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Physico-chemical Investigation on Some Mixed-Ligand Complexes of Dioxouranium(VI), Part I

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Mixed-ligand complex studies of $UO_2(VI)$ using nitrilotriacetic acid and iminodiacetic acid as primary ligands and lactic acid and protocatechuic acid as secondary ligands have been carried out potentiometrically at three different temperatures 20, 35, 50°C and $\mu = 0.2$ M (KNO_3). The thermodynamic parameters, *viz.*, ΔG, ΔH and ΔS have been evaluated. The ΔG and ΔH values have been further separated into their electrostatic components ΔG_e and ΔH_e and cratic components ΔG_c, ΔH_c. The results are correlated on the basis of structural characteristics of the chelates formed.

INTRODUCTION

Ternary and quaternary complexes of $UO_2(VI)$ with various bidentate ligands have been studied[1–4]. In a few studies polyamino acids have also been used.[5] In all ternary complexes of $UO_2(VI)$ reported so far, the coordination number of central uranium atom is six (two positions being occupied by two oxygen atoms), while in quaternary complexes the coordination number attained is eight by the expansion of coordination number of uranium. The present paper reports a systematic study on ternary complexes of $UO_2(VI)$ using tridentate iminodiacetic acid (IMDA) and tetradentate nitrilotriacetic acid (NTA) as primary ligands and bidentate lactic acid (LA) and protocatechuic acid (PCA) as secondary ligands. The study has been carried out at three different temperatures, *viz*, 20, 35 and 50°C and at $\mu = 0.2$ M KNO_3 employing modified form of Irving-Rossotti's pH titration technique.[6] The thermodynamic parameters, namely change in free enrgy (ΔG), enthalpy (ΔH) and entropy (ΔS) have been evaluated. To know the extent of covalent and ionic bonding the ΔG and ΔH values are further separated into their cratic components ΔG_c, ΔH_c and electrostatic components ΔG_e and ΔH_e.

EXPERIMENTAL

All the chemicals used were of reagent grade (BDH or E. Merck). A 0.02 M uranyl nitrate solution was prepared by dissolving requisite quantity of pure sample in known quantity of nitric acid and estimated gravimetrically.[7] The ligand solutions were prepared in double distilled water and estimated potentiometri-

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cally. Carbonate-free sodium hydroxide was prepared by standard method. All experiments were carried out under inert atmosphere by bubbling nitrogen through reaction vessel throughout the course of experiments. The "Systronics" digital pH-meter, Model No. 335, with glass-calomel electrodes was employed for pH measurements. The instrument was capable of measuring pH from 0 to 14 with a resolution of ±0.01 pH units and was provided with temperature compensation control from 0 to 100°C with ±2°C accuracy.

Procedure

The experimental procedure involved potentiometric titration of the following four mixtures:

(i) 2.0×10^{-2} M nitric acid

(ii) 2.0×10^{-2} M HNO_3 + 1.0×10^{-3} M secondary ligand

(iii) 2.0×10^{-2} M HNO_3 + 1.0×10^{-3} M primary ligand + 1.0×10^{-3} M uranyl nitrate

(iv) 2.0×10^{-2} M HNO_3 + 1.0×10^{-3} M uranyl nitrate + 1.0×10^{-3} M primary ligand + 1.0×10^{-3} M secondary ligand.

The ionic strength was maintained constant by adding required volume of KNO_3 solution. The ratio of metal (M) : primary ligand (A) : secondary ligand (L) was maintained at 1 : 1 : 1 in each system.

RESULTS AND DISCUSSION

The graphs were plotted between pH and volume of sodium hydroxide solution added. The four plots obtaied were: acid curve, secondary ligand curve, binary complexation curve and ternary complexation curve, respectively, for the mixtures (i) to (iv). Representative graphs are shown in Figs. 1–4. The proton-ligand and metal-ligand formation constants (log K_1^H and log K_{MAL}^{MA} were calculated by extended procedure of Irving and Rossotti (Table-1).

