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CONDUCTANCE BEHAVIOR OF SYMMETRICAL TETRAALKYLAMMONIUM HALIDES IN AQUEOUS SUCROSE SOLUTIONS*

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ABSTRACT

The conductance behavior of some tetraalkylammonium halides (R_4NX) in saturated, aqueous solutions of sucrose has been investigated, and data on the conductance of these salts in water saturated by sucrose at 50° are reported at several temperatures within the range 25 to 70° In these homogeneous, ternary systems, plots of $-\log K$ *versus* $1/T$ show a break at the saturation temperature, where two straight lines intersect one another Divergence of the pair of straight lines has been found to decrease with increasing chain-length of the R_4N^+ ions, in contrast to the structural behavior of common, alkali-metal ions The results are interpreted in terms of the hydrophobic nature of the tetraalkylammonium halides, as well as the salting-in behavior of these salts towards sucrose molecules

INTRODUCTION

Investigations on the nature and behavior of symmetrical tetraalkylammonium halides in aqueous solution occupy an interesting position in the physical chemistry of solutions[1] The properties of salts containing tetraalkylammonium ions differ from those of most simple electrolytes Their anomalous viscosity[2], heat capacity[3], salting-in behavior[4 5], activity coefficient[6 7], and association[8] all lead to the conclusion that these large cations locally affect the structure of water[2 9] Despite the tremendous amount of work done on the properties of water and aqueous solutions, there is still much controversy on the absolute structure of water Of more general acceptance, however, is the interpretation of changes in the structure of water that are caused by the introduction of different solutes A recent review by Vaslow[10] on the properties of aqueous solutions stressed the importance of structural changes induced by the solute In this respect, solutions of nonelectrolytes and organic salts are of special interest, as many of these salts are known to increase the structure of water According to the commonly accepted view, (*a*) small ions attract water molecules

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*Paper presented, in part, at the 170th National Meeting of the American Chemical Society, Chicago, Illinois, August, 1975 (hydrophilic hydration), (*b*) most large organic ions and molecules strengthen the hydrogen bonds of the neighboring water molecules (hydrophobic hydration), and (*c*) intermediate ions break the structure of water Much of the information on hydrophobic hydration was provided by tetraalkylammonium salts (general formula, R_4NX, R being the alkyl group, and X the halide ion), as these salts are reasonably soluble in water, and their hydrophobic character can be varied by changing the size and nature of the R group

The unusual physicochemical properties of these salts (in comparison to those of common electrolytes), which arise mainly because of the presence of nonpolar groups, have been of considerable interest in studying their effects on the structural stability of nonelectrolyte solutions Conductance studies on the interaction of sucrose with some common alkali halides[11] and the sodium salts of some lower aliphatic acids[12] in aqueous solution have been reported recently In the present communication, the structural aspects of the interaction of tetraalkylammonium halides in aqueous sucrose solution, as ascertained by employing conductance measurements, have been studied

EXPERIMENTAL

General — Tetraalkylammonium salts obtained from various sources were recrystallized from suitable solvents or their mixtures, as described in the literature[13,14] Me_4NI and Et_4NI (B D H , England) were dissolved in absolute alcohol, and precipitated from solution with ether Pr_4NI and Bu_4NI (Distillation Products Industries, U S A) were dissolved in methanol, and precipitated with ether The recrystallized salts were dried in a vacuum desiccator, and every possibility of their contact with air was avoided Me_4NBr (BDH, England) was recrystallized once from methanol, with addition of sufficient petroleum ether to produce turbidity, Et_4NBr (B D H , England) and Bu_4NBr (D P I , U S A) were recrystallized twice from acetone, with sufficient ether to produce turbidity, and dried in a vacuum desiccator Me_4NCl and Bu_4NCl, both obtained from Fluka AG (Switzerland) were highly hygroscopic They were used without further purification, after drying in a vacuum desiccator The sucrose used was of Analytical Reagent grade (B D H , England)

Methods — A suitably grounded, Kohlrausch slide-wire apparatus, as described elsewhere[11], was used for the conductance measurements Cylindrical cells (Leeds and Northrup, U S A) were used for these systems Temperature control and other experimental procedures were the same as described earlier[11]

