ELSEVIER

Thermochimica Acta 250 (1995) 173–187

thermochimica
acta

Stability trend of 1:1 and 2:1 azo malononitrile divalent chelates

M.F. Eid [a,*], F.Z. Mahmoud [b], S.M. Abozied [b]

[a] *Chemistry Department, Faculty of Education, Roxy, Cairo, Egypt*
[b] *Faculty of Education and University College for Girls, Ain Shams University, Cairo, Egypt*

Received 21 March 1994; accepted 9 June 1994

Abstract

Acid–base equilibria, and the thermodynamic formation functions of some metal ion chelates with phenyl hydrazo malononitrile (2-PHMN) and 2-acetylphenyl hydrazomalono ethyl ester nitrile (2-APHMEN) are reported from potentiometric equilibrium measurements of hydrogen ion concentrations at 10, 20, 30 and 40°C and ionic strength 0.1 M (KNO_3) in 75% dioxane–water medium. The effect of ionic strength at 0.05, 0.10, 0.15 and 0.20 M on the proton–ligand dissociation and stability constants with some divalent metals have also been studied. Solvent effect studies were carried out in 75% ethanol–water. Owing to the deep green colour of the Cu–2-APHMN chelate, its electronic absorption spectra have been studied as an example.

Keywords: Chelate; Dissociation; Dye; pH; Stability; Stability constant; Thermodynamics

1. Introduction

Azo-dyes form the largest group of synthetic dyestuffs and feature prominently in almost every type of application. Some azo-compounds which contain an active methylene group, like malononitrile or its derivatives, form a well-known class of ligands capable of forming stable complexes with various metal ions [1–6]. A survey of the literature shows that no systematic study has been made on the chelating ability of phenyl hydrazo malononitrile (PHMN), 2-acetyl phenyl hydrazo

---

* Corresponding author.

SSDI 0040-6031(94)01934-9

malononitrile (2-APHMN) or 2-acetyl phenyl hydrazomalono ethyl nitrile (2-APHMEN). In the present study, the stability constant, the thermodynamic functions via $\Delta G^{\ominus}$, $\Delta H^{\ominus}$, $\Delta S^{\ominus}$, and the effect of the solvent and the ionic strength of the metal chelates of these ligands with Cu(II), Ni(II), Zn(II), Mn(II) and UO_2(II) were studied.

2. Experimental

The organic ligands were prepared from the corresponding diazotized amino acetophenone coupled with malononitrile or its derivative in aqueous alcoholic sodium acetate solution [7]. The crude product was recrystallized from suitable organic solvents.

The dioxane and ethanol used were purified by the method described by Vogel [8]. Distilled water, redistilled over alkaline potassium permanganate, was used throughout the investigation. The medium of titration was 75:25 dioxane–water or ethanol–water (v/v) mixture. Ionic strength was maintained by adding potassium nitrate. All reagents were of analytical reagent grade. Metal nitrates of 99.9% purity (BDH) were dissolved in redistilled water. The temperature used was adjusted at the desired temperature using an ultra thermostat. A precision research pH-meter, digital WTW mode, with combined electrode was used. The changes in the pH can be measured with an accuracy of 0.005 pH unit. The experimental method of Irving and Rossotti was applied to determine the values of n' and pL (where n' is the average number of ligand molecules bound to one metal ion, and L is the concentration of the free chelating species at different pH values). The titrations were performed in duplicate to test for reproducibility. All spectrophotometric studies were in aqueous solutions using a Perkin-Elmer spectrophotometer 555 uv/vis model.

3. Results and discussion

3.1. pH-Metric study

The titration curves of the free ligands, PHMN, 2-APHMN, 2-APHMEN, and of metal–ligand mixtures in ratio 1:2 are shown in Figs. 1–3. The titration curve of the free ligands shows one weak inflection corresponding to the deprotonation of the hydrazone group. At all temperatures, the curves of the ligands exhibit one inflection point in the alkaline region ($pH > 7$). This weak inflection reflects the dissociable process of the hydrazone group as represented by Scheme 1. Accordingly, the basicities of the considered complexing agents (pK^{H} values) were found to be in the order 2-APHMEN > 2-APHMN > PHMN.

The values of the thermodynamic dissociation constants of the ligands at the investigated temperatures were determined by the Albert–Serjeant method [9] and are summarized in Table 1. The data indicate that the neutralization reactions of

