served in samples which were prepared in this manner and left exposed in the balance case for periods up to one hour. The carbon analysis reported above was obtained on such a sample.

The completeness of drying, as well as the possibility of thermal decomposition due to the treatment to which the Bis-phenol-A was subjected, was checked by a combustion of the original powdered material in which the mass burned was computed from the amount of carbon dioxide produced. As a further check, one sample for combustion was held at 200° for ten minutes before crystallization. There was no significant difference between the results of these and the other experiments.

The results of eight combustion experiments yielded for Bis-phenol-A the value $-\Delta U_B/M$ = 8184.1 cal./g. with an average deviation from the mean of ±0.01% and a maximum deviation of 0.02%. Consideration of the propagated uncertainty of the result, which is due to the respective precision error taken for the heat of combustion of benzoic acid, the calibration measurements, the combustions of Bis-phenol-A and the carbon analysis, resulted in an estimated accuracy uncertainty of ±0.03%. The derived data are presented in Table I. No value for the heat of combustion of Bis-phenol-A was found in the literature.

TABLE I

HEAT OF COMBUSTION OF 2,2'-BIS-(4-HYDROXYPHENYL)-PROPANE, $C_{15}H_{16}O_2$, Mol. Wt. = 228.278

Derived data at 25° in kcal./mole

$-\Delta U_B = 1868.2 \pm 0.4^a$

$-\Delta U_R = 1867.3 \pm 0.4$

$-\Delta H_R = 1869.1 \pm 0.4$

$-\Delta H_f = 88.2 \pm 0.5$

[a] Precision uncertainty.

Summary

The isothermal heat of combustion at 25° of 2,2'-bis-(4-hydroxyphenyl)-propane has been determined. From this value the heat of formation has been calculated.

BARTLESVILLE, OKLAHOMA RECEIVED MAY 13, 1948

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Cuprous Chloride Complexes of Maleic and Fumaric Acids

BY L. J. ANDREWS AND R. M. KEEFER

A study of the relative tendencies of different olefins to form cuprous chloride complexes as influenced by the nature of substituents at the double bond is in progress in this Laboratory. In this connection it seemed desirable to compare the degree to which certain *cis–trans* isomers will form such complexes. This paper reports the results of a study of the reaction of cuprous chloride with maleic and fumaric acids.

By measurements of the solubility of cuprous chloride in aqueous solutions of allyl alcohol,[1] it has been demonstrated that an equilibrium is established with respect to the formation of a 1–1 water soluble complex ($CH_2{=}CH{-}CH_2OH \cdot CuCl$). Using a similar procedure the solubility of cuprous chloride in aqueous solutions of maleic and fumaric acids at different hydrogen ion concentrations has been determined. Supporting evidence for the conclusions as to structure of the complexes and equilibria involved as based on these solubility measurements has been obtained by an investigation of the absorption spectra of the intensely yellow solutions of the complexes.

Experimental

Cuprous Chloride.—This material was prepared in 5-g. batches according to the procedure of Keller and Wycoff.[2] Each batch was divided into 1-g. samples which were placed in sample vials and stored in a desiccator until used.

Maleic and Fumaric Acids.—These were prepared from maleic anhydride according to the directions of Robertson.[3]

Solubility Determinations.—The method for determination of the solubility of cuprous chloride in fumaric or maleic acid solutions was essentially that used in previous work.[1] To minimize chances of oxygen entering the reaction flasks during shaking the glass stoppers were sealed with paraffin. Solutions of maleic and fumaric acids which had been standardized against standard sodium hydroxide solution were used. The analyses for water-soluble cuprous complexes in the solutions at equilibrium were determined volumetrically as described elsewhere.[4] All reported concentrations (Cu_c^+) were corrected for the slight solubility of cuprous chloride in the organic acid-free medium. All runs were temperature controlled at 25 ± 0.5°.

When solutions of maleic acid which had been partially neutralized with sodium hydroxide were shaken with cuprous chloride, a crystalline yellow solid was formed. The solid was washed with water by decantation to remove traces of cuprous chloride and was transferred to a filter and washed with absolute alcohol and anhydrous ether. After air drying the water insoluble yellow solid showed negative tests for chloride and sodium ions. Analyses of the solid by dissolving weighed portions in hydrochloric acid and titrating for cuprous content indicated that it was cuprous acid maleate dihydrate.

