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Ion-Solvent Interactions in Aqueous Solutions of Alkali Metal Salts of 2,6-Dihydroxy-, 2,4-Dihydroxy- and 2-Hydroxy-4-Aminobenzoic acids

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Measurements of the relative viscosities of aqueous solutions of a series of alkali metal salts of 2,6-dihydroxybenzoic acid and sodium salts of 2,4-dihydroxy- and 2-hydroxy-4-aminobenzoic acids in the temperature range 298–308 K show that while 2,6-dihydroxybenzoate acts as a water structure breaker, 2,4-dihydroxy- and 2-hydroxy-4-aminobenzoate systems enforce the structure of water. The structure disrupting property of 2,6-dihydroxybenzoate is due to formation of strong intramolecular hydrogen bonds between the carboxylate group and the two adjacent hydroxyl groups. A number of physico-chemical parameters such as hydration number, ionic radii and thermodynamic parameters for viscous flow (using Feakin's model) have been calculated.

INTRODUCTION

Solute-water interactions are important in understanding the physico-chemical properties of aqueous solutions. However, some of the determining factors of solute-solvent interactions in aqueous solution of organic ions remain obscure. It is well known that substitution of a hydroxyl group at the *ortho* position of the benzoic acid molecule profoundly affects the physico-chemical and biochemical properties of the resulting compound. Benzoic acid, *e.g.*, is a much weaker acid than salicylic acid which, again, is pharmacologically much more active than the former. Through measurement of fluidities of aqueous solution of alkali metal benzoates and salicylates it has been shown[1,2] that salicylate ion interacts with water structure differently than benzoate ion.

The B-coefficient of salicylate ion is smaller than that of benzoate ion and it increases with temperature in contrast to benzoate system (*loc. cit.*). In view of this observation it is urgently felt that a study of the viscosity behaviour of 2,6-dihydroxybenzoate ion in which the carboxylate group is situated in an environment of two *ortho* hydroxyl groups, is worth investigating. The work aims to obtain a deeper understanding about ion-water interactions in aqueous solution of dihydroxybenzoate systems. The present communication reports the results of viscometric and densitimetric studies of alkali metal salts of 2,6-dihydroxy-, 2,4-dihydroxy- and 2-hydroxy-4-aminobenzoic acids in the temperature range 298–308 K.

EXPERIMENTAL

Alkali metal salts of the acids were, in general, prepared by mixing equivalent amounts of the crystallised acid and an alkali metal carbonate (AR) in a minimum volume of water to obtain a clear solution (sometimes a slight warming was necessary for dissolution) from which the salt was obtained by slow crystallisation. The repeatedly crystallised salt was finally washed several times with distilled ether and dried. Stock solutions of the salts were prepared by weighing. Solutions of varying concentrations were prepared from the stock by dilution. Li-, Na-, K- and Cs- salts of 2,6-dihydroxybenzoic acid and Na-salts of 2,4-dihydroxy- and 2-hydroxy-4-aminobenzoic acids were prepared in this way.

Densities of solutions were measured by a calibrated weld-type pyknometer (40 mL) provided with a graduated stem fitted with a standard joint stopper at its upper end and placed in a thermostat regulated within ± 0.01°C. All viscosity measurements were made in a specially designed long flow time viscometer that was placed in the thermostat described above. Efflux times of solutions were measured by a 1/10th second stopwatch and were reproducible to within ±0.2 s. For calibration of the viscometer the measured flow times of fresh triply distilled water at two different temperatures, viz., 303 and 308 K, are 867.8 and 785.5 s, respectively. The viscometer constants were determined according to the equation

$$\eta/d = A't - B'/t \qquad (1)$$

where η (CP) is the viscosity, d is the density (g cm^{-3}) and t is the flow time in seconds. The viscometer constants A' and B' are 9.299×10^{-4} and 5.21109 respectively.

