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Mixed ligand chelates of Cd²⁺ with 2-(1-(aminomethyl)cyclohexyl) acetic acid and dicarboxylic acids

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ABSTRACT

The nature of mixed ligand chelates of cadmium(II) ions with 2-(1-(aminomethyl)cyclohexyl) acetic acid as a secondary ligand and dicarboxylic acids such as oxalic (ox), malonic (mal), succinic (suc), glutaric (glu), adipic (adi) and phthalic (phth) acids as primary ligands was investigated by potentiometric technique at 32 °C (± 0.1 °C) and $\mu = 0.1$ M KNO₃ in aqueous 50% (v/v) DMSO medium. The formation of mixed ligand chelates having 1:1; 1:2 and 1:3 complexes with ligands was identified. The ternary chelates are formed by simultaneous equilibrium. The stability of ternary complexes was investigated and compared with those of the corresponding binary complexes in terms of the $\Delta \log K$ parameter. The concentration distribution of the complexes in solution has been evaluated.

Key words: Dicarboxylic acids; Binary and ternary complexes; Stability constants; Potentiometry.

INTRODUCTION

Dicarboxylic acids are an important class of organic ligands and are suitable substrates for preparation for the pharmaceutical and food industries. Furthermore, they are useful materials for the preparation of fragrances, polyamides, adhesives, lubricants, and polyesters. These are present in larger amounts in natural waters and biological fluids, they are of remarkable importance in the speciation studies of these fluids. They are chemically important because of their sequestrating abilities toward several cations and play a biological fundamental role in metabolic cycles; for example oxalate is present in many natural fluids such as blood, in which its concentration is $1.4-2.8 \text{ mg L}^{-1}$ and in urine (30 mg/24h) [1]. It is contained in foods such as the succinic acid, are involved in the metabolic process in the Krebs's cycle; malonic acid is an inhibitor of succinate dehydrogenase and is present in legumes, and it is involved in developing rat brain processes [2]. 2-(1-(aminomethyl)cyclohexyl) acetic acid plays an important role in biochemistry because it functions as a anticonvulsant [3] and also in treatment of neuropathic pain in human and animal models [4-6].

The acid-base properties and the sequestrating abilities of carboxylic acids in different ionic media, temperature, ionic strengths [7-13] and their complexing abilities toward several organic and inorganic cations are reported [12-14]. The main driving force for binding of carboxylic acids or their anions in nonpolar media is intermolecular hydrogen bonding [15-17] just as in aqueous or aqueous organic media intermolecular hydrogen bonding is considerably hindered by hydration, both electrostatic and stacking interactions are become predominant [18]. In this paper, the results of potentiometric study on the protonation constants, stability constants of binary and ternary systems of cadmium(II) ion with *amcaa* and the series of dicarboxylic acids [oxalic (*ox*), malonic (*mal*), succinic (*suc*), glutaric (*glu*), adipic (*adi*), and phthalic (*phth*) acids] are reported in 50% (v/v) DMSO-water medium at 32 °C (\pm 0.1 °C) under nitrogen atmosphere.

MATERIALS AND METHODS

2.1 Chemicals and equipment

Stock solutions of $(5.0 \times 10^{-2} \text{ M})$ 2-(1-(aminomethyl)cyclohexyl) acetic acid and dicarboxylic acids (oxalic, malonic, succinic, glutaric, adipic and phthalic acids) were prepared by weighing the solid samples without further purification. Carbonate-free solution of NaOH (1. 0 M) was prepared in double distilled water and estimated by standard method. The purity of the acids (Fluka A.R) was checked by alkali metric titration with standard NaOH solution and the results were always \geq 99.5%, 1.0 M KNO₃ and 5.0×10^{-3} M cadmium(II) stock solutions were prepared from AnalaR grade samples and their purities were checked by potentiometric titration for acid and EDTA method for cadmium(II) [19]. SYSTRONIC digital pH/mV meter model 335 accurate to ±0.05 units and equipped with a glass electrode and saturated calomel electrode were used in this work.

