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CONDUCTANCE STUDIES ON THE INTERACTION OF LACTOSE WITH ALKALI-METAL HALIDES IN WATER AND IN FORMAMIDE

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ABSTRACT

The interaction of lactose with alkali-metal halides in solution in water and in formamide has been studied by employing conductance measurements Conductance data of sodium and potassium halides in water and in formamide saturated with lactose at 50 0 ±0 05° are reported at several temperatures within a range of 25 to 70° Plots of —log *K* against *l/T* showed a break at the saturation temperature, where two straight lines intersect one another Divergence of the pairs of straight lines in these ternary, homogeneous systems has been found to be highly influenced by the structural properties of the solutes The transitional behavior in the conductance values is explained for the system in terms of solute-solvent interactions involved in the electrolyte-solvent-nonelectrolyte systems

INTRODUCTION

Much work have been done[1-5] on the interaction of nonelectrolytes in electrolyte solutions Many carbohydrates and several other polyhydroxy compounds are known to interact with alkali and alkaline-earth metal salts by the formation of definite adducts[6-8] or molecular compounds[9] with these salts Such physical properties as conductance and viscosity of ionic solutions are found to change in the presence of nonelectrolyte molecules[10,11] These changes lead to abrupt, transitional behavior in ionic solutions, as well as in ionic solutions containing nonelectrolytes[12] Conductance measurements on electrolyte solutions in the presence of nonelectrolytes have been made by several workers[13-17] In the past, many attempts have been made[1-3,6-8,10,11,18] to ascertain the direction of structural changes in solvents caused by added, nonionic moieties or ionic solutes The study of the structural interaction of nonelectrolyte solutions in ionic solutes is quite recent In our laboratory, a continuing program[19-28] involves study of the structural interactions in ternary systems containing alkali-metal halides and sucrose, D-mannitol, D-xylose, urea, D-glucose,

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HMT maltose, or D-fructose, in solution in water or formamide, within a definite temperature range of 25–70°

During these studies, an abrupt transition in the conductance values of the homogeneous ternary systems of nonelectrolyte-electrolyte-solvent 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 It has been observed[19–28] that a pair of straight lines intersecting one another at the saturation temperature is obtained when the values of -log K for these systems are plotted against the reciprocal $(1/T)$ of their absolute temperature T It has also been observed’[9] that the divergence of the pairs of straight lines is highly Influenced by the structural properties of the different solutes in solution

Lactose, a reducing sugar that exists in α- and β-anomeric forms and undergoes mutarotation is of some Importance from the point of view of structural considerations in ternary systems, as the lactose molecule may take part in biochemical processes fundamentally concerned in calcium metabolism It Increases the retention of dietary calcium, apparently by improving the utilization of calcium already absorbed, and it increases the mineral content of bone”‘. It has been observed[30] that an even distribution of α-lactose monohydrate crystals in sweetened, condensed milk confers the desired texture on the milk and that, at Incorrect temperatures and under improper processing conditions, p-lactose monohydrate crystals also occur, but that the milk is then of low consumer acceptability It was, therefore, of considerable Interest to observe the conductance behavior of lactose, which has a number of hydrogen-bonding sites, in aqueous and nonaqueous solutions of electrolytes

We now report a study of the interaction of lactose with alkali-metal halides in water and in formamide, employing conductance data at various temperatures

EXPERIMENTAL

Materials — Analytical-reagent grade samples of lactose, NaBr, NaCl, NaI, KBr, KC!, and KI, obtained from BDH and E Merck. were used without further purification Formamide obtained from BDH (England) was purified as already reported”

Methods — Conductance measurements were made with a suitably grounded, Leeds and Northrup (U S A), Kohlrausch slide-wire assembly[19] A cylindrical type of conductivity cell, supplied by Leeds and Northrup (U S A), was used The temperature control and other experimental procedures were as described earlier[19] All solutions were prepared by weight, in demineralized, conductivity water (sp cond 0 5–1 0 x 10^{-6} ohm-’ cm-‘) and in pure formamide A 0 1M solution of the electrolyte was prepared, and was saturated with lactose at 50 0 ±0 05” in an oil thermostat A period of 20 to 30 h was aliowed for complete saturation of the solution Crystals from the mother liquor were separated by centrifugation within an au-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

