

Viscosity *B*-coefficients of sodium salts of some orthosubstituted benzoic acids in relation to hydrogen bonding and electronegativity

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Abstract. Viscosity *B*-coefficients of sodium salts of salicylic, thiosalicylic, anthranilic, 2,6-dihydroxy benzoic and *o*-anisic acids have been measured at 298, 303 and 308 K respectively. Temperature dependence of *B*-values suggest that the salts as well as their anions except *o*-anisate behave as structure breakers. This is further supported by energy of activation data. The observed *B*-coefficients suggest probable involvement of simultaneous intra- and intermolecular hydrogen bonding between an ortho-substituent and the carboxylate group on the one hand and between the ortho-substituent and solvent water on the other. A good correlation between *B*-coefficients and the electronegativities of oxygen, nitrogen and sulphur atoms has been noted. The probable involvement of ring π -electrons in depolymerising the water structure has been conjectured.

Keywords. Viscosity *B*-coefficients; ortho-substituted sodium benzoates; solute–solvent interactions; hydrogen-bonding; electronegativity.

1. Introduction

It is well known that a study of the perturbation of the viscous flow of a solvent by an added solute (in particular, an ionic one) yields valuable and significant information on solute–solvent interactions and hence on the structure of a solvent through evaluation of the Jones–Dole viscosity *B*-coefficient (Jones and Dole 1929). Although extensive studies in this area have been carried out with simple electrolytes in aqueous, non-aqueous and aquo-organic solvents, much less has been done on electrolytes having organic backbones, except quaternary ammonium salts (Kay *et al* 1966), amino acids (Devine and Lowe 1971), and several aliphatic acids and their salts (Lawrence and Wolfenden 1934; Patil *et al* 1979). The viscosity behaviour of alkali metal salts of benzoic and some substituted benzoic acids has been studied by several workers (Yasuda and Mizutani 1973; Mandal *et al* 1978) who noted a positive effect of substituents on ion-solvent interactions. Further, various other studies (Tamres 1952; Goldman and Crisler 1958; Kalfoglon and Bowen 1969) do confirm that solutes containing aliphatic hydrocarbons affect water structure differently from those containing aromatic hydrocarbons. The object of the present communication is to report the results of our investigations on the viscous flow of sodium salts of a series of ortho-substituted benzoic acids in relation to solute–solvent interactions in water and to explore the probable role of hydrogen bonding on solute–solvent interactions.

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2. Experimental

Sodium salts of salicylic, thiosalicylic, anthranilic, 2,6-dihydroxy benzoic and *o*-anisic acids were prepared separately by mixing equivalent amounts of the corresponding acid (AR) and sodium carbonate (AR) in minimum volume of water to obtain a clear solution (sometimes a little warming was necessary to effect solution) from which the salt was slowly crystallised out. This was purified by repeated crystallisation and finally by washing several times with distilled ether. The salt was then dried and its stock solution prepared by direct weighing. Solutions of varying concentrations were then prepared from the stock solution by dilution.

The densities of the solutions were measured by a calibrated Weld-type pycnometer (40 ml) provided with a graduated stem fitted with a standard joint stopper at its upper end and placed in a constant temperature bath controlled to within $\pm 0.01^\circ$. A specially designed long flow time Ostwald Viscometer placed in a thermostat regulated within $\pm 0.01^\circ$ was used to measure the viscosities of solutions. Efflux times (at least three) of solutions measured by a 0.1 second stop-watch and reproducible within ± 0.2 s were averaged. For calibration of the viscometer the observed flow times of freshly prepared triple-distilled water at two different temperatures, viz. 303 and 308 K were 867.8 and 785.5 s respectively. The viscometer constants were determined according to

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

where η is the viscosity (cp), d the density (g ml^{-1}) and t the flow time (s). The viscometer constants A' and B' were found to be 9.299×10^{-4} and 5.21109 respectively. Standard deviations in η/η_0 values for all the salts at three different temperatures lie in the range $(1.3-5.7) \times 10^{-4}$, while those in density data are $(1.0-9.0) \times 10^{-5}$.

