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ADSORPTION EQUILIBRIA OF CHLOROPENTAFLUOROETHANE ON ACTIVATED CARBON POWDER

Dong Ju Moon†, **Moon Jo Chung, Honggon Kim,**
Byung Gwon Lee, Sang Deuk Lee and Kun You Park

CFC Alternatives Research Center, Korea Institute of Science and Technology,
P.O. Box 131, Cheongryang, Seoul, Korea

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Abstract – An equilibrium study was conducted on the adsorption of chloropentafluoroethane (CFC-115, CF_3CF_2Cl) on activated carbon powder between 298.15 K and 373.15 K. Experimental data were fitted with several isotherm equations. Among the two-parameter equations, the BET equation showed the best results over the entire relative pressure range studied. When the pressure range was divided into two regions, a better result was obtained by applying the Langmuir equation in the lower pressure range and the BET equation in the higher relative pressure region. Among the three-parameter equations, the Langmuir-Freundlich equation gave better results than the Redrich-Peterson equation. The isosteric heat of adsorption of CFC-115 on the activated carbon powder was estimated. It was found to have the same order of magnitude with the heat of condensation, which indicates that the adsorption was primarily due to physical forces.

Key words : CFC-115, Chloropentafluoroethane, Activated Carbon, Adsorption Equilibrium, CFCs

INTRODUCTION

Chlorofluorocarbons (CFCs) have been widely used as refrigerants, blowing agents, propellants and cleaning agents due to their outstanding properties. However, international protocols restrict the release of CFCs into the atmosphere [UNEP, 1987] because CFCs deplete the stratospheric ozone layer [Cicerone and Stolarski, 1974; Molina and Rowland 1974]. This has led to various researches on methods to recover the halogenated hydrocarbons after use [Moon et al., 1997; Cho et al., 1996; Cho and Kim, 1996; Kuo and Hines, 1992; Kodama et al., 1992; Tsai and Chang, 1994]. Chlorofluoropentane (CFC-115) has been mainly used in refrigerants such as R-502, an azeotropic blend of CFC-115 and HFC-22. The recovered CFC-115 can be converted to pentafluoroethane (HFC-125), which is one of the promising substitutes for CFCs [Moon, 1998].

Activated carbon has been used as an adsorbent for the adsorption equilibria of CFC-12 [Kwang et al., 1989], CFC-113 [Lim et al., 1994; Park et al., 1995], and CFC-12/HFC-32 mixture [Lee et al., 1997] and as a support material for catalysts [Moon et al., 1998; Moon and Ihm, 1994]. One inexpensive way to reduce halogenated carbon emissions is to recover the used CFCs by using the activated carbon as an adsorbent. This technology is highly effective for low concentrations of CFCs. The adsorption equilibria are prerequisites for the design of adsorption facilities.

In this work, an equilibrium study was conducted on the adsorption of CFC-115 on activated carbon powder between 298.15 K and 373.15 K. Several two- or three-parameter isotherm equations were tested to find an equation that represented the equilibrium characteristics most satisfactorily. Isosteric heats of adsorption were also estimated at different levels of surface coverage.

EXPERIMENTAL

1. Materials

Activated carbon powder (surface area of 1,098 m^2/g, pore volume of 0.418 cc/g, pore diameter of 53.53 Å) was used as an adsorbent. Chloropentafluoroethane of 99.99 % purity was supplied from Elf Atochem.

2. Vapor Pressure of CFC-115

The vapor pressure of CFC-115 should be known in advance in order to apply the BET equation. It was calculated by Eq. (1) [Frere et al., 1994] below the critical temperature of CFC-115 and was estimated by the simulation program PRO-II (Simulation Science Inc., USA) above the critical temperature.

$$\ln (P_0) = b_1/T + b_2 + b_3 \cdot T + b_4 \cdot (1 - T/T_c)^{1.5} \qquad (1)$$

where $b_1 = -3809.75$, $b_2 = 21.78658$, $b_3 = -0.008324$,
$b_4 = 4.744543$, $T_c = 353.10$ K

3. Experimental

A volumetric sorption analyzer (Micromeritics, ASAP 2000) was used to measure the BET surface area of the activated carbon powder. A schematic diagram of the volumetric apparatus for adsorption isotherms is given in Fig. 1. Before the adsorption, the adsorbent was evacuated to 10^{-5} mm Hg at 473 K for 15 hours. A turbomolecular pump (Balzers Co., Model TSH 065D) in combination with a rotary vacuum pump (Model Duo 1.5A) was used to evacuate the system. An ion gauge and a convectron vacuum gauge (Granville-Phillips Model 307)

