SPECTROPHOTOMETRIC STUDY OF THE ACID-BASE AND OPTICAL PROPERTIES OF THE 5-BROMO AND 5-CHLORO DERIVATIVES OF 2-(2-PYRIDYLAZO)-5-(DIETHYLAMINO)PHENOL (BrPADAP, ClPADAP) AND THEIR COMPLEXATION EQUILIBRIA WITH ZINC(II) IONS

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The optical and acid-base characteristics of BrPADAP and ClPADAP were studied in mixed water–ethanol and water–DMF media and in 10% ethanol medium in the presence of cationic, anionic and nonionic tensides. The composition, optical characteristics, molar absorption coefficients and equilibrium constants of the ML and ML_2 complexes with zinc(II) ions were found by graphical analysis and numerical interpretation of the absorbance curves by the modified SQUAD-G program. Optimal conditions were found for the spectrophotometric determination of Zn(II) in the presence of 0·1% Triton X-100 or 1% Brij 35 in alkaline media with $pH = 6{\cdot}5-10$. BrPADAP and ClPADAP are the most sensitive reagents ($\varepsilon = 1{\cdot}3-1{\cdot}6 \,.\, 10^5$ mmol $^{-1}$ cm^2 at 557 and 560 nm, respectively) for the determination of zinc with high colour contrast of the reaction ($\Delta\lambda = 104$ nm) and selectivity similar to that for the other N-heterocyclic azodyes (PAN, PAR, *etc.*).

Gusev and coworkers[1,2] introduced 2-(2-pyridylazo)-5-(diethylamino)phenol and its halogen derivatives into analytical chemistry. These azodyes are very sensitive metallochromic indicators for the determination of a number of transition elements and are very sensitive reagents for the spectrophotometric determination of U(VI) (ref.[3-12]), Co (ref.[13-15]) and other elements[16-30]. PADAP and its derivatives are synthesized by reaction of 3-diethylaminophenol with the corresponding halogen-substituted 2-pyridylazonium salt[1] and subsequent recrystallization of the product from ethanol solution[4]. Compared with the other N-heterocyclic azodyes, these reagents exhibit much higher molar absorption coefficient values of the corresponding complexes ($\varepsilon \geqq 1 \,.\, 10^5$ mmol^{-1} cm^2) and better colour contrast in the reaction ($\Delta\lambda_{ML-L} \geqq 100$ nm). The selectivity of the reactions remains unchanged because of the identical chelate-forming grouping of the donor atoms.

The work describes study of the optical and acid-base characteristics of both reagents in media of 30 and 50% ethanol, 50% DMF and 10% ethanol in the presence of a 0·1% solution of a nonionic tenside Triton X-100. The optical and acid-base characteristics of ClPADAP were also determined in 10% ethanol medium in the presence of cationic and anionic tensides, cetylpyridinium bromide and sodium dodecyl sulphate (CPB, SDS), in concentrations of $1 \,.\, 10^{-3}$ mol l^{-1}. The complexation equilibria of ClPADAP and BrPADAP with zinc(II) ions were studied in similar media. The basic characteristics of ClPADAP and BrPADAP and their complexes with Zn(II) were evaluated by graphical analysis and numerical interpretation of the absorbance curves by the modified SQUAD-G program[31,32]. Optimal conditions were proposed for the spectrophotometric determination of Zn(II) in pure BrPADAP solutions and the results were evaluated statistically by the STAT program[33].

EXPERIMENTAL

Chemicals and Instruments

Stock solutions of 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (BrPADAP) and 2-(5--chloro-2-pyridylazo)-5-(diethylamino)phenol (ClPADAP) with concentrations of $1 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ mol l^{-1} were prepared by dissolving the solid BrPADAP (E. Merck, Darmstadt, GFR, Art. 10 731) or ClPADAP (Dojindo Co., Japan) in ethanol. The contents of the active components of the reagent (51·54% C, 4·86% H and 16·33% N) were found by elemental C, H, N analysis for BrPADAP alone (theoretical contents, 51·58% C, 4·91% H, 22·90% Br, 16·04% N, 4·58% O on $C_{15}H_{17}BrN_4O$, $M_r = 349{\cdot}233$ for BrPADAP and 59·12% C, 5·62% H, 11·63% Cl, 18·38% N, 5·25% O in $C_{15}H_{17}ClN_4O$, $M_r = 304{\cdot}782$ for ClPADAP). The solutions were stable for at least 14 days.

The stock solution of 0·4912 mol l^{-1} $Zn(NO_3)_2$ was prepared by dissolving doubly recrystallized *p.a.* $Zn(NO_3)_2$ (Lachema, Brno, Czechoslovakia) in 0·1M-HNO_3, *p.a.* The solution was standardized gravimetrically and by complexometric titration with EDTA. Working solutions were prepared by diluting the stock solution with 0·1M-HNO_3.

BRIJ 35 (polyoxyethylenemonododecyl ether, $n \sim 20$, $M_r \sim 900$) was the product of E. Merck, Darmstadt, GFR. The stock solution with a concentration of 10% w/v was prepared by dissolving a weighed amount of the substance in *c.* 50°C warm water and diluting to the required volume after cooling. The solution was stored in a refrigerator and was stable for at most one week. Needle-shape particles were precipitated on longer storage.

TRITON X-100 (octylphenolpolyethyleneglycol ether, analytically pure, $n \sim 10$) was a product of Koch-Light Labs. Ltd., Great Britain. The working solutions were prepared by pipetting an appropriate amount of the liquid substances at laboratory temperature immediately before the measurement.

