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Effect of Temperature on HTO-Dissociation Determined by Ion Exchange Resins

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In order to reveal the effect of temperature on (i) the dissociation equilibrium of tritiated water (HTO water) and (ii) the reactivity of each anion-exchange resin, the OT-for-OH exchange reaction between each anion-exchange resin and HTO water was studied within the range of 20˚C to 80˚C in the equilibrium state. In addition, the apparent dissociation constant (pK') for each resin was estimated by the method of pH-titration. From the observation of the OT-for-OH exchange reaction between each of the following anion-exchange resins and HTO water, the next three items have been found: (1) in the case of acryl-type anion-exchange resin, the effect of temperature on OT-for-OH exchange reaction is larger than that on the reaction in the case of styrene-type one; (2) the radioactivity incorporated into weakly basic anion-exchange resin (OH^--form) by the isotope exchange reaction is smaller than that into strongly basic one; (3) in the case of the weakly basic anion-exchange resin, the amount of radioactivity incorporated into Cl^--form resin by the hydrolysis is larger than the amount of radioactivity incorporated into OH^--form resin by the isotope exchange reaction.

Keywords OT-for-OH exchange reaction, anion-exchange resin, tritium, dissociation of tritiated water, apparent dissociation constant

The external exposure from T can be neglected because (1) the half-life of the tritium (T) is relatively long (12.3 y), and (2) the maximum energy of the β^--rays emitted from T is relatively low (18.6 keV). When T is incorporated into the body, it can be thought that T causes some internal exposure, and is exchanged with ^1H in important functional groups in the body.[1,2] The T-concentration in the atmosphere increases with increasing the number of nuclear power plants and reprocessing plants for spent nuclear fuel, and with the further study of nuclear fusion.[2]

We have studied the hydrogen-isotope exchange reactions (T-for-H exchange reactions) between T-labeled compounds and unlabeled ones having a functional group in gas-solid[2,3] and liquid-solid[2,4,5] systems. Moreover, several isotope exchange reactions between T-including atomic groups (*i.e.*, OT-for-OH exchange reactions) were recently observed in the equilibrium state.[6–8] The following have been found: (1) OT-for-OH exchange reaction occurred between HTO water and each strongly basic anion-exchange resin having styrene-divinylbenzene copolymer matrix; (2) the higher the temperature is, the smaller is the radioactivity due to OT-for-OH exchange reaction in anion-exchange resin (IRA400), and the higher the temperature is, the larger is the radioactivity due to T-for-H exchange one in the case of cation-exchange resin (IR120B); (3) the radioactivity of the resin due to exchange reaction decreases with increasing the degree of crosslinking.

HTO and ROH (where ROH means each OH^--form anion-exchange resin) dissociate as shown in Formulas (1), (2), and (3), respectively.

$$HTO \rightleftharpoons H^+ + OT^- \tag{1}$$

$$HTO \rightleftharpoons T^+ + OH^- \tag{2}$$

$$ROH \rightleftharpoons R^+ + OH^- \tag{3}$$

Consequently, the OT-for-OH exchange reaction between HTO and ROH can be expressed as Formula (4).

$$ROH + HTO \rightleftharpoons ROT + H_2O \tag{4}$$

When the H^+-form cation-exchange resin is abbreviated as R′H, the T-for-H exchange reaction between HTO and R′H can be expressed as Formula (5).

$$R'H + HTO \rightleftharpoons R'T + H_2O \tag{5}$$

Based on the above-mentioned, we aimed in this work to clarify (1) the behavior of T when tritiated water (HTO water) dissociates, (2) the effect of temperature on the dissociation equilibrium of HTO water, (3) the effect of temperature on the reactivity of each anion-exchange resin, and (4) the effect of the matrix of each anion-exchange resin on the reactivity of the resin.

