水素同位体水分子の吸脱着に関する研究：基礎的研究とトリチウム浄化システムへの応用

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Chapter IV

Adsorption-Desorption of Isotopic Waters on Activated Alumina with Multilayer Formation

- Hysteresis Model Assuming Potential Shift -

In the last chapter, the characteristics of adsorption of H$_2$O and D$_2$O on activated alumina were investigated experimentally and analytically, where the multilayer adsorption was assumed by modeling cluster decorations on alumina surface-structural hydroxyl groups with water molecules. The multilayer adsorption of isotopic waters was described with a Freundlich-type homogeneous polynomial with respect to the Polanyi potential. The multilayer model was verified by the fact that the empirical parameters for H$_2$O and D$_2$O are consistent with the relationships of structure and energy between layers in a modeled multilayer.

In the present chapter, the characteristics of desorption of H$_2$O and D$_2$O are examined as continued from the previous study, using the same apparatus and alumina specimen as for the adsorption. The experimental results show the characteristics of desorption irreversible to adsorption: hysteresis phenomena.

An attempt is made to explain the hysteresis phenomena by a model assuming a shift of chemical potential in the adsorbed phase. The difference in the potential shift is defined as an energetic factor characterizing hysteresis, and another factor quantitatively characterizing hysteresis is also defined. The equation for adsorption is modified by regarding these hysteresis factors. The modified equation can describe not only the adsorption characteristics but also the desorption characteristics.

The desorption characteristics of H$_2$O are satisfactorily approximated by this equation. The present model predicts a variety of hysteresis loops formed by adsorption-desorption swing operation under varied conditions. The comprehensive expression is verified by comparing between experimental and calculated hysteresis-loops for H$_2$O under the same operational
conditions. The desorption characteristics of D$_2$O are also approximated by the modified equation with quantitative hysteresis parameters equivalent to those for H$_2$O. An experimental hysteresis loop for D$_2$O is also simulated by the comprehensive expression. The hysteresis model and its description are thus certified by clarifying consistence with the empirical characteristics of H$_2$O and D$_2$O.


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1 INTRODUCTION

Many investigations were made for adsorption of water on alumina$^{(1)-(5)}$. The equilibrium behaviors are never sufficiently understood in detail, however. It is well-known that hysteresis phenomena are observed between adsorption and desorption in polar systems. In problems of design and operation on adsorption, it is essential to know desorption isotherms as well as adsorption isotherms. Although many types of equation were proposed for describing adsorption isotherms, there is few success in formulating desorption isotherms exhibiting hysteresis phenomena in consistence with adsorption isotherms.

Many attempts were made to interpret hysteresis phenomena as early as 1910's; there are the dry and wet surface model by Zigmond, the bottle-neck model by Kramer and McBain, the cylindrical pore model by Foster and Cohan, and so on. It is generally considered that the cylinder model is more persuasive.
than the others. The hysteresis phenomena were studied in relation to the pore-size distribution\(^{(6)-(13)}\), where various types of pore shape were modeled. Morioka\(^{(14)-(15)}\) reported the result of a hysteresis-loop simulation by the Monte Carlo method, assuming a network structure of cylinders with varied pore sizes.

All of known interpretations are fundamentally based on the capillary condensation theory which is one of the earliest adsorption theories, but its theoretical ground was questioned by Patrick et al. and Gregg who observed adsorptions conflicting with the concept of condensation, in 1920's\(^{(16)}\). Adsorption occurs by a microscopic mechanism of molecular interaction, but the capillary condensation is a macroscopic concept. Nevertheless, this theory is frequently applied to adsorption because of convenience for characterizing adsorbents with the pore-size distribution\(^{(17)-(21)}\). So far, there is no model which can construe hysteresis phenomena as ingenious as the capillary theory, however.

In Chap. III, the adsorptions of \(\text{H}_2\text{O}\) and \(\text{D}_2\text{O}\) on activated alumina were examined experimentally and characterized with the Polanyi potential, \(A=RT\ln(P_e/P)\), where the multilayer adsorption was assumed by modeling cluster decorations on alumina surface hydroxyl groups with water molecules. The adsorption characteristics were described by a Freundlich-type homogeneous polynomial. The multilayer model was endorsed in this polynomial expression. In the present study, also, the desorptions of \(\text{H}_2\text{O}\) and \(\text{D}_2\text{O}\) on activated alumina were examined experimentally as continued from the study of adsorption. Hysteresis phenome-
were observed between the adsorption and desorption characteristics of each of H$_2$O and D$_2$O.

