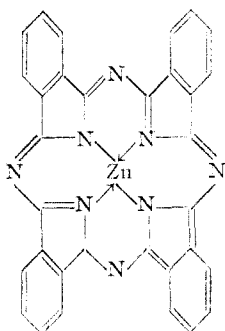


Fig. 13.—Zinc phthalocyanine in polar media.

(and thereby the porphine macrocyclic compounds in general).

Our spectrophotometric measurements on the phthalocyanines, exemplified by *zinc phthalocya-*



nine show no definite effect of polar moment of solvent on the absorption (Fig. 13). This indifference may be taken to mean that no ionized (dipolar) structures are represented in the first excited state; the resonance system is presumably by way of the two alternately covalently and coordinately

linked pairs of the four interior N-atoms,¹⁷ through

(17) The conjugation extends, of course, through the external —N= links.

the central atom, making the system resemble benzene with its basic Kekulé resonance. A notable difference from benzene, however, is the great intensity (extinction) of the longest wave absorption band.

Acknowledgment.—We desire to express our thanks for helpful suggestions and criticisms to Dr. M. L. Huggins, and to Mr. H. R. Brigham for the preparation and spectrophotometry of sublimed solid films of certain dyes.

Conclusion

The results presented in this paper extend the tentative conclusions expressed in Part I. So far as these orienting investigations go, they indicate that the sensitivity of the absorption spectra of dyes to solvent influence is rather closely related to the resonance system of the dye, and may throw some light upon this. Correlatively, it appears possible that, with increased investigation, the effect of given solvents on the absorption spectrum of selected dyes may improve our understanding of the molecular structure of liquids. The rather notable behavior of halogenated alkyls suggests a promising field for further investigation as also the observations on hydroxylated solvents.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Solubility of Calcium Oxalate Monohydrate in Pure Water and Various Neutral Salt Solutions at 25°

BY WILBUR H. MCCOMAS, JR.,¹ AND WM. RIEMAN III

Because of the importance of calcium oxalate in analytical work, accurate data on its solubility are very desirable. A survey of the literature reveals, however, very discordant figures for the solubility in pure water and very few reliable data on the effect of neutral salts.² Table I summarizes the previous work on the solubility in pure water. Since the equilibrium between calcium oxalate and its saturated solution is established rather quickly, the major source of error in

the solubility determinations probably lies in the failure to obtain pure calcium oxalate.

Solubility in Pure Water

Experimental.—Calcium oxalate monohydrate, product A, was prepared as follows:^{2a} fifty mmol. of ammonium oxalate contained in 400 ml. was added slowly (twenty-five minutes) with vigorous stirring to 60 mmol. of calcium chloride contained in 1600 ml. at room temperature. Then 200 ml. of 0.1 *N* hydrochloric acid was added with vigorous stirring. The precipitate was digested for one day at 95–100°. After cooling, the precipitate was washed by centrifugation until a negative test for chloride ion was obtained in the wash water. It was stored under water until used.

(1) This paper is taken from part of a thesis submitted by Wilbur H. McComas, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Hammersten, *Compt. rend. trav. lab. Carlsberg*, **17**, 11 (1929), has studied the effect of several salts at 37°, mostly at ionic strengths below 0.2.

(2a) Kolthoff and Sandell, *J. Phys. Chem.*, **37**, 459 (1933).

TABLE I

SOLUBILITY OF CALCIUM OXALATE IN PURE WATER AT 25°

Investigator	Solubility, molarity $\times 10^5$
Richards, McCaffrey and Bisbee ³	5.31
Herz and Muhs ⁴	23.3
Kohlrausch ⁵	4.84
Henderson and Taylor ⁶	7.13
Scholder, Gadenne and Niemann ⁷	5.23 ^a
Hammarsten ²	4.66 ^a
Medes ⁸	4.46 ^a
Kolthoff and Sandell ⁹	6.70
Pedersen ¹⁰	4.84
Shehyn and Pall ¹¹	6.00 ^a

^a Solubility at 25° calculated from Kohlrausch's value of $d \log \text{solubility}/d(1/T)$.

