[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF CHICAGO]

The Influence of Charge and Configuration on the Solvent Power of Benzene Carboxylic Acid Ions[1]

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The study of serological reactions,[2] and recognition of the necessity of inorganic ions in addition to proteins as components of certain enzyme systems, make it desirable to obtain further knowledge of phenomena in the neighborhood of electrical charges in aqueous media. In particular an earlier study[3] showed that dilute sodium mellitate solutions produced a far greater increase in the solubility of thallous iodate than that predicted by the theory of Debye and Hückel. Furthermore even in 0.001 molar mellitate the addition of a neutral salt caused an actual decrease in thallous iodate solubility instead of the increase to be expected.

The present report comprises a similar study of other members of the homologous series with particular reference to the effects resulting from differences in carboxyl group spacing.

Experimental

Materials.—Benzoic acid, *o*, *m* and *p*-phthalic acids, and trimesic acid were obtained from the Eastman Kodak Company. The *p* acid was freed from *p*-toluic acid by way of its methyl ester.[4] Pyromellitic acid and benzenepentacarboxylic acid were prepared by oxidation of the appropriate methyl substituted benzene with potassium permanganate in the cold.[5] All acids were repeatedly recrystallized from water until analyses were satisfactory.[6]

The identity of the compounds was confirmed as follows: Benzoic acid. Calcd.: C, 68.84; H, 4.95; eq. wt., 122.1. Found: C, 68.83; H, 4.96; eq. wt., 122.0; m. p. 122°. *o*-Phthalic acid. Calcd.: C, 57.83; H, 3.64; eq. wt., 83.06. Found: C, 57.83; H, 3.64; eq. wt., 83.08; m. p. 196°. *m*-Phthalic acid. Found: C, 57.88; H, 3.53; eq. wt., 83.13; m. p. 343°. *p*-Phthalic acid. Found: C, 57.78; H, 3.65; eq. wt., 83.39; m. p., >300 sublimes. Trimesic acid. Calcd.: C, 51.44; H, 2.88; eq. wt., 70.04. Found: C, 51.49; H, 2.80; eq. wt., 70.44; m. p. >362°. Pyromellitic acid. Calcd.: C, 47.25; H, 2.38; eq. wt., 63.54. Found: C, 47.18; H, 2.32; eq. wt., 63.51; m. p. 271°.[7] Benzenepentacarboxylic acid. Calcd.: C, 44.31; H, 2.03. Found: C, 44.50; H, 1.91; m. p. 239°. All melting points are corrected and agree well with reported values.

Methods.—Salts of the acids were prepared in solution by adding the equivalent amount of sodium hydroxide from sodium. Solvents were rotated with the solid phase for twenty-four hours at 25.00 ± 0.02°. Analytical methods were those of La Mer and Goldman.[8]

Results

TABLE I

SOLUBILITY OF THALLOUS IODATE IN SOLUTIONS OF THE SODIUM SALTS OF BENZENE CARBOXYLIC ACIDS

$$-\log \gamma_0 = 0.506\sqrt{0.001834} = 0.0217$$
$$-\log \gamma_\pm = 0.0217 + \log S/S_0$$

Molarity of solvent salt	Soly. $\times 10^6$ H_2O	$-\log \gamma_\pm$
0	1834	0.0217
	Sodium Benzoate	
0.02	2057	0.0715
.05	2228	.1062
.10	2429	.1437
.20	2723	.1934
	Sodium *o*-Phthalate	
0.001333	1930	0.0439
.002667	2005	.0604
.00667	2172	.0952
.01333	2377	.1343
.03333	2798	.2051
.0667	3287	.2751
	Sodium *m*-Phthalate	
0.00667	2053	0.0707
.01333	2171	.0950
.03333	2401	.1387
.0667	2655	.1824
	Sodium *p*-Phthalate	
0.00667	2046	0.0687
.01333	2156	.0919
.03333	2373	.1336
.0667	2613	.1754
	Sodium Trimesate	
0.003333	2069	0.0736
.00667	2189	.0985
.01667	2416	.1414
.03333	2661	.1833
	Sodium Pyromellitate	
0.0004	1944	0.0470
.0008	2029	.0656
.002	2214	.1035
.004	2458	.1489
.010	2818	.2082
.0152	3053	.2430
.020	3224	.2667
	Sodium Benzenepentacarboxylate	
0.0001067	1908	0.0389
.0002666	2029	.0656
.000533	2212	.1031
.001334	2636	.1792
.002666	3123	.2529

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(1) Aided in part by a grant from the Dr. Wallace C. and Clara A. Abbott Memorial Fund of the University of Chicago.

