

Full Paper

Potentiometric and thermodynamic studies of 2-mercaptobenzothiazole complexes with selected metal ions

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Abstract

The complex-formation of the copper(II), rhenium(V) and nickel(II) metal ions with 2-mercaptobenzothiazole (MBT) have been investigated in 1 M hydrochloric acid. The compositions of complexes were determined, and their stepwise stability constants were calculated at 298, 308 and 318 K. The thermodynamic parameters such as, Gibb's free energy change (ΔG), entropy change (ΔS) and enthalpy change (ΔH) associated with the complexation reactions were calculated and discussed. The dissociation process is non-spontaneous, endothermic and entropically unfavourable. The formation of the metal complexes has been found to be endothermic and entropically favourable.

Keywords: Potentiometry, Stability constant, Thermodynamic parameters.

1. Introduction

Mercapto compounds have several applications in biological, pharmaceutical and other chemical fields and are well known to form complexes with various metals [1, 2]. Gupta and coworker [3, 4] have carried out significant investigation on the electrochemical behavior of several biologically active organo-sulphur compounds and their complexation behavior with metals [5, 6]. The formation of Cu(II) coordination compounds with 1,2,4-triazolethiol in 6 M hydrobromic acid was studied at various temperatures [7]. The

metal ligand stability constants of carboxymethylmercaptosuccinic acid with some transition metals ions have been determined in dioxane-water mixture at ionic strength 0.1 M (KNO_3) at three different temperature (25, 35 and 45 °C) employing Bjerrum-Calvin pH titration technique [8]. The stability of complexes follows the order $Cu(II) > Ni(II) > Mn(II)$. The free energy, enthalpy and entropy changes involved in the complexation have also been evaluated at 35 °C in 40 % (v/v) dioxane-water mixture. Very few studies have been devoted to the

composition and structure of oxocomplexes of Tc(V) and Re(V) with mercaptoamino acids and their derivatives despite a continuous interest in the biological behavior of ^{99m}Tc complexes of cysteine and derivatives [9]. Stability constants of Re(V) metal complexes with selected medicinal drugs adenosine, isoniazid and metformin hydrochloride have been determined using a pH metric titration technique in aqueous hydrochloric acid media at different temperature (293, 303, 313 and 323 K) and an ionic strength of 0.2 M [10]. The process of complex formation of Re(V) ion and 2-mercapto-pyridine was investigated potentiometrically by evaluating the formation equilibrium, stability constants of the metal complex at a temperature range of 273-338 K [11]. These formation constants are used to derive the proportions of the various complex forms as a function of equilibrium ligand concentration. A new Re(V), Re(III) and Zn(II) complexes $[\text{ReOCl}_2(\text{L})]$, $[\text{ReO}(\text{L})_2]\text{Cl}$ and $[\text{ZnCl}_2(\text{HL})]$ (where; HL = 2-formylpyridine-N-(4-phenylthiosemicarbazone) have been synthesized and characterized [12]. The compounds of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ and $[\text{ReO}_4]^-$ in the presence of PPh_3 have been used as a starting material to prepare Re(V) and Re(III) complexes, while ZnCl_2 is used to prepare the zinc complex. Recently, profound solution studies of the Re(V) penicillamine complex have been described including the observation that the NH deprotonation does not occur in this system up to a very high pH value [13, 14].

The objective of this investigation was the following: (i) the potentiometric determination of the stability constant of MBT complexes with Cu(II), Re(V) and Ni(II) at various temperatures, (ii) the corresponding thermodynamic parameters were derived and discussed.

2. Experimental

2.1. Reagents and materials

All the chemicals used for experiment, such as copper chloride, nickel chloride, potassium iodide etc were of analytical grade and 2-mercaptobenzothiazole (Sigma Aldrich) was commercial product and used as such, double distilled water was used in preparation of various solutions. Metal ion solution of Re(V), (K_2ReOCl_5) was prepared as mentioned elsewhere [15]. The concentration of metal ion in the solution was determined spectrophotometrically at wavelength (λ) of 480 nm [15].