Polyvinylpyrollidone (Koch-Light Labs. Ltd., Great Britain), pharmaceutically pure, $M_r = 248500$. Bion NE-9 (paranonylphenol adduct of 9-ethyleneoxide, Pierce Chem. Comp.) and Slovasol 0 (W. Pieck Works, Nováky, Czechoslovakia). These substances were used as weighed amounts of the solid substance or by pipetting the required amount of the liquid substance (Bion NE-9) directly to the measured solution.

Cetylpyridinium bromide (CPB, $C_{21}H_{39}BrN$, $M_r = 384{\cdot}44$) was doubly recrystallized from hot ethanol (Lachema, Brno, Czechoslovakia). Sodium dodecyl sulphate (SDS, $C_{12}H_{25}O$ -SO_3Na, $M_r = 288{\cdot}38$) was the product of BDH Ltd., Poole, Great Britain. Both ionic tensides were used as weighed amounts of the solid crystalline substance added directly to the working solution.

The other chemicals were of "Suprapure" purity (HCl, NH_4OH and HNO_3) or *p.a.* (EDTA, KNO_3, NaOH, KOH); the solvents (ethanol containing 5% v/v methanol, dimethylformamide, *etc.*) were of *p.a.* purity and were further purified by distillation. KOH and NaOH were purified by coprecipitation of heavy metal hydroxides on barium carbonate and KNO_3 was purified by repeated recrystallization from alkaline medium (pH 9). Water was doubly distilled in a Bi-8 quartz apparatus (Heraeus Quarzschmelze, GFR). The ionic strength of the solution was maintained at a constant value of $I = 0{\cdot}10$ by a combination of appropriate volumes of solutions of HNO_3, KNO_3, KOH and NaOH.

All the spectrophotometric measurements were carried out by titrations at 25 ± 0·10°C in 10—40 mm quartz cuvettes on a Superscan^{TM} 3 double-beam digital recording spectrophotometer (Varian, Switzerland) controlled by an HP 9815A table-top calculator (Hewlett–Packard, USA). The experimental data were recorded in numerical form using a program for direct recording and treatment of experimental data on the HP 9815A table-top calculator (ref.[34]).

The solution acidity was measured using pHM 64 or pHM 84 digital pH meters (Radiometer, Denmark) with glass G 202 B and calomel K 401 electrodes. The instruments were calibrated regularly with phosphate (pH 7·00), tetraoxalate (pH 1·68), phthalate (pH 4·01) and tetraborate (pH 9·18) buffers. The pH values in the mixed media were not corrected and are designated by the symbol pH for simplicity.

Method

The absorption spectra of solutions of BrPADAP and ClPADAP and their chelates with Zn(II) were recorded in dependence on the acidity of the medium in steps of 0·3—0·5 pH unit or in dependence on $-\log c_H$ in graphical form in the wavelength interval 330—730 nm. The positions of the absorption maxima of the individual absorbing species in the solution and the positions of the isosbestic points characterizing the acid-base or complex equilibria were found from the graphical recording. Optimal wavelength values were selected for digital spectra recording and measurement of the absorbance curves from the graphical recordings.

The absorption spectra in digital form were measured in dependence on the experimental conditions in steps of 0·1—0·3 pH units or $-\log c_H$ units for 50—150 discrete wavelength values in the interval 350—650 nm. The exact position of the absorption maxima, the positions of the inflection points on the curves and possible overlapping of the absorption bands were found from the digital recording using the program for the calculation of the first and second derivatives $dA/d\lambda$ and $d^2A/d\lambda^2$ (absorption spectra of the H_2L^+ acid-base form and of the ZnL and ZnL_2 complexes for BrPADAP) (ref.[34]). Separation of the absorption spectra for the individual absorbing species was also carried out on the basis of the results of the numerical treatment of the experimental data by the SQUAD-G program in the form of the dependence $\varepsilon = f(\lambda)$ for the measured discrete wavelength values.

The absorbance-pH curves $A = f(\text{pH})$ in steps of pH = 0·1—0·2 pH units, the curves of the dependence of the absorbance on the concentration of a single component $A = f(c_L)$ or $A = f(c_M)$ and the continuous variation curves $A = f(x_L)$ were measured for 10—25 discrete wavelengths in the region of maximum absorbance of the individual absorbing species for data treatment by the SQUAD-G program. The dissociation constant, equilibrium constant and molar absorption coefficient values, complex composition and number of protons dissociating during the reaction were found by graphical analysis of selected absorbance curves and 1—2 wavelengths at the absorption maximum using the slope-intercept transformation[35] on the programmable TI-59 calculator (Texas Instruments, USA). Complete sets of experimental data for all the media employed were treated by the general minimization SQUAD-G program (ref.[31,32]), which was modified, shortened and complemented by calculation of the distribution diagrams for the medium-sized EC 1033 computer (USSR). The parameters of the calibration curves $A = f(c_M)$ were evaluated by the STAT (ref.[33]) program on the table-top 9815A calculator (Hewlett–Packard, USA).

