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Spectrophotometric Studies, Stability Constants and Thermodynamics for Complexes of *o*-Hydroxyacetophenone Isobutyroylhydrazone with Some Bivalent Transition Metal Ions

A. A. El-Bindary

Chemistry Department, Faculty of Science (Demiatta), Mansoura University, Demiatta, Egypt

Summary. The u.v. spectra of *o*-hydroxyacetophenone isobutyroylhydrazone (*HAIBuH*) were investigated in pure organic solvents as well as in Britton Robinson buffer solutions of varying *pH* values. The interaction of *HAIBuH* with Co(II), Ni(II) and Cu(II) were studied spectrophotometrically. The optimum *pH* favouring the formation of the highly coloured complexes are 8.5, 8.0 and 7.5 for Co(II), Ni(II) and Cu(II), respectively. The stoichiometries of these complexes were determined and indicated the formation of 1:2 (metal:ligand) complexes of Co(II) and Ni(II) and a 1:1 complex of Cu(II). The dissociation constants pK^H of *HAIBuH* and the overall stability constants $\log\beta$ of their complexes were determined at different temperatures (293, 303 and 313 K). The corresponding thermodynamic parameters (ΔG, ΔH and ΔS) in 20% (*v*/*v*) ethanol-water mixture were derived and discussed.

Keywords. *o*-hydroxyacetophenone isobutyroylhydrazone; Dissociation and stability constants; Thermodynamic parameters.

Spektrophotometrische Untersuchungen, Stabilitätskonstanten und Thermodynamik der Komplexe von *o*-Hydroxyacetophenonisobutyroylhydrazon mit einigen bivalenten Übergangsmetallionen

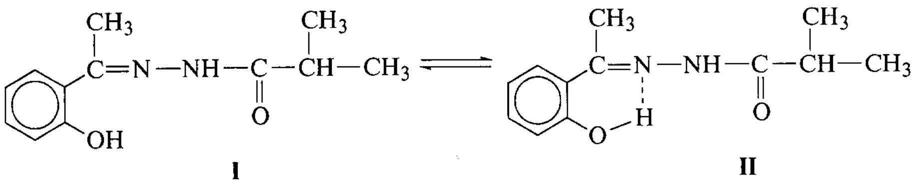
Zusammenfassung. Die UV-Spektren von *o*-Hydroxyacetophenon-isobutyroylhydrazon (*HAIBuH*) wurden in reinen organischen Solventien und in Britton-Robinson-Pufferlösungen von verschiedenem *pH* gemessen. Die Wechselwirkung von *HAIBuH* mit Co(II), Ni(II) und Cu(II) wurde spektrophotometrisch untersucht. Die optimalen *pH*-Werte zur maximalen Ausbildung der starkgefärbten Komplexe sind 8.5, 8.0 bzw. 7.5 für Co(II), Ni(II) bzw. Cu(II). Für die Stöchiometrien wurde ein Metall:Ligand-Verhältnis 1:2 für Co(II) und Ni(II) und 1:1 für Cu(II) bestimmt. Die Dissoziationskonstanten pK^H von *HAIBuH* und die Gesamtstabilitätskonstanten $\log\beta$ der Komplexe wurden bei verschiedenen Temperaturen bestimmt (293, 303 und 313 K) und die entsprechenden thermodynamischen Parameter ($\Delta G, \Delta H$ und ΔS) in 20% (*v*/*v*) Ethanol-Wasser-Mischung errechnet und diskutiert.

Introduction

The applications of stability constants are numerous [1], e.g. in life sciences, medicine, pollution, animals, and plants. Both animals and plants contain quantities of both ligands and metal ions [2]. In continuation of our earlier work [3–6] on enthalpy measurements, we report herein the thermodynamic behaviour of *o*-hydroxyacetophenone isobutyroylhydrazone and its complexes formed in solution with Co(II), Ni(II) and Cu(II). Also, the effect of *pH*, stoichiometries and the stability constants of the metal complexes were determined spectrophotometrically. Hydrazone-Co(II), Ni(II) and Cu(II) systems were chosen owing to the reported antimalarial [7] and anti-diabetics [8] agents based on hydrazones as well as the treatment of many diseases such as leprosy and tuberculosis [9]. Moreover, Cu(II), Co(II) and Ni(II) are present in all healthy tissue in man and their roles are of utmost importance.

