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Spectrophotometric Microdetermination of Divalent Cu, Ni, Pd and UO_2 Ions Using Some Naphthoic Acid Azo Dyes

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Spectrophotometric studies have been carried out on five hydroxynaphthoic acid azo dyes and their metal complexes in aqueous solution at pH 5–8. These azo dyes have been proved as good analytical reagents for the microdetermination of Cu (II), Ni (II), Pd (II) and UO_2 (II) ions based on measuring their absorbance at 470–535 nm and by the photometric titration using EDTA as a titrant. Interference of various cations and anions in this method was studied to find out the most suitable azo dyes for the microdetermination of the respective metal ions. Beer's law was obeyed for Cu (II) and Ni (II) up to 5.8 ppm, for Pd (II) up to 8.5 ppm and for UO_2 (II) ions up to 16.6 ppm.

INTRODUCTION

Hydroxynaphthoic acid azo dyes have received great interest due to their biological activity[1,2], dyeing properties[3,4] and stimulation of plant growth[5]. 4–(*o*–Carboxyphenylazo)–3–hydroxy–2–naphthoic acid has been applied for spectrophotometric determination of Pb ions (10–200 ppm) measuring at 500 nm[6]. Imurad et al. determine tetraethyllead at 440 nm using 4–(*p*–nitrophenylazo)–1–hydroxy–2–naphthoic acid after its extraction with chloroform[7]. Recently, the lanthanides have been determined using some 4-arylazo–3–hydroxy–2–naphthoic acid derivatives[8].

The present study was devoted to the spectrophotometric investigation of the complex formation between Ni (II), Cu (II), Pd (II) and UO_2 (II) and five derivatives of hydroxynaphtoic acid azo dyes as new chromogenic reagents for the microdetermination of these cations.

EXPERIMENTAL

The azo compounds under investigation were prepared as previously described[9]. They have the general structure as shown in figure I

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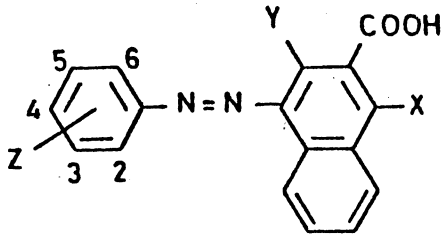

X = OH and Y = H (I), X = H and Y = OH (II), Z = OH (a), COOH (b) and 2-OH, 5-SO_3H (c).

Stock dye solutions (10^{-3} M) were prepared in ethanol except Ic and IIc which were dissolved in water. 10^{-3} M metal solutions were obtained from the corresponding solid salts dissolved in water. The solutions of Ni^{2+} and Cu^{2+} were standardized titrimetrically by EDTA[10], whereas those of Pd^{2+} and UO_2^{2+} were standardized spectrophotometrically using dithizone[11] and arsenazo I[12] respectively.

The pH (R) values measured in water-ethanol mixtures (using Chemcadet pH meter Model 5984–50) were corrected according to:

$$\delta\ pH = pH\ (R) - \delta$$

where $\delta = 0.15$ for 40% ethanol and 0.2 for 50% ethanol.

The electronic absorption of the azo compounds were measured in the visible region using PYE Unicam SP 8–100 UV Spectrophotometer. The measurements of the absorbance of solutions containing 2×10^{-4} M of azo dye and different concentrations of metal ions (0.1×10^{-4}–1.0×10^{-4} M) were carried out (i) against the same amount of dye or (ii) against the unreacted amount of dye *i.e.* optimum blank compensation.

Photometric Titrations

The azo compounds Ia, Ib, Ic and IIa could be used as metallochromic indicators in the photometric titrations with EDTA solution. To a volume 0.4–1.2 ml 10^{-3} M of metal ions, successive amounts (0.2–1.6 ml) of 10^{-3} M EDTA were added followed by addition of a volume (0.8–2.4 ml) of 10^{-3} M of the azo dye. Each mixture was diluted with buffer solution to 10 ml and measured at the recommended suitable wavelength using the azo dye as blank. Plotting the absorbance versus the ml added of EDTA gives two straight lines intersecting at the end point. All the results obtained are summarized in Table-2.

