Carbohydrate Research, 132 (1984) 7–17
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

STUDIES ON THE VISCOSITY BEHAVIOR OF CONCENTRATED ALKALI HALIDES IN AQUEOUS MALTOSE SOLUTIONS

AWADHESH K. SINGH, VINOD K. SINGH,
Department of Chemistry, Harish Chandra Post-Graduate College, Varanasi – 221001 (India)

AND VISHNU
Department of Chemistry, University of Gorakhpur, Gorakhpur (India)

(Received February 21st, 1984; accepted for publication, March 13th, 1984)

ABSTRACT

The viscosities of concentrated solutions of sodium and potassium halides (concentration range 0.125 to 3.0M) have been measured in aqueous maltose solution at 25, 30, 35, and 40°. Various equations employed for concentrated solutions of electrolytes have been tested, to ascertain the validity of the relative viscosity data. In order to elucidate the structural behavior of sodium and potassium halides in aqueous maltose solution, the molar volumes ($\bar{V}$), ionic B-coefficients, and hydration numbers (n_B) of various ions have been computed. The B_+ and B_- coefficients have been interpreted in terms of solute–solvent interactions. On the basis of the data, it has been found that, in 0.5M maltose solution, the different ions show structure-breaking tendency in the order: $I^- > Br^- > Cl^- > K^+ > Na^+$.

INTRODUCTION

Aqueous solutions have always received great attention, especially with regard to the exceptional properties of water as a solvent. The addition of nonelectrolytes to water may result in a build-up of the water structure that has often been attributed to the formation of fluctuating, clathrate structures about the nonelectrolyte molecules[1]. The properties of ionic solutes in water are often found to be strongly modified upon addition of nonelectrolytes, and a number of studies have dealt with the thermodynamic[2–5] and transport[6,7] properties of electrolytes in nonelectrolyte solutions. Understanding of aqueous ternary systems comprised of electrolyte, water, and nonelectrolyte molecules is, at present, in a deplorable state. Much of the difficulty arises because most of these studies were limited to free energies. More progress would probably be made if we had adequate data on the thermodynamic and transport properties of some model systems, consisting of electrolyte, nonelectrolyte, and water in order to test the various theoretical approaches.

0008-6215/84/$ 03.00

We are systematically studying the conductance[8-14] and viscosity[15-17] behavior of electrolytes in aqueous nonelectrolyte solutions to obtain information regarding the structural interaction of ions with nonelectrolytes. For the present work, maltose (4-*O*-α-D glucopyranosyl-D-glucopyranose), a disaccharide possessing a number of hydrogen-bonding sites and capable of interacting with the ions of electrolytes in solution, has been selected as a typical nonelectrolyte. Maltose is a reducing sugar having an α-D-(1→4)-glucosyl unit and, in the crystal, it appears[18] to contain a hydrogen bond between O-2 and O-3. Although this conformation in the crystal may or may not exist in aqueous solution, it can make a significant contribution to the structural changes in aqueous solution. Considerable attention has, therefore, been directed towards study of the structural interactions of alkali-metal halides in aqueous solutions of maltose.

EXPERIMENTAL

Materials and preparation of solutions. — Analytical-reagent grade samples of maltose (Reidel, W. Germany), and of sodium and potassium halides, obtained from BDH and E. Merck, were used as such, without purification.

Doubly distilled conductivity water (sp. conductance ~10^{-6} $\text{ohm}^{-1}.\text{cm}^{-1}$) was used for the preparation of solutions. A stock solution of maltose (0.5M) was prepared in conductivity water, and the solutions of electrolytes were prepared on the molar basis. For the measurements, 3M solution of electrolyte was first prepared in maltose solution, and other concentrations were obtained by diluting it with the stock solution.

Density and viscosity measurements. — The densities of the solutions were determined at 25. 30, 35, and 40° in the conventional way. The viscosity measurements at specified temperatures were made by using a modified, Tuan–Fuoss viscometer, described elsewhere[15]. The time flow of conductivity water was determined to be 220 ±0.1 s at 25°. All measurements were conducted in a water thermostat for controlling the temperature within ±0.05°.

