SPECTROPHOTOMETRIC STUDY OF THE COMPLEX EQUILIBRIA OF CADMIUM(II) IONS WITH 4-(2-PYRIDYLAZO)RESORCINE (PAR) USING THE SQUAD-G PROGRAM AND THE METHOD OF DETERMINING Cd(II) IONS WITH PAR

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The existence of the red-orange $CdLH^+$ complex ($\lambda_{max} = 406$ nm, $\varepsilon_{max} = 1.78 \cdot 10^4$ mmol^{-1} . cm^2, log $^*\beta_{111} = -1.66 \pm 0.04$) and CdL complex ($\lambda_{max} = 495$ nm, $\varepsilon_{max} = 3.2 \cdot 10^4$ mmol^{-1} . cm^2, log $^*\beta_{112} = -8.25 \pm 0.05$) was demonstrated in aqueous solutions of PAR with a concentration excess of Cd(II) ions. It was shown that a 10% v/v acetone medium containing Cd(II) in a concentration excess of PAR contains the following complexes: CdL_2H_2 ($\lambda_{max} = 507$ nm, $\varepsilon_{max} = 1.4 \cdot 10^4$ mmol^{-1} cm^2, log $^*\beta_{122} = -2.85 \pm 0.04$), CdL_2H^- ($\lambda_{max} = 495$ nm, $\varepsilon_{max} = 6.25 \cdot 10^4$ mmol^{-1} cm^2, log $^*\beta_{123} = -9.58 \pm 0.04$) and CdL_2^{2-} ($\lambda_{max} = 495$ nm, $\varepsilon_{max} = 9.16 \cdot 10^4$ mmol^{-1} cm^2, log $^*\beta_{124} = -17.33 \pm 0.06$). The basic parameters of the individual complexes were determined by graphical interpretation using slope-intercept transformations and by numerical interpretation using the generalized SQUAD-G program. The statistical parameters of the spectrophotometric method of determining cadmium ions were evaluated from the linear part of the calibration curve using the STAT program.

The group of N-heterocyclic azodyes (PAN, PAR, BrPADAP, *etc.*) belongs among the most useful spectrophotometric reagents for determining cadmium ions. The molar absorption coefficients of these reagents attain values of $8.0–14.0 \cdot 10^4$ mmol^{-1} cm^2, which permits their use for the determination of trace concentrations of Cd(II) ions in water and in the air.

Although the reaction of Cd(II) ions with 4-(2-pyridylazo)resorcine is very sensitive, far less attention has been paid to study of this reaction than to the corresponding reaction with Zn(II) ions. Sommer and Hniličková described the use of PAR as a metallochromic indicator in complexometric titrations of Cd(II) and other ions[1,2] and described formation of complexes of Cd(II) with PAR with a molar ratio of ML in acid medium and ML$_2$ in neutral and alkaline media ($\lambda_{max} = 496$ nm). Iwamoto[3] gives a composition with a ratio of M : L = 1 : 1 for the complex in alkaline media, while Kitano and Ueda[4] described formation of the ML$_2$ complex with an absorption maximum at 495 nm and molar absorption coefficient of $8.4 \cdot 10^4$ mmol^{-1} . cm^2, at pH 10. Geary and Nickless[5] gave a similar composition on the basis of potentiometric study of complexation equilibria. The ML$_2$ complex was used[4] for the spectrophotometric determination of Cd(II) after separation from interfering elements on strongly basic ion exchanger after masking with 5% NaF.

Because of the above ambiguities in the data on the composition of the complex and the high sensitivity of the reaction, this work was devoted to study of the com-

plex equilibria of Cd(II) with PAR in aqueous media and in 10% v/v acetone medium by spectrophotometric methods with graphical and numerical interpretation of the absorbance curves. Optimal conditions were proposed for the spectrophotometric determination of Cd(II) with PAR and the basic statistical parameters of the method were determined.

EXPERIMENTAL

Chemicals and Instruments

The commercial PAR substance (Lachema, Czechoslovakia) was purified by repeated crystallization from methanol. The content of the active component was found by elemental analysis (91·5%) and by complexometric photometric microtitration with a $Cu(NO_3)_2$ solution. The stock solutions were prepared by dissolving a weighed amount of the solid substance in 1 ml of dimethylformamide (DMF) and 2 ml of 1 mol . l^{-1} NaOH and diluting with distilled water to the required volume.

The standard solution of $0·1897$ mol l^{-1} $Cd(NO_3)_2$ in $0·1$ mol l^{-1} HNO_3 was prepared by dissolving 99·999% metallic cadmium (Metal Research Institute, Panenské Břežany Czechoslovakia) in an excess of HNO_3. The Cd(II) ions content was controlled by titration with EDTA using Eriochrome Black T indicator. The working solution was diluted with $0·1$ mol l^{-1} HNO_3. The other chemicals were of purity for semiconductors (HNO_3, NH_4OH) or *p.a.* (KNO_3, EDTA). Acetone was distilled twice. The ionic strength of the solutions was maintained constant at $I = 0·10$ by a combination of suitable volumes of $1·0$ mol l^{-1} HNO_3 and $1·0$ mol l^{-1} NaOH (Suprapur, Merck, GFR).

