

Conductance studies on the interaction of urea with ions in formamide

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Abstract. Conductance data on the interaction of urea with sodium and potassium halides and with larger tetraalkylammonium halide salts in formamide solution have been reported at several temperatures within a range of 25 to 70°. 0.1 M solution of the electrolyte in formamide was saturated with urea at 50° and the conductances of the homogeneous electrolyte-solvent-nonelectrolyte systems were measured. Pairs of straight lines have been obtained from the plots of $-\log K$ versus $1/T$, intersecting one another at the saturation temperature. Divergence of the pairs of straight lines has been found to be markedly influenced by the structural properties of various ions. Trend of the divergence of the pairs of straight lines has been found to follow the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$ and $\text{Hex}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Et}_4\text{N}^+ > \text{Me}_4\text{N}^+$. These results have been interpreted on the basis of the structure-breaking properties of urea and 'salting-in' of urea by electrolytes and of electrolytes by urea.

Keywords. Alkali halide; tetraalkylammonium halide; formamide solution; structure-making; structure-breaking and salting-in.

1. Introduction

The role of solvent structure on the interaction of urea with electrolytes has been of recent interest. In these studies, attention has largely been focussed on the solvent water, but it has now been generally believed that for the interpretation of results, data in other solvents will also be essential. Most of the workers (Franks and Clarke 1967; Arakawa and Takenaka 1967; Hargraves and Krescheck 1969; Stern and Kulluck 1969; Barone *et al* 1970; Phillip *et al* 1971, 1973) are of the opinion that urea acts as a net water structure breaker, while Hamidayyah (1965) has suggested that urea might enter the water 'clusters' and substitute some water molecules without appreciable steric effects leading to a stabilization of the water structure. Subramanian *et al* (1969, 1971) Chawla and Ahluwalia (1973), on the other hand, are of the view that urea has essentially no net effect on water structure. However, studies, e.g., ultrasonic absorption and velocity in aqueous urea solution (Beauregard and Barrett 1968), viscosity (Vidulich *et al* 1969), thermal measurements (Khamova *et al* 1966) as well as the statistical analysis (Frank and Franks 1968) of urea solutions have definitely concluded that urea acts as a structure-breaker in aqueous solution.

In this laboratory, a continuing programme has been in progress in which the ternary systems comprising electrolytes, solvent and nonelectrolytes like sucrose, xylose and mannitol have been studied employing conductance measurements (Vishnu and Singh 1974, 1975, 1977, a, b, c). These studies have been conducted in

water and in formamide, the latter being a structured polar solvent of very high dielectric constant (109.5 at 25°). The use of electrical conductivity and its variation above and below the saturation temperature provides an experimentally simple and convenient method for the study of these systems in comparison to other physico-chemical techniques, e.g. viscosity and thermochemical measurements, etc. In the present communication, conductance data on the interaction of some common and large ions with urea in formamide solutions have been presented. The choice of urea as a nonelectrolyte in our study is based on its two outstanding properties in solution, namely, its great ability to undergo hydrogen bonding with solvent because of the presence of three potential centres on each molecule and its small effect on polarity of the solvent (Mukherjee and Ray 1963).

Though aqueous solutions of urea have been the subject of various studies, it was not possible for us to study the interaction of electrolyte with urea in aqueous medium because a clear supersaturated aqueous solution of urea containing electrolytes could not be obtained—a condition fundamental for the present study. However, supersaturated solution of urea in formamide was found to be fairly stable for a long time and no significant decomposition of urea occurred even at elevated temperatures during the experiment so as to affect the conductance data.

