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Synthesis and spectrophotometric studies of some benzothiazolylazo dyes – determination of copper, zinc, cadmium, cobalt and nickel

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4-(2-Benzothiazolylazo)-2-amino-3-hydroxypyridine and its derivatives 4-(4-methyl-2-benzothiazolylazo), 4-(6-chloro-2-benzothiazolylazo) and 4-(6-bromo-2-benzothiazolyl-azo)-2-amino-3-hydroxypyridines have been synthesized. All these dyes are very sensitive chromogenic reagents for the determination of copper, cadmium, zinc, cobalt and nickel. The reagents react with the metal ions to form purple-coloured complexes (λ_{max} 540−570 nm) in aqueous acetone solution within the pH range 2.8 to 4.6. Copper can be selectively determined at pH 2.8 and most of the metal ions do not interfere except for nickel and cobalt. Cadmium, zinc, cobalt and nickel can be determined at pH 4−5. Their mutual interference can be eliminated using suitable masking reagents. A further advantage of this method is that an extraction procedure is not required and therefore the analytical procedure is very simple.

Key words: 2-aminobenzothiazole, azodyes, 2-amino-3-hydroxypyridine, spectrophotometry, analytical reagents, metal ions.

INTRODUCTION

In search of new sensitive and selective organic reagents, a thorough study of some heterocyclic azo dyes has been made. Among the heterocyclic reagents pyridylazo, thiazolylazo and benzothiazolylazo dyes are extensively used for the spectrophotometric determination of metal ions [1−22]. In this work 4-(2-benzothiazolylazo)-2-amino-3-hydroxypyridine (BTAAHP), 4-(4-methyl-2-benzothiazolylazo)-2-amino-3-hydroxy-pyridine (MBTAAHP), 4-(6-chloro-2-benzothiazolylazo)-2-amino-3-hydroxypyridine (CBTAAHP) and 4-(6-bromo-2-benzothiazolylazo)-2-amino-3-hydroxypyridine, (BBTAAHP) were prepared and a spectrophotometric method was developed for the determination of copper, zinc, cadmium, cobalt and nickel. The authors have already reported the synthesis of 4-(2-benzothiazolylazo)-2-amino-3-hydroxypyridine (BTAAHP) and the spectrophotometric determination of copper by this reagent [1].

All the reagents react instantaneously with Cu (II), Zn (II), Cd (II) and Co (II) to form reddish purple complexes. However, the formation of Ni (II) complexes requires 30 minutes time. These complexes are stable for an hour. Metal ions like Fe^{2+}, Hg^{2+}, Pb^{2+} do not interfere.

MATERIALS AND METHODS

Apparatus

Shimadzu UV double-beam spectrophotometer was used for the spectrophotometric measurements. pH adjustments were carried out with Digisun electronic pH meter model 7007. 2000 Perkin Elmer FTIR was used for IRS measurements and Thermo DFS double focusing magnetic sector mass spectrometer was applied for mass spectral measurements. Graphite furnace atomic absorption spectrometer was used for the determination of the analytes in water samples

Chemicals

2-Aminobenzothiazole and 2-amino-4-methylbenzothiazoles were prepared by cyclization of the corresponding α-phenyl thioureas [23] with thionyl chloride as described previously [24]. 2-amino-6-chloro- and 2-amino-6-bromobenzo-thiazoles were prepared from the corresponding α-phenyl thioureas, using sulphuric acid and hydrobromic acid as cyclization agents [25]. 2-amino-3-hydroxypyridine was purchased from Acros Organics (New Jersey, USA). 0.2 M sodium acetate and 0.2 M acetic acid were used for pH adjustments. BTAAHP, MBTAAHP, CBTAAHP and BBTAAHP solutions of concentration 10^{-4} M were prepared by dissolving a suitable quantity of the substance in AR acetone and these solutions were stable for several months, if stored in amber coloured bottles. All other solutions, including standard solutions of

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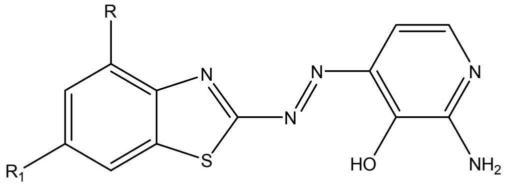
metal ions, were prepared from purified reagents in redistilled water.

EXPERIMENTAL

Synthesis of BTAAHP. Synthesis and analysis of BTAAHP were already reported by the authors [1].

