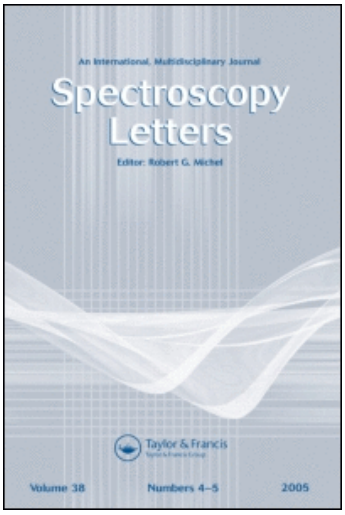

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Thermodynamics of Substituted Rhodanine IV: Potentiometric Studies of 3-(P-Tolylsulphonamido)Rhodanine Transition Metal Complexes

M. M. Ghoneim[a]; A. A. El-bindary[b]; A. Z. El-Sonbati[b]; S. A. Barakat[b]
[a] Chemistry Department, Faculty of Science, Tanta University, Egypt [b] Chemistry Department, Faculty of Science (Demiatta), Mansoura University, Demiatta, Egypt

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Thermodynamics of substituted rhodanine IV: Potentiometric studies of 3-(p-Tolylsulphonamido)rhodanine Transition Metal Complexes.

Keywords. 3-(p-Tolylsulphonamido)rhodanine, Dissociation and stability constants; Thermodynamic parameters, and stoichiometries.

M.M. Ghoneim[a], A.A. El-Bindary[b], A.Z. El-Sonbati[b] and S.A. Barakat[b].

[a] Chemistry Department, Faculty of Science, Tanta University, Egypt.

[b] Chemistry Department, Faculty of Science (Demiatta), Mansoura University, Demiatta , Egypt.

Abstract

Proton-ligand dissociation and metal-ligand stability constants of 3-(p-Tolylsulphonamido)rhodanine (TSR) with some transition metal ions were calculated potentiometrically in 0.1 M KCl and 20% (v/v) ethanol-water mixture. The order of stability constants was found to be:

$$Th^{4+} > UO_2^{2+} > Gd^{3+} > Ce^{3+} > La^{3+} > Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

The dissociation constants pK^{H} of TSR and the stability constants $\log K$ of their complexes were determined at different temperatures (303, 308 and 318 K). The corresponding thermodynamic parameters (ΔG, ΔH and ΔS) were derived and discussed. The dissociation process is non-spontaneous, endothermic and entropically unfavourable. The formation of the metal

complexes have been found to be spontaneous, exothermic or endothermic (depend on the metal) and entropically favourable. The stoichiometries of these complexes were determined spectrophotometrically and indicated the formation of 1:1 and 1:2 (metal:ligand) complexes.

INTRODUCTION

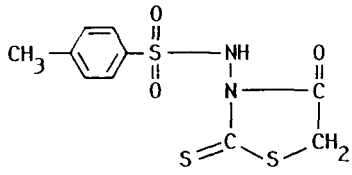
The importance of metal ions in biological process has been cited [1]. Sulphonamides constitute a class of drugs which are frequently used in pharmaceutical preparations, especially in veterinary practice [2]. Many sulphonamide drugs are prescribed as sodium salts [3], the acidic hydrogen in the sulphonamide group (SO_2NH) being displaced to give a water soluble drug. Rhodanine and its derivatives are known to play an important role in biological reactions [4,5], e.g., in the inhibition of mycobacterium tuberculosis [6]. The carbonyl oxygen of the rhodanine moiety constituents chelating backbone in most complexes and allowing the formation of enol form with displacement of a proton in the solution. In continuation of our earlier work [7-10], the objective of this investigation is to assess the following : (i) the dissociation constants of TSR at different temperatures are determined potentiometrically; (ii) moreover, the stability constant of TSR complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Gd^{3+}, UO_2^{2+} and Th^{4+} are determined; (iii) the corresponding thermodynamic parameters are derived and discussed; (iv) the stoichiometeries of these complexes are determined by molar-ratio and continuous variation methods.

EXPERIMENTAL

Preparation of the ligand

3-(p-Tolylsulphonamido)rhodanine (TSR) was prepared according to the method [11]. The purity (m.p. 159°C) was checked by elemental analysis (found: C 39.80,

H 3.40, N 9.40; calcd.: C 39.72, H 3.33, N 9.27), IR and ^{1}HNMR spectra.



Reagents and Materials

Metal ion solutions (0.001 M) were prepared from AnalaR metal salt samples (BDH) in bi-distilled water and standardized with EDTA [12]. The ligand solution (0.01M) was prepared by dissolving the accurate weight of the solid in ethanol (AnalaR). Solutions of 0.005 M KCl and 1 M KCl were also prepared in bi-distilled water. A carbonate-free sodium hydroxide solution in 20% (v/v) ethanol-water mixture was used as titrant and standardized against AnalaR oxalic acid.

