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Potentiometric and Thermodynamic Studies of Dissociation and Metal Complexation of 4-(3-Hydroxypyridin-2-ylimino)-4-phenylbutan-2-one

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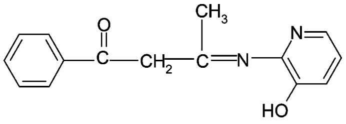
The Schiff base 3-(3-hydroxypyridin-2-ylimino)-1-phenylbutan-2-one (HPIB) was synthesized and characterized by elemental analysis and IR spectra. The proton−ligand dissociation constant of HPIB and the stepwise stability constants of its metal complexes with Cu^{2+}, Ni^{2+}, Co^{2+}, and Mn^{2+} were determined potentiometrically in a 40 % (v/v) ethanol−water mixture in the presence of 0.100 M KCl under nitrogen. The stabilities of the complexes follow the order Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}. The dissociation constants of HPIB and the stability constants, log *K*, of its metal complexes were determined at different temperatures, and the corresponding thermodynamic parameters are derived and discussed. The proton−ligand dissociation is found to be nonspontaneous, endothermic, and entropically unfavorable. The values of ΔG^0 and ΔH^0 accompanying the complex formation are related to the ionic radius, the electronegativity, the ionization enthalpy, and the hydration enthalpy of the metal ion. The order of $-\Delta G^0$ and $-\Delta H^0$ was found to obey Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}, in agreement with the Irving−Williams order. The different thermodynamic parameters suggest that the complex formation is an enthalpy-driven process. The speciation of the complexes is determined.

1. Introduction

Schiff bases are an important class of ligands and play an important role in the development of coordination chemistry as they readily form stable complexes with most transition metals.[1−5] It is well-known that some drugs exhibit increased activity when administered as metal complexes,[6−8] and several metal chelates have been shown to inhibit tumor growth.[9] There have been several reports on metal complexes of the Schiff base ligands having a variety of applications including biological, clinical, analytical, and industrial in addition to their important roles in catalysis and organic synthesis.[10−14] In continuation of our earlier work,[15−17] we report herein the dissociation constant of the free ligand (HPIB), I, the stepwise stability constants of its complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}, and thermodynamic calculations from data obtained at different temperatures. Such work may help to explain the nature and driving forces for the interactions occurring in biological systems, such as metal−protein and metal−nucleic acid interactions.



HPIB

(I)

2. Experimental

2.1. Reagents and Materials. Metal ion solutions (0.0002 M) were prepared from metal chloride (Analar) in doubly distilled water and standardized against a standard EDTA solution in the presence of a suitable indicator.[18] The ligand solution (0.001 M) was prepared by dissolving 0.02543 g in absolute ethanol, and the volume was made up to 100 mL. A solution of 1.00 M KCl was prepared by dissolving 37.2757 g in doubly distilled water, and the volume was made up to 500 mL. A carbonate-free sodium hydroxide solution in a 40 % (v/v) ethanol−water mixture was used as titrant after standardization against a standard oxalic acid solution using the appropriate indicator. All potentiometric titrations were done under N$_2$ gas.

2.2. Apparatus and Procedures. CHN analysis was obtained using a LECO-CHNS 932 analyzer. FT-IR spectra were recorded as KBr discs with a Schimadzu 2000 FT-IR spectrophotometer. The apparatus, general conditions, and methods of calculation were the same as in previous investigations.[15] The following mixtures were prepared and titrated potentiometrically at 298 K against standard 0.010 M NaOH in a 40 % (v/v) ethanol−water mixture: (i) 5.00 mL of 0.0l0 M HCl + 5.00 mL of 1.00 M KCl + 20.00 mL of ethanol; (ii) 5.00 mL of 0.010 M HCl + 5.00 mL of 1.00 M KCl + 15.00 mL of ethanol + 5.00 mL of 0.001 M ligand; (iii) 5.00 mL of 0.010 M HCl + 5.00 mL of l.00 M KCl + 15.00 mL of ethanol + 5.00 mL of 0.001 M ligand + 5.00 mL of 0.0002 M metal ion.

