

Surface Tension of Solutions of Chlorides, Bromides & Iodides of Na & K & of Tetraalkylammonium Iodides in Nonaqueous Solvents of High Dielectric Constants

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Surface tension of solutions of some tetraalkylammonium iodides like Pr_4NI , Pen_4NI , Hex_4NI and Hep_4NI in formamide, N-methylformamide (NMF) and N-methylacetamide (NMA) has been determined at different concentrations and temperatures (30-45°) employing a modified Traube's stalagmometer. Some common salts like KCl, KBr, KI, NaCl, NaBr and NaI have also been examined for the sake of comparison. Lyophilic and lyophobic interactions of these salts in these solvents have been explained on the basis of accommodation inside the intermolecular spaces of these solvents and the size of solute particles.

THE tetraalkylammonium salts containing large R_4N^+ ions (R being an alkyl chain) have been reported to possess abnormal properties in aqueous solution¹⁻¹³. This has been reported to be true for some properties, e.g. apparent and partial molal volumes of these salts even in some non-aqueous solutions¹⁴⁻¹⁸. Frank and associates¹⁹ have tried to explain the abnormal behaviour in aqueous solutions on the ground that the R_4N^+ ions, containing water repelling alkyl chains, act as water structure promoters around them. What is the exact nature of this hydrophobic or water repelling interaction of the alkyl chains has never been made quite clear in spite of numerous reports on this topic. Although the structure promotion concept of Frank and associates, specially the tetrahedral nature, has been questioned by several workers²⁰⁻²², the hypothesis seems very interesting and needs further study, specially in other solvents. If the alkyl chains attached to the central nitrogen atom of the R_4N^+ ions really repel water, these ions should be preferentially adsorbed on the surface, like surface active agents. This would result in a decrease of surface tension of water in their presence as required by the well known Gibbs adsorption equation, namely,

$$\Gamma = \frac{-C}{RT} \frac{d\sigma}{dc}$$

This has actually been found to be the case in some preliminary studies undertaken in our laboratory²³ using the R_4NX salts of the lower paraffins (R = methyl, ethyl, butyl) because the larger alkylammonium salt (alkyl > butyl) are almost insoluble in water. For a clearer understanding of the hydrophobic interaction and the general R_4N^+ -solvent interaction, it appears desirable to extend such studies in other

solvents which have high dielectric constants, so that complete dissociation of the R_4NX salts is assured and in which solvent repelling by the alkyl chains may not be expected. Solvents of this class appear to be formamide, N-methylformamide and N-methylacetamide, etc. Since these solvents and the R_4N^+ ions belong to organic class of compounds, it is very reasonable to expect that no lyophobic R_4N^+ -solvent interaction would occur in them. Some preliminary studies involving the smaller the R_4N iodides in these solvents were undertaken by Gopal and Bhatnagar²³.

In this paper, surface tension of solutions of some R_4N iodides has been determined in formamide, N-methylformamide and N-methylacetamide at different temperatures (30-45°) and concentrations with a somewhat improved technique than used previously²³. Iodides, bromides, and chlorides of sodium and potassium have also been included in the study for the sake of comparison.

Materials and Methods

The tetraalkylammonium salts, viz. Pr_4NI , Pen_4NI , Hex_4NI and Hep_4NI , were purified by several fractional crystallizations from appropriate solvents or their mixtures²⁴ (In our earlier studies²³, tetrapropylammonium iodide was not included). AR (BDH) samples of NaCl, NaBr, NaI, KCl, KBr, KI were recrystallized from conductivity water. Formamide, NMF and NMA, all from Fluka were treated with freshly ignited quicklime and distilled under reduced pressure, the middle fractions of the distillate having been collected for redistillation. The process was repeated till the electrical conductance of the distillate, in each case was in the range 10^{-5} to 10^{-6} mho. The solvents were stored in dark coloured bottles in dry nitrogen box and used, as early as possible after distillation. Aqueous solutions were prepared in fresh conductivity water (specific conductance $\approx 10^{-6}$ mho).

