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Thermochimica Acta 381 (2002) 119–131

thermochimica acta

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Dissociation constants of eriochrome black T and eriochrome blue black RC indicators and the formation constants of their complexes with Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), and Pb(II), under different temperatures and in presence of different solvents

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Received 6 February 2001; received in revised form 11 July 2001; accepted 14 July 2001

Abstract

The dissociation constants of eriochrome black T, and eriochrome blue black RC, were obtained at different temperatures (20–40 °C) by potentiometric measurements in the presence of different percentage of organic solvent–water media. The thermodynamic parameters of ionization were calculated. The formation constants of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), and Pb(II) complexes of the azo indicators were evaluated in 50% ethanol media (v/v). The thermodynamic parameters of complexation were calculated and discussed.

Keywords: Dissociation constants; Formation constants; Azo-indicators; Solvent effects; Potentiometry; Thermodynamics parameters

1. Introduction

The acid dissociation constants and stability constants of complexation have been studied for barbituric azo [1–3], pyridyl azo [4,5], and *o*,*o*-dihydroxy azo [6] compounds. Although the thermodynamics of acid dissociation of some azo compounds have been published, there is need for information on the thermodynamics of 1:1 and 1:2 complexation reactions of azo compounds.

Eriochrome black T (EBT) (I), and eriochrome blue black RC (EBB) (II) are among the most important azo indicators used in complexation titration of various metals: Ca, Mg, Mn, Cd, Hg, Pb, Cu, Al, Fe, Ti, Co, Ni, and the Pt metals [7,8]. Due to the wide applications of such systems, the present work aimed to elaborate the important usage of these indicators through the study of their acidity in different solvents and variable temperatures. The ability for these indicators for complexation with Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), and Pb(II) is aimed to be investigated. Values of acidity and stability constants and corresponding thermodynamic parameters are computed using potentiometric methods. The structures of sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate (EBT), and sodium 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulphonate (EBB) are presented below.

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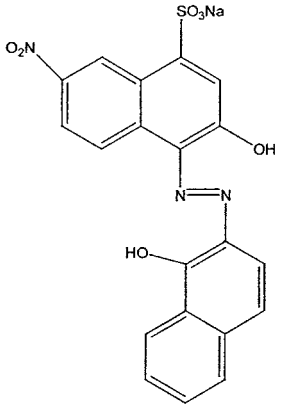
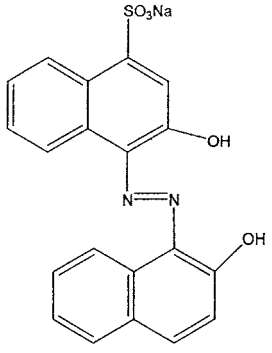
0040-6031/02/$ – see front matter
PII: S0040-6031(01)00691-8

2. Experimental

The potentiometric measurements were carried out using Denver instrument Model 225 pH. Ion selective electrode meter fitted with a combined glass electrode (reading to ±0.01 pH unit). The pH meter was calibrated from time to time at different temperatures using three standard buffers of different pH values. The chemicals used were BDH and Merck products. The solvents used are spectroquality. All solutions were prepared in deionized water. Carbonate free sodium hydroxide solution was prepared and checked by titration against standard potassium hydrogen phthalate solution. A stream of purified nitrogen gas was flushed over the solution through the whole titration. Titrations were repeated for reproducibility. The correction factor, δ, for measuring the pH values in different percentages of organic solvent–water media was calculated, using the van Uietert and Haas relation: $-\log[H^+] = B + \delta$, where B is the pH meter reading [9].



EBT
(I)



EBB
(II)

The dissociation constants of ligands were determined by introducing 50.00 ml of the ligand (1.00×10^{-3} M) into the titration cell in the presence of KCl ($\mu = 0.30$) and different percentage (v/v) of the organic solvent–water media. The titrations versus standard NaOH (1.00×10^{-2} M) were carried in 150 ml thermostatic cell. The cell compartment was kept constant at the desired temperature by using a thermostat Model Heto HMT 200 in the temperature range 20–40 °C (±0.1 °C). The obtained K_a values are used to calculate the stability constants at each temperature.

The stability constants were computed using acid–base titration technique: 50.00 ml solution in the titration cell consisted of 5.00×10^{-4} M metal ions, 1.00×10^{-3} M ligand and KCl ($\mu = 0.30$) (ligand to metal mole ratio equal 2). The pH readings were taken after the addition of increments of 0.5 ml of 1.00×10^{-2} M NaOH solution. The pH range explored to collect the complexation data is 3–11.

