proach one another closely when each method is operating under optimum conditions. Such conditions obtain when the adsorption isotherm undergoes a sharp change at a low pressure to give a well-defined "Point B" and when capillary condensation sets in at a fairly high pressure well separated from "Point B"; this is illustrated by Lambert and Foster's water-aged ferric oxide–ethyl alcohol system.[16]

The results in the table indicate that, for the most part, the adsorbents chosen for application of the equations satisfactorily fulfill the requirements of one of the original assumptions, namely, that the surface represented by the walls of capillaries constitutes practically the entire surface of the adsorbent. Otherwise, surface values from capillary radii probably would have been consistently lower than those from unimolecular adsorption.

Agreement with the surface area values from "Point B" in the case of Lambert and Foster's silica gel[12] leaves much to be desired. Since hysteresis with water occurs in this gel in capillaries of from 10.45 to 19.23 Å. radius and since these small capillaries account for only 0.0565 g. of the 0.22 g. total liquid adsorbed, the discrepancy is probably due, in part at least, to neglecting very small capillaries which contribute a large surface area. It is interesting to note that benzene and ethyl alcohol, molecules larger than water, showed no hysteresis when adsorbed on this gel. Presumably after the surface had been covered little further room remained for capillary condensation.

The writer wishes to express his appreciation to Dr. Charles Rosenblum and Professor H. S. Taylor for their kind advice during the preparation of this paper.

Summary

Equations have been developed which permit relatively easy calculation of the surface areas of porous adsorbents from the high pressure portion of adsorption isotherms. When the adsorbed layer is taken into consideration and when the desorption isotherm is used, pore radii usually give surface areas in good agreement with those obtained by the "Point B" method of Emmett and Braunauer. A tabulation of results by both methods is included for representative vapor–adsorbent systems.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Factors Affecting the Precipitation of Some Insoluble Quinaldates

BY JOHN F. FLAGG AND FRANK T. MCCLURE

Introduction

In the several publications dealing with the use of quinaldic acid (quinoline-2-carboxylic acid) as a precipitant for inorganic ions, considerable attention is given to securing the correct hydrogen ion concentration for precipitation of a given ion, or for its separation from some other ion or ions. The original investigations[1,2] on the use of quinaldic acid dealt mainly with the determination of copper, zinc and cadmium, and the separation of the former two ions from others whose quinaldates under the same conditions were more soluble. Later work by Shennan[3,4] and by Majundar[5] established more precisely some conditions for the precipitation of copper and cadmium, although agreement regarding the exact conditions for separating these ions was not reached.

Considerable work has been done in the field of organic precipitants concerning the effect of *p*H on their mode of action and, while this type of data has been applicable in special cases, it has not been amenable to a more general treatment.

It would appear that the precipitation of a metallic ion by an organic compound (when salt formation is involved) should not differ fundamentally, at least in theory, from the precipitation of, for example, a metallic sulfide. That is, the point of initial precipitation should depend upon (1) the concentration of metallic ion, (2) the concentration of precipitant, and (3) the *p*H. The solubility of the metallo-organic complex, once formed, will depend upon the excess of precipitant and the *p*H of the solution. With data showing the effect of these factors on the quantity of an ion precipitated, it becomes possible to calculate solubility products for the insoluble complexes. Then, using these, it is possible to make useful predictions concerning the behavior of any quantity of metallic ion (or ions) under any of the variable conditions.

We have attempted to collect information of this sort for several of the insoluble quinaldates, particularly the copper, cadmium and zinc salts which are of analytical interest. The line of attack has been as follows: for given concentrations of metallic ion and precipitant, the fraction precipitated has been determined as accurately as possible. Solubility products, and practical applications, have been derived from these data.

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(1) P. R. Ray and M. K. Bose, *Z. anal. Chem.*, **95**, 400 (1933).

(2) P. R. Ray and A. K. Majundar, *ibid.*, **100**, 324 (1935).

(3) R. J. Shennan, *Analyst*, **64**, 14 (1939).

(4) A. J. Lindsey and R. J. Shennan, *ibid.*, **65**, 636 (1940).

(5) A. K. Majundar, *ibid.*, **64**, 874 (1939).

Experimental Part

Quinaldic Acid.—This was prepared by the method of Hammick.[6] Yields of better than 90% of a recrystallized product were obtained; m. p. 156–157° (uncor.), reported m. p. 157°. Hammick's method requires large quantities of bromine, and a method described by Reissert[7] was found to give equally good yields in about the same length of time, at considerably less expense.

