

Potentiometric Studies on Some Binary and Mixed Ligand Complexes of $\text{UO}_2(\text{VI})$ [Part-III]

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Stability constants of binary complexes of $\text{UO}_2(\text{VI})$ with nitrilotriacetic acid (NTA), lactic acid (LA) and protocatechuic acid (PCA) as ligands and of mixed ligand complexes of $\text{UO}_2(\text{VI})$ with NTA as a primary ligand and LA and PCA as secondary ligands at 20, 35, 50° and in different ratios of water to non-aqueous solvents and at different ionic strengths have been determined. The effect of dielectric constant and ionic strength on the values of stability constants have been discussed on the basis of steric factors and structural characteristics of complex formed.

INTRODUCTION

In ternary complexes uranium is hexa-coordinated¹⁻⁴ while in quaternary complexes using bidentate ligand the coordination number exhibited is eight⁵. Some studies on mixed ligand complexes of $\text{UO}_2(\text{VI})$ using aminopoly carboxylic acid as primary ligands and bidentate secondary ligands have been reported⁶. When tridentate iminodiacetic acid is used as primary ligand^{6,7} the coordination number exhibited is seven, while using tetradentate nitrilotriacetic acid^{6,7} the coordination number is eight. In an earlier communication⁷ a systematic study on ternary complexes of $\text{UO}_2(\text{VI})$ 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 has been reported. The study was carried out at three different temperatures, viz., 20, 35 and 50°C and at ionic strength $\mu = 0.2 \text{ M KNO}_3$, employing modified form of Irving-Rossotti's pH-titration technique. In the present paper the complexation of $\text{UO}_2(\text{VI})$ with LA and PCA in binary systems and $\text{UO}_2(\text{VI})$ -NTA/LA and PCA in ternary systems under different conditions of ionic strength, temperature, using solvents with different dielectric constants have been reported.

EXPERIMENTAL

All the chemicals used were of AnalaR grade (BDH or E. Merck). Uranyl nitrate solution (0.02 M) was prepared in nitric acid to prevent hydrolysis and the uranium content was estimated gravimetrically⁸. The ligand solutions were prepared in double distilled water and estimated potentiometrically. The organic solvents used were purified by standard methods⁹. All experiments were carried out under inert atmosphere by bubbling nitrogen through reaction vessel through-

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out the course of experiment. A "Systronics" digital pH-meter, Model No. 335, with glass-calomel electrodes assembly, 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 $\pm 2^\circ\text{C}$ accuracy. Temperature was maintained constant with an accuracy of $\pm 0.02^\circ$ by dipping the reaction vessel in a thermostat.