TABLE 1

MOLAR ABSORBITIVITY ε, SPECIFIC ABSORBITIVITY **a** AND SANDEL SENSITIVITY **S** AND BEER OBEYED RANGE FOR Ni (II), Cu (II) AND UO_2 (II) COMPLEXES WITH HYDROXYNAPHTHOIC ACID.

Metal ion	$\lambda_{max, nm}$		pH	$\varepsilon \times 10^{-3}$		$a \times 10^{2}$		$S \times 10^{-3}$		Range obeyd (μg metal/10 ml)	
	(a)	(b)		(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Ia Complexes											
Ni (II)	535	535	8*	7.84	13.60	13.35	23.17	7.49	4.32	58.69	41.83
Cu (II)	512	472	7**	7.00	24.50	11.01	38.55	9.00	2.50	63.54	50.83
Pd (II)	530	520	6***	24.28	29.00	22.80	27.20	4.38	3.67	74.48	85.12
U (VI)	500	468	5**	8.84	26.66	3.71	11.20	26.93	8.93	214.23	166.62
Ib Complexes											
Cu (II)	512	512	8**	9.03	21.4	14.21	33.20	7.30	3.01	63.54	57.19
Pd (II)	530	525	6***	30.00	36.66	28.19	24.45	3.55	2.90	74.48	85.12
U (VI)	512	512	5**	10.40	18.46	4.37	7.75	22.88	12.89	166.62	166.62
Ic Complexes											
Cu (II)	535	535	7**	9.16	10.90	14.40	17.10	6.94	5.84	38.13	38.13
Pd (II)	530	530	5***	18.82	20.00	17.68	18.79	5.66	5.32	23.21	23.21
U (VI)	500	500	6**	8.41	16.42	3.53	6.90	28.30	14.50	119.02	119.02
IIa Complexes											
Ni (II)	525	525	7***	12.44	14.9	21.20	25.39	4.72	3.94	35.21	58.69
Cu (II)	525	525	7***	17.00	25.00	26.70	39.35	3.70	2.54	38.13	38.13
Pd (VI)	525	525	7*	16.84	20.83	15.82	19.57	6.32	5.11	53.21	53.21

Metal ion	$\lambda_{max, nm}$		pH	$\varepsilon \times 10^{-3}$		$a \times 10^{2}$		$S \times 10^{-3}$		Range obeyd (μg metal/10 ml)	
	(a)	(b)		(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
IIc Complexes											
Ni (II)	535	535	7***	2.15	33.04	36.03	56.29	2.78	1.78	29.35	29.35
Cu (II)	530	530	7***	15.10	29.17	23.76	45.90	4.21	2.18	50.83	44.48
Pd (II)	535	535	6***	18.18	29.33	17.08	27.65	5.83	3.63	53.21	63.85
U (VI)	555	555	6***	13.33	21.53	5.60	9.05	17.85	10.58	119.02	119.02

(a) Using the same amount of ligand as a blank.
(b) Using the optimum blank compensation techinque.
ε: Molar absorbitivity ($LM^{-1} cm^{-1}$).
a: Specific absorbitivity ($ml\ g^{-1} cm^{-1}$).
S: Sandel index ($\mu g\ cm^{-1}$).
*Hexamine buffer containng 50% ethanol.
**Hexamine aqueous.
***Universal buffer containing 40% ethanol.

TABLE 2

EFFECT OF INTERFERING IONS ON THE COMPLEX FORMATION BETWEEN Pd^{2+}, UO_2^{2+}, Cu^{2+} AND Ni^{2+} IONS AND AZO DYES Ia, Ib AND IIc.

Foreign ions	Ia				Ib			Ic			IIa			IIc			
	Ni(II)	Cu(II)	Pd(II)	U(VI)	Cu(II)	Pd(II)	U(VI)	Cu(II)	Pd(II)	U(VI)	Ni(II)	Cu(II)	Pd(II)	Ni(II)	Cu(II)	Pd(II)	U(VI)
Na^+	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Mg^{2+}	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
K^+	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Ca^{2+}	–	–	–	–	+	–	+	–	+	+	+	+	+	–	+	+	+
VO_2^{2+}	+	+	–	+	+	+	–	+	+	+	+	+	–	–	–	–	–
Cr^{3+}	+	+	+	–	+	+	–	+	+	+	+	+	–	–	–	–	–
Mn^{2+}	–	–	–	–	–	–	–	–	–	–	+	–	–	–	–	–	–
Fe^{3+}	+	+	–	–	+	–	+	+	+	+	+	–	+	+	+	+	+
Fe^{2+}	–	+	–	–	+	–	+	+	+	+	+	+	+	+	+	+	+
Co^{2+}	+	+	–	–	–	–	–	+	+	–	+	+	–	–	+	–	+
Ni^{2+}	+	+	–	–	–	–	–	–	–	–	+	+	+	+	+	+	+
Cu^{2+}	+	+	–	+	+	–	+	+	+	+	+	+	+	+	+	+	+
Zn^{2+}	–	–	–	–	–	–	–	–	+	–	+	–	–	–	+	–	+
Sr^{2+}	+	+	–	–	–	–	–	–	+	–	+	+	–	–	–	–	–