All the solutions were prepared by weight, in doubly distilled, demineralized, conductivity water (specific conductance ~ 1 μohm^{-1} cm^{-1}) A 0 1M solution of the tetraalkylammonium salt was prepared, and this was saturated with sucrose by keeping the mixture stirred at 50 0 ±0 05° in an oil thermostat A period of 20 to 30 h was allowed for complete saturation of the solution Crystals were separated from the mother liquor by electrical centrifugation within an air thermostat maintained at the same temperature (50 0 ±0 2°) Complete separation of the crystals from the mother liquor was ensured, and the centrifugate was transferred to the conductivity cell kept at the same temperature within the air thermostat The cell was then immersed in an oil bath maintained at a higher temperature (65–70°) The resistance was first measured at the highest temperature, the temperature was then lowered 2 to 4° at a time, maintained at each temperature for at least 30 to 40 min, and then the resistance was measured Resistances were measured at 20 to 25° above and below the saturation temperature Before each measurement, it was ensured that no crystallization had occurred in the cell solution

RESULTS AND DISCUSSION

Figs 1 to 4 are plots of the negative logarithm of the specific conductance against the reciprocal of the temperature for Me_4NX, Et_4NX, Bu_4NX, and R_4NI, respectively, in aqueous sucrose solution The difference between the experimentally observed values of $-\log K$ and the calculated values constitutes the deviation Plots of the deviation *versus* the temperature reciprocal for these systems are given in Figs 5 to 8 Deviation values were obtained as reported earlier[13 14] For this purpose, the best fit for the points above the saturation temperature was obtained

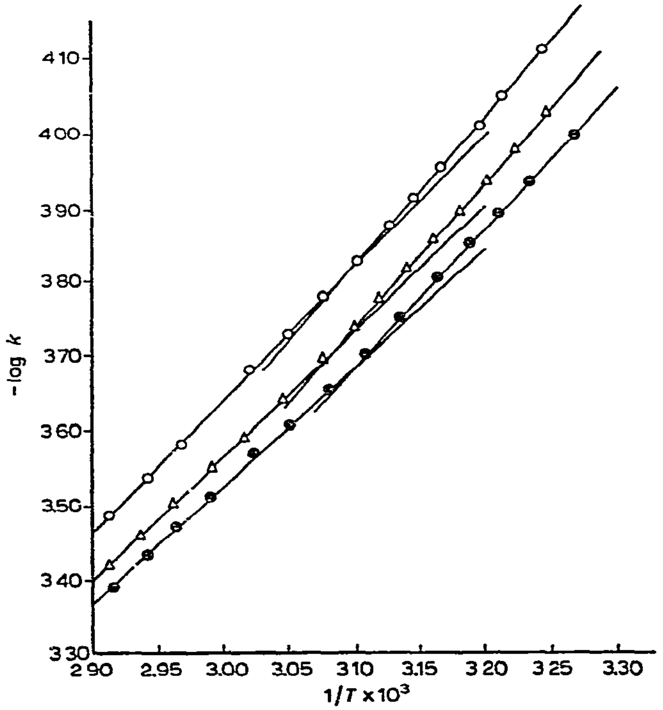

Fig 1 Plots of $-\log K$ *versus* $1/T$ for tetramethylammonium halides in aqueous sucrose solution [Key ○, Me_4NCl, △, Me_4NBr, ●, Me_4NI]

statistically, with the help of least-square calculations, and values of $-\log K$ were calculated from the regression equation for different values of $1/T$.