(2) Pressman, Grossberg, Pence and Pauling, THIS JOURNAL, **68**, 250 (1946).

(3) Failey, *ibid.*, **55**, 3112 (1933).

(4) Bayer, *Ann.*, **245**, 140 (1888).

(5) These compounds were prepared or purified in the laboratory of the Department of Biological Chemistry, College of Physicians and Surgeons, Columbia University. The author wishes to express his gratitude to Professor Hans T. Clarke for the facilities placed at his disposal.

(6) The author wishes to thank Mr. W. Saschek for carrying out the elementary analyses.

(7) In sealed tube by the plunge method.

(8) La Mer and Goldman, THIS JOURNAL, **51**, 2632 (1929).

TABLE II

SOLUBILITY OF THALLOUS IODATE IN M = 0.02 SODIUM BENZOATE TO WHICH VARYING AMOUNTS OF A THIRD SALT HAVE BEEN ADDED

Molarity of third salt	Soly. × 10^6	$-\log \gamma_{\pm}$
0	2057	0.0715
	NaCl	
0.01	2141	0.0889
.03	2285	.1172
.10	2667	.1843
	$MgCl_2$	
.00398	2145	.0897
.00994	2261	.1126
.01988	2422	.1425
.0398	2681	.1866

TABLE III

SOLUBILITY OF THALLOUS IODATE IN M = 0.00667 SODIUM *o*-PHTHALATE TO WHICH VARYING AMOUNTS OF A THIRD SALT HAVE BEEN ADDED

Molarity of third salt	Soly. × 10^6	$-\log \gamma_{\pm}$
0	2172	0.0952
	NaCl	
0.002	2182	0.0972
.004	2196	.0999
.008	2224	.1054
.01	2251	.1107
.03	2373	.1336
.06	2542	.1635
.10	2735	.1953
	$NaNO_3$	
.002	2179	.0966
.004	2193	.0993
.008	2217	.1041
.01	2229	.1064
.020	2280	.1162
.050	2416	.1414
.10	2607	.1744
.00398	2218	.1043
.00994	2306	.1212
.01988	2446	.1468
.0398	2697	.1892

TABLE IV

SOLUBILITY OF THALLOUS IODATE IN M = 0.00667 SODIUM *m*-PHTHALATE TO WHICH VARYING AMOUNTS OF A THIRD SALT HAVE BEEN ADDED

Molarity of third salt	Soly. × 10^6	$-\log \gamma_{\pm}$
0	2053	0.0707
	NaCl	
0.01	2136	0.0879
.03	2276	.1155
.06	2458	.1489
.10	2664	.1838
	$MgCl_2$	
.00398	2134	.0875
.00994	2242	.1089
.01988	2398	.1381
.0398	2660	.1832

TABLE V

SOLUBILITY OF THALLOUS IODATE IN M = 0.00667 SODIUM *p*-PHTHALATE TO WHICH VARYING AMOUNTS OF A THIRD SALT HAVE BEEN ADDED

Molarity of third salt	Soly. × 10^6	$-\log \gamma_{\pm}$
0	2046	0.0687
	NaCl	
0.01	2129	0.0865
.03	2270	.1143
.06	2452	.1478
.10	2658	.1829
	$MgCl_2$	
.00398	2131	.0869
.00994	2241	.1087
.01988	2402	.1389
.0398	2663	.1837

TABLE VI

SOLUBILITY OF THALLOUS IODATE IN M = 0.003333 SODIUM TRIMESATE TO WHICH VARYING AMOUNTS OF A THIRD SALT HAVE BEEN ADDED

Molarity of third salt	Soly. × 10^6	$-\log \gamma_{\pm}$
0	2069	0.0736
	NaCl	
0.01	2142	0.0891
.03	2279	.1160
.06	2455	.1484
.10	2661	.1833
	$MgCl_2$	
.00398	2128	.0863
.00994	2233	.1072
.01988	2393	.1372
.0398	2653	.1820

