

Potentiometric studies on the complexation equilibria involving diacetylmono(lepityl) hydrazone and bivalent metal ions in aqueous ethanolic medium

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Abstract. The ligand diacetylmono(lepityl) hydrazone(DALH) has been synthesized in four steps and characterized by melting point, thin layer chromatography, elemental analysis, NMR and IR. Complex formation between transition metal ions Mn(II), Pb(II), Cd(II), Co(II), Ni(II), Cu(II), UO₂(II) and DALH has been investigated by potentiometric measurements of hydrogen ions liberated on complexation at 25, 30, 40 and 50 ± 0.5°C in 0.02, 0.05, 0.1 and 0.2 M (NaCl) ionic strength and in 75% ethanol-water medium. From the potentiometric titration curves dissociation constants of the ligand and stability constants of its complexes have been determined. Using these stability constants, thermodynamic parameters such as free energy changes (ΔG), enthalpy changes (ΔH) and entropies (ΔS) of complex formation have calculated and reported. Thermodynamic stability constants ($\log K_f'$) have also been reported. The ligand field stabilization energy (δH) has been calculated for the first row transition metals which is in good agreement with the theory.

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

1. Introduction

Diacetylmono(lepityl) hydrazone(DALH) has analytical applications. It can be used as an indicator at a pH range between 4 and 6 and in detection and quantitative determination of several metals in micro-amounts. As the compound DALH is related to isonicotinoyl hydrazone or isonicotinic acid (antituberculosis drug), it may be used as an antituberculosis agent.

2. Experimental

2.1 Preparation of the ligand

DALH was prepared by dissolving 10 gm (0.06 mole) of 2-hydrazine-lepidine in a minimum volume of conc. HCl and adding 15 gm of crystallized sodium acetate in 100 ml of water, followed by 5 ml of diacetyl (0.06 mole) in 80 ml of water. The solution was then shaken vigorously until all the lepitylhydrazone was crystallized. It was recrystallized from ethanol.

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2.2 Characterization of the ligand

The compound was then characterized by melting point determination (203–205°C), elemental analysis, proton magnetic resonance, IR spectroscopy and thin layer chromatography.

2.2a *Elemental analysis*: The elemental analysis of DALH shows the following: C, H, N – (calc.) 69.71, 6.22, 17.43%; (found) 69.23, 6.13, 17.57%.

2.2b *¹H NMR spectra*: Proton magnetic resonance spectra of the ligand was taken in deuterated chloroform. Chemical shifts for protons (δ scale) as observed ¹H NMR (δ , ppm); 2.7 (s, 3H, –CH₃), 7.2–7.9 (m, 5H, aromatic protons), 12.68 (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, diacetyl (starting materials) and product DALH in ethanol on a TLC plate (20 × 5 cm²). A single spot for the product indicated the purity of the ligand.

On the basis of the above analysis and spectral study, structures I & II may be assigned to DALH. The sites of coordination are shown by the asterisks on the nitrogen and oxygen atoms in II.

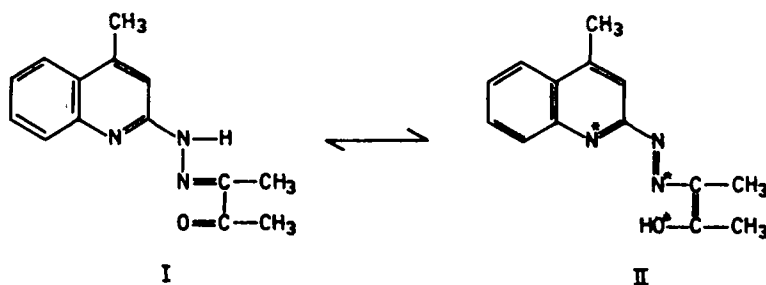


Chart 1. Diacetylmono(lepidyl) hydrazone (DALH).

2.3 Reagents

The solution of the ligand was prepared in 80% (v/v) aqueous ethanol. All the metal ion solutions were prepared and standardized by conventional procedures (Vogel 1986). Sodium chloride (E Merck) was used to keep the ionic strength constant over the various sets. A solution of sodium hydroxide (NaOH) (E Merck) in 75% ethanol (aqueous) was used as the titrant, its solution was standardized using standard oxalic acid. Ethanol was purified as described by Vogel (1978).