RESULTS AND DISCUSSION

The experimental data on relative viscosities of aqueous solutions of the solutes have been analysed according to the Jones-Dole[3] equation (2):

$$\eta/\eta_0 = 1 + AC^{1/2} + BC \qquad (2)$$

where η/η_0 is the relative viscosity of a solution of concentration C (M), A and B are constants characteristic of the electrolyte and represent the ion-ion and ion-solvent interactions, respectively. The B coefficient which depends on ion-size and ion-structure cannot be calculated a priori. The values of A and B coefficients evaluated from the intercept and slope respectively of the plot of $(\eta/\eta_0 - 1)/C^{1/2}$ versus $C^{1/2}$ are recorded in Table 1, while some typical plots are shown in Fig. 1 (a) and (b). The regression coefficients for the plots lie in the range 0.985–0.999. The standard deviations in B values are also recorded in the same table. All the salts of 2,6-dihydroxybenzoic acid have positive B coefficients increasing with temperature, suggesting their structure breaking ability. The salts of 2,4-dihydroxy- and 2-hydroxy-4-aminobenzoic acids, however, show an opposite thermal dependence supporting their structure making property. The temperature dependence of B coefficients is shown in Fig. 2. The B coefficients of these substituted benzoate ions have been calculated by Kaminsky's procedure[4] and are listed in column 3 of Table 1. The B value of 2, 6-dihydroxybenzoate ion

TABLE 1

A- AND B-COEFFICIENTS OF ALKALI METAL SALTS OF 2,6-DIHYDROXYBENZOIC ACID, SODIUM SALTS OF 2,4-DIHYDROXY- AND 2-HYDROXY-4-AMINOBENZOIC ACIDS AND B-VALUES OF THEIR ANIONS AT DIFFERENT TEMPERATURES

Salt	B_{salt}			B_{anion}			$A_{coefficient}$			Ionic Partial molal volume ($\overline{V}^{0}_{3(-)}$), 298 K	$B_{einstein}$ 298 K
	298 K	303 K	308 K	298 K	303 K	308 K	298 K	303 K	308 K		
2,6-Dihydroxy Li-benzoate	0.329 (±0.012)	0.346 (±0.009)	0.351 (±0.005)	0.180	0.202	0.213	0.006	0.008	0.007	83.88	0.210
2,6-Dihydroxy Na-benzoate	0.283 (±0.007)	0.295 (±0.007)	0.319 (±0.006)	0.197	0.210	0.234	0.010	0.006	0.005	87.21	0.218
2,6-Dihydroxy K-benzoate	0.212 (±0.015)	0.218 (±0.005)	0.250 (±0.010)	0.218	0.219	0.245	0.005	0.005	0.004	81.98	0.205
2,6-Dihydroxy Cs-benzoate	0.183 (±0.017)	—	0.200 (±0.007)	0.228	—	—	0.003	—	—	92.66	0.232
2,4-Dihydroxy Na-benzoate	0.423 (±0.018)	—	0.326 (±0.011)	0.337	—	0.241	0.006	—	0.002	100.21	0.251
4-Amino-Na- salicylate	0.420 (±0.011)	—	0.390 (±0.018)	0.334	—	0.305	0.0001	—	0.004	100.31	0.251