For each mixture, the volume was made up to 50 mL with doubly distilled water before the titration. These titrations were repeated at (308 and 318) K. The temperature was kept constant within ± 0.05 K using an ultrathermostat (Galenkamp thermostirrer 85). The pH measurements were carried out using a VWR Scientific instruments model 8000 pH-meter precise to ± 0.01 units. The pH-meter readings in 40 % (v/v) ethanol−water mixture are corrected according to the method of Van Uitert and Hass.[19] The concentration distribution diagrams were obtained using the program SPECIES[20] under the experimental conditions described.

2.3. Synthesis of the Organic Ligand. The organic compound was synthesized by addition of 3-hydroxy-2-minopyridine (0.001 mol) and benzoylacetone (0.0015 mol) in EtOH (50 mL) in the presence of 3 drops of acetic acid. The reaction mixture was refluxed on a water bath for 2 h, and the solvent was evaporated to 1/3 of its initial volume and cooled to room temperature.

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Table 1. Thermodynamic Parameters of Dissociation of HPIB in a 40 % (v/v) Ethanol−Water Mixture in the Presence of 0.100 M KCl at Different Temperatures ±[a]

T K	pK_1	$\Delta G^0{}_1$ kJ·mol^{-1}	ΔH^0 kJ·mol^{-1}	$T\Delta S^0{}_1$ 308 K	pK_2	$\Delta G^0{}_2$ kJ·mol^{-1}	ΔH^0 kJ·mol^{-1}	$T\Delta S^0{}_2$ 308 K
298	4.37 ± 0.08	24.93 ± 0.45	19.04 ± 0.87	−6.14 ± 0.42	7.75 ± 0.09	44.22 ± 0.51	12.29 ± 0.06	−20.38 ± 0.45
308	4.27 ± 0.05	25.18 ± 0.38			7.61 ± 0.09	44.88 ± 0.51		
318	4.16 ± 0.07	25.33 ± 0.40			7.48 ± 0.07	45.54 ± 0.39		

[a] Standard errors are given in parentheses.

Table 2. Stepwise Stability Constants for the Complexation of HPIB with 3d Divalent Metal Ions in a 40 % (v/v) Ethanol−Water Mixture in the Presence of 0.100 M KCl at Different Temperatures[a]

	$\log_{10} K_1 \pm \sigma$			$\log_{10} K_2 \pm \sigma$			$\log K_1 - \log K_2$		
metal ion	298 K	308 K	318 K	298 K	308 K	318 K	298 K	308 K	318 K
Mn^{2+}	5.96 ± 0.03	5.83 ± 0.02	5.70 ± 0.04	4.48 ± 0.03	4.39 ± 0.02	4.29 ± 0.04	1.48	1.44	1.4
Co^{2+}	6.80 ± 0.03	6.65 ± 0.03	6.50 ± 0.05	4.60 ± 0.03	4.50 ± 0.03	4.39 ± 0.04	2.2	2.26	2.11
Ni^{2+}	7.25 ± 0.04	7.08 ± 0.04	6.91 ± 0.04	4.70 ± 0.04	4.59 ± 0.04	4.49 ± 0.04	2.55	2.49	2.42
Cu^{2+}	7.60 ± 0.04	7.41 ± 0.05	7.25 ± 0.04	4.97 ± 0.04	4.85 ± 0.05	4.75 ± 0.04	2.63	2.56	2.50

[a] Correlation coefficients range from 0.9841 to 0.9999; σ is the standard deviation.

The solid precipitate obtained after the addition of Et_2O was filtered off and recrystallized from EtOH to give yellow crystals: % yield = 78 %.

Elemental Analysis*: *% Found (% Calcd). C, 70.59 (70.86); H, 5.60 (5.51); N, 11.26 (11.24).

IR ($\acute{\upsilon}$, cm^{-1}): 1634 ($\upsilon_{C=O}$), 1598 ($\upsilon_{C=N}$), 3386 (υ_{OH}), 2884, 2829 (υ_{CH}), 1573($\upsilon_{C=N}$)$_{Py}$.

Calculations. The average number of protons $\bar{n}_A$ associated with the reagent molecule is determined at different pH values by applying eq 1

$$\bar{n}_A = Y + \frac{(V_1 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_1)TC^\circ_L} \tag{1}$$

where 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° is the initial volume (50 mL) of the mixture; TC°_L is the total concentration of the reagent; N° is the normality of sodium hydroxide solution; and E° is the initial concentration of the free acid. The values of $\bar{n}_A$ are plotted against pH, and the values of proton−ligand stability constants p$K^{H}{}_1$, and p$K^{H}{}_2$ are calculated by interpolation at half $\bar{n}_A$ values.