Anal. Calcd. for $CuC_4H_3O_4 \cdot 2H_2O$: eq. wt., 215. Found: eq. wt., 209, 215.

A yellow solid of this type was also isolated in runs using partially neutralized fumaric acid solutions. It was, however, never isolated free from cuprous chloride.

---

[1] Kepner and Andrews, *J. Org. Chem.*, **13**, 208 (1948).

[2] Keller and Wycoff, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, pp. 1–4.

[3] Robertson "Laboratory Practice of Organic Chemistry," The Macmillan Company, New York, N. Y., 1943, pp. 316–317.

[4] Hatch and Estes, THIS JOURNAL, **67**, 1730 (1945).

Because of the complication arising from cuprous salt formation, no solubility studies were made on partially neutralized solutions of the organic acids.

Absorption Spectrum Measurements.—Absorption cells containing small amounts of cuprous chloride were almost completely filled with dilute solutions of the unsaturated acids in boiled water containing known amounts of sulfuric acid. The cells were capped, sealed with paraffin and shaken mechanically for four hours at 25°. After the undissolved cuprous chloride settled, the spectra of the cell contents were measured on the Beckman Spectrophotometer against a water blank over a range of 320–400 mμ. Aqueous solutions of maleic and fumaric acid of the concentrations used in these runs did not display appreciable absorption over this range; nor did solutions prepared by shaking cuprous chloride with dilute sulfuric acid absorb appreciably at this range.

Stability of Maleic and Fumaric Acid.—To establish that the reaction conditions used in the solubility determinations were not conducive to *cis–trans* isomerization of the acids, the following experiments were performed: maleic (0.3 *M*) and fumaric (0.06 *M*) acid solutions in 1 *N* sulfuric acid were shaken with excess cuprous chloride for four hours at 25°. Ten-ml. samples of the resulting solutions were extracted twice with 25-ml. portions of ether. The ether extracts were dried over anhydrous magnesium sulfate and were evaporated to dryness at room temperature to recover the acid. That isolated from the maleic acid run melted 129–130° uncor. (mixed m. p. with maleic acid, 129–130° uncor.). That isolated from the run using fumaric acid appeared to be pure fumaric acid, m. p. 285°.

Results

Solubility Measurements.—In this discussion, the terms maleic and fumaric acids and the acid maleate and acid fumarate ions will be designated as H_2M, H_2F, HM^- and HF^-; and the terms H_2X and HX^- will be used to designate either maleic or fumaric acid and their ions.

Table I gives the solubility of cuprous chloride in fumaric acid solutions of varying sulfuric acid concentration. The results were interpreted assuming the reaction

$$\mathrm{CuCl\,(s)} + H_2X = H_2X\cdot\mathrm{CuCl}$$

$$K_1 = \frac{(H_2X\cdot \mathrm{CuCl})}{(H_2X)} \cong \frac{(\mathrm{Cu_0}^+)}{(H_2X)_{\mathrm{init.}} - (\mathrm{Cu_0}^+)} \qquad (1)$$

Since H_2F is a weak acid[5] ($K_a = 9.48 \times 10^{-4}$), the assumption that $(H_2X) = (H_2X)_{\mathrm{init.}} - (\mathrm{Cu_c}^+)$, used in calculating K_2 values is good except for the run in which no sulfuric acid was added. Correcting this value for HF^- concentration, the value of K_1 when no sulfuric acid is present is 0.35. The values of K_1 are independent of the hydrogen ion concentration from 0.006 to 0.48 *M*.

Table I

The Solubility of Cuprous Chloride in Fumaric Acid Solutions at 25°

(H_2SO_4), mole/liter	(H_2F) init., mole/liter	$(\mathrm{Cu_0}^+)$, mole/liter	K_1	K_1 av. const. (H_2SO_4)[b]
0.477	0.0350	0.0093	0.36	
.477	.0456	.0107	.31	
.477	.0342	.0091	.36	
.477	.0504	.0116	.30	0.33
.238	.0456	.0100	.28	.28
.094	.0456	.0112	.32	.32
.0496	.0504	.0111	.28	
.0496	.0452	.0115	.34	
.0496	.0378	.0093	.33	
.0496	.0339	.0087	.35	.33
0	.0452	.0103	.30[a]	
0	.0438	.0103	.31[a]	.31

[a] Correcting for (HF^-) these values become 0.35 and 0.36. [b] These are the averages of the K_1 values for each series of runs at fixed sulfuric acid concentrations.