Experimental

HAIBuH was obtained as mentioned previously [10]. The compound has the general structures **I** and **II** [11].



I **II**

The solvents utilized were obtained from commercial sources and purified according to recommended procedures [12]. The buffers used for *pH* control were prepared as recommended by Britton and Rhobinson [13]. Stock solutions of 10^{-3} *M* *HAIBuH* and metal chlorides were prepared by dissolving an accurate weight in the appropriate volume of pure ethanol. Solutions for spectral measurements were obtained by accurate dilution of the stock ones. The buffers are usually made in 20% (*v*/*v*) ethanol-water. Solutions of the metal chlorides were estimated using standard methods of analysis [14].

The absorption spectra were recorded in the wavelength range 200–400 nm on a varian 634 spectrophotometer equipped with a thermostatted cell holder using a 1 cm matched silica cell. The temperature was controlled at 293, 303 and 313 K using a Gallenkamp thermo stirrer 85 with an accuracy of 0.05 K. The *pH* measurements were carried out at 298 K using a HANNA instruments model 8519 *pH*-meter accurate to ±0.01 *pH* units. The correction of *pH* readings in 20% (*v*/*v*) ethanol-water are taken from Irving and Mahnot [15].

Results and Discussion

Effect of Solvents

The spectrum of *HAIBuH* was recorded in organic solvents of different polarities (Fig. 1). The λ_{max} and ε_{max} values of the different bands obtained from the spectra are collected in Table 1. The electronic absorption spectra are composed of three sets of bands. The first one (A) near 215 nm is due to the medium energy ($\pi \rightarrow \pi^*$) transition corresponding to the ($^1L_a \leftarrow {}^1A$) transition. This band is obscured in the spectra in some solvents such as *DMF*, $CHCl_3$ and CCl_4 due to the opacity of these solvents in the uv region. The second one (B) in the (255–285 nm) region is due to the $\pi \rightarrow \pi^*$ transition corresponding to ($^1L_b \leftarrow {}^1A$) within the aromatic system and

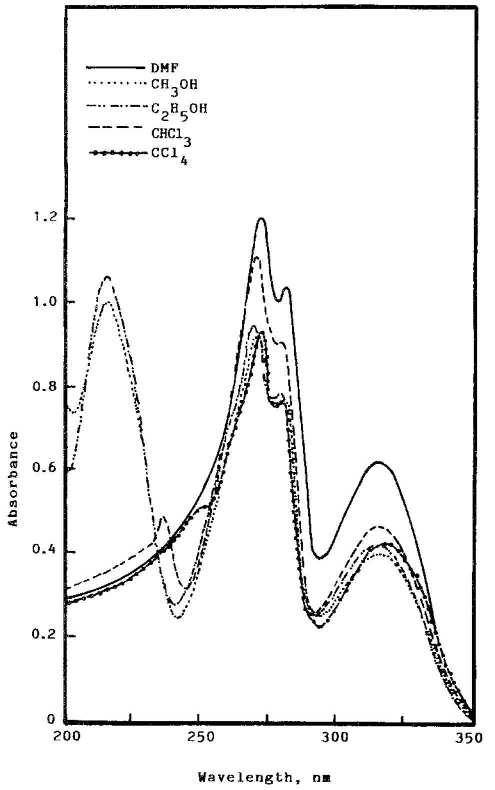


Fig. 1. The electronic absorption spectra of 5×10^{-5} *M* of *HAIBuH* in different organic solvents at 293 K