In this chapter, a hysteresis model is proposed assuming a shift of adsorbed-phase chemical potential, where two kinds of factors characterizing hysteresis phenomena are defined. The Freundlich-type equation for adsorption is modified by regarding these factors in accordance with the proposed model. A comparative analysis of the original and modified equations produces a method for determining energetic and quantitative hysteresis parameters from differences in adsorption and desorption characteristics. By this method, the hysteresis difference characteristics of H$_2$O are analyzed, and the hysteresis parameters are obtained. The Freundlich-type adsorption polynomial is reformed as a conditional polynomial comprehensively describing hysteresis adsorption-desorption of water on activated alumina. This conditional polynomial sufficiently approximates the desorption characteristics of H$_2$O and D$_2$O. According to this expression, it is predicted that a variety of hysteresis loops are obtained from adsorption-desorption swings under varied operational conditions. This prediction is confirmed by additional adsorption-desorption experiments for H$_2$O and D$_2$O.

2 EXPERIMENTAL

Desorptions of H$_2$O and D$_2$O on activated alumina were examined by the same gravimetric method using the same adsorbent specimen as the adsorption experiments. The experiments for H$_2$O and D$_2$O were respectively continued as sequential series to the
adsorption experiments for H₂O and D₂O.

At first, the desorption of H₂O was measured. As a leading experimental series, Run 1 was carried out from a condition corresponding to A of 204.9 J/mol after the adsorption beginning from the regeneration of the alumina sample by heating at 593 K. Reason of setting the condition not at the zero point of A was because of hardness to operate the equilibria closely near the absolutely saturated adsorption condition; a slightly aberrant adjustment may induce the condensation. In sequels to this series, two swings between adsorption and desorption were operated in different ranges and processes, Run 2 and 3, in order to observe varied hysteresis loops. Equilibria were conditioned at 60 points in Run 1, 29 points in Run 2 and 30 points in Run 3.

The first experiment of the desorption of D₂O was begun from a potential of 915 J/mol after the adsorption developed from the regenerated condition at 593 K, Run 1, where 31 points were measured. The subsequent experiment, Run 2, is the series of a swing operation between adsorption and desorption, comprising 30 measurement points, for the hysteresis loop observation.

Equilibrium conditions were changed by random combination of pressure and temperature but with respect to the order of the thermochemical vapor potentials corresponding to A. The experimental temperatures are indicated in captions of experimental data figures. Details of experimental conditions are described in Sec. 2 of Chap III, where equations used to estimate vapor pressures at dewpoints are shown.
3 EXPERIMENTAL RESULTS OF DESORPTION OF H₂O

Results from Run 1 for H₂O are shown in Fig. 4.1, where plots indicate the experimental data. Some of them are defaulted in the range near the saturation in order to relieve the congestion of overlapping key marks, but the defaulters are reflected in other figures. In this figure, the plots appear to be distributed on a single curve. The curve was calculated by an equation obtained from hysteresis analyses mentioned in following sections. The dotted line illustrates the curve of adsorption calculated by the following polynomial obtained in the last chapter:

\[ Q = \sum_{j=1}^{3} Q_{ej} \exp(-A/E_j) \]  \hspace{1cm} (4.1)

where the parameters are identical to ones for Eq. (3.10). The experimental data show a clear lineup deviated from the characteristic curve of adsorption: hysteresis phenomena. The desorption curve agrees with the adsorption one at least at the regeneration point, but this point disappears on such logarithmic graphics. If the hysteresis phenomena occurs by the capillary condensation, the agreement at a lower point may appear in Fig. 4.1. The disappearance suggests that the hysteresis phenomena are deduced from another mechanism.

4 MODELING OF ADSORPTION-DESORPTION HYSTERESIS MECHANISM

4.1 Hysteresis Model Assuming Chemical Potential Shift in Adsorbed Phase

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From an energetic standpoint, the difference between desorption and adsorption isotherms can be reputed as a shift of the adsorption potential. Based on this view, a model is created for the purpose of describing the desorption characteristics.

Polanyi's potential theory was originated as an energetic description for adsorption of vapor molecules in an adsorptive potential field. This theory supposes that vapors are adsorbed there finally by condensation and the adsorbed molecules are present in the saturated liquid state, where adsorption and desorption are reversible. If it is attempted to describe the characteristics of adsorption-desorption exhibiting hysteresis phenomena by this potential concept, the mechanism of change in the potential between adsorption and desorption processes must be explained.

On the other hand, Kelvin's formula\(^{(17)(22)(23)}\) based on the capillary theory gave a relation similar to \(A=RT\ln\left(\frac{P_s}{P}\right)\):

\[
RT\ln\left(\frac{P_s}{P}\right) = 2\left(\frac{\gamma V_m}{r}\right)\cos\theta
\]

where \(\gamma\) and \(V_m\) are respectively the surface tension and the molar volume of the saturated liquid, and \(\theta\) represents the contacting angle of the liquid meniscus curvature with the wall of the cylindrical capillary of the radius \(r\). The left term corresponds to \(A\). In this theory, the potential results in the surface tension of the adsorbed phase affected by the capillary wall surface, and is basically the energetic barrier for vaporizing molecules in the adsorbed phase. Hence, this potential should be recognized as "desorption potential" rather than "adsorption potential". The hysteresis phenomena are inter-
preted by the difference in meniscus formations between adsorption and desorption processes. It may be difficult that this macroscopic concept consists with the proposed model of multilayer adsorption of isotopic waters on activated alumina.

