Journal of Alloys and Compounds 408–412 (2006) 1302–1306

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Systematics of polymeric hydrolysis constants of actinide ions

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Abstract

Systematic trends observed in the polymeric hydrolysis constants of U(VI), Np(VI) and Pu(VI) were analyzed by a simple hard sphere model, in which not the formal but the effective charges of actinide ions were considered. The parameter values such as the effective charge of AnO_2^{2+} were determined by fitting the reported hydrolysis constant data to the model. Using obtained parameter values, some predictions were made for unknown values of hydrolysis constants.

Keywords: Hydrolysis constant; Hexavalent actinide; Model; Solubility

1. Introduction

The solution chemistry of actinide ions in aquatic systems relevant for radioactive waste disposal includes hydrolysis reactions together with complexation with various inorganic ligands. It is thus quite important to establish the thermodynamic database for such solution reactions. However, some of the thermodynamic data of actinide elements are still lacking, and the chemical behavior of these elements is often predicted by applying chemical analogy, that is by taking the thermodynamic data of similar kinds of the elements. It is needed to establish the basis and conditions for applying the chemical analogy.

The stability of hydrolysis and complex species has been discussed in many literatures in terms of the charge and ionic radius of the central metal ion [1–6]. In our approach, we have proposed a simple hard sphere model to describe the systematic trends in the hydrolysis behavior of actinide ions [7,8]. Reasonable agreement for higher coordination number has been obtained by taking into account the repulsive forces of hard spheres. Also, the effective charges of actinide ions have been introduced into the model by considering possible contributions of non-electrostatic interactions of actinide ions in addition to those of ordinary electrostatic ones, and systematic trends of the hydrolysis constants have been discussed by considering the additional interactions of 5f orbitals [8].

The present study is an extension of our previous one and deals with the polymeric hydrolysis constants of actinide ions. The systematic trends observed in the hydrolysis constants of actinide ions are analyzed by the hard sphere model, in which not the formal but the effective charges of actinide ions are considered. The obtained results will be important to establish the basis and conditions for applying the chemical analogy.

2. Analytical procedure

2.1. Selected hydrolysis constants

Our procedure is first to select the reference values for hydrolysis constants from the literatures, and then to apply the hard sphere model to the analysis of the selected values in order to discuss the systematic trends.

Because of the increasing needs for the reliable values, a critical and comprehensive review of available literatures has recently been performed for some of actinide elements in the NEA Thermochemical Data Base project [9,10]. The recommended values for polymeric hydrolysis constants of U(VI), Np(VI) and Pu(VI) are found in this review, and

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doi:10.1016/j.jallcom.2005.04.126

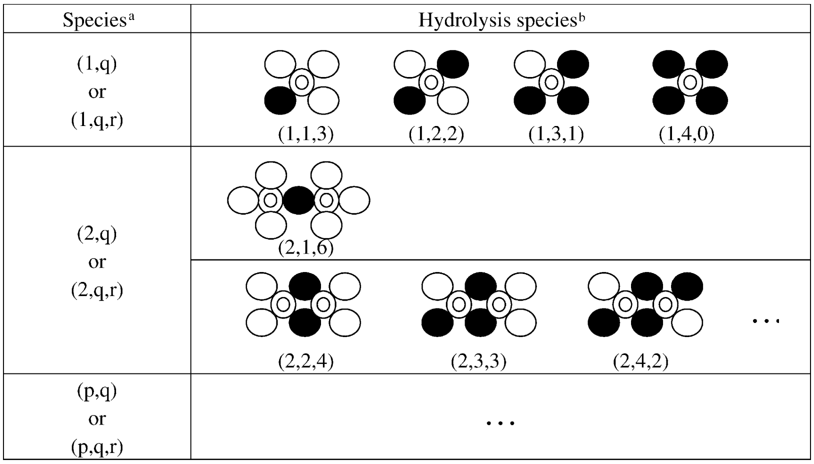
Table 1
Selected hydrolysis constants of An(VI) ions