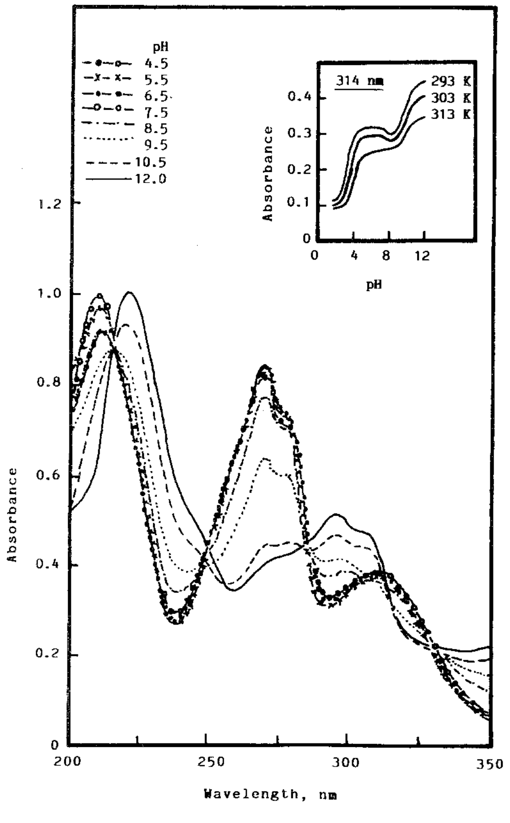


Fig. 2. The electronic absorption spectra of 5×10^{-5} *M* of *HAIBuH* in Britton universal buffer solutions containing 20% (*v*/*v*) ethanol-water mixture at 293 K

Table 1. Assignment of the electronic spectral bands of *HAIBuH* and other parameters in different organic solvents at 293 K

Solvent	λ_m nm	$\varepsilon_m/10^3$ $\mathrm{l\,mol^{-1}\,cm^{-1}}$
Dimethylformamide	260 sh	16.820
	271	24.500
	279	20.300
	314	12.120
Methanol	215	20.400
	260 sh	14.300
	269	18.840
	279	14.900
	314	7.680
Ethanol	215	21.680
	260 sh	14.520
	269	19.280
	279	15.320
	314	8.200
Chloroform	260 sh	15.940
	271	22.640
	279	17.800
	314	8.900
Carbon tetrachloride	260 sh	14.100
	271	19.200
	280	14.880
	315	8.200

its conjugation with the OH group [16]. The third band (C) around 314 nm is mainly broad and less intense and can be assigned to the $n \rightarrow \pi^*$ transition of the carbonyl group.

Effect of pH on HAIBuH

The spectra of $5 \times 10^{-5}\,M$ of *HAIBuH* in 20% (*v*/*v*) ethanol-water mixture within the *pH* range 2–12 and at 293, 303 and 313 K were recorded (Fig. 2). The spectra of *HAIBuH* in aqueous buffer solutions show regular changes with increasing *pH* of the medium, especially the band at 314 nm. The absorption spectra exhibit clear isosbestic points at 250 and 285 nm, denoting the existence of an equilibrium essentially of acid-base type between the two forms existing in solution. The protons associated with the ligand naturally dissociate in steps in solution which correspond to the two dissociation constants for the ligand. If H_2L denotes the protonated ligand and L the ligand, then the stepwise dissociation can be represented as

$$H_2L \rightleftharpoons HL^- + H^+$$
$$HL^- \rightleftharpoons L^{2-} + H^+$$

The absorption-*pH* curve constructed at 314 nm (Fig. 2) is a typical dissociation curve, revealing the existence of an acid-base equilibrium in each case.