All the spectrophotometric measurements were carried out on a double-beam digital recording Superscan 3 instrument (Varian, Switzerland) controlled on-line by an HP 9815A table-top calculator (Hewlett–Packard, USA) or a single-beam Spectromom 201 instrument (MOM, Hungary). The solution acidity was measured on a pHM 4d pH meter (Radiometer, Denmark) and an OP-205 instrument (Radelkis, Hungary) with a glass G 202B and saturated calomel K 401 electrode (Radiometer, Denmark). The instruments were calibrated with a set of aqueous NBS buffers (pH 1·68, 4·01, 7·00 and 9·18 with a precision of $\pm 0·01$ at 25°C).

The measurement was carried out in volumetric flasks by mixing suitable volumes of solvent (DMF, acetone), reagent, HNO_3, Cd(II) and NaOH to give the required acidity or in an apparatus for measurements in a closed cycle[6] with a connecting teflon tube and syringe for transport of the sample between the titration vessel and the flow-through spectrophotometer cuvette.

In solutions with a concentration excess of reagent, a red-purple complex with probable composition ML_2H_2 was deposited on the surface of the electrode, on the surface of the titration vessel and on the cuvette. In aqueous solutions and in 10% acetone medium a colloidal turbidity of the reagent was formed after two hours. Consequently, this measurement was carried out only in 10% acetone where the individual sets of experimental data were obtained from several connected measurements carried out at intervals of 5—90 minutes.

RESULTS AND DISCUSSION

The complexing equilibria were studied in solution and the optimal experimental conditions were found for development of a spectrophotometric method of determining Cd(II) using a combination of graphical and numerical interpretation of the

absorbance curves. The absorbance curves for equimolar solutions and solutions with concentration excess of one of the reactants in dependence on the acidity or component concentrations were treated for $1-2$ wavelengths in the region of maximum absorbance of the studied species by graphical and logarithmic analysis using slope-intercept transformation[7]. The resultant parameter values for the predominant complexes were used as initial data in the numerical interpretation of the complete set of experimental data by the adjusted and extended SQUAD-G program (ref.[8,9]). The molar absorption coefficients ε_{pqrk} and equilibrium constants $*\beta_{pqr}$, which best correspond to the experimental data for the selected set of stoichiometric coefficients p, q and r of the complex equilibrium considered,

$$pM + q\,LH_2 - r\,H \; \rightleftharpoons \; M_pL_qH_{2q-r} \quad *\beta_{pqr} \qquad (A)$$

were calculated by the minimization process using this program, on the basis of the additivity of the absorbances of all the absorbing species, from the set of absorbance values for the corresponding experimental conditions.

The values of the standard deviations of the determination of the absorbance $\sigma(A)$ and the logarithms of the equilibrium constants $\sigma(\log *\beta)$, which must not be greater than the measuring precision ($\sigma(A) \leqq \Delta A \approx 0\cdot010$) or must fulfill the condition $*\beta \leqq F_\sigma \cdot \sigma(*\beta)$, where F_σ is the rejection factor, are a criterion of the correctness of the tested model (p, q, r) of the absorbing species and the values of their basic parameters ($\varepsilon, *\beta$). The value $F_\sigma = 1\cdot5$ was used in this work, which corresponds to 93·3% probability for the existence of the given species.

The overall number of absorbing species in solution was found by matrix analysis of the absorption spectra by the RANKANAL program (ref.[10,11]) and the statistical parameters of the spectrophotometric method of determining Cd(II) ions with PAR were found by the linear least squares method using the STAT program (ref.[12]).

Acid–Base Equilibria of PAR

The dissociation constant values $pK_{a1} = 2\cdot76 \pm 0\cdot03$ and $pK_2 = 5\cdot41 \pm 0\cdot01$ for aqueous medium ($c_L = 2 \cdot 10^{-5}$ mol l^{-1}, $c_{EDTA} = 5 \cdot 10^{-4}$ mol l^{-1}, $365-555$ nm, $\Delta\lambda = 10$ nm, $I = 0\cdot10$) or $pK_{a2} = 5\cdot54 \pm 0\cdot01$ in 10% acetone medium ($c_L = 1 \cdot 10^{-5}$ mol l^{-1}, $c_{EDTA} = 1 \cdot 10^{-3}$ mol l^{-1}, $460-555$ nm, $\Delta\lambda = 5$ nm, $I = 0\cdot10$) were calculated from the absorbance-pH curves for 20 wavelength values using the SQUAD-G program; these values are in good agreement with the literature data.

Complex Equilibria of Cd(II) with PAR

The absorption spectra of equimolar solutions and of solutions with various concentration excesses of Cd(II) ions or of reagent (Fig. 1 and 2 and Table I) indicate

the presence of the acid–base forms of the reagent LH_3^+, LH_2 and LH^- with absorption maxima at 395 and 452 nm, 386 nm or 413 nm, respectively (ref.[13]) and at least three complexes of Cd(II) ions with PAR, whose absorption maxima lie in the range $480-515$ nm, in dependence on the experimental conditions.

