

Physico-chemical and Thermodynamic Studies of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III), and Yb(III)-chelates of N-salicylidenevaline

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The stability constants and other thermodynamic parameters of the rare-earth chelates of N-salicylidenevaline have been determined using Calvin-Bjerrum pH-titration technique as used by Irving and Rossotti in aqueous media ($\mu=0.1, 0.05$ and $0.01M$ NaClO₄) at 25°, 30° and 35° and the order of stability constants is found to be La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III) < Tb(III) < Dy(III) < Ho(III) < Yb(III) which is in agreement with the lanthanide contraction. Magnetic conductance and I.R. studies of the solid chelates have also been carried out.

A survey¹⁻³ of the literature has revealed that no work on the physico-chemical and thermodynamic studies of the rare-earth chelates of N-salicylidenevaline (H₂SV) has been carried out and hence the same was undertaken.

Apparatus and Reagents: The apparatus and the reagents employed were the same as reported earlier⁴. H₂SV and its solid chelates were synthesized by the procedure already reported^{5,6}.

Experimental

The stability constants of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III) and Yb(III)-chelates with H₂SV were determined by Calvin-Bjerrum pH-titration technique as used by Irving and Rossotti⁷. For the evaluation of the thermodynamic stability constants, experiments were carried out in media of low ionic strengths (0.1, 0.05, 0.01M NaClO₄) at 25°, 30° and 35°. H₂SV was titrated in the absence and presence of the metal ions of interest with 0.1M sodium hydroxide solution and the titration curves had the usual shapes.

Results and Discussion

The dissociation constants of H₂SV and the stability constants of its rare-earth chelates at different ionic strengths and temperatures are summarized in Table 1. The stability of the metal chelates follows the order La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III) < Tb(III) < Dy(III) < Ho(III) < Yb(III) which is in agreement with the lanthanide contraction.

The thermodynamic stability constants were obtained by the extrapolation of the experimentally

obtained constants to zero ionic strength in the plots between log of stability constants against $\sqrt{\mu}$, where μ is the ionic strength. The values of thermodynamic stability constants and other parameters obtained are summarized in Table 2.

It is further observed that ΔH is positive in all cases which suggest that reactions are endothermic. The positive values of ΔS for all the chelates indicate that entropy term is favourable for their formation.

Harned *et al*⁸ gave the relation between $\log K^H$ and temperatures as $[(pK^H - ct^2) = -2c\theta t + (pK_m^H - c\theta^2)]$ where $pK^H = -\log K^H$ at $t^\circ C$; pK_m^H is minimum pK^H value at $\theta^\circ C$ and c is a constant having the value $5.0 \times 10^{-5} \text{ deg}^{-2}$. A plot of $(pK^H - ct^2)$ vs t must be linear and this was found true in the present case. The values of θ and pK_m^H for H₂SV were found 193.3° and 16.84 respectively. ΔH values evaluated from Harned's equation were found in agreement with those received from Gibbs-Helmholtz equation.

The yield, mol. wt., magnetic moment and molar conductance values of the solid chelates are summarized in Table 3. The conductance data suggest these compounds to be nonelectrolytes.

I.R. spectrum of H₂SV shows bands at 2610, 1640 and 2570 cm⁻¹ assignable to bonded νOH , $\nu C=N$ and $\nu COOH$, respectively. It appears that the phenolic oxygen is intramolecularly hydrogen bonded to the lone pair of the azomethine N-atom⁹. νOH of the ligand around 2610 cm⁻¹ was shifted to lower frequency range of 2590-2580 cm⁻¹ suggesting the rupture of hydrogen bonding and its participation in coordination. The band at 2570 cm⁻¹

TABLE 1—DISSOCIATION CONSTANTS OF H_2SV AND THE STABILITY CONSTANTS OF ITS TRIVALENT METAL CHELATES AT DIFFERENT IONIC STRENGTHS

