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# EQUILIBRIA OF TRICHLOROMONOFLUOROMETHANE ON A CARBON PELLET

**Sung Yong Cho†, Tai Jin Lee* and Seung Jai Kim****

CFC Center, KIST, Seoul, Korea
*Young Nam University, Taegu, Korea
**Chonnam National University, Kwangju, Korea

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**Abstract** – A laboratory study on the adsorption of trichloromonofluoromethane on a pellet-type carbon was carried out at 298, 323, 348 and 373 K. Equilibrium parameters based on Freundlich, Langmuir and Dubinin-Radushkevich equations were determined. It was found that the Dubinin-Radushkevich (D-R) equation was better fitted by the experimental data of trichloromonofluoromethane on the activated carbon pellet than other two equations. In addition, the isosteric heats of adsorption were evaluated from experimental data.

*Key words*: *Carbon Pellet, Equilibria*

## INTRODUCTION

Trichloromonofluoromethane has been widely used as a foaming agent, providing polyurethane and polyisocyanurate foams with good thermal insulation. Rigid polyurethane foams blown with trichloromonofluoromethane enable cost effective structures to be built with a high level of insulation. For several decades, these characteristics have led to an important development in build, cold storage and appliances.

However, it has reported that the stratospheric ozone layer is severely attacked by ozone-depleting chemicals such as ChloroFluoroCarbons (CFCs), halons and halogenated carbons [Cicerone et al., 1974; Molina and Rowland, 1974]. International protocol and its subsequent reviews restrict the release of trichloromonofluoromethane to atmosphere [Andersen, 1991]. Under these circumstances, many researchers have been interested in the separation of the halogenated chemicals from air [Kuo and Hines, 1992; Kodama et al., 1992; Tsai and Chang, 1994].

One way to achieve the reduction of trichloromonofluoromethane's emissions is the use of 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 the high removal efficiency at low concentrations. Furthermore, this technology demands the low energy cost. In order to use the adsorption facilities, the equilibrium information and heats of adsorption are very important.

The present study includes the investigation on the laboratory adsorption of trichloromonofluoromethane vapor on the activated carbon pellet as a promising adsorbent. From experimental data, the parameters of Freundlich, Langmuir and Dubinin-Radushkevich equations were determined. Furthermore, the isosteric heats of adsorption with the variation of coverage are evaluated.

## EXPERIMENTAL

A pellet-type activated carbon (Norit B4) was employed as an efficient adsorbent for the adsorption of trichloromonofluoromethane. The structure of this carbon is depicted in Fig. 1. The BET surface area of the activated carbon pellet was measured using the nitrogen adsorption at 77 K by the automatic sorption analyzer (Quantachrome : Autosorb-1). The physical properties of this adsorbent are listed in Table 1. Trichloromonofluoromethane was employed as an adsorbate and its purity were 99.9%.

A conventional isotherm equipment was used for generation of equilibrium data (Micrometrics : Accusorb – 2100E). This equipment employs a volumetric method for the measurement of adsorption equilibria. Before the adsorption experiments, the adsorbent was regenerated in evacuated system at 393 K for about 15 hours. The weight of the sample was measured within 10 μg accuracy and the dead volume was measured using helium gas. Oil diffusion pump and mechanical vacuum pump in combination provide vacuum down to $10^{-5}$ mm Hg. Adsorption isotherms were obtained by the successive increments of the measured volume to the adsorbent. After each increment of gas admitted, time was allowed for the attainment of

