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A THERMODYNAMIC STUDY OF THE COMPLEXING OF SOME BIVALENT METAL IONS WITH *N-o*-TOLYLBENZOHYDROXAMIC ACID

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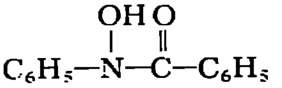
ABSTRACT

The thermodynamic stepwise formation constants and thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0 are determined for the complexation reactions of UO_2^{2+}, Be^{2+}, Cd^{2+} and Hg^{2+} with *N-o*-tolylbenzohydroxamic acid by the Bjerrum—Calvin pH titration technique. Aqueous dioxane (50% v/v) is used as the solvent medium because of inadequate water solubility of the reagent and its metal chelates. The formation of 1 : 1 and 1 : 2 complexes of these divalent metal ions is shown. The order of stability is $UO_2^{2+} > Be^{2+} > Cd^{2+} > Hg^{2+}$, and $\log K_1 > \log K_2$. Other factors which effect chelate stability of the metal ions are briefly discussed.

INTRODUCTION

N-Phenylbenzohydroxamic acid (PBHA)



$$C_6H_5—\overset{\overset{\Large OH}{|}}{N}—\overset{\overset{\Large O}{\|}}{C}—C_6H_5$$

has many analytical [1—4] and medicinal uses [5]. Analogous compounds are continually being sought in the hope of developing a reagent with superior analytical characteristics [6—8]. However, most studies with PBHA derivatives have been concerned with substitution in the C-phenyl ring. Ryan and Lutwick [9] believe that investigation of the effects of substitution in the *N*-phenyl ring would be rewarding, since such substituents should have a greater effect on the complexing of protons or metals. This has encouraged a systematic search for better reagents among the family of hydroxamic acids substituted in the *N*-phenyl ring [10].

N-o-Tolylbenzohydroxamic acid (*o*-TBHA) is already established as a specific reagent for the spectrophotometric determination of vanadium [11]. It has also been proposed as a gravimetric reagent for uranium [12], niobium and tantalum [13]. Recently, *ortho*-substituted reagents were found to be potentially useful in selective precipitation techniques because of steric hin-

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drance [14]. Donor properties of various hydroxamic acids have already been reviewed [15]. No thermodynamic data, however, have been reported on hydroxamic acids substituted in the *N*-phenyl ring, hence the need for the present investigation.

This deals with the potentiometric determination of the stepwise thermodynamic formation constants of UO_2^{2+}, Be^{2+}, Cd^{2+}, and Hg^{2+} with *o*-TBHA in dioxane—water (50% v/v) at 25 and 35 ± 0.1°C, for calculation of thermodynamic functions such as ΔG^0, ΔH^0 and ΔS^0 associated with complexing. The Bjerrum—Calvin pH titration technique [16] was used. Some thermodynamic acid association constants have already been reported [17]. The low water solubility of the reagent and its metal chelates necessitated the use of mixed solvents.

EXPERIMENTAL

Reagents and solutions

All chemicals used were of A.R. (B.D.H.) or G.R. (Merck) grades unless otherwise stated. *N*-*o*-Tolylbenzohydroxamic acid was prepared as already described [18]. The melting point was 106°C compared to the literature value of 104°C. Metal perchlorate solutions were used to minimize complexing of the metal ions by anions.

Carbonate-free KOH was prepared by the electrolytic method given by Vogel [19] and dioxane was purified by the procedure of Weissberger [20]. Pure distilled water, redistilled over alkaline permanganate and freed from carbon dioxide, was used throughout the investigation.

pH meter

A battery-operated Radiometer pH meter model pHM-4C reading in 0.01 unit of pH was used. Calibration of the pH meter was done with standard Beckman buffers at the beginning of each titration and checked after completion.

Titration procedure

A weighed quantity of *o*-TBHA, corresponding to a 0.01 M solution in a final volume of 50 ml, was placed in a dry titration vessel and 25 ml of freshly distilled dioxane was added. Then 10 ml of a 0.005 M solution of metal perchlorate and 15 ml of water was added to yield a 50 vol. % final composition of dioxane—water in the mixture. Due allowance for the contraction in volume on mixing the two solvents was made [21,22].

The titration vessel with its contents was then thermostated at 25 or 35 ± 0.1°C and nitrogen, pre-saturated with 50 vol. % aqueous dioxane, was bubbled through the solution. The glass and calomel electrodes were placed in the solution which was titrated against 0.1 M KOH, also prepared in 50 vol. % dioxane, by adding small aliquots and noting the pH meter reading.