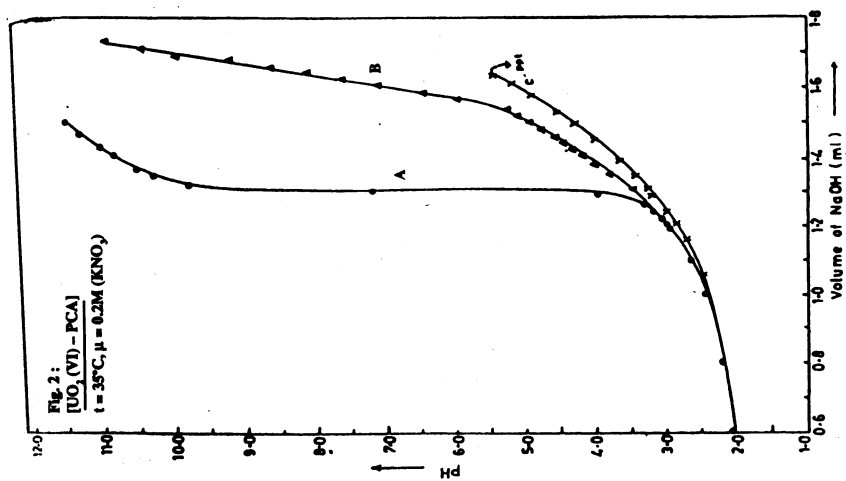
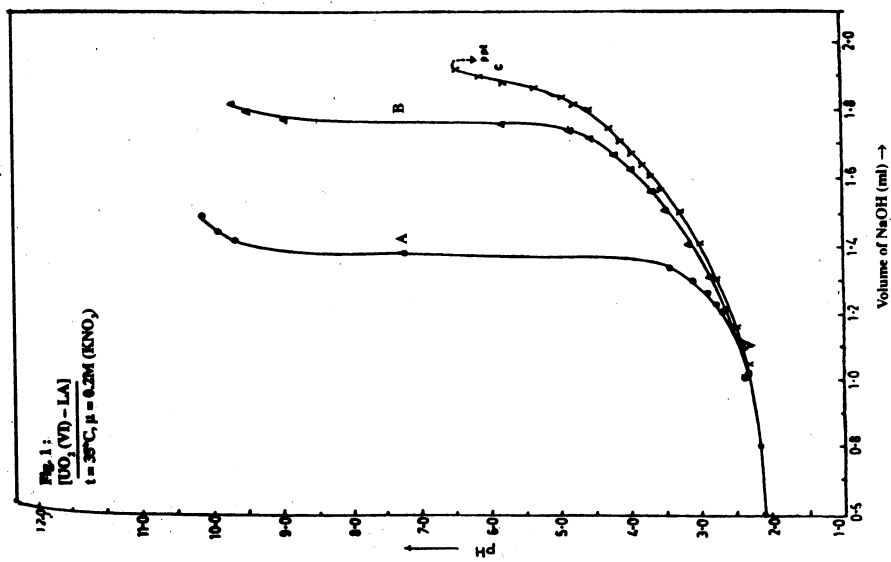
The experimental procedure for binary system was similar to one described earlier¹⁰ maintaining metal-ligand ratio to be 1 : 5, except that instead of perchloric acid, nitric acid was used in the present case. For mixed ligand system, the procedure was similar to the one described earlier^{6,7}.

