TRANSITION PHENOMENA AT SATURATION TEMPERATURE. STUDIES ON ELECTROLYTIC CONDUCTANCE OF ALKALI HALIDES IN AQUEOUS SYSTEMS

VISHNU AND AWADHESH K. SINGH

[Department of Chemistry, University of Gorakhpur, Gorakhpur (U.P.), India]

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ABSTRACT

A plot of negative logarithm of the electrical conductance (K) vs reciprocal of the absolute temperature (T) shows the existence of the transition in the systems ‘Electrolyte-Sucrose-water’, ‘Electrolyte-Mannitol-water’, and ‘Electrolyte-Xylose-water’. A saturated solution of sucrose/mannitol/xylose containing a known amount of an electrolyte was prepared at a temperature of $50.0 \pm 0.05 \degree C$ and the crystals were separated by centrifugation at the same temperature. The conductance of the centrifuge was measured in a tubular conductivity cell at different temperatures in the range between 30 \degree C to 70 \degree C. The plot of $\log_{10} K$ vs $1/T$ showed a break at the saturation temperature, the point where two straight lines appeared to intersect. The transition can be explained on the basis of change in the water structure due to the presence of ‘structure-breaking’ and/or ‘structure-making’ ions. These sucrose, xylose, and mannitol molecules due to the presence of a number of hydrogen bonding sites contribute largely toward the build up of big structures in the supersaturated state. These structures crumble as the system undergoes the transition at the saturation temperature. Different electrolytes produced more or less similar effect.

INTRODUCTION

ABRUPT transitions in homogeneous systems are normally unexpected during gradual changes in either the composition or in the physical factors such as temperature or pressure. As typical exceptions we have $\lambda$-point of liquid helium as well as the micelle formation in soap solutions. Schneider and co-workers have shown that absorption by Xenon$^1$ and sulphur fluoride$^2$ shows a maximum, as the system passes through the neighbourhood of the

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critical point although there is no heterogeneity developed in the system. This has been accounted for as caused by clustering when the substance is at low concentrations and due to development of holes when the substance is at high concentrations. Similarly, the ultrasonic absorption, the molar heat capacity at constant pressure and the viscosity of a binary liquid mixture are found to be maximum in the neighbourhood of the critical solution temperature, although there is no development of heterogeneity. The interesting results of Dodd and Hu Pak Mi have shown that the viscosity of phenyl ether shows a transition when the liquid passes through the melting point, while cooled (avoiding solidification) from the ordinary liquid to the supercooled state.

Recently, Fred Vaslow has found a critical type of transition in the case of the relationship for the apparent molal volume data. Vaslow has tentatively concluded on the basis of the evidence presented that an effect or transition does occur. The transition occurs at different concentrations for different salts and hence is not indicative of any single type of solvent group. Earlier work by Doss, Gupta and Vishnu has shown that an abrupt transition also occurs in the electrical conductivity when molasses pass through the saturation temperature, as it is cooled from the unsaturated state to the supersaturated state. In a previous communication, the author has studied the electrical conductivity of aqueous solutions of sucrose containing electrolytes over a temperature range (30°C to 70°C) covering the saturation temperature. The data obtained for 'LiCl-sucrose-water' and 'KCl-sucrose-water' systems showed the existence of a definite transition at the saturation temperature.

A continuing programme has been undertaken in this laboratory to extend these studies to a number of systems containing sucrose, xylose, and mannitol as typical nonelectrolytes, and to observe the effect of different electrolytes in relation to their aqueous solutions.

**Experimental Section**

*Materials.*—Sucrose and xylose were obtained from British Drug Houses, and the reagent grade material was used without further purification. Mannitol used was of Merck's reagent grade.

Potassium bromide used in the present work was obtained from E. Merck and Co. (Germany), while other electrolytes like potassium chloride, potassium iodide, Sodium chloride, sodium bromide, and sodium iodide were of BDH analytical reagent grade.
All the solutions were prepared by weight using double distilled demineralized conductivity water as the solvent.

Apparatus.—The bridge equipment consisted of Leeds and Northrup Kohlraush slide wire apparatus (model 4258), a Hewlett-Packard (model 200 AB) variable frequency oscillator with a transformer and oscillator, and one 10,000 Ohm decade resistance box (graduated in 0.1 Ohm intervals). The bridge arrangement was made according to Jones's design. A pair of Leeds and Northrup headphones was used as the null detecting device.

