

acetic acid. The shortened induction period, which is characteristic of titanium dioxide-pigmented drying oils containing metal-ortho-phen-

anthroline complex driers can be attributed to this reduction in the adsorption tendency.

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[CONTRIBUTION FROM THE HAYDEN MEMORIAL LABORATORIES OF NORTHEASTERN UNIVERSITY]

## The Solubility Effect in Solvents of Low Dielectric Constant. II. A Study of the Solubility Effect in Benzene<sup>1</sup>

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### I. Introduction

In continuation of the work of Vernon, Luder and Giella<sup>3</sup> this paper reports the results of further solubility measurements of quaternary ammonium salts in benzene. In addition to the literature references cited in the earlier paper by these authors it should be noted that Partington<sup>4</sup> and co-workers have reported results using alcohols as solvent. Also Geer<sup>5</sup> studied some solubility effects in acetic acid, Gross, Kuzmany and Wald<sup>6</sup> in ethyl alcohol and Anhorn and Hunt<sup>7</sup> in liquid ammonia.

### II. Experimental

**Materials.**—C. p. thiophene-free benzene, after standing for several days over anhydrous calcium chloride, was distilled from anhydrous aluminum oxide, the first and last fifth portions being discarded. It was collected and stored in five-pint, ground glass stoppered bottles.

Tetraisoamylammonium iodide was prepared by heating an equimolar mixture of Eastman Kodak Co. tri-isoamylamine and isoamyl iodide to 70° in a constant temperature oven. The crude yield was washed with petroleum ether and dissolved in hot ethyl acetate and treated while hot with alcoholic potassium hydroxide until pink to phenolphthalein. On decanting and cooling in an ice-bath, amine free iodide crystals separated out. The final leafy product was obtained after several recrystallizations from ethyl acetate (m. p. 146.5°).

Tetraamylammonium iodide was prepared similarly except that the crude yield was dissolved in 95% ethyl alcohol before treatment with potassium hydroxide. The iodide was precipitated in water and recrystallized from ethyl acetate (m. p. 134°).

The corresponding picrates were prepared by the method of Cox, Kraus and Fuoss<sup>8</sup> except that the recrystallizations were from 95% ethyl alcohol. They were tetraisoamyl-

ammonium picrate (m. p. 86°) and tetraamylammonium picrate (m. p. 73°).

Tributylammonium picrate was prepared by the method of Mead, Fuoss and Kraus.<sup>9</sup>

**Procedure.**—The method was essentially the same as described by Vernon, Luder and Giella<sup>3</sup> with the modifications that only 600 cc. of benzene was used and a water solution of silver nitrate was substituted for the alcoholic solution. It was found that using alcoholic silver nitrate, the iodide was precipitated colloiddally and on aging it settled and adhered to the bottom of the beakers. Transfer of this type of solid to a Gooch crucible was very difficult and relatively inaccurate.

On using a water solution of silver nitrate, however, the precipitated silver iodide came down immediately in flocculent form and on standing settled out at the interface of the benzene and water layers. In this form it was readily transferred to a Gooch crucible since it rode along with the interface and any small particles that adhered to the beaker wall were easily transferred using a rubber policeman and a wash bottle stream. The reproducibility of results was very good, often being within one part in five hundred. Analysis of a known weight of quaternary iodide showed this technique subject to about one per cent. error. The Gooch crucible containing the transferred silver iodide was dried for twenty-four hours over phosphorus pentoxide in a desiccator to consistent weight.

**Results.**—The results of the determinations are recorded in Tables I and II. All concentrations are in moles per liter and are the averages of duplicate measurements. Since these data are of most value when combined with

TABLE I

SOLUBILITY OF TETRAISOAMYLAMMONIUM IODIDE IN THE PRESENCE OF EITHER (a) TETRAISOAMYLAMMONIUM PICRATE OR (b) TRIBUTYLAMMONIUM PICRATE IN BENZENE AT 25°

Concn. of (a) × 10 <sup>4</sup>	Solubility of iodide × 10 <sup>4</sup>	Concn. of (b) × 10 <sup>4</sup>	Solubility of iodide × 10 <sup>4</sup>
0.00	1.13	0.00	1.13
1.28	1.32		
2.53	1.48	3.48	3.28
5.06	1.94	6.95	4.74
10.13	2.95		
15.00	3.97	13.90	7.30
20.00	5.19		
25.33	6.89	27.78	11.24

(1) Condensed from a thesis presented by John P. Masterson to the faculty of Northeastern University in partial fulfillment of the requirements for the degree of M.S. in chemistry.

