SPECTROPHOTOMETRIC STUDY OF THE COMPLEXATION EQUILIBRIA OF CADMIUM IONS WITH 5-BROMO AND 5-CHLORO DERIVATIVES OF 2-(2-PYRIDYLAZO)-5-DIETHYL-AMINOPHENOL (BrPADAP, ClPADAP)

Vlastimil KUBÁŇ and Miroslav MACKA

Department of Analytical Chemistry,
J. E. Purkyně University, 611 37 Brno

The composition, optical characteristics, molar absorption coefficients and equilibrium constants of the reactions of formation of the ML and ML_2 complexes of both reagents with cadmium(II) ions were determined by graphical analysis and numerical interpretation of the absorbance-pH curves by the modified SQUAD-G program. Optimal conditions were proposed for the spectrophotometric determination of Cd in 10% v/v ethanol medium in the presence of 0·1% w/v Triton X-100 or 1% w/v Brij 35. BrPADAP and ClPADAP are the most sensitive spectrophotometric reagents for the determination of cadmium(II) ions ($\varepsilon = 1·28-1·44 . 10^5$ mmol^{-1} cm^2 at 560 nm and pH 8·0—9·5) with a high colour contrast in the reaction ($\Delta\lambda_{max} \sim 117$ nm) and a selectivity similar to that of other N-heterocyclic azodyes (PAR, PAN, *etc.*).

The analytical chemistry of cadmium has undergone great development, especially in recent years in connection with the increasing technological importance of this element and the subsequent increased cadmium contents of the atmosphere, soil and waste waters. Cadmium metal alone is not toxic, but most of its compounds are. Cadmium compounds have the greatest toxicity on inhaling (*e.g.* CdO vapours formed in melting of cadmium, its alloys and ores), or in the digestive system. During intoxication, cadmium compounds attack the central nervous system leading to degenerative changes in the internal organs or interference in the metabolism of phosphorous and calcium exchange. The highest permissible concentration of cadmium in the atmosphere is 0·1 mg m^{-3} (hygienic standards) or 0·3—0·4 mg m^{-3} of cadmium alloy dust particles[1]. Consequently, the analytical chemistry of trace concentrations of cadmium is of great importance. In addition to atomic absorption spectrophotometric and other methods, molecular absorption spectrophotometry in the visible and UV regions is very important in many routine laboratory analyses.

Of organic analytical reagents, the greatest importance is enjoyed by the group of N-heterocyclic azodyes based on pyridine (PAR, PAN, PADAP, *etc.*) of which the most sensitive reactions are provided by 2-(2-pyridylazo)-5-dialkylaminophenol (PADAP) and its halogen derivatives, BrPADAP and ClPADAP. This reagent has the same chelating system as PAR, but the dialkylamine substituent in the *p*-position yields molar absorption coefficient values 1·5 to 2·0 times higher and much better colour contrast in the reaction.

This work deals with study of the complexation equilibria of the 5-bromo and 5-chloro derivatives of PADAP with cadmium(II) ions in mixed water–ethanol and

water–DMF media and 10% v/v ethanol medium in the presence of nonionic tensides. The basic parameters of the complexes of Cd(II) with BrPADAP and ClPADAP were evaluated by graphical analysis[2] and numerical interpretation by the SQUAD-G program (refs[3,4]) of the absorbance-pH curves of solutions with a concentration excess of ligand or cadmium ions. Conditions were proposed for development of a very sensitive spectrophotometric method for the determination of cadmium in pure solutions in 10% ethanol medium in the presence of nonionic tenside Triton X-100 or Brij 35 in a concentration of 0·1 or 1·0% w/v, respectively.