TABLE 1

Optical characteristics of the Cd(II)–PAR system. $c_L = 1.60 . 10^{-5}$ mol l^{-1}, $I = 0.10$ (HNO$_3$ + NaOH), $t = 25°C$

c_M/c_L	pH	λ_{max}, nm	$\lambda_{i.p.}$, nm
2 400[a]	<4	395, 452[b], 500	470—480
	>4	413[b], 495, 515	436
80	<5	395[b], 452[b], 500	450—480, 395
	>5	413[b], 495, 515	329, 436, 551
	~8	595, 515	
1	>6	413[b], 495, 515	330, 440
1/2	>6	413[b], 495, 515	329, 440, 550
1/5[c], 1/10[d]	>7	413[b], 495, 515	329, 440, 550
1/10[d]	>7	413[b], 495, 515	336, 447

[a] $c_L = 2.00 . 10^{-5}$ mol l^{-1}; [b] absorption maxima of the acid–base forms of the reagent, LH_3^+, LH_2 and LH^-; [c] $c_L = 4.00 . 10^{-5}$ mol l^{-1}; [d] $c_L = 8.00 . 10^{-5}$ mol l^{-1}
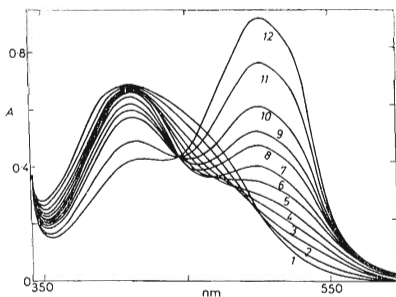

FIG. 1

Absorption spectra of a PAR solution with a concentration excess of cadmium ions. $c_M = 1.28 . 10^{-3}$ mol l^{-1}, $c_L = 1.6 . 10^{-5}$ mol l^{-1}, $c_M/c_L = 80$, $I = 0.10$ (HNO$_3$ + KOH), $l = 10$ mm, $t = 25°C$. Curve: 1 pH 3·97; 2 4·35; 3 4·80; 4 5·11; 5 5·75; 6 6·12; 7 6·45; 8 6·72; 9 6·95; 10 7·33; 11 7·45; 12 7·86

The absorbance-pH curves of aqueous solutions of PAR with a concentration excess of cadmium ions, measured for 20 discrete wavelengths in the interval 365 to 555 nm in steps of $\Delta\lambda = 10$ nm (for the experimental conditions, see Fig. 3) and for
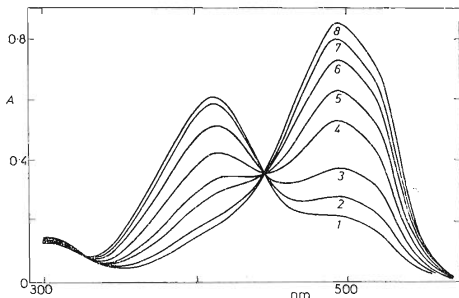

Fig. 2

The absorption spectra of a solution of Cd(II) ions with a concentration excess of PAR $c_M = 8.00 \cdot 10^{-6}$ mol l^{-1}, $c_L = 1.6 \cdot 10^{-5}$ mol l^{-1}, $c_L/c_M = 2$, $I = 0.10$ (HNO$_3$ ++ KOH), $l = 10$ mm, $t = 25°C$. Curve: 1 pH 6·37; 2 7·11, 3 7·48, 4 7·98, 5 8·35, 6 8·57, 7 9·27, 8 10·04
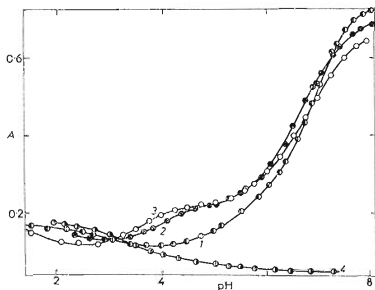

Fig. 3

The absorbance-pH curves of a PAR solution with a concentration excess of cadmium ions. $c_L = 2.00 \cdot 10^{-5}$ mol l^{-1}, $I = 0.10$ (HNO + KOH), 495 nm, c_M (mol l^{-1}) and c_M/c_L: Curve 1 $4.8 \cdot 10^{-4}$ and 24; 2 $4.8 \cdot 10^{-3}$ and 240; 3 $4.8 \cdot 10^{-2}$ and 2 400; 4 0

pH $1 \cdot 25 - 8 \cdot 00$ exhibit two formation regions at pH $2 \cdot 5 - 4 \cdot 7$ and $5 \cdot 0 - 8 \cdot 0$. Matrix analysis of the set of experimental data using the RANKANAL program confirms the simultaneous existence of four absorbing species in the whole studied pH interval. Graphical interpretation of both formation parts of the absorbance curves for 485, 495 and 515 nm using slope-intercept transformation confirms formation of the protonated CdLH complex from free components in the pH interval $2 \cdot 5 - 4 \cdot 7$ and deprotonation to the CdL complex in the second formation part of the absorbance-pH curve in the sense of the equilibria (charges are omitted)
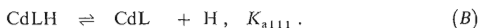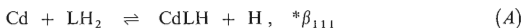
$$ Cd + LH_2 \ \rightleftharpoons \ CdLH + H , \quad {}^*\beta_{111} \qquad (A) $$

$$ CdLH \ \rightleftharpoons \ CdL + H , \quad K_{a111} . \qquad (B) $$

TABLE II

Values of the logarithms of the equilibrium constants of the reaction $p \, Cd + q \, LH_2 - r \, H \rightleftharpoons Cd_p L_q H_{2q-r}$ obtained by graphical interpretation and using the SQUAD-G program from the absorbance-pH curves $A = f(pH)$. $I = 0 \cdot 10$ (HNO$_3$ + KOH), $l = 10$ mm, $t = 25°C$