A special type of tubular conductivity cell (Fig. 1) was employed for the entire conductivity measurements. The cell was made of pyrex glass tube (B) of small and uniform diameter (5 to 7 mm) containing thick platinum wires (A₁ and A₂) as electrodes and was open at both the ends. It was placed in an oil thermostat. The temperature was maintained constant correct to ± 0.05° C with the help of a mercury-toluene thermoregulator and electronic relay. Resistance measurements were done at 1000 cycles/sec. (no change in resistance with frequency was recorded during a check measurement upto 10,000 cycles). The platinum electrodes of the cell were platinized following the method of Jones and Bollinger. The cell constant was determined in the usual manner employing KCl solutions. Before each run the cells were cleaned with conductivity water, steamed out for 0.5 hour and dried at 110° C in an oven.

The electrolyte was dissolved in the required quantity of conductivity water and the resulting solution was saturated with sucrose/xylose/mannitol by keeping the mixture stirred at 50° C in the thermostat maintained correct to ± 0.05°. Sufficient time, say 20 to 30 hours, was given for the complete saturation of the solution at this temperature. Crystals of the nonelectrolyte and mother liquor were separated by centrifugation of the solution at about 50° C and the centrifuge was sucked into the tubular cell through its lower opening. Both ends of the cell were properly stoppered and it was then immersed in the electrically maintained oil thermostat, conductivity measurements were first taken at the highest temperature. The temperature of the thermostat was then lowered 2 to 4° C at a time and maintained at each temperature for 20 to 30 minutes, before measuring the resistances of the experimental solution in the cell. Since the cell had a small diameter, the temperature equilibrium was quickly attained. Resistances were measured 25 to 30° above and below the saturation temperature after an interval of 2 to 4°. Sufficient care was taken that no crystallisation in the cell solution may occur during the experiment.
RESULTS AND DISCUSSION

The results obtained are shown in Figs. 2, 3, 4 and 5. Negative logarithm of specific conductance has been plotted against the reciprocal of abso-
lute temperature. The particular plot was chosen in conformity with Andrade's equation for variation of viscosity with temperature and the well-known inverse dependence of conductance on viscosity. It is found that the plots consist of pairs of straight lines intersecting in the neighbourhood of the saturation temperature. This is established beyond question by fitting the best straight lines to the points above the saturation temperature and plotting deviation from this line as shown in Figs 6, 7, 8 and 9. The
regression equation was first determined statistically for the points above the saturation temperature. The theoretical values of the \(-\log_{10} K\) were obtained from the regression equation for the different values of 1/T. The differences between these values and the experimental values are plotted in Figs. 6, 7, 8 and 9 against the reciprocal of absolute temperatures. These plots indicate a definite transition at the saturation temperature.

Figure 2 shows the plots of ‘potassium halide-sucrose-water’ solution saturated at 50.0 ± 0.05°C. A pair of straight lines intersecting each other at the saturation point shows the existence of a transition in each cases. In the system ‘potassium halide-sucrose-water’, the deviation of the lines are more or less of the same order, as evident from the plot 6 of their deviation versus 1/T. All the points belonging to the three different systems, however, fall on the same line.

Figure 3 shows the plots of ‘sodium halide-sucrose-water’ systems. It is evident from Figs. 3 and 7 that the deviation in sodium iodide system is the most pronounced one and it follows an order, NaI > NaBr > NaCl.

Figure 4 gives the plots of ‘potassium halide-mannitol-water’ systems. In these systems, the order is KCl > KBr > KI. The deviation plots of ‘potassium halide-mannitol-water’ systems (Fig. 8) depict these effects in a pronounced way.

Figure 5 gives the plots for ‘KI-sucrose-water’, ‘KI-xylose-water’ and ‘KI-Mannitol-water’ systems. All the three plots show definite transition at the saturation temperature. Depending upon the availability of the H-bond sites, the transition follows the order sucrose > xylose > mannitol. Moreover, because of the high conductivity of mannitol solution itself, the change in conductivity was not much pronounced for 2 to 4°C change in the temperature.

The results obtained by our studies could possibly be explained on the basis of the theoretical considerations of the following:

(i) Structure of water,
(ii) Structure of aqueous solution,
(iii) Structure of aqueous solutions containing nonelectrolytes.

Structure of water.—The actual structure of liquid water remains unknown. Although a number of models of the structure of liquid water have been proposed, so far none have been found to be entirely satisfactory, in the sense of being able to account for all the facts known about liquid
water. The models of water structure can be divided roughly into two types: the uniformistic or continuum models, which assume that only one type of molecule corresponding to the average of all the molecules need be considered and mixture models which require the existence of two or more structural units.

![Figure 3](image-url)  

Fig. 3. Plot of $-\log_{10}K$ vs. $10^3/T$ for the system ‘Sodium halide-sucrose-water’.

- NaCl-Sucrose-water
- NaBr-Sucrose-water
- NaI-Sucrose-water
The uniformistic continuum type of models of liquid water structure include the bent or distorted H bond model of Pople and the related random network model of Bernal. Neither of the two models have been examined in detail and both merit further attention.

