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CONDUCTANCE STUDIES ON THE INTERACTION OF SYMMETRICAL TETRAALKYLAMMONIUM IODIDES WITH NON-ELECTROLYTES — SUCROSE AND UREA — IN *N*,*N*-DIMETHYLFORMAMIDE

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ABSTRACT

The interaction of sucrose and urea with symmetrical tetraalkylammonium iodides in *N*,*N*-dimethylformamide (**1**) has been studied by employing conductance measurements. These studies involved the use of a rather simple, unique technique developed for study of the solute–solute and solute–solvent interactions in non-electrolyte solutions. Our results showed a break at the saturation temperature, indicating a transition in the conductance values. This behavior is explained in terms of the solute–solvent interactions involved in electrolyte–solvent–non-electrolyte systems. The results have been interpreted on the basis of the special, structure-promoting features of the (large) tetraalkylammonium (R_4N^+) ions, the hydrogen-bonding capabilities of sucrose and urea, the salting-in behavior of R_4NI salts with sucrose and urea, and the one-dimensional, hydrogen-bonded structure of molecules of **1**.

INTRODUCTION

The investigation of the changes that are induced in the structure of solvents by added solutes is of fundamental importance in many fields of chemistry. Earlier workers have directed their efforts towards elucidating the structural changes in the solvent, caused either by ionic solute or by non-ionic entities. Examination of the structural interactions of ionic species in non-ionic solutions is relatively recent. In studies of the ternary solutions of this kind, most of the attention has been focussed on water as the solvent[1–4], but it is now generally believed that, for the interpretation of the results, data for other solvents and solvent systems are also necessary. With this aim in mind, a systematic study on electrolyte–solvent–non-electrolyte interactions employing conductance[5–10] and viscosity[11,12] measurements was, therefore, undertaken in this laboratory. Besides water, another hydrogen-bonded, structured solvent, formamide, was used in conductance studies, and very interesting, comparable results were obtained[7-10]. Because both of these solvents have a high dielectric constant (D = 78 for water, and 109.5 for formamide at 25°) and are hydrogen-bonded, it was postulated that the major differences in the conductance behavior of electrolytes in these solvent systems would be due to the open, three-dimensional hydrogen-bonding in water, in contrast to the sheet-like, two-dimensional network of formamide molecules.

It was, therefore, of interest to investigate the conductance behavior of 1:1 electrolytes in the less-structured solvent *N*,*N*-dimethylformamide[13] (**1**), which possesses a chain-like, one-dimensional structure, and comparatively lower dielectric constant (D = 36.7 at 25°). Another reason for the choice of **1** as the solvent, and symmetrical tetraalkylammonium iodides as the electrolytes was based on the concept that interactions between the (large) tetraalkylammonium ions and the solvent water differ[14,15] from those between these ions and non-aqueous solvents. These differences have led to the concept of hydrophobic hydration in water, whereas such solvents as dimethyl sulfoxide (Me_2SO) and *N*,*N*-dimethylformamide do not show specific and substantial structural effects[14] on dissolution. Therefore, such a study in various solvent systems would be very interesting, as it should help to identify the factors that influence solute–solvent interactions.

During the present program for studying solute–solvent interaction in homogeneous, ternary systems, a rather new and simple technique has been developed that employs conductance measurements[5-10]. In this communication, studies on the interaction of tetraalkylammonium iodides with solutions of sucrose and urea in **1** are reported. Both sucrose and urea, having a number of hydrogen-bonding sites, were used as non-electrolytes. The presence of a non-electrolyte tends to strengthen the hydrogen bonds between the solvent near the large solute, and a relatively large structure is eventually formed. How these large structures are influenced by the introduction of R_4N^+ ions, and by the type of interactions that are involved therein, has been studied and is discussed herein.

