

Chromatographic Adsorption Measurement of Chlorinated Hydrocarbons into Zeolite

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Abstract

In this study, adsorption measurement of various chlorinated hydrocarbons on zeolites were performed using the chromatographic method to examine the adsorption phenomena. Dichloromethane (DCM), chloroform (TCM), trichloroethylene (TCE) and tetrachloroethylene (PCE) were used as the chlorinated hydrocarbons, and PQ-USY, USY-6.18, Na-Y and Pentasile-2 were used as adsorbent. Each adsorption measurement was performed to get the heat of adsorption and the activation energy of micropore diffusivity.

Introduction

Diffusion as well as adsorption equilibrium in adsorbent particles are important in designing adsorption processes. The possible mechanisms of diffusion in adsorbent particles are classified into three groups in the case of gaseous adsorption. They are diffusion in gas phase of macropores such as molecular diffusion or Knudsen diffusion, surface diffusion which occurs in the adsorbed phase, or diffusion in the micropores whose diameters are comparable with molecular diameter of adsorbates. The engineering estimation of the effective diffusivities for the first and second cases is almost possible, but when the intraparticle diffusion is controlled by the third mechanism, there are still some ambiguities in estimating the order of magnitude of the adsorption rate. Molecular sieving materials such as zeolite have micropores of well-defined structure. Micropores of zeolites have network structures. Study of micropore diffusion in molecular sieving materials is significant since they provide fundamental characteristics of diffusion in other adsorbents which possess micropores of wide varieties. Though many investigations for intracrystalline diffusion in zeolite have been made, there has been, however, little work on diffusion of chlorinated hydrocarbons in zeolite.

Micropore diffusion of adsorbate molecules occurs in the potential energy field which is due to interactions between adsorbate molecules and adsorbent lattice atoms. This diffusion is generally described as each molecule hopping from one minimum of the potential energy distribution to another, or adsorption site to site, across potential energy barriers, which separate adjacent sites. This type of micropore diffusion is a kind of activated process and is called activated diffusion.

The purpose of this work is to experimentally determine the micropore diffusivities and adsorption equilibrium constants of various chlorinated organics in zeolite at wide temperature ranges and to correlate the obtained activation energies of micropore diffusion and isosteric heats of adsorption with the properties of adsorbate gases. Chromatographic measurements were made for this purpose. By introducing the

concentration pulse of adsorbate to the carrier gas stream at the inlet of the adsorbent column, the concentration elution curve at the outlet of the column was measured. Adsorption equilibrium constant and micropore diffusivity were determined by means of moment analysis of elution curves.

Experimental Procedure and Conditions

The experimental apparatus was shown in Figure 1. The apparatus was a conventional gas chromatograph (GC-9A) (Shimadzu Co., LTD). PQ-USY, USY-6.18, Na-Y and Pentasile-2 (crashed and screened to obtain particle size between #20 and #32) were used as adsorbent. These particles were packed in a column. The carrier gas was helium.

Dichloromethane, chloroform, trichloroethylene, and tetrachloroethylene were used as adsorbate. The adsorbate was introduced as pulse into the carrier gas stream by a 6-way valve. The flow was controlled by mass flow controllers (about 25 cm/sec). The outlet signal from the TCD cell was recorded to a chart-recorder and converted into personal computer as pulse response. Column conditions were shown in Table 1.

