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CONDUCTANCE STUDIES ON THE INTERACTION OF SODIUM CARBOXYLATES WITH SUCROSE IN WATER AND IN FORMAMIDE

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ABSTRACT

Conductance data for the sodium salts of the group of aliphatic acids from formic to caproic, in water and in formamide solutions saturated with sucrose at 50°, are reported at several temperatures within the range of 25 to 70° Plots of $-\log K$ *vs.* $1/T$ showed a break at the saturation temperature, where two straight lines appeared to intersect Deviations of the two lines were found to decrease with increasing length of the hydrocarbon chain The behavior of these salts resembles that of the tetraalkylammonium salts, and the results are interpreted in terms of the effect that hydrocarbon chains have on hydrogen bonding in the saturated sucrose solutions

INTRODUCTION

The properties of tetraalkylammonium salts in aqueous and some nonaqueous solvents have been a subject of considerable interest in the past few years[1-10] The results of these studies have usually been interpreted in terms of the influence of the tetraalkylammonium (R_4N^+) ions on the solvent structure It has now been well established that, in aqueous solution, these large R_4N^+ ions, possessing hydrophobic moieties in their structure, cause increased hydrogen bonding of the solvent It has also been suggested that the structure-promoting or structure-making effect increases with increase in the length of the carbon chain of the cation The purpose of this study was to determine whether a similar structure-making effect could be observed with a salt of an ion having a hydrocarbon chain attached to a negatively charged atom. Lindenbaum[11-13] has studied the effect of this type of organic anion on the structure of water by determining the change in excess enthalpies and entropies of aqueous solutions It was similarly concluded by Snell and Greyson[14], who measured enthalpies of transfer of sodium salts of some aliphatic acids from normal to heavy water, that the hydrocarbon chains promote increased hydrogen-bonding of the solvent

In this laboratory, a continuing program has been under way in which the influence of electrolytes on the structure of nonelectrolyte solutions has been investigated by employing conductance measurements. Sucrose, having a number of hydrogen-bonding sites and being capable of interacting with electrolytes in solution, has been chosen as a typical nonelectrolyte in the program. The 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°). Ternary systems that have been studied and reported earlier[15–17] included alkali halides and tetraalkylammonium halides in both water and formamide solutions in the presence of sucrose as the nonelectrolyte. In this paper, the conductance data on the interaction of sodium salts of several low-carbon aliphatic acids with sucrose in water, as well as in formamide, solutions are reported Sodium salts of carboxylic acids were chosen for this study because they are readily soluble in both solvents and provide an opportunity to study the interaction of long hydrocarbon chains with a nonelectrolyte in aqueous and in formamide solutions.

EXPERIMENTAL

The materials used in the present investigation were either of pro Analysi (E Merck) or Analar (BDH) grade Samples of sucrose, sodium formate, and sodium acetate were obtained from BDH (England). Sodium propionate, sodium butyrate, sodium valerate, and sodium caproate were prepared by neutralizing the respective carboxylic acid with pure sodium. All samples were purified, and were oven-dried to constant weight at 105°.

Resistance measurements were made with a properly grounded, Leeds & Northrup, Kohlrausch slide-wire aseembly[15]. A cylindrical type of conductivity cell, supplied by Leeds and Northrup (U. S. A.), was used. The solutions were placed in an oil bath whose temperature was thermostatically controlled within ±0 02° in the lower and ±0.05° in the higher temperature range. Aqueous solutions were prepared in double-distilled, demineralized, conductivity water (sp conductivity, $K = 1$ µmho) Formamide (BDH, England) was treated with calcium oxide, decanted, and fractionally distilled under diminished pressure until its conductivity fell to the order of 10 µmho or less, and then used immediately.

A 0.1M solution of the electrolyte was prepared in the pure solvent. The solution was kept in a stoppered, conical flask, and was then saturated with sucrose by keeping the mixture, stirred at 50 ±0.05°, in the oil bath. Sufficient time (20 to 30 h) 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 ±0.2° 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 now transferred to the conductivity cell kept at the same temperature in the air thermostat Afterwards, the cell was well immersed in the constant-temperature oil-bath maintained at 65–70°. 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. The resistance was measured at 20 to 25° above and below the saturation temperature. Before each measurement, it was made sure that no crystallization had occurred in the experimental solution. For the formamide solutions, contact of the solvent and solutions with air was kept to the minimum. Other necessary precautions[16] were also taken.

