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Mixed Solvent Deuterium Isotope Effects on the Hydrolysis of UO_2^{2+} and Be^{2+} Ions

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Stability constants of the hydrolysis species of UO_2^{2+} ion were determined in pure light water and 80% heavy water containing 3M $NaClO_4$ as an ionic medium at 25°C, and the results were compared with those in pure heavy water. The decrease of the stability constants in hydrolysis reactions of UO_2^{2+} ion, as well as of Be^{2+} ion, was discussed in terms of the equilibrium theory of the solvent deuterium isotope effects, which is based on the assumptions that activity coefficients of chemical species in isotopic exchange equilibria remain unchanged with the change in the deuterium atom fraction in the solvent, that the solvated hydrogen ion possesses three equivalent lyons, and that the isotopic equilibria are subject to the rule of the simple geometric mean. Satisfactory agreements were found between the observed and calculated values for the relative stability constants of the hydrolysis species of UO_2^{2+} and Be^{2+} in water of various hydrogen isotopic compositions.

In the preceding papers,[2-5] we have studied on the hydrolysis reactions of Be^{2+}, UO_2^{2+}, Cu^{2+}, and Y^{3+} ions in pure heavy water and have found that the compositions of complexes formed by hydrolysis in heavy water are the same as those in light water, and that the stability constants of the complexes in heavy water are smaller than those in light water. In the study of the hydrolysis of Be^{2+} ion in mixtures of light and heavy water, it has been found that the stability constants decrease monotonously with the increase in the deuterium atom fraction.[6]

In the present paper are included results on the hydrolysis of UO_2^{2+} ion in 80% (deuterium atom fraction) heavy water as well as in light water, and a quantitative interpretation is attempted for the variation of the stability constants for hydrolysis species of UO_2^{2+} and Be^{2+} ions in H_2O-D_2O mixtures in terms of the equilibrium theory of solvent deuterium isotope effects, which have so far been applied to acid-base equilibria in light and heavy water by a number of investigators.[7]

Symbols.

Z	Average number of lyonium ions split off per metal ion
B	Total concentration of metal ion

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[2] H. Kakihana and M. Maeda, This Bulletin, **43**, 109 (1970).

[3] M. Maeda and H. Kakihana, *ibid.*, **43**, 1097 (1970).

[4] H. Kakihana, T. Amaya, and M. Maeda, *ibid.*, **43**, 3155 (1970).

[5] H. Kakihana, T. Amaya, and M. Maeda, *Trans. Royal Inst. Technol., Pure and Appl. Chem.*, **34**, 49 (1972).

[6] H. Kakihana and M. Maeda, This Bulletin, **42**, 1458 (1969).

[7] L. L. Schaleger, P. Salomaa, and F. A. Long, "Chemical Physics of Ionic Solutions," Ed. by B. E. Conway and R. G. Barradas, John Wiley & Sons, Inc., New York (1966), p. 237.

E	emf (mV), E_0 constant (mV), E_j a liquid junction potential (mV)
n	Deuterium atom fraction $\{D/(D+H)\}$
L	Lyon, H or D
$\beta_{p,q}$	Equilibrium constant for the hydrolysis reaction $qM^{z+}+2pL_2O=M_q(OL)_p^{(zq-p)+}+pL_3O^+$ Superscripts, H, D, and n represent light water, heavy water, and their mixture with the deuterium atom fraction of n.
(p,q)	Complex, $M_q(OL)_p^{(zq-p)+}$.
l	Total concentration of free lyonium ion.

Results

Values of Z, average number of lyonium ion split off per metal ion by hydrolysis, and log l at each series of B, the total concentration of the metal ion, are shown graphically in Figs. 1 and 2, respectively. A generalized least squares method was applied to determine the most probable values of stability constants of the minimum number of hydrolysis species which would suffice to account for the experimental data. Values of stability constants were so chosen that the error square sum $(\sum(Z_{calc}-Z)^2)$ becomes minimum, where Z_{calc} denotes calculated values of Z with a particular set of the constants, $\beta_{p,q}$. Among some combinations of complexes, the assumptions of formation of (2, 2), (4, 3) and (5, 3) complexes, the (4, 3) complex being a minor component, gave the most satisfactory agreement between experimental and calculated values of Z in both systems of 80% heavy water and light water. These complexes have also been found in heavy water.[3] The final values of stability constants of the complexes are listed in Table 1, together with those in pure heavy water.