Assumed species	c_M/c_L	$-\log {}^*\beta_{pqr}$	$\sigma(A)^a$	$U \cdot 10^{2 \ b}$
LH$_3$, LH$_2$, LH	$2 \ 400^c$	$1 \cdot 4^f$; $1 \cdot 8^g$		
CdLH,		$1 \cdot 666 \pm 0 \cdot 044$; $1 \cdot 4^f$; $1 \cdot 8^g$	$0 \cdot 012$	$5 \cdot 403$
CdL		$8 \cdot 246 \pm 0 \cdot 051$; $8 \cdot 55^g$		
LH$_2$, LH,	$1/10^d$, $1/21^e$			
CdL$_2$H$_2$,		$2 \cdot 812 \pm 0 \cdot 049^d$, $2 \cdot 854 \pm 0 \cdot 036^e$		
CdL$_2$H,		$9 \cdot 414 \pm 0 \cdot 052^d$, $9 \cdot 584 \pm 0 \cdot 043^e$	$0 \cdot 004$, $0 \cdot 004^e$	$1 \cdot 017$, $0 \cdot 786^e$
CdL$_2$		$17 \cdot 340 \pm 0 \cdot 066^d$, $17 \cdot 330 \pm 0 \cdot 065^e$		
LH$_2$, LH,	$1/10^d$, $1/21^e$	very high values of ε_{pqrk} for complex CdL		
CdL, CdL$_2$				

^{a} Standard deviation of absorbance determination; ^{b} sum of the squares of the deviations $U = = (A_{exp} - A_{calc})^2$; ^{c} $c_L = 2 \cdot 00 \cdot 10^{-5}$ mol l^{-1}, $c_M = 4 \cdot 80 \cdot 10^{-2}$ mol l^{-2}, 365—555 nm à 10 nm, pH $2 \cdot 73 - 7 \cdot 74$, number of measurements $n_p = 20$, calculation for species LH$_3$, LH$_2$, LH, CdL and Cd$_2$L does not converge; ^{d} $c_M = 9 \cdot 484 \cdot 10^{-6}$ mol l^{-1}, $c_L = 1 \cdot 00 \cdot 10^{-4}$ mol l^{-1}, 460—555 nm à 5 nm, pH $4 \cdot 50 - 9 \cdot 52$, number of measurements $n_p = 28$, calculation for models including the species LH$_2$, LH$^-$, CdL, CdL$_2$H$_2$, CdL$_2$H$^-$, CdL$_2^{2-}$, or LH$_2$, LH$^-$, CdL$_2^{2-}$, CdL$_2$H$_3^+$; LH$_2$, LH$^-$, CdL, CdL$_2$H$_2$, CdL$_2^{2-}$; LH$_2$, LH$^-$, CdL, CdL$_2$H$^-$, CdL$_2^{2-}$; LH$_2$, LH$^-$, CdL, CdL$_2$H$^-$, CdL$_2^{2-}$; LH$_2$, LH$^-$, CdLH$^+$, CdL$_2^{2-}$, CdL$_2^{2-}$, does not converge; ^{e} pH $= = 4 \cdot 49 - 9 \cdot 23$, number of measurements $n_p = 27$, $c_L = 2 \cdot 00 \cdot 10^{-4}$ mol l^{-1}, $c_M = 9 \cdot 484 \cdot 10^{-6}$ mol l^{-1}, 460—555 nm à 5 nm, calculation for models in d does not couverge; ^{f} ref.[2]; ^{g} graphical interpretation.

The best agreement of the experimental data and theoretically calculated $A = f(\text{pH})$ curves in numerical interpretation of the absorbance-pH curves for a concentration excess of cadmium ions of $c_M/c_L = 2\,400$ using the SQUAD-G program was found
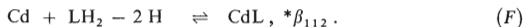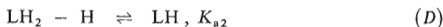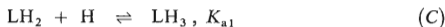
TABLE III

Molar absorption coefficient values for the CdLH, CdL, CdL$_2$H$_2$, CdL$_2$H and CdL$_2$ complexes calculated by the SQUAD-G program. For experimental conditions, see Table II

