

of the unreacted methyl ω -styryl sulfone; they were combined and dissolved in acetone, and potassium permanganate was added until a purple color persisted. The manganese dioxide was filtered off and the acetone was evaporated. Water was added and the saturated sulfone was extracted with 200 ml. of ether. Evaporation of the ether left a residue, which was recrystallized from methanol and water to give 1.8 g. of methyl β -phenyl- β , p -tolylethyl sulfone; m.p. 92–93°, total yield 2.76 g. (37% of theory).

Anal. Calcd. for $C_{16}H_{18}O_2S$: C, 69.82; H, 6.57. Found: C, 69.85; H, 6.75.

Alkylation of Toluene with p -Tolyl ω -Styryl Sulfone.—This compound⁴ (II) (10 g., 0.039 mole) was added to a stirred mixture of toluene (100 ml.) and 97% sulfuric acid (20 g.) cooled in an ice-bath. The mixture was stirred at ice-bath temperature for 1 hour and then at room temperature for 6 hours. The reaction mixture was poured into ice-water and the aromatic layer was separated. The water layer was extracted with 200 ml. of ether and the combined aromatic layer and ether extract was evaporated to dryness under an air jet. The solid obtained was dissolved in absolute methanol and crystallized in three fractions: (1) 4.3 g., m.p. 130–132°; (2) 1.5 g., m.p. 124–127°; (3) 3.8 g., m.p. 106–111°. A mixture of 0.09 g. of fraction (1) and 0.08 g. of the known sample³ (m.p. 131–132.5°) had mp. 130.5–132.5°.

Alkylations with Methyl Vinyl Sulfone.—The quantities of reactants used were: 0.1 mole of methyl vinyl sulfone,⁹ 0.22 mole of aluminum chloride, and a large excess of the

aromatic compound. In all cases a solution of the sulfone in the aromatic compound or in nitrobenzene was added to a stirred mixture of the catalyst and the aromatic compound, in some cases using nitrobenzene as the solvent. The first reactions were run at about 30° for 2 hours generally following the procedure given in ref. (2). In three cases some dry hydrogen chloride was added to the reaction mixtures containing aluminum chloride as a catalyst. When no condensation was obtained the temperature of the subsequent reactions was raised to 90°. The only result of this increase in temperature was an increase in the amount of tar-like product formed. In each case the reaction mixture was decomposed by pouring it into an ice-water–hydrochloric acid mixture. The organic layer was then separated, washed with water and steam distilled. The product, if any, should have remained in the pot residue since the sulfone produced by the condensation would be water insoluble and not appreciably steam distillable.

Methyl vinyl sulfone (10.6 g., 0.1 mole), was added to a stirred mixture of benzene (150 ml.) and sulfuric acid (97%, 20 g.) cooled to ice-bath temperature. This mixture was stirred 2 hours at ice-bath temperature, 3 hours at room temperature and 1 hour at 60°. The reaction mixture was hydrolyzed by pouring it into ice-water. The organic layer was separated and evaporated down to a small quantity of oil, which could not be crystallized. The water layer was extracted with two 100-ml. portions of ether and the ether was evaporated; however, no appreciable amount of residue remained.

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(9) G. D. Buckley, *et al.*, *J. Chem. Soc.*, 1514 (1947).

NOTES

The Adsorption of Cupric and Mercuric Ions by a Weak-base Anion Exchange Resin

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Weak-base anion-exchange resins in their "basic" form take up an anion X^- by virtue of the reaction $RNH_2 + H^+ + X^- \rightarrow RNH_3^+ + X^-$, that is, by addition of a proton to the unshared pair of the nitrogen atom. It is reasonable to expect that other cations which form ammine complexes will be adsorbed by the resin. Sussman has briefly reported on the adsorption of cupric ions by an anion-exchange resin.¹ The results of a fragmentary study of the adsorption of Cu^{++} and Hg^{++} ions by the weak-base resin, Amberlite IR-4B, are reported here.

Experimental

A sample of the resin hydrochloride was treated with excess sodium hydroxide, washed with water until on standing for 24 hours the pH remained 7–8, and stored over saturated sodium sulfate (vapor pressure 22.3 mm. at 25°, 95% relative humidity).

