

[CONTRIBUTION OF THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Adsorption of Simple and Complex Cobalt Ions on Titanium Dioxide

BY DOUGLAS G. NICHOLSON¹

It is a well-known fact that the addition of small amounts of certain metallic soaps to drying oils accelerates the rate of gelation of these substances. A recent report² has indicated that pigmented drying oil films containing drier metal ions coördinated with ortho-phenanthroline tend to absorb oxygen more rapidly and at a more uniform rate than did similarly pigmented films containing uncoördinated metal ions. In this respect the films pigmented with titanium dioxide showed the greatest differences, while those containing zinc oxide or zinc sulfide exhibited slight differences.

Authorities in the drying field agree on the fact that cobalt ions are adsorbed on the surface of titanium dioxide particles suspended in a drying oil. This adsorption has been thought to be a rather slow process involving rather long periods of time. A recent study³ has indicated that the

adsorption of a monomolecular film of cobalt ions on the surface of the titanium dioxide particles would account for the loss in catalytic drying properties of such materials.

In an effort to show that these ion adsorptions progress to a considerable extent in the early stages of the aging of suspensions of titanium dioxide and cobalt materials, as well as to account for the reported rapid oxygen absorption of drying oils containing coördinated cobalt ortho-phenanthroline materials and titanium dioxide, a conductometric study of the subject was undertaken. As the work progressed, it was decided that spectrophotometric data obtained from the experimental solutions would also yield interesting related data.

Conductometric Measurements.—To 10 ml. of conductivity water in a Freas type conductivity cell maintained in a thermostat at $25 \pm 0.1^\circ$, ten successive additions of 0.1 ml. of 0.002 *M* solutions of cobaltous acetate were made. The cell was shaken after each addition and allowed to come to the temperature of the thermostat. This experiment was then repeated except that instead of the cobaltous acetate, an equivalent solution of cobaltous ortho-phenanthroline acetate was added.

This pair of experiments was then repeated, except that in each experiment 5 g. of commercial, rutile type, titanium dioxide was first added to the conductivity water.

Another pair of similar experiments was carried out identical to the above except that the conductivity water was replaced in the first by glacial acetic acid, and in the second by glacial acetic acid 0.0005 *M* in cobaltous acetate. Small, but accurately measured, quantities of solid ortho-phenanthroline were added to each of these solutions and the resistance of the cell determined after each.

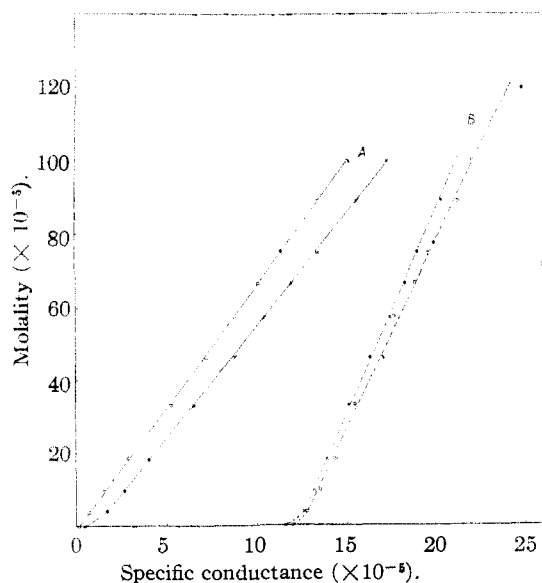


Fig. 1.—Graphical representation of conductometric data obtained by the addition of cobalt acetate and cobalt *o*-phenanthroline acetate to (A) conductivity water and (B) conductivity water containing a known quantity of commercial rutile type titanium dioxide: \circ — \circ , $\text{Co}(\text{o-A})_2\text{Ac}_2$; \times — \times , CoAc_2 ; \circ — \circ , $\text{Co}(\text{o-A})_2\text{Ac}_2 + \text{TiO}_2$; \times — \times , $\text{CoAc}_2 + \text{TiO}_2$.

(1) Present address: Chemical Warfare School, United States Army, Edgewood Arsenal, Md.

(2) Douglas G. Nicholson, paper presented before The Paint and Varnish Group of The American Chemical Society, 103rd meeting, Memphis, Tenn., April, 1942.

(3) *Am. Paint J.*, 26, 4-B, October, 29, 1941.

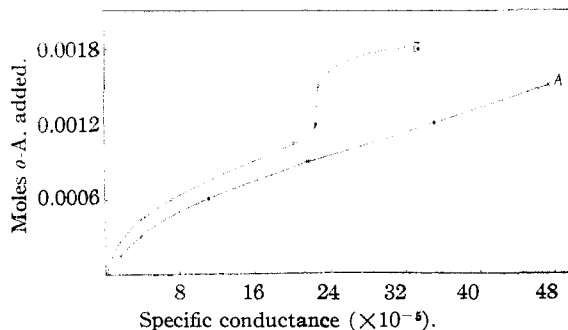


Fig. 2.—Graphical representation of conductance data obtained from the addition of *o*-phenanthroline to (A) glacial acetic acid and (B) to a 0.0005 *M* solution of cobalt acetate in glacial acetic acid: \circ — \circ , HAc + 10 cc. of 0.05 *M* CoAc_2 ; \times — \times , HAc.