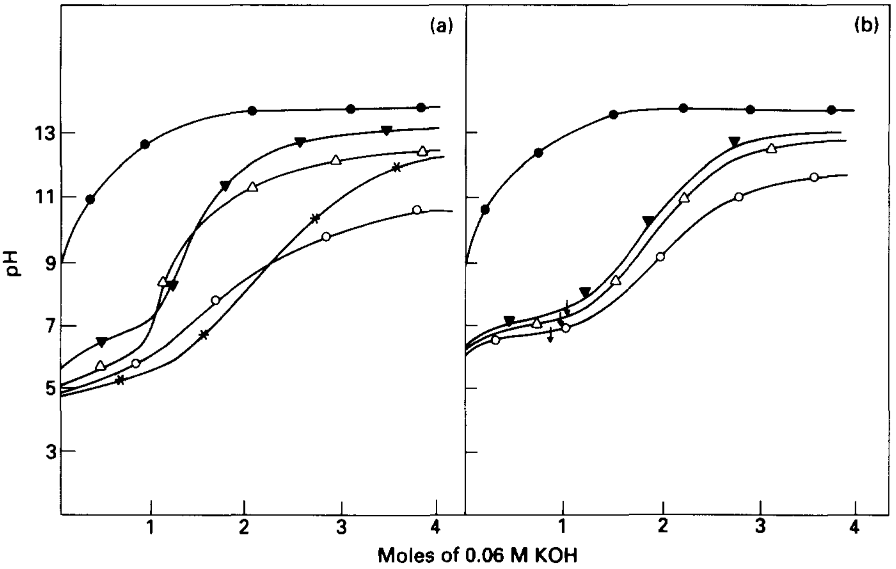


Fig. 1. Potentiometric titration curves for 2×10^{-3} M PHMN with 1×10^{-3} M transition metal ions at 30°C. (a) ●, PHMN; ○, $+ Cu^{2+}$; △, $+ Ni^{2+}$; ▼, $+ Co^{2+}$; *, $+ UO_2^{2+}$. (b) ●, PHMN; ○, $+ Zn^{2+}$; △, $+ Cd^{2+}$; ▼, $+ Mn^{2+}$. ↓ indicates precipitation.

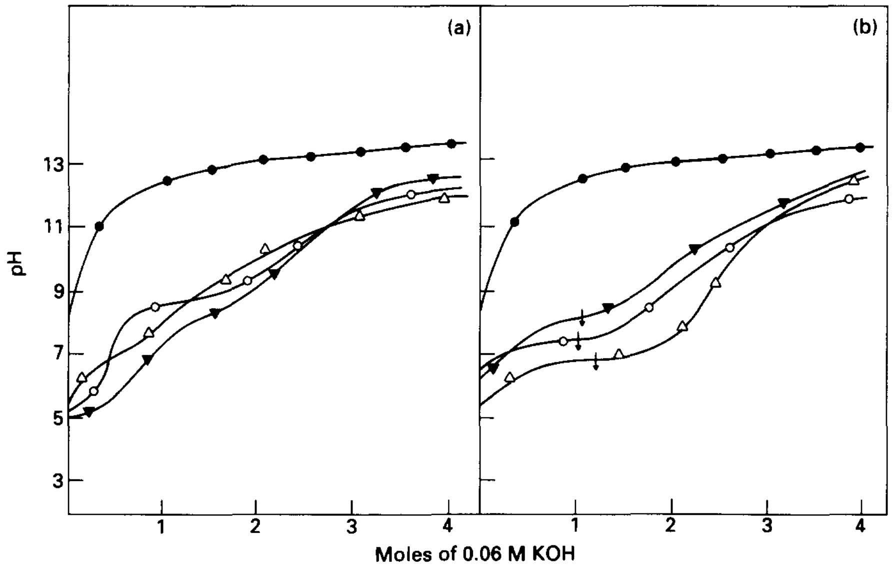


Fig. 2. Potentiometric titration curves for 2×10^{-3} M 2-APHMN with 1×10^{-3} M transition metal ions at 30°C. (a) ●, 2-APHMN; ○, $+ Cu^{2+}$; △, $+ Ni^{2+}$; ▼, $+ UO_2^{2+}$. (b) ●, 2-APHMN; ○, $+ Zn^{2+}$; △, $+ Mn^{2+}$; ▼, $+ Cd^{2+}$. ↓ indicates precipitation.

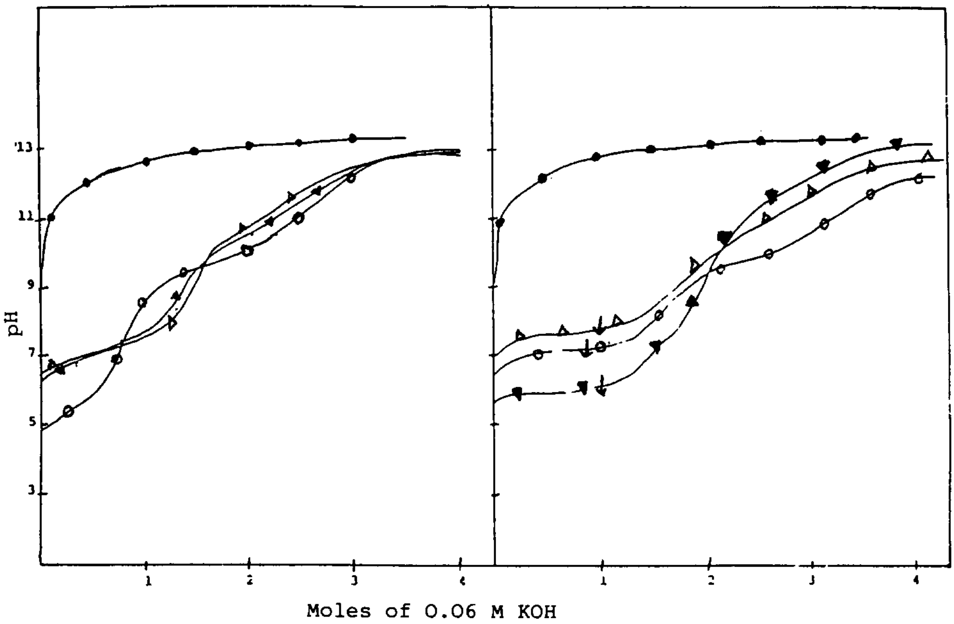
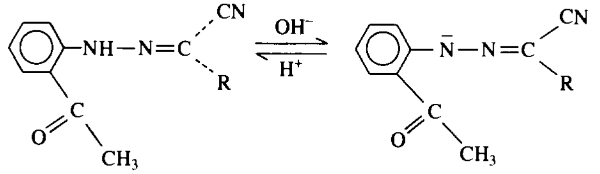


Fig. 3. Potentiometric titration curves for 2×10^{-3} M 2-APHMEN with 1×10^{-3} M transition metal ions at 30°C. (a) ●, 2-APHMEN; ○, $+Cu^{2+}$; △, $+Ni^{2+}$; ▼, $+UO_2^{2+}$. (b) ●, 2-APHMEN; ○, $+Zn^{2+}$; △, $+Mn^{2+}$; ▼, $+Cd^{2+}$. ↓ indicates precipitation.