EXPERIMENTAL

Chemicals and Instruments

The stock solution of $1·897 . 10^{-1}$ mol l^{-1} Cd(NO$_3$)$_2$ in $0·1$ mol l^{-1} HNO$_3$ was prepared by dissolving very pure (99·999%) metallic cadmium (Metal Research Institute, Panenské Břežany, ČSSR) in "Suprapure" purity HNO$_3$ (Merck, GFR). The Cd(II) content was controlled by complexometric titration with EDTA using Eriochrome Black T indicator. Working solutions were prepared by diluting the stock solution with $0·1$ mol l^{-1} HNO$_3$. The other chemicals, instruments and measuring methods and evaluation of experimental data were described in detail in an earlier work[5].

The Reactions of Cd(II) with BrPADAP and ClPADAP

The absorption spectra of a Cd(II) solution with BrPADAP were recorded in dependence on the acidity of the medium in 30% v/v ethanol in solutions with a concentration excess of cadmium ions (see Fig. 1; $c_M = 9·604 . 10^{-4}$ mol l^{-1}, $c_L = 1·0$. 10^{-5} mol l^{-1}, $c_M/c_L = 96$), in nearly equimolar solutions ($c_M = 7·804 . 10^{-6}$ mol . l^{-1}, $c_L = 1·22 . 10^{-5}$ mol l^{-1}) and in solutions with a concentration excess of BrPADAP ($c_M = 4·802 . 10^{-6}$ mol l^{-1}, $c_L = 1·5 . 10^{-5}$ mol l^{-1} or $c_M = 2·401$. 10^{-6} mol l^{-1}, $c_L = 1·5 . 10^{-5}$ mol l^{-1}, see Fig. 2). The absorption spectra of Cd(II) solutions with a concentration excess of BrPADAP in 50% v/v DMF ($c_L = 1·897$. 10^{-5} mol l^{-1}, $c_M = 3·793 . 10^{-6}$ mol l^{-1}, $c_L/c_M = 5$) were also measured. The absorption spectra of all the solutions had the same character in the wavelength region $340 - 610$ nm, with a double absorption maximum at 520 and 560 nm. The concentrations of the basic components and the optical characteristics of the absorbing species are listed in Table I.

In study of the complexation equilibria in solutions with a concentration excess of Cd(II), absorbance-pH curves were measured in a 30% v/v ethanol solution for $c_L = 9·483 . 10^{-6}$ mol l^{-1} and various concentrations of Cd(II) ions ($c_M = 9·483 . 10^{-3}$ mol l^{-1}, $c_M/c_L = 1 000$; $c_M = 4·742 . 10^{-3}$ mol l^{-1}, $c_M/c_L = 500$; $c_M = 9·483 . 10^{-4}$ mol l^{-1}, $c_M/c_L = 100$; $c_M = 4·742 . 10^{-4}$ mol l^{-1}, $c_M/c_L = 50$; $c_M = 9·483 . 10^{-5}$ mol l^{-1}, $c_M/c_L = 10$). The absorbance-pH curves were recorded

in the wavelength intervals 420−480 and 510−560 nm at constant intervals of $\Delta\lambda =$ = 10 nm. In neutral medium at pH 6−7 an amorphous $Cd(OH)_2$ precipitate began to form.

The measured dependences were evaluated only for a wavelength of 550 nm by graphical analysis assuming formation of a single complex, ML, according to the equilibrium

$$M + LH \; \rightleftharpoons \; ML + H \; (*\beta_{111}, \varepsilon_1) . \qquad (A)$$
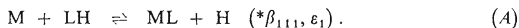
All types of slope-intercept transformations yielded very good correlation with the experimental data for all concentration excesses with the values of the equilibrium constants of reaction (A) and molar absorption coefficients ε_1 given in Table I. Calculation by the SQUAD-G program for the pH interval c. 3·5−6 for the same model and concentration excess of cadmium ions, $c_M/c_L = 100$, yielded very good agreement with the experimental data ($\sigma_A = 0·0044$ A.U.) for an equilibrium constant value of $-\log *\beta_{111} = 2·89$ and molar absorption coefficient of $\varepsilon_{max} = 7·2$. $. 10^4 \text{ mmol}^{-1} \text{ cm}^2$. These values (Table I) are in very good experimental agreement with the values obtained by graphical analysis and with the values for the corresponding complex of Zn(II) with BrPADAP (ref.[5]). Calculations for the other models tested, assuming, in addition to formation of the ML complex, also formation of the hydroxo-complexes M(OH) and $M(OH)_2$ or the mixed complex ML(OH)
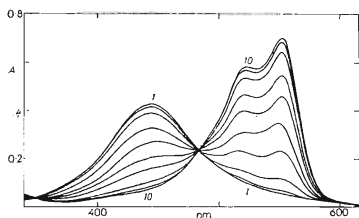