Valence	Species	$\log \beta^\circ_{p,q}$	
		Evaluated by NEA-TDB [9,10]	Calculated by the present model
U(VI)	UO_2OH^+	8.75 ± 0.24	9.19
	$UO_2(OH)_2{}^0$	15.85 ± 0.07	16.56
	$UO_2(OH)_3{}^-$	21.75 ± 0.42	20.62
	$UO_2(OH)_4{}^{2-}$	23.60 ± 0.68	22.86
	$(UO_2)_2OH^{3+}$	11.30 ± 1.00	10.70
	$(UO_2)_2(OH)_2{}^{2+}$	22.38 ± 0.04	22.51
	$(UO_2)_2(OH)_3{}^+$		31.38
	$(UO_2)_2(OH)_4{}^0$		39.09
	$(UO_2)_2(OH)_5{}^-$		44.10
	$(UO_2)_2(OH)_6{}^{2-}$		47.97
	$(UO_2)_3(OH)_4{}^{2+}$	44.10 ± 0.30	44.75
	$(UO_2)_3(OH)_5{}^+$	54.45 ± 0.12	53.54
	$(UO_2)_3(OH)_6{}^0$		61.52
	$(UO_2)_3(OH)_7{}^-$	65.80 ± 0.80	66.88
	$(UO_2)_3(OH)_8{}^{2-}$		71.44
	$(UO_2)_4(OH)_6{}^{2+}$		66.96
	$(UO_2)_4(OH)_7{}^+$	76.10 ± 1.00	75.72
	$(UO_2)_4(OH)_8{}^0$		83.86
	$(UO_2)_4(OH)_9{}^-$		89.41
	$(UO_2)_4(OH)_{10}{}^{2-}$		94.34
	$(UO_2)_5(OH)_8{}^{2+}$		89.17
	$(UO_2)_5(OH)_9{}^+$		97.91
	$(UO_2)_5(OH)_{10}{}^0$		106.15
	$(UO_2)_5(OH)_{11}{}^-$		111.82
	$(UO_2)_5(OH)_{12}{}^{2-}$		116.98
Np(VI)	NpO_2OH^+	8.90 ± 0.40	9.09
	$(NpO_2)_2(OH)_2{}^{2+}$	21.73 ± 0.21	22.13
	$(NpO_2)_3(OH)_7{}^-$	52.88 ± 0.22	52.68
Pu(VI)	PuO_2OH^+	8.50 ± 0.50	8.63
	$PuO_2(OH)_2{}^0$	14.80 ± 1.50	15.43
	$(PuO_2)_2(OH)_2{}^{2+}$	20.50 ± 1.00	20.15

then those are taken as the reference values in the present study. The values are summarized in Table 1 together with the monomeric hydrolysis constants of U(VI), Np(VI) and Pu(VI) for comparison. It may be noted, however, that some of the values are still under discussion. In his extensive study on U(VI) solution chemistry [11], for example, G. Meinrath has reported rather lower values of $\log \beta^\circ_{2,2} = 21.845 \pm 0.088$ and $\log \beta^\circ_{3,5} = 52.84 \pm 0.18$ compared with the selected values of $\log \beta^\circ_{2,2} = 22.38 \pm 0.04$ and $\log \beta^\circ_{3,5} = 54.45 \pm 0.12$ for $(UO_2)_2(OH)_2{}^{2+}$ and $(UO_2)_3(OH)_5{}^+$, respectively. There are obvious systematic deviations between the values of Meinrath and those selected by the review. Although further confirmation may be needed, it has already been pointed out that the observed discrepancy could be attributed to either a systematic error in the determination of $\log_{10} [H^+]$ or a real chemical effect caused by the difference in ionic strength and electrolyte concentration.

2.2. *Hard sphere model*

Similarly to the previous study [4], the improved hard sphere model is used in which the effective charges of central actinide ions are introduced. An octahedral structure is assumed for all the hydrolysis species, and the central actinide ion and its ligands of water molecules and hydroxide ions are all treated as single hard spheres including the oxo-complexes of $AnO_2{}^{2+}$. Thus, four corners of the octahedral structure in the equatorial plane are occupied by water molecules, which are replaced by hydroxide ions to form the hydrolysis species of $AnO_2{}^{2+}$. For the formation of polymeric hydrolysis species of $AnO_2{}^{2+}$, a polymerization process is assumed by considering the formation of the polymers bridged by hydroxide ions as shown in Fig. 1. Thomas was one of the first to interpret the polymerization phenomena in such a way as a result of his work on the hydrolysis reactions of metallic ions [12]. According to him, some irreversible elimination of water molecules, which is accompanied by the formation of oxygen bridges, may occur under appropriate conditions of high temperature, prolonged aging and/or high pH. For simplicity, however, the formation of oxygen bridges is not taken into account in the present study.



