

## Studies on the complexation behaviour of dehydroacetic acid-4-methyl-2-quinolyldiazone with bivalent metal ions

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**Abstract.** The complexation behaviour of bivalent metal complexes of dehydroacetic acid-4-methyl-2-quinolyldiazone (DAMQH) has been studied potentiometrically in 75% (v/v) aqueous dioxan medium at different ionic strengths with respect to sodium perchlorate and at different temperature in order to determine their stability constants. 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 ' $\chi^2$ ', have also been calculated. The thermodynamic stability constants and the standard free energy change ( $\Delta G$ ) have also been calculated.  $\Delta G$  values are negative in all cases. Thus complexation is spontaneous. The order of stability constants of bivalent metal complexes of DAMQH has been determined.

**Keywords.** Dehydroacetic acid-4-methyl-2-quinolyldiazone (DAMQH); bivalent ions; thermodynamic stability constant; standard free energy.

### 1. Introduction

A large number of Schiff bases were prepared in the last decade and have been characterised by elemental analysis and by spectral techniques (Ledbetter 1982; Sau *et al* 1982). Complexes of Ni(II), Co(II), Fe(II), Mn(II), and Zn(II) with Schiff bases derived from 2-hydrazinobenzoxazole and salicylaldehyde have fungicidal activity. O- and N-atoms act as donor atoms and the chelates are more effective fungicides than the ligands (Vasudha *et al* 1982). 2-Hydroxybenzylidene-2-iminopyridine-2-aminobenzoic acid and 2-hydroxybenzylidene-2-iminophenol have the highest herbicidal activity. These Schiff bases can be applied as stimulants in cultivation of monocots and dicots (Devarski 1985). A literature survey revealed that no work has been done on the bivalent metal complexes of DAMQH. Hence the present study has been undertaken to determine the solution stability constants of bivalent metal complexes with DAMQH under different experimental conditions.

### 2. Experimental

#### 2.1 Preparation of ligand

Dehydroacetic acid-4-methyl-2-quinolyldiazone was prepared by refluxing equimolar quantities of 2-hydrazinolepidine and dehydroacetic acid in ethanol. The colour of

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the final product (DAMQH) is brilliant yellow. It was finally recrystallised from dimethylformamide, m.p. 209°C, and its purity checked by TLC, elemental analysis, IR and NMR spectroscopy. A solution of 0.005 M of this compound was prepared in pure dry dioxan.

## 2.2 Reagents

All the metal ion solutions were prepared from AR quality BDH reagents and were standardised by conventional procedures. A solution of tetramethylammonium-hydroxide (TMAH) (E Merck, A G Darmstadt) in 75:25 (v/v) dioxan:water mixture was used as the titrant, and was standardised with oxalic acid. Chemically pure sodium perchlorate (Riedel) was used to maintain constant ionic strength. Perchloric acid ( $\text{HClO}_4$ ) was standardised with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). Dioxan (AR, BDH) was purified by the method given by Vogel (1956). All other chemicals used were of reagent grade.

All the measurements were made at a definite temperature maintained constant by using an MLW (West Germany) NBE-type thermostat of accuracy  $\pm 0.05^\circ\text{C}$ . An IBM 360 computer was used for calculations.

## 2.3 Instrumentation

An ECIL digital pH-meter model-5652 in conjunction with glass (0–14 pH range) calomel electrodes was used. The pH-meter was standardised with potassium hydrogen phthalate and phosphate buffers before performing the titrations. •

## 2.4 Potentiometric titration

The experimental procedure involved potentiometric titrations of the following solutions (total volume = 19.67 ml due to contraction on mixing dioxan and water) at different ionic strengths and temperatures to determine  $\bar{n}$  and  $pL$  values and thermodynamic constants of the complexes.