As a concept, it can be considered that a vapor molecule shifts one's chemical potential by interacting with neighboring molecules or/and surrounding active sites after adsorbed. If a molecule adsorbed on a site having a potential of $A$ shifts the chemical potential with a positive value of $H$, the molecule cannot be desorbed until the vapor free-energy $G$ is increased up to more than $A+H$. That is the appearance of a hysteresis phenomenon. This explanation is different from the capillary condensation model putting the potential shift on account of the irreversible meniscus formations.

We now suppose a system of adsorption described by a Freundlich-type equation with respect to $A$:

$$Q = Q_0 \exp(-A/E)$$

(4.3)

When molecules adsorbed at $A$ are assumed shifting the chemical potential homogeneously with a value of $H$ after adsorbed, a loop is drawn as illustrated in Fig. 4.2a. The line through the point $P_4$ to $P_1$ is an adsorption curve beginning from an activation condition, calculated by Eq. (4.3). The polygonal line from the point $P_1$ through $P_2$ to $P_3$ is a desorption curve affected by the potential shift. The segment between $P_1$ and $P_2$ corresponds to a band of $H$, where the desorption is obstructed during $G$ corresponding to the range from $A_1$ to $A_2$. The line from $P_2$ to $P_3$ is the desorption curve expressed by
\[ Q = Q_s \exp\left\{ -\left(\frac{A+H}{E}\right) \right\} \] (4.4)

where \( H \) is redefined as the hysteresis potential. The polygonal line from \( P_3 \) through \( P_4 \) to \( P_1 \) is a curve of adsorption returning from desorption. The segment between \( P_3 \) and \( P_4 \) is the transitional band in the adsorption process, where the adsorption is obstructed because the potential sites in the range from \( A_3 \) to \( A_4 \) are already occupied by the adsorbate molecules retained while the desorption reaches the return point \( P_3 \). After the equilibrium condition has attained to the point \( P_4 \), the adsorption occurs in the same way as the original adsorption started from the activation.

The chemical potential shift should be considered with an irregularity, but the modeling becomes too complicated. Hence, an assumption is made here to realize the hysteresis concept in empirical expressions, as follows.

Two kinds of phases are assumed in the adsorbed phase: one is of raising the shift with a constant hysteresis potential of \( H \), and the other is not of that. The total adsorbed-phase capacity \( Q_s \) comprises the capacity of the phase exhibiting hysteresis \( Q_{sh} \) and the capacity of the other phase \( Q_{sr} \), and correspondingly, the amount adsorbed \( Q \) is given as the sum of the amounts adsorbed, \( Q_r \) and \( Q_h \):

\[ Q_s = Q_{sr} + Q_{sh} \] (4.5)
\[ Q = Q_r + Q_h \] (4.6)

where the subscripts \( h \) and \( r \) respectively identify the hysteresis raising phase and the reversible adsorption-desorption
occurring phase. The adsorption and desorption in the \( r \)-phase are expressed by

\[
Q_r = Q_{sr} \exp(-A/E) \tag{4.7}
\]

On the other hand, the adsorption and desorption in the \( h \)-phase are irreversible, and the expression is conditioned: when the equilibrium operation is completely in the adsorption process,

\[
Q_h = Q_{sh} \exp(-A/E) \tag{4.8}
\]

and when completely in the desorption process,

\[
Q_h = Q_{sh} \exp(-(A+H)/E) \tag{4.9}
\]

In the same operational story as in Fig. 4.2a, a hysteresis loop is drawn as solid line curves shown in Fig. 4.2b. When the operation is completely in the adsorption process, the line from \( P_4 \) to \( P_1 \) is given by Eq. (4.3) as the aggregation of Eqs. (4.7) and (4.8). In the transitional process from adsorption to desorption, the curve from \( P_1 \) to \( P_2 \) is given by

\[
Q = Q_{sr} \exp(-A/E) + Q_{sh} \exp(-A_1/E) \tag{4.10}
\]

In this equation, the last term is constant until \( A \) reaches \( A_2 \). The segment between \( P_2 \) and \( P_3 \) is completely in the desorption process. This line is calculated by the aggregation of Eqs. (4.7) and (4.9):

\[
Q = Q_{sr} \exp(-A/E) + Q_{sh} \exp(-(A+H)/E) \tag{4.11}
\]

In the transitional process from desorption of adsorption, the curve from \( P_3 \) to \( P_4 \) is calculated by
where the last term is constant until $A$ reaches $A_4$. Within the transitional regions, therefore, the adsorption and desorption characteristics are reversible.

