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CONDUCTANCE STUDIES ON THE INTERACTION OF SUCROSE WITH SOME MULTIVALENT IONS IN AQUEOUS SOLUTION*

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ABSTRACT

The interaction of sucrose with some multivalent ions in aqueous solution has been studied by employing conductance measurements. A saturated solution of sucrose in water containing a known amount of the electrolyte was prepared at 50.0 ±0.05°. Crystals were separated by centrifugation at the same temperature, and the conductance of the centrifugate was measured at different temperatures between 30 and 70°. Plots of $-\log K$ *versus* $1/T$ gave a break at the saturation temperature, where two straight lines appeared to intersect one another, showing a transition in the conductance values. This transitional behavior in the conductance values of the ternary, homogeneous systems is explained in terms of solute–solvent interactions involved in the electrolyte–solvent–nonelectrolyte system. Some alkali-metal nitrates and sulfates, alkaline-earth nitrates and chlorides, and a few complexes have been studied, and their effect on the divergence of the pairs of straight lines is discussed on the basis of their glass-forming tendencies, their complex-forming nature with sucrose molecules, and the hydrogen-bonding capabilities of sucrose and the solvent water.

INTRODUCTION

During recent years, there has been an increasing interest in the behavior of electrolytes in aqueous solutions, with a view to investigating solute–solvent interactions. The concept of ions interacting with the solvent, and thus producing solvation, is familiar and has been widely used to describe the ion–solvent interactions that take place at infinite dilution. The quasi-lattice structure of the solvent is not the same after the ions have entered it; the ions produce effects of various kinds in the solvent structure. There arises a very interesting situation if molecules of nonelectrolytes are introduced into these ionic solutions. What happens if, in addition to ions and solvent molecules, some nonelectrolyte molecules are also present in the system? What will occur if, to a solution already containing nonelectrolyte molecules at

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saturation concentration, ions are added? These are important questions in the field of solution chemistry, and various workers have given different explanations[1-6].

The prediction of the properties of a multicomponent mixture of electrolytes and nonelectrolytes from as few measurements as possible is one of the long-range goals of a great deal of research. Many investigations have been made on equilibrium as well as on transport properties in ternary solutions, because of their importance to an understanding of solute–solute and solute–solvent interactions, which include change in solvent structure by the solute.

Measurements of electrolytic conductance in the presence of nonelectrolytes have been made by several workers[1,7-9]. Moulik and co-workers[4,5,10] reported the conductometric behavior of some "electrolyte–solvent–nonelectrolyte" systems, and developed equations that can relate the conductance of various nonhydrated and hydrated, "insulator" types of compounds. A continuing program has been undertaken in our laboratory to study the conductance behavior of several electrolytes in aqueous and structural, non-aqueous solvents saturated by nonelectrolytes (sucrose, D-xylose, D-mannitol, and urea) at certain temperatures. It has been shown[11,12] that an abrupt transition occurs in the conductance values of homogeneous, electrolyte–solvent–nonelectrolyte systems when the solution passes through the saturation temperature as it is cooled from the unsaturated to the supersaturated state, and pairs of straight lines intersecting one another at this temperature are obtained when the values of $-\log K$ for these systems are plotted against their temperature-reciprocal values. It has also been observed that the divergence of the pairs of straight lines is highly influenced by the structure-making and -breaking properties of the electrolytes. Conductance studies of these systems containing various simple[11,12], as well as hydrophobic[13-15], ions have been performed and reported.

Whereas only uni-univalent electrolytes had been studied earlier, the conductance behavior of different multivalent ions (both cations and anions) in aqueous sucrose solution is now reported. These electrolytes were chosen for the study on the basis of some of their characteristic features, *e.g.*, a glass-forming tendency in the concentrated range[16], and their molecular complex-forming nature with sucrose molecules[17]. Two complexes, namely bis(ethylenediamine)copper(II) nitrate and nitrato(pentammino)cobaltic sulfate, have also been studied, in order to help understand the effect, on the structural properties of the solvent, sucrose, and the salt itself, of various groups attached to cations.

