VISCOSITIES OF CONCENTRATED SOLUTIONS OF SODIUM AND POTASSIUM ACETATES IN AQUEOUS SOLUTIONS OF D-GLUCOSE

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ABSTRACT

The relative viscosities (η_r) of concentrated solutions of sodium and potassium acetates in 0.5M D-glucose solution at 25, 30, 35, and 40° are reported. Viscosity data have been analyzed using Vand's, Thomas's, Bresslau and Miller's, Moulik's, and a generalized treatment, at higher electrolytic concentrations. The molar volumes ($\bar{V}$), ionic B-coefficients ($B_{\pm}$), and hydration numbers (n_B) of ions were computed, and structural aspects of sodium and potassium acetates in aqueous D-glucose solutions have been interpreted by taking into account the magnitude of various parameters obtained. The temperature-dependence of B-coefficients has also been discussed. In aqueous D-glucose solutions, Na^+ and K^+ are found to act as net structure-breakers, whereas a significant structure-making trend is shown by acetate ion.

INTRODUCTION

Numerous studies have shown that viscosity measurements are useful in providing information regarding solute–solvent interactions, and particularly as regards the modifications induced by ions on the structure of solutions. The viscometric technique has generally been used in studying the behavior of electrolytes in pure solvents[1-7], but investigations of multicomponent solutions are rather scanty[8,9]. Although there are very few data available on the thermodynamic and transport properties of aqueous solutions of mixtures of electrolytes and nonelectrolytes, these mixtures provide a wealth of information about the interaction of various functional groups with ions. Such interactions are likely to play important roles in a variety of reactions.

Salts of the lower carboxylic acids have been found to cause increased hydrogen bonding of the solvent in aqueous solution[10-12]. Recently, Blokhra and coworkers made some studies on the apparent molar volume[13], ϕ_v, and viscosity B-coefficients[14,15] of alkali-metal formates and acetates in water and in aqueous methyl acetate solutions. They concluded, on the basis of experimental observa-

tions, that potassium acetate behaves as a net structure-maker in water and in methyl acetate–water mixtures. We have also observed that carboxylate ions promote the water structure, or increase the hydrogen bonding of the solvent with increasing length of the hydrocarbon chain of the anion in aqueous sucrose solution[16].

We decided to study systematically the viscometric properties of concentrated 1:1 solutions of several electrolytes in aqueous carbohydrate solutions, as we consider that such investigations may provide useful information on the effects induced by ions and the carbohydrate entities on the structure of water. We have already reported the structural interactions of alkali halides with sucrose[17], D-xylose[18], D-mannitol[19], urea[20], 1,3-dimethylurea[21], D-glucose[22], and maltose[23] in aqueous solution, employing viscosity measurements. In the present study, it was considered worth while to investigate the structural interactions of sodium and potassium acetates in D-glucose–water solutions, keeping in view the structure-forming tendency of carboxylate ions.

EXPERIMENTAL

Materials and preparation of solution. — Sodium acetate, potassium acetate, and D-glucose (BDH, Analar grade) were used, after drying, without purification.

All of the solutions were prepared on a molar basis in doubly distilled, demineralized, conductivity water (sp. cond. $\sim 10^{-6}$ ohm^{-1}.cm^{-1}). A 0.5M solution of D-glucose was prepared in conductivity water, and was used as a stock solution. Initially, a 2.0M solution of the electrolyte was prepared, and other concentrations, needed for the measurements, were obtained by diluting it with the stock solution.

Density and viscosity measurements. — The apparatus and the experimental technique used for the viscosity measurements have been described[22,23]. Densities were measured with a pycnometer. The temperature of the water bath, for both the viscometer and the pycnometer, was maintained at the chosen value ±0.05°.

RESULTS AND DISCUSSION

The relative viscosities (η_r) of sodium and potassiumacetates in D-glucose–water solutions were measured within a concentration range of 0.125 to 2.0M. The results at 25, 30, 35, and 40° are included in Table I.

