Thermochimica Acta, 190 (1991) 279–284
Elsevier Science Publishers B.V., Amsterdam

Determination of thermodynamic parameters and equilibrium constants for complexation reactions involving lanthanon(III) ions with 1,2-naphthoquinone-2-semicarbazone-4-sulphonic acid (sodium salt) (NQS · 4S)

Bhagwan S. Garg [1], Vibha Saxena and Ranjana Dixit
Department of Chemistry, University of Delhi, Delhi-110007 (India)

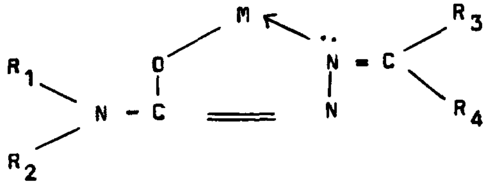
(Received 8 March 1991)

Abstract

The thermodynamic parameters and equilibrium constants of complexation reactions of 1,2-naphthoquinone-2-semicarbazone-4-sulphonic acid (sodium salt) (NQS·4S) involving lanthanon ions were evaluated by potentiometric estimation of $[H^+]$, in aqueous medium at various ionic strengths (0.02, 0.05, 0 10 and 0 20 M $NaClO_4$) and at different temperatures (20, 30, 40 and 50±0.5°C) The $\bar{n}$ and pL values calculated by the method of Bjerrum and Calvin, as modified by Irving and Rossotti, were used for the calculation of the equilibrium constants on an HCL Busy Bee PC/AT computer using the weighted least-squares method The values of S_{min} were also evaluated. The order of equilibrium constants was found to be Ho(III) > Dy(III) > Tb(III) > Y(III) > Eu(III) > Sm(III) > Gd(III) > Nd(III) > Pr(III) > Ce(III) > La(III) The thermodynamic parameters ΔG, ΔH and ΔS were also calculated at a fixed temperature (30±0.05°C) and ionic strength (0.10 M $NaClO_4$)

INTRODUCTION

Semicarbazones produce highly coloured complexes and act as very good chelating agents for metal ions by binding through oxygen and the hydrazino nitrogen atom, as shown below:



1,2-Naphthoquinone-2-semicarbazone-4-sulphonic acid was found to be highly selective for spectrophotometric determination of bismuth, as only mercury [1] and some bivalent metal complexes [2] cause interference.

---

[1] Author to whom correspondence should be addressed.

Semicarbazones of certain aldehydes and ketones have antimicrobial [3,4], herbicidal [5,6], antileukemic [7], analgesic [8] and bacteriostatic [9] activities. The semicarbazone of 5-nitrofurfural (furacin) is used as an antiseptic [10] for dressing wounds. Derivatives of 1-acetylisoquinoline semicarbazones have been found to be potential antimalarial agents [11]. Heterocyclic semicarbazones have been found to be effective against the influenza virus [12].

Because of the widespread application of metal complexes of semicarbazones, we have attempted to calculate equilibrium constants of complexation reactions involving 1,2-naphthoquinone-2-semicarbazone-4-sulphonic acid (sodium salt) (NQS · 4S) and lanthanons.

EXPERIMENTAL

Apparatus and chemicals

A digital pH meter (ECIL model pH-5652) with a glass–calomel electrode assembly was used for the pH measurements. It was calibrated with potassium hydrogen phthalate and phosphate buffers before performing the actual titrations. All measurements were made at a definite temperature maintained constant by using an MLW (NBE type) thermostat U10 (Germany). An HCL Busy Bee PC/AT computer was used for calculations.

1,2-Naphthoquinone-2-semicarbazone-4-sulphonic acid was prepared by dissolving 1,2-naphthoquinone-4-sulphonic acid (sodium salt) in a minimum amount of water and cooling to 5°C. To this solution, semicarbazide hydrochloride (which was also dissolved in the minimum amount of water) was added. The resulting mixture was cooled to 5°C with constant stirring. After stirring for 15 min., the sodium salt of 1,2-naphthoquinone-2-semicarbazone-4-sulphonic acid separated out. The salt, NQS · 4S, was recrystallised from a methanol–water mixture. The purity of the ligand was checked by thin-layer chromatography and elemental analysis. A solution of the ligand was prepared in doubly distilled water.