EXPERIMENTAL

Tetraalkylammonium iodides, obtained from various sources, were re-crystallized from suitable solvents and their mixtures, as reported in the literature[6,16]. The recrystallized salts were dried in a vacuum desiccator, and every possibility of their contact with air was avoided.

N,*N*-Dimethylformamide (**1**; E. Merck, GFR) having a specific conductance of the order of 10^{-6} $ohm^{-1}.cm^{-1}$ was used as such, without any purification.

A suitably grounded, Kohlrausch slide-wire apparatus, as described elsewhere[5], was used for measurement of the resistance. Cylindrical cells (Leeds and Northrup, USA) were used for containing these systems. Temperature control and other experimental procedures were the same as reported earlier[5,6]. A 0.02M solution of the R_4NI salt was prepared in **1**, and it was saturated with the non-electrolyte (sucrose or urea) by keeping the solution 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 electric centrifugation at the same temperature. Complete separation of the crystals from the mother liquor was ensured, and the centrifugate was transferred to the conductivity cell. The cell was then immersed in an oil thermostat maintained at a higher temperature (65–70°). The resistance of the experimental solution was first measured at the highest temperature. The temperature was then lowered 2 to 4° at a time, and maintained for at least 30–40 min before the resistance was measured at 20 to 25° above and below the saturation temperature. Before each measurement, crystallization was not allowed to occur in the cell solution.

RESULTS AND DISCUSSION

Negative logarithms of the specific conductance of the symmetrical tetraalkylammonium iodides in sucrose–$HCONMe_2$ systems are plotted against the reciprocal of their absolute temperature in Fig. 1. Similar plots for these electrolytes in urea–1 systems are depicted in Fig. 2. It is evident that, for each system, the plots consist of a pair of straight lines intersecting one another at the saturation temperature, showing a second-order transition in the conductance values of the homogeneous electrolyte–solvent–non-electrolyte systems. Figs. 3 and 4 give the plots of deviation values

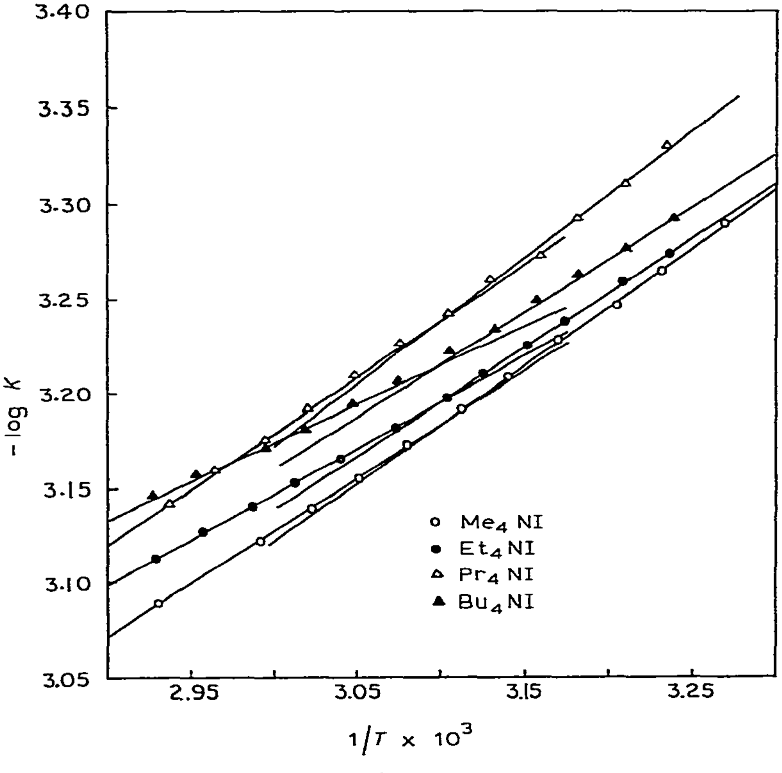

Fig. 1. Plots of $-\log K$ *versus* $1/T$ for R_4NI–sucrose–1 systems.