Scheme 1. R is CN or $CO_2C_2H_5$.

the given ligands are temperature dependent. The values of the constants pK^H were found to decrease on raising the temperature.

Plots of log K as a function of the reciprocal of the absolute temperature for 2-APHMN and 2-APHMEN and their complexes are shown in Figs. 2 and 3 respectively, from which the values of $\Delta H^\ominus$ were evaluated. The determined values of the thermodynamic parameters $\Delta H^\ominus$, $\Delta G^\ominus$ and $\Delta S^\ominus$ for the free ligands, 2-APHMN and 2-APHMEN, are given in Table 1.

The positive values of $\Delta H^\ominus$ indicate that the neutralization reactions of the two ligands are endothermic processes because ionization of these ligands is enhanced with increasing temperature. Also, the high positive values of $\Delta G^\ominus$ indicate that the dissociation of the ligands is not spontaneous and a rise in temperature shifts the equilibrium towards enhancing the dissociation of the ligands.

Table 1
Dissociation constants and thermodynamic parameters for the dissociation reaction of 2-APHMN and 2-APHMEN in 75% (v/v) dioxane-water and 0.1 M ionic strength

Ligand	10°C	20°C	30°C	40°C	$\Delta G^{\ominus}$ in kJ mol^{-1}	$\Delta H^{\ominus}$ in kJ mol^{-1}	$S^{\ominus}$ in J K^{-1} mol^{-1}	
							Method (1)	Method (2)
2-APHMN	12.843	12.493	11.920	11.790	3.99	2.734	4.218	4.749
2-APHMEN	12.896	12.811	12.638	12.487	4.14	2.945	4.011	4.316
PHMN[a]	–	–	11.413	–	–	–	–	–

[a] This ligand was included for comparative purposes.

The values of $\Delta S^{\ominus}$ calculated either from Eq. (1) (method 1)

$$\Delta S^{\ominus} = (\Delta H^{\ominus} - \Delta G^{\ominus})/T \tag{1}$$

or from the slope of $T \log K$ vs. T plots (method 2) (Figs. 4 and 5), are in good agreement, see Table 1.

The titration curves of ligand-metal ion mixtures at the four investigated temperatures for Cu-2-APHMN (Figs. 2, 3) show an inflection at $m = 1$ followed by a buffer zone and another inflection at $m = 2$ which accounts for the stepwise formation of ML and ML_2 species with 2-APHMN ligand, whereas the formation of ML species with 2-APHMEN ligand is observed with the other transition metals.

The obtained values of the stability constants, log K, of the chelates formed with Cu(II), Ni(II) and UO_2(II) at different temperatures are summarized in Table 2. It is clear that the stability of the formed complexes decreases with increasing temperature, which is favourable for the formation of complexes between the two

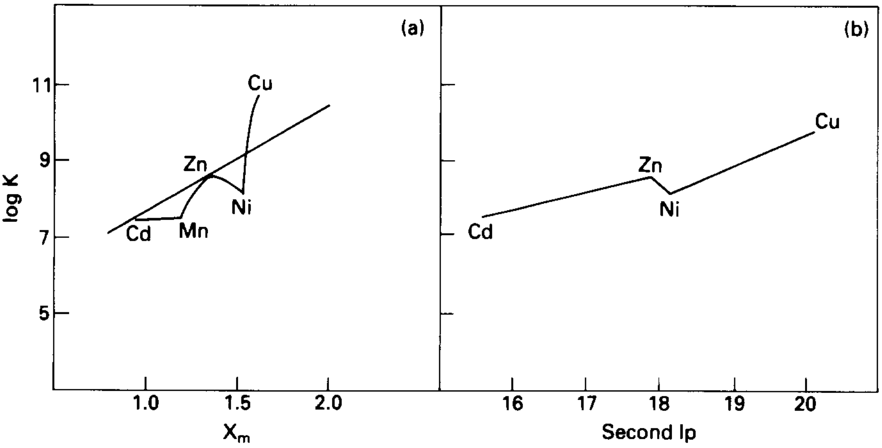


Fig. 4. Variation of log K with the electronegativity of the divalent metal. (b) Plot of log K for several metal ions vs. the 2nd ionization potential.