### 4.2 Method of Analysis of Hysteresis Parameters

A clue to hysteresis analyses based on this model is to find the transition point such as $P_2$ or $P_4$ on an experimental hysteresis loop. Since the point is located on the slope of a characteristic curve in the adsorption or desorption process, it may be hard to discriminate the position of the point from a curvature. This discrimination, however, becomes easy when the difference in amounts adsorbed between adsorption and desorption equilibria, $dQ$, is plotted as in Fig. 4.3, because the points are suggested by two peaks as $P_2$ and $P_4$ in this figure. The higher and noticeable peak $P_2$ is originated in the desorption process continued from the complete adsorption process. The modest peak posed on a mountainside, $P_4$, appears in the adsorption process continued from the complete desorption process. The former peak, therefore, is recommended for use to determine the characteristic parameters from the particular point position.

The parameters $Q_{sh}$ and $H$ are determined from the two-dimensional location of this peak point. The energy parameter $H$ is given by

$$H = A_2 - A_1$$

and $Q_{sh}$ is obtained from the following relation:
\[ dQ_p = Q_{sh} \exp(-A_1/E) - Q_{sh} \exp(-A_2/E) \]
\[ = Q_{sh} \left[ \exp(-A_1/E) - \exp(-(A_1 + H)/E) \right] \]  
(4.14)

where \( dQ_p \) is the peak height as the maximum of the difference \( dQ \). From this equation, thus

\[ Q_{sh} = \frac{dQ_p}{\left(1 - \exp(-H/E)\right)\exp(-A_1/E)} \]  
(4.15)

5 ANALYSES OF HYSTERESIS CHARACTERISTICS OF H\textsubscript{2}O

5.1 Determination of Hysteresis Parameters for Multilayer

Figure 4.4a shows the differences of the measured amounts of desorption of H\textsubscript{2}O from the amounts of adsorption calculated by Eq. (4.1). Since the adsorption characteristics of water can be stratified by the three Freundlich-type equations, three hysteresis features may be reflected in the desorption characteristics; three peaks of the \( P_2 \) type are predicted in the hysteresis difference characteristics. Among the three peaks, the peak located at the highest potential can be deduced from the first layer having the largest adsorption potential energy. The second peak is thus assumed to be deduced from the second layer.

The point \( P_{p1} \) in Fig. 4.4a was determined as the peak featured in the first layer, by anticipating that the hysteresis difference gains in the other layers can be ignored in the region around this point. A clue to determining the first peak point can be found from a profile, that the data plots on the higher potential side of the peak are distributed according to
\[ dQ = dQ_0 \exp\left(-\frac{A}{E_1}\right) \]  

(4.16)

where \( dQ_0 \) is the constant of \( dQ \) at \( A=0 \). When the plots are approximated by a curve based on this equation, the \( dQ_{pl} \) point is given on the track of the curve. The maximum \( dQ_{pl} \) is related with \( dQ_0 \) by

\[ dQ_{pl} = dQ_0 \exp\left(-\frac{A_{pl}}{E_1}\right) \]  

(4.17)

where \( A_{pl} \) is the first-peak point potential corresponding to \( A_2 \) for Eq. (4.13). From the relation of \( dQ_{pl} \) to \( dQ_0 \), Eq. (4.16) is rewritten as

\[ dQ = dQ_{pl} \exp\left(\frac{A_{pl}}{E_1}\right) \exp\left(-\frac{A}{E_1}\right) \]  

(4.18)

If \( A_{pl} \) is assumed on a point on the transverse axis, the first-layer hysteresis potential \( H_1 \) is determined by Eq. (4.13) because \( A_1 \) is decided as the experimental condition, 204.9 J/mol, and \( dQ_{pl} \) is evaluated by Eq. (4.17). Then, plots on the other side near the peak should be approximated by

\[ dQ = \frac{dQ_{pl} \{1-B_1 \exp\left(-\frac{A}{E_1}\right)\}}{\{1-\exp\left(-H_1/E_1\right)\}} \]  

(4.19)

where \( B_1 \) is the constant for the first-layer characteristics, \( \exp(204.9/E_1) \) for H2O. Equations (4.18) and (4.19) are valid at \( A \geq A_{pl} \) and \( A \leq A_{pl} \), respectively.

According to above procedure, \( P_{p1} \) was adjusted on a point of 0.507 mol/kg at 28,840 J/mol. Values of \( H_1 \) and \( Q_{sh1} \) were obtained from Eqs. (4.13) and (4.15), listed in Table 4.1a. In Fig. 4.4 two curves agreed with each other at \( P_{p1} \) were individually calculated by Eqs. (4.19) and (4.18). The curves approx-
imates the experimental plot distribution, partially but sufficiently in the region larger than about 20,000 J/mol.

