

Analysis of Cadmium Chelate Solutions with Various Ligands

HONG-WEN GAO

*School of Chemistry and Chemical Engineering
Anhui University, Hefei-230039, P.R. China*

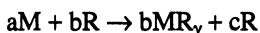
Cadmium complex's stoichiometric ratio has been determined with the following ligands, eriochrome black T (EBT), ammonium purpurate (AP), acid chrome blue K (ACBK) and calcium carboxylic acid (CCA), by the updated β -correction spectrophotometry, which is more acceptable and more simple than one of other usual methods, for example molar ratio, etc. With this principle, the complex practical molar absorptivity has been first calculated, which is higher than its apparent one at its maximum absorption wavelength. The results show that the complex ratios are: Cd/EBT = 1/2, Cd/AP = 1/4, Cd/ACBK = 1/2 and Cd/CCA = 1/1, and the practical molar adsorptivity: $\epsilon_{520\text{ nm}} = 2.72 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Cd-EBT chelate), $\epsilon_{10\text{ nm}} = 2.74 \times 10^4$ (Cd-AP chelate), $\epsilon_{510\text{ nm}} = 3.74 \times 10^4$ (Cd-ACBK chelate) and $\epsilon_{550\text{ nm}} = 0.77 \times 10^4$ (Cd-CCA chelate).

INTRODUCTION

The usual spectrophotometric determination of metal complex's stoichiometric ratio involves with the molar ratio¹, the equilibrium movement², Asmus³, the slop ratio⁴ and continuous variation⁵ methods. In this paper the determination of cadmium complex's stoichiometric ratio has been improved with four ligands *viz.*, eriochrome black T (EBT), ammonium purpurate (AP) acid chrome blue K (ACBK) and calcium carboxylic acid (CCA) by the dual-wavelength β -correction spectrophotometric method^{6,7}. The updated photometric method is different from one of other dual-wavelength methods^{8–10} in principle. It is the first to eliminate completely the interference of excess ligand from its metal coloured solution to give out the real absorbance of the formed chelate. By means of this principle, the effective complex ratio of a ligand for complexation and its chelate's practical molar absorptivity (ϵ_p) can be calculated. Especially, ϵ_p shows that the sensitivity of the β -correction method is higher than that by ordinary spectrophotometer. The results have proved that the complex's stoichiometric ratio is easier and simpler in operation and more simple in principle than that by the usual methods above. The complex ratio of Cd(II) to EBT is 1/2 at pH 9, that of Cd(II) to AP 1/4 at pH 11, that of Cd(II) to ACBK 1/2 at pH 9 and that of Cd(II) to CCA 1/1 at pH 11. Their practical molar absorptivities are equal to $2.72 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 520 nm, 2.74×10^4 at 510 nm, 3.74×10^4 at 510 nm and 0.77×10^4 at 550 nm successively.

Principle

The dual-wavelength principle can be illustrated by the following reaction example of ligand (R) with metal (M).



where a is the added molar concentration of M at the reaction beginning and b is that of R; c is the concentration of the excess of R at the reaction equilibrium;

γ is the composition ratio of the formed chelate MR_γ . The spectra are drawn in Fig. 1. We see that at the wavelength λ_2 the real absorbance (A_c) of chelate MR_γ should be expressed by⁶

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \beta \alpha} \quad (1)$$

where ΔA and $\Delta A'$ are the absorbance of the above coloured solution, against a reagent blank at λ_2 and λ_1 respectively. Both α and β are the correction coefficients and their expressions are followed respectively by

$$\beta = A_0/A'_0 \quad (2)$$

and

$$\alpha = A'_\alpha/A_\alpha \quad (3)$$

where A_0 and A'_0 are the absorbances of a reagent blank against water, and A_α and A'_α are the absorbances of a concentration MR_γ against water at λ_2 and λ_1 , respectively

From A_c value we can calculate the practical molar absorptivity (ϵ_p) of chelate MR_γ at λ_2 by the following equation

$$\epsilon_p = A_c/(\delta a) \quad (4)$$

where δ is the thickness of a used cell in cm and a is the same as in the above reaction, in mol/L.