Two series of solubility measurements were performed using maleic acid solutions. The first series at varying sulfuric acid concentration is given in Table II. Table III summarizes the data for the solubility of cuprous chloride in maleic acid solutions of varying perchloric acid concentration. In column 4 of Tables II and III appear the values of K_1.

Table II

The Solubility of Cuprous Chloride in Sulfuric Acid Solutions of Maleic Acid at 25°

(H_2SO_4), mole/liter	(H_2M) init., mole/liter	$(\mathrm{Cu_0}^+)$, mole/liter	K_1	K_1 av., const. (H_2SO_4)	(H^+),[a] mole/liter
1.19	0.152	0.0105	0.074		
1.19	.150	.0100	.072	0.073	1.20
0.595	.152	.0127	.091		
.595	.152	.0122	.087	.089	0.611
.477	.159	.0132	.091		
.477	.0794	.0069	.096		
.477	.0397	.0034	.094	.093	
.298	.150	.0134	.098		
.298	.152	.0135	.098	.098	.317
.119	.150	.0157	.117		
.119	.152	.0146	.107	.112	.142
.0595	.150	.0163	.122	.122	.087

[a] (H^+) calculated from equation (8).

Table III

The Solubility of Cuprous Chloride in Perchloric Acid Solutions of Maleic Acid at 25°

$(HClO_4)$, mole/liter	(H_2M) init., mole/liter	$(\mathrm{Cu_0}^+)$, mole/liter	K_1	$\gamma = 1$	$\gamma \neq 1$	
				(H^+)	γ	(H^+)
0.903	0.146	0.0105	0.078			
.903	.146	.0108	.080	0.904	0.84	0.906
.602	.146	.0115	.086	.605	.76	.607
.421	.146	.0125	.094	.425	.75	.428
.301	.146	.0133	.100	.307	.76	.311
.120	.146	.0148	.113	.133	.78	.139
.0602	.146	.0166	.129	.080	.80	.0865

In contrast to the results obtained using fumaric acid these values of K_1 increase with decreasing concentration of sulfuric acid or perchloric acid. Correcting the values for HM^- would cause these values to increase more rapidly with decreasing hydrogen ion concentration. In order to explain this increase the following equilibria were considered

$$H_2M + \mathrm{CuCl(s)} = H_2M\cdot\mathrm{CuCl}$$

$$K_2 = \frac{a_{H_2M\cdot\mathrm{CuCl}}}{a_{H_2M}} \qquad (2)$$

$$H_2M + \mathrm{CuCl(s)} = HM\cdot\mathrm{CuCl}^- + H^+$$

$$K_3 = a_{HM\cdot\mathrm{CuCl}^-}\, a_{H^+}/a_{H_2M} \qquad (3)$$

---

(5) Ashton and Partington, *Trans. Faraday Soc.*, **30**, 598 (1934).

and

$$H_2M = H^+ + HM^- \qquad K_4 = a_{H^+}a_{HM^-}a_{H_2M} \quad (4)$$

If $(H_2M)_{init.}$ is the initial concentration of maleic acid, then

$$(H_2M)_{init.} = (H_2M) + (H_2M{\cdot}CuCl) + HM{\cdot}CuCl^-) + (HM^-) \quad (5)$$

and

$$(Cu_c{}^+) = (H_2M{\cdot}CuCl) + (HM{\cdot}CuCl^-) \quad (6)$$

By substituting eq. 2 to 6 in eq. 1 the following equation may be derived

$$K_1\left[1 + \frac{K_4\,\gamma_{H_2M}}{\gamma_H\gamma_{HM}(H^+)}\right] = \frac{K_2\gamma_{H_2M}}{\gamma_{H_2M\cdot CuCl}} + \frac{K_3\gamma_{H_2M}}{\gamma_H\gamma_{HM\cdot CuCl}(H^+)} \quad (7)$$

In all calculations it was assumed that the activity coefficient of uncharged molecules (H_2M, $H_2M{\cdot}CuCl$) was unity. If the left-hand side of eq. 7 is plotted *versus* $1/\gamma_H\gamma_{HM\cdot CuCl}(H^+)$ a straight line should be obtained of slope K_3, and the intercept would be K_2. As a first approximation all activity coefficients were assumed to be unity. The hydrogen ion concentration in the sulfuric acid runs was calculated from the expression

$$(H^+)^2 - M_{H_2SO_4}(H^+) = K_{HSO_4^-}(HSO_4^-) + K_4[(H_2M)_{init.} - (HM^-) - (Cu_c{}^+)] \quad (8)$$

