

Potentiometric Studies of the Complexes of Pr(III) with Ethylenediaminetetraacetic Acid as Primary Ligand & Pyrogallol, Pyrocatechol, Protocatechuic Acid & Protocatechualdehyde as Secondary Ligands

T. H. MHASKE & K. N. MUNSHI

Department of Chemistry, Nagpur University Campus, Nagpur

Received 15 February 1975; accepted 11 August 1975

Binary and ternary complex formation constants K_{ML} and K_{MAL} respectively, where $M = Pr^{3+}$, $A =$ ethylenediaminetetraacetic acid and $L =$ pyrogallol, pyrocatechol, protocatechuic acid or protocatechualdehyde, have been determined at 25°, 35° and 45° and $\mu = 0.2M$ using a modified form of Irving-Rossotti technique. The 1:1:1 [Pr(III)-(EDTA)-(L)] chelates are less stable than the 1:1 [Pr(III)-L] chelates. The overall changes in ΔG , ΔH and ΔS have also been evaluated.

THE formation constants (K_{MAL}) of mixed ligand complexes (MAL) where $M = Pr^{3+}$, $A =$ ethylenediaminetetraacetic acid (EDTA), and $L =$ pyrogallol (PGL), pyrocatechol (PYC), protocatechuic acid (PCA) or protocatechualdehyde (PCAD) have been determined using pH titration technique of Irving-Rossotti¹. For comparison with K_{MAL} , the K_{ML} values have also been evaluated.

Materials and Methods

A stock solution (0.02M) of $PrCl_3 \cdot 7H_2O$ (Indian Rare Earths Ltd) was prepared in a calculated, quantity of perchloric acid and estimated spectrophotometrically². A stock solution of 0.01M EDTA (Analar, BDH) was prepared in doubly distilled water and standardized³. The stock solutions of 0.01M of PGL (Baker), PYC (Riedel) and PCA (Fluka AG) were prepared by dissolving requisite quantities in doubly distilled water. Stock solution of 0.01M PCAD (Fluka) was prepared in purified dioxan (50%, v/v) by direct weighing. Precaution was taken to avoid the oxidation of the secondary ligand solutions. All solid samples were further purified and dissolved in doubly distilled water presaturated with oxygen-free nitrogen. All the experiments were performed under atmosphere of nitrogen within 3 hr of the preparation of the solution. All these solutions were standardized potentiometrically.

Carbonate-free 1M sodium hydroxide (E. Merck) solution was prepared and standardised potentiometrically against potassium hydrogen phthalate. Sodium perchlorate (neutral) and perchloric acid was prepared by dissolving their analar samples, in doubly distilled water.

A pH-meter (Beckman H-2) with a glass-calomel electrode assembly was used. The SCE was connected to the cell externally by means of an agar-agar bridge saturated with KNO_3 , to prevent the formation of chloro complexes.

Procedure — For the calculations of K_{ML} values following solutions (total 100 ml) were prepared and

titrated: (i) $5.0 \times 10^{-3}M$ $HClO_4$, (ii) $5.0 \times 10^{-3}M$ $HClO_4 + 5.0 \times 10^{-3}M$ ligand solution, and (iii) $5.0 \times 10^{-3}M$ $HClO_4 + 5.0 \times 10^{-3}M$ ligand solution + $1.0 \times 10^{-3}M$ Pr^{3+} solution. For the study of mixed ligand complexes following solutions (total vol. 100 ml) were prepared and titrated: (iv) $1.0 \times 10^{-2}M$ $HClO_4$, (v) $1.0 \times 10^{-2}M$ $HClO_4 + 2.0 \times 10^{-3}M$ secondary ligand, (vi) $1.0 \times 10^{-2}M$ $HClO_4 + 2.0 \times 10^{-3}M$ EDTA + $2.0 \times 10^{-3}M$ Pr^{3+} solution and (vii) $1.0 \times 10^{-2}M$ $HClO_4 + 2.0 \times 10^{-3}M$ EDTA + $2.0 \times 10^{-3}M$ Pr^{3+} solution + $2.0 \times 10^{-3}M$ secondary ligand.

