

Stability Constants & Thermodynamic Parameters of Binary Complexes of 2-Hydroxy-1,4-naphthoquinone Monosemicarbazone (HNQS) with Some Lanthanons

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Stability constants of the complexes of La(III), Pr(III), Nd(III), Sm(III) and Tb(III) with 2-hydroxy-1,4-naphthoquinone monosemicarbazone (HNQS) have been determined potentiometrically in 75% (v/v) aqueous dioxan medium at various ionic strengths and at different temperatures. The method of Bjerrum and Calvin, as modified by Irving and Rossotti, has been used to find out the values of \bar{n} and pL . The stability constants have been calculated using an IBM 360 FORTRAN IV computer by the weighted least squares method. The stability constants have also been calculated by Bjerrum half \bar{n} method. The order of the stability constants is found to be: La < Pr < Nd < Sm < Tb. Thermodynamic parameters, ΔG , ΔH and ΔS , have also been calculated.

The semicarbazones and thiosemicarbazones of certain ketones and aldehydes have significant antimicrobial activities¹⁻⁶. The activity of semicarbazones is thought to be due to their ability to chelate with traces of metal ions present in biological systems. As a part of an extended study undertaken in our laboratories on the stabilities of metal complexes of biologically active α -hydroxynaphthoquinones, we report here the results of our studies on the stabilities of the complexes of some lanthanones with 2-hydroxy-1,4-naphthoquinone monosemicarbazone at different temperatures in 75% dioxan medium. The stability constants were determined using the method of Bjerrum and Calvin^{7,8} as modified by Irving and Rossotti⁹.

Experiments were conducted at 0.05 M, 0.01 M and 0.1 M ionic strengths keeping the temperature constant at 35°C. Gibb's energy, enthalpy and entropy values for various complexation reaction have been calculated at 0.1 M ionic strength.

A digital pH-meter (ECIL, model pH 5651) in conjunction with a glass electrode (0-14 pH range) was used for pH measurements. An IBM 360 FORTRAN IV computer was used for the calculations.

Preparation of ligand

2-Hydroxy-1,4-naphthoquinone (1.038 g) was dissolved in the minimum amount of ethanol and an aqueous solution containing equal amounts of semicarbazide hydrochloride (0.672 g) and anhydrous sodium acetate was added to it. The mixture was refluxed for 1 hr, filtered (if necessary) and cooled in ice.

The semicarbazone was precipitated by adding dilute hydrochloric acid and recrystallized from ethanol. 2-Hydroxy-1,4-naphthoquinone monosemicarbazone (HNQS) solution was prepared in 75% (v/v) aqueous dioxan medium.

Solutions of metal perchlorates of La(III), Pr(III), Nd(III), Sm(III) and Tb(III) were prepared from their corresponding oxides (99%, Johnson Matthey)¹⁰. These solutions were diluted to the desired concentrations and were standardised by conventional methods¹¹.

pH-Titration procedure

The following solutions were titrated against 0.05 M tetramethyl ammonium hydroxide (TMAH) in 75% aq. dioxan at various ionic strengths and temperatures. (i) 0.8 ml of HClO₄ (0.05 M) + 1.0 ml of NaClO₄ (2 M) + 15 ml of dioxan + 3.2 ml of H₂O (double distilled); (ii) 0.8 ml of HClO₄ (0.05 M) + 1.0 ml of NaClO₄ (2 M) + 10 ml of ligand (0.01 M) + 7.5 ml of dioxan + 0.7 ml of H₂O (double distilled); (iii) 0.8 ml of HClO₄ (0.05 M) + 1.0 ml of NaClO₄ (2 M) + 10 ml of ligand (0.01 M) + 7.5 ml of dioxan + 0.5 ml of metal solution (0.02 M) + 0.2 ml of H₂O (doubly distilled). These titrations were carried out in a closed double walled container in an atmosphere of nitrogen which was presaturated with the solvent.