Cupric solutions were prepared from C.P. copper nitrate and were analyzed iodometrically, using the directions of Swift.^{2a} Using 25-ml. portions of solutions at a pH of 3–5, Cu^{++} concentrations as low as $2 \times 10^{-4} M$ could be determined to 1% provided the solutions were deoxygenated by

bubbling CO_2 gas through them. Mercuric solutions, prepared from mercuric nitrate, were analyzed by thiocyanate titration.^{2b} Hydrogen ion in the Hg^{++} solutions was determined by titration with NaOH to a brom thymol blue end-point, in the presence of 0.3 M KI to complex the Hg^{++} . The first color change of the indicator gives the end-point, but it subsequently fades.

The adsorption experiments were done at an ionic strength of ca. 0.10 volume molar maintained with sodium nitrate. Weighed samples of resin were equilibrated with measured volumes of an aqueous phase in a glass-stoppered erlenmeyer flask by constant end-over-end rotation of the flask. The amount of copper or mercury adsorbed or eluted was computed from the change in concentration of the aqueous phase, and the known initial amount of metal in the resin, or, when necessary, by elution of the copper from the resin with acid. Concentrations of adsorbed constituents in the resin are reported in units of weight molality, m , *i.e.*, moles per kilogram of the free base form of the resin. Solution concentrations are reported in units of volume molarity, M . Titration curves of the resin, at the ionic strength used in our experiments, are shown in Fig. 1.

Results and Discussion

In order to do experiments at a pH at which there was no question about possible precipitation of basic copper compounds, it was necessary to use a resin which was at least 2 m in acid. Figure 2 displays the results of a series of experiments on the adsorption and elution of Cu^{++} by the resin. After 5 or 6 days exposure to the aqueous Cu^{++} solution (curves A and B), the rate of adsorption of Cu^{++} fell to a low value. The resin, which was normally amber colored, became blue-green upon adsorbing Cu^{++} and almost black when more

(1) F. C. Nachod (editor), "Ion Exchange," Academic Press, Inc., New York, N. Y., 1949, p. 244.

(2) E. H. Swift, "Introductory Quantitative Analysis," Prentice-Hall, Inc., N. Y., 1950, (a) p. 210, (b), p. 101.

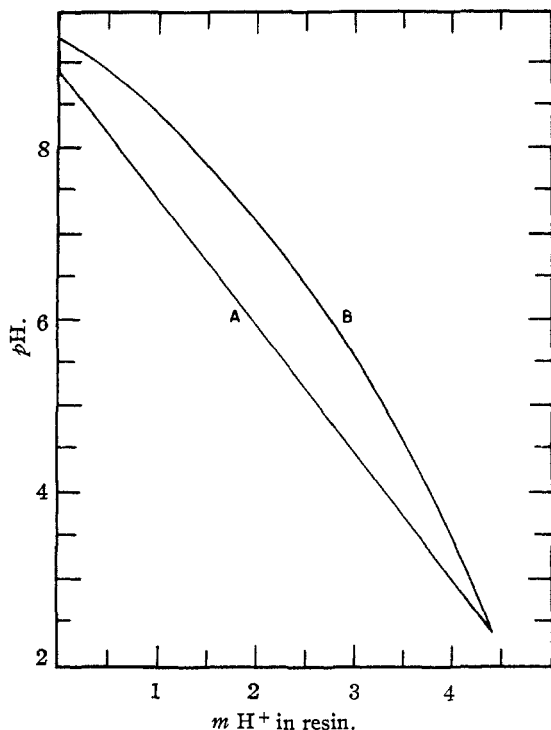


Fig. 1.—Titration curve of Amberlite IR-4B: A, nitric acid added to free base resin; B, NaOH added to resin resulting from the above titration. In each experiment, acid (or base) was added in small batches to 1.00 g. resin in 100 ml. of 0.100 M NaNO_3 and the $p\text{H}$ measured after 2 hr. stirring. The final volumes of solutions were 105 ml.; in the course of the back titration, μ increased from 0.10 to 0.14 due to NO_3^- liberated from the resin.

than 0.2 m in Cu^{++} . More Cu^{++} was adsorbed from concentrated solutions than from dilute solutions. More Cu^{++} was adsorbed on to a resin that was 2 m in H^+ than on to a resin that was 3 m in H^+ . However, on standing 90 days, much more Cu^{++} was adsorbed and there was no significant difference between the 2 m H^+ and 3 m H^+ resin (A' and B'). Elution for 90 days of resin samples that were rich in Cu^{++} (points a' and b') with 0.1 M NaNO_3 gave points which agree, within a factor of 2, with the 90 day adsorption experiments. Therefore, it seems likely that the 90 day adsorption and elution experiments define the equilibrium conditions within a factor of 2.

