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Note

Thermodynamic metal ligand stability constants of UO_2^{2+}, Be^{2+}, Cd^{2+}, and Hg^{2+} with N-phenyl-*o*-nitrobenzohydroxamic acid

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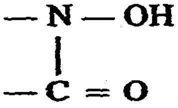
The chelate stability constants and importance of hydroxamic acids as analytical reagents have been reported by several researchers[1–10]. The complexing capacity of hydroxamic acids had already been predicted in 1908 by Werner. The substitution of different groups in the nuclei of the parent compound influences the stabilities of the resulting metal complexes. A survey of the effect of substitution in the aryl nuclei on the stability constants of metal chelates was carried out by Calvin and Wilson[11]. Such studies are important as they help predict what type of substitutents in the molecule might enhance its use for a particular purpose.

Several N-arylhydroxamic acids with the functional grouping(I) have been synthesised



$$\begin{array}{l} —N—OH \\ \quad | \\ —C=O \end{array}$$

(I)

during the last few years and their possible analytical applications were examined. Recently, the stability constants of N-phenyl-*o*-nitrobenzohydroxamic acid with some divalent metal ions have been reported by Agrawal and Tandon[1]. The present paper deals with the stability constants of UO_2^{2+}, Be^{2+}, Cd^{2+} and Hg^{2+} in 50% dioxane–water media at 25 and 35°C.

EXPERIMENTAL

Chemicals

All the chemicals used were of AR or G.R. grades of B.D.H. and E. Merck unless otherwise stated.

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Reagent and metal solutions

The N-phenyl-*o*-nitrobenzohydroxamic acid was prepared by the method as described elsewhere[12], 148° reported 148°[12].

The metal perchlorate solutions were used to minimize complexing of the metal ions by anions.

Carbonate free potassium hydroxide was prepared according to Vogel[13] and dioxane was purified by procedure of Weisberger[14].

Apparatus

A Radiometer pH meter equipped with shielded glass and a calomel electrode was used for the measurement. It is accurate to ±0.01 pH unit.

Procedure

Transfer weighed quantity of hydroxamic acid, corresponding to 0.01 M solution in a final volume of 50 ml, to a dry titration vessel and add 25 ml of freshly distilled dioxane. Next add 10 ml of 0.005 M solution of metal perchlorate and 15 ml of water to yield a final composition of dioxane–water in the mixture to the 50 vol. %. Due allowance for the contraction in volume of mixing of two solvents was made[15,16].

Next the titration vessel with its contents was thermostated at 25°C or 35 ± 0.1 °C and nitrogen, presaturated with 50 vol. % aqueous dioxane, was bubbled through the solution. Place the glass electrode and calemel electrode and the solution was titrated against 0.1 M KOH, which was also prepared in 50 vol. % dioxane, adding the same in small aliquots and noting the pH meter reading, B, each time.

RESULTS AND DISCUSSION

The thermodynamic pK_a value for N-phenyl-*o*-nitrobenzohydroxamic acid in 50 vol. % dioxane was found to be 10.80 and 10.69 at 25°C and 35°C, respectively.

A computer method was used to obtain the thermodynamic stability constants[16] and these data are listed in Table 1. There was no evidence of metal ion hydrolysis, polynuclear complexes, protonated complexes or influence of chloride, nitrate and perchlorate ions.

The log K_1 and K_2 values examined here on comparison show the following order

$UO_2^{2+} > Be^{2+} > Cd^{2+} > Hg^{2+}$

This finding is in agreement with Basolo and Pearson[17] and others[18]. With –O, –O as a donor UO_2^{2+} forms a stronger complex but the order is revised in ligands –O, –N donors. For oxygen donor, therefore, the stability order is expected to be of the same order of their respective Z^2/r values (Table 2). Values of log $K_1 > K_2$ in all the cases. Further, the log K_1 values are plotted against the reciprocal of respective electronegativities which gives a straight line and follow the order

$UO_2^{2+} > Be^{2+} > Cd^{2+} > Hg^{2+}$

The thermodynamic parameters for the N-phenyl-*o*-nitrobenzohydroxamic chelates are summarised in Table 3.

TABLE 1

THERMODYNAMIC METAL LIGAND STABILITY CONSTANTS OF N-PHENYL-*O*-NITROBENZOHYDROXAMIC ACID COMPLEXES IN 50% v/v DIOXANE–WATER

Metal ion	*Temp.* (°C)	*Log* K_1	*Log* K_2	*Log* K_1, K_2
UO_2^{2+}	25	9.80	7.69	17.49
	35	9.60	7.50	17.10
Be^{2+}	25	7.78	5.87	13.65
	35	7.66	5.69	13.35
Cd^{2+}	25	6.21	4.90	11.11
	35	6.00	4.71	10.71
Hg^{2+}	25	5.84	4.52	10.36
	35	5.65	4.35	10.00

TABLE 2

Z^2/r VALUES OF METAL IONS

Ion	*Ionic radius*[20] (*Å*)	Z^2/r	*Electronegativity*[21]
UO_2^{2+}	0.80	20.0	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

TABLE 3

THERMODYNAMIC PARAMETERS FOR N-PHENYL-*O*-NITROBENZOHYDROXAMIC ACID METAL COMPLEXES

Metal ion		$-\Delta F°$ (*kcal mol*$^{-1}$)		$-\Delta H°$ (*kcal mol*$^{-1}$)	$\Delta S°$ (*cal deg*$^{-1}$ *mol*$^{-1}$)	
		25°C	*35°C*		*25°C*	*35°C*
UO_2^{2+}	log K_1	13.38	13.55	8.4	16.70	17.25
	log K_2	10.50	10.58	7.99	11.77	8.35
	log K_1K_2	23.88	24.13	16.40	25.09	25.12
Be^{2+}	log K_1	10.62	10.81	5.05	18.68	18.09
	log K_2	8.01	8.03	5.75	7.58	9.08
	log K_1K_2	18.63	18.84	12.62	20.16	20.05
Cd^{2+}	log K_1	8.48	8.47	8.83	−1.17	−1.17
	log K_2	6.89	6.65	8.83	−6.51	−7.03
	log K_1K_2	15.17	15.12	16.83	−5.57	−5.51
Hg^{2+}	log K_1	7.97	7.97	7.99	−0.07	−0.06
	log K_2	6.17	6.14	7.15	−3.29	−3.20

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