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CONDUCTANCE STUDIES ON THE INTERACTION OF SUCROSE WITH SYMMETRICAL TETRAALKYLAMMONIUM HALIDES IN FORMAMIDE

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ABSTRACT

The interaction of sucrose with symmetrical tetraalkylammonium halides (R_4NX) in formamide has been studied by employing conductance measurements Conductance data of these salts in formamide saturated by sucrose at 50 0 $\pm$0 05° are reported in the temperature range 25 to 70° Plots of $-\log$ (specific conductance) against $1/T$ showed a break at the saturation temperature, where two straight lines intersect one another Divergence of the pairs of straight lines in these homogeneous, ternary systems was found to be highly influenced by the structure-making or -breaking properties of the electrolytes The results are interpreted in terms of the structural properties of the electrolytes and the hydrogen-bonding capabilities of the formamide and sucrose molecules A similarity in the conductance behavior of R_4N^+ ions in both aqueous and formamide solutions containing sucrose at saturation concentration has been observed The transitional effect is more pronounced for R_4N^+ ions in formamide than in aqueous systems, and this is attributed to the less-structured nature and higher dielectric constant of formamide

INTRODUCTION

The behavior of tetraalkylammonium salts containing a large R_4N^+ ion (R being an alkyl chain) in aqueous solutions has been studied in great detail by various workers[1–6] These salts are reported to possess abnormal properties which have been attributed to solvent structural changes due to the hydrophobic nature of these ions Although these structural aspects have been widely studied in aqueous solutions, less consideration has been given to such effects in nonaqueous solvents It was, therefore, of interest to investigate their behavior in solvents other than water but similar to water in respect to their high dielectric constant and high degree of structural order due to hydrogen bonding Some interesting solvents of this type are amides of lower aliphatic acids and their mono-alkyl-substituted derivatives, *e g*, formamide, *N*-methylformamide, *N*-methylacetamide, and *N*-methylpropionamide In a series of papers[7–14], Ram Gopal and his co-workers described studies of a few

properties of these salts in some of the amide solvents, and they observed the anomalous behavior of tetraalkylammonium ions, even in nonaqueous solutions

In this communication, studies on the interaction of tetraalkylammonium halides with sucrose in formamide solutions are reported, sucrose, having a number of hydrogen-bonding sites, was used as the nonelectrolyte, and formamide as the solvent, as it is known to be a highly structured liquid The presence of the nonelectrolyte tends to strengthen the hydrogen bonds between the solvent near the large solute, and a relatively large structure is effectively formed How these large structures are influenced by the introduction of these large, hydrophobic ions, and by the type of interactions that are involved therein, has been studied, and is discussed in this paper

EXPERIMENTAL

Formamide, obtained from B D H (England), was kept overnight over freshly ignited quicklime and then distilled under diminished pressure, the middle fraction of the distillate being collected The process of purification was repeated until the electrical conductance of the sample was lowered to $\sim 10\ \mu\text{ohm}^{-1}\ \text{cm}^{-1}$, or less Tetraalkylammonium halides obtained from various sources [B D H (England), Fluka (Switzerland), and Distillation Product Industries (U S A)] were purified as described elsewhere[7,15] Sucrose (analytical reagent grade, B D H) was used as such, without further purification The rest of the experimental procedure and the precision of measurements were as described in earlier communications[16,17]

RESULTS AND DISCUSSION

In Figs 1–4, the negative logarithm of the specific conductance data for R_4NX–sucrose–formamide systems is plotted against the reciprocal of the absolute temperature Figs 5–8 depict plots of the deviation *versus* $1/T$ for these systems Deviation values were obtained with the help of least-squares calculations, as described elsewhere[16,17]

From Figs 1–4, it is evident that the plots consist of pairs of straight lines intersecting one another at a point in the vicinity of the saturation temperature, as observed for alkali halide–sucrose–formamide[17] and R_4NX–sucrose–water[18] systems A perusal of Figs 1–7 clearly reveals that the divergence of the pairs of straight lines is most pronounced in the Me_4NI system, and that the divergence decreases gradually with decrease in the crystallographic radius of the anion, *i e*, deviation of the two straight lines follows the trend $Me_4NI > Me_4NBr > Me_4NCl$ Similar anionic behavior is also noticed in the tetraethyl- and tetrabutyl-ammonium halide systems

