

## Conductance studies on the interaction of D-glucose with alkali halides in water and formamide

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**Abstract.** The interaction of D-glucose with alkali halide in aqueous and formamide solutions has been studied by employing conductance measurements. Our results showed a break at the saturation temperature indicating a transition in the conductance values. This behaviour is explained in terms of solute-solvent interactions involved in the electrolyte-solvent-nonelectrolyte systems.

**Keywords.** Alkali halides; formamide solution; conductance studies; D-glucose.

### 1. Introduction

Studies on structural interactions in ternary systems comprising electrolyte-solvents nonelectrolyte, by physico-chemical techniques have been the subject of active-research in recent years. The conductance of electrolytes in the presence of nonelectrolytes have been measured by several workers (Longworth 1947; Steel *et al* 1958; Fredricksson 1969). The inability of the Walden rule or the Stokes law (Robinson and Stokes 1965) to interpret these results has been attributed to the interaction of the nonelectrolyte with the ions of the electrolyte (Fredricksson 1969; Fisher and Koval 1939; Hale and De Vries 1948). Nonelectrolytes like polyhydroxy compounds interact with electrolytes in solution (Longworth 1947; Fredericksson 1969). Definite adducts of many carbohydrates with salts and hydrated oxides of alkali and alkaline-earth metals have also been reported (Rendleman 1966; Moulik 1973). Equations relating the conductance of non-hydrated and hydrated insulator-type bodies (including several proteins and polyhydroxy compounds) have been obtained by Moulik (1972, 1973) and the change in conductance values has been attributed to the obstruction of the electrical migration of ions by the environmental nonelectrolyte entities. Similar significant changes in conductance of carbohydrate-electrolyte solutions were also reported by Moulik and Mitra (1973) who have also obtained association constant values for D-glucose and sucrose solutions.

It has been shown earlier by Vishnu and Singh (1974, 1975) that an abrupt transition occurs in the conductance values of homogeneous 'electrolyte-solvent-non-electrolyte' systems when the solution passes through the saturation temperature as it is cooled from the unsaturated to the super-saturated state, and pairs of straight lines intersecting one another at saturation temperature are obtained, when the values of  $-\log K$  for these systems are plotted against their absolute temperature reciprocal values ( $1/T$ ). The divergence of the pairs of straight lines is also influenced by the structure-making and breaking properties of the solutes.

In the present paper, D-glucose, a monosaccharide, having five hydrogen bonding sites and which can interact with electrolytes in solution has been chosen as a typical nonelectrolyte for our studies. These studies have been conducted in water and in formamide, the latter being structured, polar solvent of very high dielectric constant ( $109.5$  at  $25^\circ$ ).

## 2. Experimental

### 2.1. Materials

Analytical reagent grade samples of NaCl, NaBr, NaI, KCl, KBr, KI and D-glucose obtained from BDH and E Merck, were employed and used without further purification. Formamide obtained from BDH (England) was kept overnight over freshly ignited quicklime and 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

A suitably grounded Leeds and Northrup Kohlrausch slide wire assembly was used for conductance measurements. Tubular conductivity cells, temperature control and other experimental procedures were described earlier (Vishnu and Singh 1974).

The solutions were prepared by weight, in doubly distilled, demineralised, conductivity water (sp. conductivity  $\sim 10^{-6}$  ohm $^{-1}$  cm $^{-1}$ ) and in pure formamide. A  $0.1$  M solution of the electrolyte was prepared and saturated with D-glucose at  $50.0 \pm 0.05^\circ$  in an oil thermostat for 20 to 30 hr. Crystals from the mother liquor were completely separated by electric centrifugation within an air thermostat maintained at the same temperature ( $50.0 \pm 0.02^\circ$ ). The centrifugate was transferred to a conductivity cell kept at the same temperature within the air thermostat. The cell was then immersed in the constant temperature oil bath maintained at a higher temperature ( $65-70^\circ$  C). The resistance of the experimental solution was first measured at the highest temperature. The temperature was then lowered between  $2$  and  $4^\circ$  at a time and maintained for at least 30-40 min, before the resistance was measured at  $20$  to  $25^\circ$  above and below the saturation temperature. Before each measurement, no crystallisation was allowed to occur in the cell solution.

