THE USE OF 2-(2-HYDROXYPHENYLAZO)-7-OXO-
-5,5-DIMETHYL-4,5,6,7-TETRAHYDROBENZOTHIAZOLE
AS AN EXTRACTANT FOR Cu(II), Ni(II), Co(II), Pb(II) AND Cd(II)

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The heterocyclic azo dye, 2-(2-hydroxy-5-ethylphenylazo)-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole (*I*), was prepared. The acid–base and optical parameters of the azo dye were found spectrophotometrically and the molar absorption coefficients and concentration dissociation constants were determined. The formation of the chelates of compound (*I*) with Cu(II), Ni(II), Pb(II) and Cd(II) was studied. The molar absorption coefficients and stability constants of the chelates were determined by calculations, graphical and logarithmic analysis, based on data from the $A = f(\text{pH})$ curves. The region of optimal extraction and the extraction constants were found for the chelates of *I* with Cu(II), Ni(II), Co(II) and Pb(II).

In recent years, a number of original works have been devoted to the study of heterocyclic azo dyes considering both their theoretical properties and analytical applications. The results have been discussed in reviews[1,2] and in a number of original works. The heterocyclic azo dye group derived from 2-amino-7-oxo-5,5-dimethyl-4,5,6,7--tetrahydrobenzothiazole with passive components of substituted phenols and naphthols are studied in the works[3-6]. This work is concerned with the preparation of the heterocyclic azo dye 2-(2-hydroxy-5-ethylphenylazo)-7-oxo-5-,dimethyl--4,5,6,7-tetrahydrobenzothiazole, and study of its acid–base and chelating properties and of the experimental conditions for using the azo dye for the extraction of Cu(II), Ni(II), Cd(II) and Pb(II).

EXPERIMENTAL

Spectrophotometric measurements were carried out on the Specord UV VIS spectrophotometer (C. Zeiss, Jena) with cuvettes thermostatted at a temperature of $20 \pm 0.2°C$ using an ultrathermostat (Höppler, type NB) and VSU-1 and Spekol spectrophotometers (both C. Zeiss, Jena). The pH was measured using a PHM 64 pH meter (Radiometer, Copenhagen) with a G 202 B glass and K 401 calomel electrode from the same firm. The pH meter was standardized using standard solutions with pH of 1·68, 6·50 and 9·22 supplied with the instrument. The pH values measured in 40% ethanol solution were corrected by a correction factor of $\delta = 0.10$, including the effect of the ion solvation in aqueous-organic medium and in aqueous solutions. Thus $\text{pH}^+ = \text{pH} - \delta$ (ref.[7]). The pH^+ value is related to the activity of the solvated proton
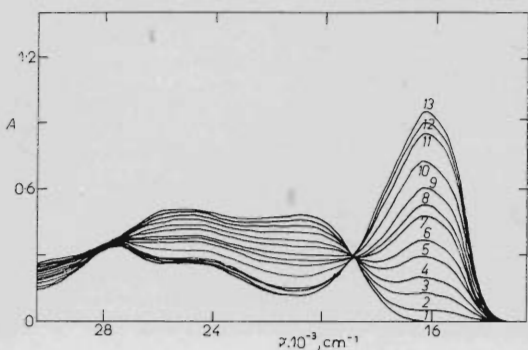
FIG. 1

Dependence of the optical absorbance of solutions of compound I on the pH value. $c_L = 4 . 10^{-5}$ mol 1^{-1}; $d = 1.0$ cm, pH: *1* 2·50; *2* 6·60; *3* 7·14; *4* 7·37; *5* 7·61; *6* 7·74; *7* 7·92; *8* 8·06; *9* 8·18; *10* 8·40; *11* 8·84; *12* 9·10; *13* 12·00
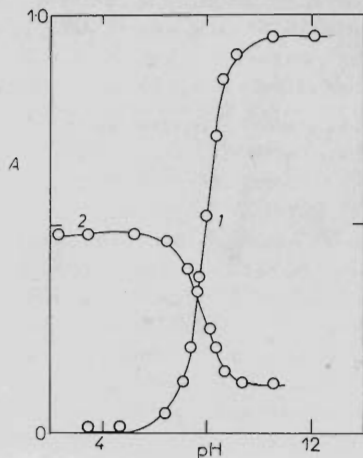

