*Thermochimica Acta*, 195 (1992) 169–175
Elsevier Science Publishers B.V., Amsterdam

# Evaluation of thermodynamic functions and stability constants of lanthanon(III) complexes with 1,2-naphthoquinone-2-thiosemicarbazone-4-sulphonic acid (sodium salt) (NQTS.4S) from potentiometric data

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

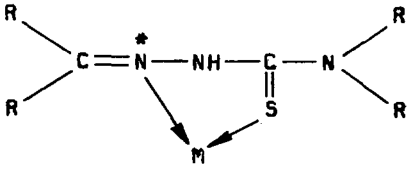
(Received 10 May 1991)

## Abstract

Stability constants and thermodynamic functions of formation of 1:1 and 1:2 binary complexes of lanthanons(III) with 1,2-naphthoquinone-2-thiosemicarbazone-4-sulphonic acid (NQTS.4S) ligand have been determined by a potentiometric technique, at various ionic strengths ($\mu = 0.02$, 0.05, 0.10 and 0.20 M $NaClO_4$) in aqueous medium and at various temperatures (20, 30, 40 and $50 \pm 0.5\,^{\circ}C$). The $\bar{n}$ and pL values have been subjected to the weighted least squares method to obtain $\beta_n$ values on an HCL Busy Bee PC/AT computer. The values of $S_{\min}$ have also been calculated. The order of stability constants has been found to be La(III) < Ce(III) < Pr(III) < Gd(III) < Sm(III) < Eu(III) < Y(III) < Tb(III) < Dy(III) < Ho(III). The thermodynamic functions ($\Delta G$, $\Delta H$, $\Delta S$) for these complexation reactions have also been evaluated under suitable conditions.

## INTRODUCTION

Thiosemicarbazones (TSCs) are a class of compounds obtained by condensation of thiosemicarbazide with suitable aldehydes or ketones. They can act as chelating agents for metal ions by bonding through sulphur and the hydrazino nitrogen atom marked with asterisk [1] as shown in Formula 1.



Formula 1.

---

[1] Author to whom correspondence should be addressed.

Thiosemicarbazones find wide applications in biological and medical fields. The antitubercular activity of *p*-acetamide benzaldehyde thiosemicarbazone, which is found to be enhanced by the presence of a small amount of copper ions [2], was reported for the first time by Domagk et al. [1]. Thiosemicarbazones show antiparasitic [3], antineoplastic [4], antiinflammatory [5] and antithyroid [6] types of activities. The metal–TSC complexes were found to be active against influenza [7], protozoa [8], smallpox [9] and pests [10]. Antibacterial activity of the 2-benzoylpyridine thiosemicarbazone and the complexes of the ligand with Ni(II), Co(II), Fe(II), Cu(II), Mn(II), Zn(II) and Cd(II) have been studied against *Escherichia coli* by De and Guha [11]. West et al. have studied chemical and antifungal properties of 2-acetyl-pyridine $^4N$-diethyl- and $^4N$-dipropylthiosemicarbazone and their Cu(II) [12], Ni(II) [13] complexes.

These findings have led recently to an increased interest in the chemistry of metal chelates of thiosemicarbazones. In this communication we report the complexation behaviour of another biologically active thiosemicarbazone, 1,2-naphthoquinone-2-thiosemicarbazone-4-sulphonic acid (NQTS.4S).

## EXPERIMENTAL

### *Apparatus*

A digital pH meter (ECIL model pH-5652) with a combined glass electrode, was used for the pH measurements. It was calibrated with potassium hydrogenphthalate and phosphate buffers before performing the actual titrations. An HCL Busy Bee PC/AT computer was used for calculations. All measurements were made at a definite temperature, maintained constant (±0.5 °C) by using an MLW (West Germany) (NBE type) thermostat U10.

### *Chemicals*

1,2-Naphthoquinone-2-thiosemicarbazone-4-sulphonic acid (NQTS.4S) $\cdot$ $2H_2O$ (sodium salt) was prepared by dissolving the requisite amount of 1,2-napthoquinone-4-sulphonic acid (Na salt) in the minimum amount of water (cooled to 5 °C) and adding to it an aqueous solution containing thiosemicarbazide hydrochloride, which was also cooled to 5 °C. After stirring for about 15 min, the sodium salt of 1,2-napthoquinone-2-thiosemicarbazone-4-sulphonic acid separated out. The NQTS.4S $\cdot$ $2H_2O$ was recrystallised from methanol–water mixture. The purity of the ligand was checked by TLC and elemental analyses. Solutions of the ligand were prepared in doubly distilled water.