[a] (p,q,r) denotes $(AnO_2)_p(OH)_q(H_2O)_r{}^{(2p-q)}$.

[b] ◎ : $AnO_2{}^{2+}$, ● : OH^-, ○ : H_2O.

Fig. 1. Formation of polymeric hydrolysis species.

By considering the Coulomb interactions between the hard spheres, the electrostatic potential energy $E_{p,q}$ of each species is given by

$$E_{p,q} = \sum_{i \neq j}^{N} (Z_i Z_j / \varepsilon d_{ij})$$

where N denotes the total number of hard spheres in the (p,q) species, Z_i and Z_j the electric charges of hard spheres i and j, respectively, ε the dielectric constant, and d_{ij} the distance between hard spheres i and j. As a substitute for the dipole moment, water molecules are assumed to have an effective charge. It is important to note that the effective charges of $AnO_2{}^{2+}$ include possible contributions of non-electrostatic interactions of actinide ions and are only for the first neighbors. For the other neighbors, the net charges of +2 are to be used.

By taking into account the coordinated water molecules as shown in Fig. 1, the polymerization process for the (p,q) species other than the (2,1) species is generally written as

$$p\mathrm{AnO_2(H_2O)_4}^{2+} + q\mathrm{OH}^- = \mathrm{(AnO_2)}_p\mathrm{(OH)}_q\mathrm{(H_2O)}_{2p-q+2}{}^{2p-q} + (2p+q-2)\mathrm{H_2O} \qquad (2)$$

while that of the (2,1) species is written as

$$2\mathrm{AnO_2(H_2O)_4}^{2+} + \mathrm{OH}^- = \mathrm{(AnO_2)_2(OH)_1(H_2O)_6}^{3+} + 2\mathrm{H_2O} \qquad (3)$$

The potential energy change ΔE in reactions (2) and (3) is then given by

$$\begin{aligned}\Delta E_{p,q} &= E_{p,q} - pE_{1,0} + [(2p+q-2) - q]E' \\ &= E_{p,q} - pE_{1,0} + (2p-2)E' \qquad (4)\end{aligned}$$

$$\Delta E_{2,1} = E_{2,1} - 2E_{1,0} + E' \qquad (5)$$

where E' denotes the contribution of a free water molecule or a hydroxide ion to the potential energy change. In the present study, no difference is considered between the free H_2O and OH^- in the potential energy change in reactions (2) and (3), and the last terms in the right hand side in Eqs. (4) and (5) are mainly due to the entropy changes. Accordingly, the standard state hydrolysis constant $\beta^\circ_{p,q}$ of each species is expressed by

$$\beta^\circ_{p,q} = \exp(-\Delta E_{p,q}/RT) \qquad (6)$$

where R and T denote the gas constant and absolute temperature, respectively.

3. Results

A least-squares fitting analysis of the selected reference $\beta^\circ_{p,q}$ values in Table 1 was carried out by using the above equations. The ionic radii of $AnO_2{}^{2+}$ were taken from the literature values for the effective radii in the equatorial plane [5] and, for the lack of data, the ionic radius of 1.38×10^{-10} m [13,14] for O^{2-} was taken for H_2O. The electric charge of OH^- was assumed to be −1. Together with the effective charge of $AnO_2{}^{2+}$, the effective charge and the dielectric constant for H_2O and the E' value were treated as free parameters in the fitting analysis. The obtained results for the effective charges of the actinide ions are summarized in Table 2, and the $\beta^\circ_{p,q}$ values obtained in the analysis are compared with the selected reference values in Table 1.

As shown in Fig. 2, the systematic behavior of the $\beta^\circ_{p,q}$ values is well described by the present model similarly to the case of monomeric species [7,8]. The $\beta^\circ_{p,q}$ values increase with increasing coordination number, but the rate of increase is not simply proportional to the coordination number due to the increasing repulsive interactions between the negatively charged ligand ions.