The Acid-Base and Optical Properties of BrPADAP *and* ClPADAP

Depending on the acidity of the medium, the solution contains four optically different acid-base forms of the reagent, LH_3^{2+}, LH_2^+, LH^0 and L^-. The doubly proton-

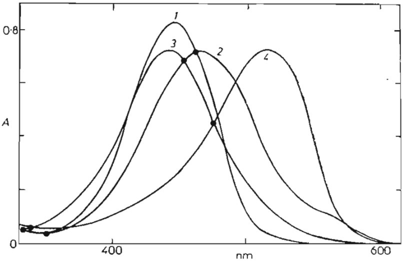

FIG. 1

The absorption curves $A = f(\lambda)$ for the individual acid-base forms of BrPADAP. $c_L = 1{\cdot}5\,.\,10^{-5}$ mol l^{-1}, 30% ethanol, $I = 0{\cdot}10$ (HNO_3 + KOH). Curve, form, pH: *1*, LH_3^{2+}, conc. H_2SO_4; *2*, LH_2^+, 1·49; *3*, LH°, 4·64; *4*, L^-, 13·42

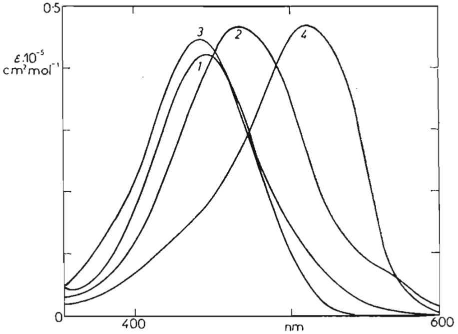

FIG. 2

The absorption spectra $\varepsilon = f(\lambda)$ for the acid-base forms of ClPADAP obtained by the SQUAD-G program. $c_L = 2{\cdot}00\,.\,10^{-5}$ mol l^{-1}, 30% ethanol, $I = 0{\cdot}10$. Curve, form: *1*, LH_3^{2+}; *2*, LH_2^+; *3*, LH°; *4*, L^-

ated species LH_3^{2+} (451 nm) is present in concentrated acid medium, in the pH interval 0–3 the solution contains the orange protonated LH_2^+ form (468–475, 563 to 569 nm) together with the LH_3^{2+} ($pH < 0$) and LH^0 ($pH > 3$) forms. The yellow molecular form LH^0 (442–445 nm) exists in a broad pH interval, pH 4–10 and, at $pH > 10$, is converted into the red completely deprotonated L^- form (513–518 nm).

The acid-base equilibria of BrPADAP and ClPADAP were studied in media of 30 and 50% ethanol, 50% DMF, 10% ethanol in the presence of 0·1% Triton X-100 and, for ClPADAP, also in 10% ethanol medium containing $1 \cdot 10^{-3}$ mol l^{-1} CPB or SDS. Where not stated otherwise, the absorbance of a $2 \cdot 0 \cdot 10^{-5}$ mol l^{-1} reagent solution was measured at 25 wavelengths in the interval 355–585 nm in steps of $\Delta\lambda = = 10$ nm in the acidity region pH = 1–13. In 50% DMF medium, measurements were carried out only to pH 11·5.

The absorption spectra of $1 \cdot 5 \cdot 10^{-5}$ mol l^{-1} BrPADAP in 30% ethanol medium or aqueous medium in the presence of various concentrations of H_2SO_4 were recorded in the classical manner on a recording spectrophotometer as the dependence $A = f(\lambda)$ for various pH or H_2SO_4 concentration values. The curves of the absorption spectra for the individual acid-base forms measured in the acidity region where the existence of a single acid-base form of BrPADAP can be assumed are given in Fig. 1. For illustration, Fig. 2 depicts the absorption spectra of the individual forms of ClPADAP obtained by fitting continuous curves to the molar absorption coefficient values for various wavelengths from the SQUAD-G program. The character of the individual curves and the positions of the absorption maxima and isosbestic points are practically identical for the two types of absorption spectra ($\Delta\lambda \leqslant 2-6$ nm) for BrPADAP and ClPADAP (Table I).

The dissociation constant values for both reagents in various media were evaluated by the SQUAD-G program for the individual formation regions of the absorbance – pH curves. The dissociation constants of BrPADAP, pK_{a1}, pK_{a2} and pK_{a3} in 50% ethanol, and pK_{a1} and pK_{a2} in 30% ethanol media, were evaluated by graphical interpretation using the slope-intercept transformation method. The dissociation constant values and optical characteristics of both reagents for all the media are given in Table I. The values obtained are in good experimental agreement with the values calculated by the SQUAD-G program and with the values given in the literature.

In Fig. 3 are depicted the absorbance-pH curves for $2 \cdot 10^{-5}$ mol l^{-1} ClPADAP at a wavelength of 505 nm in media where the greatest shift of the formation region of the absorbance-pH curves occurs. The positions of the curves and the conditional dissociation constant values for ClPADAP in all the other media and for BrPADAP in all the media used are rather similar and consequently these curves are not given in the figure. It is apparent from Fig. 3 and Table I that a more marked shift occurs only in the presence of ionic tensides (SDS and CPB). The shifts of the condi-

TABLE I

The acid-base and optical characteristics of BrPADAP and ClPADAP in various media

Medium	pK_{a2}[a]	pK_{a3}[b]	λ_{IP}, nm		λ_{max}[c], nm; (10^{-4} . ε_{max}), mmol^{-1} cm^2		
			LH_2^+/LH	LH/L^-	LH_2^+	LH^0	L^-
			BrPADAP				
50% DMF[d]	2·141 ± 0·003	11·788 ± 0·002$_5$	456	476	475 (4·5)	445 (4·2)	518 (4·5)
10% ethanol 0·1% Triton	2·134 ± 0·003	11·597 ± 0·002	448	474	469 (4·5)	445 (4·0)	515 (4·7)
50% ethanol[e]	2·028 ± 0·004	11·933 ± 0·002$_5$	452	474	468 (4·9)	443 (4·5)	516 (5·2)
30% ethanol[f]	2·388 ± 0·001	11·637 ± 0·002	454	474	469 (4·7)	443 (4·6)	513 (4·9)
30% ethanol[g]			455	475	465 (4·7)	442 (4·5)	515 (5·0)
			ClPADAP				
50% DMF	2·154 ± 0·001	11·742 ± 0·008	454	475	474 (4·5)	444 (4·1)	517 (4·6)
10% ethanol 0·1% Triton	2·217 ± 0·007	11·573 ± 0·003	447	472	466 (4·4)	445 (4·0)	511 (4·6)
50% ethanol	2·130 ± 0·002	11·091 ± 0·002	449	472	468 (4·9)	442 (4·3)	512 (4·9)
30% ethanol[h]	2·409 ± 0·004	11·634 ± 0·002	453	473	453 (4·7)	443 (4·3)	512 (4·7)
10% ethanol, 10^{-3} CPB	2·131 ± 0·001	10·663 ± 0·004	446	477	465 (4·4)	444 (3·9)	519 (4·0)
10% ethanol, 10^{-3} SDS	3·158 ± 0·002$_5$	11·402 ± 0·002	449	471	467 (4·6)	443 (4·2)	509 (4·7)

