

Evaluation of thermodynamic functions for complexation reactions involving bivalent metal ions and ethyl-2,3-dioxobutyrate-2p-bromophenylhydrazone

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MS received 4 January 1992; revised 30 May 1992

Abstract. Complexation reactions of bivalent metal ions and ethyl-2,3-dioxobutyrate-2p-bromophenylhydrazone (EDOB-2p-BPH) have been studied potentiometrically in 50% (v/v) ethanol/water medium at different ionic strengths with respect to NaClO₄ and at different temperatures and their stability constants determined. The method of Bjerrum and Calvin as modified by Irving and Rossotti has been used to determine the \bar{n} and pL values. S_{\min} values which have the same significance as ' χ^2 ' have also been calculated. The thermodynamic stability constants and standard free energy change (ΔG) have also been calculated. ΔG values are negative in all cases indicating that the reactions are spontaneous. The ligand field stabilization energy (δH) has also been calculated for the 3d transition metals.

Keywords. Stability constants; thermodynamic parameters; ethyl-2,3-dioxobutyrate-2p-bromophenylhydrazone; bivalent metal ions.

1. Introduction

Aroylhydrazones are reported to possess antitubercular, anticancer, antibacterial and antileukemic activity, which is attributed to the formation of stable chelates with transition metals present in the cells. The formation of hydrazones is also extensively used in detection, determination and isolation of compounds containing the carbonyl group. The present study has been undertaken keeping in view these applications.

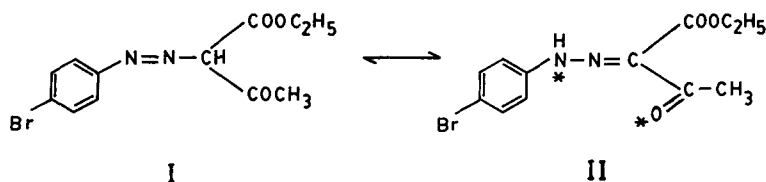
2. Experimental

2.1 Preparation of the ligand

The ligand, ethyl-2,3-dioxobutyrate-2p-bromophenylhydrazone (EDOB-2p-BPH), was prepared by general methods described by Barber *et al* (1961) and Fernandes *et al* (1975). The crude product was recrystallized from methanol. The ligand was characterized by melting point (96–98°C), elemental analysis, ¹H NMR, IR spectroscopy and thin layer chromatography.

On the basis of analysis and spectral study as reported in literature structures I and II

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Scheme 1. Ethyl-2,3-dioxobutyrate-2*p*-bromophenylhydrazone (EDOB-2*p*-BPH).

(scheme 1) may be assigned to the ligand. The sites of coordination are shown by the asterisks on the nitrogen and oxygen atoms in II.

2.2 Reagents

The solution of the ligand was prepared in ethanol. All the metal ion solutions were prepared from corresponding sulphates or nitrates (AR, BDH) in double distilled water and were standardised by conventional methods (Vogel 1978). Sodium perchlorate (Riedel) was used to maintain constant ionic strength. A solution of tetramethylammonium hydroxide (TMAH, E Merck), 0.1 M in 50% aqueous ethanol was used as the titrant and its solution standardised using standard oxalic acid. Ethanol was purified as described by Vogel (1966).

2.3 Potentiometric measurements

A digital pH-meter (Radiometer, Copenhagen, model PHM83) with a single glass-calomel electrode assembly was used for the pH measurements. The pH-meter was standardized with potassium hydrogenphthalate and phosphate buffer before titrations were performed. The solution in the titration vessel was stirred by means of a mechanical stirrer. The titrations were carried out in a nitrogen atmosphere (N_2 purity $\approx 99.9\%$) which was presaturated with 50% (v/v) aqueous ethanol before passing through the reaction mixture. The titrations were carried out in a covered double-walled glass cell.

All the measurements were made at different temperatures maintained constant by using Julabo F20 thermostat of accuracy $\pm 0.5^\circ\text{C}$.

