Thermochimica Acta, 59 (1982) 157–165
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

THERMODYNAMIC STUDY OF THE INTERACTION OF RARE EARTHS WITH *N*-ARYLVIOLURIC ACIDS

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(Received 23 April 1982)

ABSTRACT

Thermodynamic proton ligand stability constants of *N*-phenylvioluric acid (PVA), *N*-*p*-tolylvioluric acid (*p*-TVA), *N*-*o*-tolylvioluric acid (*o*-TVA) and *N*-*m*-tolylvioluric acid (*m*-TVA) and thermodynamic formation constants of the complexes of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Eu^{3+}, Dy^{3+} and Ho^{3+} with these four closely related *N*-arylvioluric acids have been determined in 50% v/v ethanol–water solvent. The order of stability for rare earths with *N*-arylvioluric acids is $La^{3+} < Ce^{3+} < Pr^{3+} < Nd^{3+} < Sm^{+3} < Gd^{3+} < Eu^{3+} < Dy^{3+} < Ho^{3+}$. The stability constants are found to decrease as the temperature increases. The thermodynamic functions ΔG^0, ΔH^0 and ΔS^0 corresponding to the stepwise complexation processes have been evaluated. The stepwise formation of complexes is predominantly enthalpy driven. The other factors affecting complex stability of metal ions are discussed.

INTRODUCTION

Violuric acids are of great importance in analytical chemistry [1–3]. They form chelates with metal ions [4–6] but no literature data are available on thermodynamic metal–ligand stability constants of rare earths with the *N*-arylvioluric acids. Hence, it is desirable to have a knowledge of the stabilities of complexes of these acids with La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+} and Ho^{3+}.

EXPERIMENTAL

The method reported in ref. [7] for the preparation of *N*-phenylvioluric acid was used for the synthesis of *N*-(*o*-*m*-*p*)-tolylvioluric acids. All these acids were used after further purification. Solutions of metal perchlorates

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were prepared in order to minimize complexing of metal ions by anions. Since pure perchlorates of the metals were not available, they were prepared by treating an excess of pure oxide of carbonate of the metal with perchloric acid of requisite strength. The solutions were filtered, boiled to remove any dissolved carbon dioxide and then suitably diluted. The concentrations of the metal ions were determined by standard methods [8,9]. All other chemicals used were of AR and GR grade of B.D.H. or Merck products unless otherwise stated.

The titrating solution was made up of metal ion (0.001 M), ligand (0.01 M) and $HClO_4$ (0.005 M) and the carbonate free sodium hydroxide was used as the titrant. The medium was 50% ethanol–water. The ionic strength of the titrating solution was maintained at 0.1 M with $NaClO_4$. Titrations were carried out in a sealed water jacketed vessel at a fixed temperature and monitored by a precalibrated expanded scale pH meter (Elico 821, India) equipped with a glass electrode and a saturated calomel electrode. The experimentation and calculations are essentially based on the method of Bjerrum [10] and Calvin and Wilson [11] as modified by Irving and Rossotti [12]. By applying various computational methods such as interpolation at half $\bar{n}$ values, interpolation at various $\bar{n}$ values, midpoint slope method and correction term method, the stepwise metal–ligand stability constants were determined. The values obtained by different methods are in fair agreement.

Titrations were performed repeatedly until two sets of values differing within ±0.001 pH units were obtained. All titrations were done with at least two different metal concentrations differing by factor of 5–10.

RESULTS AND DISCUSSION

In all metal–ligand titrations, the $\bar{n}$ value steadily increased with pH from $< 0.3 - \geqslant 3.0$ before any precipitation occurred, indicating the formation of 1:3 metal–ligand complexes as the highest complexes in these systems. The thermodynamic values for the stepwise protonation constants of acids and stepwise formation constants of the corresponding metal–ligand complexes obtained by applying activity coefficient corrections on the basis of the Davies equation [13] are summarized in Tables 1–4. Formation constants, determined as above, were reproducible to 0.04 log unit or less in replicate experiments, while variation in the initial concentration of metal and chelating agent gave results with a variation of ±0.10 log units or less.