A perusal of Figs 1–4 reveals that plots of $-\log K$ *versus* $1/T$ consist of pairs of straight lines intersecting one another at the saturation temperature, showing a transition in the conductance values of tetraalkylammonium halides in aqueous sucrose solution similar to that observed in the alkali halide–sucrose–water system^{11} Although the divergence of the straight lines is small in comparison to that obtained for alkali halides in aqueous sucrose solution^{11}, the intersection of the two straight lines is clearly established Divergence of the pair of straight lines for all the Me_4N^+, Et_4N^+, and Bu_4N^+ halides studied follows the order iodide > bromide > chloride, as is evident from Figs 5 to 7 Fig 8 presents the plots of temperature reciprocal *versus* deviation value for R_4NI compounds (R varying from Me to Bu) in sucrose–water systems Fig 8 very clearly shows that the deviation of the straight lines increases in the order $Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$, *i e*, the divergence of the pair of straight lines decreases with an increase in the cationic size Although the anionic behavior of these salts is similar to that of alkali halides in sucrose–water system^{13}, the cationic behavior contrasts with that of alkali halides, where more divergence of the pair of straight lines was noticed in potassium halide–sucrose–water systems than that of a solution containing a sodium halide

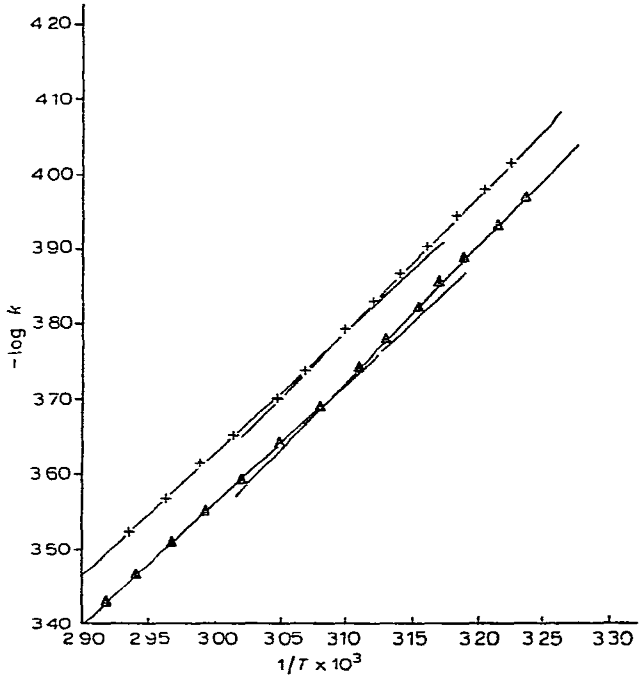

Fig 2 Plots of $-\log K$ *versus* $1/T$ for tetraethylammonium halides in aqueous sucrose solution [Key ×, Et_4NBr, ▲, Et_4NI]

These results may be explained by taking into account structural features of the solvent water, the hydrogen-bonding capabilities and hydration characteristics of sucrose molecules, and the special, hydrophobic character of tetraalkylammonium (R_4N^+) ions in aqueous medium. Water is known to be a largely associated liquid. The presence of such nonelectrolytes as sucrose or large organic ions tends to strengthen the hydrogen bonds between the water molecules, near the large solute, and a relatively large "iceberg" is effectively formed around them. Strong evidence for the correctness of this model was given by McMullan and Jeffrey[15], who succeeded in determining the structure of the clathrate hydrate of the salt Bu_4NBr containing, on the average, 32.8 molecules of water per molecule.

The effect of the simple alkali-metal, halide, and tetraalkylammonium ions on the thermal and transport properties of aqueous solutions has been widely studied[15–18]. The effects are generally ascribed to the ability of various ions to increase or decrease the structure of solvent water over that of the pure liquid. The general agreement is that such small, simple ions as Li^+ are structure-makers, whereas those of Cs^+ are structure-breakers. On the other hand, the tetraalkylammonium ions follow a pattern the reverse of that of the simple ions, and this is usually interpreted in terms of the special hydrophobic interactions of the hydrocarbon groups with water to increase its ice-like structure. Explanations for this increase in likeness to ice differ, depending