Table 2. Thermodynamic parameters and pK^H values of *HAIBuH* in 20% (*v*/*v*) ethanol-water mixture at different temperatures

	λ_{max} nm	Temp. K	Method			Mean	ΔH kJ mol^{-1}	ΔG kJ mol^{-1}	$-\Delta S$ J mol^{-1} K^{-1}
			a	b	c				
pK_1^H	314	293	3.82	3.82	3.80	3.82 ± 0.01	16.849	22.774	15.4 ± 3.0
		303	3.71	3.73	3.70	3.71 ± 0.01		21.582	
		313	3.60	3.63	3.62	3.62 ± 0.01		20.252	
pK_2^H	314	293	9.67	9.71	9.65	9.68 ± 0.02	22.737	58.013	107.8 ± 4.1
		303	9.55	9.57	9.52	9.55 ± 0.02		55.405	
		313	9.40	9.45	9.42	9.42 ± 0.02		52.847	

a = half-height method, b = limiting absorbance method, c = modified Collecter method

Increasing the *pH* leads to an increase of the absorbance till it attains a constant value at 7.5. The band at 314 nm becomes broad and exhibits a red shift as the result of the ionization of the phenolic OH group. This behaviour is due to the strong intramolecular H-bond (structure **II**). By increasing the *pH* above 7.5 the absorbance increases and exhibits a blue shift, the broad band splits into two bands at 295 and 308 nm. The bands at 255–285 nm decrease by increasing of *pH* till 12. The last changes are due to the dissociation of the hydrazo group of *HAIBuH* from the mono-ionized to the dinegative anion. The colour of the buffered solutions ranged from colourless ($pH = 3.5$) to pale yellow ($pH = 7.5$) for phenolic OH ionization, then from pale yellow to yellow ($pH = 12$) for the hydrazo form [17].

The pK_1^H and pK_2^H values of *HAIBuH* (Table 2) were obtained by applying different spectrophotometric methods, namely, the half height [18], modified limiting absorbance [19], and the modified Colleter method [20] at 293, 303 and 313 K. Moreover, the error limits in the determination of pK_1^H and pK_2^H values are given as twice of the overall estimated standard deviation of the mean.

Effect of pH on Complex Formation

This study was carried out to determine the optimum *pH* at which *HAIBuH* forms a highly coloured complex with some metal ions. Thus, solutions containing 1×10^{-4} *M* of metal ion and 1×10^{-3} *M* of *HAIBuH* in Britton universal buffer of varying *pH* and in 20% (*v*/*v*) ethanol-water mixture were used. The variations of the absorbance at the characteristic wavelength of each metal-complex with the *pH* of the solution are represented in Fig. 3. Measurements have shown that the *pH* at which the maximum complex formation occurs depend on the metal ion. The optimum *pH* value for complex formation was found to be 8.5, 8.0 and 7.5 for Co(II), Ni(II) and Cu(II), respectively. The sequence of addition metal-buffer-ligand or ligand-buffer-metal has no effect on the optimum *pH* values for the complexes. However, at *pH* values higher than these values the absorbance of the complexes decreases with increasing *pH*, which may be attributable to its decomposition or the formation of hydroxy complexes.

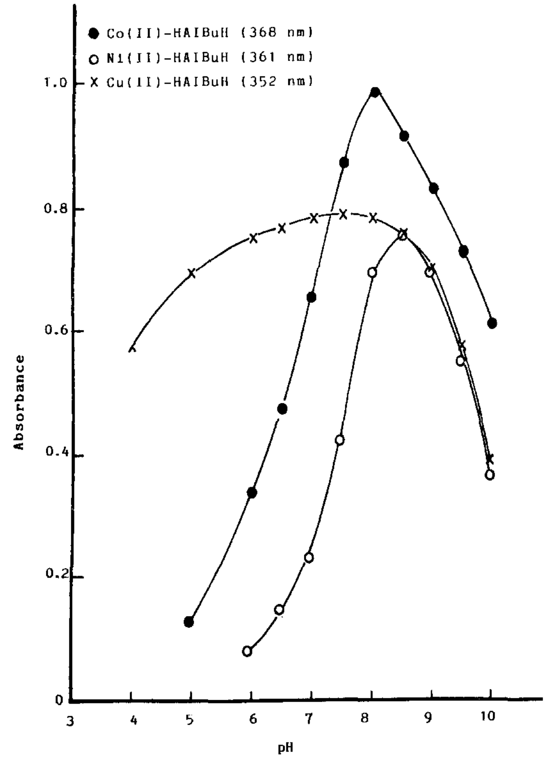


Fig. 3. The absorbance-*pH* curves of $1 \times 10^{-4} M$ of metal ion complexes with $1 \times 10^{-3} M$ of *HAIBuH* in Britton universal buffer solution of varying *pH* values in 20% (*v*/*v*) ethanol-water mixture at 293 K