The effective percentage (η) of R for complexation is expressed by⁸

$$\eta = (A_c - \Delta A)/A_0 \times 100\% \quad (5)$$

From a η value we may calculate the complexation ratio (γ) according to the following equation, if the added M will be reacted completely.

$$\gamma = 0.01 \eta b/a \quad (6)$$

where a and b have the same meanings as in the above reaction. When γ value will reach maximal and remain constant, we believe this complexation is complete and this reaction reaches the maximal sensitivity. Therefore, this maximum γ value presents the composition ratio of chelate MR_γ .

EXPERIMENTAL

Visible spectra were recorded with a Model 722 spectrophotometer (made in Shanghai 3rd Analytical Instruments, China) in a 1 cm cell.

Standard cadmium(II) solution, 10.0 mg/L was prepared with cadmium (AR, Shanghai Chemical) to dissolve in nitric acid, then diluted to the desired concentration. The following ligand solutions were prepared as follows: 2.00 mmol/L EBT (Shanghai 3rd Reagents) in 10% triethanolamine in analytical reagent gradient (Shanghai Chemicals), 3.00 mmol/L AP (Beijing Chemicals) in 2% sodium hydroxide, 2.00 mmol/L ACBK (Beijing Chemicals, China) and 2.00 mmol/L CCA (Shanghai 3rd Reagents). 4% sodium hydroxide and the ammonium buffer pH 9 were used for the described acidity.

Recommended procedure: Take 20 μg of standard cadmium in a 25 mL volumetric flask. Then, add the described colorant and 4% sodium hydroxide or the ammonium buffer solution according to Table-1. Dilute to required volume and well mix. After 10 min, measure the absorbance at the two wavelengths as shown in Table-1, against water and the reagent blank. Calculate A_c , η , γ and ϵ_p from above equations.

TABLE-1
OPERATION CONDITIONS FOR THE FORMATION OF Cd(II) CHELATES

Ligand solution and working volume added	Acidity	Wavelengths selected	
		λ_1	λ_2
2.00 mmol/L EBT, 2.0 mL	pH 9	620 nm	520 nm
3.00 mmol/L AP, 2.00 mL	pH 12	580 nm	510 nm
2.00 mmol/L ACBK, 1.0 mL	pH 9	610 nm	510 nm
2.00 mmol/L CCA, 1.5 mL	pH 12	650 nm	550 nm

RESULTS AND DISCUSSION

Fig. 1 shows the absorption spectra of 4 ligands and their cadmium coloured solutions. From curve 3, two wavelengths should be chosen such that the

