POTENTIOMETRIC AND THERMODYNAMIC STUDIES OF 5-PHENYL AZORHODANINE DERIVATIVES AND THEIR METAL COMPLEXES

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ABSTRACT

A series of 5-phenylazo-2-thioxo-4-thiazolidinone derivatives (L_1-L_5) have been prepared and characterized by elemental analysis, and IR spectra. Rhodanine and its derivatives are used as an inhibition of mycobacterium tuberculosis and in medicinal preparations . Azo compounds based on rhodanine play a central role as chelating agents for a large number of metal ions, as they form a stable six-membered ring after complexation with the metal ion and can also be used as analytical reagents. Proton-ligand dissociation constants of (L_1-L_5) and their metal-ligand stability constants of their complexes with (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, La^{3+}, Hf^{3+}, and Zr^{4+}) metal ions have been determined potentiometrically in 0.1M KCl and 40% (v/v) ethanol-water mixture. The influence of substituents on the dissociation and stability constants was examined on the basis of the electron repelling property of the substituent. The order of the stability constants of the formed complexes was found to be $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Cd^{2+} < La^{3+} < Hf^{3+} < Zr^{4+}$. 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.

تم تحضير مجموعة من مركبات الآزورودانين المحتوية على مجموعات ذات خواص إلكترونية مختلفة. يستخدم الرودانين ومركباته فى تحضير الكثير من الأدوية والمستحضرات الطبية وخصوصا المستخدمة فى مقاومة الدرن، كذلك تستخدم مركبات الآزورودانين فى الكيمياء التحليلية. تم حساب ثابت التكسير لهذه المركبات وكذلك حساب درجة الثبات لمتراكباتها مع أيونات بعــض العناصر مثل (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, La^{3+}, Hf^{3+}, Zr^{4+}) باستخدام طريقة معايرة الجهــد فى وســـط يحتــوى على ٠,١ مولر كلوريـد بوتاســيوم وكذلك ٤٠ % إيثانول ـ ماء (بالحجم). ولقد وجد أن درجة ثبات المتراكبات تكون ($Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Cd^{2+} < La^{3+} < Hf^{3+} < Zr^4$) . كذلك تم دراسة تأثير درجة الحرارة وبالتالى حساب ثوابت الديناميكا الحرارية. ولقد وجد أن طريقة تكسير المركبات تكون غير تلقائية وماصة للحرارة والأنتروبيا غير مرغوبة. بينما كانت درجة ثبات المتراكبات تلقائية وماصة للحرارة والأنتروبيا مرغوبة.

Keywords: 5-Phenylazorhodanines, Potentiometry, Complexation , Thermodynamic.

1. INTRODUCTION

Chemistry of rhodanine and its derivatives has attracted special interest due to their inhibition of mycobacterium tuberculosis [1] and as potential medicinal preparations [2]. Azo compounds based on rhodanine play a central role as chelating agents for a large number of metal ions, as they form a stable six-membered ring after complexation with the metal ion and can also be used as analytical reagents [3]. In continuation to the earlier work [4-8], herein the synthesis of 5-phenylazo-2-thioxo-4-thiazolidinone derivatives are reported. The stability constants of

Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, La^{3+}, Hf^{3+}, and Zr^{4+} complexes with 5-phenylazorhodanine derivatives at different temperatures and substituent effects on the dissociation and stability constants are also investigated. Furthermore, the corresponding thermodynamic functions of dissociation and complexation are evaluated and discussed.

2. MATERIALS AND METHODS

5-phenylazo-2-thioxo-4-thiazolidinone derivatives (L_1-L_5) were prepared. The standard chemical aniline or 4-alkyl-aniline and rhodanine were used as received from Aldrich. The experimental technique