In the complexation of metal ions by ligands, the values of the first and second stepwise stability constants, log K_1 and log K_2, of the comp1exes can be determined. The average number of the reagent molecules attached per metal ion, $\bar{n}$, and free ligand exponent, pL, can be calculated using eqs 2 and 3

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_2)\bar{n}_A TC^\circ_M} \tag{2}$$

and

$$\mathrm{pL} = \log_{10} \frac{\sum_{n=O}^{n=J} \beta^H_n \left(\frac{1}{\text{anti log pH}}\right)^n}{TC^\circ_L - \bar{n}TC^\circ_M} \cdot \frac{V^\circ + V_3}{V^\circ} \tag{3}$$

where TC°_M is the total concentration of the metal ions present in the solution and β^H_n 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, the organic ligand, and the complex, respectively. On plotting the values of $\bar{n}$ against the pL and interpolation at half $\bar{n}$ values, the stepwise stability constants of the chelates can be evaluated. All calculations were made in the pH range 2.80 to 8.00 to avoid the hydrolysis of the metal ion.

3. Results and Discussion

3.1. Proton−Ligand Dissociation Constant. To calculate the stability constants of metal chelates, the acid dissociation constant of the ligand was first determined from the titration curves for HCl in the presence and absence of the ligand. The average number of protons, $\bar{n}_A$, associated with the HPIB at different pH values was calculated according to the method previously reported.[15,17] The formation curve for the proton−ligand systems showed that the free ligand has two dissociable protons (−CH═C(OH)− and the hydroxyl group hydrogen) which are characterized by p$K^{H}{}_2$ and p$K^{H}{}_1$, respectively. Different computational methods[15,17] were applied to evaluate the dissociation constants. The number of replicates is three, and the average values obtained are listed in Table 1.

3.2. Complex 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). The ($\bar{n}$) values were calculated according to the previously reported methods.[15,17] These curves were analyzed, and the successive stability constants were determined using different computational methods[21,22] and agree within 1 % error. According to the average values in Table 2, the following general remarks can be made:

(i) The maximum values were found to be $\bar{n} \approx 2$ in all cases indicating the formation of only *ML and ML$_2$* complexes in solution.[5]

(ii) The very low concentration of metal ion solutions used in the present study was 2×10^{-5} mol·dm^{-3} and precludes the possibility of formation of polynuclear complexes.[23]

(iii) The metal titration curves are displaced to the right-hand side of the ligand titration curves along the volume axis, indicating a proton release upon complex formation. The large decrease in pH for the metal titration curves relative to ligand titration curves can be attributed to strong metal−ligand bonding.

(iv) For the same ligand at constant temperature, the stability of the chelates increases in the order $Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$.[24,25] This order largely reflects 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.[26,27]

(v) All calculations of stability constants have been successful for the low pH region. Therefore, the formation of hydroxo

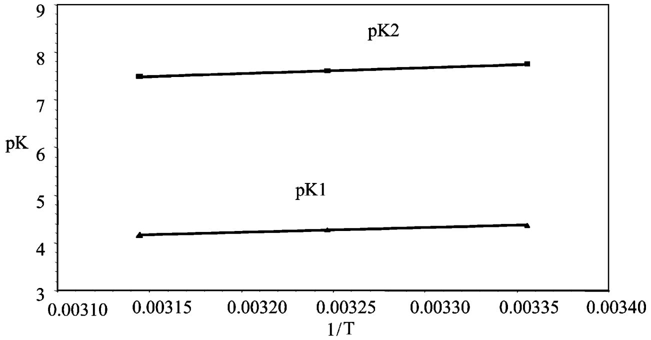

Figure 1. Van't Hoff plot of pK dissociation of HPIB against $1/T$.

