Table IV displays the results obtained. The experiments were performed by mixing the reagents in aqueous solutions in a separatory funnel containing 50 ml. of carbon tetrachloride, shaking vigorously immediately after mixing, and then separating the two phases. The manganese(III) (and higher oxidation states if they be present in these nonequilibrium solutions) and free chlorine concentrations were determined iodometrically; a distribution coefficient of 15 for chlorine between the organic and aqueous phases was used.

TABLE IV

REACTION OF PERMANGANATE WITH MANGANESE (II) AND HYDROCHLORIC ACID AT 25°

$[\mathrm{MnO_4^-}]^a$ $\times 10^3$, moles/liter	$[\mathrm{Mn^{++}}]^a/[\mathrm{MnO_4^-}]$	$[\mathrm{HCl}]^a$ moles/liter	Vol. aq. phase, ml.	Equiv. $\mathrm{Cl_2}$ / Equiv. $\mathrm{Mn^{III}}$ B[b]	C[b]
9.9	5.1	5.0	20	0.65	0.64
9.4	10.1	5.2	21	.39	.28
10.0	8.0	6.0	50	1.0	
4.0	0	8.0	15		3.0
3.0	9.8	8.5	20	1.6	1.7
2.1	14.7	8.9	19	1.7	1.3

[a] Calculated initial concentrations after mixing, but before reaction. [b] Procedure B, 0.02 *F* $\mathrm{MnO_4^-}$ soln. added through the $\mathrm{CCl_4}$ phase to the $\mathrm{Mn^{++}}$ in HCl soln.; procedure C, $\mathrm{Mn^{++}}$ in HCl added through the $\mathrm{CCl_4}$ phase to the 0.02 *F* $\mathrm{MnO_4^-}$ soln.

The results in Table IV indicate that the ratio of equivalents of free chlorine to equivalents of manganese(III) produced depends on the manganese(II)–permanganate ratio, on the acid concentration, and to some extent on the order of mixing. The result in 6 *F* acid is the same as that reported by Bobtelsky and Cohen[16] in acid of this concentration with somewhat different manganese concentrations. As expected, a high ratio of chlorine to manganese(III) is obtained when permanganate is added to hydrochloric acid alone. Probably the results of experiments like these are dependent on several variables (rates of mixing, absolute concentrations, etc.) not investigated by us. We are offering the data of Table IV merely to indicate the order of magnitude of the results and to indicate that a one-to-one ratio of free chlorine to manganese(III) is not generally obtained.

Acknowledgments.—We are indebted to the Office of Naval Research for support of this work and to Professor Dan H. Campbell for many kindnesses in connection with the use of the spectrophotometer.

Summary

The equilibrium optical density, due to a higher manganese chloride, of a solution of manganese(II) in concentrated hydrochloric acid oxidized by chlorine obeys the relation $D = K\epsilon[\mathrm{Mn^{++}}]\cdot[\mathrm{Cl_2}]^{1/2}$, implying that the colored species is a chloro-complex of manganese(III) formed by the reaction $\mathrm{Mn^{++}} + {}^1/_2\mathrm{Cl_2} = \mathrm{Mn^{III}} + \mathrm{Cl^-}$. The extinction coefficients of manganese(III) were measured, and the equilibrium constant, $K = [\mathrm{Mn^{III}}]/[\mathrm{Mn^{++}}][\mathrm{Cl_2}]^{1/2}$ (liter/moles),$^{1/2}$ in 10.1 *F* hydrochloric acid was evaluated as 0.19 (25°) and 0.33 (0°).

There is no optical interaction absorption in mixed solutions of manganese(II) and (III). Spectrophotometric evidence for the formation of chloro-complexes of manganese(II) is presented. The ratio of the amount of tripositive manganese to the amount of chlorine formed by the reaction of permanganate with a manganese(II) solution in hydrochloric acid has been investigated.

