown in Fig. 5. As the data of the activity coefficient for Bu_4NBr at 25 °C are unavailable, the data for Bu_4NBr

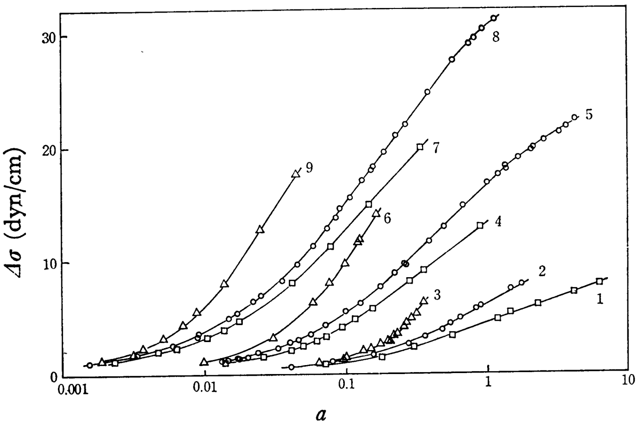

Fig. 5. Change in surface tension ($\Delta\sigma$) as a function of log a; 1, Et_4NCl; 2, Et_4NBr; 3, Et_4NI; 4, Pr_4NCl; 5, Pr_4NBr; 6, Pr_4NI; 7, Bu_4NCl; 8, Bu_4NBr; 9, Bu_4NI.

at 0 °C published by Nomura *et al.*,[11] are used. Because the activity coefficients for Pr_4NBr are independent of the temperature in the range from 0 to 25 °C,[10,11] this procedure is approximately valid. The Gibbs adsorption equation in the form of:

$$\Gamma = (1/2RT)(\mathrm{d}\Delta\sigma/\mathrm{d}\ln a) \tag{3}$$

will be applied to the data shown in Fig. 5, where Γ is the surface concentration of the solute, and a, the activity. As is shown in Fig. 5, there is fairly wide range of the linear portion on the plots between the $\Delta\sigma$ values and activities for each salt. Using the value of this slope of the linear portion in Fig. 5, the maximum surface concentration for each salt has been calculated; the results are listed in Table 3.

Table 3. The surface concentration at the maximum adsorption (in 10^{-10} mol/cm^2)

	Cl^-	Br^-	I^-
Et_4N^+	0.377	0.622	1.19
Pr_4N^+	0.838	1.05	1.61
Bu_4N^+	1.28	1.43	1.73

The large values of the surface concentration for R_4NI salts are particularly striking, as is evident in Table 3, which may be interpreted in terms of the specific interaction of R_4N^+ ion with I^- ion. The activity coefficients for R_4NI salts in water are very low compared for those of R_4NCl and R_4NBr salts; those for Et_4NI, Pr_4NI, and Bu_4NI salts are especially lower-lying than the Debye-Hückel limiting law.[10,11] These facts imply that R_4NI salts are very stable in water. Many investigators have proposed a specific interaction between R_4N^+ ions and I^- ions in terms of "water structure-enforced ion-pairing,"[12] micelle formation,[10] and structural salting-in.[13] At the surface, the adsorbed R_4N^+ ions will interact to a great extent with I^- ions as counter-ions; therefore, the electrical repulsive potential of the ionized surface will be greatly reduced.[4]

The behavior of R_4NX salts at the surface can probably be deduced if we apply the several surface chemical principles to the results of this work. However, such an attempt is beyond the scope of this paper.

The Behavior of R_4NX Salts in Concentrated Solutions. Some investigators have proposed a micelle formation for R_4NX salts in aqueous solutions. As a critical micelle concentration for Bu_4NBr, Lindenbaum and Boyd[10] reported 0.039 *m* and Rehfeld[14] reported 0.015 *m*. Wirth[15] were of the opinion that the micelle formation occurred above 4.0 *m* in Et_4NBr and above 1.4 *m* in Pr_4NBr solutions. As is evident from the curves for Pr_4NBr and Bu_4NBr in Fig. 3, the $\Delta\sigma$ value increases very rapidly as the concentration is increased, but at higher concentrations this increase is less marked; this situation is somewhat similar to what is seen when the electrolyte forms micelles. It was further observed in this study that the solution of R_4NX salts became highly viscous at higher concentrations, suggesting that the solute-solute interaction plays an important role in such concentrated solutions. However, the behavior of R_4NX salts in concentrated solutions, and especially the possibility of the micelle formation, remain as problems for the future.

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