EXPERIMENTAL

Salts [$Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $NaNO_3$, KNO_3, Na_2SO_4, K_2SO_4, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, $SrCl_2 \cdot 6H_2O$, and $BaCl_2 \cdot 2H_2O$] used in the present investigation were of analytical-reagent grade, obtained from BDH. All of the salts were recrystallized twice from conductivity water, and then oven-dried before use. Complexes used in the present work, namely [$Co(NH_3)_5 \cdot NO_3]SO_4$ and

$[Cu(en)_2](NO_3)_2$, were prepared as described elsewhere[18]. The sucrose used was of BDH AnalaR grade.

A suitably grounded, Kohlrausch slide-wire assembly, described elsewhere[11], was used for conductance measurements. Cylindrical cells obtained from Leeds and Northrup (U.S.A.) were used for these systems. Temperature control and other experimental procedure were as described earlier[11].

All the solutions were prepared by weight, in doubly distilled, demineralized, conductivity water (sp. cond. $\sim 10^{-6}$ ohm^{-1}.cm^{-1}). An 0.1M solution of the electrolyte was prepared, and was saturated 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 from the mother liquor were separated by electric centrifugation within an air thermostat maintained at 50.0 ±0.2°. Complete separation of the crystals from the mother liquor was ensured, and the centrifugate was transferred to a conductivity cell kept at the same temperature within the air thermostat. The cell was then immersed in an oil bath maintained at 65–70°. The resistance was first measured at the highest temperature; the temperature was then lowered by 2 to 4° at a time, and kept at

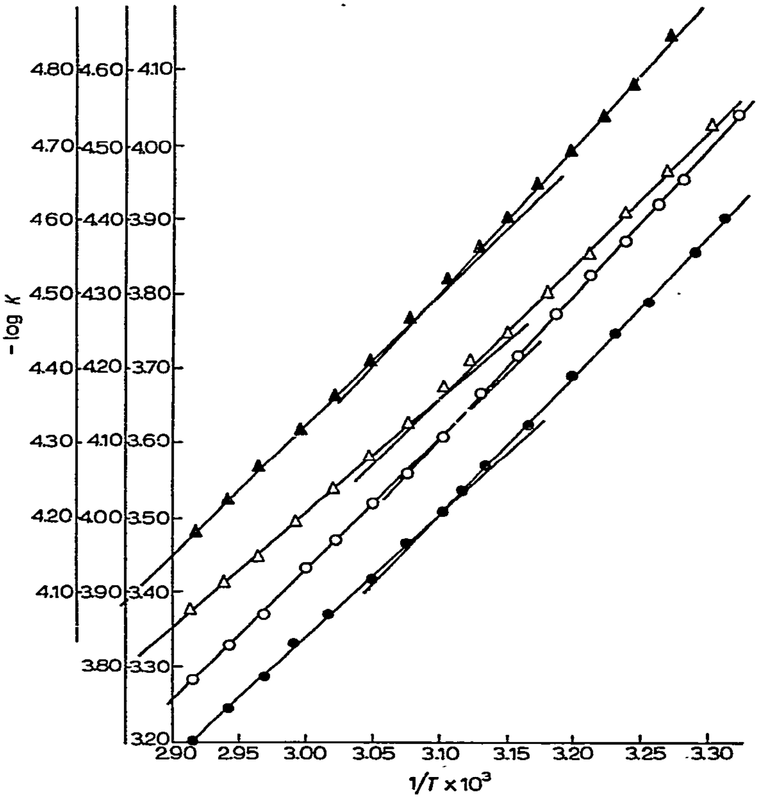

Fig. 1. Plots of —log *K versus* reciprocal of absolute temperature for alkaline-earth nitrates and complexes of Co and Cu in aqueous sucrose solution. {Key: ●, $Ca(NO_3)_2 \cdot 4H_2O$; ○, $Mg(NO_3)_2 \cdot 6H_2O$; △, $[Co(NH_3)_5NO_3]SO_4$; ▲, $[Cu(en)_2](NO_3)_2$.}

each temperature for at least 35 min before the resistance was measured. Resistances were measured at 20–25° above and below the saturation temperature. Before each measurement, it was ensured that no crystallization had occurred in the cell solution.