2.4 Potentiometric measurements

A digital pH-meter (ECIL model pH-5652) in conjunction with a glass electrode was used for 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 and was maintained at $25 \pm 0.5^\circ\text{C}$ by the circulation of thermostatted water. A stream of nitrogen,

presaturated with 75% aqueous ethanol was bubbled through the solution to protect it from air. The titrations were carried out in a covered double-walled glass cell.

The pH values in aquo-organic mixtures were corrected using the method of Van Uiter and Hass (1953) and volume correction were also applied according to the method of Rao and Mathur 1969. The following solutions were titrated potentiometrically against standard 0.05 M NaOH, in 75% (v/v) ethanol-water.

- (i) 1.5 cm³ HCl(0.05 M) + 1.0 cm³ NaCl(2.0 M) + 1.0 cm³ K₂SO₄ or KNO₃(0.01 M) + 2.75 cm³ water + 18.75 cm³ ethanol.
- (ii) 1.5 cm³ HCl(0.05 M) + 1.0 cm³ NaCl(2.0 M) + 1.0 cm³ K₂SO₄ or KNO₃(0.01 M) + 0.75 cm³ water + 10.0 cm³ ligand (0.005 M) + 10.75 cm³ ethanol.
- (iii) 1.5 cm³ HCl(0.05 M) + 1.0 cm³ NaCl(2.0 M) + 1.0 cm³ metal sulphate or nitrate (0.01 M) + 0.75 cm³ water + 10.0 cm³ ligand (0.005 M) + 10.75 cm³ ethanol.

2.5 Calculation

During complexation the acidic proton is replaced by an equivalent amount of metal (II). From the titration curves of solutions (i) and (ii) the parameter \bar{n}_H , average number of protons bound per free ligand ion, and pK_a , dissociation constant of the ligand, were determined. By using the expression given by Irving and Rossotti (1953, 1954), \bar{n} , the average number of ligands bound per metal ion, and pL , the free ligand exponent were determined. The stability constants were determined by an Upton PC plus computer using a weighted least squares programme (Sullivan *et al* 1959). The weighted least squares programme determines that set of β_n values which make the function U ,

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

nearest to zero, by minimizing S

$$S = \sum_{i=1}^I U^2(x_i, y_i, z_i),$$

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

3. Results

The dissociation constants and stability constants were calculated at four different ionic strengths (0.2, 0.1, 0.05 and 0.02 M NaCl) at 25°C, and at four different temperatures (25, 30, 40 and 50 ± 0.5°C). The values are recorded in tables 1 and 2. Thermodynamic stability constants obtained by extrapolation of a straight-line plot of log K vs. $\mu^{\frac{1}{2}}$ to zero ionic strength (figure 1) are given in table 1. The ligand field stabilization energy, δH , and $Er(\text{Mn-Zn})$, lattice energy difference for Zn²⁺ and Mn²⁺ complexes were calculated according to the method of George and McClure (1959) and listed in table 3.

The thermodynamic parameters ΔG , ΔH have been calculated by using the following relationship (Yatsimirskii and Vasilev 1960) and are given in table 4.

Table 1. Stability constants of transition metal(II) complexes of DALH at different ionic strengths and at temperature = $25 \pm 0.5^\circ\text{C}$.