Potentiometric Measurements

The apparatus, general conditions and methods of calculation were the same as in the previous work [7,8]. The following mixtures were prepared and titrated potentiometrically at 303 K against standard 0.02 M NaOH in 20% (v/v) ethanol-water mixture:

1- 5 ml 0.005 M HCl + 5 ml 1 M KCl + 10 ml ethanol.

2- 5 ml 0.005 M HCl + 5 ml 1 M KCl + 5 ml ethanol + 5 ml 0.01 M ligand.

3- 5 ml 0.005 M HCl + 5 ml 1 M KCl + 5 ml ethanol + 5 ml 0.01 M ligand + 10 ml 0.001 M metal salt.

For each mixture the volume was made up to 50 ml with bi-distilled water before the titration. These titrations were repeated for temperatures of 308 and 318 K. A constant temperature was adjusted to ±0.05 K by using an ultrathermostate (Gallenkamp thermo stirrer 85). The pH-meter readings

in 20% (v/v) ethanol-water mixture are corrected according to the Van Uitert and Hass relation [13].

Spectrophotometric Measurements

The absorption spectra were recorded in the wavelength range 200-400 nm on a Perkin-Elmer (Lambda 2) spectrometer with a thermostatted cell-holder using 1 cm matched silica cells.

RESULTS AND DISCUSSION

Potentiometric Studies

Proton-Ligand Stability Constants

The average number of protons associated with the TSR at different pH values, $\bar{n}_A$, was calculated from the titration curves of acid in the absence and presence of TSR. Thus, the formation curves ($\bar{n}_A$ vs. pH) for the proton-ligand systems were constructed and found to extend between 0 and 2 in the $\bar{n}_A$ scale. This means that TSR has two dissociable protons (the enolized hydrogen ion of the carbonyl oxygen in the rhodanine moiety and the sulphonamide proton SO_2NH). Different computational methods [14] were applied to evaluate the stepwise dissociation constants. The average values obtained are listed in Table 1.

The TSR has a lower acidic character (higher pK^H value) than 3-Phenylsulphonamidorhodanine[8]. This is quite reasonable because the presence of p-CH_3 group will enhance the electron density by their high positive mesomeric and positive inductive effects, respectively, whereby stronger N-H and O-H bonds are formed. Therefore, the electron-repelling properties of the methyl group retard the removal of the ligand protons and hence increase the basicity of the ligand[15].

Table (1) : Potentiometric thermodynamic functions for the dissociation of TSR in 20 % (v/v) ethanol-water mixture and 0.1 M KCl at different temperatures.

Temp. (K)	Dissociation Constant [a]		Free Energy Change (k J mol^{-1})			Enthalpy Change (k J mol^{-1})			Entropy change (J mol^{-1} k^{-1})		
	$p k_1^{II}$	$p k_2^{II}$	ΔG_1	ΔG_2	ΔG_β	ΔH_1	ΔH_2	ΔH_β	$-\Delta S_1$	$-\Delta S_2$	$-\Delta S_\beta$
303	4.51	9.41	26.17	54.59	80.76						
308	4.46	9.32	26.3	54.96	81.26	18.38	27.57	45.95	25.5±0.5	89.0	114.5±0.5
318	4.34	9.17	26.43	55.83	82.26						

[a] ±(0.03-0.05)

Metal-Ligand Stability Constants

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion ($\bar{n}$) versus the free ligand exponent (pL), according to Irving and Rossotti [16]. These curves were analyzed and the successive stability constants were determined using different computational methods [17,18]. The values of stability constants ($\log K_1$, $\log K_2$ and $\log \beta$) as well as the ratio $\log K_1/\log K_2$ are given in Table 2. The following general remarks can be pointed out:

(i) The maximum $\bar{n}$ values in all cases were found to be ≈2, revealing that both ML and ML_2 types of complexes are formed in solution.

(ii) No precipitate was observed in the titration vessel, indicating that the possibility of formation of metal hydroxide is excluded.

(iii) For all complexes formed, because the vacant sites of the metal ions move freely available for the binding of a first ligand than for a second one.

(iv) the order of stability constants of the metal complexes of TSR was found to be

$$Th^{4+} > UO_2^{2+} > Gd^{3+} > Ce^{3+} > La^{3+} > Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

The sequence of stability ($Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$) of the complexes of TSR are in agreement with that found by Irving and Williams [19, 20]. The order largely reflect 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 [21] and crystal-field stabilization energies [22]. The greater stability of Cu^{2+} complexes is produced by the well known Jahn-Teller effect. The stability constant of the divalent oxygenated cation complex (UO_2^{2+}) has higher value than the other divalent

cation complexes (Table 2). 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[23]. The higher values of the stability constants of Th^{4+} complexes compared to that of the other divalent metal complexes is expected in the bases of charge and ionization potential of Th^{4+} ion[8].

