EFFECTIVE SPECTROPHOTOMETRIC STUDY OF THE COMPLEXATION REACTIONS OF 2-(2-PYRIDYLAZO)-1-NAPHTHOL-4-SULPHONIC ACID WITH Zn(II) AND Cd(II) USING THE SQUAD-G PROGRAM

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The existence of the red-orange protonated MLH complexes ($\lambda_{max} = 490$ nm, $\varepsilon_{max} = 16\,700$ $mmol^{-1}\ cm^2$, $\log {}^*\beta_{111} = -0{\cdot}51$ for Zn(II) and $\lambda_{max} = 490$ nm, $\varepsilon_{max} = 20\,800$ $mmol^{-1}\ cm^2$, $\log {}^*\beta_{111} = -1{\cdot}28$ for Cd(II)) and of the red-purple ML and ML_2 complexes ($\lambda_{max} = 517$ nm, $\varepsilon_{max} = 27\,5000$ $mmol^{-1}\ cm^2$, $\log {}^*\beta_{112} = -2{\cdot}8$ and $\lambda_{max} = 527$ nm, $\varepsilon_{max} = 61\,500$ $mmol^{-1}$ . . cm^2, $\log {}^*\beta_{124} = -6{\cdot}0$ for Zn(II) and $\lambda_{max} = 522$ nm, $\varepsilon_{max} = 27\,200$ $mmol^{-1}\ cm^2$, $\log {}^*\beta_{112} = -3{\cdot}9$ and $\lambda_{max} = 522$ nm, $\varepsilon_{max} = 52\,000$ $mmol^{-1}\ cm^2$, $\log {}^*\beta_{124} = -8{\cdot}2$ for Cd(II) ions) was demonstrated in aqueous medium by numerical interpretation of the absorbance curves by the SQUAD-G minimization program. Conditions were proposed for development of a spectrotrophotometric method for the determination of Zn(II) and Cd(II) using 1-PAN-4S.

The N-heterocyclic azodye 2-(2-pyridylazo)-1-naphthol-4-sulphonic acid (further 1-PAN-4S) is a suitable indicator for metal ions in EDTA titrations and a sensitive spectrophotometric reagent for the determination of a number of elements. Both the properties of the reagent and its analytical importance have been described[1]. The complexation reactions of this reagent with Cu(II) and Ni(II) (ref.[2]), Hg(II) (ref.[3]), Ga(III), In(III) and Tl(III) (ref.[4]) and Co(III) (ref.[5]) have been studied in detail and optimal conditions have been found for the spectrophotometric determination of these elements.

This work is concerned with study of the complexation equilibria of 1-PAN-4S with Zn(II) and Cd(II) ions in aqueous media; the possibility of spectrophotometric determination of these elements with this reagent was confirmed. The general and expanded SQUAD-G program (ref.[6]), originally used in a primary version by Leggett and McBryde[7], was found very useful in the study of complexation equilibria.

EXPERIMENTAL AND RESULTS

Chemicals and Instruments

2-(2-Pyridylazo)-1-naphthol-4-sulphonic acid (further 1-PAN-4S) with a content of 91·9% of the anhydrous substance (M_r 329·3) was standardized by elemental analysis (CH N content) and photometric microtitration with a $Cu(NO_3)_2$ solution in a formate buffer solution with pH 3·6 (ref.[1]).

The $Cu(NO_3)_2$ solution was standardized by EDTA titration. The stock reagent solutions were prepared by dissolving precisely weighed amounts of the solid substance in 5 ml of 1 mol l^{-1} HNO_3, semiconductor purity, and dilution with distilled water to the required volume. The solution is stable for at least 14 days.

Zinc nitrate: $9{\cdot}824 \,.\, 10^{-2}$ mol l^{-1} in 0·1 mol l^{-1} HNO_3. The original substance of *p.a.* purity (Lachema, Czechoslovakia) was recrystallized from 0·1 mol l^{-1} HNO_3. The solution was standardized gravimetrically and by EDTA titration. Cadmium(II) nitrate, $1{\cdot}897 \,.\, 10^{-1}$ mol . . l^{-1} in 0·1 mol l^{-1} HNO_3, was prepared by dissolving a precisely weighed amount of 99·999% cadmium (Metal Research Institute, Panenské Břežany, Czechoslovakia) in an excess of HNO_3. The cadmium content was controlled by EDTA titration.

Nitric acid, semiconductor purity (Lachema, Brno, Czechoslovakia) and NaOH, Suprapure (Merck, GFR) were use for adjusting the acidity and the ionic strength to 0·10. The remaining chemicals were of *p.a.* purity or were recrystallized.

A Superscan 3 digital double-beam recording spectrophotometer (Varian, Switzerland) was used, connected to an "on-line" desk-top HP 9815A calculator (Hewlett-Packard, USA). PHM 64 and PHM 4 pH meters (Radiometer, Denmark) were used with a G 202B glass and a K401 saturated calomel electrode and were calibrated with a set of standard NBS buffers (1·68, 4·01, 7·00 and 9·18 with a precision of ±0·01 at 25°C).

Measuring Method

The absorption spectra and absorbance curves were measured in dependence on the acidity and component concentrations using a modified apparatus for measurements in a closed cycle[8] with a connecting teflon tube and hypodermic syringe for solution transport between the titration vessel and the spectrophotometer cuvette.

In a study of the acid–base equilibria of the reagent alone, two reagent solutions with the same ionic strength but different pH values were mixed. The effect of trace amounts of metal ions was eliminated by addition of EDTA in a 10—30× excess over the reagent. In study of the complexation equilibria of Zn(II) and Cd(II) ions, all the necessary components at ionic strength and at a pH value at which the complex is not formed were placed in titration vessel (A). Depending on the required acidity change, this solution was then titrated with an NaOH solution with a final concentration of 1·0, 0·10 or 0·01 mol l^{-1}. The changes in the concentrations of the individual components as a result of the titration were compensated by addition of the same volume of compensation solution (*B*) with the same ionic strength *I* and double the concentration of all the solution components compared to solution (*A*) and pH = 3—5, from another burette.

The whole system was enclosed under a protective argon atmosphere, which eliminated absorption of atmospheric CO_2 in the alkaline medium of pH 8. For rapid equilibration of the electrode potential in the region pH 5·7—7·5, it was necessary to employ NaOH with a minimal carbonate content.

Interpretation of the Absorbance Curves

The SQUAD program (ref.[7]), modified for medium-sized (Tesla 200, EC 1021, Czechoslovakia) and large (EC 1033, USSR) computer[6] was used for numerical treatment of the acid-base and complexation equilibria in the solutions and calculations of the basic complex parameters.

The SQUAD program assumes validity of the Bouguer law and the law of absorbance additivity for the *i*-th solution and *k*-th wavelength. In the case of 1-PAN-4S (abbreviated as LH_2) interaction with Zn and Cd ions the following equations are valid.

$$A_{ik} = \sum_0^P \sum_0^Q \sum_0^R [M_pL_qH_{2q-r}] \cdot \varepsilon_{pqrk} = \sum_0^P \sum_0^Q \sum_0^R {}^*\beta_{pqr}[M]_i^p \cdot [LH_2]_i^q [H]_i^{-r} \cdot \varepsilon_{pqrk}\,, \qquad (1)$$

where the ε_{pqrk} are the molar absorption coefficients of the complexes with stoichiometric coefficients p, q and r for the k-th wavelength and the ${}^*\beta_{pqr}$ are the equilibrium constants given by the relationship

$${}^*\beta_{pqr} = [M_pL_qH_{2q-r}]/[M]^p[LH_2]^q[H]^{-r} \qquad (2)$$

for the considered complexation equilibrium:

$$p\,M + q\,LH_2 - r\,H \rightleftarrows M_pL_qH_{2q-r}\,. \qquad (A)$$

The values of the molar absorption coefficients ε_{pqrk} and the equilibrium constants ${}^*\beta_{pqr}$, which correspond best to the experimental data for the selected set of stoichiometric coefficients p, q and r, are calculated by the minimization procedure from the set of absorbance values for the corresponding experimental conditions.

