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# DETERMINATION OF THERMODYNAMIC PARAMETERS AND STABILITY CONSTANTS OF THE COMPLEXES OF β-MITSC WITH TRANSITION METAL IONS

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## ABSTRACT

The consecutive stability constants of the 1:1 and 2:1 chelate species formed by the interaction of *N*-methylisatin-β-thiosemicarbazone (β-MITSC) with transition bivalent metal ions have been determined potentiometrically at different ionic strengths (0.02, 0.05, 0.1 and 0.2 M $NaClO_4$) and at different temperatures (30, 40, 45 and 50°C) in 50% dioxan–water medium. Further, the variation of $pK_a$ and log $K$ with the inverse of the dielectric constant or mole fraction of the solvent (50, 60 and 75% dioxan–water media) has also been investigated. The order of magnitude of the log $K$ values for M(II)–β-MITSC chelates is in accordance with the Irving–Williams series. The thermodynamic parameters $\Delta G$, $\Delta H$, $\Delta S$ and ligand-field stabilization energy, $\delta H$, of the complexation reaction have also been evaluated at 30°C.

## INTRODUCTION

Derivatives of isatin and *N*-methylisatin have been established to possess pharmacological activity. They have been found to act as central nervous system depressants and are used for prevention of smallpox, etc. [1]. The antimicrobial, antineoplastic, antihypotensive, analgesic, antiinflammatory and crysticidal activities of isatin derivatives are well known [2]. However, perusal of the literature reveals that no analytical work has been done on isatin and its derivatives. In view of the widespread applications of isatin and its derivatives and lack of literature involving analytical investigations, we have chosen β-MITSC as a ligand to study its interaction with bivalent metal ions. The various types of interactions have been studied in dioxan–water media, by pH titration technique and necessary corrections for activity coefficients have been made [3–5].

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## EXPERIMENTAL

### *Instrumentation*

The digital pH meter (ECIL model, pH-5651) with a single glass calomel electrode assembly was used for pH measurements.

### *Reagents*

*N*-Methylisatin-$\beta$-thiosemicarbazone ($\beta$-MITSC) was prepared by refluxing equimolar quanticies of *N*-methylisatin and thiosemicarbazide hydrochloride in alcohol. The purity of the ligand was checked by infrared (IR) spectrometry, elemental analysis and thin layer chromatography (m.p. = 232°C). A solution of the ligand was prepared in freshly distilled dioxan. All metal ions were prepared from the corresponding nitrates or sulphates (AR, B.D.H.) and were standarised by conventional methods [6], sodium perchlorate (Riedel) was used to keep the ionic strength of the medium constant. A 0.05 M solution of thetramethylammonium hydroxide (TMAH) (Merck) was used as titrant. The dioxan used was purified by the procedure of Weissberger et al. [7].

### *Potentiometric titrations*

The method of Bjerrum and Calvin, as modified by Irving and Rossotti [8,9] was used to determine $\bar{n}$ and p$L$ values. The experimental procedure involved the potentiometric titrations of the following solutions against 0.05 M TMAH in 50%, in dioxan–water media: (1) $HClO_4$ ($1.5 \times 10^{-3}$ M); (2) $HClO_4$ ($1.5 \times 10^{-3}$ M) + $\beta$-MITSC ($2.5 \times 10^{-3}$ M); (3) $HClO_4$ ($1.5 \times 10^{-3}$ M) + $\beta$-MITSC ($2.5 \times 10^{-3}$ M) + $M^{2+}$ ($0.5 \times 10^{-3}$ M). These titrations were repeated for ionic strengths, $\mu = 0.02$, 0.05, 0.1 and 0.2 M $NaClO_4$. In order to determine thermodynamic parameters, the titrations were also carried out at various temperatures: 30, 40, 45 and 50°C. Furthermore, to establish the relationship between p$K_a$, log $K$ and dielectric constant of media, the titrations were repeated for 50, 60 and 75% dioxan–water media. Temperature was maintained constant ($\pm 0.5$°C) in all the systems by using a MLW (West Germany, NBE type) thermostat. Pre-saturated nitrogen (with dioxan) was bubbled through the reaction solution.