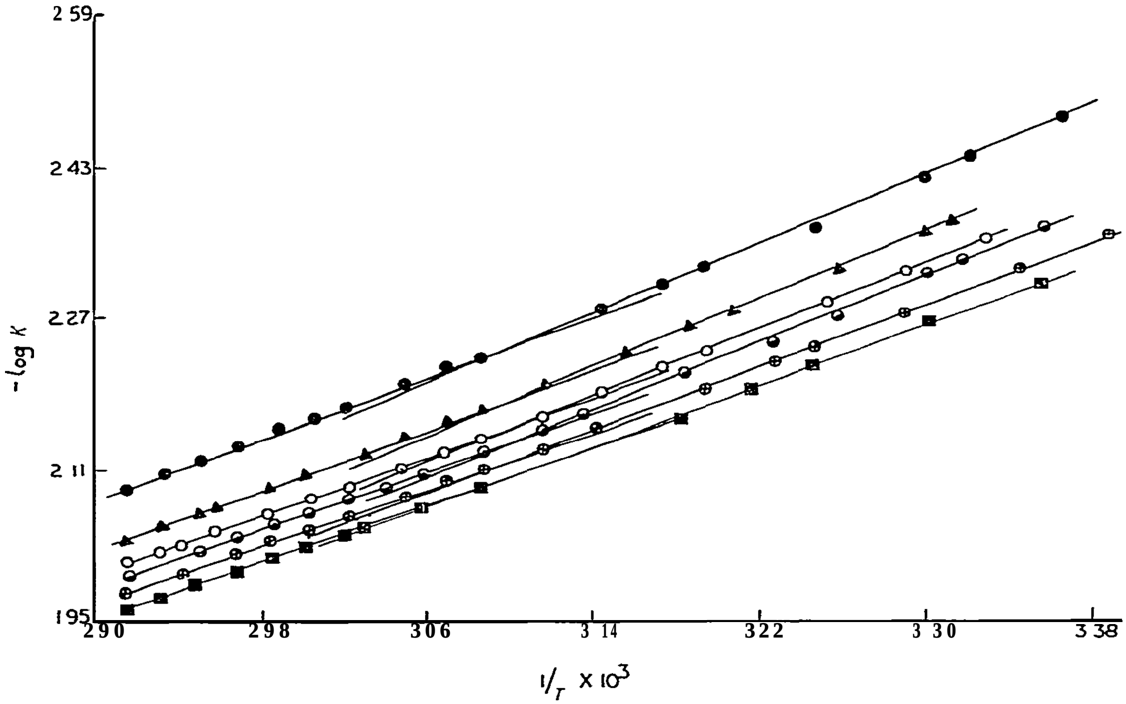

Fig I Plots of $-\log K$ vs $1/T$ for alkali-metal halides–lactose–water systems [Key ○ NaCl ▲ NaBr ● NaI ■ KCl ⊗, KBr and ◒ KI]

cell kept at the same temperature within an air thermostat The conductivity cell was then immersed in an oil thermostat maintained at 65-70° The resistance of the experimental solution was first measured at the highest temperature the temperature was then lowered 2–4° at a time, and maintained at each temperature for at least 30-35 min The resistance was 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

The negative logarithms of the specific conductance values (-log K) of alkali-metal halides in water and in formamide solutions saturated with lactose at 50° plotted against the reciprocal ($1/T$) of the absolute temperature (T), are shown in Figs 1 and 2, and the deviation values, against the temperature-reciprocals ($1/T$), for these systems are plotted in Fig 3

Values of the deviation from single straight-line behavior were obtained statistically For this purpose, the best fit for the points above the saturation temperature was obtained with the help of least-squares calculations, and the theoretical values of -log K were obtained from the regression equation for different values