A 0.04 M solution of tetramethylammonium hydroxide (TMAH) in water was used as titrant. All solutions of metal ion (as perchlorates) were prepared from the corresponding oxides [13] (purity 99%, Johnson–Matthey). The solutions were standardised complexometrically using xylenol orange as indicator. Sodium perchlorate (Fluka) was used to maintain the ionic strength constant. All other chemicals used were of reagent grade. The titrations were performed in a covered double-walled glass cell under a continuous stream of nitrogen (pre-saturated with doubly distilled water).

Titration technique

The following sets of solutions were titrated against (0.04 M) TMAH solution (in water):

(i) 2 ml of $HClO_4$ (0.02 M) + 1 ml of $NaClO_4$ (2.0 M) + 17 ml of water;

(ii) 2 ml of $HClO_4$ (0.02 M) + 1 ml of $NaClO_4$ (2.0 M) + 10 ml of ligand (0.01 M) + 7 ml of water;

(iii) 2 ml of $HClO_4$ (0.02 M) + 1 ml of $NaClO_4$ (2.0 M) + 10 ml of ligand (0.01 M) + 0.5 ml of Ln(III) perchlorate solution (0.02 M) + 6.5 ml of water. From the titration curves for solutions (i) and (ii), the values of $\bar{n}_H$ were calculated at various pH values. The pK_a value of the ligand was found by plotting log ($\bar{n}_H/1 - \bar{n}_H$) vs. pH. From the titration curves of solutions (i), (ii) and (iii), $\bar{n}$ values of the metal complexes were determined at various pH values and the corresponding pL values were calculated. The $\bar{n}$ and pL data were analysed using the weighted least-squares method developed by Sullivan et al. [14] on an HCL Busy Bee PC/AT computer. The weighted least-squares treatment determines the set of β_n values which makes up the function U

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

nearest to zero, by minimising S, where

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

with respect to variation in β_n. The parameter S_{min} has the same statistical distribution as χ^2, with K degrees of freedom and the weights defined in accordance with Sullivan et al. [15].

RESULTS AND DISCUSSION

The complexes of Ln(III) with NQS · 4S show an increase in stability from La(III) to Ho(III), in agreement with the increasing Lewis acidity of the metal ion, i.e. they follow the order La(III) < Ce(III) < Pr(III) < Nd(III) < Gd(III) < Sm(III) < Eu(III) < Y(III) < Tb(III) < Dy(III) < Ho(III). The "log K" values of NQS · 4S–Ln complexes are reported in Tables 1 and 2.

Betts and Dahlinger [16] demonstrated an agreement for the trends in the stability constants of the lanthanon complexes from measurements of changes in the free energy, entropy and enthalpy of the reaction. They showed that for lanthanons beyond europium, although enthalpy changes become positive, complex formation still proceeds because of the large entropy changes (which steadily rise on going from lanthanum to lutetium). This explains the gadolinium break. According to Rossotti [17], the stability constants of Y(III) complexes and Gd(III) complexes should be equal (both ions have no ligand-field stabilisation), but he explained that owing to the smaller size of Y(III), complexes of Y(III) are expected to have higher stability than those of Gd(III).

Stability constants of the complexes were found to decrease with the

TABLE 1

Stability constants of trivalent metal complexes of NQS·4S in aqueous medium at different ionic strengths and at a temperature of 30±0.05°C