λ, nm	ε_{pqrk}, mmol^{-1} cm^2				
	CdLH[a]	CdL[a]	CdL$_2$H$_2$[b]	CdL$_2$H[b]	CdL$_2$[b]
365	9 086 ± 314	4 494 ± 539			
375	11 890 ± 323	5 113 ± 555			
385	14 750 ± 275	5 916 ± 473			
395	16 910 ± 172	6 795 ± 295			
405	17 750 ± 82	7 533 ± 142			
415	17 140 ± 114	8 268 ± 196			
425	15 360 ± 186	9 289 ± 319			
435	13 090 ± 216	10 910 ± 371			
445	11 200 ± 199	13 710 ± 342			
455	10 260 ± 161	17 480 ± 276			
460			12 560 ± 463	37 100 ± 639	58 080 ± 379
465	10 090 ± 113	21 980 ± 193	11 490 ± 425	41 940 ± 588	64 460 ± 349
470			10 990 ± 385	46 600 ± 532	70 650 ± 316
475	10 290 ± 134	26 290 ± 230	11 060 ± 345	50 930 ± 477	76 660 ± 283
480			11 380 ± 298	55 040 ± 412	82 430 ± 244
485	10 460 ± 215	30 420 ± 369	11 800 ± 267	58 720 ± 369	87 590 ± 219
490			12 300 ± 265	61 350 ± 367	90 880 ± 218
495	10 400 ± 248	31 990 ± 426	12 990 ± 239	62 280 ± 331	91 610 ± 196
500			13 400 ± 225	61 510 ± 311	89 830 ± 184
505	9 933 ± 246	30 840 ± 423	13 780 ± 206	59 870 ± 285	86 930 ± 169
510			13 510 ± 225	57 570 ± 312	83 100 ± 185
515	9 099 ± 216	28 630 ± 371	13 370 ± 216	55 000 ± 299	79 340 ± 177
520			12 910 ± 203	52 150 ± 281	75 070 ± 167
525	7 841 ± 176	23 520 ± 303	12 040 ± 193	46 750 ± 267	67 290 ± 158
530			10 900 ± 148	38 150 ± 205	54 410 ± 122
535	6 329 ± 141	13 680 ± 241	9 884 ± 131	28 160 ± 182	39 370 ± 108
540			8 659 ± 109	19 410 ± 151	26 050 ± 89
545	4 734 ± 104	6 688 ± 180	7 444 ± 98	13 030 ± 136	16 330 ± 80
550			6 198 ± 87	8 757 ± 120	9 985 ± 71
555	3 267 ± 81	3 480 ± 139	5 103 ± 77	5 920 ± 106	6 177 ± 63

[a] Results for a concentration excess of Cd(II) ions, $c_L = 2.00 \cdot 10^{-5}$ mol l^{-1}, $c_M = 4.848 \cdot 10^{-2}$ mol l^{-1}, pH 2·73—7·74; [b] concentration excess of PAR, $c_L = 2.00 \cdot 10^{-4}$ mol l^{-1}, $c_M = 9.484 \cdot 10^{-6}$ mol l^{-1}.

for the model of reaction equilibrium with formation of the CdLH and CdL complexes with simultaneous consideration of the acid–base transitions of the reagent, LH_3/LH_2 and LH_2/LH, in the sence of the equations (charges are omitted)

$$LH_2 + H \rightleftharpoons LH_3, K_{a1} \qquad (C)$$

$$LH_2 - H \rightleftharpoons LH, K_{a2} \qquad (D)$$

$$Cd + LH_2 - H \rightleftharpoons CdLH, *\beta_{111} \qquad (E)$$

$$Cd + LH_2 - 2H \rightleftharpoons CdL, *\beta_{112}. \qquad (F)$$

The dissociation constants of the first two reactions were left unchanged during the calculation and only the equilibrium constants of reactions (E) and (F) changed together with the molar absorption coefficients of the CdLH and CdL complexes. The $\log *\beta_{111}$ and $\log *\beta_{112}$ values obtained from graphical interpretation of the curves $(\log *\beta_{111} = -4 \cdot 82, \log *\beta_{112} = -9 \cdot 50)$ were used as initial data for the actual
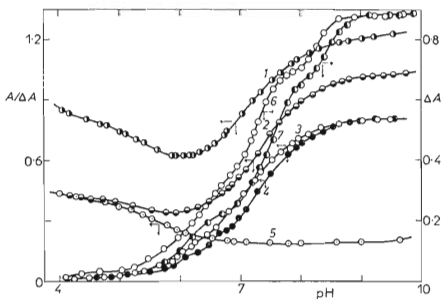

Fig. 4

The absorbance-pH curves of a solution of Cd(II) ions with various concentration excesses of PAR. $c_M = 9 \cdot 484 \cdot 10^{-6}$ mol l^{-1}, $I = 0 \cdot 10$ (HNO$_3$ + KOH), 495 nm. Curves $1-3$, $A = f(\text{pH})$, curves $4-7$, $\Delta A = A - A_{OL} = f(\text{pH})$. c_L (mol l^{-1}) and c_L/c_M: Curve 1 $2 \cdot 0 \cdot 10^{-4}$ and 21; 2 $1 \cdot 0 \cdot 10^{-4}$ and $10 \cdot 5$; 3 $1 \cdot 0 \cdot 10^{-4}$, $c_M = 0$; 4 $2 \cdot 0 \cdot 10^{-4}$ and $21 \cdot 0$; 5 $1 \cdot 0 \cdot 10^{-4}$ and $10 \cdot 5$; 6 $1 \cdot 0 \cdot 10^{-4}$ and $10 \cdot 58$; 7 $5 \cdot 00 \cdot 10^{-5}$ and $5 \cdot 29$

calculation. In consideration of further complexing equilibria (Cd_2L, $CdLH$, CdL), the calculation did not converge which, together with the small value of the standard deviation of the absorbance $\sigma(A)$, confirms the correctness of the above conclusions. A survey of the values of the molar absorption coefficients and the logarithms of the equilibrium constants of the reactions, (A), (B), (E) and (F), obtained by graphical and numerical interpretation of the absorbance curves, is given in Tables II and III.