3. Results and discussion

Experimental results of the relative viscosities of aqueous solutions of sodium salts of different ortho-substituted benzoic acids (including benzoic acid also) have been analysed by the Jones-Dole equation

$$(\eta_{\text{sp}}/\sqrt{C}) = A + B\sqrt{c}, \quad (2)$$

where $\eta_{\text{sp}} = \eta/\eta_0 - 1$, η and η_0 are the viscosities of the solution and the solvent respectively, and c is the molar concentration. A and B are characteristic constants specific to the ion and the solvent. The A -coefficient depends on the ion-ion interactions and can be calculated from physical properties of the solvent and the solution. The B -coefficient represents the ion-solvent interactions conditioned by ion-size and ion-structure and cannot be calculated a priori. The plots of $\eta_{\text{sp}}/c^{1/2}$ against $c^{1/2}$ for the electrolytes were found to be linear with least scatter in the concentration range studied. Some typical plots are presented in figure 1. The regression coefficients for the plots of $\eta_{\text{sp}}/c^{1/2}$ vs $c^{1/2}$ lie in the range 0.998-0.996.

The B -coefficients of the salts, obtained as slopes of the straight lines of the Jones-Dole plots, are shown in table 1. The viscosity B -coefficients for the ortho-substituted benzoates are positive and fairly large as compared with those of the

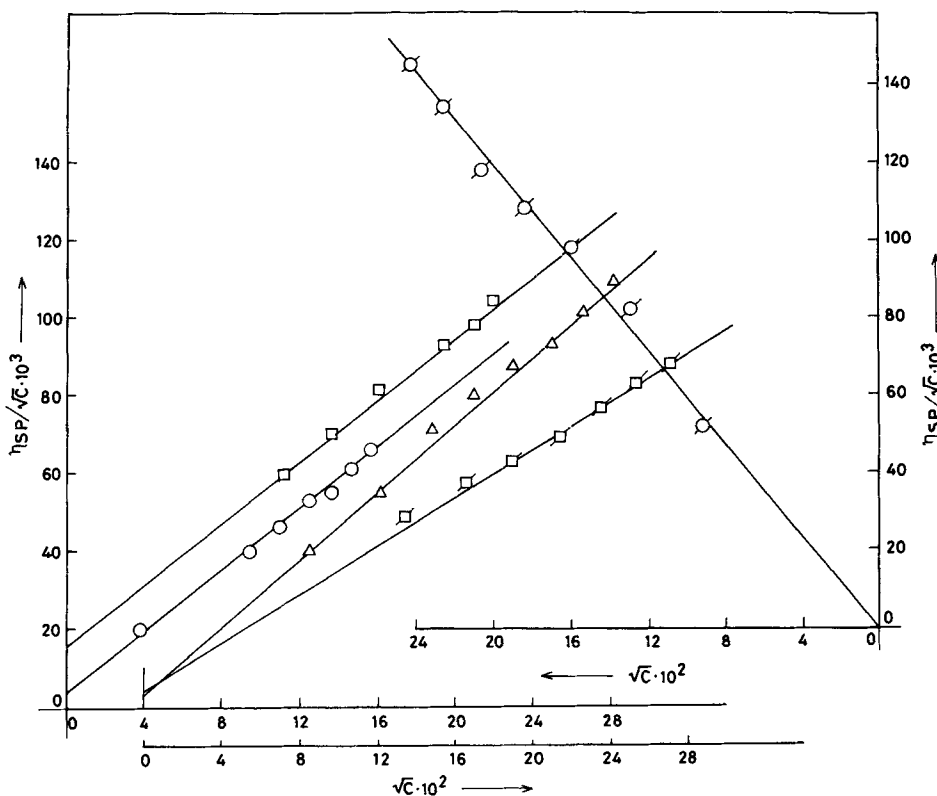


Figure 1. Plot of η_{sp}/\sqrt{C} vs \sqrt{C} . \circ - Na-salicylate; \square - Na-anthranilate; \triangle - Na-thiosalicylate; \diamond - Na-*o*-methoxybenzoate; and \square - 2,6-dihydroxy Na-benzoate at 298 K.