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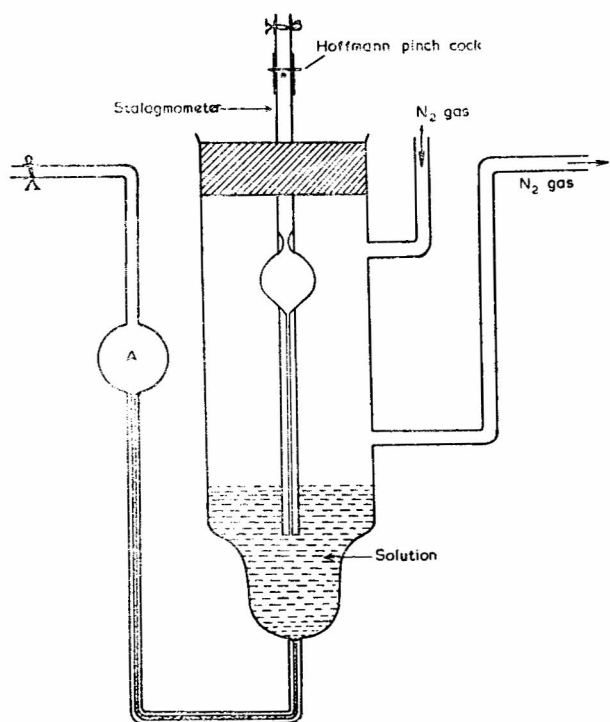


Fig. 1—Modified Traube's stalagmometer

The surface tension measurements were made with a modified Traube's stalagmometer (Fig. 1). To carry out the experiments at different temperatures, the stalagmometer was enclosed in an outer jacket, whose mouth was closed with a single bore rubber stopper, in which stalagmometer was fitted, the upper arm of the stalagmometer was connected to a propipette with a rubber tube carrying a Hoffmann pinch cock. This arrangement enabled one to suck the solution in the stalagmometer mechanically and also to allow it to fall at a slow desired rate. The solution from the wider tube was sucked in the bulb (A). Dry nitrogen atmosphere was maintained in the tube. The stalagmometer and outer jacket were thoroughly cleaned and dried before use. Every care was taken to avoid contamination of the dropping tip with grease, etc. The sufficient quantity of the solution under study was taken in the outer jacket. The jacket was placed in the thermostat maintained at the required temperature. After equilibration, the solution was first sucked in the stalagmometer with the help of propipette and the remaining solution in the outer jacket was then sucked into bulb (A), to make room for the falling drops from the stalagmometer. For each concentration and temperature, the number of drops were counted five times. Only a single drop variation was found for the same concentration. The surface tension was calculated in the usual manner from the density of that solution and by using the average value of the number of counted drops. The accuracy of the equipment and procedure was ascertained by determining the surface tension of two liquids (methyl alcohol and benzene) and the results obtained were compared with literature values at

TABLE 1—SURFACE TENSION VALUES OF METHYL ALCOHOL AND BENZENE AT DIFFERENT TEMPERATURES

Temp. °C	Surface tension (dynes/cm)			
	Expl	Lit.	Expl	Lit.
	IN MeOH		IN BENZENE	
30	21.73	21.69	26.63	27.67
35	21.31	21.30	26.98	26.96
40	20.83	20.83	26.30	26.25
45	20.49	20.49	25.50	25.56

different temperatures. The maximum deviation between experimental and literature values was found to be less than $\pm 0.2\%$ which was considered quite satisfactory. The results obtained are given in Table 1 for the sake of comparison.

Results and Discussion

σ_0 and σ , the surface tensions of pure solvent and solution at different temperatures (30-45°C) and concentrations, are given in Table 1. Relative surface tension (σ/σ_0) values at different temperatures and concentrations were calculated and curves between σ/σ_0 and C for 35° were drawn (Figs. 2-6).