The B-coefficients for the electrolytes, in aqueous D-glucose solution at different temperatures, were determined graphically, using the relation

$$\eta_r = 1 + BC, \qquad\qquad\qquad (1)$$

where C is ~ 0.1M. Eq. *1* holds good for sodium and potassium acetates in aqueous D-glucose solution (0.5M) only up to an electrolytic concentration of 0.5M. For the concentrated electrolyte solutions, representation of viscosity by one general equa-

TABLE I

RELATIVE VISCOSITY (η_r) DATA FOR ELECTROLYTES IN AQUEOUS D-GLUCOSE SOLUTION (0.5 M) AT DIFFERENT TEMPERATURES

Concentration of electrolyte (M)	Temperature (°C)			
	25	30	35	40
CH_3CO_2Na				
2.0	1.741	1.716	1.686	1.625
1.5	1.524	1.519	1.511	1.466
1.0	1.360	1.353	1.347	1.329
0.75	1.263	1.259	1.257	1.252
0.50	1.178	1.171	1.168	1.160
0.25	1.118	1.103	1.096	1.094
0.125	1.078	1.068	1.063	1.059
CH_3CO_2K				
2.0	1.543	1.527	1.430	1.425
1.5	1.423	1.364	1.322	1.321
1.0	1.239	1.238	1.221	1.207
0.75	1.194	1.168	1.158	1.157
0.50	1.131	1.130	1.117	1.117
0.25	1.067	1.064	1.058	1.054
0.125	1.043	1.041	1.038	1.034

tion is very difficult, and hence, several equations used for such solutions were taken into consideration and the validity of the experimental data was tested. An equation, proposed by Moulik[24] for concentrated electrolyte solutions, is given as

$$\eta_r^2 = M + KC^2, \tag{2}$$

where M and K are constants, and could be obtained from the slope and intercept, respectively, of the plot of η_r^2 versus C^2.

Experimental data were also analyzed by following an equation due to Thomas[25], namely,

$$\eta_r = 1 + 2.5\,\phi + 10.05\,\phi^2, \tag{3}$$

where ϕ is $\leqslant 0.25$ and denotes the volume fraction. Substitution of $\phi = C\bar{V}_e$, where $\bar{V}_e$ is the effective rigid molar volume, in Eq. 3 yields the Bresslau and Miller equation (Eq. 4).

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

The values of $\bar{V}_e$ thus obtained were used for calculating the B-coefficient, employing the relation

$$B = 2.90 \ \bar{V}_e - 0.018. \tag{5}$$

In order to test the validity of the Thomas equation in linear form, Eq. *3* was rearranged in the form

$$(\eta_r - 1)/C = 2.5 \ \bar{V} + (K_s \ \bar{V})^2 \ C, \tag{6}$$

where K_s is a generalized constant.

The validity of the data has also been examined by a generalized equation (Eq. *7*), similar to that of Thomas, namely,

$$\eta_r = 1 + 2.5 \ \phi + K\phi^2, \tag{7}$$

where K is a generalized constant. Substitution of $\phi = C\bar{V}$ in Eq. *7* yields

$$\eta_r = 1 + 2.5 \ C\bar{V} + K_1 C^2 \ \bar{V}^2, \tag{8}$$

which may be rewritten as

$$\eta_r = 1 + a_1 C + a_2 C^2, \tag{9}$$

where $\bar{V} = a_1/2.5$ and $K_1 = a_2/\bar{V}^2$. $\bar{V}$ may be determined by taking into account the values of coefficients a_1 and a_2 for different concentrations of electrolytes.

Moreover, the viscosity data have also been fitted to Vand's equation (Eq. *10*), namely,

$$\ln \eta_r = \frac{2.5 \ \phi}{1 - K \ \phi}, \tag{10}$$

where K is a generalized, particle-interaction coefficient. For analysis of data by Eq. *6*, it was rearranged into the form

$$\frac{C}{\log \eta_r} = \frac{2.303}{2.5 \ \bar{V}} - \frac{2.303 \ KC}{2.5}, \tag{11}$$

where $\bar{V}$ is the effective flowing volume and is given by the intercept of the linear plot of $C/\log \eta_r$ against C, on extrapolating it up to the zero concentration.