RESULTS AND DISCUSSION

The relative viscosities of alkali-metal halides in aqueous maltose solution were determined using the well known relationship given in Eq. *1*.

$$(\eta/\eta_0) = \frac{dt}{d_0 t_0}, \tag{1}$$

where η, d, and t are respectively the viscosity, density, and flow time of the electrolyte in aqueous maltose solution, and η_0, d_0, and t_0 denote the viscosity, density, and flow time of an aqueous solution of maltose alone. The (η/η_0) values were computed for all of the concentrations of alkali halides in aqueous maltose so-

TABLE I

RELATIVE VISCOSITY (η/η_0) DATA FOR THE MALTOSE-ALKALI HALIDE-WATER SYSTEMS AT DIFFERENT TEMPERATURES

Concentration of electrolyte (in mol/L)	*Maltose–NaCl–water system Temperature (°C)*				*Maltose–NaBr–water system Temperature (°C)*				*Maltose–NaI–water system Temperature (°C)*			
	25	*30*	*35*	*40*	*25*	*30*	*35*	*40*	*25*	*30*	*35*	*40*
3.0	1.398	1.407	1.427	1.435	1.295	1.298	1.314	1.315	1.231	1.233	1.235	1.242
2.5	1.328	1.334	1.335	1.363	1.218	1.231	1.236	1.241	1.130	1.146	1.153	1.168
2.0	1.215	1.221	1.243	1.251	1.160	1.172	1.173	1.176	1.082	1.109	1.113	1.119
1.5	1.156	1.160	1.181	1.188	1.114	1.127	1.128	1.131	1.049	1.075	1.089	1.092
1.0	1.094	1.099	1.104	1.109	1.062	1.073	1.076	1.084	1.022	1.045	1.059	1.066
0.75	1.065	1.068	1.071	1.073	1.042	1.060	1.062	1.067	1.015	1.037	1.045	1.051
0.50	1.039	1.042	1.053	1.060	1.030	1.040	1.041	1.047	1.008	1.027	1.035	1.039
0.25	1.024	1.028	1.033	1.039	1.014	1.024	1.034	1.036	1.004	1.018	1.020	1.023
0.125	1.008	1.014	1.017	1.0207	1.008	1.011	1.019	1.024	0.997	1.001	1.006	1.009
	Maltose–KCl–water system				*Maltose–KBr–water system*				*Maltose–KI–water system*			
3.0	1.033	1.043	1.068	1.093	0.957	0.983	0.998	1.004	0.974	0.981	0.987	0.990
2.5	1.024	1.037	1.054	1.086	0.952	0.968	0.986	0.996	0.964	0.971	0.976	0.979
2.0	1.015	1.027	1.042	1.071	0.955	0.971	0.988	0.997	0.945	0.954	0.956	0.960
1.5	1.010	1.017	1.032	1.058	0.960	0.972	0.989	0.999	0.934	0.936	0.941	0.946
1.0	0.996	1.004	1.021	1.045	0.967	0.973	0.992	1.0014	0.941	0.946	0.949	0.952
0.75	0.993	1.001	1.021	1.046	0.977	0.987	0.997	1.007	0.971	0.975	0.977	0.980
0.50	1.002	1.004	1.023	1.048	0.983	0.991	1.002	1.012	0.974	0.977	0.980	0.983
0.25	1.003	1.006	1.025	1.049	0.989	0.994	1.007	1.023	0.978	0.981	0.984	0.989
0.125	1.009	1.012	1.027	1.051	0.995	0.999	1.011	1.014	0.982	0.986	0.992	0.997

lution and are listed in Table I. The relative viscosity data obtained from Eq. *1* were used to calculate the B-coefficient, employing the relation in Eq. *2*.

$$(\eta/\eta_0) = 1 + BC, \qquad (2)$$

where C is ~0.1M. This relation holds good for all six electrolytes in aqueous maltose solution up to the concentration of 0.5M. These values of B-coefficients are given in Table II.