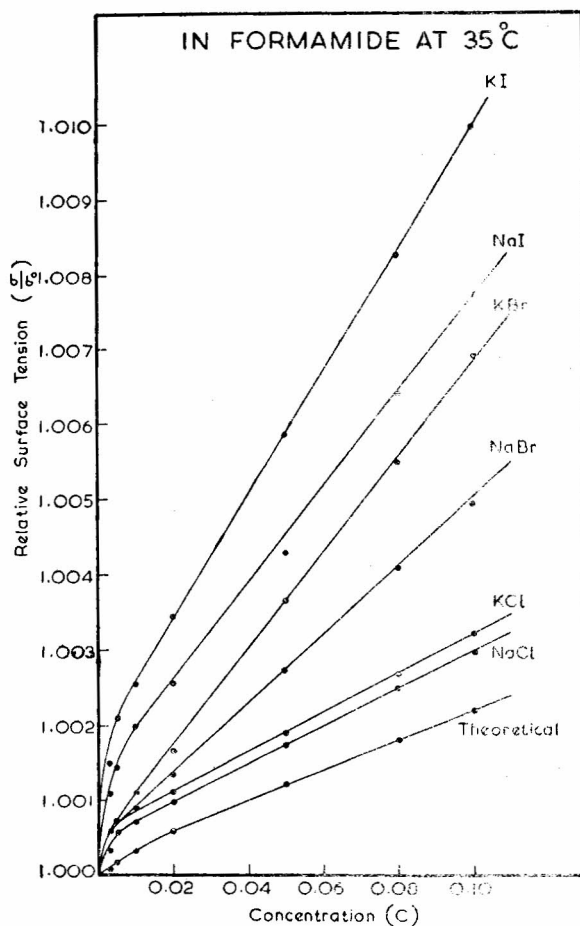


Fig. 2—Plots of relative surface tension (σ/σ_0) versus concentration for alkali metal halides in formamide

The occurrence of minimum in Me_4NI , Et_4NI and common salts at very low concentration has been observed earlier²³; no minimum appeared in the curve for Bu_4NI . The deviations from the theory are quite pronounced.

The theoretical σ/σ_0 vs C curves for 35° have also been given for these solvents for the sake of comparison. The curves for other temperatures are similar to those at 35° .

Solutions in formamide— Figs. 2 and 3 clearly show that for the common electrolytes, the deviation from the ideal behaviour are quite significant and positive. No minima in σ/σ_0 vs C curves are observed, unlike that in water²⁵. This could be associated with the tetrahedral structure of water which breaks down in the presence of the highly charged ions, thus lowering the surface tension of water. At higher concentrations, ion-ion effects become more pronounced. Since in formamide no such structure (i.e. tetrahedral) is present, minima in σ/σ_0 vs C curves do not occur.

The behaviour of the R_4NI salts is different from that of the common electrolytes. For the smaller Pr_4NI , surface tension increases with concentration and has a positive deviation from the theoretical value. The curve passes through a maximum at higher concentrations. It appears that the salts have a higher concentration in bulk than at the surface. One could, therefore, say that the salt has a lyophilic interaction in formamide at lower concentrations but at higher concentrations, the interaction is lyophobic. However, the surface