The absorbance-pH curves of Cd(II) solutions with concentration excess of PAR for 20 discrete wavelength values in the interval $460-555$ nm in steps of $\lambda = 5$ nm, measured in 10% (v/v) acetone medium (for experimental conditions, see Fig. 4) in the pH interval $3 \cdot 9 - 10 \cdot 1$ exhibit three insufficiently separated formation branches at pH $5-7$, $7-8$ and $8-9$ or $4-6$, $6-7$ and $7-9$.

Graphical interpretation of the curves for wavelengths of 495 and 515 nm in the pH interval $5 \cdot 2 - 9 \cdot 5$, assuming formation of the CdL_2H_x complexes from the free components and their interconversion, confirms the formation of a mixture of variously protonated complexes with molar $M : L = 1 : 2$. At pH $5 \cdot 75$ the CdL_2H_2 complex predominates in solution ($\varepsilon_{max} = 26 \cdot 500$, $\log *\beta_{122} = -2 \cdot 5$), at pH ~ 6 deprotonation of the CdL_2H_2 complex to the CdL_2H complex ($\varepsilon_{max} = 70\,900$) begins to occur and, finally, at pH $8-9 \cdot 5$ a further proton is dissociated to give
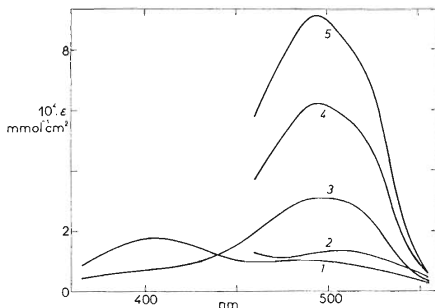

Fig. 5

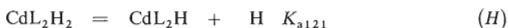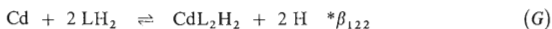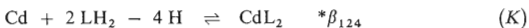The absorption spectra of the individual $CdLH^+$, CdL, CdL_2H_2, CdL_2H^- and CdL_2^{2-} complexes calculated by the SQUAD-G program. Curve, complex: *1* $CdLH^+$, *2* CdL, *3* CdL_2H_2, *4* CdL_2H^-, *5* CdL_2^{2-}

the CdL$_2$ complex $\left(\varepsilon_{max} = 87\,900\right)$ according to the equilibria (charges are omitted)

$$Cd + 2\,LH_2 \;\rightleftharpoons\; CdL_2H_2 + 2\,H \quad *\beta_{122} \qquad (G)$$

$$CdL_2H_2 \;=\; CdL_2H + H \quad K_{a121} \qquad (H)$$

$$CdL_2H \;\rightleftharpoons\; CdL_2 + H \quad K_{a120}. \qquad (I)$$

Because of the insufficient separation of the individual formation part of the curves, the equilibrium constant values change considerably with a change in the concentration excess of PAR; nevertheless, they were used as initial values in the numerical interpretation of the curves by the SQUAD-G program.

Numerical interpretation of the absorbance-pH curves for $c_L/c_M = 10.5$ and 21.0 for the whole set of experimental data confirm the existence of the CdL$_2$H$_2$, CdL$_2$H and CdL$_2$ complexes in addition to the acid–base forms of the reagent LH$_2$ and LH. In consideration of further complexes (CdL, CdL$_2$H$_3$, CdLH, etc.), the calculation for the curves with a concentration excess of PAR does not converge or the values of the molar absorption coefficients of some complexes are very high and mostly the required value of the standard deviation for the determination of the absorbance and the logarithm of the equilibrium constants are not attained (Table II). A survey of the values of the basic parameters for the CdL$_2$H$_2$, CdL$_2$H and CdL$_2$ complexes and the equilibrium constants of reaction (G) and of the reactions (charges are omitted)

$$Cd + 2\,LH_2 - 3\,H \;\rightleftharpoons\; CdL_2H \quad *\beta_{123} \qquad (J)$$

$$Cd + 2\,LH_2 - 4\,H \;\rightleftharpoons\; CdL_2 \quad *\beta_{124} \qquad (K)$$

together with the $\sigma(A)$ and $\sigma(\log *\beta_{pqr})$ values, are given in Tables II and III.

The stoichiometric compositions of the complexes were confirmed by measuring the dependence of the absorbance on the concentration of the components for wavelengths of 480, 495, 510 and 525 nm at selected pH values. The $A = f(c_M)$ curve at pH 4.0, 5.0 and 7.0, $c_L = 1.89 \cdot 10^{-5}$ mol l^{-1}, $c_M = (0.0935 - 3.78) \cdot 10^{-3}$ mol l^{-1}, evaluated by the tangent method, indicates bonding of a single Cd(II) ion in the whole pH interval. The $A = f(c_L)$ curves for $c_M = 9.45 \cdot 10^{-6}$ mol l^{-1} and $c_L = (0.10$ to $1.53) \cdot 10^{-4}$ mol l^{-1} confirm the existence of a complex with molar ratio M : L = = 1 : 2 at pH 7.5 and 8.5 and the existence of a mixture of complexes with molar ratios M : L of 1 : 1 and 1 : 2 at pH 5.25.