Effect of Time and Temperature

It was found that the complexes are completely developed spontaneously and remain constant for 48 hours. It was also found that raising the temperature up to 333 K has no effect on the formation of the complexes, whereas boiling destroys the formed complexes.

Stoichiometries and stability constants of the complexes result from measurements in the range of 200–400 nm for the complex solutions with *HAIBuH* at the optimum *pH* values with characteristic absorption maxima at 238, 361 for Co(II), 236, 368 for Ni(II), and 238, 352 nm for Cu(II). These studies were carried out to investigate the stoichiometries of the formed complexes from the molar ratio [21] and continuous variation [22] methods. Both methods indicated the formation of 1:2 (metal:ligand) complexes with Co(II) and Ni(II), whereas 1:1 (metal:ligand) complex were obtained with Cu(II) (Fig. 4a, b). The overall stability constants (log β) were determined applying the molar ratio [21] and continuous variation [22] methods at 293, 303, and 313 K (Table 3). The data in Table 3 reveal that the overall stability constants (log β) agree well with the Irving–Williams [23] and Van Uitert et al. [24] order of stabilities for *HAIBuH*: Co(II) < Ni(II).

The stability constants of the complexes were determined spectrophotometrically by measuring the absorbance of solutions containing $1 \times 10^{-5} M$ of metal ion and $1 \times 10^{-4} M$ of *HAIBuH* in 20% (*v*/*v*) ethanol-water at varying *pH* values (Fig. 3). The values of the degree of formation of the complexes ($\bar{n}$) [25] were obtained from the relationship

