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THERMODYNAMICS FOR THE FORMATION OF COMPLEXES OF LANTHANIDE(III) IONS WITH PHTHALANILIC ACIDS

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ABSTRACT

Thermodynamic step-wise stability constants for the interactions of lanthanide(III) ions with phthalanilic, 4-methylphthalanilic, 4-chlorophthalanilic, 4-bromophthalanilic and 4-nitrophthalanilic acids were determined at 22, 30 and 40 °C by the Bjerrum–Calvin titration technique as adopted by Irving and Rossotti. The order was found to be: Ho(III) > Dy(III) > Tb(III) > Gd(III) < Eu(III) > Sm(III) > Nd(III) > Pr(III) > La(III), with each anilic acid, while the stabilities of the complexes of different anilic acids with the same metal ion were in the order: phthalanilic acid < 4-methylphthalanilic acid > 4-chlorophthalanilic acid > 4-bromophthalanilic acid > 4-nitrophthalanilic acid. Free energy, enthalpy and entropy changes for the formation of these complexes were also determined which indicated that the chelation was through nitrogen of secondary amide and carboxylate groups.

INTRODUCTION

A survey of the existing literature reveals that the interactions of anilic acids with zirconium and thorium [1–3] have been used for their gravimetric and amperometric determinations. Studies have also been carried out on the interactions of bivalent transition metal ions with phthalanilic [4] and maleanilic acids [5], and of lanthanide(III) ions with maleanilic acids [6]. Anilic acids containing secondary amide and carboxylate groups as coordinating sites are very important from pharmacological, analytical and industrial points of view [7–9]. Here we report the values of the thermodynamic stability constants, ΔF, ΔH and ΔS, for the interactions of lanthanide(III) ions with phthalanilic acids.

EXPERIMENTAL

Reagents and solutions

For details, see our previous paper [5].

Physical measurement and titration procedure

The procedure was as reported earlier [5]. The accuracies of the pK values of the acids and the log K values of the complexes are ± 0.025 and ± 0.05 log units, respectively. The accuracy of these values varies from ± 3.40 to ± 5.06 kJ mol^{-1} for ΔH and from ± 4.20 to ± 6.30 J k^{-1} mol^{-1} for ΔS.

RESULTS AND DISCUSSION

The values of pK_1 and pK_2 corresponding to the deprotonation of the carboxylic group and the secondary amide group, respectively, at 22, 30 and 40 ° C and at ionic strength 0.1 M $NaClO_4$ are given in Table 1. Table 2 summarizes the values of the stability constants. The values of ΔF, ΔH and ΔS corresponding to the first, second and third step reactions are given in Table 3. The order of pK_2 values is: 4-methyl P > P > 4-chloro P ≈ 4-bromo P > 4-nitro P. Thus, the inductive and mesomeric effects influence the liberation of protons from –NH–, $-NO_2$, –Cl or –Br which reduces the electron density at the reaction centre and readily leads to proton liberation. The reverse is true for the methyl derivative. A similar trend is observed in pK_1 values. The possibility of the formation of polynuclear species can be ruled out in view of the high metal to ligand ratio (1 : 10) which was maintained in these studies. The formation curves determined from ligand–metal ratios of 10 : 1 and 15 : 1 were found to be identical. The λ_{max}

TABLE 1

Protonation constants of phthalanilic acids in 0.1 M $NaClO_4$ at 22, 30 and 40 ° C

Acid	Temp. (° C)	pK_1	pK_2
P	22	4.35	11.15
	30	4.25	11.10
	40	4.15	10.90
4-methyl P	22	4.45	11.30
	30	4.38	11.15
	40	4.33	11.00
4-chloro P	22	4.10	11.10
	30	4.00	10.95
	40	3.90	10.85
4-bromo P	22	4.12	11.13
	30	4.05	11.00
	40	4.00	10.88
4-nitro P	22	3.80	10.90
	30	3.65	10.85
	40	3.55	10.70

P = Phthalanilic acid.

