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INVESTIGATIONS OF THE COMPLEXATION EQUILIBRIA AND THERMODYNAMIC PARAMETERS OF BIOLOGICALLY ACTIVE *o*-VANILLINSEMICARBAZONE WITH LANTHANON(III) IONS

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ABSTRACT

The complexation behaviour of *o*-vanillinsemicarbazone (OVSC) with La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Gd^{III}, Sm^{III}, Eu^{III}, Tb^{III}, Y^{III}, Dy^{III} and Ho^{III} ions and the corresponding thermodynamic parameters were evaluated using a pH-titration technique in 50% (v/v) aqueous dioxan medium at various ionic strengths (0.02, 0.05, 0.1 and 0.2 M $NaClO_4$) and at various temperatures (15, 25, 35 and $45 \pm 0.1°$ C). The formation constants log β_n (calculated using the weighted least-squares method) for the complexes increased with the atomic number of the lanthanon, with a break at gadolinium. The thermodynamic parameters ΔG, ΔH and ΔS for the formation of the complexes were also evaluated. Complexation reactions were found to be entropically favoured under the experimental conditions used.

INTRODUCTION

Interest in the study of the complexation behaviour of semicarbazones has increased rapidly due to their potential chelating power towards traces of metal ions in biological systems. Domagk et al. [1] reported the antitubercular activity of metal semicarbazones. Semicarbazones also act as herbicides [2]. The semicarbazones of certain aldehydes and ketones have significant antimicrobial activity [3–7]. Some coordination compounds of vanillinsemicarbazone have been found to be biologically active [8]. Lambrou [9] has reported that the thio and semicarbazone derivatives of *o*-vanillin are potential fungistatic and tuberculostatic agents. Semicarbazones also have a large number of analytical applications [10,11]. A literature survey revealed that no study has been carried out on the complexation behaviour of *o*-vanillinsemicarbazone (OVSC) with inner transition metal ions. In this paper an attempt is made to study this.

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EXPERIMENTAL

Instrumental

A digital pH meter (model PHM 83; Radiometer, Copenhagen) with a single glass–calomel electrode assembly was used for the pH measurements.

Chemicals and reagents

o-Vanillinsemicarbazone (OVSC) was prepared by condensing equimolar quantities of semicarbazide hydrochloride and *o*-vanillin in the presence of sodium acetate and a few drops of HCl. The purity of the OVSC was checked by IR and ^{1}H NMR spectroscopies, elemental analysis and thin layer chromatography (melting point, 235–237 °C). Solutions of all metal ions (as perchlorate) were prepared from their corresponding oxides [12] (purity, 99%; Johnson Matthey). The solutions were standardized complexometrically using xylenol orange as indicator. $NaClO_4$ (Merck) was used to maintain constant ionic strength. Me_4NOH (TMAH) (Merck) (0.1 M) in 50% aqueous dioxan was used as titrant. The ligand solution was also prepared in 50% (v/v) dioxan–H_2O medium. The dioxan used was purified according to the procedure of Weissberger [13]. All chemicals used were of AnalaR grade (BDH). The titrations were carried out in a nitrogen atmosphere (N_2 purity, ~ 99.9%) which was presaturated with 50% (v/v) aqueous dioxan.

Potentiometric titrations

The method of Bjerrum and Calvin as modified by Irving and Rossotti [14] was used to determine $\bar{n}$ and pL values. The experimental procedure involved the potentiometric titration of the following solutions against 0.1 M TMAH in 50% dioxan–water medium: (i) $HClO_4$ (1.0×10^{-2} M); (ii) $HClO_4$ (1.0×10^{-2} M) + OVSC (2.5×10^{-3} M); (iii) $HClO_4$ (1.0×10^{-2} M) + OVSC (2.5×10^{-3} M) + M^{3+} (0.5×10^{-3} M).

These titrations were repeated for ionic strengths μ of 0.02, 0.05, 0.1 and 0.2 M $NaClO_4$. In order to determine the thermodynamic parameters ΔG, ΔH and ΔS, the titrations were also repeated at various temperatures (15, 25, 35 and 45 ± 0.1 °C). The experimental temperature was maintained constant within ± 0.1 °C using an MLW (Radiometer, F.R.G.) NBE-type thermostat. The pH values in aquo–organic mixtures were corrected using the method of Van Uitert and Hass [15], and volume corrections were also applied according to the method of Rao Balachandra and Mathur [16].