3. Results and discussion

3.1. Acidity constants studies

The calculation of the acid dissociation constants of the ligands by potentiometric measurements depends on the evaluation of the average proton number associated with the ligand, n_A. The value of n_A was evaluated at different pH using the following equation, $n_A = Y - V_i N / V_0 C_L$; where V_i denotes the volume of alkali required to reach a given pH on the titration curve, V_0 is the initial volume of the ligand, N the alkali concentration, C_L the total concentration of the ligand and Y is the number of displaceable hydrogen atoms in the ligand [10]. The plots of pH against n_A gave pK_{a1} and pK_{a2} values at $n_A = 0.5$ and 1.5, respectively. The point-wise method [11], was used to confirm the obtained pK values.

$$\mathrm{pH} + \log \frac{2 - n_A}{n_A - 1} = pK_1,$$

$$\mathrm{pH} + \log \frac{n_A}{1 - n_A} = pK_2$$

The plots of log n_A ratio versus pH give the required pK_a values, Tables 1–3 (Figs. 1 and 2). The data are due to deprotonations from the OH groups. The EBT compound gave lower pK values compared to the EBB compound due to the presence of the electron attracting nitro group in the former one. Meanwhile, the dependence of pH on n_A in different solvent mixtures gave that the trend in the pK_a values are in the following sequence: ethanol > DMF ~ acetonitrile > dioxane. Dioxane has the lowest dielectric constant 2.2. DMF and acetonitrile are basic solvents with high dielectric constants values of 36.7 and 37.5, respectively. Ethanol has an intermediate dielectric constant

Table 1
The pK values and thermodynamic parameters for eriochrome black T (EBT) in different percentages of ethanol–water media at (20–40 °C)[a]

Media (%)	pK					ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (e.u.)
	20 °C	25 °C	30 °C	35 °C	40 °C			
0	9.25 ± 0.02 (10.65) ± 0.02	9.18 ± 0.02 (10.58) ± 0.04	9.14 ± 0.04 (10.52) ± 0.02	9.09 ± 0.03 (10.44) ± 0.03	9.00 ± 0.05 (10.35) ± 0.02	12.53 ± 0.03 (14.44) ± 0.06	4.96 ± 0.15 (6.21) ± 0.30	−25.40 ± 0.50 (−27.60) ± 1.00
25	9.40 ± 0.08 (10.88) ± 0.02	9.31 ± 0.05 (10.80) ± 0.02	9.24 ± 0.03 (10.75) ± 0.02	9.20 ± 0.03 (10.69) ± 0.02	9.15 ± 0.09 (10.47) ± 0.02	12.70 ± 0.07 (14.74) ± 0.03	5.13 ± 0.11 (7.81) ± 0.03	−25.39 ± 0.37 (−23.24) ± 0.05
35	9.56 ± 0.04 (11.18) ± 0.02	9.42 ± 0.03 (11.04) ± 0.02	9.29 ± 0.05 (10.99) ± 0.02	9.26 ± 0.04 (10.76) ± 0.02	9.20 ± 0.09 (10.49) ± 0.02	12.85 ± 0.05 (15.06) ± 0.03	7.40 ± 0.45 (13.94) ± 0.05	−18.28 ± 1.51 (−3.76) ± 0.17
50	9.62 ± 0.02 (11.30) ± 0.02	9.54 ± 0.03 (11.13) ± 0.05	9.45 ± 0.03 (11.05) ± 0.02	9.36 ± 0.04 (10.90) ± 0.02	9.25 ± 0.15 (10.62) ± 0.02	13.02 ± 0.03 (15.19) ± 0.10	7.72 ± 0.31 (13.37) ± 0.04	−17.78 ± 1.04 (−6.10) ± 0.13
75	9.78 ± 0.10 (11.36) ± 0.02	9.62 ± 0.08 (11.20) ± 0.10	9.51 ± 0.15 (11.12) ± 0.02	9.40 ± 0.02 (11.04) ± 0.03	9.29 ± 0.20 (10.83) ± 0.02	13.13 ± 0.11 (15.28) ± 0.14	10.09 ± 0.28 (10.26) ± 0.14	−10.20 ± 0.94 (−16.84) ± 0.47

[a] Values in parenthesis are pK_2.

Table 2
The pK values and thermodynamic parameters for eriochrome blue black RC (EBB) in different percentages of ethanol–water media at (20–45 °C)[a]

Media (%)	pK						ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (e.u.)
	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C			
0	10.37 ± 0.02	10.32 ± 0.07	10.21 ± 0.02	10.01 ± 0.08	9.95 ± 0.02	9.75 ± 0.03	14.08 ± 0.10	10.67 ± 0.26	−11.44 ± 0.87
	(11.16) ± 0.02	(11.00) ± 0.09	(10.93) ± 0.02	(10.75) ± 0.11	(10.68) ± 0.03	(10.55) ± 0.02	(15.00) ± 0.12	(10.18) ± 0.21	(−16.17) ± 0.70
25	11.08 ± 0.03	10.93 ± 0.08	10.78 ± 0.03	10.62 ± 0.09	10.56 ± 0.02	10.50 ± 0.02	14.91 ± 0.11	10.14 ± 0.23	−16.00 ± 0.77
	(11.68) ± 0.02	(11.48) ± 0.06	(11.35) ± 0.02	(11.20 ± 0.04	(11.11) ± 0.02	(11.02) ± 0.08	(15.66) ± 0.08	(11.09) ± 0.30	(−15.33) ± 1.01
35	11.27 ± 0.02	11.12 ± 0.04	11.09 ± 0.02	10.74 ± 0.09	10.65 ± 0.02	10.55 ± 0.08	15.17 ± 0.05	13.02 ± 0.16	−7.21 ± 1.21
	(11.90) ± 0.02	(11.78) ± 0.02	(11.59) ± 0.02	(11.35) ± 0.05	(11.30) ± 0.02	(11.22) ± 0.10	(16.07) ± 0.03	(12.33) ± 0.46	(−12.54) ± 0.54
50	11.52 ± 0.02	11.32 ± 0.02	11.14 ± 0.02	11.05 ± 0.08	10.99 ± 0.02	10.89 ± 0.02	15.45 ± 0.03	10.29 ± 0.12	−17.31 ± 0.40
	(12.08) ± 0.08	(11.94) ± 0.06	(11.72) ± 0.04	(11.60) ± 0.10	(11.54) ± 0.02	(11.30) ± 0.09	(16.29) ± 0.08	(12.65) ± 0.42	(−12.21) ± 1.40
75	11.58 ± 0.02	11.42 ± 0.08	11.30 ± 0.02	11.24 ± 0.09	11.17 ± 0.06	11.00 ± 0.04	15.58 ± 0.11	9.00 ± 0.40	−22.07 ± 1.34
	(12.27) ± 0.02	(12.17) ± 0.02	(12.10) ± 0.03	(12.00) ± 0.07	(11.89) ± 0.02	(11.83) ± 0.08	(16.61) ± 0.03	(7.63) ± 0.42	(−30.12) ± 1.41