The continuous variation curves $\Delta A = f(x_L)$ also confirm the existence of a complex with molar ratio M : L = 1 : 2 in the whole range of experimental conditions

$(c_O = c_M + c_L = 1.89 . 10^{-5} \text{ mol l}^{-1}$, 480, 495, 510 and 525 nm, pH 6·0, 7·5 and 8·5), as the maximum on the curve lies at $x_L = 0.66$. The basic parameters differ considerably for the individual pH values, indicating the presence of a mixture of variously protonated complexes, CdL_2H_x $(x = 0-2)$.

The distribution diagrams $\delta = [M_pL_qH_{2q-r}]/c_M = f(\text{pH})$ or $\delta = [M_pL_qH_{2q-r}] / / c_L = f(\text{pH})$ for solutions with a concentration excess of Cd(II) ions (curves 3 and 4 in Fig. 6) confirm quantitative formation of the MLH and ML complexes at pH 4·5–5·0 and pH > 8, respectively. The ML_2H_2, ML_2H and ML_2 complexes are formed stepwise in solutions with a concentration excess of reagent (Fig. 6, curves 5–8). The maximal values of the distribution coefficients $\delta = 0.65$ and $\delta = = 0.55$, respectively, of the first two complexes are attained at pH 6 and pH 7·25, respectively. The ML_2 complex is formed quantitatively at pH > 9·2 and at pH > 10 the acid–base equilibrium $LH \rightleftarrows L$ of the reagent alone begins to become important $(pK_{a3} = 11.98)$. This pH interval is also most suitable for development of a spectrophotometric method for the determination of Cd(II) with PAR.

It follows from study of the complex equilibria of Cd(II) ions with PAR that the equilibrium scheme corresponds completely to the reaction scheme found by graphical methods and numerical treatment of the absorbance curves by the PRCEK[13] program for Zn(II) solutions with PAR. The complexes of Zn(II) with PAR are roughly one order of magnitude more stable than the corresponding complexes of Cd(II) and values of the molar absorption coefficients of the ZnL_2H_2, ZnL_2H and ZnL_2 complexes $(\varepsilon_{122} = 17\,000 \text{ mmol}^{-1} \text{ cm}^2$, $\varepsilon_{123} = 67\,000 \text{ mmol}^{-1} \text{ cm}^2$,
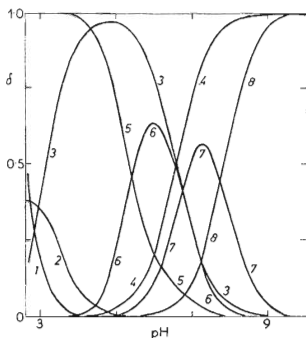

Fig. 6

Distribution curves for components of the reaction mixture of Cd(II) + PAR in solutions with a concentration excess of cadmium ions (curves 1–4) or of PAR (curves 5–8). Curves 1–4: $c_M = 4.8 . 10^{-2}$ mol l^{-1}, $c_L = = 2.0 . 10^{-5}$ mol l^{-1}, $c_M/c_L = 2\,400$; Curves 5–8: $c_M = 9.484 . 10^{-6}$ mol l^{-1}, $c_L = = 2.0 . 10^{-4}$ mol l^{-1}, $c_L/c_M = 21.0$. δ: Curve 1 $[LH_2]/c_L$, 2 $[LH]/c_L$, 3 $[MLH]/c_L$, 4 $[ML]/c_L$, 5 $[M]/c_M$, 6 $[ML_2H_2]/c_M$, 7 $[ML_2H]/c_M$, 8 $[ML_2]/c_M$

$\varepsilon_{124} = 93\,000$ mmol^{-1} cm^2 at 495 nm) are roughly $2\,000 - 5\,000$ mmol^{-1} cm^2 higher than for the corresponding CdL_2H_2, CdL_2H and CdL_2 complexes (Tables III and IV).

TABLE IV

Characteristics of the spectrophotometric method of determining Cd(II) with PAR reagent. $c_L = 1.00 \cdot 10^{-4}$ mol l^{-1}, $c_M = (0.378 - 2.26) \cdot 10^{-5}$ mol l^{-1}, 0.10 mol l^{-1} borate buffer, pH 9.22, $l = 10$ mm, $t = 25°C$

Quantity	λ, nm			
	480	496	510	525
$\varepsilon \pm d(\varepsilon)^a$	$70\,460 \pm 662$	$81\,650 \pm 862$	$75\,650 \pm 785$	$59\,820 \pm 574$
q^b	0·9993	0·9993	0·9993	0·9994
$A_{b1}{}^c$	0·450	0·248	0·156	0·097
$s_{xy}{}^d$	0·0184	0·0194	0·0177	0·0130
$10^3 \cdot U^e$	2·04	2·26	1·89	1·01
$S_I \cdot 10^2{}^f$	1·59	1·37	1·49	1·87

^{a} Molar absorption coefficient and its standard deviation, mmol^{-1} cm^2. ^{b} correlation coefficient; ^{c} blank absorbance; ^{d} estimated standard deviation for the scatter around the regression straight line, $s_{xy} = (U/(n-2))^{1/2}$ for $n = 8$; ^{e} sum of the squares of the deviations $U = \sum(A_{exp} - A_{calc})^2$; ^{f} Sandell's sensitivity index for $A = 0.010$, $S_I = 10 \cdot M_r/\varepsilon$.