### *Calculations*

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 p$L$, the free ligand exponent, were determined by the expressions described by Irving and Rossotti [8,9] in order to evaluate the p$K_a$ values of the ligand

and the stability constants of complexes. The $\bar{n}$ values (0.1–1.8) indicate the formation of 1 : 1 and 2 : 1 complexes (L : M). The stability constants were computed on an IBM 360 FORTRAN IV computer using a weighted least-squares program, patterned after that of Sullivan et al. [10]. The weighted least-squares treatment determines that set of $\beta_n$ 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

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

with respect to variation in $\beta_n$.

$S_{\min}$ has the same statistical distribution as $\chi^2$ with $K$ degrees of freedom and with weights defined in accordance with Rydberg and Sullivan [11]. $S_{\min}$ can be equated to $\chi^2$.

## RESULTS AND DISCUSSION

The dissociation constant and stability constants were calculated at four different ionic strengths (0.2, 0.1, 0.05 and 0.02 M $NaClO_4$) at 30 °C, at four different temperatures (30, 40, 45 and 50 °C) in 0.1 M $NaClO_4$, and in 50, 60 and 75% dioxan–water media with 0.1 M $NaClO_4$ at 30 °C. The values are recorded in Tables 1 and 2.

### *Order of stability constant*

It is evident, from Tables 1 and 2, that the stability constants of the complexes follow the order found by Mellor and Maley [12] and Irving and Williams [13,14]. The sequence was found to be Cu > Ni > Pb > Co > Zn > Cd > Mn; in all the cases, $\log K_1 > \log K_2$. The differences $\log K_1 - \log K_2$ observed, 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 of singly charged 1 : 1 complex 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.

### *Effect of ionic strength*

The value of the dissociation constant of the ligand ($pK_a$) decreases with increase in ionic strength of the medium, which is in agreement with the

TABLE 1
Stability constants of bivalent metal complexes with $\beta$-MITSC at different ionic strengths and in various dioxan–water media (temp. $30 \pm 0.5$ °C)

| System | Constant | Ionic strength (M $NaClO_4$)/% Solvent | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0.02/50 | 0.05/50 | 0.1/50 | 0.1/60 | 0.1/75 | 0.2/50 |
| $\beta$-MITSC | $pK_a$ | 9.760 | 9.590 | 9.380 | 9.620 | 9.980 | 9.130 |
| Cu(II)–$\beta$-MITSC | $\log K_1$ | 8.714 | 8.419 | 8.178 | 8.443 | 8.673 | 7.796 |
| | $\log K_2$ | 7.869 | 7.866 | 7.442 | 7.598 | 8.195 | 7.057 |
| | $S_{min}$ | 0.02075 | 0.01761 | 0.05637 | 0.00659 | 0.22427 | 0.19580 |
| Ni(II)–$\beta$-MITSC | $\log K_1$ | 8.221 | 8.124 | 7.910 | 8.038 | 8.310 | 7.709 |
| | $\log K_2$ | 7.697 | 7.511 | 7.117 | 7.346 | 7.614 | 6.595 |
| | $S_{min}$ | 0.01133 | 0.04027 | 0.17994 | 0.18765 | 0.18106 | 0.07935 |
| Pb(II)–$\beta$-MITSC | $\log K_1$ | 8.109 | 7.861 | 7.653 | 7.809 | 8.286 | 7.307 |
| | $\log K_2$ | 7.544 | 7.318 | 6.917 | 7.244 | 7.225 | 6.345 |
| | $S_{min}$ | 0.01525 | 0.00473 | 0.01596 | 0.01525 | 0.06017 | 0.07199 |
| Co(II)–$\beta$-MITSC | $\log K_1$ | 8.014 | 7.668 | 7.591 | 7.613 | 7.914 | 7.251 |
| | $\log K_2$ | 7.151 | 7.015 | 6.435 | 6.750 | 7.051 | 5.723 |
| | $S_{min}$ | 0.02204 | 0.04468 | 0.13430 | 0.22395 | 0.22404 | 0.05881 |
| Zn(II)–$\beta$-MITSC | $\log K_1$ | 7.820 | 7.534 | 7.423 | 7.533 | 7.731 | 7.039 |
| | $\log K_2$ | 7.035 | 6.910 | 6.248 | 6.194 | 7.093 | 5.552 |
| | $S_{min}$ | 0.06524 | 0.07744 | 0.52589 | 0.46659 | 0.06579 | 0.16828 |
| Cd(II)–$\beta$-MITSC | $\log K_1$ | 7.409 | 7.015 | 6.863 | 7.015 | 7.382 | 6.611 |
| | $\log K_2$ | 5.589 | 5.334 | 5.107 | 5.334 | 5.584 | 4.773 |
| | $S_{min}$ | 0.05585 | 0.08723 | 0.03121 | 0.08723 | 0.18708 | 0.14690 |
| Mn(II)–$\beta$-MITSC | $\log K_1$ | 6.041 | 5.820 | 5.621 | 5.909 | 6.033 | 5.439 |
| | $S_{min}$ | 0.13810 | 0.06380 | 0.05985 | 0.06142 | 0.06752 | 0.05856 |