RESULTS AND DISCUSSION

Negative logarithms of the specific conductances of the sodium salts of some lower aliphatic acids in aqueous sucrose solution are plotted against their respective, absolute-temperature reciprocals in Figs. 1 and 2; Figs. 3 and 4 give similar plots for these electrolytes in formamide solutions containing sucrose as the nonelectrolyte. Fig. 3 also includes conductance data for sodium halides[16] for comparison. Figs. 5 and 6 give the deviation *vs.* temperature-reciprocal plots for sodium carboxylates in water and formamide solutions containing sucrose as the nonelectrolyte. Similar plots for the sodium salts of some inorganic acids plotted against the temperature reciprocal are given in Fig. 7. For deviation values, the best fit for the points above the satura-

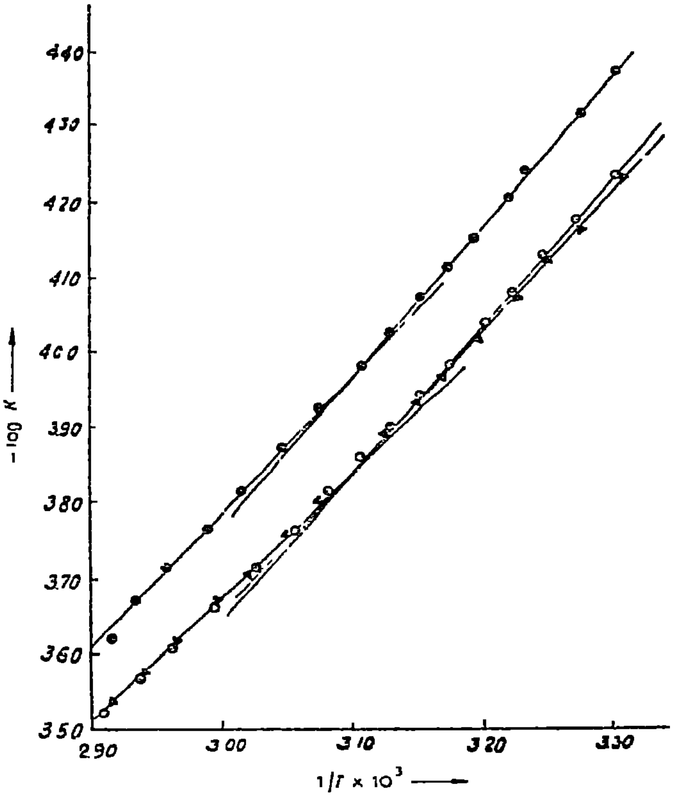

Fig 1. Plots of $-\log K$ *versus* $1/T$ for sodium carboxylates in aqueous sucrose solution [Key: ⊙, sodium formate, ▲, sodium acetate; ●, sodium propionate]

tion temperature was obtained statistically with the help of least-squares calculations, and the theoretical values of $-\log K$ were obtained from the regression equation for different values of $1/T$. The differences between the values of $-\log K$ experimentally observed and those calculated constitute the deviations.

It is evident from the $-\log K$ vs $1/T$ plots in Figs 1 to 4 that the plots consist of two straight lines intersecting in the vicinity of the saturation temperature, as in the studies reported earlier on alkali halides and tetraalkylammonium halides in water and formamide solutions$^{15-17}$. The departure of these lines from a single line is markedly influenced by cations and anions of different sizes, and the deviation is greater with structure-breaking ions, and less with structure-making ions.

