

Complexation behaviour of benzilmono(lepityl)hydrazone (BLH) toward bivalent metal ions: A potentiometric study

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Abstract. Potentiometric investigations on metal complexes of various bivalent metal ions, viz. $\text{UO}_2(\text{II})$, $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Co}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Zn}(\text{II})$ and $\text{Mn}(\text{II})$ with benzilmono(lepityl)hydrazone (BLH) have been carried out at different ionic strengths and at different temperatures in order to determine stability constants of the complexes. Thermodynamic parameters ΔG , ΔH and ΔS have also been evaluated from temperature coefficient data. The effect of varying the dielectric constant of the medium on the stability constants of complexes has also been investigated at $30 \pm 0.5^\circ\text{C}$ and $\mu = 0.1 \text{ M NaCl}$. Thermodynamic stability constants and thermodynamic stabilization energies for the first transition metals have also been discussed.

Keywords. Stability constants; thermodynamic parameters; benzilmono(lepityl)hydrazone; bivalent ions.

1. Introduction

Many of the physiologically active hydrazones find numerous applications in the treatment of several diseases such as tuberculosis, leprosy, mental disorder, cancer, tumour, bacterial infection etc. (Kitaev *et al* 1970). Hydrazones act as herbicides, insecticides, nematocides and plant growth regulators. They show spasmolytic activity, hypotensive action and activity against leukemia, sarcomas and other malignant neoplasms (Braun *et al* 1978). Various aliphatic and aromatic hydrazones containing the N, N, N', N'-bi(1, 2-ethanedyl) phosphoric diamide moiety have been found to have anticancer activity (Sosnovsky *et al* 1985).

In analytical chemistry, the formation of hydrazones is extensively used in detection, determination and isolation of compounds containing the carbonyl group. They can be used as indicators at high pH ranges (in the pH range 4 to 6). Hydrazones have been used extensively in detection and quantitative determination of several metals in micro amounts.

Hydrazones also find use as first level dyes for wool, nylon and leather.

Their property of chelation and its applications prompted us to undertake the present investigation.

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2. Experimental

2.1 Preparation of the ligand

Benzil 0.1 mol (1.26 g) was dissolved in ethanol to give a saturated solution. A saturated solution of 2-hydrazinolepidine 0.1 mol (1.73 g) in the minimum volume possible of conc. HCl was added and the mixture was refluxed for half an hour. After completion of the reaction, the mixture was cooled and filtered, to give a yellow-coloured final product which was recrystallized from ethanol.

2.2 Characterization of the ligand BLH

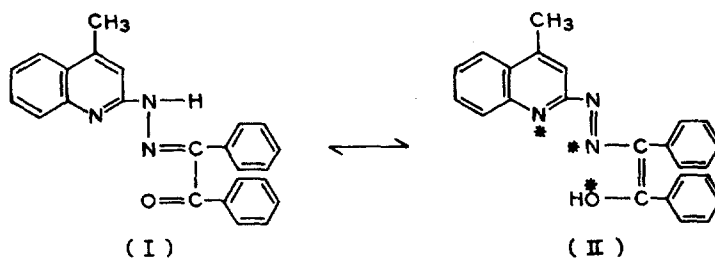
The purity of the product (BLH) was checked by NMR, elemental analysis and thin layer chromatography; m.p. 220°C.

2.2a *Elemental analysis*: The elemental analysis of BLH shows the following analysis: C, H, N – (Calc.) 78.90, 5.21, 11.51%; (Found) 79.56, 5.10, 11.39%.

2.2b *¹H NMR spectra*: Proton magnetic resonance spectra of the complexes were taken in deuterated chloroform. Chemical shifts for protons (δ scale) as observed are ¹H NMR (δ , ppm); 2.7 (s, 3H, -CH₃); 7.3–8.1 (m, 15H, aromatic protons); 10.62 (s, -OH).