Features of another peak becomes to be more discriminative by suppressing the characteristics of the first-layer hysteresis differences. Figure 4.4b shows results obtained by eliminating the calculated first-layer differences from the experimental hysteresis differences, where the results are plotted. By the same procedure as for the first peak, the second peak was assumed on a point of 0.67 mol/kg at 7,100 J/mol, $P_{p2}$, by similarly anticipating that the third-layer hysteresis characteristics hardly affect it. Based on these locational parameters, $H_2$ and $Q_{sh2}$ were evaluated as listed in Table 4.1a. The curves continued at $P_{p2}$ were calculated by Eqs. (4.18) and (4.19) using the second-layer parameters instead of the first-layer ones. The calculated curves approximate the plotted data in the region larger than about 5,000 J/mol.

By suppressing the hysteresis differences calculated for the first and second peaks, the third-peak features emerge from the experimental hysteresis difference distribution, as plots shown in Fig. 4.4c. The plots are arranged on a mountain-shaped curve similar to the model line illustrated in Fig. 3.3. The top of this mountain was assumed on a position of 3.17 mol/kg at 1,115.1 J/mol, $P_{p3}$, in the same way as for the earlier peaks. From the peak point position, $H_3$ and $Q_{sh3}$ were calculated as values included in Table 4.1a. The slope curves of both mountainsides were calculated by Eqs. (4.18) and (4.19) using $H_3$ and $Q_{sh3}$.

5.2 Comprehensive Description of Adsorption and Desorption
The hysteresis parameters are thus determined for each of the stratified characteristics of H2O on activated alumina. Equation (4.1) can be modified with the hysteresis parameters as the following conditional polynomial:

\[ Q = \sum_{j=1}^{3} Q_{srj} \exp(-A_j/E_j) + \sum_{j=1}^{3} Q_{shj} \exp(-A_{hj}/E_j) \]  

(4.20)

where \( A_{hj} \) represents the conditional potential parameter:

\[ A_{hj} = A_{tdj} \quad \text{when} \quad A_{tdj} \leq A \leq A_{tdj} + H_j \]  

(4.21a)

\[ A_{hj} = A - H_j \quad \text{when} \quad A_{tdj} + H_j < A \]  

(4.21b)

\[ A_{hj} = A_{taj} - H_j \quad \text{when} \quad A_{taj} - H_j \leq A \leq A_{taj} \]  

(4.21c)

\[ A_{hj} = A \quad \text{when} \quad A < A_{taj} - H_j \]  

(4.21d)

where \( A_{tdj} \) is the potential at a point of turn from completely adsorptive to desorptive process and \( A_{taj} \) is that at a point of turn from completely desorptive to adsorption process, for \( j \)-layer. In Fig. 4.1 the curve approximating the experimental results of desorption was calculated by Eq. (4.20) in the relations of Eqs. (4.21a) and (4.21b). This desorption curve must agree with the adsorption curve at least at the regeneration point though the agreement point disappears on the scale in this figure.

For observing an isothermal hysteresis-loop on a linear scale, the experimental data were rearranged in Fig. 4.5, where two isotherms for desorption at 300 K are shown for instance. Equilibrium pressures at this temperature were estimated by

\[ P = P_0 \exp(-A_e/RT) \]  

(4.22)
where \( A_e \) denotes the \( A \)-value calculated with measured equilibrium pressures and temperatures. This equation is identical to Eq. (3.13) in Chap. III. Two dotted lines are the adsorption and desorption isotherms calculated between the activation and saturation. The \( Q \)-values were computed by Eq. (4.20) with \( A \)-values corresponding to the relative pressure \( P/P_s \) at a temperature of 300 K. Widely ranged plots demonstrate the experimental isotherm based on the data from Run 1, and the other plots result from Run 3. Two solid lines were calculated by following the experimental desorption stories in Runs 1 and 3. The calculated curves sufficiently simulate the experimental isotherms.

Similar hysteresis isotherms are frequently observed in water adsorption systems. For example, Rajniak and Yang\(^{(24)}\) showed isotherms for water on silica gels. Desai, Hussain and Ruthven presented isotherms for adsorption and desorption of water on various aluminas in a paper\(^{(2)}\).

5.3 Hysteresis Loop Simulation

The desorption characteristics have been described in consistence with the multilayer adsorption model as endorsed in Figs. 4.1 and 4.5. According to this potential shift model, the hysteresis loop formation depends on the potential conditions at turn points in swing operation between adsorption and desorption equilibria. The conditional expression, Eq. (4.20) with Eqs. (4.21a)-(4.21d), can simulate hysteresis loops for adsorption-desorption of \( H_2O \) on activated alumina.