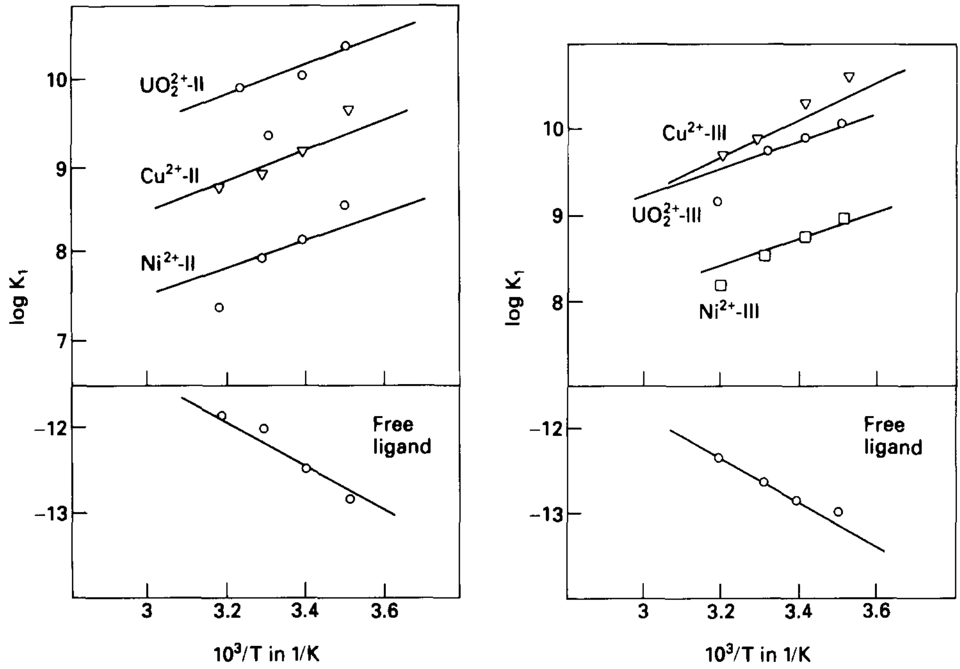


Fig. 5. (a) Relation between log K_1 and $1/T$ for 2-APHMN (II) and its complexes. (b) Relation between log K_1 and $1/T$ for 2-APHMEN (III) and its complexes.

ligands and the considered metals. The stability constants were found to follow the following trend at all investigated temperatures: Cu(II) > Zn(II) > Ni(II) > Co(II). This is in accordance with the Irving-Williams order [10].

Fig. 4 represents the relation between electronegativity (X_m) and the second ionization potential (second Ip) of the divalent metals against log K_1 for 2-APHMN complexes. The stability constant increases more or less linearly on increasing X_m and the second Ip from Cd and Ni, indicating that a gradual increase in the tendency of the formation of copper complexes in Fig. 4 is due to the great tendency of the copper ion to form stable compounds. $\Delta H^\ominus$ values of the formed complexes were obtained from Arrhenius plots shown in Fig. 5. The evaluated parameters ($\Delta G^\ominus$, $\Delta H^\ominus$ and $\Delta S^\ominus$) for the chelates of 2-APHMN and 2-APHMEN with metal ions are given in Table 3.

It was found that $\Delta G^\ominus$ increases with increasing temperature, indicating that low temperature favours complexation. The high negative values obtained for $\Delta G^\ominus$ indicates also that the complexation reaction proceeds spontaneously. These results are also confirmed by the negative values of $\Delta H^\ominus$ obtained in this study.

Values of $\Delta S^\ominus$ of the formed complexes were determined from the plots of $T \log K$ against T (Fig. 6). The positive $\Delta S^\ominus$ values observed for all the chelates may account for the stability of these compounds [11]; the results in Table 3 show that the magnitude of $\Delta S^\ominus$ for 1:1 Cu–2-APHMN chelate is positive and confirms

Table 2
Determination of the stability constants of 2-APHMN, 2-APHMEN, and PHMN complexes at different temperatures

Metal ion	2-APHMN						2-APHMEN				PHMN [a]
	10°C log K_1	20°C log K_1	30°C		40°C		10°C log K_1	20°C log K_1	30°C log K_1	40°C log K_1	30°C log K_1
			log K_1	log B	log K_1	log B					
Cu(II)	9.85	9.20	8.86	15.57	8.73	17.15	10.75	10.47	10.74	9.02	8.16
Ni(II)	8.69	8.10	7.90	–	7.30	–	9.19	8.83	8.45	8.12	7.60
Co(II)	–	–	–	–	–	–	8.77	8.56	8.32	8.18	7.17
UO_2(II)	10.51	10.00	9.17	17.39	–	–	10.03	9.22	9.72	9.53	8.58
Zn(II)	–	–	7.55	–	–	–	–	–	8.30	–	7.49
Cd(II)	–	–	7.48	–	–	–	–	–	–	–	7.19
Mu(II)	–	–	7.52	–	–	–	–	–	7.74	–	7.25

[a] This ligand was taken as a parent compound at 30°C for comparison only.

Table 3
Formation constants at different temperatures and thermodynamic parameters of M(II)–2-APHMN and M(II)–2-APHMEN

Metal ion	Temp. in °C	log K_1	$-\Delta G^\ominus$ in kJ mol^{-1}	$-\Delta H^\ominus$ in kJ mol^{-1}	$-\Delta S^\ominus$ in J mol^{-1} K^{-1}		log K_1	$-\Delta G^\ominus$ in kJ mol^{-1}	$-\Delta H^\ominus$ in kJ mol^{-1}	$\Delta S^\ominus$ in J mol^{-1} K^{-1}	
					Method (1)	Method (2)				Method (1)	Method (2)
Cu	10	9.85					10.75				
	20	9.20					10.47				
	30	8.86	2.98	1.902	3.619	3.8	9.74	3.25	2.452	2.682	2.878
	40	8.73					9.02				
Ni	10	9.69					9.19				
	20	8.10					8.83				
	30	7.94	2.603	1.709	2.999	3.064	8.45	2.813	1.902	3.057	3.167
	40	7.30					8.12				
Co	10	–					8.77				
	20	–					8.56	2.911	1.886	2.911	2.968
	30	–	–	–	–	–	8.32				
	40	–					8.18				
UO_2	10	10.51					10.03				
	20	10.00	3.163	1.823	4.503	4.522	9.92	3.191	1.824	4.589	4.749
	30	9.17					9.71				
	40	–					9.53				

