

A Complex of Cadmium (II) and Pyrocatechol Violet.

Determination of the Molar Absorptivity and Dissociation Constant

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Pyrocatechol violet, 3,3',4'-trihydroxyfuchsonone -2''- sulfonic acid, forms colored complexes with many cations. The absorption of light by mixtures of this dye and various metal ions may readily be determined by spectrophotometric means. Such colorimetric data have been used for quantitative determinations of several metal ions (4, 5). Dissociation constants of complexes of eight cations with pyrocatechol violet have been determined (3). A complex of cadmium (II) and pyrocatechol violet has been reported (1); however, the complexity constant was not given. This study was undertaken to obtain the value of the constant and to determine the molar absorptivity of the complex.

Experimental

Stock solutions of cadmium chloride and pyrocatechol violet having concentrations of 0.000989 M and 0.001013 M, respectively, were prepared. Each compound was an analytical reagent grade chemical. For purposes of dilution, the stock solutions were added from 10-ml. burets to 100-ml. "red-line" volumetric flasks. As shown in Table 1, two series of solutions were prepared. Table 1a lists samples containing only

TABLE 1

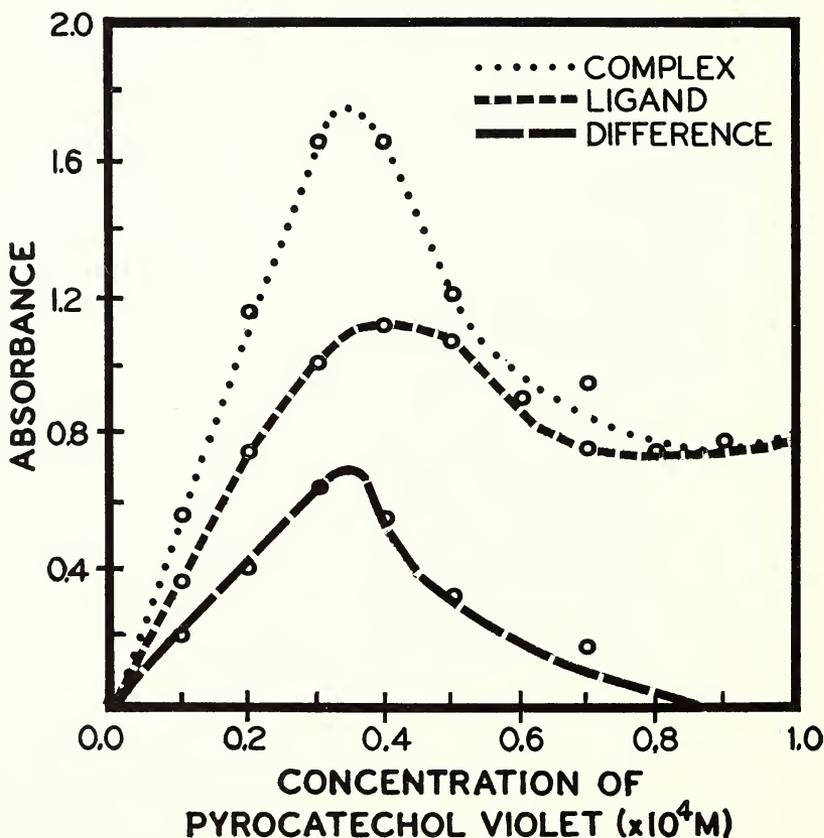
1a			1b		
Concentration of P. V. ($\times 10^4$ M)	Absorbance		Mole Fraction of P.V.	Absorbance	
	420 $m\mu$	620 $m\mu$		420 $m\mu$	620 $m\mu$
0.000	0.000	0.000	0.000	0.000	0.001
0.101	0.067	0.036	0.102	0.090	0.056
0.203	0.143	0.074	0.204	0.187	0.115
0.304	0.219	0.101	0.305	0.273	0.166
0.405	0.291	0.110	0.406	0.330	0.165
0.506	0.331	0.093	0.506	0.355	0.121
0.608	—	—	0.606	0.396	0.087
0.709	0.433	0.075	0.705	0.441	0.092
0.810	0.474	0.076	0.804	0.482	0.074
0.912	—	—	0.902	0.547	0.077
1.013	0.601	0.081	1.000	0.609	0.078
P.V. = Pyrocatechol violet					

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pyrocatechol violet, while Table 1b lists samples containing mixtures of cadmium chloride and pyrocatechol violet. In the latter case, each solution was adjusted so that the total concentration of the salt plus the ligand equaled 0.001 M. The mole fraction of each mixture in terms of pyrocatechol violet is given in Table 1b.