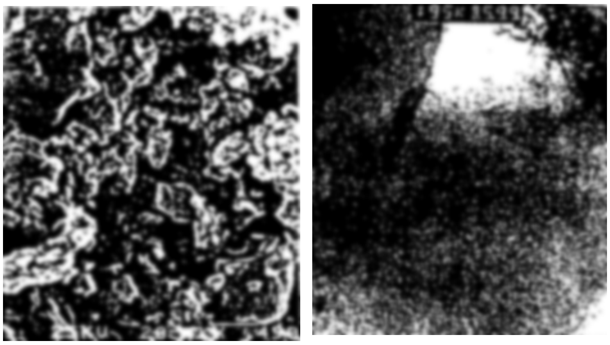

**Fig. 1. The structure of activated carbon pellet.**

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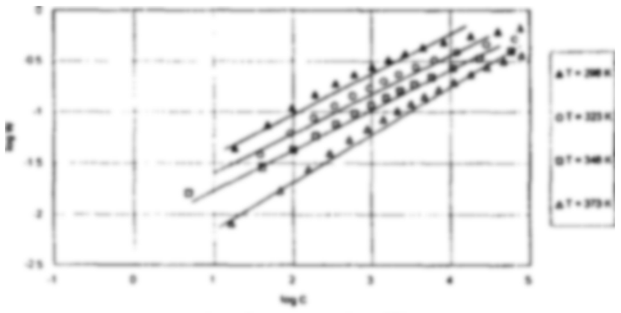
†To whom all correspondences should be addressed.

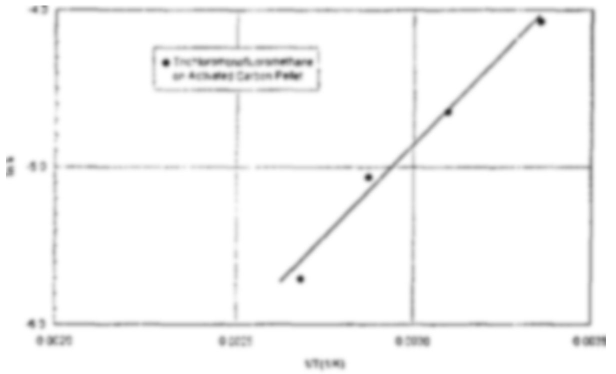
**Table 1. Physical properties of the activated carbon pellet**

| | Activated carbon pellet |
|---|---|
| Supplier (model no.) | Norit (B4) |
| Pellet diameter | 0.37 |
| Pellet length (cm) | 0.65 |
| BET surface area* ($m^2/g$) | 826 |

*from nitrogen adsorption at 77 K (0.162 $nm^2$/molecule).



(a) log C versus log W



(b) ln k versus 1/T

Fig. 2. The temperature dependence of Freundlich parameters.

equilibrium and the system pressure was then noted. A correction of the known volume of gas admitted for the amount unadsorbed in the dead space yielded a point on the adsorption isotherm. Equilibrium data for the carbon pellet were obtained by similar procedures varying the temperatures.

## RESULTS AND DISCUSSION

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 the adsorption capacity in equilibrium [Ruthven, 1984; Suzuki, 1990; Lewis et al., 1950; Cho et al., 1995; Wood, 1992].

The Freundlich isotherm was used in the form.

$$W = k \cdot C^{1/n} \tag{1}$$

where k and n are empirical constants. In general, n, has a value greater than unity and a higher value of k increases the adsorption capacity of the adsorbent. Fig. 2-a shows plots of log W versus log C for different temperatures. Although this figure shows slightly different slopes for different temperatures, the constant, n, was determined as a averaged value (=2.4) to reduce the temperature-dependent variable in Eq. (1).

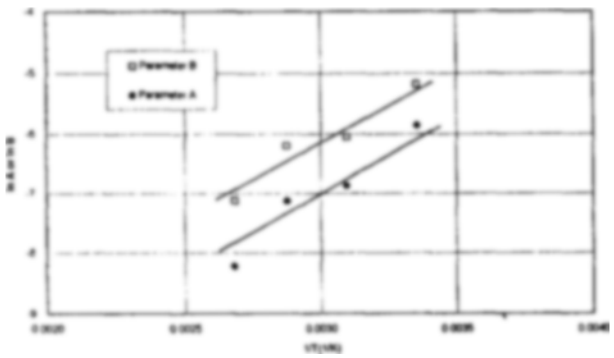


Fig. 3. The temperature dependences of Langmuir parameters.