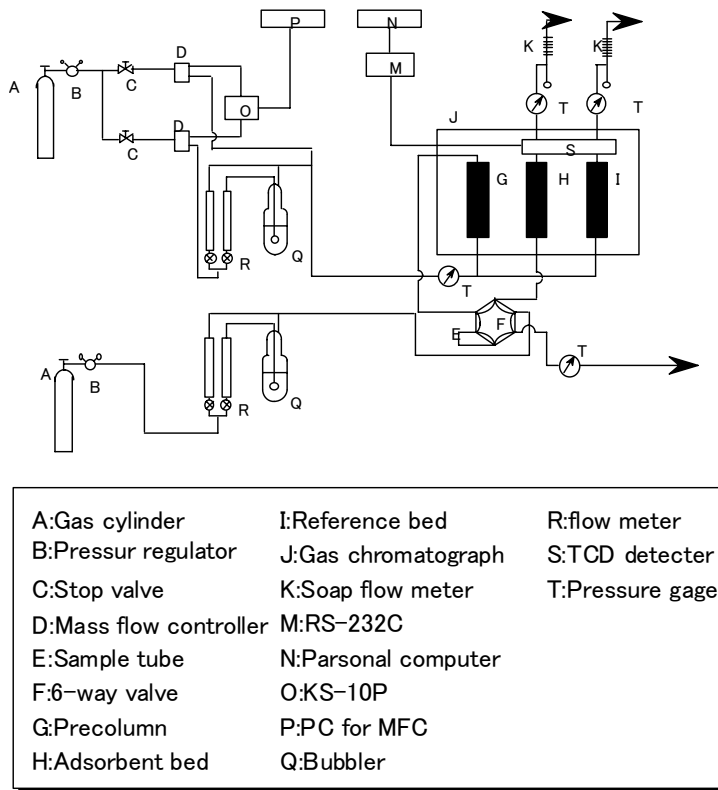


Figure1 Experimental apparatus

Table1 column and adsorbent conditions

	PQ-USY	USY-6.18	Na-Y	Pentasil-2
length of column[cm]	30.0	30.1	25.0	27.2
void fraction	0.4282	0.3849	0.3690	0.5112
bulk density[g/cm ³]	0.4299	0.4515	0.6195	0.6450
column diameter[mm]	0.30			
zeolite type	FAU			MFI
SiO ₂ /Al ₂ O ₃	70	6.18	5.6	30
macropore fraction	0.4140	0.4383	0.2854	0.2653
particle density[g/cm ³]	0.7519	0.7302	0.9816	1.3197
range of sieve openings[mm]	0.495-0.833	0.495-0.833	0.495-0.833	0.495-0.833
average particle radius[mm]	0.332			

Method of Analysis

The adsorption isotherm is given by a linear equation at near zero surface coverage:

$$q = K^* \cdot c \quad (1)$$

where q = amount adsorbed per unit mass of adsorbent [g/g], K^* = adsorption equilibrium constant [cm³/g], c = concentration in the fluid phase [g/cm³].

The resultant moment equations of the impulse response for a packed bed of spherical particles with bidispersed pore structure and size distribution of the microparticles with helium carrier are (Chihara, Suzuki and Kawazoe 1978 and Kawazoe, Suzuki and Chihara 1973).

$$\mu_1 = \frac{z}{u} (1 + \delta_0) \quad (2)$$

$$\mu_2' = \frac{2z}{u} (\delta_d + \delta_f + \delta_a + \delta_i) \quad (3)$$

where

$$\delta_0 = \frac{(1-\varepsilon)\varepsilon_a}{\varepsilon} \left(1 + \frac{\rho_p K^*}{\varepsilon_a} \right) \quad (4)$$

$$\delta_d = \frac{Ez}{u^2} (1 + \delta_0)^2 \quad (5)$$

$$\delta_f = \frac{1-\varepsilon}{\varepsilon} \cdot \frac{R}{3K_f} (\varepsilon_a + \rho_p K^*)^2 \quad (6)$$

$$\delta_a = \frac{1-\varepsilon}{\varepsilon} \cdot \frac{R^2}{15D_a} (\varepsilon_a + \rho_p K^*)^2 \quad (7)$$

$$\delta_i = \frac{1-\varepsilon}{\varepsilon} \cdot \frac{\rho_p K^*}{15D} \int_{-\infty}^{\infty} a^2 f(a) d \ln a \quad (8)$$

The size distribution of the microparticles is assumed to be the log-normal distribution as

$$f(a) = \frac{1}{\sqrt{2\pi} \cdot \sigma} \exp\left[-\frac{(\ln a - \ln a_0)^2}{2\sigma^2}\right] \quad (9)$$

By introducing Equation (9) into Equation (8), we get

$$\delta_i = \frac{1-\varepsilon}{\varepsilon} \cdot \frac{\rho_p K^*}{15D} a^2 \exp(\sigma^2) \quad (10)$$

δ_f is neglected for its small effects in the following analysis. For instance, by using Carberry's equation (Carberry 1960), k_f can be estimated for the experimental condition. Then, the value of δ_f is found to be one order of magnitude smaller than δ_a or δ_a .