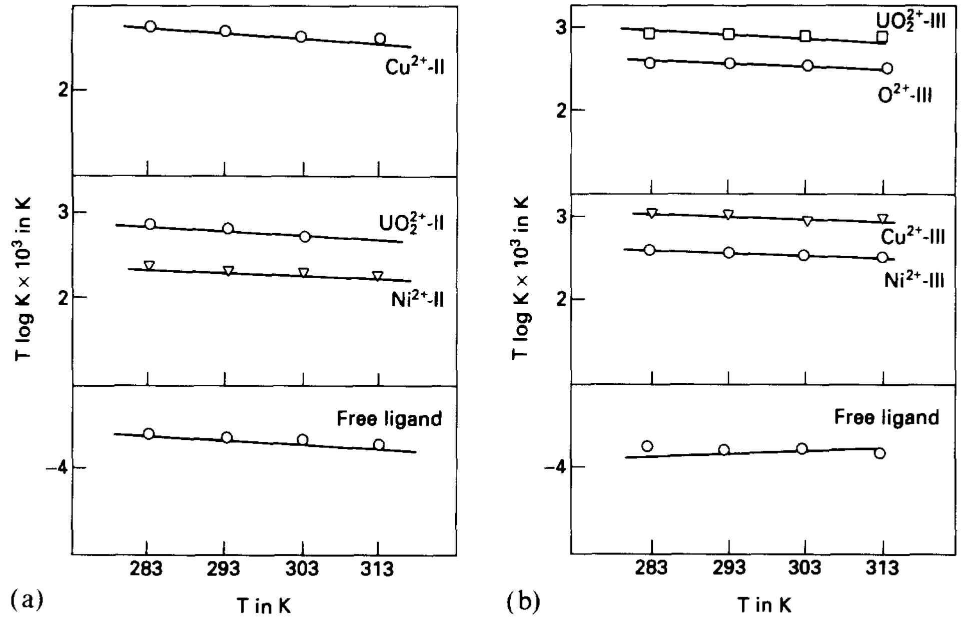


Fig. 6. (a) Relation between $T \log K$ and T for ligand 2-APHMN (II) and its complexes. (b) Relation between $T \log K$ and T for 2-APHMEN (III) and its complexes.

that the entropy effect and not to the enthalpy factor. Furthermore, the low entropy terms obtained for Co(II) chelates may be the result of these complexes being less stable than those of Cu(II) and Ni(II).

3.1.1. *Effect of ionic strength*

The complex formation of some transition metals with 2-APHMN and 2-APHMEN has been studied at different ionic strengths, namely 0.05, 0.10, 0.15 and 0.20 M. The dissociation constants of the two ligands and also the stability constants of the chelates formed with Cu(II), Ni(II), Co(II) and UO_2(II) are summarized in Table 4. It is apparent from the table that the values of the stability constants of the complexes formed decrease with decreasing ionic strength. The achieved results agree well with those reported previously [12,13].

3.1.2. *Solvent effect*

The dissociation constant (pK^H) and also the formation constants of 2-APHMN with 75% dioxane–water and 75% ethanol–water solvents are given in Table 5. The dissociation constant (pK^H) in mixed aqueous solvents decreases with three factors, namely: by increasing the dielectric constant of the solvent, by decreasing the extent of hydrogen bonding in the water by the organic solvent, and by increasing the proton solvation [14–16].

Also the higher basicity of a given ligand in aqueous dioxane than in ethanol is substantiated by Braude [17]. Table 5 also lists the stability constants for

Table 4
Effect of ionic strength on the stability constants of 2-APHMN–M^{2+} and 2-APHMEN–M^{2+} complexes (log K_1) at 30°C

Metal ion	2-APHMN							2-APHMEN			
	0.20 M	0.15 M		0.10 M		0.05 M		0.20 M	0.1 M	0.10 M	0.05 M
	log K_1	log K_1	log B	log K_1	log B	log K_1	log B	log K_1	log K_1	log K_1	log K_1
Ut	12.751	12.526	–	11.92	–	11.319	–	13.044	12.843	12.64	12.293
Cu	9.67	9.45	18.65	8.86	15.57	8.45	–	10.31	10.02	9.74	9.39
Ni	8.55	8.36	–	7.94	15.73	7.27	–	9.95	9.11	8.45	7.62
Co	–	–	–	–	–	–	–	9.99	9.38	8.32	7.54
UO_2	10.48	10.18	–	9.17	17.59	8.66	17.17	10.58	10.35	9.72	9.09

Table 5
Formation constants (log K_1) for the interaction 2-APHMN with transition metal ions in 75% ethanol–water and 75% dioxane–water

M^{2+} ion	log K_1	
	75% EtOH–H_2O	75% dioxane–H_2O
Cu(II)	7.86	9.76
Ni(II)	7.15	8.21
Zn(II)	6.61	8.55
Mn(II)	5.59	7.52
Cd(II)	5.44	7.48
UO_2(II)	8.83	9.17

2-APHMN with some bivalent metals with the two mixed solvents (75% dioxane–water and 75% ethanol–water). The stability constants of the formed chelates decrease with the increase in the dielectric constant of the mixed solvents, and this may be due to increasing the extent of solvation of the metal ion.

