

Complexation Equilibria between Cadmium(II) and 2-(5'-Ethyl-1',3',4'-thiadiazol-2'-azo)-4-methoxyphenol

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The reaction of cadmium(II) with 2-(5'-ethyl-1',3',4'-thiadiazol-2'-azo)-4-methoxyphenol in aqueous medium at $I = 0.1 \text{ mol dm}^{-3}$ was investigated spectrophotometrically. Graphical and numerical calculation methods were used to establish the equilibria in solution and to evaluate the stability constant of the complexes formed ($\log \beta_{101} = 3.67 \pm 0.03$ and $\log \beta_{102} = 7.90 \pm 0.16$). The extractions of ETDAMOF and Cd(II)—ETDAMOF complex with benzene were studied and the $\log K_{\text{ex}} = -8.17 \pm 0.22$ was calculated.

Even though heteroazophenols have been widely used as analytical reagents [1, 2] for many metal ions, in most cases little attention has been paid to their complexation equilibria in aqueous solution and to the extraction with solvents.

In this work, the complexation reaction of cadmium with 2-(5'-ethyl-1',3',4'-thiadiazol-2'-azo)-4-methoxyphenol (ETDAMOF) and extraction with benzene is described and studied by spectroscopic methods and the constants of the complex species in solution are determined.

EXPERIMENTAL

Spectrophotometers 25 (Beckman) and 200 (Hitachi—Perkin—Elmer) with 1 cm path length glass cells, digital pH-meter PHM64 (Radiometer) with glass calomel combination electrode, rotary shaker (Heidol), constant speed centrifuge M80A (Gerber), and digital computer VAS/VMX 11/780 (V.4.0) were used.

10^{-3} M and $5 \times 10^{-4} \text{ M}$ solutions of ETDAMOF in ethanol and benzene, respectively, standard 0.1 M solution of $\text{Cd}(\text{ClO}_4)_2$, prepared from $\text{Cd}(\text{NO}_3)_2$ by treatment with HClO_4 and evaluated complexometrically, were applied.

Anal. grade chemicals and deionized water were used throughout with any further purification. The ionic strength was kept constant at 0.1 mol dm^{-3} by addition of a suitable amount of 2.5 M-NaClO_4 .

RESULTS AND DISCUSSION

Spectrophotometry of the System Cd(II)—ETDAMOF in Aqueous Solution

The absorption spectra of solutions as a function of the pH at $I = 0.1 \text{ mol dm}^{-3}$ show the pres-

ence of an absorption maximum at $\lambda = 588 \text{ nm}$ and an isosbestic point at 505 nm . The variation of the absorbance at $\lambda = 588 \text{ nm}$ as a function of the pH for solutions with different Cd(II) and ETDAMOF concentration ratios (Fig. 1) shows that complexation begins at pH 4 and stabilizes at $\text{pH} \geq 8$.

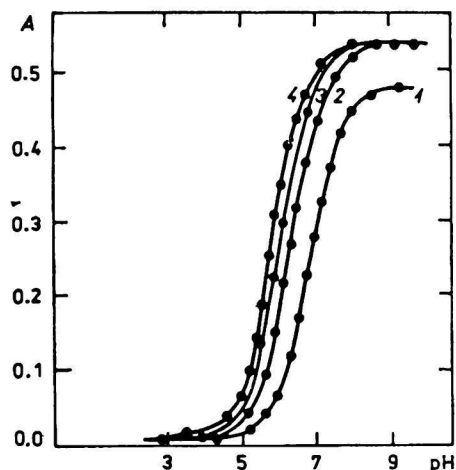


Fig. 1. Absorbance—pH curves for the system Cd(II)—ETDAMOF. $c_R = 4 \times 10^{-5} \text{ mol dm}^{-3}$; c_{Cd}/c_R : 1. 1; 2. 20; 3. 40; 4. 60.

The calculation of the stability constants β and molar absorption coefficients ϵ of the different complex species, as well as their stoichiometry, was carried out, firstly, by applying the graphical analysis method to the absorbance—pH curves [3, 4] in the interval of pH 5 to 7.5, and considering that the value of $\text{p}K_{a2}$ of ETDAMOF is 6.97 ± 0.09 [5] (Table 1). The results obtained show the existence of the species CdR in solution and that $\log \beta_{101} = 3.62 \pm 0.12$ and $\epsilon = (1351 \pm 60) \text{ m}^2 \text{ mol}^{-1}$

Table 1. Optical Characteristics of ETDAMOF Species (R)

