

Potentiometric studies on Ternary Complexes of Some Heavy Metal Ions Containing N-(2-Acetamido)-iminodiacetic and Amino Acids

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Solution equilibria of the ternary systems $\text{UO}_2(\text{II})$, $\text{La}(\text{III})$, $\text{Ce}(\text{III})$ -N-(2-acetamido)-iminodiacetic acid and dicarboxylic amino acids are studied potentiometrically. The formation of 1:1:1 mixed ligand complexes are inferred from the potentiometric titration curves. The formation constants of the different binary and ternary complexes in such system are evaluated at $t=24\pm 0.1^\circ\text{C}$ and $\mu=0.1\text{ mol dm}^{-3}$ (KNO_3). It is deduced that the ternary complex is more stable than the corresponding binary amino acid anion complex. Moreover, the order of stability of the binary or ternary complexes in terms of nature of amino acid and metal ion is investigated and discussed.

Key words: Heavy metal ions, Ternary complexes, ADA, Amino acids

INTRODUCTION

N-(2-Acetamido)-iminodiacetic acid (H_2ADA) is considered as one of the biologically important ligands. Generally, H_2ADA is applied as a complexing agent in the field of metal ion buffers suitable for use in biochemistry at physiological pH's. Furthermore, it is widely used as an important analytical chelating agent for the spectrophotometric determination of a number of metal ions (Gonzalez-Portal *et al.*, 1980; Lojo-Rocamonde *et al.*, 1981; Lojo-Rocamonde *et al.*, 1982; Gonzalez-Portal *et al.*, 1985). Though much work has been published on binary metal complexes of H_2ADA (Nakon, 1979; Lance and Nakon, 1981; Lance *et al.*, 1983; Parr *et al.*, 1983), little work has been made of ternary metal complexes containing this compound (Nakon *et al.*, 1986; Mahmoud *et al.*, 1989). On the other hand, no attention has been paid before to the ternary complexes of lanthanide and actinide metal ions with H_2ADA and amino acids. Therefore, in the present paper a systematic study on the complex formation of the ternary system: M^{+n} ($\text{La}(\text{III})$, $\text{Ce}(\text{III})$, $\text{UO}_2(\text{II})$): HADA^{-1} (in the form of monosodium salt): dicarboxylic amino acids (H_2L (aspartic and glutamic acids)) is investigated. The study includes the potentiometric determination of the formation constant of the different binary and ternary complexes formed in such system adopting the Irving and Rossotti technique (Irving and Rossotti,

1953). The stability of the formed ternary complexes has been examined and discussed in relation to the corresponding binary complex as well as in terms of nature of metal ion and amino acid moiety.

MATERIALS AND METHODS

Materials and Solutions

Metal salts: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used as A.R products. Stock solutions of these metal salts were prepared and standardized as recommended. H_2ADA was analytical grade (BDH) with purity not less than 98% and was used without further purification. Since the solubility of the free acid H_2ADA in pure aqueous media is very small, the monosodium salt was prepared by titration of H_2ADA with standard carbonate-free sodium hydroxide solution. The required concentration was then obtained by accurate dilution. All amino acids used were of extra pure products. The acid (HNO_3) and base (NaOH) used for titration as well as KNO_3 and KH phthalate were analytical reagent grade. All solutions were prepared using CO_2 -free distilled water.

Potentiometric Titrations

Numerous titrations of different $\text{M}^{+n}\text{-HADA}^{-1}$ and/or amino acid mixtures in 1:1:1 molar ratio (5×10^{-3} mol dm^{-3} for each) with a relatively high concentrated standard carbonate-free sodium hydroxide solution

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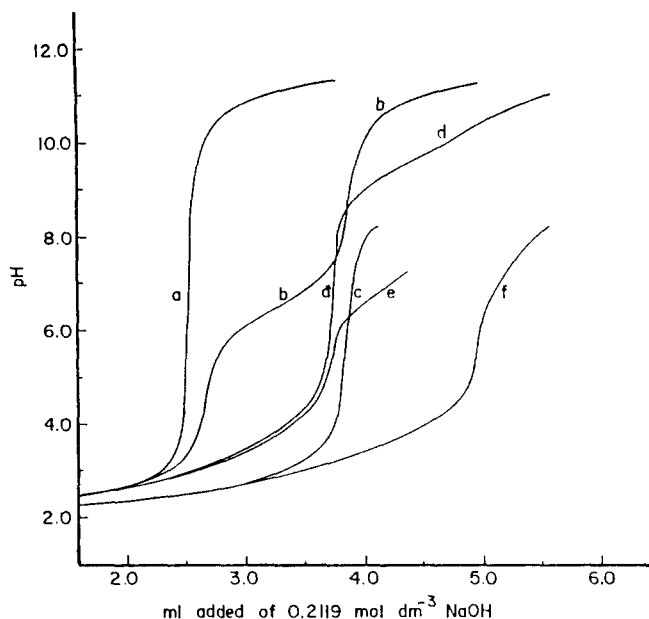


Fig. 1. Potentiometric titration curves for La(III)-HADA⁻¹ aspartic acid system at 24°C and $\mu=0.1 \text{ mol dm}^{-3} \text{ KNO}_3$ with $0.2119 \text{ mol dm}^{-3} \text{ NaOH}$.