- (i) 2.0 ml  $\text{HClO}_4$  (0.055 M) + 2.0 ml  $\text{NaClO}_4$  (2 M) + 1.0 ml  $\text{K}_2\text{SO}_4$  or  $\text{KNO}_3$  (0.01 M) + 15.0 ml dioxan.
- (ii) 2.0 ml  $\text{HClO}_4$  (0.055 M) + 2.0 ml  $\text{NaClO}_4$  (2 M) + 1.0 ml  $\text{K}_2\text{SO}_4$  or  $\text{KNO}_3$  (0.01 M) + 10.0 ml ligand solution (0.005 M) in pure dioxan + 5.0 ml dioxan.
- (iii) 2.0 ml  $\text{HClO}_4$  (0.055 M) + 2.0 ml  $\text{NaClO}_4$  (2 M) + 1.0 ml metal sulphate or nitrate (0.01 M) + 10.0 ml ligand solution (0.005 M) in pure dioxan + 5.0 ml dioxan.

A similar titration procedure was followed for titrations at other ionic strengths ( $\mu = 0.1, 0.05, 0.02$  M  $\text{NaClO}_4$ ) at  $33 \pm 0.05^\circ\text{C}$ . Three more sets of titrations were carried out at three different temperatures ( $T = 40, 45, 50 \pm 0.05^\circ\text{C}$ ). The pH meter readings were plotted against the volume of TMAH added.

The titrations were carried out in a covered double-walled glass cell in an inert atmosphere of nitrogen, which was presaturated with solvent (3:1 v/v dioxan-water) before it was passed into the reaction solution.

3. Results and discussion

Values of  $\bar{n}_H$  were calculated at various pH values from the titration curves of solutions, (i) and (ii), by employing the relationship derived by Irving and Rossotti (1954). On plotting  $\log \bar{n}_H / (1 - \bar{n}_H)$  vs. pH, a straight line with an intercept equal to  $pK_a$  on the pH axis and a slope equal to unity was obtained. From the titration curves of solutions (i), (ii) and (iii),  $\bar{n}$  values of the metal complexes were determined at various pH values. The  $\bar{n}$  values (0.1 to 1.8) indicate the formation of both 1:1 and 1:2 complexes. The stability constants were computed on an IBM 360 computer using a weighted least squares program patterned after that of Sullivan *et al* (1959) which determines the set of  $\beta_n$  values which makes the function,  $U$ ,

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

nearest to zero by minimizing

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

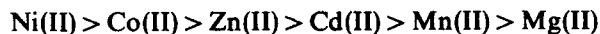
**Table 1.** Stability constants of bivalent metal complexes of DAMQH at different ionic strengths.

Temperature =  $33 \pm 0.05^\circ\text{C}$

System	Constants	Ionic strength (M NaClO <sub>4</sub> )			
		0.2	0.1	0.05	0.02
DAMQH	$pK_1$	6.33	6.43	6.76	6.79
DAMQH-Ni(II)	$\log K_1$	6.31	6.48	6.97	7.09
	$\log K_2$	6.22	6.25	6.90	6.85
	$S_{\min}$	0.0154	0.0019	0.0034	0.1467
DAMQH-Co(II)	$\log K_1$	6.08	6.38	6.72	6.91
	$\log K_2$	5.84	5.86	6.36	6.58
	$S_{\min}$	0.4412	0.0136	0.0930	0.0024
DAMQH-Zn(II)	$\log K_1$	5.88	6.14	6.58	6.76
	$\log K_2$	5.72	5.55	5.84	6.38
	$S_{\min}$	0.0429	0.8275	0.2099	0.0058
DAMQH-Cd(II)	$\log K_1$	5.56	5.79	5.92	6.23
	$\log K_2$	5.39	5.23	5.16	6.00
	$S_{\min}$	0.0120	0.0167	0.0054	0.0125
DAMQH-Mn(II)	$\log K_1$	3.86	4.00	4.20	4.47
	$\log K_2$	3.69	3.96	3.84	3.76
	$S_{\min}$	0.0044	0.0213	0.0610	0.0135
DAMQH-Mg(II)	$\log K_1$	2.72	2.80	2.95	3.23
	$\log K_2$	—	—	—	—
	$S_{\min}$	0.0005	0.0024	0.0052	0.0059

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

The order of stability constants of the bivalent metal complexes of DAMQH is (tables 1 and 2):



The order is in good agreement with the order as determined by Mellor and Maley (1948) and Irving and Williams (1948, 1953). In all the cases, the values of  $\log K_1 > \log K_2$ .