Result and Discussion

Microparticle size distribution

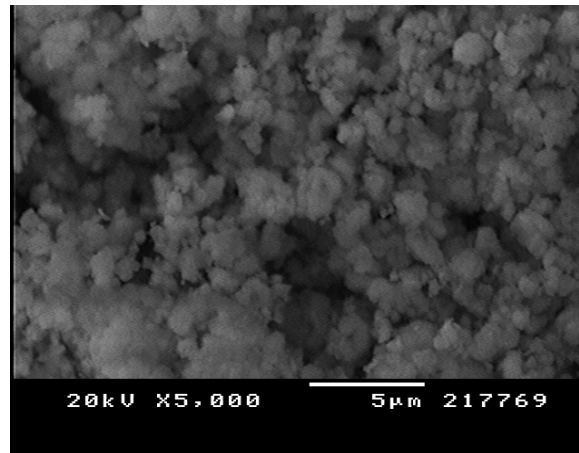


Figure2 Photomicrograph of
Pentasile-2 pellet

The size distribution of the microparticles for zeolite was determined by the scanning electron microscope. By cutting the zeolite pellet, the inner surface was photographed. A typical photomicrograph is shown in Figure2. It is apparent that the macroparticle is an agglomerate of microparticles, and the microparticles have random shapes and size distribution. The diameters in the same orientation of about 200 microparticles were measured from micrographs.

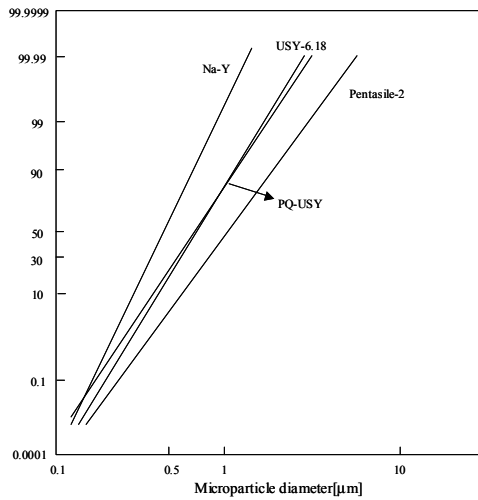


Figure3 Log-normal size distribution of the microparticles of zeolite

On the assumption that the microparticle is a sphere, the cumulative number fraction was plotted against the microparticle radius \bar{a} on a log-normal probability graph paper; a straight line was obtained as shown in Figure3. It is assumed that microparticles of zeolite have the log-normal size distribution. The radius at the peak of the probability a_0' which corresponds to a number fraction basis, and the standard deviation σ were thus found. In the case of log-normal distribution, the straight lines of distribution both on number fraction basis and on volume fraction basis are parallel on a log-normal probability paper, and the relation between the radius at the peak of the probability on a number fraction basis a_0' and that on a volume fraction basis a_0 and average radius \bar{a} are as follows (Hatch 1933). The value of \bar{a} and σ were shown in Table2.

$$a_0 = a_0' \exp(3\sigma^2) \quad (11)$$

$$\bar{a} = \frac{\int_{-\infty}^{\infty} af(a)d \ln a}{\int_{-\infty}^{\infty} f(a)d \ln a} = a_0 \exp\left(\frac{\sigma^2}{2}\right) \quad (12)$$

Table2 Average radius and standard deviation

	PQ-USY	USY-6.18	Na-Y	Pentasile-2
average radius [μm]	1.205	0.699	0.529	2.137
standard deviation [-]	0.431	0.209	0.167	0.451

Moment analysis

The concentration of adsorbate in the effluent from the adsorbent bed was detected by the thermal conductivity cell. Figure 4 shows the effluent chromatographic peaks for dichloromethane pulses at several temperatures for almost the same velocity.