2.2. Potentiometric measurements

Potentiometric titration was performed using a R3003 voltage comparator. A platinum plate was used as an indicator electrode. The redox system consisting of MBT and its oxidized form was created by oxidizing a small portion of initial MBT in 1 M hydrochloric acid with a 0.5 ml (0.1 N) iodine solution. The stepwise complexation of Cu(II), Re(V) and Ni(II), with MBT was studied using the Bjerrum method [16, 17]. For this purpose, the redox system consisting of MBT (0.0055 mole/l) and its oxidized form was titrated with a 0.00259 metal ions solution in 1 M hydrochloric acid. The equilibrium ligand concentration and the formation function at each titration point were calculated by the equations (1, 2):

$$\log[L] = \frac{E_I - E_i}{1.9837 \cdot 10^{-4} T} + \log C_L^I + \frac{1}{2} \log \frac{V_I}{V_T} \quad (1)$$

$$\bar{n} = \frac{C_L - [L]}{C_M} \quad (2)$$

where E_I is the initial equilibrium potential of the system in the absence of metal ions, E_i is the equilibrium potential of the system at a current titration point, C_L^I is the initial concentration of MBT, V_I/V_T is the ratio of the initial volume to the total volume, and T is the temperature of an experiment in K. The \bar{n}

is the degree of formation; The [L] is the equilibrium concentration of MBT at the titration and the C_M is the concentration of metal ions at each point of the titration. The stepwise stability constants were calculated at 298, 308 and 318 K.

2.3. Determination of the thermodynamic parameters

The decomposition of stability constants into their enthalpic (ΔH), Gibb's free energy change (ΔG) and entropic (ΔS) contributions is of fundamental importance to the understanding of the various factors (electronic and steric effects, solute-solvent interactions, etc) that may influence coordination [18, 19]. Enthalpy changes due to coordination reactions can always be obtained from the determination of stability constants at different temperatures according to the van't Hoff [20, 21] relationship (3, 4):

$$\Delta G = -2.303 RT \log K_i \quad (3)$$

$$\log K_i = \left(\frac{-\Delta H}{2.303R} \right) \left(\frac{1}{T} \right) + \left(\frac{\Delta S}{2.303R} \right) \quad (4)$$

where R is ideal gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), K_i is the stability constant of the complex and T is the absolute temperature in Kelvin (K). The change in enthalpy (ΔH) is calculated by plotting $\log K_i$ against $1/T$. The equation utilized for the calculation of changes in enthalpy (ΔH) is as (5):

$$\text{Slope} = -\Delta H / 2.303 R \quad (5)$$

The evaluation of changes in entropy (ΔS) is done by the following equation (6):

$$\Delta S = (\Delta H - \Delta G) / T \quad (6)$$

3. Results and discussion

3.1. Potentiometric titration

The results obtained were analyzed by an Excel program using titration data and then stability constant values were calculated [22]. The experimental data show that the equilibrium potential of the redox system increases in the process of potentiometric titration as the metal ions volume added to a titrated solution increases. During the titration no precipitates were formed indicating that there is no tendency to form hydroxo complexes [23]. The formation curves for selected metal ions with MBT in 1 M hydrochloric acid at various temperatures are plotted in Figs. 1-3.