A 0.04 M tetramethylammonium hydroxide (TMAH) solution in water was used as titrant. All metal ion (as perchlorates) solutions were prepared from their corresponding oxides [14] (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 presaturated nitrogen (with doubly distilled water).

### *Titration technique*

The method of Bjerrum and Calvin as modified by Irving and Rossotti [15] was used to determine the values of $\bar{n}$ and pL. The following solutions were titrated pH-metrically against standard 0.04 M TMAH in doubly distilled water: (i) 2.2 ml $HClO_4$ (0.02 M) + 1.0 ml $NaClO_4$ (2.0 M) + 16.8 ml $H_2O$; (ii) 2.2 ml $HClO_4$ (0.02 M) + 1.0 ml $NaClO_4$ (2.0 M) + 10 ml ligand (0.01 M) + 6.8 ml $H_2O$; (iii) 2.2 ml $HClO_4$ (0.02 M) + 1.0 ml $NaClO_4$ (2.0 M) + 10 ml ligand (0.01 M) + 0.5 ml metal solution (0.02 M) + 6.3 ml $H_2O$.

These titrations were also performed at various temperatures (20, 30, 40, $50 \pm 0.5\,^\circ$C) and at various ionic strengths ($\mu = 0.02$, 0.05 and 0.2 M $NaClO_4$). The ligand NQTS.4S possesses one ionisable hydrogen ion. From titration curves of (i) and (ii), the values of $\bar{n}_H$ were calculated at various pH values and from the plot of $\log(\bar{n}_H/1 - \bar{n}_H)$ versus pH, the p$K_a$ values of the ligand were determined. From the titration curves of solutions (i), (ii) and (iii) the values of $\bar{n}$ and pL of the metal complexes were determined at various pH values by using an HCL Busy Bee PC/AT computer. The corresponding values of stability constants were calculated using the weighted least-squares method of Sullivan et al. [16] which determines the set of $\beta_n$ values which makes the function

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

nearest to zero, by minimising

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

with respect to variation in $\beta_n$. $S_{\min}$ has the same statistical distribution as $\chi^2$ with $K$ degrees of freedom and the weights defined in accordance with Sullivan et al. [17].

## RESULTS AND DISCUSSION

The order of log $K_1$ values for NQTS.4S–Ln complexes have been found to be La(III) < Ce(III) < Pr(III) < Gd(III) < Sm(III) < Eu(III) < Y(III) < Tb(III) < Dy(III) < Ho(III).

TABLE 1

Stability constants of trivalent metal complexes of NQTS.4S in aqueous medium at different ionic strengths and temperature of 30 ± 0.5 ° C