As the symmetrical tetraalkylammonium halides form a homologous series of increasing cation size, it was of interest to study the effect of cation size on the properties of electrolytic solutions Therefore, the negative logarithms of the specific conductance data for a series of R_4NI compounds (R varying from Me to hexyl)

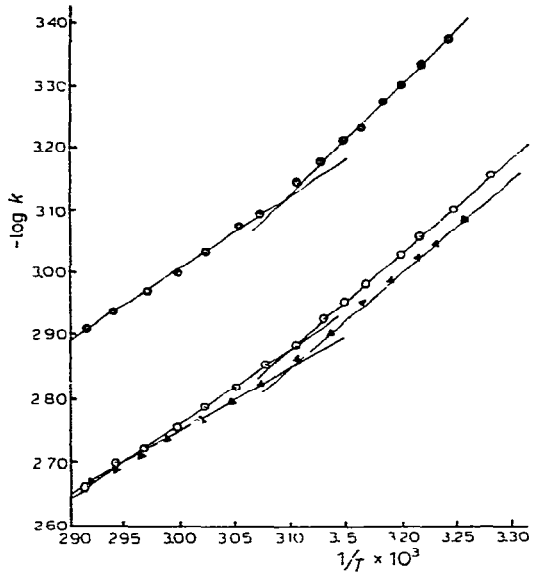

Fig 1 Plots of $-\log K$ *versus* $1/T$ for tetramethylammonium halides in sucrose–formamide solution [Key ⊙, Me_4NCl ▲, Me_4NBr, ⊜ Me_4NI]

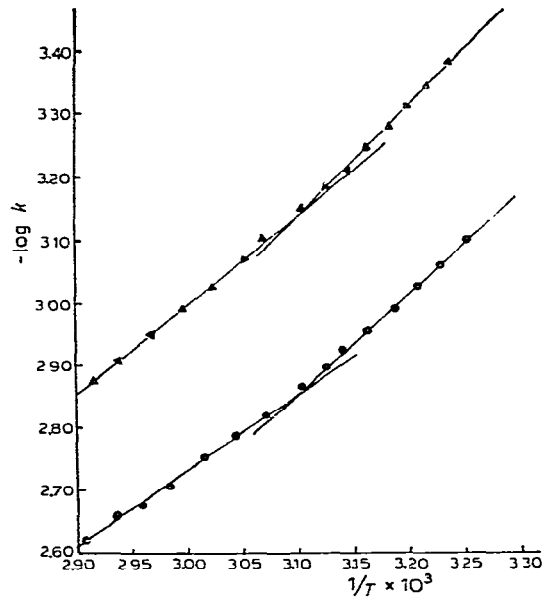

Fig 2 Plots of $-\log K$ *versus* $1/T$ for tetraethylammonium halides in sucrose–formamide solution [Key ▲, Et_4NBr, ⊜, Et_4NI]

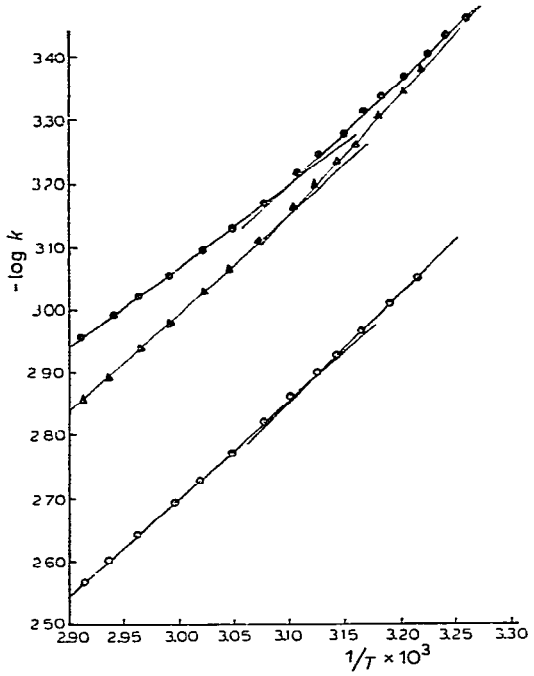

Fig 3 Plots of $-\log K$ *versus* $1/T$ for tetrabutylammonium halides in sucrose–formamide solution [Key ⊙ Bu_4NCl ▲ Bu_4NBr, ⊜ Bu_4NI]