In general, the trends for the chelate stability of the transition ion (Table 5) were found to follow the order $UO_2^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+} > Cd^{2+}$. This agrees with the conclusions of Irving and Williams [10].

3.2. Spectrophotometric studies

All studies were carried out in 50% dioxane–water solvent (v/v) using the ligand as a reference for the measurements of Cu^{2+}–2-APHMN complexes. When the effect of pH on the spectra of the ligand was studied, the reference used was the mixed solvent 50% dioxane–water (v/v).

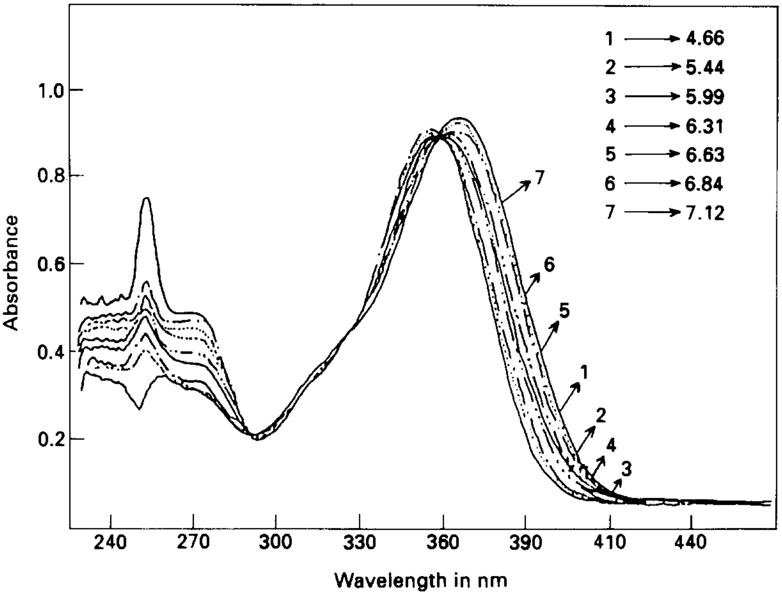


Fig. 7. Ultra-violet spectra for 2-APHMN at different pH values.

3.2.1. *Determination of pK^H for 2-APHMN ligand*

The electronic absorption spectrum of the uncomplexed 2-APHMN in 50% dioxane–water (Fig. 7) displays two absorption bands at $\lambda_{max} = 253$ and 367 nm, having molar absorptivities (ε) of 6.2 and 24 $m^2\ mol^{-1}$ respectively. These two bands may be attributed to the malononitrile branch and the $-N{=}N-$ moiety, respectively. Their high molar absorptivities suggest that $\pi-\pi^*$ transitions are involved. The $n-\pi^*$ band of the azo group of the studied ligand seems to be completely masked by the $\pi-\pi^*$ band [18]. The effect of pH in the range 6–10.5 on the spectrum of the ligand is represented in Fig. 7. The spectra exhibit two maxima: the one at $\lambda_{max} = 253$ nm is pH-independent; the other is located around the isolestic point at $\lambda_{max} = 367$ nm and is pH-dependent. The dissociation constant of the ligand pK^H was calculated by applying the limiting absorbance method [19]. The obtained value of pK^H of the ligand equals 11.50, as shown in Table 6 and Fig. 8.

3.2.2. *Effect of pH on complex formation*

This study was carried out to determine the optimum pH at which the complex of metal could be formed. Thus, solutions of known concentration of Cu^{2+} ion and an excess of the ligand at different pH values ranging between 2 and 12 were measured in the UV and visible region. The general trend observed was a slight increase from pH 2.0 to 5.0, followed by a buffered region between 5.6 and 12, which may be attributed to the formation of a hydroxo complex of the type CuHA(OH).

Table 6
Calculation of pK^H of 2-APHMN ligand using the limiting absorbance spectrophotometric method

pH	A	$A - A_{min}$	$A_{max} - A$	$\frac{A - A_{min}}{A_{max} - A}$	$\log \frac{A - A_{min}}{A_{max} - A}$
7.54	0.880	0.240	0.040	6.000	0.778
8.39	0.820	0.180	0.100	1.800	0.255
9.55	0.860	0.220	0.060	3.667	0.564
11.25	0.692	0.052	0.090	0.280	−0.130
11.60	0.740	0.100	0.180	0.556	−0.255

$A_{min} = 0.640$, $A_{max} = 0.920$ at $\lambda = 410$ nm.

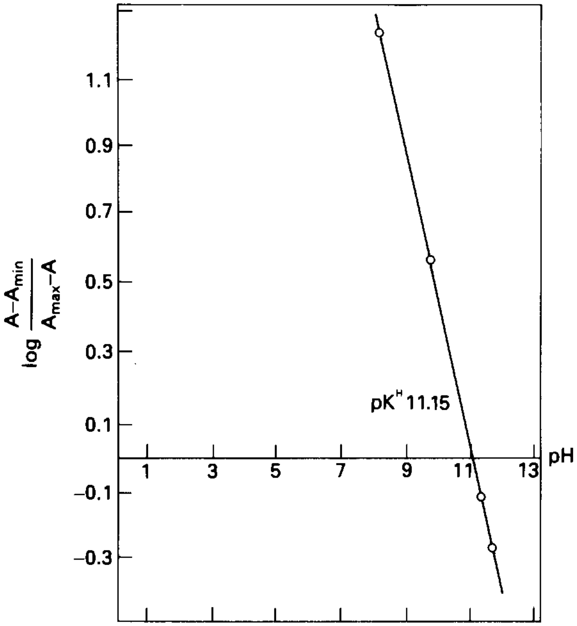


Fig. 8. Calculation of pK^H for 2-APHMN using the limiting absorbance method.