While sucrose and mannitol have been found to be structure-makers in aqueous solution by several workers (Walrafen 1966; Kozak *et al* 1968; Cassel and Wood 1974) and also by the present workers in both aqueous and formamide solutions in the presence of electrolytes (Vishnu and Singh 1974, 1975, 1977a, b, c), the urea-electrolyte interaction and its structural behaviour in formamide is not well studied. Since a marked resemblance in some of the physical properties of aqueous and formamide solutions has been observed by several workers (Gopal and Siddiqui 1969; Gopal and Singh 1970; Gopal *et al* 1971; Visser *et al* 1975; Vishnu and Singh 1975, 1977a, c), it is expected that urea in formamide may behave in the same manner to that of urea in water. Present study may, therefore, provide an insight into the structural interactions of urea and those of some alkali metal ions and larger tetraalkylammonium (R_4N^+) ions in this solvent.

2. Experimental

2.1. Materials

Urea was BDH (AnalaR) grade and dried in vacuo before use. Sodium and potassium halides used in the present investigation were either of pro Analyti (E. Merck) or AnalaR (BDH) grade. All the samples of these salts were purified by repeated crystallization from conductivity water. Tetraalkylammonium halides obtained from various sources (Fluka, Switzerland, BDH England, and Distillation Product Industries USA) were purified in the manner described by Conway *et al* (1969) and Vishnu and Singh (1977 b, c).

Formamide obtained from BDH (England), was kept overnight over freshly ignited quicklime and then distilled under reduced pressure. The middle fraction of the distillate was collected. The process of purification was repeated until the electrical conductance of the sample was reduced to about 10^{-5} mho or less.

2.2. Measurements

Resistance measurements were made with a properly grounded, Leeds and Northrup (USA) Kohrausch slide wire assembly (Vishnu and Singh 1974). Tubular conductivity cells described elsewhere (Vishnu and Singh 1974) were used for the measurement. Required solution temperature was achieved by placing the solution in an oil bath thermostatically controlled within $\pm 0.02^\circ$ in the lower and $\pm 0.05^\circ$ in the higher temperature range.

A 0.1M solution of the electrolyte was prepared in pure formamide. The solution was kept in a stoppered conical flask and saturated with urea by keeping the mixture stirred at $50.0 \pm 0.05^\circ$ in the oil bath. Sufficient time (20 to 30 hr) was allowed for complete saturation of the solution. Crystals were separated from the mother liquor by electrical centrifugation in an air thermostat maintained at $50.0 \pm 0.2^\circ$. Care was taken to achieve complete separation of the crystals from the solution, and to check for any crystallization in the clear solution. This solution was then sucked into the tubular conductivity cell kept at the same temperature in the air thermostat. Later, the cell was well immersed in the constant temperature oil bath maintained at $65-70^\circ$. 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 at each temperature for at least 30 to 40 min before measuring its resistance. Thus, resistances were measured 20 to 25° above and below the saturation temperature. Before each measurement it was ensured that no crystallization had occurred in the experimental solution. Contact of the solvent and the solution with air was kept to the minimum.

3. Results and discussion

Negative logarithm of specific conductance values of sodium and potassium halides in formamide solutions saturated with urea at 50° are plotted against their absolute temperature reciprocals in figures 1 and 2 while those of tetramethyl-, tetraethyl- and tetrabutyl- ammonium halides in urea-formamide solution is given in figures 3, 4 and 5 respectively. The plots of $-\log K$ versus $1/T$ for R_4 NI salts (R varying from Me to Hex) in urea-formamide solution are depicted in figure 6. The particular plot was chosen in conformity with Andrade's equation (Dac Andrade 1930) for variation of viscosity with temperature and the well-known inverse dependence of conductance on viscosity. All these plots depict pairs of straight lines intersecting in the neighbourhood of saturation temperature similar to those of sucrose-water (Vishnu and Singh 1974, 1977b) and sucrose-formamide (Vishnu and Singh 1975, 1977c) systems containing these electrolytes. Since the divergence of the pair of straight lines is small, deviation values from a single straight line behaviour were obtained statistically. For this purpose, the best fit for the points above the saturation temperature was obtained with the help of least square calculations, and the theoretical values of $-\log K$ were obtained from the regression equation for different values of $1/T$. The difference between the values of $-\log K$, experimentally observed, and those calculated, constitute the deviations.

