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Thermodynamic studies of 2-(5-bromo-2-pyridylazo)-5-diethylamino)phenol Cu(II), Co(II), Ni(II) and Zn(II) complexes

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Abstract

The metal–ligand mole ratios and the stability constants of the Cu(II), Co(II), Ni(II) and Zn(II) complexes at 2-(5-bromo-2-pyridylazo)-5-diethylamino)phenol were determined using a spectrophotometric method at different temperatures (20, 30, 40 and 50±0.1 °C) and ionic strengths (0.05, 0.1 and 0.2) in 30% (v/v) aqueous ethanol. Plots of thermodynamic stability constants at zero ionic strength (ln K°) versus T^{-1} gave linear curves; the ensuing complex formation (ΔH° and ΔS°) values calculated from these plots. The changes in free energy for each metal–ligand system were evaluated. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Complex formation; Pyridylazo; Stability constant; Spectrophotometric

1. Introduction

Azo dyes are the largest group of organic dyes and constitute more than 35% of the global production of all dyes and thus are used widely. However, some azo dyes have toxicological properties and therefore require sensitive, selective methods to determine their physicochemical characteristics. Such studies have mainly been concerned with aromatic azo compounds because of the importance of this group in the dyestuff industry, the interest in carcinogenic properties and the use of azo compounds for the indirect determination of metals [1]. The application of 2-pyridylazo compounds in chemical analysis has been studied extensively. The three representatives of this group, namely, pyridylazo naphthol (PAN), pyridylazo resorcinol (PAR) and pyridylazo diethylaminophenol (PADAP) have proved to be most versatile reagents for metals. These reagents can serve as chromogenic agents in the determination of many elements and have been widely used applied in tap water, metal alloys and trace analysis [2–4]. Most of these reagents are characterized by their molecular structure, in which an electron donating diethylamino group is introduced *para* to the azo linkage of the heterocyclic-azo-phenol structure. Highly sensitive and sometimes highly selective reagent towards metal ions have been obtained by introducing different groups in the ortho position to the azo linkage on the aminophenol ring [5].

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Previous studies on the polarographic and spectroscopic behaviour of azobenzenes, pyridylazo derivatives and their metal chelates have been studied extensively in aqueous buffer solution in order to clarify the mechanism of the electrode process, kinetic parameters of complex formation, characterization of molecular structure and use in analytical applications [6–13].

The present study concerns the thermodynamic stability constants and thermodynamic parameters of the complexes of 2-(5-bromo-2-pyridylazo)-5-diethylamino)phenol (5-Br-PADAP) with Cu(II), Co(II), Ni(II) and Zn(II), evaluated using a spectrophotometric method.

2. Experimental

2.1. Instruments

Spectra were recorded using a UNICAM UV/VIS Spectrometer UV2 from 190 to 800 nm using a 1cm quartz cuvette. A Jenway 3040 ion analyzer was used to monitor the pH of buffer solutions and a Grant LTD 6G model circulating thermostatic bath was used.

2.2. Reagents

The dye solution 5-Br-PADAP (Merck), was prepared fresh prior to each determination. A 1×10^{-3} M stock solution was prepared by dissolving the compound in absolute ethanol. 1×10^{-3} M 100 ml $Cu(NO_3)_2$, $Co(NO_3)_2$, $Zn(NO_3)_2$ and $Ni(NO_3)_2$ stock solutions were also prepared. All reagents were of analytical grade. Buffer solutions were of acetate (0.05 M, pH 2–6), Tris (tris(hydroxymethyl)aminomethane) (0.05 M) (pH 7–9) and borate (0.05 M) (pH 10–12). Tris buffer showed a higher ε and better complex stability than borate or phosphate therefore used in pH range 7–9.

2.3. Procedures

2.3.1. Optimum pH

The influence of the pH on the complexes was determined using buffer solutions in the range pH 2–12. The changes in absorbance at the wavelength of maximum absorption (λ_{max}) of each complex were recorded.