Table 1. *B*-coefficients at different temperatures of sodium salts of benzoic and several *o*-substituted benzoic acids and of benzoate and *o*-substituted benzoate ions in water. Energy of activation for viscous flow for the anions at 298 K.

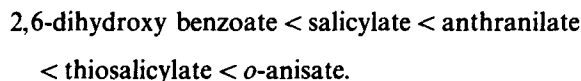
Salt	<i>B</i> _{salt} at <i>T</i> (K) =			<i>B</i> _{anion} at <i>T</i> (K) =			ΔE^{**} (kJ mol ⁻¹)
	298	303	308	298	303	308	
Sodium salicylate	0.368	0.379	0.394	0.282	0.293	0.309	-1.294
Sodium anthranilate	0.391	0.414	0.427	0.300	0.330	0.340	-2.268
Sodium thiosalicylate	0.437	—	0.485	0.351	—	0.400	-2.473
2,6-Dihydroxy sodium benzoate	0.283	0.296	0.319	0.197	0.210	0.234	-1.524
Sodium <i>o</i> -anisate	0.593	—	0.549	0.509	—	0.464	2.033
Sodium benzoate	0.540	—	0.500	0.454	—	0.415	

Taking $\Delta E_{Na^+}^ = 0.084$ kJ mol⁻¹ (Nightingale 1966)

simple electrolytes. In order to obtain better insight into solute-water interaction, the division of *B*-values is desirable. This has been done for the ortho-substituted benzoate ions at all the three temperatures assuming the additive property of the total *B*-coefficient ($B_K^+ = B_{C1}^-$) and using the necessary data of B_{Na^+} values, at different temperatures from the literature (Stokes and Mills 1965), although at 303 K, the

required B^+ value has been calculated by interpolation technique of Kaminsky (1957). Ionic B -values are also recorded in the same table 1.

From table 1 it is observed that except sodium benzoate and sodium ortho-anisate the B -coefficient increases with rise in temperature for each of the remaining four salts whose anions exhibit the same trend, suggesting that the salts as well as the anions derived from them behave as structure breakers. This is supported by the values of energy of activation for viscous flow which, as shown in table 1, are negative, a characteristic property of solvent structure disruptors. The B -coefficients for the salts as well as their anions follows the increasing order:



The fact (as seen from table 1) that the B^- values of the different ortho-substituted benzoate ions except the *o*-anisate ion are lower than that of the benzoate ion (Mandal *et al* 1978) suggests a probable involvement of the ortho-substituent, viz. $-\text{OH}$, $-\text{NH}_2$ and $-\text{SH}$ groups, in depolymerising the water structure and reducing the B -value of the corresponding ortho-substituted benzoate ion over that of the benzoate ion. This has been confirmed by studying the viscosities of *o*-methoxy benzoate in the temperature range 298–308 K. At any given temperature the B -coefficient of the *o*-methoxy benzoate ion is greater than that of the salicylate ion and like that of the benzoate ion, decreases with increasing temperature.