The skeletal structures of PVA, *o*-TVA, *m*-TVA and *p*-TVA are identical but they contain different groups which cause a great change in the distribution of electron density in the ring and hence the electron density at any particular point is also affected. With this change in electron density distribution, the protonation–deprotonation equilibria and the complexation

TABLE 1

Thermodynamic stability constants of *N*-phenylvioluric acid at different temperatures, and thermodynamic functions at 25°C

Cation	$\log K_1$		$\log K_2$		$\log K_3$		$-\Delta H^0$ (kcal mole^{-1})			$-\Delta S^0$ (cal mole^{-1} deg^{-1})		
	25°C	35°C	25°C	35°C	25°C	35°C	$-\Delta H_1^0$	$-\Delta H_2^0$	$-\Delta H_3^0$	$-\Delta S_1^0$	$-\Delta S_2^0$	$-\Delta S_3^0$
H^+	10.44	10.23	4.42	4.18								
La^{3+}	6.98	6.53	5.46	5.22	4.26	4.12	18.72	9.98	5.82	31.00	8.62	0.30
Ce^{3+}	7.10	6.62	5.60	5.34	4.42	4.27	19.96	10.81	6.24	34.63	10.77	0.80
Pr^{3+}	7.38	6.86	5.89	5.61	4.71	4.55	21.63	11.64	6.65	39.09	12.21	0.83
Nd^{3+}	7.54	6.99	6.03	5.73	4.84	4.65	22.88	12.48	7.90	42.41	14.39	4.46
Sm^{3+}	7.60	7.02	6.10	5.77	4.90	4.69	24.12	13.72	8.73	46.30	18.25	6.97
Eu^{3+}	7.85	7.21	6.33	5.96	5.16	4.92	26.62	15.39	9.98	53.55	22.78	9.96
Gd^{3+}	7.69	7.07	6.19	5.84	4.99	4.76	25.79	14.56	9.56	51.51	20.63	9.32
Dy^{3+}	8.02	7.36	6.54	6.14	5.34	5.08	27.45	16.64	10.81	55.57	26.20	11.94
Ho^{3+}	8.08	7.39	6.60	6.16	5.40	5.12	28.70	18.30	11.64	59.49	31.34	14.46

TABLE 2

Thermodynamic stability constants of *N*-*m*-tolylvioluric acid at different temperatures and thermodynamic functions at 25°C

Cation	log K_1		log K_2		log K_3		$-\Delta H^0$ (kcal mole^{-1})			$-\Delta S^0$ (cal mole^{-1} deg^{-1})		
	25°C	35°C	25°C	35°C	25°C	35°C	$-\Delta H_1^0$	$-\Delta H_2^0$	$-\Delta H_3^0$	ΔS_1^0	$-\Delta S_2^0$	$-\Delta S_3^0$
H^+	10.62	10.42	4.76	4.58								
La^{3+}	7.14	6.65	5.65	5.37	4.56	4.37	20.38	11.64	7.90	35.83	13.70	5.73
Ce^{3+}	7.25	6.73	5.75	5.55	4.68	4.48	21.63	12.48	8.32	39.53	16.14	6.61
Pr^{3+}	7.54	6.98	6.04	5.72	4.95	4.74	23.29	13.31	8.73	43.79	18.45	6.74
Nd^{3+}	7.69	7.10	6.21	5.86	5.11	4.89	24.54	14.56	9.15	47.31	21.34	7.41
Sm^{3+}	7.75	7.13	6.25	5.88	5.17	4.93	25.79	15.39	9.98	51.20	23.35	9.93
Eu^{3+}	8.04	7.36	6.50	6.09	5.38	5.12	28.28	17.05	10.81	58.25	27.58	11.74
Gd^{3+}	7.85	7.19	6.34	5.95	5.28	5.03	27.45	16.22	10.40	56.34	25.53	10.83
Dy^{3+}	8.17	7.47	6.70	6.26	5.58	5.30	29.12	18.30	11.64	60.46	30.87	13.62
Ho^{3+}	8.25	7.52	6.76	6.28	6.68	6.36	30.36	19.96	13.31	64.26	36.17	14.22

TABLE 3

Thermodynamic stability constants of *N-o*-tolylvioluric acid at different temperatures and thermodynamic functions at 25°C