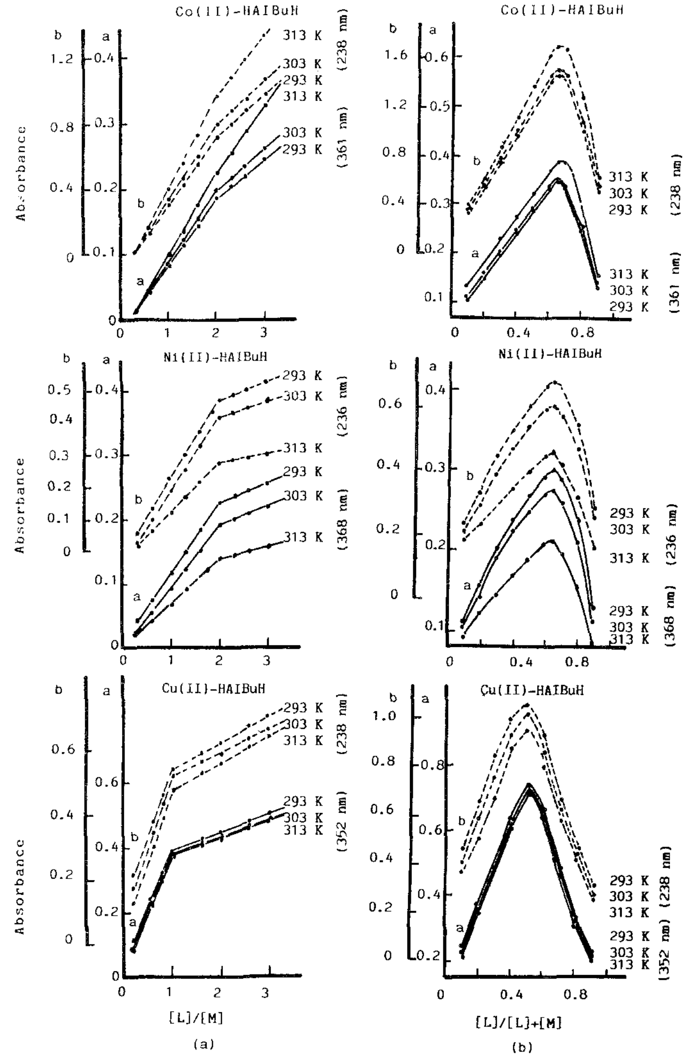


Fig. 4. Determination of the stoichiometry of M(II)-*HAIBuH* complexes by (a) molar ratio (constant $M(\text{II}) = 5 \times 10^{-5}\,M$) and (b) continuous variation method (total $2 \times 10^{-4}\,M$), and in 20% (v/v) ethanol-water mixture at 293, 303 and 313 K

$$\bar{n} = \frac{A_x - A_L}{A_{ML} - A_L} \tag{1}$$

where A_X, A_L and A_{ML} are the absorbances at a specific pH value of the partially formed complex, the free ligand and the fully formed complex, respectively. The value of A_L of the ligand has been cancelled out, since the same concentration of ligand solution was used as a reference throughout the measurements. The negative logarithm of the concentration of the non-protonated ligand [pL] was obtained using Eq. (2) [26].

$$pL = \log\left[\frac{\beta_0^{\mathrm{H}} + \beta_1^{\mathrm{H}}[\mathrm{H}^+] + \beta_2^{\mathrm{H}}[\mathrm{H}^+]^2}{T_L - \bar{n}T_M}\right] \tag{2}$$

where $\beta_0^{\mathrm{H}} = 1$, β_1^{H} and β_2^{H} are the reciprocals of the acid dissociation constants of the ligand, respectively. T_L and T_M are the stoichiometric concentrations of the ligand

Table 3. Thermodynamic parameters and overall stability constants of *M*(II)-*HAIBuH* complexes in 20% (*v*/*v*) ethanol-water mixture by molar ratio (M.R.) and continuous variation (C.V.) methods at different temperatures

Compound	Method	λ_{max} nm	Stoichiometry	Temperature T, K	$\log\beta$	ΔH kJ mol^{-1}	$-\Delta G$ kJ mol^{-1}	ΔS J mol^{-1} K^{-1}
Co(II)-*HAIBuH* $pH = 8.5$	M.R.	238	1:2	293	9.03	+13.403	50.659	218.44±0.25
				303	9.08		52.678	
				313	9.18		55.016	
		361	1:2	293	9.13	+14.801	51.220	225.04±0.23
				303	9.20		53.375	
				313	9.27		55.555	
	C.V.	238	1:2	293	9.08	+11.967	50.940	214.46±0.29
				303	9.13		52.968	
				313	9.20		55.136	
		361	1:2	293	9.15	+11.967	51.333	216.12±0.08
				303	9.23		53.549	
				313	9.29		55.675	
Ni(II)-*HAIBuH* $pH = 8.0$	M.R.	236	1:2	293	9.98	−29.582	55.989	90.39±0.19
				303	9.83		57.030	
				313	9.66		57.893	
		368	1:2	293	9.88	−28.280	55.428	92.57±0.38
				303	9.73		56.449	
				313	9.58		57.413	

Table 3. (Continued)