FIG. 2

The $A = f(\text{pH})$ dependence for compound I. $c_L = 4 . 10^{-5}$ mol 1^{-1}; *1* $\tilde{\nu} = 16\,200$ cm^{-1}, *2* $\tilde{\nu} = 20\,800$ cm^{-1}
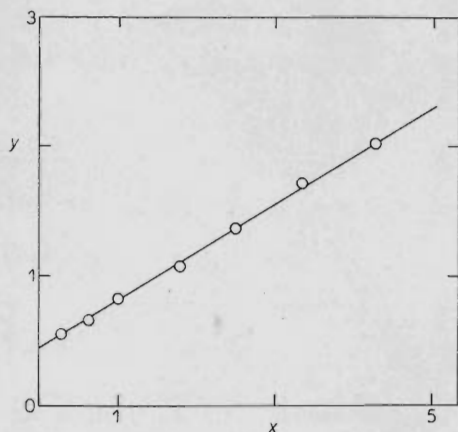

FIG. 3

Graphical analysis of the $A = f(\text{pH})$ curves for compound I. $\tilde{\nu} = 16\,200$ cm^{-1}; $x = [(A - \varepsilon_L c_L)[H^+]/A] . 10^8$; $y = (c_L/A) . 10^4$.
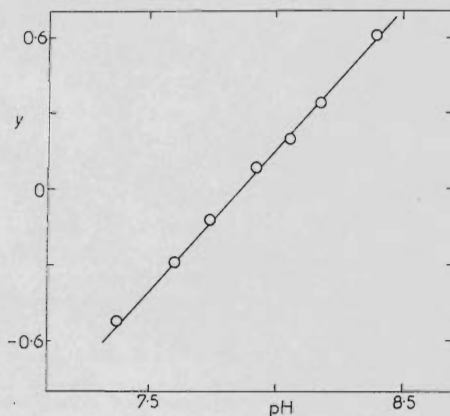

FIG. 4

Logarithmic analysis of the $A = f(\text{pH})$ curve $\tilde{\nu} = 16\,200$ cm^{-1}; $y = \log [(A - \varepsilon_L c_L)/(\varepsilon_L c_L - A)]$

in the particular medium, which is related to the standard state, which is an infinitely dilute solution in the same solvent. An AAS model 306 instrument (Perkin–Elmer) with atomization in an acetylene–air flame was used to determine the metal concentrations. Single-element hollow cathode lamps from the same firm were employed as sources of monochromatic light.

2-(2-*hydroxy-5-ethylphenylazo*)-7-*oxo*-5,5-*dimethyl*-4,5,6,7-*tetrahydrobenzothiazole* (*I*) was prepared according to the procedure given in work[5] with a yield of 68%, m.p. (Kofler) 170 to 172°C. For $C_{17}H_{19}N_2O_2S$ (M_r 329·4) calculated: 12·76% N, 9·73% S, found: 12·74% N, 9·53% S. The uniformity of the azo dye was verified using ascending chromatography on What- man No 1 paper in the systems: isobutanol–ammonia–water (15 : 4 : 1), butyl acetate–pyridine– –water (1 : 5 : 10), amyl acetate–HCl–water (1 : 1 : 5), butanol–HCl–water (10 : 1·5 : 2·7). The stock solutions of the metal salts (10^{-3} mol l^{-1}) were prepared from the metal nitrates of *p.a.* purity in redistilled water. The solution concentrations were controlled chelometrically[8]. The pH was adjusted using acetate buffer solutions, Britton–Robinson buffer solutions, per- chloric acid and sodium hydroxide. The ionic strength was adjusted with $NaClO_4$. All the chemicals were of *p.a.* purity. The solution of the test substance was prepared in concentrations of 10^{-2} and 10^{-3} mol l^{-1} in redistilled ethanol, chloroform, isoamylalcohol and carbon tetrachloride.
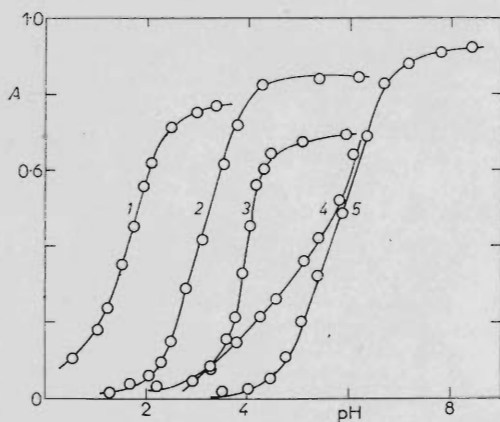