TABLE VII

SOLUBILITY OF THALLOUS IODATE IN M = 0.002 SODIUM PYROMELLITATE TO WHICH VARYING AMOUNTS OF A THIRD SALT HAVE BEEN ADDED

Molarity of third salt	Soly. × 10^6	$-\log \gamma_{\pm}$
0	2214	0.1035
	NaCl	
0.01	2252	0.1109
.03	2359	.1310
.06	2517	.1592
.10	2709	.1911
	$MgCl_2$	
.000796	2183	.0974
.001988	2160	.0928
.00398	2162	.0932
.00994	2245	.1095
.01988	2401	.1387
.0398	2665	.1840

TABLE VIII

SOLUBILITY OF THALLOUS IODATE IN M = 0.001334 SODIUM BENZENEPENTACARBOXYLATE TO WHICH VARYING AMOUNTS OF A THIRD SALT HAVE BEEN ADDED

Molarity of third salt	Soly. × 10^6	$-\log \gamma_\pm$
0	2636	0.1792
	NaCl	
0.01	2587	0.1711
.03	2607	.1744
.06	2701	.1898
.10	2842	.2119
	$MgCl_2$	
.000796	2424	.1428
.001988	2253	.1111
.00398	2195	.0997
.00994	2258	.1120
.01988	2408	.1400
.0398	2671	.1850

Discussion

In Figures 1, 2 and 3 are plotted the deviations of the activity coefficient of thallous iodate from the Debye–Hückel limiting law, the ordinate being $-\log \gamma_\pm - 0.506 \sqrt{\mu}$ and the abscissa $\sqrt{\mu}$. The ionic strength was determined, as usual, from the total concentration of added and dissolved ions.

Figure 1 shows that when sodium *o*-phthalate is the solvent, there is an anomalously high solubility of thallous iodate, corresponding to the excess of $-\log \gamma_\pm$ over the limiting law value. The curve for *m*-phthalate indicates a negative deviation, as would be expected from the ionic size factor in the Debye–Hückel equation. Sodium benzoate, and *p*-phthalate fall respectively above and below *m*-phthalate.

Addition of sodium chloride to sodium *o*-phthalate of fixed concentration, or of magnesium chloride to *m*-phthalate does not alter the deviations from the limiting law, but magnesium chloride added to *o*-phthalate, or sodium chloride added to *m*-phthalate reduce and even change the sign of the deviation.

In Figure 2 is seen the more pronounced solvent power of pyromellitate ion with its carboxyl groups in the 1,2 and 4,5 positions. Addition of sodium chloride brings about a decrease in the ordinate, and magnesium chloride added to 0.002 molar sodium pyromellitate causes an actual decrease in thallous iodate solubility. The symmetrical trivalent trimesate ion does not differ greatly from *m*-phthalate in behavior.

Figure 3 which includes data from reference 3 shows the very pronounced solvent action of the ion of benzenepentacarboxylic acid and of the hexavalent mellitate ion. The repression by added sodium chloride and to a greater extent by magnesium chloride is evident.

It is apparent that anomalously high solubilities are found only in the presence of ortho carboxyl groups, although it would seem dangerous to generalize this to include all organic ions of high valence.