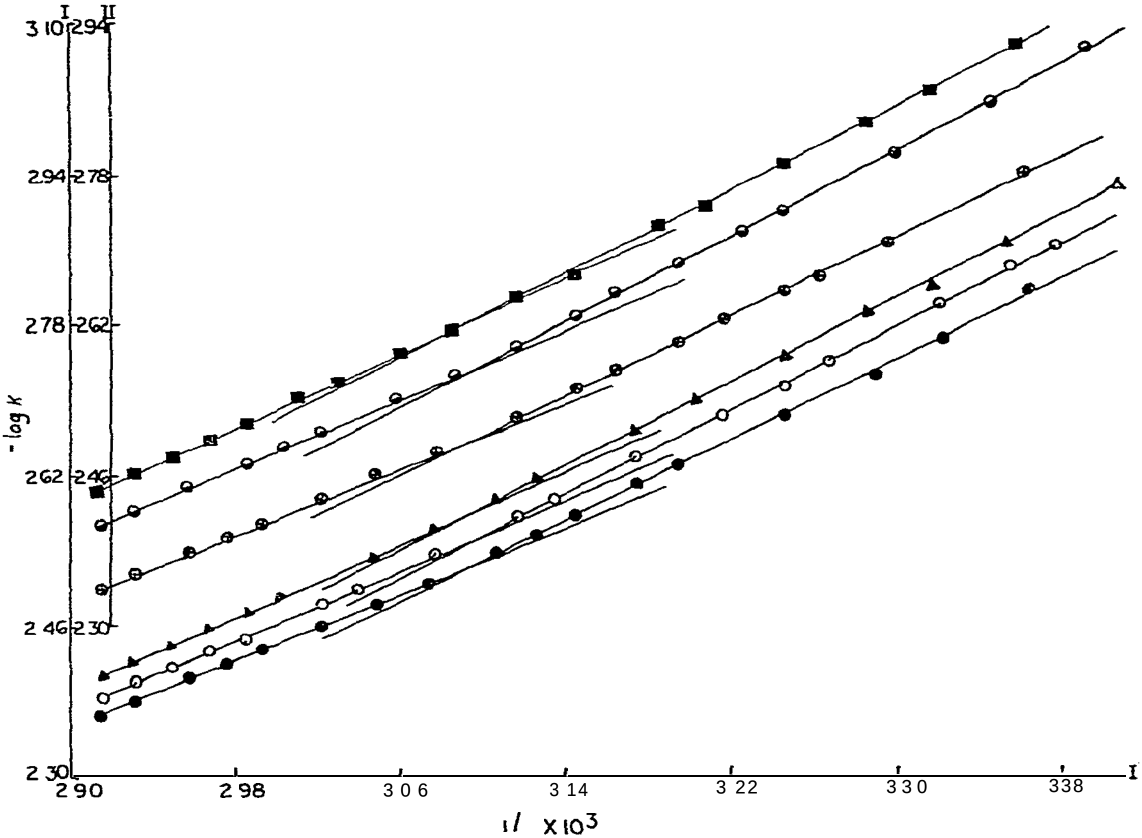

Fig 2 Plots of —log *K* vs 1/*T* for alkali-metal halides–lactose–formamide systems [Key 0, NaCl (scale I-I), ▲, NaBr [scale I-I) ● NaI (scale I-I), ■ KCl (scale II-I), ⊗, KBr (scale II-I), and ⊖ KI (scale I I-I)]

of 1/*T* The **differences between the experimentally observed values of -log *K* and those calculated theoretically are termed "deviations**

It may be seen that plots of -log *K* vs 1/T (see Figs 1 and 2), consist of two straight lines intersecting in the neighborhood of the saturation temperature, as in the studies reported previously$^{19-28}$ The departure of these lines from a single straight line is markedly influenced by catrons and anions of different sizes in both water and in formamide solutions

The trend of deviations of the pairs of straight lines [see Figs 3a(ii) and 3b(ii)] follows the order KI > KBr > KCl for potassium halides–lactose–water and potassium halides–lactose–formamide systems, whereas the deviation values for sodium halides–lactose–water and sodium halides–lactose–formamide systems [see Figs 3a(i) and 3b(i)] exhibit no anionic behavior, and the points fall on a single, straight line, irrespective of the nature of the halide ions Furthermore, it is also noted that potassium halides produce greater deviations than sodium halides in lactose-water