Deviation values versus temperatures reciprocal plots for these systems are given in figures 7-12. The significance of these plots could be attributed to the occurrence

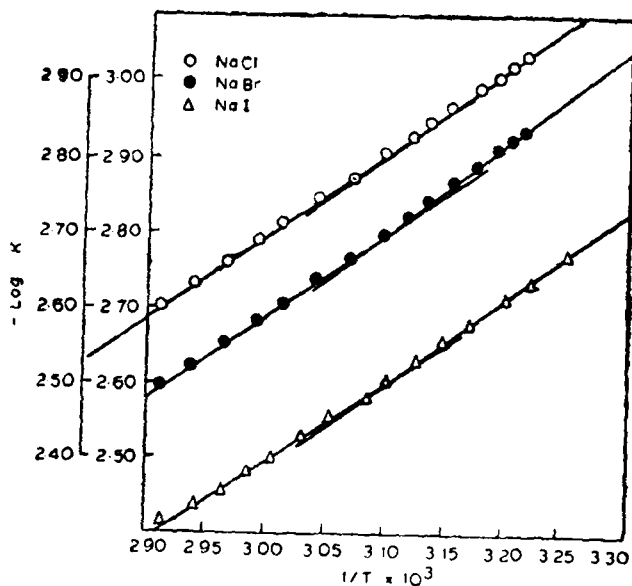


Figure 1. Plots of $-\log K$ vs $1/T$ in urea-formamide solution for sodium halides

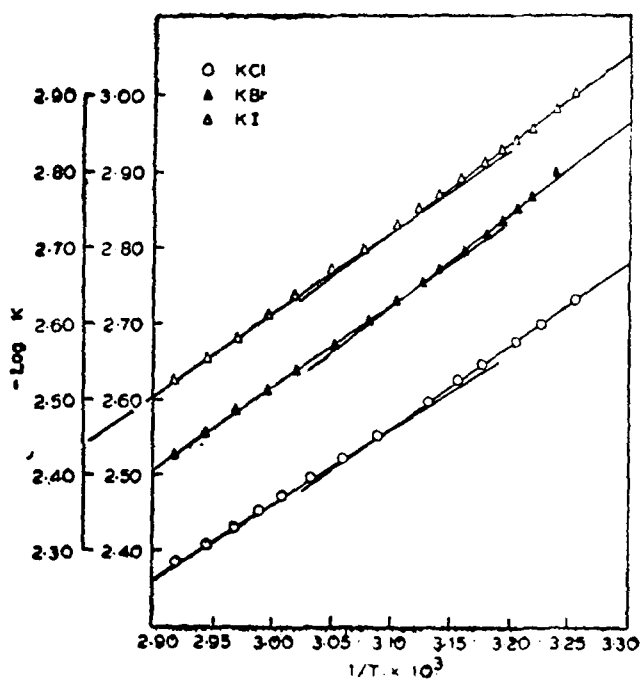


Figure 2. Plots of $-\log K$ vs $1/T$ in urea-formamide solution for potassium halides

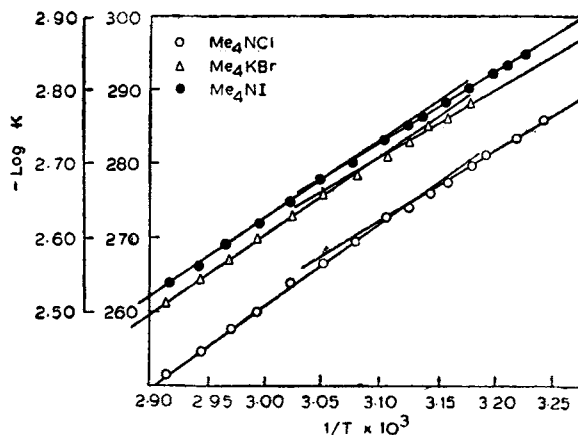


Figure 3. Plots of $-\log K$ vs $1/T$ in urea-formamide solution for tetramethylammonium halides