Experimental

Sample material

Anion-exchange resins used were Amberlite IRA400 (strongly basic styrene type) which has quaternary ammonium salt as a functional group, IRA458 (strongly basic acryl type) having the same functional group as IRA400, and IRA96SB (weakly basic styrene type) having tertiary amine as a functional group. The cation-exchange resin used for comparison was Amberlite IR120B having sulfonate as a functional group (strongly acid styrene type). The structure of the functional group in each ion-exchange resin is shown in Fig. 1. HTO water (specific radioactivity: 185 MBq g^{-1}) was purchased from Japan Radioisotope Association (JRIA), and was diluted to 0.9 MBq g^{-1} in this experiment. The specific radioactivity of HTO water thus prepared was precisely measured with a liquid scintillation counter (Aloka LSC-5101).

Isotope exchange reaction

The experimental procedure for isotope exchange reaction is generally the same as that mentioned before.[8] The method can be summarized as follows. (1) About 60 mg of each regenerated resin was placed in a vial. (2) After 0.300 cm^3 of HTO water was added into the vial, the vial was shaken for 1 h. (3) After that, the vial was vacuum-dehydrated for 3 h by using a vacuum line. (4) An aliquot of the resin (*ca.* 20 mg) was placed into another vial, and was weighed precisely. (5) In case of each anion-exchange resin, 5.00 cm^3 of 1 mol dm^{-3} HCl was added to the vial. In case of the cation-exchange resin, 0.5 mol dm^{-3} NaOH solution was used instead of 1 mol dm^{-3} HCl solution. In case of a weakly anion-exchange resin, 5.00 cm^3 of organic solvent was added to the vial, and the vial was vacuum-dehydrated for 3 h; then 5.00 cm^3 of 1 mol dm^{-3} HCl was added. (6) The resin in each vial was filtered out. (7) The radioactivity of 1.00 cm^3 of the filtrate was measured with a liquid scintillation counter.

pH-titration curve

The procedure for making a pH-titration curve was as follows. (1) Each regenerated anion-exchange resin (*ca.* 0.5 g) was weighed precisely, and put into a vessel (500 cm^3) with 200 cm^3 distilled and CO_2-free water. (2) A pH electrode (HORIBA 6366-10D) and a buret for dropping the titrant (0.100 mol dm^{-3} HCl) were set into the vessel. (3) After the solution was degassed with nitrogen, the HCl solution was dropped into the vessel in a nitrogen atmosphere. In case of Amberlite IR120B, the titrant was 0.100 mol dm^{-3} KOH. The pH value of the solution was measured with a pH meter (HORIBA F-13) when the proper amount of the titrant was added to reach an equilibrium. The procedure for measuring total ion-exchange capacity was generally based on the literature.[10,11]

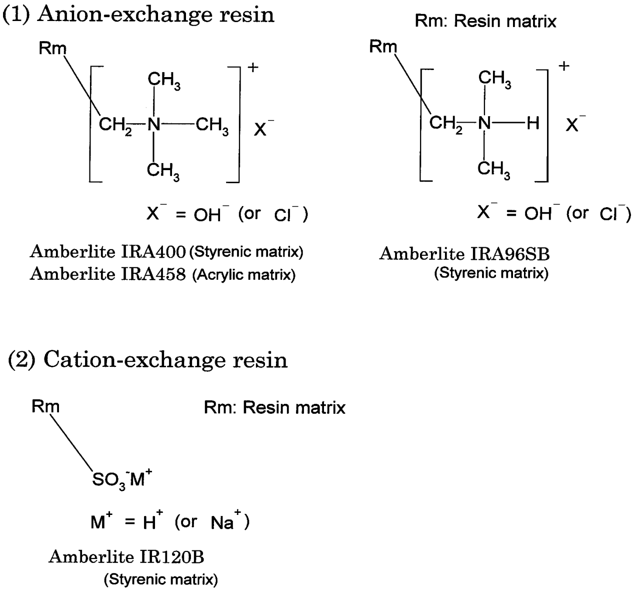

Fig. 1 The structure of the functional group in each ion-exchange resin used.

Results and Discussion

Determination of the apparent dissociation constant for each resin

In order to investigate the effect of the ionic dissociation of the resin on the isotope exchange reaction, an apparent dissociation constant (pK')[11–13] was estimated for each resin. Although pK' is different from pK (which represents the strength of acid-base), it is an useful indication for estimating the degree of the dissociation in each ion-exchange resin.