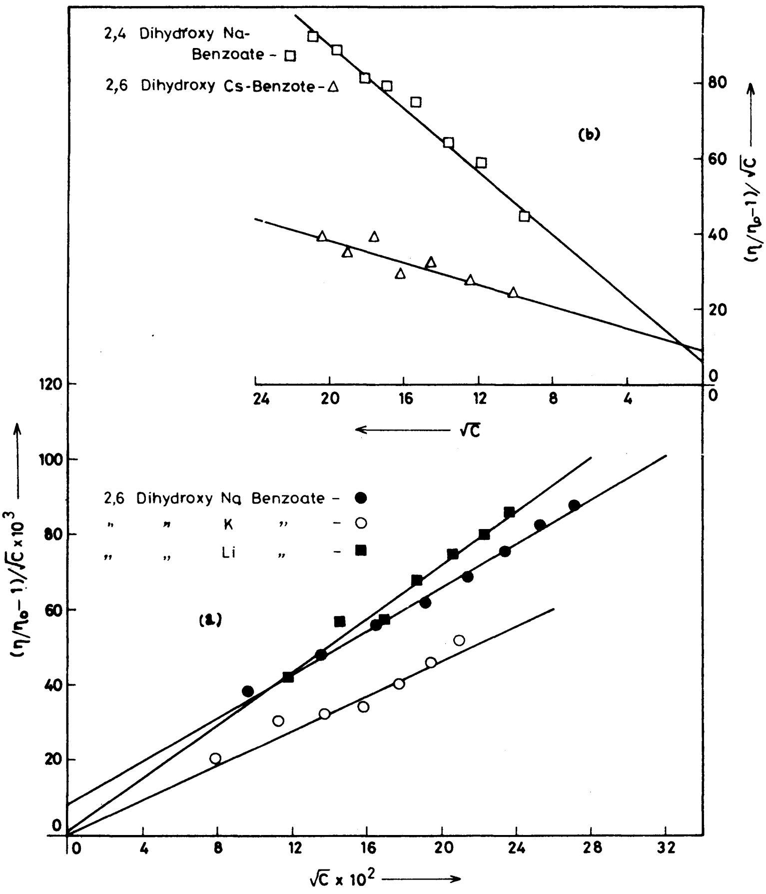

Fig. 1 Plot of $(\eta/\eta_0 - 1)\sqrt{C}$ vs $\sqrt{C}$

exhibits the same thermal dependence as that of the parent salt, suggesting that the anion, like the salt, is a structure breaker. A comparison of B coefficients of 2,6-dihydroxy- and 2-hydroxybenzoate ions[2] shows that the former is a more efficient structure breaker than the latter. The most probable explanation for this may be that the two *ortho* hydroxyl groups in 2,6-dihydroxybenzoate ion form strong intramolecular hydrogen bonds with the carboxylate group and hence reduces the electrostrictive structure making ability of this group in 2,6 dihydroxybenzoate ion more than that caused by the single—OH group in the salicylate ion. Evidence in favour of formation of intramolecular hydrogen bond in 2,6-dihydroxybenzoate has come from a study of IR spectra[5] and ionisation constant of the free acid[6]. The structure disrupting property of 2,6-dihydroxybenzoate is further supported by the values of the free energies of activation for viscous flow of the anion as shown in columns 2 and 3 of Table 3, which increase with temperature. The interesting observation made in the present study is that while dB/dT is positive for *ortho*-hydroxybenzoate, it is negative in the case of

2,4-dihydroxy- and 2-hydroxy-4-aminobenzoates. The solute-solvent interaction is drastically altered by substitution at the *para*-postion of *ortho*-hydroxybenzoate.

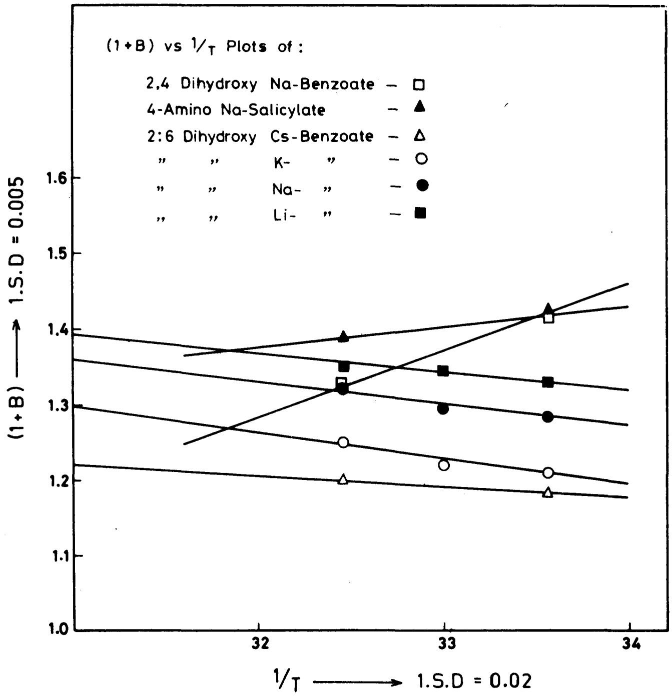

Fig. 2 Plot of (1 + *B*) vs 1/*T*

TABLE 2
PARTIAL MOLAL VOLUME AND HYDRATION NUMBER OF SALTS AND RADII OF ANIONS

Salts	Hydration number of salt (^nH_2O)	Radius of Anion r_s (Å)	r_v (Å)	ϕ_v^0 (ml mol^{-1}) 298 K	303 K	308 K
2,6-Dihydroxy Li-benzoate	2.70	3.05	3.21	83	86	90
2,6-Dihydroxy Na-benzoate	1.51	3.15	3.26	86	90	95
2, 6-Dihydroxy K-benzoate	-0.354	3.26	3.19	91	95	104
2,6-Dihydroxy Cs-benzoate	-2.26	3.31	3.32	114	—	118
2,4-Dihydroxy Na-benzoate	3.90	3.76	3.41	99	—	101.5
4-Amino-Na-salicylate	3.81	3.75	3.91	99.1	—	98.5

r_s = Radii of anions calculated from B_{anions}.
r_v = Radii of anions calculated from ionic partial molal volume.

