Potentiometric and Thermodynamic Studies
of 2-Thioxothiazolidin-4-one and its Metal Complexes

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Proton—ligand dissociation constants of 2-thioxothiazolidin-4-one and metal—ligand stability constants of its complexes with some metal ions have been determined potentiometrically in 0.1 M-KCl and ethanol—water (volume ratio = 2 : 3). The order of the stability constants of the formed complexes increases in the sequence Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, La^{3+}, Hf^{3+}, and Zr^{4+}. The effect of temperature was studied and the corresponding thermodynamic parameters (ΔG, ΔH, and ΔS) were derived and discussed. The dissociation process is nonspontaneous, endothermic, and entropically unfavourable. The formation of the metal complexes has been found to be spontaneous, endothermic, and entropically favourable.

Chemistry of rhodanine and its derivatives has attracted special interest due to their inhibition of *Mycobacterium tuberculosis* [1] and application as potential medicinal preparations [2]. Thiazolidinones play a central role as chelating agents for a large number of metal ions, and can also be used as analytical reagents [3]. In continuation of the earlier works [4—8], the stability constants of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, La^{3+}, Hf^{3+}, and Zr^{4+} complexes with 2-thioxothiazolidin-4-one (TT) at different temperatures are reported here. Furthermore, the corresponding thermodynamic functions of complexation are evaluated and discussed.

The average number of the protons associated with the reagent molecule TT, $\bar{n}_A$, was determined at different pH values applying the following equation

$$\bar{n}_A = Y + \frac{(V_1 - V_2)(N^\circ + E^\circ)}{(V^\circ - V_1)TC_L^\circ} \qquad (1)$$

where Y is the number of available protons in TT ($Y = 2$) and V_1 and V_2 are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid and reagent, respectively, V° is the initial volume (50 cm^3) of the mixture, TC_L° is the total concentration of the reagent, N° is the concentration of sodium hydroxide solution, and E° is the initial concentration of the free acid. The titration curves ($\bar{n}_A$ *vs.* pH) for the proton—ligand systems were constructed and found to extend between 0 and 2 on the $\bar{n}_A$ scale. This means that TT has two dissociable protons (the hydrogen ions of —SH group, pK_{a1} and —OH group, pK_{a2}) in the rhodanine moiety. Different computational methods [9] were applied

to evaluate the dissociation constants. Three replicate titrations were performed; the average values obtained are listed in Table 1.

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions ($\bar{n}$) *vs.* the free ligand exponent (pL), according to *Irving* and *Rossotti* [10]. The average number of the reagent molecules attached per metal ion, $\bar{n}$, and free ligand exponent, pL, can be calculated using the equations

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V^\circ - V_2)\bar{n}_A TC_M^\circ} \qquad (2)$$

and

$$pL = \log_{10} \frac{\sum_{n=0}^{n=J} \beta_n^H \left(\frac{1}{\text{anti}\log pH} \right)^n}{TC_L^\circ - \bar{n}TC_M^\circ} \cdot \frac{V^\circ + V_3}{V^\circ} \quad (3)$$

where TC_M° is the total concentration of the metal ions present in the solution, β_n^H is the overall proton—reagent stability constant. V_1, V_2, and V_3 are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid, organic ligand, and complex, respectively. These curves were analyzed and the successive stability constants were determined using different computational methods [11, 12]. The values of the stability constants ($\log\{K_1\}$ and $\log\{K_2\}$) are given in Table 2.

The following general remarks can be made:

i) The maximum value of $\bar{n}$ was ≈ 2 indicating the formation of 1 : 1 and 1 : 2 (n(metal) : n(ligand)) complexes only.

