

Research Article

Potentiometric and Thermodynamic Studies of Some Schiff-Base Derivatives of 4-Aminoantipyrine and Their Metal Complexes

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Received 12 June 2012; Accepted 20 September 2012

Academic Editor: Dimosthenis L. Giokas

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The proton-ligand dissociation constant of 4-(4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino)-phenol (L_1) and 4-(4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino)-benzoic acid (L_2) and metal-ligand stability constants of their complexes with metal ions (Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+}) have been determined potentiometrically in $0.1\text{ mol}\cdot\text{dm}^{-3}$ KCl and 10% (by volume) ethanol-water mixture and at 298, 308, and 318 K. The stability constants of the formed complexes increase in the order Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} . 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.

1. Introduction

Schiff-base coordination complexes have attracted great attention over the past decades due not only to their facile syntheses, their wide application, and the accessibility of diverse structural modifications, but also to their biological modeling applications, catalysis, design of molecular ferromagnets, and materials chemistry [1–6]. It is well known that N atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules [7]. The Schiff bases of 4-aminoantipyrine and their coordination complexes have been extensively investigated because of their biological, clinical, pharmacological, analytical and material applications [8–11]. Also some drugs showed increased activity when administered as metal chelate rather than as free organic compounds [12, 13]. In continuation of earlier work [14–18], we report here the dissociation constant of 4-(4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino)-phenol (L_1) and 4-(4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino)-benzoic acid (L_2) and the stability constants of their complexes with Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} at different temperatures. Furthermore, the corresponding

thermodynamic functions of complexation are evaluated and discussed.

2. Experimental

4-(4-Amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino)-phenol (L_1) and 4-(4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino)-benzoic acid (L_2) (Figure 1) were prepared by refluxing a mixture of hot solution of 4-aminoantipyrine (0.1 mmol) and 4-hydroxyaniline or 4-carboxyaniline (0.1 mmol) in 50 cm^3 ethanol for 2 h [19, 20]. The formed solid product was separated by filtration, purified by crystallization from ethanol, washed with diethyl ether, and dried in a vacuum over anhydrous calcium chloride.

A ligand solution ($0.001\text{ mol}\cdot\text{dm}^{-3}$) was prepared by dissolving an accurately weighed amount of the solid in ethanol (Analar). Metal ion solutions ($0.0001\text{ mol}\cdot\text{dm}^{-3}$) were prepared from Analar metal chlorides in bidistilled water and standardized with EDTA [20]. Solutions of $0.001\text{ mol}\cdot\text{dm}^{-3}$ HCl and $1\text{ mol}\cdot\text{dm}^{-3}$ KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 10%

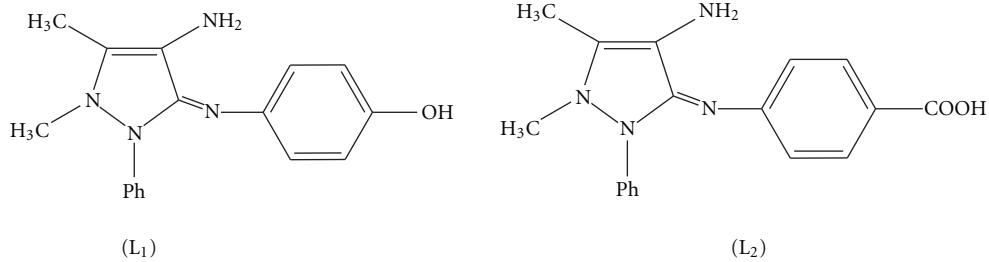


FIGURE 1

TABLE 1: Thermodynamic functions for the dissociation of ligand (L_i) in 10% (by volume) ethanol-water mixture and $0.1 \text{ mol} \cdot \text{dm}^{-3}$ KCl at different temperatures.