An average value for $K_{HSO_4^-}$ (0.015) at the ionic strengths involved was obtained by assuming $\gamma_H\gamma_{HSO_4} = 0.8^2$ and using the value for $K_{HSO_4^-}$ from Harned and Owen.[6] The value for K_4[5] was taken as 0.0142. The equation was solved for (H^+) by successive approximations assuming first that (HSO_4^-) was equal to $M_{H_2SO_4}$ and neglecting (HM^-). With the approximate value of (H^+) obtained, values of (HSO_4^-) and (HM^-) were calculated and substituted in eq. (8) to obtain the final values of (H^+) appearing in column 6 of Table II. For the perchloric acid determinations the (H^+) was determined by adding the (H^+) resulting from ionization of the maleic acid to the concentration of perchloric acid. These values appear in column 5 of Table III. As may be seen from curve I of Fig. 1, a straight line is obtained when the left-hand side of eq. 7 is plotted against $1/(H^+)$ except at high hydrogen ion concentrations. Within the limits of experimental error the results for sulfuric acid and perchloric acid lie on the same curve.

Since the ionic strength was not held constant, the activity coefficients in eq. (7) would vary considerably over the range of concentration of acids used. In order to estimate the effect of the activity coefficients, it was assumed that

$$\gamma^2_{\pm HCl} = \gamma_H\gamma_{HM} = \gamma_H\gamma_{HM\cdot CuCl} = \gamma_H\gamma_{ClO_4}$$

Column 6 of Table III gives the values of $\gamma_{\pm HCl}$ used which were taken from Harned and Owen.[6] The concentration of hydrogen ion appearing in column 7 of Table III was calculated using K_4 and the activity coefficients. As may be seen from curve II of Fig. 1, the introduction of activity coefficients gives better agreement, but the values still decrease too rapidly at high hydrogen ion concentrations. By extrapolation K_2 is found to be 0.083. From the slope of the straight line the value of K_3 is 0.0043.

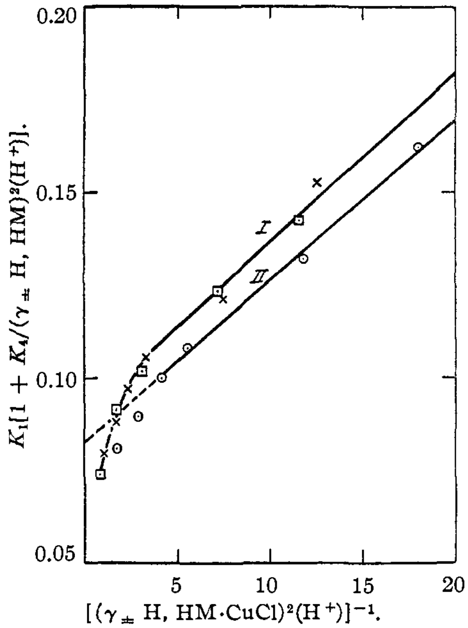


Fig. 1.—The solubility of cuprous chloride in maleic acid solution: curve I, ⊡ values for H_2SO_4 and × values for $HClO_4$ solutions assuming $\gamma_\pm = 1$; curve II, ⊙ for $HClO_4$ solutions correcting for activities.

It may be seen from the value of K_2 that fumaric acid complexes cuprous chloride to a greater extent than does maleic acid. It is also interesting to note that the acid maleate ion complexes cuprous chloride to a greater extent than maleic acid as may be shown by subtracting eq. 4 from eq. 3.

$$HM^- + CuCl(s) = HM{\cdot}CuCl^-$$
$$K_9 = a_{HM\cdot CuCl}/a_{HM} = 0.31 \quad (9)$$

The Absorption Spectra.—Within the limits of experimental error the spectra of the solutions obtained by shaking cuprous chloride with solutions of fixed fumaric acid concentration were identical ($\lambda_{max.}$ = 360 mμ), although the sulfuric acid concentrations of the medium were varied from 0.5 to 0.05 *M*. Curves I and II, Fig. 2, are representative of results obtained. At very low sulfuric acid concentrations the position of the absorption maximum was shifted toward the ultraviolet (Curve III), and the maximum optical density was somewhat less than at higher acid concentrations. It is presumed that this results from the formation of some $HF{\cdot}CuCl^-$ at low sulfuric acid concentration.