The calculated molar absorption coefficient values must be real and non-negative and must satisfy the relationships for a change in the ε_{pqrk} values on coordination of a greater number of ligand molecules.

The criteria for the correctness of the tested models for stoichiometric coefficients p, q and r for the absorbing species and their basic parameters (${}^*\beta_{pqr}$, ε_{pqrk}), in addition to agreement of the stoichiometric coefficients with chemical concepts of the studied system, are the values of the standard deviations of the determined absorbance $\sigma(A)$, which must be less than the measuring precision $\Delta(A)$. The values of the standard deviations of the logarithms of the equilibrium constants σ (log ${}^*\beta_{pqr}$) must also satisfy the relationship ${}^*\beta_{pqr} \geqq F_\sigma \cdot \sigma({}^*\beta_{pqr})$. The value of the "rejection factor" F_σ was selected as $F_\sigma \geqq 2{\cdot}0$, corresponding to 97·7% probability for the existence of the given absorbing species.

In testing the correctness of the selected model, it is neccessary to adjust the basic complex parameters and stoichiometric coefficients p, q and r until the standard deviation of the absorbance $\sigma(A)$ is less than or equal to the estimated or determined precision and reproducibility

TABLE I

Dissociation constants of 2-(2-pyridylazo)-1-naphthol-4-sulphonic acid in aqueous solutions (I 0·1)

pK_{a1}	pK_{a2}
2·795 ± 0·001[a]	8·0036 ± 0·0008[a]
2·817 ± 0·002[b]	
2·78; 2·81[c]	
2·879 ± 0·030[d]	7·89 ± 0·02[d]

[a] From 36 wavelengths using the SQUAD-G program; [b] using the PRCEK T200 program (average from wavelengths of 495, 505, 515, 520 and 525 nm); [c] from graphical analysis of the $A = f$(pH) curves for 500 and 520 nm; [d] using the SPEKTFOT 4 program (ref. [4]).

of the absorbance measurement $\sigma(A) \leqq \Delta(A) \leqq 0{\cdot}010$. When the data were treated using an incorrect model for the stoichiometric coefficients p, q and r, the calculation generally did not converge even after a larger number of cycles ($n \geqq 20$), or the molar absorption coefficient values for the individual absorbing species were unrealistic. When using the SQUAD program, use of the criterion F_σ is of lesser importance than the other criteria.

The program permits solution of systems containing one or two different cations M_1 and M_2 and one or two ligands L_1 and L_2, including interaction with H^+ or OH^- ions. In addition to final values of the equilibrium constants $^*\beta_{p,q,r}$, stoichiometric coefficients p, q and r and molar absorption coefficients ε_{pqrk}, the results yielded information on the shape of the absorption spectra of all the absorbing species.

Using a segmented[6] SQUAD-G program (the overall length including the COMMON blocks using double precission is 114·6 kB) on the Tesla 200 computer enables treatment of sets for maximally 26 wavelength values under 20 different experimental conditions and simultaneously to change up to 4 equilibrium constants of the ten possible simultaneous complexation equilibria. When using the EC 1033 computer, sets can be computed for a maximum of 36 wavelengths under 50 different experimental conditions with simultaneous adjustment of 6-equilibrium constant values (requirements on the operational memory equal 320 kB). Both versions permit calculation of up to 10 sets of molar absorptivities, *i.e.* 260 and 360 absorptivity values for one solution on the Tesla 200 and EC 1033 computers, respectively, using an overall capacity of the operational memory of 128 and 512 kB, respectively.

Testing of the dependence of the obtained values of the basic parameters of the absorbing species on changed experimental conditions indicates that sufficiently precise and accurate parameters can be determined from measurement of the absorbance curves for a sufficient number of wavelengths (≈ 30) in a broad spectral region for the region of maximum absorbance of all the absorbing species at a larger number of sufficiently different concentrations of the reacting components and various solution acidities (25—35 values). The total measured absorbance value for the individual conditions should not be less than $A = 0{\cdot}03$.

The initial estimates of the equilibrium constants $^*\beta_{pqr}$ may differ from the correct values by up to 6—7 orders[6]. Thus the initial data may be estimates from the half-waves of the absorbance-pH curves $A = f(\text{pH})$ or $\Delta A = A - A_L - A_M = f(\text{pH})$ for solutions with a concentration excess of metal or ligand. Thus, in determination of an optimal model for the complexing equilibria in solution, prior determination of the values of the parameters[6,9] using graphical methods with slope-intercept transformation[4,10] is not necessary; however, determination of the predominant species and of their parameters with sufficient precision may shorten the time necessary for choice of an exact model and for calculation of the corresponding parameters of minor complexes in the given system using the SQUAD-G program.

The Likussar and Boltz program[14], modified for the Tesla 200 computer (ref.[11]) was used for calculation of the conditional formation constants for the complexes from the continuous variation curves. The distribution diagrams for all the components of the system were constructed from calculations using the HALTAFALL-SPEFO-GRAPH program (ref.[11,12]), under various experimental conditions and concentrations of the reacting components, from the equilibrium constant values of the existing complexation equilibria, calculated by the SQUAD-G program.

Acid-Base Properties of 1-PAN-4S

The values of the dissociation constants of the acid-base transitions LH_2/LH and LH/L and the molar absorption coefficients of the individual acid-base forms of 1-PAN-4S were found from the absorbance-pH curves for 36 wavelength values in the region 360 – 580 nm, $c_L = 3{\cdot}0 \,.\, 10^{-5}$ mol l^{-1} and pH 1·0 – 10·1 using numeri-

TABLE II

Molar absorption coefficients of the individual acid-base forms of 1-PAN-4S, calculated by the SQUAD-G program. $c_L = 3{\cdot}0 \,.\, 10^{-5}$ mol l^{-1}, $c_{EDTA} = 1{\cdot}0 \,.\, 10^{-3}$ mol l^{-1}, I 0·1