For concentrated solutions, representation of viscosity by one general relation is very difficult, and hence several equations were put forward. These equations have been described in detail in an earlier communication[17].

One of these equations, as proposed by Moulik[19], and valid only for concentrated solutions, is given as

$$(\eta/\eta_0)^2 = M + KC^2, \qquad (3)$$

where M and K are constants that could be obtained from the slope and intercept of the plot of $(\eta/\eta_0)^2$ *versus* C^2. For the present work, M and K values were ob-

TABLE II

B-COEFFICIENT VALUES OF ALKALI-METAL HALIDES IN MALTOSE SOLUTION

Temperature (°C)	*Electrolytes*	*B*[a]	*B*[b]	*B*[c]
25	NaCl	0.087	0.078	0.078
	NaBr	0.061	0.048	0.054
	NaI	0.024	−0.017	0.01
	KCl	−0.0062	0.01	−0.0042
	KBr	−0.026	−0.031	−0.058
	KI	−0.062	−0.087	−0.076
30	NaCl	0.092	0.089	0.089
	NaBr	0.073	0.073	0.070
	NaI	0.038	0.028	0.036
	KCl	0.0068	0.021	0.005
	KBr	−0.019	−0.028	−0.037
	KI	−0.048	−0.068	−0.073
35	NaCl	0.10	0.100	0.1003
	NaBr	0.075	0.083	0.083
	NaI	0.049	0.043	0.048
	KCl	0.021	0.057	0.04
	KBr	−0.003	0.006	−0.0067
	KI	−0.030	−0.06	−0.062
40	NaCl	0.1014	0.118	0.11
	NaBr	0.081	0.096	0.092
	NaI	0.051	0.045	0.057
	KCl	0.025	0.126	0.092
	KBr	0.0045	0.023	0.006
	KI	−0.0255	−0.043	−0.051

[a] B-coefficient values obtained from the plot of $(\eta/\eta_0 - 1)$ *versus* C. [b] B-coefficient values obtained from Eq. *12*. [c] B-coefficient values obtained from the Bresslau–Miller equation; $B = 2.90, \bar{V}_c = -0.018$.

tained from the plot for all six electrolytes in 0.5M maltose solution; they are reported in Table III.

The viscosity data have also been fitted in the relation (Eq. *4*) due to Thomas[20], for $\phi \leqslant 0.25$ (ϕ = volume fraction).

$$(\eta/\eta_0) = 1 + 2.5\,\phi + 10.05\,\phi^2 \tag{4}$$

The substitution of $\phi = C\bar{V}_c$, where $\bar{V}_c$ is the average effective rigid molar volume, in Eq. *4*, yields the Bresslau–Miller[21] Eq. *5*.

$$\bar{V}_c = \frac{-2.5C + [(2.5C)^2 - 4\,(10.05C^2)\,(1 - \eta/\eta_0)]^{1/2}}{2(10.05)\,C^2} \tag{5}$$

The value of $\bar{V}_c$ thus obtained was used for calculating the B-coefficient by employing Eq. *6*, namely,

$$B = 2.90\,\bar{V}_c - 0.018, \tag{6}$$

TABLE III

VALUES OF DIFFERENT PARAMETERS (AT MALTOSE CONCENTRATION OF 0.5M AND AT SALT CONCENTRATION OF 0.125–3M, EXCEPT WHEN INDICATED OTHERWISE)