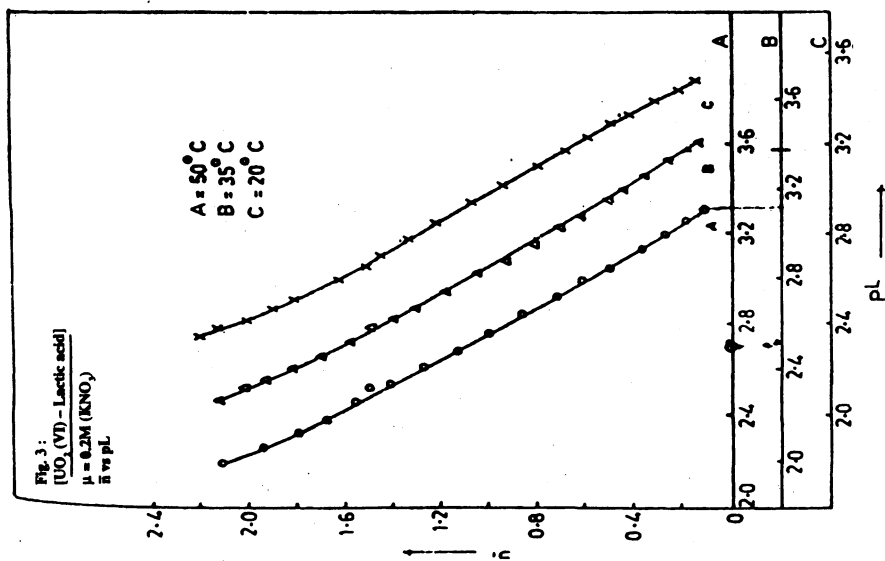
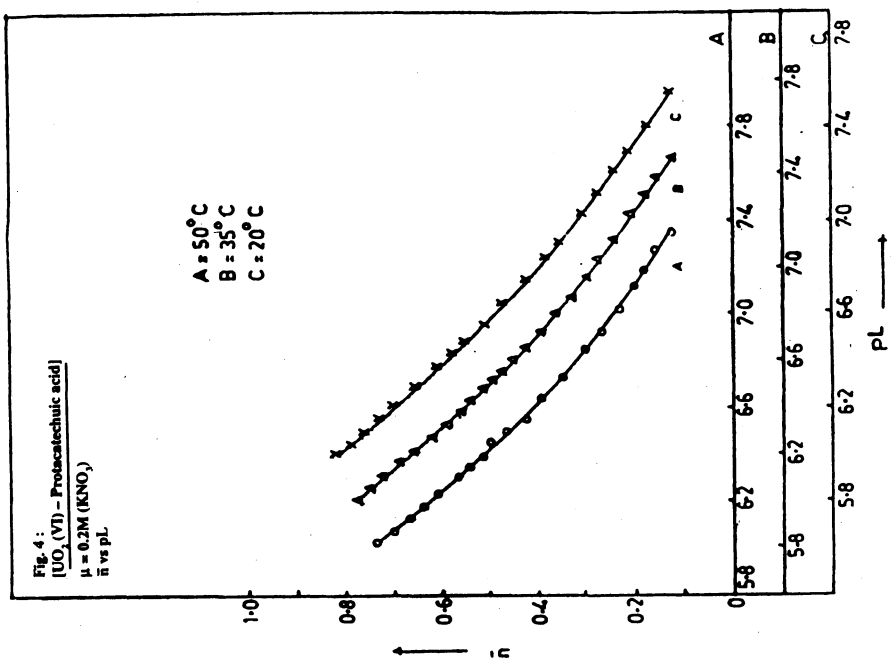
Irving-Rossotti's pH-titration technique¹¹ as modified by Bhattacharya and coworkers was used for calculating stability constants. Titrations were carried out at 20, 35 and 50°C and at ionic strength $\mu_0 = 0.2$ M (KNO_3). The representative curves are shown in Figs. 1 and 2. For studying the effect of dielectric constant of the medium, the titrations were performed in dioxane-water, methanol-water, and ethanol-water media containing 15, 30, 45 and 60% (v/v) dioxane, methanol or ethanol at 35°C and $\mu = 0.2$ M. The effect of change in ionic strength ($\mu = 0.1, 0.2, 0.3$ and 0.4 M) at 20, 35 and 50°C was also studied for the binary and ternary systems in aqueous medium only.

RESULTS AND DISCUSSION

The binary $[\text{UO}_2(\text{VI})\text{-NTA}]$ complex was formed at pH *ca.* 2.0 and the \bar{n} reached a value of unity at pH ≈ 3.0 . The \bar{n} value remained unaltered up to pH *ca.* 5.6 but increased at pH > 5.6 due to hydrolysis of the complex. The stability constant of $[\text{UO}_2(\text{VI})\text{-NTA}]$ 1 : 1 primary complex as determined at 35°C and $\mu = 0.2$ M (KNO_3) is 9.83. The value is in good agreement with the value reported before^{6,12}. In case of $[\text{UO}_2(\text{VI})\text{-LA}]$ system, the formation curves for metal-ligand stability constants at different temperatures drawn between \bar{n} and pL (Fig. 3) are found to be extended between 0 to 2.2 in \bar{n} scale, showing formation of 1 : 1 and 1 : 2 complex in stepwise manner. The precipitation was observed after pH 6.50. The formation curves (Fig. 4) for $[\text{UO}_2(\text{VI})\text{-PCA}]$ drawn between \bar{n} and pL, at different temperatures, do not extend beyond the \bar{n} value of 0.82, thus confirming formation of only one 1 : 1 complex. Precipitation was observed after pH 5.5.