Effect of Temperature

The dissociation constants (pK_1^H and pK_2^H) for TSR as well as the stability constants of its complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Gd^{3+}, UO_2^{2+} and Th^{4+} have been evaluated at 303, 308 and 318 K, and are given in Tables 1 and 2. The slope of the plot (pK^H or log K vs. $1/T$) was utilized to evaluate the enthalpy change (ΔH) for the dissociation or complexation process, respectively. From the free energy change (ΔG) and (ΔH) values one can deduce the entropy change (ΔS) using the well known relationships (1) and (2):

$$\Delta G = -2.303\ RT \log K = 2.303\ RT\ pK \quad \text{..... (1)}$$

$$\Delta S = (\Delta H - \Delta G)/T \quad \text{..... (2)}$$

All thermodynamic parameters of the dissociation process of TSR are recorded in Table 1. Inspection of these values reveals that:

(i) The stepwise pK^H values decreases with increasing temperature revealing that its acidity increases with increasing temperature.

(ii) A positive value of ΔH indicating that its dissociation is accompanied by adsorption of heat and the process is endothermic.

Table (2) : Stepwise stability constants for ML and ML_2 complexes of TSR in 20 % (v/v) ethanol-water mixture and 0.1 M KCl at different temperatures.

M^{n+}	303 K				308 K				318 K			
	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/\log K_2$	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/\log K_2$	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/\log K_2$
Mn^{2+}	6.66	5.60	12.26	1.19	6.50	5.19	11.69	1.25	5.79	4.78	10.57	1.21
Co^{2+}	7.58	5.68	13.26	1.33	7.18	5.64	12.82	1.27	6.78	5.60	12.38	1.21
Ni^{2+}	7.25	4.20	11.45	1.73	7.44	4.69	12.13	1.59	7.62	5.17	12.79	1.47
Cu^{2+}	10.35	6.44	16.79	1.6	10.10	6.36	16.46	1.59	9.8	6.28	16.08	1.56
Zn^{2+}	7.90	4.70	12.60	1.68	7.39	4.53	11.92	1.63	6.88	4.36	11.24	1.58
La^{3+}	7.90	7.22	15.12	1.09	7.48	7.00	14.48	1.07	7.30	6.95	14.25	1.05
Ce^{3+}	8.00	7.63	15.63	1.05	7.88	7.33	15.21	1.08	7.28	7.15	14.43	1.02
Gd^{3+}	7.62	7.14	14.76	1.07	7.42	7.07	14.49	1.05	7.22	7.00	14.22	1.03
UO_2^{2+}	8.65	7.60	16.25	1.14	8.36	7.53	15.89	1.11	8.00	7.30	15.3	1.10
Th^{4+}	10.58	8.48	19.06	1.25	10.90	9.10	20	1.20	11.08	9.32	20.4	1.19

(iii) A large positive value of ΔG indicating that the dissociation process is not spontaneous.

(iv) A negative value of ΔS is obtained, due to increased order as a result of solvation processes.

All the thermodynamic parameters of the stepwise stability constants of TSR complexes are recorded in Table 3. It is known that the divalent metal ions exist in solution as octahedrally hydrated species and the obtained values of ΔH and ΔS can then be considered as sum of two contributions:

(a) release of H_2O molecules, and

(b) metal-ligand bond formation.

It was suggested [24] that the ions in aqueous solution, order the water molecules around them and during complex formation between oppositely charged ions (ligand L^{2-} and M^{n+}) will lead to the breakdown of metal-water arrangement resulting in positive entropy and enthalpy changes. Examination of these values shows that:

(i) The stepwise stability constants ($\log K_1$ and $\log K_2$) for TSR complexes decreases with increasing temperature in the case of Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Gd^{3+} and UO_2^{2+} whereas in the case of Ni^{2+} and Th^{4+} the reverse happens, i.e., its stability constants increase with increasing the temperature.

(ii) The negative values of ΔG for the complexation process of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Gd^{3+}, UO_2^{2+} and Th^{4+} with TSR suggests a spontaneous nature of such process.

Table (3) : Thermodynamic functions for ML and ML_2 complexes of TSR in 20 % (v/v) ethanol-water mixture and 0.1 M KCl.