PASADENA, CALIFORNIA

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The Properties of Benzhydrol in Sulfuric Acid Solution

BY CLARK M. WELCH AND HILTON A. SMITH

When triphenylcarbinol is dissolved in sulfuric acid it ionizes according to the equation

$$(\mathrm{C_6H_5})_3\mathrm{COH} + 2\mathrm{H_2SO_4} \longrightarrow (\mathrm{C_6H_5})_3\mathrm{C^+} + \mathrm{H_3O^+} + 2\mathrm{HSO_4^-}$$

This ionization is demonstrated by the light absorption of the solution,[1] by the molar freezing point depression which is four times that caused by a non-ionized solute,[2] and by the reaction of the carbonium ions in the sulfuric acid solution with alcohols to form ethers.[3]

These characteristics naturally led to interest in the behavior of benzhydrol (diphenylcarbinol) when dissolved in sulfuric acid. The solutions are reddish-brown in color, indicating the presence of carbonium ions. Fuson and Jackson[4] reported that when such a solution was poured into cold methanol, and treated in the usual manner, no benzhydryl methyl ether was found, but two unidentified products were obtained. One of these was a liquid boiling at 178–182° (16 mm.), while the other was a hard resin at ordinary temperatures. The combined weight of these fractions was less than 50% of the weight of benzhydrol used. These same workers found that when dimesitylcarbinol was dissolved in sulfuric acid, a deep red solution resulted, and that essentially quantitative yields of dimesityl-

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[1] A. Hantzsch, *Ber.*, **54**, 2573 (1921).

[2] A. Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908); L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **55**, 1900 (1933).

[3] H. A. Smith and R. J. Smith, *ibid.*, **70**, 2400 (1948).

[4] R. C. Fuson and H. L. Jackson, *ibid.*, **72**, 351 (1950).

methyl ether could be obtained by the procedure of Smith and Smith.[3]

In the research reported here, it was found that the deep red-brown solutions containing 0.2–0.4 g. of benzhydrol in 100 g. of sulfuric acid gave "*i*" factors of 4.6–5.2 thirty minutes after the solid had been added. A rapid drift in the freezing point indicated that reactions were taking place. After twenty-four hours the "*i*" factors became constant at values ranging from 5.0–6.1 for various samples. When these solutions were poured into water, they were instantly decolorized. Extraction with ether yielded only a small fraction of the original weight of benzhydrol. These results indicate the probability of sulfonation of the carbonium ion, for this could easily result in "*i*" factors as great as six, and the product from reaction with water would not be extractable with ether.

It was noted that when the proportion of benzhydrol to sulfuric acid was as great as 1:10 by weight, no recognizable compounds could be separated from the amorphous ether-soluble fraction. This is in agreement with the findings of Fuson and Jackson[4] who used the reactants in a 1:7.5 ratio.

When solid benzhydrol was added to sulfuric acid, solution was achieved very slowly. During the solution period sulfonation occurred to a considerable extent. When the benzhydrol was first dissolved in the inert solvent carbon tetrachloride, and subsequently extracted by stirring with sulfuric acid, the benzhydrol was quickly brought into solution. When this clear red solution was poured into water, or methanol and then water, fairly good yields of dibenzhydryl ether and benzhydryl methyl ether, respectively, were obtained. The instantaneous nature of the reactions make it appear reasonably certain that benzhydryl carbonium ions were present in solution.

It was also noted that benzhydryl acetate could be obtained when a solution of benzhydrol in sulfuric acid was poured into glacial acetic acid and subsequently into water.

Work on similar compounds is in progress.

Experimental

Freezing Point Studies.—The freezing point apparatus was similar to that previously described.[5] It was equipped with a stirrer which passed through a glass sleeve fitted with a collar of Tygon tubing. The collar and the ground glass joint on the Beckmann thermometer were lubricated with Silicone grease.

The sulfuric acid solvent had a freezing point of 10.2°, the freezing point of the pure acid having been depressed 0.3° by addition of 96% sulfuric acid. The apparatus was checked for moisture leaks by allowing it to stand for more than 300 hours. The total freezing point lowering over this period of time was 0.011°. Freezing points were taken by supercooling the acid not more than 1.5°, and then inducing crystallization by touching the side of the tube with a piece of solid carbon dioxide. Successive freezing points on the acid usually agreed within 0.003°, and no drift in the readings was apparent.

The solute (0.1–0.2 g.) was added from an L-shaped vial to a weighed amount (usually 55 g.) of sulfuric acid. This gave a freezing point depression of 0.4–0.6°. Check measurements on triphenylcarbinol gave "*i*" factors of 3.97, 4.00 and 3.89, using 6.15° for the molal freezing point depression of sulfuric acid.

Eastman Kodak Co. benzhydrol was recrystallized from ligroin; m. p., 66.0–67.2°.