2.2c *Thin layer chromatography*: The solvent system used was acetone–benzene (1:4), the spots were applied using solutions of compounds 2-lepidyl hydrazine, benzil (starting materials) and product BLH in ethanol on a TLC plate (20 × 5 cm²). Spots were detected by exposure to iodine vapour. A single spot for the product showed the purity of the ligand. Spots for the product and starting materials were observed at different heights from the base of the plate.

On the basis of above analysis and spectral study, structures I and II may be assigned to BLH.



Benzilmono (lepidyl) hydrazone (BLH)

The sites of coordination are shown by the asterisks on nitrogen and oxygen atoms in H.

2.3 Instrumentation:

A digital pH meter (ECIL model pH 5651) in conjunction with a glass electrode was used for pH measurements. The pH meter was standardised with potassium hydrogenphthalate buffer before performing the titration.

2.4 Reagents:

All the metal ion solutions were prepared and standardised by conventional procedures. Ligand solution was prepared in freshly distilled alcohol. NaCl (E Merck) was used to maintain constant ionic strength. A solution of sodium hydroxide (NaOH) (E Merck) in 75% aqueous alcohol was used as the titrant, and was standardised with oxalic acid. All other chemicals used were of reagent grade. The titrations were carried out in a covered double-walled glass cell in a nitrogen atmosphere, which was presaturated with 75% (v/v) aqueous ethanol. Ethanol was purified by the method given by Vogel (1956).

2.5 Potentiometric titrations

The following solutions were titrated potentiometrically against standard 0.05M NaOH, in 75% (v/v) ethanol-H₂O.

- (i) 1.5 ml HCl (0.05M) + 2.0 ml NaCl (2.0M) + 1.0 ml K₂SO₄ or KNO₃ (0.01M) + 0.5 ml H₂O + 15.0 ml ethanol.
- (ii) 1.5 ml HCl (0.05M) + 2.0 ml NaCl (2.0M) + 1.0 ml K₂SO₄ or KNO₃ (0.01M) + 0.5 ml H₂O + 10.0 ml ligand (0.005M) + 5.0 ml ethanol.
- (iii) 1.5 ml HCl (0.05M) + 2.0 ml NaCl (2.0M) + 1.0 ml metal sulphate or nitrate (0.01M) + 0.5 ml H₂O + 10.0 ml ligand (0.005M) + 5.0 ml ethanol.

In other sets NaCl was added as required to maintain the ionic strength at 0.1, 0.05 or 0.02M.

In order to determine the thermodynamic parameters, the titrations were also carried out at various temperatures 30, 40 and 50 ± 0.5°C. Further, to establish the relationship between pK_a , $\log K$ and the dielectric constants of the media, the titrations were repeated for 50, 60 and 75% (v/v) ethanol-H₂O, 75% (v/v) acetone-H₂O and 75% (v/v) dioxan-H₂O. In all the systems, temperature was maintained constant (± 0.5°C) by using an MLW (West Germany) (NBE type) thermostat.

The pH values in aquo-organic mixtures were corrected using the method of Van Uitert and Hass (1953) and volume corrections were also applied according to the method of Rao and Mathur (1969).

2.6 Calculations

From the above titration curves of solutions (i), (ii) and (iii) the parameters, \bar{n}_H , the average number of protons bound per free ligand ion, \bar{n} , the average number of ligand molecules bound per metal ion and pL , the free ligand exponent, were determined by the expressions described by Irving and Rossotti (1954) in order to evaluate the pK_a values of the ligand and the stability constants of the complexes. The corresponding

values of stability constants were calculated using the weighted least-squares program (Rydberg and Sullivan 1959; Sullivan *et al* 1959) computed on an Uptron PC plus computer, which determines the set of β_n values which make the function

$$U, \left[U = \sum_{n=0}^N (y - x - nz)\beta_n x^n \right]$$

nearest to zero by minimizing S ,

$$\left[S = \sum_{i=1}^I W_i U^2(x_i, y_i, z_i) \right]$$

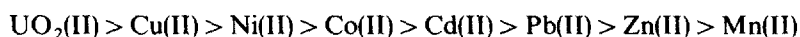
with respect to the variation in β_n . We report the S_{\min} values for different metal complexes. S_{\min} has the same statistical distribution as χ^2 with K degrees of freedom and with weights defined in accordance with Sullivan *et al* (1959). S_{\min} can be equated to χ^2 .