Values of $\bar{V}_e$ and $\bar{V}$ obtained from Eqs. *4*, *6*, *9*, and *11* are included in Table II, along with some other parameters derived from different equations.

TABLE II

VALUES OF DIFFERENT PARAMETERS AT D-GLUCOSE CONCENTRATION = 0.5M AND ELECTROLYTE CONCEN-
TRATION = 0.5–2.0 M, EXCEPT INDICATED OTHERWISE

Temp. (°C)	Thomas Eq. $\bar{V}$ (extra-polated)	Vand Eq. $\bar{V}$ (extra-polated)	Calc. from Eq. 9 $\bar{V}$	K	Bresslau and Miller Eq. $\bar{V}_e$	Moulik Eq. M	K
CH_3CO_2Na							
25	0.131	0.139	0.144	0.261	0.127^a	0.99	0.416
30	0.124	0.136	0.130	0.059	0.119^a	0.80	0.400
35	0.121	0.133	0.127	0.490	0.115^a	0.66	0.375
40	0.119	0.128	0.124	0.950	0.111^a	0.46	0.300
CH_3CO_2K							
25	0.088	0.090	0.091	0.508	0.088^a	1.06	0.300
30	0.083	0.085	0.087	1.150	0.084^a	0.86	0.277
35	0.080	0.079	0.082	0.967	0.077^a	0.67	0.210
40	0.078	0.076	0.079	0.489	0.074^a	0.48	0.193

[a]Valid for an electrolyte concentration of 0.125 to 3.0M.

B-coefficients were determined with the help of $\bar{V}$, employing the relation

$$B = 2.5 \, \bar{V}. \tag{12}$$

B-Coefficients obtained with the help of different equations for aqueous D-glucose solution at 25, 30, 35, and 40° are given in Table III.

TABLE III

B COEFFICIENTS OF ELECTROLYTES IN 0.5M D-GLUCOSE–WATER SOLUTION AT DIFFERENT TEMPERATURES.
(ELECTROLYTE CONCENTRATION RANGE, 0.125–2.0 M, NUMBER OF DATA POINTS EMPLOYED, 7)

Electrolytes	Temperatures (°C)	B^a	B^b	B^c
CH_3CO_2Na	25	0.401	0.409	0.351
	30	0.383	0.385	0.327
	35	0.369	0.377	0.315
	40	0.350	0.366	0.302
CH_3CO_2K	25	0.277	0.277	0.237
	30	0.246	0.240	0.225
	35	0.235	0.238	0.205
	40	0.218	0.225	0.196

[a]Values from the plot of η_r versus C. [b]Values from equation, $B = 2.5 \, \bar{V}$. [c]Values from Bresslau and Miller's equation: $B = 2.90$, $\bar{V}_e -0.018$.

TABLE IV

VALUES OF IONIC PARAMETERS IN AQUEOUS D-GLUCOSE SOLUTION (0.5M) AT DIFFERENT TEMPERATURES

Temp. (°C)	Ion	$r_\pm$	$\bar{V}^0_\pm$ $(cm^3.mol^{-1})$	$B_\pm$ $(L.mol^{-1})$	$\bar{V}_\pm$ $(cm^3.mol^{-1})$	n_B
25	Na⁻	1.17[a]	4.040	0.126	50.4	7.0
	K⁺	1.49[a]	8.340	0.002	0.8	−1.15
	CH₃CO₂⁻	4.50[b]	229.62	0.275	110.0	−18.07
30	Na⁺	1.17[a]	4.040	0.139	55.6	7.78
	K⁺	1.49[a]	8.340	0.0024	1.0	−1.108
	CH₃CO₂⁻	4.50[b]	229.6	0.243	97.2	−20.0
35	Na⁺	1.17[a]	4.040	0.141	56.0	7.84
	K⁺	1.49[a]	8.340	0.007	2.8	−0.83
	CH₃CO₂⁻	4.50[b]	229.6	0.226	90.4	−21.03
40	Na⁺	1.17[a]	4.040	0.143	57.2	8.03
	K⁺	1.49[a]	8.340	0.105	4.2	−0.62
	CH₃CO₂⁻	4.50[b]	229.6	0.207	83.0	−34.67

[a]Gourary–Adrian radii. [b]Ionic radii of $CH_3CO_2^-$ in aqueous solution.