has been described previously [6-8]. Chemical structure of azorhodanine derivatives is shown in Fig.(1). In a typical preparation, 25 ml of bidistilled water containing 0.01 mole hydrochloric acid were added to 0.01 mole aniline or 4-alkyl-aniline. To the resulting mixture stirred and cooled to 0°C, a solution of 0.01 mole sodium nitrite in 20 ml of water was added dropwise. The so formed diazonium chloride was consecutively coupled with an alkaline solution of 0.01 mole 2-thioxo-4-thiazolidinone, in 20 ml of pyridine. The coloured precipitate, which formed immediately was filtered, washed several times with water. The crude product was purified by recrystallization from hot ethanol, yield 65% then dried in vacuum desicator over P_2O_5. The ligands were also characterized by elemental analysis (Table 1) and I.R. spectroscopy.
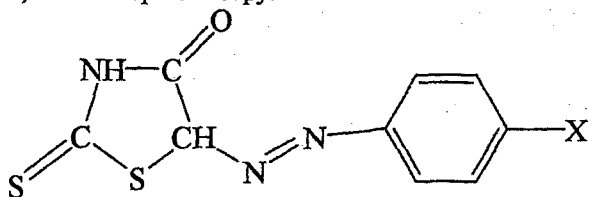

Fig. 1 Derivatives chemical structure ; X = OCH₃
(L₁), CH₃ (L₂), H (L₃), Cl (L₄) and NO₂ (L₅)

Metal ion solutions (0.0002 M) were prepared from Analar metal chloride in bidistilled water and standardized with EDTA [9]. The ligand solution (0.001 M) was 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 40% (v/v) ethanol-water mixture 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 work [6-8]. The following mixtures (i)-(iii) were prepared and titrated potentiometrically at 298 K against standard 0.02 M NaOH in 40% (v/v) ethanol-water mixture:

i- 5 mL 0.01 M HCl + 5 mL 1 M KCl + 20 mL ethanol.

ii- 5 mL 0.01 M HCl + 5 mL 1 M KCl + 15 mL ethanol + 5 mL 0.001 M ligand.

iii- 5 mL 0.01 M HCl + 5 mL 1 M KCl + 15 mL ethanol + 5 mL 0.001 M ligand + 5 mL 0.0002 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. A constant temperature was maintained at ± 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 ± 0.01 units. The pH-meter readings in

40% (v/v) ethanol-water mixture are corrected according to the Van Uitert and Hass relation [10].

3. RESULTS AND DISCUSSION

3.1 Proton-ligand stability constants

The average number of protons associated with the ligands at different pH values, $\bar{n}_A$, were calculated from the titration curves of the acid in the absence and presence of a ligand. 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. Ligands (L₁-L₅) have two ionizable protons (the enolized hydrogen ions of the –SH group in the rhodanine moiety, pK_1^H and in hydrazo from, pK_2^H) [11]. It can be seen that for the same volume of NaOH added the ligand titration curves had a lower pH value than the acid titration curve. The displacement of a ligand titration curve along the volume axis with respect to the acid titration curve is an indication of proton dissociation. The proton-ligand stability constants were calculated using the method of Irving and Rossotti [12]. The –SH group is known to be highly acidic, indicating a weaker bonding between the proton and the sulphur donor. This means that the proton-ligand stability constant of pK_1^H of (L₁-L₅) should be low due to the dissociation of the –SH group [13].Three types of tautomerism can be suggested for the compounds L₁-L₅ as follows [7].
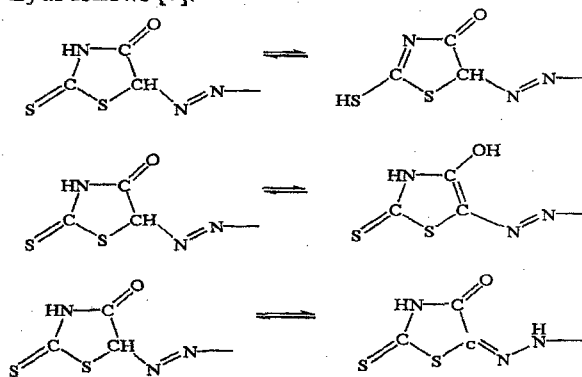
3.2 Substituent effect on pK

An inspection of the results in Table 2 reveals that the pK^H values of 5-phenyl azorhodanine (L₃) and its substituted derivatives are influenced by the inductive or mesomeric effect of the substituents. The p-OCH₃ and p-CH₃ derivatives (L₁ and L₂) have a lower acidic character (higher pK^H values) than the p-Cl and p-NO₂ derivatives (L₄ and L₅). This is quite reasonable because the presence of p-OCH₃ and p-CH₃ groups (i.e. an electron donating effect) will enhance the electron density by their high positive inductive or mesomeric effect, where by a stronger O-H bond is formed. The presence of p-Cl and p-NO₂ groups (i.e. an electron withdrawing effect) will lead to the opposite effect. The results are also in accordance with Hammett's para substituent constant

values σ^x [7,14]. Straight lines are obtained on plotting pK^H values at different temperatures versus σ^x (Figs.2 , 3). The para substituents have a direct influence on the pK^H values of the investigated compounds, revealing the co-planarity of the molecule and thus affording a maximum resonance via delocalization of its π-system.

