Carbohydrate Research, 70 (1979) 13–18
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ACTIVATION ENERGIES OF TRANSITION FOR SOME ELECTROLYTE–SUCROSE–WATER SYSTEMS, FROM CONDUCTANCE DATA

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(Received May 11th, 1978; accepted for publication, May 31st, 1978)

ABSTRACT

The conductance behavior of some electrolyte–sucrose–water systems has been investigated at several temperatures above and below the saturation temperature (50°). Arrhenius plots (—log K *vs.* $1/T$) gave a pair of straight lines intersecting one another at the saturation temperature, showing a structural transition in the homogeneous system. Activation energies of conduction have been computed for the two processes, and the difference in activation energies is attributed to the activation energy of transition.

INTRODUCTION

During the past few years, thermodynamic and transport properties of mixed electrolyte solutions have been extensively investigated[1–4], both theoretically and experimentally, but not for electrolyte–nonelectrolyte systems. A better understanding of such ternary, aqueous systems necessitates systematic investigations of model systems under various conditions. Model solutes or cosolutes should include ionic and nonionic components known to have vastly different effects on the structure of water. The most typical hydrophilic and hydrophobic electrolytes are probably[5] NaCl and Bu_4NBr. Of the nonionic components, sucrose appears to be a strong structure-maker for water, as it has eight hydrogen-bonding sites[6].

In this laboratory, we have undertaken a continuing program to study the conductance behavior of various electrolytes in aqueous solutions saturated by nonelectrolytes (mainly sucrose) at temperatures between 30 and 70°. A rather new technique has been developed for studying solute–solvent interactions in homogeneous, ternary systems that employs conductance measurements[7–10].

During these studies[7–10], an abrupt transition in the conductance value of the homogeneous, ternary system was found to occur in the vicinity of the saturation temperature, as the system passes from an unsaturated to a supersaturated state (through the saturation temperature). Pairs of straight lines intersecting one another at the saturation temperature are obtained when the values of —log (specific conductance) 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 structural properties of different electrolytes.

In this communication, the activation energies of conduction for supersaturated and unsaturated states have been computed from the Arrhenius plots (—log *K* *vs.* 1/*T*) for the two straight lines. The differences in the activation energies of the two processes of conduction at 50° for several electrolyte–sucrose–water systems have been computed, and are now reported.

EXPERIMENTAL

The electrolytes employed in the present investigation, *viz.*, alkali halides (NaCl, NaBr, NaI, KCl, KBr, and KI), sodium carboxylates (formate, acetate, propionate, butyrate, valerate, and caproate), and symmetrical tetraalkylammonium halides (Me_4NCl, Me_4NBr, Me_4NI, Et_4NBr, Et_4NI, Pr_4NI, Bu_4NCl, Bu_4NBr, and Bu_4NI) were of the same purity as those used previously[7-10]. The sucrose was of BDH AnalaR grade.

The experimental procedures were the same as those reported in earlier communications[7,8], as follows. All of the solutions were prepared by weight, in double-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 with sucrose 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 at the same temperature (50.0 ±0.2°). Complete separation of the crystals from the solution was ensured, and the centrifugate was transferred to the conductivity cell. 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 each temperature for at least 30 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 experimental solution.

RESULTS AND DISCUSSION

As reported earlier[7-10], the negative logarithm of the specific conductance of each system was plotted against the reciprocal of the absolute temperature. All of the plots of —log *K* *vs.* 1/*T* consist of pairs of straight lines intersecting one another at the saturation temperature, showing a second-order transition in the conductance values of the system in the vicinity of the saturation temperature. The best fit for the two straight lines was obtained statistically, with the help of least-square calculations, and the activation energy of conduction for each straight line was computed from the Arrhenius plots (—log *K* *vs.* 1/*T*). Differences (ΔE) in the activation energies of the two straight lines at 50° for the electrolyte–sucrose–water systems under study are presented in Table I.

The abrupt change in the conductance values of homogeneous, ternary systems may be interpreted on the basis of the occurrence of a second-order transition in

TABLE I

ACTIVATION ENERGY OF TRANSITION (ΔE) AT THE SATURATION TEMPERATURE (50°) FOR HOMOGENEOUS, ELECTROLYTE–SUCROSE–WATER SYSTEMS

Electrolyte	ΔE *(kJ.M^{-1})*	*Electrolyte*	ΔE *(kJ.M^{-1})*
NaCl	3.646	Me_4NCl	3.369
NaBr	4.130	Me_4NBr	4.071
NaI	5.141	Me_4NI	4.671
KCl	5.338	Et_4NBr	3.101
KBr	5.455	Et_4NI	4.201
KI	5.488	Pr_4NI	3.670
HCO_2Na	5.241	Bu_4NCl	1.505
CH_3CO_2Na	4.614	Bu_4NBr	2.123
$C_2H_5CO_2Na$	4.130	Bu_4NI	2.659
$C_3H_7CO_2Na$	4.033		
$C_4H_9CO_2Na$	3.992		
$C_5H_{11}CO_2Na$	3.043		

these systems. These systems could be envisaged as a network of electrolyte–solvent–nonelectrolyte structures held together by hydrogen bonding, and the abrupt transition could be explained on the basis of the change in the water structure brought about in the vicinity of the saturation temperature by the presence of the electrolyte and sucrose molecules. The solute molecules (both electrolyte and nonelectrolyte) have a tendency to enter into the spaces in the water structure without disrupting it. As the concentration of the solute increases, the water structure becomes unstable, and is eventually transformed in a cooperative way. As the temperature is increased, the degree of disorder increases, and, in a sense, the structure gradually "melts" or is disrupted, as a result of which a transition occurs. Actually, the water structure is retained intact in the unsaturated state, and gives way in the supersaturated state. Similar changes have been found to occur in heat capacity, expansion coefficient, viscosity[11], and apparent molal volume data[12]. 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 noted for supercooled liquids[13].