3. Results and discussion

Dissociation constants and stability constants were calculated at four different ionic strengths (0.2, 0.1, 0.05 and 0.02M NaCl) at 30°C, at three different temperatures (30°, 40° and 50°C) in 0.1M NaCl and 50, 60 and 75% ethanol–water media with 0.1M NaCl at 30°C.

3.1 Order of stability constant

The order of stability constants in the metal complexes of BLH has been found to be:



which is in good agreement with the order found by Mellor and Maley (1947) and by Irving and Williams (1948). Log K_1 , log K_2 and S_{\min} values for the bivalent metal ion complexes are summarized in tables 1 and 2.

3.2 Effect of ionic strength

The values of dissociation constants of ligand (pK) have been found to decrease with increasing ionic strength of the medium (table 1) in agreement with the Debye–Huckel equation (Nasanen and Ekman 1952).

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

A similar variational trend has been observed in the case of the stability constants of complexes.

3.3 Effect of temperature

In the present investigation, it has been observed that the stability constants decrease with increase in temperature along with the pK_a values (table 2). These results are in

Table 1. Stability constants of bivalent metal complexes with BLH at different ionic strengths (μ) (M NaCl) and in various organic solvent-water ($v_2, v_1/v$) media (temperature = $30 \pm 0.5^\circ\text{C}$).

System	Constant	0.02			0.05			0.1			0.2			
		Ethanol-H ₂ O	Ethanol-H ₂ O	75	Ethanol-H ₂ O	Ethanol-H ₂ O	75	Acetone-H ₂ O	Dioxan-H ₂ O	Ethanol-H ₂ O	Ethanol-H ₂ O	Ethanol-H ₂ O	75	
BLH	pK_a	5.50			5.32			5.28			5.60			4.52
	$\log K_1$	5.24			4.82			5.04			5.42			4.36
	$\log K_2$	4.82			3.78			4.38			4.80			3.45
Cu(II)-BLH	S_{\min}	0.00			0.00			0.00			0.00			0.00
	$\log K_1$	5.10			4.74			4.98			5.36			4.29
	$\log K_2$	4.71			3.67			4.24			4.68			3.35
Ni(II)-BLH	S_{\min}	0.00			0.00			0.00			0.00			0.00
	$\log K_1$	4.98			4.69			4.86			5.20			4.20
	$\log K_2$	4.51			3.49			4.08			4.64			3.21
Co(II)-BLH	S_{\min}	0.00			0.00			0.00			0.00			0.00
	$\log K_1$	4.94			4.66			4.79			5.14			4.12
	$\log K_2$	4.10			3.37			3.93			4.50			3.12
Cd(II)-BLH	S_{\min}	0.00			0.00			0.00			0.00			0.00
	$\log K_1$	4.90			4.57			4.66			5.06			4.01
	$\log K_2$	3.75			3.21			3.68			4.32			2.77
Pb(II)-BLH	S_{\min}	0.00			0.00			0.00			0.00			0.00
	$\log K_1$	4.83			4.44			4.56			4.90			3.80
	$\log K_2$	3.68			2.94			3.60			4.28			2.58
Zn(II)-BLH	S_{\min}	0.00			0.00			0.00			0.00			0.00
	$\log K_1$	4.67			4.24			4.24			4.82			3.67
	$\log K_2$	3.56			2.74			3.22			3.98			2.22
Mn(II)-BLH	S_{\min}	0.00			0.00			0.00			0.00			0.00
	$\log K_1$	4.50			3.97			4.12			4.52			3.43
	$\log K_2$	3.42			2.39			2.94			3.68			1.85
	S_{\min}	0.00			0.00			0.00			0.00			0.00

Table 2. Stability constants and thermodynamic parameters of bivalent metal complexes with BLH at different temperatures ($\mu = 0.1\text{M NaClO}_4$).