Based on the following dissociation equilibrium in the resin phase (Formula (6)), the pK_a' value for each cation-exchange resin (R′H) can be estimated as follows.[11–13]

$$R'H \rightleftharpoons R'^{-} + H^{+} \tag{6}$$

$$K_a' = \frac{[R'^{-}][H^{+}]}{[R'H]},\ pK_a' = -\log K_a' \tag{7}$$

$$pK_a' = pH^0 + \log[K^0] - \log[X^0/2] \tag{8}$$

where $[X^0]$ is the concentration of the functional group in the resin, which is determined from the end point value of the KOH titration and is equal to the total ion-exchange capacity.[11] Here pH^0 and $[K^0]$ are the pH and the KOH concentration at half-volume point of the titration, where half the volume of KOH titrant has been added to the solution.

Similarly, in case of anion-exchange resin (ROH), based on the dissociation constant, the pK_b' value is calculated as follows using the autoprotolysis constant (K_w) for H_2O:

$$K_b' = \frac{[R^{+}][H^{-}]}{[ROH]},\ pK_b' = -\log K_b' \tag{9}$$

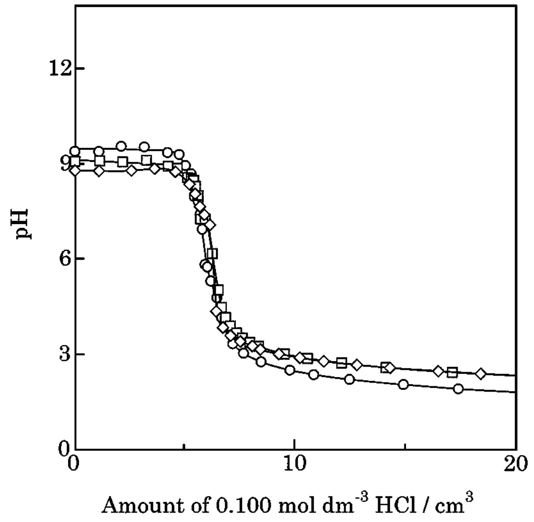

Fig. 2 pH-titration curves for IRA400. ○: 20˚C; □: 40˚C; ◇: 60˚C.

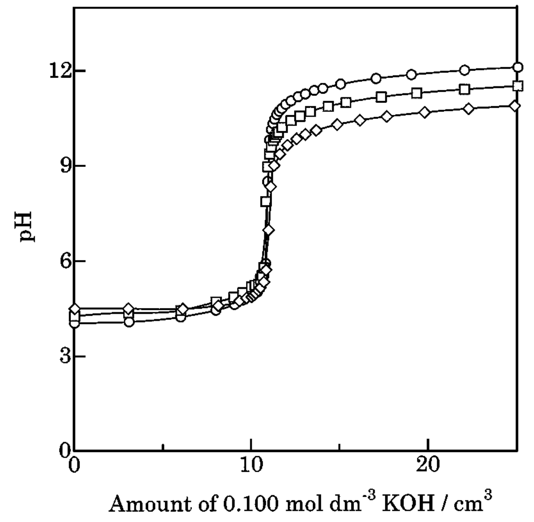

Fig. 3 pH-titration curves for IR120B. ○: 20˚C; □: 40˚C; ◇: 60˚C.

$$pK_b'=-\log K_w-pH^0+\log[Cl^0]-\log[X^0/2] \quad (10)$$

where $[X^0]$ is the concentration of the functional group in the resin, which is determined from the end point value of the HCl titration and is equal to the total ion-exchange capacity. Here pH^0 and $[Cl^0]$ are the pH and the HCl concentration at half-volume point of the titration, where half the volume of HCl titrant is added to the solution.

The pH-titration curves for IRA400 and IR120B are shown in Figs. 2 and 3, and the total ion-exchange capacity for each resin is shown in Table 1. From these values, pK' values for the resins were calculated using Eq. (8) or (10), as shown in Table 2. The pK_b' value for IRA96SB is also calculated at each temperature (Table 2) by using the pH-titration curve, total ion-exchange capacity (Table 1) and Eq. (10).