The results suggest that the probable involvement of simultaneous hydrogen bonding between (i) the carboxylate group and the ortho-substituent and (ii) the ortho-substituent and solvent water might be responsible for the resultant depolymerisation of the water structure. The first mechanism (intramolecular hydrogen bonding) reduces the electrostrictive action and hence the structure forming ability of the carboxylate group. Since hydrogen bonding of the type $\text{Y}^- \dots \text{H}^+ - \text{X}^-$ depends

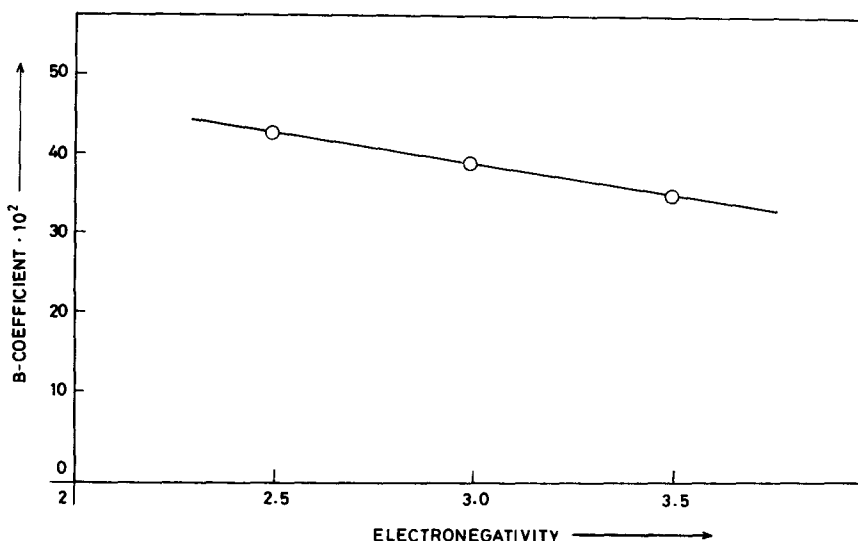


Figure 2. Plot of B -coefficient vs electronegativity of atoms.

on the electronegativity of X, it is greatest with 2,6-dihydroxy benzoate ion and least with thiosalicylate ion. The observed order of *B*-values is in complete accord with this expectation. The observation of a linear correlation (as shown in figure 2) between the viscosity *B*-coefficients and the electronegativities of oxygen, nitrogen and sulphur atoms are further support for this expectation. The second mechanism suggests that apart from what has been happening at the carboxylate end, the hydroxyl group, by virtue of its capacity for hydrogen bonding with bulk water molecules (a weak protonic acid), cleaves the cage of the water structure present around the benzene ring where the hydration may be expected to be hydrophobic due to large size of the benzene ring according to Wen and Saito (1964). They have shown that the *B*-coefficient of tetra-(2-hydroxy ethyl) ammonium ion is lower than that of tetrapropyl ammonium ion of similar size, suggesting that the introduction of a hydroxyl group into the alkyl group destroys the hydrophobic character of the alkyl chains. The probable involvement of ring π -electrons in disrupting water structure by forming hydrogen bonds with water molecules (a weak protonic acid) has been suggested by some workers (Kalfoglon and Bowen 1969).

Further support to the hydrogen bonding theory mentioned above is obtained by studying the viscosity behaviour of sodium orthomethoxy benzoate. From the data recorded in table 1 it can be concluded that *o*-methoxy benzoate ion manifests structure-making behaviour since its *B*⁻ value decreases with rise in temperature. In this anion, the -OCH₃ group cannot form any intra or intermolecular hydrogen bonds whereas the -OH group(s) in salicylate and 2,6-dihydroxy benzoate ions can form both types of hydrogen bonds. Therefore, it may reasonably be supposed that the capacity of the -OH group(s) in the ortho position(s) towards hydrogen bond formation leads to a special type of behaviour of the salicylate and 2,6-dihydroxy benzoate ions in aqueous solution. Similar behaviour has been observed in case of anthranilate and thiosalicylate anions.

