

Studies in Stability Constant of Lanthanum(III) and Samarium(III) Complexes with Valine in Non-Aqueous Medium

M.M. SUVARNA*, V.S. PANSE, U.P. FULWADVA and (Late) P.K. JADHAV
*Department of Physical Chemistry, Institute of Science,
Madam Cama Road, Bombay-400 032, India*

Formation constants of lanthanum(III) and samarium(III) with L-valine have been determined pH-metrically using Irving-Rossotti titration technique adopted by Calvin and Bjerrum using various solvent systems at $28 \pm 0.1^\circ\text{C}$. The results are discussed in terms of effect of dielectric constant and mol fraction of solvent on proton-ligand stability constants and formation constants.

INTRODUCTION

Studies on amino acids have achieved great importance because of their practical significance in physiological and analytical chemistry. A survey of literature shows that not much work has been reported with valine complexes of rare earths in various solvent media. Hence it was proposed to undertake these studies so as to have useful information regarding the effect of dielectric constant on the stability constants of the valine complexes of lanthanum(III) and samarium(III).

EXPERIMENTAL

All chemicals were of A.R. grade. Solvents used were of L.R. grade and were purified¹. Valine was estimated by using Sorensen-Formol technique². Metal(III) nitrate solutions were prepared from the oxides and standardised against 0.05 M EDTA using xylenol yellow indicator. Ionic strength was maintained using 0.05 M KCl solution. A systronic digital pH meter model 335 was used for measurement of pH. The combined single electrode supplied with the instrument was used. It was standardised by making use of buffers of pH 4.01, 7.01 and 9.18. Calvin-Bjerrum^{3,4} technique as adopted by Irving and Rossotti⁵ is used. The titration were carried out in a double jacketed 150 mL closed cell. The temperature of the cell was controlled with the help of thermostat at $28 \pm 0.1^\circ\text{C}$.

The following titrations were carried out against carbonate-free NaOH solution:

1. 0.049 M HCl.
2. 0.049 M HCl + 0.048 M ligand.
3. 0.049 M HCl + 0.048 M ligand + 0.047 M metal nitrate.

SOLVENT COMPOSITION

Water	100	80	60	40	30
Methanol	0	20	40	60	70
Ethanol	0	20	40	60	70
Isopropanol	0	20	40	60	70

A graph of pH-metre reading, B vs V, the volume of alkali added is shown in Fig. 1