[a] Values in parenthesis are pK_2.

Table 3
The pK values and thermodynamic parameters for eriochrome blue black RC (EBB) in different percentages of DMF–water media at (20–40 °C)[a]

Media (%)	pK					ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (e.u.)
	20 °C	25 °C	30 °C	35 °C	40 °C			
25	10.51 ± 0.11	10.40 ± 0.03	10.29 ± 0.02	10.21 ± 0.02	10.02 ± 0.02	14.20 ± 0.04	9.82 ± 0.41	−14.69 ± 1.38
	(11.28) ± 0.02	(11.18) ± 0.07	(11.05) ± 0.02	(10.95) ± 0.02	(10.83) ± 0.02	(15.26) ± 0.10	(9.48) ± 0.34	(−19.39) ± 1.14
35	10.73 ± 0.02	10.63 ± 0.10	10.45 ± 0.07	10.35 ± 0.02	10.24 ± 0.02	14.51 ± 0.14	10.55 ± 0.22	−13.28 ± 0.74
	(11.79) ± 0.02	(11.55) ± 0.03	(11.33) ± 0.19	(11.21) ± 0.03	(11.09) ± 0.02	(15.76) ± 0.04	(14.62) ± 0.06	(−3.82) ± 0.20
50	10.93 ± 0.03	10.68 ± 0.03	10.50 ± 0.02	10.45 ± 0.03	10.40 ± 0.02	14.57 ± 0.04	10.86 ± 0.07	−12.44 ± 0.24
	(11.96) ± 0.02	(11.92) ± 0.02	(11.78) ± 0.02	(11.64) ± 0.02	(11.52) ± 0.03	(16.27) ± 0.03	(9.70) ± 0.09	(−22.04) ± 0.30
75	10.98 ± 0.02	10.88 ± 0.02	10.80 ± 0.02	10.76 ± 0.03	10.58 ± 0.02	14.85 ± 0.03	7.73 ± 0.06	−23.88 ± 0.20
	(12.96) ± 0.02	(12.86) ± 0.03	(12.71) ± 0.11	(12.64) ± 0.03	(12.47) ± 0.02	(17.55) ± 0.04	(10.06) ± 0.05	(−25.12) ± 0.17

[a] Values in parenthesis are pK_2.