Using maleic acid solutions all of the same concentration, $(H_2M)_{init.}$, the optical densities at the absorption maximum (340 mμ) diminished even as the sulfuric acid concentrations of the solutions

---

[6] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Company, New York, N. Y., 1943.

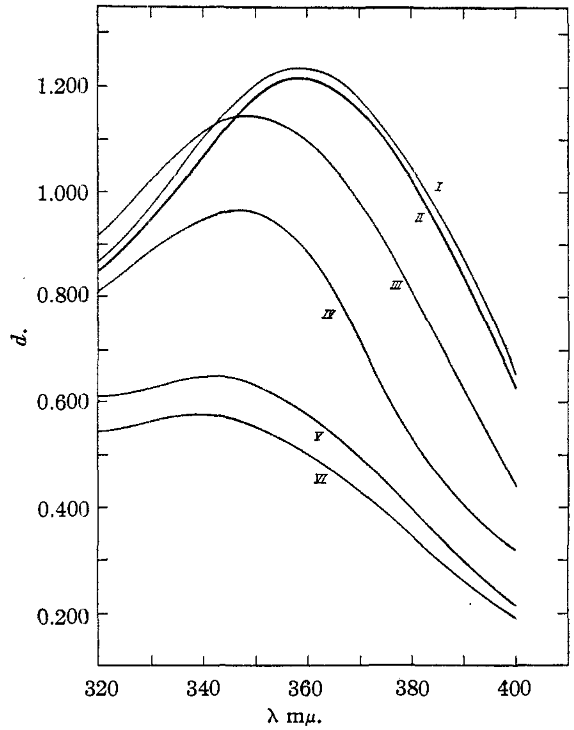


Fig. 2.—The absorption spectra of aqueous solutions of cuprous chloride complexes of maleic and fumaric acids: curves I, II and III for solutions of $(H_2F)_{init.} = 2.63 \times 10^{-3}$ *M;* curves IV, V and VI for solutions of $(H_2M)_{init.} = 3.00 \times 10^{-3}$ *M;* H_2SO_4 concns. 0.47 *M* for I and VI, 0.24 *M* for II and V, 0.0025 *M* for III; 0.050 *M* for IV.

changed from 0.5 to 0.25 *M* (Curves V and VI, Fig. 2). As the sulfuric acid concentration was decreased, the position of the absorption maximum shifted toward the visible; and the measured optical densities increased markedly (Curve IV, Fig. 2). These observations are consistent with the results of the solubility studies which indicated that considerable amounts of $HM\cdot CuCl^-$ are formed even in media of reasonably high hydrogen ion concentration. It appears that the extinction coefficient for $HM\cdot CuCl^-$ is considerably larger than that for $H_2M\cdot CuCl$.

For solutions of $H_2F\cdot CuCl$ it was observed that the magnitude of the optical density was directly proportional to the original fumaric acid concentration of the solution as may be seen from Fig. 3. This constitutes further evidence that one molecule each of fumaric acid and cuprous chloride are associated in the complex. The extinction coefficient for $H_2F\cdot CuCl$ has been calculated from equation (10) assuming $K_1 = 0.32$, $d_{360\,m\mu} = 1.22$ (see Curves I and II, Fig. 2) where $(H_2F)_{init.} = 2.63 \times 10^{-3}$ *M.*

$$\epsilon_{360\,m\mu} = (1 + K_1)d_{360\,m\mu}/K_1(H_2F)_{init.} = 1900 \quad (10)$$

An estimate was also made of the extinction coefficients at 340 mμ for $H_2M\cdot CuCl$ (ϵ_1) and $HM\cdot CuCl^-$ (ϵ_2) using equation (11).

$$d_{340\,m\mu} = \epsilon_1(H_2M\cdot CuCl) + \epsilon_2\,(HM\cdot CuCl^-) \quad (11)$$