The average number of protons bound per free ligand $\bar{n}_H$, the average number of ligands bound per metal ion $\bar{n}$ and the free ligand exponent pL were determined from the expression given by Irving and Rossotti [14] to

TABLE 1

Stability constants of lanthanon(III)–OVSC complexes at various ionic strengths at 35 ± 0.1° C

System	Stability constants	Ionic strength (M $NaClO_4$)				
		0.2	0.1	0.05	0.02	0.00 [a]
OVSC	log K_1^H	10.30	10.40	10.52	10.62	–
La^{III}–OVSC	log K_1	7.06	7.32	7.36	7.63	7.85
	S_{min}	0.00798	0.00273	0.08691	0.01508	–
Ce^{III}–OVSC	log K_1	7.47	7.82	7.87	7.98	8.20
	S_{min}	0.00289	0.00163	0.06865	0.00345	–
Pr^{III}–OVSC	log K_1	7.60	7.92	8.08	8.25	8.55
	S_{min}	0.01275	0.01560	0.05172	0.00833	–
Nd^{III}–OVSC	log K_1	7.79	8.07	8.22	8.44	8.70
	S_{min}	0.02114	0.01290	0.05950	0.01823	–
Gd^{III}–OVSC	log K_1	8.06	8.22	8.40	8.62	8.87
	S_{min}	0.03676	0.02762	0.05762	0.09231	–
Sm^{III}–OVSC	log K_1	8.12	8.43	8.57	8.73	9.00
	S_{min}	0.05125	0.05057	0.07684	0.04229	–
Eu^{III}–OVSC	log K_1	8.35	8.60	8.77	8.86	9.13
	S_{min}	0.00732	0.02169	0.12345	0.02764	–
Tb^{III}–OVSC	log K_1	8.49	8.69	8.93	9.00	9.26
	S_{min}	0.01429	0.02170	0.09707	0.06492	–
Y^{III}–OVSC	log K_1	8.57	8.89	9.12	9.16	9.47
	S_{min}	0.03036	0.01390	0.08126	0.02903	–
Dy^{III}–OVSC	log K_1	8.70	9.02	9.20	9.23	9.62
	S_{min}	0.03739	0.01774	0.06316	0.05882	–
Ho^{III}–OVSC	log K_1	8.83	9.16	9.24	9.51	9.85
	S_{min}	0.06782	0.00493	0.06863	0.01933	–

[a] Obtained by extrapolation of log K_1 vs. $\mu^{1/2}$.

evaluate pK_a of the ligand and the metal–ligand stability constant log β_n. The stability constants were computed on an H.P. 9050 FORTRAN 77 computer using a weighted least-squares program similar to that of Sullivan et al. [17].

The weighted least-squares treatment gives that set of β_n values which allows function (1) to be nearest to zero by minimizing function (2) as β_n varies

$$\sum_{n=0}^{N} (y - x - nz)\beta_n X^n \tag{1}$$

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

TABLE 2

Stability constants of the lanthanon(III)–OVSC complexes at $\mu = 0.1$ M $NaClO_4$ at various temperatures and the thermodynamic parameters at $\mu = 0.1$ M $NaClO_4$ at 35 ± 0.1°C