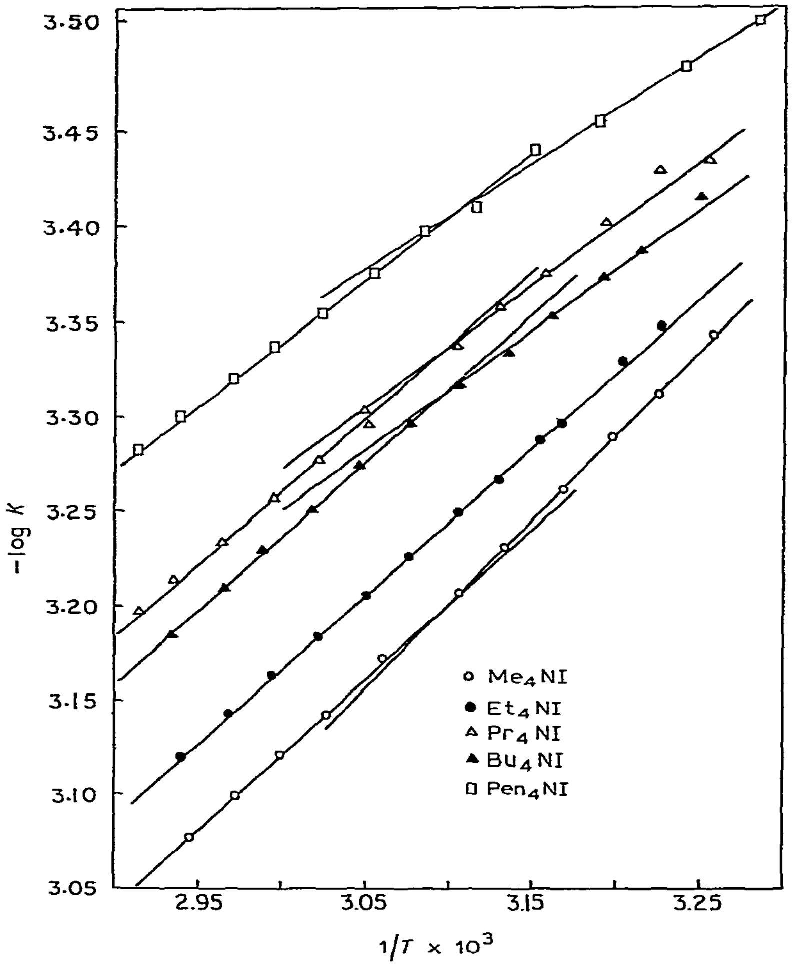

Fig. 2. Plots of $-\log K$ *versus* $1/T$ for R_4NI–urea–**1** systems.

against the temperature-reciprocal for these systems. Deviation values were obtained statistically with the help of least-squares calculations. For this purpose, the best fit for the points above the saturation temperature was obtained statistically, and the values of $-\log K$ were computed from the regression equation for different values of $1/T$. (The differences between the observed values of $-\log K$ and those calculated are termed deviations.)

It is evident from Figs. 1 and 3 that the divergence of the pair of straight lines in sucrose–**1** systems increases with increasing size of the cation of the tetraalkylammonium iodide. Departure of straight lines from a single-straight-line behavior in these systems follows the order $Bu_4NI > Pr_4NI > Et_4NI > Me_4NI$.