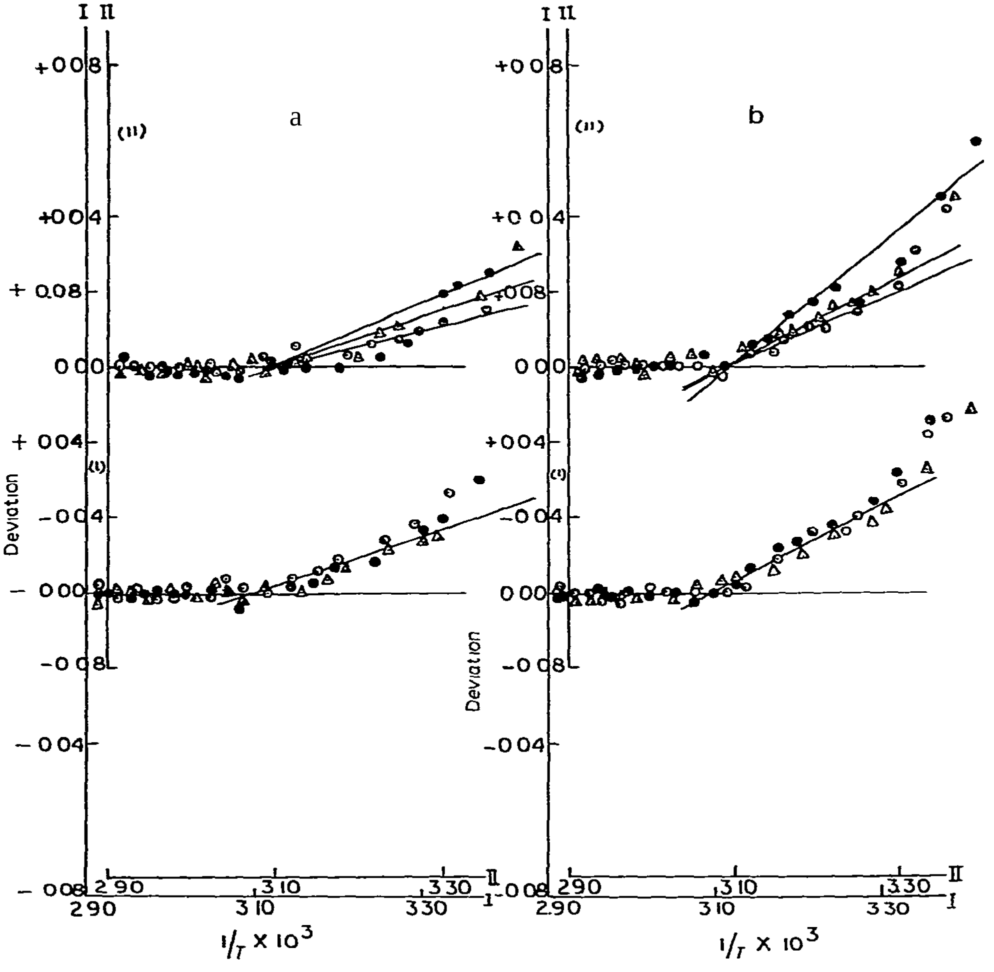

Fig 3 a(i), Plots of deviation vs 1/T for sodium halides–lactose–water systems [Key ○, NaCl, △ NaBr, and ●, NaI], a(ii) Plots of deviation vs 1/T for potassium halides–lactose–water systems [Key ○, KCl, △, KBr, and ●, KI], b(i) Plots of deviation vs 1/T for sodium halides–lactose–formamide systems [Key ○ NaCl, △ NaBr, and ●, NaI], b(ii) Plots of deviation vs 1/T for potassium halides–lactose–formamide systems [Key 0, KCl, A, KBr, and ●, KI I

as well as in lactose–formamide systems, and the deviation produced in the case of the latter system is greater than those of the former system for alkali-metal halides