The ionic strength was maintained at $\mu = 0.2M$ by adding appropriate amount of $NaClO_4$. In the case of PCAD 50% v/v aqueous dioxan media was maintained. In each case for K_{MAL} the ratio between Pr^{3+} , EDTA and secondary ligand (L) was kept 1:1:1. Titrations with NaOH (1.063M) were carried out under nitrogen atmosphere at 25°, 35° and 45°.

Results and Discussion

Proton-ligand stability constants — The values of practical proton-ligand stability constants of secondary ligands have been evaluated at three different temperatures (Table 1). These values of protonation constants have been used for the calculation of the formation constants of binary and ternary complexes.

Metal-ligand stability constants (K_{ML}) — The formation constants K_{ML} have been obtained at different temperatures by plotting \bar{n} against pL using the method of Irving-Rossotti¹. Typical plots for Pr^{3+} — PGL system are given in Fig. 1. Only $\log K_1$ values could be obtained under the present conditions of study and values are given in Table 1.

Stability constants (K_{MAL}) of mixed ligand complexes — The titration curve for the system (iii) shows that primary complex formation starts at very low pH. The value of \bar{n} obtained shows that the formation of 1:1 complex between Pr(III) and EDTA is complete by pH 4. Beyond this pH and up to pH

TABLE 1 — PROTON-LIGAND STABILITY CONSTANTS OF SECONDARY LIGAND AND STABILITY CONSTANTS FOR THE BINARY AND TERNARY SYSTEMS AT $\mu = 0.2M$ (NaClO_4)

System	Stability constant	Values at		
		25°C	35°C	45°C
H-PGL	$\log K_1^H$	10.72	10.60	10.42
	$\log K_2^H$	8.70	8.63	8.51
H-PYC	$\log K_1^H$	11.78	11.31	10.96
	$\log K_2^H$	9.27	9.03	8.73
H-PCA	$\log K_1^H$	8.62	8.48	8.34
	$\log K_2^H$	4.32	4.28	4.22
*H-PCAD	$\log K_1^H$	11.74	11.64	11.48
	$\log K_2^H$	8.58	8.42	8.28
Pr(III)-PYC	$\log K_{ML}$	8.72	8.47	8.21
Pr(III)-PGL	$\log K_{ML}$	9.78	9.64	9.53
Pr(III)-PCA	$\log K_{ML}$	5.74	5.56	5.32
*Pr(III)-PCAD	$\log K_{ML}$	9.39	9.34	9.28
Pr(III)-(EDTA)(PYC)	$\log K_{MAL}$	5.26	4.93	4.84
Pr(III)-(EDTA)(PGL)	$\log K_{MAL}$	4.27	4.53	4.62
Pr(III)-(EDTA)(PCA)	$\log K_{MAL}$	3.40	3.22	3.06
*Pr(III)-(EDTA)(PCAD)	$\log K_{MAL}$	5.18	5.06	4.98

*Experiments in 50% dioxan.

 TABLE 2 — THERMODYNAMIC PARAMETERS OF BINARY AND TERNARY SYSTEMS AT $\mu = 0.2M$ (NaClO_4)

System	ΔG	ΔH	ΔS
	kcal/mole	kcal/mole	cal deg ⁻¹ mole ⁻¹
Pr(III)-(PYC)	-11.94	-10.22	+5.6
Pr(III)-(PGL)	-13.59	-5.76	+27.4
Pr(III)-(PCA)	-7.85	-9.15	-4.3
*Pr(III)-(PCAD)	-13.10	-3.22	+35.5
Pr(III)-(EDTA)(PYC)	-7.05	-8.99	-6.30
Pr(III)-(EDTA)(PGL)	-6.29	+7.56	+45.00
Pr(III)-(EDTA)(PCA)	-4.41	-7.31	-9.0
*Pr(III)-(EDTA)(PCAD)	-7.12	-4.37	+8.9

*Experiments in 50% dioxan.

10.5 hydrolysis of the complex is not observed. The formation of the ternary complex, i.e. the attachment of the secondary ligand to the primary complex species, $[\text{Pr(III)-EDTA}]$ starts after pH 4 for PGL, PYC and PCAD. However for PCA, self dissociation of the primary complex starts even before it attaches to the primary complex species.

