

Viscosities of Concentrated Solutions of Polyhydroxy Nonelectrolytes, Glucose, Sucrose, Mannitol & Sorbitol in Relation to Solute-Solvent Interaction & a Universal Viscosity Equation

S. P. MOULIK & D. P. KHAN

Department of Chemistry, Jadavpur University, Calcutta 700032

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The viscosities of aqueous solutions of glucose, sucrose, mannitol and sorbitol have been analysed in the light of Vand's equation. The evaluation of hydration number from viscosity is only partial. Local water structure disruption at the microscopic level around the polyhydroxy compounds should be considered vital to account for the temperature variation of the constant term that appears in the equations of Vand and Einstein. The viscosity of concentrated aqueous solutions of the above referred polyhydroxy compounds as well as several electrolytes can well be described by the equation of Vand, Moulik and Thomas. Differential forms of these equations have been observed to have a common basis. Interrelation of these equations can thus generate a universal equation whose validity has been established.

SOLUTIONS of non-spherical particles and even concentrated solutions of spherical particles do not obey Einstein's viscosity equation¹

$$\eta_r = 1 + 2.5\phi \quad \dots(1)$$

where η_r is the relative viscosity of the solution and ϕ is the volume fraction of the solute.

Under these situations the equation of Vand² has shown much success.

$$\ln \eta_r = a\phi/(1-Q\phi) = 2.5 V_h C/(1-QV_h C) \quad \dots(2)$$

where a is a constant (a depends on the axial ratios of the particles and ≥ 2.5 for non-spherical particles), Q is an interaction constant (it accounts for the interaction of the flow patterns among the neighbouring particles), V_h is the molar volume of the solute including rigidly held solvent molecules due to hydration and C is the molar concentration of the solute.

The scope of solute-solvent interaction is absent in both the above equations. This effect can alter the magnitude of a and a deviation from 2.5 can then be both dimensional³⁻⁶ and interactional⁷. Though dimensional effect has been analysed^{6,8}, the interactional part has not been analysed particularly when the solution is concentrated. It would, therefore, be worthwhile to study the latter aspect using solutes of known geometry and to see what bearing this has on the constant terms whose magnitude may as well indicate the effectiveness of such an interaction. The class of compounds selected in the present study consists of several industrially and biologically important polyhydroxy compounds, such as glucose, sucrose, mannitol and sorbitol. But for sucrose, no systematic measurements of viscosities of their aqueous solutions have been elaborately made at different temperatures. The results of such measurements have been analysed according to the equation of Vand which is truly

applicable to sucrose² and other polyhydroxy compounds in general⁹.

In recent papers^{9,10,12} it has been established that viscosity of concentrated solutions of both electrolytes and nonelectrolytes more or less obey the equations of Vand² (Eq. 2), Moulik¹⁰ (Eq. 3) and Thomas¹¹ (Eq. 4).

$$\eta_r^2 = I + MC^2 \quad \dots(3)$$

$$\eta_r = 1 + 2.5 V_h C + 10.05 V_h^2 C^2 \quad \dots(4)$$

where I and M are two constants and the other terms have got their usual significance. We believe that there is a common basis for these equations since these originate from the basic equation of Einstein; only different ways of manipulation give different formulations. A mathematical comprehension of these equations may give some insight into this. This is described in the following. The analysis is with reference to spherical shape of the solute particles. (For non-spherical shapes the value of the constant term^{6,8} will be other than 2.5).

Eqs. (1-3) on differentiation with respect to C give Eqs. (5-7) respectively.

$$\frac{d\eta_r}{dC} = 2.5 V_h = K_E \quad \dots(5)$$

$$\frac{d\eta_r}{dC} \left\{ \frac{(1-Q'C)^2}{\eta_r} \right\} = 2.5 V_h = K_V \quad \dots(6)$$

where $Q' = QV_h$.

$$\frac{d\eta_r}{dC} \left(\frac{\eta_r}{C} \right) = M = K_M \quad \dots(7)$$

Thomas' equation (4) can be rewritten as Eq. (8).

$$\eta_r = 1 + 2.5 V_h C + K'_s C^2 \quad \dots(8)$$

where $K'_s = 10.05 V_h^2$.