The acid was dissolved in water to make solutions approximately 0.05 *M* and 0.03 *M*; these solutions were neutralized to phenolphthalein using dilute sodium hydroxide. The exact molarity was determined by precipitating the quinaldic acid in 20.00 or 25.00 ml. aliquots with excess copper nitrate at a *p*H near 3. The precipitates were filtered on No. 4 Jena glass filtering crucibles, dried to constant weight at 115°, and weighed as $Cu(C_{10}H_6O_2N)_2 \cdot H_2O$.

Copper Nitrate, 0.02238 *M*.—355.7 mg. of pure copper foil was dissolved in 20 ml. of nitric acid; this solution was diluted to 250.0 ml.

Zinc Nitrate, 0.01541 *M*.—251.9 mg. of reagent grade zinc was dissolved in 20 ml. of nitric acid; this solution was diluted to 250.0 ml. The concentration was checked by precipitation with quinaldic acid, as recommended by Ray and Bose.[1]

Cadmium Sulfate, 0.01633 *M*.—Reagent grade cadmium sulfate was dissolved in water, and the solution standardized by precipitating 10.00-ml. aliquots with excess quinaldic acid.[1]

Solutions of other ions, for use in less carefully made studies, were prepared as follows:

Cobalt Sulfate, 0.01013 *M*.—Approximately 2.8 g. of reagent grade $CoSO_4 \cdot 7H_2O$ was dissolved in 1 liter of water. The solution was standardized by electrolysis of 100.0-ml. aliquots.

Nickel Sulfate, 0.0100 *M*.—Prepared by dissolving 2.63 g. of reagent grade $NiSO_4 \cdot 6H_2O$ in water, and standardized by precipitating 25.00-ml. aliquots with dimethylglyoxime.

Palladous Chloride, 0.01 *M*.—Prepared by dissolving 178 mg. of C. P. $PdCl_2$ in 100.0 ml. of water.

Silver Nitrate, 0.01002 *M*.—Prepared by dissolving 1.7020 g. of reagent grade silver nitrate in water and diluting to exactly 1 liter.

The following solutions, approximately 0.01 *M*, were prepared by dissolving the proper quantity of reagent grade salt in water, and diluting to 1 liter: $Hg_2(NO_3)_2$, $Hg(NO_3)_2$, $Pb(NO_3)_2$, Na_2WO_4, $(NH_4)_2MoO_4$.

All other chemicals used were of highest purity obtainable. Normax volumetric ware was used throughout.

Data for the accurate determination of the solubility products of copper, zinc, and cadmium were obtained as follows.

(a) **Copper.**—To 100.0 ml. of water in a 250-ml. beaker was added 10.00 ml. of copper nitrate solution, plus 10.00 ml. of quinaldic acid solution. Dilute sodium hydroxide was then added slowly from a buret, while stirring the solution, until a faint opalescence appeared in the solution. The *p*H at this point was measured with a Beckman glass electrode *p*H meter, calibrated previously with standard buffers. The *p*H measured at this point was probably slightly above the true equilibrium value for initial precipitation, since some solid had precipitated and the end-point had been reached comparatively rapidly. Accordingly, another solution was prepared as before; its *p*H was adjusted to about 0.1 unit less than the former measured value. If no precipitate appeared in this solution after about thirty minutes, another drop of base was added, and longer standing allowed. Eventually, a point was reached at which visible precipitation just began, in about thirty minutes. From the amounts of water, copper nitrate, quinaldic acid, and sodium hydroxide added, the concentrations of copper and quinaldic acid in the solution could be calculated. The *p*H was measured to about 0.02 unit.

Other solutions were then prepared by adding known amounts of copper to 100.0 ml. of water. The *p*H was adjusted as before to values 0.1, 0.2, etc., units higher than the value previously measured. These solutions were heated to boiling and a measured excess of the quinaldic acid solution added. The precipitate that formed was allowed to stand for five to six hours with frequent stirring, after which it was filtered, washed with nitric acid having approximately the same *p*H as the filtrate, dried and weighed. From the known weight of copper taken, the fraction precipitated could be calculated. The measured *p*H of the filtrate (washings not included) was taken to be the equilibrium value under the particular conditions. In some experiments the reactants were added to 50.00 ml. of water.

(b) **Zinc.**—The procedure followed was similar to that used for copper in all details.

(c) **Cadmium.**—The procedure differed from that used for copper and zinc only in that precipitation was made at room temperature.

The conditions used in precipitating the quinaldates were those recommended by the original investigators as giving compounds of definite and reproducible composition.