Stability constants and S_{\min} value	Weighted least squares method							
	Mn(II)	Pb(II)	Zn(II)	Cd(II)	Co(II)	Ni(II)	Cu(II)	UO ₂ (II)
$\log K_1^0$	4.13	4.24	4.34	4.40	4.45	4.57	5.62	4.71
$\mu = 0.2 \text{ M NaCl}, pK_a = 4.96$								
$\log K_1$	3.54	3.61	3.63	3.77	3.86	3.95	4.08	4.22
$\log K_2$	1.92	2.23	2.53	2.77	2.88	3.01	3.25	3.28
$\log \beta_2$	5.46	5.84	6.16	6.54	6.74	6.96	7.33	7.50
S_{\min}	0.00015	0.00032	0.00081	0.00042	0.00017	0.00063	0.00020	0.00025
$\mu = 0.1 \text{ M NaCl}, pK_a = 5.14$								
$\log K_1$	3.57	3.69	3.81	3.93	4.01	4.18	4.34	4.39
$\log K_2$	2.07	2.34	2.60	2.79	2.89	3.09	3.30	3.55
$\log \beta_2$	5.64	6.03	6.41	6.72	6.90	7.27	7.64	7.94
S_{\min}	0.01470	0.00410	0.01700	0.00300	0.00410	0.00340	0.00040	0.00047
$\mu = 0.05 \text{ M NaCl}, pK_a = 5.24$								
$\log K_1$	3.72	3.88	4.00	4.09	4.16	4.26	4.37	4.51
$\log K_2$	2.19	2.38	2.88	3.04	3.25	3.40	3.51	3.66
$\log \beta_2$	5.91	6.26	6.88	7.13	7.41	7.66	7.88	8.17
S_{\min}	0.00940	0.00110	0.00160	0.00020	0.00013	0.00013	0.00007	0.00003
$\mu = 0.02 \text{ M NaCl}, pK_a = 5.30$								
$\log K_1$	3.88	4.05	4.23	4.29	4.32	4.37	4.45	4.59
$\log K_2$	2.84	3.05	3.25	3.68	3.72	3.79	3.97	4.05
$\log \beta_2$	6.72	7.10	7.48	7.97	8.04	8.16	8.44	8.64
S_{\min}	0.00021	0.00067	0.00150	0.00630	0.00500	0.00380	0.00780	0.00730

Table 2. Stability constants of transition metal(II) complexes of DALH at different temperatures(I) and at ionic strength $\mu = 0.1 \text{ M NaCl}$.

Stability constants	Weighted least squares method							
	Mn(II)	Pb(II)	Zn(II)	Cd(II)	Co(II)	Ni(II)	Cu(II)	UO ₂ (II)
$T = 25^\circ\text{C}, pK_a = 5.14$								
$\log K_1$	3.57	3.69	3.81	3.93	4.01	4.18	4.34	4.39
$\log K_2$	2.07	2.34	2.60	2.79	2.89	3.09	3.30	3.55
$\log \beta_2$	5.64	6.03	6.41	6.72	6.90	7.27	7.64	7.94
S_{\min}	0.01470	0.00410	0.01700	0.00300	0.00410	0.00340	0.00040	0.00047
$T = 30^\circ\text{C}, pK_a = 4.98$								
$\log K_1$	3.35	3.59	3.73	3.79	3.87	4.04	4.11	4.22
$\log K_2$	2.32	2.56	2.58	2.70	2.86	2.89	3.38	3.60
$\log \beta_2$	5.67	6.15	6.31	6.49	6.73	6.93	7.49	7.82
S_{\min}	0.00079	0.00033	0.00031	0.00027	0.00022	0.00400	0.00110	0.00120
$T = 40^\circ\text{C}, pK_a = 4.74$								
$\log K_1$	3.32	3.48	3.63	3.76	3.84	4.00	4.08	4.17
$\log K_2$	2.03	2.32	2.63	2.68	2.80	2.82	3.21	3.31
$\log \beta_2$	5.35	5.80	6.26	6.44	6.64	6.82	7.29	7.43
S_{\min}	0.00005	0.00004	0.00018	0.00034	0.00032	0.00017	0.00110	0.00140
$T = 50^\circ\text{C}, pK_a = 4.50$								
$\log K_1$	3.19	3.36	3.53	3.67	3.79	3.95	4.00	4.05
$\log K_2$	1.60	1.79	2.15	2.44	2.57	2.71	3.01	3.13
$\log \beta_2$	4.79	5.15	5.68	6.11	6.36	6.66	7.01	7.18
S_{\min}	0.00002	0.00001	0.00001	0.00004	0.00010	0.00080	0.00020	0.00150

