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ADSORPTION EQUILIBRIA OF TWO HALOGENATED CARBONS ON A CARBON FIBER

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Abstract – Chlorofluorocarbons (CFCs) are presently considered to be the prime contribution to stratospheric ozone depletion. In this study, a microporous activated carbon felt (KF-1500) was used as a useful adsorbent for adsorption of trichlorofluoromethane and methylene chloride. The isotherms of these organic vapors on a microporous carbon felt were measured and the equilibrium parameters based on Dubinin-Radushkevich correlation were evaluated. Besides, the isosteric heats of adsorption were evaluated from the equilibrium data. It was found that equilibrium data for this carbon felt were well described by Dubinin-Radushkevich correlation.

Key words : Halogenated Carbons, Carbon Fiber, Adsorption

INTRODUCTION

Trichlorofluoromethane and methylene chloride have been used as the excellent solvents and especially attractive as the forming and cleaning solvents. Furthermore, these are widely used as an extraction solvent in food and pharmaceutical processing where its high volatilities are desirable [Wolf et al., 1991]. In spite of its usefulness, the 1987 Montreal Protocol on substances that deplete the ozone layer restricts the releases of trichlorofluoromethane to atmosphere [Andesen, 1991; Cicerone et al., 1974].

On the other hand, American Conference of Governmental Industrial Hygienists (ACGIH) reported that the Threshold Limit Value (TLV) for methylene chloride is 50 ppmv as the 8 hour Time-Weighted Average (TWA) [Tsai and Chang, 1994]. The repeated contact with methylene chloride may result in dermatitis, headache, giddiness, tingling in the limbs [Allen, 1989]. The ACGIH has classified it as a suspected human carcinogen (Group A2). Because of the toxicity of methylene chloride, it has been listed as one of hazardous air pollutant in the US Clean Air Act Amendments (CAAA) of 1990.

One way to control the emission of these chemicals is the carbon adsorption. This technology is very common one because it offers some advantages. The advantages include the possibility of the recovery of raw materials for recycling and high removal efficiency at low concentration. Furthermore, this technology demands the low energy costs. The adsorption equilibria and heats of adsorption are the important factors for the design of adsorption facilities.

In this study, the adsorption isotherms of two chemicals on microporous carbon felt were investigated. From the experimental data, the parameters based on Dubinin-Raduskevich equation and the isosteric heats of adsorption for each adsorbates are evaluated, respectively.

EXPERIMENT

A microporous carbon felt (KF-1500), supplied by Toyobo Co. Ltd., was employed as a useful adsorbent for two adsorbates. The physical properties and SEM (Scanning Electron Microscopy) of this adsorbent are listed in Table 1 and Fig. 1, respectively.

Trichlorofluoromethane and methylene chloride were employed as adsorbates. The purity of these adsorbates was 99.9% and the physical properties of two adsorbates as the functions of temperature were listed in Table 2.

A conventional isotherm equipment was used for generation of equilibrium data [Cho et al., 1995]. This equipment employs a volumetric method for measurement of adsorption equilibria. Oil diffusion pump and mechanical vacuum pump in combination provide vacuum down to 10^{-6} mm Hg.

The adsorbent was regenerated in evacuated system at 473 K and regeneration time typically required about 20 hours. The weight of the sample was measured within 10 μg accuracy and the dead volume was measured using helium gas. Using the adsorption of nitrogen at 77 K, the BET surface area for this adsorbent was measured by the automatic sorption analyzer (Quantachrome Autosorb-1). Adsorption isotherms were obtained by the successive increments of the measured volume to the adsorbents. After each increment of gas admitted, time was allowed for the attainment of equilibrium and system pressure was then noted. The correction of the known volume of gas admitted for the amount unadsorbed in the dead space yielded a

Table 1. Physical properties of the activated carbon felt

	Activated carbon felt
Fiber diameter* d_f (μm)	19.14
BET surface area** (m^2/kg)	964×10^3
Mean pore diameter (nm)	1.604
Micropore volume*** (m^3/kg)	0.67×10^{-3}

*from scanning electron microscopy (SEM).
**from nitrogen adsorption at 77 K (0.162 nm^2/molecule).
***from D-R plot.