From the plots given in Figs 1, 2, and 5, it is observed that, in these systems, sodium formate shows the maximum deviation from single-straight-line behavior, and sodium caproate shows the minimum deviation. In other words, departure of the two straight lines from one another decreases as the number of carbon atoms in the anion increases. It is believed that, for these longer-chain carboxylates, aggregation or micelle formation is responsible for the effect. The decrease in deviation values with increase in the number of carbon atoms in the carboxylate chain is

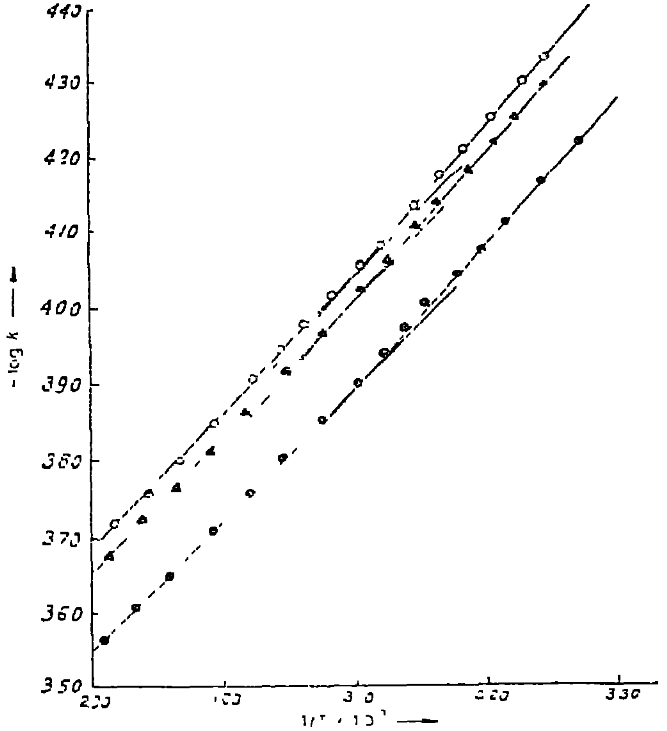

Fig 2 Plots of $-\log K$ *versus* $1/T$ for sodium carboxylates in aqueous sucrose solution [Key ●, sodium butyrate, ⊙, sodium valerate, ▲, sodium caproate]

similar to the behavior found for the tetraalkylammonium halides[17] This suggests that, in both cases, the hydrophobic, alkyl chains cause increased solvent hydrogen-bonding of the water molecule

It has now been well established[18] that the B coefficient of the Jones-Dole viscosity equation has large values for these hydrophobic ions, and that, the larger the ion, the more positive the B coefficient This is in contrast to the behavior of alkali-metal ions, which show decreasing B values with increase in their ionic size The same trend has been reported in our previous communications[15-17] For alkali-metal iodides, deviation values obtained from the experimental and theoretical values of specific conductance increase with increasing size of the cation[16], whereas, for the large, organic cations, they decrease markedly with increase in the cation size Similar behavior has been noticed in the present study on comparing the conductance data for the sodium salts of some inorganic acids with those for sodium salts of some carboxylic acids In Fig 7 are depicted the plots of deviation *vs* 1/*T* for some sodium salts having inorganic anions of different crystallographic sizes The trend of deviation follows the order $(NaPO_3)_n > Na_2SO_4 > NaI > NaCl$ The

