NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2226—2227 (1973)

The Viscosity *B*-Coefficients of the Anionic Species of Benzoic Acid and Its Monosubstituted Derivatives

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(Received March 14, 1972)

The viscosities of aqueous electrolyte solutions have been measured for a large number of electrolytes. According to Jones and Dole,[1] who first measured accurately the viscosity of the aqueous electrolyte solutions up to the range of extremely high dilution, the specific viscosity, η_{sp}, of aqueous solutions of strong electrolytes is related to the solute molarity, c, by the equation:

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1 = A\sqrt{c} + Bc$$

where η and η_0 are the viscosities of the solution and of water respectively. A is a coefficient depending on the ion-ion interaction between the solute ions; it can be calculated theoretically. B is a coefficient depending on the size of the ions and on the interaction between the ions and the surrounding solvent; it is usually called the Jones-Dole's viscosity B-coefficient.

In the course of measurements of the B-coefficients of isomers of metal complexes, we felt that a thorough study of the viscosity of the benzoate anion and its derivatives might supply useful information concerning the contribution of substituents to the viscosity. A study was, therefore, made of the viscosities of the benzoic acid and its derivatives.

Experimental

Measurements. The viscosities were measured with a Cannon-Fenske capillary viscometer with an efflux time of *ca.* 300 seconds for distilled water. The viscosities and densities of the solutions were measured in a water bath maintained at 25±0.01 °C. The efflux times, measured with a stopwatch to 0.1 sec, were easily reproducible to 0.2 sec.

Materials. Samples of benzoic acid and its derivatives of a guaranteed reagent grade were used. From stock solutions, prepared from benzoic acids and potassium hydroxide, solutions containing 0.04—0.15 mol/l potassium benzoate were made by dilution and were then used for the viscosity and density measurements. In each case, the pH value of the solution was controlled so as to be about 2 or 3 pH units higher than the pK value of the parant acid.

Calculations. The B-coefficient was evaluated by plotting $\eta_{sp}/\sqrt{c}$ *vs.* $\sqrt{c}$ (Fig. 1). A straight line was obtained in each case at concentrations below 0.15 mol/l. The intersection of the resulting straight line on the ordinate gives the value of the A-coefficient. In each case, the A-coefficient was found to be zero within the limits of experimental error. The slope of the resulting straight line gives the value of the B-coefficient. As has been discussed by Gurney,[2] the B-coefficient is composed additively of contributions from each of the solute species present in the solution. Moreover, the B-value of the benzoate anion can be obtained by subtracting a correction for the other solute species present in the solution.

Results and Discussion

As the pH value of the solution was at least 2 pH units higher than the pK value of the parent benzoic acid, the contribution of the un-ionized benzoic acid to the viscosity of the solution may be practically neglected. The concentrations of the hydrogen and hydroxide ions are very low compared with that of the benzoate anion in the pH range (5—10) studied here. Moreover, their B-coefficients are themselves quite small compared with that of the benzoate anion,[2] and so their contribution to the viscosity of the solution may also be practically neglected. On the other hand, the concentration of the potassium ion is comparable to that of the benzoate anion. Hence, a correction, a relatively small one, for the potassium ion is necessary, although its B-value is actually the lowest of those of the chemical species under consideration.[2] The B-coefficients studied here are listed in Table 1.

TABLE 1. VISCOSITY B-COEFFICIENTS OF BENZOATE DERIVATIVES

Substituent	*o*-	*m*-	*p*-
H		(0.41)	
OH	0.31	0.41	0.45
CH_3	0.49	0.49	~0.49
Cl	0.49	0.47	0.47
NO_2	0.44	0.41	0.41
OCH_3	0.50	—	0.46
COO^-	0.61	0.61	0.61

As has been reported by Charles,[3] the values of η_{sp}/c for the copper chelate with an enforced planar *cis*-configuration about the metal were higher than those found for the corresponding alkyl-substituted chelates with planar *trans*-configurations, evidently the result of the permanent dipole moment associated with the *cis*-configuration. However, as may be seen from Table 1, no essential difference between the B-coefficients of *o*-, *m*-, and *p*-isomers is found, even for COO^--derivatives, with the exception of the OH-derivatives. In the latter case, the B-value of the *o*-hydroxybenzoate, *i.e.*, the salicylate anion, is appreciably lower than that

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[1] G. Jones and M. Dole, *J. Amer. Chem. Soc.*, **51**, 2950 (1929).

[2] R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Company, New York (1953).

[3] R. G. Charles, *J. Amer. Chem. Soc.*, **81**, 1793 (1959).

of its isomers. This may by due mainly to the formation of an intramolecular hydrogen bond, as has been discussed by Davies and Malpass[4] in connection with the difference in *B*-values between maleic acid and its isomer, fumaric acid.

For *o*-phthalic acid, the viscosity measurements were carried out over the 4.4—11.8 pH range. The slope of the straight lines obtained by plotting $\eta_{sp}/\sqrt{c}$ *vs.* $\sqrt{c}$ depend on the pH values lower than about 6. However, for the pH values higher than about 6.7, where phthalic acid, H_2A, is present virtually as the A^{2-} anion the satisfactory agreement of all the points with a single straight line indicates that the *B*-value of the phthalate anion, A^{2-}, is independent of the pH value, as has been expected.

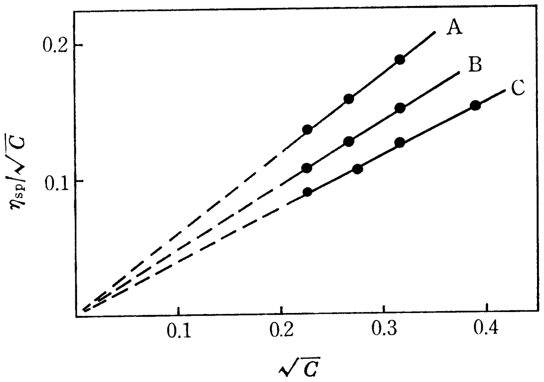

Fig. 1. $\eta_{sp}/\sqrt{C}$ for aqueous potassium benzoate and potassium *o*-phthalate solutions at 25 °C as a function of $\sqrt{C}$
A: potassium *o*-phthalate, pH=7.2, B: potassium *o*-phthalate. pH=4.6, C: potassium benzoate, pH=10.0.

Figure 1 shows two straight lines at the pH values of 4.6 and 7.2. The *B*-coefficient of hydrogenphthalate, HA^-, was tentatively calculated as 0.42 using the data for the lower pH range, where the A^{2-} and HA^- species are present predominantly, together with the *B*-value of A^{2-} and the acid dissociation constants of phthalic acid.

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[4] C. W. Davies and V. E. Malpass, *Trans. Faraday Soc.*, **60**, 2075 (1964).