Eq. (8) on differentiation with respect to C yields Eq. (9).

$$\frac{d\eta_r}{dC} - 2K'_s C = 2.5 V_h = K_T \quad \dots(9)$$

On the consideration^{6,12}, $2.5 V_h = B$, it can be stated that the differential forms of the equations of Einstein, Vand and Thomas lead to a constancy which is the solute-solvent interaction coefficient (B coefficient) proposed by Jones and Dole¹³.

The yet undefined constant term K_M of Eq. (7) may have a relation¹² also with B . Now, the more or less general validity of all these equations¹² suggests that the factors, $(1-Q'C)^2/\eta_r$, η_r/C , and $2K'_s C$ of Eqs (6), (7) and (9) respectively appear to be appropriate correction factors. They curb down the nonlinear variation of $d\eta_r/dC$ (evident for high concentration) to a constant whose value is $2.5 V_h$ or B . Q' , K_M and K'_s then stand as different manipulative parameters. Now a critical survey of the actual values of these parameters shows that K_M is $1B$ for monovalent electrolytes, and $4B$ for polyvalent electrolyte and non-electrolytes.

Eq. (7) is thus

$$\frac{d\eta_r}{dC} \left(\frac{\eta_r}{nC} \right) = B = 2.5 V_h \quad \dots(10)$$

where $n = 1$ or 4 .

Since none of these equations performs uniquely, an intercombination of all of them or any two of them should become more general. These are given below:

$$\text{Vand-Moulik: } \eta_r = \sqrt{nC}(1-Q'C) \quad \dots(11)$$

$$\text{Vand-Thomas: } \eta_r = 1 + 2(K'_s - Q')C + \left(Q'^2 - \frac{4K'_s Q'}{B} \right) C^2 + \frac{2K'_s Q'^2 C^3}{B} \quad \dots(12)$$

Moulik-Thomas:

$$\eta_r = \frac{n^2 BC}{B + 2K'_s C} \quad \dots(13)$$

The results of the earlier analysis¹² show that K'_s varies in the range 3-22. Taking $K'_s = K_s V_h^2$ and $2.5 V_h = B$, K'_s values fall in the range $1B^2-7B^2$. For a generalized approach K'_s may be replaced by a term mB^2 . Eqs (12) and (13) then take the forms of Eqs (14) and (15) respectively.

$$\eta_r = 1 + 2(mB^2 - Q')C + (Q'^2 - 4mBQ')C^2 + 2mBQ'^2 C^3 \quad \dots(14)$$

$$\eta_r = \frac{C}{\frac{1}{n^2} + \frac{2mBC}{n^2}} \quad \dots(15)$$

For a unified approach intercombination of all the three equations is considered. From (10) and (9) we have

$$\frac{d\eta_r}{dC} - 2mB^2 C = \frac{d\eta_r}{dC} \left(\frac{\eta_r}{nC} \right) \quad \dots(16)$$

This on rearrangement gives Eq. (17).

$$\frac{d\eta_r}{dC} \left(1 - \frac{\eta_r}{nC} \right) = 2mB^2 C \quad \dots(17)$$

From (9) and (17)

$$\frac{B\eta_r}{(1-Q'C)^2} \left(1 - \frac{\eta_r}{nC} \right) = 2mB^2 C \quad \dots(18)$$

Rearranging Eq. (18), we get

$$\eta_r \left(1 - \frac{\eta_r}{nC} \right) = 2mB (1-Q'C)^2 C \quad \dots(19)$$

or

$$\left[\frac{\eta_r}{C} \left(1 - \frac{\eta_r}{nC} \right) \right]^{\frac{1}{2}} = (2mB)^{1/2} - (2mB)^{1/2} Q' C \quad \dots(20)$$

Eq. (20) gives the final general form of the intercombined equations of Vand, Moulik and Thomas.

This equation will be tested using literature data on concentrated solutions of electrolytes and the presently measured viscosity data on glucose, sucrose, mannitol and sorbitol.

Materials and Methods

Mannitol (Difco, USA), sorbitol (S. Merck, pro-analysis), glucose and sucrose (BDH, analar) were used as such. Doubly distilled water having specific conductance 1.5×10^{-6} mho cm^{-1} at 25° was used as the medium.

Ostwald viscometers and a pycnometer were used for viscosity and density measurements respectively at desired temperatures maintained with an accuracy of $\pm 0.1^\circ$.