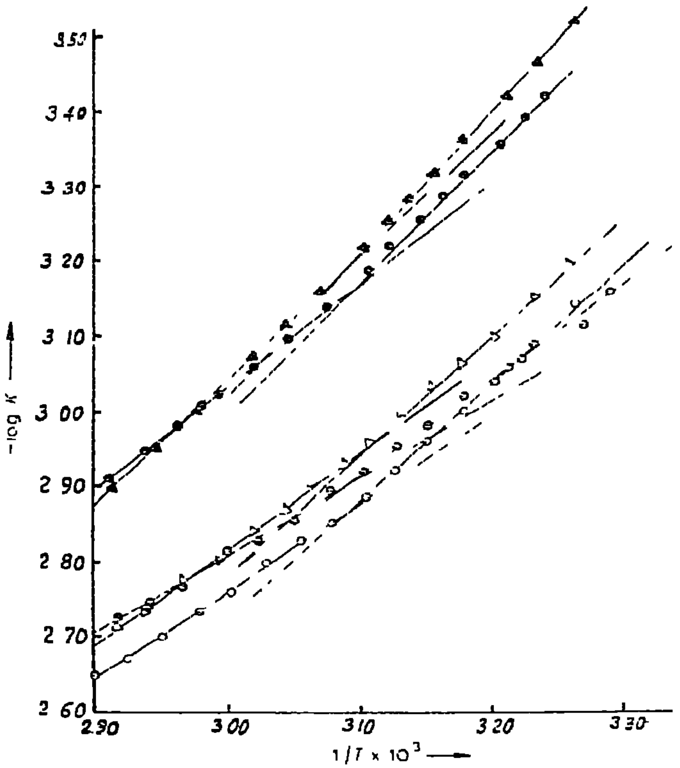

Fig 3 Plots of −log κ *versus* 1/*T* for electrolytes in formamide solutions containing sucrose [Key ⊙, sodium chloride, ◎ sodium bromide △, sodium iodide, ●, sodium formate, ▲, sodium acetate]

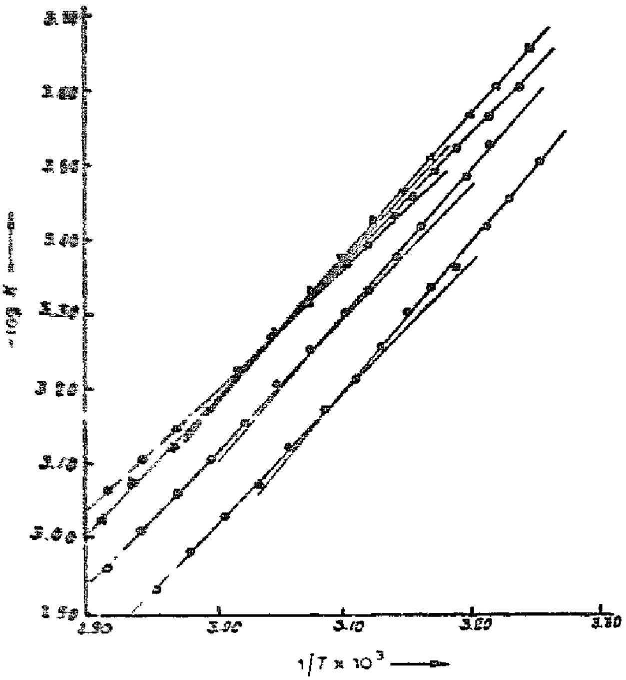

Fig. 4. Plots of $-\log K$ *versus* $1/T$ for sodium carboxylates in formamide solutions containing sucrose. [Key: ⊘, sodium propionate; ◎, sodium butyrate; ●, sodium valerate; △, sodium caproate.]

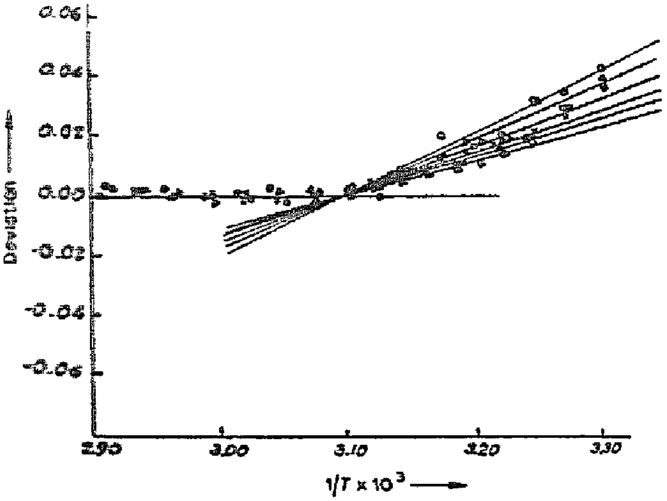

Fig. 5. Plots of deviation *versus* $1/T$ for sodium carboxylates in aqueous systems. [Key: ◎, sodium formate; △, sodium acetate; ●, sodium propionate; ×, sodium butyrate; ▲, sodium valerate; ☐, sodium caproate.]