[a] pK_{a2} = 2·02 ± 0·05 (ref.[4]), pK_{a2} = 1·96 ± 0·03 (ref.[27]) for BrPADAP, pK_{a2} = 2·12 ± 0·08 (ref.[27]) for ClPADAP; [b] pK_{a3} = 11·30 ± 0·04 (ref.[4]), pK_{a3} = 11·72 ± 0·15 (ref.[27]) for BrPADAP, pK_{a3} = 11·78 ± 0·12 (ref.[27]) for ClPADAP; 450 nm (pH 1), 440 nm (pH 5·2) and 510 nm (pH 12) for BrPADAP (ref.[2]); 460 nm (LH form after extraction into $CHCl_3$), ref.[19]; 480 nm (LH form after extraction into $CHCl_3$; (ref.[24]); 440 nm for the LH form (ref.[26]); 445 nm for the LH form (ref.[27,13]) all for BrPADAP; 445 mn for the LH form of ClPADAP (ref.[27]); [c] the values given in parenthesis are the molar absorption coefficient values ε_{max} for the given absorption maximum. [d] c_L = 1·8967 . 10^{-5} mol l^{-1}; [e] c_L = 1·5 . 10^{-5} mol l^{-1}, 395–565 nm in steps of 10 nm, values from the graphical interpretation for 505 nm; pK_{a1} = 0·05 (c_L = = 2·0 . 10^{-5} mol l^{-1}, 420 nm, 440, 480 and 500 nm), pK_{a2} = 2·06, pK_{a3} = 11·90; [f] c_L = 1·5 . 10^{-5} mol l^{-1}, 395–565 nm in steps of 10 nm, values from graphical interpretation for 505 nm; pK_{a1} = −0·29 (c_L = 2 . 10^{-5} mol l^{-1}, 420, 440, 480 and 500 nm, I = 1·0, below pH 0 the ionic strength is variable), pK_{a2} = 2·39, pK_{a3} = 11·64; [g] values from the classical absorption spectra in Fig. 1; [h] pK_{a1} = −0·228 ± 0·003 at I = 1·023, SQUAD-G program.

tional dissociation constant pK_{a2} to higher values in the presence of anionic dodecyl-sulphate and of pK_{a3} to lower values in the presence of cationic cetylpyridinium probably result from formation of reagent-tenside ion associates with composition $(LH_2^+.T^-)$ or $(L^-.T^+)$, whose formation has been described for a number of other organic analytical reagents. A change in the character of the solvation sphere, a change in the dielectric constant of the solvent, *etc.* may also be important, as has been found for nonionic tensides or in mixed media.

Complexation Equilibria of Zn(II) *with* BrPADAP *and* ClPADAP

The complexation equilibria of Zn(II) with both reagents were studied in mixed media of 30% ethanol, 50% DMF and 10% ethanol in the presence of 0·1% Triton X-100 (BrPADAP, ClPADAP), 1% Brij 35 (BrPADAP) or $1 \cdot 10^{-3}$ mol l^{-1} CPB or SDS (ClPADAP).

The absorption spectra of a Zn(II) solution containing BrPADAP were recorded in the presence of a concentration excess of metal ion ($c_M = 4{\cdot}912 \cdot 10^{-4}$ mol l^{-1}, $c_L = 1 \cdot 10^{-5}$ mol l^{-1}, $c_M/c_L = 50$, see Fig. 4), in equimolar solutions ($c_M = 1{\cdot}18 \cdot 10^{-5}$ mol l^{-1}, $c_L = 1{\cdot}25 \cdot 10^{-5}$ mol l^{-1}, $c_M/c_L \sim 1$) and in solutions with a concentration excess of reagent ($c_M = 1{\cdot}965 \cdot 10^{-6}$ mol l^{-1}, $c_L = 1{\cdot}75 \cdot 10^{-5}$ mol l^{-1}, $c_L/c_M = 8{\cdot}9$, see Fig. 5). In acid medium with pH 3, the absorption spectra have the same shape and exhibit a single absorption maximum at 445 nm, corresponding to the absorption maximum of the molecular acid-base form of the reagent LH^0. With increasing pH, the characteristic double absorption maximum corresponding to the formation of the Zn(II) complex of BrPADAP gradually appears in the wavelength region 510–550 nm. The formation of this complex appears on the individual absorption spectra as a sharp isosbestic point at 480 nm. Only the curves in the acid region, where the simultaneous LH_2^+/LH^0 equilibrium of BrPADAP appears, do not pass through this isosbestic point. The concentrations of the basic components, wavelength regions of spectra recording and optical characteristics of the solutions are listed in Table II.