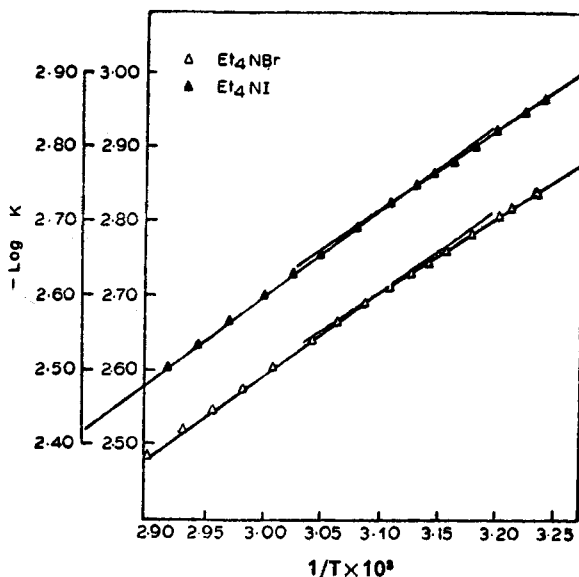
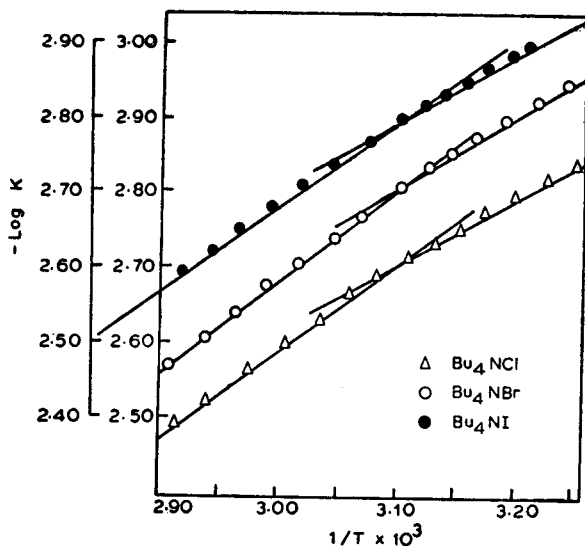


Figure 4. Plots of $-\log K$ vs $1/T$ in urea-formamide solution for tetraethylammonium halides

of a second order transition in the conductance values of the homogeneous electrolyte-solvent-nonelectrolyte systems whereas the structural behaviour of ions is projected on the divergence of the pairs of straight lines obtained at the saturation temperature, as reported in an earlier communication (Vishnu and Singh 1974).

An examination of figures 1 and 2 reveals that the divergences of the pairs of straight lines in alkali halide-urea-formamide systems are very small as compared to those obtained for sucrose-water (Vishnu and Singh 1974) and sucrose-formamide (Vishnu and Singh 1975) solutions of these electrolytes. Deviation plots (figures 7 and 8) of these electrolytes clearly show that the trend of deviation of the pairs of straight lines follows the order $\text{NaCl} > \text{NaBr} > \text{NaI}$ and $\text{KCl} > \text{KBr} > \text{KI}$. It may be recalled here

that a similar anionic behaviour was also observed for mannitol-water (Vishnu and Singh 1974) and mannitol-formamide (Vishnu and Singh 1975) systems containing



Figures 5. Plots of $-\log K$ vs $1/T$ in urea-formamide solution for tetrabutylammonium halides