TABLE 2

Thermodynamic stability constants of metal complexes of phthalanilic acids

Acids	Temp. (°C)	Formation constants	La^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Td^{3+}	Dy^{3+}	Ho^{3+}
P	22	log K_1	6.60	6.98	7.00	7.58	7.83	7.57	8.50	9.50	9.75
		log K_2	6.40	6.90	6.95	7.38	7.57	7.45	7.90	9.15	9.45
		log K_3	6.29	6.75	6.77	7.23	7.42	7.25	7.60	8.02	8.32
		log β_3	19.29	20.63	20.72	22.19	22.82	22.28	24.00	26.67	27.52
	30	log K_1	6.52	6.89	6.91	7.47	7.71	7.47	8.37	9.34	9.56
		log K_2	6.35	6.82	6.86	7.29	7.46	7.34	7.77	9.02	9.31
		log K_3	6.25	6.70	6.73	7.18	7.35	7.19	7.52	7.95	8.24
		log β_3	19.12	20.41	20.50	21.94	22.52	22.00	23.66	26.31	27.11
	40	log K_1	6.43	6.78	6.81	7.35	7.58	7.35	8.24	9.15	9.35
		log K_2	6.28	6.73	6.77	7.18	7.33	7.22	7.64	8.88	9.10
		log K_3	6.21	6.64	6.67	7.12	7.28	7.13	7.44	7.88	8.15
		log β_3	18.92	20.15	20.25	21.65	22.19	21.70	23.32	25.91	26.60
4-methyl P	22	log K_1	8.42	8.55	8.61	8.74	8.78	8.81	8.95	9.58	9.83
		log K_2	7.90	8.02	8.11	8.21	8.36	8.30	8.43	9.10	9.44
		log K_3	7.37	7.74	7.79	8.01	8.15	8.11	8.22	8.52	8.78
		log β_3	23.69	24.31	24.51	24.96	25.29	25.22	25.60	27.20	28.05
	30	log K_1	8.28	8.40	8.45	8.58	8.61	8.65	8.77	9.38	9.61
		log K_2	7.81	7.92	8.01	8.10	8.24	8.18	8.30	8.96	9.29
		log K_3	7.32	7.69	7.72	7.93	8.06	8.02	8.12	8.40	8.64
		log β_3	23.41	24.01	24.18	24.61	24.81	24.85	25.19	26.74	27.54
	40	log K_1	8.13	8.23	8.29	8.40	8.43	8.47	8.48	9.14	9.38
		log K_2	7.71	7.82	7.90	7.98	8.11	8.06	8.17	8.81	9.14
		log K_3	7.26	7.62	7.65	7.85	7.96	7.93	8.01	8.26	8.48
		log β_3	23.10	23.67	23.84	24.23	24.50	24.46	24.66	20.21	27.00
4-chloro P	22	log K_1	8.05	8.25	8.34	8.94	9.13	8.99	9.20	9.80	9.97
		log K_2	7.77	8.06	8.12	8.19	8.30	8.21	8.46	9.18	9.40
		log K_3	7.28	7.45	7.57	7.66	7.77	7.70	7.85	8.30	8.35
		log β_3	23.10	23.76	24.03	24.79	25.20	24.90	25.51	27.28	27.72

	30	log K_1	7.92	8.12	8.19	8.80	8.88	8.85	9.05	9.60	9.75
		log K_2	7.70	7.97	8.04	8.10	8.20	8.12	8.35	9.05	9.26
		log K_3	7.23	7.39	7.51	7.60	7.70	7.64	7.78	8.19	8.25
		log β_3	22.85	23.48	23.74	24.50	24.78	24.61	25.18	26.84	27.26
	40	log K_1	7.78	7.96	8.05	8.64	8.72	8.70	8.77	9.40	9.52
		log K_2	7.60	7.86	7.94	8.00	8.07	8.01	8.23	8.90	9.10
		log K_3	7.17	7.32	7.45	7.53	7.62	7.58	7.70	8.08	8.14
		log β_3	22.55	23.14	23.44	24.17	24.41	24.29	24.70	26.38	26.76
4-bromo P	22	log K_1	7.94	8.15	8.23	8.83	8.92	8.85	9.11	9.60	9.83
		log K_2	7.68	7.81	7.89	8.14	8.23	8.20	8.36	8.72	9.04
		log K_3	7.17	7.36	7.50	7.62	7.70	7.67	7.76	8.20	8.30
		log β_3	22.79	23.32	23.62	24.59	24.85	24.72	25.23	26.52	27.17
	30	log K_1	7.81	8.02	8.09	8.69	8.76	8.69	8.94	9.41	9.62
		log K_2	7.61	7.74	7.81	8.05	8.12	8.09	8.25	8.60	8.90
		log K_3	7.12	7.31	7.44	7.56	7.64	7.61	7.69	8.12	8.19
		log β_3	22.54	23.07	23.34	24.30	24.52	24.39	24.88	26.13	26.71
	40	log K_1	7.67	7.88	7.94	8.53	8.59	8.53	8.76	9.20	9.40
		log K_2	7.54	7.66	7.73	7.94	8.00	7.98	8.13	8.45	8.74
		log K_3	7.07	7.25	7.37	7.49	7.56	7.54	7.61	8.02	8.08
		log β_3	22.28	22.79	23.04	23.96	24.15	24.05	24.50	25.67	26.22
4-nitro P	22	log K_1	7.98	8.16	8.33	8.43	8.57	8.43	8.75	9.60	9.85
		log K_2	7.40	7.66	7.75	7.88	7.91	7.84	7.92	9.03	9.18
		log K_3	7.00	7.17	7.28	7.50	7.54	7.38	7.50	8.14	8.31
		log β_3	22.38	22.99	23.36	23.81	24.02	23.65	24.23	26.77	27.34
	30	log K_1	7.85	8.02	8.18	8.27	8.41	8.28	8.57	9.41	9.64
		log K_2	7.31	7.56	7.65	7.77	7.79	7.73	7.80	8.90	9.04
		log K_3	6.94	7.10	7.21	7.43	7.46	7.30	7.48	8.05	8.21
		log β_3	22.10	22.69	22.94	23.47	23.60	23.31	23.85	20.36	26.89
	40	log K_1	7.71	7.88	8.02	8.10	8.23	8.11	8.38	9.20	9.41
		log K_2	7.21	7.45	7.53	7.65	7.67	7.61	7.67	8.75	8.90
		log K_3	6.88	7.02	7.13	7.35	7.37	7.22	7.39	7.95	8.10
		log β_3	21.80	22.35	22.68	23.10	23.27	22.94	23.44	25.90	26.41