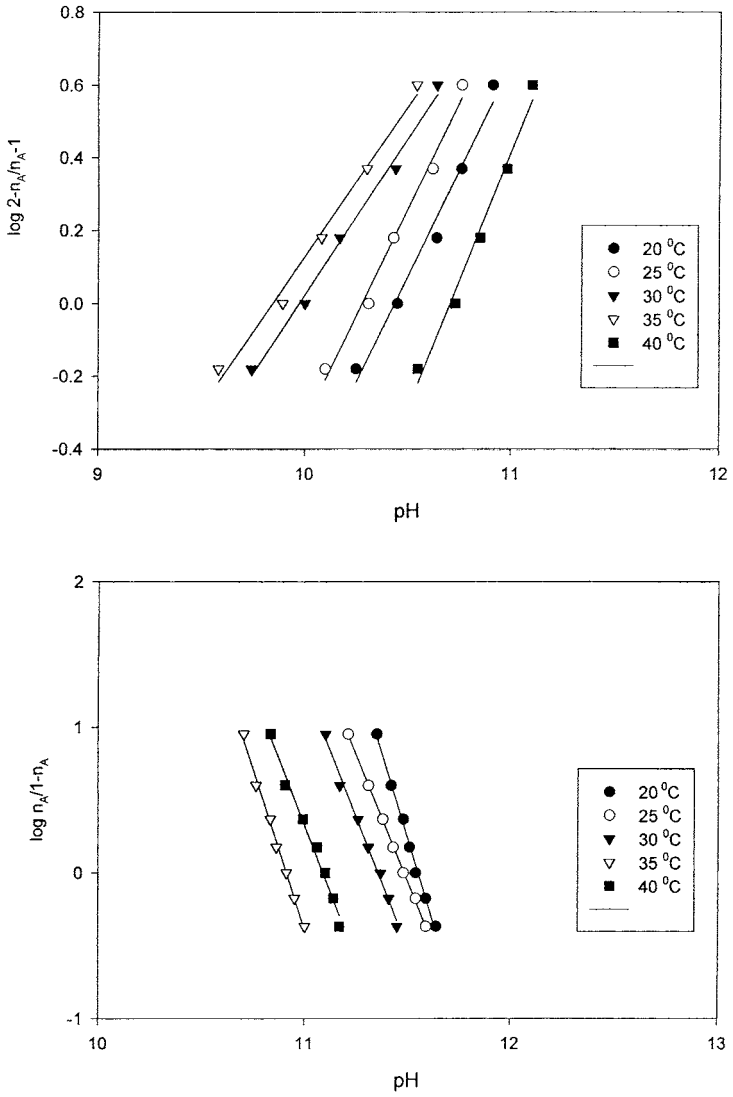


Fig. 1. Point-wise plot for EBB in 50% dioxane at different temperature.

value of 24.3 but is a hydrogen bonding solvent that leads to association.

The pK_a values decreased with increasing temperature, and are dependent upon the nature and the proportion of organic cosolvent, where the increase in the organic cosolvent content in the medium results in an increase in the pK_a value, Tables 1–3 (Fig. 2).

The acidity constant in pure aqueous medium (K_a) can be related to that in water–organic solvent mixture (K'_a) by the equation: $K_a = K'_a\,(\gamma_{H^+}\gamma_{A^-}/\gamma_{HA})$, where γ is the activity coefficient for the subscripted species in a partially aqueous medium to that in pure aqueous one. So the electrostatic effects of solvents operate only on the activity coefficients of charged species, i.e. the increase in the amount of the organic cosolvent in the medium will increase the activity coefficients terms, leading to a decrease in the acid dissociation constant (higher pK_a value) [12].

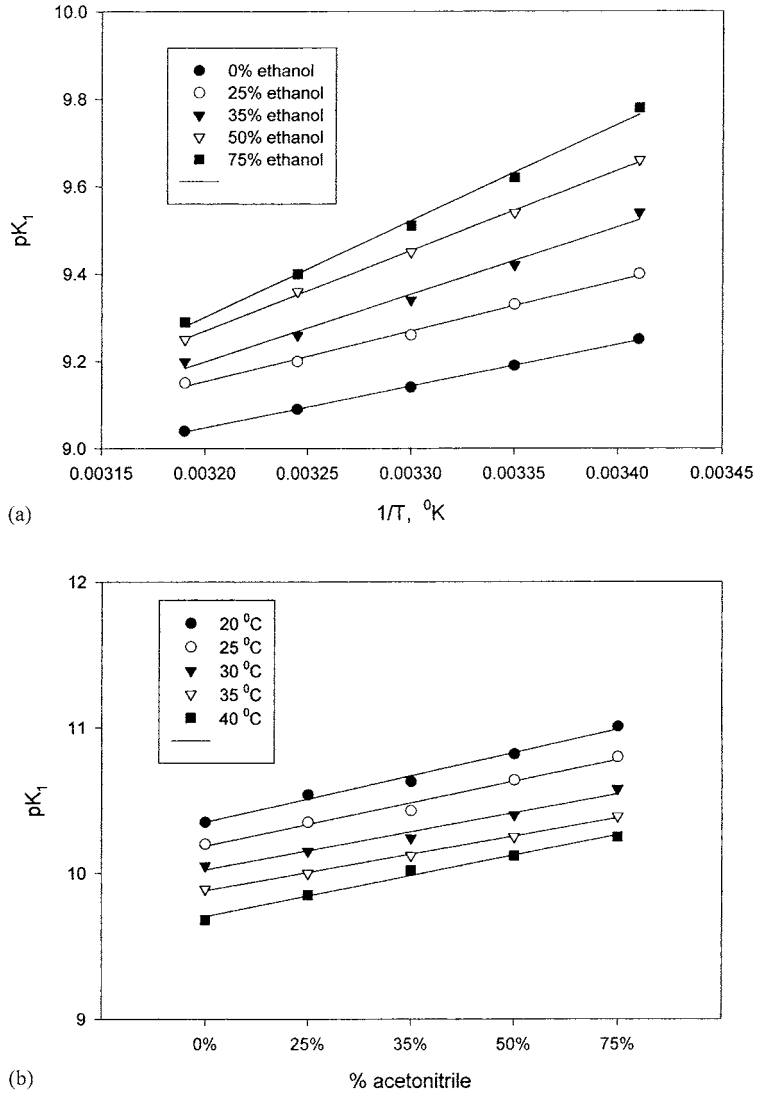


Fig. 2. (a) pK_1 of EBT vs. 1/T (K) at different percentage of ethanol; (b) pK_1 of EBB vs. percentage of acetonitrile at different temperatures.

3.2. Thermodynamic parameters of ionization

The thermodynamic of ionization of azo indicators was investigated in the temperature range 20–40 °C, where ΔG, ΔH and ΔS values are evaluated, Tables 1–3.

On plotting the pK values versus 1/T, straight lines are obtained with a slope of $\Delta H/2.3R$, from which the ΔH values (kcal/mol) are computed (Van't Hoff method). The free energy values ΔG (kcal/mol) are calculated at 25 °C using the equation $\Delta G = 2.303RT$ pK, whereas the entropy term ΔS (e.u.) is given as $\Delta S = 10^3(\Delta H - \Delta G)/T$.

