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DETERMINATION OF STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF COMPLEXES OF DIACETYLMONO(LEPIDYL)HYDRAZONE (DALH) WITH LANTHANONS

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ABSTRACT

The consecutive stability constants of the 1:1 and 2:1 chelate species formed by the interaction of diacetylmono(lepidyl)hydrazone (DALH) with lanthanon ions have been determined potentiometrically at various ionic strengths (0.02, 0.05, 0.1 and 0.2 M NaCl) and temperatures (25, 30, 40 and 50 °C ± 0.5 °C) in 75% ethanol/water medium. The method of Bjerrum and Rossotti was used to calculate the values of $\bar{n}$ and pL. Stability constants, and the values of $S_{\min}$ and the thermodynamic parameters ΔG, ΔH and ΔS are reported.

INTRODUCTION

In view of the widespread applications of hydrazones, it was decided to study the interaction of diacetylmono(lepidyl)hydrazone (DALH) with metal ions. Recent surveys have reported that hydrazones are used as anti-bacterial, anti-viral, anti-fungal, anti-microbial, anti-amoebiodal, anti-cancer, anti-liver inhibition and anti-tumour agents. In analytical chemistry, the formation of hydrazones is extensively used in the detection, determination and isolation of compounds containing the carbonyl group. They can be used as indicators over ranges of high pH. Hydrazones have also been used extensively in the detection and quantitative determination of several metals in micro amounts; and they give fast level dyes for wool, nylon and leather.

EXPERIMENTAL

Instrumentation

A digital pH meter (ECIL Model, pH 5651) with a glass electrode (0–14 pH range) was used for the pH measurements. The pH meter was standar-

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dized using potassium hydrogen phthalate and phosphate buffers before the titrations were performed.

Reagents

DALH was prepared by dissolving 10 g (0.06 mol) of 2-hydrazinolepidine in the minimum volume of concentrated HCl and adding 15 g of crystallized sodium acetate in 100 ml of water, followed by a solution of 5 ml of diacetyl (0.06 mol) in 80 ml of water. The solution was then shaken vigorously in a 1 l flask with a cork until all the lepidylhydrazone was crystallized. The purity of the ligand was checked by IR spectroscopy, proton magnetic resonance, elemental analysis, thin-layer chromatography and melting point (m.p. 203–205 ° C). The solution of the ligand was prepared in 80% (v/v) aqueous ethanol. All the metal ion solutions were prepared and standardized by conventional procedures. Sodium chloride (E. Merck) was used to keep the ionic strength constant over the various sets. A solution of sodium hydroxide (NaOH) (E. Merck) in 75% ethanol (aqueous) was used as the titrant. Ethanol was purified as described by Vogel [1].

Potentiometric titrations

The method of Bjerrum and Calvin as modified by Irving and Rossotti [2,3] was used to determine $\bar{n}$ and pL values. The experimental procedure involved potentiometric titration of the following solutions against 0.05 M NaOH in 75% ethanol/water medium.

(i) 1.5 ml HCl (0.05 M) + 1.0 ml NaCl (2.0 M) + 3.75 ml water + 18.75 ml ethanol

(ii) 1.5 ml HCl (0.05 M) + 1.0 ml NaCl (2.0 M) + 1.75 ml water + 10.0 ml ligand (0.005 M) + 10.75 ml ethanol

(iii) 1.5 ml HCl (0.05 M) + 1.0 ml NaCl (2.0 M) + 0.75 ml water + 10.0 ml ligand (0.005 M) + 10.75 ml ethanol + 1.0 ml metal solution (0.01 M).

These titrations were repeated for ionic strengths 0.02, 0.05, 0.1 and 0.2 M NaCl. In order to calculate the thermodynamic parameters, the same titrations were also carried out at temperatures of 25, 30, 40 and 50 ° C ± 0.05 ° C. The temperature was maintained at a constant level (±0.05 ° C) in all the systems using a MLW (FRG) NBE-type thermostat. Pre-saturated nitrogen with 75% (v/v) ethanol (aqueous) was bubbled through the reaction solution.