## 3. Results and discussion

Negative logarithm of the specific conductance values ( $-\log K$ ) of sodium and potassium halides in water and formamide solutions saturated with D-glucose at

$50^\circ$  plotted against the reciprocal of the absolute temperature ( $1/T$ ) are shown in figures 1 and 2. Figures 3 and 4 give the deviation values, against  $1/T$  values for these systems. The deviation values were obtained with least-square calculations. For this purpose, the best fit for the points above the saturation temperature was obtained statistically, and the theoretical values of  $-\log K$  were obtained from the regression equation for different values of  $1/T$ . The difference between the observed values of  $-\log K$  and the calculated values are termed deviations. The plots in figures 1 and 2 consisted of two straight lines intersecting in the vicinity of the saturation temperature (Vishnu and Singh 1974, 1975, 1977b). The divergence of the pairs of straight lines is markedly influenced by the cation and anions of different sizes in both water and formamide solvents. The divergence of the two straight lines in formamide solution is less than that of the aqueous solutions.

The trend of deviation of the pairs of straight lines (figure 3a) follow the order  $\text{NaI} > \text{NaBr} > \text{NaCl}$  for sodium halides-glucose-water systems while for potassium halides-glucose-water system the deviation is more or less of the same order (figure 3a), i.e., the points fall on a single straight line irrespective of the nature of

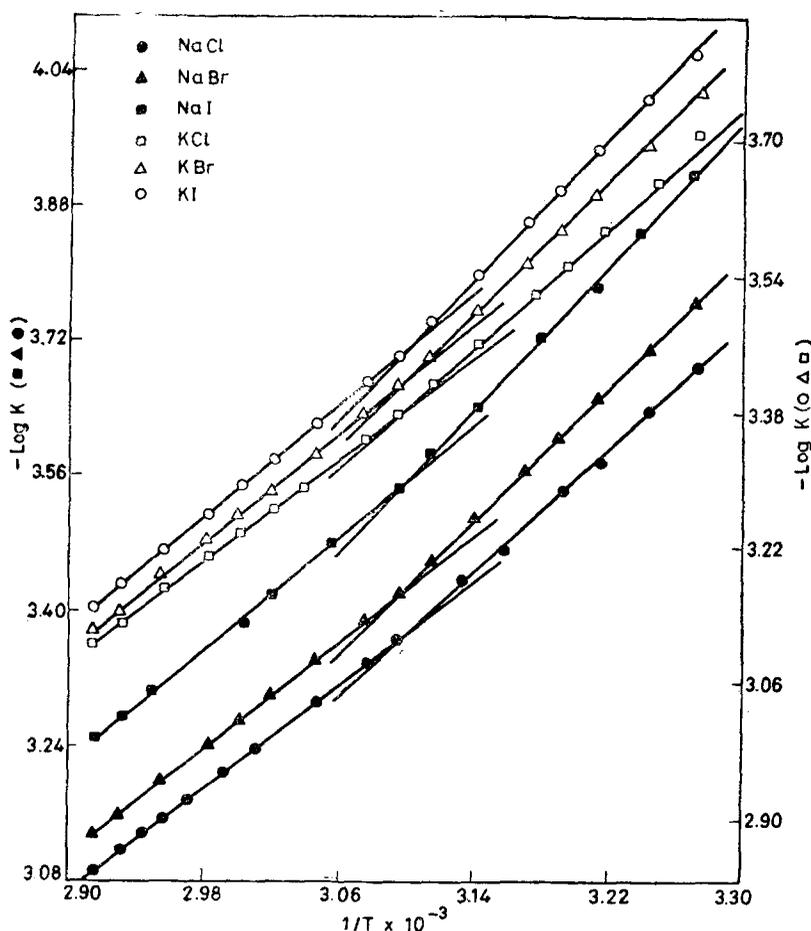


Figure 1. Plots of  $-\log K$  versus  $1/T$  for alkali halides-glucose-system.