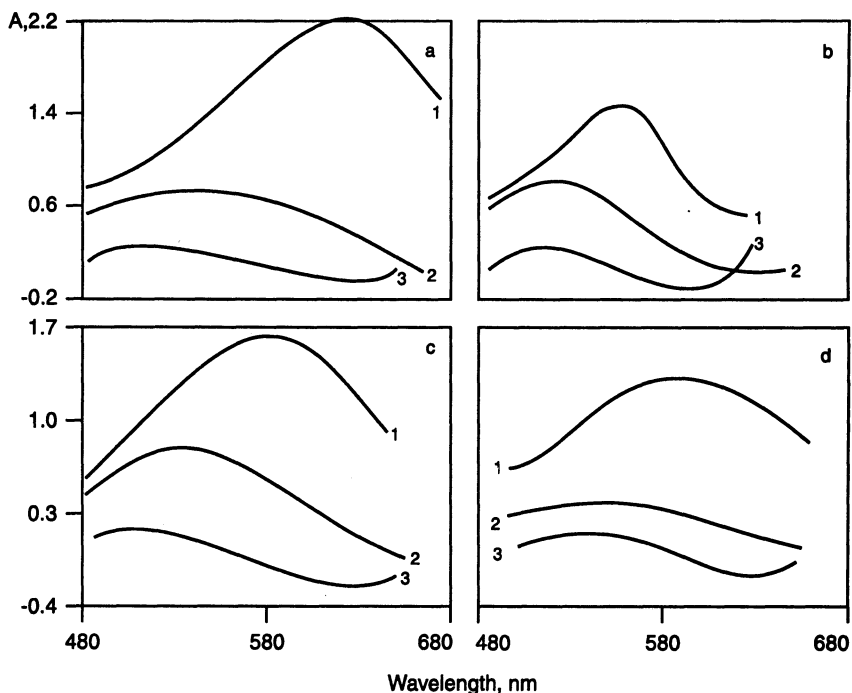


Fig. 1. The absorption spectra of four ligands and their coloured solution with cadmium: a-1, 0.16 mmol/L EBT at pH 9 against water; a-2, complex containing 50 mg/L Cd and 0.08 mmol/L EBT at pH 9 against water; 3, the coloured solution containing 0.80 mg/L Cd and 0.16 mmol/L EBT at pH 9 against a reagent blank; b-1, 0.24 mmol/L AP at pH 11 against water; b-2, complex containing 50 mg/L Cd and 0.12 mmol/L AP at pH 11 against water; b-3, 0.80 mg/L Cd coloured solution containing 0.24 mmol/L AP at pH 11 against a reagent blank; c-1, 0.08 mmol/L ACBK at pH 9 against water; c-2, only complex containing 50 mg/L Cd and 0.04 mmol/L ACBK at pH 9 against water; c-3, 0.80 mg/L Cd coloured solution containing 0.08 mmol/L ACBK at pH 9 against a reagent blank; d-1, 0.12 mmol/L CCA at pH 11 against water; d-2, only complex containing 50 mg/L Cd and 0.06 mmol/L CCA at pH 11 against water; d-3, 0.80 mg/L Cd coloured solution with 0.12 mmol/L CCA at pH 9 against a reagent blank.

difference in absorbances was maximum at the peak and the valley, as shown in Table-1. From curve 1, we can calculate each β value and from curve 2, each α can be computed. Their calculated values have been listed in Table-2. From equation (1), α and β of each we may express A_c as shown in Table-2.

TABLE-2
DETERMINATION OF α AND β AND EXPRESSION OF A_c

Ligand used	β	α	A_c
EBT	0.493	0.561	$1.38(\Delta A - 0.493\Delta A')$
AP	0.943	0.287	$1.37(\Delta A - 0.943\Delta A')$
ACBK	0.663	0.150	$1.11(\Delta A - 0.663\Delta A')$
CCA	0.697	0.284	$1.25(\Delta A - 0.697\Delta A')$