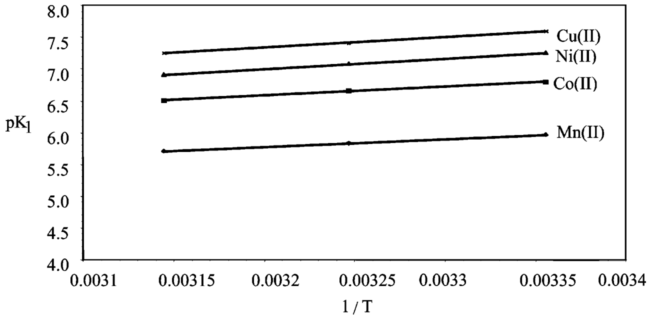

Figure 2. Van't Hoff plot of log K_1 of M(II) complexes with HPIB against $1/T$.

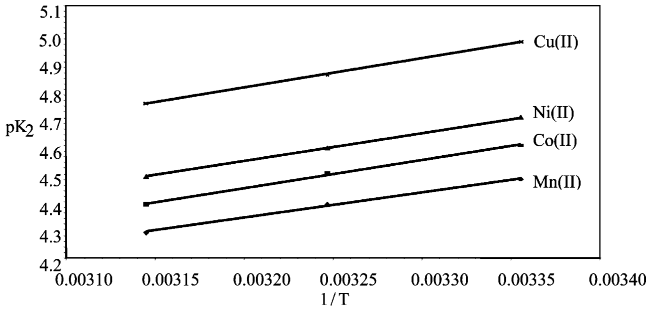

Figure 3. Van't Hoff plot of log K_2 of M(II) complexes with HPIB against $1/T$.

species (e.g., [ML(OH)], $[MS_{x-1}(OH)]^+$, where L is the ligand, S is the solvent molecule, and x is the number of solvent molecules bound) could be neglected.

(vi) The values of log K_1 − log K_2 in Table 2 are positive in all cases. This means that the coordination of the first ligand to the metal ion is more favorable than the bonding of the second ligand molecule. As shown in Table 2, this difference lies within 1.4 to 2.91 log units, revealing the importance of electrostatic and steric effects resulting from the addition of the second ligand molecule, since the statistical effect contributes only 0.68 log units.[22]

3.3. Effect of Temperature. The pK_a for HPIB as well as the stability constants of its complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} have been evaluated at (298, 308, and 318) K and are given in Tables 1 and 2. The enthalpy change (ΔH^0) for the dissociation or complexation process was calculated from the slope of the plot (pK_a or log K vs $1/T$) (Figures 1 to 3) using the graphical representation of Van't Hoff's equation

$$-2.303\, RT \log K = \Delta H^0 - T\Delta S^0 \tag{4}$$

or

$$\log K = -(\Delta H^0/2.303R)(1/T) + \Delta S^0/R \tag{5}$$

From the free-energy change (ΔG^0) and ΔH^0 values, the entropy change (ΔS^0) could be calculated using the well-known relationships eqs 6 and 7

$$\Delta G^0 = -2.303RT \log K \tag{6}$$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0)/T \tag{7}$$

where R (ideal gas constant) = 8.314 $J \cdot K^{-1} \cdot mol^{-1}$; K is the dissociation constant for the ligand or the stability constant of the complex; and T is the absolute temperature.

The calculated thermodynamic parameters of HPIB are given in Table 1. The data show: (i) the positive ΔH^0 for the dissociation follows the general pattern for ionization processes which is endothermic;[27](ii) the negative ΔS^0 indicates that the total number of solvent molecules bound with the dissociated ligand is greater than that bonded to the undissociated form; and (iii) the large positive value of ΔG^0 indicates that the dissociation process is not spontaneous.[15,17,28]

The stepwise stability constants of the complexes formed at different temperatures are calculated, and the average values are given in Table 2. The decrease of the values of the stepwise stability constant with temperature indicates that the complex formation process is more favorable at lower temperature. The thermodynamic parameters of metal complexes (Table 3) are calculated by a procedure similar to that used for the dissociation of HPIB.

It is known that the divalent metal ions exist in solution as octahedrally hydrated species,[26] and the obtained values of ΔH^0 and ΔS^0 are considered as a sum of two contributions: (a) release of H_2O molecules and (b) metal−ligand bond formation. From these results the following conclusions can be made:

(i) All values of ΔG^0 for complexation are negative, indicating that the chelation process proceeds spontaneously.

(ii) The negative value of ΔH^0 shows that the chelation process is exothermic, indicating that the complexation reactions are favored at low temperatures. Furthermore, when a coordinate bond between the ligand and the metal ion is formed, the electron density of the metal ion generally increases. Consequently, its affinity for a subsequent molecule ligand decreases, leading to an increase in ΔG^0 and ΔH^0 of complexation.

