

canted. Addition of a small amount of ether gave a second oily layer which also was separated. On further addition of ether and scratching, crystallization commenced and was allowed to proceed on standing in a cold room at 2–5°. The solution was filtered, yielding 1 g. of a hydrochloride; m. p. 110–120°. This was recrystallized by dissolving in a minimum of absolute alcohol, adding 2–3 volumes of acetone and finally ether until crystallization took place; m. p. 123–125°. This hydrochloride gave a strong positive ferric chloride test similar to that shown by vitamin B₆.

Anal. Calcd. for C₁₀H₁₆O₃NCl: C, 51.39; H, 6.85; N, 6.00. Found: C, 51.14; H, 7.12; N, 6.49.

2-Methyl-3-hydroxy-4,5-di-(bromomethyl)-pyridine Hydrobromide, XI.—A solution containing 0.5 g. of the hydrochloride of 2-methyl-3-hydroxy-4-ethoxy-methyl-5-hydroxymethylpyridine, X, in 25 cc. of 48% hydrobromic acid was heated at the boiling point for ten minutes. On cooling in ice water, crystals separated and were filtered, washed with water, acetone and ether; m. p. 223–224°, showing partial decomposition at 219°; yield 0.53 g. (66%).

This compound apparently is identical with the one described by Kuhn and Wendt¹⁴ as having a melting point of 217°. They obtained it from the β -methyl ether of natural vitamin B₆ by the use of 66% hydrobromic acid.

Anal. Calcd. for C₈H₁₀ONBr₃: C, 25.53; H, 2.66; N, 3.72. Found: C, 25.95, 25.90; H, 2.89, 2.84; N, 3.73.

Vitamin B₆ Hydrochloride or 2-Methyl-3-hydroxy-4,5-di-(hydroxymethyl)-pyridine Hydrochloride, XII.—The 2-

(14) Kuhn and Wendt, *Ber.*, **72**, 311 (1939).

methyl-3-hydroxy-4,5-di-(bromomethyl)-pyridine hydrobromide (1.78 g.), XI, was converted to vitamin B₆ hydrochloride by boiling in 150 cc. of water for twenty minutes and removing the bromide ions with freshly prepared silver chloride. The filtrate was evaporated to dryness, dissolved in 1 cc. of water and 5 cc. of alcohol, filtered with charcoal and crystallized by adding acetone; m. p. 206–208°, mixed m. p. with natural vitamin B₆ hydrochloride, 206–208°. The yield was 0.42 g. of crystals plus 0.30 g. of crystalline residue making the total yield about 75%.

Anal. Calcd. for C₈H₁₂NO₃Cl: C, 46.72; H, 5.84; N, 6.81. Found: C, 46.64; H, 5.69; N, 6.75.

Acknowledgments.—The authors wish to thank Drs. Major, Engels, Stevens and Keresztesy for helpful advice and encouragement, Messrs. Hayman and Reiss for the microanalyses, and Messrs. Sletzing and Wilson for technical assistance.

Summary

A complete synthesis of vitamin B₆ starting with ethoxyacetylacetone and cyanoacetamide has been accomplished. The synthetic vitamin B₆ hydrochloride is identical with the natural vitamin B₆ hydrochloride. A single dose of 100 gamma of synthetic vitamin B₆ hydrochloride gave a curative effect which paralleled that of the natural vitamin B₆.

RAHWAY, N. J.

RECEIVED APRIL 11, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MICHIGAN COLLEGE OF MINING AND TECHNOLOGY]

Chelate Compounds as Flotation Reagents. I

BY C. C. DE WITT AND FREDERICK VON BATCHELDER

The purpose of this paper is to present quantitative data obtained with a new series of flotation reagents.¹ The present report deals with a compound of known chelate structure, salicylaldoxime, and its isomers, meta and para hydroxybenzaldoxime. It is perhaps significant that the ortho derivative when used as a flotation reagent recovers in commercial yields not only the copper sulfides, but also the copper carbonates and cuprous oxide from a siliceous gangue. The only existing report on the use of oximes as flotation reagents of which the authors are aware is that of Holman,² who used dimethylglyoxime as a flotation reagent for the recovery of oxidized nickel ores.

(1) Previous work by the senior author in this Laboratory had shown the effectiveness of certain chelate compounds including salicylaldoxime in the separation of heavy metal minerals from siliceous gangue.

(2) B. W. Holman, *Bull. Inst. Min. and Met. Nr.*, 314 (1930).