For the purposes of conforming the formation of varied hysteresis loops, two series of adsorption-desorption experiments,
Runs 2 and 3, were carried out. Run 2 is the operation of the adsorption returning from the desorption after the adsorption developed from the regenerated condition. The results are shown with plots on the route of a-b-c in Fig. 4.6a, Loop-1. Run 3 is the operation of the desorption returning from the adsorption after the desorption beginning from the adsorption developed from the regenerated condition. The results are shown with plots on the route of a-b-c-d in Fig. 4.6b, Loop-2. In these figures, the adsorption and desorption processes are differentiated by two or three kinds of circle keys. Dotted lines are the calculated curves of the adsorption and desorption to/from the saturation. The solid lines approximating the plotted distributions result from the computations obeying the same operational conditions as the experiments. In both figures, the experimental results are satisfactorily traced by the numerical loops.

The prediction has been validated by the agreements of the numerical and experimental results, where it has been endorsed that hysteresis phenomena occur in the range between regenerated and saturated conditions.

6 VERIFICATION OF HYSTERESIS MODEL BY EXPERIMENTAL AND ANALYTICAL RESULTS OF D2O

Results from Run 1 of experimental series of D2O desorption are plotted in Fig. 4.7. Two dotted lines are the adsorption and desorption curves calculated between the regenerated and saturated conditions. The solid line approximating the results was calculated by following the experimental conditions.
These three lines were computed by Eq. (4.20) conditioned by Eqs. (4.21a)-(4.21d), with the hysteresis parameters comprised in Table 4.1b. The characteristics of desorption of D₂O on the same alumina appears to be analogous to that of H₂O. The hysteresis parameters were obtained by the same procedures as for H₂O, as follows.

Figure 4.8a shows the differences of the measured amounts of desorption of D₂O from the amounts of adsorption calculated by (4.1), where the results are plotted. The plots appears to be distributed in features similar to the distribution in Fig. 4.4a for H₂O. The point P₁ was assumed to be the peak gained in the first layer, locating on a position of 0.492 mol/kg at 30,620 J/mol (determination of A₁ and dQ₁). The parameter H₁ was obtained as 29,710 J/mol by Eq. (4.13), where A₁ of 915 J/mol was decided as the experimental condition. The parameter Qsh₁ was evaluated at 0.585 mol/kg by Eq. (4.15). Two curves drawing a wave through P₁ were individually calculated by Eqs. (4.18) and (4.19). The Qsh₁-value is comparable to 0.584 mol/kg for H₂O.

Figure 4.8b shows plots of the experimental differences suppressed by the first-layer hysteresis differences indicated by the curves in Fig. 4.8a. The point P₂ was assumed as the second peak, and a position of 0.511 mol/kg at 8,070 J/mol was given it (determination of A₂ and dQ₂). By Eqs. (4.13) and (4.15), H₂ and Qsh₂ were respectively calculated as 2,450 J/mol and 0.785 mol/kg. The Qsh₂-value is comparable to 0.788 mol/kg for H₂O, as well as the Qsh₁-values for H₂O and D₂O. With these values of H₂ and Qsh₂, the curves reaching P₂ were calculated
by Eqs. (4.18) and (4.19).

By eliminating the hysteresis gains in the first and second layers, a mountain-shaped profile is discriminated from the experimental hysteresis characteristics, as shown with plots in Fig. 4.8c. The third peak was assumed on a point of 0.852 mol/kg at 1860 J/mol, $P_{p3}$ (determination of $A_{p3}$ and $dQ_{p3}$). By Eqs. (4.13) and (4.15), $H_3$ and $Q_{sh3}$ were evaluated at 530 J/mol and 5.76 mol/kg. The $Q_{sh3}$-value is equivalent to that for H2O.

The illustrated mountainside slopes were numerically drawn using Eqs. (4.18) and (4.19) with the values of $H_3$ and $Q_{sh3}$.

The calculated solid line in Fig. 4.7, bases on above analyses, sufficiently describes the desorption characteristics of D2O on activated alumina. In addition, similarly to the case of H2O, the measured data were rearranged as an isotherm for desorption at 300 K in Fig. 4.9, for observing the hysteresis characteristics in a linear scale. Equilibrium pressures at 300 K were estimated from the experimental potential conditions by Eq. (4.22). The corrected experimental results are plotted in this figure. The dotted lines indicate the adsorption and desorption isotherms between regenerated and saturated conditions, estimated by Eq. (4.20). The solid line approximating the plots were drawn by calculating Eq. (4.20) with all parameters included in Table 4.1b. The plotted isotherm is satisfactorily described by the numerical curve.

Run 2 of experiment series of D2O desorption was carried out for confirming a hysteresis loop formation. Results from Run 2 are shown with plots in Fig. 4.10, where two kinds of keys differentiate the adsorption and desorption equilibria. The
plots indicated by a, b and c are the turn points in operational swings between adsorption and desorption. The operation was performed following a course of the desorption returning from the adsorption continued from the desorption beginning from the adsorption developed from the regenerated condition: the route of a-b-c. The solid lines tracing the plots were computed by Eq. (4.20) conditioned by Eqs. (4.21a)-(4.21d), in accordance with the operational story of Run 2. The numerical curve sufficiently simulates the experimental hysteresis loop. This result of simulation demonstrates that D$_2$O behaves adsorption-desorption on activated alumina in the same manner as H$_2$O.

