Potentiometric Studies on the Complexation Reactions of *N*-(2,2-[1-(3-Aminophenyl)ethylidene]hydrazino-2-oxoethyl)benzamide with Ni^{2+}, Cu^{2+}, and Cd^{2+} Ions in Aqueous Dioxane and Micellar Media

Promila Devi Thangjam and Lonibala Rajkumari*

Department of Chemistry, Manipur University, Canchipur 795 003, Manipur, India

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N-(2,2-[1-(3-Aminophenyl)ethylidene] hydrazino-2-oxoethyl)benzamide, aehb, was prepared by condensation of *N*-benzoyl glycine hydrazide with 3-aminoacetophenone and characterized on the basis of elemental and spectral data. Potentiometric studies of the Ni(II), Cu(II), and Cd(II) complexes of aehb were carried out at a constant ionic strength (I, $mol \cdot dm^{-3} = 0.10$ M KNO_3) at different temperatures, $T =$ (290, 300, and 310) K, in aqueous dioxane (40 %) and in nonionic and anionic micellar media. The ligand accepted one proton in the pH range of 5.0 to 11.0 and reacted with the Ni^{2+}, Cu^{2+}, and Cd^{2+} ions in all media to form only 1:1 metal−ligand complexes. The protonation constant of aehb and the stability constants of the complexes had been evaluated from the pH metric titration curves employing Irving and Rossotti's pH metric titration technique. The stability constant of the complexes was in the following order: Cu(II) > Ni(II) > Cd(II). Thermodynamic parameters associated with the protonation and complexation reactions of aehb were also calculated. The values of ΔG and ΔH were negative for all of the systems in all of the media, which suggested that all of the reactions were exothermic and enthalpy-driven. The presence of surfactants in the media resulted in a decrease of the protonation constant of the ligand and stability constants of the complexes due to the compartmentalizing action of the micelles on the reacting species, and the values in different media followed this trend: aqueous > Triton X-100 (Tx-100) > Labs.

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1. Introduction

Metal complexes of Schiff bases have played a central role in the development of coordination chemistry. Development of the field of bioinorganic chemistry has also led to an increased interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species especially for metalloenzymes,[1] and have a variety of applications including biological, clinical, analytical, and industrial ones in addition to their important roles in catalysis and organic synthesis.[2−7] It is also well-known that some drugs exhibit increased activity when administered as metal complexes.[8] To understand the complex formation ability of the ligands and the activities of the complexes, it is necessary to have detailed knowledge about the thermodynamic and solution equilibria involved in the reactions. The extent to which a ligand binds to a metal ion is normally expressed in terms of the stability constant, and information about the concentration of a metal complex in an equilibrium mixture can be predicted on the basis of the formation constants in solution. A survey of the literature reveals that most of the reported studies on the formation and stability constants of the complexes of Schiff bases are carried out in aqueous or mixed aqueous organic solvent media. Although there are reports[9,10] that the presence of micelles in the systems affects many chemical reactions, not enough attention has been given to understand the effect of micelles on metal complexation reactions. Since micelles represent a multiphase system where a species may be distributed in both the bulk aqueous phase and on the micelle's surface, a study of metal/Schiff base complexation reactions in micellar media would assume critical significance in view of the fact that reaction behavior observed at surfactant interfaces is expected to be more representative of many biological reactions than reactions studied in dilute aqueous solutions.[11] Protonation constants of ciprofloxacin and formation constants of Fe(III) complexes were greatly influenced[12] by the presence of sodium dodecyl sulfate and cetyl trimethylammonium bromide (CTAB), and the effects of surface active substances could be used in modeling studies of iron based antianemia drugs or multivitamin formulations and ciprofloxacin interactions in vivo. It has also been reported[13−15] that metal complexes show better micellization and biocidal properties than the parent compounds. Shin et al.[16,17] evaluated the values of formation constants of Cu(II) and Cd(II) complexes of SCN^- in both aqueous and micellar phases. The study suggested that the anionic complexes $[M(SCN)_3]^-$ may form ion pairs in micelles to keep electric neutrality and be stabilized in the hydrophobic environment of micelles. The behavior of metal complex formation in surfactant micellar solutions has been demonstrated in aqueous solution[18] and employed in removing heavy metals from soils, under acidic and alkaline conditions, through direct complexation followed by solubilization.

Thus, in an attempt to quantify the influence of the micelles on the protonation and metal complex formation, we have measured the acid dissociation constant of a new Schiff base, *N*-(2,2-[1-(3-aminophenyl)ethylidene]hydrazino-2-oxoethyl)benzamide (aehb, Figure 1) and the formation constants of Ni(II), Cu(II), and Cd(II) complexes in aqueous dioxane, nonionic Triton X-100 (Tx-100), and anionic Labs micellar media at a constant ionic strength and at three different temperatures. We report herein the equilibrium and stability constants of the complexes and thermodynamic parameters associated with the protonation and complexation reactions calculated based on

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* Corresponding author. E-mail: lonirk@yahoo.co.uk. Fax: 0385-2435145.