Cation	$\log K_1$		$\log K_2$		$\log K_2$		$-\Delta H^0$ (kcal mole^{-1})			$-\Delta S^0$ (cal mole^{-1} deg^{-1})		
	25°C	35°C	25°C	35°C	25°C	35°C	$-\Delta H_1^0$	$-\Delta H_2^0$	$-\Delta H_3^0$	$-\Delta S_1^0$	$-\Delta S_2^0$	$-\Delta S_3^0$
H^+	10.54	10.24	4.46	4.28								
La^{3+}	7.02	6.55	5.52	5.26	4.38	4.22	19.55	10.81	6.65	33.62	11.10	2.34
Ce^{3+}	7.15	6.65	5.65	5.37	4.50	4.32	20.08	11.64	7.48	34.79	13.32	4.49
Pr^{3+}	7.43	6.89	5.94	5.64	4.82	4.62	22.46	12.48	8.32	41.51	14.79	5.97
Nd^{3+}	7.59	7.02	6.10	5.78	4.88	4.67	23.71	13.31	8.73	44.96	16.87	7.04
Sm^{3+}	7.65	7.05	6.17	5.82	5.02	4.79	25.96	14.56	9.56	52.24	20.73	9.19
Eu^{3+}	7.92	7.26	6.40	6.01	5.25	4.99	27.45	16.22	10.81	56.00	25.26	12.34
Gd^{3+}	7.73	7.09	6.23	5.86	5.09	4.85	26.62	15.39	9.98	54.09	23.25	10.30
Dy^{3+}	8.08	7.40	6.56	6.14	5.43	5.16	28.28	17.47	11.23	58.08	28.72	12.95
Ho^{3+}	8.14	7.43	6.66	6.20	5.54	5.25	29.53	19.13	12.06	61.97	33.82	15.23

TABLE 4

Thermodynamic stability constants of *N*-*p*-tolylvioluric acid at different temperatures, and thermodynamic functions at 25°C

Cation	$\log K_1$		$\log K_2$		$\log K_3$		$-\Delta H^0$ (kcal mole^{-1})			$-\Delta S^0$ (cal mole^{-1} deg^{-1})		
	25°C	35°C	25°C	35°C	25°C	35°C	$-\Delta H_1^0$	$-\Delta H_2^0$	$-\Delta H_3^0$	$-\Delta S_1^0$	$-\Delta S_2^0$	$-\Delta S_3^0$
H^+	10.75	10.52	5.07	4.80								
La^{3+}	7.27	6.76	5.77	5.46	4.71	4.54	21.21	12.89	7.07	38.05	16.94	2.24
Ce^{3+}	7.39	6.86	5.88	5.55	4.83	4.64	22.04	13.72	7.90	40.26	19.22	4.49
Pr^{3+}	7.69	7.11	6.18	5.83	5.14	4.83	24.12	14.56	8.73	45.90	20.70	5.87
Nd^{3+}	7.83	7.22	6.35	5.97	5.30	5.08	25.37	15.80	9.15	49.46	24.09	6.54
Sm^{3+}	7.90	7.26	6.43	6.03	5.38	5.14	26.62	16.64	9.98	53.32	26.54	8.95
Eu^{3+}	8.17	7.51	6.68	6.25	5.64	5.38	27.87	17.88	10.81	56.27	29.56	10.57
Gd^{3+}	7.96	7.31	6.47	6.06	5.49	5.24	27.04	17.05	10.40	54.46	27.71	9.86
Dy^{3+}	8.32	7.57	6.82	6.36	5.77	5.48	31.20	19.13	12.06	66.77	33.21	14.16
Ho^{3+}	8.38	7.60	6.90	6.41	5.84	5.54	32.44	20.38	12.48	70.67	36.94	15.26

equilibria of these acids in the presence of rare earths have been greatly varied.