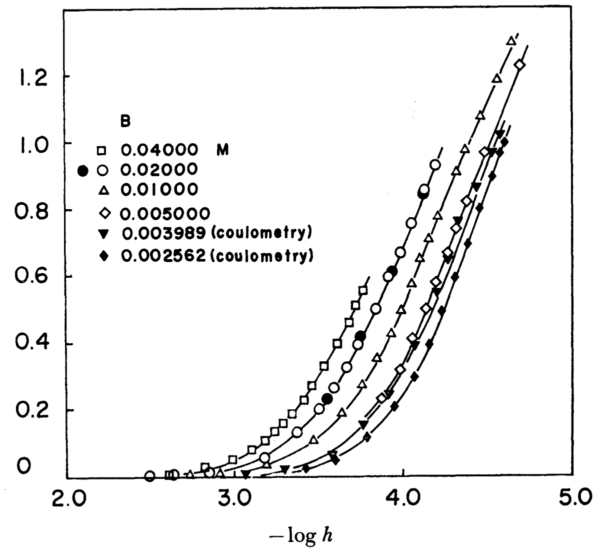

Fig. 1. Average number, Z, of OH bound per UO_2^{2+}, as a function of log h for the system of light water. Drawn curves were calculated with the stability constants given in Table 1. Open symbols denote the forward titrations and filled symbols the back titrations.

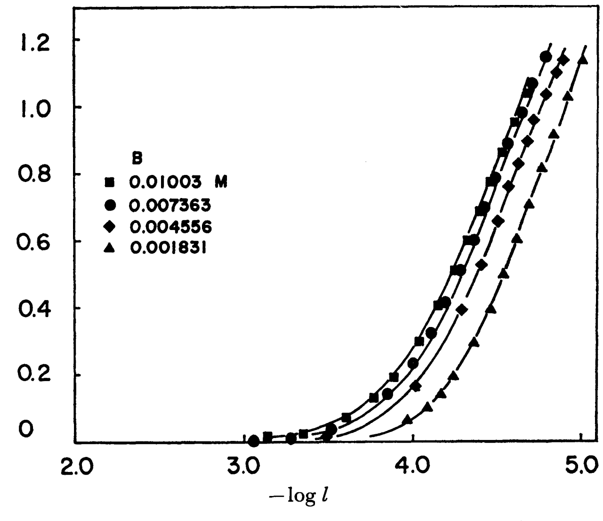

Fig. 2. Average number, Z, of OL bound per UO_2^{2+}, as a function of log l for the system of 80% heavy water. Drawn curves were calculated with the stability constants given in Table 1.

Table 1. Stability constants of uranyl hydroxo complexes in light and heavy water and 80% heavy water

	Light water[a]	80% Heavy water[a]	Heavy water[a]
$-\log\beta_{2,2}$	6.17±0.02	6.61±0.03	6.80±0.02
$-\log\beta_{4,3}$	12.92±0.1$_5$	14.28±0.2$_0$	14.00±0.1$_5$
$-\log\beta_{5,3}$	17.04±0.03	18.16±0.04	18.63±0.02

a) The uncertainties of the constants were estimated as 3σ.

The present results for the light water system were compared with those obtained by Sillén *et al.*[15] in the same ionic medium(3 M $NaClO_4$). Values for $\beta_{p,q}$ they obtained were $-\log\beta_{1,1}\simeq6.10$, $-\log\beta_{2,2}=6.04\pm0.02$, $-\log\beta_{4,3}\simeq13.21$ and $-\log\beta_{5,3}=16.53\pm0.02$. For the (4, 3) complex almost the same stability constant was found in the present study. For the (2, 2) and (5, 3) complexes, on the other hand, the smaller stability constants were obtained in this work than those of their work. No (1, 1) complex found by Sillén *et al.* was detected.