2.2 pH – metric measurements

The pH –metric measurements were carried out in a thermostatically controlled cell at 32 °C (\pm 0.1 °C) using a "SYSTRONIC – 335" pH meter with a precision less than 0.05 pH units. The pH meter was calibrated before and after each titration set with suitable buffer solutions (pH 4.0 and 9.2). The mixed ligand was titrated in the absence of, and in the presence of metal ions of interest. The titrations were carried out in 50% (v/v) DMSO-water at 32 °C (\pm 0.1 °C). The ionic strength was maintained constant at 0.1 M by adding requisite amounts of potassium nitrate solution. The total volume in each case was 30 ml. The reaction mixture was titrated with carbon dioxide free sodium hydroxide solution (0.1 M). The measurements were made with pH meter fitted with glass and calomel electrode. The mixtures for the mixed ligand systems were prepared as follows. (4.0×10^{-2} M) HNO₃ + (1.0 M) KNO₃ (a); a + *amcaa* (4×10^{-2} M) (b); b + metal ion (5×10^{-3} M) (c); a + dicarboxylic acid (1.5×10^{-2} M) (d); d + metal ion (e) and a + *amcaa* + dicarboxylic acid + metal ion (f).

The recorded pH meter reading was converted to hydrogen ion concentration by means of the equation given by van Uitert and Hass [20].

$$-\log \left[\mathrm{H}^{+}\right] = \mathrm{B} + \log \mathrm{U}_{\mathrm{H}} - \log \left(1/\gamma^{2}\right) \tag{1}$$

where γ is the activity coefficient of the solvent composition and U_H is the correction factor at zero ionic strength of the solution.

RESULTS AND DISCUSSION

3.1 Proton - ligand constants

Normal biochemical processes occur in aqueous solution close to neutral pH. Certain functional groups found in biological molecules, in particular carboxylic acids or amino groups, can gain or lose H^+ depending on the availability of hydrogen ions (or protons) in the solution. Representative potentiometric titration curves for the free and metal complexed ligands are depicted (Cd-*amcaa-ox*) in FIG-1.

The acid dissociation constants of *amcaa* and dicarboxylic acids in 50% (v/v) DMSO-water were determined from curves (a) and (d) using a computer program based on Irving-Rosotti pH titration techniques [21]. The values of the dissociation constants of *amcaa, ox, mal, suc, glu, adi* and *phth* were determined under the same experimental conditions (32 °C (± 0.1 °C), $\mu = 0.1$ M KNO₃). The SCOGS [22] computer program was used to refine the overall protonation constants by minimizing the standard deviation of the fit (σ fit) between the observed and calculated pH values. The pKa values as borne out for acids by table-1 refer to the following protonation equilibrium shown below.

$$A^{-} + H^{+} \underbrace{\longrightarrow}_{AH} AH$$

$$K_{1}^{H} = \frac{[AH]}{[A^{-}][H^{+}]}$$

$$HA + H^{+} \underbrace{\longrightarrow}_{H_{2}A^{+}} H_{2}A^{+}$$

$$K_{2}^{H} = \frac{[H_{2}A^{+}]}{[HA][H^{+}]}$$
(2)
(3)

The quality of the fit was judged by the values of the sample standard deviation. The obtained pKa values are given in table-1 and fairly agree with the data reported previously in literature after allowing for changes in experimental conditions as well as methods of calculation. The pKa values increase with the increases DMSO content (volume fraction of DMSO) because of the decrease in dielectric constant of bulk solution [23].

3.2 Metal – ligand stability constants of binary complexes

The stability constants of both 1:1 and 1:2 binary complexes of the chosen ligands were determined at 32 °C (\pm 0.1 °C) and μ = 0.1 M KNO₃. It can be observed that the stability constants of the different 1:2 metal-ligand complexes are lower than those of the corresponding 1:1 systems, as expected from statistical considerations. Analysis of the complexed ligand curves (d) and (e) (FIG-1) indicates that the free ligand solutions shift the buffer region of the ligand to lower pH values. This shows that complexation reaction proceeds by releasing of protons from such ligands. The curves reveal that the magnitude of the horizontal displacement of the complex curves (d) and (e) from the free ligand curves (b) and (c) is longer with Cd(II). This means that Cd(II) strongly interacts with the same ligand. Generally, it is observed that MA complexes (curve c) begin to form at higher pH range (~ 3.4) than MB complexes (curve e) (pH \leq 5.5). The complexes are quite stable up to high pH values (pH \approx 9.3). Precipitation occurred at pH > 9.9 and thus, no calculations could be performed beyond this point. Therefore, the hydroxide species likely to be formed after precipitation point could not be investigated.