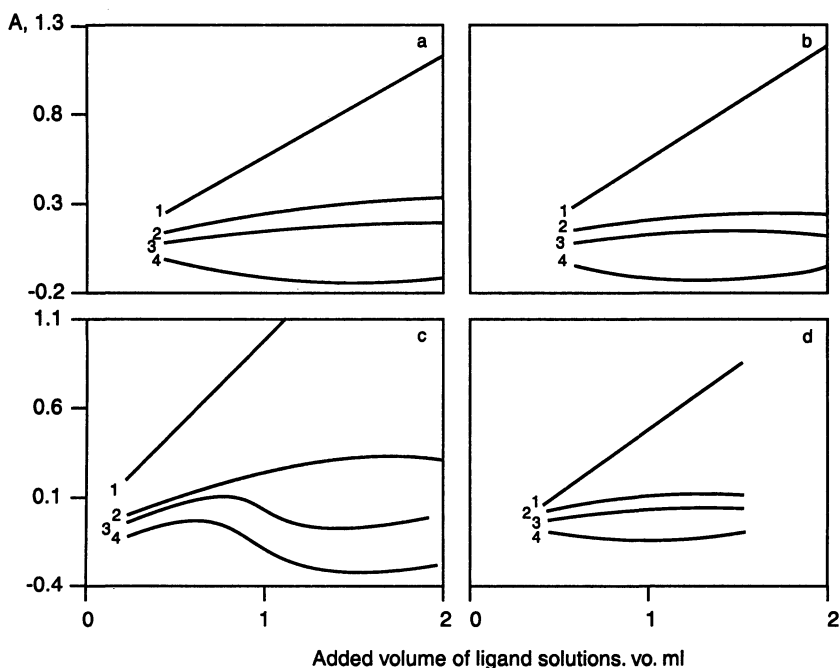


Fig. 2. Effect of the added volume (V_0 , mL) of ligand solutions on the absorbance of four indicator solutions and their cadmium coloured solution at pH = 9 (a and c) and 11 (b and d): a-1, EBT solution against water at 520 nm; a-2, A_c of 0.80 mg/L Cd chelate with EBT at 520 nm; a-3, 0.80 mg/L Cd coloured solution with EBT at 520 nm against a reagent blank; a-4, the solution same as a-3 at 620 nm; b-1, AP solution against water at 510 nm; b-2, A_c of 0.80 mg/L Cd complex with AP at 510 nm; b-3, 0.80 mg/L Cd coloured solution with AP at 510 nm against a reagent blank; b-4, same as b-3 at 580 nm; c-1, ACBK solution against water at 510 nm; c-2, A_c of Cd complex with ACBK at 510 nm; c-3, the coloured solution containing 0.80 mg/L Cd at 510 nm against a reagent blank; c-4, same as c-3 but at 610 nm; d-1, CCA solution against water at 550 nm; d-2, A_c of Cd complex with CAA at 550 nm; d-3, the coloured solution containing 0.80 mg/L Cd at 550 nm against a reagent blank; d-4, same as d-3 but at 650 nm.

Effect of ligands: Fig. 2 shows the effect of the added volume (V_0) of the ligands on its solution and its cadmium coloured solution. A_c value of curve 2 was computed from curves 3 and 4 with equations in Table-2. We find from curve 3 because the inflection point is difficult to find accurately, the inaccurate stoichiometric ratio of a complex will be given with the usual molar ratio method. To compare curve 2 with 3 we see $A_c > \Delta A$; the analytical sensitivity by the dual-wavelength spectrophotometry is therefore higher than that by the single wavelength method. According to the conditions in Table-1 and from A_c and ΔA values in Fig. 1, both ϵ_a and ϵ_p values at the sensitive wavelength can be calculated as shown in Table-3.

TABLE-3
DETERMINATION OF MOLAR ABSORPTIVITY

Ligand used	Wavelength (nm)	Absorbance (A_c)	Measured (ΔA)	Molar absorptivity ($L \text{ mol}^{-1} \text{ cm}^{-1}$)
EBT	520	0.194	0.086	$\epsilon_m = 1.21 \times 10^4$ $\epsilon_p = 2.72 \times 10^4$
AP	510	0.195	0.061	0.86×10^4 2.74×10^4
ACBK	510	0.266	0.029	0.41×10^4 3.74×10^4
CCA	550	0.055	0.002	0.77×10^4 0.03×10^4

Determination of η and γ : From $a = 0.178 \mu\text{mol}$ ($= 20 \mu\text{gcd}$) and each b as shown in Table-1, η and γ of each coloured solution have been calculated at any V_0 and their results shown in Figure 3. From curve 2 we find at $V_0 > 1.0 \text{ mL}$, γ remains constant and maximum as 2 for EBT, 4 for AP, 2 for ACBK and 1 for CCA. Therefore, the cadmium complex can be expressed by $\text{Cd}(\text{EBT})_2$, $\text{Cd}(\text{AP})_4$, $\text{Cd}(\text{ACBK})_2$ and $\text{Cd}(\text{CCA})$. From Table-4 we see at the working ligand in 0.80 mg/L cadmium occupies over 80%. It is therefore indubitable that the excess ligand affects seriously in the determination of the real absorbance of the formed complex.