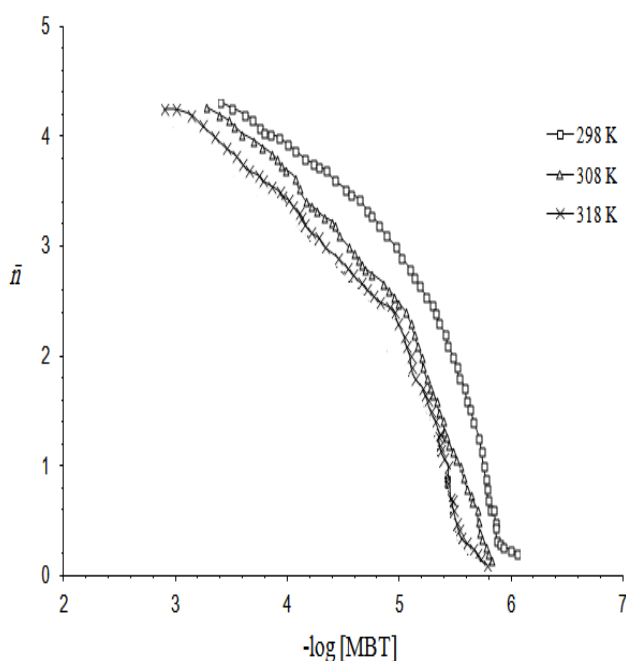


Fig. 1: Formation curves of Cu(II) with MBT complexes in 1 M HCl at various temperatures.

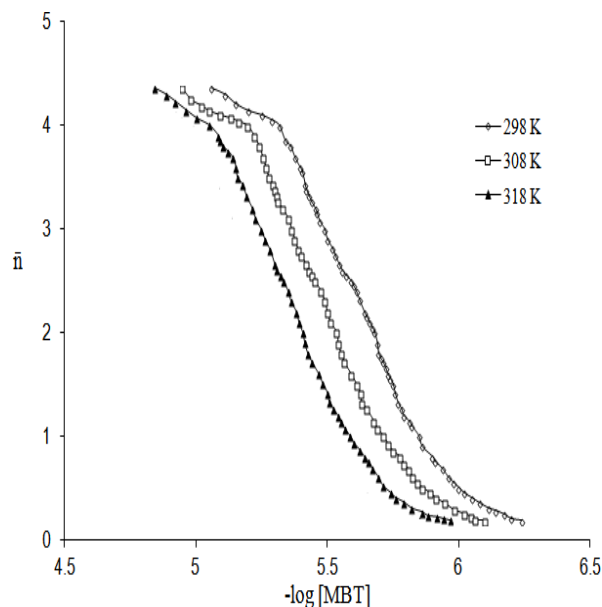


Fig. 2: Formation curves of Re(V) with MBT complexes in 1 M HCl at various temperatures.

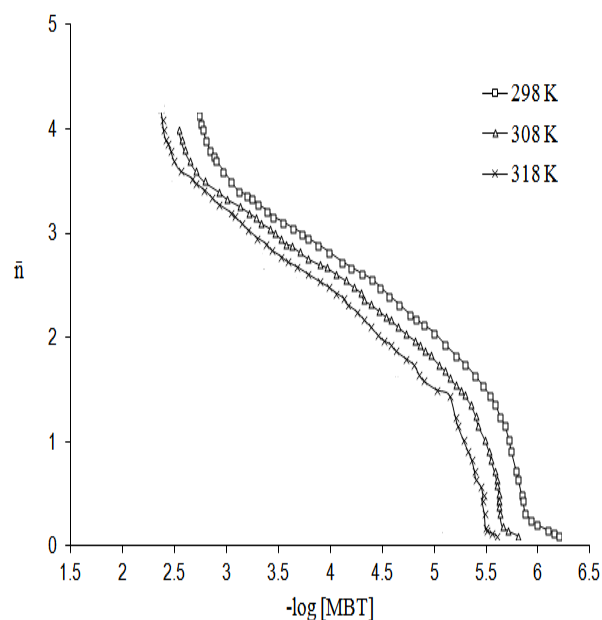


Fig. 3: Formation curves of Ni(II) with MBT complexes in 1 M HCl at various temperatures.