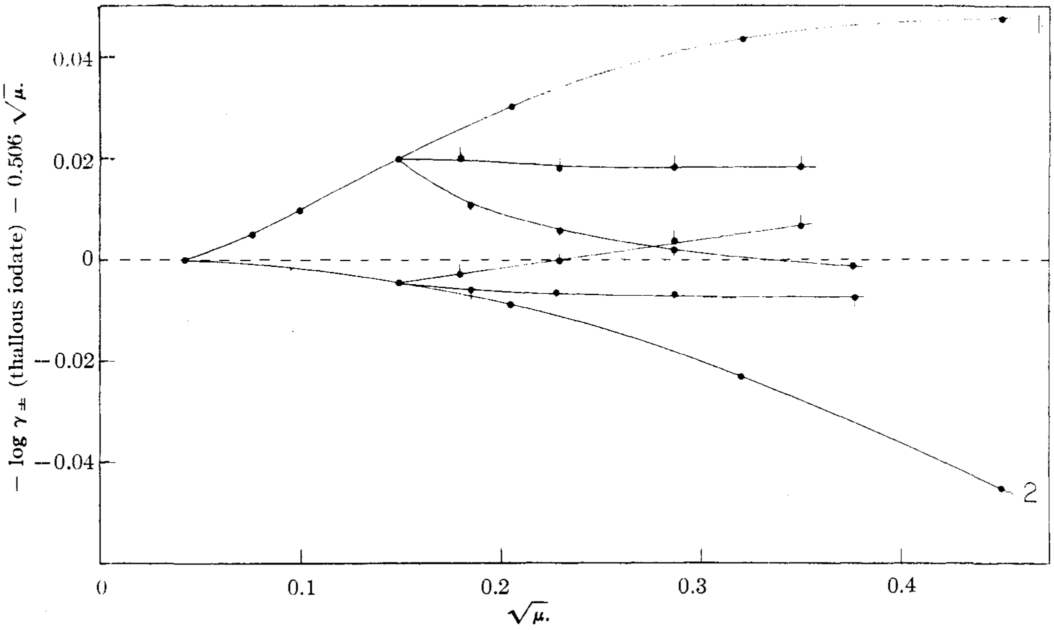

Fig. 1.—Deviation of the activity coefficient of thallous iodate from the Debye–Hückel limiting law in the presence of sodium *o*-phthalate, and of sodium *m*-phthalate with and without the addition of a third salt: 1, *o*-phthalate; 2, *m*-phthalate; ●, sodium chloride added; ●, magnesium chloride added.

Ion Association Theory

One plausible explanation for the high solubilities observed in the presence of *o*-phthalate is to be found in the hypothesis that undissociated com-

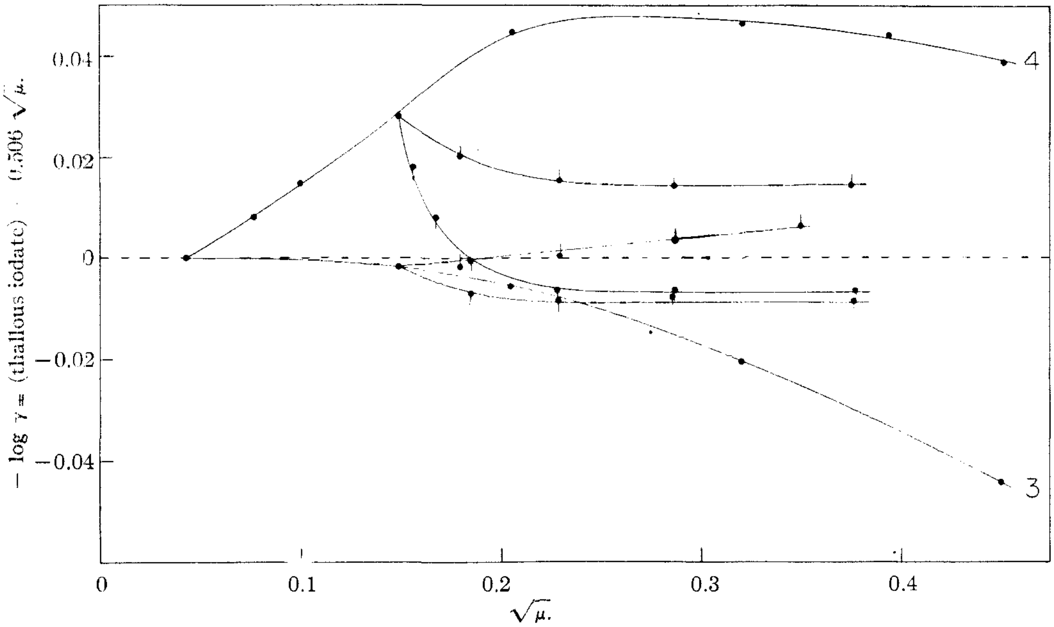

Fig. 2.—Deviation of the activity coefficient of thallous iodate from the Debye–Hückel limiting law in the presence of sodium trimesate, and of sodium pyromellitate, with and without the addition of a third salt: 3, trimesate; 4, pyromellitate; ●, sodium chloride added; ⧪, magnesium chloride added.

plexes are formed, containing one *o*-phthalate anion and one or more thallous cations. The removal of bound thallous ion from the solubility product equilibrium would then cause additional thallous iodate to dissolve.