Temperature (°C)	Calculated from						
	Thomas Eq.	*Eq.* 12		*Vand Eq.*	*Bresslau–Miller Eq.*[a]	*Moulik Eq.*	
	$\bar{V}$ *(extrapolated)*	$\bar{V}$	*K*	$\bar{V}$ *(extrapolated)*	$\bar{V}_c$	*M*	*K*
	Maltose–NaCl–water system						
25	0.030[b]	0.0312	21.9	0.032	0.033	1.101	0.0927
30	0.031	0.0354	15.07	0.034	0.0368	1.125	0.0937
35	0.033	0.039	11.4	0.036	0.040	1.160	0.098
40	0.035[b]	0.047	7.5	0.038	0.044	1.212	0.10
	Maltose–NaBr–water system						
25	0.021[b]	0.019	56.02	0.023	0.025	1.073	0.0697
30	0.023[b]	0.029	13.113	0.025	0.030	1.082	0.072
35	0.024[b]	0.033	20.86	0.027	0.035	1.097	0.0735
40	0.032[b]	0.038	12.7	0.031	0.038	1.102	0.075
	Maltose–NaI–water system						
25	0.0025[b]	0.0068	192.3	0.0052	0.0097	1.003	0.031
30	0.014[b]	0.011	87.7	0.0149	0.018	1.05	0.042
35	0.023[b]	0.017	69.2	0.024	0.023	1.063	0.047
40	0.031[b]	0.018	19.7	0.029	0.026	1.08	0.050
	Maltose–KCl–water system						
25	0.001	0.004	123.7	0.0019	0.0047	0.975	0.0108
30	0.003	0.008	43.8	0.0033	0.008	0.987	0.0156
35	0.008	0.022	−8.42	0.0073	0.020	0.997	0.017
40	0.019	0.05	−13.08	0.0203	0.038	1.062	0.0179
	Maltose–KBr–water system						
25	−0.015	−0.012	33.9	−0.017	−0.0112	0.925	0.0055
30	−0.012	−0.0110	59.8	−0.0105	−0.0068	0.947	0.0061
35	−0.005	0.0025	69.4	−0.006	0.004	0.952	0.007
40	0.004	0.009	144.01	—	0.008	0.962	0.0097
	Maltose–KI–water system						
25	−0.0335	−0.035	20.9	−0.033[c]	−0.021	0.862	0.0049
30	−0.0329	−0.027	30.4	−0.031[c]	−0.019	0.875	0.0056
35	−0.0285	−0.023	35.2	−0.0263[c]	−0.015	0.889	0.0065
40	−0.0193	−0.017	48.08	−0.018[c]	−0.011	0.897	0.0093

[a] Valid between 0.125 and 3.0M. [b] Valid between 0.25 and 3.0M. [c] Valid between 0.75 and 3.0M.

and the results obtained from Eq. 6 are given in Table II.

Furthermore, the relative viscosity data have also been fitted in the equation given by Vand[22],

$$\ln (\eta/\eta_0) = \frac{2.5\phi}{1 - K\phi}, \tag{7}$$

where K is the generalized particle interaction coefficient. Rearrangement of Eq. *7* gives

$$C/\log(\eta/\eta_0) = \frac{2.303}{2.5\,\bar{V}} - \frac{2.303\,KC}{2.5}, \tag{8}$$

where $\bar{V}$ is the effective flowing volume. $\bar{V}$ has been obtained from the intercept of the linear plot of C/log (η/η_0) *versus* C on extrapolating it to zero concentration.

In order to test the validity of the Thomas equation in the linear form, Eq. *4* has been rearranged to give

$$\frac{(\eta/\eta_0 - 1)}{C} = 2.5\,\bar{V} + (K_s\bar{V})^2\,C, \tag{9}$$

where K_s is a generalized constant.

The viscosity data have also been fitted in a generalized Eq. *10* that is similar to the Thomas equation,

$$(\eta/\eta_0) = 1 + 2.5\phi + K_1\phi^2, \tag{10}$$

where K_1 is a constant. On substituting the value $\phi = C\bar{V}$, the equation yields Eq. **11**.

$$(\eta/\eta_0) = 1 + 2.5\,C\bar{V} + K_1C^2\bar{V}^2 \tag{11}$$

Eq. *11* may be written as

$$(\eta/\eta_0) = 1 + a_1C + a_2C^2, \tag{12}$$

where $\bar{V} = a_1/2.5$ and $K_1 = a_2/\bar{V}^2$. This relation has also been utilized, and coefficients a_1 and a_2 have been calculated for different concentrations using it. The average value of $\bar{V}$ obtained from the relation is also given in Table III.