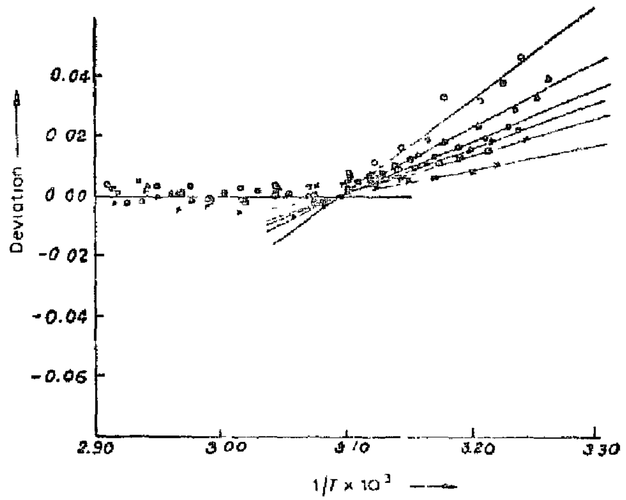

Fig. 6. Plots of deviation *versus* $1/T$ for sodium carboxylates in formamide systems [Key ◈, sodium formate; △, sodium acetate, ◉, sodium propionate; ▲, sodium butyrate, □, sodium valerate, ×, sodium caproate.]

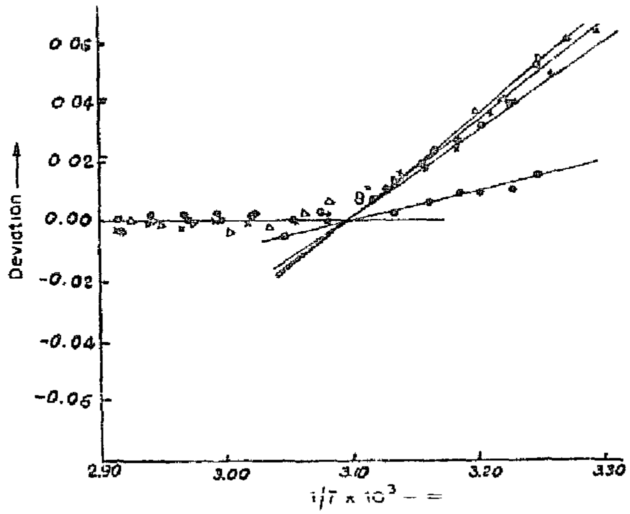

Fig. 7. Plots of deviation *versus* $1/T$ for sodium salts of inorganic acids in aqueous systems [Key △, sodium polyphosphate; ○, sodium sulfate; ×, sodium iodide; ◉, sodium chloride.]

polyphosphate anion, having the bigger crystallographic size, has been found to produce maximal deviation, whereas the deviation is minimal for the (smaller) chloride ion This is in contrast to the results obtained for sodium carboxylates in sucrose solution The results for sodium carboxylates in aqueous sucrose solutions suggest that these anions, like R_4N^+ cations, also promote water structure, or increase hydrogen bonding of the solvent, with increase in their carbon chain-length

It is clear from Figs 3, 4, and 6, which present the conductance data for sodium carboxylate–sucrose–formamide systems, that similar behavior of the carboxylate ions is also found in formamide solutions However, in these systems, the break of the two straight lines is more pronounced in comparison to those observed with aqueous solutions In Fig 3, the conductance data for sodium halides are given for comparison, they show a similar type of behavior, *i e*, a greater departure of the straight lines in the case of sodium halides This enhanced deviation for these electrolytes in formamide solutions may be attributed to the less-structured nature of the solvent It is well known that water can form four hydrogen bonds of tetrahedral orientation, resulting in the formation of a three-dimensional structure, but formamide can have a maximum of three hydrogen bonds per molecule, enabling the formation of a sheet-like structure

Sucrose, like many other polyhydroxy compounds, is known to interact with electrolytes in solution[19, 20]. It readily dissolves in water and such other structured solvents as formamide in large excess The association with water in the saturated solution is found to the extent of 14 water molecules bound per sucrose molecule[21]. Ordinarily, it has been observed that only 5 molecules of water bind with a molecule of sucrose[22] However, the interaction of such electrolytes with nonelectrolytes is generally discussed in terms of the structural properties of the electrolytes, the nonelectrolyte, and the solvent Actually, sucrose, having a number of hydrogen-bonding groups, has a greater tendency to participate in hydrogen-bond formation In our systems, the measurements have been conducted at temperatures above and below the saturation temperature, to form unsaturated and supersaturated states. The concentration of hydrogen-bonded sucrose molecules increases with decrease in temperature, *i e*, at temperatures below the saturation temperature, the association of the sucrose molecules with solvent molecules reaches its maximum and, at this stage, the 'structure-making' or 'structure-breaking' properties of the electrolytes very readily influence the solution structure This is why a sudden change in the conductance behavior is noted, leading to a transition at the saturation temperature This transitional behavior had been explained[15, 16] on the basis of structural changes brought about by the solute molecules, and in terms of solute–solvent interactions