The absorbance-pH curves of a BrPADAP solution with a concentration excess of Zn(II) were measured in 30% ethanol medium ($c_L = 1{\cdot}2576 \cdot 10^{-5}$ mol l^{-1}, $c_M = 1{\cdot}2676 \cdot 10^{-5}$ mol l^{-1}, $c_M/c_L = 1$; $c_M = 1{\cdot}277 \cdot 10^{-4}$ mol l^{-1}, $c_M/c_L = 10{\cdot}15$; $c_M = 1{\cdot}277 \cdot 10^{-3}$ mol l^{-1}, $c_M/c_L = 101{\cdot}5$) at wavelengths of 550, 547·5, 540, 530, 520, 455, 445 and 435 and 435 nm or 552, 550, 545, 540, 530, 520, 455, 445, 440 and 435 nm ($c_L = 1{\cdot}2576 \cdot 10^{-5}$ mol l^{-1}, $c_M = 4{\cdot}912 \cdot 10^{-4}$ mol l^{-1}, $c_M/c_L = 39{\cdot}06$). All the curves had the same shape with a single formation branch; with increasing Zn(II) concentration, the curves were shifted into the more acid region. A $Zn(OH_2)$ precipitate began to be formed in solutions with a high overall Zn(II) concentration at pH 7.

Numerical treatment of the absorbance-pH curve for $c_M = 4{\cdot}912 \cdot 10^{-4}$ mol l^{-1} by the SQUAD-G program yielded the best agreement with the experimental data

($\sigma_A = 0{\cdot}0047$ A.U.) and the values $-\log {}^*\beta_{ML} = 1{\cdot}4082 \pm 0{\cdot}0006$ and $\varepsilon_{max} = 69\,000\ \text{mmol}^{-1}\ \text{cm}^2$ for the model corresponding to formation of the ZnL complex according to reaction equilibrium (A):

$$M + LH \rightleftharpoons ML + H \quad ({}^*\beta_{ML}, \varepsilon) \tag{A}$$

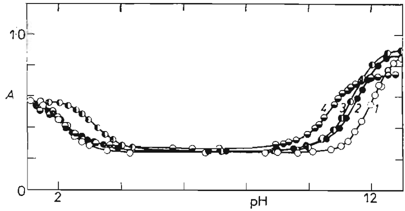

FIG. 3

The absorbance-pH curves for ClPADAP in various media. $c_L = 2{\cdot}00 \cdot 10^{-5}$ mol l^{-1}, 505 nm, $I = 0{\cdot}10$. Curve, medium: *1*, 50% ethanol; *2*, 10% ethanol with 0·1% Triton X-100; *3*, 10% ethanol with $1 \cdot 10^{-3}$ mol l^{-1} SDS; *4*, 10% ethanol with $1 \cdot 10^{-3}$ mol l^{-1} CPB

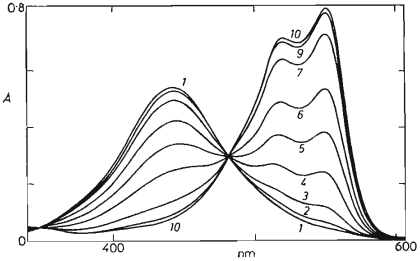

FIG. 4

The absorption curves $A = f(\lambda)$ for BrPADAP with a concentration excess of Zn(II). $c_L = 1{\cdot}00 \cdot 10^{-5}$ mol l^{-1}, $c_M = 4{\cdot}932 \cdot 10^{-4}$ mol l^{-1}, $I = 0{\cdot}10$, 30% ethanol. Curve, pH: *1*, 2·84; *2* 3·19; *3*, 3·60; *4* 3·95; *5* 4·39; *6* 4·72; *7* 5·06; *8* 5·44; *9* 6·05; *10* 6·64

Calculations for models assuming that, in addition to the ML complex, the hydroxocomplexes $M(OH)_2$ or $M(OH)^+$ or the mixed hydroxocomplex ML(OH) are formed, did not converge.

The dependences for $c_L = 1{\cdot}2576 \, . \, 10^{-5} \, mol \, l^{-1}$, $c_M = 1{\cdot}277 \, . \, 10^{-4} \, mol \, l^{-1}$ or $c_M = 4{\cdot}912 \, . \, 10^{-4} \, mol \, l^{-1}$ ($c_M/c_L = 10{\cdot}15$ or $39{\cdot}06$) were also treated by graphical methods for a wavelength of 550 nm. Graphical interpretation of the absorbance-pH curves for $c_M = 1{\cdot}277 \, . \, 10^{-4} \, mol \, l^{-1}$ yielded the values $-\log {}^*\beta_{ML} = 1{\cdot}12$ (A-transformation) or 1·27 (logarithmic transformation) and $\varepsilon_{550} = 68{\cdot}200 \, mmol^{-1} \, cm^2$. Interpretation of the second curve yielded the values $-\log {}^*\beta_{ML} = 1{\cdot}41$ (A-transformation), $-\log {}^*\beta_{ML} = 1{\cdot}42$ (c_L/A-transformation) and $-\log {}^*\beta_{ML} = 1{\cdot}49$ (logarithmic transformation) and the values of the molar absorption coefficient $\varepsilon = 67\,500$ or $68\,400 \, mmol^{-1} \, cm^2$ (A or c_L/A-transformation). The calculated values of the equilibrium constants and molar absorption coefficients are given in Table II. The values are in good agreement with the experimental data.

Numerical interpretation of the absorbance curves for the Zn(II) system with ClPADAP in 30% ethanol medium ($c_L = 1{\cdot}0 \, . \, 10^{-5} \, mol \, l^{-1}$ and $c_M = 4{\cdot}912 \, . \, 10^{-4} \, mol \, l^{-1}$, $c_M/c_L = 49{\cdot}12$, $\lambda = 355 - 595$ nm in steps of 10 nm) using the SQUAD-G program also confirmed the existence of a single ML complex ($\sigma_A = 0{\cdot}0027$ A.U.). The calculations for the other models considered, as for BrPADAP, did not converge. The calculated equilibrium constant values and optical characteristics are listed in Table II.