The results of these experiments are shown in graphical form in Figs. 1 and 2.

Spectrophotometric Measurements.—Samples of cobaltous acetate and of cobaltous ortho-phenanthroline acetate, 0.025 *M* in cobalt ion, were prepared and spectrophotographic transmittancy curves obtained for each by means of a General Electric Recording Spectrophotometer. Additional portions of each of these solutions were shaken with commercial, rutile type, titanium dioxide and after allowing approximately twelve hours of standing and filtering off the pigment, transmittancy curves were again obtained from the resulting solutions.

These data appear in graphical form in Figs. 3 and 4.

Discussion.—Figure 1 shows that the solutions containing the coordinated cobalt ions are poorer conductors than are uncoordinated solutions of equal ion concentration. When titanium dioxide is present in the solution, the reverse effect is true. Thus it appears that the loss of conductivity of the uncoordinated ions may be due to adsorption of some on the surface of the pigment particles. The presence of the large coordinating molecules surrounding the cobalt ions, apparently reduces the tendency for this adsorption, with the result that the coordinated ions are better conductors when the pigment is present.

Figure 2 shows quite conclusively that cobalt acetate does form a coordination compound with ortho-phenanthroline in glacial acetic acid. The break in the curve occurs at approximately three molecules of the coordination agent per ion of cobalt. The data appearing in this graph also indicate that ortho-phenanthroline also reacts with the glacial acetic acid, with the probable formation of ortho-phenanthroline acetate.

Figures 3 and 4 show, respectively, the transmissivity curves obtained from the uncoordinated and the coordinated cobalt acetate-glacial acetic acid solutions, before and after the suspension of titanium dioxide pigment. It is to be noted (Fig. 3) that there is an increased transmissivity after the titanium dioxide contact with the solution. This tends to indicate that some of the coloring material (cobalt ions) had been removed by the treatment. This point supports the adsorption idea. In Figure 4, there is actually a slight loss of transmissivity after the contact with the titanium dioxide. No explanation is offered to justify this anomalous behavior. However, there is little doubt regarding the fact that the pigment reacts differently toward the simple and the coordinated cobalt ions of equal concentration. These spectrophotometric data support the in-

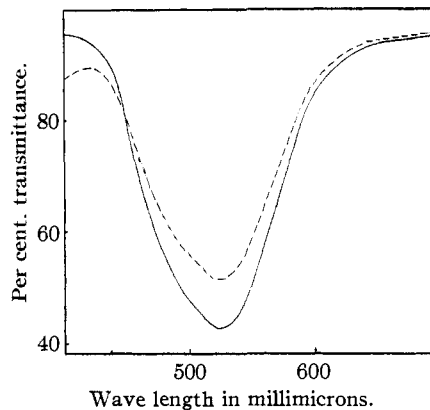


Fig. 3.—Spectrophotometric transmittancy curves obtained from 0.025 *M* cobalt acetate dissolved in glacial acetic acid: (a) solid line is control material; (b) dotted line is same material after having titanium dioxide suspended and filtered.

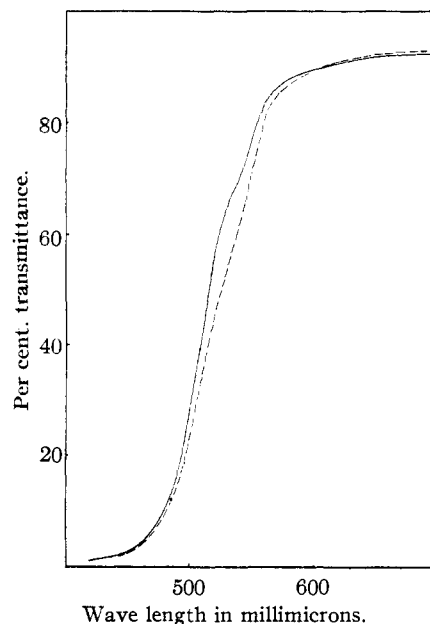


Fig. 4.—Spectrophotometric curves obtained from 0.025 *M* cobalt *o*-phenanthroline acetate dissolved in glacial acetic acid: (a) solid line is control solution; (b) dotted line is same solution after exposure to titanium dioxide.

formation obtained from the conductometric portion of this work.

Summary

Titanium dioxide suspended in water or glacial acetic acid solutions of cobalt acetate adsorbs cobalt ions in a relatively short time.

Coordination of cobalt ions with ortho-phenanthroline materially reduces this adsorption tendency. Ortho-phenanthroline forms a coordination compound with cobalt acetate in glacial

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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The Solubility Effect in Solvents of Low Dielectric Constant. II. A Study of the Solubility Effect in Benzene¹

BY ARTHUR A. VERNON AND JOHN P. MASTERSON²

I. Introduction

In continuation of the work of Vernon, Luder and Giella³ 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 Partington⁴ and co-workers have reported results using alcohols as solvent. Also Geer⁵ studied some solubility effects in acetic acid, Gross, Kuzmany and Wald⁶ in ethyl alcohol and Anhorn and Hunt⁷ 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 Fuoss⁸ 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.⁹

Procedure.—The method was essentially the same as described by Vernon, Luder and Giella³ 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 ⁴	Solubility of iodide × 10 ⁴	Concn. of (b) × 10 ⁴	Solubility of iodide × 10 ⁴
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).