Table 1. Thermodynamic Functions for the Dissociation of TT in Ethanol—Water (volume ratio = 2 : 3) and 0.1 M-KCl at Different Temperatures

Temp.	Dissociation constant		Gibbs energy change kJ mol^{-1}		Enthalpy change kJ mol^{-1}		Entropy change J mol^{-1} K^{-1}	
K	pK_{a1}	pK_{a2}	ΔG_1	ΔG_2	ΔH_1	ΔH_2	$-\Delta S_1$	$-\Delta S_2$
298	6.15	9.32	35.09	53.71	24.50	19.96	35.53	113.25
308	6.00	9.20	35.38	54.25			35.32	111.33
318	5.88	9.10	35.80	55.40			35.53	111.45

Table 2. Stepwise Stability Constants for ML and ML$_2$ Complexes of TT in Ethanol—Water (volume ratio = 2 : 3) and 0.1 M-KCl at Different Temperatures

| M^{n+}	298 K		308 K		318 K	
	log $\{K_1\}$	log $\{K_2\}$	log $\{K_1\}$	log $\{K_2\}$	log $\{K_1\}$	log $\{K_2\}$
Mn^{2+}	8.69	4.82	8.85	4.98	9.00	5.12
Co^{2+}	8.83	4.95	8.99	5.12	9.13	5.28
Ni^{2+}	8.96	5.10	9.13	5.26	9.27	5.41
Cu^{2+}	9.10	5.28	9.26	5.45	9.40	5.59
Cd^{2+}	9.24	5.56	9.41	5.72	9.56	5.87
La^{3+}	9.42	5.78	9.58	5.95	9.72	6.10
Hf^{3+}	9.53	5.96	9.70	6.12	9.86	6.26
Zr^{4+}	9.67	6.13	9.84	6.30	10.00	6.44

ii) The metal ion solution used in the present study was very dilute $(2 \times 10^{-5}$ mol dm$^{-3})$, hence there was no possibility of formation of polynuclear complexes [13].

iii) The metal titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves points to the formation of strong metal complexes [14].

iv) In most cases, the colour of the solution after complex formation was observed to be different from the colour of the ligand at the same pH.

v) For the same ligand at constant temperature, the stability of the chelates increases in the order Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, La^{3+}, Hf^{3+}, and Zr^{4+} [15, 16]. This order largely reflects the changes in the heat of complex formation across the series from a combination of the influence of both the polarizing ability of the metal ion [17] and the crystal-field stabilization energies [18].

The dissociation constants (pK_a) for TT as well as the stability constants of its complexes have been evaluated at 298 K, 308 K, and 318 K, and are given in Tables 1 and 2. The enthalpy change (ΔH) for the dissociation and complexation process was calculated from the slope of the plot pK_a or log$\{K\}$ vs. $1/T$ (Figs. 1—3) using the graphical representation of Van't Hoff equation
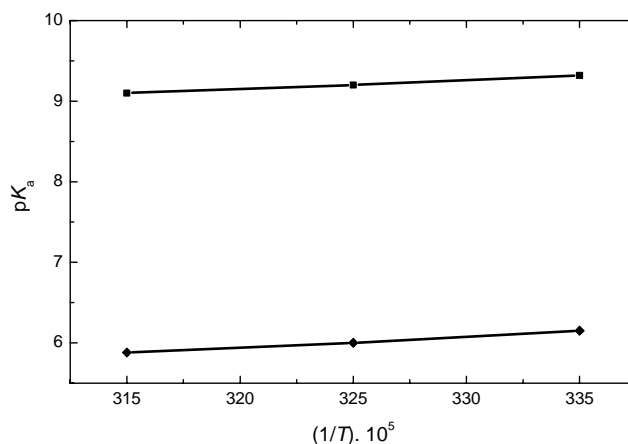
Fig. 1. Van't Hoff plot pK_a of TT against $1/T$: ◆ pK_{a1}, ■ pK_{a2}.