Table 1 Total ion-exchange capacity of each ion exchange resin at several temperatures

Temperature/˚C	Total ion-exchange capacity/mmol g^{-1}		
	IRA400	IRA96SB	IR120B
20	1.97	2.24	2.35
40	1.91	2.36	2.35
60	1.94	2.43	2.31

Table 2 The pK' value for each resin

Temperature/˚C	pK_b'		pK_a'
	IRA400	IRA96SB	IR120B
20	4.5	10	4.2
40	4.3	9.6	4.4
60	4.0	9.2	4.4

Estimation of the adsorbed water in each resin

In general, it is difficult to remove the moisture adsorbed in the interior of an ion-exchange resin completely because the resin is porous.[9] Accordingly, the radioactivity obtained from each ion-exchange resin includes both the radioactivity adsorbed as HTO water and the radioactivity of OT^- (and T^+) exchanged with X^- (and M^+) in the resins shown in Fig. 1.

It is thought that the hydrolyses of Cl^--form of IRA400, Cl^--form of IRA458, and Na^+-form of IR120B do not occur, but Cl^--form of IRA96SB causes hydrolysis, because the former are strongly basic (and acidic) types and the latter is weakly basic type.

Therefore, in case of IRA458, the real radioactivity incorporated into each resin by exchange reaction was estimated by subtracting the radioactivity adsorbed in the Cl^--form resin from the radioactivity in the OH^--form resin as in the case of IRA400.[8] On the other hand, in the case of IRA96SB, another estimation method using each organic solvent was applied. As for the results for IRA458 and IRA96SB, see the latter sections.

Effect of temperature on the dissociation equilibrium of HTO water

Using the data in Table 2, we normalized the K' values at 40˚C and 60˚C for IRA400 (or IR120B) to that at 20˚C.

$$\text{IRA400 (20˚C):(40˚C):(60˚C)}=1.0:1.6:3.2 \quad (11)$$

$$\text{IR120B (20˚C):(40˚C):(60˚C)}=1.0:0.63:0.63 \quad (12)$$

Further, the temperature dependence of the ratios of radioactivity incorporated into IRA400 (or IR120B) was obtained by using the data in Ref.8.

$$\text{IRA400 (20˚C):(40˚C):(60˚C)}=1.0:1.1:0.77 \quad (13)$$

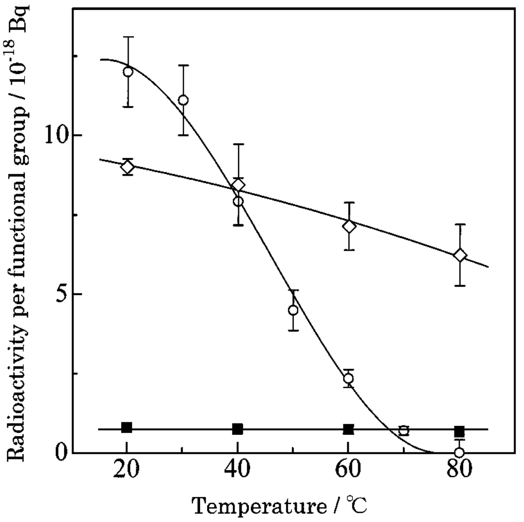

Fig. 4 Radioactivity per functional group in IRA458 (and IRA96SB) *vs.* temperature. ○: IRA458; ■: IRA96SB (OH^--form); ◇: IRA96SB (Cl^--form).

$$\text{IR120B } (20^\circ\text{C}):(40^\circ\text{C}):(60^\circ\text{C})=1.0:1.5:1.7 \qquad (14)$$

In the case of IRA400, when the temperature rises from 20˚C to 60˚C, the dissociation of IRA400 increases by a factor of 3.2, while the radioactivity in the OT-for-OH exchange reaction becomes 0.77 times. Then, the decreasing rate of “$HTO \rightleftharpoons H^+ + OT^-$” is estimated to be 0.24 (0.77×1.0/3.2) if one raises the temperature from 20˚C to 60˚C.

In case of IR120B, when the temperature rises from 20˚C to 60˚C, the dissociation of IR120B decreases by a factor of 0.63, while the radioactivity in the T-for-H exchange reaction becomes 1.7 times. Then, the increasing rate of “$HTO \rightleftharpoons T^+ + OH^-$” is estimated to be 2.7 (1.7×1.0/0.63) if one raises the temperature from 20˚C to 60˚C.