Debye–Hückel equation [15]

$$pK_a^0 - \left[A\sqrt{\mu}/1 + \alpha\sqrt{\mu}\right] + C\mu = pK_a$$

A similar trend of variation has been observed in the case of the stability constants of complexes. The thermodynamic stability constants are obtained by extrapolating the straight line plot of $\log K_1$ vs. $\sqrt{\mu}$ to zero ionic strength.

## *Effect of temperature*

The thermodynamic parameters $\Delta G$, $\Delta H$ and $\Delta S$ have been calculated by using the following relationship [16] and values are given in Table 2.

$$\Delta G = -RT \ln K$$

$$d \log K/d(1/T) = \Delta H/(2.303R)$$

$$\Delta S = (\Delta H - \Delta G)/T$$

TABLE 2
Stability constants and thermodynamic parameters of bivalent metal complexes with β-MITSC at different temperatures ($\mu = 0.1$ M $NaClO_4$) [a]

| System | Stability constant | Temperature (°C) | | | $-\Delta G$ (kcal $mol^{-1}$) | $\Delta H$ (kcal $mol^{-1}$) | $\Delta S$ (cal $mol^{-1}$) |
|---|---|---|---|---|---|---|---|
| | | 40 | 45 | 50 | | | |
| β-MITSC | $pK_a$ | 9.520 | 9.580 | 9.660 | – | – | – |
| Cu(II)–β-MITSC | log $K_1$ | 8.289 | 8.634 | 8.741 | 11.339 | 8.054 | 64.003 |
| | log $K_2$ | 7.683 | 7.789 | 7.898 | (10.319) | (9.152) | (64.261) |
| | $S_{min}$ | 0.03430 | 0.02072 | 0.00378 | – | – | – |
| Ni(II)–β-MITSC | log $K_1$ | 7.998 | 8.091 | 8.163 | 10.799 | 7.893 | 61.690 |
| | log $K_2$ | 7.458 | 7.627 | 7.713 | (10.051) | (10.616) | (68.208) |
| | $S_{min}$ | 0.30349 | 0.03571 | 0.04396 | – | – | – |
| Pb(II)–β-MITSC | log $K_1$ | 7.852 | 7.992 | 8.065 | 10.611 | 8.955 | 64.572 |
| | log $K_2$ | 7.183 | 7.465 | 7.582 | (9.590) | (9.608) | (63.363) |
| | $S_{min}$ | 0.01368 | 0.01466 | 0.02372 | – | – | – |
| Co(II)–β-MITSC | log $K_1$ | 7.806 | 7.914 | 7.963 | 10.526 | 8.122 | 61.544 |
| | log $K_2$ | 6.674 | 7.050 | 7.218 | (8.923) | (8.694)(58.142) | |
| | $S_{min}$ | 0.17620 | 0.22404 | 0.12053 | – | – | – |
| Zn(II)–β-MITSC | log $K_1$ | 7.645 | 7.654 | 7.919 | 10.293 | 8.008 | 60.399 |
| | log $K_2$ | 6.644 | 7.011 | 7.137 | (8.663) | (16.416) | (82.768) |
| | $S_{min}$ | 0.20689 | 0.06359 | 0.06522 | – | – | – |
| Cd(II)–β-MITSC | log $K_1$ | 7.184 | 7.599 | 7.899 | 9.530 | 9.838 | 63.921 |
| | log $K_1$ | 5.404 | 5.638 | 5.938 | (7.096) | (12.813) | (65.706) |
| | $S_{min}$ | 0.14110 | 0.03309 | 0.03319 | – | – | – |
| Mn(II)–β-MITSC | log $K_1$ | 5.849 | 5.942 | 5.948 | 7.794 | 6.864 | 48.376 |
| | $S_{min}$ | 0.07041 | 0.37193 | 0.28200 | – | – | – |