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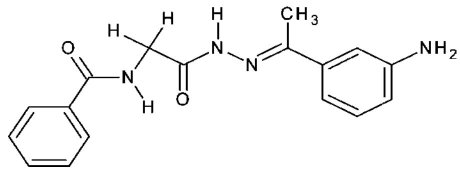


Figure 1. Structure of aehb.

the formation constants. The effects of the nonionic and anionic micelles on the protonation of the ligand and formation of the metal complexes have also been reported.

2. Experimental Section

2.1. Materials and Solutions. *N*-Benzoyl glycine, 3-aminoacetophenone, 1,4-dioxane, KOH, KNO_3, and metal salts $MCl_2 \cdot nH_2O$ (M = Ni, Cu, and Cd) were purchased from Merck. The surfactants used in this study (Tx-100 and Labs) were from Sigma-Aldrich and used as obtained without any purification. All of the other chemicals were of AnalaR grade. The solutions used in the potentiometric titrations were prepared in double-distilled water. The KOH solution was standardized[19] with standard oxalic acid solution (0.05 M), and the standard alkali solution was again used for the standardization of HNO_3. The metal salt solutions were also standardized.[19] Since the ligand was not soluble in water, the stock solution of the ligand was prepared in 40 % aqueous dioxane solution. The critical micellar concentrations (CMCs) of Tx-100 and Labs are (0.24 and 1.6) mmol, respectively. Therefore, the concentration of the solutions of the nonionic surfactant Tx-100 and anionic surfactant Labs used for preparing the reaction mixtures for the potentiometric titrations in micellar media was 5 mmol each, well above the CMCs of the surfactants, so that the surfactant molecules would aggregate to form micelles.

2.2. Apparatus and Procedure: Potentiometric Titration. A digital pH meter, Eutech Cyberscan pH 1100, with a glass calomel electrode was employed for the potentiometric titrations at three different temperatures [(290, 300, and 310) K]. The desired temperature for the titrations was maintained using a thermostat model (D8-G Haake Mess-Techinik). The pH meter was standardized before each titration with standard buffer solutions of pH 4.00, 7.00, and 9.00 obtained from Eutech Instruments, Singapore.

For evaluating the protonation constant of the ligand and the formation constants of the complexes in aqueous dioxane media, the following three sets of reaction mixtures, (a) 2.5 mL of HNO_3 (0.001 M) + 5 mL of 0.1 M KNO_3, (b) 2.5 mL of HNO_3 (0.001 M) + 5 mL of 0.1 M KNO_3 + 1.5 mL of aehb (0.0006 M), and (c) 2.5 mL of HNO_3 (0.001 M) + 5 mL of 0.1 M KNO_3 + 1.5 mL of aehb (0.0006 M) + 0.75 mL of $MCl_2 \cdot nH_2O$ (0.0003 M), were prepared. Low concentrations of metal ions were used to preclude the possibility of the formation of polynuclear complexes,[20] while the metal−ligand ratio was maintained at 1:2 molar concentrations. The volume of each set was made up to 25 mL with 40 % (v/v) aqueous dioxane mixture. The ionic strength of the solutions was maintained at 0.1 M using KNO_3 as the background electrolyte. The reaction mixtures were potentiometrically titrated against standard 0.02 M KOH solution at 290 K. For the titration in micellar media, 1.20 mL (5 mmol) of Tx-100 and 2.25 mL (5 mmol) of Labs were added separately in each set of the above reaction mixtures before making up the volume to 25 mL, and the reaction solutions were also potentiometrically titrated against the standard alkali solution at 290 K. These titrations in both aqueous dioxane and micellar media were repeated at (300 and 310) K. All of the titrations were stopped when the pH readings became unstable because of the hydrolysis of the metal ions. In all cases, no calculations were performed beyond the precipitation point. Therefore, the hydroxyl species likely to be formed beyond this point could not be studied.