Synthesis of MBTAAHP. 1.64 g of 2-amino-4-methylbenzothiazole was dissolved in concentrated sulphuric acid (14 mL) and diluted with 24 mL of water. The amine was diazotized using nitrosyl sulphuric acid (prepared by adding 0.72 g of sodium nitrite to 5 mL of concentrated sulphuric acid at 70−90°C) at 0−5°C [7]. The diazotized mixture was kept for 2 hours at 0−5°C and then added to a solution containing 1.1 g of 2-amino-3-hydroxypyridine in 400 mL of 7% NaOH. The pH of the mixture was adjusted to 5 with ammonia and acetic acid, it was kept overnight and filtered. Brownish-red solid of MBTAAHP was dried and recrystallized from chloroform. The reagent was further purified by column chromatography using silica gel and 10% acetone in chloroform as eluent.

4-(6-chloro-2-benzothiazolylazo)-2-amino-3-hydroxypyridine (CBTAAHP) (and 4-(6-bromo-2-benzothiazolylazo)-2-amino-3-hydroxypyridine (BBTAAHP) were prepared as it was described above starting with 2-amino-6-chlorobenzothiazole (1.84 g) and 2-amino-6-bromobenzothiazole (2.29 g). The structure of the obtained substances is shown in Fig. 1.



BTAAHP [R = H, R_1 = H],
MBTAAHP [R = CH_3, R_1 = H]
CBTAAHP [R = H, R_1 = Cl],
BBTAAHP [R = H, R_1 = Br].

Fig. 1. Structure of the dye.

Analysis of MBTAAHP. $C_{13}H_{11}N_5OS$ requires 54.74% C, 3.86% H and 24.56% N; found 54.8% C, 3.78% H and 24.5% N; reddish-brown powder (m.p. 242°C decomposes). Mass spectrum: M^+ ion peak at 285. IR spectrum (KBr pellets): 3472, 3431 cm^{-1} (str) (N–H), 3301 cm^{-1} (str) (O–H), 1473 cm^{-1} (str) (N=N).

Analysis of CBTAAHP. $C_{12}H_8N_5OSCl$ calculated 47.13% C, 2.62% H and 22.91% N; found 47.1% C, 2.6% H and 22.89% N; reddish-brown powder (m.p. 248°C decomposes). Mass spectrum: M^+ ion peak is at 305.5. IR spectrum (KBr pellets): 3461 cm^{-1}, 3432 cm^{-1} (str) (N–H), 3332 cm^{-1} (str) (O–H), 1471 cm^{-1} (str) (N=N).

Analysis of BBTAAHP: $C_{12}H_8N_5OSBr$ calculated 41.14% C, 2.28% H and 20.0% N; found 41.2% C, 2.26% H and 20.0% N; reddish-brown powder (m.p. 252°C decomposes). Mass spectrum: M^+ ion peak is at 350 m/z. IR spectrum (Nujol): 3478 cm^{-1}, 3448 cm^{-1} (str) (N–H), 3348 cm^{-1} (str) (O–H), 1490 cm^{-1} (str) (N=N). Spectral data for these dyes are represented in Table.1.

Table 1. Spectral data for the azo dyes.

Parameters	BTAAHP	MBTAAHP	CBTAAHP	BBTAAHP
Color in acetone	Reddish-orange	Reddish-orange	Reddish-orange	Reddish-orange
λ_{max}	470 nm	470 nm	470 nm	470 nm
ε_{max}, $L\cdot mol^{-1}\cdot cm^{-1}$ (in acetone)	5.52×10^4	3.85×10^4	4.26×10^4	2.42×10^4
ε_{max}, $L\cdot mol^{-1}\cdot cm^{-1}$ (pH 2.8)	4.4×10^4	3.55×10^4	3.88×10^4	2.39×10^4
ε_{max}, $L\cdot mol^{-1}\cdot cm^{-1}$ (at pH 4.45)	3.16×10^4	3.68×10^4	2.97×10^4	2.0×10^4
ε_{max}, $L\cdot mol^{-1}\cdot cm^{-1}$ (pH 4.63)	3.78×10^4	3.63×10^4	2.0×10^4	2.5×10^4

Preparation of metal standard solutions. Stock solutions (10^{-5} M) of copper, zinc, cadmium, cobalt were prepared from their corresponding analytical grade acetate salts; that of nickel was prepared from its sulphate salt.