The experimental results obtained may be explained on considering the structural behavior of lactose and the various ions in aqueous solution as well as in formamide, the hydrogen-bonding capabilities, and the hydration properties of the lactose molecule The hydration of a large number of polyhydroxy compounds has been studied[31], and their aggregation with water has been confirmed The hydration properties of six-membered-ring, polyhydroxy compounds are found[32] to depend on the conformations adopted, besides the number of hydroxyl groups present, in solutions of such compounds Lactose (4-O-β-D-galactopyranosyl-D-glucopyranose[33]) has 8 hydroxyl groups and on hydrolysis, one molecule yields one molecule of D(+)-glucose and one molecule of D(+)-galactose both having the $^4C_1$ conformation Strong hydrogen-bonding would be expected between water and the hydroxyl groups of lactose, because of the fact that, in β-lactose, the majority of the hydroxyl groups are equatorially disposed and thus they fit very well with the water-tetrahedral arrangement[32] Recent n m r studies[32] disclosed the hydration of the pyranose ring in carbohydrates, and provided evidence for hydrophilic interactions The two six-membered rings [O-β-D-galactopyranosyl-(1→4)-β-D-glucopyranose] in the β anomer of lactose produce a greater hydration effect than a single six-membered ring

Furthermore, in aqueous solution, lactose undergoes "simple' mutarotation, and the equilibrium mixture consists mainly of the 'ı- and β-pyranose forms[34] The proportion of the y-form in equilibrium may be calculated from the theoretical, free-energy values by use of the equation $AG = -RT\ln K$ The measured value of the optical rotation of c/-lactose in water corresponds closely to predictions made from the crystal structure[35] With electrolytes, lactose is found to Interact in solution, like many other polyhydroxy compounds[13,14] In the present study, a sudden change in the conductance value giving a transition at the saturation temperature, is observed when the conductance measurements have been made at temperatures above and below the saturation temperature The transition in the electrolytic conductance is due to the transition occurring in the viscosity of the system by formation of large clusters of solute molecules below the saturation temperature, and to the anomeric changes of the lactose molecules taking place in solution In the unsaturated state, the lactose is mostly in the β-anomeric form, whereas in the supersaturated state, the α anomer may preponderate The change from the unsaturated to the supersaturated state is brought about, presumably, by a change from the β-anomeric to the α-anomeric form through the formation of a cyclic transition-complex of the α anomer of the lactose molecule, which is heavily hydrated Such a transformation is also affected by the structure-making and -breaking properties of metal ions through interactions in solution

The transition may also take place as a consequence of the sudden change in the activation energy of conduction at the saturation temperature of alkali-metal halides–lactose systems in water and in formamide The conductance is found to vary 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[36] The two straight lines observed in the system imply two activation energies for conduction. The change in activation energy *(AE)* at the saturation temperature may possibly be due to (a) change in the solvent structure brought about by the structural changes produced by the lactose molecule at the saturation temperature as the system passes from the unsaturated to the supersaturated state, and (*b*) change in the mobilities of the ions in the two states The change in activation energy *(AE)* of the two straight lines at 50° for alkali-metal

TABLE I

ACTIVATION ENERGY OF TRANSITION (ΔE) AT THE SATURATION TEMPERATURE (50°) FOR HOMOGENEOUS, ELECTROLYTE-LACTOSE-WATER AND ELECTROLYTE-LACTOSE-FORMAMIDE SYSTEMS

Electrolyte	ΔE (*kJ* M^{-1})	
	Lactose–water	*Lactose-formamide*
NaBr	2 13	3 43
NaI	2 00	2 85
NaCl	1 88	2 38
KI	2 34	4 44
KBr	1 28	3 77
KCl	0 29	1 55

halides in lactose-water and lactose–formamide systems is given in Table I this may be termed the activation energy of transition