$$-2.303RT \log\{K\} = \Delta H - T\Delta S \qquad (4)$$

or

$$\log\{K\} = (-\Delta H/2.303R)(1/T) + (\Delta S/2.303R) \quad (5)$$

From the Gibbs energy change (ΔG) and (ΔH) values one can deduce the entropy changes (ΔS) using the well known relationships

$$\Delta G = -2.303\,RT \log\{K\} \qquad (6)$$

Table 3. Thermodynamic Functions for ML and ML$_2$ Complexes of TT in Ethanol—Water (volume ratio = 2 : 3) and 0.1 M-KCl

| M^{n+} | Temp. | Gibbs energy change | | Enthalpy change | | Entropy change | |
| | | kJ mol^{-1} | | kJ mol^{-1} | | J mol^{-1} K^{-1} | |
	K	$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
Mn^{2+}	298	49.58	27.50	28.13	27.22	260.77	183.62
	308	52.19	29.36			260.77	183.70
	318	54.79	31.17			260.75	183.61
Co^{2+}	298	50.38	28.24	27.22	29.95	260.40	195.26
	308	53.01	30.19			260.48	195.25
	318	55.59	32.14			260.40	195.25
Ni^{2+}	298	51.12	29.09	28.13	28.13	265.93	192.01
	308	53.84	31.01			266.13	192.01
	318	56.44	32.94			265.94	192.04
Cu^{2+}	298	51.92	30.12	27.22	28.13	265.57	195.46
	308	54.60	32.14			265.64	195.68
	318	57.23	34.03			265.56	195.47
Cd^{2+}	298	52.72	31.72	29.03	28.13	274.32	200.83
	308	55.49	33.73			274.41	200.84
	318	58.20	35.74			274.30	200.84
La^{3+}	298	53.74	32.97	27.22	29.03	271.67	208.05
	308	56.49	35.08			271.78	208.14
	318	59.18	37.14			271.69	208.08
Hf^{3+}	298	54.37	34.01	29.94	27.22	282.91	205.46
	308	57.20	36.09			282.92	205.55
	318	60.03	38.11			282.92	205.44
Zr^{4+}	298	55.17	34.97	29.94	28.13	285.60	211.74
	308	58.02	37.15			285.58	211.94
	318	60.88	39.21			285.59	211.76
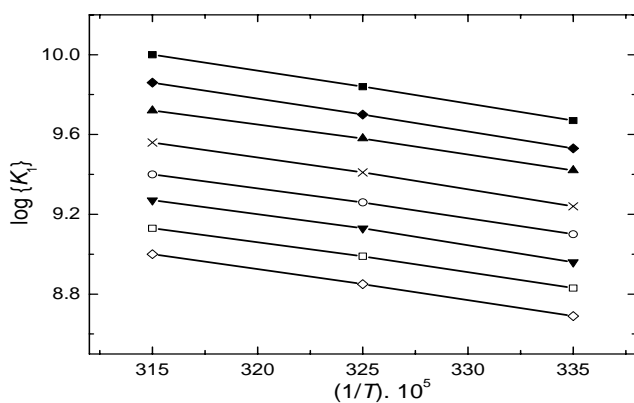
Fig. 2. Van't Hoff plot of log $\{K_1\}$ of M^{n+} complexes with TT against $1/T$: ■ Zr^{4+}, ♦ Hf^{3+}, ▲ La^{3+}, × Cd^{2+}, ○ Cu^{2+}, ▼ Ni^{2+}, □ Co^{2+}, ◇ Mn^{2+}.
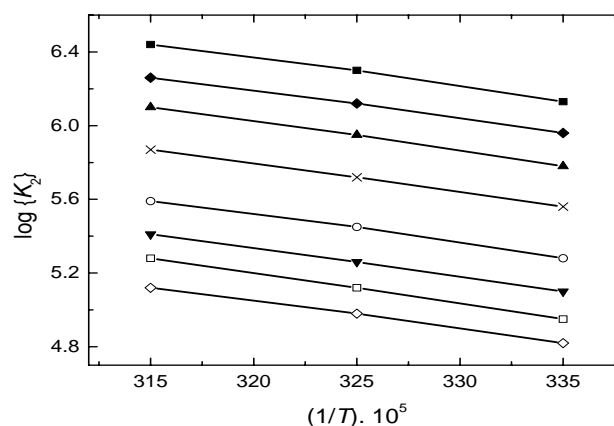
Fig. 3. Van't Hoff plot of log $\{K_2\}$ of M^{n+} complexes with TT against $1/T$: ■ Zr^{4+}, ♦ Hf^{3+}, ▲ La^{3+}, × Cd^{2+}, ○ Cu^{2+}, ▼ Ni^{2+}, □ Co^{2+}, ◇ Mn^{2+}.