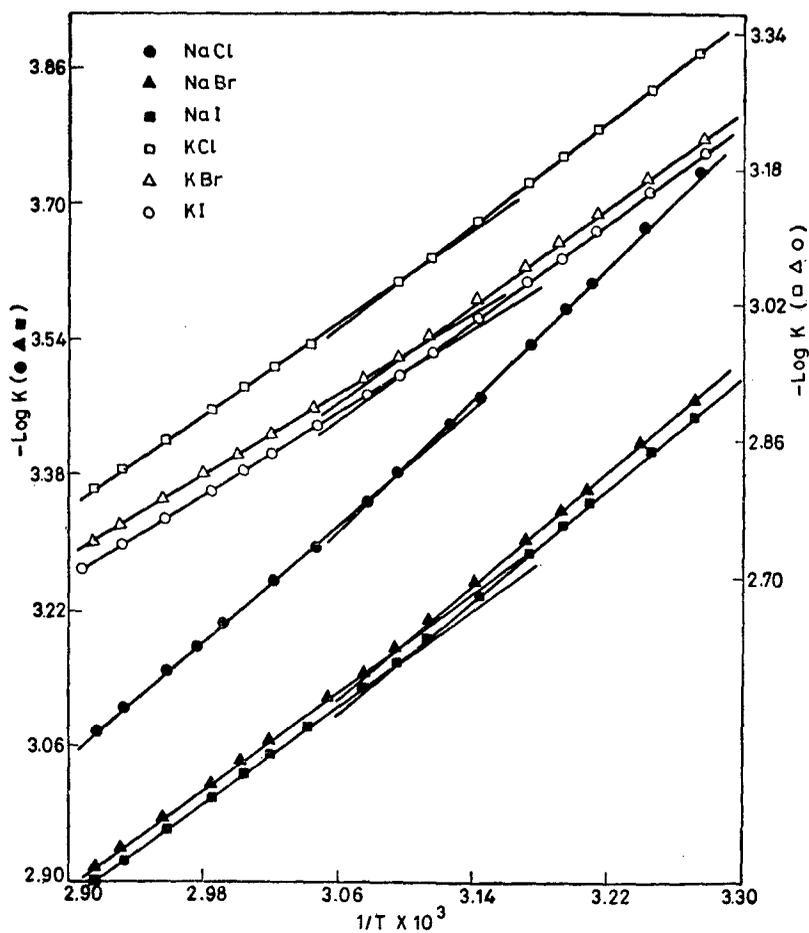


Figure 2. Plots of  $-\log K$  versus  $1/T$  for alkali halides-glucose-formamide system

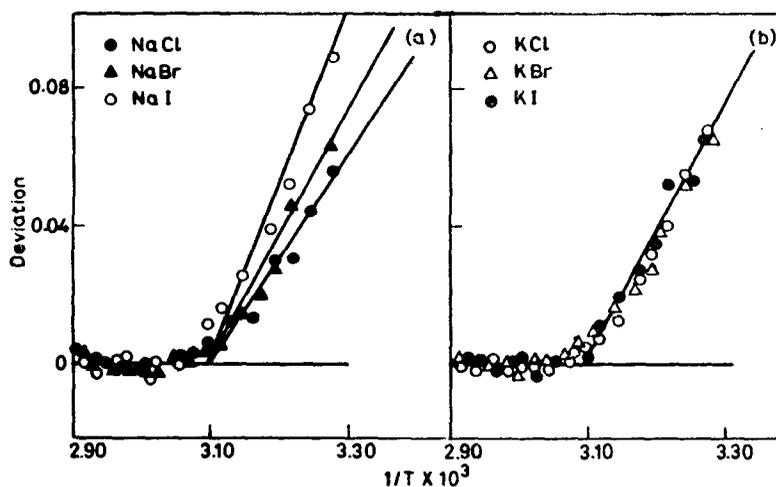


Figure 3. (a) Deviation plots for the sodium halides-glucose-water system, (b) Deviation plots for the potassium halides-glucose-water system.