(2) Present address: Fremont, Nebraska.

(3) Vernon, Luder and Giella, *THIS JOURNAL*, **63**, 862 (1941).

(4) King and Partington, *Trans. Faraday Soc.*, **23**, 522 (1927); Hawkins and Partington, *ibid.*, **24**, 518 (1928); Partington and Winterton, *ibid.*, **30**, 619 (1934).

(5) Geer, Thesis, University of Kansas, 1935.

(6) Gross, Kuzmany and Wald, *THIS JOURNAL*, **59**, 2692 (1937).

(7) Anhorn and Hunt, *J. Phys. Chem.*, **45**, 351 (1941).

(8) Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

(9) Mead, Fuoss and Kraus, *THIS JOURNAL*, **61**, 3257 (1939).

TABLE II

SOLUBILITY OF TETRAAMYLAMMONIUM IODIDE IN THE PRESENCE OF EITHER (a) TETRAAMYLAMMONIUM PICRATE OR (b) TRIBUTYLAMMONIUM PICRATE IN BENZENE AT 25°

Concn. of (a) $\times 10^4$	Solubility of iodide $\times 10^4$	Concn. of (b) $\times 10^4$	Solubility of iodide $\times 10^4$
0.00	0.539	0.00	0.539
1.00	0.583	1.00	1.07
5.00	0.992	3.00	2.04
10.00	1.43	10.00	3.85
20.00	2.50	30.00	7.39
		50.00	10.65

previous results, they are plotted in Fig. 1 with the curves previously obtained by Vernon, Luder and Giella.<sup>3</sup>

### III. Discussion

A usual treatment of solubility data is to compare the curve of variation of activity coefficient *versus* the square root of salt concentration with that predicted by the Gronwall, LaMer and Sandved equations using arbitrary values of "ionic diameters." If the experimental and theoretical curves can be made to agree closely by assigning "reasonable" values to the "ionic diameter" then the theoretical equation is considered applicable in the region investigated.

To apply such calculations to the solutions investigated in benzene is fruitless. In such a low dielectric solvent, conductivity and freezing point measurements indicate that association becomes very manifest and the electrolytes behave as if incompletely dissociated. Obviously the value of an "ionic diameter" of a supposed single ion would have little meaning under such conditions.

An approach such as that of Gronwall, Sandved and LaMer might be possible if there were some means of calculating the number of charged ion aggregates in the solution. At present this is not the case.

The increase in solubility in every case on the

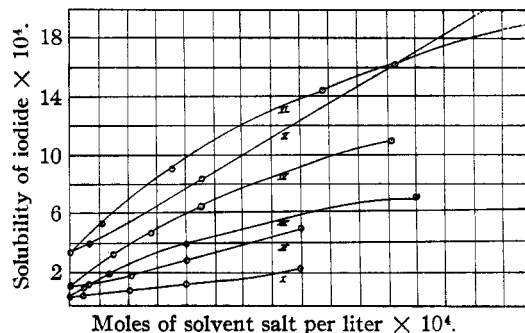


Fig. 1.—I,  $(\text{Am})_4\text{NI}$  in presence of  $(\text{Am})_4\text{N}$  picrate; II,  $(\text{Isoamyl})_4\text{NI}$  in presence of  $(\text{isoamyl})_4\text{N}$  picrate; III,  $(\text{Am})_4\text{NI}$  in presence of  $(\text{Bu})_3\text{HN}$  picrate; IV,  $(\text{Isoamyl})_4\text{NI}$  in presence of  $(\text{Bu})_3\text{HN}$  picrate; V,  $(\text{Bu})_4\text{NI}$  in presence of  $(\text{Bu})_4\text{N}$  picrate; VII,  $(\text{Bu})_4\text{NI}$  in presence of  $(\text{Bu})_4\text{N-NO}_2$ .

addition of an electrolyte whether with or without a common ion seems to be further proof of other than single ion phenomena. If the predominant effect were that of single ions we should expect a decrease in solubility on adding a common ion. The fact that the tri salt gives a greater solubility increase than the tetra-salt with tetraisoamylammonium iodide may be due to a greater inter-ionic attraction.

### IV. Summary

1. The solubility of tetraisoamylammonium iodide in benzene solutions of tetraisoamylammonium picrate and tributylammonium picrate was determined.

2. The solubility of tetraamylammonium iodide in benzene solutions of tetraamylammonium picrate and tributylammonium picrate was determined.

3. An increase in solubility of the saturating salt was found in both cases and the relation of this to multiple ion phenomena is indicated.

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