The present hysteresis model held validity in the analyses of the desorption of D$_2$O as well as H$_2$O, in consistence with the multilayer adsorption model. The parameter analyses revealed an interesting fact that the quantitative ratios $Q_{shj}/Q_{sj}$ are equivalent between H$_2$O and D$_2$O. This suggests that the sites inducing the chemical potential shift are decided in the water multilayer or that the probability of presence of molecules shifting the chemical potential in each layer is equivalent between H$_2$O and D$_2$O. The $H_j$-values for D$_2$O are relatively larger than those for H$_2$O, while the $E_j$-values for the former are relatively reduced in comparison with those for the latter. The isotope effect on these energetic factors are discussed in detail in the next chapter, and Relationships of $Q_{ej}$, $Q_{arj}$, $Q_{shj}$, $E_j$ and $H_j$ are comprehensively considered there.

7 CONCLUSIONS

Hysteresis phenomena were observed between the adsorption and
desorption of H$_2$O and D$_2$O on activated alumina. The empirical adsorption-desorption characteristics were successfully described by the conditional polynomial expression. Throughout the experiments and analyses, it has been verified that the hysteresis model is valid in consistence with the multilayer model. Therefore, the hysteresis phenomena can be explained to result in the shift of the chemical potential of adsorbate molecules in the adsorbed phase.

According to the present model, the potential shift produces four processes: the completely adsorptive process, the transitional desorption process, the completely desorptive process, and the transitional adsorption process. In the transitional processes, the adsorption-desorption is reversible. The hysteresis-loop formation is determined by the potential condition at a point of return from the completely adsorptive or desorptive process. The conditional expression has made it possible to predict varied isotherms for adsorption and desorption of H$_2$O and D$_2$O on activated alumina.

The deviation between adsorption and desorption equilibria is promoted by the hysteresis potential defined by the difference in the shift. The isotope effect appears not only on the adsorption potential but also on the hysteresis potential.

Two types of adsorbed phase are assumable: one is of appearance of hysteresis phenomena and the other of disappearance. This assumption is convenient for formulating the hysteresis adsorption-desorption characteristics observed actually. The present ratio of the two types in each layer adsorbed-phase is equivalent between H$_2$O and D$_2$O.
[ NOMENCLATURE ]

\( A \) = Polanyi's adsorption potential \([\text{J} \cdot \text{mol}^{-1}]\)

\( A_e \) = experimental value corresponding to \( A \) \([\text{J} \cdot \text{mol}^{-1}]\)

\( A_h \) = conditional potential parameter for Eq. (4.20) \([\text{J} \cdot \text{mol}^{-1}]\)

\( A_p \) = \( A \) at \( dQ_p \) \([\text{J} \cdot \text{mol}^{-1}]\)

\( A_{ta} \) = \( A \) at point of turn to adsorption \([\text{J} \cdot \text{mol}^{-1}]\)

\( A_{td} \) = \( A \) at point of turn to desorption \([\text{J} \cdot \text{mol}^{-1}]\)

\( A_{1-4} \) = particular values of \( A \) \([\text{J} \cdot \text{mol}^{-1}]\)

\( B \) = constant for Eq. (4.19) \([-\text{]}\)

\( dQ \) = hysteresis difference in \( Q \) between adsorption and desorption \([\text{mol} \cdot \text{kg}^{-1}]\)

\( dQ_p \) = peak point value of \( dQ \) \([\text{mol} \cdot \text{kg}^{-1}]\)

\( dQ_0 \) = constant for Eq. (4.16) \([\text{mol} \cdot \text{kg}^{-1}]\)

\( E \) = characteristic potential energy \([\text{J} \cdot \text{mol}^{-1}]\)

\( G \) = vapor free-energy corresponding to \( A \) \([\text{J} \cdot \text{mol}^{-1}]\)

\( H \) = hysteresis potential \([\text{J} \cdot \text{mol}^{-1}]\)

\( j \) = ordinal number of adsorption layers \([-\text{]}\)

\( P \) = equilibrium vapor pressure \([\text{Pa}]\)

\( P_s \) = saturation vapor pressure \([\text{Pa}]\)

\( Q \) = amount adsorbed \([\text{mol} \cdot \text{kg}^{-1}]\)

\( Q_{zh} \) = amount adsorbed in irreversible phase \([\text{mol} \cdot \text{kg}^{-1}]\)

\( Q_z \) = amount adsorbed in reversible phase \([\text{mol} \cdot \text{kg}^{-1}]\)

\( Q_w \) = limiting amount adsorbed \([\text{mol} \cdot \text{kg}^{-1}]\)