The difference between the solvent powers of *o* and *m* phthalate ions may be explained by extending Bjerrum's[9] theory of ion association to cover ions possessing two separate charges at some distance from one another. Harned and Owen[10] give the equation

$$(1 - \alpha) = \frac{4\pi Nc}{1000}\int_b^q r^2 \exp\,(|z_1z_2|e^2/DrkT)\mathrm{d}r \qquad (1)$$

where $(1 - \alpha)$ = the degree of association, N = Avogadro's number, c = the molarity of *associating* ions, as distinguished from the oppositely charged central ion whose degree of complex formation is being considered, r = the distance from the center of that ion, z_1 and z_2 are the valencies, e = the electronic charge, D = the effective dielectric constant, k = the Boltzmann constant, T = the absolute temperature, b = the distance of closest approach, and q is the value of r at which the integrand reaches a minimum.

This is a special case of the more general relation

$$(1 - \alpha) = \frac{Nc}{1000}\int\!\!\int\!\!\int \exp\,(\varphi/kT)\mathrm{d}v \qquad (2)$$

Here φ is the work necessary to remove the *associating* ion from the volume element dv to an infinite distance, and the integration is to be performed throughout the volume surrounding the central ion within which any second ion is considered an associated ion.

Each phthalate ion may, for simplification, be regarded as two negative charges held a fixed distance d apart. The value of d was taken as 3.53 Å. for the *o* acid and 6.12 Å. for the *m*, these figures having been arrived at by assuming each effective charge to lie halfway between the carboxyl oxygen atoms. The equipotential surfaces surrounding such an ion satisfy the equation

$$1/l + 1/n = 2/a \qquad (3)$$

Where l and n are the distances from a point on the surface to the two charges, and a is a parameter which becomes identical with r the distance from the center of a spherical divalent ion as d vanishes.

Call $v(a, d)$ the volume enclosed by the equipotential surface defined by given values of a and d. Let

$$v(a, d)\Big/\frac{4}{3}\pi a^3 = g(a, d) = g(a/d) \qquad (4)$$

Values of the functions $g(a/d)$ and dg/d(a/d) were estimated graphically and plotted against (a/d)

$$(\partial v/\partial a)_d = 4/3\pi a^3(\partial g/\partial a)_d + 4\pi a^2 g \qquad (5)$$

Then if the positive ions are univalent equation (3) becomes

$$(1 - \alpha) = \frac{4\pi Nc}{1000}\int_p^q \{1/3a^3(\partial g/\partial a) + a^2 g\}\exp(2e^2/DkaT)\mathrm{d}a \qquad (6)$$

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[9] Bjerrum, *Kg. Danske Videnskab. Selskab, Math-fys. Medd.*, **7**, no. 9 (1926).

[10] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 42 and 43. See also R. H. Fowler, "Statistical Mechanics," Cambridge University Press, 1936, pp. 552 and 553.