There was a small but significant release of H^+ by the resin to the aqueous phase as Cu^{++} was adsorbed. In effect, therefore, most of the Cu^{++} was adsorbed by the reaction, $\text{RNH}_2 + \text{Cu}^{++}(\text{aq.}) \rightarrow \text{RNH}_2\text{Cu}^{++}$, rather than by $\text{RNH}_3^+ + \text{Cu}^{++}(\text{aq.}) \rightarrow \text{RNH}_2\text{Cu}^{++} + \text{H}^+(\text{aq.})$. Typical values of the amount of H^+ liberated are listed in the legend to Fig. 2.

The long time required to achieve equilibrium in adsorption indicates that the rate of diffusion of Cu^{++} into the resin particles is quite slow. It is probable therefore that much of the Cu^{++} adsorbed in the 5–6 day experiments was on the outside of the spherical particles. There was a greater release of H^+ per Cu^{++} adsorbed from the 3 m resin in the 5–6 day experiments than in the 90 day experiment.

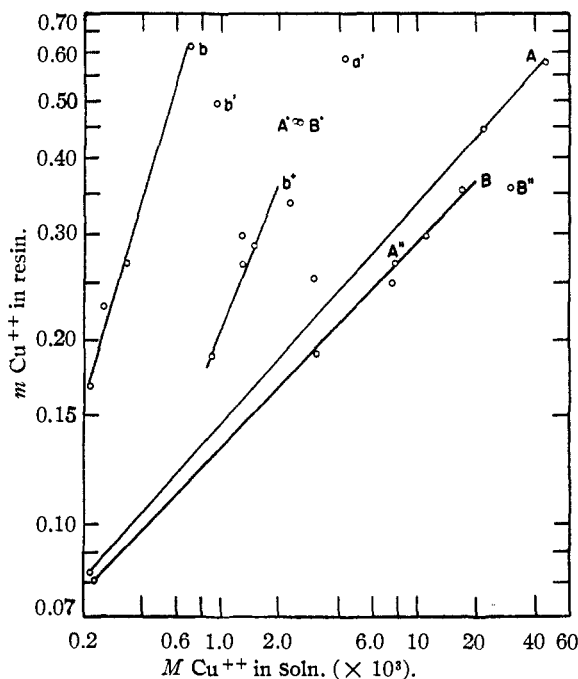


Fig. 2.—Adsorption of Cu^{++} by Amberlite IR-4B: 1 g. resin/100 ml. aqueous phase; constant stirring, 28.3°; final ionic strength, 0.09–0.10 (NaNO_3). A' , 2 m H^+ in resin (one point), adsorption, 5 days; A , (four points), 6 days; A' , 90 days; a' , elution, 90 days; B' , 3 m H^+ in resin, adsorption, 5 days; B , (five points), 6 days; B' , 90 days; b , elution, 6 days; b' , 90 days; b'' , elution of 2 m H^+ resin with 0.01 M HNO_3 so that resin became 3 m in H^+ . Some typical values of the ratio, r , of moles H^+ displaced/moles Cu^{++} adsorbed are: Curve B, (Cu^{++}) = 0.0031 M , r = 0.045, (Cu^{++}) = 0.017 M , r = 0.083; B'' , (Cu^{++}) = 0.030 M , r = 0.13; B' , (Cu^{++}) = 0.0026 M , r = 0.020. Curve A, (Cu^{++}) = 0.0030 M , r = 0.0007; (Cu^{++}) = 0.022, r = 0.0027; (Cu^{++}) = 0.046, r = 0.0043; A' , (Cu^{++}) = 0.0024, r = 0.0010.

This probably indicates that H^+ was displaced from the outside of the resin particles by the concentrated Cu^{++} but was re-adsorbed as Cu^{++} diffused into the center of the resin particles and the external Cu^{++} decreased.