Data for calculating solubility products of other quinaldates were obtained as follows. To 40.00 ml. of water was added 5.00 ml. of a solution of the ion to be tested, plus 5.00 ml. of quinaldic acid solution. In some cases, 90.0 ml. of water was used to dilute the same quantities of reactants. Then 1 *N* sodium hydroxide or nitric acid was added until the point at which the precipitate would just form (or dissolve) was reached. This point was approached from the acid side several times, and an average *p*H was obtained. This was taken to be the *p*H of initial precipitation, subject to the same qualification as in the previous cases.

Results and Discussion

In Table I are given the results of the experiments, together with the solubility products calculated from them. The following method of calculating the solubility products has been used.

TABLE I

Ion	$[M_0^{+n}]$	$[HQ_0]$	α	*p*H	*pS*
Ag^+	1.00×10^{-3}	3.00×10^{-3}	0	~0	17.9
Cd^{++}	2.33×10^{-3}	8.40×10^{-3}	.976	3.25	12.44
	2.33×10^{-3}	8.40×10^{-3}	.389	2.45	12.14
	2.43×10^{-3}	6.14×10^{-3}	.860	3.19	12.24
				Av.	12.3
Co^{++}	1.0×10^{-3}	3.00×10^{-3}	0	3.50	10.9
	5.0×10^{-4}	1.50×10^{-3}	0	4.10	10.6
				Av.	10.8
Cu^{++}	2.43×10^{-3}	7.71×10^{-3}	0	0.50	15.68[a]
	1.65×10^{-3}	5.23×10^{-3}	.817	0.81	16.94
	1.65×10^{-3}	5.23×10^{-3}	.560	0.68	16.56
	4.13×10^{-4}	13.1×10^{-4}	.441	1.50	16.52
	4.13×10^{-4}	13.1×10^{-4}	.890	1.74	17.20
	4.13×10^{-4}	13.1×10^{-4}	.954	2.00	17.12
				Av.	16.8
Fe^{+++}	1.0×10^{-3}	3.00×10^{-3}	0	0.5	16.9
Hg_2^{++}	1.0×10^{-3}	3.00×10^{-3}	0	~0	17.9
Hg^{++}	2.0×10^{-3}	4.8×10^{-3}	0	0.16	16.8
MoO_4^-	1×10^{-3}	3.00×10^{-3}	>0	<0	..
Ni^{++}	1.00×10^{-3}	3.00×10^{-3}	0	3.90	10.1
Pb^{++}	1.00×10^{-3}	3.00×10^{-3}	0	3.6	10.6
Pd^{++}	1.0×10^{-3}	2.4×10^{-3}	0	2.50	13.0
	5.0×10^{-4}	1.5×10^{-3}	0	2.99	12.8
				Av.	12.9
WO_4^-	1×10^{-3}	3.00×10^{-3}	>0	<0[b]	..
Zn^{++}	1.30×10^{-3}	4.76×10^{-3}	0	1.85	12.78[a]
	1.30×10^{-3}	4.76×10^{-3}	.483	2.30	13.32
	1.30×10^{-3}	4.76×10^{-3}	.900	2.50	14.04
	1.30×10^{-3}	8.90×10^{-3}	.916	2.18	13.84
	1.30×10^{-3}	8.90×10^{-3}	.961	2.35	13.82
				Av.	13.8

[a] Not included in average. [b] Quantitative between *p*H 0 and *p*H 1. Solubility of molybdate and tungstate complexes increases with *p*H; both dissolve completely at *p*H 4.

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[6] D. L. Hammick, *J. Chem. Soc.*, **123**, 2882 (1923).

[7] A. Reissert, *Ber.*, **38**, 1610 (1905).

Consider the equilibrium

$$MQ_2 \rightleftarrows M^{++} + 2Q^-$$

(letting Q^- represent the quinaldate ion, $C_{10}H_6O_2N^-$, and replacing activities by molar concentrations).

$$S = [M^{++}][Q^-]^2 \qquad (1)$$

The ionization constant of quinaldic acid is given as[8]

$$K_a = \frac{[H^+][Q^-]}{[HQ]} = 1.2 \times 10^{-5} \qquad (2)$$

Substituting for $[Q^-]$ in (1)

$$S = \frac{[M^{++}][K_a]^2[HQ]^2}{[H^+]^2}$$

or

$$[H^+] = \frac{K_a\sqrt{[M^{++}]}[HQ]}{\sqrt{S}} \qquad (3)$$

Let $[M_0{}^{++}]$ and $[HQ_0]$ represent initial concentrations of these reactants. When the fraction α of the metallic ion has precipitated

$$[M^{++}] = [M_0{}^{++}](1 - \alpha)$$
$$[HQ] = [HQ_0] - 2\alpha[M_0{}^{++}]$$

At this point, the hydrogen ion concentration will be given by

$$[H^+] = \frac{K_a\sqrt{[M_0{}^{++}](1 - \alpha)}}{\sqrt{S}}\{[HQ_0] - 2\alpha[M_0{}^{++}]\} \qquad (4)$$

Equation (4) was solved for $\sqrt{S}$ from experimental data. The results are included in Table I.