The positive ΔH values indicate that the acid dissociation is endothermic mechanism. The negative ΔS values for all compounds in presence of different percentages of organic solvent–water mixture are attributed to the presence of intermolecular

hydrogen bonding and hydrogen bonding to solvent which promote a higher degree of ordering [13]. Increasing the percentage of organic solvent in the medium resulted in an increase in pK_a and ΔG values systematically.

Assuming that the J factor, represents a solvent-transfer number characteristic of the tested chemical reaction which can be attributed to the transfer of the solvent, the following equation [14] is tested:

$$J\log[S] - \log K = -\frac{\Delta G_t}{2.303RT} - W\log\frac{[H_2O]}{[S]} + J\log[H_2O],$$

where

$$\log\frac{[H_2O]}{[S]} = X, \qquad J\log[S] - \log K = Y.$$

[S] and ΔG_t represent the solvent concentration and the free energy, respectively. The data are collected in Table 4 is plotted against $-X$ (Fig. 3). Trial values of $J = 1$, 2, 3, 4 are used to find values of W for the gradients of Y versus $-X$. The data obtained may throw light on the role of aquation and solvation during the dissociation. For pK_1 and pK_2 of EBB and EBT in different organic solvent–water media, and at temperatures 20–40 °C, the W values are lowest for $J = 1$, i.e. the aquation is predominant. At $J = 2$–4, the W values are increased, and hence, the solvation process increases.

3.3. Formation constant studies

The acid–base properties of the free ligand facilitates the investigation of the coordinating behavior of these ligands towards cobalt(II), nickel(II), copper(II), iron(III), mercury(II), lead(II), zinc(II), and cadmium(II). Comparing the pH titration curves of the free ligands with that of the complex solutions reveals a drop in pH, indicating that the mechanism of complexation is based on hydrogen ion liberation, where the ligands are of stronger coordinating ability [15]. The free ligand exponent (pA) and the degree of formation of the system (n) were calculated; [A^{2-}] is the concentration of free ligand anion, and n is the average number of mole of ligand bound per mole of metal ion. Thus, the stability constants of the metal ligand complexes can be computed. By plotting n values versus pA, the log K_1, and log K_2 values are obtained at the pA values equivalent to $n = 0.5$ and 1.5, respectively [16]. The data are collected in Tables 5 and 6. The formation constants log K_{f1} are obtained for all metals with EBB and EBT. Whereas log K_{f2} are obtained for Fe with EBT and for Fe, Ni, and Cu with EBB.

Studies of EBB and EBT metal complexation in 50% ethanol at 25 °C reveals that log K_{f1} follow the following trends:

EBB complexes : Fe > Cu > Zn > Ni > Co > Cd > Pb
EBT complexes : Fe > Cu > Co > Ni > Zn > Pb > Cd > Hg

The trends in the stabilities constants of these metal complexes are in accordance with the Irving–Williams order. For EBT complexes and except for copper, the stability constants decreased systematically with an increase in atomic number of the metal.

The radii of metal ion increase in the following order for complexes:

$$Fe^{3+} < Ni^{2+} < Cu^{2+} < Co^{2+} < Zn^{2+} < Cd^{2+} < Hg^{2+} < Pb^{2+}$$

Thus, the stability constants of EBB complexes decrease with an increase in radii of metal ion except for Ni and Zn. The stability constant of EBT complexes decreased with an increase in radii of metal ion except for Ni, and Pb.

The log K_{f1} values for EBB metal complexes are higher than the corresponding EBT metal complexes, although both ligands undergo the same modes of coordination with the metals, i.e. from two OH groups and the azo group. The electron attracting property of the nitro group in the EBT complexes causes an increase in its acidity with respect to EBB, since it stabilizes the conjugate base by electron density withdrawing effect. EBB is being a more basic ligand and shows stronger chelation with the metals. The difference in flexibility of the ligands may also affect the strength of chelation.

The values of log K_{f1} and log K_{f2} at 25 °C of various cations with EBB and EBT are compared with the

Table 4
X–Y data for EBT and EBB in different percentages of ethanol–water media at different temperatures