Discussion

As has been seen from results in systems of Be^{2+},[2,6] Cu^{2+},[4] and Y^{3+},[5] the compositions of complexes formed by hydrolysis in heavy water are the same as those in light water, while the stability constants of the complexes are smaller in heavy water than in light water. Essentially the same results were found in the system of uranyl ions.

The first attempt of interpretation of the solvent deuterium isotope effect was made by Gross and his co-workers[8] for acid catalyzed reactions, and the Gross' treatment has been applied to acid dissociation equilibria of water itself[9] and some acids such as am-

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8) P. Gross, H. Steiner, and F. Krauss, *Trans. Faraday Soc.*, **32**, 877 (1936); P. Gross and H. Wischler, *ibid.*, **32**, 879 (1936); P. Gross, H. Steiner, and H. Suess, *ibid.*, 863 (1936).

9) P. Salomaa, L. L. Schaleger, and F. A. Long, *J. Amer. Chem. Soc.*, **86**, 1 (1964).

monium ion[10] and phosphoric acid,[9] as well as to reaction kinetics.[11]

Since hydrolysis reactions are regarded as acid dissociation reactions of aquated metal ions, essentially similar treatments as Gross' may be used for analysis of hydrolysis schemes of metal ions in H_2O-D_2O mixtures. In the equilibrium theory first proposed by Gross,[8] the following assumptions are made; (1) Activity coefficients of chemical species do not change through the exchange of protons in a molecule with deuterons, (2) a solvated hydrogen ion possesses three lyons, and (3) isotopic disproportionation equilibria are subject to the rule of the simple geometric mean. Under these assumptions and with knowledge of values of stability constants of hydrolysis species in light and heavy water, variations of stability constants of hydrolysis species of UO_2^{2+} and Be^{2+} ions with the deuterium atom fraction in the solvent were discussed.

(1) Solvent Deuterium Isotope Effects on the Hydrolysis of UO_2^{2+}. On the basis of the above assumptions, prevailing equilibria among the various solvent species, protons, and deuterons along with their equilibrium constants are written as follows.

$$H_2O + D_2O = 2HDO \ ; \ 4 \tag{1}$$

$$2H_3O^+ + D_3O^+ = 3H_2DO^+ \ ; \ 27 \tag{2}$$

$$H_3O^+ + 2D_3O^+ = 3HD_2O^+ \ ; \ 27 \tag{3}$$

$$1/3H_3O^+ + 1/2D_2O = 1/3D_3O^+ + 1/2H_2O \ ; \ \psi \tag{4}$$

From Eq.(1), the concentrations of waters in a solvent mixture of a deuterium atom fraction n become

$$[H_2O] = (1-n)^2 \tag{5}$$

$$[HDO] = 2n(1-n) \tag{6}$$

$$[D_2O] = n^2 \tag{7}$$

The total concentration of lyonium ions, $\sum[L_3O^+]$ is expressed by Eq. (8) in terms of $[H_3O^+]$, n and ψ by means of Eqs. (1)—(7).

$$\begin{aligned}\sum[L_3O^+]&=[H_3O^+]+[H_2DO^+]+[HD_2O^+]\\&+[D_3O^+]=[H_3O^+](1-n+n\psi)^3(1-n)^{-3}\end{aligned} \tag{8}$$

Let us consider a solution of the (2, 2) complex in a mixed H_2O-D_2O solvent. There are three different types of complexes, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_2(OH)(OD)^{2+}$ and $(UO_2)_2(OD)_2^{2+}$. The following two deuterium fractionation factors are defined;

$$(UO_2)_2(OH)_2^{2+}+D_2O=(UO_2)_2(OD)_2^{2+}+H_2O \ ; \ \Phi_{20}$$

$$\begin{aligned}&(UO_2)_2(OH)_2^{2+}+1/2D_2O\\&\quad=(UO_2)_2(OH)(OD)^{2+}+1/2H_2O \ ; \ \Phi_{21}\end{aligned}$$

and they are given as

$$\begin{aligned}\Phi_{20}&=\{[UO_2)_2(OD)_2^{2+}]/[(UO_2)_2(OH)_2^{2+}]\}\\&\times\{(1-n)/n\}^2=(\beta^D{}_{2,2}/\beta^H{}_{2,2})\psi^{-6}\end{aligned} \tag{9}$$

$$\begin{aligned}\Phi_{21}&=\{[(UO_2)_2(OH)(OD)^{2+}]/[(UO_2)_2(OH)_2^{2+}]\}\\&\times\{(1-n)/n\}=K(\beta^D{}_{2,2}/\beta^H{}_{2,2})\psi^{-3}\end{aligned} \tag{10}$$

