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The Ortho Effect. A Correlation Using Ebullioscopy

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Association of the solute benzoic acid and the ortho substituted benzoic acid solutes 2-bromo, 2-chloro, 2-methoxy, and 2-methyl in CCl₄ solutions was studied using ebullioscopy in the 0.04 to 0.4 m concentration range. Association numbers for solutes and observed equilibrium constants for solute dimerization reactions at 76.7 °C + ΔT_b at 1 atm pressure were calculated.

In this study the association of selected ortho substituted benzoic acid solutes and of benzoic acid in CCl₄ has been correlated with concentration and with the ortho substituent. The ortho effect has been primarily interpreted to be a steric effect; for ortho substituted benzoic acids the substituent may force the carboxyl group out of the plane of the benzene ring, decrease the resonance of the molecule, and affect the activity of the carboxyl group (δ). There are, however, very little reliable experimental data relating association of benzoic acids in aprotic solvents with the ortho substituent (2, 4). Correlation of data has been extremely difficult due to variations of solvent, temperature, and especially concentration. In this present study ortho substituents chosen for comparison, and where only intermolecular association is involved, are the chloro, bromo, and methyl groups. The effect of the ortho group on association can be quantitatively compared independent of steric differences for the chloro and methyl groups since their van der Waals radii are virtually the same at 1.75 and 1.72 Å, respectively (1). For these latter ortho groups, the group which causes the greatest increase in carboxyl bond polarity through inductive and resonance effects should most enhance hydrogen bonding between solute molecules, as indicated by increased intermolecular association. An ortho group such as methoxy, which can form an intramolecular hydrogen bond with the carboxyl group can be expected to have decreased intermolecular association due to this effect. The influence of such a group on intermolecular association must be considered separately from ortho groups which do not involve intramolecular association.

Experimental Section

The apparatus used has been previously described (7) and consisted of an improved Cottrell ebullioscope (3). All mea-

surements made use of a second apparatus with solvent only to correct for pressure fluctuations. In this study the lowest concentrations measured were approximately 0.04 m; below this concentration the temperature elevation became less than 0.100° and the Beckmann differential thermometers used measured only two significant figures. The upper concentration in the study was about 0.4 m to ensure solute solubility. The approximately one order of magnitude concentration range studied permitted study of association which is primarily interpreted as solute dimerization. Chemicals were reagent grade and were carefully checked for purity by melting point or boiling point and refractive index measurements before use. All solution concentrations were determined from careful weighings of solute and solvent.

Results and Discussion

Figure 1 shows the association of the solutes studied in CCl₄ where the association number, i , the ratio of the measured solute molecular weight to the true solute molecular weight, is plotted as a function of solution molality. It can be seen from the figure that choice of the concentration for purposes of comparison between solutes is significant. At approximately 0.10 m, for example, solute association number is close to 2.00 for chloro and bromo substituted benzoic acids whereas for the methyl substituted benzoic acid and for benzoic acid, association at this concentration is approximately 13% less than 2.00. Association at 0.10 m indicates a greater ionic character to the carboxyl-carboxyl bond for solutes with chloro and bromo ortho groups as compared with the methyl group; this greater ionic character may be primarily attributed to the inductive effect of the chloro and bromo ortho groups. The association shown in the figure demonstrates that, for the chloro and bromo ortho groups compared with benzoic acid at approximately 0.10 m any steric effect of the groups has not caused a decrease in association. In the case of the ortho methoxy group the figure shows that at almost all concentrations the intermolecular association is less than for benzoic acid, a fact that may be attributed to intramolecular hydrogen bonding.

Table I shows experimental results, including observed equilibrium constants in mole fraction concentration units, K_X ,

Table I. Association Number and Observed Dimerization Equilibrium Constant Data for Solutes in Carbon Tetrachloride at 76.7 °C + ΔT_b and 1 Atm Pressure. Ebullioscopic Constant, K_b , 5.03 (5)

Molality	ΔT_b	i	K_x (obsd)
Benzoic Acid			
0.0358	0.111	1.61	4.01
0.0431	0.132	1.63	4.60
0.0649	0.192	1.69	7.11
0.1035	0.294	1.76	13.2
0.1530	0.432	1.76	13.2
0.1544	0.429	1.80	20.1
0.2411	0.651	1.84	32.8
0.2964	0.775	1.89	74.1
0.4111	1.058	1.92	142
2-Bromobenzoic Acid			
0.0411	0.145	1.42	1.24
0.0548	0.172	1.60	0.674
0.0737	0.209	1.76	13.2
0.0926	0.231	2.00	—
0.1091	0.268	2.03	—
2-Chlorobenzoic Acid			
0.0586	0.190	1.54	2.54
0.0601	0.196	1.53	2.40
0.0621	0.187	1.66	5.69
0.0767	0.215	1.78	16.0
0.0860	0.211	2.03	—
0.1627	0.396	2.05	—
2-Methylbenzoic Acid			
0.0371	0.111	1.67	6.12
0.0687	0.199	1.73	10.0
0.1029	0.297	1.72	9.13
0.1309	0.376	1.73	10.0
2-Methoxybenzoic Acid			
0.0368	0.171	1.07	0.0811
0.0792	0.281	1.40	1.11
0.1072	0.371	1.44	1.40
0.1338	0.436	1.52	2.25
0.1828	0.511	1.78	16.0
0.2386	0.596	1.98	2.50×10^3

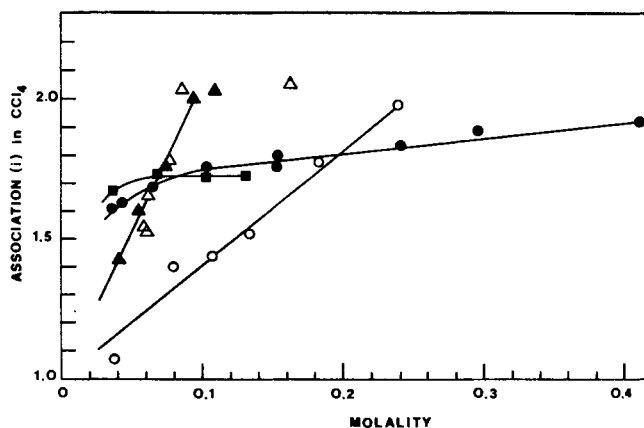


Figure 1. Association number-concentration curves for ortho substituted benzoic acids in CCl_4 at 76.7 °C + ΔT_b and 1 atm: ●, benzoic; ○, 2-methoxy; ■, 2-methyl; ▲, 2-bromo; △, 2-chloro.

calculated assuming dimerization to be the primary type of association. Table I shows that the magnitude of i , the association number, only slightly exceeds 2.00 for a few concentrations, supporting dimerization as the principle type of association in this study. However, trimers and higher polymers may also exist at higher concentrations. The procedure used for calculation of equilibrium constants has been recently reviewed (7).

In conclusion, in spite of previous studies, relatively little systematic data existed for the systems described in this paper. This study correlates association obtained from ebullioscopic data with concentration and nature of ortho substituents for selected benzoic acid solutes.

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