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pH Metric Studies on the Mixed Ligand Complexes of Ruthenium(III) with DL-2-Amino-3-Hydroxy Butanoic Acid and Nitrilotriacetic Acid in Aqueous Media

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The stability constants of the mixed ligand complexes of ruthenium(III) with DL-2-amino-3-hydroxy butanoic acid (DL-threonine) as secondary ligand and nitrilotriacetic acid (NTA) as primary ligand have been determined by employing well known Irving- Rossotti method as modified by Chidambaram and Bhattacharya under varying conditions of temperature and ionic strength. It has also been found that values of stability constants for Ru(III)-DL-2-amino-3-hydroxy butanoic acid-nitrilotriacetic acid mixed ligand metal complex is significantly less as compared to the first formation constant value for Ru(III)-DL-2-amino-3-hydroxy butanoic acid binary metal complex which has been explained on the basis of factors involving properties like coulombic interaction between various ligand anion species present and steric hindrance caused by the bulky NTA molecule. Thermodynamic parameters have also been evaluated.

INTRODUCTION

The study of mixed ligand complexes involving biologically important ligands is useful in explaining many biochemical reactions as many metalloenzyme reactions have been shown to involve the formation of ternary complexes.[1–5] The stability constants and structures of such ternary complexes are of interest for understanding the role of metal and nature of two ligands in determining the stability of ternary complexes.[6]

The literature survey reveals few references[7, 8] on the mixed ligand complexes on metal-amino acid-nitrolotriacetic acid. It was therefore considered of interest to undertake a systematic study on the mixed ligand metal complexes of Ru(III) DL-threonine and NTA under varying conditions of temperature of 20°, 30° and 40°C and ionic strength of 0.1 M, 0.2 M, 0.5 M and 1.0 M KNO_3 employing Irving-Rossotti method as modified by Chidambaram and Bhattacharya.[7] The thermodynamic parameters have also been evaluated at 20°C in aqueous media. NTA forms stable complexes with metal ions at low pH which are stable even at higher pH; therefore, NTA is commonly used as a primary ligand in the study of a variety of ternary complexes.[9–12]

EXPERIMENTAL

$RuCl_3$ was supplied by Johnson Mathey Co. Ltd., London. DL-Threonine was supplied by E. Merck India Pvt. Ltd. NTA was supplied by BDH. All other chemicals used were of AnalaR grade. Double distilled conductivity water was used for carrying out the studies. The pH measurements were made on EC digital pH meter (accuracy ± 0.01 pH) using combined glass-calomel electrode assembly. The temperature of the cell was maintained constant by thermostat.

The experimental procedure involves the titration of following solutions:

(A) $HClO_4$ M [0.05 M]
(B) A + NTA [2 mM]
(C) B + Ru(III) [2 mM]
(D) A + DL-threonine [2 mM]
(E) C + DL-threonine [2 mM]

against standard 0.5 M NaOH and pH of solution was measured. The formation function n and pL_{MAL} were calculated as usual using standard equation[13, 14]. $\bar{n}$ Values were plotted against pL_{MAL} values to get the formation curves for metal complexation equilibria and log K_{MAL} value *i.e.* the formation constant was evaluated which corresponds to pL_{MAL} value at $\bar{n}_{MAL} = 0.5$.

RESULTS AND DISCUSSIONS

The values of the formation constants for the mixed ligand complexes of Ru(III)-NTA-DL-threonine at varying temperatures and ionic strengths have been recorded in Table-1.