Foreign ions	Ia				Ib			Ic			IIa			IIc			
	Ni(II)	Cu(II)	Pd(II)	U(VI)	Cu(II)	Pd(II)	U(VI)	Cu(II)	Pd(II)	U(VI)	Ni(II)	Cu(II)	Pd(II)	Ni(II)	Cu(II)	Pd(II)	U(VI)
Hg^{2+}	–	+	–	–	–	–	–	–	–	–	–	–	–	–	+	+	+
Bi^{+3}	+	+	–	–	–	+	+	+	+	+	+	+	–	+	+	+	+
Pb^{2+}	+	+	–	+	–	–	–	+	+	+	–	–	–	–	–	+	+
Ba^{2+}	–	+	+	–	–	+	–	–	–	–	+	–	–	–	–	–	–
NO_3^-	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
SO_4^{2-}	+	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
CN^-	+	+	+	–	+	+	–	+	–	–	+	–	+	+	–	–	–
F^-	–	–	–	–	–	–	+	–	–	+	–	–	–	–	–	–	–
Cl^-	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Br^-	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
I^-	–	–	+	–	–	+	–	–	–	–	–	–	–	–	–	–	–
Acetate	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Tartrate	+	+	–	–	+	+	+	+	–	+	–	–	–	–	–	–	–
$C_2O_4^{2-}$	+	+	+	–	+	+	+	+	+	+	–	–	+	–	–	–	–
$PhCOO^-$	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
EDTA	+	+	+	–	+	+	+	+	+	+	+	+	+	+	+	+	–

+: Interfere; –: do not interfere.

TABLE 3
SPECTROPHOTOMETRIC TITRATION OF Ni (II), Cu (II), Pd (II) and UO_2 (II) IONS WITH EDTA USING THE DYES Ia, Ic, Ib, AND IIa.

Dye	Metal ion	λ_{max}(nm)	pH	µg metal/10 ml		
				Taken	Found	% Error
Ia	Ni	535	8*	23.48	23.48	0.00
				35.21	35.21	0.00
				46.95	46.95	0.00
				58.69	58.69	0.00
				70.43	70.43	0.00
	Cu	512	7*	38.12	38.12	0.00
				50.83	50.83	0.00
				63.54	62.90	0.01
				76.2	73.71	0.03
	Pd	520	6***	63.85	63.85	0.00
				85.14	85.14	0.00
				106.42	106.42	0.00
Ib	Cu		8*	38.12	38.12	0.00
				50.83	50.83	0.00
				63.54	63.54	0.00
				76.25	76.25	0.00
	Pd	530	6***	63.85	63.85	0.00
				85.14	85.14	0.00
				106.42	106.42	0.00
				127.70	134.09	0.05
Ic	Cu	535	7**	38.12	38.12	0.00
				50.83	50.83	0.00
				63.54	63.54	0.00
				76.25	76.25	0.00
				101.66	97.85	0.04
	Pd	530	5***	42.57	42.57	0.00
				63.85	63.85	0.00
				85.14	85.14	0.00
				106.42	106.42	0.00
				127.70	126.64	0.008
IIa	Ni	525	7***	23.47	23.47	0.00
				35.51	35.51	0.00
				46.95	46.95	0.00
				58.69	58.69	0.00
				70.43	70.43	0.00
	Cu	525	7***	25.43	25.43	0.00
				38.12	38.12	0.00
				50.83	50.83	0.00
				63.54	63.54	0.00
				76.25	76.25	0.00
	Pd	530	7*	63.85	63.85	0.00
				85.14	85.14	0.00