FIG. 5

The $A = f(pH)$ dependence for solutions of compound *I* with copper, nickel, cobalt, cadmium and lead *I*. $c_L = 4 . 10^{-5}$ mol l^{-1}, $c_M = 4 . 10^{-3}$ mol l^{-1};   1 Cu, $\tilde{\nu} =$ $= 15\,300$ cm^{-1};   2 Ni, $\tilde{\nu} = 15\,600$ cm^{-1}; 3 Co, $\tilde{\nu} = 16\,000$ cm^{-1};   4 Pb, $\tilde{\nu} =$ $16\,100$ cm^{-1}; 5 Cd, $\tilde{\nu} = 16\,300$ cm^{-1}
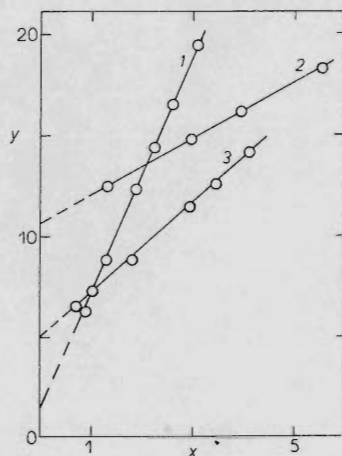
FIG. 6

Graphical analysis of the $A = f(pH)$ depen- dence for solutions of compound *I* with excess of metal solution. $c_L = 4 . 10^{-5}$ mol l^{-1}, $c_M = 4 . 10^{-3}$ mol l^{-1};   1 Co, $x = ([H^+]\sqrt{A}/A$. $. 10^4$, $y = (c_L/A) . 10^5$;   2 Pb, $x = ([H^+]/ /c_M) . 10^5$, $y = (c_L/A) . 10^5$;   3 Cu, $x =$ $= ([H^+]/c_M) . 10^2$, $y = (c_L/A) . 10^4$

RESULTS AND DISCUSSION

The test substance (I) exists in two acid–base forms in the pH range, $1-11$, depending on the pH value. The coexistence of the individual forms can be schematically depicted as $LH \rightleftharpoons L^- + H^+$, confirmed by the existence of a sharp isosbestic point at a wavenumber of $18\,190\ cm^{-1}$. In media of $1-5\ mol\ l^{-1}\ HClO_4$, the heterocyclic nitrogen becomes protonated, in the equilibrium $LH_2^+ \rightleftharpoons LH + H^+$. It can be seen in Figs 1 and 2 that, from pH 2 to 6 the test substance exists as a yellow molecular species, LH, with maximum absorbance at a wavenumber of $20\,830\ cm^{-1}$. At pH 6 the proton of the —OH group begins to dissociate and from pH 10 the azo-dye exists in a blue form, L^-, with maximum absorbance at a wavenumber of $16\,190\ cm^{-1}$. On the basis of the relationships, $K_a = [H^+][L^-]/[HL]$, $A = A_{L^-} + A_{HL}$, $C_L = = [L^-] + [HL]$, calculation and graphical and logarithmic analysis of the curves of the dependence $A = f(\mathrm{pH})$ yield the molar absorption coefficient ε_{L^-} and dis-
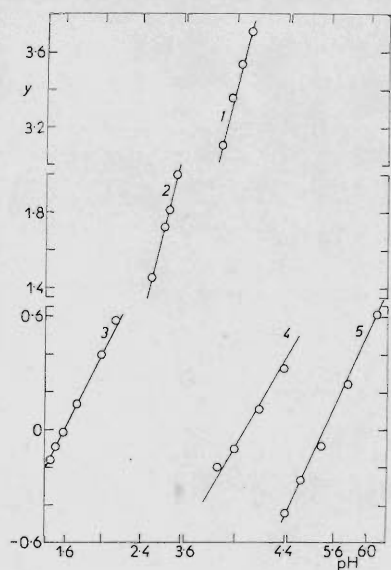
FIG. 7