Here, K is the isotopic disproportionation factor for the reaction,

$$\begin{aligned}&1/2(UO_2)_2(OH)_2^{2+}+1/2(UO_2)_2(OD)_2^{2+}\\&\quad=(UO_2)_2(OH)(OD)^{2+} \ ; \ K\end{aligned} \tag{11}$$

From Eqs. (8)—(10), the total concentration of the (2, 2) complexes is given as follows.

$$\begin{aligned}&\sum[(UO_2)_2(OL)_2^{2+}]=[(UO_2)_2(OH)_2^{2+}]\\&\quad\times\{1+\Phi_{20}(n/(1-n))^2+\Phi_{21}(n/(1-n))\}\end{aligned} \tag{12}$$

The equilibrium constant, $\beta_{2,2}$ in a mixed solvent, which is accessible to experimental measurement is made up of the total concentrations of the various isotopic species involved.

$$\begin{aligned}\beta^n{}_{2,2}&=\{\sum[(UO_2)_2(OL)_2^{2+}]\cdot\sum[L_3O^+]^2\}/\\&\{[UO_2^{2+}]^2\sum[L_2O]^4\}\end{aligned} \tag{13}$$

Introducing the expressions for the total concentration of the (2, 2) complexes (Eq. (12)) and of lyonium ions (Eq.(8)) into Eq. (13), we obtain

$$\begin{aligned}\beta^n{}_{2,2}&=[\{[(UO_2)_2(OH)_2^{2+}][H_3O^+]^2\}/\{[UO_2^{2+}]^2(1-n)^6\}]\\&\times\{1+\Phi_{20}(n/(1-n))^2+\Phi_{21}(n/(1-n))\}(1-n+n\psi)^6\end{aligned} \tag{14}$$

If we assume that the equilibrium constant of the reaction $2UO_2^{2+} + 4H_2O = (UO_2)_2(OH)_2^{2+} + 2H_3O^+$ in a mixed solvent with a deuterium atom fraction n is equal to that of the same reaction in pure light water, the following equation is readily obtained.

$$\begin{aligned}\beta^n{}_{2,2}/\beta^H{}_{2,2}&=(1-n+n\psi)^6\\&\times\{(1-n)^2+\Phi_{20}n^2+\Phi_{21}n(1-n)\}\end{aligned} \tag{15}$$

The application of the rule of the geometric mean to the equilibrium(11) leads to K=2.[12] As the values for $\beta^H{}_{2,2}$ and $\beta^D{}_{2,2}$ have been obtained experimentally and the value for ψ has been reported to be 0.69,[13] the relative stability constant, $\beta_{2,2}/\beta_{2,2}$ can be calculated using Eqs.(9) and (10).

The relative stability constant, $\log(\beta^n{}_{2,2}/\beta^H{}_{2,2})$ at $n=0.8$ thus calculated is shown in Table 2. The agreement between the experimental and calculated values is satisfactory.

TABLE 2 CALCULATED AND OBSERVED RELATIVE STABILITY CONSTANTS, $\log(\beta^n{}_{p,q}/\beta^H{}_{p,q})$ AT $n=0.8$

Complex	$\log(\beta^n{}_{p,q}/\beta^H{}_{p,q})$	
	Calcd	Obsd
$(UO_2)_2(OL)_2^+$	−0.46	−0.44
$(UO_2)_3(OL)_5^+$	−1.17	−1.12

In general, Eq. (15) can be written, for the (p,q) complex, as follows;

$$\beta^n{}_{p,q}/\beta^H{}_{p,q}=(1-n+n\psi)^{3p}\cdot\{\sum_m\Phi_{pm}n^{(p-m)}(1-n)^m\} \tag{16}$$

and Φ_{pm} is given as

$$\Phi_{pm}=\mathrm{K}_m(\beta^D{}_{p,q}/\beta^H{}_{p,q})^{(p-m)/p}\cdot\psi^{-3(p-m)} \tag{17}$$

where K_m denotes the equilibrium constant of the following isotopic disproportionation reaction (charges are omitted);

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10) P. Salomaa, L. L. Schaleger, and F. A. Long, *J. Phys. Chem.*, **68**, 416 (1964).

