Oct., 1936

The tie lines do not all pass exactly through the points corresponding to the composition of the three solid phases mentioned, but it must be considered that the analytical errors become greatly magnified as the tie lines are extended. No evidence of the existence of solid phases other than the three mentioned was obtained. So far as the writers are aware, the compound MgSO4·CO- $(NH_2)_2 \cdot 3H_2O$  has not been reported previously.

A curious feature of this isotherm is the practically unchanged solubility of magnesium sulfate over a wide range of urea concentration (0-21%). Mixtures of solid urea and MgSO4·7H2O, of such composition that the resulting equilibrium solution falls in the range represented by the middle branch of the isotherm, at first go completely or almost completely into solution, but on continued stirring the reaction

 $MgSO_4 \cdot 7H_2O + CO(NH_2)_2 =$ 

 $MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O + 4H_2O$ 

takes place quite rapidly and is probably complete in an hour or so after it starts. The crystals of the complex so obtained are very small. Attempts to prepare large crystals for detailed examination have, so far, been unsuccessful.



Fig. 1.—The system magnesium sulfate-urea-H<sub>2</sub>O at 30°.

#### Summary

Data were obtained establishing the 30° isotherm of the system magnesium sulfate-ureawater. It was found to consist of three branches corresponding to the solid phases MgSO<sub>4</sub>·7H<sub>2</sub>O,  $MgSO_{i} \cdot CO(NH_{2})_{2} \cdot 3H_{2}O$  and  $CO(NH_{2})_{2}$ . WASHINGTON, D. C.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE COLLEGE]

# Optical Crystallographic Data for Some Salts of the Cinchona Alkaloids

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### Introduction

Very few data on the optical properties of the salts of quinine, quinidine, cinchonidine and cinchonine can be found in the literature. Groth,<sup>1</sup> Poe and Swisher,<sup>2</sup> Wright,<sup>3</sup> and Wherry and Yanovsky<sup>4</sup> have listed some optical properties of these four alkaloids. However, the information is very scant.

Many salts of quinine were available, while just a few of quinidine, cinchonidine and cinchonine could be obtained. All salts were of commercial origin.

### **Optical Crystallographic Data**

The optical properties, given in the table, were

- (2) Poe and Swisher, THIS JOURNAL, 57, 748 (1935).
- (3) Wright, ibid., 38, 1647 (1916).
- (4) Wherry and Yanovsky, ibid., 40, 1063 (1918).

determined by methods given by Chamot and Mason.<sup>5</sup> Refractive indices were determined by the Becke line method. In several cases it was impossible to determine the indices because the crystals dissolved in the immersion oils. The quartz wedge and selenite plate were used in various determinations.

The fluorescence of the salt and its aqueous solution were determined by means of an ultraviolet lamp.

All crystals were found to be biaxial and to give parallel extinction, except in the case of quinine bihydrochloride carbamate and quinine tetrasulfate where oblique extinction was obtained. The sign of elongation was positive in all cases except quinine nitrate and picrate.

<sup>(1)</sup> Groth, "Chemische Krystallographie," 1908-1919.

<sup>(5)</sup> Chamot and Mason, "Handbook of Chemical Microscopy." Vol. I, John Wiley and Sons, Inc., New York, New York, 1930.

