

Thermodynamics of the complexation reactions of UO_2^{2+} , Be^{2+} and Cu^{2+} with methoxybenzoic acids

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Abstract. The stability constants and thermodynamic parameters of complexation reactions of UO_2^{2+} , Be^{2+} and Cu^{2+} with some methoxybenzoic acids in 76% (v/v) dioxane water medium and $\mu = 0.1 \text{ M NaClO}_4$ have been potentiometrically investigated. All the metal ions form 1 : 1 complexes. The $\log K_1$ varies linearly with mole fraction of dioxane but nonlinearly with the reciprocal of dielectric constant in the case of UO_2^{2+} chelates. In all the complexes ΔG values follow the Basolo Pearson stability order : $\text{UO}_2^{2+} > \text{Be}^{2+} > \text{Cu}^{2+}$.

Keywords. Stability constants; Gibbs-Helmholtz equation; Born equation.

1. Introduction

In continuation of our earlier work on rare earth chelates of methoxybenzoic acids (Mali and Pethe 1978a), we report in this paper the results of our studies on complexation reactions of UO_2^{2+} , Be^{2+} and Cu^{2+} with substituted methoxybenzoic acids at different temperatures in order to evaluate the different thermodynamic parameters. The effect of change in dielectric constant on the complexation reactions of UO_2^{2+} with different methoxybenzoic acids was also studied.

2. Experimental

All the chemicals used were of A.R. grade obtained from E. Merck or Fluka. The metal solutions were prepared by dissolving the respective nitrates in 0.1 M HClO_4 and were analysed for the metal contents by standard procedures (Vogel 1973). All the solutions were prepared in double distilled water. Dioxane was purified by standard procedure (Vogel 1956). The details regarding the pH-meter and the titration procedure is given in Mali and Pethe (1978a). The pH-meter readings B obtained for dioxane water medium were corrected according to the method of Van Uitert and Haas (1953), in order to get the thermodynamic values.

3. Results and discussion

The pK values were calculated by the method of Irving and Rossotti (1954) and are reported in Pethe and Mali (1978b). For the determination of metal ligand stability constant ($\log K_1$) the metal ligand titration curve should deviate from the ligand titration curve, before the onset of hydrolysis of the metal ion. However, it was observed that there was no such deviation for Cu^{2+} and Be^{2+} in dioxane water mixtures below 60% (v/v) for all the ligands. Hence a comparative study of these metal ion complexes was undertaken only in 76% (v/v) dioxane water medium. However, UO_2^{2+} complexes were studied at different dioxane percentages, data of which are given in table 1.

In all the three ions studied only 1 : 1 complexes are formed. The possibility of 1 : 2 complexes cannot be considered since \bar{n} above 1.0 were erratic due to the onset of hydrolysis of the metal ion at higher pH. This was confirmed by comparing the experimental formation curve with the theoretical formation curve—(Irving and Rossotti 1953), by plotting \bar{n} (theoretical) and \bar{n} (experimental) versus pL values. The representative data are given in table 2. The agreement between the theoretical and experimental values is good over the entire B range. The $\Delta\bar{n}$ values were used to calculate the standard deviation, which indicate high precision of the experimental results. The $\log K_1$ values at different temperatures are reported in table 3.

3.1. Effect of change in dielectric constant

The formation of a metal complex is either an ion-ion or ion-dipole interaction. The coulombic forces involved in such interactions are dependent on dielectric constant of the medium. Naturally, the decrease in the dielectric constant of the medium is expected to enhance the stability of the complex species. Such a study

Table 1. Thermodynamic $\log K_1$ values for UO_2^{2+} , chelates of methoxybenzoic acids at different dioxane-water medium.

Temp. $30 \pm 0.1^\circ \text{C}$

$\mu = 0.1 \text{ M (NaClO}_4\text{)}$

Benzoic acid	$\log K_1$ values in dioxane % (v/v)			
	20 $n_2 = 0.05$	40 $n_2 = 0.12$	60 $n_2 = 0.24$	76 $n_2 = 0.40$
2-Methoxy-	3.63	4.50	5.78	7.67
4-Methoxy-	3.92	4.80	6.17	8.19
2,3-Dimethoxy-	3.31	4.03	5.47	7.37
2,4-Dimethoxy-	4.29	5.20	6.54	8.49
2,6-Dimethoxy-	3.25	4.12	5.46	7.21
2,4,5-Trimethoxy-	4.11	4.94	6.38	8.52
2,4,6-Trimethoxy-	3.60	4.55	5.80	7.76

n_2 = mole fraction of dioxane.

Table 2. Comparison of $\bar{n}_{\text{exp.}}$ and $\bar{n}_{\text{calc.}}$.

Temp. $30 \pm 0.1^\circ \text{C}$ Medium : 76% (v/v) dioxane-water;
 $\mu = 0.1 \text{ M (NaClO}_4\text{)}$

p^L	$\bar{n}_{\text{exp.}}$	$\bar{n}_{\text{calc.}}$	$\Delta \bar{n}$
UO₂²⁺-2,4,6-trimethoxybenzoic acid system			
8.05	0.220	0.337	-0.117
7.96	0.331	0.384	-0.053
7.86	0.441	0.434	+0.007
7.78	0.496	0.511	-0.015
7.68	0.551	0.541	+0.010
7.50	0.717	0.644	+0.073
standard deviation = 0.04			
Be²⁺-2-methoxybenzoic acid system			
7.34	0.281	0.343	-0.062
7.27	0.375	0.384	-0.009
7.16	0.413	0.443	-0.030
6.98	0.569	0.544	+0.025
6.92	0.613	0.576	+0.037
6.80	0.712	0.644	+0.068
standard deviation = 0.040			
Cu²⁺-2,6-dimethoxybenzoic acid system			
6.63	0.233	0.265	-0.032
6.45	0.331	0.357	-0.026
6.28	0.451	0.447	+0.004
6.08	0.557	0.562	-0.005
5.91	0.648	0.658	-0.010
standard deviation = 0.020			

Table 3. Thermodynamic log K_1 values of UO₂²⁺, Be²⁺ and Cu²⁺ chelates of methoxybenzoic acids at different temperatures.