Six viscometers having capillaries of different bores and times of water flow in the range 60-240 sec were selected. Solutions of the polyhydroxy compounds were prepared and placed in the viscometers such that the time of flow for the most dilute solution was always at least 30 sec more than the time of flow for water. Six solutions in six viscometers after equilibration for 30 min were handled to note the time of clearance one after another in succession. This procedure was repeated 3 to 4 times and the average of these readings was recorded. Each batch was repeated twice to ensure reproducibility of the results. The final readings were then the average of these two sets. To check upon the efficiency of the viscometers and the working conditions, the set of data at 30° on sucrose were compared with the literature¹¹ data. A correlation within 1% was observed. We report that the uncertainties of the measured viscosities and the densities were within $\pm 0.8\%$ and $\pm 0.20\%$ respectively. The measurements were made at 27° , 35° , 55° and 65° .

Results

The rearranged form of Vand's equation has been used. Provided this linearly formulated Eq. (21) holds, one can evaluate V_h and Q from the slope and intercept respectively with a prior knowledge of a , from the axial ratio^{6,8}. (These axial ratios for glucose, sucrose, sorbitol and mannitol are 1.95, 2.00, 2.50 and 2.50 respectively).

$$1/\log \eta_r = -2.303Q/a + 2.303/aV_h \times 1/C \quad \dots(21)$$

The validity of this equation for the aqueous solution of the polyhydroxy compounds is illustrated in Figs. 1-3. Q , V_h and hence the hydration number h calculated for different temperatures are given in Table 1. The solubility of mannitol is much low. For this compound V_h and hence h have been calculated using the equation of Simha^{9,14} ($\eta_r = 1 + aV_h C$), recommended for dilute solutions of nonspherical

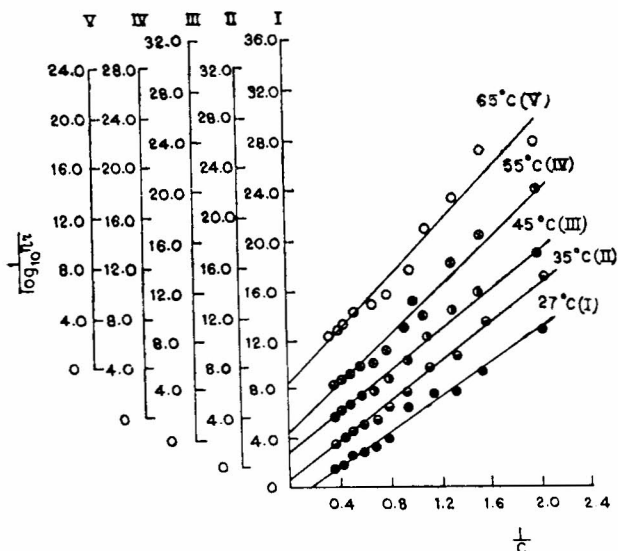
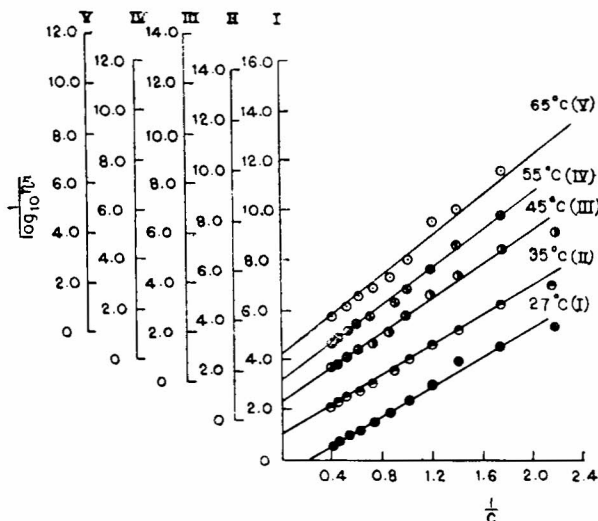
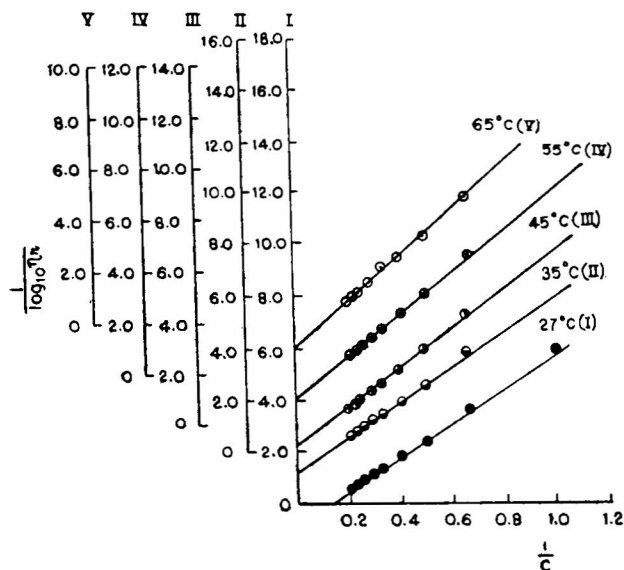
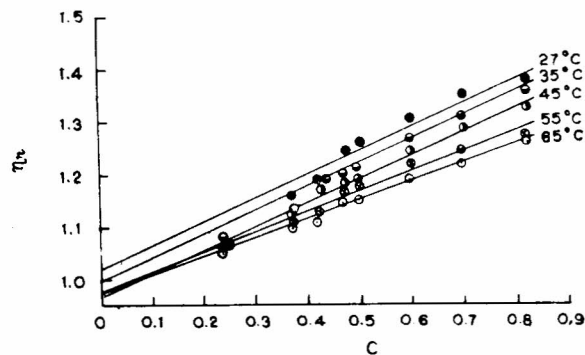
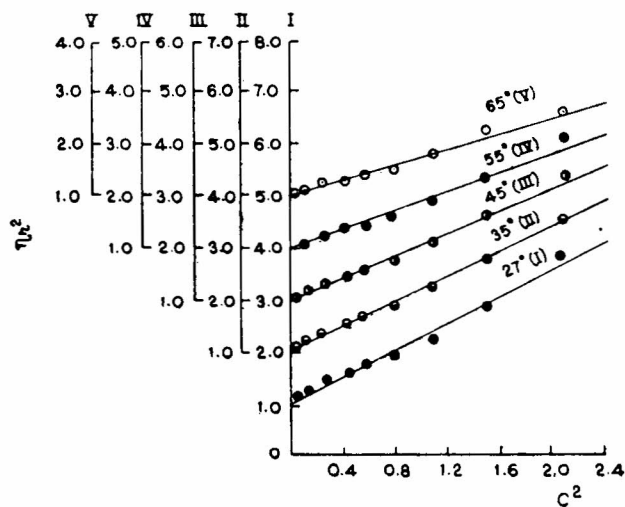