3.2.3. *Effect of ligand concentration*

The effect of ligand concentration on the absorption of Cu^{2+} ions at pH 5.0 is shown in Fig. 9, using the same concentration of ligand as reference. An increase in the maximum absorbance at $\lambda = 470$ nm occurs on increasing the ligand concentration until it reaches a 1:1 ratio. On exceeding the ratio 1 : 1, a steady increase in the absorbance is observed, indicating that the predominate species is that of a 1 : 1 ratio.

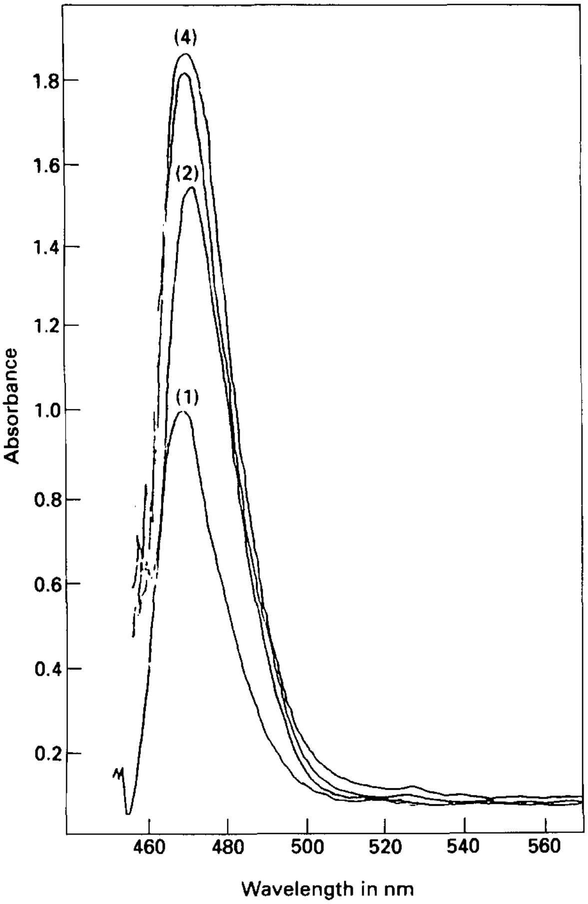


Fig. 9. Effect of concentration of ligand on Cu–2-APHMN complexes with reference ligand (pH 5.0 ± 0.1): (1), 0.5:1; (2), 1.0:11; (3), 2.0:1; (4), 3.0:1 [Lig]:[Cu].

3.2.4. Stoichiometry of the complex

The composition of the Cu^{2+}–2-APHMN complex was determined by applying the continuous variation method [20], the slope ratio method [21], the limiting logarithmic method [22] and the molar ratio method [23]. The measurements were carried out at the optimum pH = 5. Job's method is represented in Fig. 10 and is given as an example. The composition of the complexes determined by the different methods shows that the ratio Cu^{2+} :ligand is 1 : 1.

3.2.5. Determination of the formation constant of 1 : 1 complexes

The formation constant of (1 : 1) Cu^{2+} :2-APHMN complex was determined spectrophotometrically by applying:

(1) The continuous variation method [20]

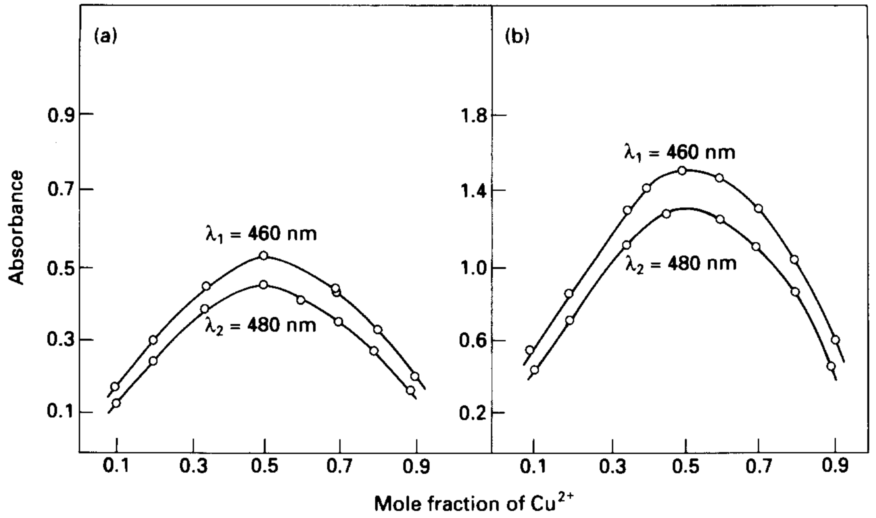


Fig. 10. Job's method for Cu–2-APHMN complexes with reference ligand and 50% dioxane–water, pH = 5.0 ± 0.1. (a) [L] = [Cu^{+2}] = 5 × 10^{-4} M. (b) [L] = [Cu^{+2}] = 1 × 10^{-3} M.