| Metal ion | Stability constant | Ionic strength | | | | $\log K_1$ |
|---|---|---|---|---|---|---|
| | | 0.02 | 0.05 | 0.10 | 0.20 | |
| $H^+$ | | 8.19 | 8.04 | 7.93 | 7.68 | 5.85 |
| Ho(III) | $\log K_1$ | 6.06 | 5.94 | 5.85 | 5.79 | |
| | $\log K_2$ | 5.40 | 5.28 | 5.19 | 5.14 | |
| | $S_{\min}$ | 0.0234 | 0.0233 | 0.0222 | 0.0328 | |
| Dy(III) | $\log K_1$ | 5.80 | 5.76 | 5.70 | 5.65 | 5.70 |
| | $\log K_2$ | 4.62 | 4.58 | 4.52 | 5.47 | |
| | $S_{\min}$ | 0.0078 | 0.0064 | 0.0063 | 0.0062 | |
| Tb(III) | $\log K_1$ | 5.58 | 5.54 | 5.50 | 5.44 | 5.50 |
| | $\log K_2$ | 4.41 | 4.36 | 4.33 | 4.27 | |
| | $S_{\min}$ | 0.0085 | 0.0086 | 0.0084 | 0.0081 | |
| Y(III) | $\log K_1$ | 5.40 | 5.38 | 5.34 | 5.26 | 5.34 |
| | $\log K_2$ | 4.18 | 4.14 | 4.06 | 3.96 | |
| | $S_{\min}$ | 0.0379 | 0.0086 | 0.0365 | 0.0053 | |
| Eu(III) | $\log K_1$ | 5.26 | 5.20 | 5.14 | 5.02 | 5.14 |
| | $\log K_2$ | 3.87 | 3.81 | 3.75 | 3.63 | |
| | $S_{\min}$ | 0.0057 | 0.0061 | 0.0056 | 0.0046 | |
| Sm(III) | $\log K_1$ | 5.05 | 5.00 | 4.92 | 4.82 | 4.92 |
| | $\log K_2$ | 3.82 | 3.77 | 3.69 | 3.60 | |
| | $S_{\min}$ | 0.0318 | 0.0300 | 0.0270 | 0.0044 | |
| Gd(III) | $\log K_1$ | 4.76 | 4.72 | 4.64 | 4.57 | 4.64 |
| | $\log K_2$ | 3.69 | 3.65 | 3.57 | 3.48 | |
| | $S_{\min}$ | 0.0077 | 0.0073 | 0.0060 | 0.0052 | |
| Nd(III) | $\log K_1$ | 4.52 | 4.46 | 4.38 | 4.30 | 4.38 |
| | $\log K_2$ | 3.61 | 3.55 | 3.47 | 3.39 | |
| | $S_{\min}$ | 0.0059 | 0.0052 | 0.0044 | 0.0372 | |
| Pr(III) | $\log K_1$ | 4.48 | 4.28 | 4.20 | 4.10 | 4.20 |
| | $\log K_2$ | 3.45 | 3.35 | 3.29 | 3.11 | |
| | $S_{\min}$ | 0.0077 | 0.0060 | 0.0022 | 0.0016 | |
| Ce(III) | $\log K_1$ | 4.20 | 4.08 | 4.00 | 3.90 | 4.00 |
| | $\log K_2$ | 3.48 | 3.32 | 3.31 | 3.21 | |
| | $S_{\min}$ | 0.0130 | 0.0115 | 0.0105 | 0.0091 | |
| La(III) | $\log K_1$ | 3.96 | 3.89 | 3.82 | 3.72 | 3.82 |
| | $\log K_2$ | 2.94 | 2.86 | 2.68 | 2.58 | |
| | $S_{\min}$ | 0.0035 | 0.0028 | 0.0003 | 0.0002 | |

Log $K_1$ (Tables 1 and 2) values have been found to increase with the increase in atomic number from lanthanum(III) to holmium(III), in agreement with increasing acidity of the metal ion. Betts and Dahlinger [18] gave an agreement for the trends in the stability constant of the lanthanon complexes from measurements of changes in free energy, entropy and enthalpy of the reaction. They showed that for lanthanons beyond europium, though enthalpy changes become positive, complex formation still

TABLE 2

Stability constants of trivalent metal complexes of NQTS.4S in aqueous medium at ionic strength $\mu = 0.10$ M $NaClO_4$ and at different temperatures, with overall free energy enthalpy and entropy changes at 30 ± 0.5 °C