The present study shows that 1:1 and 1:2, metal : ligand type of species are the important types in both metal ion-*amcaa* (A) and dicarboxylic acid (B) systems. This is based on the presence of two inflections in case of MA species and a single steep two in case of MB species, after

addition of two moles of NaOH per 1 mole of ligand. This suggests that the dissociation of two protons from *amcaa* is in stepwise manner. These equilibria can be shown as follows:

$$M + A \xrightarrow{K_{MA_2}^{MB}} MA$$

$$MA + A \xrightarrow{K_{MB_2}^{MB}} MA_2$$

$$\log K_{MA}^M = \log [MA] - (\log [M] + \log [A])$$

$$\log K_{MA_2}^M = \log [MA_2] - (\log [M] + 2 \log [A])$$
(4)

Similarly for secondary ligands (B)

$$\begin{array}{c} M+B \\ MB+B \end{array} \xrightarrow{K_{MB}^{M}} MB \\ MB_{2} \\ \log K_{MB}^{M} = \log \left[MB \right] - \left(\log \left[M \right] + \log \left[B \right] \right) \\ \log K_{MB_{2}}^{M} = \log \left[MB_{2} \right] - \left(\log \left[M \right] + 2 \log \left[B \right] \right) \end{array}$$
(6)
 (7)

Table-1: Proton-ligand constants and stability constants of binary systems

Ligand	$log\beta_{H_1}$	$log\beta_{H_2}$	Cd (II)		
			$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
amcaa	10.51	15.69	5.45	10.91	-
	10.28^{a}	-	-	-	-
ox	5.46	8.27	4.04	8.08	12.13
	1.27^{b}	4.26^{b}	2.78°	4.00°	5.20 ^c
	3.92 ^d	5.06^{d}	3.35 ^e	-	-
mal	6.68	10.13	3.95	7.91	-
	5.22 ^f	2.64 ^f	2.75^{e}	-	-
	5.39 ^d	8.05 ^d	-	-	-
SUC	6.56	11.67	4.02	8.08	-
	5.32 ^d	9.35 ^d	-	-	-
glu	5.61 ^g	3.01 ^g	-	-	-
	5.98	11.27	3.34	6.68	-
	3.70 ^h	2.69 ^h	2.0^{i}	2.68^{i}	-
	5.03 ^d	9.25 ^d	-	-	-
adi	6.13	11.56	2.8	5.60	
	4.08 ^h		1.4 ^J	2.11 ^j	3.16 ^j
	5.05 ^d	9.34 ^d	-	-	-
phth	6.97	10.84	3.55	7.11	
	2.74 ^k	4.92^{k}	1.98 ^j	2.40^{j}	3.62 ^j
	2.67 ^k	5.06 ^k	-	-	-

Temp = 32 °C (± 0.1 °C), $\mu = 0.1 M KNO_3$

a. Glen Brookes, Lesile D. Petlit, J. Chem. Soc., Dalton, 1977, 1918. 0.15 M NaClO₄ at 37 °C (water medium).

b. R Goldberg, N. Kishore, Lennen, J. Phys. Chem. Ref. Data, 2002, 31(2), 231(Water medium).

c. D.G. Dhuley, D.V. Jahagirdar, D.D. Khanolkar, J. Inorg. Nucl. Chem., 1975, 37, 2135 $\mu = 2.0M \text{ KNO}_3 \text{ at } 25 \,^\circ \text{C}$).

d. Francesco Crea, Alessandro De Robertis, Silvio Sammartano, J. Solu. Chem., 2004, 33, $\mu = 0.1 M$ NaCl, at 25 °C).

e. Pavel Janos, J. Chromatogrphy, **1993**, 641, 229 μ = 0.04*MLiClO4* at 25 °C).

f. M. Srinivas Mohan, D. Bancroft, E.H. Abbott. J. Inorg, Chem., 1979, 18, No.6, 1527. (µ = 0.2M KNO₃ at 25 °C).

g. Fernando, Rived, Marti Roses, Elisabeth. Anal. Chim. Acta, 1998, 374, 309. M.S. Balakrishnan, M. Santappa. J. Inorg, Nucl. Chem. 1975, 37, 1229 ($\mu = 0.1M$ NaClO₄ water medium at 25 °C).

h.

A.E. Martell, R.M. Smith, Critical stability constants 1977, 3. i. $(\mu = 0.1M \text{ KNO}_3 40\% (v/v) \text{ ethanol-water at } 25 \,^{\circ}\text{C}).$

j. Pratap D. Jadhav, Ramesh A. Bhobe. J. Inorg. Nucl. Chem., 1978, 41, 853 ($\mu = 2.5M \text{ NaNO}_3 40\% (v/v)$ ethanol-water at 25°C).

k. Giuseppe Arena, Enrico Rizzarelli, Silvio Sammartano, Talanta, 1978, 1979, .26, 1.