The following solutions (total volume = 19.70 ml due to contraction on mixing ethanol and water) were titrated potentiometrically against standard 0.1 M TMAH, in 50% ethanol-water medium.

- (i) 2.5 ml HClO_4 (0.02 M) + 2.0 ml NaClO_4 (1.0 M) + 0.5 ml KNO_3 or K_2SO_4 (0.02 M) + 5.0 ml H_2O + 10.0 ml ethanol.
- (ii) 2.5 ml HClO_4 (0.02 M) + 2.0 ml NaClO_4 (1.0 M) + 0.5 ml KNO_3 or K_2SO_4 (0.02 M) + 5.0 ml H_2O + 10.0 ml ligand in ethanol (0.01 M).
- (iii) 2.5 ml HClO_4 (0.02 M) + 2.0 ml NaClO_4 (1.0 M) + 0.5 ml M^{2+} (nitrates or sulphates) (0.02 M) + 5.0 ml H_2O + 10.0 ml ligand in ethanol (0.01 M).

These titrations were repeated for varying ionic strengths ($\mu = 0.2, 0.1$ and 0.05 M NaClO_4) at $35 \pm 0.5^\circ\text{C}$, and for different temperatures ($T = 20, 35, 45 \pm 0.5^\circ\text{C}$).

3. Results and discussion

From the titration curves of solutions (i) and (ii) the parameter \bar{n}_H , the average number of protons bound per free ligand, was calculated by employing the relationship derived by Irving and Rossotti (1954). pK_a values were determined by plotting $\log \bar{n}_H/(1 - \bar{n}_H)$ vs. pH. \bar{n} and pL values were calculated from the titration curves of solutions (i), (ii) and (iii) at various pH values. The \bar{n} values (0.1 to 1.7) indicate the formation of both 1:1 and 1:2 complexes. The stability constants were computed on an Upton PC plus computer using a weighted least squares program patterned after that of Sullivan *et al* (1959) which determines the set of β_n values which makes the function U ,

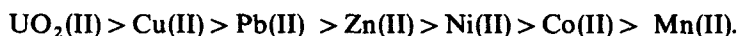
$$U = \sum_{n=0}^N (y - x - nz)\beta_n \chi^n,$$

nearest to zero, by minimizing S ,

$$S = \sum_{i=0}^I W_i U^2(x_i, y_i, z_i),$$

with respect to variation in β_n . S_{\min} has the same statistical distribution as χ^2 with K degrees of freedom and with weights defined in accordance with Rydberg and Sullivan (1959). S_{\min} can be equated to χ^2 .

The order of stability constants of the bivalent metal complexes of EDOB-2p-BPH is (table 1):



This order is in good agreement with the order as determined by Mellor and Maley (1948) and Irving and Williams (1948, 1953). In the recent past our group (Garg and Sarkar 1987; Garg and Dixit 1991) also found the same order. In all the cases, the values of $\log K_1$ are greater than those of $\log K_2$.

3.1 Effect of ionic strength and temperature

The values of the dissociation constant of the ligand, pK_a , decrease with increase in ionic strength of the medium, which is in good agreement with the Debye-Huckel treatment (Nasanen & Ekman 1952),

$$pK_a^0 - [A\mu^{1/2}/(1 + \mu^{1/2})] + C\mu = pK_a.$$

A similar trend of variation has been observed in the case of stability constants of complexes. Stability constants have also been found to decrease with increasing temperature along with pK_a values (Garg and Dixit 1987; Garg and Sarkar 1987).

3.2 Thermodynamic stability constants and ligand field stabilization energy

Thermodynamic stability constants obtained by extrapolating the straight line plots of $\log K_1$ vs. $(\mu)^{1/2}$ to zero ionic strength are given in table 2. The order of thermodynamic

Table 1. Stability constants of complexes of bivalent metals with EDOB-2p-BPH at various ionic strengths (μ) and temperature (T) in 50% ethanol-water medium.