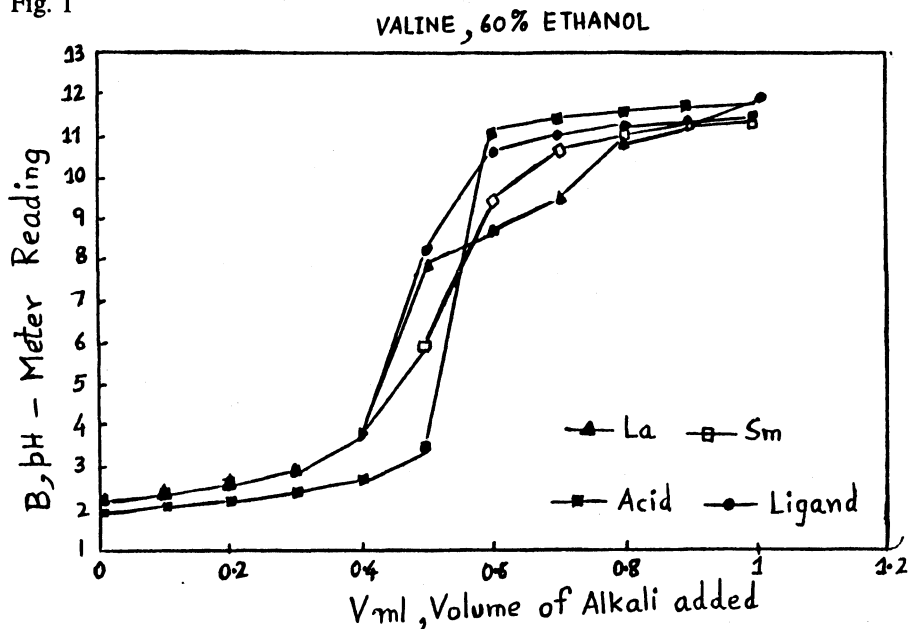


Fig. 1. Plot of pH-metre reading versus volume of alkali

RESULTS AND DISCUSSION

Proton-ligand stability constants and formation functions were calculated using \bar{n} method and least squares method. Calculations were performed on an IBM PC AT 286 computer using Lotus 1-2-3.

RANGE OF \bar{n}_A

Composition % v/v solvent	20	40	60	70
Methanol	0.507-1.465	0.538-1.373	0.692-1.681	0.555-1.217
Ethanol	0.107-1.958	0.230-1.896	0.540-1.987	0.386-1.926
Isopropanol	0.169-1.988	0.569-1.864	0.198-1.927	0.075-1.926

\bar{n}_A values for different solvent compositions under investigation ranged from 0 to 2 in all the cases except methanol where it ranged from 0 to 1. It indicated

the formation of proton-ligand stability complexes in the ratio of 1:2 in ethanol and isopropanol and 1:1 in methanol.

TABLE-1
EFFECT OF DIELECTRIC CONSTANT ON PROTON
LIGAND STABILITY CONSTANT

Solvent	% (v/v)	ϵ	$\log \beta_1$	$\log \beta_2$
Water	100	76.75	6.554	9.185
Ethanol	20	72.95	10.218	14.444
Ethanol	40	67.69	7.763	11.500
Ethanol	60	59.94	7.608	11.601
Ethanol	70	54.50	8.178	12.505
Isopropanol	20	73.48	8.673	13.192
Isopropanol	40	68.76	7.876	11.444
Isopropanol	60	61.36	6.943	11.213
Isopropanol	70	55.84	7.971	12.027

In mixed aqueous solvents proton-ligand stability constants are dependent on solvent characteristics *e.g.* dielectric constant ϵ of the media. If water is partially replaced by organic solvents the dielectric constant would decrease with increase in protonation of organic solvent and thus resulting in the increase in proton-ligand stability constants as seen in Table-1.

Effect of Mol Fraction: The graphs of overall proton-ligand stability constants versus mol fraction of solvents were plotted. one of the graphs is shown in Fig. 2. The graph shows a U-shaped curve in all the cases with a minima mol