Chemical Studies

Addition of Solid Benzhydrol to 100% Sulfuric Acid.—A 0.5 g. quantity of benzhydrol was added to 50 g. of the stirred acid. After ten minutes, solution was almost complete and the red-brown liquid was poured into 250 g. of ice-water mixture. The color was discharged immediately. The water solution was extracted with two 150-ml. portions of ether. On evaporation, the ether extract yielded 0.12 g. of residue, which indicates that most of the benzhydrol had undergone sulfonation.

Preparation of Benzhydryl Carbonium Ion Solution.—A solution of 0.5 g. of benzhydrol in 10 ml. of carbon tetrachloride was stirred into 50 g. of 100% sulfuric acid. The lower acid layer was deep red, while the upper layer remained colorless. The mixture was stirred for five minutes, then was used immediately.

Reaction of the Benzhydryl Carbonium Ion Solution with Water.—The red acid solution (together with the carbon tetrachloride) was poured into 250 g. of water. The colorless, cloudy liquid was extracted with two 50-ml. portions of ether. The combined extracts were dried over potassium hydroxide pellets, filtered, and evaporated to dryness. The 0.39 g. of yellow sirup remaining was dissolved in hot methanol, concentrated to 3 ml. and cooled to effect crystallization. The resulting slightly yellow dibenzhydryl ether melted at 106.5–107.8°; the yield was 0.32 g. (67%). Decolorization and further recrystallization from methanol raised the melting point to 109.1–109.5° (cor.). An authentic sample prepared by the method of Ward[6] melted at 109.1–109.6°. The mixed melting point of the two samples was 109.1–109.6°.

Reaction of the Benzhydryl Carbonium Ion Solution with Methanol.—The carbonium ion solution was stirred into 150 ml. of methanol. The resulting colorless solution was immediately poured into 250 g. of ice-water mixture, and the latter extracted as quickly as possible with two 150-ml. portions of ether. The combined ether extracts were shaken with aqueous potassium carbonate, dried and the ether evaporated. One ml. of petroleum ether was added to the liquid residue, and the solution chilled in a methanol–solid carbon dioxide bath to effect crystallization. The petroleum ether was removed by suction as the solution temperature was gradually raised, and the crystals then melted at 16.0–19.0°. The yield was 0.36 g. (67% calculated as benzhydryl methyl ether). The product was recrystallized several times from petroleum ether, methanol and ether. The melting point of the purified material was 19.3–20.4°; n^{27}_{D} 1.6632. An authentic sample of benzhydryl methyl ether prepared by the method of von Kostanecki and Lampe[7] had the following physical constants: b. p. 153.2–153.5° (14.5 mm.)[8]; m. p. 20.4–21.3°; n^{27}_{D} 1.6637. The two compounds were shown to be identical by mixed melting points (19.0–20.3°).

This procedure was repeated a second time, the only difference being the use of 10 ml. of petroleum ether in the crystallization process. Here a small amount of polymeric material insoluble in the petroleum ether was precipitated. After removal of this solid, the yield of product was 0.27 g. (51%, m. p. 16–19°).

A 50-g. quantity of 100% sulfuric acid was dissolved in 150 ml. of methanol and the solution cooled to 25°. To

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[5] L. P. Hammett and A. J. Deyrup, ref. 2; H. P. Treffers and L. P. Hammett, *ibid.*, **59**, 1708 (1937).

[6] A. M. Ward, *J. Chem. Soc.*, 2291 (1927).

[7] St. von Kostanecki and V. Lampe, *Ber.*, **39**, 4019 (1906).

[8] *Cf.*, G. Wittig and W. Happe, *Ann.*, **557**, 205 (1947); E. Bergmann and J. Hervey, *Ber.*, **62**, 915 (1929).

this was added 0.50 g. of benzhydrol dissolved in 10 ml. of carbon tetrachloride. As soon as the stirred mixture became homogeneous it was poured into 250 g. of ice–water mixture. The solution was extracted with ether, the extract dried, filtered, and the benzhydrol, 0.47 g. (93% of the original weight) melting at 60–65°, was recovered.

When the benzhydryl carbonium ion solution was added to methanol under such conditions that the temperature of the mixture was kept below 25°, no benzhydrol could be recovered from the reaction mixture. These experiments show that the reaction to form methyl benzhydryl ether was not a simple acid-catalyzed etherification.