Metal ion	Stability constant	Ionic strength μ				$\log K_1^0$
		0.02 M	0.05 M	0.10 M	0.20 M	
H^+		8.00	7.88	7.68	7.44	
Ho(III)	$\log K_1$	6.08	6.05	5.98	5.90	6.16
	$\log K_2$	5.49	5.43	5.36	5.31	
	S_{min}	0.0109	0.0327	0.0327	0.0108	
Dy(III)	$\log K_1$	5.97	5.93	5.88	5.80	6.04
	$\log K_2$	5.15	5.11	5.06	4.98	
	S_{min}	0.0069	0.0069	0.0068	0.0067	
Tb(III)	$\log K_1$	5.74	5.71	5.69	5.65	5.78
	$\log K_2$	4.55	4.41	4.48	4.35	
	S_{min}	0.0556	0.0065	0.0546	0.0064	
Y(III)	$\log K_1$	5.51	5.47	5.46	5.45	5.56
	$\log K_2$	4.75	4.79	4.61	4.69	
	S_{min}	0.0131	0.0011	0.0161	0.0129	
Eu(III)	$\log K_1$	5.35	5.31	5.27	5.27	5.41
	$\log K_2$	4.50	4.50	4.44	4.43	
	S_{min}	0.0016	0.0032	0.0016	0.0047	
Sm(III)	$\log K_1$	5.18	5.12	5.06	4.97	5.25
	$\log K_2$	4.37	4.24	4.23	4.09	
	S_{min}	0.0215	0.02116	0.0206	0.0199	
GD(III)	$\log K_1$	4.87	4.83	4.81	4.73	4.92
	$\log K_2$	4.00	3.96	3.94	3.90	
	S_{min}	0.0007	0.0008	0.0007	0.0009	
Nd(III)	$\log K_1$	4.58	4.52	4.50	4.46	4.64
	$\log K_2$	3.38	3.34	3.32	3.28	
	S_{min}	0.0065	0.0058	0.0055	0.0050	
Pr(III)	$\log K_1$	4.43	4.39	4.37	4.34	4.47
	$\log K_2$	3.50	3.46	3.44	3.42	
	S_{min}	0.0087	0.0079	0.0075	0.0033	
Ce(III)	$\log K_1$	4.25	4.21	4.19	4.15	4.30
	$\log K_2$	3.14	3.14	3.08	3.08	
	S_{min}	0.0002	0.0000	0.0003	0.0000	
La(III)	$\log K_1$	4.07	4.01	3.98	3.89	4.15
	$\log K_2$	2.93	2.88	2.83	2.74	
	S_{min}	0.0001	0.0000	0.0000	0.0000	

increasing ionic strength of the medium (Table 1) which is in good agreement with the Debye–Hückel equation (in ref. 18). The values of thermodynamic stability constants, which are obtained by plotting $\log K_1$ vs. $\sqrt{\mu}$ and extrapolating to zero ionic strength, are given in Table 1.

In the present case, it was found that the pK_a values and equilibrium constants decrease with increase in temperature. The values of $\log K_1$ were plotted against $1/T$, and the overall free energy, enthalpy and entropy

TABLE 2

Stability constants of trivalent metal complexes of NQS·4S in aqueous medium (at ionic strength $\mu = 0.10$ M $NaClO_4$) at different temperatures, and thermodynamic parameters (at 30 ± 0.05 °C)

