

EVALUATION OF THERMODYNAMIC PARAMETERS AND STABILITY CONSTANTS OF BIVALENT METAL COMPLEXES OF BIOLOGICALLY ACTIVE *o*-VANILLINSEMICARBAZONE

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(Received 25 February 1988)

ABSTRACT

Thermodynamic parameters ΔG , ΔH and ΔS and stability constants of Mg, Mn, Pb, Zn, Co and Ni complexes of *o*-vanillinsemicarbazone have been determined using the pH titration technique in 50% (v/v) aqueous dioxane at different ionic strengths (0.02, 0.05, 0.1 and 0.2 M NaClO₄) and at different temperatures (25, 35, 40 and $45 \pm 0.1^\circ\text{C}$). The stability constants for the complexes have been found to be entropically favoured.

INTRODUCTION

Currently, considerable interest is being devoted to the study of complexation equilibria of semicarbazones, owing to their great chelating power towards trace metal ions of biological importance. Lambrou [1] has reported the thio and semicarbazone derivatives of *o*-vanillin as potential fungistatic and tuberculostatic agents. Some coordination compounds of vanillinsemicarbazone have also been found to be biologically active [2]. Semicarbazones which have a large number of analytical applications [3,4] have also been found to have antitubercular and herbicidal properties [5,6]. In view of the widespread applications of semicarbazones and considering the biological potentialities of *o*-vanillinsemicarbazone (OVSC), we have chosen OVSC as a ligand to study its complexation equilibria towards bivalent metal ions (transition and non-transition).

EXPERIMENTAL

Instrumental

A digital pH meter (Radiometer Copenhagen, model PHM83) with a single glass calomel electrode assembly was used for pH measurements.

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Chemicals and reagents

o-Vanillinsemicarbazone 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 OVSC was checked by IR and ^1H NMR spectroscopy, elemental analysis and thin layer chromatography; m.p. = 235–237°C. All metal ion solutions were prepared from their corresponding sulphates or nitrates (AR, BDH) in double distilled water and standardized by conventional methods. NaClO_4 (Merck) was used to maintain constant ionic strength. 0.1 M Tetramethylammonium hydroxide (TMAH) (Merck) in 50% aqueous dioxan was used as titrant and the ligand solution was prepared in 100% dioxan medium. The dioxan used was purified by Weissberger's [7] procedure. The titrations were carried out in a nitrogenous atmosphere (N_2 purity ~ 99.9%). The N_2 was presaturated with 50% (v/v) aqueous dioxan before passing through the reaction mixture.

Potentiometric titrations

The method of Bjerrum and Calvin, as modified by Irving and Rossotti [8,9], was used to determine the values of \bar{n} , the average number of ligand molecules bound per metal ion and pL, the free ligand exponent. The experimental procedure involved the potentiometric titrations of the following solutions against 0.1 M TMAH in 50% (v/v) dioxan–water media: (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^{2+} (5.0×10^{-4} M). These titrations were also repeated for different ionic strengths: $\mu = 0.02, 0.05, 0.1, 0.2$ M NaClO_4 . In order to determine thermodynamic parameters such as ΔG , ΔH and ΔS the titrations have also been repeated at various temperatures (25, 35, 40 and $45 \pm 0.1^\circ\text{C}$). The experimental temperature was kept constant within $\pm 0.1^\circ\text{C}$ by using a MLW (F.R.G.) NBE-type thermostat. The pH values in aqueous–organic mixtures have been corrected using the method of van Uitert and Hass [10] and corrections to the volume have also been performed according to the method of Rao and Mathur [11].

Calculations

The parameters \bar{n}_{H} , the average number of protons bound per free ligand ion, \bar{n} and pL ligand exponent were evaluated using the expressions described by Irving and Rossotti [8,9]. Using these parameters, the $\text{p}K_{\text{a}}$ values of the ligand and stability constants of its complexes were calculated. The stability constants were computed on an H.P. 9050 FORTRAN 77 computer using a weighted least squares program designed after that of Sullivan et al.

[12]. By this method the 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 was determined by minimizing

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

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 [13]. S_{\min} can be equated to χ^2 .

RESULTS AND DISCUSSION

The pK_a values and metal–ligand formation constants thus evaluated at four different ionic strengths (0.02, 0.05, 0.1 and 0.2 M NaClO₄) at $35 \pm 0.1^\circ\text{C}$ and at four different temperatures (25, 35, 40 and $45 \pm 0.1^\circ\text{C}$) at 0.1 M NaClO₄ are given in Tables 1 and 2. The thermodynamic parameters ΔG , ΔH and ΔS for the complexation reactions were calculated by the standard method [14] and are also given in Table 2.