TABLE I

QUININE									
Salt	Color	Soly. in water	Habit	Refractive indices Alpha Beta Gamma		Bire- fringence	Fluo <b>resce</b> nce Salt Soln.		
Acetate	Colorless	Soluble	Needles	••	1.62	1.68	Weak	Neg.	Blue
Anisate	Yellow	Insol.	Diamond	1.58	1.62	••	Moderate	Faint	Faint
Arsenate	Pink	Insol.	Rods	1.61	1.62	1.69	Strong	Neg.	Blue
Benzoate	Colorless	Insol.	Rods	1.60	1.66	1.69	Strong	Neg.	Blue
Bihydrobromide	Yellow	Slight	Rods	1.58	1.61	1.69	Strong	Yellow	Blue
Bihydrochloride carbamate	Colorless	Slight	Rods	1.58	1.64	1.72	Strong	Faint	Blue
Bisulfate	Colorless	Soluble	Rods	1.58		1.67	Strong	Blue	Intense blue
Borate	Yellow	Insol.	Plates	••	••	• •		Yellow	Green
Camphorate	Yellow	-Insol.	Rods	1.58	1.61	1.62	Moderate	Neg.	Intense blue
Chlorate	Colorless	Soluble	Rođs	1.62	1.64	1.69	Moderate	Neg.	Intense blue
Chromate	Yellow	Insol.	Rođs	••	1.65	1.69	Moderate	Neg.	Neg.
Citrate	Colorless	Insol.	Rođs	1.58	1.65	••	Strong	Faint	Intense blue
Ferrocitrate	Yellow	Insol.	Plates	••		••		Neg.	Green
Formate	Colorless	Insol.	Rođs	••	1.62	1.69	Strong	Neg.	Intense blue
Hydrobromide	Colorless	Insol.	Rods	1.61	1.63	1.68	Strong	Neg.	Intense blue
Hydrochloride	Colorless	Soluble	Rođs	1.59	1.61	1.67	Strong	Neg.	Intense blue
Hydroferrocyanide	Green	Insol.	Amorph.		••	••		Neg.	Faint
Hydrofluosilicate	Colorless	Insol.	Rods	1.56	1.58	1.62	Strong	Neg.	Intense blue
Hypophosphite	Colorless	Slight	Rođs	1.69	1.62	1.65	Moderate	Faint	Intense blue
Hyposulfite	Colorless	Pptd.	Rods		1.64	1.70	Strong	Neg.	Neg.
Lactate	Brown	Insol.	Amorph.	••	••	• •		Neg.	Green
Nitrate	Orange	Insol.	Rods	1.56	1.61	1.64	Strong	Neg.	Intense blue
Oxalate	Colorless	Insol.	Rods	1.60	1.61	1.69	Strong	Neg.	Intense blue
Phosphate	Colorless	Insol.	Rođs	1.58		1.64	Moderate	Neg.	Faint
Phthalate	Colorless	Soluble	Rođs	1.61	1.62	1.69	Moderate	Neg.	Intense blue
Picrate	Yellow	Insol.	Rođs	1.61	1.64	1.72	Strong	Neg.	Green
Ouinolate	Colorless	Insol.	Amorph.					Neg.	Faint
Salicylate	Colorless	Insol.	Rods	1.62	1.63	1.67	Strong	Faint	Intense blue
Succinate	Colorless	Insol.	Rods		1.59	1.68	Strong	Neg.	Intense blue
Sulfate	Colorless	Insol.	Rods	1.62	1.63	1.67	Moderate	Neg.	Intense blue
Sulfoiodide	Grav	Insol.	Plates					Neg.	Intense blue
Tannate	Vellow	Insol.	Amorph.					Neg.	Intense blue
Thiocyanate	Colorless	Slight	Rods		1.61	1.69	Moderate	Neg.	Intense blue
Valerate	Brown	Insol	Plates					Faint	Intense blue
TT - Just manual J	0-11	0-1-1-1-	Dede	1 50	1 60	1 60	Sterra	Faint	Interne blue
Hydrobromide	Colorless	Soluble	Rods	1.08	1.00	1.08	Strong	Fame	Intense blue
Sulfate	Colorless	Soluble	Rods	1.59	1,01	1.05	Moderate	ineg.	Intense blue
CINCHONIDINE									
Free base	Colorless	Insol.	Rods	1.61	1.62	1.68	Moderate	Neg.	Neg.
Acetate	Colorless	Slight	Rođs	1.59	1.61	1.64	Moderate	Neg.	Faint
Bihydrochloride	Colorless	Slight	Rođs	1.59	••	1.70	Strong	Slight	Faint
Hydrobromide	Colorless	Insol.	Rođs	••	1.66	1.72	Strong	Neg.	Neg.
Hydrochloride	Colorless	Insol.	Fragments	••	••	••	• • • • •	Neg.	Neg.
Tetrasulfate	Colorless	Slight	Rođs	1.55	1.56	1.65	Strong	Bright	Intense blue
Cinchonine									
Free base	Colorless	Insol.	Rođs	1.58	1.62	1.69	Strong	Neg.	Neg.
Bisulfate	Colorless	Insol.	Rods	1.56		1.62	Moderate	Blue	Blue
Hydrobromide	Colorless	Insol.	Rods	1.61		1.69	Moderate	Neg.	Neg.
Hydrochloride	Colorless	Soluble	Rods	1.55	1.62	1.67	Strong	Neg.	Faint
Sulfate	Colorless	Insol.	Rods	1.59	1.64	1.66	Moderate	Neg.	Faint
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## Summary

The crystallographic data for four cinchona alkaloids—quinine, quinidine, cinchonine and

cinchonidine—have been worked out. The fluorescent properties in ultraviolet light also have been determined.

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