Table 2
Parameter values used and obtained in the analysis of hydrolysis constants

An(VI)	U(VI)	Np(VI)	Pu(VI)
Z_{An}	2.22 ± 0.05[a]	2.21 ± 0.05[a]	2.13 ± 0.06[a]
Z_{OH}	−1	−1	−1
Z_{H_2O}	-0.50 ± 0.07[a]	-0.50 ± 0.07[b]	-0.50 ± 0.07[b]
r_{An} (nm)	0.104 [5]	0.104 [5]	0.102 [5]
r_{OH} (nm)	0.138 [13,14]	0.138 [13,14]	0.138 [13,14]
r_{H_2O} (nm)	0.138 [13,14]	0.138 [13,14]	0.138 [13,14]
ε	7.0 ± 1.7[a]	7.0 ± 1.7[b]	7.0 ± 1.7[b]
E' (kJ/mol)	-1.6 ± 1.6[a]	-1.6 ± 1.6[a]	-1.6 ± 1.6[a]

[a] Standard errors.

[b] Taken from the values determined for U(VI).

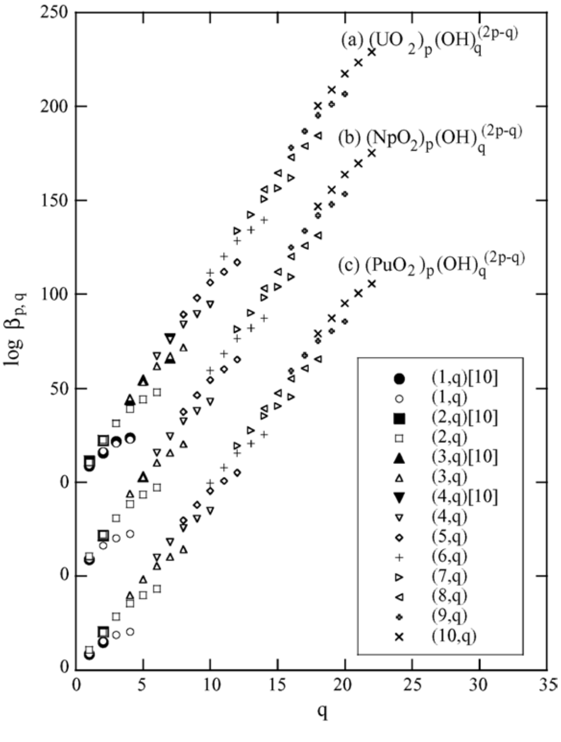


Fig. 2. log $\beta^\circ_{p,q}$ values of An(VI) as a function of the q number: (a) $(UO_2)_p(OH)_q{}^{(2p-q)}$; (b) $(NpO_2)_p(OH)_q{}^{(2p-q)}$, (c) $(PuO_2)_p(OH)_q{}^{(2p-q)}$.

4. Discussion

4.1. Obtained parameter values

As shown in Table 2, the effective charges of AnO_2^{2+} are obtained to be 2.22, 2.21 and 2.15 for UO_2^{2+}, NpO_2^{2+} and PuO_2^{2+}, respectively. It is noticed that the obtained values are much smaller than such values as reported to be 3.2, 3.0 and 2.9 for UO_2^{2+}, NpO_2^{2+} and PuO_2^{2+}, respectively, by Choppin and Rao [2]. However, this difference may be explained by considering different definitions of the effective charge in the two models. In fact, the effective charge of the central An atom in the AnO_2^{2+} was obtained in their model by applying the extended Born equation to the AnO_2F complexation while the overall charge of the AnO_2^{2+} was obtained in the present model by treating the AnO_2^{2+} as a single hard sphere. The present values are also smaller than the values obtained in our previous study [8], in which the effective charges of 2.428, 2.391 and 2.374 have been determined for UO_2^{2+}, NpO_2^{2+} and PuO_2^{2+}, respectively. For this difference, it is noted that the ionic radii, which were obtained from the measured distances between atoms in solution species, were used in the present study while the ionic radii in crystals were used in the previous study. Thus this difference may be due to the differently selected ionic radii. As shown in Table 2, the effective charges of the AnO_2^{2+} are larger than the formal charge of +2 and decrease with the increasing atomic number. Similarly to the previous study [8], the present result suggests that these actinide ions have not only the electrostatic interactions but also additional non-electrostatic interactions. Such contributions of 5f orbital electrons to the additional interactions would decrease with the increasing atomic number.