 Fig. 1 — Plot of $1/\log_{10} \eta_r$ versus $1/C$ for glucose

 Fig. 2 — Plot of $1/\log_{10} \eta_r$ versus $1/C$ for sucrose

 Fig. 3 — Plot of $1/\log_{10} \eta_r$ versus $1/C$ for sorbitol

 Fig. 4 — Plot of η_r versus C for mannitol


Fig. 5 — Test of Eq. (3) on glucose

particles (see Fig. 4). The results furnished in Table 1 have been derived following a linear regression analysis and the data are presented with appropriate standard deviations.

Eq. (20) has been tested for several electrolytes and the polyhydroxy nonelectrolytes presently studied. For the source of viscosity data of aqueous electrolyte solutions and their processing we refer to our previous publications^{10,12,15}. These viscosity data have been observed to satisfy all the individual equations up to a stage of high concentration (Figs. 5 and 6). The applicability of Eq. (20) on sucrose and glucose is exemplified in Fig. 7. It is observed that the valid range in the case of multivalent electrolyte (Fig. 8) is more on the lower side of the concentration compared to that of univalent electrolytes (Fig. 9).

Discussion

Although results incorporated in Figs. 1-3 indicate validity of Eq. (3), the h and Q values show variations, of which the most striking feature is the negative hydration exhibited by most of the solutes more or less at a temperature which is only 27°. Only sucrose shows a positive hydration ($h \approx 4$) which has been known from thermodynamics of its aqueous solution⁶. The Q value predicted by Vand for sucrose is 0.61. We see that the value of Q is greater than 0.61 and it increases with temperature.