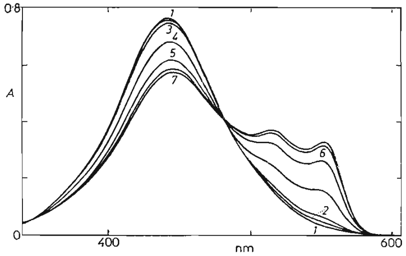

FIG. 5

Absorption curves $A = f(\lambda, pH)$ of Zn(II) with a concentration excess of BrPADAP. $c_L = 1{\cdot}75 \, . \, 10^{-5} \, mol \, l^{-}$, $c_M = 1{\cdot}965 \, . \, 10^{-6} \, mol \, l^{-1}$, 30% ethanol, $I = 0{\cdot}10$ Curve, pH: *1* 4·10; *2* 4·72; *3* 5·14; *4* 5·60; *5* 6·11; *6* 6·55; *7* 7·02

TABLE II

The equilibrium constants and optical characteristics of the complexes of Zn(II) with BrPADAP and ClPADAP

Medium	λ_{IP}, nm	λ_{max}, nm	$\varepsilon_{max} \cdot 10^{-4}$ cm^{2} mmol^{-1}	$-\log {}^{*}\beta$	$c_L \cdot 10^5$, mol l^{-1}; $c_M \cdot 10^5$, mol l^{-1} λ, nm; $\Delta\lambda$, nm
30% ethanol^{a}	480	444^{b}, 519, 537	—	—	1,0; 49·12; 340—605; —
30% ethanol^{a}	482	443^{b}, 520, 551	—	—	1·25; 1·18; 340—605; —
30% ethanol^{a}	481	442^{b}, 515, 552	—	—	1·75; 0·1965; 340—605; —
30% ethanol	—	519, 547	6·9^{g}	1·41 ± 0·001	1·2576; 49·12; 552, 550, 545, 540, 530, 520, 455, 445, 440, 435; —
30% ethanol^{c}	—	520, 545	6·84^{g}6·75^{e},	1·41^{e}, 1·42; 1·49^{d}	1·2576; 49·12; 550; —
30% ethanol^{c}	—	520, 545	6·82^{g}	1·12; 1·27^{d}	1·2576; 1·277; 550; —
1% BRIJ 35^{f}	—	525, 557	15·4^{g}	2·21 ± 0·005	3·930; 0·3930; 557—507; 5
0·1% Triton	473	525, 555	14·5^{g}	1·96 ± 0·007	4·00; 3·930; 355—595; 10
			ClPADAP		
30% ethanol	479	519, 545	7·1^{g}	1·42 ± 0·001	1·00; 49·12; 355—595; 10
0·1% Triton	473	525, 555	16·0^{g}	1·97 ± 0·0004	4·00; 0·3930; 355—595; 10
10^{-3} mol l^{-1} CPB	472	525, 555	14·4^{g}	1·41 ± 0·0002	4·00; 0·3930; 355—595; 10

[a] Data obtained from spectra recording; [b] absorption maximum of the reagent; [c] results obtained from graphical interpretation of the absorbance-pH curves, A transformation; [d] results of graphical logarithmic analysis; [e] results of graphical interpretation, c_L/A transformation; [f] $\varepsilon = 1{\cdot}466 \cdot 10^5$; $1{\cdot}458 \cdot 10^5$ and $1{\cdot}494 \cdot 10^5$ mmol^{-1} cm^2, $-\log {}^{*}\beta = 2{\cdot}71$, 3·34 and 2·41 ($A$-tansformation) or $-\log {}^{*}\beta = 2{\cdot}59$, 2·29 and 2·34 (logarithmic transformation) for $c_M = 3{\cdot}93 \cdot 10^{-6}$ mol l^{-1}, $c_L = 1{\cdot}965 \cdot 10^{-5}$ mol l^{-1}, $c_L = 3{\cdot}93 \cdot 10^{-5}$ mol l^{-1} and $c_L = 5{\cdot}895 \cdot 10^{-5}$ mol l^{-1} and wavelength of 552 nm; [g] data for the long wavelength maximum.

In aqueous ethanolic solutions of Zn(II) with BrPADAP and ClPADAP with a concentration excess of reagent, a slight turbidity or precipitate of the chelate of Zn(II) with the reagent appeared in the pH region of complex formation; its formation was suppressed only in the presence of 50% v/v DMF. With the other solvents tested (acetone, ethanol, *etc.*), colloid formation could not be eliminated completely even at larger solvent contents. Because of the poor suitability of solutions containing 50% DMF for practical applications and the flat shape of the absorbance-pH curve with a narrow pH region suitable for analytical applications, solutions of nonionic and ionic tensides – Triton X-100, Brij 35, Bion NE-9, polyvinylpyrrolidone and Slovasol O in the presence of 10% ethanol – were tested for solubilization of the complex formed. The absorption spectra (340–620 nm, $c_L = 1{\cdot}965 \,.\, 10^{-5}$ mol l^{-1}, $c_M = 1{\cdot}965 \,.\, 10^{-6}$ mol l^{-1}) recorded in the narrow pH interval 8·4–9·1 in dependence on the concentration of the individual tensides were identical with the spectra in the absence of tenside. The absorption maxima lie in the region 512–557 nm. The optimal concentration for the actual measurement was found from the dependence of the absorbance on the tenside concentration. In the presence of Slovasol O, the absorbance increased practically linearly with concentration, indicating contamination of the substance by heavy metal ions (attempts to purify this substance by common methods were not successful). In the presence of polyvinylpyrollidone, the dependence exhibited a narrow maximum for a concentration of *c.* 0·8%, but the absorbance values were lower than for the other solutions. In the presence of Triton X-100, the concentration dependence was not marked. A concentration of 0·1% was sufficient for complete solubilization of the complex. In the presence of Bion NE-9, the absorbance in the optical concentration region 0·1–0·35%, was lower than for the other tensides except for Brij 35, for which the dependence increased linearly up to a concentration of about 1% and the absorbance was then independent of the concentration. Considering these results and the availabilities of the tensides, Triton X-100 and Brij 35 with concentrations of 0·1 or 1·0%, respectively, were selected for further applications.