3.3 Metal-ligand stability constants

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions ($\bar{n}$) versus the free ligand exponent (pL), according to Irving and Rossotti [15]. These curves were analyzed and the successive stability constants were determined using different computational methods [16,17] which agree within 1% error. Accordingly, the average values are represented in Table 3. The following general remarks can be pointed out:

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

(ii) The metal ion solution used in the present study was very dilute (2×10^{-5} M), hence there was no possibility of formation of polynuclear complexes [18].

(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 point to the formation of strong metal complexes [19].

(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 $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Cd^{2+} < La^{3+} < Hf^{3+} < Zr^{4+}$ [20,21]. 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 [22] and the crystal-field stabilization energies [23].

3.4 Effect of the substituent X on the stability of the complexes

An inspection of the results in Table 3 reveals that the stability constant values of the complexes of L_3 and its substituted derivatives are influenced by the inductive or mesomeric effect of the substituents. This behaviour correlates with the effect of substitution on the phenyl ring as follows:

(i) The high stability of L_1 and L_2 complexes can be attributed to the presence of the -OCH_3 and -CH_3 groups in the p-position relative to the azo group, respectively. This is quite reasonable because the presence of p-OCH_3 and p-CH_3 groups (i.e. an electron donating effect) will enhance the electron density by their high positive indicative or

mesomeric effect, whereby stronger chelation was formed and therefore the stability of the complexes.

(ii) The low stability of L_5 and L_4 complexes can be attributed to the presence of the -NO_2 and -Cl groups in the p-position relative to the azo group, respectively. This is caused by the negative indicative effect of the -NO_2 and -Cl groups which decreases its ability for chelation and therefore the stability of the complexes.

(iii) For the ligands with the same metal ion at constant temperature, the stability of the chelates decreases in the order $L_1 > L_2 > L_3 > L_4 > L_5$ [7,24].

3.5 Effect of temperature

The dissociation constant (pK^H) for 5-phenyl azorhodanine (L_3) and its derivatives, as well as the stability constants of their complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, La^{3+}, Hf^{3+} and Zr^{4+} have been evaluated at 298, 308 and 318 K, and are given in Table 2 and 4. The enthalpy change(ΔH) for the dissociation or complexation process were calculated from the slope of the plot (pK^H or log K vs. $^1/_T$) (Figs. 4-7) using the graphical representation of van't Hoff equation:

$$-2.303RT\log K = \Delta H - T\Delta S \qquad (1)$$

or

$$\log K = (-\Delta H/2.303R)(1/T) + (\Delta S/2.303R) \qquad (2)$$

From the free energy change (ΔG) and (ΔH) values one can deduce the entropy changes (ΔS) using the well known relationships (3) and (4) :

$$\Delta G = -2.303RT\log K \qquad (3)$$

$$\Delta S = (\Delta H - \Delta G)/T \qquad (4)$$

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 L_3 and its derivatives are recorded in Table 2. From these results the following conclusions can be made:

(a) The pK^H values decrease with increasing temperature, i.e., the acidity of the ligands increases, independent of the nature of the substituent [7].

(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 [25].

(d) The dissociation processes for L_3 and its derivatives have negative values of ΔS due to increase order as a result of the solvation processes.

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in Table 4. It is known that the metal ions exist in solution as octahedrally hydrated species [17] 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 increases with increasing temperature, i.e., its stability constants increase with increasing the temperature.

(ii) The negative value of ΔG for the complexation process suggests the spontaneous nature of such process [24].

(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 [5].

4. CONCLUSIONS

The following conclusions can be withdrawn from this research:

1. The order of the stability constants of the formed complexes were found to be $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Cd^{2+} < La^{3+} < Hf^{3+} < Zr^{4+}$.