From the plots shown in Figs. 2 and 4, it was observed that, in urea–**1** systems, the deviation values for Me_4NI are very small, but positive, in nature, whereas they

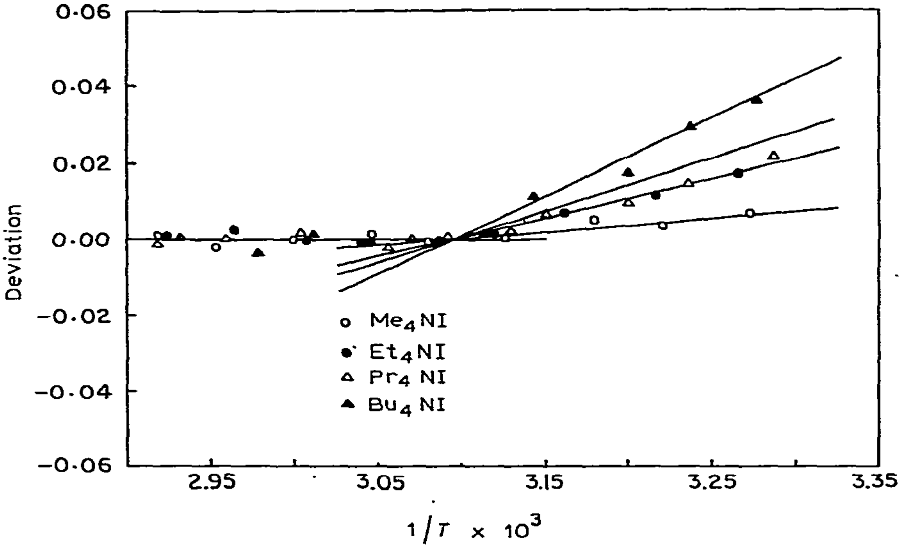

Fig. 3. Plots of deviation *versus* $1/T$ for R_4NI–sucrose–1 systems.

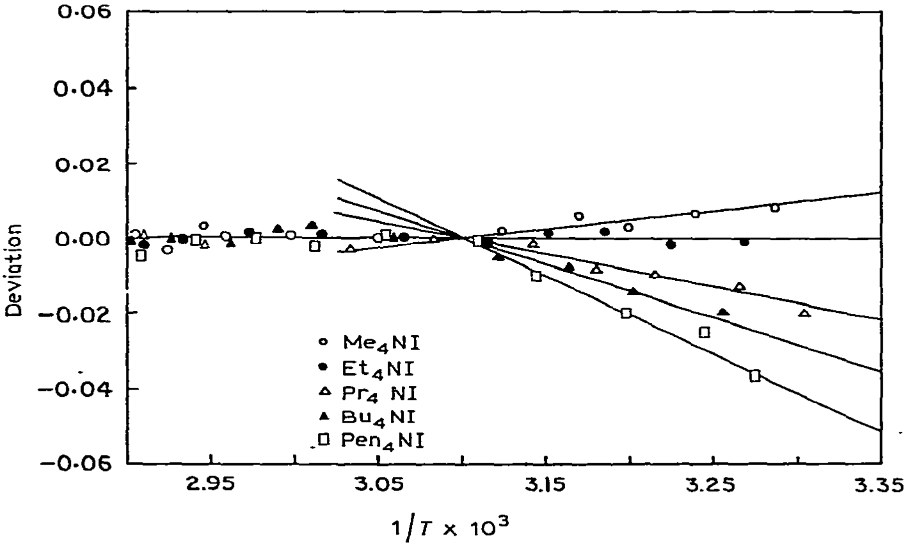

Fig. 4. Plots of deviation *versus* $1/T$ for R_4NI–urea–1 systems.

are negative for Pr_4NI, Bu_4NI, and Pen_4NI. At the same time, a single-straight-line behavior is observed for Et_4NI–urea–1 systems. In other words, the transitional effect almost vanishes for Et_4NI in urea–1 solution.