(a) $9.54 \times 10^{-3} \text{ mol dm}^{-3} \text{ HNO}_3$, (b) solution(a) + $5.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ HADA}^{-1}$, (c) solution(b) + $5.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ La(III)}$, (d) solution(a) + $5.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ aspartic acid}$, (e) solution(d) + $5 \times 10^{-3} \text{ mol dm}^{-3} \text{ La(III)}$, (f) solution(e) + $5 \times 10^{-3} \text{ mol dm}^{-3} \text{ HADA}^{-1}$.

were performed at $24 \pm 0.1^\circ\text{C}$. The constant temperature was achieved by using an air thermostat box. A constant ionic strength was obtained with $0.1 \text{ mol dm}^{-3} \text{ KNO}_3$ and total volume was kept constant at 50 ml. pH's were measured with Orion pH-meter model 701 A (accurate to $\pm 0.005 \text{ pH unit}$). The different solutions titrated can be represented according to the following scheme: HNO_3 (a); $\text{HNO}_3 + \text{HADA}^{-1}$ (b); $\text{HNO}_3 + \text{HADA}^{-1} + \text{M}^{+n}$ (c); $\text{HNO}_3 + \text{amino acid}$ (d); $\text{HNO}_3 + \text{amino acid} + \text{M}^{+n}$ (e); $\text{HNO}_3 + \text{HADA}^{-1} + \text{amino acid} + \text{M}^{+n}$ (f).

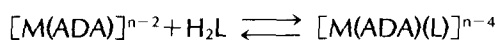
RESULTS AND DISCUSSION

Fig. 1 displays representative set of experimental titration curves obtained according to the sequence described in the experimental part for the different $\text{M}^{+n}(\text{HADA})^{-1}$: amino acid systems studied. The second and third acid dissociation constant values pK_{a2} and pK_{a3} of aspartic and glutamic amino acids were determined from the titration curves a and d making use of the Rossotti and Irving formulate (Irving and Rossotti, 1953, 1953). The obtained values are in good agreement with the corresponding ones reported in the literature (Weast, 1980). The second acid dissociation constant value pK_{a2} for the monosodium salt of N-(2-acetamido)-iminodiacetic acid (HADA)⁻¹, has

been determined under identical conditions from the titration curves a and b. The obtained value (6.51) is in agreement with the corresponding literature one (Perin and Demposey, 1974). The constructed titration curves (c.f. Fig. 1) clearly reveal that the different 1:1 binary $[\text{M}(\text{ADA})]^{n-2}$ complexes are formed at lower pH's (~ 2.0). This is attained from the appeared divergence of the 1:1 binary $\text{M}^{+n}\text{-HADA}^{-1}$ titration curve c from that of the corresponding free $(\text{HADA})^{-1}$ solution, curve b. The complex solutions of such binary systems do not show any precipitation due to hydrolysis up to $\text{pH}'s \geq 6$ where nearly complete complex formation is occurred. This behaviour strongly suggests that the ligand $(\text{HADA})^{-1}$ is characterized by high tendency to form metal complexes.

With respect to the titration curves of the different M^{+n} -dicarboxylic amino acids studied, it is evident that these complexes begin to form at pH's (3.3-3.5). However, La(III) and Ce(III)-complexes undergo hydrolysis reaction where hydroxy complex species are likely formed. Accordingly, in such cases a further study could not be possible beyond the precipitation point.

The titration curves of the different studied 1:1:1 ternary complexes are strongly overlap with the corresponding ones of the $[\text{M}(\text{ADA})]^{n-2}$ at lower pH's. Generally, above certain pH value which is largely dependent on the nature of amino acid as well as metal ion, one observes a divergence of the ternary titration curve from that of the corresponding binary $[\text{M}(\text{ADA})]^{n-2}$ titration curve. This shows the coordination of the dicarboxylic amino acid with the binary $[\text{M}(\text{ADA})]^{n-2}$ complex in stepwise manner as represented by the following equation:



$\text{M} = \text{La(III)}, \text{Ce(III)}, \text{UO}_2(\text{II}),$

$\text{H}_2\text{L} = \text{dicarboxylic aspartic and glutamic acids.}$

Accordingly, it may be assumed that the dicarboxylic amino acid would combine with $[\text{M}(\text{ADA})]^{n-2}$ binary complex species in ternary systems as it does with $[\text{M}(\text{H}_2\text{O})_x]^{+n}$ in a binary system. The horizontal distance between the curves c and f was measured and used for the calculation of \bar{n}_{mix} (average number of the secondary ligand aspartate or glutamate anion attached per $[\text{M}(\text{ADA})]^{n-2}$). The equation used for the calculation of \bar{n}_{mix} was the same as in the original paper (Irving and Rossotti, 1953, 1954)

$$\bar{n}_{\text{mix}} = \frac{(V_i - V_o)(n^{\circ} + E^{\circ} + T_m^{\circ}(Y - \bar{n}_H))}{(V_o + V_i)\bar{n}_H T_m^{\circ}} \quad (1)$$

