[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

The Solubility of Thallous Iodate in Solutions of Sodium Mellitate[1]

BY CRAWFORD F. FAILEY

The modern conception of protein salts as polyvalent ions and recent studies on immunologically specific polysaccharides of high valence[2] lend increased interest to simpler ions of definitely known structure bearing several charges. Mellitic acid, $C_6(COOH)_6$, was chosen as a suitable substance of this type.

Preparation.—The acid was prepared by oxidizing hexamethylbenzene with potassium permanganate in the cold, according to Friedel and Crafts.[3] The lead salt was precipitated, decomposed with hydrogen sulfide, and the crude acid twice recrystallized from nitric acid diluted with one-fifth part of water. Calcd. for $C_{12}H_6O_{12}$: C, 42.10; H, 1.77. Found: C, 42.28; H, 2.02. The neutralization to phenolphthalein of 0.1056 g. of acid required 18.42 ml. of 0.0999 *N* sodium hydroxide, the end-point being very poor owing to hydrolysis. Equivalent weight calcd. 57.0; found, 57.4.

Titration Curve.—In view of the buffering shown at a comparatively high *P*H it was considered worth while to investigate electrometrically the dissociation of this polyvalent acid. Table I and Fig. 1 show the *P*H of 0.02 normal solution of mellitic acid to which varying amounts of sodium hydroxide have been added. Each solution was made up to volume separately and its *P*H determined by means of a Clark rocking electrode in an air-bath at 25°. As considerable poisoning of the electrodes occurred and it was necessary to replate them frequently, the results were checked with a quinhydrone electrode. One-tenth normal hydrochloric acid was the reference standard, its *P*H being assumed to be 1.08.

TABLE I

TITRATION OF MELLITIC ACID AGAINST SODIUM HYDROXIDE

MELLITIC ACID 1.140 G. PER LITER = 0.02 *N*

Equivalents of base	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.05
*P*H	2.29	2.36	2.43	2.52	2.62	2.74	2.89	3.07	3.35	3.66	4.03	4.37	4.75	5.12	5.43	5.79	6.12	6.41	6.73	7.17	8.44	10.89

The acid buffers uniformly from *P*H 3 to *P*H 7, and the shape of the curve is similar to that typical of a protein.

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(1) This work was aided by a grant from The Chemical Foundation.

(2) Heidelberger and Kendall, *J. Biol. Chem.*, **95**, 127 (1932).

(3) Friedel and Crafts, *Ann. chim. phys.*, [6] **1**, 449 (1884).

Solubility Measurements.—The preparation of thallous iodate and the method of analysis were those of La Mer and Goldman.[4] A stock solution of sodium mellitate was prepared by adding an equivalent amount of sodium hydroxide from sodium to 0.025 mole of the acid and making up to 0.5 liter. Solvents were rotated with the solid phase in a water-bath at 25.00 ± 0.01°.

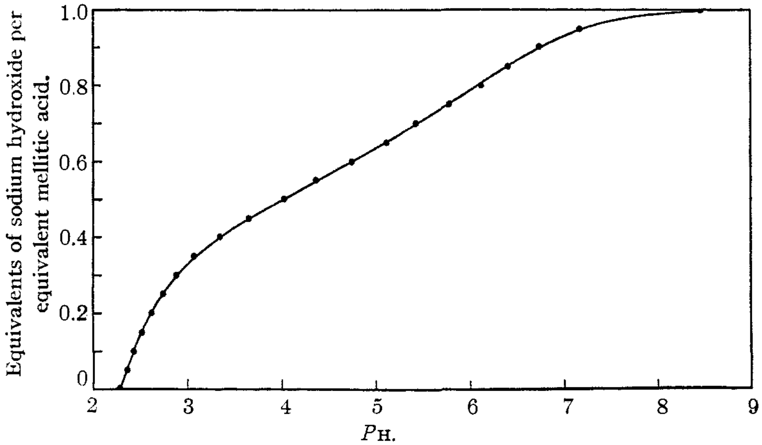

Fig. 1.