TABLE 1 — TEMPERATURE DEPENDENCE OF HYDRATION AND INTERACTION PARAMETERS FOR POLYHYDROXY COMPOUND-WATER SYSTEMS

Temp. °C	Glucose	Sucrose	Sorbitol	Mannitol
	MOLAR VOLUME OF THE SOLUTE (V_h)			
27	0.115 ± 0.003	0.278 ± 0.008	0.108 ± 0.0013	0.137 ± 0.030
35	0.107 ± 0.003	0.274 ± 0.007	0.106 ± 0.0016	0.139 ± 0.013
45	0.103 ± 0.005	0.237 ± 0.007	0.094 ± 0.0009	0.142 ± 0.012
55	0.085 ± 0.003	0.221 ± 0.009	0.087 ± 0.0008	0.108 ± 0.012
65	0.076 ± 0.005	0.206 ± 0.010	0.079 ± 0.001	0.113 ± 0.008
	HYDRATION NUMBER (h)			
27	-0.094 ± 0.132	3.41 ± 0.05	-5.00 ± 0.09	-0.88 ± 0.31
35	-0.545 ± 0.160	3.20 ± 0.39	-5.11 ± 0.08	-1.09 ± 0.73
45	-0.767 ± 0.280	1.12 ± 0.43	-5.79 ± 0.06	-0.92 ± 0.52
55	-1.811 ± 0.160	0.22 ± 0.51	-6.14 ± 0.02	-2.20 ± 0.67
65	-2.287 ± 0.320	-0.58 ± 0.50	-6.60 ± 0.05	-2.50 ± 0.45
	CONSTANT a			
27	1.73 ± 0.05	2.57 ± 0.008	1.78 ± 0.025	2.84 ± 0.53
35	1.61 ± 0.05	2.55 ± 0.006	1.75 ± 0.028	2.86 ± 0.26
45	1.55 ± 0.07	2.21 ± 0.007	1.55 ± 0.014	2.93 ± 0.20
55	1.26 ± 0.04	2.05 ± 0.009	1.44 ± 0.015	2.45 ± 0.25
65	1.34 ± 0.08	1.92 ± 0.009	1.31 ± 0.017	2.34 ± 0.19
	INTERACTION CONSTANT Q			
27	1.24 ± 0.38	0.75 ± 0.17	1.10 ± 0.08	—
35	1.63 ± 0.50	0.72 ± 0.13	0.99 ± 0.01	—
45	1.07 ± 0.51	0.95 ± 0.18	1.19 ± 0.05	—
55	2.14 ± 0.54	1.04 ± 0.28	1.28 ± 0.07	—
65	2.35 ± 1.0	0.96 ± 0.34	1.40 ± 0.06	—
	INTERACTION CONSTANT Q^a			
27	0.76 ± 0.13	0.676 ± 0.048	0.599 ± 0.027	—
35	0.94 ± 0.12	0.644 ± 0.030	0.531 ± 0.037	—
45	0.74 ± 0.25	0.734 ± 0.040	0.564 ± 0.035	—
55	0.95 ± 0.14	0.747 ± 0.080	0.564 ± 0.024	—
65	0.93 ± 0.34	0.643 ± 0.038	0.558 ± 0.037	—
Av.	0.864 ± 0.19	0.689 ± 0.055	0.565 ± 0.032	—