The thermodynamic parameters, *viz*, ΔG, ΔH and ΔS have been evaluated making use of temperature coefficients and Gibbs-Helmholtz equation[8] and tabulated in Table-2. The ΔG and ΔH values have been further separated into their cratic components ΔG_c and ΔH_c and electrostatic components ΔG_e and ΔH_e by the method of Nancollas.[9] The final forms of the equations used to find out ΔG_c, ΔH_c, ΔG_e and ΔH_e are

$$\Delta G_e = -\nu(\Delta S + \Delta nRT \ln 55.5) \quad (1)$$

$$\Delta H_e = (T - \nu)(\Delta S + \Delta nRT \ln 55.5) \quad (2)$$

$$\Delta G_c = \Delta G - \Delta G_e - \Delta nRT \ln 55.5 \quad (3)$$

$$\Delta H_c = (\Delta H - \Delta H_e) \quad (4)$$

where ν is temperature characterstic of the solvent (219°C for water) and T is 298 K.

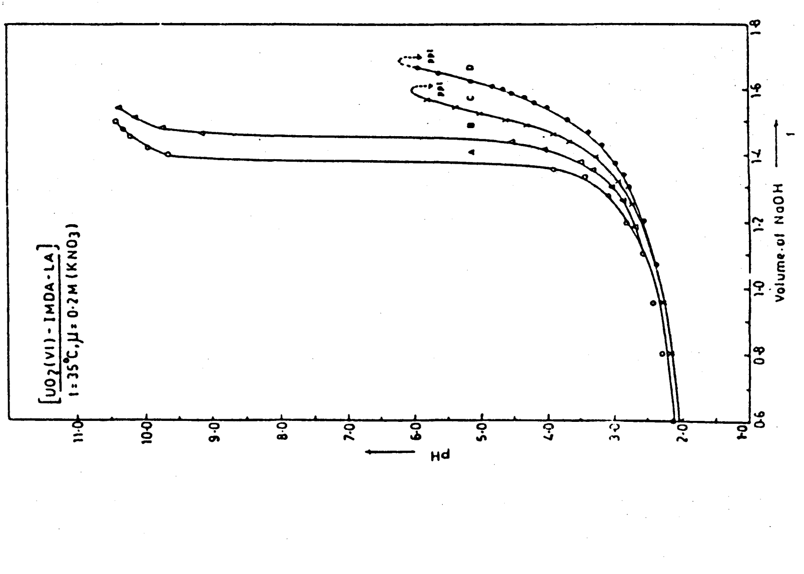
[UO2(VI) - IMDA-LA]
t = 35°C, μ = 0·2M (KNO3)
pH
11·0
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0·6
0·8
1·0
1·2
1·4
1·6
1·8
Volume of NaOH
A
B
C
D
ppt
ppt

Fig. 1A

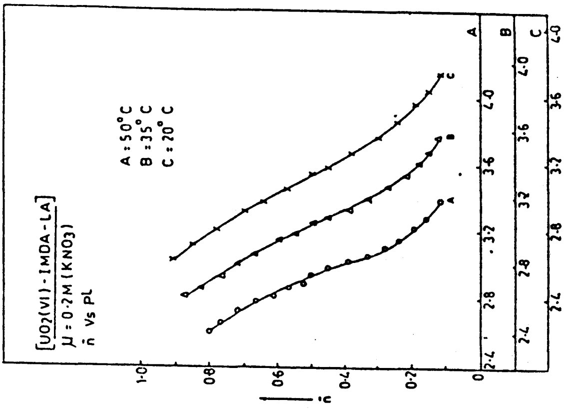
[UO2(VI) - IMDA-LA]
μ = 0·2M (KNO3)
n̄ Vs pL
A : 50°C
B : 35°C
C : 20°C
n̄
1·0
0·8
0·6
0·4
0·2
0
2·4
2·8
3·2
3·6
4·0
A
B
C
pL