System	Stability constant	Temperature ($^{\circ}\text{C}$)			$-\Delta G$ (kcal/mol)	$-\Delta H$ (kcal/mol)	ΔS (kcal $\text{K}^{-1} \text{mol}^{-1}$)
		30 ± 0.5	40 ± 0.5	50 ± 0.5			
BLH	pK_a	4.76	4.66	4.52	—	—	—
UO ₂ (II)-BLH	$\log K_1$	4.68	4.59	4.31	6.5	5.4	0.0
	$\log K_2$	3.69	3.41	3.35	5.1	5.0	0.0
	S_{min}	0.00	0.03	0.00	—	—	—
Cu(II)-BLH	$\log K_1$	4.44	4.34	4.23	6.2	5.0	0.0
	$\log K_2$	3.67	3.23	3.24	5.1	4.6	—
	S_{min}	0.00	0.00	0.00	—	—	—
Ni(II)-BLH	$\log K_1$	4.29	4.20	4.07	5.9	5.0	—
	$\log K_2$	3.45	3.14	3.05	4.8	4.6	—
	S_{min}	0.00	0.00	0.00	—	—	—
Co(II)-BLH	$\log K_1$	4.24	4.04	3.99	5.9	4.6	0.0
	$\log K_2$	3.22	2.86	2.75	4.5	4.1	—
	S_{min}	0.00	0.00	0.00	—	—	—
Cd(II)-BLH	$\log K_1$	4.16	3.97	3.88	5.8	4.6	—
	$\log K_2$	2.99	2.78	2.52	4.1	4.1	—
	S_{min}	0.00	0.00	0.00	—	—	—
Pb(II)-BLH	$\log K_1$	4.03	3.90	3.73	5.6	4.6	—
	$\log K_2$	2.90	2.63	2.25	4.0	3.7	—
	S_{min}	0.00	0.00	0.00	—	—	—
Zn(II)-BLH	$\log K_1$	3.90	3.81	3.57	5.4	4.1	—
	$\log K_2$	2.73	2.38	1.91	3.8	3.2	—
	S_{min}	0.00	0.00	0.00	—	—	—
Mn(II)-BLH	$\log K_1$	3.71	3.64	3.43	5.1	3.7	—
	$\log K_2$	2.34	2.14	1.66	3.2	2.7	—
	S_{min}	0.00	0.00	0.00	—	—	—

good agreement with those of Pitzer (1937). The overall free energy, enthalpy and entropy changes at $30 \pm 0.5^{\circ}\text{C}$ are reported in table 2. The results indicate that ΔH and ΔG are negative, which indicate that complexation takes place spontaneously. The entropy is almost zero. Hence, entropy has virtually no effect on complexation.

Thermodynamic stability constants obtained by extrapolating the straight line plots of $\log K_1$ vs. $(\mu)^{\frac{1}{2}}$ to zero ionic strength are given in table 3 and figure 1 along with the thermodynamic stabilization energy δH . The δH and $Er(\text{Mn}-\text{Zn})$ values have been calculated according to the method of George and McClure (1959) and are listed in table 3 and figure 2. The hydration energies (ΔH_H) are those given by George and McClure (1959). The order of ' δH ' is:



3.4 Effect of dielectric constant

The proton-ligand constants and the formation constants of metal complexes with BLH have been measured in ethanol-water, dioxan-water and acetone-water media. The dielectric constants of the media were varied by varying their organic solvent content.