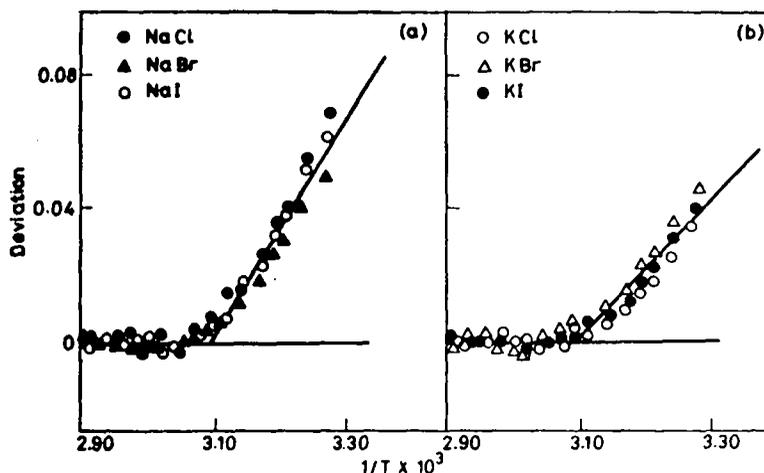


Figure 4. (a) Deviation plots for the sodium halides–glucose–formamide system, (b) Deviation plots for the potassium halides–glucose–formamide system.

the halide ions. It has also been observed that the deviation is larger in the case of sodium halides in glucose–water system than the potassium halides (figures 3a and 3b) for the above system.

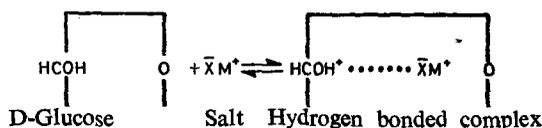
The hydration of several polyhydroxy compounds and their aggregation with water has been obtained by analysing the viscosity data of their aqueous solutions (Moulik and Khan 1977). The hydration properties of the D-glucose, which has 5 OH groups, are not related to the number of OH groups or oxygen atoms in the molecule, probably the result of the conformation which the D-glucose adopts in aqueous solution (Tait *et al* 1972). It has been shown (Angyl 1969) that D-glucose has C 1 conformation. The majority of the OH groups are in an equatorial configuration and the distance between the groups in this configuration or the same side of the ring, e.g., OH groups attached to carbon atoms 1,3 and 5 of  $\beta$ -D-glucose is 4.86 Å (Warner 1962). This agrees with the second nearest neighbour distance in water of 4.9 Å (Danford and Levy 1962) which is derived from the x-ray data for water assuming a tetrahedral structure, and supports the proposal that hydrogen bonding would be expected between water and the D-glucose OH groups (Kabayama *et al* 1958). Experiment reveals that D-glucose forms a stable monohydrate in aqueous solution (Tait *et al* 1972) which has been isolated having melting point 83° C (Heilbon and Bunbury 1965). The pyranose form of D-glucose is therefore stabilised by the interaction with water (Lemieux and Stevens 1966; Angyl 1969) and the NMR measurements of Tait and others provide evidence for the greater hydration of the 6-membered ring conformation in D-glucose and offer a description of the nature of the hydrophilic interactions. In proton magnetic relaxation studies of D-glucose in D<sub>2</sub>O (Suggett 1976) one proton (H 1 in the  $\alpha$ -form only) is susceptible to intermolecular proton-proton interactions while the remaining protons are very effectively shielded. This is consistent with the conformational and hydration properties of D-glucose.