Fig. 1B

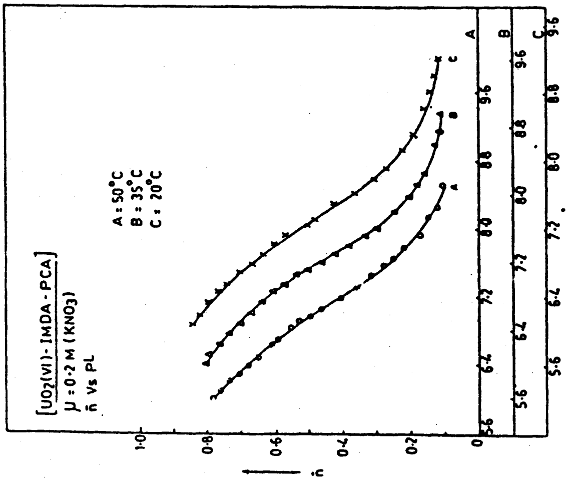
[UO2(VI)-IMDA-PCA]
μ = 0·2 M (KNO3)
n̄ Vs pL
A : 50°C
B : 35°C
C : 20°C
A
B
C
0
0·2
0·4
0·6
0·8
1·0
n̄
5·6
6·4
7·2
8·0
8·8
9·6
pL

Fig. 2B

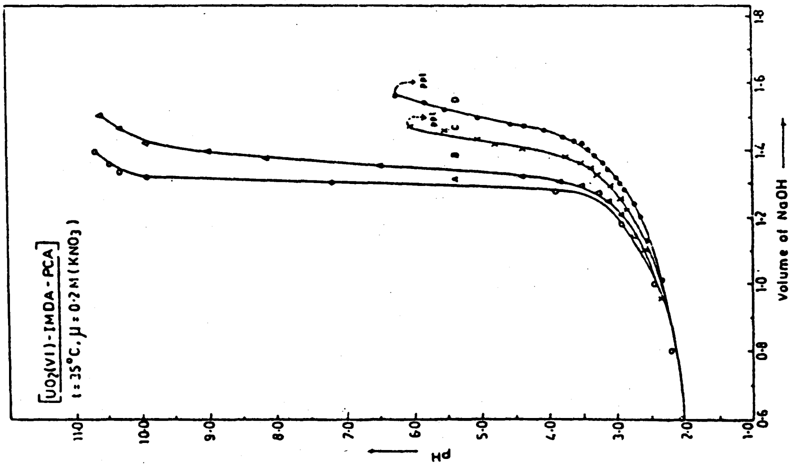
[UO2(VI)-IMDA-PCA]
t = 35°C, μ = 0·2 M (KNO3)
A
B
C
D
ppt
ppt
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10·0
11·0
pH
0·6
0·8
1·0
1·2
1·4
1·6
1·8
Volume of NaOH

Fig. 2A

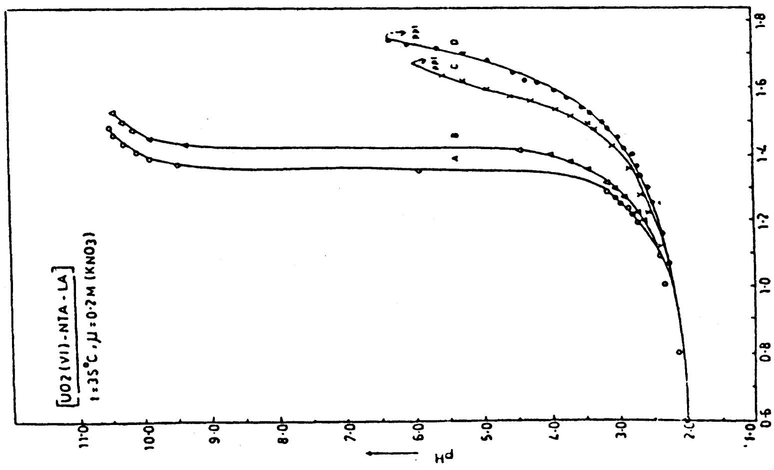
[UO2(VI)-NTA-LA]
t : 35°C, μ : 0·2 M (KNO3)
pH
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10·0
11·0
Volume of NaOH
0·6
0·8
1·0
1·2
1·4
1·6
1·8
A
B
C
D