RESULTS AND DISCUSSION

In Fig. 1 are plotted the negative logarithms of the values of the specific conductance of two alkaline-earth nitrates, as well as of two complexes of cobalt and copper, against their temperature-reciprocal. 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 transition in the conductance values of the homogeneous system. In Fig. 4 are depicted the plots of deviation values against the temperature-reciprocal for these systems. Deviation values were obtained statistically with the help of least-square 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 the calculated values are termed "deviations".) It is evident from these figures that the divergence of the pair of straight lines is much more pronounced for the $Ca(NO_3)_2 \cdot 4H_2O$ system than for the $Mg(NO_3)_2 \cdot$

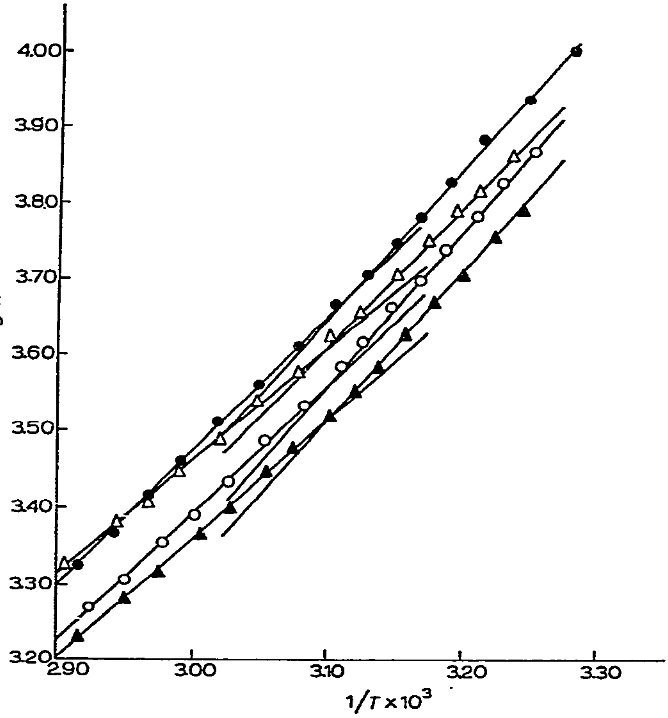

Fig. 2. Plots of $-\log K$ *versus* $1/T$ for alkaline-earth chloride–sucrose–water systems. (Key: ●, $MgCl_2 \cdot 6H_2O$; △, $CaCl_2 \cdot 2H_2O$; ○, $SrCl_2 \cdot 6H_2O$; ▲, $BaCl_2 \cdot 2H_2O$.)

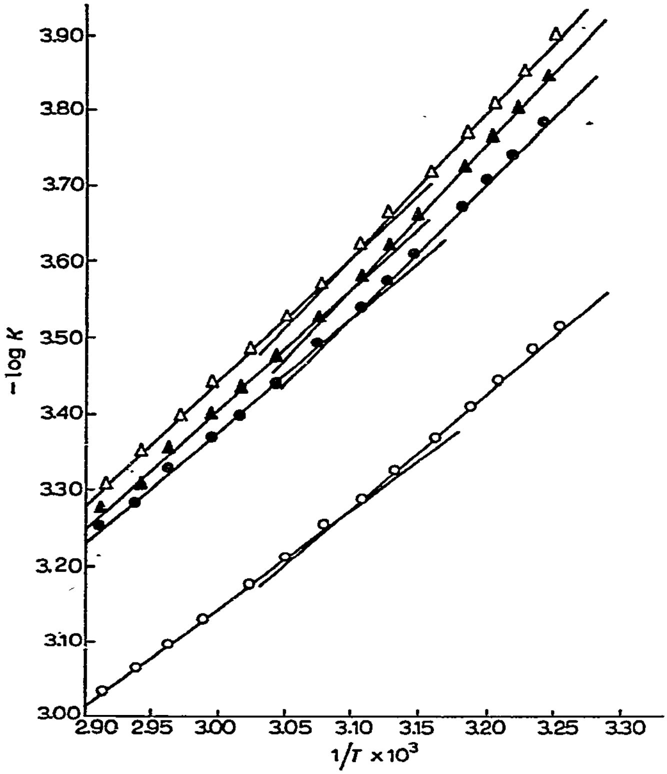

Fig. 3. Plots of $-\log K$ *versus* $1/T$ for alkali nitrate/sulfate–sucrose–water systems. (Key: ○, $NaNO_3$; ●, KNO_3; △, Na_2SO_4; ▲, K_2SO_4.)