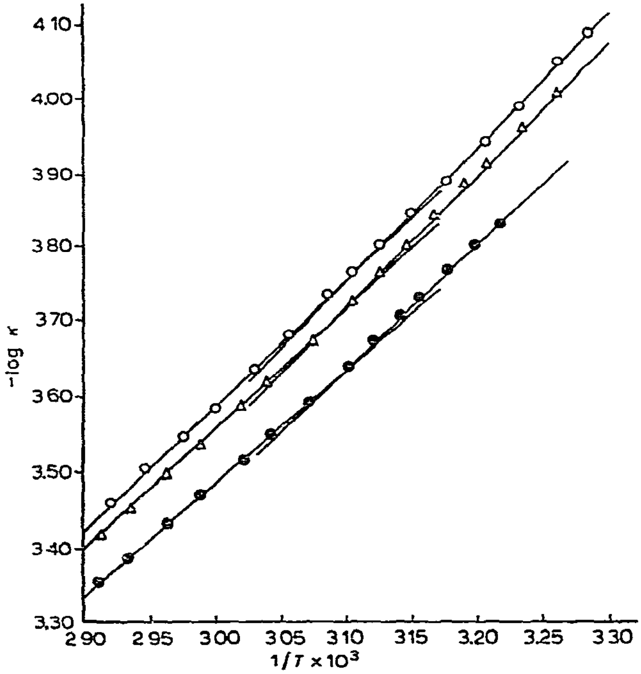

Fig. 3. Plots of $-\log K$ *versus* $1/T$ for tetrabutylammonium halides in aqueous sucrose solution. [Key ○, Bu_4NCl, ●, Bu_4NBr, △, Bu_4NI.]

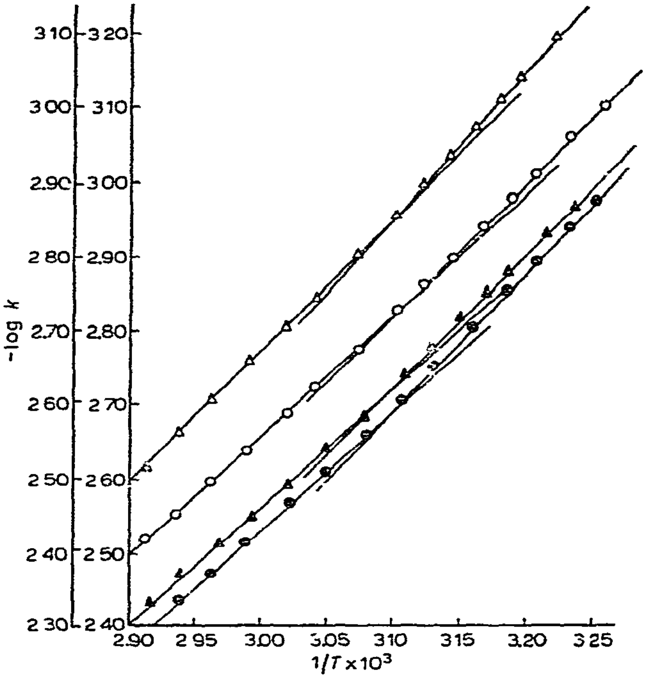

Fig 4 Plots of $-\log K$ versus $1/T$ for tetraalkylammonium iodides in aqueous sucrose solution [Key ●, Me_4NI, ▲, Et_4NI, △, Pr_4NI, ○, Bu_4NI]

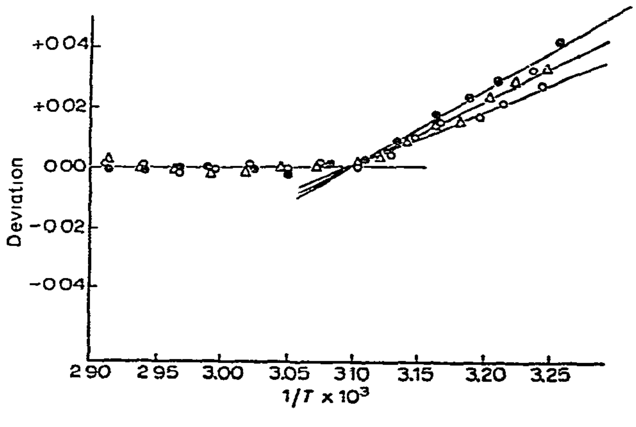

Fig 5 Plots of deviation *versus* $1/T$ for tetramethylammonium halides in aqueous sucrose solution. [Key ○, Me_4NCl, △, Me_4NBr, ●, Me_4NI]