11) C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, **83**, 3890 (1961).

12) J. Bigeleisen, *J. Chem. Phys.*, **23**, 2264 (1955).

$$\frac{m}{p}M_q(OH)_n + \frac{p-m}{p}M_q(OD)_p = M_q(OH)_m(OD)_{p-m} \; ; \; K_m \qquad (18)$$

Φ_{pp}, K_0, and K_p are defined as 1.

Variation of the stability constant of the $(UO_2)_3(OL)_5^+$ complex, $\log(\beta^n{}_{5,3}/\beta^H{}_{5,3})$, can be calculated from Eq. (16); in this case $K_1=5$, $K_2=10$, $K_3=10$, and $K_4=5$ are given under the assumption of the geometric mean.[12]

The calculated results at $n=0.8$ are represented in Table 2.

For the $(UO_2)_3(OL)_4^{2+}$ complex, the formation of which is quite small, uncertainties of the stability constants are so large that the discussion of the variation of the stability constant with the solvent composition can hardly be made.

(2) Solvent Deuterium Isotope Effects on the Hydrolysis of Be^{2+}. In the previous studies for the hydrolysis of Be^{2+} ion in light water,[2,14] heavy water,[2] and their mixtures,[6] we found that the main product of the reaction is $Be_3(OL)_3^{3+}$ in all systems examined and the stability constant of the species decreases with the increase of the deuterium atom fraction in the solvent. The continued variation of the relative stability constant of the (3, 3) species with the change in the deuterium atom fraction in the solvent has been determined experimentally as follows.[6] If only the (3, 3) species is present in appreciable amounts in mixed H_2O-D_2O solvents, the following equation can be derived:

$$1/2 \log Z - 3/2 \log(1-Z) = 1/2 \log 3 + 1/2 \log \beta_{3,3} + \log B - 3/2 \log l \qquad (19)$$

Differentiation of Eq. (19) with respect to the deuterium atom fraction at constant B and Z values gives the equation:

$$\partial \log \beta_{3,3} = 3\, \partial \log l \qquad (20)$$

The variation of the stability constant can be determined according to Eq. (20) if the change in l with the deuterium atom fraction is measured. In order to determine the variation of l with the deuterium atom fraction, the change in emf, ΔE, with the solvent composition was measured at constant B (0.02 and 0.04 M) and Z values ($Z \simeq 0.5$, where the (3, 3) species has been found to be predominant), and the change in E_0, that is ΔE_0, with the deuterium atom fraction was also measured by the similar titration procedure without beryllium ions. From the values for ΔE and ΔE_0 at any given solvent composition the change in l, $\Delta \log l$, could be evaluated by the equation $\Delta \log l = (\Delta E - \Delta E_0)/59.15$. The observed changes in $\beta_{3,3}$ with varying deuterium atom fraction from 0 to 0.8 are shown in Fig. 3.

Calculation of the relative stability constant of the $Be_3(OL)_3^{3+}$ complex in water of different hydrogen isotopic compositions was carried out by substituting the relation $K_1=K_2=3$[12] into Eq. (16). The results are compared with the experimental ones in Fig. 3. We see that the agreement is satisfactory.