Since the dissociation of $[\text{Pr(III)-(EDTA)}]^-$ primary complex does not take place in the range of dissociation of the secondary ligands, it can be considered that the secondary ligands combine with $[\text{Pr(III)-(EDTA)}]^-$ just as it does with $[(M-aq)]^{3+}$ in binary systems and the formation of $[\text{Pr(III)-(EDTA)-(OH)}_n]$ is suppressed. \bar{n} , the average number of phenolic ligands bound per $[\text{Pr(III)-(EDTA)}]^-$ can be calculated from Eq. (1).

$$\bar{n} = \frac{(N+E^{\circ})(V_3-V_2)}{(V^{\circ}+V_1)\bar{n}_A T^{\circ}_{CM}} \quad \dots(1)$$

where, V_2 = horizontal distance between curves A and B, V_3 = horizontal distance between curves C and D, V° = initial volume of the titration solution

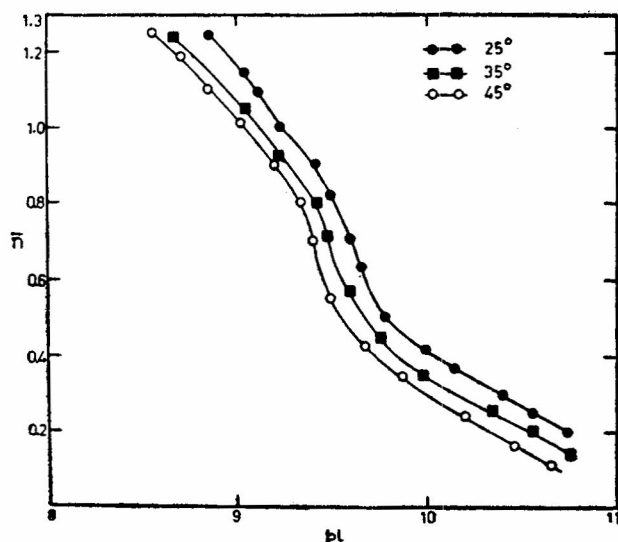


Fig. 1 — Formation curves of $[\text{Pr(III)-(PGL)}]$ at three different temperatures and at $\mu = 0.2M$

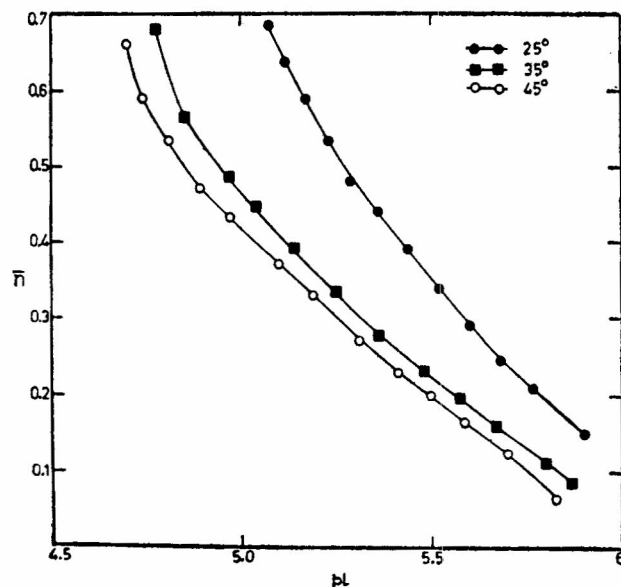


Fig. 2 — Formation curves of $[\text{Pr(III)-(EDTA)-(PYC)}]$ at three different temperatures at $\mu = 0.2M$

V_1 = volume of alkali consumed in the titration of mixture (A) and T°_{CM} = concentration of $[\text{Pr(III)-(EDTA)}]^-$ complex or $[\text{Pr(III)}]$. \bar{n} and pL were calculated at different pH . At $\bar{n} = 0.5$ in the formation curve, $pL = \log K_{MAL}$. Typical plots for \bar{n} against pL for $[\text{Pr(III)-(EDTA)-(PYC)}]$ system at different temperatures are shown in Fig. 2. The values of $\log K_{MAL}$ calculated from the formation curves are given in Table 1.