Hydration of the solutes: The number of water molecules ($n_{\text{H}_2\text{O}}$) bound per mole of the solute can be calculated (Patel *et al* 1973) using the following equation

$$B = 2.5 \times 10^{-3} M_2 \left(\frac{\phi_v^0}{M_2} + \frac{\omega_1}{d_0} \right), \quad (3)$$

where ϕ_v^0 is the partial molal volume of the solute at infinite dilution, M_2 is the solute molecular weight, ω_1 is the weight of water per unit weight of the solute and d_0 is the density of water. The values of $n_{\text{H}_2\text{O}}$ shown in table 2 suggest that the order of hydration of the solutes follow the same trend as that of the *B*-coefficients of the solutes. Since all the solutes are associated with the same cation, viz., Na⁺ ion, the hydration behaviour of the *o*-substituted benzoate ions runs parallel to their *B*-values. On the basis of available hydration number (4) of Na⁺ ion (Antropov 1977) (literature data show a wide variation), the ortho-substituted benzoate ions (except thiosalicylate and *o*-methoxy benzoate anion) are found to have negative hydration numbers – a characteristic associated with structure breaking properties (Woldan 1988).

The radii of the substituted benzoate anions have been calculated (Einstein 1906) from the following equation:

$$B_{\text{anion}} = 2.5 \bar{V} = 2.5 \times \frac{4}{3} \pi \frac{R^3 N}{1000}, \quad (4)$$

Table 2. Partial molal volume, hydration number and radii of anions at 298 K.

Salt	ϕ_r^0 anion (ml mol ⁻¹)	Hydration no. of anion	Radii of anion ^a (Å)	Radii of anion ^b (Å)
Sodium salicylate	92.76	-0.92	3.55	3.22
Sodium anthranilate	98.41	-0.72	3.62	3.39
Sodium thiosalicylate	90.21	+0.75	3.82	3.29
2,6-Dihydroxy sodium benzoate	87.21	-3.05	3.15	3.26
Sodium <i>o</i> -anisate	101.21	+3.60	4.32	3.42
Sodium benzoate	87.17 ^c	—	4.15	3.26

^aAnion radii calculated from B_{anion}

^bAnion radii calculated from ionic partial molal volume

^cData from Mohanty *et al* (1983)

assuming that the ion behaves like a rigid sphere with an effective radius R moving in a continuum. The values of R are recorded in table 2 and they agree with the radii calculated from partial ionic molal volumes of the anions.

Viscosity data have also been analysed on the basis of the transition state theory of the relative viscosities of electrolyte solutions as suggested by Feakins *et al* (1974). The B -coefficient (Feakins *et al* 1974), is expressed by the equation

$$B = \frac{\bar{V}_1^0 - \bar{V}_3^0}{1000} + \frac{\bar{V}_1^0}{1000} \left(\frac{\Delta\mu_3^{0\ddagger} - \Delta\mu_1^{0\ddagger}}{RT} \right), \quad (5)$$

where \bar{V}_1^0 and \bar{V}_3^0 are the partial molal volumes of the solvent and solute respectively, $\Delta\mu_3^{0\ddagger}$ is the contribution per mole of the solute to the free energy of activation for viscous flow of the solution. $\Delta\mu_1^{0\ddagger}$, the free energy of activation per mole of the pure solvent, is given (Glasstone *et al* 1941) by

$$\Delta\mu_1^{0\ddagger} = RT \ln(\eta_1 V_1/hN), \quad (6)$$

where η_1 is the viscosity of the solvent in poise. $\Delta\mu_3^{0\ddagger}$ can be calculated from (5) after substituting for the value of $\Delta\mu_1^{0\ddagger}$ obtained from (6). The activation parameters for viscous flow for the electrolytes and pure solvent are presented in table 3.

