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Formation Constants of Ternary Complexes of Some Heavy Metal Ions with *N*-(2-Acetamido)iminodiacetic Acid and Aliphatic or Aromatic Acids

Maher M. A. Hamed,*[†] **Mohamed B. Saleh,**[‡] **Iman T. Ahmed,**[‡] **and Mohamed R. Mahmoud**[†]

Department of Chemistry, Faculty of Science, Assiut University, Assiut, Egypt, and Department of Chemistry, Faculty of Science, El-Minia University, El-Minia, Egypt

Solution equilibria of the ternary systems involving La(III), Y(III), Ce(III), and UO_2^{2+}, *N*-(2-acetamido)iminodiacetic acid, and some aliphatic or aromatic acids have been investigated potentiometrically. The formation of 1:1:1 mixed ligand complexes is inferred from the potentiometric titration curves. Formation constants of the different binary and ternary complexes formed in such systems were determined at 25 ± 0.1 °C and μ = 0.1 mol dm^{-3} (KNO_3). It is deduced that the mixed ligand complexes are more stable than the corresponding binary complexes containing the aliphatic or aromatic acidate moiety. The order of stability of the binary and ternary complexes is investigated and discussed in terms of the nature of both the metal ion and the secondary ligand (aliphatic or aromatic acid).

Introduction

N-(2-Acetamido)iminodiacetic acid (H_2ADA) is considered as one of the biologically important ligands. It is used as a complexing agent in the field of metal ion buffers working at the physiological pH range. Furthermore, it is widely used as an analytical chelating agent for the spectrophotometric determination of metal ions (*1–4*). Though much work has been carried out on binary metal complexes of H_2ADA (*5–8*), little work is reported concerning ternary metal complexes containing this ligand (*9–10*). No studies have been made on the ternary complexes of the lanthanide and actinide ions containing H_2ADA. This paper presents a potentiometric study of the ternary systems M^{n+} + $HADA^{1-}$ (in the form of monosodium salt) + aliphatic or aromatic acids. The metal ions used are Y(III), La(III), Ce(III) and UO_2^{2+}, and the acids used are succinic, tartaric, malic, citric, salicylic, anthranilic, and phthalic. The study adopts the Irving and Rossotti technique (*11*) for the evaluation of the formation constants of the different binary and ternary complexes. The stability of the complexes is examined and discussed in terms of the nature of the metal ion and the secondary ligand.

Experimental Section

Materials and Solutions. Metal salts $Y(NO_3)_3 \cdot 6H_2O$, $La(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $UO_2(NO_3)_2 \cdot 6H_2O$ were AR (Merck or BDH) products. Stock solutions were prepared by dissolving an accurately known mass in the appropriate volume of bidistilled water. H_2ADA of analytical reagent grade (BDH) with purity not less than 98% was used without purification. Since the solubility of the free acid (H_2ADA) in pure aqueous medium is low, the monosodium salt was prepared by dissolving 1.902 g of H_2ADA in 10 cm^3 of NaOH (0.1 mol dm^{-3}) and dilution to 100 cm^3 with bidistilled water. The required concentration was then obtained by accurate dilution. The acid (HNO_3) and base (NaOH) as well as potassium hydrogen phthalate were of analytical reagent grade, and their solutions were prepared using CO_2-free distilled water. Stock solutions of the various aliphatic acids used were prepared by dissolving the requisite quantity of each in double-distilled water. Aromatic acid solutions were prepared in absolute ethanol. The molarity of the base solution was checked by its titration with the standard potassium hydrogen phthalate solution. Then the molarities of the aliphatic and aromatic acid solutions under investigation were checked with standard NaOH solution.