*Hexamine buffer containing 50% ethanol
**Hexamine aqueous
***Universal buffer containing 40% ethanol

RESULTS AND DISCUSSION

The spectra of Ni^{2+}, Cu^{2+}, Pd^{2+} and UO_2^{2+} complexes with the hydroxynaphthoic acid azo dyes Ia, Ib, Ic, IIa and IIc show a maximum absorption at 470–535 nm. The complexes are formed instantaneously and remain stable for 24 hrs. except the UO_2–Ib which is stable for only 1 hr. and UO_2–Ia which precipitates with time.

The spectra of the complexes measured within 400–600 nm were recorded in solution of pH 4–10 using either the universal (40% alcoholic) buffer (1) or aqueous hexamine buffer (2) or 50% alcoholic hexamine buffer (3). The Ni^{2+} and Cu^{2+} complexes with (IIa, IIc), (Ib, Ic) and Ia have maximum absorbance at pH 7–8 using the buffer (1), (2) and (3) respectively.

The complexes of Pd(II) ions with IIc and those of UO_2 (II) with Ia and IIa absorb maximally at pH 5–6 using buffers (1) and (2). The low absorption of the complexes at pH less than 4 may be attributed to the competition between the metal ions and hydrogen ions. The optimum pH values for the complex formation could be predicted from the absorbance - pH curve for each complex. At these pH values, the respective azo dyes can be used as analytical reagents for the microdetermination of the metal ions. Fig. 1 represents the effect of varying the pH value on the absorbance of the Cu^{2+}-complexes at wavelength 520 nm.

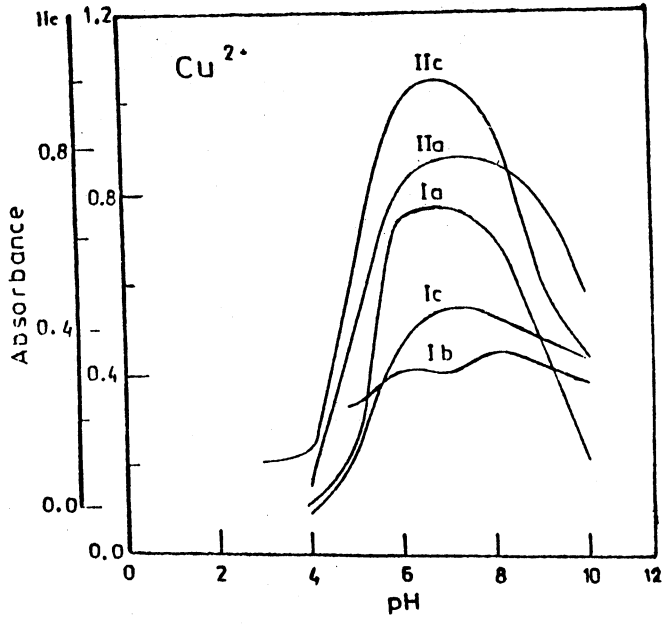

Fig. 1. pH-dependence of the absorption of Cu(II) complexes with Ia, Ib, Ic, and IIc azo dyes.

In order to obtain stable complexes having highest absorbance at 470–530 nm, the stuitable sequence of addition (after many trials) was found to be: metal–dye–buffer except for the UO_2–Ib complex where the sequence metal-buffer-dye is much better.

The stoichiometry of the formed complexes was investigated using the molar ratio method[13]. According to this method, the plot of the absorbance (A_{max}) of the complex ML versus the [L]/[M] ratio consists of two straight lines intersecting at the most stable molar ratio of the formed coloured complex species. Fig (2) shows the molar ratios plots of the UO_2 (II) complex species 1 : 1 and 1 : 2 with different ligands Ia, Ib and Ic.