Available overall stability constants for the formation of MBT metal complexes are reported in Table 1-3. Some of these deserve some comments. We used the formation curves to find approximate numerical values of stepwise constants at 298-318 K. Since the formation constants were found graphically,

they were refined via data processing by solving the following equation [24] (7):

$$\bar{n} = \frac{\beta_1[L] + 2\beta_2[L]^2 + 3\beta_3[L]^3 + 4\beta_4[L]^4}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \beta_4[L]^4} \quad (7)$$

where β is the overall stability constant and $[L]$ is the equilibrium ligand concentration. To solve this equation, we have developed a program in the Borland Delphi environment [24]. The equilibrium ligand concentration was found for all from 0.1 to 4.2 (Table 1). The comparison of the data of Table 1 show that the trend in the refined stepwise constants slightly differs from their trend before refinement. However, the trend of the constants to decrease with an increase in either temperature or number of ligand molecules is retained after refinement [25].

Table 1: Stepwise stability constants of complexes of Cu(II) with MBT in the presence of 1 M HCl

Complex species (Cu(II) : MBT)	log K_i	Temperature, K		
		298	308	318
(1 : 1)	log K_1	5.86 (5.90)*	5.71 (5.75)	5.45 (5.47)
(1 : 2)	log K_2	5.63 (5.65)	5.48 (5.51)	5.20 (5.24)
(1 : 3)	log K_3	5.27 (5.31)	5.04 (5.08)	4.85 (4.97)
(1 : 4)	log K_4	4.56 (4.57)	4.14 (4.16)	3.91 (3.93)

* The values of stepwise constants by solving the equation [24]

Table 2: Stepwise stability constants of complexes of Re(V) with MBT in the presence of 1 M HCl

Complex species (Re(V) : MBT)	log K_i	Temperature, K		
		298	308	318
(1 : 1)	log K_1	6.01	5.86	5.73
(1 : 2)	log K_2	5.74	5.61	5.49
(1 : 3)	log K_3	5.58	5.46	5.34
(1 : 4)	log K_4	5.41	5.28	5.05

Table 3: Stepwise stability constants of complexes of Ni(II) with MBT in the presence of 1 M HCl

Complex species (Ni(II) : MBT)	log K_i	Temperature, K		
		298	308	318
(1 : 1)	log K_1	5.84	5.61	5.47
(1 : 2)	log K_2	5.50	5.24	5.01
(1 : 3)	log K_3	4.46	4.22	3.96
(1 : 4)	log K_4	3.03	2.81	2.64

It is known that the Re(V) metal ion exists in solution as octahedral specie [26]. Re (V)-ligand stability constants log K_i for 1:1, 1:2, 1:3 and 1:4 complexes respectively are summarized in Table 2 in the presence of 1 M hydrochloric. There is no such appreciable difference between the log K_i values at a same temperature (Table 2). The order of log $K_1 > \log K_2 > \log K_3 > \log K_4$ is observed. The reason is statistically effective, statistically coordination of a second molecule is difficult when compare to the first due to availability of less number of coordinating sites on the metal ion for the second ligand. From the data of Tables 1-3 it can be seen that an increase in temperature from 298 to 318 K decreases the stability constants of the metal ion complexes. These values shows that less temperature is favorable for the formation of stable complexes and follow the order Re(V) > Cu(II) > Ni(II). The maximum \bar{n} value in all cases were found to be ≈ 4 , revealing that M(MBT), M(MBT)₂, M(MBT)₃ and M(MBT)₄ types of complexes are formed in solution. No precipitate was observed in the titration vessel, indicating that the possibility of metal hydroxide formation is excluded [27, 28]. The order reflects the changes in the heat of complex formation across the series and arise from combination of the influence of both polarizing ability of the metal ion and crystal-field stabilization energies [29]. The stability constant of the pentavalent cation complex is higher than the other divalent and

tetravalent cation complexes [30]. This may be attributed to the bonded oxygen atoms, which may increase the electrostatic attraction between the metal ion and the coordinated ligands and overcome any steric hindrance offered by the oxygen of the oxygenated cation [31].