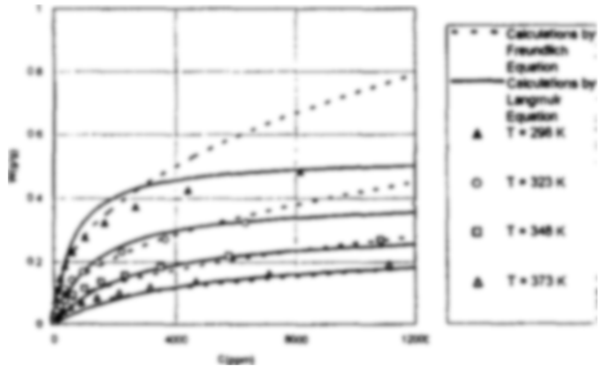


Fig. 4. Comparable plots of calculated curves by Freundlich and Langmuir equations with experimental data.

Fig. 2-b illustrates the temperature dependence of constant, k. The values of k decrease with increasing the temperatures, indicating that the adsorbent has a higher adsorption capacity at lower temperatures. The optimum expression of constant, k, is as follows.

$$k = 1.1 \times 10^{-5} \cdot e^{(2171/T)} \tag{2}$$

The Langmuir isotherm can be represented by

$$W = \frac{A \cdot C}{1 + B \cdot C} \tag{3}$$

where the constant, A, is equal to $B \cdot W_m$, $W_m$ is the adsorption capacity at monolayer saturation and B is the adsorption equilibrium constant.

Fig. 3 illustrates the temperature dependence of constants, A and B. Both A and B decreased with increasing temperatures. It indicates that the adsorbent has a higher adsorption affinity and capacity at lower temperature. The expressions of A and B as the functions of temperature are presented in the following forms:

$$A = 7.90 \times 10^{-8} \cdot e^{(2740/T)} \tag{4}$$

$$B = 3.75 \times 10^{-8} \cdot e^{(2740/T)} \tag{5}$$

Fig. 4 shows the comparable plot of calculated curves by Eqs. (1) and (3) with experimental data. The Freundlich isotherm appears to fit the experimental data reasonably at low concentration, but the deviations increase with increasing the concentration. In addition, Langmuir isotherm shows the deviations between calculated and experimental data in low concentrations.

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; Wood, 1992]. On the basis of the micropore volume filling theory and the Polanyi's concept of the adsorption potential, isotherm equation can be expressed as [Wood, 1992]:

$$W/d_L = w_o \exp[-(K/\beta^2)\cdot\{RT\cdot\ln(P_{sat}/P_i)\}^2] \tag{6}$$

The plots of $\ln(W/d_L)$ vs. $\{RT\cdot\ln(P_{sat}/P_i)\}^2$ give the values of $-K/\beta^2$, where K is the carbon structure constant and $\beta$ is the vapor affinity coefficient. Three debates have concerned which the adsorbate properties (molar polarization, molar liquid volume, molecular parachor) correlate the parameter, $\beta$, in Eq. (6) [Noll et al., 1989; Reucroft et al., 1971].

Noll et al. [1989] reported that there is no obvious difference in accuracy of the isotherm prediction for the above methods. Furthermore, they recommend the molar volume method to predict isotherms at different temperatures, because of its simplicity and requirements for easily obtainable physical parameter. Since both the refractive index and liquid density decrease with increasing temperature, the variation in molar polarization is small. Therefore, the range of the molar polarization is too narrow to get a meaningful correlation of $K/\beta^2$. In this study, molar volume method was used, in order to express $K/\beta^2$ as a function of temperature.