Here T_m° is the concentration of $[\text{M}(\text{ADA})]^{n-2}$ which is equal to the concentration of M^{+n} used; $Y = \text{number of dissociable protons of aspartic and glutamic acids}$ ($Y=2$ in both cases); $V_o = \text{original volume (50 ml)}$; V_i, V_f are the volume of alkali consumed to reach the

Table 1. Formation constants for the binary complexes $[M(L)]^{n-2}$ ($\log k_{ML}^M$) and those for the mixed ligand complexes $[M(ADA)(L)]^{n-4}$ ($\log k_{M(ADA)(L)}^{M(ADA)}$) at 24°C and $\mu=0.1 \text{ mol dm}^{-3} \text{ KNO}_3$.

Amino acid	Log k_{ML}^M			Log $k_{M(ADA)(L)}^{M(ADA)}$									$\Delta \log K$ UO ₂ (II)
	UO ₂ (II)			La(III)			Ce(III)			UO ₂ (II)			
	i	ii	mean	i	ii	mean	i	ii	mean	i	ii	mean	
Aspartic acid	8.40	8.38	8.39±0.01	8.60	8.63	8.62±0.06	8.85	8.88	8.87±0.04	8.90	8.88	8.89±0.01	+0.50
Glutamic acid	8.25	8.33	8.29±0.08	8.10	8.14	8.12±0.02	8.20	8.25	8.23±0.05	8.50	8.41	8.46±0.06	+0.17

i) the average value method. ii) the straight line method.

same pH value in curves c and f. All other symbols have their usual meaning (Irving and Rossotti, 1953, 1954). \bar{n}_H for secondary ligand, amino acid, at different pH values were available from the determination of amino acids formation constant values as described above. From the values of \bar{n}_{mix} obtained, free secondary ligand exponent, pL_{mix}^- was calculated using the equation:

$$pL_{mix}^- = \log \left(\frac{\sum_{Y=2}^{Y=2} \beta_Y^H \left(\frac{1}{10^B} \right)^Y}{T_L - \bar{n}_{mix} T_M} \cdot \frac{V_o + V_f}{V_o} \right) \quad (2)$$

β_Y^H = second and third formation constant values for the applying amino acids.

B = the pH meter reading.

The stability constants of the different binary complexes $[M(L)]^{n-2}$ and those for the mixed complexes $[M(ADA)(L)]^{n-4}$ were determined from the corresponding formation curves (curves d, e and c, f respectively) using the Irving and Rossotti equations(11). The different $\log k_{ML}^M$ and $\log k_{M(ADA)(L)}^{M(ADA)}$ values were obtained from the average value and straight line methods. The values obtained along with the error as calculated by applying the least-squares method are listed in Table 1.

Examination of the different formation constant values of the same metal ion binary or ternary complex in terms of nature of the dicarboxylate amino acid moiety clearly reveals that the stability of the ternary complex containing the α , β -dicarboxylic aspartate is higher than that containing the α , γ -dicarboxylic glutamate. This can be mainly explained on the principle of steric effects, since both dicarboxylate amino acid anions behave as tridentate $\bar{O}\bar{O}N$ ligand where two chelated rings are formed (five and six membered rings in case of aspartate and five and seven membered chelate rings in case of glutamate). On the other hand, the order of stability of the different $[M(ADA)(L)]^{n-4}$ ternary complexes in terms of nature of metal ion follow the order $UO_2(II) > Ce(III) > La(III)$. This is in accordance with the complex forming tendency of these metal ions (Cotton and Wilkinson, 1972).

The stability of the ternary complex $[M(ADA)(L)]^{n-4}$ compared to that of the corresponding binary amino

acid complex $[ML]^{n-2}$ (L=aspartate or glutamate) is expressed in terms of $\Delta \log K$ (c.f. Table 1). It is evident that, the formation constant corresponding to the association of amino acid anion with $[M(ADA)]^{n-2}$ is higher than that corresponding to the reaction of the same amino acid anion with $[M(H_2O)_x]^{+n}$ i.e the former has higher stability relative to the latter one ($\Delta \log K$ is positive). This behaviour can be likely ascribed to the presence of two five membered chelate rings in the ternary complex due to coordination of the primary N, O, O tridentate $(ADA)^{-2}$ ligand on compared to the 1:1 binary M^{+n} : amino acid complex $[M(L)]^{n-2}$.

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