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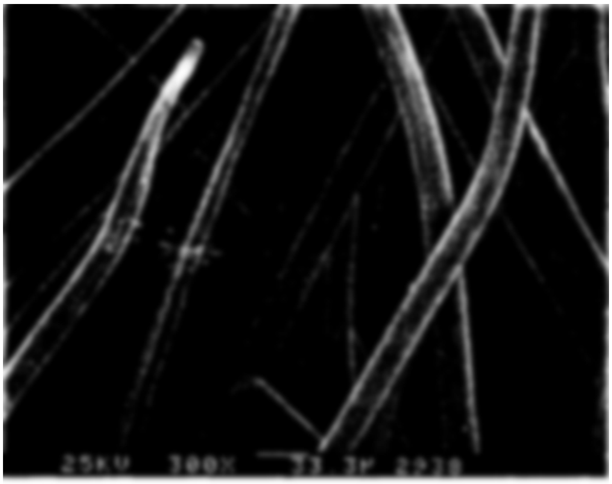
(A) shape of carbon felt



(B) SEM of carbon felt

Fig. 1. SEM photo of carbon felt.

Table 2. Physical properties of two adsorbates

Temp. [K]	Vap. press. [kPa]	Liq. den. [kg/m^3]	Molar polarization* [m^3/mol]$\times 10^6$	Molar vol.* [m^3/mol]$\times 10^6$
Trichlorofluoromethane [Wolf et al., 1991; Wood, 1992]				
298	106.99	1475.7	21.57	93.13
323	231.73	1414.4	21.87	97.15
348	437.72	1357.4	21.94	101.45
373	741.90	1300.9	22.13	105.59
Heat of condensation, $q_{Condensation}$, [kJ/mol]=29.40 at 300 K				
Methylene chloride [Yaws, 1981]				
298	57.96	1309.4	16.46	64.92
323	145.50	1279.9	16.45	66.41
348	318.57	1216.1	16.76	69.90
373	623.35	1145.6	17.19	74.20
Heat of condensation, $q_{Condensation}$, [kJ/mol]=28.86 at 300 K				

*calculated values.

point on the adsorption isotherm. Equilibrium data for this adsorbent were obtained by similar procedure varying the concentration and temperature.

RESULTS AND DISCUSSION

The adsorbent which used in this study has a felt-type shape and relatively regular pore distribution as shown in Fig. 2. Because of these geometries, this carbon felt can be of avail in adsorption facilities.

One of the important factors for designing an adsorption facility is the adsorption equilibria of adsorbates on the adsorbents. It is very convenient that adsorption equilibria are represented by explicit equations. Therefore, many isotherm correlations are derived to describe the effects of vapor concentration and temperature on an adsorbed capacity in equilibrium.

Adsorption equilibria of adsorbates on microporous adsorbents have been correlated by means of Polanyi's potential theory [Ruthven, 1984] in several cases. Adsorption of vapors in micropores has been recognized as a volume filling and adsorbed phase has generally been assumed as liquid state [Cho et al., 1995; Lewis et al., 1950; Reucroft et al., 1971]. The adsorption potential, A, based on the Polanyi's theory can be written as:

$$A = RT \cdot \ln[P_{sat}/P_i] \tag{1}$$

where P_{sat} is the saturation pressure of gas at temperature, T, and P_i is the partial pressure of gas at equilibrium. Dubinin and Radushkevich proposed the following equation to correlate the adsorption of gases on microporous adsorbents.

$$V/w_0 = \exp[-K(A/\beta)^2] \tag{2}$$

Based on the micropore volume filling theory and the Polanyi's concept of adsorption potential, isotherm equation can be expressed as [8]:

$$W^*/d_L = w_o \exp[-(K/\beta^2) \cdot \{RT \cdot \ln(P_{sat}/P_i)\}^2] \tag{3}$$

The plots of $\ln(W^*/d_L)$ vs. A^2 give the values of $-K/\beta^2$, where K is the carbon structure constant and β is the vapor affinity coefficient.