Preparation of Oximes.—Salicylaldoxime and the *m*- and *p*-hydroxybenzaloximes were prepared by the method of Brady and Dunn.³ The crude salicylaldehyde⁴ was purified by bisulfite precipitation, washing this precipitate with alcohol to remove phenol, etc., followed by recrystallization from water, acidification and steam distillation, drying, and finally distillation at atmospheric pressure. The *m*- and *p*-hydroxybenzaldehydes were Eastman best grade; these were carefully recrystallized from alcohol.

Preparation of Synthetic Copper Ores.—The copper minerals used were authentic, massive samples of relatively pure chalcocite, covellite, azurite, malachite and cuprite procured from a reputable source. These samples were examined mineralogically by Professor W. A. Seaman and analyzed for copper content in this Laboratory. These minerals were crushed and sized. Those portions which passed through a 40-mesh sieve and were retained on a 60-mesh sieve were reserved for flotation tests. The

(3) Brady and Dunn, *J. Chem. Soc.*, **105**, 821 (1914).

(4) Acknowledgment is made to the Dow Chemical Company for generous amounts of crude salicylaldehyde supplied for this work.

gangue material selected was of siliceous nature. It was likewise crushed and sized to pass a 40-mesh sieve and be retained on a 60-mesh sieve. The analyses were as follows

	Cu found, %	Cu calcd., %
Chalcocite, Cu_2S	74.79	79.75
Covellite, CuS	61.0	66.45
Azurite, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	45.8	55.25
Malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	51.1	57.5
Cuprite, Cu_2O	68.15	88.82

The sulfide samples contained siliceous material and small amounts of pyrites. The azurite and malachite both contained notable amounts of calcite and siliceous materials. The cuprite contained larger amounts of siliceous material.

Frothing Agent.—The pine oil used as frothing agent was the regular flotation grade furnished by the Hercules Powder Company. It was used in the form of an ethanol solution, one volume of pine oil to nine volumes of ethanol. The amount used in each flotation run was 2.5 mg. for each 50-g. sample (0.2 lb. per ton).

pH Measurements.—pH measurements were made by means of the quinhydrone electrode. These measurements were checked frequently by use of the glass electrode. pH measurements were made on the liquid remaining in the flotation cell after the tests were completed. Adjustments of pH were made before the test by the addition of acid or alkali.

Flotation Cell.—The flotation cell used was the 50-g. enameled cast iron type formerly sold by the Reilly Tar and Chemical Company. The cell stirrer speed was 1750 r. p. m.

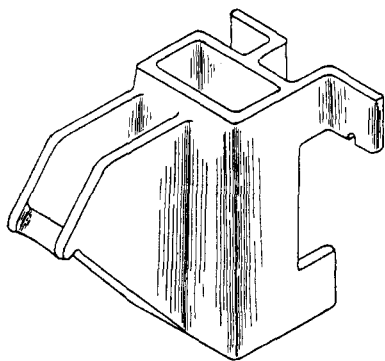


Fig. 1.—Flotation cell.

Operative Technique.—The general technique for the runs was as follows: 50 g. of the siliceous gangue material was placed in the cell together with exactly 0.5 g. of the ore. Approximately 200 cc. of distilled water was added and the stirrer started. Then the stated amount of oxime in water solution was added. Stirring was continued for three minutes and then 2.5 mg. of pine oil was added. The frothing began almost immediately. The froth was collected over a period of three minutes, filtered on a Gooch crucible, dried, weighed and analyzed for copper content. The residual gangue was likewise treated and analyzed in several instances to ascertain whether any inconsistencies developed due to previous errors in the analysis of the ore.

Since none were found in the course of the work, these analyses were not reported.

TABLE I
FLOTATION OF COPPER MINERALS BY SALICYLALDOXIME

pH	Oxime, g.	Lb. oxime per ton	G. concn.	Cu recov., %
Chalcocite				
4.9	0.0025	0.1	0.246	1.33
4.5	.005	.2	.491	36.3
4.9	.01	.4	.779	65.0
4.3	.05	2.0	.697	75.1
4.1	.05	2.0	1.052	83.1
4.0	.05	2.0	...	83.6
4.0	.100	4.0	1.390	91.7
3.6	.200	8.0	1.551	79.7
4.6	.000	0.0	1.013	0.54
Malachite				
5.5	0.0000	0.00	0.825	2.3
4.95	.005	.2	.246	5.63
4.7	.01	.4	.563	90.0
4.3	.05	2.0	.736	97.0
4.8	.05	2.0	1.053	97.7
4.0	.100	4.0	1.171	97.0
Covellite				
4.8	0.0000	0.00	1.071	70.5
4.6	.0025	.1	0.665	81.6
4.6	.005	.2	.658	86.2
4.9	.01	.4	.717	91.4
4.7	.01	.4	.920	95.8
4.7	.02	.8	.953	96.4
4.2	.05	2.0	1.093	97.6
Azurite				
4.6	0.000	0.00	0.947	1.88
4.4	.005	.2	.244	3.47
4.6	.01	.4	.613	81.8
4.6	.05	2.0	.739	95.6
3.9	.05	2.0	.731	97.3
4.4	.100	4.0	1.097	96.3
Cuprite				
4.8	0.0000	0.00	0.662	0.44
5.3	.01	.4	.228	3.75
4.1	.100	4.0	.600	39.8
4.1	.200	8.0	1.091	89.7
4.3	.500	20.0	1.393	78.0
Chalcocite, Covellite, Malachite, Azurite and Cuprite				
4.8	0.0000	0.00	1.032	0.62
4.6	.005	.2	0.594	27.2
4.3	.01	.4	.635	66.2
4.1	.05	2.0	.720	80.5
4.1	.100	4.0	.864	84.1