2.3. Calculations. The equations of Irving and Rossotti[21,22] were used to determine the protonation constant of the ligand and the stability constants of the complexes. The average number of protons associated with the ligand ($\bar{n}_H$) at various pH meter readings was determined from the acid and ligand titration curves employing eq 1 of Irving and Rossotti.

$$\bar{n}_{\mathrm{H}} = Y - \frac{(V_{\mathrm{L}} - V_{\mathrm{A}})(N + E^0)}{(V_0 + V_{\mathrm{A}})T_{\mathrm{L}}^0} \qquad (1)$$

where Y is the number of dissociable protons present in the ligand. V_L and V_A are the volumes of KOH of concentration N (0.02 M) consumed by solutions (a) and (b), respectively, for the same pH reading, and ($V_L - V_A$) measures the displacement of the ligand curve with respect to the acid curve. V_0 is the initial volume of the reaction mixture (25 mL), and E^0 and T_L^0 are the resultant concentrations of nitric acid (0.001 M) and the ligand (0.0006 M) in the reaction mixture, respectively. The protonation curves for the proton−ligand systems were obtained by plotting $\bar{n}_H$ versus pH, and the protonation constants have been evaluated from the protonation curves at half $\bar{n}_H$ values using Bjerrum's half integral method.[23]

$\bar{n}$, the average number of ligands attached per metal ion, and pL, the free ligand exponent, were calculated from the experimental titration curves using eqs 2 and 3.

$$\bar{n} = \frac{(V_{\mathrm{M}} - V_{\mathrm{L}})(N + E^0)}{(V_0 + V_{\mathrm{A}})T_{\mathrm{M}}^0\bar{n}_{\mathrm{H}}} \qquad (2)$$

and

$$\mathrm{pL} = \log_{10}\left[\frac{\sum_{n=0}^{n=j}\beta_n H\left(\frac{1}{\mathrm{antilog\,pH}}\right)^n}{T_{\mathrm{L}}^0 - \bar{n}T_{\mathrm{M}}^0} \cdot \frac{V_0 + V_{\mathrm{M}}}{V_0}\right] \qquad (3)$$

where N, E^0, V_L, V_0, and V_A have the same meaning as in eq 1. V_M is the volume of alkali added to solution c to attain the pH reading as that of V_A and V_L, and T_M^0 is the metal ion concentration (0.0003 M) in the reaction mixture. $\beta_n H$ is the overall proton−ligand stability constant. The metal−ligand stability constants have been determined from the metal−ligand formation curves obtained by plotting the values of $\bar{n}$ against pL.

2.4. Preparation and Characterization of the Ligand. *N*-Benzoyl glycine hydrazide was prepared from *N*-benzoyl glycine as previously reported.[24] *N*-(2,2-[1-(3-Aminophenyl) ethylidene] hydrazino-2-oxoethyl) benzamide, aehb, was prepared by refluxing ethanolic solutions of *N*-benzoyl glycine hydrazide (0.02 M, 1.0 g in 30 mL) and 3-aminoacetophenone (0.02 M, 0.7 g in 10 mL) for 4 h. The white precipitate obtained on slow cooling of the reaction mixture was filtered and washed repeatedly with ethanol. It was then recrystallized from hot ethanol and dried at room temperature (% yield = 60 %; mp of (486 to 488) K; M^+ peak at 311 as the base peak in the mass spectrum of the ligand; see Figure 2).

Elemental Analysis: Found % (calcd %) for $C_{17}H_{18}N_4O_2$. C, 65.60 (65.80); H, 5.80 (5.80); N, 17.89 (18.06); N_2H_4, 10.40 (10.32).

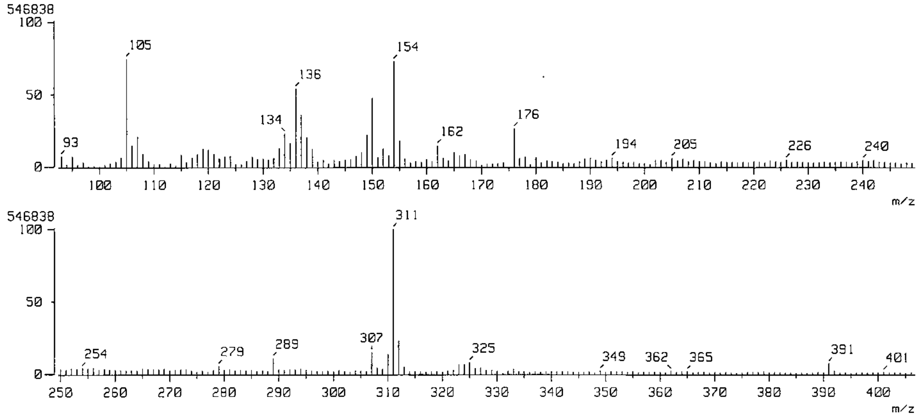


Figure 2. Mass spectrum of aehb.

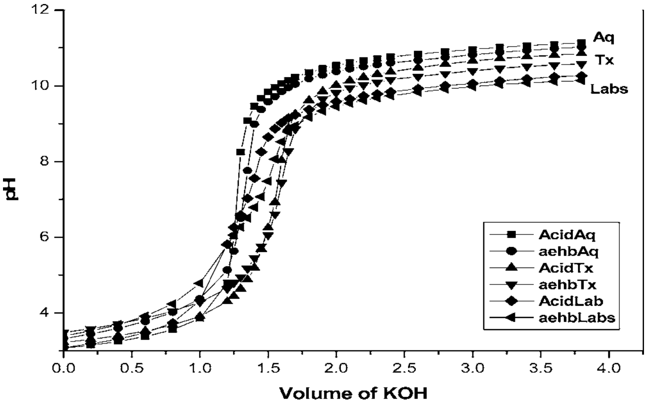


Figure 3. Acid and ligand potentiometric titration curves at 300 K and $I = 0.10\ \mathrm{mol \cdot dm^{-3}}$ KNO_3 in different media.