P = Phthalanilic acid

TABLE 3

$\Delta F^{\ominus}$ and $\Delta H^{\ominus}$ values (kcal mol^{-1}) and $\Delta S^{\ominus}$ values (cal k^{-1} mol^{-1}) at 22° C

Acids	Thermodynamic parameters	La^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}
P	$-\Delta F^{\ominus}$	108.82	116.48	117.15	125.73	128.87	126.02	135.48	150.75	155.56
	$-\Delta H$	39.62	40.15	52.17	56.23	60.46	57.11	62.93	71.96	77.53
	ΔS	232.71	238.32	219.95	235.14	231.17	233.59	245.64	266.35	261.79
4-methyl P	$-\Delta F^{\ominus}$	133.73	137.32	138.23	141.01	142.80	142.43	144.34	153.76	158.58
	$-\Delta H$	56.48	61.50	64.81	65.98	75.35	70.71	80.83	93.05	98.49
	ΔS	261.67	256.52	242.71	239.53	227.94	242.59	214.81	205.06	202.25
4-chloro P	$-\Delta F^{\ominus}$	130.54	134.14	135.73	140.20	141.96	140.75	144.31	154.18	156.81
	$-\Delta H$	54.68	56.40	58.99	64.18	66.48	61.71	72.93	83.93	92.97
	ΔS	256.94	263.26	260.04	257.69	251.29	268.03	241.63	237.48	216.23
4-bromo P	$-\Delta F^{\ominus}$	128.49	131.17	133.48	138.90	140.58	139.66	142.72	150.04	153.64
	$-\Delta H$	47.28	52.47	56.94	60.58	67.57	63.18	71.80	82.01	89.37
	ΔS	274.76	267.27	259.16	256.90	247.07	258.91	239.83	229.87	217.19
4-nitro P	$-\Delta F^{\ominus}$	126.49	129.70	131.96	134.35	135.73	133.80	137.06	151.16	154.56
	$-\Delta H$	57.07	60.04	64.39	69.33	72.17	67.99	76.82	82.63	91.63
	ΔS	234.72	235.43	228.78	222.13	215.52	222.76	204.10	231.67	212.67

P = Phthalanilic acid.

of these solutions in the visible region further confirmed the presence of identical species. The highest value of $\bar{n}$ (average number of ligands attached per metal ion) was found to be 3, indicating a 1 : 3 stoichiometry in the complexes. The values of log K_1, log K_2, log K_3 and log β_3 regularly increase from lanthanum(III) to holmium(III) except in the case of gadolinium (III). Such behaviour has also been observed in other systems [10,11]. This exception in the case of Gd(III) complexes may be due to the combined effect of ligand field stabilization energy and the hydration number of the metal ion.

The large entropy values for the formation of these complexes are due to the contributions from both translational and configurational changes. The decrease in entropy change for the second and third steps of the reaction may be attributed to statistical effects which are also reflected in the values of ΔF and log K (stepwise values). As there is no change in the structure, the transitional entropy change should be less significant than the changes due to the gradual increase in bond strength and steric hindrance as the ionic radius decreases. The high exothermic values of enthalpy changes indicate the involvement of nitrogen in the coordination because the contribution due to the involvement of the carboxylate group is either very small or endothermic.

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REFERENCES

1 S.K. Datta, Z. Anal. Chem., 23 (1960) 174.
2 C.L. Sharma and R.S. Arya, Talanta, 26 (1979) 577.
3 C.L. Sharma and R.S. Arya, Anal. Lett., 12 (1979) A-9.
4 C.L. Sharma, S.S. Narvi and R.S. Arya, Acta Chim. Hung., 114 (1983) 349.
5 C.L. Sharma, R.S. Arya and S.S. Narvi, Thermochim. Acta, 105 (1986) 231.
6 C.L. Sharma, S.S. Narvi, R.S. Arya and H.O. Gupta, J. Indian Chem. Soc., 60 (1983) 920.
7 L.P. Epstein and F. Stohlman, Jr., Blood, 24 (1964) 69.
8 S. Malcohn and D. Pressman, J. Am. Chem. Soc., 76 (1954) 2863.
9 Y. Himeno, T. Hotatsu, K. Arisawa, S. Koshimura and R. Hirata, Annu. Rep. Res. Inst. Tuberc. Kanazawa Univ., 2(5) (1954) 12.
10 G. Schwarzenbach, R. Gut and G. Anderegg, Helv. Chim. Acta, 37 (1954) 937.
11 R. Hardar and S. Chaberk, J. Inorg. Nucl. Chem., 11 (1959) 197.