M^{n+}	Tmp. (K)	Free Energy Change (k J mol^{-1})			Enthalpy Change (k J mol^{-1})			Entropy change (J mol^{-1} k^{-1})		
		$-\Delta G_1$	$-\Delta G_2$	$-\Delta G_\beta$	ΔH_1	ΔH_2	ΔH_β	ΔS_1	ΔS_2	ΔS_β
Mn^{2+}	303	38.64	32.49	71.13	-111.05	-94.2	-205.25	-238	-205	-443
	308	38.33	30.61	68.94				(±1.5)	(±1.5)	(±1.5)
	318	35.25	29.1	64.35						
Co^{2+}	303	43.98	32.95	76.93	-95.35	-7.66	-102.63		83.5	-83.5
	308	42.34	33.26	75.60					(±0.5)	±(0.5)
	318	41.28	34.10	75.38						
Ni^{2+}	303	42.06	24.37	66.43	47.29	84.82	132.11	295.5	364	659.5
	308	43.88	27.66	71.54				(±0.5)	(±2)	±(0.5-2)
	318	46.40	31.48	77.88						
Cu^{2+}	303	60.06	37.36	97.41	-52.65	-25.66	-78.31	23	39	62
	308	59.56	37.51	97.07				(±1)	(±1)	(±1)
	318	59.67	38.24	97.91						
Zn^{2+}	303	45.83	27.27	73.10	125.03	-39.06	-164.09	-262.5	-39.5	-302
	308	43.58	26.71	70.29				(±1.5)	(±0.5)	±(0.5-1.5)
	318	41.90	26.55	68.45						
La^{3+}	303	45.83	41.89	87.72	-68.55	-34.46	-89.03		23.5	23.5
	308	44.11	41.28	85.39					(±1.5)	±(1.5)
	318	44.45	42.32	86.77						

Ce^{3+}	303	46.41	44.27	90.68	-91.91	-61.27	-153.18	-149.5 (±0.5)	-57.5 (±1.5)	-207 ±(0.5-1.5)
	308	46.47	43.23	89.7						
	318	44.33	43.53	87.86						
Gd^{3+}	303	44.21	41.42	85.63	-47.68	-17.81	-65.49		78	78
	308	43.76	41.69	85.45						
	318	43.96	42.62	86.58						
UO_2^{2+}	303	50.18	44.1	94.28	-113.4	-38.29	-151.69		19.5 (±0.5)	-19.5 ±(0.5)
	308	19.3	44.41	93.71						
	318	48.71	44.45	93.16						
Th^{4+}	303	61.38	49.20	110.58	63.76	107.22	170.98	414.5 (±1.5)	519 (±3)	933 ±(1.5-3)
	308	64.28	53.67	117.95						
	318	67.46	56.75	124.21						

Error is given between parentheses.

Table (4) : Stoichiometry of M^{n+}-TSR complexes in 20% (v/v) ethanol-water mixture by Molar Ratio (M.R.) and Continous Variation (C.V.) methods at 298 K.

Metal	pH	λ_{max} nm	M.R.		C.V.	
Mn^{2+}	9	380	1:1	1:2	-	1:2
Co^{2+}	9	380	1:1	1:2	1:1	-
Ni^{2+}	9	360	1:1	1:2	1:1	-
Cu^{2+}	9	360	1:1	1:2	1:1	-
Zn^{2+}	9	370	1:1	1:2	-	1:2
La^{3+}	9	365	1:1	1:2	-	1:2
Ce^{3+}	7	320	1:1	1:2	-	1:2
UO_2^{2+}	9	320	1:1	1:2	-	1:2

(iii) The ΔH values are negative in the case of Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Gd^{3+} and UO_2^{2+} whereas in the case of Ni^{2+} and Th^{4+} are positive. This means that these processes are exothermic and favourable at lower temperatures for Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Gd^{3+} and UO_2^{2+} complexes, while in the case of Ni^{2+} and Th^{4+} complexes the process are endothermic and favourable at higher temperature.

(iv) The positive values of ΔS for the complexation process of TSR with Co^{2+}, Ni^{2+}, Cu^{2+}, La^{3+}, Gd^{3+}, UO_2^{2+} and Th^{4+} confirming that the complex formation is entropically favourable. In contrary, the Mn^{2+}, Zn^{2+} and Ce^{3+} complexes have negative values of ΔS. Such negative entropy change can be attributed to the extensive solvation of metal chelates in

aqueous-ethanol medium. This may be due to the exposure of the polar oxygen, nitrogen and metal ion of the chelate to solvent molecules [25].

Spectrophotometric studies

Stoichiometries

Stoichiometries of the complexes of TSR with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+} and UO_2^{2+} result from the measurements in the range 200-400 nm at the optimum pH values. These studies were carried out to investigate the stoichiometries of the formed complexes at the characteristic absorption maximum from the molar ratio [26] and continuous variation [27] methods. Both methods indicated the formation of 1:1 and 1:2 (metal:ligand) complexes (Table 4).

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