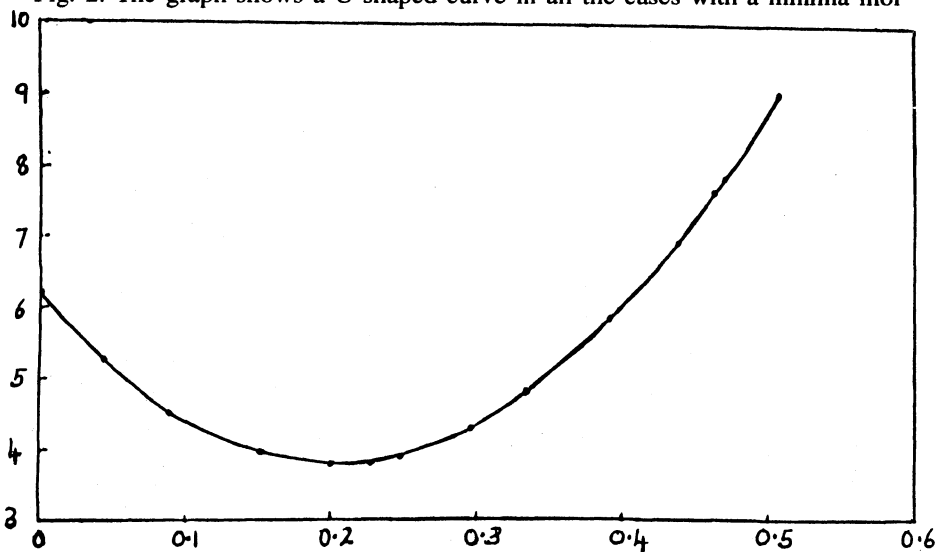


Fig. 2. Plot of proton-ligand stability constant versus molfraction of methanol

fraction of the solvent. It should be noted that the minima occur in the range of 0.2 to 0.3 *i.e.* in the range of water-solvent ratio from 2.5 to 3.5. It is known that when a solvent is added to water, the 3-dimensional hydrogen-bond network of water breaks down. Although the alcohols show a tendency to form hydrogen bonding, it decreases from water to the higher homologues of alcohols. It is possible that maximum solvent-solvent interaction takes place at this stage where a minima is observed in the proton-ligand stability values.

In general it is seen that the stability of the complexes increases with decrease in dielectric constant of the ligand; thus there is a general increasing trend in metal-ligand stability constant with increasing percentage of organic solvent, as seen in Table-2.

TABLE-2
METAL-LIGAND STABILITY CONSTANTS OF LANTHANUM(III)
AND SAMARIUM(III) COMPLEXES

Solvent % (v/v.)	ϵ	$\log \beta_1$	$\log \beta_2$
Lanthanum(III) Complexes			
Water	76.750	7.844	14.493
20% Methanol	72.250	4.301	7.304
40% Methanol	66.460	4.478	7.801
20% Ethanol	72.950	4.118	7.122
40% Ethanol	67.690	4.766	8.433
20% Isopropanol	73.480	8.879	12.334
40% Isopropanol	68.760	4.394	6.998
Samarium(III) Complexes			
20% Methanol	72.250	7.808	4.480
40% Methanol	66.460	7.319	3.886
20% Ethanol	72.950	4.362	6.204
40% Ethanol	67.690	4.766	8.433
20% Isopropanol	73.480	4.102	6.043
40% Isopropanol	68.760	4.3.03	8.740

In case of lanthanides, due to lanthanide contraction, the metal-ligand stability constants are expected to increase with decreasing ionic radii. It means that samarium should have greater stability than lanthanum. It is observed from the stability constant obtained in the present investigation that the above trend is not strictly observed by lanthanum and samarium in the solvent systems studied. Lanthanum is known to show abnormal trends. The reasons for such deviations have been discussed by many authors⁶⁻⁹. It is suggested¹⁰ that these trends in the values of formation constants may be due to varying degrees of stabilisation arising out of the interactions of 4f metal orbitals with ligand field.

REFERENCES

1. A.I. Vogel, A Text book of Practical Organic Chemistry, ELBS, pp.366-370 (1971).
2. Kirk Othmer, Encyclopedia of Chemical Technology, 3rd Ed., pp. 410-421 (1978).
3. M. Calvin and K.W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).
4. J. Bjerrum, Metal Ammine Formation in Aqueous Solutions, P. Hass and Sons, Copenhagen (1941).
5. H. Irving and H. Rossotti, *J. Chem. Soc.*, 2904 (1954).
6. T. Moeller and E.P. Horwitz, *J. Inorg. Nucl. Chem.*, **12**, 49 (1954).
7. E.H. Wheelright, F.H. Speeding and G. Schwarzenbach, *J. Am. Chem. Soc.*, **75**, 4196 (1953).
8. G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chem. Acta*, **39**, 1989 (1956).
9. F.J.C. Rossotti, *Discuss. Farad. Soc.*, **26**, 183 (1958).
10. L.A.K. Stavely and J. Randell, *Discuss Farad. Soc.*, **26**, 157 (1958).

(Received: 23 April 1994; Accepted: 22 November 1994)

AJC-897