Three debates have concerned which the adsorbate properties (molar polarization, molar liquid volume, molecular parachor) correlate the parameter, β, in Eq. (3) [Reucroft et al., 1971; Wood, 1992; Noll et al., 1989].

For the nonpolar and weakly polar adsorbates, dispersion forces play a dominant role in determining adsorptive interactions [Noll et al., 1989]. In this case, the affinity coefficient can be expressed as:

$$\beta = \frac{V}{V_{ref}} \tag{4}$$

Where $V = M_w/d_L$

$V_{ref} = V$ at 298 K

On the other hand, for polar adsorbates, Reucroft et al. [Reucroft et al., 1971] pointed out that the adsorptive interaction may be influenced more by electronic forces than by dispersion forces. They suggested that the ratio of electronic polarizations, Pe, can be used to calculate the affinity coefficient. The electronic polarization is given by

$$\beta = \frac{Pe}{Pe_{ref}} \tag{5}$$

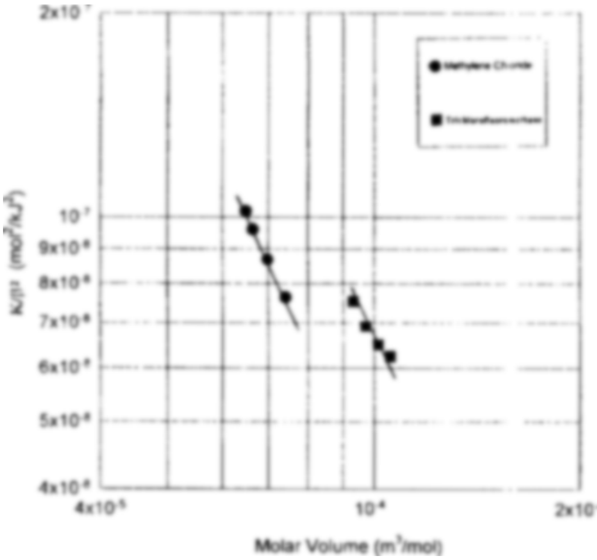


Fig. 2. Plot of K/β^2 vs. molar volume.

$$\text{where } Pe=\left(\frac{n_{D,T}^2-1}{n_{D,T}^2+2}\right)\frac{M_w}{d_L}$$

$$Pe_{ref}=Pe \text{ at } 298\text{ K}$$

Noll et al. [1989] reported that there is no obvious difference in accuracy of the isotherm prediction for the above two method and they recommend the molar volume method to predict isotherms at different temperatures, because of its simplicity and requirements for easily obtainable physical parameter.

Furthermore, since both $n_{D,T}$ and d_L decrease with increasing temperature, the variation in Pe is as small as 2.6% for trichlorofluoromethane and 4.9% for methylene chloride, as shown in Table 2. Therefore, the range of the molar polarization is too narrow to get a meaningful correlation of K/β^2. In this study, molar volume method was used, in order to express the K/β^2 as a function of temperature.

Fig. 2 illustrates the relationships of the K/β^2 between the molar volume, V. The slope of the lines in this figure was determined as 2. As a result, equilibria of two adsorbates on this microporous carbon felt can be expressed by the following form:

$$W^*=w_o\cdot d_L\cdot\exp[-b_i\cdot\{(RT/V)\cdot\ln(P_{sat}/P_i)\}^2] \qquad (6)$$

Fig. 3 shows the typical D-R plots for trichlorofluoromethane and methylene chloride, respectively. The slopes of lines in this figure illustrate the constants, b_i, in Eq. (6) for each adsorbate, respectively. Furthermore, the intersect of these lines means the micropore volume, w_o. The micropore volume of this carbon felt was determined as 0.67×10^{-3} m³/kg, using the extrapolation method. This value is larger than that of the commercial granular activated carbons (GACs) made from bituminous coal (BPL) and coconus shell (PCB) that were reported in Chang's study [Tsai and Chang, 1994] for the adsorption of methylene chloride (0.4531×10^{-3} m³/kg for BPL and 0.5744×10^{-3} m³/kg for PCB). This result suggests that the microporous carbon felt is very useful for the adsorption of volatile organic compounds.