General procedure for determination of metal ions. 5 mL of the standard dye solutions of concentration 5×10^{-4} M were diluted to 100 mL with acetone. From these solutions, 5 mL were used for the determination of metal ions. Absorption measurements were made at 540−580 nm, depending upon the kind of metal ions at a pH value, where the absorption was maximal. The reagent blank was prepared by pipetting 5 mL of the dilute dye solution (0.02 $mg\cdot L^{-1}$) to 5 mL of buffer solution and 10 mL of acetone, making up to 25 mL with water.

RESULTS AND DISCUSSION

Effect of pH

The absorbance of various metal chelates of BTAAHP, MBTAAHP, CBTAAHP and BBTAAHP at different pH values was measured. The pH of maximal absorption was selected for the pH range for the determination of the metal ions, as listed in Table 2.

The copper complexes of all the dyes were determined at pH 2.8 at λ_{max} = 540 nm, the selectivity of the reagents is excellent and metal ions like zinc, cadmium, iron, lead, mercury, do not interfere except for nickel and cobalt.

Metal ions like Cu^{2+}, Zn^{2+}, Cd^{2+},$Co^{2+}$and Ni^{2+} show strong interference with one another within the pH range 4 to 5. Therefore, determination of any one of these metal ions requires either complete separation or masking of the other four metal ions.

Characteristics of the complexes

BTAAHP, MBTAAHP, CBTAAHP, and BBTAAHP form 1:1 (1igand to metal) complexes with copper, zinc, cadmium, cobalt and nickel. Calibration graphs were drawn by the general procedure. Beer's law was obeyed in the concentration range 0.03−0.3 $mg \cdot L^{-1}$.

The reagents react instantaneously with copper, zinc, cadmium and cobalt at the pH values listed in Table 2 to form reddish-purple coloured complexes. The reagents require 30 minutes to form a stable nickel complex. All these complexes were stable in aqueous acetone solution for an hour. The empirical formulae of the complexes were determined by Job's and mole ratio methods. The optical characteristics such as optimum range for the determination of metals, molar absorptivity, Sandell's sensitivity (S) are shown in Table 2.

The empirical formulae of the complexes were determined by Job's and mole ratio methods. The optical characteristics such as optimal range for the determination of metals, molar absorptivity and Sandell's sensitivity (S) are shown in Table 2.

To test the validity of the method, the experimental data were interpreted statistically by the linear regression method. The high correlation coefficient (r) (about 0.98) is evidence for the linear dependence of the absorbance on metal ion concentration. Correlation coefficients (r), slopes and intercepts for the various metal ion complexes are listed in Table 2.

Effect of diverse ions

The selectivity of BTAAHP, MBTAAHP, CBTAAHP, and BBTAAHP for copper, zinc, cadmium, cobalt and nickel is excellent. The effect of foreign ions with respect to MBTAAHP is represented in Table 3.

Copper determination in industrial effluents

Effluent samples were collected from battery producing industries and electroplating industries. These effluents contain mainly copper, cadmium, zinc and lead in trace amounts. Suitable amounts of the effluent solutions were completely evaporated and 10 mL of concentrated nitric acid were added to these solutions. The mixtures were heated until decomposition of all nitrates. The obtained residues were extracted with diluted acetic acid made up to 25 mL with redistilled water. The determination of copper ions was carried out as it is described in the general procedure using BTAAHP as analytical reagent. The results obtained by the proposed method agreed with those of the AAS method (Table 4).

Table 2. Spectral data for the metal complexes at various pH conditions.