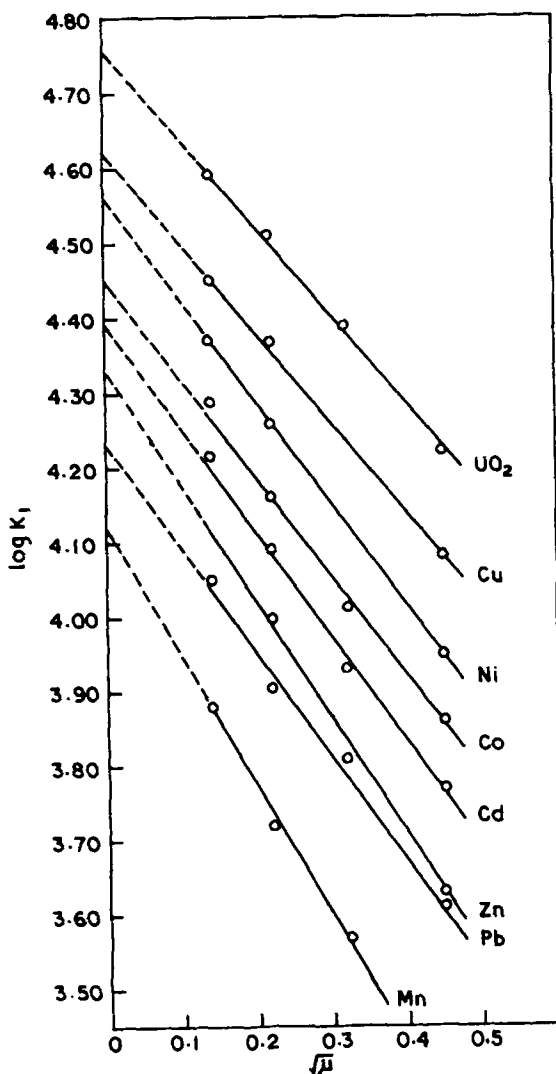
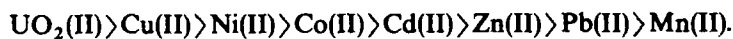


Figure 1. Plot of $\log K_1$ vs. μ^\pm of bivalent metal complexes of DALH in 75% ethanol-water medium at $25 \pm 0.5^\circ\text{C}$.

4. Discussion

The \bar{n} values (0.1 to 2.2) indicate the formation of 1:1 and 1:2 complexes (M:L). From tables 1 and 2, it is evident that the stability constants of the complexes follow the order:



The same trend was observed by several workers (Garg and Dixit 1987; Garg and Sarkar 1987). In all the cases $\log K_1 > \log K_2$, the observed differences in $\log K_1 - \log K_2$, have shown no definite trend and it seems probable that the cation is so modified by the addition of first ligand, that the forces leading to the interaction

Table 3. $Er(Mn-Zn)$ and δH values (kJ mol^{-1}) for complexes of DALH.

Parameters	Metal ions				
	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$\log K_1^0$	4.13	4.45	4.57	4.62	4.34
$\Delta G(\text{kJ/mol}^{-1})$	23.95	25.81	26.51	26.80	25.17
ΔG_R	—	1.86	2.56	2.85	1.22
ΔH_H	—	179.87	259.35	263.53	196.60
ΔH_L	—	181.73	261.91	266.38	197.82
$[(n-5)/5]Er$	—	79.13	118.70	158.26	—
δH	—	102.60	143.21	108.12	—

ΔG = free energy change = $2.303 RT \log K_1^0$, where R , T & K_1^0 have their usual significance and temperature = 303 K (30°C);

ΔG_R = change in heat content for the formation of the complexes in solution;

ΔH_H = heat of hydration of metal ion;

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;

$\log K_1^0$ = thermodynamic stability constant at zero ionic strength as plotted in figure 1 for values given in table 1.

Table 4. Thermodynamic parameters of bivalent metal complexes with DALH at temperature = $30 \pm 0.5^\circ\text{C}$ ($\mu = 0.1 \text{ M NaCl}$).