TABLE 1

Thermodynamic formation constants of complexes of *N*-*o*-tolylbenzohydroxamic acid [a]

Complexing ion	25°C					35°C					Method of computation [c]
	log K_1	log K_2	log K_{AV}	log (K_1/K_2) [b]	$\bar{n}$ range	log K_1	log K_2	log K_{AV}	log (K_1/K_2) [b]	$\bar{n}$ range	
H^+	11.12					10.95					
UO_2^{2+}	10.98	9.00	9.99	1.98	0.24–1.88	10.80	8.91	9.86	1.89	0.28–1.77	L
	10.92	9.05				10.76	8.94				G
	10.92	9.06				10.85	8.86				H
	11.00	9.11				10.88	8.99				A
Be^{2+}	8.25	6.79	7.52	1.46	0.29–1.77	8.11	6.63	7.37	1.48	0.26–1.87	L
	8.29	6.82				8.15	6.69				G
	8.28	6.71				8.19	6.60				H
	8.31	6.83				8.22	6.71				A
Cd^{2+}	7.38	6.11	6.75	1.27	0.22–1.81	7.23	6.03	6.63	1.20	0.23–1.78	L
	7.43	6.09				7.28	6.01				G
	7.41	6.19				7.20	6.11				H
	7.45	6.18				7.19	6.13				A
Hg^{2+}	6.14	4.99	5.57	1.15	0.21–1.79	5.88	4.76	5.32	1.12	0.25–1.70	L
	6.09	4.93				5.92	4.77				G
	6.12	4.92				5.91	4.69				H
	6.18	5.04				5.84	4.72				A

[a] [Metal] = 0.001 M; [*o*-TBHA] = 0.01 M; [KOH] = 0.1 M. Medium: 50% (v/v) dioxane—water.

[b] Values of log K_{AV} and log(K_1/K_2) have been computed from log K_1 and log K_2 obtained by the least-square method.

[c] L: values obtained by the least-squares method, maximum scatter in log K_1 or log K_2 is ± 0.05 log unit. G: values calculated by Goldberg's method. H: values calculated by interpolation at half $\bar{n}$ values. A: values calculated by the successive approximations method. The values of log K_1 and log K_2 are the average of at least ten titration points.

Titrations were performed repeatedly until two sets of values differing by only ±0.01 pH unit were obtained.

CALCULATIONS

The calculation of stepwise first and second formation constants, K_1 and K_2, of the complexes from the results of the metal—ligand titrations was done by the least-squares method as described by Albert and Serjeant [23]. Other computational methods, viz. interpolation at half $\bar{n}$ values [24], the successive approximation method [24], and Goldberg's modified calculation procedure [25], were used to determine the stepwise metal—ligand stability constants; values are summarized in Table 1. Compared to graphical methods, these computational methods are valuable in that they provide greater statistical accuracy and yield true thermodynamic constants at all points.

Values of the overall change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) accompanying complexation were determined from the temperature coefficient and the Gibbs—Helmholtz equation [26] (Table 2). The ligational standard free energy change was obtained from

$$\Delta G^0 = -2.303\ RT \log K_n$$

The standard enthalpy change, ΔH^0, was calculated from Van't Hoff's equation [27] at two temperatures T_1 (298.2 K) and T_2 (308.2 K)

$$-\Delta H^0 = \frac{4.576(\log K_n^{T_1} - \log K_n^{T_2})}{(1/T_1 - 1/T_2)}$$

which simplifies to

$$\Delta H^0 = 42.06(\log K_n^{308.2} - \log K_n^{298.2})$$

Finally, $\Delta G^0 = \Delta H^0 - T\Delta S^0$ was followed to estimate the standard entropy change (ΔS^0) accompanying the metal—ligand reactions.

RESULTS AND DISCUSSION

The value of stepwise formation constants $\log K_1$ and $\log K_2$ evaluated by the various computational methods are in fair agreement (Table 1). The stabilities of the complexes decrease with increase in temperature, thereby showing that formation of the complexes is favoured at lower temperatures. It is also evident that all the metal chelates are quite stable. Since activity coefficient corrections have been applied, the $\log K_n$ values reported here are thermodynamic constants. The stability constants, determined as above, were reproducible to 0.05 log units or less in replicate determinations, while variation in the initial concentration of metal and chelating agent gave results with a variation of ±0.10 log units or less. An error of 0.01 pH unit in the pH measurements was found to affect the log K values by approximately 0.1 log unit. There was no evidence of metal ion hydrolysis, polynuclear complexes, protonated complexes or influence of Cl^-, NO_3^-, ClO_4^-, K^+ or Na^+ on values of

TABLE 2

Thermodynamic paramters for *N*-*o*-tolylbenzohydroxamic acid chelates [a]