T/K	Dissociation constant pK^H	Gibbs energy $\text{kJ} \cdot \text{mol}^{-1}$ ΔG_1	Enthalpy $\text{kJ} \cdot \text{mol}^{-1}$ ΔH_1	Entropy $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ $-\Delta S_1$
298	9.25 (0.10)	52.77		70.56
308	9.07 (0.09)	53.48	31.75	70.57
318	8.90 (0.09)	54.19		70.56

Standard deviations are given in parentheses.

TABLE 2: Thermodynamic functions for the dissociation of ligand (L_2) in 10% (by volume) ethanol-water mixture and $0.1 \text{ mol} \cdot \text{dm}^{-3}$ KCl at different temperatures.

T/K	Dissociation constant pK^H	Gibbs energy $\text{kJ} \cdot \text{mol}^{-1}$ ΔG_1	Enthalpy $\text{kJ} \cdot \text{mol}^{-1}$ ΔH_1	Entropy $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ $-\Delta S_1$
298	4.26 (0.09)	24.31		24.92
308	4.09 (0.09)	24.12	31.73	24.72
318	3.91 (0.08)	23.81		24.92

Standard deviations are given in parentheses.

(by volume) 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 previous work [15–18]. The following mixtures (i)–(iii) were prepared and titrated potentiometrically at 298 K against standard $0.002 \text{ mol}\cdot\text{dm}^{-3}$ NaOH in a 10% (by volume) ethanol-water mixture:

- (i) 5 cm^3 $0.001 \text{ mol}\cdot\text{dm}^{-3}$ HCl + 5 cm^3 $1 \text{ mol}\cdot\text{dm}^{-3}$ KCl + 5 cm^3 ethanol.

(ii) 5 cm^3 $0.001 \text{ mol}\cdot\text{dm}^{-3}$ HCl + 5 cm^3 $1 \text{ mol}\cdot\text{dm}^{-3}$ KCl + 5 cm^3 $0.001 \text{ mol}\cdot\text{dm}^{-3}$ ligand.

(iii) 5 cm^3 $0.001 \text{ mol}\cdot\text{dm}^{-3}$ HCl + 5 cm^3 $1 \text{ mol}\cdot\text{dm}^{-3}$ KCl + 5 cm^3 $0.001 \text{ mol}\cdot\text{dm}^{-3}$ ligand + 10 cm^3 $0.0001 \text{ mol}\cdot\text{dm}^{-3}$ metal chloride.

For each mixture, the volume was made up to 50 cm³ with bidistilled water before the titration. These titrations were repeated for temperatures of 308 K and 318 K. The temperature was controlled to within ± 0.05 K by circulating

thermostated water (Neslab 2 RTE 220) through the outer jacket of the vessel. The pH measurements were performed with a Metrohm 836 Titrando (KF & Potentiometric Titrator) equipped with a combined porolyte electrode. The pH-meter readings in the nonaqueous medium were corrected [21]. The electrode system was calibrated according to the method of Irving et al. [22]. All titrations have been carried out between pH 3.0 and 11.0 and under nitrogen atmosphere.

3. Results and Discussion

The average number of the protons associated with ligands (L_1 and L_2) at different pH values, \bar{n}_A , was calculated from the titration curves of the acid in the absence and presence of ligands (L_1 and L_2). Apply (1):

$$\bar{n}_A = Y + \frac{(V_1 - V_2)(N^0 + E^0)}{(V^0 + V_1)TC_l^0}, \quad (1)$$

where Y is the number of available protons in ligands (L_1 and L_2) ($Y = 1$) 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^0 is the initial volume (50 cm^3) of the mixture, TC_L^0 is the total concentration of the reagent, N^0 is the normality of sodium hydroxide solution, and E^0 is the initial concentration of the free acid. Thus, the formation curves (\bar{n}_A versus pH) for the proton-ligand systems were constructed and found to extend between 0 and 1 in the \bar{n}_A scale. This means that ligands (L_1 and L_2) have one ionizable proton (the enolized hydrogen ion of the $-\text{OH}$ and $-\text{COOH}$ group, pK^H), respectively. Different computational methods [23] were applied to evaluate the dissociation constant. Three replicate titrations were performed; the average values obtained are listed in Tables 1 and 2. The completely protonated form of ligands (L_1 and L_2) has one dissociable proton that dissociates in the measurable pH range.