(iii) It is generally noted that $-\Delta G_1{}^0 > -\Delta G_2{}^0$ and $-\Delta H_1{}^0 > -\Delta H_2{}^0$. This may be attributed to the steric hindrance produced by the entrance of a second molecule and the charge neutralization concept.

(iv) The ΔS^0 values for all investigated complexes are positive, indicating that the increase in entropy by the release of bound solvent molecules on chelation is greater than the decrease resulting from the chelation process itself. It occurs because the solvent molecules are arranged in an orderly fashion around the ligand, and the metal ion has acquired a more random configuration on chelation. This is referred to as a gain in configurational entropy.

3.4. Species Distribution Curves. Estimation of equilibrium concentrations of metal(II) complexes as a function of pH provides a useful picture of metal ion binding in solutions. All of the species distributions were calculated with the aid of the Species computer program.[20] The concentrations of metal ligand complexes increase with increasing pH. The species distribution pattern for the Co−(HPIB) complex, taken as representative of metal ligand complexes, is given in Figure 4. The Co−(HPIB) complex starts to form at pH ~ 4 and reaches its maximum concentration of 86 % at pH ~ 5.2, whereas the Co−$(HPIP)_2$ complex species reaches a maximum concentration of 72 % at pH ~ 7.2.

Table 3. Thermodynamic Parameters for ML and ML_2 Complexes of of HPIB with 3d Divalent Metal Ions in a 40 % (v/v) Ethanol−Water Mixture in the Presence of 0.100 M KCl at Different Temperatures[a]

	$-\Delta G_1^0$ (kJ·mol^{-1})			$-\Delta G_2^0$ (kJ·mol^{-1})			$-\Delta H_1^0$	$-\Delta H_2^0$	$T\Delta S_1^0$	$T\Delta S_2^0$
metal ion	298 K	308 K	318 K	298 K	308 K	318 K	kJ·mol^{-1}	kJ·mol^{-1}	308 K	308 K
Mn^{2+}	34.01 (±0.17)	34.38 (±0.11)	34.71 (±0.23)	25.56 (±0.17)	25.89 (±0.11)	26.12 (±0.23)	23.58 (±0.44)	17.22 (±0.85)	10.8 (±0.27)	8.67 (±0.74)
Co^{2+}	38.80 (±0.17)	39.22 (±0.17)	39.58 (±0.28)	26.25 (±0.17)	26.54 (±0.17)	26.73 (±0.23)	27.21 (±0.51)	19.03 (±0.88)	12.06 (±0.34)	7.51 (±0.71)
Ni^{2+}	41.37 (±0.23)	41.75 (±0.23)	42.97 (±0.23)	26.82 (±0.23)	27.07 (±0.17)	27.34 (±0.23)	30.84 (±0.58)	19.06 (±0.17)	10.91 (±0.35)	8.01 (±0.06)
Cu^{2+}	43.36 (±0.23)	43.69 (±0.28)	44.14 (±0.23)	28.35 (±0.28)	28.60 (±0.17)	28.92 (±0.23)	31.77 (±0.98)	19.97 (±0.67)	11.92 (±0.75)	8.95 (±0.39)

[a] Standard deviation errors are given in parentheses.