Complex formation constants for binary systems expressed in terms of overall formation constants $\{\log \beta = \log K_{MB}^{M} + \log K_{MB_2}^{M}\}$ are compared using standard procedures based on the calculation of the average number of ligands bound per metal ion.

The data listed in table-1, clearly reveals that the stability of metal-dicarboxylic acids are very close to those already published after allowing for changes in experimental conditions. The stability constants of the oxalate complexes are larger than the other ligands. Hence Cd^{2+} is most probably chelated by $C_2O_4^{2-}$. The results show that the stability order of binary systems in terms of the dicarboxylic acids is ox > suc > mal > phth > glu > adi. In the Cd(II) – dicarboxylate, the stability of the chelate ring decreased with increase in ring size from oxalic to phthalic acid. On the other hand, the results indicate that MA complex is more stable than those of MB complexes. This behaviour can be interpreted based on the bidentate nature of amcaa which coordinated through the amino nitrogen and the carboxylic oxygen atoms and also two and seven membered complex is more stable under the experimental conditions. Kumar and Malik [24] reported the stability of amcaa with Cu(II), Cd(II), Co(II), Ni(II), Pb(II) and Zn(II) using potentiometric method in 50% (v/v) dioxane-water medium at an ionic strength of 0.1M (KNO₃). $\log \beta_2 = 6.12$ at 35 °C for Cd(*amcaa*)₂. Which is four log unit lesser than Cd(*amcaa*)₂ in 50% (v/v) DMSO-water medium, it indicates that binary complex is more stable in DMSO-water medium is best compared with water-dioxane medium. The studies of complex formation were carried out using several cadmium(II) concentrations to ascertain the formation of polynuclear complexes. Analysis of the complexed ligand curves (FIG-1) indicates that only mononuclear species were formed in appreciable concentration within the concentration range used.

3.3 Metal- ligand stability constants of ternary complexes

The cadmium-*amcaa-ox* mixed systems were studied at 32 °C (\pm 0.1 °C) and μ = 0.1 M KNO₃ in 50% (v/v) DMSO-water medium. The determination of the composition and the evaluation of stability constants of the mixed ligand complexes show that there is positive replacement of ligand ions in the systems. The mixed ligand complexes are formed when both the ligands are attached to the metal ion simultaneously. The simultaneous displacement of water molecules during the mixed ligand complexation will also lead to a favourable entropy factor [25].

From the purely statistical consideration the value should be 0.6 [26]. The difference between the observed and the statistical value is attributed normally to factors such as steric and electrostatic effects. Electrostatic effects may be neglected, since both the ligands in the mixed complexes have the different charges. It is felt that steric effects have a predominating influence. This is borne out by the increased pK_a values.

A representative set of experimental titration curves obtained for the different 1:2 Cd(II)-*amcaa*, and 1:1:2 Cd(II)-*amcaa*- ox systems at 32 °C (\pm 0.1 °C) and μ = 0.1 M are shown in FIG-1 (curve f) and other mixed systems show similar behaviour. In our study, *amcaa* (A) is considered as a secondary ligand and dicarboxylic acids (B) as primary ligand, since MB species is formed at lower pH values (FIG -3) than MA species. The observed lowering of ternary MAB₂ curve (f) in comparison to binary MA₂ and MB₂ curves (c) and (e) as well as its deviation from the theoretical composite curve constructed by graphical addition of the horizontal distance of the 1:1 MA (or MB) curve to free ligand B (or A) titration curve, indicates the formation of ternary complexes in solution. Analysis of these curves in terms of the species distribution curves indicate that these systems are involved the ternary complexes MAB₂H₂ and MAB₂ for other than oxalic acid system. The formation constants for these complexes are given in table-2.