TABLE-1
log K_{MAL} VALUE FOR Ru(III)-NTA DL-THREONINE SYSTEM IN AQUEOUS MEDIA AT VARYING TEMPERATURES AND IONIC STRENGTHS

Stability constant	Temperature (μ = 0.1M)			
	20°C	30°C	40°C	
log K_{MAL}	12.0	12.4	12.7	
	Ionic strengths (Temperature = 20°C)			
	0.1 M	0.2 M	0.5 M	1.0 M
log K_{MAL}	12.0	12.4	12.8	13.2

It is evident from the plots of pH values against volume of alkali for acid curve (A), primary ligand curve (B), secondary ligand curve (D), primary complex curve (C) and ternary complex curve (E) [Fig. 1] that metal-NTA complex formation takes place at pH ≤ 2 which is in agreement with the fact that NTA generally combines with metal ions at low pH and forms very stable complexes which do not undergo dissociation even at higher pH[9]. Primary complex curve (C) and ternary complex curve (E), however, overlap at pH *ca.* 2.5 which indicates that DL-threonine does not combine with metal ion in this pH range where

primary complexation takes place; however, curve (E) diverges from curve (C) around pH *ca.* 3.0 suggesting the co-ordination of DL-threonine primary complex does not occur at higher pH.

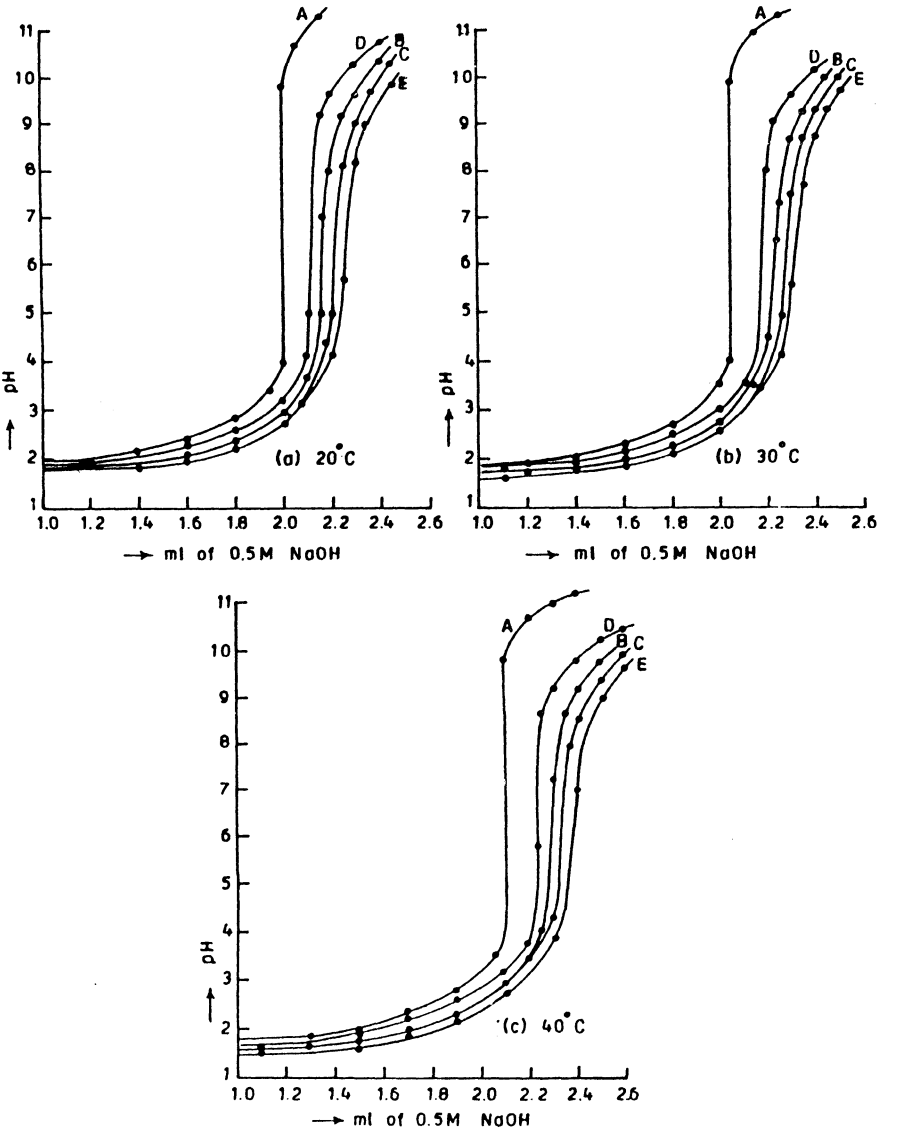

Fig. 1A. Titration curves for Ru (III)-NTA-DL-threonine system at varying temperatures.