The abrupt change in the conductance values of the homogeneous, ternary systems may be interpreted on the basis of the occurrence of a second-order transition in these systems. Such systems could be envisaged as consisting of a network of electrolyte–solvent–non-electrolyte structures held together by hydrogen bonds, and the abrupt transition could be explained on the basis of the change in the solvent structure brought about, in the vicinity of the saturation temperature, by the presence of the electrolyte and non-electrolyte molecules possessing several hydrogen-bonding sites. In the present study, as the system passes from an unsaturated to a supersaturated state, through the saturation temperature (avoiding crystallization), it undergoes a change in the entropy, due to a change in the solvent structure. The entropy change thus represents a change in the bulk-solvent structure occurring as a result of molecular rearrangement of higher order, *i.e.*, a decrease in entropy. This decrease in entropy is similar to the decrease of entropy noticed for supercooled liquids[17].

The results may further be explained by taking into account the structural features of the solvent (*N*,*N*-dimethylformamide), the hydrogen-bonding capabilities of sucrose and urea molecules, and the structural behavior of R_4N^+ ions in non-aqueous solvents. *N*,*N*-Dimethylformamide is a dipolar, aprotic solvent possessing intramolecular hydrogen-bonding in its structure. It has a less structured, one-dimensional structure. The presence of a non-electrolyte such as sucrose, with eight hydrogen-bonding sites, and of urea, with three potential centers for hydrogen-bonding, tends to strengthen the hydrogen bonding between molecules of **1** that are near to large solute molecules, and a relatively large cluster is eventually formed around them. The structural properties of R_4N^+ ions in **1** influence these clusters to different extents and that explains the variation in the divergence of pairs of straight lines obtained for various systems.

It had already been reported[3] that the behavior of R_4NX salts in sucrose–formamide solutions is similar to that[6] of the sucrose–water solutions. The divergence of the pairs of straight lines in aqueous and formamide solutions was found to follow the order $Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$, in contrast to what has been observed in sucrose–**1** systems. It is well known that water has a three-dimensional structure, whereas formamide consists of a two-dimensional network, and the structure allows R_4N^+ ions to be accommodated into it, forming big structures, a process that is facilitated by the presence of sucrose molecules with their eight hydrogen-bonding sites. This situation is not encountered in the case of solutions in **1**, whose molecule, already mentioned, is a chain-like, one-dimensional, crystal lattice, and, hence, it is not possible for the bigger R_4N^+ ions to enter into the voids of this molecule; this is why, in this solvent, R_4N^+ ions behave as common alkali-metal ions. Similarity of the structural behavior of the common alkali-metal ions and R_4N^+ ions in this solvent is further understandable, because the special, structure-promoting features of the larger R_4N^+ ions in water would be missing in **1**, owing to the similarity of the constituents[16,18] of the R_4N^+ ions and the $HCONMe_2$ molecule (*e.g.*, the presence of alkyl groups).

In R_4NI–urea–**1** systems, a peculiar difference from those of sucrose–**1** systems is noticed; whereas the deviation values for all of the latter systems are positive, positive deviation values are obtained only for Me_4NI in the urea–**1** mixture. Negative deviation values were obtained for Pr_4NI, Bu_4NI, and Pen_4NI, and the transitional effect seems to be almost absent in the Et_4NI–urea–**1** system (see Figs. 2 and 4). Urea in aqueous solutions is known to act like a statistical, water-structure breaker[19,20]. This structure-breaking behavior of urea has also been found valid for some structured, amide solvents, such as formamide, *N*-methylformamide, and *N*,*N*-dimethylformamide[13]. From experimental evidence, Somsen and co-workers concluded that the interaction of urea with water and with amide solvents is of the same order of magnitude[13]. Perhaps this structure-breaking mechanism of urea predominates in the R_4NI–urea–**1** systems, causing negative deviation values with larger R_4N^+ ions.

The results for such systems may further be interpreted on the basis of change in activation energies of conduction for unsaturated and supersaturated regions, due to a change in the mobilities of ions in the two states. In sucrose–**1** mixtures, the mobilities of ions in the supersaturated region are restricted, owing to the formation of bigger structures, whereas such structures are not to be expected in urea–**1** mixtures, because of the structure-breaking properties of urea, and hence, an increase in the mobilities of ions is found in urea solutions.

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