The stability constant of the complex ML$_n$ can be obtained from

$$K = \frac{C'_3}{C_t(1-X) - C_3(C_tX - nC_3)^n} = \frac{C'_3}{C'_t(1-X) - C'_3(C'_tX - nC'_3)^n} \tag{2}$$

Hagenmuller [24] found that, if only ML complex is formed, i.e. $X = 0.5$ and $n = 1$, then Eq. (2) can be written in the simple formula

$$K = \frac{C_3}{(0.5C_t - C_3)^2} = \frac{C'_3}{(0.5C'_t - C'_3)^2} \tag{3}$$

Table 7
Stability constants of Cu^{2+}–2-APHMN complex by applying the molar ratio method [Cu^{2+}] = b = 4 × 10^{-3} M

[L] = a 4 × 10^{-3}	A	A/A_m	$(a - b\,A/A_m)$ 4 × 10^{-3}	$(1 - A/A_m)$	K [a] × 10^{-3}	log K
0.2	0.105	0.223	0.023	0.777	3.1196	3.494
0.3	0.130	0.277	0.0234	0.723	4.0910	3.612
0.4	0.160	0.340	0.0596	0.660	2.1649	3.336
0.5	0.195	0.415	0.0851	0.585	2.0831	3.319
0.6	0.230	0.489	0.1106	0.511	2.1662	3.336
0.7	0.260	0.553	0.1468	0.447	2.1085	3.324
0.8	0.290	0.617	0.1830	0.383	2.2010	3.343
0.9	0.315	0.670	0.2298	0.330	2.2109	3.345
1.0	0.345	0.734	0.2660	0.266	3.5338	3.548
1.2	0.380	0.809	0.3915	0.192	2.6962	3.431

[a] $K = \dfrac{A/A_m}{(a - b\,A/A_m)(1 - A/A_m)}$.

where $A/A' = C/C'$, and C and C' are the concentrations of the formed complexes. A and A' are the absorbances corresponding to the concentrations C_3 and C'_3 respectively. From Fig. 7, for Cu^{2+}–2-APHMN complex, $A = 0.450$ and $A' = 1.330$ at $\lambda = 470$ nm for $C_t = 5.0 \times 10^{-4}$ and $C'_t = 1.0 \times 10^{-3}$ M respectively. The obtained values of log K on substitution either by C_3 or C'_3 in Eq. (3) has been found to be 3.544.

(2) Molar ratio method

The detailed calculations for a 1:1 Cu^{2+} : ligand type of complex are given in Table 7. The average value of log K_1 was found to be 3.409 ± 0.101.

References

[1] J.E. Powell, J. Inorg. Nucl. Chem., 30 (1968) 2223.
[2] T. Kruch, et al., Z. Naturforsch. Teil B, 28 (1973) 38.
[3] B. Haymore and R.D. Felthan, Inorg. Synth., 14 (1973) 81.
[4] D. Gwost and K.G. Caulton, J. Chem. Soc. Chem. Commun., (1973) 64.
[5] B.A. El Shetary, et al., J. Chin. Chem. Soc., 32 (1985) 41.
[6] A.A. Ramadan, G. El. Inany and M.F. Eid, Asian J. Chem., 3 (1991) 351.
[7] R. Adams, Organic Reactions, Vol. 10, Chapman and Hall, London, 1959.
[8] A.A. Vogel, A Test Book of Practical Organic Chemistry, 3rd edn., Longmans, London, p. 177.
[9] A. Albert and E.P. Serjeant, Ionization Constants of Acids and Bases, Methuen, London, 1st edn., 1962, p. 31.
[10] H. Irving and R.J.P. Williams, J. Chem. Soc., (1953) 3192.
[11] M.S. Abdel Moez, B.A. Elshetary and M.F. Eid, Thermochim. Acta, 128 (1988) 81.
[12] S. Shrivastava and P.B. Chakrwarted, J. Indian Chem. Soc., 7 (1980) 607.
[13] A. Bhattacharry and S.C. Lahivi, J. Indian Chem. Soc., 7 (1981) 607.
[14] B.A. El Shetary, A.M. Zahra, A.A. Taha and A.I. Ibrahim, J. Chin. Chem. Soc., 32 (1975) 41.
[15] N. Kole and A.K. Chaudhury, J. Inorg. Nucl. Chem., 43 (1981) 2471.
[16] A. Gergely and T. Kiss, J. Inorg. Nucl. Chem., 39 (1977) 109.
[17] E.A. Braude, J. Chem. Soc., (1948) 1971.
[18] C.N.R. Rao, Ultra-Violet and Visible Spectroscopy, Chemical Applications, 3rd edn., Butterworths, London, 1978, p. 50.
[19] R.M. Issa and A.H. Zewail, Egypt. J. Chem., 14 (1971) 461.
[20] P. Job, Ann. Chim., 9 (1928) 113; 11 (1936) 97.
W.C. Vosburgh et al., J. Am. Chem. Soc., 63 (1941) 437; 64 (1942) 1630.
[21] A.E. Harvey and D.L. Manning, J. Am. Chem. Soc., 72 (1950) 4488.
[22] H.E. Bent and C.L. French, J. Am. Chem. Sc., 63 (1941) 568.
[23] J. Yoe and A. Johes, Indust. Eng. Chem. Anal. Ed., 16 (1944) 14.
[24] P.H. Hagenmuller, Ann. Chim. Paris, 6 (1951) 5.