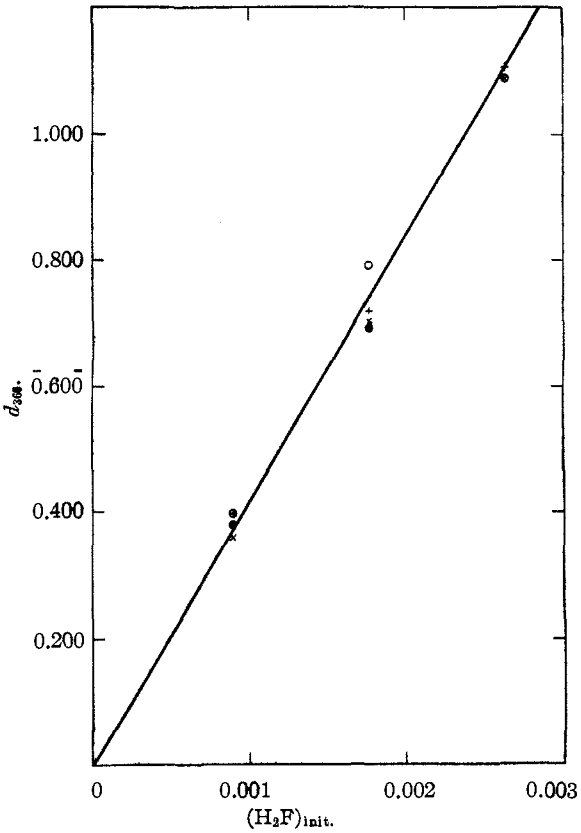
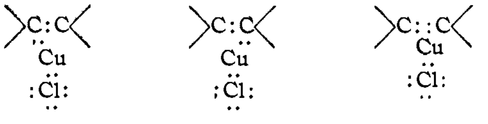


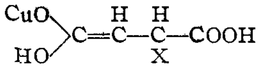
Fig. 3.—The optical densities of $H_2F\cdot CuCl$ at 360 mμ as a function of fumaric acid concentration; H_2SO_4 concentrations: +, 0.005 *M;* ×, 0.050 *M;* ●, 0.24 *M;* ○, 0.47 *M.*

It was observed for solutions in which $(H_2M)_{init.} = 3.0 \times 10^{-3}$ *M* that the $d_{340\,m\mu}$ values for the cuprous chloride complexes were 0.948 and 0.576, respectively, when the sulfuric acid concentrations of the solutions were 0.050 and 0.48 *M.* Applying these values and the values for K_2, K_3 and K_4 to equation (11), the values for ϵ_1 and ϵ_2 were found to be 2000 and 3800, respectively.

The Structure of the Complexes.—It seems most reasonable to classify these complexes as being of the metal–olefin type as postulated for silver ion–olefin complexes.[7] For a simple olefin the following resonance structures would represent the complex



Since both maleic and fumaric acids readily form cuprous chloride complexes, the spectra of which are similar, it seems unlikely that the structure of the maleic acid complex is of the chelate type, in which both carboxyl groups are concerned.



$$\begin{matrix}CuO \\ HO\end{matrix}\!\!>\!C{=}\overset{H}{C}{-}\underset{X}{\overset{H}{C}}{-}COOH$$

---

(7) Winstein and Lucas, THIS JOURNAL, 60, 836 (1939).

Structures of the type comparable to those proposed[8] as intermediates in the acid-catalyzed isomerization of maleic to fumaric acid seem inappropriate since no evidence for isomerization of maleic acid as catalyzed by cuprous chloride was obtained. Also the equilibrium for formation of a cuprous complex appears to be independent of the nature of anions (X^-) present in the medium.[9]

Summary

Solubility measurements have been used to study the equilibria for formation of water soluble complexes of cuprous chloride with maleic and fumaric acids. The results indicate that with fumaric acid a 1–1 complex of the type $H_2F \cdot CuCl$ is formed. In the case of maleic acid evidence for the formation of not only $H_2M \cdot CuCl$ but also of $HM \cdot CuCl^-$ was obtained even in solutions of reasonably high hydrogen ion concentration. Supporting evidence for these conclusions was obtained by studies of the absorption spectra of the complexes.

Davis, California Received April 6, 1948

---

[8] Nozaki and Ogg, This Journal, **63**, 2583 (1941).

[9] Preliminary studies of certain other olefins indicate that the solubility of cuprous chloride in aqueous solutions of the unsaturates is influenced by chloride ion concentration. Further studies of maleic and fumaric acids are planned in the light of this observation.