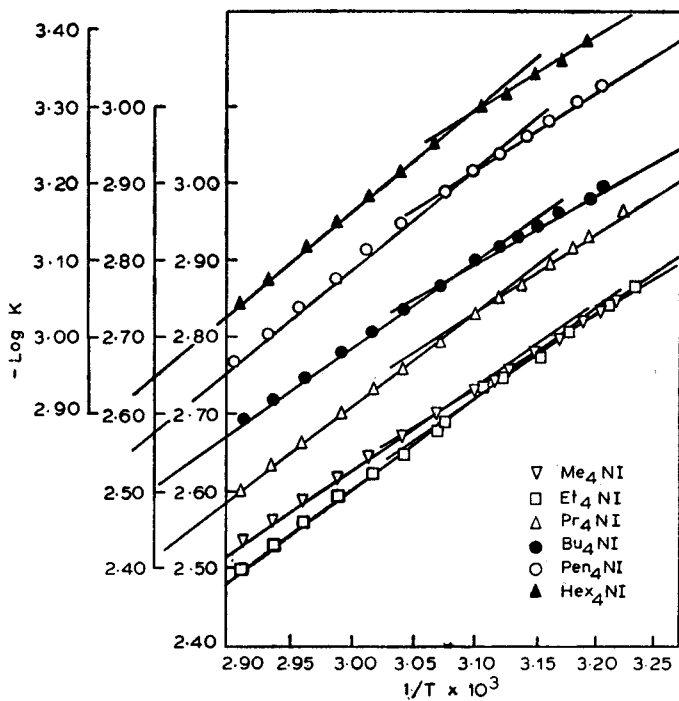


Figure 6. Plots of $-\log K$ vs $1/T$ in urea-formamide solution for tetraalkylammonium iodides.