λ, nm	ε_{LH_2}, mmol^{-1} cm^2	ε_{LH}, mmol^{-1} cm^2	ε_L, mmol^{-1} cm^2
580	69 ± 3	501 ± 2	546 ± 2
570	89 ± 3	641 ± 2	1 206 ± 2
565	119 ± 3	738 ± 3	1 792 ± 2
560	117 ± 4	898 ± 4	2 623 ± 3
555	285 ± 4	1 178 ± 3	3 771 ± 4
550	418 ± 4	1 602 ± 3	5 182 ± 4
545	649 ± 5	2 299 ± 4	6 907 ± 4
540	977 ± 5	3 315 ± 4	8 835 ± 5
535	1 470 ± 6	4 712 ± 5	10 890 ± 4
532	1 845 ± 6	5 709 ± 5	12 110 ± 4
530	2 121 ± 6	6 461 ± 5	12 950 ± 4
527	2 614 ± 6	7 630 ± 6	14 150 ± 4
525	2 981 ± 6	8 442 ± 5	14 920 ± 6
522	3 582 ± 7	9 645 ± 6	16 000 ± 5
520	4 037 ± 7	10 490 ± 6	16 710 ± 4
517	4 739 ± 7	11 700 ± 7	17 710 ± 7
515	5 300 ± 9	12 450 ± 8	18 310 ± 7
510	6 693 ± 10	14 230 ± 9	19 620 ± 6
505	8 258 ± 11	15 850 ± 10	20 670 ± 5
500	9 859 ± 12	17 340 ± 11	21 360 ± 6
495	11 530 ± 14	18 760 ± 12	21 720 ± 6
490	13 160 ± 16	19 970 ± 14	21 730 ± 6
485	14 710 ± 17	20 840 ± 15	21 430 ± 7
480	16 060 ± 18	21 230 ± 16	20 480 ± 7
470	17 920 ± 18	20 610 ± 16	19 100 ± 6
460	18 470 ± 18	18 820 ± 16	17 040 ± 6
450	17 870 ± 18	16 260 ± 16	15 070 ± 5
440	16 310 ± 16	13 230 ± 14	13 040 ± 4
430	14 340 ± 14	10 520 ± 12	10 890 ± 5
420	12 200 ± 21	8 398 ± 19	8 792 ± 4
410	10 320 ± 9	6 783 ± 8	6 741 ± 8
400	9 494 ± 8	6 062 ± 7	4 910 ± 6
390	10 870 ± 9	6 615 ± 8	3 468 ± 4
380	14 300 ± 10	8 975 ± 9	2 796 ± 5
370	16 720 ± 12	11 640 ± 11	3 562 ± 6
360	17 130 ± 13	12 670 ± 12	6 108 ± 7

cal calculation by the SQUAD-G program. The results were compared with data obtained by the PRCEK T200 program (ref.[13-15]) and by graphical interpretation using slope-intercept transformations for selected wavelengths and from older data[4] (Table I). The molar absorption coefficient values for various acid-base forms of the reagent are given in Table II.

Complexation Equilibria of 1-PAN-4S *with* Zn(II) *Ions*

The isosbestic point at 485 nm on absorption curves with a concentration excess of Zn(II) ions (c_M/c_L = 16·3, c_L = 3·0 . 10^{-5} mol l^{-1}, 340–590 nm, pH 1·70–6·81) indicates transition from the acid-base form of the reagent LH_2 with maximum absorbance at 363 and 460 nm to the red-purple complex with Zn(II) with a maximum at 517 nm (Fig. 1). The absorption spectra (Fig. 2) of solutions with a concentration excess of ligand (c_L/c_M = 3·05, c_M = 9·824 . 10^{-6} mol l^{-1}, 350–600 nm, pH 2·39 to 10·11) indicate formation of a complex with a maximum at 525 nm and acid-base transitions LH_2/LH and LH/L of the free reagent (λ_{max} = 362, 460 and 480 nm, respectively).

The absorbance-pH curves of solutions with a concentration excess of Zn(II) ions (c_M/c_L = 163, 81·9, 16·3, c_L = 3·0 . 10^{-5} mol l^{-1}) or concentration excess of the reagent (c_L/c_M = 3·05, 6·11, 7·63, c_M = 9·824 . 10^{-6} mol l^{-1}) were measured in the region 380–580 nm in steps of $\Delta\lambda$ = 2–10 nm in the pH region 1·2–6·6 or 2·75 to 9·66. The computer calculations were carried out using experimental points from the curve for the final two concentration excesses of metal ion or reagent (Fig. 3 and 4).

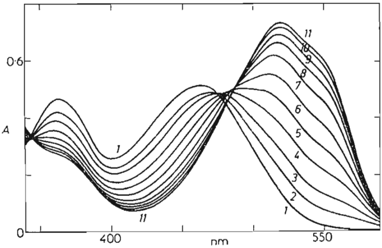

FIG. 1

Absorption curves of a 1-PAN-4S solution with excess Zn^{2+}; c_M = 4·912 . 10^{-4} mol . l^{-1}, c_L = 3·0 . 10^{-5} mol l^{-1}, I 0·1. pH: Curve *1* 1·70; *2* 2·40; *3* 2·73; *4* 3·05; *5* 3·30; *6* 3·55; *7* 3·84; *8* 4·11; *9* 4·39; *10* 4·91; *11* 6·81

Of the considered probable models for the complexation equilibria in solutions with concentration excess of Zn(II) ions, the best agreement with experimental conditions was found for the model including the acid-base forms of the reagent LH_2 and LH as well as the ZnLH and ZnL complexes (Table III). The ZnLH complex is present in solutions with highest concentration excess ($c_M \geqq 2{\cdot}456 . 10^{-3}$ mol l^{-1}) at pH 0·9 – 3·7 and at wavelengths in the region of maximum absorbance of the ZnL complex (λ_{max} 517 nm), which is optically quite similar (λ_{max} 490 nm to the ZnLH complex.

In the search for the optimal model for the complexation equilibria in solutions with a concentration excess of reagent (c_L/c_M = 6·11 and 7·63), in addition to the ZnL and ZnLH complexes, further complexes with molar ratio M : L = 1 : 2 and two-step reagent dissociation (LH_2/LH, LH/L) were considered. The best agreement with the experimental data was obtained for simultaneous presence of the following complexation equilibria:

$$\mathrm{Zn} + \mathrm{LH_2} \rightleftharpoons \mathrm{ZnLH} + \mathrm{H} \quad {}^*\beta_{111} \tag{B}$$

$$\mathrm{Zn} + \mathrm{LH_2} \rightleftharpoons \mathrm{ZnL} + 2\,\mathrm{H} \quad {}^*\beta_{112} \tag{C}$$

$$\mathrm{Zn} + 2\,\mathrm{LH_2} \rightleftharpoons \mathrm{ZnL_2} + 4\,\mathrm{H} \quad {}^*\beta_{124} \tag{D}$$

(Table III). The values of the equilibrium constants ${}^*\beta_{111}$ and molar absorption coefficients of the ZnLH complexes, calculated from the curves for solutions with

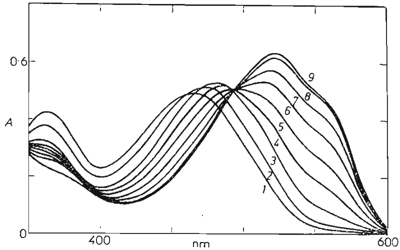

FIG. 2

Absorption curves of a Zn^{2+} solution with excess 1-PAN-4S. $c_M = 9{\cdot}824 . 10^{-6}$ mol . l^{-1}, $c_L = 3{\cdot}0 . 10^{-5}$ mol l^{-1}; *I* 0·1. pH: Curve *1* 2·39; *2* 3·01; *3* 4·17; *4* 4·72; *5* 5·12; *6* 5·61; *7* 6·17; *8* 7·55; *9* 10·11 a concentration excess of Zn(II), were retained in constant calculations, as this complex makes a negligible contribution to the overall absorbance. The other models considered yielded worse agreement (LH_2, LH, L, ZnL_2) or the calculation did not converge. All the complexes, ZnL_2H, ZnL_2H_2 and $Zn(LH_2)LH$, were rejected in the calculation by the SQUAD-G program because of unrealistic molar absorption coefficient values and large standard deviations for the equilibrium constants of the equilibria

$$\mathrm{Zn} + 2\,\mathrm{LH_2} \rightleftharpoons \mathrm{ZnL_2H} + 3\,\mathrm{H} \quad {}^*\beta_{123} \qquad (E)$$

$$\mathrm{Zn} + 2\,\mathrm{LH_2} \rightleftharpoons \mathrm{ZnL_2H_2} + 2\,\mathrm{H} \quad {}^*\beta_{122} \qquad (F)$$

$$\mathrm{Zn} + 2\,\mathrm{LH_2} \rightleftharpoons \mathrm{Zn(LH_2)LH} + \mathrm{H} \quad {}^*\beta_{121} \qquad (G)$$

or the iteration process did not converge, indicating that the model considered is not realistic[6,9].