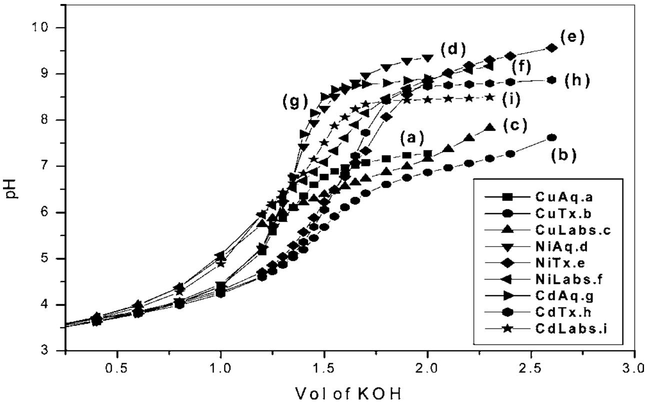


Figure 4. Potentiometric titration curves of M(II)−aehb complexes at 300 K and $I = 0.10\ \mathrm{mol \cdot dm^{-3}}$ KNO_3 in different media.

IR (ν, cm^{-1}). 1688 (amide I), 1577 (amide II), 1329 (amide III) of hydrazidic moiety, 1634 (amide I), 1552 (amide II), 1311 (amide III) of benzamide moiety, 1597 (CN), 995 (NN).

^{1}H NMR (δ). 10.74, 10.92 (d, N*H*CO), 8.98, 9.14 (d, C_6H_5CONH), 2.50 (d, NC-CH_3), 4.77 (s, CH_2), 5.44 (s, NH_2), 6.93 to 8.22 (m, ring protons).

^{13}C NMR (ppm). 171.07 (s, > *C*O hydrazide), 166.82, 165.93 (d, > *C*O benzamide), 41.37 (s, *C*H_2), 148.55 (s, N*C*), 13.57, 14.24 (d, *C*H_3), 111.45 to 138.81 (9s, ring carbons).

2.5. Physical Measurements. Hydrazine was determined volumetrically[19] by titrating against KIO_3 after subjecting the compound to acid hydrolysis for 4 h. C, N, and H were microanalyzed using a Perkin-Elmer C, H, and N analyzer model 240C. An IR spectrum was obtained using a Shimadzu Fourier transform infrared (FTIR) spectrophotometer 8400S in KBr medium, while the mass spectrum was recorded on a JEOLSX102/DA6000 mass spectrophotometer and the ^{1}H and ^{13}C NMR spectra on a Jeol AL 300 FT NMR spectrometer.

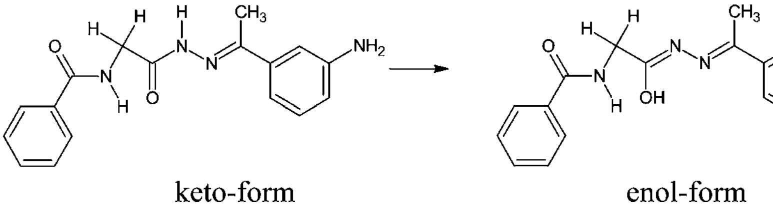
3. Results and Discussion

3.1. Titration Curves. The ligand was potentiometrically titrated with standard KOH at $I = 0.1\ \mathrm{mol \cdot dm^{-3}}$ KNO_3 and at three different temperatures [(290, 300, and 310) K] in aqueous dioxane and in Tx-100 and Labs micellar media. The potentiometric titration curves at 300 K in different media are given in Figures 3 and 4, where Figure 3 represents the acid and the ligand titration curves, and the metal−ligand titration curves for Ni(II), Cu(II), and Cd(II) complexes in aqueous dioxane and in Tx-100 and Labs micellar media are exhibited in Figure 4.

Figure 3 shows that at a constant temperature, for the same volume of alkali added to the reaction solution, the acid and ligand titration curves in Tx-100 and Labs micellar media in the initial stage were shifted to a higher pH as compared to those in aqueous dioxane media. This indicates that the presence of the surfactants caused an increase in the basicity of the ligand. However, as the ligand protonated, there was a decrease in the basicity of the ligand, and the drop in the basicity was comparatively more in the presence of Labs.