In all the calculations pH correction and volume correction factors have been applied for dioxan-water mixture. From the titration curves of solutions (i) and (ii) the values of \bar{n} were calculated at various pH values. On plotting $\log(\bar{n}_H/1-\bar{n}_H)$ versus pH, linear plots having intercept equal to pK_a and slope equal to unity were obtained. From the titration curve of solutions (i), (ii) and (iii), \bar{n} values of the metal complexes were determined at various pH values. From pK_a and \bar{n} values at different pH values, the corresponding values of pL were calculated. The \bar{n} and pL data were subjected to the weighted least squares method developed by Sullivan *et al.*¹² on an IBM 360 FORTRAN IV computer to get β_n values. The weighted least squares treatment determined the set of β_n values which make the function U

$$U = \sum_{n=0}^N (y - x - nz) \beta_n x^n$$

nearest to zero, by minimizing S ,

$$S = \sum_{i=1}^I W_i U^2(x_i, y_i, z_i)$$

with respect to variation in β_n . S_{\min} has the same statistical distribution as χ^2 with K degrees of freedom and

Table 1—Stability Constants of Lanthanon Complexes with HNQS

Metal ion/ ligand	Dissociation/ stability constant	Weighted least squares method					
		μ at 35°C			μ at 40°		μ at 45°
		0.05M	0.01M	0.1M	0.1M	0.1M	
H +	log K_1	7.00	7.35	6.60	6.45	6.30	
	log K_2	—	—	—	—	—	
	log β_2	—	—	—	—	—	
La(III)	log K_1	4.71	5.12	4.01	3.98	4.10	
	log K_2	4.40	4.15	3.36	3.40	2.17	
	log β_2	8.11	9.27	7.37	7.38	6.27	
Pr(III)	log K_1	4.73	5.34	4.54	4.24	4.41	
	log K_2	4.25	4.47	3.68	3.39	3.27	
	log β_2	8.98	9.81	8.22	7.63	7.68	
Nd(III)	log K_1	5.05	5.37	4.87	4.21	4.43	
	log K_2	4.10	4.65	3.62	3.94	3.61	
	log β_2	9.15	10.02	8.49	8.15	8.04	
Sm(III)	log K_1	5.28	5.65	5.00	4.62	4.57	
	log K_2	4.27	4.77	3.48	3.90	3.83	
	log β_2	9.55	10.42	8.48	8.52	8.40	
Tb(III)	log K_1	5.27	6.04	5.45	4.94	4.75	
	log K_2	4.67	4.90	3.43	4.06	3.99	
	log β_2	9.94	10.94	8.88	9.00	8.74	

the weight defined in accordance with Sullivan *et al.*¹³. S_{\min} can be equated to χ^2 . The ΔH was calculated by the graphical method of Yatsimirskii *et al.*¹⁴ while ΔG and ΔS were calculated by conventional methods.

In the present investigations it has been noticed that the values of acid dissociation constants pK_a and stability constants decrease with increasing ionic strength and temperature of the medium (Table 1) which is in agreement with Debye-Huckel¹⁵ equation. The order of stability constants of the metal complexes of HNQS is found to be: La < Pr < Nd < Sm < Tb.

Moeller and Hseu¹⁶ and Choppin and Graffeo¹⁷ have observed similar trends. The results are in good agreement with those of Nair and Srinivasulu¹⁸ and Vishwanath and Ananta Krishnan¹⁹. The values of change in Gibb's energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complex formation are reported in Table 2.

The stabilities of lanthanides complexes with HNQS show an increase from La(III) to Tb(III) in agreement with the increasing acidity. This trend suggests that metal-ligand interaction may be predominantly electrostatic.

In general $\log K_1 > \log K_2$ for a given metal ion; however, the difference in the values between the two constants is not too much, indicating that there is almost an equal tendency for the formation of neutral complex species. In fact, the maximum \bar{n} values observed in our present experiments are ~ 2.0 which support our assumption of 1:2 stoichiometry.

Table 2—Thermodynamic Parameters of Lanthanon Complexes with HNQS

Metal ions	$\{\mu = 0.1M NaClO_4 \text{ and Temp.} = 35 \pm 0.5^\circ\}$		
	$-\Delta G$ (kcal mol ⁻¹)	$-\Delta H$ (kcal mol ⁻¹)	ΔS (kcal degree ⁻¹ mol ⁻¹)
La(III)	5.65	1.82	+0.0124
Pr(III)	6.39	5.48	+0.0030
Nd(III)	6.86	18.28	-0.0371
Sm(III)	7.04	20.11	-0.0424
Tb(III)	7.80	34.73	-0.0874

Finally, in view of the very low ($5.0 \times 10^{-4} M$) concentration of metal ions used in the titration, it has been assumed that the possibility of formation of poly nuclear complex is negligible.

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