$$\Delta S = (\Delta H - \Delta G)/T \qquad (7)$$

where the gas constant $R = 8.314$ J K^{-1} mol^{-1}, K is the dissociation constant for the ligand or the stability constant of the complex, and T absolute temperature.

All thermodynamic parameters of the dissociation process of TT are recorded in Table 1. From these results the following conclusions can be made:

a) The pK_a values decrease with increasing temperature, i.e. the acidity of the ligands increases [6].

b) A positive value of ΔH indicates that the process is endothermic.

c) A large positive value of ΔG indicates that the dissociation process is not spontaneous [19].

d) A negative value of ΔS is obtained due to the increased order as a result of solvation processes.

All the thermodynamic parameters of the stepwise stability constants of complexes are given in Table 3. It is known that the divalent metal ions exist in solution as octahedrally hydrated species [12] and the obtained

values of ΔH and ΔS can then be considered as the sum of two contributions: a) release of H_2O molecules and b) metal—ligand bond formation. Examination of these values shows that:

i) The stepwise stability constants ($\log\{K_1\}$ and $\log\{K_2\}$) for ligand complexes increase with increasing temperature, i.e. their stability constants increase with increasing the temperature [8].

ii) The negative value of ΔG for the complexation process suggests the spontaneous nature of such process [5].

iii) The ΔH values are positive, meaning that these processes are endothermic and favourable at higher temperature.

iv) The ΔS values for the ligand complexes are positive, confirming that the complex formation is entropically favourable [4].

EXPERIMENTAL

2-Thioxothiazolidin-4-one, TT, was used as received from Aldrich. Metal ion solutions ($c = 0.0002$ mol dm^{-3}) were prepared from Analar metal chloride in bidistilled water and standardized with EDTA [20]. The ligand solutions ($c = 0.001$ mol dm^{-3}) were prepared by dissolving the accurate mass of the solid in ethanol (Analar). Solutions of 0.01 M-HCl and 1 M-KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in ethanol—water (volume ratio = 2 : 3) was used as titrant and standardized against oxalic acid (Analar).

The apparatus, general conditions, and methods of calculation were the same as in the previous works [4—8]. The following mixtures i—iii were prepared and titrated potentiometrically at 298 K against standard 0.02 M-NaOH in ethanol—water (volume ratio = 2 : 3):

i) 5 cm^3 0.01 M-HCl + 5 cm^3 1 M-KCl + 20 cm^3 ethanol,

ii) 5 cm^3 0.01 M-HCl + 5 cm^3 1 M-KCl + 15 cm^3 ethanol + 5 cm^3 0.00l M-ligand,

iii) 5 cm^3 0.01 M-HCl + 5 cm^3 l M-KCl + 15 cm^3 ethanol + 5 cm^3 0.001-M ligand + 5 cm^3 0.0002 M-metal salt.

For each mixture, the volume was made up to 50 cm^3 with bidistilled water before the titration. These titrations were repeated for temperatures of 308 K and 318 K. A constant temperature was maintained at $\pm$ 0.05 K by using an ultrathermostat (Neslab 2 RTE 220). The pH measurements were carried out using VWR Scientific Instruments, Model 8000 pH-meter accurate to $\pm$ 0.01 units. The pH-meter readings in ethanol—water (volume ratio = 2 : 3) are corrected according to the Van Uitert and Hass relation [21].

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