TABLE-4
DETERMINATION OF η and γ AT THE WORKING V_0

Ligand used	Working V_0 (mL)	$\eta\%$	γ	Ligand's excess
EBT	2.0	9.7	2	91.3%
AP	2.0	11	4	89.0%
ACBK	1.0	18	2	82.0%
CCA	1.5	6.2	1	93.8%

Precision of A_c and ΔA : According to the recommended procedures for 10 replicated determinations of 0.80 mg/L cadmium, the relative standard deviations (RSDs) have been listed in Table-5. We find A_c has the much higher precision than ΔA .

TABLE-5
PRECISION OF αC AND ΔA for 0.80 mg/L Cd(II)

Ligand used	Wavelength (nm)	Relative standard deviation (RSD)	
		Ac	ΔA
EBT	520	2.3%	7.9%
AP	510	1.6%	5.1%
ACBK	510	3.2%	12%
CCA	550	4.5%	21%

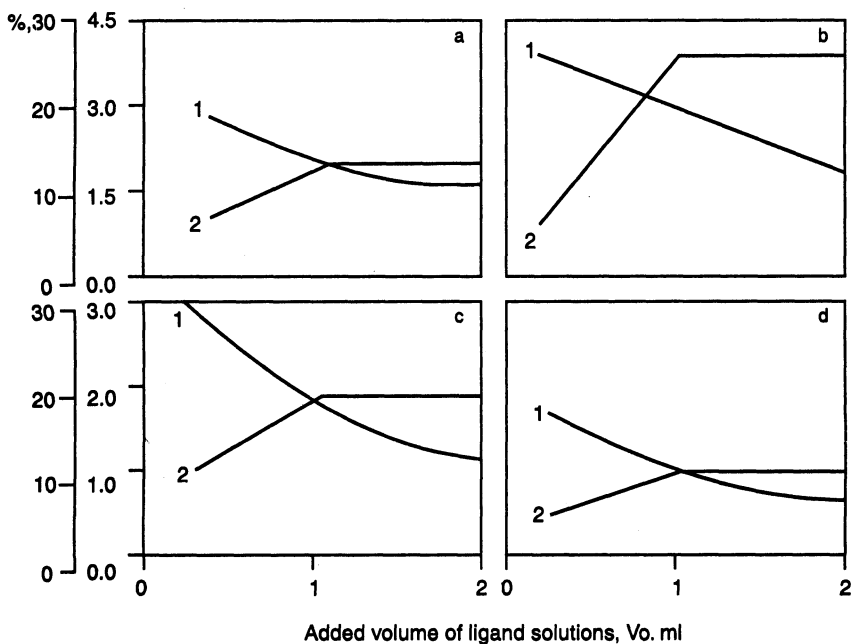


Fig. 3. Curve of η and γ against V_o : a, effect of EBT; b, that of AP; c, that of ACBK; d, that of CCA; 1, $\eta\%$; 2,

REFERENCES

1. L.C. Kamra, *Anal. Chim. Acta*, **78**, 423 (1975).
2. H.E. Beut, *J. Am. Chem. Soc.*, **64**, 568 (1941).
3. E. Asmus, *Z. Anal. Chem.*, **178**, 104 (1960).
4. B. Tamhina, *Anal. Chim. Acta*, **76**, 417 (1975).
5. W. Likussar, *Anal. Chem.*, **45**, 1926 (1973).
6. H.W. Gao and P.F. Zhang, *Analyst.*, **119**, 2109 (1994).
7. H.W. Gao and H.L. Shi, *Spectroscopy*, **9**, 47 (1994).
8. H.W. Gao, *Huanjing Kexue*, **14**, 82 (1993).
9. H. Watanabe and H. Ohmori, *Talanta*, **26**, 959 (1979).
10. K.L. Ratzlaff, *Anal. Chem.*, **49**, 2170 (1977).