At 300 K, the protonation of the ligand occurred over the pH range of 5.0 to 11.0 in aqueous dioxane, 5.5 to 10.5 in Tx-100, and 6.5 to 9.8 in Labs micellar media. A single inflection point observed in the pH range of 5.0 to 11.5 in the ligand curves in all of the media showed the neutralization of only one proton. The addition of a metal ion to the free ligand solution shifted the buffer region of the ligand to a lower pH value as observed in the curves a to i in Figure 4. This was an indication that complex formation was proceeded by releasing protons from the base. A large decrease in pH for the metal titration curves relative to the ligand curve might be attributed to strong metal−ligand interaction. The metal−ligand curves were well-separated from the ligand curves. However, the pH ranges at which the separation of the complex curves from the ligand curves occurred were different in different media. The curve containing the Cu^{2+} ion started separate from the ligand curve at pH of 5.5, 5.0, and 5.7 and showed a wide divergence at pH 7.0, 6.6, and 6.5 in aqueous dioxane, Tx-100, and Labs media, respectively, indicating that the complexes were formed in these pH ranges in the respective media. Similarly, the formation of the Ni(II) complex occurred in the pH ranges of 6.2 to 8.8, 6.4 to 8.8, and 6.6 to 8.6, while Cd(II) complexes were formed at pH 6.2 to 8.7, 6.4 to 8.7, and 7.8 to 8.4 in aqueous, Tx-100, and Labs media, respectively. The acid−ligand and metal−ligand

Scheme 1



(1)

titration curves at (290 and 310) K showed similar features, though the pH ranges at which the protonation of the ligand and the formation of the complexes occurred were found to vary. The presence of the surfactants in the media caused a shift in the complex curves toward a higher pH value. These observations would suggest stronger proton−ligand and metal−ligand interactions in aqueous dioxane media as compared to those in surfactant media.

Hydrazones are reported[25−27] to bond to metal ions through the carbonyl oxygen and hydrazinic nitrogen/nitrogen of the imino group in the aqueous medium where there is a conjugate chelate ring formed by ligand enolization in the complexes. Thus, aehb was also expected to exhibit keto−enol tautomerism, and the amido proton could be dissociated through enolization. As shown by Figure 2, two dissociable amido protons are present in the ligand. However, pH metric studies indicated the dissociation of only one proton from the base. Studies[23,28−31] on the metal complexes of hydrazones derived from the *N*-benzoyl glycine hydrazide showed that of the two amide groups, only the hydrazidic group would deprotonate and be involved in the complexation with metal ions, while the benzamide group would not participate in complex formation. Therefore, for aehb, too, only the amido proton of the hydrazidic group would be dissociated through enolization, and the keto−enol tautomerism exhibited by the ligand might be as shown in Scheme 1.

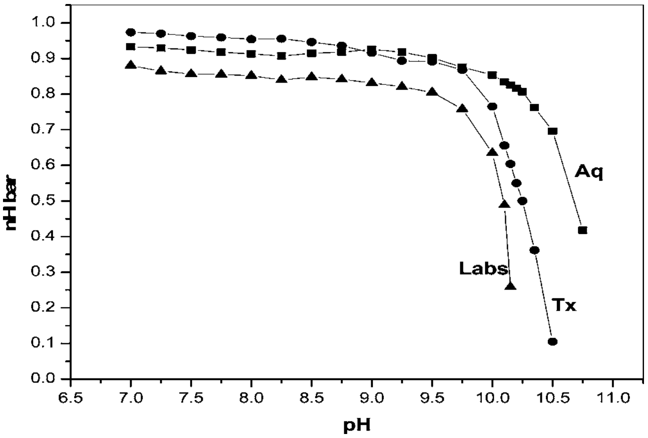


Figure 5. Proton−ligand formation curves at 300 K and $I = 0.10$ mol·dm^{-3} KNO_3 in different media.

3.2. Protonation Constant. The protonation curves for the ligand at three different temperatures, (290, 300, and 310) K, in aqueous dioxane and in Tx-100 and Labs micellar media were obtained by plotting $\bar{n}_H$ versus pH, and Figure 5 represents the protonation curves for the ligand at 300 K in different media. The curves extended from 0.1 to 1.0 on the $\bar{n}_H$ scale, showing that only one proton dissociated from the ligand in all media. The dissociation constants (log K^H_{aehb}) of the ligand at different temperatures and in different media were evaluated from the curves using Bjerrum's half integral method[23] and are collected in Table 1. In all media, the values of log K^H_{aehb} were observed to decrease with an increase in temperature, showing that the dissociation of the ligand was exothermic and favorable at lower temperatures. The values so obtained were in good agreement with the reported data.[22]

At constant temperature, the protonation constants decreased in the presence of surfactants. The trend in the protonation constant values in aqueous dioxane and in Tx-100 and Labs micellar media, aqueous > Tx-100 > Labs, showed that the affinity of the ligand for protons decreased in presence of the surfactants in the media.