2.3.2. Determination of molar absorption coefficients

Into a 10 ml volumetric flask were added 2 ml of buffer solution, 0.35 ml of 1 M potassium nitrate solution, 2.1 ml of ethanol and 1 ml of 5-Br-PADAP solution. This mixture was diluted with distilled water to 7 ml, and mixed thoroughly. This mixture was warmed for 15 min at 25 ± 0.1 °C and then 100 µl of stock metal solution (kept under the same conditions) was added to the mixture with a micropipette and the mixture was shaken. Five mixtures of different metal concentration were prepared for each metal at different ionic strengths ($I=0.05$, 0.1 and 0.2). After complex formation was complete, the changes in absorbance at the λ_{max} were recorded against the same solution containing no metal ion (Table 1).

2.3.3. Determination of metal to ligand mole ratio and stability constants

The continuous variation (Job's) method was used to determine stoichiometry [14]. To a screw cap test tube 2.1 ml ethanol, 0.1–0.5 ml of 1.10^{-4} M stock metal solution, 2 ml of buffer solution, 0.35 ml 1 M KNO_3 and an appropriate volume of distilled water were added such that the total volume was 7 ml. Five mixtures of different metal concentrations were prepared and the mixtures were kept for 10 min at 20 °C in a thermostatic bath. Keeping the ligand to metal ratio at 2, the reaction was initiated by adding 1.10^{-4} M 5-Br-PADAP solution. The ensuing mixture was shaken and thermostated for 15 min at 20 °C and the changes in absorbances at the λ_{max} were measured.

Table 1
Spectrophotometric properties of the complexes

Complex	λ_{max}	ε ($dm^3\ mol^{-1}\ cm^{-1}$)			pH
		$I=0.05$	$I=0.1$	$I=0.2$	
Cu–5-Br-PADAP	552	54,932	55,329	55,691	4
Co–5-Br-PADAP	556	78,146	78,598	79,089	4
Ni–5-Br-PADAP	560	158,186	158,681	159,091	7.5
Zn–5-Br-PADAP	552	112,931	113,107	114,808	7.5

Similar experiments were repeated for 30, 40 and 50 °C at different ionic strengths.

3. Results and discussion

The absorption spectra of the 5-Br-PADAP complex solutions were nearly identical for all of the complexes studied. All spectra showed a large bathochromic shift of about 100 nm on complex formation. The complexes were purple and reached maximal absorbances some 15 min after mixing; they were stable for at least 12 h. The wavelengths $\lambda_{\max}$ and molar absorptivities of the chelates are given in Table 1.

As shown in Fig. 1 the complex stoichiometries were found to be 1:2 for Ni, Zn, Co and 1:1 for Cu [15]. The stoichiometry ratio of 1:1 is indicative of square planar and tetrahedral complexes with three donor atoms from 5-Br-PADAP being involved (the pyridine nitrogen, the β-azo nitrogen and the *o*-hydroxy oxygen atom) and a monodentate ligand such as H_2O from water or buffer [16,17]. A 1:2 stoichiometry is indicative of an octahedral complex. The three pK_a values of ligand at 1.0, 3.0 and 11.2 show that at optimal pH, divalent cationic complexes are formed [18,19].

In the content of the effect of pH on the metal–5-Br-PADAP systems, it was found that the absorbances of the copper and cobalt complexes remained virtually unchanged over all pH values used. The absorbances were maximum and constant in the pH range 7–9 for Ni and Zn (Fig. 2). Thus, determinations were carried out at pH 4 and 7.5 for Cu, Co and Ni, Zn, respectively.

The complex formation reaction can be written as follows:

$$M^{2+} + n(\mathrm{Dye}) = \left[M(\mathrm{Dye})_n\right]^{2+}$$

the formation constant being given by: I and II.

$$K_\mathrm{f} = \frac{\left[M(\mathrm{Dye})_n\right]^{2+}}{[M^{2+}][\mathrm{Dye}]^n} \tag{1}$$

$$K_\mathrm{f} = \frac{\left[M(\mathrm{Dye})_n\right]^{2+}}{\left(C_{M^{+2}} - \left[M(\mathrm{Dye})_n\right]^{2+}\right)\left(C_{(\mathrm{Dye})} - \left(n\left[M(\mathrm{Dye})_n\right]^{2+}\right)\right)^n} \tag{2}$$

At equilibrium, the complex concentration can be calculated from Beer's law. The formation constant was calculated from the equilibrium concentration of the reactants using Eq. (2) while the formation constants of the complexes (K_f) have been previously determined [20].