The absorbance-pH curves of Zn(II) solutions containing BrPADAP in 10% ethanol in the presence of 1·0% Brij 35 ($c_M = 3{\cdot}930 \,.\, 10^{-6}$ mol l^{-1}, $c_L = 1{\cdot}965 \,.\, 10^{-5}$ mol l^{-1}, $3{\cdot}930 \,.\, 10^{-5}$ mol l^{-1} and $5{\cdot}895 \,.\, 10^{-5}$ mol l^{-1}, 557–507 nm in steps of 5 nm, pH = 3–10) or 0·1% Triton X-100 ($c_M = 3{\cdot}930 \,.\, 10^{-6}$ mol l^{-1}, $c_L = 4{\cdot}00 \,.\, 10^{-5}$ mol l^{-1}, 355–595 nm in steps of 10 nm, pH = 3–11) had the same shape with a single formation branch. With increasing reagent concentration, the curves were shifted to the acid region. In a broad pH region, pH = 6·5–9, the absorbance was practically independent of the experimental conditions (Fig. 6).

Graphical analysis of the measured absorbance-pH curves for a wavelength of 552 nm and for various concentration excesses of the reagent indicate formation of the ML_2 complex, whose optical parameters are listed in Table II. The values of the slopes of the logarithmic transformations ($q = 1{\cdot}75$, 1·81, *etc.*) suggest the

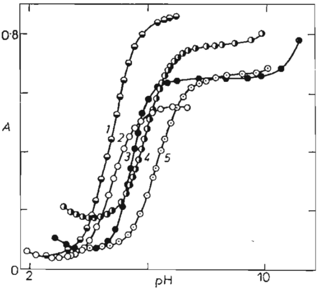

FIG. 6

Absorbance-pH curves of Zn(II) with BrPADAP and ClPADAP. Curve, reagent, $c_L \, . \, 10^5$ (mol l^{-1}), $c_M \, . \, 10^5$ (mol l^{-1}), λ(nm): *1* BrPADAP 1·2576 49·12 550; 2 ClPADAP 1·00 49·12 555; *3* BrPADAP 4·00 0·393 555 10% ethanol with 0·1% Triton X-100; *4* BrPADAP 7·587 0·393 550; *5* ClPADAP 4·00 0·393 555; 30% ethanol for curves *1* and 2, 50% DMF for curves *4* and *5*

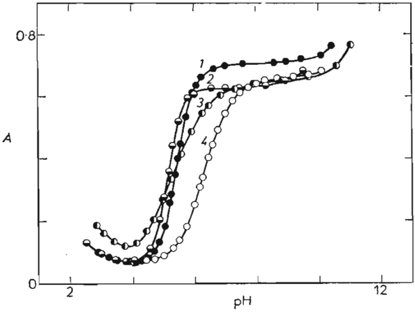

FIG. 7

Absorbance-pH curves of a Zn(II) solution with a concentration excess of ClPADAP in 10% ethanol medium with tensides or DMF. $c_L = 4{\cdot}00 \, . \, 10^{-5}$ mol l^{-1}, $c_M = 3{\cdot}93 \, . \, 10^{-6}$ mol l^{-1}, 555 nm, $I = 0{\cdot}10$. Curve tenside c_T (mol l^{-1} or %): *1* Triton X-100 0·1% 2 CPB 1 . 10^{-3} *3* SDS 10^{-3}; *4* 50% DMF possibility of a side reaction with dissociation of a single proton according to equilibria (*A*)–(*C*):

$$\mathrm{M} + 2\,\mathrm{LH} \rightleftharpoons \mathrm{ML_2} + 2\,\mathrm{H} \qquad (B)$$

$$\mathrm{M} + 2\,\mathrm{LH} \rightleftharpoons \mathrm{ML_2H} + \mathrm{H} \qquad (C)$$

Calculations by the SQUAD-G program for the same model considering the formation of the ML, ML_2 and ML_2H complexes or a combination thereof yielded satisfactory agreement only in consideration of independent equilibrium (*B*) for both media ($\sigma_A = 0{\cdot}0049$ or 0·0046 A.U. for Brij 35 or Triton X-100, respectively). The other calculations did not converge. The determined optical parameters and equilibrium constants of reaction (*B*) are given in Table II.

Neither graphical nor numerical interpretation of the experimental data measured in 50% DMF medium ($c_L = 7{\cdot}587 \cdot 10^{-5}$ mol l^{-1}, $c_M = 3{\cdot}930 \cdot 10^{-6}$ mol l^{-1}, 510–560 nm in steps of 5 nm, pH = 3–11) yielded satisfactory agreement with the experimental data for any of the above models. It follows, however, from the molar absorption coefficient values in the pH region pH $\gtrsim$ 8·5 that complex ML_2 is also formed quantitatively in this medium, while several complexes are present simultaneously at lower pH values.