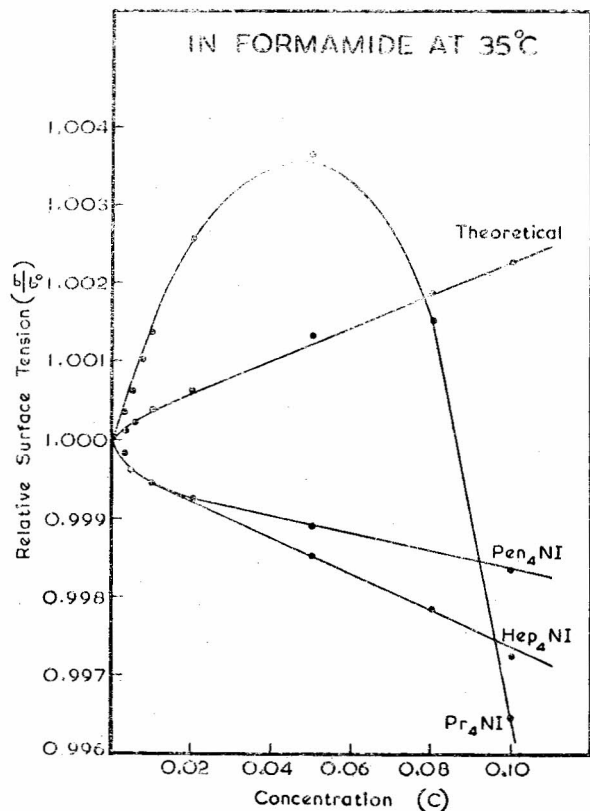


Fig. 3—Plots of σ/σ_0 versus concentration for tetraalkylammonium iodides in formamide

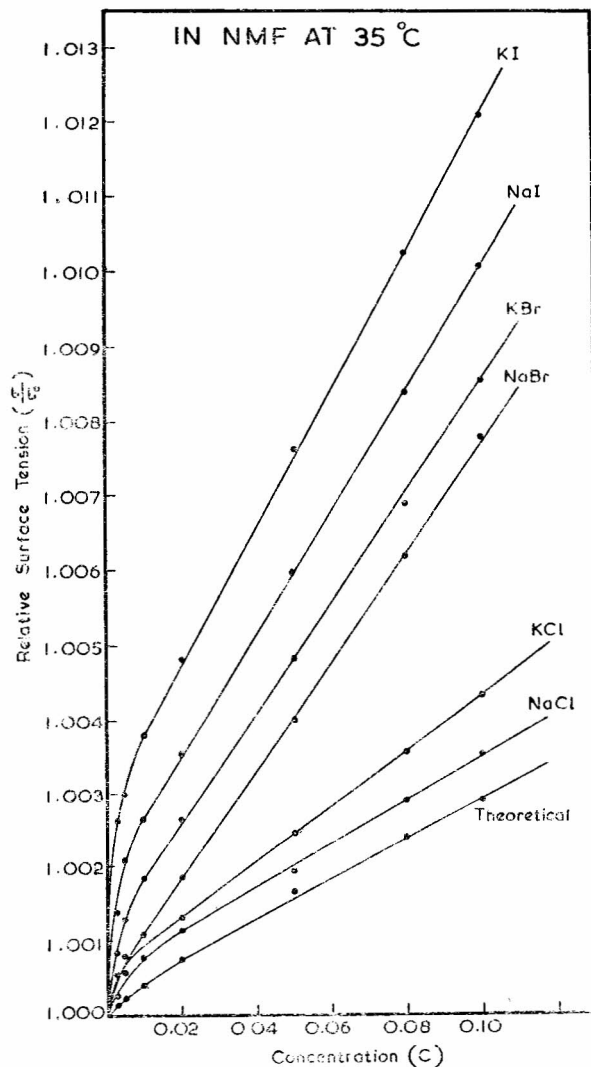


Fig. 4—Plots of σ/σ_0 versus concentration for alkali metal halides in N-methylformamide (NMF)

tension of the larger Pen_4NI and Hex_4NI salts decreases with the increase in concentration even in low concentration region and the deviation from the theoretical value is negative. Apparently, the behaviour appears to be lyophobic. This is rather an unexpected result and appears to be connected with the large size of the Pen_4N^+ and Hex_4N^+ ions.