were plotted against $1/T$ in Fig 4 Plots of the temperature reciprocal *versus* the deviation for these systems are given in Fig 8 In these systems, the most striking feature is that the divergence of the pairs of straight lines decreases with increasing cation size of the tetraalkylammonium iodides Departure of the straight lines in these systems follows the order $Me_4NI > Et_4NI > Pr_4NI > Bu_4NI >$ pentyl$_4$NI > hexyl$_4$NI Similar cationic behavior is also observed for the R_4NBr and R_4NCl compounds

Before the results obtained here are discussed, those of earlier studies, on alkali halides in formamide solutions[17], and on tetraalkylammonium halides in aqueous sucrose solution[18], should be considered The trend of deviations in alkali halide–sucrose–formamide systems was found to be in the order iodide > bromide > chloride Greater departure of the straight lines was observed for potassium salts than for sodium salts in each system, indicating increasing divergence of the straight lines with increase in the crystallographic radius of the common cations

It has already been established that the divergence of the pairs of straight lines increases with increase in the structure-breaking properties of the electrolytes From viscosity data, McDowal and Vincent[19] showed that the structure-breaking properties of halide ions in formamide increases in the order iodide > bromide > chloride, and the same trend has been observed in our systems, both for common and for tetraalkylammonium halides in formamide solution

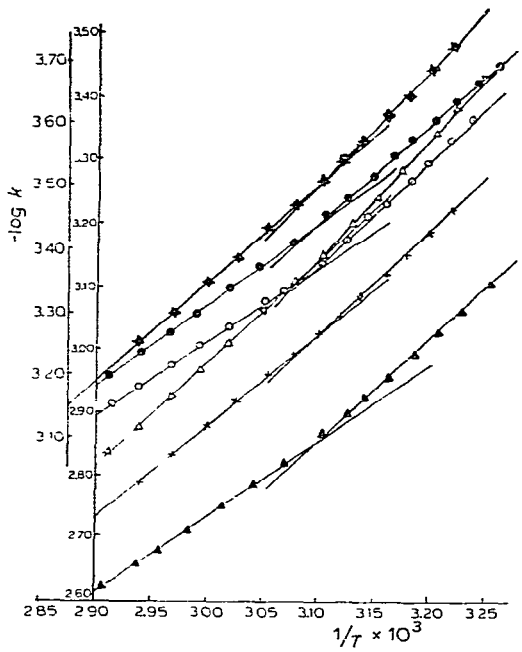

Fig 4 Plots of $-\log K$ *versus* $1/T$ for tetraalkylammonium iodides in sucrose–formamide solution [Key ⊙, Me_4NI, ▲, Et_4NI, △, Pr_4NI, ●, Bu_4NI, +, pentyl$_4$NI, ⊕, hexyl$_4$NI]

The general behavior of symmetrical tetraalkylammonium halides in formamide is somewhat similar to that in aqueous solution As the dielectric constant of the formamide is higher than that of water, an overall, pronounced effect is to be expected On the other hand, the different nature of the R_4N^+–water (hydrophobic) and R_4N^+–formamide (lyophilic) interactions[20] may lead to dissimilarities in their behavior in the two solvents

In water, the smaller departure of the pair of straight lines for R_4NX salts containing large R_4N^+ ions has been explained as due to the hydrophobic (R_4N^+–water) interactions Although the divergence of the pair of straight lines is more pronounced in formamide systems, a marked similarity in the behavior of R_4NX compounds, (*i e*, a decrease in the deviation with an increase in the size of the R_4N^+ ions) is observed for both systems This type of similarity in other properties of R_4NX compounds in formamide solution had also been observed by Gopal and co-workers[9–11] As the similar behavior in R_4N^+ ions in water and in formamide, in both of which hydrophobic interaction between the alkyl chains of R_4N^+ ions and the solvent molecules was not expected, it is concluded that the factor responsible for this similarity should, in general, differ from the interaction between the solvent and solute particles