Ternary system	logβCdAB ₂ H ₂	$\log \beta_{CdAB}$	pK ^H _{CdAB2H2}	logK ^{CdA} _{CdAB}	∆ log K			
Cd ²⁺ -amcaa-ox	-	15.40	-	9.95	1.87			
Cd ²⁺ -amcaa-mal	29.13	13.85	15.28	8.40	0.49			
Cd ²⁺ -amcaa-glu	27.24	13.48	13.76	8.03	1.35			
Cd ²⁺ -amcaa-suc	28.20	13.05	15.15	7.60	-0.48			
Cd ²⁺ -amcaa-adi	27.45	12.93	14.54	7.33	1.88			
Cd ²⁺ -amcaa-phth	27.73	12.21	15.52	6.76	-0.35			
Temp: 32 \mathcal{C} (+0.1 \mathcal{C}): $\mu = 0.1 M KNO$, 50% (v/v) DMSO-water medium								

Table-2: Stability constants of Cd²⁺-*amcaa* – dicarboxylic acid ternary systems

Temp: 32 \mathcal{C} ($\pm 0.1 \, \mathcal{C}$); $\mu = 0.1 \, M \, KNO_3 \, 50\% \, (v/v) \, DMSO$ -water medium

Further, it is worth mentioning that these systems show no precipitation during titration. Thus, they are not hydrolyzed under the experimental conditions, even at high ≈ 9 pH's. This behaviour may be explained on the basis of the electron density on the metal-ligand bonds in ternary chelates which are redistributed in such a way that the ternary chelates are more polar than the binary chelates.

To discuss the stabilization of ternary chelates, the following stepwise formation constants for equilibrium could be

$$MB_2 + A \xrightarrow{K_{MB_2A}^{MB_2}} MB_2A$$

$$MB_2 + MA \xrightarrow{K_{MB_2A}} MB_2A + M$$

The difference in stability of the binary complex with that of the ternary complex, $\Delta \log K$, was calculated by equation (8) for all types of ternary complexes detected in the systems.

$$\Delta \log K = \log K_{MB_2A}^{MB_2} - \log K_{MA}^M$$
(8)

3.4 Comparison of stability of binary and ternary complexes

According to Sigel [27], the relative stability of ternary complex MAB₂ as compared with that of the binary complex MB₂ can be quantitatively expressed in different ways. The most suitable comparison is in terms of $\Delta \log K$. This parameter can be calculated from the reaction of secondary ligand (A) either with MB₂ or with free metal ion, hence $\Delta \log K =$ $\log K_{MAB_2}^{MB_2} - \log K_{MA}^M.$

The $\Delta \log K$ values are given in table-2 for ternary mixed ligand complexes. $\Delta \log K$ represents the difference in stability for ternary complexes. The positive values of $\Delta \log K$ indicate that the ternary complexes are more stable than the binary complexes. It should be kept firmly in mind that the magnitudes of $\Delta \log K$ is strongly influenced by statistical differences in the formation of complex as well as difference in bonding. The negative values for $\Delta \log K$ can be attributed to the fact that there are fever coordination positions are available on the complex and also less flexibility of ligands. The much more negative values for $\Delta \log K$ can be due to a combination of the statistical effect resulting from the reduction in available binding sites.

Equilibrium measure the tendency of dicarboxylic to form mixed-ligand complexes. The constant $K_{CdAB_2}^{CdA}$ measure the addition of two dicarboxylic to the binary MA complex to form the ternary CdAB₂ complex. The $\Delta \log K$ values listed in table 2 are negative for succinic and phthalic acids indicating that dicarboxylic binds better to Cd(II) than to the binary MA complexes. The positive $\Delta \log K$ values for systems in table 2 indicate that the Cd-*amcaa* complex interacts better with the anionic oxygen donors than Cd(II) itself.