Fig. 3A

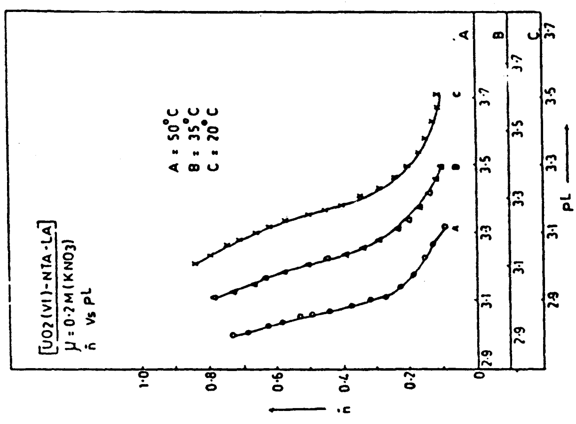
[UO2(VI)-NTA-LA]
μ = 0·2 M (KNO3)
n̄ Vs pL
A : 50°C
B : 35°C
C : 20°C
n̄
0
0·2
0·4
0·6
0·8
1·0
pL
2·9
3·1
3·3
3·5
3·7
A
B
C

Fig. 3B

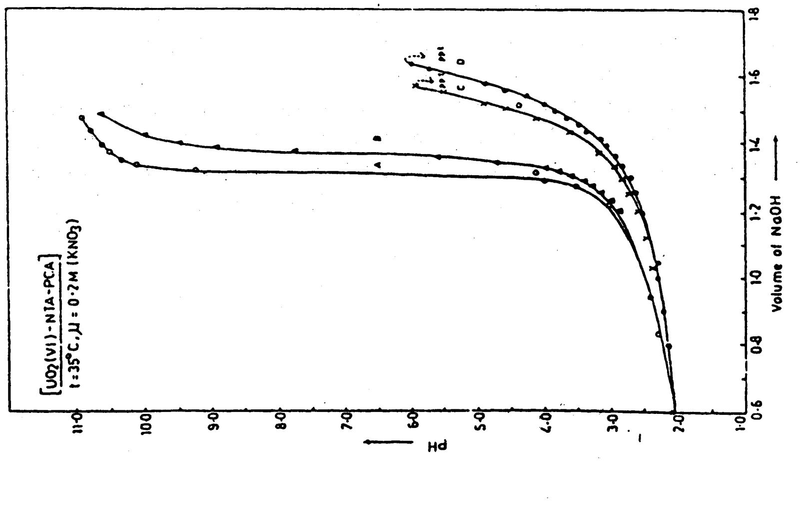
[UO2(VI)-NTA-PCA]
t = 35°C, μ = 0·2M (KNO3)
pH
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10·0
11·0
Volume of NaOH
0·6
0·8
1·0
1·2
1·4
1·6
1·8
A
B
C
D

Fig. 4A

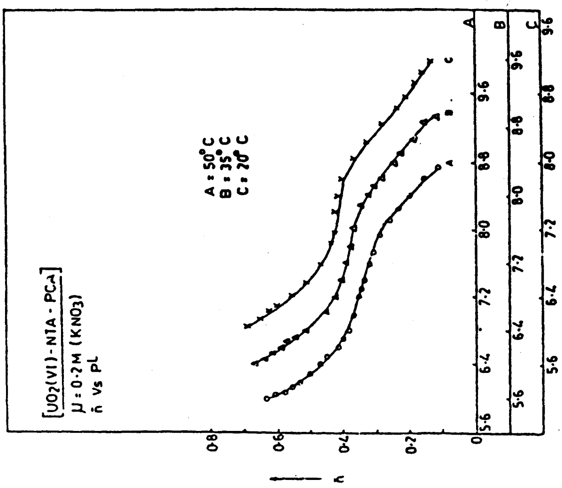
[UO2(VI)-NTA-PCA]
μ = 0·2M (KNO3)
n̄ Vs pL
A : 50°C
B : 35°C
C : 20°C
n̄
0
0·2
0·4
0·6
0·8
pL
A 5·6 6·4 7·2 8·0 8·8 9·6
B 5·6 6·4 7·2 8·0 8·8 9·6
C 5·6 6·4 7·2 8·0 8·8 9·6

Fig. 4B

TABLE-1
PROTON AND METAL-LIGAND STABILITY CONSTANTS AT DIFFERENT TEMPERATURES $\mu = 0.2$ M (KNO_3)