| Metal ion | Stability constants | Temperature ($T \pm 0.5$ °C) | | | $-\Delta G$ (kJ mole$^{-1}$) | $-\Delta H$ (kJ mole$^{-1}$) | $\Delta S$ (kJ K$^{-1}$ mole$^{-1}$) |
|---|---|---|---|---|---|---|---|
| | | 20 | 40 | 50 | | | |
| $H^+$ | | 8.32 | 7.89 | 7.53 | | | |
| Ho(III) | log $K_1$ | 6.10 | 5.69 | 5.54 | 32.35 | 27.71 | 0.0150 |
| | log $K_2$ | 5.44 | 5.03 | 4.88 | | | |
| | $S_{min}$ | 0.0225 | 0.0219 | 0.0216 | | | |
| Dy(III) | log $K_1$ | 5.76 | 5.55 | 5.42 | 31.39 | 20.82 | 0.0347 |
| | log $K_2$ | 4.58 | 4.37 | 4.24 | | | |
| | $S_{min}$ | 0.0064 | 0.0061 | 0.0058 | | | |
| Tb(III) | log $K_1$ | 5.64 | 5.34 | 5.22 | 30.31 | 24.24 | 0.0196 |
| | log $K_2$ | 4.47 | 4.17 | 4.05 | | | |
| | $S_{min}$ | 0.0091 | 0.0075 | 0.0067 | | | |
| Y(III) | log $K_1$ | 5.50 | 5.20 | 5.10 | 29.59 | 26.00 | 0.0117 |
| | log $K_2$ | 4.20 | 3.93 | 3.80 | | | |
| | $S_{min}$ | 0.0061 | 0.0322 | 0.0046 | | | |
| Eu(III) | log $K_1$ | 5.37 | 5.00 | 4.86 | 28.56 | 27.71 | 0.0112 |
| | log $K_2$ | 3.96 | 3.60 | 3.45 | | | |
| | $S_{min}$ | 0.0171 | 0.0044 | 0.0034 | | | |
| Sm(III) | log $K_1$ | 5.06 | 4.77 | 4.67 | 27.21 | 26.00 | 0.0038 |
| | log $K_2$ | 3.85 | 3.52 | 3.40 | | | |
| | $S_{min}$ | 0.0325 | 0.0211 | 0.0172 | | | |
| Gd(III) | log $K_1$ | 4.81 | 4.50 | 4.38 | 24.24 | 0.0046 | 25.66 |
| | log $K_2$ | 3.74 | 3.41 | 3.29 | | | |
| | $S_{min}$ | 0.0078 | 0.0048 | 0.0035 | | | |
| Nd(III) | log $K_1$ | 4.50 | 4.24 | 4.12 | 22.53 | 0.0054 | 24.16 |
| | log $K_2$ | 3.59 | 3.33 | 3.21 | | | |
| | $S_{min}$ | 0.0057 | 0.0034 | 0.0026 | | | |
| Pr(III) | log $K_1$ | 4.26 | 4.01 | 3.88 | 20.82 | 0.0067 | 22.86 |
| | log $K_2$ | 3.34 | 3.10 | 2.97 | | | |
| | $S_{min}$ | 0.0026 | 0.0012 | 0.0008 | | | |
| Ce(III) | log $K_1$ | 4.10 | 3.89 | 3.79 | 19.06 | 0.0100 | 22.11 |
| | log $K_2$ | 3.35 | 3.20 | 3.05 | | | |
| | $S_{min}$ | 0.0132 | 0.0090 | 0.0061 | | | |
| La(III) | log $K_1$ | 3.92 | 3.70 | 3.60 | 20.82 | 0.0008 | 21.15 |
| | log $K_2$ | 2.78 | 2.54 | 2.44 | | | |
| | $S_{min}$ | 0.0005 | 0.0002 | 0.0001 | | | |

proceeds because of the large entropy changes (which readily rise from lanthanum to lutetium). This explains the gadolinium break. According to Rossotti [19], the stability constant of Y(III) complexes and Gd(III) complexes should be equal (both ions have no ligand field stabilisation) but he explained that due to the smaller size of Y(III), complexes of Y(II) are expected to have higher stability than those of Gd(III).

The stability constants of the complexes have been found to decrease with increasing ionic strength of the medium, which is in agreement with the Debye–Huckel equation (in ref. 19). The results are summarised in Table 1.

The stability constants decrease with increase in temperature [18] along with $pK_a$ values (Table 2). These results are in good agreement with those of Pitzer [20]. There are no absolute regularities in thermodynamic functions among the lanthanon(III) ions, which indicates that the ligand field stabilisation energy is negligible for these complexes.

The thermodynamic parameters ($\Delta G$, $\Delta H$ and $\Delta S$) were calculated by using the relationships

$$\Delta G = -RT \ln K$$

$$\mathrm{d} \log K/\mathrm{d}(1/T) = -\Delta H/2.303R$$

and

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

The overall free energy change, enthalpy and entropy changes at 30 ± 0.5 °C are reported in Table 2. The negative free energy change ($\Delta G$) in each case indicates that the complexation is spontaneous.

The enthalpy changes are exothermic. The positive values for $\Delta S$ indicate that complexation reactions are entropically favoured under the experimental conditions used.