The $\Delta \log K$ values obtained for the ternary systems generally do not deviate from the statistical expectations, where the statistical steric and electrostatic factors result in the lower stability constants for the ternary complexes as compared to the corresponding binary systems. The absence of stabilization is compatible with the explanations given by Sigel et al [28-31] for the possible stabilization of ternary complexes. The data indicate that the $\Delta \log K$ values obtained for Cd-amcaa-ox species more positive than the values obtained for other species indicating the marked stability of Cd-amcaa-ox₂. The log β_{CdAB_2} and log $K_{CdB_2A}^{CdB_2}$ values in Table 2 for cadmium-amcaa(A)-ox(B), -mal(B), -suc(B), -adi(B), -phth(B) systems decrease in the order of $B = ox > mal > suc \approx phth > glu > adi$. This indicates that the ring size order 5 > 6 > 7 > 8 > 9and also basicity of ligand. The results in table-2 show that $\Delta \log K_{CdB,A}$ values in Cd(II)amcaa-suc and Cd(II)-amcaa-phth systems are negative compared to their other ternary systems in this investigation. The data indicate that succinic and phthalic acid ternary systems are less stable than other ternary systems. Succinic and phthalic acids interligand interaction is less, are compared with other dicarboxylic acids ternary systems. These results demonstrate that formation of CdB₂A from their binary depends on the size and interligand interaction. The protonated ternary complexes, CdB₂AH₂ in the Cd(II)-amcaa(A)-dicarboxylic acids (B) systems were found to be more favoured near pH 5.5, with regards to the site of protonation in these complexes, its possibility with the dicarboxylic, primary (B) may be ruled out because in the cadmium(II)-dicarboxylic binary system no protonated binary complex species were detected. Hence, the extra protons in CdB₂AH₂ complexes must be attached to the secondary ligand like amcaa. For example, the $pK_{CdB_2AH_2}^{H_2}$ value of 15.28 in cadmium(II)-amcaa(A)-mal_2(B) system compares well with $pK_{AH_2}^{H_2}$ value of *amcaa* ($log\beta cdAB_2H_2 - log\beta_{AH_2}^{H_2} = 15.29$ for CdAB₂H₂ with A = 15.29). This demonstrates with that the protons in the $CdAB_2H_2$ complexes are attached to the amino and carboxylic groups of amcaa. This is due to the limited tendency of oxalate for interligand interaction. Based on the fact that $\Delta \log K$ values depend on the coordination number of metal ion and the ligands [32], the change in $\Delta \log K$ values obtained may also be attributed to the change in the geometry of the complex. For square planar complexes with bidentate ligand, the $\Delta \log K$ values are -0.6 units. For a regular and distorted octahedral geometry, the values are -0.4 and -0.9 units, respectively [33].

3.5. Binding nature of ligands

The relative stability $(\log \beta_{MAB_2})$ of the ternary complexes is also calculated by the following method [34].

%RS (A) =
$$\left[(\log K_{MB_2A}^{MA} - \log K_{MB_2}^{M}) / \log K_{MB_2}^{M} \right] \times 100$$
 [9]

These values indicate that the binding nature of the ligands A and B with metal ion in the complexes formed (ie. % RS(A) = 23.14, for cadmium-*amcaa*(A)-*ox*(B), = 6.20, for cadmium-*amcaa*(A)-*mal*(B), = -5.94 for cadmium-*amcaa*(A)-*suc*(B), =20.21,for cadmium-*amcaa*(A)-*glu*(B), =35.18, cadmium-*amcaa*(A)-*adi*(B) and = -4.92 for cadmium-*amcaa*(A)-*phth*(B)). The

results reflecting that MAB_2 system is more stable than both MA_2 and MB_2 , this stability enhancement is referred to as a "ligand effect" which is related to the electrostatic factors originated from charge neutralization, since in the formation of MAB_2 , two positive charge of Cd^{+2} is neutralized by ligand B⁻, this leads to increased σ covalence.

3.5 Distribution diagrams

Using the stability constants of the complexes and equilibrium constants of the ligands under the same experimental conditions, the percentage concentration of each complex species involving metal ion and ligand as a function of pH has been calculated [35]. A representative the pH species distribution profiles for the Cd-*amcaa* and Cd-*ox* binary systems are shown in FIGS-2 and 3. Similar trends were obtained for other systems. The distribution profiles for Cd-*ox* binary and ternary systems show that at lower pH's (2.0 - 3.0) almost all Cd(II) ($\alpha = 88\%$) over pH range 3.8 - 5.5 the predominant change is the conversion of Cd(II) into Cd-*ox* with a maximum degree of formation 80% at less than pH 5.5.

In the case of ternary system, the plots (FIG-4) show that between pH 6.0 and 8.0 the concentration of Cd-*ox* complex decreases, while the concentration of Cd-*amcaa-ox* ternary system increases. At pH 8 the ternary system reaches a maximum, $\alpha = 57\%$ while the concentration of binary systems becomes very small ($\alpha \le 40\%$). Similar trend was observed in other ternary systems.



FIG-4 Species distribution curves of Cd(II)-amcaa- ox at 1:3:3 molar ratio

The pH metric studies on Cd(II)-*amcaa*(A)-*ox*, *mal*, *suc*, *glu*, *adi*, *phth* (B) ternary complex systems at 32 °C (\pm 0.1 °C) and I = 0.1M (KNO₃) show that the ternary complex species have, in general, higher stability compared to the binary analogues. This enhancement may be attributed to the mutual interaction between the two kinds of ligands in the mixed complexes. The results show that the stability constants of mixed ligands studied here decrease continually as the size of the organic ligand increases. The stability constant values of binary, ternary systems and complex formation are better by aqueous DMSO media than in aqueous medium.

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