Potentiometric Titrations. Numerous titrations of M^{n+} + ADA^{2-} and/or aliphatic or aromatic acid mixtures in the 1:1:1 molar ratio (5 × 10^{-3} mol dm^{-3} of each) with a relatively highly concentrated standard NaOH solution were performed at 25 ± 0.1 °C. The constant temperature was maintained by using an air thermostat box. The ionic strength was kept constant using 0.1 mol dm^{-3} KNO_3 solution, and a total volume of 50 cm^3 was used in each titration. The pH's were measured with an Orion 701 A pH meter, accurate to ±0.005 pH unit. Since the aromatic acids were dissolved in ethanol, 20 mass % ethanol + water was used in the titrated solutions containing them. In these cases, and in order to account for the differences in acidity, basicity, dielectric constant, and ion activities on transfer from pure aqueous medium to an ethanol + water mixed solvent, the measured pH values of the latter medium were corrected by the procedure of Douheret (*12, 13*). A value of 0.04 pH unit was subtracted from each pH meter reading (correction value for 20 mass % (w/w) ethanol + water (*14*)) where the instrument is standardized using aqueous buffer solutions. The different solutions titrated were according to the following scheme: (a) HNO_3, (b) HNO_3 + $HADA^{1-}$, (c) HNO_3 + $HADA^{1-}$ + M^{n+}, (d) HNO_3 + aliphatic or aromatic acid, (e) solution d + M^{n+}, (f) solution e + $HADA^{1-}$.

Results and Discussion

Figures 1 and 2 display a representative set of experimental titration curves obtained according to the above-described sequence for the different M^{n+} + $HADA^{1-}$ + aliphatic or aromatic acid systems. The second acid dissociation constant (pK_{a_2}) for $HADA^{1-}$ as well as the proton–ligand dissociation constants of the different aliphatic and aromatic acids have been determined under identical conditions from the titration curves a, b and a, d, respectively, making use of the Rossotti and Irving formulation (*11*). These values are in good agreement with the corresponding literature values (*14–16*). The titration curves (cf. Figures 1 and 2) indicate that the different 1:1 binary $[M(ADA)]^{(n-2)+}$ complexes are formed at

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[†] Assiut University.
[‡] El-Minia University.

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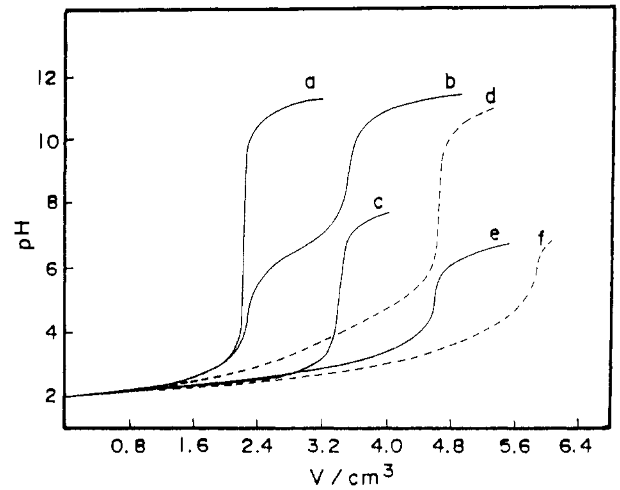

Figure 1. Titration curves of pH against volume of NaOH, V, for Y(III) + ADA^{2-} + malic acid at 25 °C and μ = 0.1 mol dm^{-3} KNO$_3$ with 0.2119 mol dm^{-3} NaOH: (a) 9.54 × 10^{-3} mol dm^{-3} HNO$_3$ + 0.1 mol dm^{-3} KNO$_3$, (b) solution a + 5.0 × 10^{-3} mol dm^{-3} HADA^{1-}, (c) solution b + 5.0 × 10^{-3} mol dm^{-3} Y(III), (d) solution a + 5.0 × 10^{-3} mol dm^{-3} malic acid, (e) solution d + 5.0 × 10^{-3} mol dm^{-3} Y(III), (f) solution e + 5.0 × 10^{-3} mol dm^{-3} HADA^{1-}.