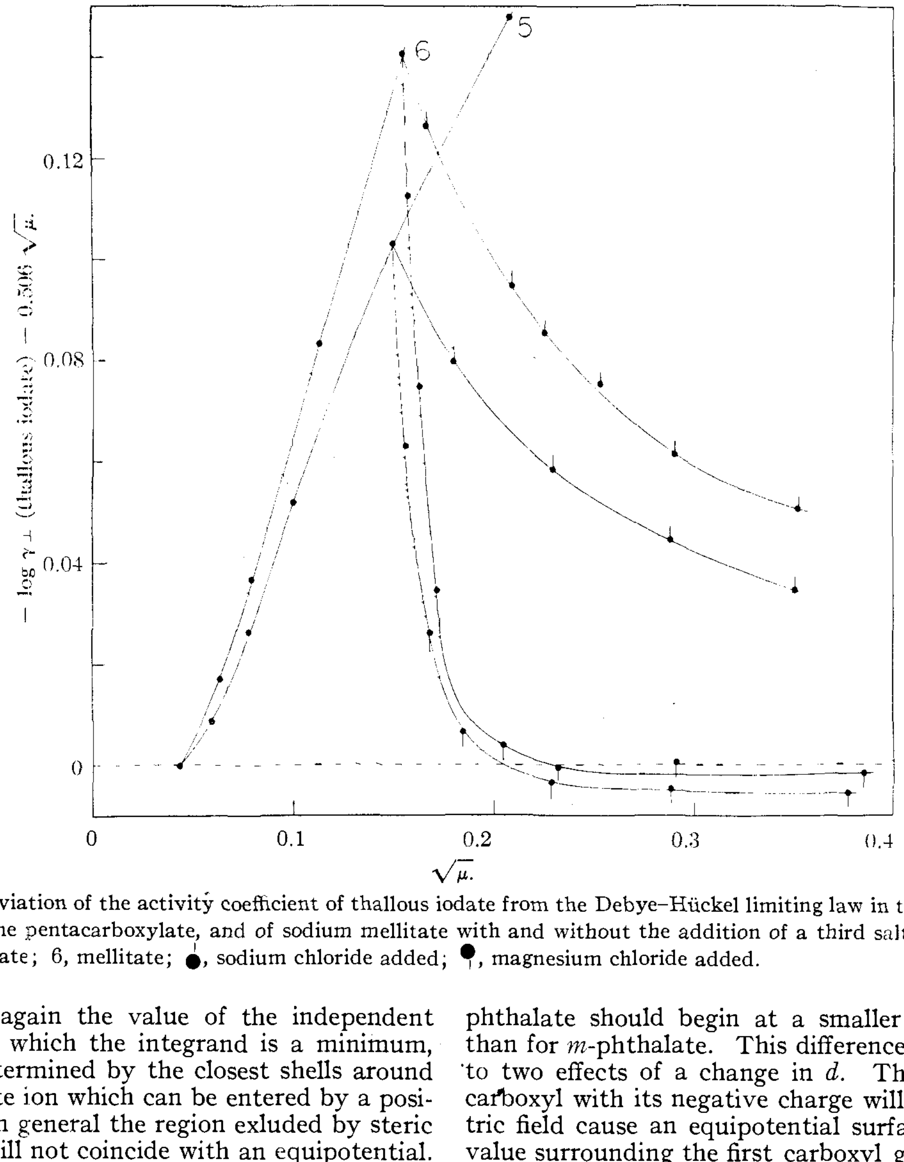

Fig. 3.—Deviation of the activity coefficient of thallous iodate from the Debye–Hückel limiting law in the presence of sodium benzene pentacarboxylate, and of sodium mellitate with and without the addition of a third salt. 5, benzene pentacarboxylate; 6, mellitate; $\overset{|}{\bullet}$, sodium chloride added; $\underset{|}{\bullet}$, magnesium chloride added.

where q is again the value of the independent variable for which the integrand is a minimum, and p is determined by the closest shells around the phthalate ion which can be entered by a positive ion. In general the region exluded by steric hindrance will not coincide with an equipotential.

The integrand of equation (6) is called W and is plotted in Fig. 4 against a in Å. The separate curves represent different values of d.

The degree of association $(1 - \alpha)$ is estimated by determining the area under the curve from the proper value of a, corresponding to the effective distance of closest approach to the upper limit q which lies at 7.19×10^{-8} cm., and multiplying by $Nc/1000$. It may be observed that for given limits of integration $(1 - \alpha)$ decreases with increasing d. This is in accord with the experimental data. However, it is also apparent that the degree of association should be less than twice as high for *o*-phthalate as for *m*-phthalate. The thallous iodate solubilities indicate a greater difference.

The above considerations apply to identical limits of integration, but closer scrutiny suggests that the integration to determine $(1 - \alpha)$ for *o*-phthalate should begin at a smaller value of a than for *m*-phthalate. This difference will be due to two effects of a change in d. The second *o*-carboxyl with its negative charge will by its electric field cause an equipotential surface of given value surrounding the first carboxyl group to enclose a greater volume, and thus to lie further from the center of the carboxyl. This influence will be greater for small d values. If then there is a distance of closest approach between a cation and a carboxyl group, the cation can penetrate into a deeper potential shell in the case of *o*-phthalate. This means that the integration starts at a smaller a value, and because of the shape of the curves in Figure 4 there will be a considerable increase in $(1 - \alpha)$. In addition, a second negative group nearby would presumably enhance the lowering of the effective dielectric constant[11] and cause marked changes in the exponential and therefore in $(1 - \alpha)$.