[*S*] (%)	−log[*S*]	−*X*	*Y*											
			20 °C				25 °C				30 °C			
			J = 1	*J* = 2	*J* = 3	*J* = 4	*J* = 1	*J* = 2	*J* = 3	*J* = 4	*J* = 1	*J* = 2	*J* = 3	*J* = 4
EBT														
25	0.602	−0.477	8.80 (10.28)	8.20 (9.68)	7.59 (9.07)	6.99 (8.47)	8.71 (10.20)	8.11 (9.60)	7.50 (8.99)	6.90 (8.39)	8.64 (10.15)	8.04 (9.55)	7.43 (8.94)	6.83 (8.34)
35	0.456	−0.269	9.10 (10.72)	9.65 (10.27)	8.19 (9.81)	7.74 (9.36)	8.96 (10.58)	8.50 (10.13)	8.05 (9.67)	7.59 (9.21)	8.83 (10.53)	8.37 (10.08)	7.92 (9.62)	7.46 (9.17)
50	0.301	0	9.32 (11.00)	9.02 (10.70)	8.72 (10.40)	8.42 (10.10)	9.24 (10.83)	8.94 (10.53)	8.64 (10.23)	8.34 (9.93)	9.15 (10.75)	8.85 (10.45)	8.55 (10.15)	8.25 (9.85)
75	0.125	0.477	9.66 (11.24)	9.53 (11.11)	9.41 (10.99)	9.28 (10.86)	9.50 (11.08)	9.37 (10.95)	9.25 (10.83)	9.12 (10.70)	9.39 (11.00)	9.26 (10.87)	9.14 (10.74)	9.01 (10.62)
EBB														
25	0.602	−0.477	(10.48 (11.08)	9.88 (10.48)	9.27 (9.87)	8.67 (9.27)	10.33 (10.88)	9.73 (10.28)	9.12 (9.67)	8.52 (9.07)	10.18 (10.75)	9.58 (10.15)	8.97 (9.54)	8.37 (8.94)
35	0.456	−0.269	(10.81 (11.44)	10.36 (10.99)	9.90 (10.53)	9.45 (10.08)	10.66 (11.32)	10.21 (10.87)	9.75 (10.41)	9.30 (9.96)	10.63 (11.13)	10.18 (10.68)	9.72 (10.22)	9.27 (9.77)
50	0.301	0	11.22 (11.78)	10.92 (11.48)	10.62 (11.18)	10.32 (10.88)	11.02 (11.64)	10.72 (11.34)	10.42 (11.04)	10.11 (10.74)	10.84 (11.42)	10.54 (11.12)	10.24 (10.82)	9.94 (10.52)
75	0.125	0.477	11.46 (12.15)	11.33 (12.02)	11.21 (11.90)	11.08 (11.77)	11.30 (12.05)	11.17 (11.92)	11.05 (11.80)	10.92 (11.67)	11.18 (11.98)	11.05 (11.85)	10.93 (11.73)	10.80 (11.60)

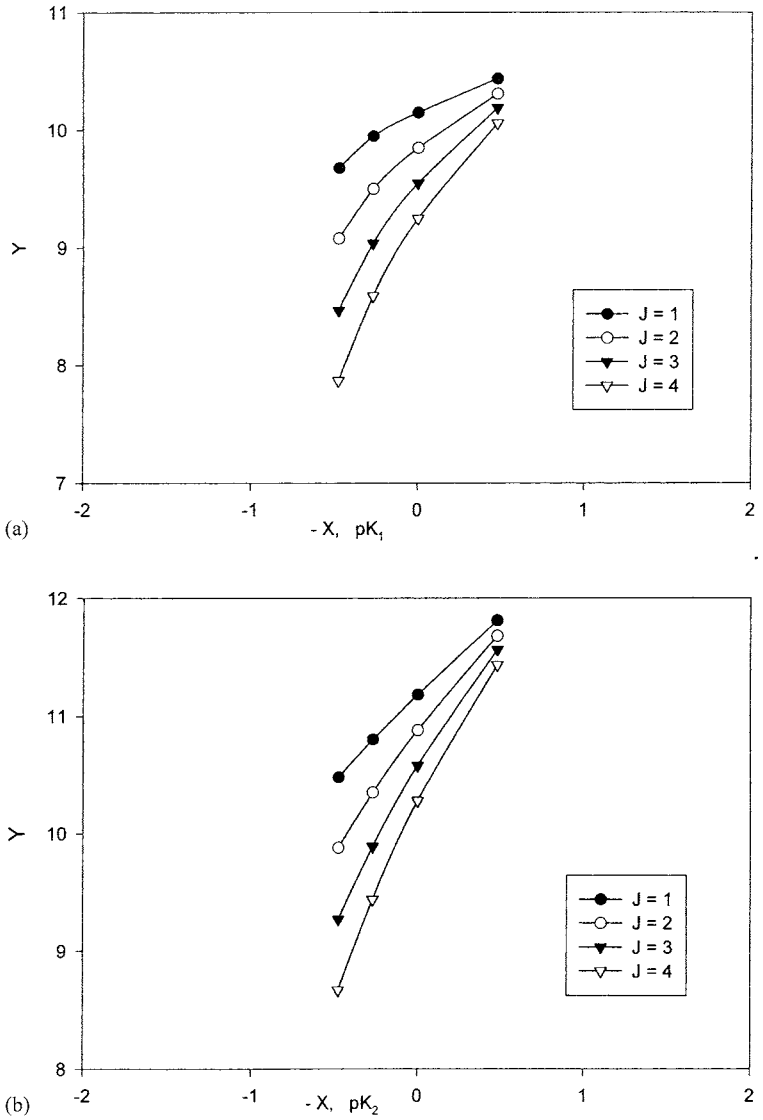


Fig. 3. (a) *X–Y* relationship for pK_1 of EBB in different % of dioxane–water media at 25 °C. (b) *X–Y* relationship for pK_2 of EBB in different percentage of dioxane–water media at 25 °C.

related tridentate azo ligands HNPR [6], and PAAP [17], Table 7. EBT and EBB, represented as H_2L, are dibasic tridentate ligands (Strucures I and II). The ligands coordinate to the metal via the azo-nitrogen and the two phenolic oxygen atoms. HNPR is 2-hydroxy-4-nitrophenylazo resorcinol, it also coordinates to the metal ions through the azo-nitrogen and the two *o*,*o*-hydroxyl oxygens. PAAP is 6-(2-pyridylazo)-3-acetamidophenol, it coordinates to the metal ions through the pyridine nitrogen, azo nitrogen and the *o*-hydroxyl oxygen.

