Isothermal gas chromatography study of Zr and Hf tetrachlorides using radiotracers of ^{88}Zr and ^{175}Hf—Towards investigation of gas-phase chemistry of Rf—†

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The gas-phase chemical study of Rf, $Z = 104$, has been carried out for its tetrachloride together with $ZrCl_4$ and $HfCl_4$, which are homologues of Rf in the periodic table.[1] Zvára pointed out that the reported values of adsorption enthalpy ($\Delta_{ads}H$) were quite different between experiments and attributed this to the differences in the modification of the surface of the quartz glass column by different chlorinating reagents.[2] To overcome this problem, the present study aimed at obtaining reliable $\Delta_{ads}H$ values of $ZrCl_4$ and $HfCl_4$ by using isothermal gas chromatography.

The apparatus consisted of four components: (i) a reaction part; (ii) a chloride collection part; (iii) an isothermal part; and (iv) a measurement part. Parts (i)–(iii) were heated individually using an electric tube furnace, and part (iv) was cooled with water to collect the chloride passed through the isothermal column. A straight quartz glass tube passed through the four parts. The inner diameter of the isothermal part was 4 mm, and its length was 30 cm.

The radioactive tracers of ^{88}Zr and ^{175}Hf were produced via ^{89}Y$(d,3n)$ and ^{nat}Lu(d,xn) reactions, respectively, by a 24 MeV deuteron beam supplied by the RIKEN K70 AVF cyclotron. Zr and Hf tracers were reacted with CCl_4 at 600°C for 90 min, and the formed chloride was collected on carbon filter put upstream of the isothermal part. Then, the chloride was evaporated at 400°C, and cumulative yields of the chloride were obtained with γ-ray measurement.

The surface-chlorinated quartz column was examined to study the effect of the surface state of the column on the behaviors of $ZrCl_4$ and $HfCl_4$ in the isothermal chromatography. The column was chlorinated with CCl_4 at 600°C for 2 h. After the chlorination, the $ZrCl_4$ and $HfCl_4$ chromatography was carried out. Chromatography experiments were performed at column tempetatures of 135–160°C for the non-treated column and at 100–140°C for the chlorinated column.

In the column-migration model applied to isothermal chromatography,[3] the average retention time ($\bar{t}_r$) is expressed as the following eqation:

$$\ln\left(\bar{t}_r\sqrt{T_{iso}}\right) = -\frac{\Delta_{ads}H}{R}\frac{1}{T_{iso}} + k$$

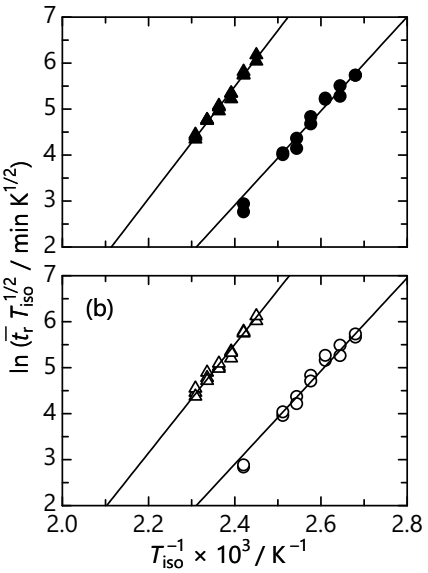

Fig. 1. Plot of $\ln\left(\bar{t}_r\sqrt{T_{iso}}\right)$ versus $1/T_{iso}$ for $ZrCl_4$ (a) and $HfCl_4$ (b). Triangles and circles indicate the type of the column, non-treated and chlorinated, respectively. The solid lines are the results of a least-square fitting.

where k is a constat value including the experimental parameters. Therefore, a plot of $\ln\left(\bar{t}_r\sqrt{T_{iso}}\right)$ against $1/T_{iso}$ is expected to yield a straight line and from its slope, $\Delta_{ads}H$ can be obtained independent of the ambiguous experimental parameters.

Figure 1 plots the results of $\ln\left(\bar{t}_r\sqrt{T_{iso}}\right)$ against $1/T_{iso}$. From the slopes of the fitted lines, the values of $\Delta_{ads}H$ free from parameters were obtained for the first time and those of $ZrCl_4$ and $HfCl_4$ for the non-treated column were -101.3 ± 4.0 kJ mol^{-1} and -98.1 ± 3.1 kJ mol^{-1}, respectively. For the chlorinated column, $\Delta_{ads}H$ of $ZrCl_4$ was -85.1 ± 4.5 kJ mol^{-1} and that of $HfCl_4$ was -84.2 ± 3.3 kJ mol^{-1}.

Comparing with the theoritical calculation by Pershina *et al.*,[4] in both types of column, this is more likely to include a physisorption of MCl_4. If this adsorption mechanism is adopted, $RfCl_4$ is expected to have an enthalpy close to that of the homologues.[4]

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