Logarithmic analysis of the $A = f(\mathrm{pH})$ dependence for solution with excess metal 1 Co, 2 Ni, 3 Cu, 4 Pb, 5 Cd. y for 1, 2 = $= \log (\varepsilon_2 A/(\varepsilon_2 C_L - 2A)^2)$, y for 3, 4, 5 = $= \log (A/\varepsilon_1 C_L - A)$

FIG. 8

Dependence of the extraction of the chelates of metals with I into $CHCl_3$ on the pH of the aqueous phase. $c_M = 5 \cdot 10^{-5}\ mol\ l^{-1}$, $c_L = 10^{-3}\ mol\ .\ l^{-1}$, $I = 0.10$; 1 Cu, 2 Co, 3 Cd, 4 Pb, 5 Ni

sociation constant K_a according to the equations

$$C_L/A = 1/\varepsilon_{L^-} + [H^+](A - \varepsilon_{LH})/K_a\varepsilon_{L^-}A \tag{1}$$

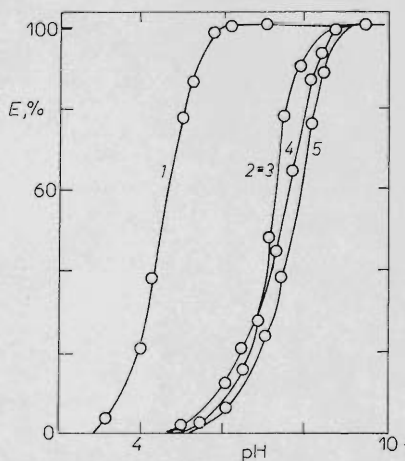$$pK = pH - \log[(A - \varepsilon_{HL}C_L)/(\varepsilon_L \cdot C_L - A)] \tag{2}$$

(Figs 3 and 4). The ε_{HL} value can be found from the simple relationship $\varepsilon_{HL} = A/C_L$ assuming that the necessary values are taken from that part of the $A = f(\text{pH})$ curve where the test substance exists in the molecular form at a cuvette thickness equal to unity. For a wavenumber of $16\,190\,\text{cm}^{-1}$, $\varepsilon_L\,(1\,\text{mol}^{-1}\,\text{cm}^{-1}) = 2\cdot32\,.\,10^4$, $pK_a = 7\cdot87 \pm 0\cdot03$ and the confidence limits calculated from the range for $1 - \alpha = 0\cdot95$ for 6 results; a value of $7\cdot89$ is obtained from the results of graphical analysis and $7\cdot86$ from the results of logarithmic analysis.

In acid medium, azo compound (*I*) forms green coloured chelates with Cu(II), Cd(II), Pb(II), Ni(II) and Co(II). The formation, composition and stability of these chelates were studied in 40% aqueous ethanol solution by the spectrophotometric method. The Job plot method was used to determine the composition of the chelates. The molar absorption coefficients and stability constants of the chelates were found
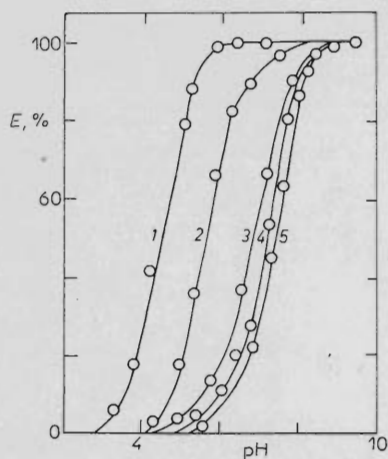
FIG. 9