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**Fig. 4.** Plot of $-\log_{10} K$ vs. $10^3/T$ for the system ‘Potassium halide-Mannitol-water’,

- KCl-Mannitol-water
- KBr-Mannitol-water
- KI-Mannitol-water
The mixture models of the structure of water can be subdivided into network/cluster models and cell/cage models. In the network/cluster type of model, liquid water is regarded as a mixture of 'clusters' of water molecules, each internal molecule being linked to four others, and single
water molecules which occupy the space between the clusters (Fig. 10). The clusters are continuously being built up and broken down and single molecules are added on and split off in a rapid interchange. For regions with four co-ordinated structure (Fig. 10), an average of 91 water molecules per cluster was calculated at 0°C, decreasing to about 25 at 70°C. Two effects may play an important role in the formation of these short lived clusters of water molecule. One is the co-operative behaviour in the formation and breakdown of H-bonded structure, the total energy of the H-bonds inside a cluster being greater than the sum of the individual \( O' \ldots H \ldots O'' \) bonds between the constituent water molecules. The other effect is that the polarization of one lone electron pair accompanying the formation of a H-bond between two water molecules leads to the polarization of all the other electron pairs in the two molecules, facilitating further H-bonding with neighbouring water molecules. Thus there may occur a co-operative resonance effect over a large group of molecules which resonate together to form a 'flickering iceberg'.

![Graph](image-url)

Fig. 6. Deviation plot for the system, 'Potassium halide-sucrose-water'.
- KCl-Sucrose-water
- KBr-Sucrose-water
- KI-Sucrose-water
In the second type of mixture model, the water is assumed to contain two components. One of them is a bulky, ice-like framework of tetrahedrally co-ordinated water molecules. The other component consists of single water molecules in the cavities of this framework, where they rotate without restraint because they do not participate in any H-bonding.

Evidently, the molecular processes occurring in liquid water and in aqueous solutions are complex. It is likely that a model able to correlate and account for all the known properties of water will include some of the salient characteristics of both the mixture and continuum type models.

The structure of aqueous solutions.—The most familiar interaction between a solute particle and water is the hydration of ions. A water molecule can be represented as a dipole and it tends to orient towards the centre of positive or negative change. The water molecules in the vicinity of charged particles are kept in the potential well of the ion-dipole interaction, the ion

![Graph](image-url)

**Fig. 7.** Deviation plot for the system 'Sodium halide-sucrose-water'.
being the anion or cation of the dissolved salt, and the dipole, the water molecule. The depth of this potential energy minimum corresponds to the energy of hydration. This first layer of water molecules around an ion, the first hydration shell, is an ordered or 'structural' region since the molecules within it are more rigidly oriented with respect to one another than in pure water. The H₂O molecule in the second hydration shell will be more mobile than in the pure water and hence this region is known as a region of structure-breaking’.

Considerable attention has recently been given to the Gurney cosphere model¹⁸ for structural interactions in aqueous systems.¹⁹, ²⁰, ²¹ The Gurney model in its simplest terms states that the solute particles in aqueous systems are surrounded by spherical shells of solvent modified in structure from that in the pure solvent.

Division of the influence of dissolved ions on solvent structure into long and short-range ordering has been discussed at length by Kaminsky,²² who
proposed that viscosity effects resulted from a combination of the influence of the ions on the bulk structure of the solvent as well as on primary solvation. Thus, high charge density and strongly solvating relatively small species like Li\(^+\), Na\(^+\), H\(_2\)O\(^+\), Ca\(^{2+}\), Ba\(^{2+}\), Mg\(^{2+}\), Al\(^{3+}\), HO\(^-\), F\(^-\) and others, such as tetra-alkylammonium ions, acetate ions and formate ions orient water at a distance and are strong 'structure-makers', while weakly hydrating K\(^+\), NH\(_4\)^{+}, Rb\(^+\), Cs\(^+\), Cl\(^-\), Br\(^-\), I\(^-\), NO\(_3\)^{−}, ClO\(_4\)^{−} ions compete for water molecules with structured component of the bulk solvent and in so doing cause structure disruption.

![Deviation plot for the system 'KI-Non-electrolyte-water'.](image)

**Fig. 9.** Deviation plot for the system 'KI-Non-electrolyte-water'.

- ■ KI-Sucrose-water
- ▲ KI-Xylose-water
- ○ KI-Mannitol-water

It appears not unreasonable that the hydration of small ions could be consistent with normal hydrogen bonded structural groupings of liquid water.\(^{23}\) Assuming now that this is so, some possible speculative conse-
quences can be discussed. Firstly, as to the nature of the structural groups, water has an open structure with many holes. It is possible that structure forming ions as Li$^+$ or Na$^+$ can fit into these holes, distorting but not disrupting the structure, while potassium and larger ions which are structure-breaking would presumably not fit into these holes. An example of such a hole, which may exist in liquid water and which seems compatible with the hydration requirements of Na$^+$ ion, is given by the 5-membered hydrogen-bonded ring that occurs in the dodecahedron-based structure suggested by Pauling.\textsuperscript{34} For the hydrogen bond distance of ice, the ring has a centre opening just long enough for an Na$^+$ ion but not for a K$^+$ ion.