As is well known, the B-coefficient may be regarded as a result of two contributions, that from the cation and that from the anion, which are independent and, consequently, additive. Ionic B-coefficients contribute independently to solute–solvent interactions and, hence, their magnitude might be very helpful in understanding the structural interaction of different ions in aqueous carbohydrate solutions already possessing a number of hydrogen-bonding sites. Keeping this concept in mind, ionic B-coefficients were computed on the separation basis, taking potassium chloride solution under consideration. In order to determine the B-coefficient for KCl in D-glucose–water, the relative viscosities (η_r) of KCl in D-glucose solution (0.5M) were measured at specified temperatures, and the ionic contribution of K⁺ was calculated by taking $B_{K^+} = B_{Cl^-}$. Values of B_{K^+} thus obtained were substituted in the B-values of sodium and potassium acetates, and the ionic contributions of other ions at different temperatures were determined.

Ionic molar volumes ($\bar{V}_\pm$) of electrolytes in D-glucose solutions were also determined with the help of the relation

$$B_\pm = 2.5\,\bar{V}_\pm. \tag{13}$$

Hydration numbers (n_B) of the ions under study were calculated by making use of the relation

$$\bar{V}_\pm = \bar{V}^0_{ion} + n_B\,\bar{V}^0_s, \tag{14}$$

where $\bar{V}^0_s$ is the volume of water equal to 6.62 $cm^3.mol^{-1}$ and $\bar{V}^0_{ion}$ is the free ion

volume, which may be obtained from the relation $\bar{V}_{ion} = 2.52\, r_0^3$ (r_0 being the radius in Ångström units, taken from Gourary–Adrian radii).

Eq. *14* may be rearranged in the form

$$n_B = \frac{V_{\pm} - \bar{V}_{ion}^0}{\bar{V}_s^0},\tag{15}$$

and may be further modified, with the help of Eq. *13*, as

$$n_B = \frac{0.4\,B_{\pm} - \bar{V}_{ion}^0}{\bar{V}_s^0}.\tag{16}$$

Ionic B-coefficients ($B_{\pm}$), ionic molar volumes ($\bar{V}_{\pm}$), and ionic hydration numbers (n_B), obtained with the help of the aforementioned equations, are given in Table IV, along with some other ionic parameters.

It had already been established[26] that the B-coefficient of the Jones–Dole equation has large positive values for hydrophobic ions, and that the larger the ion, the more positive the B-coefficient. A perusal of Table III reveals that the B-values for sodium and potassium acetates in aqueous D-glucose solution decrease with increasing temperature. Negative B-coefficients are generally associated with structure-breaking effects of electrolytes in solution. A number of workers consider that the viscosities B-coefficient is a measure of ion–dipole interaction between the ions and solvent molecules. From the data in Table IV, it may be seen that the ionic B-coefficients for Na^+ and K^+ in aqueous D-glucose solution increase, whereas the B-coefficient for CH_3COO^- decreases, with increase in temperature. Thus, when ionic B-coefficients are correlated with temperature, it is found that dB/dT for Na^+ and K^+ are positive, and, for CH_3COO^-, is negative in D-glucose solution. The value of dB/dT is a better criterion for determining solute–solvent interactions. As regards the acetate ion, $dB_-/dT < 0$ shows that it behaves as a net structure-maker in D-glucose–water. Moreover, in the case of sodium and potassium ions, we obtain $dB_+/dT > 0$, which indicates the structure-breaking tendency of these ions in aqueous D-glucose solution.