CALCULATIONS

The average number of protons bound per metal ion $\bar{n}_H$, and the free ligand exponent pL were determined by the expressions described by Irving and Rossotti in order to evaluate the pK_a values for the ligand and the stability constants for the complexes. The $\bar{n}$ values (0.1–2.2) indicate the formation of 1 : 1 and 2 : 1 complexes (L : M). The stability constants were computed on an Uptron PC plus computer using a weighted least-squares program modelled on that of Sullivan et al. [4]. The weighted least-squares treatment determines that set of β_n values which make the function

$$U\left[U = \sum_{n=0}^{N} (y - x - nz)\beta_n \chi^n\right]$$

nearest to zero by minimizing

$$S\left[S = \sum_{i=1}^{I} U^2(x_i y_i z_i)\right]$$

TABLE 1

Stability constants of lanthanon complexes of DALH at various ionic strengths at $T = 25\,^\circ C \pm 0.5\,^\circ C$ in 75% (v/v) ethanol/water medium

System	Stability constant	Ionic strength (M NaCl)			
		0.02	0.05	0.1	0.2
DALH	pK_a	5.32	5.24	5.14	4.98
Ho(III)–DALH	$\log K_1$	4.32	4.20	4.14	3.91
	$\log K_2$	3.00	3.36	3.23	2.80
	S_{min}	0.01480	0.00670	0.00001	0.00240
Dy(III)–DALH	$\log K_1$	4.29	4.06	4.00	3.86
	$\log K_2$	3.59	3.27	3.16	2.51
	S_{min}	0.00170	0.00580	0.02010	0.01610
Tb(III)–DALH	$\log K_1$	4.26	3.96	3.94	3.79
	$\log K_2$	3.34	3.18	2.96	2.42
	S_{min}	0.00230	0.02030	0.01900	0.00530
Sm(III)–DALH	$\log K_1$	4.19	3.84	3.80	3.69
	$\log K_2$	3.20	2.93	2.87	2.39
	S_{min}	0.00460	0.00610	0.01090	0.00430
Nd(III)–DALH	$\log K_1$	4.10	3.75	3.68	3.57
	$\log K_2$	3.08	2.80	2.72	2.30
	S_{min}	0.00090	0.00200	0.00640	0.00310
Gd(III)–DALH	$\log K_1$	4.01	3.60	3.54	3.47
	$\log K_2$	2.86	2.59	2.51	2.26
	S_{min}	0.00080	0.00210	0.00360	0.00400
Pr(III)–DALH	$\log K_1$	3.89	3.57	3.51	3.36
	$\log K_2$	2.58	2.30	2.36	2.17
	S_{min}	0.00020	0.00240	0.00140	0.00150
La(III)–DALH	$\log K_1$	3.72	3.48	3.36	3.27
	$\log K_2$	2.29	2.08	2.04	2.08
	S_{min}	0.00010	0.00180	0.00270	0.00120

with respect to variation in β_n. S_{min} has the same statistical distribution as χ^2 with K degrees of freedom and with weights defined in accordance with Rydberg and Sullivan [5], and can be equated to χ^2.

RESULTS AND DISCUSSION

The stability constants calculated in this way are given in Tables 1 and 2. ΔH was calculated by the graphical method of Yatsimirskii and Vasilev [6];

TABLE 2

Stability constants of lanthanon complexes of DALH at various temperatures ($\mu = 0.1$ M NaCl)

System	Stability constant	Temperature (°C)			
		25	30	40	50
DALH	pK_a	5.14	4.96	4.74	4.50
Ho(III)-DALH	log K_1	4.14	3.91	3.71	3.60
	log K_2	3.23	3.14	3.11	2.90
	S_{min}	0.00001	0.00240	0.00210	0.00100
Dy(III)-DALH	log K_1	4.00	3.78	3.62	3.50
	log K_2	3.16	2.99	2.89	2.74
	S_{min}	0.02010	0.00140	0.00170	0.00020
Tb(III)-DALH	log K_1	3.94	3.70	3.53	3.40
	log K_2	2.96	2.88	2.74	2.66
	S_{min}	0.01900	0.00042	0.00620	0.00350
Sm(III)-DALH	log K_1	3.80	3.56	3.38	3.28
	log K_2	2.87	2.78	2.67	2.56
	S_{min}	0.01090	0.00580	0.00095	0.01260
Nd(III)-DALH	log K_1	3.68	3.50	3.30	3.20
	log K_2	2.72	2.65	2.56	2.44
	S_{min}	0.00640	0.00380	0.00097	0.00030
Gd(III)-DALH	log K_1	3.54	3.46	3.24	3.10
	log K_2	2.51	2.49	2.40	2.30
	S_{min}	0.00360	0.00620	0.00024	0.00040
Pr(III)-DALH	log K_1	3.51	3.38	3.17	3.02
	log K_2	2.36	2.30	2.24	2.12
	S_{min}	0.00140	0.00420	0.00120	0.02540
La(III)-DALH	log K_1	3.36	3.28	3.09	2.96
	log K_2	2.08	2.04	2.00	1.98
	S_{min}	0.00270	0.00800	0.00025	0.03200