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†To whom all correspondence should be sent.
E-mail : djmoon@kistmail.kist.re.kr

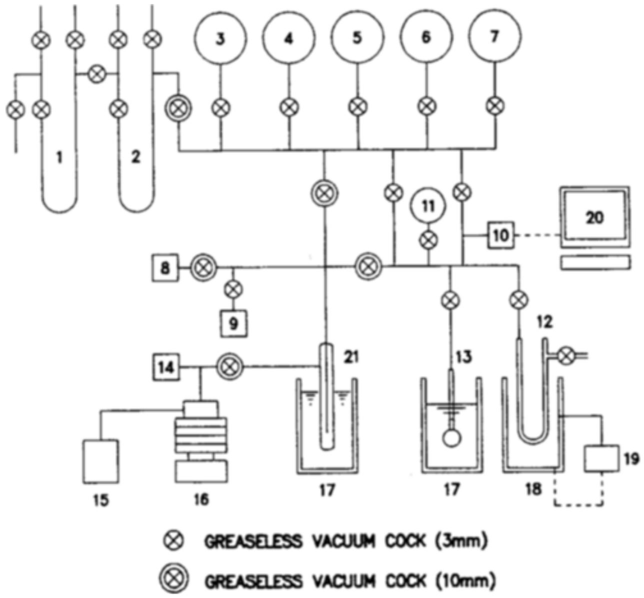


Fig. 1. Schematic diagram of the volumetric adsorption system.

1. Moisture trap
2. Oxygenation trap
3. H_2 reservoir (2 l)
4. CFCs reservoir (2 l)
5. N_2 reservoir (2 l)
6. He reservoir (2 l)
7. O_2 reservoir (2 l)
8. Ion vacuum gauge
9. Convectron vacuum gauge
10. Baratron vacuum gauge
11. Reference volume
12. Chemisorption cell
13. Bet cell
14. Compact full range gauge
15. Rotary vacuum pump
16. Turbomolecular pump
17. Liquid N_2 duar
18. Electric heater
19. Temperature controller
20. Personal computer
21. Trap

were used for the measurement of vacuum. During the adsorption run, pressure changes were measured by an MKS absolute pressure transducer (Model 690A-13T) and a power supply readout instrument (Type 270). The dead volume of the system was determined by helium gas, and the weight of the adsorbent was measured within ±10 μg precision.

Adsorption isotherms were obtained by admitting successive increments of a known volume of the sample gas to the adsorbent sample. After each increment, the equilibrium pressure of the system was measured. Correction was made with a consideration of the dead volume to determine each point on the adsorption isotherm. The equilibrium data at different temperature levels were obtained by the same procedure.

RESULTS AND DISCUSSION

The adsorption data of CFC-115 on the activated carbon powder were obtained at five temperatures (298.15, 308.15, 318.15, 348.15, and 373.15 K). The data points were reproducible within ±1 %.

It would be very convenient if the adsorption equilibria could be represented by an explicit equation. Therefore, many isotherm correlations were suggested to describe the adsorption equilibrium [Tsai and Chang, 1992; Ruthven, 1984; Cho et al., 1995]. The applicability of various isotherm equations can be determined by a comparison of the absolute error (*Abs. Err.*) defined as Eq. (2),

$$Abs.\ Err. = \left(\frac{1}{N}\right)\sum_{i=1}^{N}\left|\frac{V_i^{cal}-V_i^{exp}}{V_i^{cal}}\right| \tag{2}$$

where V_i^{cal} and V_i^{exp} are a calculated value and an experimental value, respectively, and N is the number of data points at a given temperature.