Metal ion	Stability constant	Temperature (°C)			$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	ΔS (kJ K^{-1} mol^{-1})
		20	40	50			
H^+		7.78	7.51	7.33			
Ho(III)	log K_1	6.16	5.91	5.79			
	log K_2	5.57	5.29	5.17	33.09	17.33	0.0518
	S_{min}	0.0110	0.0324	0.0322			
Dy(III)	log K_1	6.05	5.72	5.63			
	log K_2	5.23	5.32	4.81	32.48	25.99	0.0213
	S_{min}	0.0070	0.0158	0.0063			
Tb(III)	log K_1	5.86	5.49	5.40			
	log K_2	4.59	4.22	4.19	31.48	31.19	0.0008
	S_{min}	0.0091	0.0083	0.0481			
Y(III)	log K_1	5.64	5.37	5.24			
	log K_2	4.88	4.69	4.37	30.21	20.79	0.0309
	S_{min}	0.0133	0.0010	0.0150			
Eu(III)	log K_1	5.43	5.16	5.00			
	log K_2	4.58	4.32	4.20	29.16	20.79	0.02758
	S_{min}	0.0017	0.0042	0.0023			
Sm(III)	log K_1	5.21	4.94	4.81			
	log K_2	4.40	4.06	4.00	28.00	20.79	0.0238
	S_{min}	0.0217	0.0196	0.0181			
Gd(III)	log K_1	4.99	4.65	4.54			
	log K_2	4.13	3.80	3.71	26.61	24.26	0.0079
	S_{min}	0.0007	0.0006	0.0000			
Nd(III)	log K_1	4.69	4.39	4.29			
	log K_2	3.49	3.21	3.12	24.90	19.06	0.0192
	S_{min}	0.0083	0.0042	0.0032			
Pr(III)	log K_1	4.47	4.23	4.13			
	log K_2	3.54	3.32	3.22	24.18	20.79	0.0112
	S_{min}	0.0095	0.0024	0.0041			
Ce(III)	log K_1	4.31	4.06	3.92			
	log K_2	3.22	2.95	2.85	23.18	19.06	0.0138
	S_{min}	0.0010	0.0001	0.0000			
La(III)	log K_1	4.10	3.86	3.70			
	log K_2	2.96	2.51	2.53	22.02	20.79	0.0037
	S_{min}	0.0001	0.0000	0.0000			

changes (ΔG, ΔH and ΔS) at 30 ± 0.05 °C were calculated and are reported in Table 2. The results show that complexation reactions are favourable at ordinary temperatures. The entropy changes for the complexation reactions were found to be positive, which indicates that the complexation between lanthanons and NQS · 4S is entropically favoured.

REFERENCES

1 T. Ueda, A. Takada and K. Kosugi, Yakugaku Zasshi, 92 (1972) 332.

2 S. Mukherjee, B.S. Garg and R.P Singh, Acta Cienc. Indica, [Ser.] Chem., 9 (1983) 4

3 P A Barrett, Nature (London), 206 (1965) 1340.

4 J R. Doamaral, E.J. Blanz and F A. French, J. Med. Chem., 12 (1969) 21.

5 K.K. Showa Denko, Japan Kokai Tokkyo Koho JP 60, 11458 (8511, 458); Chem Abstr., 102 (1985) 220598r

6 R J Anderson, M M Leippe and J. Bamberg, Eur Pat Appl. EP258 182 (Cl. C07 D2t5/02), 2 March 1988, U.S. Pat. Appl. 894 990, 8 August 1986

7 J R Dimmock, D C. Smith, J.M Brenner, S.S. Jonnalagadda, M.S. Sardesai, J D. Wood and G E. Bigam, Eur J Med. Chem.-Chim Ther., 21 (3) (1986) 187

8 A Burger, Relation of chemical structure and biological activity, in Medicinal Chemistry, Edn. 3, Wiley, New York, 1970, p. 65.

9 Y. Fang, Z Sun, Z. Ren, J. Xiang, Z Xue and T. Li, Yingyong Huaxue, 4(5) (1987) 69

10 N.M Samus, E N. Shlyakhov, T A Burdanka, T.S. Chaika, V I Tsapkov and N G. Mukutsa, Khim. Farm. Zh, 20 (1986) 1071

11 D. Klayman, J.P. Scovill and J.F. Bartosevich, J. Med. Chem., 27 (1) (1984) 84.

12 A B. Tomchin, V.S Dmitraukha, V.I Ilenko and V G Platnov, Khim. Farm Zh, 17 (1983) 691

13 N E. Topp, The Chemistry of Rare Earth Elements, Elsevier, London, 1965, p 115

14 J C. Sullivan, J Rydberg and W.F Miller, Acta Chem. Scand., 13 (1959) 2023

15 J C. Sullivan, J. Rydberg and W.F Miller, Acta Chem Scand., 13 (1959) 2059

16 R H Betts and O.F. Dahlinger, Can J. Chem., 37 (1959) 91

17 F.J.C Rossotti, Discuss Faraday Soc, 26 (1958) 190.

18 R Nasanen and A. Ekman, Acta Chem. Scand., 6 (1952) 1389