The set of molar absorption coefficient values, the corresponding equilibrium constants and a survey of the tested models are given in Tables III and IV.

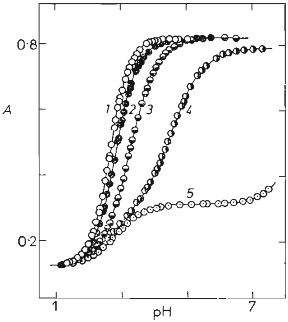

FIG. 3

Absorbance-pH curves for the Zn^{2+}–1-PAN-4S system for solutions with excess Zn^{2+}. $c_L = 3{\cdot}0 \cdot 10^{-5}$ mol l^{-1}, I 0·1, 520 nm; c_M (mol l^{-1}): Curve *1* 4·912 . 10^{-3}; *2* 2·456 . 10^{-3}; *3* 4·912 . 10^{-4}; *4* 2·947 . 10^{-5}; *5* only reagent

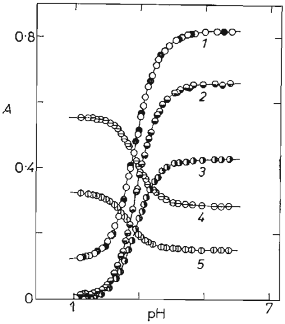

FIG. 4

Absorbance-pH curves for 1-PAN-4S solutions with a concentration excess of Zn^{2+}. $c_L = 3{\cdot}0 \cdot 10^{-5}$ mol l^{-1}, $c_M = 2{\cdot}456 \cdot 10^{-3}$ mol l^{-1}, I 0·1; Curve *1* 520 nm; *2* 550 nm; *2* 550 nm; *3* 565 nm; *4* 460 nm; *5* 390 nm

TABLE III

Results of numerical minimization of the absorption data in the Zn^{2+}–1-PAN-4S system by the SQUAD-G program.

Model (assumed species in solution)	c_M/c_L pH	$ZnLH^+$	ZnL	ZnL_2^-	$\sigma_{(A)}$ [d]	U . 10^3 [e]
		log $^*\beta_{111}$ ε, $mmol^{-1}$ cm^{-2} 490 nm	log $^*\beta_{112}$ ε, $mmol^{-1}$ cm^{-2} 517 nm	log $^*\beta_{124}$ ε, $mmol^{-1}$ cm^{-2} 527 nm		
LH_2, LH, ZnL[a] $>c_M$	81·9		−2·767 ± 0·002 27 090 ± 66		0·0105	99·71
	16·3		−2·768 ± 0·002 27 270 ± 79		0·01	86·95
LH_2, LH, ZnLH, ZnL[a] $>c_M$	81·9	−0·513 ± 0·014 16 710 ± 202	−2·758 ± 0·005 27 480 ± 23		0·0018	2·875
	16·3	−0·440 ± 0·057 17 800 ± 313	−2·827 ± 0·005 27 540 ± 18		0·0014	1·707
LH_2, LH, L, ZnL_2 $>c_L$	0·131			−5·765 ± 0·020 69 460 ± 2121	0·0889	153·9

LH_2, LH, L, ZnLH, ZnL, ZnL_2	0·131	−0·513	−2·758 ± 0·005 27 480 ± 23	−5·990 ± 0·002 61 930 ± 146	0·0030	9·659
$>c_L$	0·163	−0·513	−2·758 ± 0·005 27 480 ± 23	−5·998 ± 0·003 61 150 ± 169	0·0037	7·069
LH_2, LH, L, ZnLH, ZnL, ZnL_2 $c_M \simeq c_L$	0·990	−0·513	−2·625 ± 0·005 28 450 ± 119	−5·990 ± 0·002	0·050	17·06
LH_2, LH, ZnL $\gtrsim c_M$	5·0[b]		−2·689 ± 0·053 26 130 ± 89[c]		0·020	28·486
LH_2, LH, L, ZnL, ZnL_2 $\gtrsim c_L$	6·25[b]			−6·292 ± 0·052 55 040 ± 253[c]	0·0058	1·991

[a] Input estimate $\log {}^*\beta_{111} = -0·6$ or $\log {}^*\beta_{112} = -3·3$ from the halfwave value on the absorbance-pH curves for $c_M/c_L = 81·9$ and 16·3; [b] pH; [c] 515 nm; [d] standard deviation of the calculated A values relative to the experimental absorbance values at the same wavelength; [e] sum of the squares of the deviations $U = \sum(A_{exp} - A_{calc})^2$.

Numerical analysis of the absorbance-pH curves for equimolar solutions ($c_M = 2{\cdot}947 \,.\, 10^{-5}$ mol l^{-1}, $c_L = 3{\cdot}00 \,.\, 10^{-5}$ mol l^{-1}, 380–580 nm, pH 2·60–7·75) for 30 wavelength values yielded an optimal model for the LH_2, LH, L, ZnL, ZnLH and ZnL_2 species, while the calculation did not converge for the other tested models.

TABLE IV

Molar absorption coefficients of the complex of Zn^{2+} with 1-PAN-4S. $c_M = 2{\cdot}456 \,.\, 10^{-3}$ mol l^{-1}; $c_L = 3{\cdot}0 \,.\, 10^{-5}$ mol l^{-1}; $I = 0{\cdot}1$ (for the complex with Zn : L = 1 : 1); $c_M = 9{\cdot}824 \,.\, 10^{-6}$ mol l^{-1}, $c_L = 7{\cdot}5 \,.\, 10^{-5}$ mol l^{-1} (for the complex with Zn : L = 1 : 2)

λ, nm	ε, mmol^{-1} cm^2 $ZnLH^+$	ε, mmol^{-1} cm^2 ZnL	ε, mmol^{-1} cm^2 ZnL_2
580	2 965 ± 156	5 085 ± 17	25 260 ± 83
570	4 076 ± 283	10 960 ± 31	40 760 ± 347
565	4 058 ± 246	14 470 ± 27	47 020 ± 97
560	4 184 ± 214	17 710 ± 23	50 910 ± 104
555	4 120 ± 169	20 320 ± 18	53 230 ± 103
550	4 486 ± 157	22 090 ± 17	54 610 ± 116
545	5 009 ± 176	23 250 ± 19	56 030 ± 128
540	5 888 ± 173	24 040 ± 19	58 000 ± 140
535	6 830 ± 174	24 850 ± 19	60 220 ± 144
532	7 451 ± 184	25 420 ± 20	61 300 ± 148
530	8 034 ± 181	25 840 ± 20	61 740 ± 148
527	8 753 ± 184	26 370 ± 20	61 930 ± 146
525	9 121 ± 200	26 860 ± 22	61 730 ± 146
522	10 000 ± 197	27 270 ± 21	60 800 ± 147
520	10 410 ± 201	27 450 ± 22	59 820 ± 143
517	11 180 ± 216	27 480 ± 23	57 880 ± 155
515	11 560 ± 229	27 350 ± 25	56 430 ± 139
510	12 830 ± 246	26 460 ± 27	52 080 ± 130
505	13 880 ± 235	25 010 ± 25	47 700 ± 119
500	15 050 ± 211	23 320 ± 23	43 600 ± 114
490	16 710 ± 202	20 120 ± 22	35 370 ± 125
460	15 460 ± 143	9 550 ± 16	11 970 ± 182
450	13 480 ± 137	6 952 ± 15	7 612 ± 175
440	11 530 ± 145	4 917 ± 16	4 879 ± 150
430	9 766 ± 125	3 507 ± 14	3 603 ± 136
420	8 599 ± 80	2 764 ± 9	3 657 ± 110
410	8 183 ± 88	2 783 ± 10	5 310 ± 82
400	8 319 ± 86	3 486 ± 9	8 263 ± 62
390	9 275 ± 84	5 068 ± 9	13 040 ± 80
380	11 430 ± 124	7 386 ± 14	16 760 ± 100