3.2. The distribution diagrams

The distribution diagrams were drawn in the titration where the metal to ligand mole ratio was 1:4. They were obtained with the aid of SPE program [32] and the concentration of total metal ion presents 5.5×10^{-3} M set at 100 %. In Figure 4, the species $[\text{Ni}(\text{MBT})_3(\text{H}_2\text{O})_3]^{2-}$ (X_3) for the system MBT and metal ion Ni(II) reaches a maximum of 69 %. The second species $[\text{Ni}(\text{MBT})_2(\text{H}_2\text{O})_4]^{2-}$ (X_2) reaches a maximum of 61 %, and the $[\text{Ni}(\text{MBT})(\text{H}_2\text{O})_5]^{2-}$ (X_1) complex species reaches a maximum of 47 %. The analysis of the temperature-dependent distribution function shows that the yield of the complexes decreases with increasing temperature. The analysis of the distribution curves provides the possibility to elucidate the predominance region for some complex depending on temperature and concentration. These data were used to develop optimal methods for the preparation of Ni(II) complexes with MBT in 1 M hydrochloric acid.

3.3. Thermodynamic functions

The values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complex reactions have been determined at 298, 308 and 318 K with the help of van't Hoff equation. The slope of the plot (log K_i vs. $1/T$) was applied to evaluate the enthalpy change (ΔH) for the dissociation or complexation process, respectively (Fig. 5). The values of ΔG , ΔH and ΔS in 1 M hydrochloric acid are given in Tables 4-6.

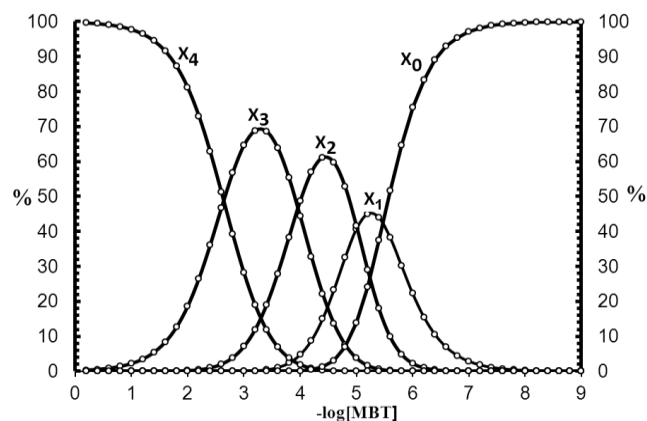


Fig. 4: Species distribution curves of the metal ion Ni(II) and the MBT as a function of $-\log [\text{MBT}]$ in 1M HCl at 318 K for a solution initially containing 5.5×10^{-3} M Ni(II) ion and 2.59×10^{-3} M MBT.

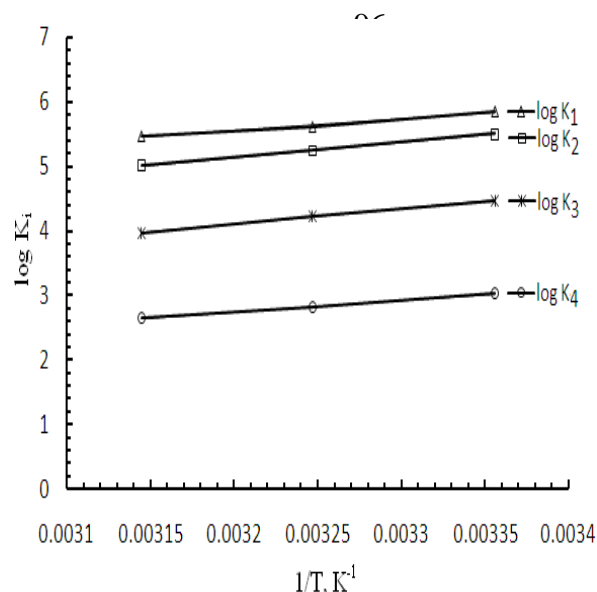


Fig. 5: Vant Hoff plot of $\log K_i$ of Ni(II) complexes with MBT against $1/T$.