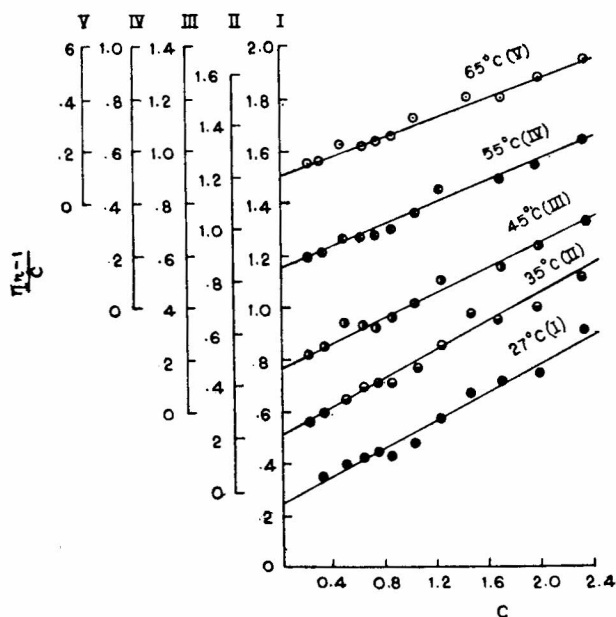


Fig. 6 — Test of Eq. (4) on glucose

Within the short range of temperature the change of Q is not expected. Now, considering that the hydration numbers of the polyhydroxy compounds remain unaltered in the working range of temperature, the magnitude of a can be calculated from the intercept. For such a calculation the hydration numbers of glucose, sucrose, sorbitol and mannitol have been taken to be 5, 4, 2 and 2 respectively^{6,9,16} with the assumption that the axial ratios are independent of these states of hydration². The a values for glucose, sucrose, sorbitol and mannitol, using Simha's equation are 2.83, 2.85, 3.27 and 3.27 respectively. Recalculation of Q using this a from the slope has been made and are listed in Table 1 under the heading Q^a . These Q^a values for sucrose are almost constant and close to the predicted value of 0.61; those for the other compounds are also nearly constant at all the temperatures. The constancy of Q^a suggests the analysis to be in the expected direction. When compared the increasing order of this constant is glucose > sucrose > sorbitol. The highest position of glucose can be due to the presence of a reacting group (reducing end) on its one carbon atom. A weak interacting possibility