Product B was prepared by an identical method except that the precipitation was performed in the presence of excess oxalate ions. Fifty mmol. of calcium chloride in 400 ml. were added to 60 mmol. of ammonium oxalate in 1600 ml., etc.

The solubility of each product was determined by agitating about a gram of precipitate with two liters of pure water for an hour at 25.0 \pm 0.2°. Longer periods of saturation did not alter the result. The solution was separated from the precipitate by means of a porcelain micro filter stick. The first portions of the filtrate were rejected. Then 200-ml. portions were titrated with 0.02 *N* ceric sulfate by the method of Willard and Young.¹² Appropriate blank titrations were performed. The mean of six determinations for the solubility of product A was $(4.46 \pm 0.04) \times 10^{-5}$ molar. The mean of seven determinations for product B was $(4.63 \pm 0.03) \times 10^{-5}$ molar.

Discussion.—The close agreement between these two results is evidence for the purity of the products. The mean, 4.55×10^{-5} *M*, is in good agreement with the results of Kohlrausch, Hammarsten, Medes and Pedersen.

Solubility in Salt Solutions

Experimental.—About 1 g. of the pure calcium oxalate monohydrate in aqueous suspension was centrifuged and

(3) Richards, McCaffrey and Bisbee, *Z. anorg. Chem.*, **28**, 71 (1901).

(4) Herz and Muhs, *Ber.*, **36**, 3717 (1903).

(5) Kohlrausch, *Z. physik. Chem.*, **64**, 129 (1908).

(6) Henderson and Taylor, *J. Phys. Chem.*, **20**, 663 (1916).

(7) Scholder, Gadenne and Niemann, *Ber.*, **60**, 1510 (1927).

(8) Medes, *Proc. Soc. Exp. Biol. Med.*, **30**, 281 (1932).

(9) Kolthoff and Sandell, *THIS JOURNAL*, **55**, 2170 (1933).

(10) Pedersen, *ibid.*, **61**, 334 (1939).

(11) Shehyn and Pall, *J. Phys. Chem.*, **44**, 166 (1940).

(12) Willard and Young, *THIS JOURNAL*, **55**, 3260 (1933).

washed three times with portions of the standard salt solution. This precipitate was then added to about 2 liters of the standard salt solution, and the solubility was determined as in pure water.

Results.—The results are given in Table II. Each value in Column 4 is the mean of six determinations.

TABLE II

SOLUBILITY OF CALCIUM OXALATE IN SALT SOLUTIONS

Salt	Molarity of salt	Ionic strength	Solubility, molarity $\times 10^5$	pS'	
				Found	Calculated
None	0.000	0.00018	4.55	8.684	8.670
NaCl	.100	.100	11.79	7.856	7.815
	.200	.20	15.47	7.621	7.623
	.300	.30	17.64	7.507	7.505
	.400	.40	19.50	7.420	7.415
	.500	.50	21.10	7.350	7.353
	.600	.60	22.58	7.292	7.300
	.700	.70	23.79	7.247	7.255
	.800	.80	24.82	7.210	7.216
	.900	.90	26.10	7.166	7.182
	1.000	1.00	27.08	7.135	7.151
KCl	0.64	0.64	22.99	7.277	7.281
HCOONH ₄	.36	.36	22.34	7.302	7.450
Na ₂ SO ₄	.213	.64	34.94	6.913	7.282

Since none of the solutions listed in Table II were sufficiently acid to change significant quantities of secondary oxalate ion to the primary anion, the classical solubility product, S' , is simply the square of the molar solubility. Extrapolation of the experimental values of pS' to $\mu = 0$, gives 8.730 for the thermodynamic solubility exponent, pS . This figure was then used in conjunction with the equation of Gronwall, LaMer and Sandved¹³ to calculate theoretical values of pS' . When a is 4.85 Å., the figures of Column 6 are obtained. These values are in good agreement with the experimental data for sodium and potassium chlorides to surprisingly high ionic strengths.

Summary

The solubility of pure calcium oxalate in water and in solutions of sodium chloride, potassium chloride, ammonium formate and sodium sulfate at 25° has been determined.

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(13) Gronwall, LaMer and Sandved, *Physik. Z.*, **29**, 358 (1928).