Fig. 1

The absorption curves of a BrPADAP solution with a concentration excess of Cd(II) ions in 30% v/v ethanol medium. $c_L = 1·0$. $. 10^{-5} \text{ mol l}^{-1}$, $c_M = 9·604 . 10^{-4} \text{ mol l}^{-1}$, $I = 0·10$, HNO_3 + KOH, $t = 25·0°C$. Curve pH: *1* 3·81, *2* 4·27, *3* 4·87, *5* 5·60, *6* 5·85, *7* 6·18, *8* 6·62, *9* 7·12, *10* 7·65.
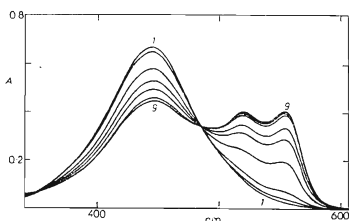
Fig. 2

The absorption curves of Cd(II) ions in a concentration excess of BrPADAP in 30% v/v ethanol medium. $c_L = 1·5 . 10^{-5} \text{ mol l}^{-1}$, $c_M = 2·401 . 10^{-6} \text{ mol l}^{-1}$, for the other conditions, see Fig. 1. Curve pH: *1* 4·67, *2* 6·04, *3* 6·63, *4* 7·33, *5* 7·78, *6* 8·05, *7* 8·67, *8* 9·52, *9* 10·10
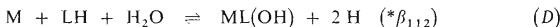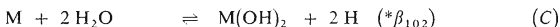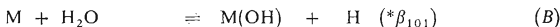
TABLE I

Basic characteristics of the complex of Cd(II) ions with BrPADAP and CIPADAP. 30% v/v ethanol, $I = 0.10$ HNO_3 + KOH, $t = 25.0°C$

$c_L \cdot 10^5$ mol/l	$c_M \cdot 10^5$ mol/l	$\langle \lambda \rangle$ nm	λ_{1P} nm	λ_{max} nm	ε_{max} mmol⁻¹ cm²	$-\log \beta_{mnx}$	Note
BrPADAP							
1.0	96.04	340—615	483	445[a], 523, 552			
1.22	0.78	340—620	483	445[a], 521, 552			
1.50	0.4802	340—505	483	443[a], 521, 554			
1.50	0.2401	340—605	483	445[a], 520, 554			
1.897	0.3793	340—610[b]	484	443[a], 520, 555			
0.9483	94.83	420—460 à 10 / 510—560 à 10	—	520, 550	71 771 ± 299[c]	$2.89_2 \pm 0.0007^c$	*β_{j111}
4.0	0.3793	355—595 à 10[d]	475	528, 560	139 553 ± 3 147	$4.10_2 \pm 0.0032$	*β_{112}
CIPADAP							
1.0	94.83	355—595 à 10	481	441[a], 519, 549	67 482 ± 260	2.87 ± 0.0029	*β_{111}
4.0	0.3793	355—595 à 10[d]	481	440[a], 530, 562	144 601 ± 3 110	4.12 ± 0.0030	*β_{122}