Ligand NQTS.4S has been compared with NQS.4S (semicarbazone) for its chelating ability towards lanthanons. Results presented in Table 3 show that the stability of NQS-4S–Ln complexes is higher than that of NQTS.4S–Ln complexes.

TABLE 3

Comparison of log $K_1$ values of lanthanon complexes of NQS.4S and NQTS.4S at ionic strength $\mu = 0.10$ M $NaClO_4$ and temperature = 30 ± 0.5 °C in aqueous medium

| Metal ion | log $K_1$ | |
|---|---|---|
| | NQS.4S | NQTS.4S |
| Ho(III) | 5.98 | 5.85 |
| Dy(III) | 5.88 | 5.70 |
| Tb(III) | 5.69 | 5.50 |
| Y(III) | 5.46 | 5.34 |
| Eu(III) | 5.27 | 5.14 |
| Sm(III) | 5.06 | 4.92 |
| Gd(III) | 4.81 | 4.64 |
| Nd(III) | 4.50 | 4.38 |
| Pr(III) | 4.37 | 4.20 |
| Ce(III) | 4.19 | 4.00 |
| La(III) | 3.98 | 3.82 |

This is explained on the hard–soft acid–base (HSAB) principle. Oxygen is a harder base than sulphur. The lanthanons behave as typical hard acids, bonding preferentially to oxygen donor ligands. Therefore the stability of lanthanon complexes of 1,2-naphthoquinone-2-semicarbazone-4-sulphonic acid (sodium salt) (NQS.4S) is higher than that of lanthanon complexes of NQTS.4S. In both the cases 1 : 1 and 1 : 2 complexes were found to be formed.

## ACKNOWLEDGEMENT

One of the authors (V.S.) is grateful to C.S.I.R., New Delhi (India) for providing her with financial assistance.

## REFERENCES

1 G. Domagk, R. Behnisch, F. Mietzsch and H. Schmidt, Naturwissenschaften, 33 (1946) 315.
2 K.Z. Libermeister, Naturforsch, Teil B, (1950) 79.
3 D.R. Sridhar, K.S. Rao, K. Rastogi and N.L. Jain, Indian J. Chem., Sect. 8, 26(6) (1987) 596.
4 F.A. Gollmick, E. Shutter, Stud. Biophys., 117 (1987) 41.
5 I.P. Singh, A.K. Saxena, J.N. Sinha and K. Shaker, Eur. J. Med. Chem. Chim. Ther., 20(3) (1985) 283.
6 V.K. Tiwari and P.K. Srivastava, Indian J. Pharm. Sci., 49(2) (1987) 52.
7 N.N. Orlova, V.A. Aksenova, D.A. Selidovkin, N.S. Bogdanova and G.N. Pershin, Russ. Pharmacol. Toxicol. (Moscow), 31 (1968) 725.
8 K. Butter, U.S. Patent 3,382,266 (1968).
9 D.J. Bauer, L.Sb. Vineent, C.H. Kempe and A.W. Downe, Lancet, 2 (1963) 494.
10 C.W. Johnson, J.W. Joyner and R.P. Perry, Antibiot. Chemother. (Washington D.C.), 2 (1952) 636.
11 K. De and A.K. Guha, Indian J. Chem., Part A, 29 (1990) 605.
12 D.X. West, C.S. Carlson and C.P. Galloway, Transition Met. Chem., 15 (1990) 91.
13 D.X. West, C.S. Carlson, A.E. Liberta, J.N. Albert and C.R. Daniel, Transition Metal Chem., 15 (1990) 341.
14 N.E. Topp, The Chemistry of Rare Earth Elements, Elsevier, London, 1965, p. 115.
15 H.M. Irving and H.S. Rossotti, J. Chem. Soc., (1954) 2904.
16 J.C. Sullivan, J. Rydberg and W.F. Miller, Acta Chem. Scand., 13 (1959) 2023.
17 J.C. Sullivan, J. Rydberg and W.F. Miller, Acta Chem. Scand., 13 (1959) 2059.
18 R.H. Betts and O.F. Dahlinger, Can. J. Chem., 37 (1959) 91.
19 F.J.C. Rossotti, Discuss. Faraday Soc., 26 (1958) 190.
20 K.S. Pitzer, J. Am. Chem. Soc., 50 (1937) 2365.