1. Isotherm Equations

1-1. The Langmuir Equation

The Langmuir equation is the most widely used two-parameter equation, represented as Eq. (3) [Langmuir, 1918],

$$\theta = \frac{V}{V_m} = \frac{B\cdot P}{1+B\cdot P} \tag{3}$$

where θ is the fractional coverage and V_m is the adsorbed amount per unit mass of adsorbent corresponding to the complete monolayer coverage. B is the Langmuir constant. V_m and B are obtained by the intercept and the slope of a plot of 1/V vs 1/P at a given adsorption temperature. In the present study, the expressions of V_m and B as functions of temperature were obtained as Eq. (4) and Eq. (5) by non-linear regression analysis:

$$V_m = 541.18\cdot \exp\left(\frac{576.02}{T}\right) \tag{4}$$

$$B = 7.4\times 10^{-6}\cdot \exp\left(\frac{2657.18}{T}\right) \tag{5}$$

1-2. The Freundlich Equation

The Freundlich equation is an empirical one represented as Eq. (6) [Yang, 1962],

$$Q = K\cdot P^{(1/n)} \tag{6}$$

where K and n are empirical constants. In general, n has a value greater than unity. A plot of ln Q vs ln P gives K and n from the intercept and the slope. In the present study, the expressions of K and n as functions of temperature were obtained as Eq. (7) and Eq. (8) by non-linear regression analysis:

$$K = 9.805\times 10^{-2}\cdot \exp\left(\frac{2716}{T}\right) \tag{7}$$

$$n = 2.329\times 10^{-1}\cdot \exp\left(\frac{847.37}{T}\right) \tag{8}$$

1-3. The BET Equation

The Brunauer, Emmett and Teller (BET) isotherm equation shown as Eq. (9) was derived from the theoretical model for multilayer adsorption on the free surface [Brunauer et al., 1938].

$$\frac{P}{V(P_o-P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C}\left(\frac{P}{P_o}\right) \tag{9}$$

The BET isotherm's parameters, V_m and C, were obtained from the slope and the intercept of the BET plots of $P/V(P_0-P)$ against P/P_0 represented in Fig. 2. Expressions of V_m and C as functions of temperature were obtained as Eq. (10) and Eq. (11) by non-linear regression analysis.

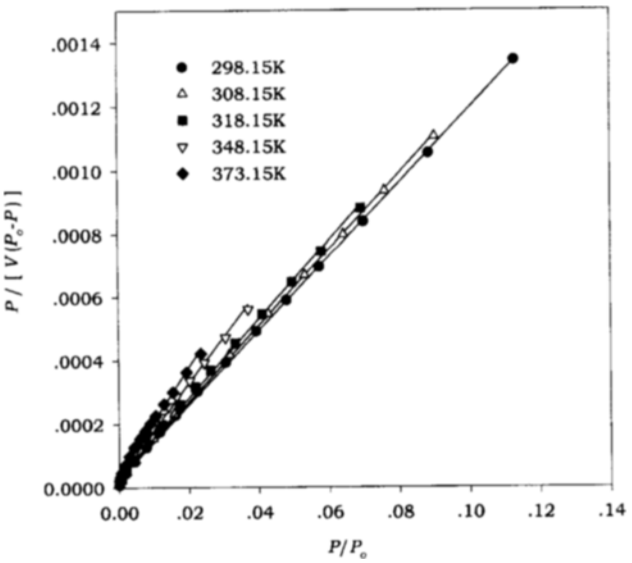


Fig. 2. The BET plots of P/P_0 vs $P/[V(P-P_0)]$ in the entire range of relative pressure.

$$V_m = 17.948 \cdot \exp\left(\frac{474.01}{T}\right) \tag{10}$$

$$C = 152.94 \cdot \exp\left(\frac{192.10}{T}\right) \tag{11}$$

Fig. 3 shows the calculated isotherms by the Langmuir equation, the Freundlich equation and the BET equation. The amount of CFC-115 adsorbed increased with increasing pressure and decreased with increasing temperature. The absolute error between the experimental data and the calculated values by the Langmuir equation was considerably large, i.e., about 24 %. The main deviation was seen in lower pressures under 15 torr, but the Langmuir isotherm was well fitted at higher pressures. The absolute error by the Freundlich equation was 9 %. The Freundlich isotherms appeared to fit the experimental data reasonably at low pressures compared to the Langmuir isotherm, but the deviation increased with increasing pressure. The Freundlich isotherm over the entire range was well fitted compared to the Langmuir isotherm. Among the two-parameter equations, the BET equation gave the best result to represent the experimental data over the entire range studied.