Out of the various transition elements studied for complexation reactions, stability constants of Cd, Fe, U and Cu could not be determined by this

TABLE 1

Stability constants of the bivalent–OVSC complexes at $35 \pm 0.1^\circ\text{C}$ at different ionic strengths

System	Stability constant	Ionic strength (M NaClO ₄)				
		0.2	0.1	0.05	0.02	0.00 *
OVSC	Log K_1^H	10.30	10.40	10.52	10.64	–
Mg ^{II} –OVSC	Log K_1	3.55	3.72	3.93	4.05	4.30
	S_{\min}	0.00366	0.00130	0.00285	0.03165	
Mn ^{II} –OVSC	Log K_1	5.08	5.28	5.45	5.49	5.77
	S_{\min}	0.04301	0.01677	0.01737	0.01196	
Pb ^{II} –OVSC	Log K_1	6.91	6.94	7.17	7.29	7.45
	S_{\min}	0.00142	0.01375	0.00334	0.00659	
Zn ^{II} –OVSC	Log K_1	7.07	7.12	7.27	7.38	7.50
	S_{\min}	0.00158	0.00144	0.00136	0.00019	
Co ^{II} –OVSC	Log K_1	7.24	7.43	7.53	7.79	8.02
	S_{\min}	0.00513	0.00286	0.00062	0.00213	
Ni ^{II} –OVSC	Log K_1	7.78	8.14	8.24	8.40	8.72
	S_{\min}	0.00282	0.00467	0.00312	0.00425	

* Obtained by extrapolation of the log K vs. $\mu^{1/2}$ plot.

TABLE 2

Stability constants of the bivalent OVSC complexes at $\mu = 0.1$ M NaClO₄ at different temperatures and their thermodynamic parameters at $\mu = 0.1$ M NaClO₄ and $35 \pm 0.1^\circ$ C

System	Stability constant	Temperature ($^\circ$ C)			$-\Delta G$ (kcal mol ⁻¹)	$-\Delta H$ (kcal mol ⁻¹)	ΔS (kcal K ⁻¹ mol ⁻¹)
		25	40	45			
OVSC	Log K_1^H	10.51	10.31	10.20	—	—	—
Mg ^{II} -OVSC	Log K_1	4.10	3.68	3.63	5.24	3.90	0.00435
	S_{min}	0.00134	0.00059	0.01092			
Mn ^{II} -OVSC	Log K_1	5.35	5.19	4.93	7.44	4.55	0.00938
	S_{min}	0.01793	0.00708	0.02611			
Pb ^{II} -OVSC	Log K_1	7.04	6.84	6.74	9.78	8.67	0.00360
	S_{min}	0.01482	0.00381	0.01323			
Zn ^{II} -OVSC	Log K_1	7.23	7.06	6.97	10.03	8.02	0.00652
	S_{min}	0.00159	0.00157	0.00196			
Co ^{II} -OVSC	Log K_1	7.57	7.38	7.33	10.47	5.42	0.01639
	S_{min}	0.00435	0.00324	0.00139			
Ni ^{II} -OVSC	Log K_1	8.23	7.97	7.83	11.47	7.37	0.01331
	S_{min}	0.03294	0.01700	0.01030			

technique as in some cases (Cu, U) the complexation equilibria shifted to the right immediately after mixing the reactants even at very low pH values. In other cases (Cd, Fe) the complexes formed are readily hydrolyzed even at lower pH values. Only results for Mg, Mn, Pb, Co, Ni and Zn are reported in Tables 1 and 2. The formation constants follow the general order of Mellor and Maley [15] and Irving and Williams [16,17].

The values of the dissociation constant of the ligand (pK_a) decrease with increase in ionic strength of the medium, which is in agreement with the Debye-Hückel equation [18]

$$pK_a^0 - [A\mu^{1/2}/(1 + \alpha\mu^{1/2})] + C\mu = pK_a$$

A similar trend of variation has also been observed in the case of the stability constants of complexes. The thermodynamic stability constants (at $\mu = 0.00$ M NaClO₄) are given in Table 1 and were obtained by extrapolating the straight line plot of $\log K_1$ against $\mu^{1/2}$ to zero ionic strength.

The various thermodynamic parameters ΔG , ΔH and ΔS for complexation reactions have been calculated by using the following relationship [14] and values are given in Table 2.

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

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

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

The results indicate that ΔG and ΔH are negative which shows that complexation reactions are favourable at ordinary temperatures. The change in entropy upon complexation of a bivalent metal ion is related both to

changes in the number of particles in the system and to changes in the mode of vibration of these particles. In aqueous systems, complexation by chelation is favoured by the release of bound water molecules [19]. The entropy change for the present complexation reactions are positive which indicates that complexes are entropically favoured.

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