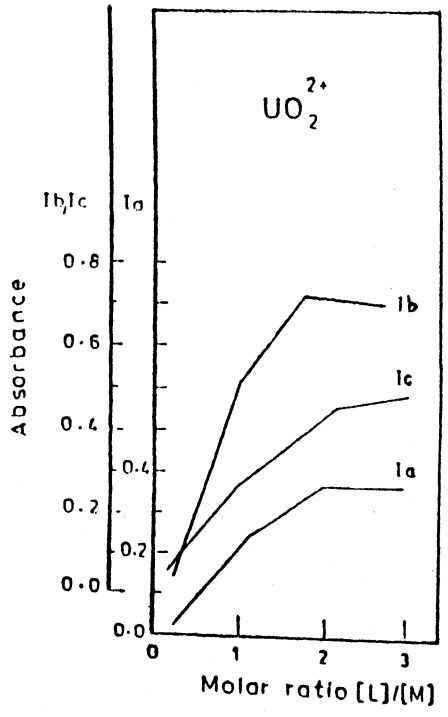

Fig. 2 Molar ratio method for UO_2(II) complexes.

The results indicate that 1 : 1 and 1 : 2 complex species are formed with Cu (II), Ni (II), Pd (II) and UO_2(II) and that only 1 : 2 species is found in Ni–Ia and Pd–IIa complexes.

Validity of Beer's law

In order to find the suitable concentration range of metal ions for their microdetermination, the M–L complexes with different M^{2+} concentrations ($0.1 - 1 \times 10^{-4}$ M) are measured at the selected λ_{max}. Beer's law is satisfactorily

obeyed for metal ions up to 16.6 ppm. The molar absorbitivity (ε, in LM^{-1} cm^{-1}), specific absorbitivity[14] (a, in ml g^{-1} cm^{-1}) and Sandell index[15] (s, in μg cm^{-1}) were calculated and their values are listed in Table (1). the results indicate the high sensitivity of the method (Fig.-3). The appreciable difference in slopes of line (1) and line (2) indicates that the use of the optimum blank compensation increases the sensitivity of the present method.

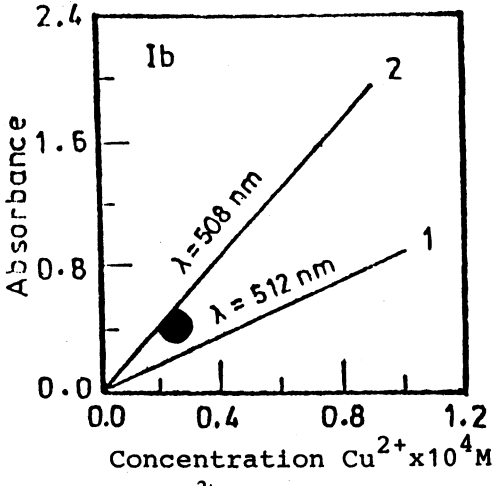

Fig. 3 Validity of Beer's law for Cu^{2+}-Ib complex, (1) dye of blank (2) optimum blank compensation.*

Interfering Ions

The interference due to several anions and cations was studied in detail by carrying out the spectrophotometric measurements in the presence of 30 foreign ions. The obtained data (Table-2) lead to the conclusion that Ia is more selective for both Pd^{2+} and UO_2^{2+} ions whereas Ib is selective for Cu^{2+} ions and IIc is selective for Ni^{2+} ions. Up to 10-folds of Na^+, Mg^{2+}, K^+, Ca^{2+}, VO_2^{2+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, CO^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sr^{2+}, Hg^{2+}, Bi^{3+}, Pb^{2+}, NO_3^-, SO_4^{2-}, F^-, Cl^-, Br^-, acetate, benzoate, tartrate donot interfere for example with Pd^{2+}–Ia complexation. The Cr^{3+}, Ba^{2+}, CN^-, I^-, oxalate and EDTA interfere and must be excluded. The Ia dye can be used for the determination of UO_2^{2+} ions spectrophotometrically since only few ions (Pb^{2+}, Cu^{2+}, VO_2^{2+}) can interfere.

Spectrophotometric Titrations

The application of the azo dyes of hydroxy naphthoic acids (Ia, Ib, Ic, IIa) as indicators in the spectrophotometric titrations of Ni^{2+}, Cu^{2+} and Pd^{2+} ions with

*Line (1) using only one blank and line (2) applying the optimum blank compensation method i.e. measuring the absorbance against blanks containing the unreacted reagent only.

EDTA has been carried out. The present method is accurate and highly reproducible as indicated by the low per cent error (Table 2). However, the results whow that Ni^{2+}, Cu^{2+} and Pd^{2+} ions can be successfully determined up to 20–120 μg metal ion per 10 ml.

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