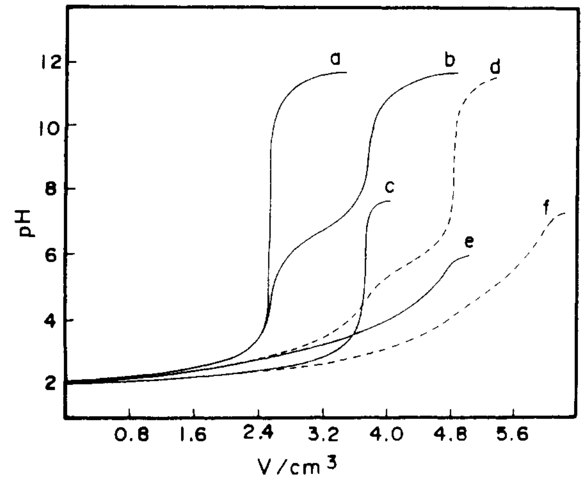

Figure 2. Titration curves of pH against volume of NaOH, V, for Ce(III) + ADA^{2-} + phthalic acid at 25 °C and μ = 0.1 mol dm^{-3} KNO$_3$ with 0.2083 mol dm^{-3} NaOH: (a) 9.54 × 10^{-3} mol dm^{-3} HNO$_3$ + 0.1 mol dm^{-3} KNO$_3$, (b) solution a + 5.0 × 10^{-3} mol dm^{-3} HADA^{1-}, (c) solution b + 5.0 × 10^{-3} mol dm^{-3} Ce(III), (d) solution a + 5.0 × 10^{-3} mol dm^{-3} phthalic acid, (e) solution d + 5.0 × 10^{-3} mol dm^{-3} Ce(III), (f) solution e + 5.0 × 10^{-3} mol dm^{-3} HADA^{1-}.

lower pH's (2.8–3.6). This is attained from the observed divergence of the 1:1 binary M^{n+} + HADA^{1-} titration curve c from that of the corresponding free HADA^{1-} titration curve (curve b). The complex solutions of such binary systems do not show any precipitation due to hydrolysis up to pH ⩾ 6, where nearly complete complex formation is achieved. This behavior strongly suggests that the ligand (HADA^{1-}) is characterized by a high tendency to form metal complexes. With respect to the titration curves of the different binary M^{n+} + aliphatic or aromatic acids under investigation, it is evident that the pH at which the binary complex is formed depends primarily upon the nature of both the secondary ligand and the metal ion. In general, for the same metal ion, the pH at which binary complex formation starts is increased as the aliphatic acid is changed in the direction citric → tartaric → malic → succinic. This denotes a low tendency of the aliphatic acid toward complex formation, under the mentioned conditions, in the same direction. Also, Y(III) and UO$_2^{2+}$ binary complex formation begins at lower pH's than La(III) and Ce(III) do with the same aliphatic acid. However, M(III) + succinic acid binary complex solutions (except that of UO$_2^{2+}$) and those of La(III) and Ce(III) + tartaric as well as Y(III) and Ce(III) + salicylic acid complex solutions show precipitation at low pH's (3.5–4.5), indicating the formation of hydroxo complexes. Other binary M^{n+} + aliphatic or aromatic acid complex solutions under investigation do not show precipitation up to pH ⩾ 6.0. However, in all cases, calculations could not be possible beyond the precipitation point.

The titration curves of the different 1:1:1 ternary complexes strongly overlap with the corresponding titration curves of [M(ADA)]$^{(n-2)+}$ at lower pH's. Generally, above a certain pH value, depending upon the type of the metal ion and the nature of the aliphatic or aromatic acid secondary ligand, one observes a divergence of the ternary titration curve from that of the binary complex titration curve. This shows the coordination of the secondary ligand (aliphatic or aromatic acid) to the binary [M(ADA)]$^{(n-2)+}$ complex in a stepwise manner, as represented by the equation

$$[\mathrm{M(ADA)}]^{(n-2)+} + \mathrm{H}_m\mathrm{L} \rightleftharpoons [\mathrm{M(ADA)L}]^{(n-(2+m))+}$$

where M = Y, La, Ce, or UO$_2$, n = 3 or 2, and m = 1, 2, or 3.