The first absolute moment and the second central moment were evaluated from the effluent peak $C_e(t)$ as follows:

$$\mu_1 = \frac{\int_0^{\infty} C_e(t) t dt}{\int_0^{\infty} C_e(t) dt} \quad (13)$$

$$\mu_2' = \frac{\int_0^{\infty} C_e(t) (t - \mu_1)^2 dt}{\int_0^{\infty} C_e(t) dt} \quad (14)$$

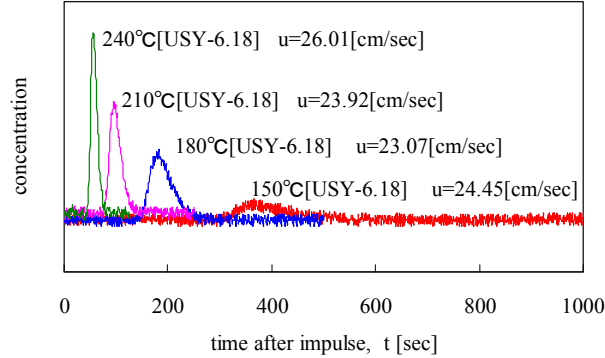


Figure4 Typical chromatographic peaks for dichloromethane [USY-6.18]

In Table3, the upper and lower limits of the moment obtained moment data are shown as μ_1 and μ_2 corresponding to the experimental condition ranges of temperature and interstitial velocity.

The analysis of second moment was simplified by first dividing Equation(3) by $[\mu_1/(z/u)]^2$ obtained from Equation(2). The result was

$$H = \frac{\mu_2'}{\mu_1^2} \left(\frac{z}{2u} \right) = H_0 + \frac{Ez}{u^2} \quad (15)$$

where

$$H_0 = \frac{\delta_a + \delta_i}{(1 + \delta_0)^2} \quad (16)$$

Ez was expected to be proportional to u in the experimental condition. H_0 was able to be obtained as an intercept to the ordinate when H were plotted against $1/u$ according to Equation(15). Since δ_a could be estimated by the established evaluation equation for macropore diffusion and Equation(7), δ_i was obtained by Equation(16).