Thus, the presumption[6,8] that Formula (2) is more predominant than Formula (1) at high temperature could be quantitatively expressed in this work.

Effect of the matrix of anion-exchange resins on the OT-for-OH exchange reaction

In order to survey the effect of the matrix of anion-exchange resins on the OT-for-OH exchange reaction, IRA458 was used and the results were compared with those of IRA 400.[8] The radioactivity incorporated into IRA458 by the OT-for-OH exchange reaction is shown in Fig. 4. It is found that the higher the temperature is, the smaller is the radioactivity due to the OT-for-OH exchange reaction in IRA458. The trend is similar to that of IRA400[8]. In addition, the decreasing rate for IRA458 is larger than that for IRA400. In other words, the effect of temperature on the OT-for-OH exchange reaction in acryl type anion-exchange resin is larger than that in styrene type one. This may be attributed to the heat-resistant difference between the two types of resins. The result suggests that the exchange capacity for acryl type anion-exchange resin decreases much more rapidly than that for styrene type one with raising the temperature. It can be presumed that the decomposition of the functional group may be gradually caused as the temperature increases.

Table 3 Radioactivity per functional group in IRA96SB (OH^--form and Cl^--form) at each temperature

Temperature/˚C		Total[a] 10^{-18} Bq	1,4-Dioxane[b] 10^{-18} Bq
20	OH^--form	1.71±0.15	0.90±0.02
	Cl^--form	14.50±0.21	5.49±0.15
40	OH^--form	1.58±0.11	0.83±0.05
	Cl^--form	12.70±1.21	4.26±0.41
60	OH^--form	1.49±0.01	0.75±0.02
	Cl^--form	11.50±0.67	4.36±0.34
80	OH^--form	1.30±0.06	0.67±0.06
	Cl^--form	10.60±0.68	4.36±0.36

a. "Radioactivity of OT^- due to exchange reaction (or due to the hydrolysis)" + "Radioactivity of HTO adsorbed".
b. "Radioactivity of HTO adsorbed".

In order to confirm this, the total ion-exchange capacity for IRA458 (OH^--form) was measured after heating at 80˚C for 5 h. A large decrease (about 20% decrease) of total ion-exchange capacity for the resin was found, but the total ion-exchange capacity was not equal to zero.

Baumann[15,16] suggested that the decomposition reaction in anion-exchange resin occurs according to a Hoffmann-decomposition of quaternary ammonium base.

$$R\text{-}CH_2\text{-}N^+(CH_3)_3OH^- \longrightarrow R\text{-}CH_2OH+N(CH_3)_3 \qquad (15)$$

$$R\text{-}CH_2\text{-}N^+(CH_3)_3OH^- \longrightarrow R\text{-}CH_2N(CH_3)_2+CH_3OH \qquad (16)$$

Trimethylamine ($N(CH_3)_3$) has the smell of ammonia, and the aqueous solution shows basic. Accordingly, we suppose that HCl was neutralized with $N(CH_3)_3$ produced by Reaction (15) when the ion-exchange capacity of heat-treated IRA458 was measured. In the heat-treated operation, trimethylamine ion was detected. Therefore, total ion-exchange capacity was decreased.

Effect of temperature on the reactivity of weakly basic anion-exchange resin

The total radioactivity in IRA96SB (OH^--form and Cl^--form) is shown in Table 3. It is found that the total radioactivity in Cl^--form resin is much larger than the radioactivity in OH^--form resin in the case of weakly basic resin.