Compared with the results of the previous study [8], a little different values were obtained for the effective charge and the dielectric constant for H_2O. The effective charge was obtained to be -0.50 in the present study, which was less negative than the previous value of -0.57 [8]. Also the dielectric constant was obtained to be 7.0, which were larger than the previous value of 5.7 [8]. Similarly to the above, these are considered to be due to differently selected ionic radii.

4.2. Predicted hydrolysis constants of polymeric species

As seen above, the parameter values of the present model is dependent on the selected reference values. In spite of this constraint, however, it provides a basis not only to check abnormal experimental data but also to predict unknown values from a systematic point of view. For example, Table 1 shows the hydrolysis constant values predicted by the present model. It is interesting to compare such predicted values with some experimental results and to see what the consequence is.

Fig. 3 shows a comparison of the predicted solubility curve with the experimental results of U(VI) [15–17]. In this case, the predicted solubility curve and its component concentrations are calculated with the hydrolysis constants, which are predicted by the present model and are corrected by the specific ion interaction theory (SIT) [9,10]. For the lack of information, the ion interaction parameter values for polymeric species are temporarily assumed to 0.5, 0.46, -0.06, 0, -0.09 and -0.16 for net ionic charges of +3, +2, +1, 0, -1 and -2, respectively. Also, the solubility limiting solid phase is assumed to be $UO_3{\cdot}2H_2O$ with the solubility product value of $\log K^{\circ}_{sp} = -22.46$ [16] and to be $Na_2U_2O_7{\cdot}xH_2O$ with $\log K^{\circ}_{sp} = -29.45$ [17]. As shown in Fig. 3, the predicted solubility curve agrees rather well with the experimental results.

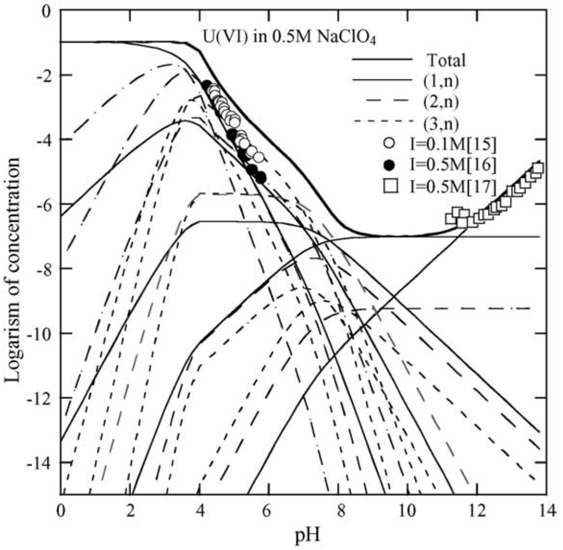


Fig. 3. Solubility and its component concentrations of U(VI) at 0.5 M $NaClO_4$ as a function of pH. Bold curve denotes the total solubility including all the (p,q) species of $p \leq 10$.

It is one of the findings in this comparison that there are considerably high contributions of polymeric species to the predicted solubility curve. Those are from the known species of $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^{+}$ and from the unknown but predicted species of $(UO_2)_2(OH)_3^{+}$ and $(UO_2)_2(OH)_4^{0}$ as shown in Fig. 3. Thus, it will be interesting and important to check the presence of these predicted species experimentally. In this case, however, it is noted that some physical interaction may also act between the polymeric species having less net charges in solutions of the polymeric species. Then, larger species may be formed by such interactions, which are sensitive to filtration. A careful examination may be needed.

5. Conclusions

Similarly to the case of monomeric hydrolysis species, the hydrolysis constants of polymeric species were well explained by a simple hard sphere model in which the effective charges of the central actinide ions were introduced. The obtained effective charges of the central actinide ions are larger than the formal charges, and not only the electrostatic interactions but also some additional non-electrostatic interactions are found to contribute to the stability of the species of actinide ions. Although the parameter values of the present model is much dependent on the selected reference values, it provides a basis not only to check abnormal experimental data but also to predict unknown values from a systematic point of view. It is thus interesting to extend the present model from hexavalent ions to the others such as tetravalent ions.

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