[a] Thermodynamic parameters are calculated at 30°C. Values in parantheses are for the reactions involving formation of 1 : 2 complexes.

The results indicate that $\Delta G$ is negative, which shows that complex formation reactions take place spontaneously. The enthalpy changes are endothermic. In spite of these unfavourable enthalpy changes, the complexes are stabilized by relatively large positve entropy change.

The ligand-field stabilization energy, $\delta H$, and $E_r$(Mn–Zn) values were calculated according to the method of George and McClure [17] and are listed in Table 3 and Fig. 1. The order of ligand-field stabilization energy, $\delta H$, is: Co < Ni > Cu.

### *Effect of dielectric constant*

The dielectric constant of the medium was changed by varying the percentage of the organic component of the media. It is seen that with an increase in the organic content of the solvent, the $pK_a$ value is increased.

TABLE 3

$E_r$(Mn–Zn) and $\delta H$ values (in kcal $mol^{-1}$) for complexes of $\beta$-MITSC

| Parameter [a] | Metal ions | | | | |
|---|---|---|---|---|---|
| | $Mn^{2+}$ | $Co^{2+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Zn^{2+}$ |
| $\log K_1^0$ | 6.230 | 8.340 | 8.500 | 9.060 | 8.160 |
| $\Delta F$ | 8.638 | 11.563 | 11.786 | 12.562 | 10.455 |
| $\Delta F_R$ | – | 2.925 | 3.148 | 3.924 | 1.817 |
| $\Delta H_H$ | – | 43.000 | 62.000 | 63.000 | 47.000 |
| $\Delta H_L$ | – | 45.925 | 65.148 | 66.924 | 48.817 |
| $[(n-5)/5]E_r$ | – | 19.526 | 29.290 | 39.054 | – |
| $\delta H$ | – | 26.399 | 35.858 | 27.870 | – |

[a] Free energy change, $\Delta F = 2.303\ RT \log K_1^0$; where $R$, $T$ and $K_1^0$ have their usual significance and $T = 303$ K. $\Delta F_R$, change in heat for the formation of the complex in solution. $\Delta H_H$, heat of hydration of metal ion. $\Delta H_L$, heat of complexation referred to metal ion in gaseous and ligand in solution state. $n$, Number of electrons in $3d$ orbital. $[(N-5)/5]E_r$, lattice energy difference for $Zn^{2+}$ and $Mn^{2+}$ complexes. $\delta H$, thermodynamic stabilization energy. $\log K_1^0$, values employed for the above calculations, have been obtained by extrapolating the $\log K_1$ vs. $\sqrt{\mu}$ (straight line) to zero ionic strength.