Furthermore, the transitional behavior in these system could also be envisaged in terms of a sudden change in the activation energy of conduction at the saturation temperature. It is known that conductance varies exponentially with temperature, and the Arrhenius plot ($-\log K$ *vs.* $1/T$) is a straight line showing a definite activation-energy required for conduction in the liquid, as well as in the fused, state. The main conclusion emerging from our results is that the two straight lines observed in these plots[7–10] may imply two activation energies for conduction due to a change in the mobilities of ions in the two states. The mobilities of the ions would be different for the unsaturated and supersaturated states, as the molecules are highly influenced by the structural and environmental changes produced by the sucrose and water. The changes in activation energies (ΔE) presented in Table I constitute the activation energies of structural transition, and may be termed activation energies of transition. The system undergoes a structural transition at the saturation temperature, due to the decay of large, hydrogen-bonded solvent-structures and formation of new, less-structured entities through solute–solute and solute–solvent interactions.

A perusal of Table I reveals that a regular increase in the activation energies of transition (ΔE) with increasing radii of the halide ions always persists, no matter whether these anions are attached to common, alkali-metal anions or to those of the (larger) tetraalkylammonium (R_4N^+) ions having hydrophobic character. On the other hand, whereas ΔE for each potassium halide is greater than that for the corresponding sodium halide, the activation energies of transition decrease markedly with increasing chain-length of the R_4N^+ ions. This behavior of R_4N^+ ions may be visualized from Fig. 1, in which ΔE has been plotted against the radii of the R_4N^+

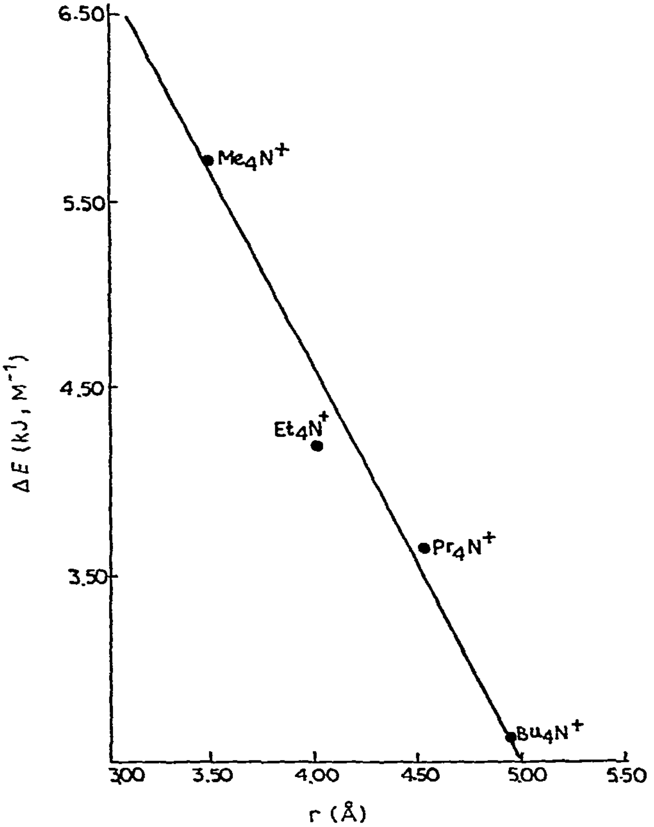

Fig. 1. Variation of activation energies of transition (ΔE) with size (r) of the R_4N^+ ions (Stokes radii)[14] in sucrose–water systems.

ions[14]. A straight line is obtained that shows decrease of ΔE with increase in size of the R_4N^+ ions. It is also evident from Table I that activation energies of transition (ΔE) decrease with increase in the chain-length of the carboxylate ions.

The results may be interpreted by taking into account the structural features of water and of sucrose (the nonelectrolyte), and the structure-making or -breaking properties of electrolytes. In a real sense, sucrose, having many hydrogen-bonding sites, has a greater tendency to participate in hydrogen-bond formation. In the present study, the possibility of hydrogen-bond formation is maximal in the supersaturated region, *i.e.*, at temperatures below the saturation temperature. In this region, the structural properties of electrolytes can influence the structure of the system very conveniently, and this is, presumably, why a sudden change in the conductance values of the system occurs once the electrolytes have entered into the solvent structure.

It has also been observed that ΔE increases with increase in the structure-breaking properties of the electrolytes, and it decreases with the increase in the structure-making tendency of the electrolytes. This behavior may be readily understood in light of the model just suggested. It has already been well established that R_4N^+ ions, possessing hydrophobic entities in their structure, cause increased hydrogen bonding of the solvent[15,16], and, hence, lessen the activation energy of transition (ΔE), the greater the hydrophobicity of the ions. A similar trend of decrease in the ΔE value with increase in the length of the hydrocarbon chain of the carboxylate anion attached to Na^+ cation also supports the view that increased hydrophobicity, no matter whether caused by cations or anions, decreases the activation energy of transition in these systems. Lindenbaum[16,17] and Snell and Greyson[18] also concluded that an increase in the length of the hydrocarbon chain of cations or anions having hydrophobic character increases the hydrogen bonding of the solvent.

ACKNOWLEDGMENTS

We are grateful to Prof. R. P. Rastogi, Head of the Chemistry Department, University of Gorakhpur, for providing necessary facilities and for his kind interest in the work. One of us (A.K.S.) also thanks CSIR (India) for the award of a Post-Doctoral Fellowship.

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