Accordingly, it may be assumed that the secondary ligand (carboxylic acids) would combine with [M(ADA)]$^{(n-2)+}$ binary complex species in a ternary system as it does with [M(H$_2$O)$_x$]$^{n+}$ in a binary system. The horizontal distance between curves c and f was measured and used for the calculation of $\bar{n}_{\mathrm{mix}}$ (average number of the secondary ligand anions attached to the [M(ADA)]$^{(n-2)+}$ molecule. The equation used for calculating $\bar{n}_{\mathrm{mix}}$ is the same as in the original paper (*11*):

$$\bar{n}_{\mathrm{mix}} = \frac{(V_{\mathrm{f}} - V_{\mathrm{c}})[N^\circ + E^\circ + T_{\mathrm{L}}{}^\circ\,(Y - \bar{n}_{\mathrm{H}})]}{(V_0 + V_{\mathrm{c}})\bar{n}_{\mathrm{H}}T_{\mathrm{M}}{}^\circ}$$

Here $T_{\mathrm{M}}{}^\circ$ is the concentration of M(ADA)$^{(n-2)+}$ which equals the concentration of M^{n+} used, Y = number of dissociable protons of the secondary ligand, V_0 is the original volume (50 cm^3), and V_{c} and V_{f} are the volumes of alkali consumed to reach the same pH value in curves c and f. All other symbols have their usual meaning (*11*). Values of $\bar{n}_{\mathrm{H}}$ for the secondary ligands, aliphatic and aromatic acids, at the different pH's were available from the determination of acid constants as described before. From the so-obtained $\bar{n}_{\mathrm{mix}}$ values, the free secondary ligand exponent (pL$_{\mathrm{mix}}$) was calculated using the equation

$$\mathrm{pL}_{\mathrm{mix}} = \log\left(\frac{\sum_{Y=0}^{Y=i}\beta_Y^{\mathrm{H}}\left(\frac{1}{10^B}\right)^Y}{T_{\mathrm{L}}{}^\circ - \bar{n}_{\mathrm{mix}}T_{\mathrm{M}}{}^\circ}\,\frac{V_0 + V_{\mathrm{f}}}{V_0}\right)$$

where β_Y^{H} = second and third dissociation constant values of the applying acids (secondary ligands), B = the pH meter reading, and i = 1, 2 or 3.

The stability constants of the different binary complexes [M(ADA)]$^{(n-2)+}$ and [M(L)]$^{(n-m)+}$ and those for the mixed ligand complexes [M(ADA)L]$^{(n-(m+2))+}$ were determined from the corresponding formation curves (curves b, c and d, e and c, f, respectively) using the Irving and Rossotti equations. The different $\log K^{\mathrm{M}}_{\mathrm{M(ADA)}}$, $\log K^{\mathrm{M}}_{\mathrm{ML}}$, and $\log K^{\mathrm{M(ADA)}}_{\mathrm{M(ADA)(L)}}$ values were obtained from the average value and straight line

Table 1. Formation Constant Values for the Different Binary 1:1 M^{n+} + ADA^{2-} and those for M^{n+} + Carboxylic Acid Complexes[a] at 25 °C and $\mu = 0.1$ mol dm^{-3} KNO_3

ADA or carboxylic acid	log $K^{M}_{M(ADA)}$ and log $K^{M}_{M(\text{aliphatic or aromatic acid})}$			
	Y(III)	La(III)	Ce(III)	UO_2^{2+}
ADA	7.48 ± 0.06	6.70 ± 0.11	6.85 ± 0.03	7.03 ± 0.03
citric	8.86 ± 0.03	6.52 ± 0.05	6.55 ± 0.04	8.37 ± 0.01
	(7.81 ± 0.06)	(6.90 ± 0.2)	(7.38 ± 0.06)	(7.4 ± 0.2)
succinic				5.26 ± 0.03
		(1.48 ± 0.08)		(3.68 ± 0.03)
malic	4.18 ± 0.03	4.49 ± 0.05	4.39 ± 0.02	5.19 ± 0.06
		(4.04 ± 0.04)	(5.00 ± 0.01)	(6.10)
tartaric	4.12 ± 0.05			5.05 ± 0.06
	(4.07)	(2.89)	(5.50)	
phthalic	3.81 ± 0.01	3.71 ± 0.01	3.74 ± 0.01	4.96 ± 0.05
	(4.04)	(3.18)	(3.96)	(4.81)
anthranilic	2.51 ± 0.04	2.55 ± 0.02	2.65 ± 0.03	3.58 ± 0.03
		(3.14)	(3.18)	
salicylic		2.51 ± 0.03		2.95 ± 0.01
		(2.64)	(2.66)	

[a] Values in parentheses are those taken from ref 16.