System (Change omitted)	Constant	Temp. (°C)		
		20	35	50
LA-H	$\log K_1^H$	3.94	3.74	3.56
PCA-H	$\log K_1^H$	8.96	8.86	8.74
	$\log K_2^H$	4.56	4.38	4.22
[UO_2(VI)-LA]	$\log K_1$	3.28	3.14	3.04
	$\log K_2$	2.60	2.52	2.46
[UO_2(VI)-PCA]	$\log K$	6.50	6.46	6.36
[UO_2(VI)-IMDA-LA]	$\log K_{LA}^{IMDA}$	3.12	3.02	2.94
[UO_2(VI)-IMDA-PCA]	$\log K_{PCA}^{IMDA}$	7.20	7.06	6.94
[UO_2(VI)-NTA-LA]	$\log K_{LA}^{NTA}$	3.15	3.09	3.05
[UO_2(VI)-NTA-PCA]	$\log K_{PCA}^{NTA}$	6.46	6.26	6.16

TABLE-2
THERMODYNAMIC PARAMETERS

System (Charge omitted)	ΔG	ΔH	ΔS	ΔG_e	ΔH_e	ΔG_c	ΔH_c
		kcal mol^{-1}		cal $degree^{-1}$ mol^{-1}		kcal mol^{-1}	
[UO_2(VI)-IMDA-LA]	4.79	3.1	5.5	4.70	1.9	5.01	1.2
[UO_2(VI)-IMDA-PCA]	10.29	3.1	23.5	8.61	3.5	6.60	0.4
[UO_2(VI)-NTA-LA]	4.62	4.1	1.5	3.84	1.6	5.70	2.6
[UO_2(VI)-NTA-PCA]	9.02	6.2	9.0	5.51	2.2	8.43	4.0

The primary complexes with NTA and IMDA start forming at lower pH. In [UO_2(VI)-IMDA] the formation is complete up to pH 3.3 and [UO_2(VI)-NTA] is complete up to pH 3.0. The mixed-ligand complex formations with [UO_2(VI)-IMDA] and [UO_2(VI)-NTA] take place between 3.2 to 6.00, which is extended to 6.30–6.40 where the mixed-ligand complex hydrolyses. The formation of mixed-ligand complex is evident from:

[1] Horizontal distance $[(V_4 - V_3) - (V_2 - V_1)]$ which increases till ñ value reaches *ca.* 0.9 [UO_2(VI)-IMDA-LA], *ca.* 0.8 [UO_2(VI)-IMDA-PCA], *ca.* 0.8 [UO_2(VI)-NTA-LA] and *ca.* 0.7 [UO_2(VI)-NTA-PCA] where the pL value symmetrically decreases; and

[2] Increase in pH value of precipitation from *ca.* 6.0 to *ca.* 6.30 for [UO_2(VI)-IMDA-L] and from *ca.* 6.0 to *ca.* 6.4 for [UO_2(VI)-NTA-L] where L is the secondary ligand. Stepwise formation is evident from the fact that the

horizontal distance $[(V_4 - V_3) - (V_2 - V_1)]$ is negligible in pH range of formation of primary complex indicating non-involvement of secondary ligands in the pH region of formation of primary complex.

The formation of mixed ligand complex is favoured by positive values of entropy. The negative ΔH values indicate exothermic nature of the reaction, while the negative value of ΔG indicates spontaneity of the reaction. The comparison of electrostatic and cratic components from Table-2 indicates that, in case of [UO_2(VI)-IMDA-LA] and [UO_2(VI)-NTA-LA], it is not possible to decide the type of bonding existing in the complexes. In case of [UO_2(VI)-IMDA-PCA] the ΔG_e values are more negative than ΔG_c values. This trend suggests that electrostatic forces are stronger than non-electrostatic forces in formation of this complex. The $\Delta H_e > \Delta H_c$ indicates less exothermic nature of the reaction. In case of [UO_2(VI)-NTA-PCA] mixed ligand complex, the reverse trend in the values is observed, indicating more effective non-electrostatic interaction.

The work leads to the conclusion that the mixed-ligand complex formation in case of [UO_2(VI)-IMDA-L] expands the coordination number of the central uranium atom to seven and eight in [UO_2(VI)-NTA-L] complexes. The stability of the complex is governed by (i) basicity of the ligand, (ii) size of the chelate ring formed, and (iii) chelating characteristics of the ligand. When basicities of the two secondary ligands are compared, PCA is found to form more stable complex which may be because of the lone-COO^- present and also due to conjugate double bond. In LA, the electron withrawing —COOH is involved in chelation due to which the complexes are less stable.

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