[a] Absorption maximum of the LH reagent form; [b] 50% v/v DMF; [c] $-\log *\beta_{111}$ values from graphical interpretation: 2.81 ($c_M/c_L = 100$, c_L/A), 2.75, 2.77, 2.81, 2.99 and 3.15 ($c_M/c_L = 10, 50, 100, 500$ and 1 000) 2.66, 2.81, 2.80, 2.98 and 3.15 ($c_M/c_L = 10, 50, 100, 500$ and 1 000 from logarithmic analysis); [d] 10% v/v ethanol in the presence of 0.1% w/v Triton X-100; [e] c_{max} values from graphical interpretation: 67 500, 67 400, 67 900, 70 900, 70 900 and 72 200 for $c_M/c_L = 10. 50. 100, 500$ and 1 000.

in the sense of equilibria $(B)-(D)$ did not converge:

$$M + H_2O \quad\rightleftharpoons\quad M(OH) \quad + \quad H \quad (*\beta_{101}) \qquad (B)$$

$$M + 2\,H_2O \quad\rightleftharpoons\quad M(OH)_2 \quad + \quad 2\,H \quad (*\beta_{102}) \qquad (C)$$

$$M + LH + H_2O \quad\rightleftharpoons\quad ML(OH) + 2\,H \quad (*\beta_{112}) \qquad (D)$$

In ClPADAP solutions with a concentration excess of Cd(II), absorbance-pH curves were measured for $c_L = 1.0 \cdot 10^{-5}$ mol l^{-1} and $c_M = 9.483 \cdot 10^{-4}$ mol l^{-1} in 30% ethanol for wavelengths of $355-595$ nm at constant steps of $\Delta\lambda = 10$ nm (Fig. 3). Data for the pH interval $3.5-6$ were treated only by the SQUAD-G program under the same assumptions as those for BrPADAP. Very good agreement was obtained between the theoretical and experimental absorbance values for an equilibrium constant of reaction (A) of $-\log*\beta_{111} = 2.87$ ($\sigma_A = 0.0015$ A.U.). The other models tested did not converge, as for BrPADAP. The molar absorption coefficient value, $\varepsilon_{max} = 6.8 \cdot 10^4$ mmol^{-1} cm^2, is close to the value of the molar absorption coefficient for the corresponding complexes of Cd(II) with BrPADAP and Zn(II) with BrPADAP and ClPADAP (ref.[5]).

Absorbance-pH curves were measured in a solution of 0.1% w/v Triton X-100 in 10% v/v ethanol medium at wavelengths of $355-595$ nm at constant steps of $\Delta\lambda = 10$ nm for a concentration excess of BrPADAP $c_L/c_M = 10.54$ ($c_L = 4.0 \cdot 10^{-5}$ mol l^{-1}, $c_M = 3.793 \cdot 10^{-6}$ mol l^{-1}). Treatment of the experimental data by the SQUAD-G program for a model of formation of a single complex ML_2 according to equilibrium E:

$$M + 2\,H \quad\rightleftharpoons\quad ML_2 + 2\,H \quad (*\beta_{122}) \qquad (E)$$
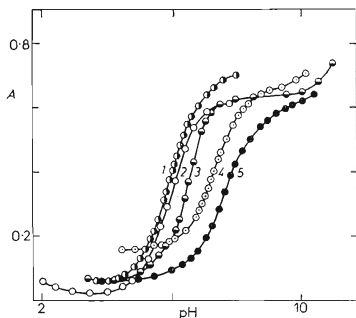
FIG. 3

Absorbance-pH curves for Cd(II) solutions with BrPADAP and ClPADAP. Conditions as in Fig. 1. Curve c_L (mol l^{-1}) c_M (mol l^{-1}) λ (nm) medium: *1* $9.483 \cdot 10^{-6}$ $9.483 \cdot 10^{-4}$ 550 30% ethanol, *2* $1.0 \cdot 10^{-5}$ $9.483 \cdot 10^{-4}$ 555 30% ethanol, *3* $4.0 \cdot 10^{-5}$ $3.793 \cdot 10^{-6}$ 555 10% ethanol with 0.1% Triton X-100, *4* $7.587 \cdot 10^{-5}$ $3.793 \cdot 10^{-6}$ 555 50% DMF, *5* $4.0 \cdot 10^{-5}$ $3.793 \cdot 10^{-6}$ 555 50% DMF