Interpretation of the curves of the concentration dependence $A = f(c_M)$ for 6 wavelengths ($c_L = 3{\cdot}00 \,.\, 10^{-5}$ mol l^{-1}, $c_M = \langle 1{\cdot}474 - 7{\cdot}859 \rangle \,.\, 10^{-4}$ mol l^{-1}, 515 to 560 nm, pH = 5·00) and the analogous dependence $A = f(c_L)$ for the same wavelengths ($c_M = 9{\cdot}8234 \,.\, 10^{-6}$ mol l^{-1}, $c_L = \langle 6{\cdot}00 - 90{\cdot}0 \rangle \,.\, 10^{-6}$ mol l^{-1}, pH 6·25) demonstrated the existence of a mixture of the ZnL and ZnL_2 complexes in addition to all the reagent forms. For both the concentration dependences, an excess of the determined species ZnL or ZnL_2 was found in only a small number of solutions. The contribution of the ZnLH complex to the overall absorbance value is small even in solutions with a concentrations excess of Zn(II) ions, especially at wavelengths which are very far away from the absorbance maximum of the given complex (λ_{max} 490 nm). This complex practically does not exist in solutions with a concentration excess of reagent (Figs. 5 and 6).

The stoichiometry of the complexes was confirmed by measuring of the continuous variation curves at 515, 520, 525, 535, 550 and 560 nm for $c_0 = c_L + c_M = 9{\cdot}0 \,.\, 10^{-5}$ mol l^{-1}. Numerical treatment of the curves using the KONVAR2 (ref. [14]) program demonstrated the existence of the ZnL complex at pH 4·35 and of the ZnL_2 complex at pH 5·50 and 6·60. The calculated conditional formation constants for the

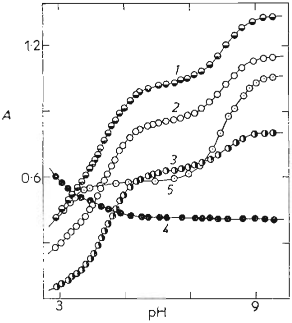

FIG. 5

Absorbance-pH curves of Zn^{2+} solutions with a concentration excess of reagent. $c_M = 9{\cdot}824 \,.\, 10^{-6}$ mol l^{-1}, $c_L = 7{\cdot}5 \,.\, 10^{-5}$ mol l^{-1}; I 0·1; Curve 1 527 nm; 2 535 nm; 3 550 nm; 4 410 nm; 5 527 nm ($c_M = 0$)

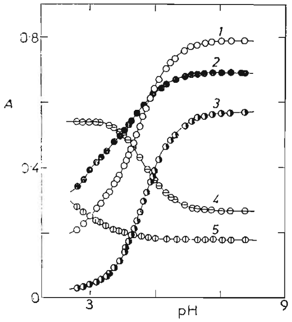

FIG. 6

Absorbance-pH curves for equimolar solutions of Zn^{2+} and 1-PAN-4S. $c_M = 2{\cdot}947 \,.\, 10^{-5}$ mol l^{-1}; $c_L = 3{\cdot}0 \,.\, 10^{-5}$ mol l^{-1}; I 0·1; Curve 1 520 nm; 2 505 nm; 3 560 nm; 4 460 nm; 5 390 nm

ZnL and ZnL_2 complexes were recalculated to yield equilibrium constants according to the relationship

$$\log {}^*\beta_{pqr} = \log \beta'_{pqr} + q \log K_{ai} - q \text{ pH},$$

where β'_{pqr} is the conditional stability constant, calculated using the KONVAR2 program, and K_{ai} is the dissociation constant for the reagent for the transition LH_2/LH. Comparison with the corresponding constants, calculated by the SQUAD-G program, is given in Table V.

TABLE V

Survey of equilibrium constants and molar absorption coefficients at λ_{max} for the complexes of Zn^{2+} and Cd^{2+} with 1-PAN-4S.

Complex	$\log {}^*\beta_{pqr}$	ε_{max}
$ZnLH^+$	-0.513 ± 0.014^a	$16\,710 \pm 202^a$ (490 nm)
ZnL	-2.758 ± 0.005^a	$27\,480 \pm 23^a$ (517 nm)
	-2.827 ± 0.005^b	$27\,540 \pm 18^b$ (517 nm)
	-2.689 ± 0.053^c	$26\,160 \pm 90^c$ (520 nm)
ZnL_2^-	-5.990 ± 0.002^d	$61\,930 \pm 146^d$ (527 nm)
	-5.998 ± 0.003^e	$61\,150 \pm 169^e$ (527 nm)
	-6.13^f	$57\,290 \pm 252^g$ (515 nm)
$CdLH^+$	-1.279 ± 0.033^h	$20\,820 \pm 261^h$ (490 nm)
CdL	-3.877 ± 0.005^h	$27\,200 \pm 20^h$ (522 nm)
	-3.805 ± 0.001^i	$27\,050 \pm 21^i$ (522 nm)
	-3.808 ± 0.004^j	$26\,930 \pm 91^j$ (522 nm)
CdL_2^-	-8.218 ± 0.007^k	$51\,480 \pm 330^k$ (522 nm)
	-8.225 ± 0.009^l	$52\,930 \pm 434^l$ (522 nm)
	-8.25^f	$52\,250 \pm 366^m$ (515 nm)

[a] From the $A = f(\text{pH})$ curve, $c_M/c_L = 81.9$; [b] from the $A = f(\text{pH})$ curve, $c_M/c_L = 16.3$; [c] from the $A = f(c_M)$ dependence, pH 5·00 for 6 wavelengths between 515–560 nm; [d] from the $A = f(\text{pH})$ curve, $c_L/c_M = 7.63$; [e] from the $A = f(\text{pH})$ curve, $c_L/c_M = 6.11$; [f] from relationship (3) from the conditional stability constant values calculated by the KONVAR 2 program; [g] from the $A = f(c_L)$ dependence, pH 6·25, 515 nm; [h] from the $A = f(\text{pH})$ curve, $c_M/c_L = 126.5$; [i] from the $A = f(\text{pH})$ curve, $c_M/c_L = 63.2$; [j] from the $A = f(\text{pH})$ curve, $c_L/c_M = 1.054$; [k] from the $A = f(\text{pH})$ curve, $c_L/c_M = 6.33$; [l] from the $A = f(\text{pH})$ curve, $c_L/c_M = 7.91$; [m] from the $A = f(c_L)$ dependence, pH 7·50, 515 nm,

It is apparent from the shape of the distribution curves for solutions with a concentration excess of Zn(II) ions ($c_M/c_L = 81{\cdot}9$) that, at pH $< 0{\cdot}9$, the ZnLH complex with maximum at 490 nm begins to be formed and contributes about 10% to the overall absorbance value in the region of maximum formation at pH ~ 2. At pH > 2, the ZnLH complex is converted to the non-protonated ZnL complex with an absorption maximum at 517 nm, which is formed quantitatively at pH $> 5{\cdot}5$. In equimolar solutions and solutions with a concentration excess of reagent, $c_L/c_M = 7{\cdot}63$, the mixture contains only the ZnL and ZnL_2 complexes. The ZnL complex is formed at pH $> 2{\cdot}6$ or $2\,6 - 6{\cdot}5$ and the ZnL_2 complex at pH $> 3{\cdot}9$ or $> 3{\cdot}5$, and is formed quantitatively at pH $\geqq 7{\cdot}5$ (Fig. 7–9).