To obtain thermodynamic formation constants, the averages of the formation constants were plotted as a function of ionic strength at each temperature used and straight lines were extrapolated to zero ionic strength [21].

The values of ln K° were plotted against T^{-1} and a straight line obtained. Considering that ΔH° and ΔS° are independent of temperature, ΔH° was calculated from the slope of the line $(-\Delta H^\circ/R)$ and ΔS° from the intercept at $T^{-1} = 0$ $(\Delta S^\circ/R)$. Using

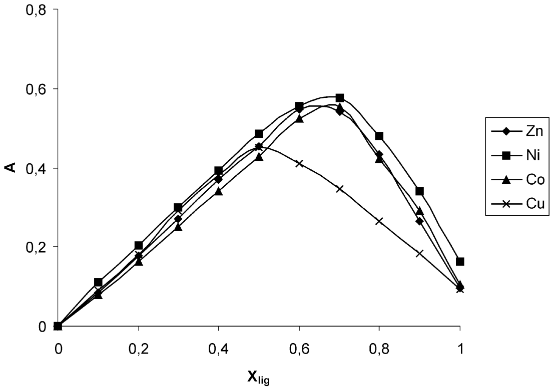

Fig. 1. The change of absorbance as a function of mole fraction.

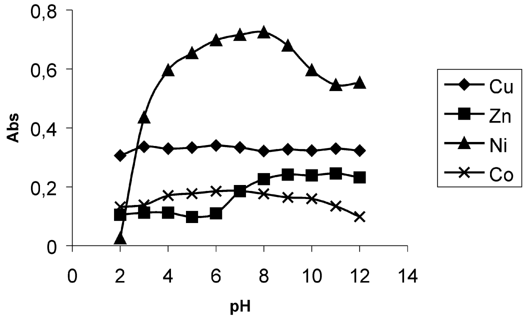

Fig. 2. The effect of pH on absorbance.

Table 2
Thermodynamic properties of the metal–5-Br-PADAP complexes

Complex	Temperature (°C)	Ln K			Ln K°	$-\Delta G^{\circ}$ (kJ mol^{-1})	$-\Delta H^{\circ}$ (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
		$I=0.2$	$I=0.1$	$I=0.05$				
Cu	20	15.29	15.21	14.94	14.90	36.31	19.68	57.09
	30	15.03	14.88	14.79	14.71	37.08	19.68	57.09
	40	14.85	14.70	14.48	14.40	37.49	19.68	57.09
	50	14.58	14.44	14.27	14.20	38.15	19.68	57.09
Co	20	29.14	28.88	28.76	28.63	69.79	15.73	185.16
	30	28.82	28.76	28.58	28.55	71.97	15.73	185.16
	40	28.73	28.65	28.43	28.38	73.89	15.73	185.16
	50	28.63	28.55	28.11	28.07	75.42	15.73	185.16
Ni	20	26.09	25.89	25.79	25.69	62.62	14.70	163.72
	30	25.83	25.78	25.61	25.58	64.47	14.70	163.72
	40	25.69	25.60	25.37	25.32	65.91	14.70	163.72
	50	25.44	25.32	25.22	25.16	67.59	14.70	163.72
Zn	20	29.61	28.88	28.71	28.34	69.08	46.41	78.20
	30	27.96	27.94	28.15	27.85	70.20	46.41	78.20
	40	27.41	27.31	27.23	27.19	70.78	46.41	78.20
	50	27.15	27.01	26.79	26.73	71.81	46.41	78.20

the equation $\Delta G^{\circ}=-RT\ \ln\ K^{\circ}$, values of ΔG° were calculated for complexes. The thermodynamic properties of the complexes are shown in Table 2.

Negative values of ΔH and ΔG were observed upon complex formation for all metals (Table 2). The stability constants of the complexes decreased with temperature and followed Cu > Ni > Co > Zn order. Mainly ΔH is responsible for the complex formation.

4. Conclusions

Stability constants of the metal–5-Br-PADAP complexes were evaluated by using a spectrophotometric method. Stability of the complexes in aqueous-ethanol solution is effected by pH, temperature and ionic strength in which measurements are performed. The stability of all the complexes decreased with increasing temperature, increased with ionic strength. Thermodynamic properties of the complexes were evaluated from thermodynamic stability constants at zero ionic strength in various temperatures.

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