Assuming that the primary hydration structure is only slightly compressible and that outside this structure the electrostriction for each ion is about the same, then according to these ideas H$^+$, being a structural unit, would have the largest volume, Li$^+$ having some structural properties but mainly fitting into holes, would have the next largest volume, and Na$^+$, fitting only into holes, would have the least volume.
Structure of aqueous solutions containing non-electrolytes.—The presence of non-electrolytes or large organic ions tends to strengthen the hydrogen bond between the water molecules near the large solute and a cage or ‘iceberg’ is effectively formed around them. In the present work, sucrose,

![Diagram of sucrose molecule showing two intramolecular H-bonds](image)

**Fig. 11.** The structure of sucrose molecule showing two intramolecular H-bonds $0(1)'-H-0(2)$ and $0(6)'-H-0(5)'$. 
xylose and mannitol with a number of hydrogen-bonded sites are used as typical non-electrolytes. Sucrose with 8 hydrogen bonding groups has two intramolecular H-bonds involving the two hydroxy methyl groups of the furanoside residue and the ring O(5) and the hydroxyl O(2) of the pyranoside residue as is evident from Fig 11. Mannitol has got six hydrogen bonding sites while only four hydrogen bonding groups are present there in xylose.

According to Snell and Greyson, saturated hydrocarbon moieties increase the degree of hydrogen bonding among neighbouring water molecules in proportion to their carbon number, as well as they increase the apparent structuring in water. Thus, sucrose, mannitol and xylose all the three in their saturated state will definitely increase the water structure in proportion to their carbon number and respective hydrogen bonding sites.

Keeping the above discussion in view, the transition in electrolytic conductance is to be interpreted as due to the transition occurring in viscosity of the system, presumably due to the sudden increase in the development of large clusters of solute molecules below the saturation temperature.

A final aspect of such transition concerns the possibility of co-operative changes in the solvent structure induced by the solute. The physical evidence of such changes consists in relatively abrupt changes in the slope or curvature of the various properties. Such abrupt changes probably cannot be due to a site filling effect in which the solute molecules enter a lowest energy group of sites and the transition occurs when this lowest set is filled. In order that there be a sharp separation of the two types of sites, a large difference in the free energy per site is necessary.

The explanation for this type of transition offered is that the solute molecules enter spaces in water structure without destroying the structure. As the concentration of solute increases, the structure becomes unstable and eventually is transformed in a co-operative manner. As the temperature increases, the degree of order decreases and, in a sense, the structure gradually melts. As a consequence a transition occurs.

The results can further be interpreted on the basis of these experimental evidences. In the ‘potassium halide-sucrose-water’ system transition is more or less of the same order, this is probably due to the smaller structure breaking properties of K+, Cl−, Br−, and I− ions. Deviation is much pronounced due to the eight hydrogen bonding sites of the sucrose molecule. In Fig. 3, we have ‘sodium halide-sucrose-water’ systems. Transition is of the order NaI > NaBr > NaCl which may be attributed to the
structure-making behaviour and small size of Na$^+$ ions. Na$^+$ ions according to hole theory are fitted in the holes among the water structure without any disruption of structure.

In the case of 'potassium halide-mannitol-water' systems, transition is of the order KCl > KBr > KI. This may also be explained on the basis of structure-breaking behaviour of K$^+$ and Cl$^-$, Br$^-$ and I$^-$ ions. Order is probably reversed due to the presence of 6 hydrogen bonding sites and high conductivity of mannitol itself. In Fig. 5 plots of 'KI-sucrose-water', 'KI-xylose-water' and 'KI-mannitol-water' systems are depicted. Transition is of the order sucrose > xylose > mannitol, which could be explained from the above considerations.

Concluding, our results could possibly be explained by inferring this transition, as a critical type of transition. As pointed out earlier, this type of transitions are not very uncommon. The water structure changes as we pass from the unsaturated to supersaturated state. Largely, the interaction is of solute-solvent type. Clusters or structures are being formed and broken, involving the hydration of sucrose/xylose/mannitol molecules. However, the role of electrolytes is yet to be understood. It may further involve some electrostatic interaction among the ions, but such effect is not clearly understood.

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REFERENCES


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27. ——— Ibid., 1969, 73, 3745.