Benzoic acid	UO ₂ ²⁺				Be ²⁺				Cu ²⁺		
	20	30	40	50	20	30	40	50	20	30	40
2-Methoxy	7.74	7.67	7.59	7.51	7.10	7.06	7.00	6.93	6.42	6.29	6.09
4-Methoxy	8.35	8.19	7.99	7.92	7.41	7.31	7.28	7.18	6.53	6.41	6.22
2,3-Dimethoxy	7.50	7.37	7.31	7.24	6.79	6.64	6.55	6.44	6.21	6.15	6.06
2,4-Dimethoxy	8.51	8.49	8.46	8.42	7.66	7.59	7.48	7.37	6.70	6.61	6.49
2,6-Dimethoxy	7.34	7.21	7.09	7.04	6.86	6.80	6.74	6.68	6.31	6.19	6.04
2,4,5-Trimethoxy	8.55	8.52	8.38	8.25	7.94	7.80	7.74	7.62	6.65	6.49	6.39
2,4,6-Trimethoxy	7.84	7.76	7.58	7.53	7.39	7.26	7.15	7.08	6.59	6.49	6.41

has been carried out for UO_2^{2+} , in which stability constants vary linearly with mole fraction of dioxane. It is generally a practice to plot $\log K_1$ values versus $1/D$ (D = dielectric constant) in order to analyse the Born (1920) equation. However, such plots are found to be nonlinear and lead to no definite conclusion. As the dioxane content of the system increases the possibility of the dioxane molecules entering into the co-ordination sphere of the interacting species increases and the micro dielectric constant differs from the macro or bulk dielectric constant of the medium.

3.2. Effect of temperature on the stability of metal complexes

The stability constant ($\log K_1$) and the total free energy change (ΔG) are related by equation; $\Delta G = -RT \ln K$. The value of enthalpy change (ΔH) was determined from the slope of the curve obtained by plotting $\log K_1$ against $1/T$. This resulted in a straight line, indicating that the assumption in Gibbs-Helmholtz equation, that ΔH is constant at different temperatures is true. The overall entropy change (ΔS) was obtained from $(\Delta H - \Delta G)/T$. The thermodynamic parameters ΔG , ΔH and ΔS thus calculated are listed in table 4. As the values of $\log K_1$ reported in table 3 are accurate to ± 0.03 log units, the values of ΔH and ΔS are reliable to ± 0.5 k cal/mole and ± 2.0 cal/mole/deg respectively.

The values of $\log K_1$ decreases with increase of temperature for all the complexes. The free energy of complex formation has more negative values with increase of temperature, showing that the complex formation is a spontaneous process. The ΔS values are positive in all the cases indicating favourable entropy for the formation of complexes. It will be observed that the changes in the ΔS and ΔH values of the chelates of the metal ions with the same ligand, do not show any regularity as is observed in ΔG values in most of the cases, following the Basolo Pearson order.

Table 4. Thermodynamic quantities of ΔG , ΔH and ΔS for UO_2^{2+} , and Cu^{2+} chelates of methoxybenzoic acids at 30° C in 76% (v/v) dioxane-water medium.

Benzoic acid	UO_2^{2+}			Be^{2+}			Cu^{2+}		
	$-\Delta G$ k cal/ mole	$-\Delta H$ k cal/ mole	$+\Delta S$ cal/ mole/ deg.	$-\Delta G$ k cal/ mole	$-\Delta H$ k cal/ mole	$+\Delta S$ cal/ mole/ deg.	$-\Delta G$ k cal/ mole	$-\Delta H$ k cal/ mole	$+\Delta S$ cal/ mole/ deg.
2-Methoxy	10.63	3.5	24.0	9.78	2.6	24.0	8.72	7.3	5.0
4-Methoxy	10.35	6.9	11.0	10.13	3.5	22.0	8.88	7.0	6.0
2,3-Dimethoxy	10.21	3.6	22.0	9.20	5.0	14.0	8.52	3.7	16.0
2,4-Dimethoxy	11.77	1.8	33.0	10.52	4.2	21.0	9.16	4.6	15.0
2,6-Dimethoxy	9.99	4.6	18.0	9.42	2.9	21.0	8.58	5.7	9.0
2,4,5-Trimethoxy	11.81	5.0	22.0	10.81	4.4	21.0	8.99	6.2	9.0
2,4,6-Trimethoxy	10.75	5.3	18.0	10.06	4.2	19.0	8.99	3.9	17.0

The stability of a metal complex depends on the charge (Z) and ionic radius (r) of the metal ion. The free energy change is expected to be a function of Z^2/r of the cation. Hence the Basolo Pearson stability order $\text{UO}_2^{2+} > \text{Be}^{2+} > \text{Cu}^{2+}$ is found to be obeyed by all the ligands.

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