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

In the present studies it has been observed that values of proton dissociation constants of DAMQH and stability constants of bivalent metal complexes at 0.1 M  $\text{NaClO}_4$  ionic strength increase with increasing temperature. This trend is also observed by other workers (Sandhu and Kumaria 1976). The order of thermodynamic stability constants ( $\log K_1^0$ ) follows the same trend as the stoichiometric stability constants. Thermodynamic stability constants obtained by extrapolating the straight line plots

**Table 2.** Stability constants of bivalent metal complexes of DAMQH at different temperatures.

$\mu = 0.1 \text{ M NaClO}_4$

System	Stability constant	$\log K_1^0$	Temperature °C		
			40	45	50
DAMQH	$pK_1$	—	6.50	6.56	6.63
DAMQH-Ni(II)	$\log K_1$	7.38	6.62	6.68	6.75
	$\log K_2$		6.26	6.25	6.47
	$S_{\min}$		0.01282	0.04420	0.14480
DAMQH-Co(II)	$\log K_1$	7.24	6.57	6.63	6.71
	$\log K_2$		6.02	6.02	6.03
	$S_{\min}$		0.01152	0.00816	0.00416
DAMQH-Zn(II)	$\log K_1$	7.05	6.18	6.34	6.41
	$\log K_2$		5.82	5.85	5.90
	$S_{\min}$		0.00165	0.01378	0.00357
DAMQH-Cd(II)	$\log K_1$	6.32	5.81	5.82	5.84
	$\log K_2$		5.28	5.38	5.58
	$S_{\min}$		0.01437	0.02256	0.05324
DAMQH-Mn(II)	$\log K_1$	4.72	4.10	4.20	4.30
	$\log K_2$		3.44	3.83	3.74
	$S_{\min}$		0.01143	0.00217	0.01363
DAMQH-Mg(II)	$\log K_1$	3.41	2.83	2.89	2.92
	$\log K_2$		—	—	—
	$S_{\min}$		0.00254	0.00209	0.00363

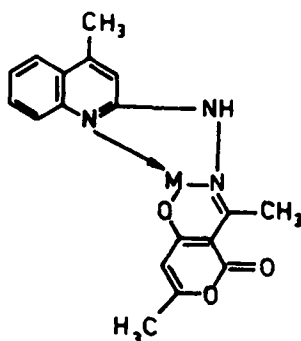
**Table 3.** Thermodynamic stability constants and standard free energy change of some bivalent metal complexes of DAMQH at  $33 \pm 0.05^\circ\text{C}$ .

Metal ion	$-\Delta G^0$ (kcal/mole)
Ni(II)	10.32
Co(II)	10.12
Zn(II)	9.86
Cd(II)	8.93
Mn(II)	6.60
Mg(II)	4.77

$\Delta G^0$  values are rounded up to the second decimal place

of  $\log K_1$  vs.  $(\mu)^{1/2}$  to zero ionic strength are given in table 3. Negative values of standard free energy change are obtained at  $33 \pm 0.05^\circ\text{C}$  which is strong support for the feasibility and spontaneous nature of the processes.

The ligand DAMQH has only one dissociable proton on the hydroxy group of the pyran ring and three nitrogen atoms with a lone pair. Taking into account the Schiff base chelate (Rao *et al* 1980) and the availability of lone pair electrons on the nitrogen atoms the following type of bonding is expected. Five- and six-membered rings are expected from the minimum strain point of view. 1:2 M:L complexes are formed in each case except  $\text{Mg}^{2+}$ .



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