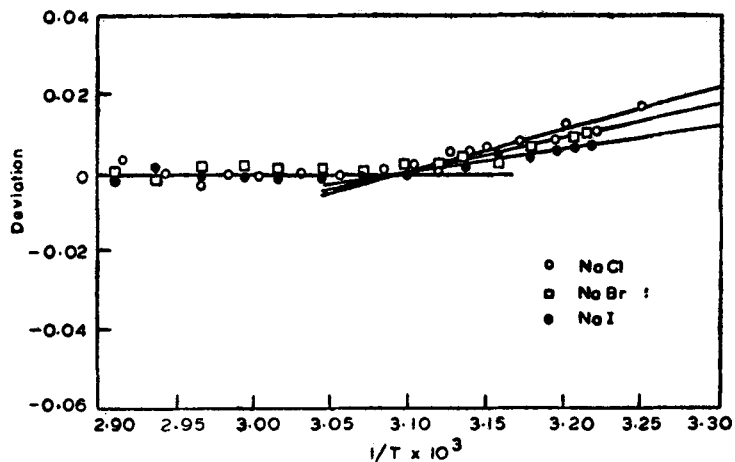


Figure 7. Plots of deviation vs $1/T$ in urea-formamides for NaX

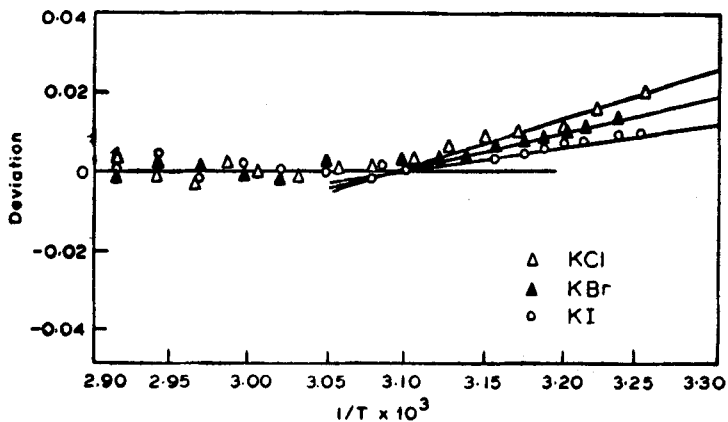


Figure 8. Plots of deviation vs $1/T$ in urea-formamides for KX

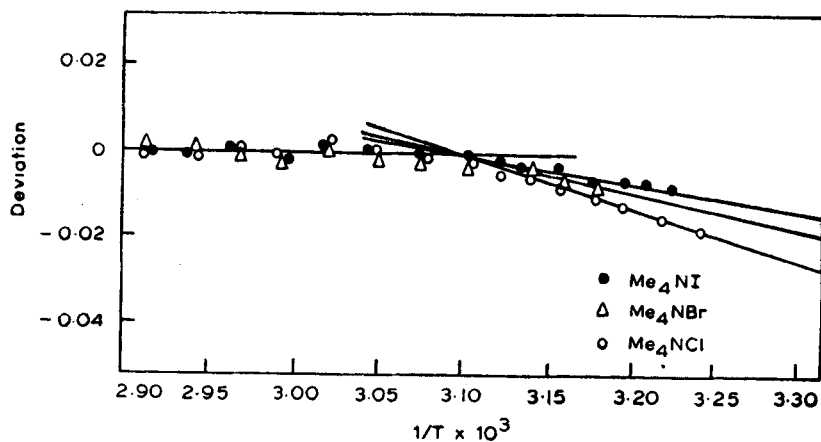


Figure 9. Plots of deviation vs $1/T$ in urea-formamides for Me_nNX

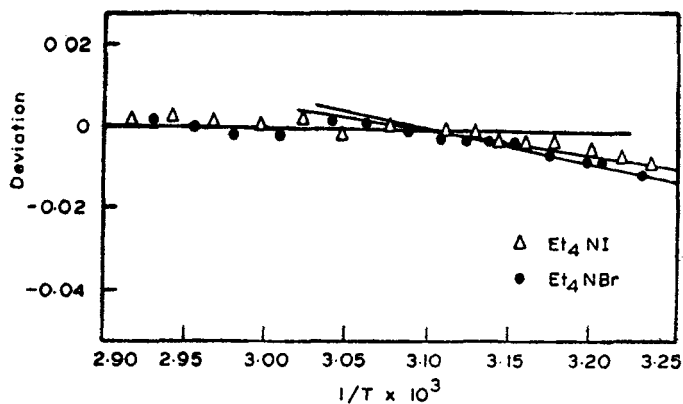


Figure 10. Plots of deviation vs $1/T$ in urea-formamides for Et_4NX

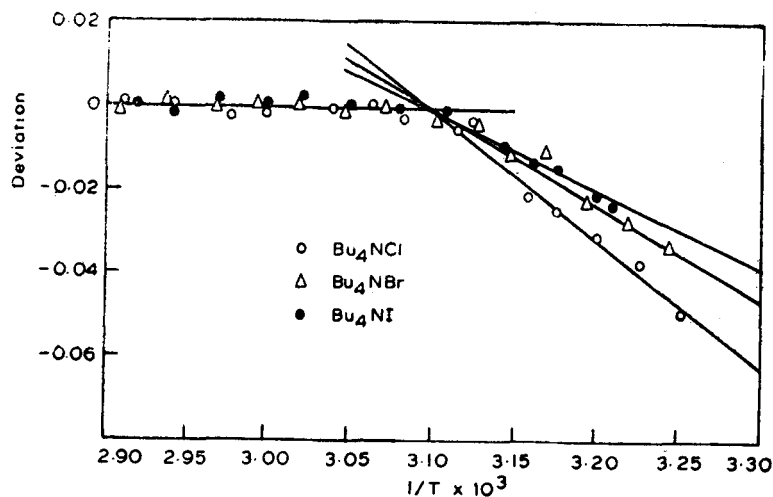


Figure 11. Plots of deviation vs $1/T$ in urea-formamide for Bu_4NX

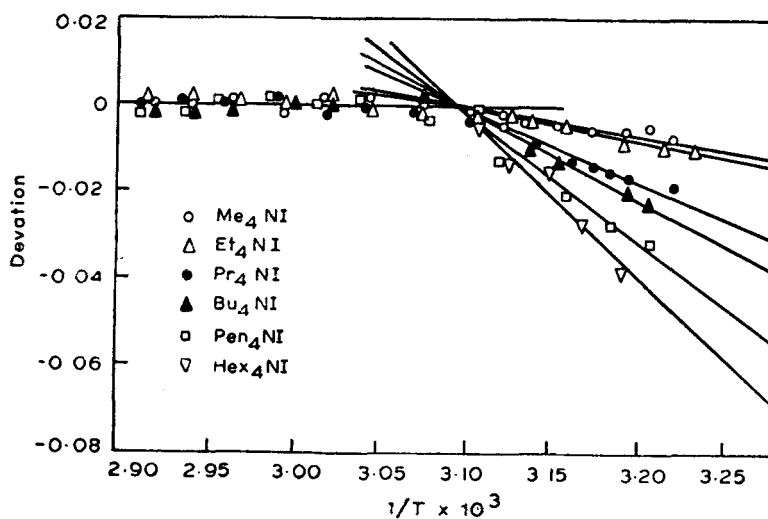


Figure 12. Plots of deviation vs $1/T$ in urea-formamides for R_4NI

some of the alkali halide salts. This behaviour of halide ions is in contrast to that obtained for sucrose solutions containing these electrolytes in both water and in formamide solutions. Trend of deviation in sucrose systems was found to be iodide > bromide > chloride (Vishnu and Singh 1974, 1975).

Pairs of straight lines are also obtained for Me_4NX , Et_4NX and Bu_4NX salts in urea-formamide solutions (figures 3-5). A peculiar difference from those of sucrose systems is noticed in these systems. While the deviation values obtained for R_4NX salts in both aqueous and formamide solutions containing sucrose as nonelectrolyte were positive, the values obtained for 'R₄NX-urea-formamide' solutions are negative. The behaviour of 'R₄NX-urea-formamide' systems is more clearly understood from the examination of figures 9-11, where deviation values of these systems are plotted against their temperature reciprocal. Another important point to note in these systems is the anionic behaviour of electrolytes in urea solutions. Divergences of the pairs of straight lines in all these systems are found to increase in the order chloride > bromide > iodide. This type of anionic behaviour is in contrast to the general behaviour of these salts in sucrose solution (Vishnu and Singh 1977 b, c).