By measuring the conductance of various electrolytes in solutions of D-glucose and sucrose, the hydration of these compounds and their association with electro-

lytes have been examined and it was found that both D-glucose and sucrose complex associate with the electrolytes (Moulik and Khan 1974). It had earlier been established that the deviations produced in electrolyte-solvent-nonelectrolyte ternary systems increases with increase in the structure-breaking properties of electrolytes (Vishnu and Singh 1974). The greater deviation values observed with alkali halides in glucose-water system than in sucrose-water reveals that D-glucose is a less structure-maker in electrolyte-solvent-nonelectrolyte system than sucrose. It is known that sucrose has 8 hydrogen bonding groups possessing two intramolecular H-bonds involving the two hydroxy methyl groups of the furano residue and side the ring O (5) and the hydroxyl O (2) of the pyranoside residue, as previously reported (Vishnu and Singh 1974).

Figures 3a and 3b indicate that the deviations are more pronounced in  $\text{Na}^+$  ions than  $\text{K}^+$  ions for alkali halides-glucose-water systems, and thus the structure-making properties of  $\text{Na}^+$  ions and the structure-breaking properties of  $\text{K}^+$  ions are effectively perturbed. As a result the  $\text{Na}^+$  ions act as a less structure-maker in glucose-water system than  $\text{K}^+$  ions and the anionic deviation trend for the above cation follow the order  $\text{I}^- > \text{Br}^- > \text{Cl}^-$ . The similar deviation for potassium halides in the potassium halides-glucose-water system (figure 3b) may be due to the smaller structure-breaking properties of  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  ions in D-glucose solution.

Our results could be explained by comparing the work of Frank and his associates (Frank and Evans 1945, Frank and Wen 1957, Frank 1965) who examined the effects of solute on the structure of water. In solution, nonelectrolytes like D-glucose may act as insulator to the permeating electric current which conducts the ions of the electrolytes (Moulik 1972). Association of many ions with nonelectrolytes (Fredricksson 1969; Fisher and Koval 1939; Hale and De Vries 1948) may further reduce their migration. The ion-nonelectrolyte association could be mainly responsible for the large decrease of the conductance values of alkali halides in D-glucose. Steel *et al* (1958) observed that the ionic mobility decreases in the presence of several polyhydroxy compounds. It has also been observed by Moulik and Mitra (1971, 1973) that D-glucose binds the electrolytes of greater charge density more strongly than sucrose even though the hydrogen bonding sites in sucrose are greater (8) than D-glucose (5). The probable reaction scheme may be depicted as following—



where  $\text{M}^+$  is a metal ion and  $x^-$  is its counter ion.

This clearly indicates that in D-glucose solution the mobility of  $\text{Na}^+$  ions is slower than  $\text{K}^+$  ions contrary to the behaviour of these ions in pure water.

The transport property is also affected by the interaction between solvent water and ionised groups as well as by the ordered structure of water around the non-polar groups (Uedaria and Uedaira 1964, 1965). The water molecule in the immediate vicinity of non-polar group like D-glucose becomes less mobile than pure water. In other words, the entropy of the aqueous D-glucose solution is less than pure