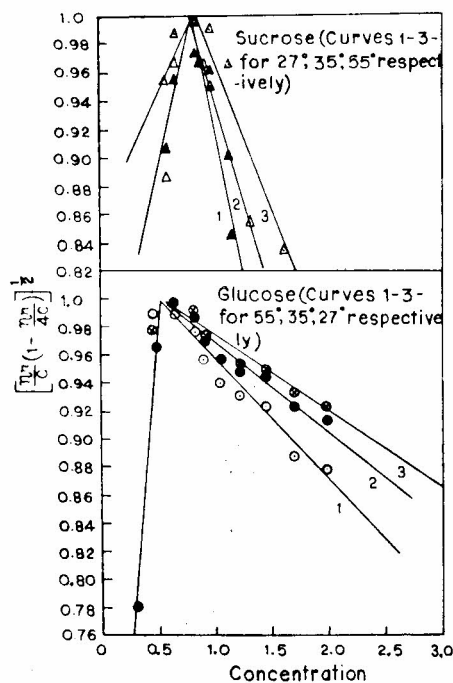


Fig. 7 — Test of Eq. (20) on glucose and sucrose

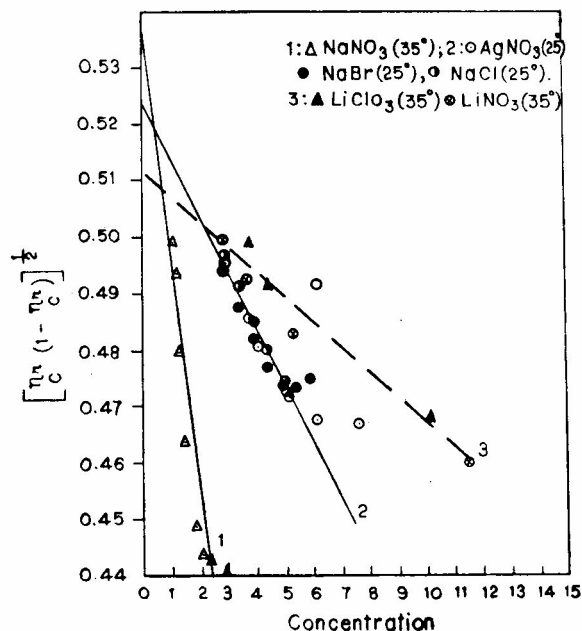


Fig. 9 — Test of Eq. (20) on uni-univalent electrolytes

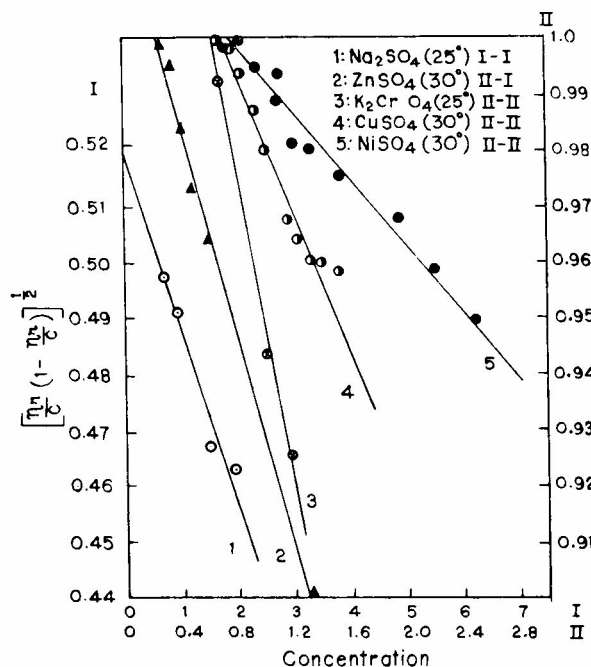


Fig. 8 — Test of Eq. (20) on multivalent electrolytes

has been observed for sucrose which for sorbitol is almost nil^{16,17}.

Recently, Merker and Scott⁷ have reported from the viscosity of tetrakisilylmethane in various solvents that the constant term of Einstein's equation is less than 2.5 and this is due to structure breaking effect of the solute on the solvent. The decrease in the values of a with temperature employed in the present study, therefore, provides a qualitative measure of the effects of the solutes. It is possible that there exists a microscopic region

or zone of disrupted medium⁷ in the immediate vicinity of the hydrated solute molecules. Flow of solvent layers in this region takes place comparatively easily and the microscopic viscosity differs from the bulk viscosity. At constant temperature such an effect depends on the type of the solvent medium⁷. Taking the magnitude of a to be a direct measure of the intensity of solute-solvent interaction, activation energy of such a process has been calculated from the temperature coefficient of a in a manner analogous to the analysis of a chemical reaction using Arrhenius' equation. These values are observed to fall in the range 7-11 kJ mole⁻¹ for the treated cases. The low magnitude of the energy barrier suggests that at the microscopic level the aqueous environment is susceptible to disruption by the presence of the polyhydroxy compounds. A region of disrupted water medium beyond the secondary hydration zone of ions was proposed by Frank and Evans¹⁸ from thermodynamic considerations of electrolyte solutions.

Our previous findings and the results reported herein as well are in favour of the general validity of all the three equations of Vand, Moulik and Thomas for concentrated solutions of both electrolytes and nonelectrolytes. This may mean either the fortuitous nature of each of these or the adequacy of all of them, only the mode of approach being different. We consider the latter to be true, and the empirical and semiempirical constants of the equations of Vand, Moulik and Thomas may then have some correlation. They are indicative of the same effect manifested in different ways. The relation of the constant M of Moulik's equation with B coefficient has been shown in Eq. (10). However, the interaction constant Q' occurring in Vand's equation remains still to be fully known.

Examination of Eq. (20) shows that the occurrence of constant term, n , having a value either 1 or 4 makes a scope for the validity of this equation towards the direction of lower concentration. When the electrolyte is multivalent, the term $(1-\eta_r/nC)$ then fixes the minimum theoretical limit of validity of Eq. (20). When $\eta_r/nC > 1$ ($1-\eta_r/nC$) is negative, the equation becomes imaginary. Equation (20) has been tested for both electrolyte and nonelectrolyte solutions of which the latter should be more adequate since the basic equations used are primarily formulated on nonionic systems. We have ultimately seen that their extensions to concentrated electrolyte solutions can become useful^{10,12}. In Figs. 1 and 2 crossing of two lines (having positive and negative slopes) at a point are shown only for glucose and sucrose. Such crossings can be observed for all the cases if the data are processed more on the lower side of concentration. This point is considered as the lower limit of validity of the final Eq. (20) as well as the individual equations from which it has been derived. This may then be the upper limit of validity of Einstein's equation discussed earlier¹⁰.

In conclusion, the proposition of non-changeable a occurring in the equation of both Vand and Einstein (and the modified equation of Simha as well) may provide wrong hydration numbers for the polyhydroxy compounds studied. Like hydrated ions of electrolyte, solute-solvent interaction may end up with a structure breaking zone at the microscopic level also in the near vicinity of the hydrated polyhydroxy compounds. This is reflected upon the magnitude of a whose temperature coefficient advocates the process to be involved

with an energy equivalent to that of hydrogen bond breaking. The viscosity equation of Vand, Moulik, and Thomas valid for concentrated solutions of electrolytes and nonelectrolytes have a common basis on which a universal viscosity equation has been formulated.

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