TABLE V

The effect of some ions on the determination of Cd(II). $c_L = 1.00 \cdot 10^{-4}$ mol l^{-1}, $c_{Cd} = 4.52 \cdot 10^{-6}$ mol l^{-1}, 495 nm, pH 9.22, 0.10 mol l^{-1} borate buffer, $l = 10$ mm, $t = 25°C$

Ion	Δ, %^{a}	Ion	Δ, %^{a}
Co(II)	31·7; 7·5^b	NO$_3^-$	1·5^c
Cu(II)	64·8; 17·1^b	ClO$_4^-$	1·5^c
Zn(II)	71·5; 19·6^b	Cl$^-$	1·5^d
Ni(II)	51·6; 14·0^b	SO$_4^{2-}$	1·5^{d,e}
		J$^-$	1·5^e

^{a} Relative error of determining the absorbance in %, $100(A_x - A)/A$; ^{b} data for a concentration ratio of $c_{Cd}/c_X = 1.0$ or $1/4$; ^{c} data for $c_X = 0.5$ mol l^{-1}, $c_X/c_{Cd} = 1.11 \cdot 10^5$; ^{d} $c_X = 1.0$ mol l^{-1}, $c_X/c_{Cd} = 2.22 \cdot 10^5$; ^{e} $c_X = 0.1$ mol l^{-1}, $c_X/c_{Cd} = 2.22 \cdot 10^4$, c_X is the concentration of the interfering ion in mol l^{-1}; A_X is the absorbance of a solution of $c_{Cd} = 4.52 \cdot 10^{-6}$ mol l^{-1} for the concentration ratio c_M/c_X given in notes $b-e$; A is the absorbance of a solution with $c_{Cd} = 4.52 \cdot 10^{-6}$ mol l^{-1}.

The Spectrophotometric Method for the Determination of Cd(II) *with* PAR

Detailed study of the complex equilibria of cadmium ions with PAR has shown that the only complex suitable for development of a determination method is the CdL_2 complex $(\lambda_{max} = 495$ nm, $\varepsilon_{max} = 91\,600$ mmol^{-1} cm$^2)$, which is formed quantitatively in solutions with a concentration excess of PAR $(c_M = 9\cdot45 \cdot 10^{-6}$ moll^{-1}, $c_L/c_M = 5\cdot29, 10\cdot5$ and $21\cdot0)$ at pH 9. At higher pH values, pH > 10, the LH/L acid–base equilibrium begins to become important and the strongly absorbing L acid–base form is present $(\lambda_{max} = 488$ nm, $\varepsilon_{max} = 2\cdot4 \cdot 10^4$ mmol^{-1} cm$^2)$. The optimum acidity conditions lie in the pH interval pH $9\cdot0 - 9\cdot7$.

For acidity adjustment, $0\cdot02 - 0\cdot5$ mol l^{-1} borate solutions (pH $9\cdot22$) and ammonia buffer (pH $9\cdot50$) were tested. The relative error when using $0\cdot05$ mol l^{-1} ammonia buffer or $0\cdot10$ mol l^{-1} borate buffer, $100(A_T - A)/A$ was approximately $1\cdot5\%$, so that further measurements were carried out using $0\cdot10$ mol l^{-1} borate buffer with pH $9\cdot22$.

It follows from the dependence of the absorbance on the PAR concentration $\Delta A = f(c_L)$ under the above experimental conditions $(c_M = 9\cdot45 \cdot 10^{-6}$ mol l^{-1}, $c_L = (0\cdot0503 - 1\cdot01) \cdot 10^{-4}$ mol l^{-1}, pH $9\cdot22)$ that a concentration excess of PAR of $c_L/c_M \geqq 4$ is sufficient for quantitative formation of the CdL_2 complex. A final concentration of $c_L = 1 \cdot 10^{-4}$ mol l^{-1} was chosen for the actual determination ensuring sufficient concentration excess of PAR in the whole range of the calibration curve. The calibration curve is linear in the cadmium ion concentration range $c_M = (0\cdot378 - 2\cdot26) \cdot 10^{-5}$ mol l^{-1}. The basic statistical parameters of the calibration curve for 480, 495, 510 and 525 nm indicate (Table IV) that the determination method is most sensitive and precise at 495 nm.

The effect of some selected cations and anions is given in Table V. Among cations, Cu(II), Co(II), Zn(II) and Ni(II) strongly interfere, while anions do not interfere in quite high concentrations, which is advantageous for separation of cadmium ions as the halogen complexes.

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