TABLE II

SOLUBILITY OF THALLOUS IODATE IN SODIUM MELLITATE, SODIUM CHLORIDE AND IN SODIUM HYDROXIDE SOLUTIONS

$$-\log \gamma_0 = 0.505\sqrt{0.001843} = 0.0217$$

$$-\log \gamma_{\pm} = 0.0217 + \log S/S_0$$

Molarity of solvent salt	Soly. × 10^6	$-\log \gamma_{\pm}$	Molarity of solvent salt	Soly. × 10^6	$-\log \gamma_{\pm}$
	H_2O				
	1843	0.0217			
				NaCl	
	$C_{12}O_{12}Na_6$				
0.0001	1967	0.0491	0.02	2118	0.0821
.0002	2092	.0768	.04	2277	.1136
.0005	2426	.1412	.10	2629	.1760
.001	2901	.2188		NaOH	
.002	3636	.3168	.01	2003	.0579
.005	4980	.4534			
.01	6184	.5475			

From Table II and Fig. 2 is evident the marked increase in the solubility of thallous iodate brought about by sodium mellitate, whose contribution to the ionic strength is $(6 + 6^2)/2$ or twenty-one times its molarity. The values of $-\log \gamma_{\pm}$ fall considerably above the theoretical limiting tangent and do not approach it asymptotically at the highest dilutions which could

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[4] La Mer and Goldman, THIS JOURNAL, **51**, 2632 (1929).

be reached. This great effect on $\gamma_{\pm}$ is not related to the slight alkalinity of the solutions for the solubility in hundredth normal sodium hydroxide, namely, 2003×10^{-6}, is approximately the same as in any other uni-univalent electrolyte.

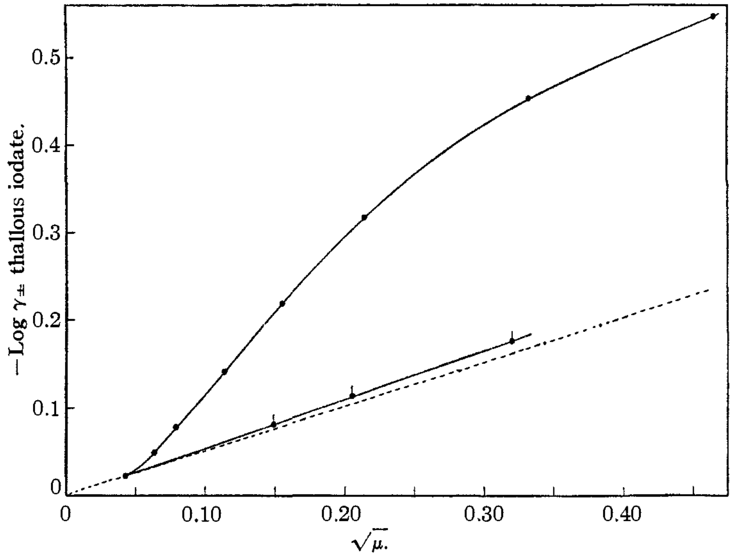

Fig. 2.—●, Sodium mellitate; ●, sodium chloride. The broken line is the Debye limiting tangent.

The unexpectedly high solubility of thallous iodate in solutions of sodium mellitate suggested that addition of a third salt, by modifying the electrical fields around the hexavalent ions, might cause a diminution in solubility instead of the increase to be expected as a result of the increased ionic strength.

TABLE III

SOLUBILITY OF THALLOUS IODATE IN $M/1000$ SODIUM MELLITATE TO WHICH VARYING AMOUNTS OF A THIRD SALT HAVE BEEN ADDED

$$-\log \gamma_{\pm} = 0.0217 + \log S/S_0$$

Molarity third salt	Soly. $\times 10^6$	$-\log \gamma_{\pm}$	Molarity third salt	Soly. $\times 10^6$	$-\log \gamma_{\pm}$
0	2901	0.2188			
	$NaNO_3$			$MgCl_2$	
0.004	2844	0.2101	0.000408	2732	0.1927
.012	2786	.2012	.00102	2520	.1576
.020	2762	.1978	.00204	2319	.1215
.028	2750	.1955	.00612	2243	.1070
.040	2746	.1949	.01020	2295	.1170
.060	2768	.1984	.02040	2460	.1471
.080	2802	.2037	.04080	2731	.1925

TABLE III (*Concluded*)

Molarity third salt	Soly. × 10^6	$-\log \gamma_{\pm}$	Molarity third salt	Soly. × 10^6	$-\log \gamma_{\pm}$
	NaCl			$MgSO_4$	
0.004	2850	0.2110	0.000420	2738	0.1936
.020	2781	.2004	.001050	2538	.1607
.028	2781	.2004	.00210	2373	.1315
.040	2797	.2029	.00420	2306	.1191
.060	2843	.2100	.0105	2360	.1291
.100	2967	.2285	.0210	2505	.1550
	Na_2SO_4		.0420	2696	.1869
.004248	2858	0.2123			
.01062	2872	.2144			
.02124	2894	.2177			