From an inspection of the data in column 3 of Table 1 it will not be prudent to assign any unique value to the B coefficient of 2,6-dihydroxybenzoate ion at any particular temperature since B_{anion} value depends on the nature of the cation partner and changes systematically from Li to K at all the three temperatures. For

TABLE 3

FREE ENERGY OF ACTIVATION FOR VISCOUS FLOW OF SOLUTES AND THEIR ANIONS AT DIFFERENT TEMPERATURES AND ENTHALPY AND ENTROPY OF ACTIVATION FOR VISCOUS FLOW OF SOLUTES AND THEIR ANIONS AT 298 K

Salts	$\Delta\mu_3^{0\#}$ KJ mol^{-1}			$\Delta\mu_{3\,\text{anion}}^{0\#}$ KJ mol^{-1}			$T\Delta S_3^{0\#}$ KJ mol^{-1} 298 K	$\Delta H_3^{0\#}$ KJ mol^{-1} 298 K	$T\Delta S_{3(-)}^{0\#}$ KJ mol^{-1} 298 K	$\Delta H_{3(-)}^{0\#}$ KJ mol^{-1} 298 K
	298 K	303 K	308 K	298 K	303 K	308 K				
2,6-Dihydroxy Li-benzoate	63.29 (±1.64)	66.68 (±1.25)	68.75 (±0.71)	36.18	40.24	42.95	−162.71	−99.42	−201.75	−165.57
2-6-Dihydroxy Na-benzoate	57.37 (±0.96)	60.19 (±0.97)	64.93 (±0.79)	38.97	41.88	46.65	−225.30	−167.90	−182.26	−143.87
2,6-Dihydroxy K-benzoate	48.21 (±2.06)	50.80 (±0.69)	56.39 (±1.42)	41.20	42.44	48.01	−243.76	−195.55	−202.94	−161.74
2,6-Dihydroxy Cs-benzoate	47.46 (±2.33)	—	51.31 (±0.99)	43.97	—	44.54	−114.73	−67.27	−16.98	26.98
2,4-Dihydroxy Na-benzoate	78.31 (±2.47)	—	66.78 (±1.56)	53.91	—	48.50	343.59	421.90	340.02	399.93
4-Amino-Na-salicylate	77.91 (±1.51)	—	75.40 (±2.54)	59.91	—	57.12	74.79	152.70	83.14	143.05
Solvent*	9.21	9.04	8.94							

J.Chem. Soc. Faraday Trans. I, **72**, 656 (1976).

Free energies of activation for the alkali metal cations at 298 K have been calculated from eq. (6) using their standard B values and partial molal volumes available in the literature.

this anion at 298 K the same trend is observed from Li to Cs also. This type of observation of cation sensitiveness of the B-coefficient has been made previously in the case of salicylate ion[2]. The present observation suggests that the resultant structure of aqueous solution of alkali metal salts of 2,6-dihydroxybenzoic acid is built up cooperatively by both the cation and anion. Cationic influences on viscous flow activation energies have been noted in aqueous solutions of alkali metal acetates[7] and benzoates[8]. More recently such influences on the equilibrium constant in the molecular iodine-metal iodide systems in DMF medium have been observed by some Russian workers[9].

The contribution to the ionic B coefficient due to einstein effect has been calculated from the following equation

$$B_{\text{ion}} = 2.5\,\overline{V}_i \tag{3}$$

where $\overline{V}_i$ is the partial ionic molal volume which has been assumed to be equal to rigid molal volume. The results only at 298 K are shown in column 5 of Table 1. For 2,4-dihydroxybenzoate and 4-aminosalicylate ions the observed B coefficients are higher than the corresponding einstein B values at 298 K. An explanation of the excess B coefficient must be sought in the components $B_{\text{ion}}^{\text{orient}}$ and $B_{\text{ion}}^{\text{reinf}}$ where $B_{\text{ion}}^{\text{orient}}$ is the positive increment arising from the structure making action of the electric field of the ion on the dipoles of the solvent molecules and $B_{\text{ion}}^{\text{reinf}}$ is the positive increment due to the effect of reinforcement of water structure by the large structure of these aromatic anions. However, quantitative evaluation of these parameters is difficult to carry out at present. The B coefficients of 2,6-dihydroxybenzoate ion are, however, a little less than the einstein contribution when the counterions are Li^+ and Na^+ and are almost same when the counter ions are K^+ and Cs^+.