Figure 6 depicts the $(1/T, -\log K)$ plots for R_4NI salts in urea-formamide systems. While the divergence of the pairs of straight lines in Me_4NI and Et_4NI salts are very small, a much pronounced deviation has been observed in the case of Pen_4NI and Hex_4NI systems. However, it is evident from figure 12 that the divergence of the pairs of straight lines increases with increasing chain length of the R_4N^+ ions.

Since formamide is a protic solvent having comparable H bonding capabilities to that of water (Thomas and Evans 1970) and possesses similar physical properties to that of water, as pointed out earlier, one may expect a similarity in the structural behaviour of urea in both the solvents. An exact knowledge of the structural behaviour of urea in aqueous solutions would, therefore, be helpful for the interpretation of our results. Association model of urea in aqueous solutions (Stokes 1967) and two species mixture model of urea (Frank and Franks 1968) represent this compound as acting like statistical water structure-breaker. According to these models, the structure-breaking mechanism of urea on water would be different from that of electrolytes while some other workers (Mathieson and Conway 1974) are of the view that aqueous urea solutions are similar to water but with less structure. Very recently, Visser and coworkers (1975) have reported the enthalpies of solutions of urea in binary mixtures of water and some amides at 25°C and have concluded that the interaction of urea with water and with formamide is of the same order of magnitude.