The effectiveness of added magnesium chloride in suppressing the solvent action of *o*-phthalate is understandable from the above as a divalent cation would be expected to displace a uni-

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[11] Reference 2, footnote 21.

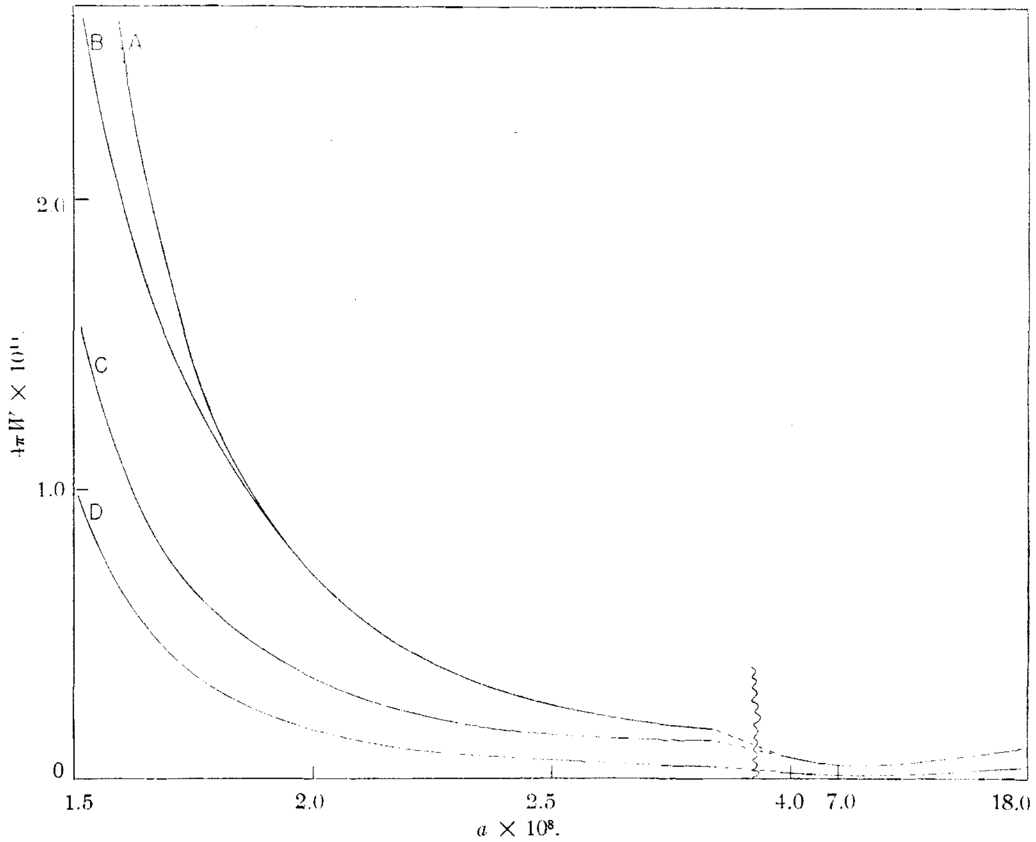

Fig. 4.—Plot of W, the integrand of equation (6), against the parameter a: for A, $d = 0$; for B, $d = 3.53$ Å.; for C, $d = 6.12$ Å.; and for D, d = infinity.

valent one from such a complex[12] formed through coulomb interaction.

Summary

Solubilities of thallous iodate higher than those predicted by the limiting law of Debye and Hückel have been observed in solutions of the sodium salts of *o*-phthalic, pyromellitic and benzene pentacarboxylic acids. The addition of neutral salts depresses this effect. In solutions of *m*-phalate, *p*-phthalate, or of trimesate, solubility falls below the limiting law value. The phenomena observed with *o*-phthalate are ascribed to ion association and a theoretical treatment is developed.

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[12] An attempt to calculate a dissociation constant for the phthalate–cation complex from the solubility data, by assuming that sodium and thallous ions were equally bound, and allowing for changes in μ with successive approximations, gave values for the degree of association much higher than permitted by existing conductivity data. One is led to the conclusion that thallous ion enters into complex formation more readily than sodium ion.