Dissociation/ stability constant	μ at 25°C			μ at 30°C			μ at 35°C		
	0.1M	0.05M	0.01M	0.1M	0.05M	0.01M	0.1M	0.05M	0.01M
H_2SV									
$\log K_1^H$	10.29	10.4	10.5	10.24	10.35	10.45	10.2	10.27	10.36
$\log K_2^H$	7.97	8.10	8.20	7.93	8.02	8.12	7.90	7.95	8.05
La(III)									
$\log K_1$	4.46	4.55	4.70	4.66	4.75	4.90	4.86	4.96	5.10
$\log K_2$	1.53	1.64	1.75	1.93	2.07	2.25	2.34	2.50	2.66
Ce(III)									
$\log K_1$	5.29	5.45	5.65	5.41	5.60	5.83	5.54	5.71	5.92
$\log K_2$	2.61	2.80	3.05	2.71	2.93	3.16	2.81	3.03	3.25
Pr(III)									
$\log K_1$	5.76	5.92	6.13	5.83	6.02	6.25	5.91	6.10	6.30
$\log K_2$	3.10	3.35	3.60	3.18	3.42	3.63	3.26	3.49	3.75
Nd(III)									
$\log K_1$	6.21	6.45	6.74	6.28	6.55	6.85	6.36	6.60	6.91
$\log K_2$	3.31	3.60	3.95	3.38	3.68	4.04	3.46	3.75	4.09
Sm(III)									
$\log K_1$	6.51	6.75	7.03	6.58	6.82	7.12	6.66	6.88	7.15
$\log K_2$	3.64	3.87	4.15	3.81	4.08	4.35	3.98	4.21	4.50
Gd(III)									
$\log K_1$	6.91	7.08	7.30	6.93	7.14	7.36	6.96	7.16	7.40
$\log K_2$	4.29	4.46	4.67	4.39	4.60	4.79	4.49	4.66	4.88
Tb(III)									
$\log K_1$	7.15	7.30	7.50	7.2	7.35	7.60	7.25	7.42	7.65
$\log K_2$	4.9	6.01	5.15	5.03	5.15	5.30	5.15	5.25	5.40
Dy(III)									
$\log K_1$	7.40	7.57	7.80	7.45	7.65	7.85	7.50	7.70	7.90
$\log K_2$	5.45	5.55	5.66	5.50	5.60	5.75	5.55	5.72	5.80
Ho(III)									
$\log K_1$	7.70	7.80	7.95	7.75	7.85	8.00	7.80	7.90	8.05
$\log K_2$	5.65	5.75	5.90	5.72	5.85	6.05	5.80	5.92	6.02
Yb(III)									
$\log K_1$	7.90	7.95	8.02	7.95	8.02	8.10	8.0	8.1	8.17
$\log K_2$	5.91	6.08	6.2	6.02	6.10	6.30	6.1	6.25	6.40

 TABLE 2—THERMODYNAMIC STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF RARE-EARTH CHELATES OF H_2SV

Metal chelates	$\log K^\circ$			$-\Delta F$ k cal/mole			ΔH k cal/mole	ΔS cal/deg/mole
	25°C	30°C	35°C	25°C	30°C	35°C	at 30°C	at 30°C
La(III)	6.65	7.36	8.00	9.06	10.19	11.28	46.43	187.40
Ce(III)	9.10	9.35	9.52	12.41	12.96	13.42	18.90	105.00
Pr(III)	10.12	10.26	10.40	13.80	14.22	14.66	13.02	89.95
Nd(III)	11.20	11.45	11.60	15.27	15.88	16.35	13.19	95.72
Sm(III)	11.80	12.00	12.15	16.09	16.63	17.13	20.58	122.70
Gd(III)	12.30	12.55	12.70	16.77	17.40	17.90	10.50	91.85
Tb(III)	13.00	13.20	13.40	17.22	18.30	18.80	14.70	108.70
Dy(III)	13.78	13.90	14.00	18.32	19.27	19.73	8.39	91.31
Ho(III)	14.10	14.20	14.30	19.23	19.67	20.16	10.50	99.65
Yb(III)	14.40	14.60	14.80	19.63	20.24	20.86	11.76	107.70

The values of ΔF of all the chelates are more negative at 35° and 30° than at 25°.

TABLE 3—YIELDS, MOL. WT., MAGNETIC MOMENT AND MOLAR CONDUCTANCE VALUES OF METAL CHELATES OF H₂SV

Composition	Yield %	Mol. wt.		Magnetic moment at 303°K B.M.	Molar conductance ohm ⁻² cm ² mole ⁻¹
		Found	Calcd		
[LaC ₂₄ H ₂₇ N ₃ O ₆]	74	566.5	578.5	—	2.5
[CeC ₂₄ H ₂₇ N ₃ O ₆]	76	568.5	579.5	2.21	2.7
[PrC ₂₄ H ₂₇ N ₃ O ₆]	75	570.9	580.4	3.32	3.5
[NdC ₂₄ H ₂₇ N ₃ O ₆]	79	573.0	583.8	3.65	4.2
[SmC ₂₄ H ₂₇ N ₃ O ₆]	80	580.0	589.9	1.47	5.7
[GdC ₂₄ H ₂₇ N ₃ O ₆]	77	583.0	596.8	7.82	6.8
[TbC ₂₄ H ₂₇ N ₃ O ₆]	78	590.0	598.5	9.48	6.9
[DyC ₂₄ H ₂₇ N ₃ O ₆]	76	591.0	602.0	10.40	7.1
[HoC ₂₄ H ₂₇ N ₃ O ₆]	75	596.0	604.4	10.42	7.2
[YbC ₂₄ H ₂₇ N ₃ O ₆]	78	601.0	612.6	4.85	7.4

These compounds gave satisfactory C, H, N and metal analyses.

disappeared suggesting coordination through the carboxylate group. In the spectra of the metal chelates bands in the region 1570-1560 cm⁻¹ due to antisymmetric ν COO⁻ were also observed. ν C=N of H₂SV around 1640 cm⁻¹ was shifted to lower frequency range (1615-1600 cm⁻¹) on complexation showing the involvement of the azomethine nitrogen in coordination.

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