Compound	Method	λ_{max} nm	Stoichiometry	Temperature T, K	$\log\beta$	ΔH kJ mol^{-1}	$-\Delta G$ kJ mol^{-1}	ΔS J mol^{-1} K^{-1}
	C.V.	236	1:2	293	9.95	−29.582	55.821	89.62 ± 0.05
				303	9.78		56.739	
				313	9.62		57.653	
		368	1:2	293	9.92	−28.280	55.652	93.41 ± 0.05
				303	9.75		56.565	
				313	9.60		57.533	
Cu(II)-*HAIBuH* *pH* = 7.5	M.R.	238	1:1	293	5.28	−14.648	29.621	51.06 ± 0.03
				303	5.19		30.110	
				313	5.11		30.625	
		352	1:1	293	5.22	−13.403	29.285	54.28 ± 0.07
				303	5.15		29.878	
				313	5.07		30.385	
	C.V.	238	1:1	293	5.24	−14.016	29.397	52.57 ± 0.08
				303	5.16		29.936	
				313	5.09		30.505	
		352	1:1	293	5.16	−10.397	28.948	63.44 ± 0.20
				303	5.12		29.704	
				313	5.04		30.205	

Table 4. Stability constants of M(II)-*HAIBuH* complexes in 20% (v/v) ethanol-water mixture at 293 K ($T_L = 1 \times 10^{-3}\,M$, $T_M = 1 \times 10^{-4}\,M$, and $pK_1^{\mathrm{H}} = 3.82$ and pK_2^{H} of *HAIBuH* $= 9.68$)

Complex	$\lambda_{\max}$ nm	pH	A_x	A_{ML}	$\bar{n}$	pL	$\log K_1$
Co(II)-*HAIBuH*	368	6.00	0.080	0.756	0.106	4.499	3.573
$pH = 8.5$		6.50	0.415	0.756	0.192	3.613	2.989
		7.00	0.230	0.756	0.304	3.128	2.768
		7.50	0.428	0.756	0.566	3.140	3.255
		7.75	0.575	0.756	0.761	3.039	3.542
		8.00	0.695	0.756	0.919	3.043	4.098
							mean value 3.371 ± 0.43
Ni(II)-*HAIBuH*	361	5.50	0.210	0.975	0.512	5.491	4.928
$pH = 8.0$		6.00	0.300	0.975	0.308	4.508	4.156
		6.50	0.475	0.975	0.487	3.626	3.603
		7.00	0.653	0.975	0.670	3.145	3.453
		7.50	0.874	0.975	0.896	3.054	3.989
		7.75	0.940	0.975	0.964	3.048	4.476
							mean value 4.101 ± 0.50
Cu(II)-*HAIBuH*	352	5.50	0.730	0.790	0.924	5.524	6.608
$pH = 7.5$		5.75	0.740	0.790	0.937	5.027	6.200
		6.00	0.750	0.790	0.949	4.538	5.807
		6.50	0.770	0.790	0.975	3.649	5.240
		6.75	0.775	0.790	0.981	3.336	5.049
		7.00	0.780	0.790	0.987	3.160	5.040
							mean value 5.657 ± 0.60

and metal ion. The equation of the formation curve is

$$\bar{n} + (1 - \bar{n})K_1[L] = 0 \tag{3}$$

where K_1 is the stability constant of the complex. The values of $\bar{n}$ extended from 0 to 1 indicating that the only 1:1 (metal:ligand) complex is formed in the pH 6.0–8.0, 5.50–7.75 and 5.50–7.00 range for Co(II), Ni(II) and Cu(II), respectively. The values of $\log K_1$ calculated using Eq. (3) are shown in Table 4. The data in Table 4 reveal that the stability constants ($\log K_1$) agree well with the Irving–Williams [23] and Van Uitert et al. [24] order of stabilities for *HAIBuH*: Co(II) < Ni(II) < Cu(II).

Effect of Temperature on Dissociation and Stability Constants

The dissociation constant pK^{H} for *HAIBuH* was calculated for various temperatures (293, 303 and 313 K). The values obtained are given in Table 2. These values indicate that the dissociation process of the ligand is temperature dependent and the acidity constants increase with increasing temperature in accordance with the weak acid nature of *HAIBuH*. The values of the free energy change, ΔG, for the dissociation of the ligand are calculated from Eq. (4). The enthalpy change, ΔH, for such a process was determined from the slope of the Arrhenius plots of pK^{H} versus $1/T$ (Fig. 5).