In ternary complex, the secondary ligands do not participate till pH *ca.* 3.20 (LA) and pH *ca.* 2.80 (PCA). The \bar{n} value increases upto *ca.* 0.8 $[\text{UO}_2(\text{VI})\text{-NTA-LA}]$ and *ca.* 0.7 $[\text{UO}_2(\text{VI})\text{-NTA-PCA}]$, where the pL value systematically decreases and the pH of precipitation of primary complex is *ca.* 6.00, which is extended to *ca.* 6.40, where the mixed ligand complex hydrolyses. The proton-ligand and metal-ligand stability constants at three temperatures are incorporated in Table-1. The observed stabilities of binary and ternary complexes are in the sequence of $\text{NTA} > \text{PCA} > \text{LA}$ and $\text{PCA} > \text{LA}$, respectively. 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 $-\text{COO}^-$ present, and also due to conjugate double





bond. In LA the electron withdrawing $-\text{COOH}$ is involved in chelation due to which the complexes are less stable.

TABLE-1
PROTON-LIGAND, METAL-LIGAND STABILITY CONSTANT OF BINARY AND MIXED LIGAND COMPLEXES OF $\text{UO}_2(\text{VI})$ IN AQUEOUS MEDIUM AT DIFFERENT TEMPERATURES AND DIFFERENT IONIC STRENGTHS

Ligand/System (Charge omitted)	Constant	Temp ($^{\circ}\text{C}$)	Ionic strength			
			0.1	0.2	0.3	0.4
LA	$\log K_1^{\text{H}}$	20	3.96	3.94	3.90	3.80
		35	3.78	3.74	3.70	3.64
		50	3.60	3.56	3.56	3.50
	$\log K_1^{\text{H}}$	20	9.06	8.96	8.88	8.84
		35	8.96	8.86	8.78	8.74
		50	8.86	8.74	8.68	8.64
PCA	$\log K_2^{\text{H}}$	20	4.58	4.56	4.50	4.44
		35	4.48	4.38	4.26	4.24
		50	4.38	4.22	4.16	4.10
	$\log K_1$	20	3.42	3.28	3.10	3.04
		35	3.32	3.14	3.06	2.92
		50	3.22	3.04	2.96	2.80
[$\text{UO}_2(\text{VI})$ -LA]	$\log K_2$	20	2.80	2.60	2.44	2.38
		35	2.72	2.52	2.38	2.30
		50	2.66	2.46	2.30	2.26
[$\text{UO}_2(\text{VI})$ -PCA]	$\log K_1$	20	6.60	6.50	6.46	6.36
		35	6.50	6.46	6.40	6.20
		50	6.40	6.36	6.30	6.10
[$\text{UO}_2(\text{VI})$ -NTA-LA]	$\log K_{\text{LA}}^{\text{NTA}}$	20	3.25	3.15	3.12	3.08
		35	3.15	3.09	3.08	3.02
		50	3.10	3.05	3.02	3.98
[$\text{UO}_2(\text{VI})$ -NTA-PCA]	$\log K_{\text{PCA}}^{\text{NTA}}$	20	6.52	6.46	6.32	6.28
		35	6.30	6.26	6.24	6.22
		50	6.18	6.16	6.12	6.12

The proton-ligand and metal-ligand stability constants are considerably influenced by the dielectric constant and ionic strength of the medium because of the fact that at least one of the constituents is either charged or polar. The present

study on the effect of variation of dielectric constant and ionic strength of the medium on $\log K_n^H$ of secondary ligand (LA and PCA), $\log K_{ML}^M$ of binary complexes of $\text{UO}_2(\text{VI})$ with LA and PCA and $\log K_{MAL}^{MA}$ of the mixed ligand complexes of $\text{UO}_2(\text{VI})$ ion reveals that as dielectric constant of the medium decreases the $\log K_n^H$, $\log K_{ML}^M$ and $\log K_{MAL}^{MA}$ values increase, while these values decrease with increase in ionic strength of the medium. For these values, in different organic solvent-water media, the sequence was found to be:

dioxane-water > ethanol-water > methanol-water,

as shown in Table-2.