Solutions in N-methylformamide (NMF)— The common electrolytes in this solvent behave in the same way as in formamide, i.e. σ/σ_0 increases with concentration and deviation from the ideal behaviour is positive. The common ions are, therefore, lyophilic in this solvent as well.

However, the similarity of the behaviour of Pr_4NI , Pen_4NI , Hex_4NI and Hep_4NI is a significant observation. The σ/σ_0 vs C curves for all of them have a positive slope and deviation is positive at the lower concentration, i.e. σ increases with the increase in concentration (Fig. 4). However, the curves pass through a maximum around $0.04M$ in all the cases after which σ begins to decrease. Thus it appears that tetraalkylammonium ions are lyophilic

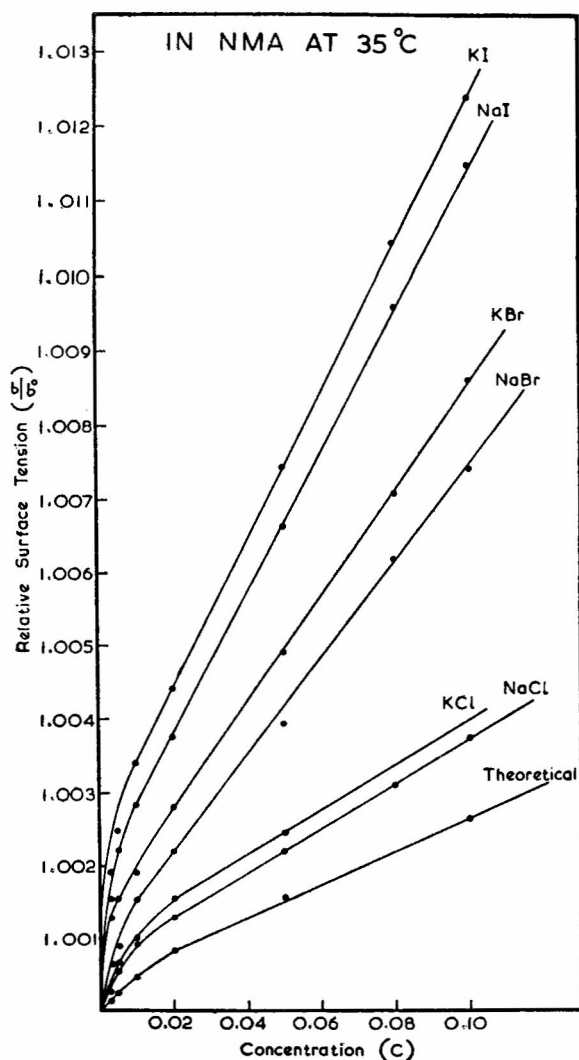


Fig. 5—Plots of σ/σ_0 versus concentration for alkali metal halides in N-methylacetamide (NMA)

at lower concentrations, and become lyophobic at higher concentrations, i.e. according to usual concept, the initial negative adsorption on the surface changes to positive adsorption at the higher concentrations.

Solutions in N-methylacetamide (NMA)—It may be noted that the common salts appear to have lyophilic interaction in this solvent also as in formamide and NMF. However, the behaviour of the R_4NI salts appear to be quite different as σ/σ_0 goes on increasing* with the increase in concentration (Fig. 5) without any tendency for a decrease so that both the smaller and larger R_4N^+ ions are lyophilic in NMA even up to 0.1M concentration.

The results obtained appear to lead to the following tentative conclusions.

The common ions which are small and could, therefore, be easily accommodated inside the intermolecular spaces of these solvents, including water, have a lyophilic interaction, i.e. these have no

*Preliminary studies by Gopal and Bhatnagar²³ showed σ to decrease with increase in concentration of NMA. It is believed that the present results are more reliable.