The formation constant K_{f1} for 1:1 complexation with EBB or EBT can be due to the interaction of M^{2+} with H_2L to form ML and loss of $2H^+$. When water

Table 5
The log K_f and thermodynamic parameters for metal complexes with EBT in 50% ethanol at 25–40 °C[a]

Media	log K_f				ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (e.u.)
	25 °C	30 °C	35 °C	40 °C			
Co(II)	6.64 ± 0.03	6.57 ± 0.05	6.41 ± 0.04	6.31 ± 0.03	−9.06 ± 0.04	−9.86 ± 0.09	−2.68 ± 0.17
Ni(II)	6.18 ± 0.04	6.10 ± 0.03	5.95 ± 0.02	5.87 ± 0.02	−8.43 ± 0.06	−9.24 ± 0.17	−2.72 ± 0.37
Cu(II)	7.29 ± 0.04	7.17 ± 0.05	6.91 ± 0.05	6.75 ± 0.06	−9.95 ± 0.06	−16.11 ± 0.79	−20.66 ± 0.73
Fe(III)	7.52 ± 0.03	7.42 ± 0.04	7.21 ± 0.06	6.94 ± 0.05	−10.26 ± 0.07	−16.74 ± 0.74	−21.73 ± 0.67
	(4.99) ± 0.06	(4.85) ± 0.04	(4.73) ± 0.05	(4.52) ± 0.05	(−6.81) ± 0.08	(−13.10) ± 0.80	(−21.10) ± 0.72
Cd(II)	3.91 ± 0.02	3.89 ± 0.02	3.87 ± 0.03	3.84 ± 0.02	−5.34 ± 0.03	−1.97 ± 0.15	11.30 ± 0.39
Pb(II)	4.67 ± 0.03	4.64 ± 0.02	4.62 ± 0.04	4.59 ± 0.02	−6.37 ± 0.04	−2.22 ± 0.16	13.92 ± 0.40
Zn(II)	5.18 ± 0.02	5.16 ± 0.02	5.12 ± 0.03	5.09 ± 0.02	−7.07 ± 0.03	−2.66 ± 0.06	14.79 ± 0.10
Hg(II)	3.47 ± 0.02	3.44 ± 0.02	3.43 ± 0.02	3.41 ± 0.02	−4.74 ± 0.03	−1.62 ± 0.05	10.46 ± 0.07

[a] Values in parenthesis are log K_{f2}.

Table 6
The log K_f and thermodynamic parameters for metal complexes with EBB in 50% ethanol at 25–40 °C[a]

Media	log K_f				ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (e.u.)
	25 °C	30 °C	35 °C	40 °C			
Co(II)	8.95 ± 0.04	8.89 ± 0.03	8.81 ± 0.02	8.74 ± 0.06	−12.21 ± 0.06	−6.08 ± 0.39	20.56 ± 1.11
Ni(II)	9.42 ± 0.02	9.35 ± 0.03	9.23 ± 0.02	9.10 ± 0.02	−12.85 ± 0.03	−9.26 ± 0.40	12.04 ± 1.24
	(3.85) ± 0.05	(4.05) ± 0.04	(4.52) ± 0.03	(4.80) ± 0.07	(−5.25) ± 0.07	(28.45) ± 0.71	(113.0) ± 2.15
Cu(II)	10.74 ± 0.03	10.69 ± 0.02	10.57 ± 0.03	10.43 ± 0.02	−14.65 ± 0.05	−9.02 ± 0.45	18.88 ± 1.34
	(4.95) ± 0.04	(5.22) ± 0.03	(5.59) ± 0.10	(6.69) ± 0.09	(−6.75) ± 0.06	(48.07) ± 2.20	(183.9) ± 7.18
Fe(III)	13.50 ± 0.03	13.71 ± 0.04	14.00 ± 0.05	14.44 ± 0.04	−18.42 ± 0.04	26.41 ± 0.88	150.36 ± 2.82
	(10.28) ± 0.02	(10.24) ± 0.02	(10.21) ± 0.03	(10.18) ± 0.02	(−14.03) ± 0.03	(−2.82) ± 0.16	(37.60) ± 0.44
Cd(II)	7.10 ± 0.03	6.68 ± 0.11	6.40 ± 0.05	6.14 ± 0.08	−9.69 ± 0.04	−26.94 ± 1.80	−57.86 ± 5.90
Pb(II)	6.50 ± 0.05	6.27 ± 0.05	6.11 ± 0.02	5.92 ± 0.06	−8.87 ± 0.07	−16.22 ± 0.40	−24.65 ± 1.11
Zn(II)	9.72 ± 0.06	9.28 ± 0.08	9.02 ± 0.04	8.71 ± 0.09	−13.26 ± 0.08	−28.06 ± 1.91	−49.64 ± 3.09

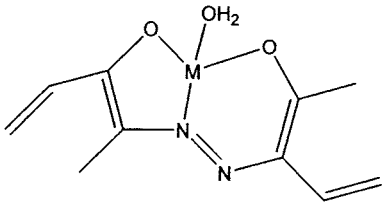
[a] Values in parenthesis are log K_{f2}.