It may be mentioned that DL-threonine combines with the species M(III)-NTA just as it does with $[M(aq)]^{3+}$ in simple systems. As such the horizontal distance between the curves D and E can be used for the calculation of $\bar{n}_{MAL}$, the average number of DL-threonine molecules associated with [M(III)-NTA], using the equation derived by Irving-Rossotti. $\bar{n}_{MAL}$ and pL_{MAL} values were calculated at

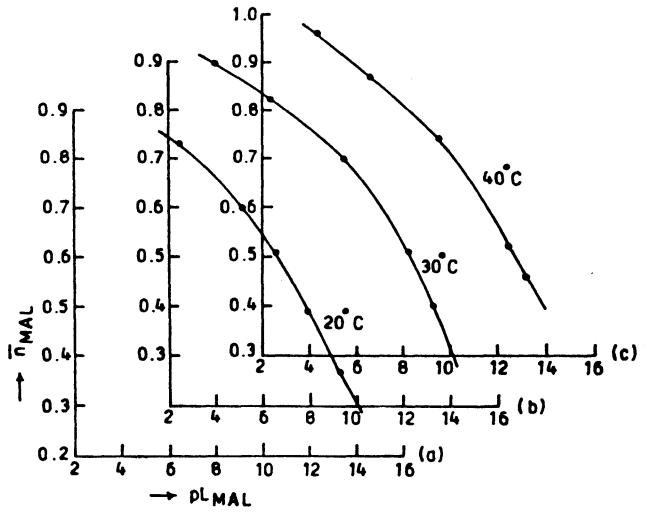

Fig. 1B. Formation curves for Ru(III)-NTA-DL-threonine at varying temperatures

different points in the pH range 3.0–7.0 and at $\bar{n}_{MAL}$ values = 0.5 in the formation curves (Fig. 1) $pL_{MAL} = \log K_{MAL}$.

It is noteworthy that the value of log K_{MAL} (Table-1) is significantly less than log K_{ML1} *i.e.* first step formation constant of simple Ru(III)-DL-threonine system but greater than log K_{ML2} and log K_{ML3} values of simple Ru(III)-DL-threonine system (Table-2). The formation constants for simple binary Ru(III)-DL-threonine system have also been determined under similar experimental conditions and the values have been recorded in Table-2.

TABLE-2
log K_{ML1}, log K_{ML2} AND log K_{ML3} VALUES OF Ru(III)-DL-THREONINE SYSTEM IN AQUEOUS MEDIA AT VARYING TEMPERATURES AND IONIC STRENGTHS

log K_{MLn}	Temperature (μ = 0.1M)		
	20°C	30°C	40°C
log K_{ML1}	13.3	13.7	14.1
log K_{ML2}	7.0	7.5	7.9
log K_{ML3}	3.0	3.1	3.2
log K_{MLn}	Ionic strength (Temperature = 20°C)		
	0.1 M	0.2 M	0.5 M	1.0 M
log K_{ML1}	13.3	13.9	14.4	14.8
log K_{ML2}	7.0	7.4	7.6	7.8
log K_{ML3}	3.0	3.0	3.0	3.0

The lower value of log K_{MAL} as compared to log K_{ML} can be explained on the basis of coulombic interaction between various ligand anion species present. In the mixed ligand complex formation there is a repulsion between two negative charges from the NTA anion. The repulsion would obviously be more than in simple $[M(aq)]^{3+}$ species where there is no such interaction resulting in log K_{ML1} > log K_{MAL}.