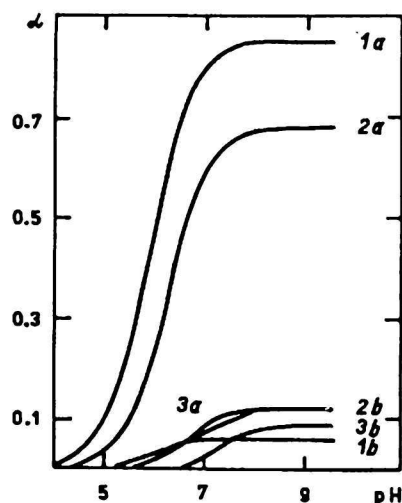
Species	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/(\text{m}^2 \text{mol}^{-1})$	$\text{p}K_{\text{a}}$
H_2R^+	503	725	-0.70 ± 0.02 ($\text{p}K_{\text{a}1}$)
HR	470	675	6.97 ± 0.09 ($\text{p}K_{\text{a}2}$)
R^-	565	1550	

Secondly, the numerical calculations of the absorbance—pH curves were performed by means of the LETAGROP—SPEFO program [6] based on the least squares method.

Initially, the species model obtained by means of the graphical method was used as base for the numerical method. Subsequently, variations of the mentioned model were introduced with a view to determine the one that best fitted the experimental curves. The results obtained are given in Table 2 and from the values of the function U (minimum sum of squares of residuals) and $s(A)$ (minimum standard deviation of absorbances) it can be de-

Table 2. Values of U , $s(A)$, $\log \beta_{\text{pqr}}$ and ϵ_{pqr} for the Different Models Tested by the LETAGROP—SPEFO Method

Species	$p M + q H + r R \rightleftharpoons M_p H_q R_r$			
	U	$s(A)$	$\log \beta_{\text{pqr}}$	$\epsilon_{\text{pqr}}/(\text{m}^2 \text{mol}^{-1})$
CdR	0.920×10^{-3}	0.009	—	—
CdR_2	0.499×10^{-1}	0.023	—	—
CdR	0.107×10^{-1}	0.011	—	—
CdHR_2	0.896×10^{-2}	0.010	—	—
CdR	0.575×10^{-3}	0.003	3.67 ± 0.03	1401 ± 4.8
CdR_2			7.90 ± 0.16	1411 ± 179
CdR_2	0.495×10^{-1}	0.023	—	—
CdOHR			—	—

**Fig. 2.** Species distribution diagrams for the system Cd(II)—ETDAMOF. a) CdR; b) CdR_2 . $c_{\text{Cd}}/c_{\text{R}}$: 1. 60; 2. 20; 3. 1.

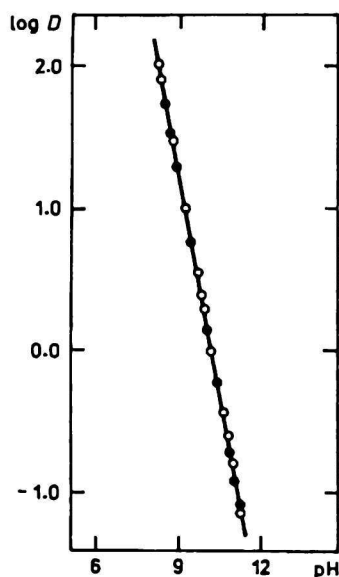
duced that the model formed by the species CdR and CdR_2 is more suitable than that formed by a single species.

On comparing the results obtained by the graphical and numerical method it was found that, despite the fact that the former only fits the CdR species and the latter a mixture of CdR and CdR_2 , an acceptable agreement exists between the parameters obtained by each method for the common species, CdR, which is attributed to the fact that the concentration of the CdR_2 species present under those experimental conditions is very limited as can be seen in the species distribution diagrams, obtained using the HALTAFALL program [7] (Fig. 2).

Extraction of ETDAMOF and the Cd(II)—ETDAMOF Complexes

Previous tests showed that the complexes as well as the reagent could be extracted with chloroform, benzene, toluene, and petroleum ether. Benzene was chosen as the absorbances were higher and stable for more than 24 h and the extraction was complete after 10 min of mechanical shaking.

ETDAMOF is extracted with benzene in a wide pH range from 0 to 11 and the extracts show absorption maxima at $\lambda = 344$ and 487 nm, indicating that the neutral HR species of the reagent is responsible for the extraction. The agreement of the values of D at each pH for different concentrations of reagent indicates that no polymerization takes place in the organic phase (Fig. 3).

**Fig. 3.** $\log D$ vs. pH for the ETDAMOF reagent. $c_{\text{R}}/(\text{mol dm}^{-3})$: 2×10^{-5} (O) and 10^{-4} (●).

The distribution process of the reagent can be written



and the distribution coefficient D can be defined as

$$\log D = \log K_D - \log (1 + K_{a2}/[\text{H}^+]) \quad (1)$$

where K_D is the partition constant and K_{a2} is the second ionization constant of the reagent.

