BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2889—2890 (1973)

# The Hydrolysis of $Y^{3+}$, $La^{3+}$, $Gd^{3+}$, and $Er^{3+}$ Ions in Heavy Water[1]

Toshihiko AMAYA,[2] Hidetake KAKIHANA, and Masunobu MAEDA*
*Research Laboratory of Nuclear Reactors, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152*
**Department of Electrochemistry, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152*

(Received March 2, 1973)

In the preceding papers,[3-6] we studied the hydrolysis reactions of $Be^{2+}$, $UO_2^{2+}$, and $Cu^{2+}$ ions in heavy water, and found that the compositions of the hydrolysis species formed in heavy water are the same as those in light water, while the stability constants of the complexes in heavy water are smaller than those in light water.

In the present work, the hydrolysis reactions of $Y^{3+}$, $La^{3+}$, $Gd^{3+}$, and $Er^{3+}$ ions in heavy water have been studied and the results have been compared with those previously obtained in light water.[7]

## Symbols

The symbols used are the same as those described in Refs. 3 and 7.

## Experimental

*Reagents and Apparatus.* The reagents used were, unless otherwise stated, prepared and analyzed as has been described in Ref. 7. A rare-earth perchlorate solution of heavy water was prepared from its solution of light water by repeated evaporation under an infrared lamp, while adding heavy water.

All the apparatuses employed were the same as those used in Ref. 7.

*Procedures.* All the measurements were carried out in a paraffin-oil thermostat kept at 25.00±0.01 °C and placed in a room thermostated at 25±1 °C.

The hydrolysis of the rare-earth ions was investigated by measurements of the deuterium-ion concentration with a glass electrode. A hydrolyzed test solution prepared by the procedures described in the preceding paper[7] was electrolyzed to generate $D^+$ ions by means of constant-current coulometry. The same cell assembly as that described in Refs. 3 and 7 was used for the emf measurements and the constant-current coulometry.

## Results and Discussion

The $Z(\log d)_B$ data for $Y^{3+}$, $La^{3+}$, $Gd^{3+}$, and $Er^{3+}$ ions are graphically represented in Fig. 1.

The experimental data were analyzed by the methods

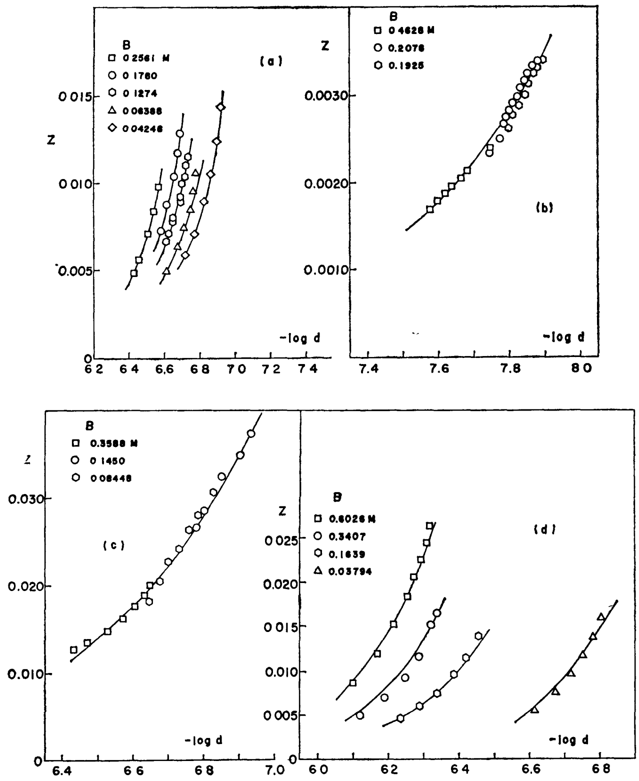

Fig. 1. Average number, $Z$, of OD bound per a) Y(III), b) La(III), c) Gd (III) and d) Er (III), as a function of $-\log d$. The drawn curves were calculated with the stability constants listed in Table 1.