According to Fig. 1, a resin that is 2 m in H^+ is in equilibrium with an aqueous phase at a $p\text{H}$ of 6–7. Bjerrum^{3a} quotes a value of 10^{-7} M for the acid constant of $\text{Cu}(\text{OH}_2)_4^{++}$. At a $p\text{H}$ of 6–7 there would be a possibility of adsorption of $\text{Cu}(\text{OH})^+$ or of precipitation of basic copper salts. However, the acid released in the adsorption experiment decreased the $p\text{H}$ to 5.5 or less for most of the samples and thus decreased the importance of hydrolysis of Cu^{++} . In effect, adsorption of Cu^{++} increases the acid constant of the resin. The slope of curve A of Fig. 1, $\Delta p\text{H}/\Delta (\text{H}^+) = -1.45$ m^{-1} . In the 90 day adsorption experiment (point A' of Fig. 2), the $p\text{H}$ decreased from 6.49 to 5.30 and the resin was 0.46 m in Cu^{++} , $\Delta p\text{H}/2\Delta (\text{Cu}^{++}) = -1.30$ m^{-1} . That is, charge for charge, Cu^{++} and H^+ increase the acid constant of the resin about the same amount.

Figure 2 also displays several elution experiments

(3) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941; (a) p. 69; (b) pp. 128, 173.

on resin samples which were exposed to Cu^{++} for 6 days and then eluted for 6 days. They have only qualitative, descriptive significance, since equilibrium was not reached and since the adsorbed Cu^{++} was probably not uniformly distributed through the resin. When the 3 *m* resin was eluted with 0.10 *M* NaNO_3 for 6 days, relatively small amounts of Cu^{++} were extracted into the aqueous phase (curve b). When the 2 *m* resin was treated for 6 days with a solution containing enough HNO_3 to make the resin 3 *m* in H^+ , more Cu^{++} was eluted, although curve B was not reached.

The results of the experiments on the adsorption of Hg^{++} are shown in Table I. To avoid possible precipitation of basic mercuric salts, the solutions initially were at a *pH* of *ca.* 2 and the resin was 4 to 5 *m* in H^+ . After 8 days, a large fraction of the mercuric ion was taken up by the resin. The ratio of H^+ liberated/ Hg^{++} adsorbed was above unity. Table I and the data of Fig. 1 show that on a charge basis Hg^{++} and H^+ are about equally effective in increasing the acid constant of the resin.

TABLE I

ADSORPTION OF Hg^{++} BY AMBERLITE IR-4B

1 g. resin/100 ml. aqueous phase; constant stirring; temp., 28.3°; ionic strength, 0.09 to 0.10; 8 days equilibration.

<i>m</i> Hg^{++} in resin	<i>M</i> Hg^{++} in soln.	<i>m</i> H^+ in resin	<i>M</i> H^+ in soln.	H^+ liberated Hg^{++} adsorbed
0	0	4.52	0.0040	..
.22	.000025	4.12	.0077	1.7
.50	.00049	3.84	.0100	1.2
.67	.0043	3.35	.0142	1.5
.81	.0029	3.35	.0142	1.2 ^a
1.01	.0120	2.55	.0207	1.7
1.13	.0218	2.24	.0221	1.6

^a 16 days equilibration.

The resin did not appreciably change color on adsorbing Hg^{++} . The greater affinity of the resin for Hg^{++} as compared to Cu^{++} is in accordance with the relative affinity of NH_3 for these two ions; $\text{Hg}^{++} + \text{NH}_3 = \text{HgNH}_3^{++}$, $\log K = 8.8$; $\text{Cu}^{++} + \text{NH}_3 = \text{CuNH}_3^{++}$, $\log K = 4.15$.^{3b}

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CONTRIBUTION NO. 1798 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY CALIFORNIA INSTITUTE OF TECHNOLOGY PASADENA 4, CALIF.

p-Dimethylaminophenylquinaldylcarbinol

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Bahner and Pace² were unable to isolate *p*-dimethylaminophenylquinaldylcarbinol from the reaction mixture of quinaldine and *p*-dimethylaminobenzaldehyde. Other substituted benzaldehydes did combine with quinaldine under the same

conditions. From the Elderfield³ summary of the various procedures used for the synthesis of these carbinols it is evident that *p*-dimethylaminobenzaldehyde will not condense.