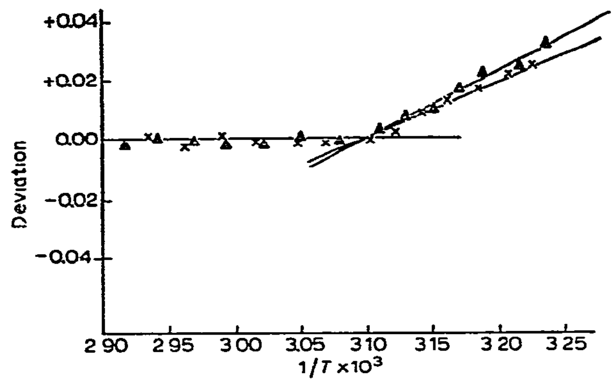

Fig 6 Plots of deviation *versus* $1/T$ for tetraethylammonium halides in aqueous sucrose solution [Key: ×, Et_4NBr, ▲ Et_4NI]

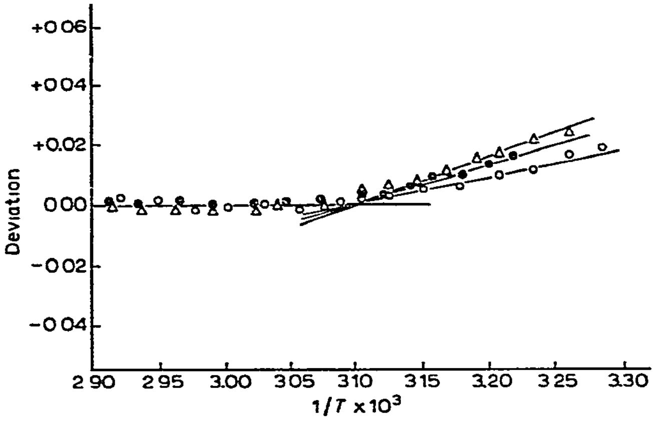

Fig 7 Plots of deviation *versus* $1/T$ for tetrabutylammonium halides in aqueous sucrose solution [Key ○, Bu_4NCl, ◉, Bu_4NBr, △, Bu_4NI]

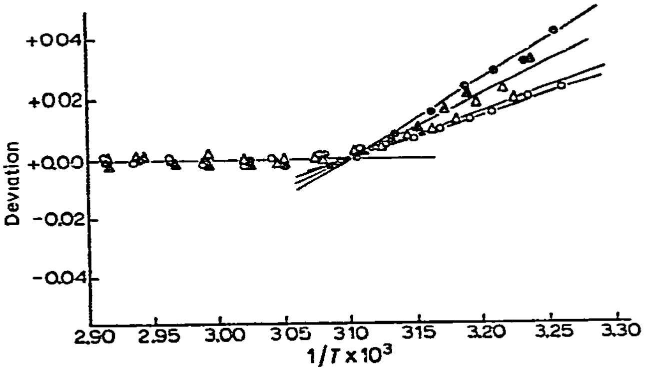

Fig 8 Plots of deviation *versus* $1/T$ for tetraalkylammonium iodides in aqueous sucrose solution [Key ◉, Me_4NI, ▲, Et_4NI, △, Pr_4NI, ○, Bu_4NI]

on the model used for liquid water, there may be an increase in the number of stabilized, ice-like clusters near the solute[9,19], or a time-average clathrate hydrate may be formed around it[20 21] Nevertheless, independent of the model used, it is now accepted that, in the intermediate vicinity of nonpolar molecules or nonpolar groups, there is a strengthening of the hydrogen bonds between the water molecules This hydration is thus quite different from the usual solute–solvent interactions brought about by the hydrophobic part of the solute, and it has been called "hydrophobic hydration" Kay and co-workers[22] concluded that Pr_4N^+ and Bu_4N^+ ions are excellent structure-promoters, that the Me_4N^+ ion is a slight structure-breaker, and that the structure-breaking and -making effects almost balance one another for the Et_4N^+ ion in aqueous solution