Fig. 4 and 5 illustrate the comparisons of calculated values with the experimental data for two adsorbates, respectively. These figures show that the Dubinin-Raduskevich correlation gives the good fits of data within 9% error. These figures show that the amounts of trichlorofluoromethane adsorbed per unit mass of microporous carbon felt are larger than those of methylene chloride adsorbed per unit mass of microporous carbon felt.

The isosteric heats of adsorption were calculated at constant adsorption loading from the following relationship;

$$q=-R\cdot\left[\frac{\partial(\ln C)}{\partial(1/T)}\right]_{W^*} \qquad (7)$$

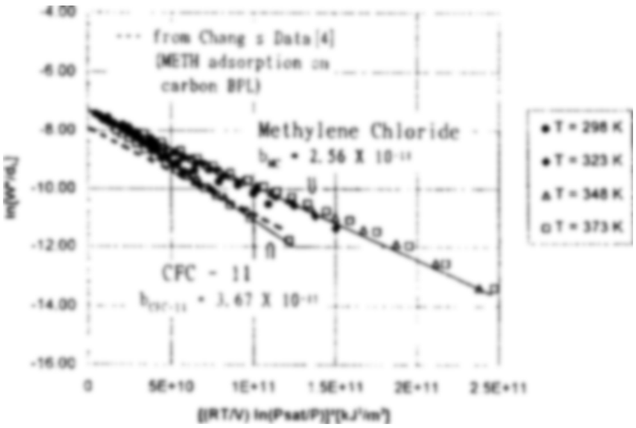
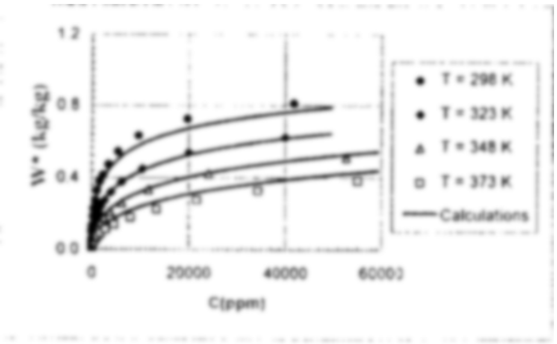
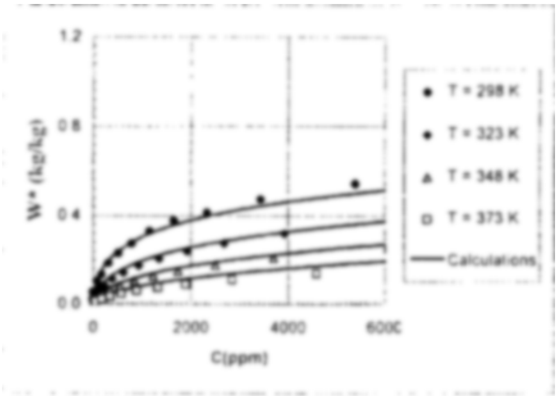


Fig. 3. Plots of ln $[W^*/d_L]$ vs. $[(RT/V)\cdot\ln(P_{sat}/P_i)]^2$.

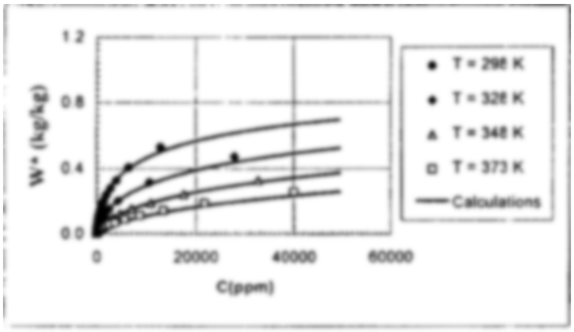


(a) in high concentration ranges

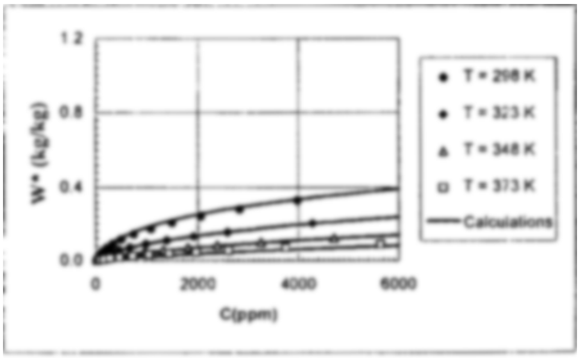


(b) in low concentration ranges

Fig. 4. Comparable plots of calculated values with experimental data for trichlorofluoromethane.