With the assumption that $K/\beta^2$ is related to $V^{-2}$ by the proportionality constant, b, Eq. (6) is expressed by the following form:

$$W = w_o \cdot d_L \cdot \exp[-b\cdot\{(RT/V)\cdot\ln(P_{sat}/P_i)\}^2] \tag{7}$$

where $P_{sat} = 101.325.10^{[34.8838 - \frac{2303.95}{T} - 11.7406\cdot \log T + 0.0064249\cdot T]}$ [Benning and McHarness, 1940]

$$\begin{aligned} d_L &= 1.5342 - 0.002282(T-273) - 0.00000230(T-273)^2, \\ &\quad \text{(at 233 - 333 K)} \\ &= 1.5191 - 0.001792(T-273) - 0.00000642(T-273)^2, \\ &\quad \text{(at 333 - 398 K)} \end{aligned}$$

[Benning and McHarness, 1940]

Fig. 5 illustrates the relationship of $\ln(W/d_L)$ vs. $\{(RT/V)\cdot\ln(P_{sat}/P_i)\}^2$. From the slope of the line in this figure, constant, b, for trichloromonofluoromethane is determined. Furthermore, the intersect of this line indicates the micropore volume, $w_o$, of the carbon pellet. Estimated values of micropore volume, $w_o$, and constant, b, for this carbon pellet are as follows.

$w_o = 0.49\ \mathrm{cm^3/g}$
$b = 30.28.$

The value of the micropore volume is similar to 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 $\mathrm{cm^3/g}$ for BPL and 0.5744 $\mathrm{cm^3/g}$ for PCB). This result suggests that this carbon pellet is of avail for the adsorption of volatile organic compounds. Furthermore, this carbon pellet merit attention commercially, because of its regular size and hardness.

Fig. 6 illustrates the comparisons of calculated curves by D-R equation with the experimental data. This figure shows that the Dubinin-Raduskevish correlation gives better fits of experimental data than the Freundlich and Langmuir correlations. It may be concluded that the D-R equation gives better fits for adsorption of volatile organic vapors on porous carbons because it was formulated based on the condensation inmicropores.

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

$$q = -R\cdot\left[\frac{\partial(\ln C)}{\partial(1/T)}\right]_w \tag{8}$$

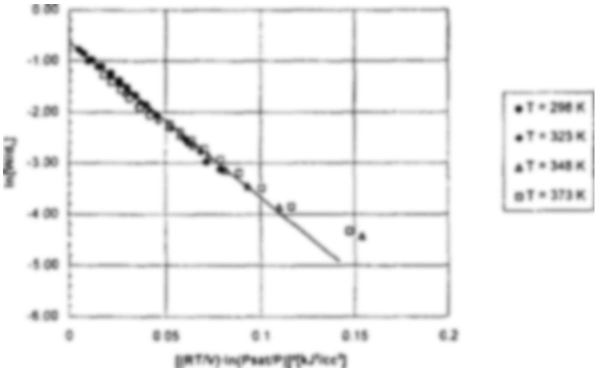
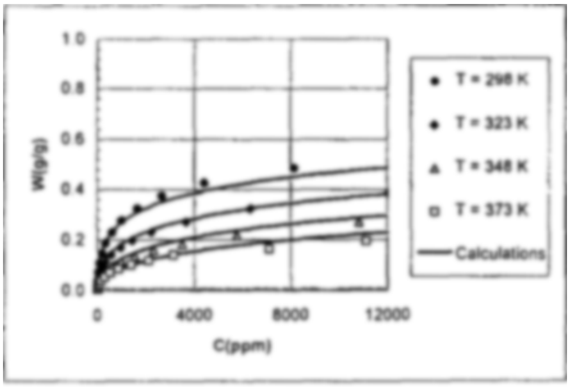
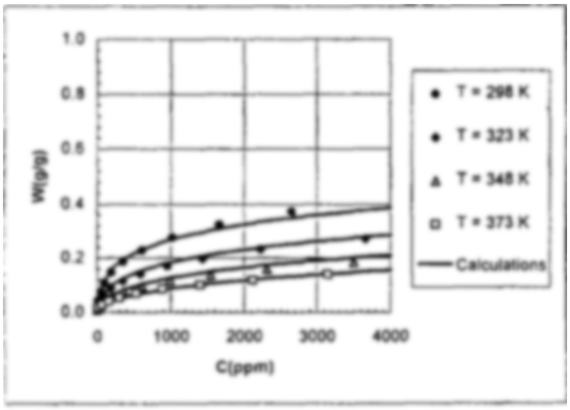