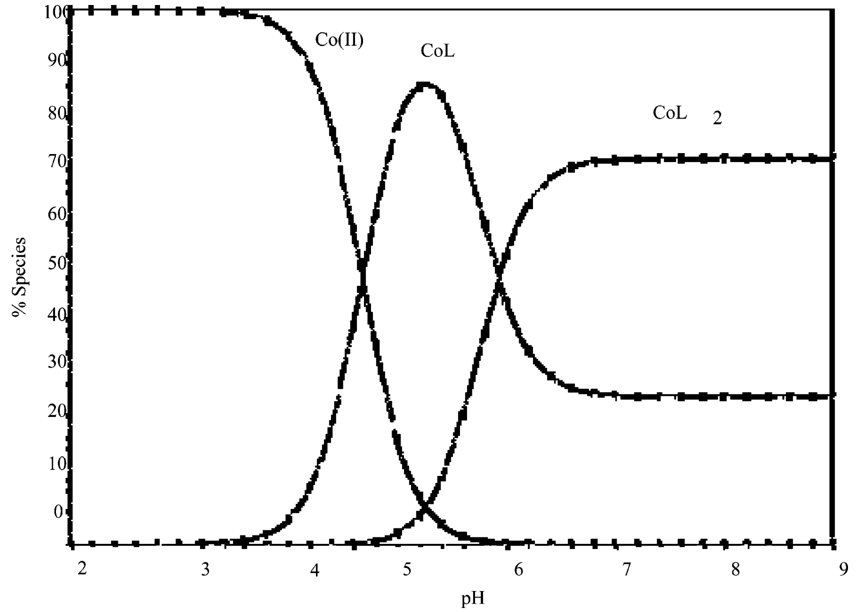

Figure 4. Concentration distribution of various species as a function of pH in the cobalt(II)−HPIB system at $[Co^{2+}] = 0.020 \cdot 10^{-3}$ M, $[HPIB] = 0.100 \cdot 10^{-3}$ M, and $[KCl] = 0.100$ M at (308 ± 1) K.

3.5. Thermodynamic Parameters of Complexation as a Function of the Properties of the Metal Ions. The stability constants and the different thermodynamic parameters are correlated with some of the properties of the metal ion such as the ionic radius, ionization enthalpy, hydration enthalpy, and electronic configuration to explain the selectivity of the ligand for complexation with certain metal ions.

The overall ΔG^0 and ΔH^0 for the formation of the titled complexes are correlated with the reciprocal ionic radius of the metal ion (Figure 5), the total ionization enthalpy at 25 °C for the process $M(gas) \rightarrow M^{2+}(gas) + 2e^-$ (Figure 6), and the enthalpy of hydration, ΔH_H (Figure 7). Moreover, $-\Delta G$ and $-\Delta H$ increase with increasing electronegativity of the metal. This is in accord with the fact that increasing electronegativity of the metal will decrease the electronegativity difference between the metal atom and the donor atom of the ligand. Thus, the metal−ligand bond would have more covalent character, which may lead to greater stability (higher $-\Delta G$ and $-\Delta H$ values) of the metal complexes.

It is found that the overall $-\Delta G$ and $-\Delta H$ (Figure 8) values for the complexation of HPIB with the divalent metal ions follow the order $Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$, which is in agreement with the Irving−Williams series.[15,17,24,28] This is in line with the fact that the greater the electron acceptor ability of a metal, the stronger the complexes that it forms will be and, hence, the more negative the values of ΔG and ΔH.

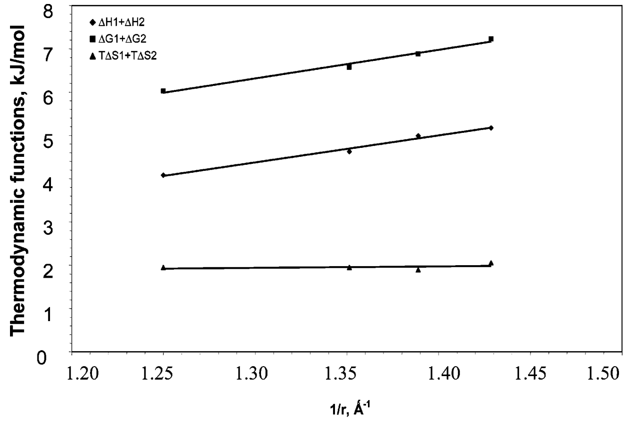

Figure 5. Variation of the overall thermodynamic functions at 308 K for the complexes with the reciprocal of the radius of the divalent metal ions.

It is apparent that the transition metal complexes of HBIB are stabilized by both favorable enthalpy (negative values) and entropy (positive values) changes (Table 3). The relatively small constant values of $T\Delta S^0$ coupled with large values of ΔH^0 suggest that enthalpy is the main driving force for complex formation in solution ($T\Delta S^0$ at 35 °C $= T\Delta S_1^0 + T\Delta S_2^0 = 19.62$ kJ·mol^{-1}).

In general, it is noted that the thermodynamic functions of the Cu^{2+} complex are higher than those of other metal ions. This is due to the extra stabilization exerted by its unique electronic configuration (d^9), which is subject to the Jahn−Teller effect.