As may be seen in Table II, $\bar{V}$ values, evaluated from Vand's equation, a modified form of the Thomas equation, Bresslau and Miller's relation, and the generalized equation, are in reasonable agreement with each other and, thus, show the validity of these equations for concentrated electrolyte solutions in D-glucose–water. At all temperatures, values of $\bar{V}$ for sodium and potassium acetates are found to decrease with increasing temperature, showing a structure-breaking trend in solution[27].

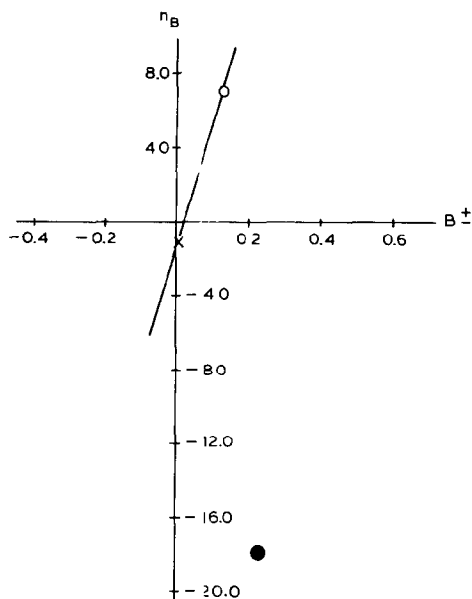The values of ionic molar volume ($\bar{V}_{\pm}$), presented in Table IV, increase

Fig. 1. Plot of hydration number (n_B) versus $B_\pm$ in alkali acetate–glucose (0.50M)–water system at 25°. (Key: ○ = Na$^+$, × = K$^+$, and ● = CH$_3$CO$_2^-$.)

slightly with temperature, except in the case of acetate ion, where $\bar{V}_\pm$ shows a decreasing trend with increase in temperature. This further indicates the structure-breaking trend of Na$^+$ and K$^+$, and the structure-forming tendency of acetate ion in aqueous D-glucose solution. Hydration numbers (n_B) of ions in D-glucose–water, given in Table IV, show that the hydration numbers of Na$^+$ and K$^+$ differ in sign. This is in agreement with the known relation between hydration of ions and solution structure. The structure-forming ions possess a positive hydration number and a positive ionic molar volume, whereas a negative hydration number and a negative ionic molar volume have been attributed to structure-distorting ions. On correlating the hydration numbers of Na$^+$, K$^+$, and CH$_3$CO$_2^-$ with their ionic radii, it was observed that Na$^+$ and K$^+$ fall on one straight line, whereas the acetate ion is beyond the line adjoining sodium and potassium ions (see Fig. 1). The behavior of these ions in D-glucose–water is supported by the work of Krestov[28], who made a correlation between ionic hydration numbers and ionic radii for alkali-metal halides, and found that alkali-metal ions fall on one straight line, and halide ions fall on another.

An effect of temperature on hydration number has also been observed, and it is seen from Table IV that the hydration numbers of Na$^+$ and K$^+$ increase with temperature, whereas the number decreases with increasing temperature for CH$_3$CO$_2^-$ in D-glucose–water. This further strengthens the view that Na$^+$ and K$^+$ are structure-breaking or negative hydrating[29] ions, whereas CH$_3$CO$_2^-$ is a structure-making or positive hydrating ion in aqueous D-glucose solution.

The correlation of hydration numbers (n_B) with their ionic B-coefficients ($B_\pm$) shows that hydration numbers of cations and anions have different linear relationships with their corresponding $B_\pm$ values, supporting the concept[30] that structure-making ions have positive ionic molar volumes, positive hydration numbers, and positive entropy changes, and that structure-breaking ions have negative values of these parameters. Thus, on the basis of the experimental evidence, the magnitude of our results conclusively indicates that Na^+ and K^+ act as structure-breakers, whereas $CH_3CO_2^-$ acts as a net structure-maker in aqueous D-glucose solutions.

ACKNOWLEDGMENT

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