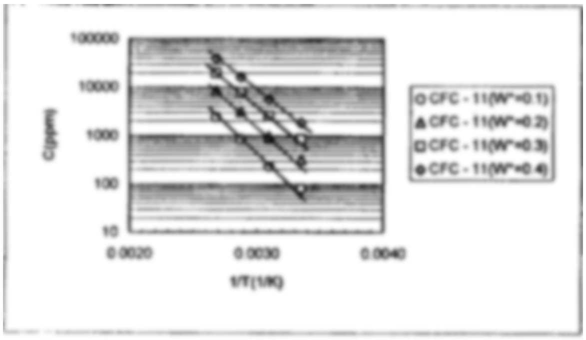


(a) in high concentration ranges

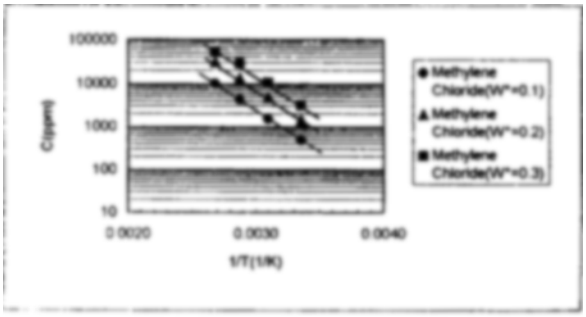


(b) in low concentration ranges

Fig. 5. Comparable plot of calculated values with experimental data for methylene chloride.



(a) Trichlorfluoromethane



(b) Methylene Chloride

Fig. 6. The van't Hoff plot for two adsorbates.

Fig. 6 illustrates the van't Hoff plot of ln C versus 1/T at constant loading . The isosteric heats of adsorption are estimated as about 46 kJ/mol for trichlorofluoromethane and nearly independent of the mass adsorbed. The isosteric heats of adsorption for methylene chloride on this microporous carbon felt are slightly less than that for trichlorofluoromethane, but are also nearly constant with increasing the adsorbate loading. The isosteric heats of adsorption for these adsorbates are of the same order of magnitude as the heats of condensation listed in Table 2, it may be considered that the adsorption of trichlorofluoromethane and methylene chloride on this activated carbon felt is due primarily to physical forces.

CONCLUSIONS

It was suggested that a microporous carbon felt is a prominent adsorbent for adsorption of trichlorofluoromethane and methylene chloride.

Adsorption equilibria of trichlorofluoromethane and methylene chloride on this carbon felt having the relatively uniform pore structure can well be expressed by Dubinin-Radushkevich (D-R) correlation over wide concentration and temperature ranges.

From the vant' Hoff plots, the isosteric heats of adsorption for trichlorofluoromethane and methylene chloride on this microporous carbon felt are slightly higher than the heats of condensation.

NOMENCLATURE

A : RT · ln(P_{sat}/P_i) [kJ/mol]
b_i : constants for i component in Eq. (6)
C : concentration in vapor phase [ppm=9869 · P_i]
d_L : liquid density [kg/m^3]
K : carbon structure constant [mol^2/kJ^2]
M_w : molecular weight [kg/mol]
$n_{D,T}$: refractive index [-]
P_i : partial pressure of adsorbate [kPa]
Pe : molar polarization [m^3/mol]
P_{sat} : vapor pressure at saturation [kPa]
q : isosteric heat of adsorption [kJ/mol]
$q_{condensation}$: heat of condensation [kJ/mol]
R : gas constant [kJ/(mol · K)]
T : absolute temperature [K]
V : molar volume of adsorbate in equilibrium [m^3/mol]
W* : mass of gas adsorbed per unit weight of adsorbent [kg/kg]
w_o : micropore volume [m^3/kg]
β : affinity coefficient [-]

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