A Bausch and Lomb Spectronic 505 recording spectrophotometer was used to determine the spectrum of pyrocatechol violet. The plot of absorbance showed a broad peak at $420\text{ m}\mu$ and a broad trough at $620\text{ m}\mu$. The data listed in Table 1 were obtained with a Beckman Model DU quartz spectrophotometer equipped with 1-cm. cuvettes. The cuvette compartment was thermostated at $25.0 \pm 0.1\text{ }^\circ\text{C}$.

The data showed deviations from Beer's law. The solutions changed colors upon dilution, going from a red-brown color at higher concentrations to a blue-green color at lower concentrations. The curve of pyrocatechol violet at $620\text{ m}\mu$ is shown in Figure 1. The deviation from a



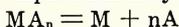
straight-line plot is quite large. Thus actual data for the absorbance were used in subsequent calculations rather than theoretical values as predicted by Beer's law.

The absorbance of pyrocatechol violet also varied somewhat with time. To minimize errors from this source, the same stock solutions were used to prepare solutions containing only the ligand and those containing the ligand plus the cation. Further, the dilute solutions were prepared at measured time intervals and absorbances were determined after identical time periods for each sample.

Calculations and Results

Job's method of continuous variations was applied to the spectrophotometric data (2, 6). The calculations were applied to the data at 620 $m\mu$. At this wave length the difference in absorbance of the ligand and the complex was the greatest.

The dissociation of a complex ion may be written as



and the dissociation constant as

$$K = \frac{[M][A]^n}{[MA_n]} \quad (1)$$

If the total concentration of M plus A is m molar and the fraction of A present is x , then the added amount of A is mx moles/liter and that of M is $m(1-x)$ moles/liter. At equilibrium between M, A, and MA_n

$$[M] = m(1-x) - [MA_n] \quad (2)$$

$$[A] = m(x) - n[MA_n] \quad (3)$$

Differentiating equation (1) gives

$$\frac{K}{[A]^n} \frac{d[MA_n]}{dx} = n \frac{[M]}{[A]} \frac{d[A]}{dx} + \frac{d[M]}{dx} \quad (4)$$

The concentration of the complex is a maximum when $\frac{d[MA_n]}{dx} = 0$.

Differentiating equations (2) and (3) and applying the test for the maximum gives $\frac{x}{(1-x)} = n$ (5)

That is, the maximum concentration of the complex results when the concentrations of M and A are added in the same ratios as the formula of the most stable complex, MA_n . Similar derivations can be used to show that if a complex ion absorbs light, the maximum absorption occurs at the mole fraction indicated by the formula MA_n .

Figure 1 shows that the maximum absorbance occurred at a concentration of 0.0000333 M pyrocatechol violet and a concentration of 0.0000667 M cadmium ion, indicating a complex of type M_2A . Analysis of the data at 420 $m\mu$ resulted in the same formula, indicating the formation of only one stable complex. Further, only one maximum was found on each curve, another indication of the formation of but one stable complex.

The determination of the molar absorptivity and the dissociation constant was accomplished by applying a method of successive approximations to the spectrophotometric data. Let C_A = total concentration of ligand added, a_A = molar absorptivity of the pure ligand, a_c = the molar absorptivity of the complex, and A_t = the total absorbance of solutions containing mixtures of metal ion and ligand. The cadmium ion absorbed no light in the visible region, thus $a_M = 0$. Then

$$A_t = a_A (C_A - [M_2A]) + a_c[M_2A] \quad (6)$$

The successive approximations were applied to the data at 0.00001 M ligand and 0.0000333 M ligand. The molar absorptivity of the complex was assumed to remain constant with concentration, i.e., Beer's law was accepted as valid. The value of a_A depended upon concentration and had to be calculated separately for each of the concentrations chosen.

The method of successive approximations for determining K and a_c was applied by calculating the appropriate value for a_A and assuming some value for a_c . The assumed value, along with the absorbance data and the proper value for a_A , were substituted into equation (6). From this equation, an approximation for the $[M_2A]$ was determined. Then an approximate value for K was readily calculated. The approximate K permitted the determination of a better value for a_c , and the process was repeated alternately at the two chosen concentrations until no change was noted in the dissociation constant or the molar absorptivity of the complex. The final values were $K = 1.44 \times 10^{-10}$ and $a_c = 5813$.

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