Three of these carbinols were made⁴ by treating the lithium derivative of 6-ethoxyquinaldine, 6-methoxyquinaldine and quinaldine itself with *p*-dimethylaminobenzaldehyde. Although the yields were only fair, the by-products formed presented no difficulty in the purification. These carbinols were easily dehydrated to the corresponding styryl derivatives by heating with acetic anhydride or hydrochloric acid.

Experimental

Quinaldines.—Quinaldine was Eastman Kodak Co., white label grade and was used with no further purification. 6-Methoxyquinaldine was prepared by modifying the procedure of Cocker and Turner.⁵

A solution of 123 g. (1.0 mole) of *p*-anisidine in 200 ml. of concentrated hydrochloric acid was cooled to 0°. With constant stirring, 137 g. (1.0 mole) of paraldehyde was added over a period of one-half hour. Stirring was discontinued, and the reaction mixture was allowed to stand overnight. The brown material was refluxed on a water-bath for four hours (additional paraldehyde was added from time to time to compensate for the unavoidable loss through the condenser). The solution was cooled and poured with vigorous stirring into a large excess of 6 *M* ammonium hydroxide (*ca.* 1000 ml.). The dark viscous oil formed was separated, washed three times with 200-ml. portions of water dissolved in ether and dried over KOH. The ether was removed and the remaining oil was distilled under reduced pressure, b.p. 145–150° (3 mm.).⁶ The pale yellow oil solidified in the receiver and formed lemon color cubic crystals. Crystallization from ligroin gave white crystals. Yield was 54 g. (31%); m.p. 64°.

6-Ethoxyquinaldine was made by the above method. From 137 g. (1.0 mole) of *p*-phenetidine, 23 g. of 6-ethoxyquinaldine (12.7%) were obtained by fractionating at 173° at 14 mm., the bath temperature being 248°. A white product was obtained from the ether-petroleum ether crystallization; m.p. 71°.⁷

***p*-Dimethylaminophenylquinaldylcarbinol.**—To a phenyl lithium solution⁸ cooled in an ice-salt-bath was added an equivalent amount of the quinaldine dissolved in 20 ml. of dry ether; the color turned brick red. Stirring was continued for one-half hour after the addition of the quinaldine. An equal molar amount of *p*-dimethylaminobenzaldehyde suspended in 35 ml. of ether was added portionwise. The color gradually changed from brick-red to orange and then to yellow. The solution was stirred for two hours and then allowed to warm to room temperature by standing overnight. The lithium salt was decomposed with 95% alcohol. The carbinol was isolated by dilution and crystallized from a dilute alcohol solution. Pale straw-yellow plates were obtained which did not turn red if kept dry. Yield was 14.3%; m.p. 130°.

*Anal.*⁹ Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_2$: C, 78.02; H, 6.91. Found: C, 78.10; H, 6.90.

***p*-Dimethylaminophenyl-6-methoxyquinaldylcarbinol** was made as described above, but the mixture was refluxed prior to decomposition of the lithium salt until the color changed to yellow. The salt was hydrolyzed with 50% alcohol, the top layer was separated, and the water layer was extracted

(3) R. C. Elderfield, "Heterocyclic Compounds," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1952, p. 295.

(4) A. Furst, Dissertation, Stanford University 1948.

(5) W. Cocker and D. G. Turner, *J. Chem. Soc.*, 143 (1941).

(6) If a sharp fraction is not taken the oil fails to solidify. At times recrystallization from ligroin will give the desired solid, but most of the time two layers separate making redistillation necessary. The dry solid turns pink almost at once and will keep indefinitely. Moist products turn brown and decompose in a matter of days.

(7) W. T. K. Brauholtz, *J. Chem. Soc.*, 121, 169 (1922).

(8) H. Gilman, E. A. Zoellner and W. M. Selby, *THIS JOURNAL*, 55, 1252 (1933).

(9) Microanalysis by C. W. Koch, Albany, California.

(1) Deceased 1946.

(2) C. T. Bahner and E. S. Pace, *THIS JOURNAL*, 74, 3932 (1952).