The structural interaction of alkali-metal halides in aqueous maltose solution may be interpreted by taking into account the structural features of solvent water, structural changes produced by nonelectrolyte, hydration characteristics of maltose, and structural behavior of various ions in aqueous solution.

It is well known that water has a unique capacity to form relatively strong, three-dimensional hydrogen-bonds in the liquid state. The presence of a nonelectrolyte such as maltose may further strengthen the hydrogen bonds between water molecules and a relatively large "iceberg" or clathrate may be effectively formed around it[23].

Maltose possesses an unattached anomeric carbon atom and a hemiacetal grouping, and is a reducing sugar. It has 8 free hydroxyl groups and, on hydrolysis, yields two molecules of D-glucose having the $^4C_1$ conformation[24]. The hydration properties of maltose are not simply related to the number of hydroxyl groups or oxygen atoms in the molecule, but may be highly influenced by the conformation adopted by maltose in aqueous solution. Sugget[25] considered the effect of conformational changes in maltose, due to the possibilities of rotation about the glycosidic bond, as well as intramolecular interaction between the D-glucosyl group and the D-glucose residue. Rees and Thom[26] found that the optical rotation of maltose is strongly dependent on the solvent and the temperature, indicating the existence of different energy minima, based on conformational interchanges. The linkage rotation in an aqueous solution of maltose decreases with decreasing temperature. These changes may reflect distortion of a chair form, and show the negative hydration. However, in aqueous solution, the linkage-rotation measurement by Rees and Thom[26] suggested that the molecule spends a large proportion of its time in a chair conformation. Such a conformation has, in fact, been suggested[27] to account for the apparent specific expansibility of maltose, where the two D-glucose units have folded together to screen their hydrophobic surfaces from the solvent. Such a folded conformation may present a hydrophilic surface more compatible with the tetrahedral arrangement of water molecules.

When added to an aqueous solution of maltose, metal ions shift the position of the $\alpha \leftrightarrow \beta$ anomeric equilibrium towards the formation of more of the α form in

TABLE IV

VALUES OF IONIC PARAMETERS AT DIFFERENT TEMPERATURES

Temperature (°C)	*Ion*	$r_{\pm}$[a] *(Å)*	$\bar{V}^0$ *(cm^3.mol^{-1})*	$B_{\pm}$ *(L.mol^{-1})*	$\bar{V}_{\pm}$ *(cm^3.mol^{-1})*	n_B
25	Na$^+$	1.17	4.04	0.089	35.6	4.76
	K$^+$	1.49	8.34	−0.0031	−1.24	−1.44
	Cl$^-$	1.64	11.12	−0.0031	−1.24	−1.86
	Br$^-$	1.80	14.7	−0.029	−11.6	−3.97
	I$^-$	2.05	21.7	−0.065	−26.0	−7.2
30	Na$^+$	1.17	4.04	0.089	35.6	4.76
	K$^+$	1.49	8.34	0.0034	1.36	−1.05
	Cl$^-$	1.64	11.12	0.0034	1.36	−1.47
	Br$^-$	1.80	14.7	−0.016	−6.4	−3.18
	I$^-$	2.05	21.7	−0.051	−20.4	−6.35
35	Na$^+$	1.17	4.04	0.089	35.6	4.76
	K$^+$	1.49	8.34	0.0105	4.2	−0.625
	Cl$^-$	1.64	11.12	0.0105	4.2	−1.045
	Br$^-$	1.80	14.7	−0.013	−6.2	−3.15
	I$^-$	2.05	21.7	−0.04	−16.0	−5.69
40	Na$^+$	1.17	4.04	0.089	35.6	4.76
	K$^+$	1.49	8.34	0.0125	5.0	−0.504
	Cl$^-$	1.64	11.12	0.0125	5.0	−0.92
	Br$^-$	1.80	14.7	−0.008	−3.6	−2.76
	I$^-$	2.05	21.7	−0.038	−15.2	−5.57

[a] Gourary–Adrian radii.

solution, permitting a hydration geometry almost compatible with the characteristics of liquid water.