Complexation Equilibria of 1-PAN-4S *with* Cd(II) *Ions*

The diffuse isosbestic point on the curves of the absorption spectra for pH $1 - 3{\cdot}5$. indicate simultaneous attainment of the acid–base equilibrium of the reagent LH_2/LH and formation of the complex with maximum absorbance at 522 nm (pH $> 3{\cdot}5$) in solutions with a concentration excess of Cd(II) ions ($c_L = 1{\cdot}6 \,.\, 10^{-5}$ mol l^{-1},

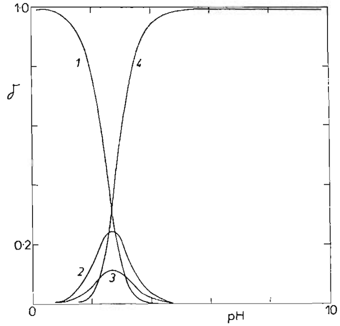

FIG. 7

Distribution curves in the Zn^{2+}-1-PAN-4S system. $c_L = 3{\cdot}0 \,.\, 10^{-5}$ mol l^{-1}, $c_M = 2{\cdot}456 \,.\, 10^{-3}$ mol l^{-1} ($c_M/c_L = 81{\cdot}9$), I 0·1; δ: Curve 1 $[LH_2]/c_L$; 2 $[LH]/c_L$; 3 $[ZnLH]/c_L$; 4 $[ZnL]/c_L$

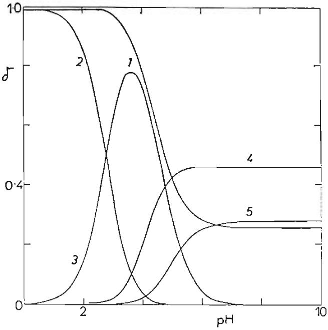

FIG. 8

Distribution curves in the Zn^{2+}-1-PAN-4S system. $c_M = 2{\cdot}947 \,.\, 10^{-5}$ mol l^{-1}, $c_L = 3{\cdot}0 \,.\, 10^{-5}$ mol l^{-1}; I 0·1; δ: Curve 1 $[Zn]/c_M$; 2 $[LH_2]/c_L$; 3 $[LH]/c_L$; 4 $[ZnL]/c_M$; 5 $[ZnL_2]/c_M$

$c_M/c_L = 118{\cdot}5$). The absorption spectra of solutions with a concentration excess of reagent ($c_M = 9{\cdot}48 \,.\, 10^{-6}$ mol l^{-1}, $c_L/c_M = 3{\cdot}16$) contain a diffuse (pH $< 4{\cdot}5$) or sharp (pH $> 4{\cdot}5$) isosbestic point indicating simultaneous formation of the acid-base equilibria of the reagent ($pK_{a1} = 2{\cdot}80$) and formation of the complex with an absorption maximum at 522 nm (Fig. 10 and 11).

The absorbance-pH curves of solutions with a concentration excess of Cd(II) ions ($c_L = 3{\cdot}00 \,.\, 10^{-5}$ mol l^{-1}, $c_M/c_L = 126{\cdot}5$, $63{\cdot}2$, $12{\cdot}65$; 360–570 nm) and with a con-

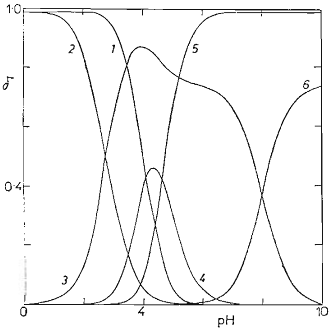

FIG. 9

Distribution curves of the components in the Zn^{2+}-1-PAN-4S system. $c_M = 9{\cdot}824 \,.\, 10^{-6}$ mol l^{-1}, $c_L = 7{\cdot}5 \,.\, 10^{-5}$ mol l^{-1}, I 0·1; δ: Curve *1* $[Zn]/c_M$; *2* $[LH_2]/c_L$; *3* $[LH]/c_L$; *4* $[ZnL]/c_L$; *5* $[ZnL_2]/c_M$; *6* $[L]/c_L$

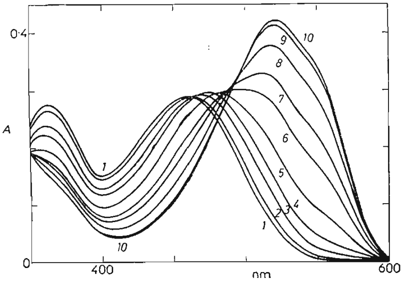

FIG. 10

Absorption curves for a 1-PAN-4S solution with a concentration excess of Cd^{2+}, $c_M = 1{\cdot}8967 \,.\, 10^{-3}$ mol l^{-1}, $c_L = 1{\cdot}6 \,.\, 10^{-5}$ mol l^{-1}. pH: Curve *1* 1·06; *2* 2·04; *3* 2·71; *4* 3·03; *5* 3·41; *6* 3·82; *7* 4·07; *8* 4·58; *9* 5·55; *10* 7·00 centration excess of reagent ($c_M = 9{\cdot}485 \,.\, 10^{-6}$ mol l^{-1}, $c_L/c_M = 1{\cdot}05$, 4·75, 6·32, 7·91; 360–570 nm) are completely analogous in the whole interval pH 1·5–7·0 or 2·9–10·1 to the curves of the Zn(II)-1-PAN-4S system; they are, however, shifted to the alkaline region.

Numerical evaluation of data for solutions with a concentration excess of Cd(II) ions ($c_M/c_L = 126{\cdot}5$ and 63·2) for a set of 30 wavelength values (Table VI) using the SQUAD-G program demonstrated the existence of a mixture of CdLH and CdL complexes in addition to the acid-base forms of the reagent LH_2 and LH. In equimolar solutions ($c_M = 2{\cdot}845 \,.\, 10^{-5}$ mol l^{-1}, $c_L = 3{\cdot}00 \,.\, 10^{-5}$ mol l^{-1}) and in solutions

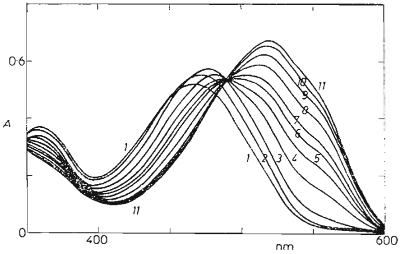

FIG. 11

Absorption curves of a Cd^{2+} solution with an excess of 1-PAN-4S. $c_L = 3{\cdot}0 \,.\, 10^{-5}$ mol . l^{-1}, $c_M = 9{\cdot}484 \,.\, 10^{-6}$ mol l^{-1}; I 0·1. pH: Curve *1* 2·94; *2* 3·45; *3* 4·21; *4* 5·05; *5* 5·57; *6* 5·97; *7* 6·38; *8* 6·81; *9* 7·32; *10* 7·81; *11* 8·52

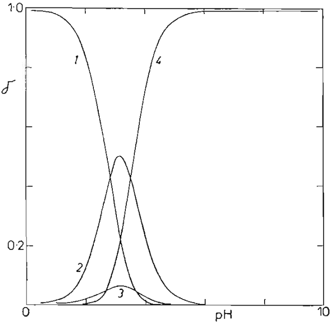

FIG. 12

Distribution curves for the components in the Cd^{2+}-1-PAN-4S system. $c_L = 3{\cdot}0 \,.\, 10^{-5}$ mol l^{-1}, $c_M = 3{\cdot}793 \,.\, 10^{-3}$ mol l^{-1}, I 0·1. δ: Curve *1* $[LH_2]/c_L$; *2* $[LH]/c_L$; *3* $[CdLH]/c_L$; *4* $[CdL]/c_L$