Besides this, the steric hindrance caused by the bulky NTA molecule accounts for the lower stability of ternary metal NTA complexes and the stereochemical effects are more significant than electrostatic repulsion. This accounts for the lower value of log K_{MAL} as compared to log k_{ML_1} value for the simple Ru(III)-DL-threonine binary system.

Effect of Temperature and Ionic Strength

The log K_{MAL} values increase with rise in temperature as evident from the results recorded in Table-1, which shows that higher temperature favours the complex formation. Similarly values of formation constants increase with increase in ionic strength from 0.1 M to 1.0 M KNO_3 as evident from the results recorded in Table-1. Linear plots were observed on plotting log K_{MAL} values against 1/T.[15] log K_{MAL} values were plotted against ionic strengths which on extrapolation to zero ionic strength gives the thermodynamic formation constants. The values have been recorded in Table-2 as log K_{MAL} ($\mu \rightarrow 0$).

Thermodynamic Parameters

The values of free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) changes accompanying complexation reaction have been determined at 20°C with the help of standard equations[16] and the values have been recorded in Table-3.

TABLE -3
VALUE OF THERMODYNAMIC FUNCTIONS IN AQUEOUS MEDIA AT 20°C

Stability constants	$\Delta G°$ kcals/mole	$\Delta H°$ kcals/mole	$\Delta S°$ cal/deg/mole
log K_{MAL} ($\mu \rightarrow 0$) = 11.75	16.09	14.71	105.11

The negative value of $\Delta G°$ shows that the reaction tends to proceed spontaneously. The positive ΔH values indicate the endothermic nature of the reaction suggesting that higher temperature favours the complexation process in fair agreement to increasing stability with temperature. It may be seen that values of $\Delta S°$ are positive which strongly favour the complex formation.

REFERENCES

1. P.S. Hallman, D.D. Perrin and A.G. Waat, *J. Biochem.*, **121**, 549 (1970).
2. A.S. Mildran and M. Cohn, *Ad. Enzymenol.*, **1**, 33 (1970).
3. D.D. Perrin, *Soumen Kemistilehti*, **42**, 205 (1969).

4. H. Sigel and D.B. McCormic, *Acc. Chem. Res.*, **3**, 201 (1970).
5. H.L. Vallcu and Walker, in H. Neurath (Ed.), Protein Consumption Structure and Function. Academic Press, New York, Vol. 15 (1966).
6. P.K. Bhattacharya and V. Manjula, *Indian J. Chem.*, **29A**, 400 (1990).
7. M.V. Chidambaram and P.K. Bhattacharya, *Acta Chem. Acad. Sci. Hungary*, **75**,123 (1973).
8. P.C. Parikh and P.K. Bhattacharya, *Bull. Acad. Pol. Sci.*, **23**, 289 (1975).
9. A.E. Martell and G.H. Carey, *J. Am. Chem. Soc.*, **83**, 4699 (1961); **89**, 2859 (1967).
10. T. Lagrange and P. Lagrange, *Bull. Soc. Chim. Fr.*, **718**, 1455 (1975).
11. D. Hopgood and R.L. Angelici, *J. Am. Chem. Soc.*, **90**, 2508 (1968).
12. Y.J. Israeli, *Canad. J. Chem.*, **4**, 2710 (1963).
13. M.Y. Chidambaram and P.K. Bhattacharya, *J. Inorg. Nucl. Chem.*, **32**, 327 (1970); *Indian J. Chem.*, **9**, 1294 (1971); *J. Inst. Chem. (India)*, **44**, 144 (1972).
14. H. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1954); 3397 (1953).
15. K.S. Pitzer, *J. Am. Chem. Soc.*, **59**, 2365 (1937).
16. K.B. Yatsimirskii and V.P. Vasilev, Instability Constants of Complex Compounds, Pergamon Press, Oxford, p. 63 (1960).

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