Dependence of the extraction of chelates of metals of *I* into CCl$_4$ on the pH of the aqueous phase. $c_M = 5\,.\,10^{-5}\,\text{mol}\,\text{l}^{-1}$, $c_L = 10^{-3}$ mol . l^{-1}, *I* 0·10; *1* Cu, *2* Co, *3* Ni, *4* Cd, *5* Pb
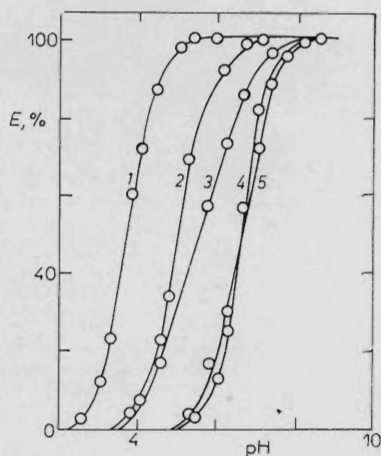
FIG. 10

Dependence of the extraction of chelates of metals with compound *I* into isoamyl alcohol on the pH of the aqueous phase. $c_M = 5\,.\,10^{-5}\,\text{mol}\,\text{l}^{-1}$, $c_L = 10^{-3}\,\text{mol}.\text{l}^{-1}$, *I* 0·01; *1* Cu, *2* Co, *3* Ni; *4* Cd, *5* Pb

TABLE I

Spectrophotometric characteristics of the chelates of reagent I with Cu(II), Cd(II), Pb(II), Ni(II) and Co(II)

Metal	ν cm^{-1}	ε_{max}(ML) l cm^{-1} mol^{-1}	$K_1{}^a$ calculation	$K_1{}^a$ graphical analysis	$K_1{}^a$ logarithmic analysis	$\log \beta_1$(ML)^b calculation	$\log \beta_1$(ML)^b graphical analysis	$\log \beta_1$(ML)^b logarithmic analysis	$k_L{}^c$
Cu	15 300	$(2 \cdot 050 \pm 0 \cdot 142) \cdot 10^4$	6·11	7·82	5·99	$8 \cdot 62 \pm 0 \cdot 10$	8·81	8·70	1·00
Cd	16 400	$(2 \cdot 047 \pm 0 \cdot 179) \cdot 10^4$	$0 \cdot 57 \cdot 10^{-3}$	$0 \cdot 63 \cdot 10^{-3}$	$0 \cdot 72 \cdot 10^{-3}$	$4 \cdot 67 \pm 0 \cdot 11$	4·17	4·78	1·10
Pb	16 100	$(9 \cdot 991 \pm 0 \cdot 249) \cdot 10^3$	$2 \cdot 12 \cdot 10^{-2}$	$1 \cdot 93 \cdot 10^{-2}$	$1 \cdot 98 \cdot 10^{-2}$	$6 \cdot 17 \pm 0 \cdot 24$	6·20	6·22	0·85

Metal	ν cm^{-1}	ε_{max}(ML$_2$) l cm^{-1} mol^{-1}	$K_{1,2}{}^d$ calculation	$K_{1,2}{}^d$ graphical analysis	$K_{1,2}{}^d$ logarithmic analysis	$\log \beta_2$(ML$_2$)^e calculation	$\log \beta_2$(ML$_2$)^e graphical analysis	$\log \beta_2$(ML$_2$)^e logarithmic analysis	$k_L{}^c$
Ni	15 600	$(2 \cdot 673 \pm 0 \cdot 025) \cdot 10^4$	$7 \cdot 24 \cdot 10^{-1}$	$7 \cdot 31 \cdot 10^{-1}$	$7 \cdot 42 \cdot 10^{-1}$	$15 \cdot 57 \pm 0 \cdot 20$	15·59	15·59	1·85
Co	16 000	$(2 \cdot 633 \pm 0 \cdot 056) \cdot 10^4$	$1 \cdot 17 \cdot 10^{-2}$	$1 \cdot 14 \cdot 10^{-2}$	$1 \cdot 22 \cdot 10^{-2}$	$13 \cdot 72 \pm 0 \cdot 08$	13·78	13·78	2·00