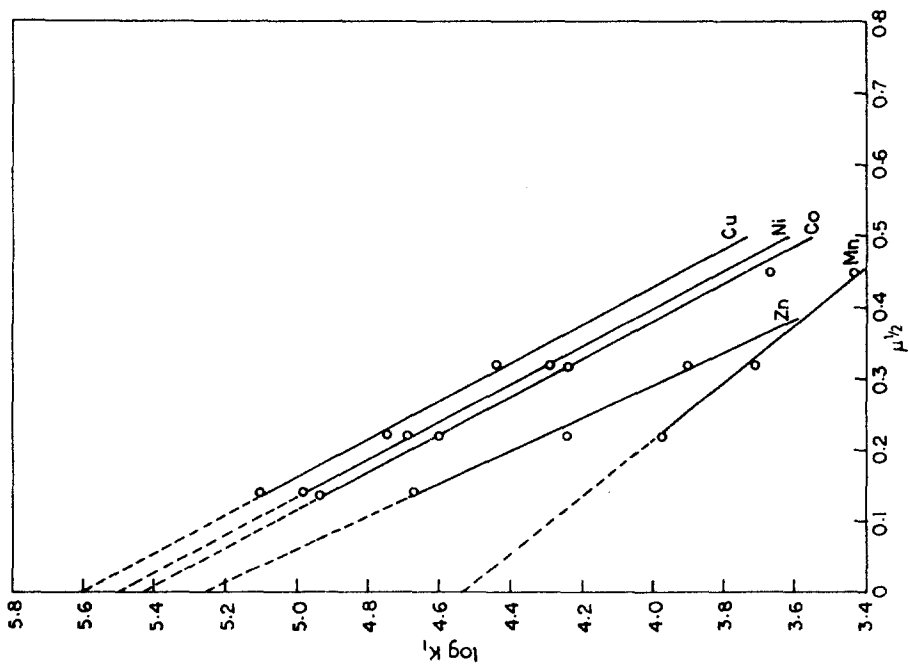


Figure 1. Plots of $\log K_1$ vs $(\mu)^{1/2}$ of bivalent metal complexes of BLH in 75% ethanol-water medium at temperature = $30 \pm 0.5^\circ\text{C}$.

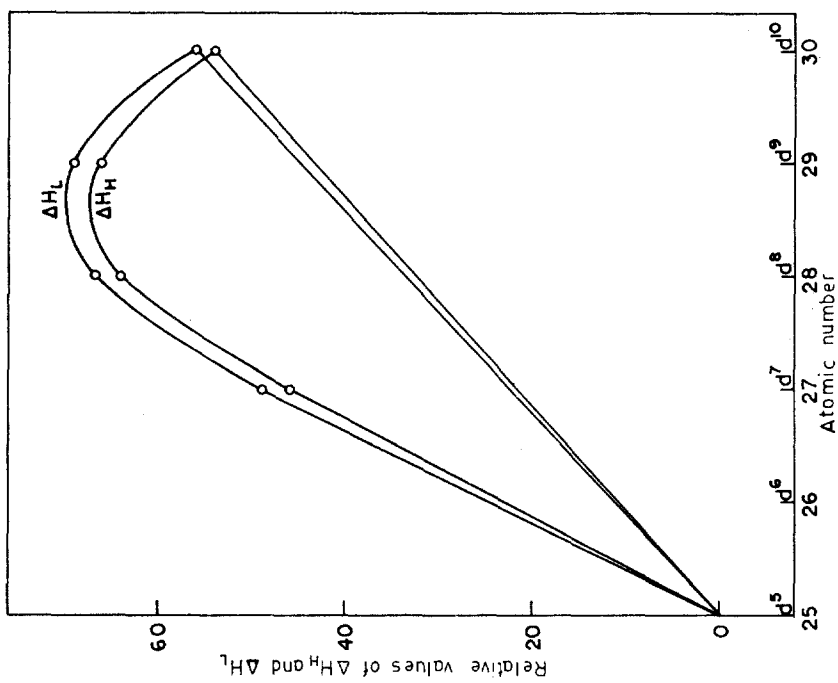


Figure 2. Plots of relative values of ΔH_H and ΔH_L against the number of 3d electrons for BLH complexes.