Metal complex	pH	λ_{max}, nm	$\varepsilon_{max} \times 10^4$ $L \cdot mol^{-1} \cdot cm^{-1}$	Beer-Lambert's range, $mg \cdot L^{-1}$	Sensitivity ($\mu g \cdot cm^{-2}$)	Linear regression equation		
						Correlation coefficient r	Intercept	Slope
Cu-BTAAHP	2.8	540	4.4	0.316−1.0	1.71×10^{-3}	0.9794	−0.068	0.1278
Zn-BTAAHP	4.63	545	2.9750	1.8−0.53	2.2×10^{-3}	0.9952	0.005	0.1956
Cd-BTAAHP	4.63	545	2.2750	0.074−1.0	4.94×10^{-3}	0.9991	0.0003	0.3523
Co-BTAAHP	4.45	555	3.0	0.25−0.57	2×10^{-3}	0.9964	−0.006	0.2255
Ni-BTAAHP	4.63	550	3.78	1.27−0.26	1.6×10^{-3}	0.9780	0.018	0.1699
Cu-MBTAAHP	2.8	540	2.9513	0.23−0.47	2.14×10^{-3}	0.9824	−0.002	0.1588
Zn-MBTAAHP	4.63	550	3.0945	0.24−0.48	2.1×10^{-3}	0.9998	−0.001	0.2327
Cd-MBTAAHP	4.63	550	2.5605	0.25−0.6	4.4×10^{-3}	0.9999	−0.001	0.4829
Co-MBTAAHP	4.45	570	3.6891	0.12−0.28	1.6×10^{-3}	0.9788	0.025	0.1962
Ni-MBTAAHP	4.63	560	4.6756	0.13−0.35	1.62×10^{-3}	0.9998	−0.001	0.1275
Cu-CBTAAHP	2.8	540	4.259	0.06−0.27	1.72×10^{-3}	0.9954	0.002	0.5515
Zn-CBTAAHP	4.63	540	1.98	0.01−0.29	3.3×10^{-3}	0.9947	0.002	0.2811
Cd-CBTAAHP	4.63	550	1.52	0.165−0.58	7.39×10^{-3}	0.9922	−0.001	0.5069
Co-CBTAAHP	4.45	560	3.51	0.081−0.201	1.7×10^{-3}	0.9599	0.0155	0.1996
Ni-CBTAAHP	4.63	550	3.810	0.109−0.22	1.54×10^{-3}	0.9800	−0.001	0.1266
Cu-BBTAAHP	2.8	540	2.3275	0.038−0.195	2.7×10^{-3}	0.9982	−0.002	0.0883
Zn-BBTAAHP	4.63	540	2.3275	0.08−0.363	2.8×10^{-3}	0.9946	−0.003	0.5548
Cd-BBTAAHP	4.63	540	1.7456	0.82−1.16	6.44×10^{-3}	0.9738	−0.003	1.561
Co-BBTAAHP	4.45	560	2.4568	0.019−0.071	2.4×10^{-3}	0.9426	0.014	0.5572
Ni-BBTAAHP	4.63	550	3.3624	0.02−0.085	1.76×10^{-3}	0.9746	0.005	0.1611

Table 3. Effect of interferents on the spectrophotometric determination of metal ions with MBTAAHP.

Substance	Amount added, mg·L^{-1}	Copper added (3.12 mg·L^{-1})		Nickel added (2.27 mg·L^{-1})		Cobalt added (1.7 mg·L^{-1})		Zinc added (1.36 mg·L^{-1})		Cadmium added (1.97 mg·L^{-1})	
		Cu found, mg·L^{-1}	Error, mg·L^{-1}	Ni found mg·L^{-1}	Error, mg·L^{-1}	Co found, mg·L^{-1}	Error, mg·L^{-1}	Zn found, mg·L^{-1}	Error, mg·L^{-1}	Cd found, mg·L^{-1}	Error, mg·L^{-1}
KCl	296	3.12	0.0	2.27	0.0	1.73	0.03	1.36	0.0	1.97	0.0
K_2SO_4	696	2.84	−0.28	1.98	−0.29	1.48	−0.22	1.25	−0.11	1.73	−0.24
KNO_3	399	3.12	0.0	2.27	0.0	1.70	0.0	1.36	0.0	1.97	0.0
Thiourea	320	2.76	−0.36	2.0	−0.27	1.48	−0.22	1.29	−0.07	1.81	−0.16
NaF	168	3.4	0.28	1.74	−0.53	1.76	0.06	1.26	−0.1	1.88	−0.09
Na-K Tartrate	250	2.5	−0.62	1.45	−0.82	0.7	−1.00	0.68	−0.68	1.22	−0.75
Dimethyl-glyoxime	2387	3.0	0.12	0.1	−2.17	1.0	−0.7	1.23	−0.13	1.61	−0.36
H_2O_2 (6%)	0.1 mL	3.02	0.1	1.9	−0.37	0.0	−1.7	1.10	−0.26	1.83	−0.14
EDTA (0.1 M)	0.05 mL	0	−3.12	0	−2.27	0	−1.7	0	−1.36	0	−1.97
NaH_2PO_4	400	3.3	0.19	2.01	−0.26	1.64	−0.06	0.65	−0.71	1.9	−0.07
Hg^{2+}	0.54	3.06	−0.06	2.0	−0.27	1.68	−0.02	1.20	−0.16	1.79	−0.18
Pb^{2+}	0.41	2.98	−0.14	2.18	−0.09	1.6	−0.1	1.3	−0.06	1.92	−0.05
Fe^{2+}	2.84	3.01	−0.11	2.01	−0.26	1.54	−0.16	1.12	−0.24	1.89	−0.08
Cd^{2+}	0.97	3.12	0.0	3.24	0.97	2.6	0.9	2.34	0.98	-	-
Zn^{2+}	1.47	3.12	0.0	3.74	−1.47	3.17	1.47	-	-	3.44	1.47
Co^{2+}	1.94	5.28	2.16	4.21	1.94	-	-	3.3	1.94	3.91	1.94
Ni^{2+}	1.82	6.39	3.27	-	-	3.5	1.8	3.18	1.82	3.79	1.82
Cu^{2+}	1.56	-	-	3.83	1.56	3.26	1.56	2.92	1.56	3.53	1.56