The radioactivity of T incorporated as adsorbed water in the resin was estimated by rinsing each dried resin with some organic solvents after the OT-for-OH exchange reaction. Eight organic solvents of ethanol, 1-propanol, 2-propanol, 1-buthanol, 1,4-dioxane, *N*,*N*-

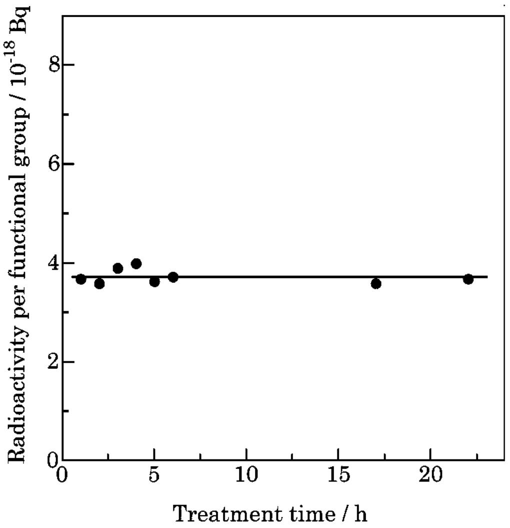

Fig. 5 Radioactivity per functional group in IRA96SB (Cl^--form) *vs.* treatment time with 1,4-dioxane. Reaction temp.: 40˚C.

dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and ethylenediamine were used because each of them has a strong affinity for water and is expected not to cause the OT-for-OH exchange reaction in the resins. The radioactivity removed from IRA96SB (Cl^--form) by treating with each organic solvent, and that removed with HCl solution after organic solvent-treatment, were also measured. It is found that the radioactivity rinsed with 1,4-dioxane is the least, and is supposed that the other organic solvents may react with the resin. Ethers such as 1,4-dioxane are generally chemically inert.[17]

In order to confirm whether 1,4-dioxane induces the exchange reaction of OT^- with OH^- in IRA96SB, the relation between the radioactivity in the Cl^--form resin and treatment time was studied (Fig. 5). The figure shows that the radioactivity in the resin is unvaried with time. Therefore 1,4-dioxane is the most suitable solvent for estimating the radioactivity of T adsorbed as HTO water in the resin.

By subtracting the radioactivity rinsed with 1,4-dioxane from the total radioactivity in Table 3, the relation between the real radioactivity of IRA96SB due to the exchange reaction (or due to the hydrolysis) and the temperature is also shown in Fig. 4. Based on the figure, the following four points can be suggested and discussed.

(i) The radioactivity incorporated into the Cl^--form resin is much larger than that into the OH^--form resin in case of IRA96SB. Thus, for IRA96SB, the incorporation of OT^- by the hydrolysis is much larger than that by the OT-for-OH exchange reaction.

(ii) The higher the temperature is, the smaller is the amount of radioactivity incorporated into IRA96SB (Cl^--form). Related to this result, OT^- (and OH^-) can be supposed to be incorporated into "the Cl^--form weakly basic anion-exchange resin (RCl)" by the hydrolysis as shown in Formulas (17) – (19).

$$RCl \rightleftharpoons R^+ + Cl^- \tag{17}$$

$$R^+ + HTO \rightleftharpoons ROT + H^+ \tag{18}$$

$$R^+ + HTO \rightleftharpoons ROH + T^+ \tag{19}$$

Here, it can be considered that OT^- (and OH^-) incorporated by the hydrolysis are based on the dissociation of HTO water. When OT^- (and OH^-) are incorporated into the resin by the hydrolysis, the degree of the incorporation of OT^- into the resin depends on the rate of the dissociation of HTO water. As described above, Formula (2) is more predominant than Formula (1) at high temperature. Accordingly, it can be considered that the higher the temperature is, the smaller is the amount of OT^- incorporated by the hydrolysis of IRA96SB (Cl^--form).

(iii) The radioactivity incorporated into IRA96SB (OH^--form) is 1/5 to 1/3 times the radioactivity into IRA400.[8] From Table 2, K_b' for IRA96SB is less than that for IRA400 by a factor of 10^5 at each temperature. Therefore, the radioactivity incorporated into "the weakly basic anion-exchange resin (OH^--form)" is smaller than the amount incorporated into the strongly basic one.

(iv) The radioactivity incorporated into IRA96SB (OH^--form) is less affected by temperature than the radioactivity incorporated into IRA458 (and IRA400[8]).

From this work, both the effects of temperature on the dissociation equilibrium of HTO water and on the reactivity of each anion-exchange resin in the OT-for-OH exchange reaction could be quantitatively revealed. Moreover, the data obtained in this work can be useful for the prevention of T-contamination.

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