3.3. Metal−Ligand Stability Constant. The metal−ligand formation curves at temperatures of (290, 300, and 310) K and in aqueous dioxane and in Tx-100 and Labs micellar media were obtained by plotting $\bar{n}$ versus pL, calculated using eqs 2 and 3. The metal−ligand formation curves at 300 K in aqueous dioxane and in Tx-100 and Labs micellar media are shown in Figure 6. It has been observed from the figure that the formation curves of Cu(II) complexes in all three media extended from 0.2 to 1.0, while those of Ni(II) and Cd(II) complexes extended from 0.1 to 0.85 on the $\bar{n}$ scale. Thus, the values of $\bar{n}$, $0.1 < \bar{n} < 1.5$, indicated the formation of only 1:1 metal−ligand complexes in all media. The metal−ligand stability constants (log K^M_{aehb}) of Cu(II), Ni(II), and Cd(II) complexes at temperatures of (290, 300, and 310) K and in aqueous dioxane and in Tx-100 and Labs micellar media evaluated from these curves are given in Table 2. There was a gradual decrease in the stability constants of the complexes in all media with an increase in temperature showing that the complexation reactions were exothermic in nature and hence favorable at lower temperature. This behavior might also be ascribed to the thermal hydrolysis of the metal complexes.[22]

Table 1. Protonation Constant (log K^H_{aehb}) of aehb and Thermodynamic Parameters of the Dissociation Reaction of the Ligand at Different Temperatures and at $I = 0.10$ mol·dm^{-3} KNO_3 in 40 % (v/v) Aqueous Dioxane and in Tx-100 and Labs Micellar Media

medium	temperature (K)	log K^H_{aehb}	$-\Delta G$ (kJ·mol^{-1})	$-\Delta H^a$ (kJ·mol^{-1})	$-\Delta S^a$ (J·deg^{-1}·mol^{-1})
aqueous dioxane	290	10.84 ± 0.02	60.19 ± 0.01	51.34 ± 0.02	+33.37 ± 0.05
	300	10.68 ± 0.03	61.35 ± 0.01		
	310	10.24 ± 0.02	60.78 ± 0.03		
Tx-100	290	10.75 ± 0.02	59.69 ± 0.02	61.54 ± 0.04	8.87 ± 0.05
	300	10.25 ± 0.13	58.88 ± 0.04		
	310	10.05 ± 0.03	59.65 ± 0.02		
Labs	290	10.26 ± 0.03	56.97 ± 0.05	37.93 ± 0.02	+66.77 ± 0.02
	300	10.09 ± 0.05	57.96 ± 0.01		
	310	9.82 ± 0.01	58.29 ± 0.01		

[a] ΔH and ΔS were computed using the linear fit program.

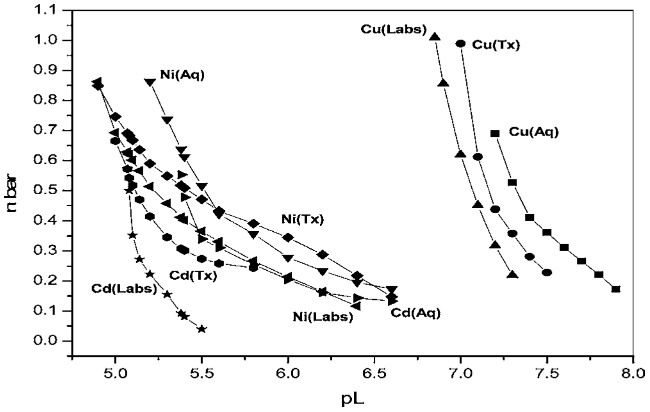


Figure 6. Metal−ligand formation curves of M(II)−aehb chelates at 300 K and $I = 0.10$ mol·dm^{-3} KNO$_3$ in different media.

Table 2. Stability Constants (log K^{M}_{aehb}) of M(II)−aehb Chelates (1:1) at Different Temperatures and $I = 0.10$ mol·dm^{-3} KNO$_3$ in 40 % (v/v) Aqueous Dioxane and in Tx-100 and Labs Micellar Media

medium	temperature (K)	metal ions Cu	Ni	Cd
aqueous dioxane	290	7.41 ± 0.03	5.92 ± 0.00	5.49 ± 0.11
	300	7.32 ± 0.04	5.54 ± 0.01	5.39 ± 0.05
	310	7.25 ± 0.01	5.23 ± 0.01	5.16 ± 0.13
Tx-100	290	7.35 ± 0.01	5.60 ± 0.01	5.26 ± 0.08
	300	7.16 ± 0.01	5.40 ± 0.01	5.12 ± 0.06
	310	7.03 ± 0.01	5.21 ± 0.04	4.96 ± 0.07
Labs	290	7.30 ± 0.01	5.25 ± 0.02	5.18 ± 0.03
	300	7.07 ± 0.04	5.19 ± 0.03	5.08 ± 0.09
	310	6.97 ± 0.05	4.88 ± 0.01	4.88 ± 0.08