It will be noted that the solubility products calculated from the point $\alpha = 0$ for copper and zinc have not been included in the average calculated from the other points. It would appear that the recorded *p*H values are considerably too high, and that precipitation should take place under those conditions much nearer *p*H zero.

In the case of the other ions we have relied, however, upon these points to calculate the solubility products. While this can only lead to approximate values, they may yet suffice for many practical purposes. The silver and mercury quinaldates, for example, precipitate at such low *p*H's that their interference in any analysis could not be avoided, while the more soluble nickel, cobalt and lead quinaldates are not likely to interfere in the region around *p*H 2-3, where copper, zinc, and cadmium are usually precipitated. In fact, it is not at all certain that at these higher *p*H values a quinaldate of definite composition precipitates. The lead quinaldate precipitates have been analyzed and found to contain more than the theoretical amount of lead that would correspond to the formula $Pb(C_{10}H_6O_2N)_2$. These latter solubility products must be taken as extremely rough, indicating the order of magnitude only, and probably too high.

Applications

Several applications of practical interest may be made from the foregoing data.

1. **Calculation of Minimum *p*H for Precipitation.**—The minimum *p*H necessary for quantitative precipitation of a given quantity of copper, zinc, or cadmium with a given amount of quinaldic acid may be predicted. Since the *p*H range for complete precipitation of an ion is generally large, it is frequently necessary to know only the lowest *p*H at which all of an ion will be precipitated. If the maximum quantity of cation present be estimated, and some given excess of quinaldic acid used for precipitation, then if $[HQ_0]/[M_0{}^{++}] = R$, the $[H^+]$ required for 99.9% precipitation may be calculated from the relation

$$[H^+] = \frac{3.79 \times 10^{-7}}{\sqrt{S_M}}[M_0{}^{++}]^{3/2}(R - 2)$$

2. **Predict the Possibility of Separation.**—The conditions for separating two ions, each of which forms an insoluble quinaldate, may be established in the following manner. First, the minimum *p*H required for 99.9% precipitation of M^{++}, using an excess of quinaldic acid sufficient to react with both ions, is calculated. This is done as indicated previously. Then the *p*H at which N^{++} begins to precipitate is calculated, assuming that in the solution after precipitation of M^{++}, the concentration of quinaldic acid is $[HQ_0] - 2[M^{++}]$. The hydrogen ion concentration at the point of initial precipitation of N^{++} is given by

$$[H^+] = \frac{1.2 \times 10^{-5}}{\sqrt{S_N}}[N_0{}^{++}]^{3/2}R'$$

in which R' is the new ratio, $[HQ]/[N_0{}^{++}]$.

If pH_N is greater than pH_M, a separation is theoretically possible. The safe range for the precipitation would be $pH_N - pH_M$, and the value chosen for precipitation would be $(pH_N + pH_M)/2$. If pH_M equalled or were less than pH_N, no separation would be possible.

Two cases of separations are cited to show the applicability of this treatment.

(a) **The Separation of Copper from Zinc.**—Coprecipitation of zinc with copper quinaldate has been reported[9] to make the separation of copper from zinc impossible when using quinaldic acid. This may be the case under certain conditions, but not under all conditions. By the method outlined above, it can be shown that with certain combinations of copper, zinc, and quinaldic acid a separation can be made. Specifically, if there is about 10% as much zinc as copper, and a two-fold excess of quinaldic acid over that required to precipitate the copper, a separation at or near *p*H 1 should be possible.

To test this, a solution was prepared containing 63.62 mg. of copper and 6.50 mg. of zinc in 50.00 ml. The *p*H was adjusted to 0.88 by means of solid sodium carbonate, the solution heated to boiling, and treated with 50.00 ml. of a solution containing 0.6920 g. of pure quinaldic acid. The precipitate of copper quinaldate was filtered

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[8] W. Ostwald, *Z. physik. Chem.*, **3**, 395 (1889).