The order of $\log K_1$ and $\log K_2$ also becomes almost similar to $1/\epsilon$ sequence, but there is a gradual deviation from linearity when $\log K_1$ (Fig. 2) is plotted against the inverse of the dielectric constant. The same observation has been made by Gergely and Kiss [18] while studying the stability constants of copper and nickel complexes of alanine in dioxan–water and methanol–water media.

The stability constants of the metal complexes are strongly affected by the dielectric constant of the medium and the solvation properties of the solvent

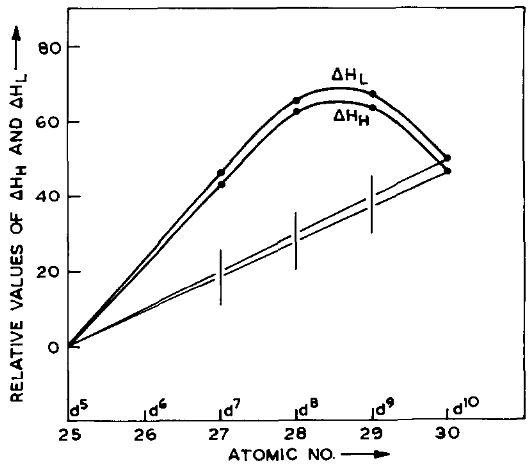

Fig. 1. Plots of relative values of $\Delta H_H$ and $\Delta H_L$ against the number of $3d$ electrons for $\beta$-MITSC complexes.

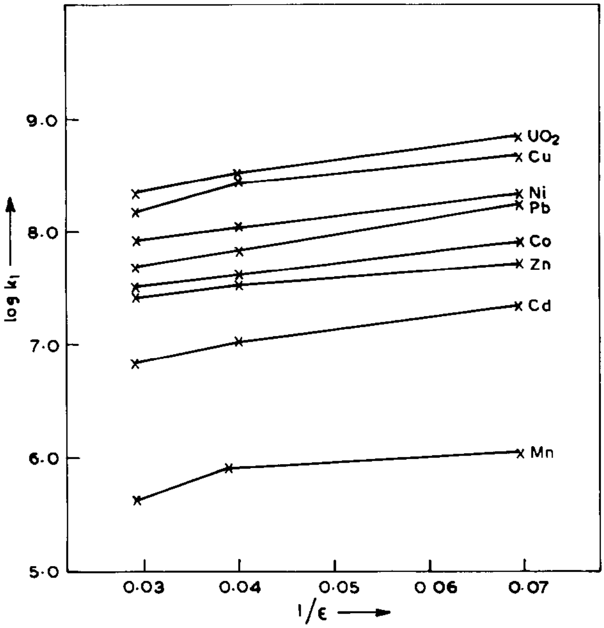

Fig. 2. Plot of log $K_1$ of β-MITSC vs. 1/ε for dioxan–water medium.

[19]. Basalo and Murmann [20] reported the effect of solvent on the complexes containing N–metal links and concluded that the organic content of the solvent had little influence on the stabilities of the complexes.

In general, the stability of complexes containing either an O–H or O–M link increases with increasing organic content of the solvent [21] due to the decrease in the dielectric constant of the bulk solvent. As the dielectric constant decreases, the ion–ion interaction, involving the proton (or metal ion) and anionic oxygen donor of the ligand, increases to a greater extent than the ion–dipole interaction between the proton (or metal ion) and the solvent molecules.

The effect of solvent composition on the stability of complexes that contain both an O–M and N–M bond has not been investigated systematically. Van Uitert et al. [22] have pointed out that, by analogy with simpler complexes, and increase in the organic content of the solvent should increase the stability of complexes in which the O–M bond is predominant but should have a lesser effect on the stability of complexes containing a strong N–M bond. Thus, the variation in stability with solvent composition of a bidentate complex may allow the assessment of the relative importance of the two donor metals bonds. The present complexes contain both O–M and N–M links, the observed increase in stability may be due to the O–M link which is strongly affected.

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