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 ligands exponent (p_L), according to Irving and Rossotti [24]. The average number

TABLE 3: Stepwise stability constants for ML and ML_2 complexes of ligand (L_1) in 10% (by volume) ethanol-water mixtures and $0.1 \text{ mol} \cdot \text{dm}^{-3}$ 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+}	6.84 (0.08)	6.04 (0.11)	7.02 (0.09)	6.22 (0.10)	7.19 (0.10)	6.40 (0.11)
Co^{2+}	6.95 (0.09)	6.13 (0.10)	7.13 (0.09)	6.31 (0.10)	7.31 (0.11)	6.48 (0.11)
Ni^{2+}	7.02 (0.09)	6.19 (0.09)	7.20 (0.10)	6.37 (0.09)	7.38 (0.11)	6.54 (0.10)
Cu^{2+}	7.15 (0.09)	6.34 (0.09)	7.34 (0.09)	6.52 (0.10)	7.53 (0.11)	6.70 (0.10)

Standard deviations are given in parentheses.

TABLE 4: Stepwise stability constants for ML and ML_2 complexes of ligand (L_2) in 10% (by volume) ethanol-water mixtures and $0.1 \text{ mol} \cdot \text{dm}^{-3}$ 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+}	7.33 (0.08)	6.74 (0.09)	7.50 (0.09)	6.90 (0.10)	7.67 (0.10)	7.07 (0.10)
Co^{2+}	7.54 (0.09)	6.85 (0.10)	7.72 (0.10)	7.02 (0.10)	7.90 (0.10)	7.20 (0.11)
Ni^{2+}	7.63 (0.09)	6.92 (0.10)	7.80 (0.11)	7.10 (0.09)	7.98 (0.11)	7.27 (0.10)
Cu^{2+}	7.78 (0.09)	7.07 (0.10)	7.97 (0.10)	7.26 (0.10)	8.16 (0.11)	7.44 (0.10)

Standard deviations are given in parentheses.

of the reagent molecules attached per metal ion, \bar{n} , and free ligands exponent, pL , can be calculated using (2) and:

$$\begin{aligned}\bar{n} &= \frac{(V_3 - V_2)(N^0 + E^0)}{(V^0 + V_2)\bar{n}_A T C_M^0}, \\ pL &= \log_{10} \frac{\sum_{n=0}^{n=J} \beta_n^H [1/\text{anti log pH}]^n}{TC_L^0 - \bar{n} T C_M^0} \cdot \frac{V^0 + V_3}{V^0},\end{aligned}\quad (2)$$

where TC_M^0 is the total concentration of the metal ion present in the solution and 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 metal-ligand stability constants were determined using different computational methods [25, 26]. The values of the stability constants ($\log K_1$ and $\log K_2$) are given in Tables 3 and 4. 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 [27].
- (ii) The metal ion solution used in the present study was very dilute ($2 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$); hence there was no possibility of formation of polynuclear complexes [28, 29].
- (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 [30, 31].

(iv) For the same ligand at constant temperature, the stability of the chelates increases in the order Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} [19, 32, 33]. This order largely reflects that the stability of Cu^{2+} complexes is considerably larger than those of other metals of the 3d series. Under the influence of both the polarizing ability of the metal ion [34] and the ligand field [35] Cu^{2+} will receive some extra stabilization due to tetragonal distortion of octahedral symmetry in its complexes. The greater stability of Cu^{2+} complexes is produced by the well-known *Jahn-Teller* effect [35].