Table 4. Determination of Cu(II) and Zn(II) in industrial effluents with BTAAHP.

Sample	Copper determination by proposed method, mg L^{-1}	Copper determination by AAS, mg·L^{-1}	Error, mg·L^{-1}	Zinc determination by proposed method, mg·L^{-1}	Zinc determination by AAS, mg·L^{-1}	Error, mg·L^{-1}
1	0.0204	0.02	−0.004	0.062	0.07	0.008
2	0.0224	0.02	−0.0024	0.0098	0.01	0.0002
3	0.0315	0.03	−0.015	0.008	0.01	0.002
4	0.367	0.35	−0.017	6.6	6.8	0.2

Zinc determination in industrial effluents

Copper, zinc and cadmium form complexes with BTAAHP. As the effluent solutions contain all the three ions, the determination of each one of them requires masking of the other two. The determination of zinc was carried out in a suitable aliquot of the effluent solution as it is described in the general procedure using BTAAHP as analytical reagent and masking copper and cadmium with 1 mL of 2% $Na_2S_2O_3$. The results are represented in Table 4.

CONCLUSION

BTAAHP, MBTAAHP, CBTAAHP and BBTA-AHP are sensitive spectrophotometric reagents for the determination of metal ions - copper, zinc, cadmium, cobalt and nickel due to their high absorptivity and the reasonable stability of their complexes. Determination of copper by these reagents at pH 2.8 is relatively free from interference; hence copper can be determined in the presence of metal ions like zinc and cadmium. Determination of zinc, cadmium, cobalt and nickel can be done above pH 4–5. Zinc can be determined in the presence of copper and cadmium by masking them with 1 ml of 2% $Na_2S_2O_3$ solution. The method was successfully applied tor the determination of copper and zinc in industrial effluents.

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СИНТЕЗ И СПЕКТРОФОТОМЕТРИЧНИ ИЗСЛЕДВАНИЯ НА НЯКОИ БЕНЗОТИАЗОЛИЛАЗО-БАГРИЛА – ОПРЕДЕЛЯНА НА МЕД, ЦИНК, КАДМИЙ, КОБАЛТ И НИКЕЛ

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(Резюме)

Синтезирани са 4-(2-бензотиазолилазо)-2-амино-3-хидроксипиридин и производните му 4-(4-метил-2-бензотиазолилазо), 4-(6-хлоро-2-бензотиазолилазо) и 4-(6-бромо-2-бензотиазолилазо)-2-амино-3-хидроксипиридини. Всички тези багрила са много чувствителни хромегенни реагенти за определяне на мед, кадмий, цинк, кобалт и никел. Реагентите взиамодействат с металните йони с образуване на пурпурно оцветен комплекс (λ_{max} 540−570 nm) във воден разтвор на ацетон с pH в областта 2.8–4.6. Медта може да бъде определена селективно при pH 2.8 и повечето от металните йони не пречат освен за никел и кобалт. Кадмий, цинк, кобалт и никел могат да бъдат определени при pH 4–5. Тяхното взаимно пречене може да бъде елиминирано с използване на подходящи маскиращи реагенти. Допълнително предимство на метода е че процедурата на екстракция не е необходима и процедурата за анализ е много опростена.