The absorbance-pH curves of solutions containing 4·00 . 10^{-5} mol l^{-1} ClPADAP

TABLE III

Comparison of some reagents for the spectrophotometric determination of Zn(II)

Quantity	PAR	PAN	Dithizone	BrPADAP
Optimum pH	8–10	8–10	5·1–5·9	6·5–10
λ_{max}, nm; LH/ML_2	412/495	480/520, 560	435, 618/535	445/525, 557
λ_{opt}, nm; complex ML_2	495	560	535	557
$\varepsilon \pm d(\varepsilon)$; cm^2 mmol^{-1}	9·05 ± 0·27	4·90 ± 0·08	7·30 ± 0·18	15·36 ± 0·27
Intercept on the absorbance axis	0·31 ± 0·004	0·00 ± 0·003	0·27 ± 0·005	0·10 ± 0·005
s_{xy}[a]	0·0045	0·0037	0·0040	0·0071
S_I[b] for A = 0·010, ppm	0·0067	0·0133	0·0089	0·0043

[a] Standard deviation of the scatter around the regression straight line; [b] the Sandell sensitivity index.

and $3{\cdot}930 . 10^{-6}$ mol l^{-1} Zn(II) were measured in the wavelength interval 355–595 nm in constant steps of 10 nm in 50% DMF and 10% ethanol in the presence of 0·1% Triton X-100, 1·0% Brij 35 or $1{\cdot}0 . 10^{-3}$ mol l^{-1} CPB or SDS (Fig. 7). Numerical treatment of the experimental data for Triton X-100 and CPB yielded the best agreement with the experimental data ($\sigma = 0{\cdot}0059$ ot 0·0022 A.U., resp.) for the model of formation of a single complex, ML_2, according to equilibrium (B). The calculations for the other models and for 50% DMF and $1{\cdot}0 . 10^{-3}$ mol l^{-1} SDS did not yield satisfactory agreement.

The complex composition in solutions with a concentration excess of reagent was verified for the complex of Zn(II) with BrPADAP by the method of continuous variations. The dependences of the absorbance on the mole fraction of reagent $A = f(_L) = f(c_L/(c_L + c_M))$ in a solution of 1% Brij 35 with 10% ethanol in the presence of 0·10 mol l^{-1} TRIS buffer with pH = 7·5 and $c_0 = c_M + c_L = 1{\cdot}965 . 10^{-5}$ mol l^{-1} and at wavelengths of 510, 520, 530, 540, 550 and 560 nm exhibit maximum absorbance at a mole fraction of $x_L = 0{\cdot}70$, corresponding to the ML_2 complex ($x_L = 0{\cdot}67$).

In the development of a method for the determination of Zn(II) with BrPADAP or ClPADAP, a 10% ethanol medium containing 1·0% Brij 35 or 0·1% Triton X-100 was seletced. It was found by measuring the dependence of the absorbance on the reagent concentration at pH 5·75, 6·10, 6·50 and 8·00 that a concentration excess of reagent of $c_L/c_M \geqq 3$ (pH 8·00) or 10 (pH ~ 6·50) is sufficient for quantitative formation of the ML_2 complex. As other elements may be present in the matrix, an excess greater than 10-fold was used. An optimal pH interval for the determination in the range pH = 6·5–10, where the complex is formed quantitatively and the acid-base transition of the reagent LH/L does not interefere by absorbing in the region of maximum absorbance of the ML_2 complex (550 nm), was selected on the basis of the absorbance-pH curves for the above conditions.

Of the buffer solutions tested for adjusting the optimal pH value (TRIS, TEA, HMT, $NH_4OH + NH_4Cl$), ammoniacal and TRIS buffers with concentrations of 0·10 mol l^{-1} were selected, as they did not interfere in the absorbance of Zn(II) solutions containing BrPADAP or ClPADAP.

The calibration dependence for the determination of Zn(II) with BrPADAP was measured in pure solutions in a 10% ethanol medium containing 1% Brij 35 and concentration $c_L = 3{\cdot}930 . 10^{-5}$ mol l^{-1} at pH 7·0, 7·5, 8·0 and 9·0 at a wavelength of 552 nm. The calibration curves were linear in the Zn(II) concentration interval $0{\cdot}4716-3{\cdot}930 . 10^{-6}$ mol l^{-1}. The parameters of the calibration dependence are given in Table III together with data for some other spectrophotometric reagents for determining Zn(II).

The values of the molar absorption coefficients of the ML_2 complexes of both reagents with Zn(II) indicate that BrPADAP and ClPADAP are at present the most sensitive spectrophotometric reagents.

DISCUSSION

Study of the acid-base properties of BrPADAP and ClPADAP demonstrated the existence of four acid-base forms of the reagent. Comparison of the dissociation constant values of the two reagents with those of PAR enables assignment of the individual acid-base equilibria to step-wise protonation of the phenolic acid oxygen (pK_{a3}), pyridine nitrogen (pK_{a2}) and the nitrogen of the amino-group (pK_{a1}). The conclusions of Johnson and Florence[4], who attribute the second protonation to the proton bonded to the amino-group, follow from comparison of the dissociation constants of BrPADAP and pyridine-2-azodimethylaniline ($pK_{NR_2} = 4{\cdot}5$) and those of the pyridine nitrogen of some N-heterocyclic azodyes ($pK_N = 1-3$). No unambiguous conclusions can be drawn at this stage.

The complexation equilibria of Zn(II) with BrPADAP and ClPADAP in various media confirm the formation of two complexes with mole ratio M : L = 1 : 1 or 1 : 2 depending on the concentration ratio c_L/c_M. The structures of the complexes are most probably similar to those of the complexes of other N-heterocyclic azodyes with similar groups of donor atoms (O,N,N).

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