2. The dissociation process of 5-phenyl azorhodanine and its derivatives is nonspontaneous, endothermic and entropically unfavourable.

3. The formation of the metal complexes has been found to be spontaneous, endothermic and entropically favourable.

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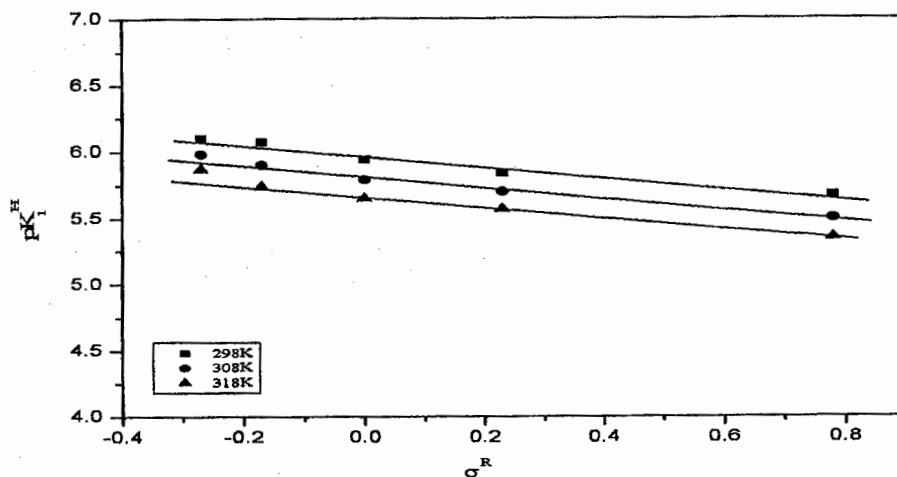
Fig. 2 Correlation of pK_1^H with Hammett's constant σ^R at 298, 308 and 318 K
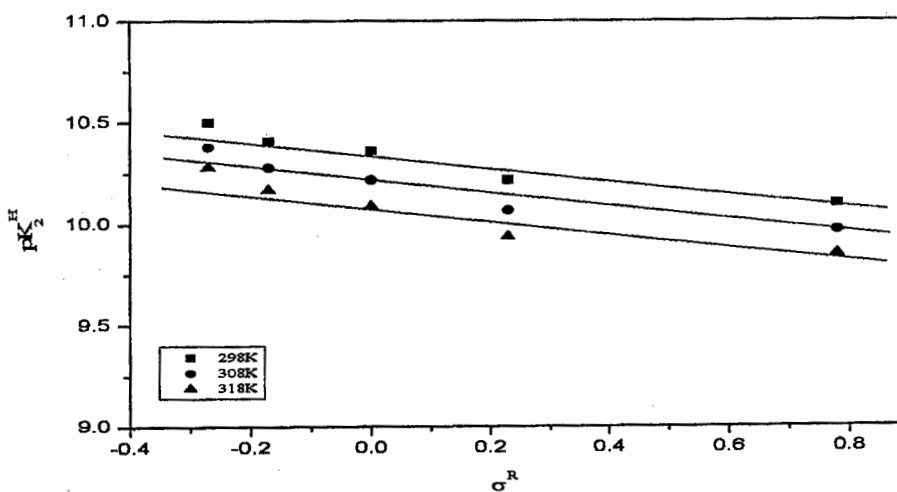

Fig. 3 Correlation of pK_2^H with Hammett's constant σ^R at 298, 308 and 318 K
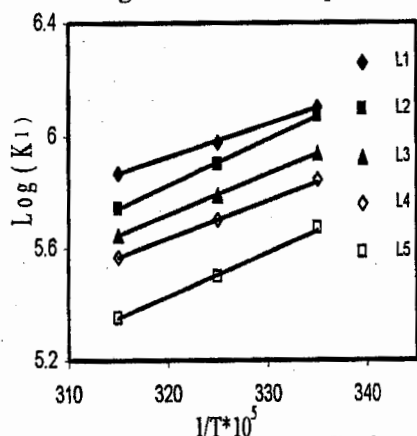

Fig. 4 : Van't Hoff plots of Log (K_1) for
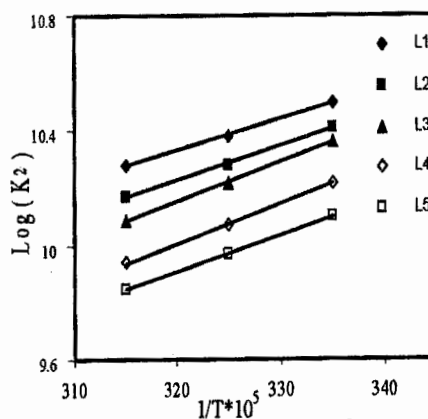different derivatives against 1/T.

