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Thermodynamics of Substituted Rhodanine III: Potentiometric and Spectrophotometric Studies of Complexes of Some Transition Metals with 3-Phenylsulfonamidorhodanine

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Summary. The dissociation constants of 3-phenylsulfonamidorhodanine (*PSR*) were determined potentiometrically in 0.1 *M* KCl and 20% (v/v) ethanol-water. The stepwise stability constants of the complexes of $Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Gd^{3+}, UO_2^{2+}$, and Th^{4+} with *PSR* were determined. The stabilities of the complexes were found as follows: $Th^{4+} > UO_2^{2+} > Gd^{3+} > Ce^{3+} > La^{3+} > Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. The thermodynamic parameters for *PSR* and its complexes were evaluated and discussed. The dissociation process is non-spontaneous, endothermic, and entropically unfavourable. The formation of the complexes was found to be spontaneous, exothermic or endothermic (depending on the metal), and entropically favourable. The stoichiometries of the complexes were determined spectrophotometrically and indicate the formation of 1:1 and 1:2 (metal:ligand) complexes.

Keywords. 3-Phenylsulfonamidorhodanine; Dissociation; Stability constants; Thermodynamic parameters.

Thermodynamik von substituiertem Rhodanin III: Potentiometrische und spektrophotometrische Untersuchungen der Komplexe einiger Übergangsmetalle mit 3-Phenylsulfonamidorhodanin

Zusammenfassung. Die Dissoziationskonstanten von 3-Phenylsulfonamidorhodanin (*PSR*) in 0.1 *M* KCl und 60% (v/v) Ethanol-Wasser wurden potentiometrisch ermittelt. Die stufenweisen Stabilitätskonstanten seiner Komplexe mit $Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Gd^{3+}, UO^{2+}$ und Th^{4+} wurden bestimmt. Die Stabilitätsreihenfolge lautet $Th^{4+} > UO^{2+} > Gd^{3+} > La^{3+} > Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. Die thermodynamischen Parameter von *PSR* und seinen Komplexen werden diskutiert. Der Dissoziationsprozeß verläuft nicht-spontan, endotherm und entropisch ungünstig. Die Komplexbildung ist spontan, exo- oder endotherm je nach Metall und entropisch begünstigt. Die Zusammensetzung der Komplexe wurde spektrophotometrisch bestimmt; es entstehen 1:1- und 1:2-Komplexe (Metall:Ligand).

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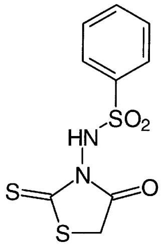
Introduction

Although stability constants of transition metal complexes have been studied extensively, no investigation including 3-phenylsulfonamidorhodanine (*PSR*) and its substituted derivatives as ligands has been reported. In continuation of our earlier work [1–4] on metal complexes in solution and in view of the importance of these ligands [5–7], we report herein the dissociation constants of *PSR* and the stability constants for 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+} at different temperatures. The corresponding thermodynamic parameters are derived and discussed. Moreover, the stoichiometries of the complexes are determined spectrophotometrically.

Experimental

Preparation of the ligand

3-Phenylsulfonamidorhodanine (*PSR*) was prepared by adding equimolar amounts of trithiocarbodiglycolic acid [8] to a solution of phenylsulfonyl hydrazide in bidistilled water with constant stirring on a steam bath for 6 hours. The white precipitate was filtered off, washed with hot bidistilled water, and recrystallized from absolute ethanol (m.p.: 140°C, molecular weight: 288.36). Its purity was checked by elemental analysis (found: C 37.60, H 3.0, N 9.90; calcd.: C 37.48, H 2.8, N 9.72), IR and ^1H NMR spectra.



PSR

Reagents and materials

Metal ion solutions (0.001 *M*) were prepared from AnalaR metal chlorides in bidistilled water and standardized with *EDTA* [9]. The ligand solution (0.01 *M*) was prepared by dissolving the accurate weight of the solid in ethanol (AnalaR). A solution of 1 *M* KCl was also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 20% (v/v) ethanol-water was used as titrant and standardized against AnalaR oxalic acid.

Apparatus and procedures

Apparatus, general conditions, and methods of calculation were the same as in previous investigations [1–3]. The following mixtures were prepared and titrated potentiometrically at 303 K against standard 0.02 *M* NaOH in 20% (v/v) ethanol-water:

1) 5 ml 0.005 *M* HCl + 5 ml 1 *M* KCl + 10 ml EtOH
2) 5 ml 0.005 *M* HCl + 5 ml 1 *M* KCl + 5 ml EtOH + 5 ml 0.01 *M* ligand
3) 5 ml 0.005 *M* HCl + 5 ml 1 *M* KCl + 5 ml EtOH + 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 bidistilled water before the titration. These titrations were repeated for temperatures of 308 and 318 K. Temperature was kept constant within ±0.05 K using an ultrathermostate (Gallenkamp thermo stirrer 85). The *pH*-meter readings in 20% (v/v) ethanol-water are corrected according to *van Uitert* and *Hass* [10].