Discussion

In order to be effective as a flotation reagent an organic compound must possess several characteristics. Most important of these characteristics are: (1) the reagent must be selectively adsorbed on or react with the surface of the min-

TABLE II
FLOTATION OF COPPER MINERALS BY *m*-HYDROXYBENZAL-

<i>p</i> H	Oxime, g.	Lb. oxime per ton	G. concn.	Cu recov., %
Chalcocite				
4.6	0.0000	0.00	1.013	0.54
3.9	.1	4.0	0.896	2.03
4.3	.5	20.0	1.094	9.63
Malachite				
5.5	0.0000	0.00	0.825	2.3
...	.200	8.00	.334	2.3
5.0	.500	20.00	.543	2.68
Covellite				
4.8	0.0000	0.00	1.152	71.5
4.6	.100	4.0	1.006	61.6
Azurite				
4.6	0.0000	0.00	0.947	1.88
5.2	.200	8.0	.774	1.40
Cuprite				
4.8	0.0000	0.00	0.662	0.44
4.5	.2	8.0	.794	1.17

TABLE III
FLOTATION OF COPPER MINERALS BY *p*-HYDROXYBENZAL-

<i>p</i> H	Oxime, g.	Lb. oxime per ton	G. concn.	Cu recov., %
Chalcocite				
4.6	0.0000	0.00	1.013	0.54
4.8	.100	4.0	0.509	0.4
4.4	.200	8.0	.458	4.5
Malachite				
5.5	0.0000	0.00	0.825	2.3
4.9	.200	8.0	.614	2.68
Covellite				
4.8	0.0000	0.00	1.152	71.5
4.7	.1	4.0	0.682	66.7
Azurite				
4.6	0.0000	0.00	0.947	1.88
4.8	.200	8.0	.607	1.22
Cuprite				
4.8	0.0000	0.00	0.662	0.44
4.5	.200	8.00	.573	0.82

eral particle; (2) any reaction product must adhere tenaciously to the mineral surface; (3) the reagent used must not precipitate from the solution any material which adsorbed on the surface of the gangue will cause the latter to float as if it were the sought mineral; (4) the slopes of the surface tension-concentration curves of

the water solutions of flotation reagents found useful to date are negative.

The objective of items (1) and (2) is apparent in that the purpose of a flotation reagent is to cover the mineral particle at least partially with a film of an organic compound. Item (3) requires that the heavy metal ions be substantially absent from the solution, or that the solubility product of the metallic compound which might be precipitated by the addition of the flotation reagent be so large that it will have no sensible effect on the subsequent flotation. Or, if precipitation does occur, the particles in a colloidal state of subdivision must have an electric charge of the same magnitude and sign as the gangue material.

In the present paper advantage is taken of the peculiar characteristics of the chelate compounds, particularly of salicylaldoxime. The function of the ortho hydroxyl group in giving such compounds chelate structures has long been known. In the present argument it is of interest to relate that when the ortho hydroxyl group is replaced by a methoxy group the resulting methoxybenzaloxime is no longer of any use in the present work as a flotation reagent.

Reference to the various tables shows that in general the presence of small amounts of the salicylaldoxime causes a lowering of the total amount of gangue material per unit of copper recovered. This same effect is noticeable to a lesser degree with the meta and para hydroxybenzaloximes.

It should be emphasized that the gangue was siliceous in nature. The separation of copper carbonates and oxides as well as sulfides from alkaline earth gangues will be the subject of a later paper. Other known chelate compounds are at present under observation as to their ability to effect the separation of heavy metal minerals from their various gangue materials.

Summary

Data are presented which show that salicylaldoxime is an effective flotation reagent for the separation of chalcocite, covellite, azurite, malachite and cuprite from siliceous gangue materials.