Table3 Typical date of μ_1 , μ_2 , K^* and D

DCM									
adsorbent	temaperature[°C]	u[cm/sec]	μ_1 [sec]	μ_2 [sec ²]	δ_d [%]	δ_α [%]	δ_t [%]	K^* [cc/g]	D [cm ² /sec]
PQ-USY	120	25.26	192	1154	18	0.002	79	157	4.05E-10
	150	25.21	83.8	190	21	0.002	76	67.7	1.10E-09
	180	26.01	46.1	48.7	24	0.002	72	37.7	2.46E-09
USY-6.18	150	24.45	370	2520	30	0.003	65	256	1.46E-10
	180	23.07	194	787	26	0.002	70	126	2.28E-10
	210	23.92	99.1	124	44	0.003	50	66.0	1.01E-09
	240	26.01	57.6	37.6	49	0.003	45	41.2	2.16E-09
Na-Y	180	25.06	550	3906	52	0.004	41	327	1.27E-10
	210	26.44	266	1027	46	0.003	48	167	2.01E-10
	240	24.92	163	380	47	0.002	47	96.2	3.37E-10
Pentasil-2	180	22.74	1064	8796	79	0.009	2.2	704	3.28E-08
	210	19.39	494	1831	82	0.007	1.3	278	1.25E-07
	240	18.15	263	506	84	0.006	0.4	138	7.12E-07
TCE									
adsorbent	temaperature[°C]	u[cm/sec]	μ_1 [sec]	μ_2 [sec ²]	δ_d [%]	δ_α [%]	δ_t [%]	K^* [cc/g]	D [cm ² /sec]
PQ-USY	150	24.15	336	2006	31	0.003	62	265	5.20E-10
	180	25.21	145	358	33	0.003	61	118	1.28E-09
	210	25.38	79.8	109	32	0.002	61	64.9	2.26E-09
USY-6.18	150	25.86	1183	14925	52	0.005	38	869	1.35E-10
	180	25.66	489	2065	64	0.005	25	356	6.25E-10
	210	24.79	249	633	54	0.003	37	175	6.90E-10
Na-Y	210	25.50	1023	9663	72	0.004	17	621	2.37E-10
	240	25.49	539	2878	67	0.003	23	326	3.02E-10
	270	26.64	294	929	62	0.003	29	186	4.00E-10
	300	25.86	178	343	61	0.003	31	108	6.23E-10
Pentasil-2	240	37.12	236	1009	34	0.005	56	255	2.56E-09
	270	37.51	107	179	39	0.005	49	116	7.38E-09
	300	37.75	58.5	51.7	41	0.004	48	63.3	1.41E-08
TCM									
adsorbent	temaperature[°C]	u[cm/sec]	μ_1 [sec]	μ_2 [sec ²]	δ_d [%]	δ_α [%]	δ_t [%]	K^* [cc/g]	D [cm ² /sec]
PQ-USY	120	24.34	290	1837	26	0.003	69	230	4.39E-10
	150	26.14	133	325	30	0.003	64	113	1.23E-09
	180	24.36	81.8	103	36	0.003	58	64	2.60E-09
USY-6.18	240	24.33	322	2790	21	0.001	76	222	9.77E-11
	270	25.10	211	682	36	0.002	59	150	3.40E-10
	300	24.43	121	176	46	0.002	48	82.5	9.10E-10
Na-Y	240	25.84	420	4419	27	0.001	70	257	5.05E-11
	270	26.06	227	979	35	0.002	61	140	1.42E-10
	300	26.59	147	355	41	0.002	54	92.5	2.83E-10
Pentasil-2	210	36.97	911	34000	15	0.002	80	980	2.03E-10
	240	36.63	529	15560	11	0.001	86	563	2.41E-10
	270	37.24	333	6960	10	0.001	88	361	3.32E-10
300	38.33	271	4383	10	0.001	87	302	4.31E-10	
PCE									
adsorbent	temaperature[°C]	u[cm/sec]	μ_1 [sec]	μ_2 [sec ²]	δ_d [%]	δ_α [%]	δ_t [%]	K^* [cc/g]	D [cm ² /sec]
PQ-USY	150	25.70	780	8774	39	0.004	52	656	3.30E-10
	180	25.34	348	2337	29	0.003	65	288	4.44E-10
	210	24.32	178	584	30	0.002	64	140	9.15E-10
USY-6.18	210	25.34	577	3421	54	0.003	37	415	3.00E-10
	240	25.82	278	911	47	0.003	45	203	4.39E-10
	270	25.81	160	255	55	0.003	36	116	1.13E-09
Na-Y	240	24.10	1051	29119	25	0.001	71	603	1.90E-11
	270	24.28	529	4802	39	0.002	56	305	7.38E-11
	300	24.39	291	1225	46	0.002	48	168	1.86E-10
Pentasil-2	210	37.94	305	2987	19	0.003	74	336	8.36E-10
	240	45.43	112	221	35	0.006	53	147	5.82E-09
	270	42.39	52.3	44.9	37	0.005	50	63.6	1.39E-08
300	42.61	30.3	13.2	43	0.005	44	36.6	3.09E-08	

Adsorption equilibrium constant

Equation(2) and (4) were used along with the \square_1 to obtain the adsorption constant K^* . The isosteric heat of adsorption q_{st} is related with K^* for each gas by Van't Hoff's equation:

$$\frac{K^*}{T} = \left(\frac{K^*}{T} \right)_{\frac{1}{T} \rightarrow 0} \exp\left(\frac{q_{st}}{R_g T} \right) \quad (17)$$

Here it is assumed that the gas is ideal.