Table 4: Thermodynamic parameter ΔG , ΔH and ΔS of Cu(II) complexes with MBT 1 M HCl

T (K)	$-\Delta G$ (kJ.mol ⁻¹)				$-\Delta H$ (kJ.mol ⁻¹)				ΔS (J.mol ⁻¹ .K ⁻¹)			
	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔS_1	ΔS_2	ΔS_3	ΔS_4
298	33.4	76.5	76.5	66.2					5.8	153.4	128.8	23.7
308	33.7	80.1	73.7	60.5	31.7	30.8	38.1	59.1	6.4	160.2	115.5	4.5
318	33.6	77.1	70.7	56.9					5.8	145.5	102.3	-6.8

Table 5: Thermodynamic parameter ΔG , ΔH and ΔS of Re(V) complexes with MBT 1 M HCl

T (K)	$-\Delta G$ (kJ.mol ⁻¹)				$-\Delta H$ (kJ.mol ⁻¹)				ΔS (J.mol ⁻¹ .K ⁻¹)			
	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔS_1	ΔS_2	ΔS_3	ΔS_4
298	34.3	83.1	83.1	80.6					29.8	202.7	205.8	197.2
308	34.6	84.2	81.9	79.2	25.4	22.7	21.7	21.8	29.7	199.7	195.4	186.6
318	34.9	83.2	80.9	78.3					29.8	190.3	186.0	177.8

Table 6: Thermodynamic parameter ΔG , ΔH and ΔS of Ni(II) complexes with MBT 1 M HCl

T (K)	$-\Delta G$ (kJ.mol ⁻¹)				$-\Delta H$ (kJ.mol ⁻¹)				ΔS (J.mol ⁻¹ .K ⁻¹)			
	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔS_1	ΔS_2	ΔS_3	ΔS_4
298	33.3	64.5	64.5	43.8					-1.1	67.4	64.5	28.3
308	33.1	75.3	60.6	40.3	33.6	44.4	45.3	35.4	-1.8	100.1	49.7	16.1
318	33.3	72.4	57.3	38.2					-1.1	88.0	37.6	8.7

It is known that the di and pentavalent metal ions exist in solution as octahedrally hydrated species and the values of ΔH and ΔS can then be considered as a sum of two contributions: (a) release of H_2O molecules, and (b) metal-ligand bond formation. Examination of these values shows that: (i) The negative values of ΔG for the complexation process of Cu(II), Re(V) and Ni(II) with MBT suggest a spontaneous nature of such process [33]; (ii) ΔH values are negative in the case of Cu(II), Re(V) and Ni(II). This means that these processes are favourable at lower temperatures, the metal-ligand binding process is enthalpy driven and metal-ligand bonds are fairly strong [34]; (iii) The positive values of ΔS for the complexation process of MBT with Cu(II) and Re(V). Confirm that the complex formation is entropically favourable [35]. The negative change in entropy (ΔS) values indicated a highly solvated metal complex and indicated that the formation of these complexes was entropy favored.

4. Conclusion

The less difference between $\log K_i$ values indicates the complex formation between Cu(II), Re(V) and Ni(II) metal ions and MBT occurring simultaneously. The maximum value of \bar{n} was 4 indicating these metal ions forms 1:1, 1:2, 1:3 and 1:4 complexes with MBT. The metal ions solution used in the present study were very dilute (5.5×10^{-3} M), hence there was no possibility of formation of polynuclear complexes or hydrolysis of the metal ions. In most cases, the colour of the solution after complex formation was observed to be different from the colour of the ligand before beginning the titration. For the same ligand at constant temperature, the stability of the chelates increases in Re(V)-MBT than Cu(II)-MBT and Ni(II)-MBT complexes. 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 and the crystal-field stabilization energies. The negative values of change in enthalpy (ΔH) for the complexation suggest that all the complexation reactions are exothermic, favorable at lower temperature. The negative change in free energy (ΔG) values indicates that both dissociation of the ligand and the complexation process are spontaneous.

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