\( Q_{sh} \) = capacity of irreversibly adsorbed phase \([\text{mol} \cdot \text{kg}^{-1}]\)

\( Q_{sr} \) = capacity of reversibly adsorbed phase \([\text{mol} \cdot \text{kg}^{-1}]\)

\( R \) = gas constant \([\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]\)

\( r \) = radius of capillary \([\text{m}]\)
\( T \) = temperature [K]

\( V_m \) = molar volume of saturated liquid [m\(^3\)·mol\(^{-1}\)]

\( \gamma \) = radius of curvature of meniscus [m]

\( \theta \) = contacting angle of meniscus [rad]

<subscripts>

1,2,3 = identification of ordinal layers

\( j \) = identification of \( j \)-layer

--- REFERENCES ---


(20) Sing, K.S.W.: "Characterization of Porous Solids II",


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*: identical to values listed in Table 3.1

Table 4.1b Parameters obtained from hysteresis model analyses of adsorption-desorption characteristics of D₂O

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*: identical to values listed in Table 3.1
Fig. 4.1 Desorption characteristics of H₂O on activated alumina from near saturation toward evacuation with respect to adsorption potential.
Fig. 4.2a Hysteresis loop illustrated by model assuming shift of chemical potential of adsorbate in adsorbed phase
Fig. 4.2b Hysteresis loop modified by assumption of two types of adsorbed phase exhibiting reversible behavior and irreversible behavior
Fig. 4.3 Hysteresis characteristics of quantitative difference between adsorption and desorption
Fig. 4.4a  Hysteresis difference characteristics of H₂O on activated alumina. Temperatures in potential order from 17.46 to 52.61 kJ/mol: 399.4, 407.0, 422.4, 430.9, 436.6, 446.1, 453.4, 468.6, 481.3, 493.5, 500.7, 509.8, 515.3, 522.6, 539.6, 547.6, 561.4, 561.4, 571.1 and 571.7 K
Fig. 4.4b Hysteresis difference characteristics of H₂O with suppression of first-layer difference-characteristics. Temperatures in potential order from 4.25 to 15.87 kJ/mol: 312.5, 311.6, 313.6, 322.1, 319.6, 325.3, 329.0, 335.0, 344.1, 347.8, 355.7, 366.0, 372.6, 374.2, 382.4 and 388.5 K
Fig. 4.4c Hysteresis difference characteristics of H$_2$O with suppression of first and second layers difference-characteristics.
Temperatures in potential order from 0.453 to 3.99 kJ/mol:
302.9, 303.4, 302.9, 302.4, 302.9, 302.9, 300.0, 302.9, 302.6, 302.8, 302.6,
304.8 and 308.2 K; 302.4 K at turn point of 0.205 kJ/mol
Fig. 4.5 Isotherms estimated for desorption of H₂O on activated alumina at 300 K
Fig. 4.6a Adsorption-desorption characteristics of H₂O on activated alumina and hysteresis loop simulation, Loop-1.

Experimental temperatures in order of route a-b-c: 320.6(a), 320.6, 320.6, 320.8, 320.2, 320.8, 321.1, 321.2, 391.5, 411.4, 411.4, 411.4, 436.4, 492.8(b), 483.6, 482.5, 466.7, 448.5, 430.3, 399.7, 384.2, 347.8, 340.0, 332.9, 329.2, 324.1, 318.4, 314.7 and 311.2 K
Fig. 4.6b Adsorption-desorption characteristics of H₂O and hysteresis loop simulation, Loop-2.
Experimental temperatures in order of route a-b-c-d: 302.0(a), 301.9, 300.7, 311.9, 319.9, 327.2, 332.9, 350.8, 357.1, 365.4, 377.4, 391.5, 549.8, 549.8(b), 557.1, 514.1, 417.6, 403.7, 403.6, 382.4, 366.6(c), 366.6, 366.6, 366.6, 366.6, 366.6, 407.0, 424.4 and 561.4 K
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Fig. 4.8c Hysteresis difference characteristics of D_2O with suppression of first and second layers difference-characteristics
Temperature = 300K

- : Calculated
  desorption curve

Experimental
  • : desorption
  ○ : adsorption

Fig. 4.9 Isotherm estimated for desorption of D₂O on activated alumina at 300 K
Fig. 4.10 Adsorption-desorption characteristics of DzO on activated alumina and hysteresis loop simulation. Experimental temperatures in order of route a–b–c:
559.0(a), 540.8, 520.9, 498.3, 482.5, 459.5, 426.7, 408.5, 389.1, 377.5, 360.2, 338.6, 304.0(b), 308.0, 319.9, 330.2, 330.2, 330.2, 346.9, 363.0, 387.2, 404.9, 425.5, 444.4, 476.8, 498.3, 515.3, 534.2, 559.0 and 578.9 K