System	Stability constants	Temperature (°C)			$-\Delta G$ (kcal mol^{-1})	$-\Delta H$ (kcal mol^{-1})	ΔS (kcal K^{-1} mol^{-1})
		15	25	45			
OVSC	$\log K_1^H$	10.70	10.51	10.20	–	–	–
La^{III}–OVSC	$\log K_1$	7.59	7.37	7.25	10.31	2.63	0.02483
	S_{min}	0.00794	0.00223	0.00602			
Ce^{III}–OVSC	$\log K_1$	7.93	7.90	7.62	11.02	2.22	0.02857
	S_{min}	0.00252	0.00310	0.00551			
Pr^{III}–OVSC	$\log K_1$	8.03	8.00	7.76	11.16	3.64	0.02441
	S_{min}	0.01121	0.01530	0.00545			
Nd^{III}–OVSC	$\log K_1$	8.24	8.12	7.93	11.37	4.25	0.02311
	S_{min}	0.00294	0.00886	0.01940			
Gd^{III}–OVSC	$\log K_1$	8.34	8.26	8.10	11.58	3.23	0.02711
	S_{min}	0.02525	0.07027	0.05380			
Sm^{III}–OVSC	$\log K_1$	8.55	8.44	8.30	11.88	3.44	0.02740
	S_{min}	0.01651	0.04786	0.04036			
Eu^{III}–OVSC	$\log K_1$	8.74	8.63	8.42	12.12	4.45	0.02490
	S_{min}	0.01104	0.01818	0.03415			
Tb^{III}–OVSC	$\log K_1$	8.90	8.80	8.50	12.24	4.25	0.02594
	S_{min}	0.01077	0.00223	0.06780			
Y^{III}–OVSC	$\log K_1$	9.08	9.01	8.56	12.52	3.85	0.02814
	S_{min}	0.00675	0.00489	0.05790			
Dy^{III}–OVSC	$\log K_1$	9.28	9.13	8.71	12.71	7.28	0.01762
	S_{min}	0.01387	0.00202	0.06591			
Ho^{III}–OVSC	$\log K_1$	9.32	9.30	8.81	12.90	3.23	0.3139
	S_{min}	0.00092	0.00053	0.07566			

The minimized function (2), designated as 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 [18]. It can be equated to χ^2.

The pK_a values and metal–ligand formation constants evaluated at four different ionic strengths (0.2, 0.1, 0.05 and 0.02 M $NaClO_4$ at 35 ± 0.1°C) and at four different temperatures (15, 25, 35 and 45 ± 0.1°C at 0.1 M $NaClO_4$) are given in Tables 1 and 2. The thermodynamic parameters ΔG, ΔH and ΔS for the complexation reactions were calculated using the standard method [19] and the values are given in Table 2.

RESULTS AND DISCUSSION

The complexes of lanthanon(III) with OVSC show an increase in stability from lanthanum(III) to holmium(III) in agreement with the increasing Lewis acidity of the metal ion. The log K_1 values are in the order: $\mathrm{La^{III}} < \mathrm{Ce^{III}} < \mathrm{Pr^{III}} < \mathrm{Nd^{III}} < \mathrm{Gd^{III}} < \mathrm{Sm^{III}} < \mathrm{Eu^{III}} < \mathrm{Tb^{III}} < \mathrm{Y^{III}} < \mathrm{Dy^{III}} < \mathrm{Ho^{III}}$.

If the bonds between ligand and metal were ionic, the Born relation, $E = z^2(1 - 1/D)/2r$, would hold for the energy change on complexation of a gaseous ion of charge z and radius r in a medium of dielectric constant D. However, the plot of log K_1 vs. z^2/r is not linear, and is consistent with covalent bonding. The values of log K_1 of the complexes gradually increase from lanthanum(III) to holmium(III) in accordance with the decrease in ionic radii, with the exception of gadolinium and yttrium. The value of gadolinium is lower than that of samarium, illustrating the famous gadolinium break [20,21]. The value of yttrium is lower than that of dysprosium. The values of log K_2 could not be determined due to the hydrolysis of the 1 : 1 (M : L) complexes.

The stability constants of the complexes decrease with increasing ionic strength of the medium, which is in agreement with the Debye–Hückel equation [22]. A plot of log K_1 vs. $\mu^{1/2}$ is linear and the extrapolation to zero ionic strength gives the thermodynamic stability constants. The values of the thermodynamic stability constants are given in Table 1.

The thermodynamic parameters (ΔG, ΔH and ΔS) for the complexation reactions were calculated using the following relationships

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

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

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

The overall free energy, enthalpy and entropy changes at 35 ± 0.1°C are reported in Table 2. The results indicate that ΔG and ΔH are negative, which shows that complexation reactions are favourable at ordinary temperatures. The change in entropy on complexation is related to the changes in the modes of vibration of these molecules. In aqueous systems, chelation is favoured by the release of bound water molecules [23]. There are no absolute regularities in the thermodynamic functions of the lanthanon ions, which indicates that the ligand field stabilization energy is negligible in these complexes. The entropy changes for the complexation reactions are positive, which indicates that the complexes are entropically favoured.

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