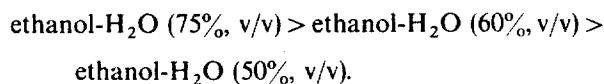
Table 3. $Er(\text{Mn-Zn})$ and δH values for complexes of BLH.

Parameters (kcal/mol)	Metal ions				
	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$\log K_1^0$	4.54	5.43	5.50	5.60	5.25
ΔF	6.29	7.53	7.63	7.76	7.28
ΔF_R	—	1.24	1.34	1.47	0.99
ΔH_H	—	43.00	62.00	63.00	47.00
ΔH_L	—	44.24	63.34	64.47	47.99
$[(n-5)/5]Er$	—	19.20	28.79	38.39	—
δH	—	25.04	34.55	26.08	—

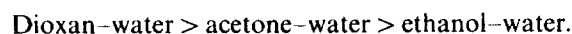
ΔF – Free energy change on complexation = $2.303RT \log K_1^0$, where R , T and K_1^0 have the usual significance, $T = 303\text{K}$.
 ΔF_R – Change in heat content for the formation of the complex in solution relative to Mn^{2+} .
 ΔH_H – Heat of hydration of metal ions relative to Mn^{2+} .
 ΔH_L – Heat of complexation referred to metal ion in gaseous and ligand in solution state.
 n – Number of electrons in $3d$ orbital.
 $[(n-5)/5]Er$ – Lattice energy difference for Zn^{2+} and Mn^{2+} complexes.
 δH – Thermodynamic stabilization energy.
 $\log K_1^0$ – Values have been obtained by extrapolating the $\log K_1$ vs $\mu^{\frac{1}{2}}$ to zero ionic strength.

From table 1, for a given mixed aqueous solvent [alcohol–water, 50% (v/v), 60% (v/v), 75% (v/v)] it is clear that the pK_a of the ligand increases with increase in organic content of the aquo–organic solvent. This may be due to decrease in the dielectric constant of the medium, increase in the proton solvation and decrease in the hydrogen-bonding ability of the solvent.

The stability constants of the metal complexes are strongly affected by the dielectric constant of the medium and the solvation property of the solvent (Braude *et al* 1948; Rorabacher *et al* 1971). The data in table 1 show that the metal–ligand formation constants increase with increase in the percentage of organic solvent in the medium, i.e.



For a particular composition (75%, v/v) of the solvent– H_2O mixtures, the stability constants of metal complexes of BLH and pK_a values follow the order:



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References

- Braude E A 1948 *J. Chem. Soc.* 1971
Braun R, Dittmar W and Goricke D 1978 *Naturwissenschaften* **65** 267
George P and McClure D S 1959 *Prog. Inorg. Chem.* **1** 428
Irving H and Williams R J P 1948 *Nature (London)* **162** 746
Irving H M and Rossotti H S 1954 *J. Chem. Soc.* 2904
Kitaev Yu P, Buzykin B I and Troepol T V 1970 *Russ. Chem. Rev.* 441
Meller D P and Maley L 1947 *Nature (London)* **159** 370
Nasanen R and Ekman A 1952 *Acta Chem. Scand.* **6** 1389
Pitzer K S 1937 *J. Am. Chem. Soc.* **50** 2365
Rorabacher D B, Mackeller W J, Shu F R and Bonavita M 1971 *Anal. Chem.* **43** 561
Rydberg J and Sullivan J C 1959 *Acta Chem. Scand.* **13** 2059
Sosnovsky G, Rao M and Uma N 1985 *Cancer Litt. (Shannon Irel.)* **29** 309
Sullivan J C, Rydberg J and Miller W E 1959 *Acta Chem. Scand* **13** 2023
Rao U B and Mathur H B 1969 *Indian J. Chem.* **7** 1234
Van Uitert L G and Hass C G 1953 *J. Am. Chem. Soc.* **75** 451
Vogel A I 1956 *A text book of practical organic chemistry* (New York: Longman) p. 166