Our results are in agreement with the view of these workers[22] regarding the structural properties of tetraalkylammonium ions in aqueous solution. It has been pointed out[12] that the divergence of the pair of straight lines decreases with increase in the structural properties of the electrolyte The smallest deviation of Bu_4N^+ ions (as compared to other R_4N^+ ions) and the increase in the deviation values with decrease in the carbon chain-length of the cation, as observed in Fig 8, may be clearly explained on the basis of the foregoing discussion Our findings are further supported by Fig 9, in which the crystal radii of R_4N^+ ions as estimated by Robinson and Stokes[23] are plotted against the slope of deviation values obtained for R_4N^+ ions (from Fig 8) It is found that the slope of the deviation $\propto 1/r$, *i e* , the greater the ionic radius of the R_4N^+ ion, the less the slope of the deviation, in other words, the deviation of the lines decreases with increase in the carbon chain-length of the R_4N^+ ions or with increase in the structural properties of the cation The anionic behavior

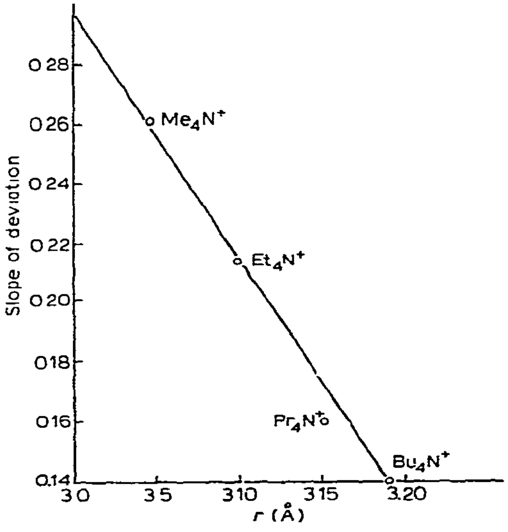

Fig 9 Variation of slope of deviations with size of the R_4N^+ ions (Stokes' radii, *r*) in aqueous sucrose solution

of these electrolytes may be explained on the same basis It is well known that the structure-breaking properties of halide ions increase with increase in their radii, and, hence, the deviation trend is in the order chloride<bromide<iodide

The less-pronounced divergence of the pair of straight lines in R_4N^+–sucrose–water systems as compared to alkali halide–sucrose–water systems[11] may further be interpreted on the basis of hydration of the sucrose molecule, as well as of the interaction of the tetraalkylammonium halide with sucrose in aqueous solution Whereas the presence of most salts tends to decrease the solubility of nonelectrolytes, tetraalkylammonium salts cause a significant increase in the solubility of nonelectrolytes[4 5 24 25] Desnoyers and co-workers[5] reported that, with the symmetrical R_4NX compounds, this type of salting-in appears to be a linear function of the number of carbon atoms of the cations (R_4N^+) As already discussed, the presence of neutral molecules increases the ice-like structure of water, this corresponds to a decrease in the entropy or an increase in the free energy of water In a system of R_4N^+ ions, sucrose, and water, both the sucrose and the large ion will tend to increase the water structure The system will, therefore, tend to minimize the increase in the free energy through association, the surface area of this association complex being smaller than that of the two particles separately As the length of the organic chain increases, the number of molecules forming the association complex probably increases, and, at the limit, micelles containing sucrose molecules in their centers are formed The solubility of a nonelectrolyte in water is limited to a large extent by the increase in the structure of water, the presence of structure-inducing ions will, therefore, facilitate the dissolution of the neutral molecules, as less work needs to be done by the nonelectrolyte against the structure of water The present results with the R_4NX compounds show that the sugar molecules would introduce more hydrophobicity in aqueous solution, and, hence, a less-pronounced divergence of the pair of straight lines This possibility is merely suggested, and is by no means conclusive However, the speculative nature of these suggestions warrants further investigations of solute–solvent interaction employing some structured, nonaqueous solvents

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