Results and Discussion

Proton-ligand stability constants

The average number of protons associated with *PSR* at different *pH* values, $\bar{n}_A$, was calculated from the titration curves of acid in the absence and presence of *PSR*. Thus, the formation 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 *PSR* has two dissociable protons (the enolized hydrogen ion of the carbonyl oxygen in the rhodanine moiety and the sulfonamide proton). Different computational methods [11] were applied to evaluate the stepwise dissociation constants. The average values obtained are listed in Table 1.

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

T(K)	Dissociation constant [a]		ΔG (kJ · mol^{-1})			ΔH (kJ · mol^{-1})			ΔS (J · mol^{-1}K^{-1})		
	pK_1^H	pK_2^H	ΔG_1	ΔG_2	ΔG_β	ΔH_1	ΔH_2	ΔH_β	$-\Delta S_1$	$-\Delta S_2$	$-\Delta S_\beta$
303	4.42	9.1	25.64	52.79	78.43	20.30	31.78	52.08	18.00	69.5±1.7	87.5±1.7
308	4.36	9.02	25.71	53.19	78.9						
318	4.26	8.85	25.94	53.89	79.83						

[a] ±(0.03 – 0.05)

Table 2. Stepwise stability constants for *ML* and *ML*$_2$ complexes of *PSR* in 20% (v/v) ethanol-water and 0.1 *M* KCl at different temperatures

	303 K				308 K				318 K			
	logK_1	logK_2	logK_β	logK_1/logK_2	logK_1	logK_2	logK_β	logK_1/logK_2	logK_1	logK_2	logK_β	logK_1/logK_2
Mn^{2+}	7.00	5.00	12.00	1.40	6.53	4.93	11.46	1.32	6.05	4.86	10.91	1.24
Co^{2+}	4.60	4.35	8.95	1.06	5.36	5.09	10.45	1.05	7.00	5.83	12.83	1.20
Ni^{2+}	6.57	3.44	10.01	1.91	6.80	4.77	11.57	1.43	7.20	6.10	13.30	1.18
Cu^{2+}	9.88	6.08	15.96	1.60	10.03	7.46	17.49	1.34	10.30	8.32	18.62	1.24
Zn^{2+}	7.51	5.00	12.51	1.50	7.61	5.74	13.35	1.30	7.71	6.47	14.18	1.19
La^{3+}	7.27	6.26	13.53	1.16	7.60	6.36	13.96	1.19	7.92	7.00	14.92	1.13
Ce^{3+}	7.47	7.00	14.47	1.07	7.42	6.91	14.33	1.07	7.36	6.82	14.18	1.08
Gd^{3+}	7.28	6.95	14.23	1.05	7.22	6.9	14.12	1.05	7.15	6.85	14.00	1.04
UO_2^{2+}	8.43	7.39	15.82	1.14	9.09	7.86	16.95	1.16	9.75	8.32	18.07	1.17
Th^{4+}	10.3	9.14	19.94	1.13	10.37	9.4	19.77	1.10	10.44	9.66	20.10	1.08

Metal-ligand stability constants

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion ($\bar{n}$) *vs*. the free ligand exponent (pL) according to *Irving* and *Rossotti* [12]. These curves were analyzed, and the successive stability constants were determined using different computational methods [13, 14]. 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 $\simeq 2$, 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 can be excluded.

(iii) For all complexes, 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 *PSR* 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 *PSR* are in agreement with that found by *Irving* and *Williams* [15, 16]. The order reflects the changes in the heat of complex formation across the series and arise from a combination of the influence of both the polarizing ability of the metal ion [17] and crystal field stabilization energies [18]. The greater stability of Cu^{2+} complexes result from the well known *Jahn-Teller* effect. The stability constant of the divalent oxygenated cation complex (UO_2^{2+}) is higher than that of 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 [19]. The higher values of the stability constants of Th^{4+} complexes compared to those of the other divalent metal complexes is expected on the basis of charge and ionization potential of Th^{4+}.

Effect of temperature

The dissociation constants (pK_1^H and pK_2^H) for *PSR* 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 of (pK^H or $\log K$ *vs*. $\frac{1}{T}$) was utilized to evaluate the enthalpy change for the dissociation or complexation process, respectively. From the free energy change and ΔH values one can deduce the entropy changes (ΔS) using Eqs. (1) and (2).

$$\Delta G = -2.303 RT \log K = 2.303\ RT \cdot pK \tag{1}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{2}$$

Table 3. Thermodynamic functions for *ML* and ML_2 complexes of *PSR* in 20% (v/v) ethanol-water and 0.1 *M* KCl (error values in parentheses)