yielded very good agreement with the experimental data $(\sigma_A = 0.0115 \text{ A.U.})$ for an equilibrium constant of $-\log *\beta_{122} \approx 4.10$ and molar absorption coefficient at the maximum of $\varepsilon_{\max} = 1.4 \cdot 10^5 \text{ mmol}^{-1} \text{ cm}^2$. Completely analogous results were obtained for the absorbance-pH curves of Cd(II) with ClPADAP (measured in 10% v/v ethanol medium in the presence of 0.1% w/v Triton X-100) for the equilibrium constant and molar absorption coefficient values given in Table I. Treatment for the other models given did not yield good agreement with the experimental data $(\sigma_A > 0.020 \text{ A.U.})$ or the calculations did not converge even after the required 20 computation cycles.

It is apparent from Table I that the values of the basic characteristics of all the complexes of Cd(II) with both reagents, as well as the values obtained by graphical and numerical treatment of the absorbance curves are very well correlated. Slight differences between the values of the absorption maxima $\lambda_{\max}$ and of the molar absorption coefficients $\varepsilon_{\max}$ obtained by spectra recording in the classical manner and the values of the corresponding quantities obtained by numerical treatment of the set of absorbance-pH curves for a large number of wavelengths in a broad spectral interval by the SQUAD-G program can be explained by instrumental and chemical factors.

From an instrumental point, the difference can be explained by the fact that, in measuring the absorption spectra of the solutions, the instrument monochromator shifts at a constant rate (usually $50-100 \text{ nm/min}$) and the absorbance values are recorded with a constant delay, while in measurement of discrete absorbance values using the HP 9815A table-top calculator, the monochromator is brought to a stand-still before each measurement. The differences resulting from this factor may attain values of up to $\Delta\lambda_{\max} = 15 \text{ nm}$ for sharp maxima at a change from the monochromator shift rate from 1 nm/min to 100 nm/min (ref.[6]).

The difference in the values of the absorption maxima of the calculated absorption curves may also occur as a result of neglecting some side equilibria that are present to a very small degree in the solution (ligand interactions with other ions or impurities). The absorption spectra obtained numerically also represent the curves of individual absorbing species, while the classical absorption spectra are always summation curves.

In solutions with a concentration excess of Cd(II) ions for both reagents, only the mononuclear complex ML was formed according to equilibrium (A) with equilibrium constant values of $-\log *\beta_{111} = 2.89$ and 2.87 and molar absorption coefficients of $\varepsilon_{\max}^{550} \ 7.2 \cdot 10^4$ and $\varepsilon_{\max}^{549} \ 6.8 \cdot 10^4 \text{ mmol}^{-1} \text{ cm}^2$ for BrPADAP and ClPADAP, respectively. These values are in very good agreement with the values for the Zn(II) complex with both reagents and for complexes with other elements (Table II).

In solutions with a concentration excess of reagent in aqueous media or in mixed water–ethanol media, a turbidity or precipitate of the poorly soluble neutral ML_2^0

complex was formed. The complexes formed become soluble in 10% v/v ethanol medium in the presence of nonionic tensides Triton X-100 (0·1% w/v) or Brij 35 (1·0% w/v) or ionogenic cetylpyridinium bromide $(1 . 10^{-3} \text{ mol } l^{-1})$ and sodium

TABLE II

Comparison of the basic characteristics of the BrPADAP and ClPADAP complexes with some metal ions