Water has the property of being both a strong hydrogen-bond donor and acceptor[37] and possesses a unique capacity to form relatively strong three-dimensional hydrogen-bonds in the liquid state[38] A nonelectrolyte such as lactose or a large organic ion tends to strengthen the hydrogen bonds between the water molecules, and a cage or “Iceberg” is effectively formed around it Formamide is an Important protic solvent, having comparable hydrogen-bonding capacities, **and** it is **less structured than** water[39] By definition, such a protic **solvent** is a **strong,** hydrogen-bond donor, and will interact strongly with such a solute as the lactose molecule which is a strong hydrogen-bond acceptor[40] It has been observed that dispersion interactions[41], or mutual polarizability[42], are indicated by the molecular polarizability of the solvent [43], and will decrease in the order HCONH, $>H_2O$ for the solvents formamide and water Large anions, and some “organic transition-states fit poorly into highly structured solvents whose **molecules are** small[44] Structure-breaking interactions **decrease the** solvation of large solutes by water and formamide[40], this interaction accounts, in part, for the positive, solvent-activity coefficients of large anions in water and formamide[40] It is difficult to separate “structure’ interactions from mutual polarizability, but the poor solvation of large solutes by highly structured solvents is also observed for cations and a nonelectrolyte[40] such as lactose, where polarizability is less important

The structural aspects of ion-solvent interactions in aqueous solution had been studied[45,46] for alkali-metal and alkaline-earth metal salts Morris[47] showed that the standard free-energy of solution of alkali-metal halides is maximal (minimum solubility) when the difference between the (conventionally assigned) free energies of hydration of the cation and anion is zero Cations are generally smaller, and less polarizable, than anions, and are not hydrogen-bond acceptor?’ The common interactions[40] to be considered between such ions and solvent are cation–dipole and structure-making or -breaking Such small, “closed-shell’ cations as Na$^+$ and K$^+$

ions are very much more solvated by water and formamide[40] The structure-making properties of such ions are found to decrease with an increase in their cationic radii[48] It had earlier been shown[19,20] that the divergence of the pair of straight lines in our systems[21–28] increases with an increase in the structure-breaking properties of the electrolytes Our experimental results can be interpreted on the basis of these facts

The results [see Figs 3a(ii) 3a(i), 3b(ii), and 3b(i)] indicate that the deviation is more pronounced in the case of K^+ than Na ions for alkali-metal halides–lactose–water, as well as alkali-metal halides–lactose–formamide systems, and the concept[45,48], is further supported, as K^+ ions are found to be more structure-breaking than Na^+ ions in the systems Born[49] assumed that ion-dipole interactions are related to the dielectric constant of the solvent and the charge density on the anion Small anions having localized charge are more solvated than large ones Water and formamide will tend to solvate all anions more strongly than will other solvents of lower dielectric constant?' Anions that are strong hydrogen-bond acceptors have strong, general, hydrogen-bonding interactions with protic solvents" Furthermore, the "hydrogen-bonding" interactions of protic solvents[40] with anions is an extreme case of an anion–dipole, electrostatic interaction where the positive center of the solvent is in a most favorable atom

The trend in anionic deviation observed for our systems, namely, potassium halides–lactose–water and potassium halides–lactose–formamide [see Figs 3a(ii) and 3b(ii)] is $I^- > Br^- > Cl^-$ and shows an increase in structure-breaking properties of halide ions, from Cl^- to I^-, for the systems, and this also agrees with McDowall and Vincent's opinion[51] for halide ions in formamide The similar anionic behavior in deviation, for sodium halides–lactose–water and sodium halides–lactose–formamide [see Fig 3a(i) and 3b(i)], is, perhaps, due to the similar structure-breaking capabilities of Na', Cl^- Br^- and I^- ions in water as well as in formamide Furthermore, as the potassium halide deviations are greater than the sodium halide deviations in lactose-water and lactose–formamide systems, the potassium halides show greater structure-breaking tendencies than sodium halides in these ternary systems In a similar way, lactose is found to act as a greater structure-breaker in formamide than in water, for the alkali-metal halides as the deviations observed are greater for lactose-formamide than for lactose-water for the aforementioned metal halides

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