TABLE VI

Results of numerical minimization of the absorption data in the Cd^{2+}–1-PAN-4S system by the SQUAD-G program

Model (assumed species in solution)	c_M/c_L pH	$CdLH^+$ loh $^*\beta_{111}$ ε, $mmol^{-1} cm^{-2}$ 490 nm	CdL loh $^*\beta_{112}$ ε, $mmol^{-1} cm^{-2}$ 522 nm	CdL_2^- log $^*\beta_{124}$ ε, $mmol^{-1} cm^{-2}$ 522 nm	$\sigma_{(A)}$[c]	U . 10^3[d]
LH_2, LH, CdL $>c_M$	126·5 63·2		−3·848 ± 0·003 26 910		0·0122	170·0
			−3·728 ± 0·004 26 660		0·0141	178·6
LH_2, LH, CdLH, CdL $>c_M$	126·5	−1·279 ± 0·033 20 820 ± 261	−3·877 ± 0·003 27 200 ± 20	 27 200 ± 20	0·0019	3·867
	63·2	−1·110 ± 0·054 20 040 ± 234	−3·804 ± 0·001 27 050 ± 21		0·0021	3·869
LH_2, LH, L, CdLH, CdL, CdL_2 $>c_L$	0·158	−1·279	−3·877 ± 0·005 27 200 ± 20	−8·218 ± 0·007 51 480 ± 330	0·0048	20·12
	0·126	−1·279	−3·877 ± 0·005 27 200 ± 20	−8·225 ± 0·010 52 930 ± 434	0·0059	25·75
LH_2, LH, L, CdLH, CdL, CdL_2 $c_M \cong c_L$	0·952	−1·279	−3·808 ± 0·004 26 930 ± 85	−8·218 ± 0·007	0·0035	8·543
LH_2, LH, CdL $\gtrless c_M$	6·00[a]		−3·360 ± 0·054 26 560 ± 92[b]		0·0211	24·259
LH_2, LH, L, CdL, CdL_2 $\gtrless c_L$	7·50[a]			−8·379 ± 0·057 52 360 ± 261[b]	0·0127	9·763

[a] pH; [b] 520 nm; [c] $\sigma(A)$, see Table III; [d] sum of the squares of the deviations $U = \sum(A_{exp} - A_{calc})^2$.

with a concentration excess of reagent ($c_L/c_M = 6{\cdot}32$ and $7{\cdot}91$), the best agreement with the experimental data was found for a model with the CdLH, CdL and CdL_2 complexes in a mixture with the acid-base forms of the reagent LH_2, LH and L, where only the initial models were adjusted in the calculation for the given set of absorbance values. Calculations for all the models with protonated complexes with molar ratio M : L = 1 : 2 also did not converge. The existence of these species, as for the complexation equilibria of Zn(II) with 1-PAN-4S, can be excluded. A survey of the results for the individual models and values of the molar absorption coefficients for the CdLH, CdL and CdL_2 complexes are given in Tables VI and VII.

Numerical interpretation of the concentration dependence $A = f(c_M)$ for 5 wavelengths in the region 515–550 nm ($c_L = 3{\cdot}00 \,.\, 10^{-5}$ mol l^{-1}, $c_M = \langle 9{\cdot}485 - 758{\cdot}7\rangle \,.\, 10^{-6}$ mol l^{-1}, pH = 6·0) and of the dependence $A = f(c_L)$ for similar wavelengths ($c_M = 9{\cdot}485 \,.\, 10^{-6}$ mol l^{-1}, $c_L = \langle 0{\cdot}3 - 9{\cdot}0\rangle \,.\, 10^{-5}$ mol l^{-1}, pH 7·5) yields the best agreement for the considered models, LH_2, LH, L, CdL or LH_2, LH, L, CdL and CdL_2. The contents of minority complexes is not important in these two mixtures, so that the equilibrium constants found in this way are less precise than for the equilibrium of Zn(II) ions with 1-PAN-4S.

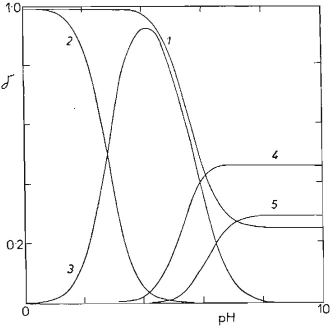

FIG. 13

Distribution curves of components in the Cd^{2+}-1-PAN-4S system. $c_M = 2{\cdot}845 \,.\, 10^{-5}$ mol l^{-1}, $c_L = 3{\cdot}0 \,.\, 10^{-5}$ mol l^{-1}, I 0·1, δ: Curve 1 $[Cd]/c_M$; 2 $[LH_2]/c_L$; 3 $[LH]/c_L$; 4 $[CdL]/c_M$; 5$[CdL_2]/c_M$

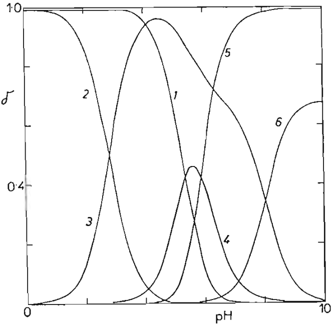

FIG. 14

Distribution curves of components in the Cd^{2+}-1-PAN-4S system. $c_M = 9{\cdot}484 \,.\, 10^{-6}$ mol l^{-1}; $c_L = 6{\cdot}0 \,.\, 10^{-5}$ mol l^{-1}, I 0·1; δ: Curve 1 $[Cd]/c_M$; 2 $[LH_2]/c_L$; 3 $[LH]/c_L$; 4 $[CdL]/c_M$; 5 $[CdL_2]/c_M$; 6 $[L]/c_L$

The continuous variation curves and their numerical analysis by the KONVAR2 program for wavelengths of 515, 525, 535 and 550 nm and for $c_0 = 9{\cdot}000 \,.\, 10^{-5}$ mol l^{-1} confirm the stoichiometric ratio of the components in the complexes M : L = 1 : 1 at pH 5·1. and the mixture of complexes ML and ML_2 at pH 6·3. At pH 7·0 and 7·7,

TABLE VII

Molar absorption coefficients in the Cd^{2+}–1-PAN-4S system, calculated by the SQUAD-G program. $c_M = 3{\cdot}793 \,.\, 10^{-3}$ mol l^{-1}, $c_L = 3{\cdot}0 \,.\, 10^{-5}$ mol l^{-1}, (for complexes with Cd : L = = 1 : 1); I 0·1; $c_M = 9{\cdot}484 \,.\, 10^{-6}$ mol l^{-1}, $c_L = 6{\cdot}0 \,.\, 10^{-5}$ mol l^{-1} (for complexes with Cd : L = = 1 : 2)