Fig. 5. The plot of $\ln(W/d_L)$ vs. $\{(RT/V)\cdot\ln(P_{sat}/P_i)\}^2$.



(a) in high concentrations



(b) in low concentrations

Fig. 6. Comparable plots of calculated curves by D-R equation with experimental data.

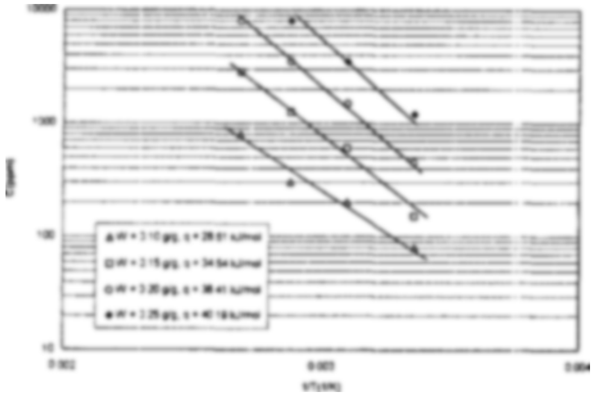


**Fig. 7. Heats of adsorption with variations of coverage.**

Fig. 7 illustrates the heats of adsorption at constant loading with the variation of coverage. This figure shows that the isosteric heats of adsorption for trichloromonofluoromethane on the activated carbon pellet are slightly increasing with the amount of trichloromonofluoromethane adsorbed per unit mass of the activated carbon pellet.

The isosteric heats of adsorption for trichloromonofluoromethane on the activated carbon pellet are of the same order of magnitude as the heat of condensation [Benning and McHarness, 1934]. It may be considered that the adsorption of trichloromonofluoromethane on this activated carbon pellet is due primarily to physical forces.

## CONCLUSIONS

The adsorption of trichloromonofluoromethane, which deplete the ozone layer, on the activated carbon pellet was investigated. The adsorption equilibria on this adsorbent has been obtained at various temperatures. The micropore volume and equilibrium constants, based on the Freundlich, Langmuir and Dubinin-Radushkevich equations, are obtained from experimental data. It was found that the Dubinin-Raduschkevich equation gives better fits than other two equations through the wide concentration ranges.

Furthermore, it was found that the isosteric heats of adsorption are of the same order of magnitude as the heat of condensation of trichloromonofluoromethane.

## NOMENCLATURE

A : Langmuir parameter [1/ppm]
B : Langmuir parameter [1/ppm]
b : constant in D-R equation
C : concentration in vapor phase [ppm ]
$d_L$ : liquid density [g/cm$^3$]
k : parameter of Freundlich equation [ppm$^n$]
K : carbon structure constant [mol$^2$/J$^2$]
$M_w$ : molecular weight [g/mol]
n : constant in Freundlich equation [-]
$P_i$ : partial pressure of adsorbate [kPa]
$P_{sat}$ : vapor pressure at saturation [kPa]
q : isosteric heats of condensation [kJ/mol]
R : gas constant [kJ/(mol·K)]
T : absolute temperature [K]
V : molar volume of adsorbate in equilibrium [cm$^3$/mol]
W : mass of gas adsorbed per unit weight of adsorbent [g/g]
$W_m$ : adsorption capacity at monolayer saturation [g/g]
$w_o$ : micropore volume [cm$^3$/g]
$\beta$ : affinity coefficient [-]

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