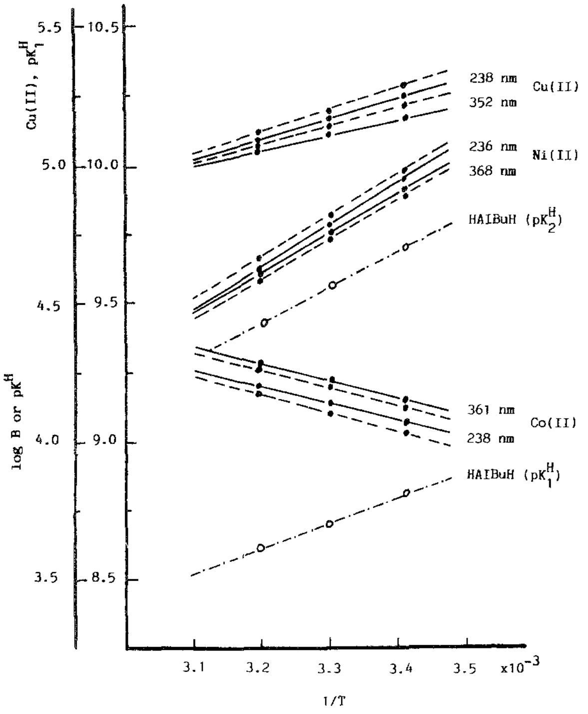


Fig. 5. Arrhenius plots of pK^H of *HAIBuH* and $\log\beta$ of *M*(II)-*HAIBuH* complexes *vs.* $1/T$ (values for molar ratio, – – –; and continuous variation method, ———)

From the ΔG and ΔH values one can deduce the entropy change ΔS applying Eq. (5).

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

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

All thermodynamic parameters of the dissociation process of *HAIBuH* are recorded in Table 2. Inspection of these values reveals that:

i. A positive value of ΔH (as for the dissociation of a weak acid) is obtained in 20% (*v*/*v*) ethanol-water solution for *HAIBuH* indicating that its dissociation is accompanied by absorption of heat and the process is endothermic;
ii. A negative value of ΔS is obtained which may be due to the increased order produced by solvation process, i.e. the total sum of the "bound" water molecules is more than the water molecules originally accompanying the undissociated ligand;
iii. A large positive value of ΔG is obtained indicating that the dissociation process for the ligand is not spontaneous.

Values of the overall stability constants were obtained at different temperatures and are listed in Table 3. The enthalpy change, ΔH, for such process was determined from the slope of the Arrhenius plots of $\log\beta$ versus $1/T$ (Fig. 5). The corresponding thermodynamic parameters for the Co(II), Ni(II) and Cu(II) complexes with *HAIBuH* were deduced from similar equations as in the case of the dissociation process (Eqs. 4 and 5) and are tabulated in Table 3. From the latter one can notice that:

i. The stability constant values decrease with a rise in temperature from 293 to

313 K in the case of Ni(II) and Cu(II) complexes, whereas in the case of the Co(II) complex the reverse happens, i.e. its stability constants increase with increasing the temperature. This suggests that the formation of Ni(II) and Cu(II) complexes with *HAIBuH* is favourable at lower temperature. On the other hand, the complexation of Co(II) with *HAIBuH* is enhanced with the temperature;

ii. ΔG is negative for Ni(II) and Cu(II) complexes which means that these complexation processes are spontaneous. But the complexation process for Co(II) is non-spontaneous since ΔG is positive. The lowest value for ΔG of Cu(II) indicates that this ion has the highest tendency for interaction with the ligand *HAIBuH*;

iii. The enthalpy values are negative for Ni(II) and Cu(II) complexes and its value is positive for the Co(II) complex. This supports the idea that a lower temperature is favourable for both Ni(II) and Cu(II), whereas in the case of Co(II) a higher temperature is favourable;

iv. The positive entropy values for Ni(II) and Cu(II) complexes favour the formation of such complexes which is contrary to the Co(II) complex where ΔS is negative.

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