It has been observed that B-coefficients obtained from the various equations (see Table II) are in the same order, and increase with increasing temperature. The individual B-coefficient (ionic) values have been obtained on the separation basis by taking $B_{K^+} = B_{Cl^-}$ in potassium chloride for all of the temperatures. The ionic B-coefficients of other electrolytes have also been computed, using the available B values of different salts at different temperatures. The results are given in Table IV. It has been observed that the B-coefficient for Na^+ remains constant, whereas the B values for K^+, Cl^-, Br^-, and I^- increase with increasing temperature. Thus, dB/dT for Na^+ remains zero, but those for K^+, Cl^-, Br^-, and I^- are positive in aqueous maltose solution, indicating interaction between the ions and the water dipole through hydrogen bonding. Frank and Wen's model[28], the Gurney cosphere model[29], and Nightingale's hydrated ion radius model[30] suggested that a positive value of dB/dT indicates the ability of ions to disrupt the water structure in their cosphere and show the structure-breaking tendency.

The B-coefficient can then be related to $\bar{V}$ by using the relation

$$B = 2.5\,\bar{V}. \qquad (13)$$

Estimates of $\bar{V}$ are often based on the hydrated or crystal radii of solute ions. In fact, this effect is used to estimate the degree of hydration. $\bar{V}_c$ values from Bresslau and Miller's relation[21], and $\bar{V}$ from Vand's[22], Thomas's[20], and the generalized Eq. *12*, are in the same order, and increase with increasing temperature for all six electrolytes in aqueous maltose solution (see Table III), indicating electrostatic attraction between water dipoles and ions, and a large number of water molecules present in the cosphere of an ion due to thermal agitation. By examining the $\bar{V}$ of ions as a function of size, charge, and temperature, it is possible to study the effect of these parameters on ion–water interaction, with the intent of obtaining a better understanding of interactions in aqueous solution. The division of $\bar{V}$ values of all of the electrolytes into their ionic components can be made from $B_\pm$ coefficients by employing the relation

$$B_\pm = 2.5\,\bar{V}_\pm. \qquad (14)$$

The hydration number (n_B) of the ions may be evaluated from the equation

$$\bar{V}_\pm = \bar{V}^0_{ion} - n_B\bar{V}^0_s, \qquad (15)$$

where $\bar{V}^0_{ion}$ is the free-ion volume, which can be calculated from the relation $\bar{V}^0_{ion} = 2.52\, r^3$, where r is the radius in Ångström units taken from Gourary–Adrian radii, and $\bar{V}^0_s$ is the volume of the water, equal to 6.62 cm^3/mol taking Pauling's radius of water as 1.38 Å.

Thus, the hydration number of ions is given by the relation

$$n_B = \frac{\bar{V}_\pm - \bar{V}^0_{ion}}{\bar{V}_s} \qquad (16)$$

On substituting the value of $\bar{V}_\pm$ from Eq. *14* in Eq. *16*, we get

$$n_B = \frac{0.4\,B_\pm - \bar{V}^0_{ion}}{\bar{V}^0_s} \qquad (17)$$

The results obtained from Eq. *17* are given in Table IV.