water. The interaction of the ions with the solvent molecules further affects the entropy of the system. The system undergoes a change in entropy due to change in the bulk structure as a result of molecular rearrangement of a higher order, i.e., a decrease in entropy. This decrease is similar to that noted for supercooled liquids (Kauzmann 1948). In the present study, as the system passes from an unsaturated to a supersaturated state through the saturation temperature, the decrease in entropy results in a change of the molecular geometry of glucose-water molecular assembly bringing about a change in the structure of D-glucose as well as water, thus affecting the equilibrium between  $\alpha$ - and  $\beta$ -anomers of D-glucose. In the unsaturated state the D-glucose is mostly in the  $\beta$ -form while in the supersaturated state the  $\alpha$ -anomer may predominate. The change from unsaturated to supersaturated state is brought about by a change from  $\beta$ -anomer to  $\alpha$ -anomer through the formation of a cyclic transition complex of the  $\alpha$ -anomer of D-glucose which is heavily hydrated. Addition of metal ions shifts the position of the  $\alpha$ - and  $\beta$ -anomers equilibrium towards the formation of more of  $\alpha$ -anomer (Finar 1975), thus permitting a hydration geometry which is in its molecular spacings and orientation almost compatible with those regarded as characteristics of liquid water. Such a hydration state could therefore be formed with a minimum of perturbation in the hydrogen bonding pattern of water. The presence of ions also affect this equilibrium by associating with  $\alpha$ -anomer of D-glucose (Finar 1975), which in turn affects the mobility of ions in the supersaturated state and a decrease in the conductance value. Thus the solute-solvent interactions play an important role as compared to solute-solute interaction. However there is no evidence for the self association of D-glucose molecules in aqueous electrolyte solutions. The hydration of D-glucose molecule and the change in the solvent structure brought about by the ions as well as the D-glucose molecules is mainly responsible for the change in the conductance value. This change is sensitive to rationalise the molecular interaction occurring in these ternary systems. Thus the deviation is greater for  $\text{Na}^+$  ions than  $\text{K}^+$  ions as well as an anionic effect in potassium halides-glucose-water systems showing a difference in the structural interactions for the various ions.

Deviation plots (figures 4a and 4b) for the electrolyte-glucose-formamide system show a greater deviation in sodium halides than potassium halides in glucose-formamide. The explanation of this is similar to that of glucose-water system because 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 (Vishnu and Singh 1975). One may therefore expect a similarity in the structural behaviour of D-glucose in both the solvents.

Further, the greater deviation values observed in sodium and potassium-halide-glucose-water indicate that D-glucose is less structure-maker in water-electrolyte system than in formamide-electrolyte system. These results could also be explained by calculating the activation energies of the alkali halide-glucose systems in water and formamide solutions. Table 1 gives the activation energies of conduction for each straight line computed from the Arrhenius plots ( $-\log K$  vs  $1/T$ ).

The transition in conductance values of the alkali halide-glucose systems in water and formamide has been taken in terms of different activation energies for supersaturated and unsaturated regions and the differences in the activation energies of the two homogeneous processes, termed as activation energies of transition

Table 1. Activation energy change ( $\Delta E$ ) at saturation temperature (50°) for 1 : 1 electrolytes in 'D-glucose-water' and 'D-glucose-formamide' systems.

Electrolytes	$\Delta E (KJM^{-1})$	
	D-glucose-water	D-glucose-formamide
NaCl	5.323	4.255
NaBr	6.835	4.786
NaI	7.645	5.698
KCl	3.979	3.804
KBr	5.059	4.687
KI	6.576	5.053

( $\Delta E$ ), has been attributed to the change in the solvent structure due to the presence of electrolytes and nonelectrolytes with many hydrogen-bonding sites at saturation concentration.

D-glucose molecules with five hydrogen bonding sites adhere the water as well as formamide molecules and form a bigger cluster near the ionic solutes. In super-saturated solution, these bigger structures are easily approached by the structure-making/breaking properties of ions and this is the reason for the difference in  $\Delta E$  for different ions.

It is evident from table 1 that  $\Delta E$  values for D-glucose-water systems are greater than those obtained for D-glucose-formamide systems of the corresponding ions. This is probably because D-glucose is less structure-maker in water-electrolyte than in formamide-electrolyte systems, which further supports the lesser deviation observed in D-glucose-formamide than D-glucose-water systems with alkali halides. The  $\Delta E$  values for sodium halides are higher than potassium halides in D-glucose-water and D-glucose-formamide systems, which strongly supports the less structure-making tendencies as well as the higher deviations of sodium halide than potassium halides in D-glucose-water and D-glucose-formamide systems.

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