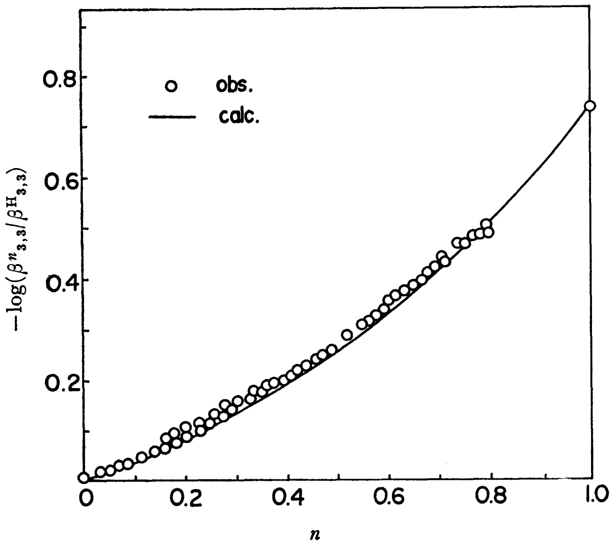

Fig. 3. Observed and calculated values of $-\log(\beta^n{}_{3,3}/\beta^H{}_{3,3})$ for the (3, 3) complex of Be^{2+} in H_2O-D_2O mixtures.

Conclusion

1) Stability constants of hydrolysis species of UO_2^{2+} ion were determined in light and 80% heavy water containing 3 M $NaClO_4$ as an ionic medium at 25°C. The results are tabulated in Table 1.

2) Relative stability constants of hydrolysis species of UO_2^{2+} and Be^{2+} ions in various H_2O-D_2O mixtures were estimated by application of the equilibrium theory of solvent deuterium isotope effects. Satisfactory agreements were found between the observed and calculated values.

Experimental

Reagents. Reagents used were, unless otherwise stated, prepared and analyzed as have been described in Refs. 2 and 3.

Uranyl percholrate solution was prepared and analyzed with the same procedures as those described in Ref. 15. *Uranyl perchlorate in* 80% *heavy water* was prepared by the repeated evaporation of uranyl perchlorate solution under an infrared lamp, while adding 80% heavy water.

NaOL solution in 80% *heavy water* was prepared by electrolysis of sodium perchlorate in 80% heavy water.

Apparatus. *A Wilhelm type half-cell*[17] was used for emf measurements, and a modified one for constant-current coulometry.

Glass electrodes of Beckman No. 40498 were used in combination with *a Radiometer PHM-4C pH-meter (Copenhagen).*

A coulometric analyzer (Leeds & Northrup Co., Philadelphia) was used as a constant current power source.

Procedures. Hydrolysis of uranyl ions in 80% heavy water and in light water was investigated by measurements of the total concentration of free lyonium ion using a glass electrode. Sodium perchlorate was used as an ionic medium in order to keep the total concentration of perchlorate ion to be 3 M. The total concentration of uranyl ion was kept constant in each series of experiments.

The lyonium ion concentration was measured by means

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13) P. Salomaa, *Acta Chem. Scand.*, **23**, 2095 (1969).

14) H. Kakihana and L. G. Sillén, *ibid.*, **10**, 985 (1956).

15) H. S. Dunsmore, S. Hietanen, and L. G. Sillén, *ibid.*, **17**, 2644 (1963).

16) S. Hietanen, B. R. L. Row, and L. G. Sillén, *ibid*, **17**, 2735 (1963).

of the cell;

$$\text{GE}|\text{Test Solution}|\text{Ref} \qquad \text{(A)}$$

where GE denotes a glass electrode and Ref, the reference half cell containing 2.99 M $NaClO_4$—0.01 M $AgClO_4$ solution and a silver-silver chloride electrode. The liquid junction between the reference half cell and the test solution was constructed with 3 M $NaClO_4$ in 80% heavy water or in light water.

For the system of light water, both coulometric and ordinary titrations were employed. Since no difference has been observed between the results by these two methods, a coulometric titration was used for the system of 80% heavy water.

The emf of the cell(A) is given, at 25°C, as follows:[18]

$$E = E_0 + 59.15 \log l + E_j \qquad (21)$$

E_j, a liquid junction potential was negligible under the present experimental condition.

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17) W. Forsling, S. Hietanen, and L. G. Sillén, *ibid.*, **6**, 901 (1952).

18) H. Kakihana, M. Maeda, and T. Amaya, This Bulletin, **43**, 1377 (1970).