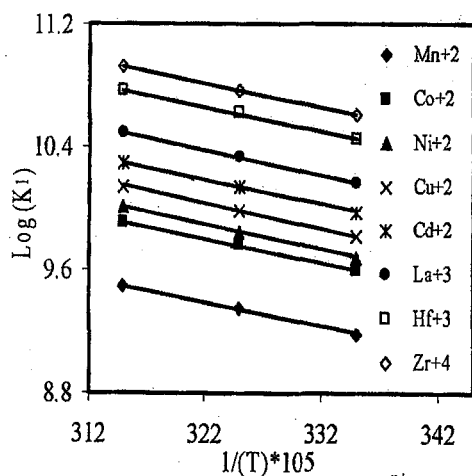Fig.5 : Van't Hoff plot of Log (K_2) for
different derivatives against 1/T.

Fig. 6: Van't Hoff plot of Log (K_1) of M^{n+} complexes with L_1 against $1/T$.
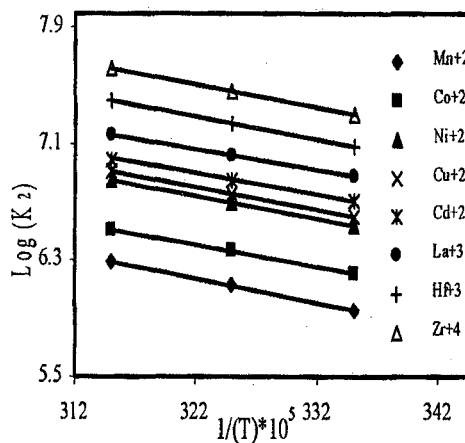
Fig. 7: Van't Hoff plot of Log (K_2) of M^{n+} complexes of L_1 against $1/T$.

Table 1 Analytical data of 5-phenylazorhodanine derivatives $(L_1$-$L_5)$

Compound	Empirical formula	Formula Weight (g/mol)	Colour	m.p. °C	Calc. (Exp.)%		
					C	H	N
L_1	$C_{10} H_9 N_3 O_2 S_2$	267	Red	198	44.94	3.37	15.73
					(44.82)	(3.25)	(15.85)
L_2	$C_{10} H_9 N_3 O S_2$	251	Orange	203	47.81	3.58	16.73
					(47.88)	(3.76)	(16.61)
L_3	$C_9 H_7 N_3 O S_2$	237	Red	139	45.56	2.95	17.72
					(45.68)	(2.80)	(17.85)
L_4	$C_9 H_6 N_3 O S_2 Cl$	271	Yellow	239	39.85	2.21	15.49
					(39.65)	(2.35)	(15.58)
L_5	$C_9 H_6 N_4 O_3 S_2$	282	Brown	245	38.29	2.13	19.85
					(38.42)	(2.25)	(19.98)

Table 2 Thermodynamic Functions for the Dissociation of L_1-L_5 in 40% (v/v) Ethanol-Water Mixture and 0.1 M KCl at Different Temperatures