TABLE 1. STABILITY CONSTANTS FOR THE HYDROLYSIS SPECIES OF THE RARE-EARTH IONS IN HEAVY WATER AND IN LIGHT WATER[a)]

| | $Y^{3+}$ | | $La^{3+}$ | | $Gd^{3+}$ | | $Er^{3+}$ | |
|---|---|---|---|---|---|---|---|---|
| | in $D_2O$ | in $H_2O$ | in $D_2O$ | in $H_2O$ | in $D_2O$ | in $H_2O$ | in $D_2O$ | in $H_2O$ |
| $-\log \beta_{1,1}$ | — | — | 10.35<br>±0.01 | 10.04<br>±0.01 | 8.34<br>±0.02 | 8.20<br>±0.01 | — | — |
| $-\log \beta_{2,1}$ | 17.0<br>±0.1 | 16.8<br>±0.1 | — | — | — | — | 17.4<br>±0.1 | 17.2<br>±0.1 |
| $-\log \beta_{2,2}$ | 14.75<br>±0.03 | 14.04<br>±0.01 | — | — | — | — | 14.29<br>±0.01 | 13.72<br>±0.01 |

a) The uncertainties of the constants were estimated as $3\sigma$.

---

[1] Ionic Equilibria in Heavy Water (Part VIII).

[2] Present address: NGK Insulators Co., Mizuho, Nagoya.

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

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

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

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

[7] T. Amaya, H. Kakihana, and M. Maeda, This Bulletin, **46**, 1720 (1973).

described in Ref. 7.

The most probable values for the stability constants of the hydrolysis species, calculated by means of the generalized least-squares method with the aid of an electronic computer (HITAC 5020), are listed in Table 1; the results in light water previously reported[7] are also listed for the sake of comparison.

The conclusions which we derived in the preceding works were confirmed in the present study; that is, the compositions of the species formed in heavy water are the same as those in light water, while the values of the equilibrium constants are smaller in heavy water than in light water.

We plotted the difference in the $\log \beta_{2,2}$ values in light and heavy water, $\Delta \log \beta_{2,2} = \log \beta_{2,2}(\text{in } H_2O) - \log \beta_{2,2}(\text{in } D_2O)$ against $\log \beta_{2,2}(\text{in } H_2O)$ for the (2,2) hydrolysis species of $Y^{3+}$ and $Er^{3+}$ ions, as well as those of the $(CH_3)_2Sn^{2+}$,[8] $UO_2^{2+}$, and $Cu^{2+}$ ions.[4-6] The plot is shown in Fig. 2. The figure shows that $\Delta \log \beta_{2,2}$ is practically independent of the change in $\log \beta_{2,2}$ (in $H_2O$) at about 0.7.

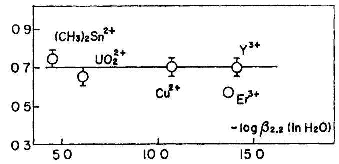

Fig. 2. $\Delta \log \beta_{2,2} = \log \beta_{2,2}$ (in $H_2O$) $- \log \beta_{2,2}$ (in $D_2O$) as a function of $-\log \beta_{2,2}$ (in $H_2O$).

Many workers[9] have reported that $\Delta pK$ (the difference in the $pK$ values of an acid in light and heavy water) increased with $pK$(in $H_2O$). In contrast with these conclusions, Ohtaki and Maeda[10] have pointed out that $\Delta pK$ is independent of $pK$(in $H_2O$) for many organic acids with a similar structure for which a linear free-energy relationship holds. It is interesting that the same tendency has been found for the hydrolysis of the metal ions; it can be regarded as a dissociation reaction of weak acids, although no simple relation like the LFER for organic acids has been found between the acidities and other physico-chemical properties of aquated metal ions.

The authors wish to thank Dr. Hitoshi Ohtaki for his valuable discussions.

---

[8] R. S. Tobias and M. Yasuda, *J. Phys. Chem.*, **68**, 1820 (1964).

[9] P. M. Laughton and R. E. Robertson, "Solute-Solvent Interactions," ed. by J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York (1969), p. 399.

[10] H. Ohtaki and M. Maeda, *Z. Naturforsch.*, **B27**, 571 (1972).