M^{n+}	M : L (metbod)	$e_{max} . 10^{-4}$	λ_{max}	pH_{opt}	Note	Ref.
		BrPADAP				
Zn^{2+}	1 : 1 (B)^j	8·5	540	6·5—8·5	$c_L/c_M = 3$	7, 8
	1 : 1 (A, C)	6·9	547	7·0—9·5		5
	1 : 2 (A, C)	15·4^b	557	7·0—9·5		5
Cd^{2+}	1 : 2 (A, B)	14·1	555	8·0—10·5	extn.^{d}	9
	1 : 1 (A, C)	7·2	550			this
	1 : 2 (A, C)	14·4^a	560	9·0—9·5		paper
UO_2^{2+}	1 : 1 (A, B)^h	5,63, 4·65	586, 554	4·1		10
	1 : 1 : 1^g	6·40	580, 646	7·3		10
Pd^{2+}	1 : 1 (A, B)	4·3	575			11
Pb^{2+}	1 : 1 (B, F)	4·9	575	7—9	extn.^{f}	12
Co^{2+}	1 : 2 (A, D, E)	9·8	580			13
Co^{3+}	1 : 2 (B)	9·2^c	586	6·98		15
Bi^{3+}	1 : 1		590			8
Ga^{3+}	1 : 2 (A, B, C)^i	12·3 ± 0·3	570	3—5		14
Tl^{3+}	1 : 2 (A, B, D)		570	2	extn.^{e}	17
		ClPADAP				
Ga^{3+}	1 : 2 (A, B, D)	11·5 ± 0·4	565	3—5	ClPADAP^k	14
Co^{2+}	1 : 2 (B, D)	10·6 ± 0·95	580	3—9	ClPADAP^l	14
Cd^{2+}	1 : 1 (A, C)	6·9	549		ClPADAP	this
	1 : 2 (A, C)	14·5^a	562		ClPADAP	paper
Zn^{2+}	1 : 1 (A, C)	7·1	545		ClPADAP	5
	1 : 2 (A, C)	15·0^b	555		ClPADAP	5

^{a} 10% v/v ethanol and 0·1% w/v Triton X-100 or 1% w/v Brij 35; ^{b} 10% v/v ethanol and 1·0% w/v Brij 35; ^{c} 10% DMF and 0·1% w/v Triton X-100; ^{d} 3-methyl-1-butanol; ^{e} benzene; ^{f} chloroform; ^{g} ternary complex in excess F$^-$, $\beta' = 4·4—4·5 . 10^2$; ^{h} $\beta' = 1·3 . 10^{-5}$; ^{i} *β = (4·65 ± ± 0·2) . 10^4; ^{j} 1/*β = 6·7 . 10^{-6}; ^{k} *β = 5·0 ± 0·1; ^{l} *β = 19·15. A continuous variations, B molar ratio, C interpretation of absorbance-pH curves, D tangent method, E Asmus straight line method, F elemental analysis after isolation, β' conditional stability constant, *β equilibrium constant.

dodecyl sulphate $(1 . 10^{-3} \text{ mol l}^{-1})$, and also in 50% v/v DMF medium. Because of the higher molar absorption coefficient values and broader pH region for complex formation, it is preferable to use nonionic tensides both for analytical applications as well as for study of the complex equilibria.

The presence of the neutral ML_2 complex formed according to equilibrium (E) was unambiguously demonstrated in nonionic tenside medium in solutions with a concentration excess of ligand. The equilibrium constant and molar absorption coefficient values are again in good agreement with the corresponding values for the BrPADAP and ClPADAP complexes with Zn(II) and other elements (Table II).

It follows from comparison of the equilibrium constant values that the stabilities of the cadmium(II) complexes of the two reagents is roughly the same, but less than that of the Zn(II) complex. The molar absorption coefficients of the BrPADAP complexes with both metals in a concentration excess of the reagent are almost identical, but those of the corresponding complexes with ClPADAP are about 10% higher. All the high molar absorption coefficient values enable development of sensitive spectrophotometric methods for determination of Cd(II) in 10% v/v ethanol medium in the presence of 0.1% w/v Triton X-100 or 1% w/v Brij 35 at a wavelength of 560 nm, with a ten-fold reagent excess $(c_L = 4 . 10^{-5} \text{ mol l}^{-1})$ and at pH 8.0 to 9.5 in ammoniacal or Tris buffer[16].

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