Table 2. Formation Constant Values for the Different 1:1:1 M^{n+} + ADA^{2-} + Aliphatic or Aromatic Acid Complexes at 25 °C and $\mu = 0.1$ mol dm^{-3} KNO_3

acid	log $K^{M(ADA)}_{M(ADA)(\text{aliphatic or aromatic acid})}$			
	Y(III)	La(III)	Ce(III)	UO_2^{2+}
citric	9.56 ± 0.02	7.11 ± 0.03	7.16 ± 0.03	9.00 ± 0.02
succinic	4.90 ± 0.08	4.72 ± 0.05	4.60 ± 0.02	5.87 ± 0.03
malic	4.85 ± 0.02	4.70 ± 0.02	4.53 ± 0.09	5.63 ± 0.10
tartaric	4.69 ± 0.01	4.38 ± 0.01	4.43 ± 0.03	5.16 ± 0.05
phthalic	4.99 ± 0.03	4.43 ± 0.02	4.67 ± 0.01	5.19 ± 0.07
anthranilic	3.24 ± 0.01	2.86 ± 0.01	3.44 ± 0.02	3.78 ± 0.06
salicylic	3.22 ± 0.14	2.81 ± 0.02	2.96 ± 0.06	3.14 ± 0.03

methods (*11*). The values obtained along with the estimated error using least-squares refinement are listed in Tables 1 and 2. Examination of these data clearly indicates that the formation constants of the ternary complexes $[M(ADA)L]^{(n-(m+2))+}$ are higher than those of binary $[ML]^{(n-m)+}$. This behavior can be mainly ascribed to the presence of two extra five-membered chelate rings in the ternary complex as a result of the coordination of the ADA^{2-} moiety (N, O, O donor) compared to the corresponding 1:1 binary metal + carboxylic acid (aliphatic or aromatic) complex. On the other hand, the stability of the ternary complexes containing aliphatic acid moieties is, in general, more than that of the complexes containing aromatic acid moieties. Also, the stability of the formed binary or ternary complexes, of the same metal ion, decreases in the following order: citrate ion ($pK_{a_1} = 3.13$, $pK_{a_2} = 4.76$, $pK_{a_3} = 6.40$) $\gg$ succinate ion ($pK_{a_1} = 4.21$, $pK_{a_2} = 5.64$) > malate ion ($pK_{a_1} = 3.40$, $pK_{a_2} = 5.05$) > tartarate ion ($pK_{a_1} = 3.04$, $pK_{a_2} = 4.37$) (*15*) and phthalate ion ($pK_{a_1} = 2.45$, $pK_{a_2} = 5.42$) > anthranilate ion ($pK_{a_1} = 2.11$, $pK_{a_2} = 4.95$) > salicylate ion ($pK_{a_1} = 3.0$, $pK_{a_2} = 12.38$) (*16*).

This behavior can be ascribed to the decrease in basicity of the conjugate bases of these acids in the same direction, i.e., a decrease in σ-donor ability along the same sequence. The observed remarkably high stability of the binary or ternary complex containing the tricarboxylate citrate moiety can be attributed to the behavior that this ligand is expected to act as a good σ-donor compared to the dicarboxylate ions succinate, malate, and tartarate. Furthermore, the tricarboxylate citrate ion acts as an O^-, O^-, O^- tridentate ligand, leading to formation of two metal chelated rings (both are seven-membered).

In terms of the nature of the coordinated metal ion, the stability of these complexes generally follows the order UO_2^{2+} > Y(III) > Ce(III) > La(III), which is in accordance with the usual order of stability of such metal ion complexes (*17*, *18*).

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