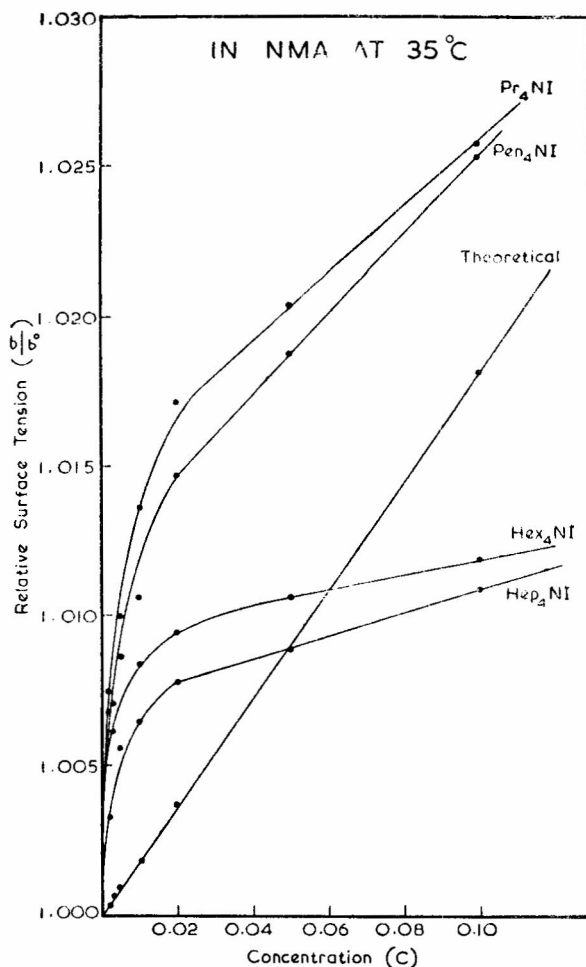


Fig. 6—Plots of σ/σ_0 versus concentration for tetra-alkylammonium iodides in NMA

tendency to be preferentially adsorbed on the surface layers. In water, the smaller Me_4N^+ and Et_4N^+ ions appear to behave like small common ions²⁶; however, the larger Pr_4N^+ are preferentially adsorbed on the surface even at very low concentrations, i.e. the interaction is lyophobic, apparently due to their large size and hence cannot be fitted in the water structure. The behaviour of the R_4N^+ ions in formamide, NMF and NMA seems to lead to a similar conclusion, i.e. lyophilic and lyophobic interactions seem to depend on the relative size of the ion with respect to the spaces available in the solvent as well as on the concentration. In formamide, for example, having the smaller molecule as compared to those of NMF and NMA, only Me_4N^+ , Et_4N^+ , Pr_4N^+ and Bu_4N^+ ions show lyophilic interaction at lower concentrations and this interaction changes to a lyophobic one at the higher concentrations; the larger Pen_4N^+ and Hex_4N^+ show lyophobic interaction from the very beginning. In NMF, with a little larger molecule, R_4N^+ ions from Pr_4N^+ to Hep_4N^+ , show an initial lyophilic interaction, but at higher concentrations, this interaction changes into a lyophobic one. Similarly, in NMA which has the largest size amongst these

solvents, no lyophobic interaction is observed even up to 0.1M concentration and the behaviour is lyophilic all through this range.

Thus it appears that if the ion is small enough to be accommodated inside the solvent spaces, the interaction is lyophilic; when these spaces are more or less occupied, the R_4N^+ ions are preferentially thrown out of the solution to the surface and R_4N^+ solvent interaction becomes lyophobic at higher concentrations. Thus the lyophilic and lyophobic interactions seem to be connected with the possibility of accommodation or to the lack of vacancy inside the solvent and may occur even with the solvents similar in nature to the solutes. The usual concept that all alkyl chains, both large and small, are water repelling, appear to be fallacious. The alkyl chains bearing smaller Me_4N^+ and Et_4N^+ ion are lyophilic interaction in water at least at lower concentrations as is also shown by the apparent and partial molal volume^{13,14} and viscosity studies⁴.

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