System	Stability constant	Conditions*				
		0.05 (35)	0.1 (20)	0.1 (35)	0.1 (45)	0.2 (35)
EDOB-2p-BPH	$\log K_1^H$	10.87	11.15	10.60	10.47	10.38
Mn(II)-EDOB-2p-BPH	$\log K_1$	4.42	4.52	4.24	3.92	3.99
	$\log K_2$	4.21	3.94	3.63	3.61	3.76
	S_{\min}	0.039693	0.076711	0.093812	0.077404	0.038535
Co(II)-EDOB-2p-BPH	$\log K_1$	4.91	4.75	4.53	4.40	4.42
	$\log K_2$	4.72	4.42	4.34	4.19	4.27
	S_{\min}	0.066571	0.119310	0.201660	0.040323	0.096300
Ni(II)-EDOB-2p-BPH	$\log K_1$	5.03	5.00	4.76	4.58	4.58
	$\log K_2$	4.83	4.70	4.53	4.40	4.25
	S_{\min}	0.048464	0.078711	0.235540	0.063561	0.082993
Zn(II)-EDOB-2p-BPH	$\log K_1$	6.35	6.69	6.15	5.84	5.98
	$\log K_2$	—	—	—	—	—
	S_{\min}	0.044799	0.018401	0.026210	0.067154	0.093690
Pb(II)-EDOB-2p-BPH	$\log K_1$	6.89	7.12	6.69	6.05	6.58
	$\log K_2$	—	—	—	—	—
	S_{\min}	0.055921	0.047398	0.114080	0.097903	0.257580
Cu(II)-EDOB-2p-BPH	$\log K_1$	7.31	7.24	7.04	6.70	6.81
	$\log K_2$	6.59	7.06	6.38	6.49	6.39
	S_{\min}	0.178760	0.120220	0.675700	0.064824	0.183510
UO ₂ (II)-EDOB-2p-BPH	$\log K_1$	8.53	8.61	8.35	7.88	8.05
	$\log K_2$	8.01	8.10	7.56	7.46	7.87
	S_{\min}	0.030478	0.029869	0.097535	0.058404	0.079374

* Numbers in parentheses are the temperatures at which measurements were made.

Table 2. Thermodynamic stability constants and values of standard free energy change of some bivalent metal complexes of EDOB-2p-BPH at $35 \pm 0.5^\circ\text{C}$.

Metal ions	$\log K_1^0$	$-\Delta G^0$ (kJ/mol)	δH	$[(n-5)/5]Er$
Mn(II)	4.85	28.49	—	—
Co(II)	5.35	31.42	99.87	82.96
Ni(II)	5.40	31.71	138.15	124.47
Cu(II)	7.75	45.52	114.64	165.97
Zn(II)	6.70	39.32	—	—

$\log K_1^0$ = values obtained by extrapolating the $\log K_1$ vs. $(\mu)^{\frac{1}{2}}$ to zero ionic strength.

$-\Delta G^0$ = standard free energy change = $-2.303 RT \log K_1^0$, where R , T and K_1^0 have the usual significance (values are rounded off upto the second decimal place).

δH = thermodynamic stabilization energy.

$[(n-5)/5]Er$ = lattice energy difference for Zn^{2+} and Mn^{2+}
 n = number of electrons in $3d$ orbitals.

stability constants ($\log K_1^0$) follows the same trend as the stoichiometric stability constants. The ligand field stabilization energy, δH , and $Er(\text{Mn} - \text{Zn})$, the lattice energy difference for Zn^{2+} and Mn^{2+} complexes, were calculated according to the method of George and McClure (1959) and are listed in table 2. The order of values of ligand field stabilization energies, δH , was found to be:



which is in good agreement with the theory. Negative values of standard free energy change are obtained at $35 \pm 0.5^\circ\text{C}$ (table 2) which is strong support for the feasibility and spontaneous nature of the processes.

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