TABLE-2
PROTON-LIGAND, METAL-LIGAND STABILITY CONSTANTS IN
AQUEOUS-ORGANIC MIXTURES, TEMP. = 35°C, $\mu = 0.2 \text{ M}$

Ligand/System	Constant	Media	0%	15%	30%	45%	60%
LA	$\log K_1^H$	Dioxane-water	3.74	3.86	3.96	4.10	4.20
PCA	$\log K_1^H$		8.88	9.10	9.18	9.26	9.30
	$\log K_2^H$		4.38	4.46	4.48	4.52	4.55
LA	$\log K_1^H$	Ethanol-water	3.74	3.76	3.84	3.96	4.08
PCA	$\log K_1^H$		8.88	9.00	9.08	9.14	9.20
	$\log K_2^H$		4.38	4.40	4.44	4.50	4.54
LA	$\log K_1^H$	Methanol-water	3.74	3.74	3.76	3.84	3.92
PCA	$\log K_1^H$		8.88	8.90	8.96	9.00	9.10
	$\log K_2^H$		4.38	4.36	4.42	4.44	4.50
[$\text{UO}_2(\text{VI})$ -LA]	$\log K_1$	Dioxane-water	3.14	3.44	3.54	3.60	3.74
	$\log K_2$		2.52	2.70	2.86	2.98	3.20
[$\text{UO}_2(\text{VI})$ -PCA]	$\log K$		6.46	7.48	7.56	7.68	7.80
[$\text{UO}_2(\text{VI})$ -LA]	$\log K_1$	Ethanol-water	3.14	3.16	3.20	3.28	3.40
	$\log K_2$		2.52	2.60	2.68	2.74	2.80
[$\text{UO}_2(\text{VI})$ -PCA]	$\log K$		6.46	7.09	7.20	7.40	7.64
[$\text{UO}_2(\text{VI})$ -LA]	$\log K_1$	Methanol-water	3.14	3.16	3.18	3.22	3.30
	$\log K_2$		2.52	2.55	2.58	2.64	2.70
[$\text{UO}_2(\text{VI})$ -PCA]	$\log K$		6.46	6.80	7.00	7.20	7.50
[$\text{UO}_2(\text{VI})$ -NTA-LA]	$\log K_{LA}^{NTA}$	Dioxane-water	3.09	3.80	4.00	4.10	4.26
[$\text{UO}_2(\text{VI})$ -NTA-PCA]	$\log K_{PCA}^{NTA}$		6.26	6.46	6.60	6.70	6.80
[$\text{UO}_2(\text{VI})$ -NTA-LA]	$\log K_{LA}^{NTA}$		3.09	3.22	3.32	3.40	3.50
[$\text{UO}_2(\text{VI})$ -NTA-PCA]	$\log K_{PCA}^{NTA}$	Ethanol-water	6.26	6.38	6.58	6.60	6.70
[$\text{UO}_2(\text{VI})$ -NTA-LA]	$\log K_{LA}^{NTA}$		3.09	3.12	3.24	3.34	3.44
[$\text{UO}_2(\text{VI})$ -NTA-PCA]	$\log K_{PCA}^{NTA}$	Methanol-water	6.26	6.30	6.40	6.48	6.60

Error Limit: $\log K_1^H = \pm 0.03$, $\log K_2^H = \pm 0.05$

$\log K_{MA}^M$ and $\log K_{MAL}^M = \pm 0.07$

The plots of $\log K$ vs. $1/D$ (D , dielectric constant) were non-linear while those of $\log K$ vs. mole fraction of solvents in the medium were linear over the entire

range, for all systems. Hence, it may be concluded that the ion-ion interaction, involving metal ion and anionic oxygen donor of the ligand, increases to a greater extent, as compared to the ion-dipole interaction between the metal and solvent molecules, as the dipole moment and so the dielectric constant of the medium decreases¹¹.

Conclusion

In the ternary systems reported, it is assumed that due to high stability of primary complex, which is formed at lower pH region, metal ion and primary ligand (NTA) are present in the form of 1 : 1 chelate, at the beginning of the ternary complex formation. Hence, there is addition of secondary bidentate ligand (LA/PCA) to primary complex to form a mixed ligand chelate. The stability constants of binary and mixed ligand complexes are in the trend of PCA > LA. This order is evidently due to higher basicity of PCA. The coordination number of uranium atom is expanded from six to eight in all NTA complexes.

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