Moreover, it has been observed that the divergence of the pairs of straight lines increases with increase in the size of the alkali-metal ions[16 17], and that there is

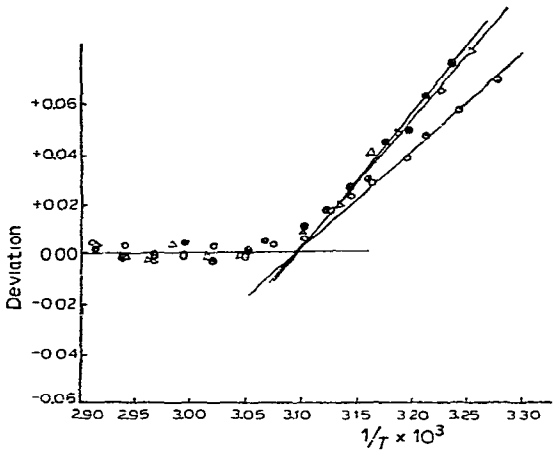

Fig 5 Fig 5 Plots of deviation *versus* $1/T$ for the system tetramethylammonium halide–sucrose–formamide [Key ⊙, Me_4NCl, △, Me_4NBr, ● Me_4NI]

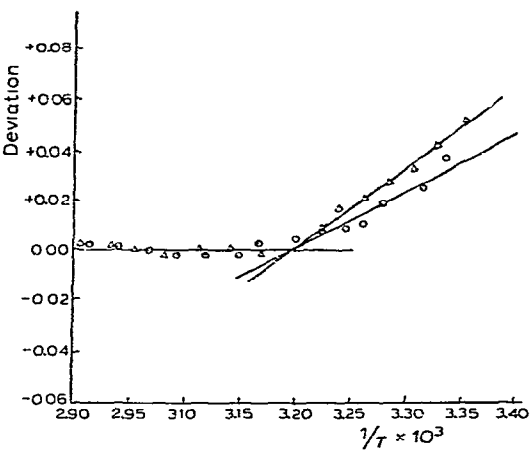

Fig 6 Plots of deviation *versus* $1/T$ for the system tetraethylammonium halide–sucrose–formamide [Key ⊙, Et_4NBr △, Et_4NI]

a marked decrease in deviation values with increase in the size of the R_4N^+ ions This type of effect of the increasing size of R_4NI compounds is seen in Fig 9, in which the Stokes radii of R_4N^+ ions have been plotted against the slope of the deviation values of these ions in sucrose–formamide solutions The foregoing results may be attributable to the fact that formamide and R_4N^+ ions are organic, and so the R_4N^+ ions are bigger than Na^+ and K^+ ions. It is expected that, in formamide solution, R_4N^+ ions penetrate the solvent structure, and that voids formed by the (larger) R_4N^+ ions are filled up by the (smaller) solvent molecules[9–11 21], whereas

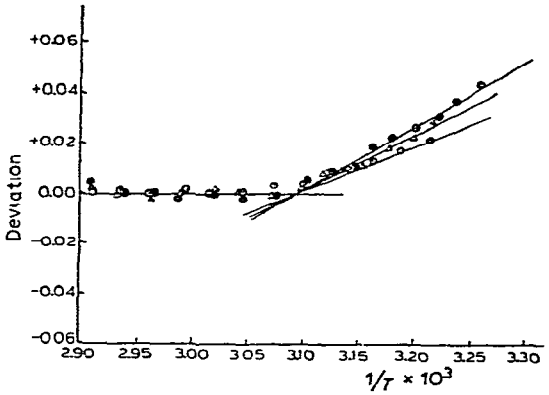

Fig 7 Plots of deviation *versus* $1/T$ for the system tetrabutylammonium halide–sucrose–formamide [Key ⊙, Bu_4NCl, △, Bu_4NBr, ●, Bu_4NI]