M^{n+}	T (K)	ΔG ($kJ \cdot mol^{-1}$)			ΔH ($kJ \cdot mol^{-1}$)			ΔS ($J \cdot mol^{-1} \cdot K^{-1}$)		
		$-\Delta G_1$	$-\Delta G_2$	$-\Delta G_\beta$	ΔH_1	ΔH_2	ΔH_β	ΔS_1	ΔS_2	ΔS_β
Mn^{2+}	303	40.61	29.01	69.62						
	308	38.51	29.07	67.58	−121.2	−17.81	−139.01		37	37
	318	36.84	29.59	66.43					(±1)	(±1)
Co^{2+}	303	26.69	25.24	51.93						
	308	31.61	30.02	61.63	306.35	189.56	495.91	1098	710	1808
	318	42.62	35.50	78.12				(±1)	(±2)	(±2)
Ni^{2+}	303	38.12	19.96	58.08						
	308	40.10	28.13	68.23	80.42	338.9	419.32	391	1186	1577
	318	43.84	37.14	80.98				(±3.7)	(±3.7)	(±3.7)
Cu^{2+}	303	57.32	35.27	92.59						
	308	59.15	43.99	103.14	53.61	285.29	338.9	366	1061	1427
	318	62.71	50.66	113.37				(±5.3)	(±5.3)	(±5.3)
Zn^{2+}	303	43.57	29.01	72.58						
	308	44.88	33.85	78.73	25.47	187.64	213.11	288	716	1004
	318	46.94	39.39	86.33				(±2)	(±2)	(±2)
La^{3+}	303	42.18	36.32	78.5						
	308	44.82	37.51	82.33	82.33	93.82	176.15	412	428	840
	318	48.22	42.62	90.84				(±1)	(±1.7)	(±1.7)
Ce^{3+}	303	43.34	40.61	83.95						
	308	43.76	40.75	84.51	−13.98	−22.98	−36.96	97	58	155
	318	44.81	41.53	86.34				(±1.5)	(±1.5)	(±1.5)
Gd^{3+}	303	42.24	40.32	82.56						
	308	42.58	40.69	83.27	−16.66	−12.83	−29.49	84.5	91	175.5
	318	43.53	41.71	85.24				(±0.5)	(±0.5)	(±0.5)
UO_2^{2+}	303	48.91	42.87	91.78						
	308	53.61	46.35	99.96	168.49	118.71	287.20	719	534.5	837.71
	318	59.37	50.66	110.03				(±1.7)	(±1.5)	(±1.5−1.7)
Th^{4+}	303	59.76	53.03	112.79						
	308	61.16	55.43	116.59	17.81	66.44	84.25	256	395	651
	318	63.57	58.82	122.39				(±1)	(±1)	(±1)

All thermodynamic parameters of the dissociation process of *PSR* are given in Table 1. Inspection of these values reveals that

(i) the stepwise pK^H values decrease with increasing temperature, demonstrating that its acidity increases with increasing temperature;
(ii) ΔH is positive, indicating that dissociation is accompanied by adsorption of heat and the process is endothermic;
(iii) ΔG is positive, indicating that the dissociation process is not spontaneous;
(iv) ΔS is negative due to increased order as a result of the solvation process.

All thermodynamic parameters of the stepwise stability constants of *PSR* complexes are given in Table 3. It is known that the divalent 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: release of H_2O molecules and metal-ligand bond formation.

It has been suggested [20] that ions in aqueous solution order the water molecules around them. During complex formation between oppositely charged ions (L^{2-} and M^{n+}), a breakdown of this metal-water arrangement will occur resulting in positive entropy and enthalpy changes. The following statements can be made:

(i) The stepwise stability constants ($\log K_1$ and $\log K_2$) for *PSR* complexes decrease with increasing temperature for Mn^{2+}, Ce^{3+}, and Gd^{3+}, whereas with $Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, UO_2^{2+}$, and Th^{4+} the reverse takes place, *i.e.* its stability constants increase with increasing 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 *PSR* suggests a spontaneous nature.

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

(iv) The positive values of ΔS for the complexation process of *PSR* with $Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Gd^{3+}, UO_2^{2+}$, and Th^{4+} indicate that the arrangement of the solvent around the metal ion is lost when the complex is formed.

Stoichiometries

The stoichiometries of the complexes of *PSR* with $Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$, La^{3+}, Ce^{3+}, and UO_2^{2+} result from spectrophotometric measurements in the range of 200–400 nm at the optimum *pH* values. These studies were carried out both according to the molar ratio [21] and continuous variation [22] methods. Both methods indicated the formation of 1:1 and 1:2 (metal:ligand) complexes (Table 4).

Table 4. Stoichiometry of M^{n+}-*PSR* complexes in 20% (v/v) ethanol-water by molar ratio (MR) and continuous variation (CV) methods at 298 K

	pH	λ_{max} (nm)	MR		CV	
Mn^{2+}	8	380	1:1	1:2	1:1	–
Co^{2+}	9	280	1:1	1:2	1:1	–
Ni^{2+}	9	450	1:1	1:2	–	1:2
Cu^{2+}	7	420	1:1	1:2	–	1:2
Zn^{2+}	8	380	1:1	–	1:1	–
La^{3+}	9	380	1:1	1:2	1:1	1:2
Ce^{3+}	7	380	1:1	1:2	1:1	–
UO_2^{2+}	6	380	–	1:2	–	1:2

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