According to Equation(17), the obtained K^* divided by T was plotted against $1/T$ for various gases in Figure5, and the isosteric heat of adsorption q_{st} and $(K^*/T)_{1/T=0}$ were determined and listed in Table4.

Table4 Properties of gases for adsorption

adsorbent	adsorbate	ΔH [kJ/mol]	q_{st} [kJ/mol]	$(K^*/T)_{1/T \rightarrow 0}$ [cm ³ /g ^o *K]	E [kJ/mol]	D_0 [cm ² /sec]
PQ-USY	DCM	28.0	38.8	2.7E-06	19.0	3.0E-04
	TCM	29.4	40.1	2.9E-06	18.6	2.7E-04
	TCE	31.4	43.6	2.5E-06	15.2	8.6E-05
	PCE	34.7	47.5	2.2E-06	12.6	9.2E-05
Pentasil-2	DCM	28.0	56.3	8.0E-08	43.4	2.0E+05
	TCM	29.4	34.4	3.0E-04	8.71	3.2E-08
	TCE	31.4	61.1	2.8E-07	30.0	4.1E-02
	PCE	34.7	61.5	1.6E-07	38.5	6.0E-02
USY-6.18	DCM	28.0	40.6	5.5E-06	25.6	1.9E-03
	TCM	29.4	44.8	1.3E-05	33.0	1.4E-02
	TCE	31.4	49.2	1.7E-06	15.8	9.4E-05
	PCE	34.7	50.6	2.8E-06	20.9	4.1E-05
Na-Y	DCM	28.0	42.0	1.9E-05	8.0	4.4E-08
	TCM	29.4	51.0	9.4E-06	19.0	3.9E-06
	TCE	31.4	48.2	1.0E-05	25.4	5.4E-05
	PCE	34.7	52.2	7.4E-06	10.9	5.5E-08

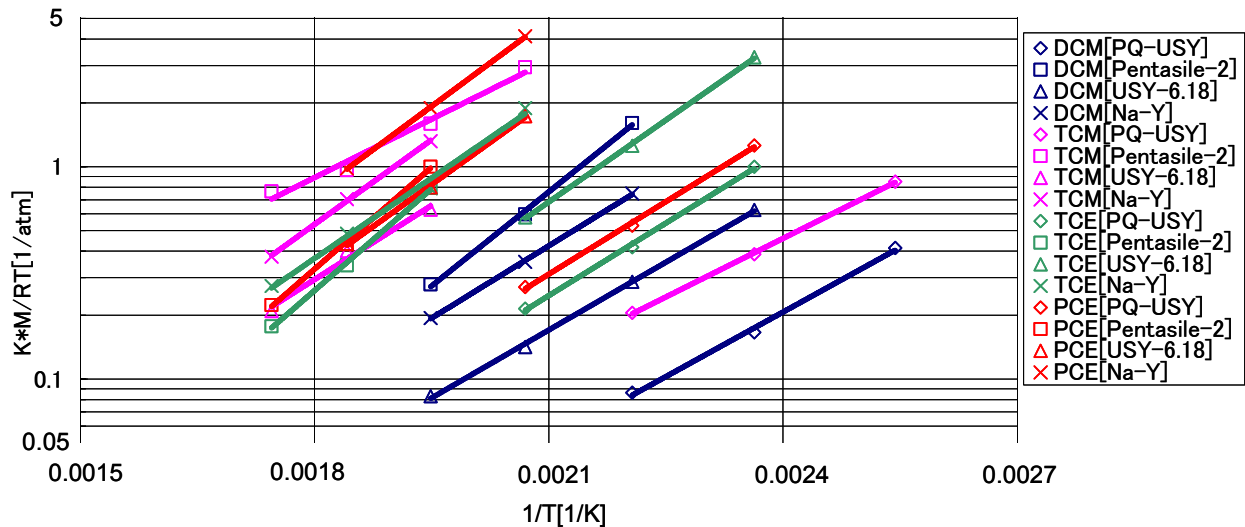


Figure5 Van't Hoff plot of adsorption equilibrium constants

Axial dispersion

Equation(15) shows that the contribution of axial dispersion to H must be evaluated first to estimate H_0 from experimental value of H . In packed beds, Ez is expressed as a sum of a molecular diffusion (D_M) term and a term due to the velocity profile:

$$Ez = \frac{D_M}{\tau_{ext}} + \frac{d_p u}{Pe} \quad (18)$$

The second term of equation(18) is expected to be dominant (Suzuki and Smith 1971), and H in Equation(15) should depend linearly on $1/u$. Peclet number was evaluated(0.78) from the empirical correlation (Suzuki and Smith 1971) given as:

$$Pe=1.2dp : dp \text{ in mm} \quad (19)$$

Diffusion in macropore

H_0 includes the effect of the macropore diffusion and the micropore diffusion. The following established relation (Satterfield 1970) was used to estimate the diffusivity in the macropore:

$$D_a = \frac{\varepsilon_a}{\tau_p} \cdot D_M \quad (20)$$

where D_a = diffusivity in macropores D_M = molecular diffusivity ε_a =void fraction of macropore.

Equation (7) was then applied to estimate δ_a . Then, δ_i was obtained by Equation (16).

Diffusion in micropore

Since the size distribution of the microparticle for zeolite was already obtained by the electron microscope, diffusivities in micropores D were evaluated from δ_i and K^* , a , and σ by using Equation(10). The values of D for different temperatures were plotted according to the following Arrhenius' equation in Figure5.

$$D/a^2 \exp(\sigma^2) = \left[D_0/a^2 \exp(\sigma^2) \right] \exp\left(-\frac{E}{RT}\right) \quad (21)$$

From Figure6, the activation energy E was determined from the slope of the straight line corresponding to the data points for each gas: the preexponential factor $D_0 \exp(\sigma^2)$ was obtained as the interception to the ordinate at $1/T=0$. These figures were listed in Table4.