TABLE 3

Thermodynamic parameters of lanthanon complexes of DALH at $\mu = 0.1$ M NaCl and $T = 30\,^{\circ}\mathrm{C} \pm 0.5\,^{\circ}\mathrm{C}$

System	$\log K_1^{\ominus}$	$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	ΔS (kJ K^{-1} mol^{-1})
Ho(III)-DALH	4.49	22.676	32.540	−0.03254
Dy(III)-DALH	4.46	21.923	24.885	−0.00979
Tb(III)-DALH	4.43	21.458	24.885	−0.01129
Sm(III)-DALH	4.01	20.656	22.969	−0.00765
Nd(III)-DALH	3.93	20.300	26.796	−0.02146
Gd(III)-DALH	3.73	20.066	24.885	−0.01288
Pr(III)-DALH	3.71	19.606	24.885	−0.01744
La(III)-DALH	3.67	19.024	22.969	−0.01300

and ΔG and ΔS were calculated by conventional methods (Table 3).

Order of stability constants

Complexes of lanthanons with DALH show an increase in stability from La(III) to Ho(III), in accordance with increasing acidity of the metal ion. The order of stability constants of the complexes with DALH was found to be: La(III) < Pr(III) < Gd(III) < Nd(III) < Sm(III) < Tb(III) < Dy(III) < Ho(III). In all cases, $\log K_1 > \log K_2$. The differences $\log K_1 - \log K_2$ show no definite trend and it seems likely that the cation is modified by the addition of the first ligand in such a way that the forces leading to the interaction of the singly charged 1 : 1 complex with the second ligand molecule are of a different type from those operating between the solvated metal ions and the first ligand molecule.

Effect of ionic strength

The values of the ligand dissociation constants $\mathrm{p}K_a$ decrease with increasing ionic strength of the medium, which is in agreement with the Debye–Hückel equation [7]

$$\mathrm{p}K_a^{\ominus} - \left(A\sqrt{\mu}/1 + \alpha\sqrt{\mu}\right) + C = \mathrm{p}K_\mathrm{a}$$

A similar trend of variation was observed for the stability constants of the complexes. The thermodynamic stability constants were obtained by extrapolating the straight-line plot of $\log K_1$ vs. $\sqrt{\mu}$ to zero ionic strength (Table 3, Fig. 1).

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

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

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

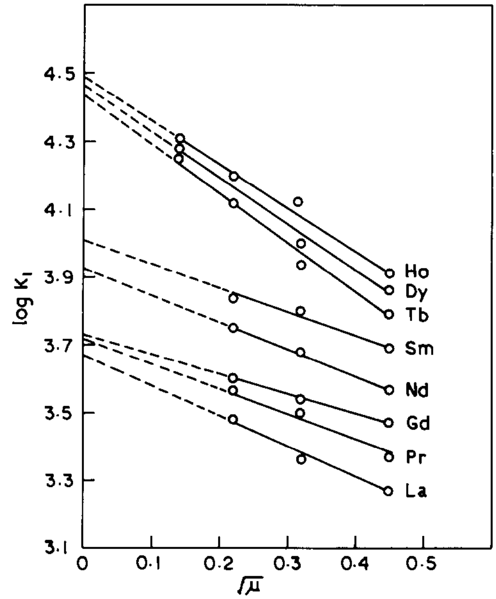

Fig. 1. Plot of log K_1 vs. $\sqrt{\mu}$ of lanthanon complexes of DALH in 75% ethanol–water medium at $30 \pm 0.5\,^{\circ}$C.

The results show that ΔG is negative, which indicates that complexation takes place spontaneously. The enthalpy changes are exothermic. However, the entropy is negative for all the chelates, indicating that the entropy is not favourable for the formation of complexes in this case.

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REFERENCES

1 A.I. Vogel, A Text Book of Practical Organic Chemistry, Longman, New York, 1956, p. 166.
2 H.M. Irving and H.S. Rossotti, J. Chem. Soc., (1953) 3397.
3 H.M. Irving and H.S. Rossotti, J. Chem. Soc., (1954) 2904.
4 J.C. Sullivan, J. Rydberg and W.F. Miller, Acta Chem. Scand., 13 (1959) 2023.
5 J. Rydberg and J.C. Sullivan, Acta Chem. Scand., 13 (1959) 2057.
6 K.B. Yatsimirskii and V.P. Vasilev, Instability Constants of Complex Compounds, Van Nostrand, New York, 1960, p. 63.
7 R. Nasanen and A. Ekman, Acta Chem. Scand., 6 (1952) 1389.