Table 7
The formation constants K_{f1} and K_{f2} of the complexes with EBB, EBT, HNPR and PAAP at 25 °C

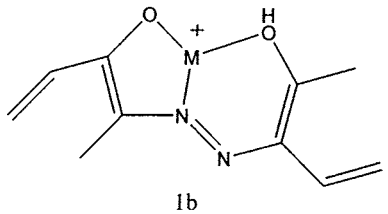
	log K					
	Co	Ni	Cu	Fe	Zn	Cd
EBB	8.95	9.42 (3.85)	10.74 (4.95)	13.5 (10.28)	9.72	7.10
EBT	6.64	6.18	7.29	7.52 (4.99)	5.18	3.91
HNPR[a]	7.60 (6.80)	7.70 (6.90)	8.20 (7.25)	7.95 (7.00)		
PAAP[b]	5.55	5.93	7.99	7.16	8.70	5.84

[a] [6].
[b] [17].

molecule is also coordinated product $ML(H_2O)$ forms with skeleton 1a.



1a



1b

The formation constant K_{f1} can also be obtained when H_2L interacts with M^{2+} with loss of H^+ to form $[M(HL)]^+$, skeleton 1b. Further reaction of $M(HL)^+$ with a second H_2L form octahedral $M(HL)_2$ also with loss of H^+. K_{f2} for 1:2 complexation is obtained from this step. In the case of Fe^{3+}, cationic complex $[Fe(HL)_2]^+Cl^-$ is formed. Interaction of one water molecule with $M(HL)^+$ can give the four-coordinate complex $[M(HL)H_2O]^+Cl^-$, while interactions of three water molecules with $[M(HL)]^+$ form the octahedral complex $[M(HL)(H_2O)_3]^+Cl^-$.

The reactions of hydrated cobalt, nickel, copper, iron, zinc, mercury, cadmium and lead chlorides with EBT or EBB in presence of ammonia in hot ethanol afforded the corresponding metal complexes as bluish black precipitates. The obtained complexes from the reaction of Co(II), Ni(II), and Cu(II) with EBT are octahedral $Co(HL)_2$, $Ni(HL)_2$, and four-coordinate $Cu(L)(H_2O)$, indicated by elemental analysis, magnetic susceptibility, FTIR, and electronic absorption [8]. The remaining complexes are characterized by measuring the electronic absorption spectra, which show peaks due to d–d electronic transitions in addition to the n–π^* transition of the azo group [8,18]. The complexes are also analyzed by polarograhy. The reduction differential pulse polarographic peaks (E_p) of azo complexes show negative shift with respect to the corresponding azo ligands [19].

3.4. Thermodynamic parameter of complexation

The thermodynamic parameters for metal complexation with EBT and EBB are listed in Tables 5 and 6 respectively. The enthalpy of complexation, ΔH (kcal/mol) were determined from the plot of $\log K_f$ versus $1/T$. Straight lines were obtained with a slope of $-\Delta H/2.303R$. The free energy ΔG (kcal/mol) was calculated at 25 °C from the relation $\Delta G = -2.303RT \log K_f$. The entropy ΔS (e.u.) is given as $\Delta S = 10^3(\Delta H - \Delta G)/T$. The negative values of ΔG_1 and ΔG_2 indicate that the formation of 1:1 and 1:2 metal ligand complexes in all the cases are thermodynamically favored process. The values of ΔH lead to the same conclusion. The high negative values of ΔH_1 and ΔH_2 in most cases indicate that the enthalpy effect is more predominant than the entropy effect.

The stabilities of complexes are influenced by cation size, type of donor atom of chelate, flexibility of ligand and solvation effects. The ΔH values of EBB complexes with Co, Ni, Cu, and Fe are smaller than those of Cd, Pb, and Zn due to strong solvation of the ions with decreasing ionic size, that also causes the entropy to be highly positive, Table 6.

The strong solvation interactions with EBT ligand such as hydrogen bonding is responsible for the positive entropy of complexation with large ions Cd, Pb, Zn and Hg, Table 5. Since the larger the size of the ion the weaker the bonding interaction between the complex ion and all donor atoms of the ligand, therefore the stability constant and enthalpy of reaction decrease while the entropy become positive. Positive entropy values have been also obtained in the complexation of alkali and alkali earth metal with crown ethers [20,21].

An attempt was made to relate the dissociation constants of the ligands and the stability constants of their complexes [22]. The linearity between $\log K_{c1}$ and pK_1 could be checked from the relation:

$$\log K_{c1} = a\,pK_1 + b$$

Table 8
Slopes of $\log K_{c1}$ – pK_{a1} plots for the transition metals complexes

Metal	Zn	Cu	Ni	Cd	Co	Pb
Slope	2.55	1.94	1.82	1.79	1.30	1.03

where a and b are constants. The slope 'a' of log K_{c1}/pK_1 would be unity if the bonding is similar in both the ligand and the complex. However, deviations from unity results from metal complexes with π-bonding. The latter is apparent for cations function as π-electron donors, and 'a' will exceed unity for cations acting as π-electron acceptor. The vacant d-orbitals of the metals are susceptible to accept the ligand electrons on complexation. The slopes for the systems under investigation (Table 8) indicated that both σ- and π-interactions coexist.

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