Compound	Temp. (K)	Dissociation constant		Free energy change (kJ.mol^{-1})		Enthalpy change (kJ. mol^{-1})		Entropy change (J. mol^{-1}.K^{-1})	
		pK_1^H	pK_2^H	ΔG_1	ΔG_2	ΔH_1	ΔH_2	$-\Delta S_1$	$-\Delta S_2$
L_1	298	6.1	10.50	34.80	59.91			46.74	134.10
	308	5.98	10.38	35.26	61.21	20.87	19.96	46.72	133.93
	318	5.87	10.28	35.74	62.59			46.76	134.1
L_2	298	6.07	10.41	34.63	59.39			15.75	126.21
	308	5.90	10.28	34.79	60.62	29.94	21.77	15.74	126.13
	318	5.74	10.17	34.94	61.92			15.72	126.25
L_3	298	5.94	10.36	33.89	59.11			25.43	116.14
	308	5.79	10.22	34.14	60.27	26.31	24.50	25.42	116.13
	318	5.65	10.09	34.40	61.43			25.44	116.13
L_4	298	5.84	10.22	33.32	58.31			29.59	110.43
	308	5.70	10.07	33.61	59.38	24.50	25.40	29.57	110.32
	318	5.57	9.94	33.91	60.52			29.59	110.44
L_5	298	5.67	10.10	32.35	57.62			8.08	117.24
	308	5.50	9.97	32.43	58.79	29.94	22.68	8.08	117.24
	318	5.35	9.85	32.51	59.97			8.08	117.26

Table 3 Stepwise Stability Constants for ML_1 and ML_2 Complexes of (L_1-L_5) in 40% (v/v) Ethanol-Water Mixtures and 0.1 M KCl at Different Temperatures

Compound	M^{n+}	298 K		308 K		318 K	
		$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
L_1	Mn^{2+}	9.18	5.96	9.35	6.13	9.49	6.28
	Co^{2+}	9.59	6.21	9.76	6.37	9.91	6.51
	Ni^{2+}	9.68	6.53	9.85	6.70	10.01	6.85
	Cu^{2+}	9.82	6.60	9.99	6.76	10.15	6.91
	Cd^{2+}	9.98	6.71	10.15	6.86	10.30	7.00
	La^{3+}	10.17	6.88	10.34	7.03	10.50	7.17
	Hf^{3+}	10.46	7.09	10.62	7.25	10.77	7.40
	Zr^{4+}	10.61	7.31	10.77	7.47	10.92	7.62
L_2	Mn^{2+}	9.04	5.81	9.19	5.96	9.33	6.10
	Co^{2+}	9.43	6.02	9.60	6.19	9.75	6.35
	Ni^{2+}	9.57	6.33	9.74	6.50	9.90	6.66
	Cu^{2+}	9.70	6.41	9.86	6.58	10.01	6.73
	Cd^{2+}	9.88	6.58	10.05	6.75	10.21	6.91
	La^{3+}	9.97	6.69	10.14	6.86	10.30	7.01
	Hf^{3+}	10.27	6.92	10.43	7.08	10.58	7.23
	Zr^{4+}	10.42	7.11	10.59	7.26	10.75	7.40
L_3	Mn^{2+}	8.92	5.68	9.09	5.84	9.25	5.99
	Co^{2+}	9.23	5.93	9.39	6.08	9.55	6.22
	Ni^{2+}	9.35	6.12	9.52	6.32	9.68	6.51
	Cu^{2+}	9.49	6.27	9.66	6.44	9.82	6.60
	Cd^{2+}	9.72	6.38	9.88	6.55	10.03	6.72
	La^{3+}	9.86	6.58	10.02	6.74	10.18	6.89
	Hf^{3+}	9.98	6.82	10.15	6.97	10.31	7.12
	Zr^{4+}	10.24	7.00	10.39	7.16	10.52	7.32
L_4	Mn^{2+}	8.77	5.57	8.94	5.72	9.10	5.86
	Co^{2+}	9.07	5.70	9.23	5.86	9.38	6.00
	Ni^{2+}	9.23	6.10	9.38	6.25	9.52	6.39
	Cu^{2+}	9.39	6.23	9.55	6.38	9.69	6.51
	Cd^{2+}	9.58	6.35	9.74	6.51	9.88	6.65
	La^{3+}	9.68	6.40	9.85	6.56	10.00	6.71
	Hf^{3+}	9.79	6.65	9.95	6.80	10.10	6.94
	Zr^{4+}	9.98	6.78	10.14	6.94	10.28	7.10
L_5	Mn^{2+}	8.69	5.37	8.85	5.54	9.00	5.70
	Co^{2+}	8.90	5.60	9.07	5.76	9.22	5.90
	Ni^{2+}	9.07	5.98	9.24	6.13	9.40	6.26
	Cu^{2+}	9.28	6.08	9.44	6.24	9.58	6.39
	Cd^{2+}	9.37	6.18	9.54	6.34	9.70	6.49
	La^{3+}	9.56	6.29	9.72	6.46	9.86	6.62
	Hf^{3+}	9.66	6.52	9.83	6.66	9.98	6.80
	Zr^{4+}	9.83	6.58	9.98	6.75	10.12	6.91

Table 4 Thermodynamic Functions for ML_1 and ML_2 Complexes of (L_1-L_5) in 40% (v/v) Ethanol-Water Mixture and 0.1 M KCl at 298 K.