^{a} $K_1 = [\mathrm{ML}][\mathrm{H}]/c_M[\mathrm{LH}]$, ^{b} $\beta_1(\mathrm{ML}) = K_1/K_a$, ^{c} $k_L =$ the slope of the straight line obtained from logarithmic analysis, ^{d} $K_2 = [\mathrm{ML}_2][\mathrm{H}]^2/c_M[\mathrm{LH}]^2$, ^{e} $\beta_2(\mathrm{ML}_2) = K_2/K_a^2$.

by calculation, by graphical and logarithmic analysis of the curves of the $A = f(\text{pH})$ dependence for a 100-fold excess of metal cations (Fig. 5). Graphical analysis of the $A = f(\text{pH})$ dependence was carried out using the relationships given in the work[9] (Fig. 6) assuming the equilibrium $M^{2+} + LH \rightleftharpoons ML^+ + H^+$ characterized by equilibrium constant $K_1 = [ML^+][H^+]/[M^{2+}][LH]$ and equilibrium $M^2 + 2LH \rightleftharpoons ML_2 + 2H^+$ with equilibrium constant $K_2 = [ML_2][H^+]^2/[M^{2+}][LH]^2$. The assumed equilibrium was confirmed by logarithmic analysis of the $A = f(\text{pH})$ dependence for $C_M \gg C_L$ (Fig. 7). The molar absorption coefficients, equilibrium constants and stability constants β_1 and β_2 of the chelates are given in Table I.

The chelates of reagent I with some metal cations are soluble in organic solvents such as chloroform, tetrachloromethane, isoamyl alcohol and methyl isobutyl ketone. Extractions were carried out at $V_{\text{org}} = V_{\text{aq}} = 10$ ml at room temperature for 2 hours on a mechanical extractor.

The extraction was carried out using a metal solution $(5 \cdot 10^{-5} \text{ mol } l^{-1})$ in buffer solutions of various pH values at an ionic strength of $I = 0 \cdot 10$, shaken to equilibrium with a solution of the reagent $(1 \cdot 10^{-3} \text{ mol } l^{-1})$ in the solvent. After phase separation, the equilibrium pH of the aqueous phase was measured. The decrease in the concentration of the metal in the organic phase was found by the AAS method. The concentration of the metal in the organic phase was found after back-extraction with an equal volume of $(1 : 1)$ HNO_3, by intense two-minute shaking at room temperature. The evaluation was carried out using analytical calibration curves drawn up using suitably diluted standard solutions, modelled by HNO_3 and $NaClO_4$, saturated with the organic solvents used. Figs 8 – 10 depict the extraction curves $\% E = f(\text{pH})$ for the studied ions. The optimal extraction region and the values of $\text{pH}_{1/2}$ as well as the extraction constant values found from the relationship

$$1/2 \, pK_{\text{ext}} = \text{pH}_{1/2} + \log [\text{HL}]_{\text{org}} \qquad (3)$$

TABLE II

The values of $\text{pH}_{1/2}$ and log K_{ext} for the extraction of copper, cadmium, lead, cobalt and nickel with reagent I into organic solvents at a reagent concentration of 10^{-3} mol l^{-1}

Metal	CHCl₃		CCl₄		C₅H₁₁OH	
	$\text{pH}_{1/2}$	log K_{ext}	$\text{pH}_{1/2}$	log K_{ext}	$\text{pH}_{1/2}$	log K_{ext}
Cu	4·6	−1·6	4·5	−1·5	3·75	−0·75
Cd	7·2	−4·2	7·2	−4·2	6·65	−3·65
Pb	7·5	−5·5	7·4	−4·4	6·65	−3·65
Co	7·2	−8·4	6·6	−7·2	5·00	−4·00
Ni	7·7	−9·4	6·8	−7·6	5·55	−5·11

were obtained. The results are given in Table II. The studied azo dye was found to be useful in the extraction of some metal cations. However, the rather high $pH_{1/2}$ for the extraction is a disadvantage.

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