Because the various components of $\bar{V}_\pm$ may be small compared to the size of an ion (crystal volume), it is difficult to determine the importance of individual components, or to separate the overlapping effects. Recently, Millero and coworker[31,32] tried to solve the problem by examining the effect of temperature on $\bar{V}_\pm$. On correlating the $\bar{V}_\pm$ value with the temperature, the results obtained for our systems were found to be in a good agreement with the findings of Millero[32] and Curthoys and Mathieson[33]. The $\bar{V}_\pm$ value increases with increasing temperature in maltose solution, except in the case of Na^+. In the case of Na^+, the $\bar{V}_\pm$ value remains constant. This indicates that K^+, Cl^-, Br^-, and I^- are disordered structure-breaking ions, or negative hydration ions, and the order of the structure-breaking effects is $I^- > Br^- > Cl^- > K^+ > Na^+$ in aqueous maltose solution.

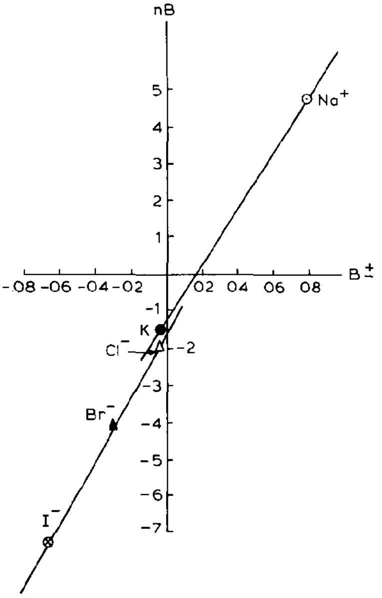

Fig. 1. Plot of hydration number *versus* ionic B-coefficient at 25°.

The hydration number is closely related to the structure of solution, and plays an important role in the interpretation of structure of solution. Structure-making ions possess positive hydration numbers, whereas the hydration number of structure-breaking ions has been found to be negative. The results given in Table IV indicate that the hydration numbers of Na^+ and K^+ differ in sign. On correlating the hydration numbers with ionic radii, it was noticed that the hydration numbers of alkali-metal ions fall on a straight line, but that those of halide ions in aqueous maltose solution fall on another straight line (see Fig. 1). This observation is supported by the work of Krestov[34], who also correlated the change in entropy of water in ionic solutions with ionic radii, and found a linear relationship between these two parameters.

An effect of temperature on the hydration number has also been observed. It was found that the hydration numbers of K^+, Cl^-, Br^-, and I^- increase with increasing temperature (see Table IV), but the hydration number of Na^+ remains constant in aqueous maltose solution. The breaking of water–water bonds leads to strengthening of the hydration in solution. Thus, when the structure of water is broken due to increase in temperature, close hydration of ions is reinforced to a certain extent. The reinforcement of close hydration of ions with increasing temperature has been demonstrated by Ivoilov *et al.*[35] by measuring the spin of deuterium nuclei in solution. Thus, the increase of hydration numbers with temperature confirms the negative hydration or structure-breaking tendency in aqueous maltose solution. It indicates that the exchange of water molecules near the ion occurs more frequently in comparison to bulk water. This fact is further supported from the work of Engel and Sare[36].

On correlating the hydration number with the ionic B-coefficient, it was observed that hydration numbers of cations and anions have a different linear relationship with their ionic B-coefficients, supporting the idea that structure-making ions have a positive ionic molar volume, a positive hydration number, and a positive entropy change, whereas structure-breaking ions have a negative ionic molar volume, a negative hydration number, and a negative entropy change. This observation strongly confirms the discovery made by Engel and Sare[36] that Na^+ is an electrostrictive, structure-maker ion, whereas K^+, Cl^-, Br^-, and I^- ions are structure-breaking.

Thus, the magnitudes of the hydration numbers (see Table IV) suggest that the structure-breaking tendency in aqueous maltose solution is in the order $I^- > Br^- > Cl^- > K^+ > Na^+$.

ACKNOWLEDGMENT

Financial support from UGC (New Delhi) to conduct the present work is thankfully acknowledged.