Thermodynamic parameters — From the overall changes in the energy (ΔG) at three temperatures the enthalpy (ΔH), and entropy (ΔS) changes for binary and ternary complex formation have been calculated at $\mu = 0.2M$ (NaClO_4) using temperature coefficients and Gibbs-Helmholtz equation⁴ (Table 2).

According to Bhattacharya and coworkers⁵, complexation of Pr³⁺ with all these ligands takes place through two *ortho*-hydroxy groups. However the present study reveals that during complexation two protons are liberated from two *ortho*-phenolic groups in the case of PYC and PCAD but in the case of PCA the second phenolic proton and in PGL the third phenolic proton are not liberated during complexation. Sogani and coworkers⁶ have also shown from potentiometric and IR studies that only one proton is replaced during complexation by metal ion forming covalent bond and the oxygen of other phenolic group acts as a co-ordinating atom.

An observation of the K_{ML} values indicate that the order of formation constants of Pr(III) complexes with different ligands is PGL > PYC > PCA which is further supported by the thermodynamic data given in Table 2.

The tendency of [Pr(aq)_n]³⁺ to receive the secondary ligands is more than that of [Pr(III)-(EDTA)]⁻ and hence the value of log K_{MAL} is significantly lower than log K_{ML} . The [Pr(III)-(EDTA)]⁻ species where EDTA acts as a hexadentate ligand has large stability^{7,8} and hence ligand exchange is eliminated. The larger size of the Pr(III) should allow sufficient room for the secondary ligand molecule to become attached to [Pr(III)-(EDTA)]⁻ species⁹⁻¹³. These secondary ligands form 5-membered rings through two phenoxide ions. If the coordination number of Pr(III) is higher than six, secondary ligands with two phenolic hydroxyl groups would displace the coordinated water molecules on seventh and eighth sites of the [Pr(III)-(EDTA)]⁻ chelate. Thus these mixed ligand chelates

do not hydrolyse even at higher pH values. The order of stability constant for the ternary systems with respect to secondary ligand is PYC > PGL > PCA. This can also be explained on the basis of ΔH and ΔS values recorded in Table 2.

Acknowledgement

We thank Prof R. H. Sahasrabudhey, Head, Chemistry Department, Nagpur University, Nagpur, for providing necessary research facilities.

References

1. IRVING, H. M. & ROSSOTTI, H. S., *J. chem. Soc.*, (1954), 2904.
2. MUNSHI, K. N. & DEY, A. K., *Microchem. J.*, **8** (1964), 152.
3. VOGEL, A. I., *Quantitative inorganic analysis* (Longmans, Green, London), (1961), 433.
4. YATISIMIRSKI, K. B. & VASIL'EV, V. P., *Instability constants of complex compounds* (Pergamon Press, London), (1960).
5. MAVANI, P., JEJURKAR, C. R. & BHATTACHARYA, P. K., *J. Indian chem. Soc.*, **49** (1972), 469.
6. AGRAWAL, M. D., BHANDARI, C. S. & SOGANI, N. C., *Bull. Acad. pol. Sci. Ser. Sci. chim.*, **21** (1973), 917.
7. SCHWARZENBACH, G., GUT, R. & ANDREGG, G., *Helv. chim. Acta*, **37** (1954), 937.
8. BETTS, R. H. & DAHLINGER, O. F., *Can. J. Chem.*, **37** (1959), 91.
9. THOMPSON, L. C. & LORAAS, J. A., *Inorg. Chem.*, **2** (1963), 89.
10. AFGHAN, B. K. & ISRAELI, J., *Talanta*, **16** (1969), 1605.
11. CARRY, G. H. & MARTELL, A. E., *J. Am. chem. Soc.*, **89** (1967), 2859.
12. OZER, U. Y., *J. inorg. nucl. Chem.*, **32** (1970), 1279.
13. HOARD, H. L., LIND, M. & SILVERTON, J. V., *J. Am. chem. Soc.*, **83** (1961), 2770.