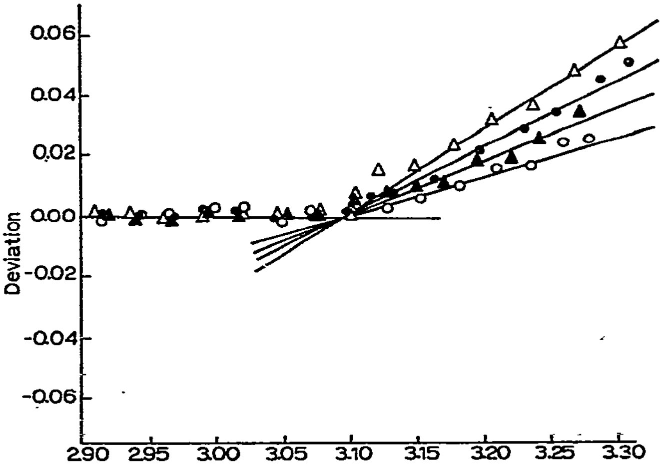

Fig. 4. Plots of deviation *versus* $1/T$ for alkaline-earth nitrates, and complexes of Co and Cu in aqueous sucrose solution. {Key: ●, $Ca(NO_3)_2 \cdot 4H_2O$; ○, $Mg(NO_3)_2 \cdot 6H_2O$; △, $[Co(NH_3)_5NO_3]SO_4$; ▲, $[Cu(en)_2](NO_3)_2$.}

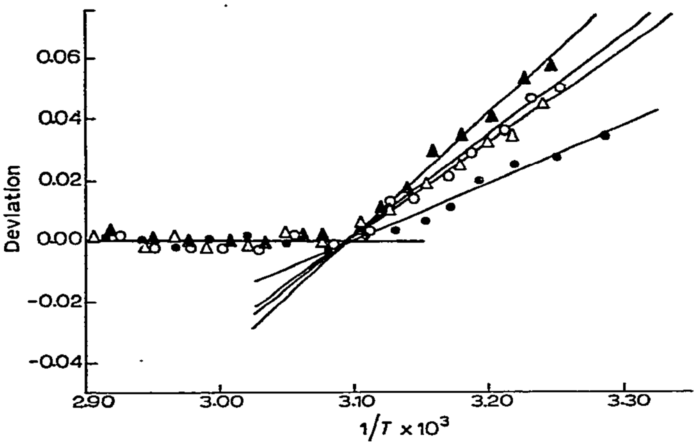

Fig. 5. Plots of deviation *versus* 1/T for alkaline-earth chloride–sucrose–water systems. (Key: ●, $MgCl_2 \cdot 6H_2O$; △, $CaCl_2 \cdot 2H_2O$; ○, $SrCl_2 \cdot 6H_2O$; ▲, $BaCl_2 \cdot 2H_2O$.)

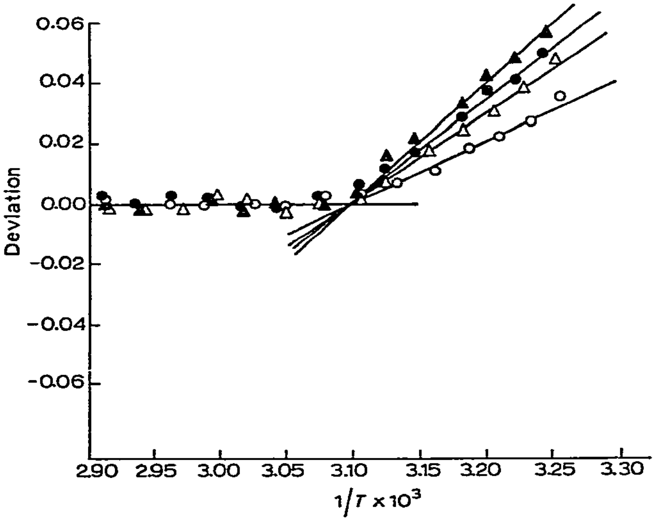

Fig. 6. Plots of deviation *versus* $1/T$ for alkali nitrate/sulfate–sucrose–water systems. (Key: ○, $NaNO_3$, ●, KNO_3; △, Na_2SO_4; ▲, K_2SO_4.)

$6H_2O$ system. The copper complex having ethylenediamine groups attached to it exhibits a smaller divergence of the straight lines compared to the cobalt complex.

Fig. 2 presents the temperature reciprocal *versus* $-\log K$ plots of alkaline-earth chlorides. In Fig. 3 are given similar plots for sodium and potassium nitrate and sulfate. Figs. 5 and 6 respectively are deviation *versus* $1/T$ plots for these systems.