At constant temperature, the stability constants of the complexes in aqueous dioxane and in Tx-100 and Labs micellar media fell in the Irving−Williams order[21,22] where Cu(II) > Ni(II) > Cd(II). The values of stability constants for the Cu(II) complex were higher than those for Ni(II) and Cd(II) complexes in all media. The extra stabilization of the Cu(II) complex could be attributed to the unique electronic configuration on Cu^{2+} and the Jahn−Teller effect. As observed in the protonation curves of the ligand in different media, Figure 6 also showed that the presence of anionic and nonionic surfactants in the media caused a shift in the formation curves of all of the complexes toward the left.

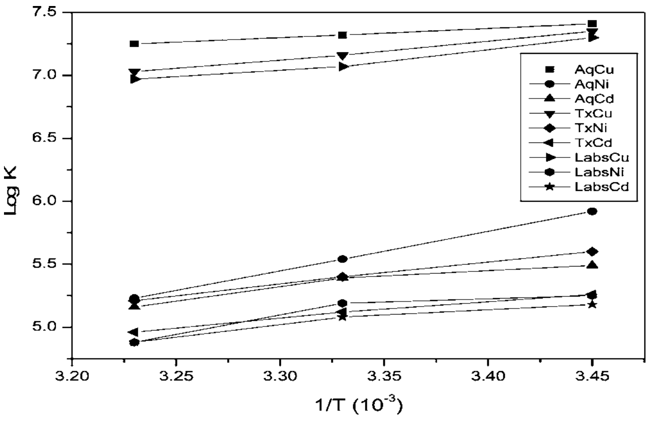


Figure 7. Plot of log K^{M}_{aehb} vs $1/T$ in different media.

3.4. *Effect of Temperature.* The thermodynamic parameters associated with the protonation of aebh and the formation of 1:1 complexes in the systems (M(II) + aehb) were also studied at $I = 0.10$ mol·dm^{-3} KNO$_3$ in different media. The change in free energy (ΔG) was calculated from the formation constant values (log K) at various temperatures and in different media using the following equation:

$$\Delta G = -2.303RT \log K \qquad (4)$$

where R (ideal gas constant) = 8.314 J·K^{-1}·mol^{-1}; K = protonation constant of aehb or stability constant of the complexes; T = absolute temperature (K).

The enthalpy change (ΔH) for the dissociation of the ligand and complexation reactions in different media was evaluated from the slope of the plot of log K_1^{H} or log K versus $1/T$ (Figure 7) using the graphical representation of the van't Hoff eq 5, and the change in entropy (ΔS) could then be calculated using relationship from eq 6:

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

$$\Delta S = (\Delta H - \Delta G)/T \qquad (6)$$

The calculated thermodynamic parameters for the dissociation of the ligand in both aqueous dioxane and micellar media are included in Table 1, and those for the complexation reactions are collected in Table 3.

In the aqueous dioxane media, the ΔG values for both protonation and complexation reactions were negative, indicating the spontaneity of the reactions. The tables show that the ΔG values had no sharp behavior with temperature, indicating the independent nature of the reactions with respect to temperature.[32] Negative ΔH values and positive ΔS values for the protonation of the ligand suggest that the reaction was both enthalpy and entropy-driven in aqueous dioxane media. The ΔG and ΔH values associated with the complexation reactions were negative. Thus, it is evident that the reactions were spontaneous and enthalpy-driven and the values followed the order Cu(II) > Ni(II) > Cd(II), which is consistent with the Irving−Williams series.[21,22] Positive ΔS terms for Cu(II) and Cd(II) complexes indicated that the formation of these complexes was entropy-favored, while ΔS values were negative for the Ni(II) complex suggesting a highly solvated metal complex.

Table 3. Thermodynamic Parameters of M(II)−aehb Chelates (1:1) at Different Temperatures and $I = 0.10$ mol·dm^{-3} KNO$_3$ in 40 % (v/v) Aqueous Dioxane and in Tx-100 and Labs Micellar Media