Hydration of Solute

The number of water molecules (^nH_2O) bound per mole of the solute has been calculated[10] from the following equation (4):

$$B = 2.5 \times 10^{-3} M_2 \left(\frac{\phi_V^0}{M_2} + \frac{\omega_l}{d_0} \right) \tag{4}$$

where ϕ_v^0 is the partial molal volume of the solute at infinite dilution, M_2 is the solute molecular weight, ω_l is the weight of water per unit weight of the solute and d_0 is the density of water. Some representative plots of ϕ_v versus $C^{1/2}$ for these systems are plotted, which are fairly linear, the reliance being given to high concentration data. The values of ^nH_2O are recorded in Table 2. For salts of 2,6-dihydroxybenzoic acid the hydration number decreases from Li- to Cs-salt. The hydration number of 2,6-dihydroxybenzoate ion shown in the same table is found to be negative, a characteristic of structure breakers. 2,4-dihydroxy and 2-hydroxy-4-amino sodium benzoates are almost equally hydrated, their hydration numbers being practically equal to 4.

Radii of anions

The Stokes radii of the anions have been calculated from the following equation (5):

$$B_{\text{anion}} = 2.5\,\overline{V} = 2.5 \times \frac{4}{3}\pi\frac{r_s^3 N}{1000} \qquad (5)$$

assuming the ion to behave like a rigid sphere with an effective radius r_s moving in a continuum. The values of r_s shown in Table 2 agree fairly closely with the partial molal radii (r_V) calculated from partial molal anionic volumes recorded also in the same table.

Transition state theory treatment

Viscosity data have been analysed on the basis of the transition state theory of the relative viscosity of electrolyte solutions as suggested by Feakins *et al*[11]. The B coefficient, according to Feakins (*loc. cit.*) is expressed by the equation (6):

$$B = \frac{\overline{V}_1^0 - \overline{V}_3^0}{1000} + \frac{\overline{V}_1^0}{1000}\left(\frac{\Delta\mu_3^{0\#} - \Delta\mu_1^{0\#}}{RT}\right) \qquad (6)$$

where $\overline{V}_1^0$ and $\overline{V}_3^0$ are the partial molal volumes of the solvent and solute respectively, $\Delta\mu_3^{0\#}$ is contribution per mole of the solute to the free energy of activation for viscous follow of the solution. $\Delta\mu_1^{0\#}$, the molal free energy of activation of the pure solvent, is given[12] by

$$\Delta\mu_1^{0\#} = \Delta_{G_1}^{\#} = RT\ln\left(\frac{\eta_1 V_1}{hN}\right) \qquad (7)$$

The free energies of activation for viscous flow for the salts, their anions and pure solvent are presented in Table 3.

According to Feakins *et al.*[13], $\Delta\mu_3^{0\#} > \Delta\mu_1^{0\#}$ for solutes having positive B values. Further $\Delta\mu_3^{0\#}$ increases with temperature for solutes having positive values of dB/dT. This is nicely demonstrated in the case of 2,6-dihydroxybenzoate which acts as water-structure breaker. The structure making ability of 2,4-dihydroxy- and 2-hydroxy-4-aminobenzoates is supported by the negative temperature coefficient of $\Delta\mu_3^{0\#}$ for these systems. The magnitude depends on the relative values and signs of $\Delta H_3^{0\#}$ and sign of $\Delta\mu_3^{0\#}$ and $T\Delta S_3^{0\#}$. The values of $\Delta H_3^{0\#}$ and $T\Delta S_3^{0\#}$ for the salts and their anions have been calculated at a particular temperature, *viz.*, 298 K, and the results are shown in Table 3. It is observed that while the enthalpy and entropy of activation are negative for 2,6-dihydroxybenzoate ion, they are positive for 2,4-dihydroxy- and 2-hydroxy-4-aminobenzoate ions. The negative values of enthalpy and entropy of activation for viscous flow suggest that for 2,6-dihydroxybenzoate ion the ion-solvent interactions are strong in the transition state solvent as observed by Feakins[13] for several structure breakers in aqueous solution. In the case of 2,4-dihydroxy- and 2-hydroxy-4-aminobenzoates both the enthalpy and entropy of activation are positive and $\Delta H_3^{0\#} > T\Delta_{S_3}^{0\#}$, suggesting that solute-solvent interaction for these anions is nearly complete or so in the ground state. Similar observations have been made by Feakins *et al.*[13] in aqueous solution of LiCl.

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