SOLUBILITY OF THALLOUS IODATE IN $M/200$ SODIUM MELLITATE TO WHICH VARYING AMOUNTS OF SODIUM NITRATE HAVE BEEN ADDED

Molarity of $NaNO_3$	Soly. × 10^6	$-\log \gamma_{\pm}$
0	4980	0.4534
0.05	4210	.3805
.10	4004	.3587
.20	3936	.3513
.50	4352	.3949

Whatever the cause, on adding small amounts of other electrolytes to moderately dilute sodium mellitate solutions, the mellitate concentration being held constant, there is observed a lessened solubility of thallous

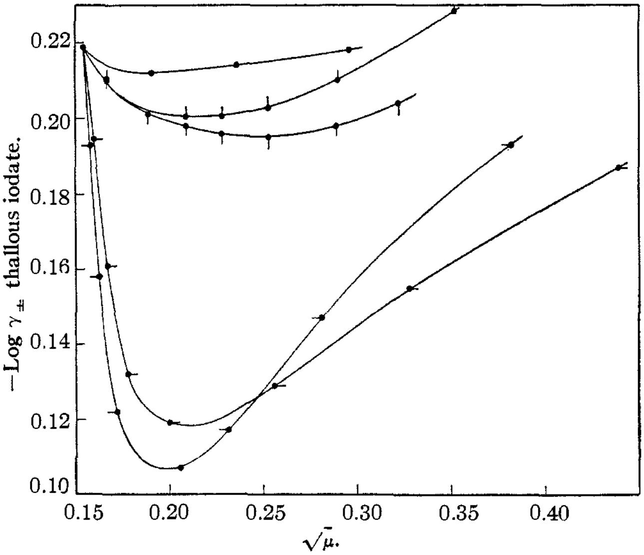

Fig. 3.—Activity coefficients of thallous iodate in $M/1000$ sodium mellitate to which varying amounts of other salts have been added: ●, Na_2SO_4; ●, NaCl; ●, $NaNO_3$; ●-, $MgSO_4$; -●, $MgCl_2$.

iodate, corresponding to an increase in its mean activity coefficient. The solubility continues to decrease on further addition of salt until it reaches a minimum when the ionic strength has been about doubled or tripled, after which it again increases. That the explanation of these effects is to be sought in the high fields of the mellitate ions is made more probable by consideration of results with divalent ions. While magnesium chloride and sulfate have a much greater influence than the corresponding sodium salts, the chlorides and sulfates of a given base have nearly equal action.

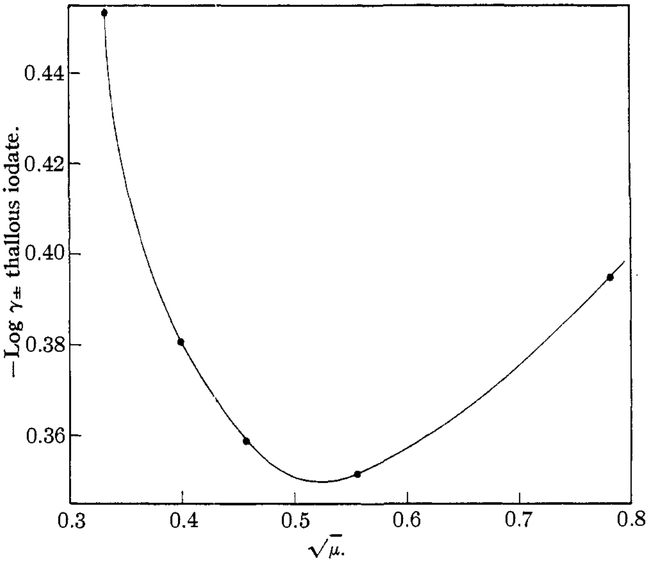

Fig. 4.—Activity coefficient of thallous iodate in $M/200$ sodium mellitate to which varying amounts of sodium nitrate have been added.

The phenomenon of an activity coefficient first increasing and then decreasing on the addition of electrolyte to a moderately dilute solution disagrees not only quantitatively but also qualitatively with predictions from the principle of the ionic strength and from the theory of Debye, and has not, so far as the author is aware, been observed before. One may hazard the suggestion that the great decrease in the mean activity coefficient is due principally to changes in the free energy of the positive thallium ion.

Summary

Mellitic acid has been titrated with alkali and the *P*H changes measured. The solubility of thallous iodate has been determined in the presence of sodium mellitate both with and without the addition of a third salt and certain anomalous solvent effects observed.

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