medium	M(II)−aehb complexes	−ΔG (kJ·mol^{-1}) 290 K	300 K	310 K	−ΔH[a] (kJ·mol^{-1})	−ΔS[a] (J·deg^{-1}·mol^{-1})
aqueous dioxane	Cu	41.14 ± 0.04	42.05 ± 0.02	43.03 ± 0.01	13.94 ± 0.02	+93.70 ± 0.02
	Ni	32.87 ± 0.02	31.82 ± 0.02	31.04 ± 0.01	60.07 ± 0.02	94.17 ± 0.03
	Cd	30.48 ± 0.06	30.96 ± 0.05	30.63 ± 0.03	28.30 ± 0.04	+8.87 ± 0.04
Tx-100	Cu	40.81 ± 0.03	41.13 ± 0.01	41.73 ± 0.01	27.93 ± 0.01	+44.00 ± 0.02
	Ni	31.09 ± 0.03	31.02 ± 0.01	30.92 ± 0.02	33.87 ± 0.02	9.50 ± 0.03
	Cd	29.21 ± 0.06	29.41 ± 0.04	29.44 ± 0.06	25.98 ± 0.04	+11.43 ± 0.04
Labs	Cu	40.53 ± 0.01	40.61 ± 0.02	41.37 ± 0.02	28.98 ± 0.02	+38.77 ± 0.01
	Ni	29.15 ± 0.02	29.81 ± 0.02	28.96 ± 0.02	27.04 ± 0.02	5.50 ± 0.03
	Cd	28.76 ± 0.05	29.18 ± 0.04	28.96 ± 0.07	25.77 ± 0.05	+11.37 ± 0.05

[a] ΔH and ΔS were computed using the linear-fit program.

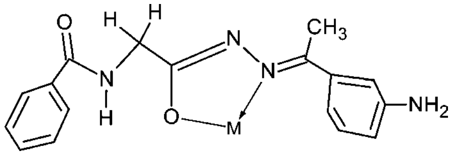


Figure 8. Representative structure showing the bonding sites of the ligand. M = Cu, Ni, or Cd.

A decrease in log *K* with an increase in temperature and the negative values of ΔH for all of the reactions in all of the media showed exothermic and enthalpy-favored reactions. This result would suggest the importance of the enthalpy rather than the entropy factor in both the protonation and the complexation processes.

Tables 1 and 3 show that the thermodynamic parameters were perturbed by the presence of surfactants in the reacting systems. Though all of the reactions were spontaneous and enthalpy-driven in micellar media, a gradual decrease in the ΔG values for the protonation and complexation reactions in the presence of surfactants, in the order aqueous > Tx-100 > Labs, was observed, while the ΔH and ΔS values varied randomly. The ΔS value for the protonation of aehb was negative in Tx-100 media, showing that the protonation had an unfavorable change of entropy in the presence of Tx-100, while it was evident from the negative ΔH and positive ΔS values that the reaction was both enthalpy and entropy-driven in other media.

3.5. Effect of Micelles on the Stability Constants. Micelles can incorporate reactant molecules in their hydrophobic core because of their solubilizing properties. The solubilization of the species into the micellar pseudophase can affect the absolute and relative concentrations of the reacting species and thus affect the reaction equilibria.[33] If there was an increasing partitioning of the ligand in favor of the micellar pseudophase and the actual complexation reaction was assumed to take place in the bulk aqueous phase, the possibility of complex formation would decrease, resulting in a fall of the formation constant.

It has been observed for all of the M(II)−aehb systems under study that the presence of the nonionic (Tx-100) and anionic (Labs) surfactants in the reaction mixtures resulted in shifting of the complex formation curves toward much lower pH values in comparison with those in aqueous dioxane media. This shows that complex formation was more favorable in aqueous dioxane media and the presence of micelles had apparently led to destabilizing the complex. A decrease in the stability of the M(II)−aehb complexes in the presence of surfactants was quite significant, and the order of stability for all of the complexes in different media at all of the temperatures was found to be aqueous > Tx-100 > Labs.

The decrease in the stability of the complex in micellar media would suggest that the ligand molecules with a large hydrophobic moiety in them were preferably drawn inside the hydrophobic core of the micelles, while the metal ions were dispersed between the stern layer and the bulk solution.[17,34] This would limit the ligands available for complexation since only the metal ions in the vicinity of the stern layer could interact with the ligand, thereby bringing about a decrease in the overall stability constant. The decrease in the stability of the complexes in micellar media might also be due to a decrease in the dielectric constant of the media with the addition of the surfactant molecules. Polarity due to the presence of surfactant molecules in the medium might also lead to the decrease of the stability constant as there was strong competition from the solvent molecules. From the observed trend, it would appear that the ligand was better stabilized in the core of the anionic micelles.

On the basis of the foregoing discussion, the chelation of the base with Cu^{2+}, Ni^{2+}, and Cd^{2+} ions appeared to be through the enolic oxygen of the hydrazinic carbonyl group forming the covalent bond and the azomethine nitrogen forming a coordinate covalent bond, as shown in Figure 8.

Supporting Information Available:

Tables 1, 2, and 3 containing values of $\bar{n}$ and pL for Cu(II), Ni(II), and Cd(II) complexes, respectively, in different media (aqueous dioxane, Tx-100, and Labs) at 300 K at different pH values. This material is available free of charge via the Internet at http://pubs.acs.org.

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