Metal ion		$-\Delta G°$ (kcal mole^{-1})		$-\Delta H°$ (kcal mole^{-1})	$\Delta S°$ (cal deg^{-1} mole^{-1})	
		25°C	35°C		25°C	35°C
UO_2^{2+}	log K_1	14.98	15.23	7.57	24.85	24.85
	log K_2	12.28	12.57	3.79	28.47	28.49
	log K_2K_2	27.26	27.80	11.36	53.32	53.34
Be^{2+}	log K_1	11.26	11.44	5.89	18.01	18.01
	log K_2	9.27	9.35	6.73	8.52	8.50
	log K_1K_2	20.52	20.79	12.62	26.49	26.51
Cd^{2+}	log K_1	10.07	10.19	6.31	12.61	12.59
	log K_2	8.34	8.50	3.37	16.67	16.64
	log K_1K_2	18.41	18.70	9.68	29.28	29.27
Hg^{2+}	log K_1	8.38	8.29	10.94	−8.59	−8.60
	log K_2	6.81	6.71	9.67	−9.59	−9.60
	log K_1K_2	15.19	15.01	20.61	−18.18	−18.17

[a] Thermodynamic data computed from formation constants obtained by the least squares method.

formation constants. In all metal—ligand titrations, the $\bar{n}$ value steadily increased with pH from ~0.2 to >1.5 ≤ 2 before precipitation occurred, indicating that 1 : 2 metal—ligand compounds represented the highest degree of complexation achieved.

The log K_1 and K_2 values indicate the following order of stability: UO_2^{2+} > Be^{2+} > Cd^{2+} > Hg^{2+}. This is in accordance with the results of Basolo and Pearson [28], which is the order expected from their electronic configuration. If the metal—ligand bond is considered to be purely electrostatic in nature, the strength of the bond should increase linearly with increase in ionic potential, Z^2/r, where Z is the effective nuclear charge and r is the radius of the metal ion. Thus the above stability order is justified on the basis of Z^2/r values for these metal ions (Table 3).

As normally encountered, the average stability constants, log K_{AV}, are con-

TABLE 3

Ionic potential (Z^2/r) and electronegativity of metal ions

Ion	Ionic radius [a] (Å)	Z^2/r	Electronegativity [b]
UO_2^{2+}	0.80	20.00	1.38
Be^{2+}	0.35	11.43	1.57
Cd^{2+}	1.03	3.88	1.69
Hg^{2+}	1.12	3.57	2.00

[a] M.J. Sienko and R.A. Plane, Physical Organic Chemistry, W.A. Benjamin, New York, 1963, p. 124.

[b] A.L. Allred, J. Inorg. Nucl. Chem., 17 (1961) 215.

sistently lower than T_pK_a of *o*-TBHA. Separation factors between the first and second stability constants are well within the expected range and the absence of high values implies there is little or no steric hindrance to the addition of a second chelate group. In the case of chelating agents containing bulky substituents near the donor atoms, such steric hindrance causes K_1/K_2 to be unusually high. This has been demonstrated [29] for *N*-substituted ethylenediamine complexes of Ni^{2+}. Furthermore, as the tendency of a metal ion to take up ligand is proportional to the number of vacant sites, the ratio between consecutive constants is, to a certain extent, statistically determined [30]. For an anionic ligand, coulombic attraction is greater for M^{2+} compared to MA^-. As such, $\log K_1 - \log K_2$ is usually positive [31]. Table 1 shows that for all systems studied here, $\log K_1 - \log K_2$ is positive and lies in the range 1.12—1.89 log unit.

Thermodynamic functions

The error in ΔG^0 and ΔH^0 values lies in the range 0.2—0.5 kcal mole^{-1} and that for ΔS^0 is 0.5 cal deg^{-1} mole^{-1}. From Table 2 it is evident that the reactions of UO_2^{2+}, Be^{2+}, Cd^{2+} and Hg^{2+} with *o*-TBHA are exothermic and explain why the formation constants have higher values at lower temperatures. The free energies of formation (ΔG^0) of the complexes have more negative values as the temperature increases, showing complex formation to be a spontaneous process. Both enthalpy (ΔH^0) and entropy (ΔS^0) changes seem to favour the formation of complexes.

The net entropy changes associated with the metal—chelate formation can be attributed to a combination of the following: (i) increase in ΔS^0 values owing to release of water of hydration; (ii) decrease in entropy of translation on formation of one chelate from two species, i.e. the metal ion and the ligands; and (iii) decrease in configuration entropy of the ligand on complex formation. For reactions with charged donor groups, the entropy changes associated with (i) predominate because of neutralization of charge on the metal ion; this results in a greater release of water of hydration and hence greater disorder of the partially immobilized and oriented water dipoles. The entropy changes accompanying the formation of UO_2^{2+}, Be^{2+} and Cd^{2+} complexes are positive for both the first and second steps, indicating that the water of hydration is removed during the formation of both 1 : 1 and 1 : 2 complexes. The only exception is Hg^{2+}, which has maximum ligational enhalpy charges. The negative values of both enthalpy and entropy encounted here suggest that the enthalpy term is favourable and the entropy term unfavourable for complex formation. This might be due to substitution of solvent molecules attached to the metal ion by the ligand, resulting in release of these solvent molecules.

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