According to Feakins *et al* (1986) $\Delta\mu_3^{0\ddagger} > \Delta\mu_1^{0\ddagger}$ for solutes having positive B -values. Again, for substances showing an increase in B -value with temperature, $\Delta\mu_3^{0\ddagger}$ also increases; the opposite behaviour in $\Delta\mu_3^{0\ddagger}$ is shown by solutes having negative dB/dT values. This is demonstrated nicely by the results shown in table 3. The corresponding values for the anions are shown in table 4 which incorporates the values for the ionic enthalpy and entropy of activation for viscous flow at a particular temperature viz. 298 K. The greater the value of $\Delta\mu_3^{0\ddagger}$, the greater is the structure-making ability of the solute. From this view point it is concluded that while the ortho-anisate ion is an efficient structure-maker, the anion of 2,6-dihydroxy benzoic acid is least so. The magnitude and sign of $\Delta\mu_3^{0\ddagger}$ depends on the relative values and signs of $\Delta H_3^{0\ddagger}$ and $T\Delta S_3^{0\ddagger}$. The values of $\Delta H_3^{0\ddagger}$ and $T\Delta S_3^{0\ddagger}$ for the salts as well as their anions have been calculated at a particular temperature, viz. 298 K and are shown in tables 3 and 4 respectively. Both $\Delta H_3^{0\ddagger}$ and $\Delta S_3^{0\ddagger}$ are negative (except for *o*-anisate) and $\Delta H_3^{0\ddagger} > T\Delta S_3^{0\ddagger}$.

Table 3. Activation parameters for viscous-flow of the solutes and the solvent.

Salt	$\Delta\mu_3^{0*}$ (kJ mol ⁻¹) at <i>T</i> (K)			ΔH_3^{0*} (kJ mol ⁻¹) at 298 K	$T\Delta S_3^{0*}$ (kJ mol ⁻¹) at 298 K
	298	303	308		
Sodium salicylate	69.75	72.57	75.26	-94.54	-164.29
Sodium anthranilate	73.67	78.64	80.08	-117.32	-190.99
Sodium thiosalicylate	78.86	—	88.33	-203.35	-282.21
2,6-Dihydroxy sodium benzoate	57.33	60.26	63.33	-121.47	-178.80
Sodium <i>o</i> -anisate	101.76	—	73.40	946.89	845.13
Solvent*	9.21	9.04	8.94		

*Water. Data from McDowall *et al* (1976)**Table 4.** Ionic free energy, enthalpy and entropy of activation for viscous flow at 298 K.

Salt	$\Delta\mu_{3(-)}^{0*}$ (kJ mol ⁻¹)	$\Delta H_{3(-)}^{0*}$ (kJ mol ⁻¹)	$T\Delta S_{3(-)}^{0*}$ (kJ mol ⁻¹)
Sodium salicylate	51.35	-116.40	-167.75
Sodium anthranilate	55.27	-139.18	-194.45
Sodium thiosalicylate	60.46	-225.00	-285.46
2,6-Dihydroxy sodium benzoate	38.93	-143.87	-182.26
Sodium <i>o</i> -anisate	83.36	925.03	841.67

The negative values of enthalpy and entropy of activation for viscous flow suggest that solute-solvent interactions are strong in the transition state solvent. Negative values of ΔH_3^{0*} and ΔS_3^{0*} have been observed by Feakins *et al* (1986) for several structure-breakers in aqueous solution. In the case of *o*-anisate both the enthalpy and entropy of activation are positive and the former exceeds the latter. This suggests that for this system solute-solvent interaction is complete or nearly so in the ground state. Similar observations have been reported by Feakins *et al* (1974) in aqueous solutions of LiCl.

The ionic *B*-coefficients are fairly large and cannot be accounted for by the Einstein effect alone as can be seen by calculation according to

$$B_{\text{ion}} = 2.5 \bar{V}_i, \quad (7)$$

where \bar{V}_i is the partial ionic molal volume. An explanation of the excess *B*-coefficient must be sought for 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 conditioned by the effect of reinforcement of water structure by the large ortho-substituted benzoate ions due to hydrophobic hydration. However, quantitative evaluation of these parameters is difficult to carry out at present. The *B*-coefficient of 2,6-dihydroxy benzoate ion is, however, a little less than that calculated according to (7) suggesting that the presence of this anion makes the water more fluid.

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