It is observed from figures 1-6 that the deviation values for sodium and potassium halides although very small are positive in nature, while deviation values for R_4NX salts are negative and the trend of deviation of the negative slope increases with increasing size of the R_4N^+ ions, as evident from figure 13 which depicts a plot of radii of these ions (Robinson and Stokes 1959) versus the negative slopes of their deviation plot. These results may be interpreted in the light of the structural behaviour of urea and those of various ions in aqueous as well as in formamide solutions. The presence of the large R_4N^+ ions would increase the degree of hydrogen bonding between the formamide molecules and enforce a shell of solvent around it in a two-dimensional structure. In saturated solutions, how does urea interact with various ions and to what extent it modifies the net structure of the system have been the main aim of our present study. Wen and Chen (1969) have reported the salting-in

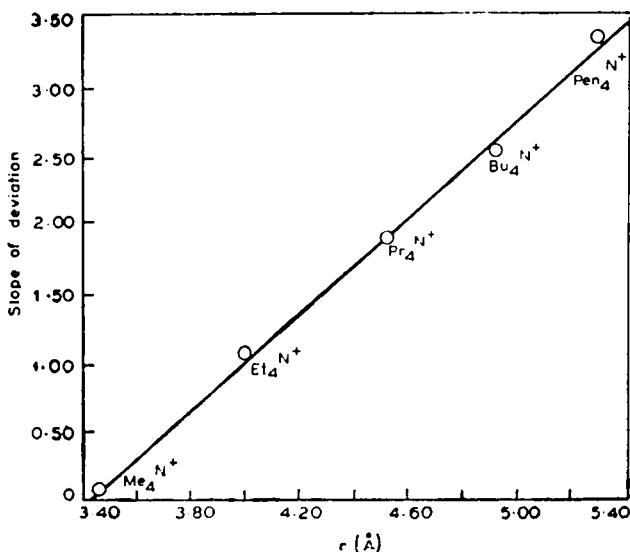


Figure 13. Variation of slope of deviation values with size of the R_4N^+ ions (Stokes' radii) in urea-formamide solution

effect of tetraalkylammonium salts towards urea in aqueous solution and found that this effect in H_2O -urea- Bu_4NBr system was much greater than that in H_2O -urea- Me_4NBr system.

The salting-in effect increases with the cationic size of the tetraalkylammonium salts and that the sodium chloride has a comparatively small effect toward urea. Our results also support the view of these workers. Examination of figures 7–12 reveals clearly the fact that sodium and potassium salts show comparatively very low salting-in effect toward urea in formamide solutions, which explains the small positive deviation observed in these systems. Negative deviation in the case of R_4NX salts in urea-formamide solution increases with increasing chain-length of the cation showing an enhanced salting-in effect with increase in cation size of the R_4NX salts toward urea in formamide.

In all the salts studied in urea-formamide solutions, trend of deviation of the pairs of straight lines has been found to increase in the order chloride > bromide > iodide. On the basis of the foregoing discussion, it is speculated that the chloride salts show more tendency of salting-in toward urea than those of corresponding bromide and iodide salts in formamide solution.

Negative derivation trend of R_4NX salts in urea-formamide solutions may be attributed to the structure-breaking properties of urea and the greater tendency of salting-in of urea by R_4NX salts and of R_4NX salts by urea. Another important difference between the behaviour of these ions in sucrose-formamide solutions (Vishnu and Singh 1977c) and in the present urea-formamide systems may be observed while taking into consideration the deviation vs $1/T$ plots of R_4NI salts in sucrose-formamide and in urea-formamide solution. In sucrose-formamide systems, positive deviation trend has been found to decrease with increase in the carbon number of the alkyl chain, while in urea systems the negative deviation increases with increase in the chain length of the cation. This type of behaviour of the R_4N^+ ions may be explained

on the basis of hydration (solvation) of sucrose and association of urea in these ternary systems.

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