λ, nm	ε, mmol^{-1} cm^2 $CdLH^+$	ε, mmol^{-1} cm^2 CdL	ε, mmol^{-1} cm^2 CdL_2^-
570	4 096 ± 283	12 780 ± 17	29 570 ± 352
560	5 298 ± 324	18 600 ± 19	38 410 ± 396
555	5 211 ± 321	20 730 ± 19	41 450 ± 394
550	6 387 ± 335	22 280 ± 20	43 670 ± 404
545	6 998 ± 323	23 460 ± 19	45 610 ± 393
540	7 917 ± 326	24 470 ± 19	47 420 ± 395
535	8 853 ± 334	25 470 ± 20	49 150 ± 383
530	10 530 ± 337	26 430 ± 20	50 650 ± 374
527	11 370 ± 344	26 870 ± 20	51 250 ± 360
525	12 050 ± 352	27 060 ± 21	51 390 ± 351
522	12 220 ± 344	27 200 ± 20	51 480 ± 330
520	13 830 ± 332	27 170 ± 20	51 330 ± 326
517	14 930 ± 329	26 920 ± 19	50 760 ± 301
515	15 080 ± 310	26 630 ± 18	50 230 ± 290
510	16 950 ± 299	25 530 ± 18	48 300 ± 253
505	18 110 ± 283	24 090 ± 17	45 800 ± 216
500	19 680 ± 256	22 490 ± 15	43 010 ± 197
490	20 820 ± 261	19 260 ± 15	36 870 ± 176
470	18 850 ± 307	12 090 ± 18	23 050 ± 216
460	16 460 ± 365	9 055 ± 22	17 310 ± 221
450	13 000 ± 405	6 700 ± 24	12 790 ± 211
440	10 480 ± 390	4 879 ± 23	9 297 ± 204
430	8 254 ± 343	3 570 ± 20	6 979 ± 176
420	7 609 ± 300	2 808 ± 18	5 778 ± 151
410	8 567 ± 232	2 562 ± 14	5 632 ± 97
400	9 577 ± 161	2 928 ± 10	7 091 ± 75
390	9 369 ± 192	4 189 ± 11	10 590 ± 161
380	7 193 ± 345	6 252 ± 20	14 860 ± 236
370	4 223 ± 368	8 030 ± 22	17 700 ± 217
360	2 253 ± 397	9 616 ± 23	19 470 ± 140

the solution contains only the ML_2 complex. The conditional formation constants calculated by the KONVAR2 program for pH 5·1 and 6·3 were recalculated to equilibrium constants using relationship (*3*) and are given in Table V.

It follows from the distribution diagrams for the complexes with a concentration excess of Cd(II) ions ($c_M/c_L = 126{\cdot}5$) that the relative content of the CdLH complex is less than for ZnLH, that it begins to be formed at $pH > 1{\cdot}7$ and that the maximal concentration is formed at $pH \sim 3{\cdot}1$. At $pH > 2{\cdot}6$ the CdL complex is formed, with quantitative formation at $pH > 6{\cdot}5$. At equimolar concentrations of Cd(II) and 1-PAN-4S a mixture of the CdL ($pH > 3{\cdot}7$) and CdL_2 ($pH > 4{\cdot}5$) complexes is formed, where the content of the CdLH complex is low. In the presence of a concentration excess of reagent ($c_L/c_M = 6{\cdot}33$) under optimal conditions $pH \sim 5{\cdot}5$, only about 40% of the Cd is bonded in the CdL complex, which is formed in the pH region 4–8. At $pH > 4{\cdot}5$, the CdL_2 complex begins to be formed and is formed quantitatively at $pH > 9$, *i.e.* in the region where the solution contains the strongly absorbing acid-base form of the reagent L^{2-} ($pK_{a2} = 8{\cdot}00$). This considerably complicates the use of 1-PAN-4S for the development of a spectrophotometric method for the determination of Zn(II) and Cd(II) because of the high blank absorbance (Fig. 12–15).

CONCLUSIONS

In the presence of a concentration excess of cadmium or zinc(II) ions, the orange-red protonated MLH^+ complex with maximum absorbance at 490 nm ($\varepsilon_{max} = 1{\cdot}67 \,.\, 10^4$ for Zn(II) and $2{\cdot}08 \,.\, 10^4\ mmol^{-1}\ cm^2$ for Cd(II) ions) is formed in strongly acid medium at $pH > 0{\cdot}9$ for Zn(II) and $pH > 1{\cdot}6$ for Cd(II) with 1-PAN-4S. Of the possible structures for the protonated complexes ZnLH and CdLH (Schemes I and II), structure *II* seems most probable because of the closeness of the absorption

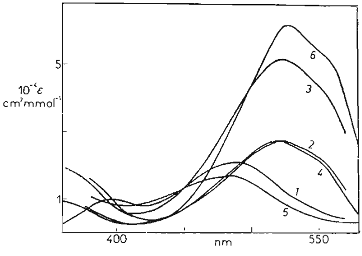

FIG. 15

Spectra of the individual complexes of Zn^{2+} and Cd^{2+} with 1-PAN-4S, calculated by the SQUAD-G program. Curve *1* $CdLH^+$ (λ_{max} 490 nm); *2* CdL (λ_{max} 522 nm); *3* CdL_2^- (λ_{max} 522 nm); *4* ZnL (λ_{max} 517 nm); *5* $ZnLH^+$ (λ_{max} 490 nm); *6* ZnL_2^- (λ_{max} 527 nm) maxima of the MLH and ML complexes to that of the LH acid-base form ($\lambda_{max} = 480$ nm), in contrast to the HgHL complex, which is formed in strongly acid medium in solutions with a concentration excess of Hg(II) ions ($\lambda_{max} = 385$ and 479 nm) and whose optical characteristics are very similar to those of the LH_2 acid-base form ($\lambda_{max} = 365$ and 464 nm) in 30% v/v ethanol medium[3]. Unambiguous conclusions cannot, however, be drawn on the basis of quantitative analysis of the absorption spectra.

In acid media with a concentration excess of metal ions, the red-purple ZnL complex (Scheme III) is formed ($\lambda_{max} = 517$ nm, $\varepsilon_{max} = 2{\cdot}75 \,.\, 10^4$ mmol^{-1} cm^2) or the CdL complex ($\lambda_{max} = 522$ nm, $\varepsilon_{max} = 2{\cdot}72 \,.\, 10^4$ mmol^{-1} cm^2).

In equimolar solutions (pH > 2·5 for Zn(II) and pH > 3·5 for Cd(II) ions) and in solutions with a concentration excess of reagent (pH > 3·5 for Zn and pH > 4·6 for Cd), a mixture of complexes ML and ML_2 is formed, where the ML_2 complex predominates at all excesses and in the alkaline region. Quantitative formation of the higher ML_2 complex is attained at pH > 7·5 for Zn(II) and pH > 9·0 for Cd(II) ions. These complexes, which are the only ones useful for the development of a spectrophotometric method for the determination of both elements, are formed in a region where the acid-base transition LH/L occurs and the strongly absorbing acid-base form of the reagent appears. The high blank absorbance (reagent absorbance) and the necessity of exact acidity adjustment decrease the suitability of 1-PAN-4S as a spectrophotometric reagent of the determination of Zn and Cd ions.

The relatively low value of the molar absorption coefficient of the ML_2 complex, compared with the corresponding value for PAR $\varepsilon = 9{\cdot}05$ or $8{\cdot}7 \,.\, 10^4$ mmol^{-1} cm^2) (ref.[16,17]) decrease the importance of this reagent for the determination of these two elements.

The existence of a protonated complex with a molar ratio of M : L = 1 : 2 demonstrated in 1-PAN-4S systems with Hg(II) and Ni(II) ions in solutions with a concentration excess of reagent, was not demonstrated for systems containing Zn(II) and Cd(II) ions.

The final values of the molar absorption coefficients, equilibrium constants and other parameters of all the complexes of 1-PAN-4S with Cd(II) and Zn(II) ions are listed in Table V.

The SQUAD-G *programs for the Tesla* 200 *and EC* 1033 *computers are available on request at the Department of Analytical Chemistry, J. E. Purkyně University, 611 37, Brno. All the calculations were carried out on the Computer Laboratory of the Technical University in Brno and in the Computing Techniques Institute, Purkyně University, Brno.*

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