Since the ease of removal of a proton is the determining factor in both the deprotonation and metal complex formation, the pK_a values of the acids and $\log K$ of metal complexes should be related linearly. All the violuric acids do indeed show a linear relationship between pK_a and $\log K$ for all the metal systems. It is evident from the order to pK_a values of the acids and that of $\log K$ of the complexes that the introduction of a methyl group into the *ortho, meta* and *para* positions of the *N*-phenyl ring of the PVA molecule has a parallel effect on the proton–ligand and metal–ligand stability constants; for example, the pK_a order is PVA < *o*-TVA < *m*-TVA < *p*-TVA, which is identical to the order of $\log K$. The parallel orders of $\log K$ and pK_a also emphasize the fact that the net electron demand in metal association remains the same as in protonation in spite of a chelate ring, most probably non-coplanner with the violurate ring, being produced.

The $\log K_1$ values of various rare earth chelates were plotted against Z/r^2 when a regular graph with a break at Gd^{3+} was obtained. This break has also been observed in the case of other ligands [14] and can be attributed to the half-filled 4 *f* shells. The increase in stability of rare earth metal complexes with decrease in ionic or crystal radii indicates the absence of extensive covalent bonding due to the unavailability of 4 *f* electrons for bond formation.

In the present study, since all the rare earth ions were in +3 oxidation state and are more or less of the same size, the electrostatic contribution to the metal–ligand bond in the first complexes formed with the same ligand is assumed to be very nearly the same. Therefore, log K_1 values fot the metal complexes with different ligands were plotted against the respective overall ionization potential of rare earths [15] to observe the effect of the electron affinity of the rare earth ions on the stability of the complexes they formed. In each case a straight line was obtained, indicating that in each ligand system the stability of the first complex formed was directly proportional to the total ionization potential of the central atom.

A comparison of the $\log K_1$, $\log K_2$ and $\log K_3$ values for rare earth metal complexes examined here shows the following order irrespective of substituents in *N*-arylvioluric acids: $La^{3+} < Ce^{3+} < Pr^{3+} < Nd^{3+} < Sm^{3+} < Gd^{3+} < Eu^{3+} < Dy^{3+} < Ho^{3+}$. This finding is in agreement with those of Stagg and Powell [16]. The $\log K_1$ values for metal complexes with acids plotted against the atomic number exhibit a more or less regularly increasing stability with increasing atomic number from La^{3+} to Eu^{3+}, followed by a decrease at Gd^{3+} and an increase to Dy^{3+} and slightly higher values for Ho^{3+}. The same trend has also been observed in other instances [17].

The values at 35°C indicate that the temperature increases the acidity of ligands and reduces the stability of the complexes, but to a small degree. The values of standard enthalpy change, ΔH^0, were calculated using van't Hoff's equation [18] at two temperatures, T_1 (298 K) and T_2 (308 K).

$$\Delta H^0 = \frac{4.576\ (\log K_1 - \log K_2)}{[1/T_1 - 1/T_2]}$$

The free energy change, ΔG^0, and ΔS^0 were calculated from the relationships

$$-\Delta G^0 = 2.303Rt \log K$$

and

$$\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$$

The error in ΔH^0 values lies in the range 0.2–0.5 kcal mole^{-1} and that for ΔS^0 is 0.5 cal deg^{-1} mole^{-1}. It is evident from Tables 1–4 that the reactions of rare earths with these acids are exothermic which explains why the formation constants have high values at lower temperatures.

The entropy changes associated with consecutive complexation processes are: (1) charge neutralization; (2) liberation of ordered solvent molecules from the solvation shell; and (3) loss of vibrational and rotational degrees of freedom of the ligand by complexation phenomena. Considering that violurates and rare earth metal cations behave as soft donors and soft acceptors, respectively, only (2) gives a small positive contribution to entropy because for a soft–soft interaction, a very weak solvation shell occurs. The coordinations may actually involve a considerable net loss of entropy owing to the rotational and conformational constraints to which the ligands are subjected in the complex. Therefore, the contribution of (1) and (3) together more than offset that due to (2) and hence all steps have negative ΔS^0 values. Thus the complexation of the *N*-arylvioluric acids with rare earth ions in solution appears to be an enthalpy driven process. In addition there is a stronger dependence of $\log K$ on the ionization potential of metal ions, so it may be concluded that the metal–ligands have more of a covalent character.

ACKNOWLEDGEMENTS

Thanks are due to the Department of Chemistry, University of Roorkee, and Sahu Jain College, Najibabad, for providing the necessary facilities, and to U.G.C., India.

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