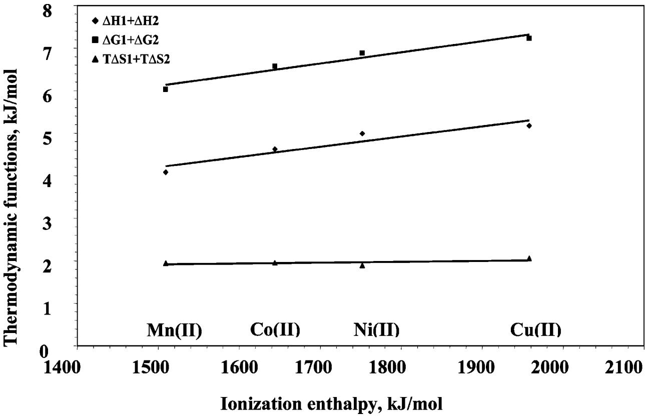

Figure 6. Variation of the overall thermodynamic functions at 308 K for the complexes with the ionization enthalpy of the divalent metal ions.

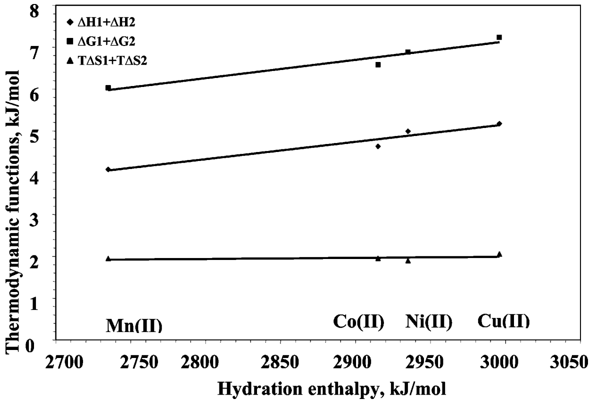

Figure 7. Variation of the overall thermodynamic functions at 308 K for HPIB complexes with the enthalpy of hydration of the divalent metal ions.

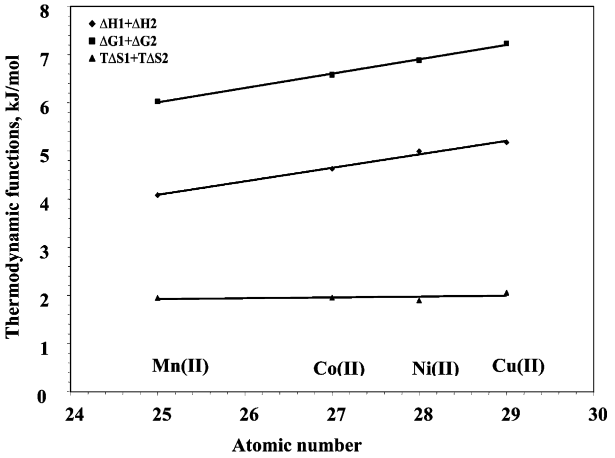

Figure 8. Variation of the overall thermodynamic functions at 308 K for HPIB complexes with the atomic number of the divalent metal ions.

Conclusion

The formation equilibria of HPIB with Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} are investigated potentiometrically in a 40 % (v/v) ethanol−water mixture in the presence of 0.100 M KCl in the temperature range of (298 to 318) K. From the values of the thermodynamic parameters, the following points could be abstracted:

(i) The values of the proton−ligand dissociation are found to be nonspontaneous, endothermic, and entropically unfavorable.

(ii) The stability of the metal complexes increases in the order $Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$.

(iii) Furthermore, the values of $\log K_1 - \log K_2$ are positive, indicating that the coordination of the first ligand molecule to the metal ion is more favorable than the bonding to the second one.

(iv) The complex formation in solution is shown to be an enthalpy driven process.

(v) The values of the thermodynamic parameters for the copper(II) complexes are higher than those of the other metal ions which could be attributed to the extra stabilization due to the unique electronic configuration of Cu^{2+}.

(vi) The values of ΔG^0 and ΔH^0 for all complexes are related to the ionic radius, the electronegativity, the ionization enthalpy, and the hydration enthalpy of the metal ion. The order of $-\Delta G^0$ and $-\Delta H^0$ is found to to be in the order $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$.

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