REFERENCES

1 M. Dollet, J. Juillard, and R. Zana, *J. Solution Chem.*, 9 (1980) 827–840.

2 T. M. Herrington and C. P. Meunier, *J. Chem. Soc., Faraday Trans. 1*, 78 (1982) 225–236.

3 H. L. Welles, Jr., M. J. Kustek, and R. E. Lindstrom, *J. Solution Chem.*, 4 (1975) 391–398.

4 H. L. Welles, Jr., and R. E. Lindstrom, *J. Solution Chem.*, 5 (1976) 155–162.

5 A. Cesaro, *J. Solution Chem.*, 5 (1976) 319–323.

6 S. Fredericksson, *Acta Chem. Scand.*, 23 (1969) 1995–2003.

7 S. P. Moulik and D. P. Khan, *Carbohydr. Res.*, 41 (1975) 93–104.

8 Vishnu and A. K. Singh, *Proc. Indian Acad. Sci., Sect. A*, 80 (1974) 57–74.

9 Vishnu and A. K. Singh, *Carbohydr. Res.*, 54 (1977) 149–157; 58 (1977) 307–316.

10 Vishnu and A. K. Singh, *Carbohydr. Res.*, 70 (1979) 13–18.

11 Vishnu and V. S. Mishra, *Indian J. Chem.*, 19A (1980) 1065–1069.

12 Vishnu and V. S. Mishra, *Proc. Indian Acad. Sci., Sect. A*, 89 (1980) 153–161.

13 Vishnu and V. S. Mishra, *Electrochim. Acta*, 25 (1980) 1513–1517.

14 Vishnu and V. S. Mishra, *Carbohydr. Res.*, 89 (1981) 55–63.

15 Vishnu and V. P. Mishra, *Carbohydr. Res.*, 59 (1977) 35–46; 60 (1978) 29–37; 63 (1978) 29–40.

16 Vishnu and V. P. Mishra, *Electrochim. Acta*, 23 (1978) 839–844.

17 Vishnu and V. K. Singh, *Indian J. Chem.*, 20A (1981) 24–29.

18 S. S. C. Chu and G. A. Jeffrey, *Acta Crystallogr.*, 23 (1967) 1038–1047.

19 S. P. Moulik, *J. Phys. Chem.*, 72 (1968) 4682–4684.

20 D. G. Thomas, *Colloid Sci.*, 20 (1965) 267–277.

21 B. R. Bresslau and I. F. Miller, *J. Phys. Chem.*, 74 (1970) 1056–1061.

22 V. Vand, *J. Phys. Colloid Chem.*, 52 (1948) 277–283.

23 T. C. W. Mac, *J. Chem. Phys.*, 43 (1965) 2799–2805.

24 S. J. Angyal, *Angew. Chem.*, 8 (1969) 57–68.

25 A. Suggett, in F. Franks (Ed.), *Water: A Comprehensive Treatise*, Vol. 4, Plenum, New York, 1975.

26 D. A. Rees and D. Thom, *J. Chem. Soc., Perkin Trans. 2*, (1977) 191–201.

27 J. L. Neal and D. A. I. Goring, *Can. J. Chem.*, 48 (1970) 3745–3758.

28 H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, 24 (1957) 133–140.

29 R. M. Gurney, *Ionic Processes in Solution*, McGraw-Hill, New York, 1953.

30 E. R. Nightingale, *J. Phys. Chem.*, 66 (1962) 894–897.

31 F. J. Millero and W. Drost-Hansen, *J. Phys. Chem.*, 72 (1968) 1758–1763.

32 F. J. Millero, *J. Phys. Chem.*, 72 (1968) 4589–4593.

33 G. Curthoys and T. G. Mathieson, *Trans. Faraday Soc.*, 66 (1970) 43–58.

34 G. A. Krestov, *Zh. Strukt. Khim.*, 8 (1962) 402–412.

35 N. K. Ivoilov, V. I. Ionov, and R. K. Mazitov, *Dokl. Akad. Nauk. SSSR*, 183 (1968) 863–868.

36 C. A. Engel and E. J. Sare, *J. Chem. Phys.*, 52 (1969) 1058–1062.