The abrupt change in the conductance values of these ternary systems may be interpreted on the basis of the occurrence of a second-order transition in these systems. It has been pointed out by Kauzmann[19] that, for supercooled liquids, the entropy of the liquid may decrease with decreasing temperature at a higher rate than for the crystalline phase, and that, at considerably low temperatures, a state may be reached when the entropy of the liquid may become less than that of the crystal. To avoid this "paradox", a transition to the amorphous state may occur (in order to increase the entropy of the system) which subsequently results in an abrupt change. Similar changes have also been found to occur in heat capacity, expansion coefficient, compressibility and viscosity[20], and apparent molal-volume data[21]. In the systems in the present study, as the system passes on from an unsaturated to a supersaturated state through the saturation temperature (avoiding crystallization), it undergoes change in the entropy due to a change in the solvent structure and to cluster formation.

The results may be further explained by taking into account structural features of the solvent-water, hydrogen-bonding capabilities and hydration characteristics of the sucrose molecule, and the structural behavior of various ions in aqueous solution. Water is known to be a highly associated liquid. The presence of a non-electrolyte such as sucrose tends to strengthen the hydrogen bonds between the water molecules near the large solute, and a relatively large "iceberg" is effectively formed around them. Structure-making/-breaking properties of various electrolytes influence this model to different extents and that explains the variation in the divergence of pairs of straight lines for different systems.

A final aspect of such a transition concerns the possibility of cooperative changes in the solvent structure induced by the solute[22]. The physical evidence of such changes consists in relatively abrupt changes in the slope or curvature of the graph of various properties.

The effect of various alkali halides on the structure of aqueous sucrose solution has already been discussed[11]. Taking into account Figs. 3 and 6, the concept that the structure-making properties of alkali halides decrease with an increase in their cationic radii[23] is further supported. It had earlier been established that the divergence of the pair of straight lines in these ternary systems increases with increase in the structure-breaking properties of the electrolytes. For ions of an alkali metal having both nitrate and sulfate anions attached, divergence of the pair of straight lines is more pronounced in the case of potassium (K^+) ions than of Na^+ ions. Departure of the lines for sulfates is comparatively more pronounced than for nitrates, and this may also be attributed to the structure-breaking properties of SO_4^{2-} ions.

On considering the system alkaline-earth chloride–sucrose–water, divergence of the pair of straight lines is found in the order $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. To attribute structure-breaking behavior to the larger alkaline-earth cations appears, at least superficially, to be in conflict with conclusions drawn from other measurements. The viscosity B coefficients for these ions are positive. Therefore, it would have been expected that they would behave as structure makers. However, in terms of structural influences, many other properties do not necessarily parallel viscosity effects. On the basis of their results for entropies of transfer between heavy and normal water for alkaline-earth chlorides, Greyson and Snell[24] tentatively concluded that alkaline-earth chlorides behave as structure-breaking salts. They found the order of structure-breaking influence to be: $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. Our results are in accord with these results. The results are further supported when the deviation plots of alkaline-earth nitrate–sucrose–water systems are considered; these show a greater divergence of the pair of straight lines for calcium nitrate than for magnesium nitrate.

Moreover, division of the influence of disolved ions on solvent structure into long- and short-range ordering has been widely discussed by Kaminsky[25], who proposed that the viscosity effects result from a combination of the influence of ions on the bulk structure of the solvent as well as on the primary solvent. Thus, high charge-density and such strongly solvating species as magnesium or lithium also orient water at a distance and are structure-makers, whereas the weakly hydrating potassium or chloride ions compete for water molecules with the structured component of the bulk solvent, and, in so doing, cause disruption of structure.

On considering the behavior of cobalt and copper complexes, a pronounced deviation is observed in the case of nitrato(pentammino)cobaltic sulfate, whereas the departure from straight lines for the bis(ethylenediamine)copper(II) nitrate–sucrose–water system is comparatively very small, indicating that this complex possesses structure-making tendencies. Perhaps this type of structure-promoting effect of this complex is due to the presence of the chelating group (ethylenediamine), whereas the cobalt complex, having an open pentammine group attached to it, behaves as a structure-breaker.

It is concluded that both ion–solvent and electrolyte–nonelectrolyte interactions are predominant in these systems, and that hydration of ions and the hydrogen-bonding tendencies of sucrose and water also play an important role.

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