Metal ion	$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	ΔS ($\text{kJ K}^{-1} \text{ mol}^{-1}$)
$UO_2(II)$	24.475	22.969	0.00497
$Cu(II)$	23.839	22.969	0.00286
$Ni(II)$	23.433	17.226	0.03723
$Co(II)$	22.446	17.226	0.02355
$Cd(II)$	21.982	15.314	0.02200
$Zn(II)$	21.634	15.314	0.02087
$Pb(II)$	20.823	19.141	0.00556
$Mn(II)$	19.430	19.141	0.00096

of singly charged 1:1 complexes with the second molecule of ligand are of a different type from those operating between the solvated metal ions and the first molecule of ligand. In view of the fact very low concentrations of metal ions have been used in the titrations, the possibility of formation of polynuclear complexes is negligible.

4.1 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 and Ekman 1952),

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

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

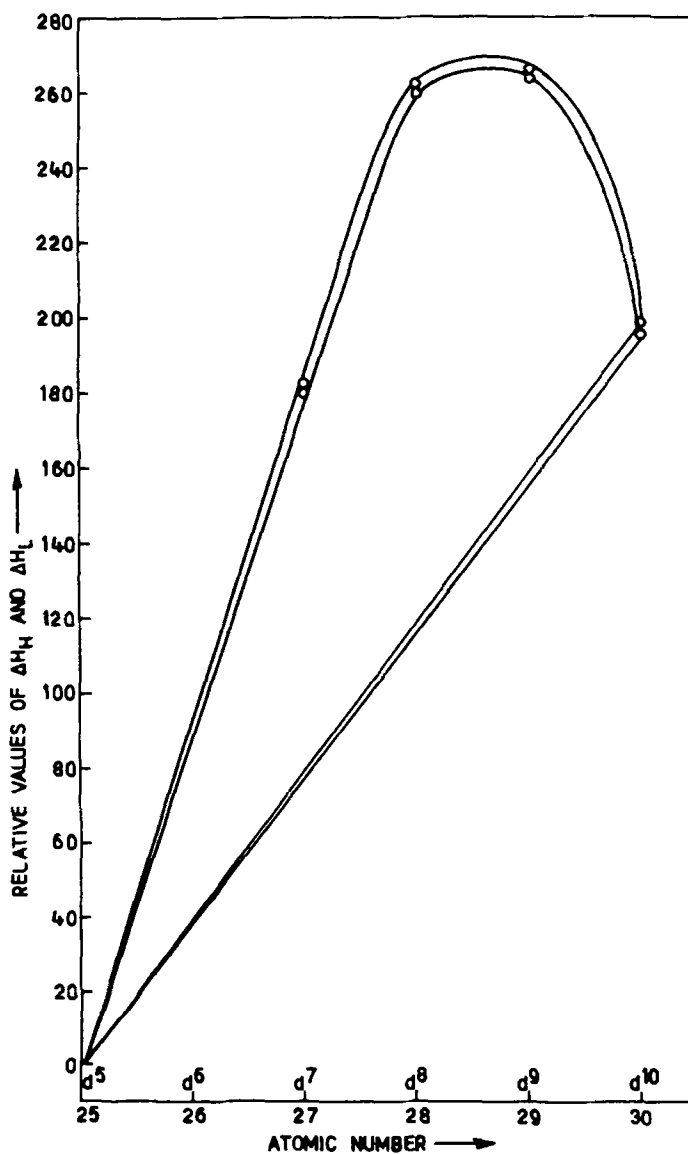


Figure 2. Plots of relative values of ΔH_H and ΔH_L against the number of 3d electrons for DALH complexes.

4.2 Ligand field stabilization energy and lattice energy

The order of ligand field stabilization energy δH was found to be $\text{Co} < \text{Ni} > \text{Cu}$, which is in good agreement with theory. The plots of ΔH_L and ΔH_H of bivalent complexes as a function of the number of d electrons in the metal ion are shown in figure 2.

The values in table 4 show that ΔG is negative, which indicates that complex formation reactions are spontaneous. The enthalpy changes are exothermic. The entropy is positive for all the chelates showing that the entropy is favourable for the formation of complexes.

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