The results may also be interpreted in terms of the Gurney cosphere model[23] for structural interactions in solution The model provides an almost ideal explanation for the results obtained in aqueous sucrose solutions The Gurney model states that the solute particles in aqueous systems are surrounded by spherical shells of solvent that is modified in structure from that of the pure solvent The concentration-dependence of properties attributable to structural interactions results from the increasing overlap of the spherical shells with increasing concentration, *i e*, the concentration of cosphere solvent per mole of solute decreases with increase in the solute concentration More or less the same interpretation is also valid for the (less-structured) formamide solutions As water is more structured than formamide, deviations are less pronounced in aqueous systems

In passing from sodium formate to sodium caproate, a gradual decrease in the values of deviations is observed, as is evident from Figs 5 and 6 Such results are in accord with the view that, in proportion to their number of carbon atoms, saturated hydrogen-bonding among neighboring solvent molecules and apparent structuring in the solvent occur

Alhough our results are in accordance with those of many workers[11–14], classification of solutes as "structure-maker" or "structure-breaker" is frequently ambiguous, and is dependent on the properties under examination Different properties may emphasize to a different extent the relative contributions of solute-solute and solute-solvent interactions

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REFERENCES

1 H S Frank and W Y Wen, *Discuss Faraday Soc*, 24 (1957) 133-140
2 H S Frank, *J Phys Chem*, 67 (1963) 1554–1558
3 W Y Wen S Saito and C M Lee, *J Phys Chem*, 70 (1966) 1244–1248
4 S Lindenbaum, *J Phys Chem*, 70 (1966) 814–820, 73 (1969) 4334
5 F Franks, in A K Covington and P Jones (Eds), *Hydrogen Bonded Solvent Systems*, Taylor & Francis, London, 1968
6 R Gopal and A K Rastogi, *J Indian Chem Soc*, 43 (1966) 269-272
7 J Padova and I Abrahmer, *J Phys Chem* 71 (1967) 2112-2116
8 R D. Singh, P P Rastogi, and R Gopal, *Can J Chem*, 46 (1968) 3525-3550
9 R Gopal and K Singh, *Z Phys Chem*, 69 (1970) 81–87, 91 (1974) 98–107
10 R Gopal and J R Singh, *J Phys Chem* 77 (1973) 554–556
11 S Lindenbaum, *J Phys Chem* 74 (1970) 3027-3028
12 S Lindenbaum, *J Chem Thermodyn*, 3 (1971) 625–629
13 S Lindenbaum, *J Phys Chem* 75 (1971) 3733-3737
14 H Snell and J Greyson *J Phys Chem*, 74 (1970) 2148-2152
15 Vishnu and A K Singh, *Proc Indian Acad Sci Sect A*, 80 (1974) 57-74
16 Vishnu and A K Singh, *Proc Indian Acad Sci Sect A*, 81 (1975) 220–231
17 Vishnu and A K Singh, to be published
18 R L Kay, T Vituccio, C Zawoyski, and D F Evans, *J Phys Chem*, 70 (1966) 2336–2341
19 L G Longsworth, *J Am Chem Soc*, 69 (1947) 1288-1291
20 S Fredericksson, *Acta Chem Scand*, 23 (1969) 1993-2003
21 S P Moulik, *Electrochim Acta*, 18 (1973) 981-987
22 R H Stokes and R Mills, *International Encyclopedia of Physical Chemistry and Chemical Physics*, Vol 3, Pergamon Press, London, 1968
23 R W Gurney, *Ionic Processes in Solution*, Dover Publications, San Francisco Calif, 1964