The dissociation constant (pK^H) for ligands (L_1 and L_2), as well as the stability constants of its complexes with Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} , has been evaluated at 298 K, 308 K, and 318 K and is given in Tables 1, 2, 5, and 6, respectively. The enthalpy (ΔH) for the dissociation and complexation process was calculated from the slope of the plot pK^H or $\log K$ versus $1/T$ using the graphical representation of *van't Hoff* equations (3) and (4):

$$\Delta G = -2.303RT \log K = \Delta H - T\Delta S, \quad (3)$$

or

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

From the ΔG and ΔH values one can deduce the entropy ΔS using the well-known relationships (3) and (5):

$$\Delta S = \frac{(\Delta H - \Delta G)}{T}. \quad (5)$$

All thermodynamic parameters of the dissociation process of ligands (L_1 and L_2) are recorded in Tables 1 and 2. From these results the following conclusions can be made.

TABLE 5: Thermodynamic functions for ML and ML_2 complexes of ligand (L_1) in 10% (by volume) ethanol-water mixture and $0.1 \text{ mol} \cdot \text{dm}^{-3}$ KCl.

M^{n+}	T/K	Gibbs energy/ $\text{kJ} \cdot \text{mol}^{-1}$		Enthalpy/ $\text{kJ} \cdot \text{mol}^{-1}$		Entropy/ $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
		$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
Mn^{2+}	298	39.03	34.46			237.52	225.21
	308	41.39	36.68	31.75	32.65	237.50	225.10
	318	43.78	38.97			237.52	225.21
Co^{2+}	298	39.66	34.98			242.64	223.92
	308	42.05	37.21	32.64	31.75	242.52	223.91
	318	44.51	39.46			242.64	223.92
Ni^{2+}	298	40.06	35.32			243.98	225.07
	308	42.46	37.57	32.65	31.75	243.87	225.06
	318	44.94	39.82			243.98	225.07
Cu^{2+}	298	40.79	36.18			252.55	230.96
	308	43.29	38.45	34.46	32.65	252.43	230.84
	318	45.85	40.79			252.55	230.96

TABLE 6: Thermodynamic functions for ML and ML_2 complexes of ligand (L_2) in 10% (by volume) ethanol-water mixture and $0.1 \text{ mol} \cdot \text{dm}^{-3}$ KCl.

M^{n+}	T/K	Gibbs energy/ $\text{kJ} \cdot \text{mol}^{-1}$		Enthalpy/ $\text{kJ} \cdot \text{mol}^{-1}$		Entropy/ $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
		$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
Mn^{2+}	298	41.82	38.46			243.82	229.45
	308	44.23	40.69	30.83	29.92	243.72	229.25
	318	46.70	43.05			243.82	229.45
Co^{2+}	298	43.02	39.09			253.93	237.64
	308	45.53	41.39	32.65	31.73	253.82	237.44
	318	48.01	43.83			253.93	237.65
Ni^{2+}	298	43.54	39.48			252.58	239.05
	308	45.99	41.87	31.73	31.75	252.38	239.04
	318	48.59	44.27			252.58	239.05
Cu^{2+}	298	44.39	40.34			264.61	248.00
	308	47.48	42.81	34.46	33.56	264.50	247.99
	318	49.68	45.30			264.62	248.05

- (i) The pK^H values decrease with increasing temperature; that is, the acidity of the ligand increases [17].
- (ii) A positive value of ΔH indicates that the process is endothermic.
- (iii) A large positive value of ΔG indicates that the dissociation process is not spontaneous [36].
- (iv) A negative value of ΔS is obtained due to the increased order as a result of the solvation process.

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in Tables 5 and 6. It is known that the divalent metal ions exist in solution as octahedrally hydrated species [26], 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 the following.

- (i) The stability constants ($\log K_1$ and $\log K_2$) for ligands (L_1 and L_2) complexes increase with increasing temperature; that is, its stability constants increase with increasing temperature [37].
- (ii) The negative value of ΔG for the complexation process suggests the spontaneous nature of such processes [38].
- (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 [16].

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