[Contribution from the Floridin Company]

Low Temperature Nitrogen Adsorption Studies on Attapulgite (Floridin)

By W. T. Granquist and R. C. Amero*

Introduction

Recently Marshall and Caldwell[1] have presented an excellent survey of the colloid chemistry of attapulgite (floridin, fullers earth); their data on clay films exhibit an interesting variation in mean refractive index with temperature of preheating. A differential thermal curve presented by Grim and Rowland[2] and included in this paper indicates definite changes in this mineral with temperature. Finally, in adsorption problems involving the percolation of a fluid through a bed of granular fullers earth, it has long been known in the trade that there are various heat activation optima for the adsorbent depending on the nature of the adsorbate. Little information of this type has been published; however, FitzSimons, Amero and Capell[3] report data correlating the yield of decolorized bright stock solution with the activation temperature of the clay, which exhibit an optimum between 590 and 650°.

On the basis of this past work, it seemed to be of interest to conduct an investigation into the variation of the properties of the adsorbent with activation temperature. This paper presents the results of a low-temperature nitrogen isotherm study; later, data will be presented in an attempt to correlate optimum activation temperature with molecular weight of adsorbate in a number of adsorbate–solvent systems. This study has been extended to include a sample of extruded fullers earth, since high pressure extrusion results in a marked increase in oil decolorizing ability.[4,5]

Experimental

Preparation of Samples.—Crude clay was ground in an attrition mill and screened to 30/60 mesh for low temperature nitrogen adsorption. For extrusion, the crude was pulverized in the laboratory Raymond mill, kneaded with sufficient water to give a free moisture content of 50%, and extruded through a Chambers Bros. Type 3B auger-type extrusion machine equipped with a die 2 cm. thick, containing 8 holes 1 cm. in diameter. The rods were air-dried, ground and screened to 30/60 mesh. The crude samples were activated at 218, 316, 427, 538, 649, 704 and 816° (425, 600, 800, 1000, 1200, 1300, 1500° F.), and the extruded sample at 649°. This activation was carried out in a laboratory muffle furnace equipped with a Leeds and Northrup Micromax controller. Heating was continued for one hour after activation temperature had been reached; the samples were then placed in a drying oven at 110° and allowed to cool before sealing in small sample bottles.

Low-Temperature Nitrogen Adsorption.—Adsorption-desorption isotherms were determined with the apparatus described by Emmett and Brunauer[6] and by Emmett.[7] The pressure arm of the manometer was equipped with a zero-indicating device to assist in maintaining the volume of the free space essentially constant—a condition necessary for precision in a given series of measurements. The liquid nitrogen-bath was agitated with a stream of gaseous nitrogen to prevent temperature stratification and to decrease the rate of condensation of atmospheric oxygen into the bath.

The nitrogen used as the adsorbate was a special high purity nitrogen supplied by the Linde Air Products Co., and this was further purified while filling the nitrogen reservoir by batch distillation from a trap cooled in liquid nitrogen. The helium utilized for measuring the free space in the samples was obtained from the Ohio Chem. and Mfg. Co. and its purity was enhanced by passing the gas during filling through active carbon cooled to liquid nitrogen temperatures.

Between 0.5 and 1.0 g. of the sample in question was weighed into the sample tube, and was then outgassed at 200° and *ca.* 10^{-5} mm. for one hour. The various points on the isotherm were determined in the usual way. To determine the final points at or very near saturation the volume of the system was decreased and the pressure observed; as soon as the pressure fell below P_0, the volume

---

* The present address of R. C. Amero is Johns-Manville Research Center, Manville, New Jersey.

[1] C. E. Marshall and O. G. Caldwell, *J. Phys. Colloid. Chem.*, **51**, 311 (1947).

[2] R. E. Grim and R. A. Rowland, *Am. Mineral.*, **27**, 746–761, 801–818 (1942).

[3] O. FitzSimons, R. C. Amero and R. G. Capell, Ref. Tech. Ed., *Nat. Petroleum News*, Oct., 1941.

[4] F. W. K. Hartshorne, U. S. Patent 2,079,854, May 11, 1937.

[5] R. C. Amero and R. G. Capell, *Pet. Ref.*, **22**, 22–26 (1943).

[6] P. H. Emmett and S. Brunauer, This Journal, **56**, 35 (1934).

[7] "Advances in Colloid Science," Vol. I, Interscience Pub. Co., New York, N. Y., 1942.