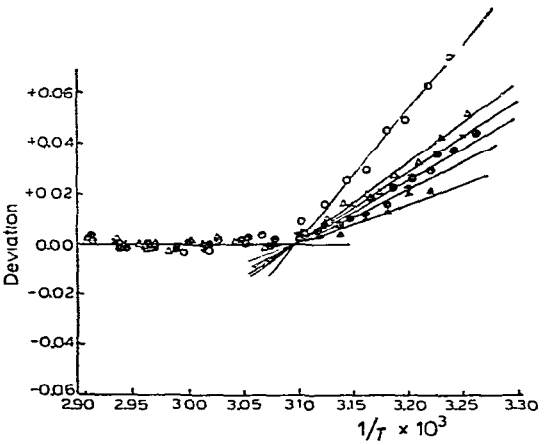

Fig 8 Plots of deviation *versus* $1/T$ for the system tetraalkylammonium iodide–sucrose–formamide [Key ⊙, Me_4NI, △, Et_4NI, ×, Pr_4NI, ●, Bu_4NI, ⊕, $pentyl_4NI$, ▲, $hexyl_4NI$]

the common alkali-metal ions are compact and, perhaps, smaller than the molecules of formamide, this suggests the possibility of accommodation of small ions in the voids formed by the formamide molecules, so that these ions will not contribute much to the structural properties of the system As formamide is less structured than water, it is easier for an ion to form a cavity in the bulk of a solution in formamide and to become highly solvated When such solvated ions encounter sucrose molecules, the adhering solvent molecules interact with sucrose molecules through hydrogen bonding, building up cage-like structures similar to those in water and thus giving rise to a transition in the homogeneous system, which is highly influenced by the structural properties of the electrolytes It appears that the structure-breaking effect continues

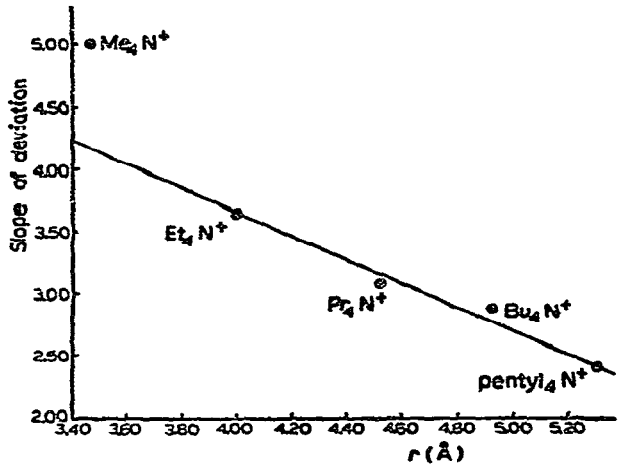

Fig 9 Variation of slope of deviations with size of the R_4N^+ ion (Stokes radii) in sucrose–formamide solution

to decrease with increase in the radius of the R_4N^+ ion This may be expected, because the larger R_4N^+ ions have low surface-charge density, so the electrostatic, ion–solvent interaction is not strong enough to break the hydrogen-bonded structure of the solvent

Ram Gopal and associates[7–14] made a detailed study of the behavior of R_4NX compounds in various, high-dielectric, amide solvents, such as *N*-methylformamide, *N*-methylacetamide, and *N*-methylpropionamide They observed an overall structure-breaking behavior of R_4NX compounds in these solvents, quite the opposite of their behavior (structure-making) in aqueous solution This tendency of the R_4N^+ ions has been attributed[7] to the fact that the special structure-promoting features (hydrophobic hydration in aqueous solution) of the larger R_4N^+ ions in water would be missing in these solvents, because of the similarity of the constituents of the R_4N^+ ions and the alkyl-substituted derivatives of the amides of lower aliphatic acids (*e g*, the presence of an alkyl group) Monica and co-workers reported[22 23] the conductance behavior of some large ions in formamide and certain other structured, nonaqueous solvents In such solvents as *N,N*-dimethylformamide, dimethyl sulfoxide, and sulfolane, they observed an anomalous, Walden product of tetraamylammonium ions, and interpreted their results in the light of the structure-breaking properties of large ions in these solvents, a hypothesis similar to that of Gopal and co-workers[7–14]. The authors[22 23] could not reach any definite conclusion regarding the structural behavior of R_4N^+ ions in formamide solution

Although no conclusive evidence was educed by earlier workers for the behavior of these salts in formamide solution[24], we have observed a similarity in the behavior of these salts in both aqueous and formamide solutions The transitional effect is more pronounced for these ions in formamide, compared to that in aqueous systems[18],

this may be attributed to the high dielectric constant and less-structured nature of formamide[25]

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