Reaction of Benzhydryl Carbonium Ion Solution with Glacial Acetic Acid.—The carbonium ion solution was poured into 150 ml. of stirred glacial acetic acid. The red color remained, indicating the presence of carbonium ions. The mixture was poured immediately into 250 g. of ice–water mixture, and instant decolorization resulted. The mixture was extracted immediately with two 150-ml. portions of ether, and the extract treated with sodium carbonate solution. It was then dried, filtered and the solvent evaporated. The residual sirupy liquid was dissolved in 0.5 ml. of petroleum ether and chilled in a methanol–solid carbon dioxide bath. The solid formed was allowed to stand at room temperature until all of the solvent had evaporated. The yield was 0.34 g. (55% calculated as benzhydryl acetate) of a solid melting at 36.5–40.5°. The recrystallizations from petroleum ether resulted in a melting point of 40.3–41.0. The literature gives a value of 42°.[9]

Saponification of the solid acetate with methanolic sodium hydroxide yielded benzhydrol, identified by melting point and mixed melting point.

Summary

When solid benzhydrol is added to sulfuric acid, solution is slow, and considerable sulfonation apparently takes place. This solution has "*i*" factors as high as six. A solution of relatively stable benzhydryl carbonium ions can be prepared by dissolving the benzhydrol in carbon tetrachloride, and extracting with sulfuric acid. By pouring the acid solution into water, methanol and glacial acetic acid, dibenzhydryl ether, methyl benzhydryl ether, and benzhydryl acetate, respectively, may be prepared in reasonable yields.

[9] E. Berner and A. Hjulstad, *Ber.*, **71B**, 2053 (1938).

KNOXVILLE, TENNESSEE RECEIVED MARCH 27, 1950

[CONTRIBUTION FROM THE EXPERIMENT STATION, HERCULES POWDER COMPANY]

Bound Metal in Ethyl Cellulose Effect on Dilute Solution Properties

BY EVAN F. EVANS AND HAROLD M. SPURLIN

Introduction

Our knowledge of the behavior of linear high polymers in dilute solution is usually considered fairly complete. When the situation is analyzed, however, it becomes apparent that our information is really good for only the two extremes, ionic polymers in water and simple non-ionic polymers in organic solvents. Recent work by Fuoss[1] gives some information about ionic polymers that are soluble in polar organic solvents. In the literature are also data on the properties of concentrated solutions in organic solvents of cellulose derivatives containing some bound metal ions.[2,3,4] The fact remains, however, that there has not been adequate recognition of the fact that many commercial polymers contain bound ions in amount sufficient to influence markedly even dilute solution properties.

About ten years ago the methods for measuring the amount of metal ions bound to carboxyl or sulfuric half-ester groups in cellulose derivatives were well advanced. It became apparent that there was frequently as much as one equivalent of bound metal per cellulose chain. The question immediately arose whether these bound ions would influence the usual methods for estimation of molecular weight. It might be anticipated that the metal ions would be osmotically active, leading to high values of osmotic pressure. There was even more reason to fear that the bound metal ions, particularly if divalent, would lead to cross-linking and therefore to higher viscosities than would correspond to the length of the basic polymer chain.

As will be shown, the effects on viscosity and osmotic pressure are very pronounced. Fortunately, they tend to disappear in dilute solution. There is no evidence that the bound metal ions contribute to osmotic pressure when extrapolated to infinite dilution. All observed effects can be attributed to association.

When it became apparent that the degree of association could be controlled by varying the amount and nature of bound metal, the significance of these data with regard to methods for determining solvent power was realized. It will be shown that as the tendency for association rises the polymer gets less soluble, the slope of the reduced viscosity–concentration curve rises, and the slope of the reduced osmotic pressure–concentration curve falls.

Selection of Materials.—It was desired to vary independently the amount and nature of bound metal as well as the chain length of the polymer. These requirements could be fulfilled, however, only if the polymer would survive chemical manipulation without change of degree of polymerization or substitution. Also, the methods of manipulation had to be such that

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[1] R. M. Fuoss, *et al.*, *J. Polymer Sci.*, **3**, 246, 602, 603 (1948); *ibid.*, **4**, 97, 191, 457 (1949); *Ann. N. Y. Acad. Sci.*, **51**, 836 (1949).

[2] H. M. Spurlin, in E. Ott, "Cellulose and Cellulose Derivatives," Interscience Publishers, Inc., New York, N. Y., 1943, p. 872.

[3] C. J. Malm, U. S. Patents, 2,126,488–9 (1936).

[4] C. J. Malm, *et al.*, *Ind. Eng. Chem.*, **42**, 730 (1950).