[9] P. R. Ray and N. K. Dutt, *Z. anal. Chem.*, **115**, 265 (1939).

after twenty minutes, washed with nitric acid of *p*H 1, and dried in the usual manner. The *p*H of the filtrate was 1.10. In two experiments, 63.4 and 63.5 mg., respectively, of copper was found. The precipitates of copper quinaldate were examined spectrographically for zinc, and faint lines at 3345, 3072 and 3035 Å. were observed. No attempt was made to estimate the amount of zinc present. The filtrate from one determination gave a negative test for copper with hydrogen sulfide. As the results were slightly low, it would appear that no appreciable amount of zinc had been entrained; likewise, no copper remained unprecipitated.

In the above solution, copper should be quantitatively precipitated at *p*H 0.72 and upward, while zinc begins to precipitate at *p*H 1.22. A better separation would doubtless have been obtained at a lower *p*H, even though only enough zinc precipitated to be detected spectroscopically under the conditions used.

(b) **The Separation of Copper from Cadmium.**—Majundar[5] and Shennan[3,4] have disagreed on the feasibility of this separation. Recalculating some data given by Majundar,[5] it appears that with $[Cu^{++}] = 2 \times 10^{-3}$ and $[Cd^{++}] = 2.5 \times 10^{-3}$, and using about 5×10^{-3} molar quinaldic acid, a quantitative separation of the copper was obtained at a *p*H of about 2. This corresponds closely to the theoretical value, as nearly as it can be estimated using the approximate molar concentrations calculated from the experiments described.

It can be shown that the safe range for separation of equimolar quantities of copper and cadmium is about 0.7 *p*H unit, with cadmium quinaldate precipitating at the higher value. Thus the results of Majundar,[5] which are satisfactory from an analytical standpoint, also seem well based theoretically.

Separations involving other ions listed in Table I may be treated analogously. Certain quinaldates, such as silver, mercury (I) and (II), tungsten, and molybdenum, are insoluble at such low *p*H values that their interference in any determination of copper, zinc, or cadmium would be certain.

3. **Calculation of Fraction Precipitated.**—A third possible application of this type of data is the calculation, for any given concentration of metallic ion, hydrogen ion, and precipitant, of the fraction that will precipitate. If the ratio of quinaldic acid to metallic ion is R, then $R = [HQ_0]/[M_0^{++}]$, and α is given by

$$-4\alpha^3 + 4\alpha^2(R+1) - \alpha(4R+R^2) + R^2 = \frac{[H^+]^2 S}{[M_0^{++}]^3[K_a]^2}$$

The solution of the cubic equation is most readily found by making successive approximations, as the useful root will lie between zero and one.

The authors wish to acknowledge the assistance of Mr. Roman Dreywood in preparing the quinaldic acid, and in conducting qualitative tests on the reactions of quinaldic acid.

Summary

1. The solubility products of some insoluble quinaldates have been determined by a method involving fractional precipitation.

2. Applications of solubility data to problems of precipitation and separation with quinaldic acid are cited.

ROCHESTER, NEW YORK RECEIVED JULY 29, 1943

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY AND THE SPECTROGRAPHIC LABORATORY OF THE MEDICAL CENTER OF THE UNIVERSITY OF CALIFORNIA]

The Ultraviolet Absorption Spectra and Resonance in Benzene Derivatives—Sulfanilamide, Metanilamide, *p*-Aminobenzoic Acid, Benzenesulfonamide, Benzoic Acid and Aniline

BY W. D. KUMLER AND L. A. STRAIT

It is well known that the absorption of light by molecules is associated with the phenomenon of resonance.[1,2,3,4] In this communication are reported measurements of the absorption spectra of some benzene derivatives in acid, basic and water or sodium chloride solutions. An interpretation of the resulting spectra is given in terms of the resonance forms used by organic chemists for about a decade[5,6,7,8] to account for various other properties of such molecules.

Experimental

The spectrophotometric data were obtained with the aid of a Hilger Spekker photometer and a Hilger medium quartz flat-field spectrograph (E498). The source of ultraviolet light was the continuous spectrum of hydrogen

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[1] Bury, THIS JOURNAL, **57**, 2115 (1935).

[2] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

[3] Sklar, *J. Chem. Phys.*, **5**, 669 (1937).

[4] Pauling, *Proc. Natl. Acad. Sci.*, **25**, 557 (1939).

[5] Ingold, *Chem. Rev.*, **15**, 225 (1934).

[6] Kumler and Porter, THIS JOURNAL, **56**, 2549 (1934).

[7] Sutton, *Trans. Faraday Soc.*, **30**, 789 (1934).

[8] Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941.