The value of D could not be calculated accurately at $\text{pH} < 8$ due to the fact that the extraction of the reagent is practically quantitative at those pH values. Taking $\text{p}K_{a2} = 6.97 \pm 0.09$ it can be obtained from the graph that $K_D = 1548$. Eqn (1) can also be written

$$D^{-1} = K_D^{-1} + K_{a2} K_D^{-1} [\text{H}^+]^{-1}$$

and from the graphical plot D^{-1} vs. $[\text{H}^+]^{-1}$ it can be obtained that $K_D = 1549$. This value of K_D falls within the orders of magnitude described for similar products by other authors [8–10].

Afterwards the experimental data were treated by means of the LETAGROP—DISTR program [11] using the values found by graphical treatment as starting values. The results obtained are $\log K_D = 3.18 \pm 0.052$, $U = 0.063$, and $\varepsilon = 0.0067 \text{ m}^2 \text{ mol}^{-1}$.

The absorption spectra of the extracted Cd—ETDAMOF complex with benzene show the presence of an absorption maximum at $\lambda = 610 \text{ nm}$.

The variation of the distribution coefficient was studied as a function of the concentration of reagent and the pH. In the first case, the relationship

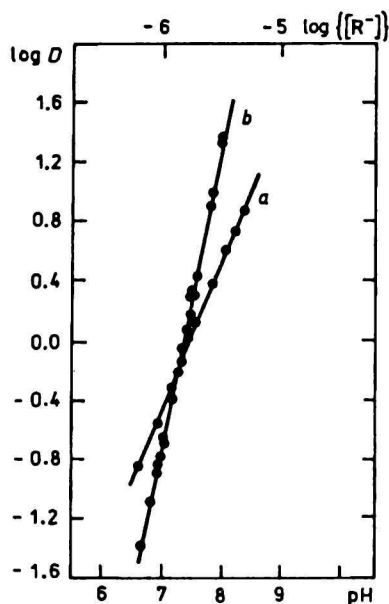


Fig. 4. a) $\log D$ vs. $\log [R^-]$ for the system Cd(II)—ETDAMOF. $c_{\text{Cd}} = 2 \times 10^{-5} \text{ mol dm}^{-3}$; $I_{\text{aq}} = 0.1 \text{ mol dm}^{-3}$ (with NaClO_4); $\text{pH} = 8.5$ ($\text{NH}_3/\text{NH}_4^+$). b) $\log D$ vs. pH for the system Cd(II)—ETDAMOF. $c_{\text{Cd}} = 2 \times 10^{-5} \text{ mol dm}^{-3}$; $c_{\text{R}} = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $I_{\text{aq}} = 0.1 \text{ mol dm}^{-3}$ (with NaClO_4).

between both parameters is given by the expression

$$D = (K_D^{\text{Cd}} \beta_n [\text{R}^-]^n) / \alpha_{\text{Cd}}$$

where $\alpha_{\text{Cd}} = 1 + \sum \beta_i [\text{NH}_3]^i + \sum \beta_j [\text{OH}^-]^j$ (considering the concentration of the cadmium complexes with the reagent in aqueous phase to be negligible under these working conditions). Fig. 4 shows how the graphical plot of $\log D$ vs. $\log [R^-]$ is a straight line of the equation

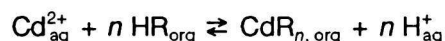
$$\log D = 11.90 + 2.08 \log [R^-]$$

which indicates that the stoichiometry of the extracted species is CdR_2 and substituting $\log \beta_{102} = 7.90$, $\alpha_{\text{Cd}} = 2.215$ [12] it is obtained that $K_D^{\text{Cd}} = 22\,131$ ($\log K_D^{\text{Cd}} = 4.34$).

A study of the variation of the distribution coefficient as a function of the pH leads to the equation

$$\log D = \log K_{\text{ex}} + n \log [\text{HR}]_{\text{org}} + n \text{pH}$$

K_{ex} is the constant of the extraction equilibrium



Operating at an excess and constant $[\text{HR}]_{\text{org}}$ the graphical plot (Fig. 4) is a straight line of the equation

$$\log D = -14.67 + 1.99 \text{pH}$$

indicating that two protons are split off, the species extracted is CdR_2 and $K_{\text{ex}} = 8.59 \times 10^{-9}$ ($\log K_{\text{ex}} = -8.07$).

The treatment of the experimental data with the LETAGROP—DISTR program [11] leads to the following results: $\log K_{\text{ex}} = -8.17 \pm 0.22$, $U = 0.070$, and $s = 0.068$.

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