Compound	M^{n+}	Gibbs energy change (kJ. mol^{-1})		Enthalpy change (kJ. mol^{-1})		Entropy change (J. mol^{-1}.K^{-1})	
		$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
L_1	Mn^{2+}	52.37	34.01	28.13	29.03	270.13	211.54
	Co^{2+}	54.71	35.43	29.03	27.22	281.01	210.23
	Ni^{2+}	55.23	37.25	29.94	29.03	285.80	222.41
	Cu^{2+}	56.03	37.65	29.94	28.13	288.48	220.73
	Cd^{2+}	56.94	38.28	29.03	26.31	288.48	216.74
	La^{3+}	58.02	39.25	29.94	26.31	295.16	220.00
	Hf^{3+}	59.68	40.45	28.13	28.13	294.66	230.13
	Zr^{4+}	60.53	41.70	28.13	28.13	297.51	234.39
L_2	Mn^{2+}	51.58	33.15	26.31	26.31	261.37	199.53
	Co^{2+}	53.80	34.34	29.03	29.94	277.95	215.70
	Ni^{2+}	54.60	36.11	29.94	29.94	283.69	221.64
	Cu^{2+}	55.34	36.57	28.13	29.03	280.10	220.13
	Cd^{2+}	56.37	37.54	29.94	29.94	289.63	226.44
	La^{3+}	56.88	38.17	29.94	29.03	291.34	225.50
	Hf^{3+}	58.59	39.48	28.13	28.13	291.01	226.87
	Zr^{4+}	59.45	40.56	29.94	26.31	299.96	224.39
L_3	Mn^{2+}	50.89	32.40	29.94	28.13	271.24	203.12
	Co^{2+}	52.66	33.83	29.03	36.31	274.12	201.81
	Ni^{2+}	53.34	34.91	29.94	35.39	279.46	235.90
	Cu^{2+}	54.14	35.77	29.94	29.94	282.14	220.50
	Cd^{2+}	55.46	36.40	28.13	30.85	280.50	225.67
	La^{3+}	56.43	37.54	29.03	28.31	286.77	220.36
	Hf^{3+}	56.94	38.91	29.94	27.22	291.54	221.91
	Zr^{4+}	58.42	39.94	25.40	29.03	281.27	231.44
L_4	Mn^{2+}	50.03	31.78	29.94	26.31	268.35	194.93
	Co^{2+}	51.75	32.52	28.13	26.22	268.05	200.46
	Ni^{2+}	52.66	34.80	26.31	26.31	265.00	205.06
	Cu^{2+}	53.57	35.54	27.22	25.40	271.10	204.49
	Cd^{2+}	54.66	36.23	27.22	27.22	274.76	212.91
	La^{3+}	55.23	36.51	29.03	28.13	282.75	216.91
	Hf^{3+}	55.85	36.51	28.13	26.31	281.81	210.80
	Zr^{4+}	56.94	38.68	27.22	29.03	282.41	227.21
L_5	Mn^{2+}	49.58	30.64	28.13	29.94	260.77	203.28
	Co^{2+}	50.78	31.95	29.03	27.22	267.81	198.55
	Ni^{2+}	51.75	34.12	29.94	25.40	274.12	199.73
	Cu^{2+}	52.94	34.69	27.22	28.13	268.99	210.80
	Cd^{2+}	53.46	35.26	29.94	28.13	279.86	212.71
	La^{3+}	54.54	35.88	27.22	29.94	274.36	220.87
	Hf^{3+}	55.11	37.20	29.03	25.40	2 82.34	210.06
	Zr^{4+}	56.08	37.54	26.31	29.94	276.47	226.44