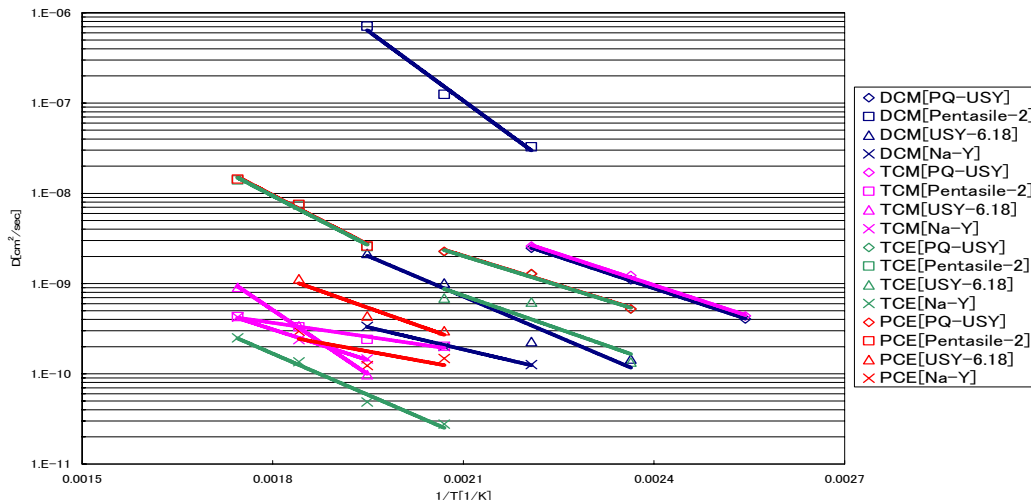


Figure6 Arrhenius plot

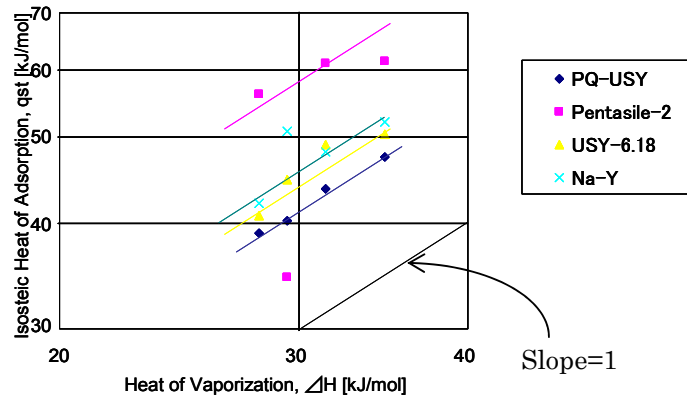


Figure7 Correlation of isosteric heat of adsorption with heat of vaporization

Discussion

The isosteric heat of adsorption obtained with the chromatographic method of zeolite in this study is characterized, so that, the estimated values are for zero coverage, or initial isosteric heats of adsorption. Therefore, these values correspond entirely to the interaction between the adsorbate molecule and the adsorbent lattice atoms, excluding the interaction among adsorbate molecules.

Isosteric heat of adsorption q_{st} for four adsorbate with four adsorbent are plotted against the heat of vaporization ΔH of corresponding adsorbate in Figure 7. (Barrer and Lee 1968) showed that the ratios $q_{st}/\Delta H$ for zeolite L slightly exceeded 2.

Diffusion in the micropore of the zeolite is so called activated diffusion and is described as the molecules hopping from an adsorption site to another across the energy barrier which separates adjacent sites, which is similar to surface diffusion.

Conclusion

Chromatographic measurements were made for various gas adsorptions on zeolite at three kind of temperatures, for zero coverage.

Adsorption equilibrium constants in the Henry's law region and diffusivities in the micropores in zeolite were determined from the first absolute moment and the second central moment where the effects of all the other possible transport processes in the case of bidispersed pore structure and also the log-normal size distribution of the microparticle were taken into account.

The amount adsorbed and isosteric heats of adsorption became low, when $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of zeolite became high. The isosteric heats of adsorption were roughly 1.4 to 2.0 of the heats of vaporization.

Notation

a	= radius of microparticle, cm
a_0	= a at the peak of the probability on a volume fraction basis, cm
a_0'	= a at the peak of the probability on a number fraction basis, cm
\bar{a}	= arithmetic average radius of microparticles defined
C_e	= concentration in the effluent gas, mol/cm ³
c	= concentration in the fluid phase, mol/cm ³
c'	= concentration in the particle, mol/cm ³
D	= diffusivity in micropores based on amount adsorbed gradient driving force, cm ² /s
D_0	= preexponential factor for the Arrhenius' plot of D , cm ² /s
D_a	= diffusivity in macropores, cm ² /s
D_M	= molecular diffusivity, cm ² /s
d_p	= particle diameter, cm
E	= activation energy for micropore diffusion, kJ/mol
E_z	= axial dispersion coefficient based on void spaces in the bed, cm ² /s
$f(a)$	= distribution function of the radii of microparticles
H	= defined by Equation (13), s
H_0	= defined by Equation (14), s
ΔH	= heat of vaporization, kJ/mol
K^*	= adsorption equilibrium constant, cm ³ /g
k_f	= external mass transfer coefficient, cm/s
P_e	= Peclet number, $d_p u / E_z f$
q	= amount adsorbed per unit mass of adsorbent, mol/g
q_{st}	= isosteric heat of adsorption, kJ/mol
R	= radius of particles, cm
R_g	= gas constant, Kcal/mol · K
T	= absolute temperature, K
t	= time, s
u	= interstitial velocity of fluid, cm/s
v	= volumetric flow rate, cm ³ /s
z	= longitudinal position in the bed, cm

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