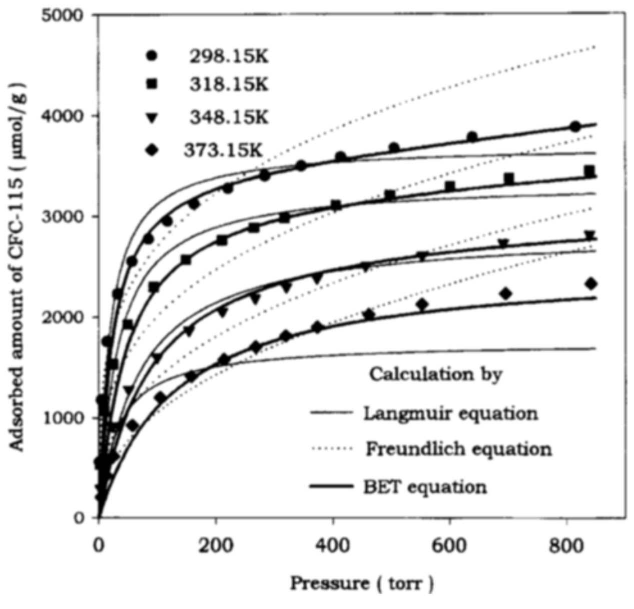
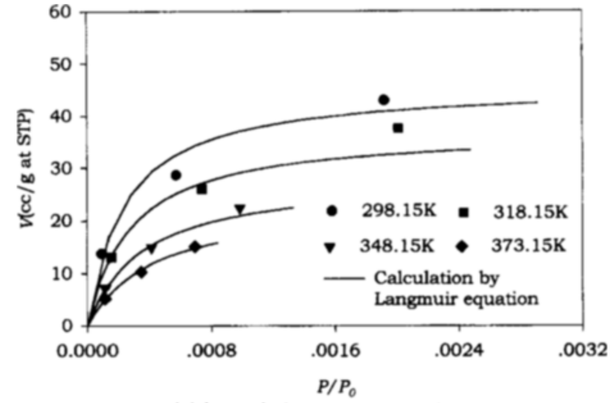


Fig. 3. The calculated isotherms by the Langmuir equation, the Freundlich equation and the BET equation.

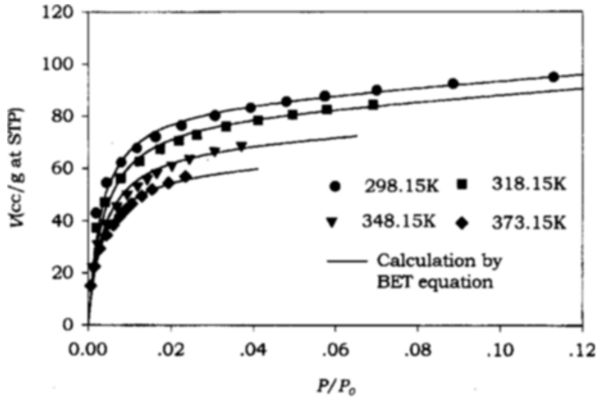
The BET equation is known to show good agreement with adsorption data in a high relative pressure range of $0.05 \leq P/P_0 \leq 0.3$ [Brunauer et al., 1938]. On the other hand, the Langmuir equation can be expected to represent the equilibrium satisfactorily in a low relative pressure range since it is based on submonolayer coverage. Therefore, it was attempted to divide the relative pressure range into two regions, and the Langmuir equation and the BET equation were applied in the low relative pressure range and in the high relative pressure range, respectively. When the boundary was set to $P/P_0=0.002$, the Langmuir equation gave a good representation within 4 % absolute error in the low pressure range, and the BET equation gave a good result within 4 % absolute error in the high pressure range. The result is shown in Fig. 4, and the parameters of the Langmuir equation and the BET equation in the corresponding pressure ranges are listed in Table 1 and Table 2, respectively.

1-4. The Redrich-Peterson Isotherm

The Redrich-Peterson isotherm expressed as Eq. (12) is a



(a) low relative pressure region



(b) high relative pressure region

Fig. 4. The calculated isotherms by the Langmuir equation in the low relative range and the BET equation in the high relative range.

Table 1. The Langmuir isotherm parameters in the low relative pressure range of $0.0001 \leq P/P_0 \leq 0.002$

Temperature T (K)	Monolayer uptake V_m (cc/g)	Langmuir constant B [$torr^{-1}$]
298.15	42.499	0.6884
308.15	41.971	0.4061
318.15	40.210	0.2585
348.15	28.220	0.1330
373.15	22.702	0.0719

Table 2. The BET isotherm parameters in the high relative pressure range of $0.002 \leq P/P_0 \leq 0.12$

Temperature T (K)	Monolayer uptake V_m (cc/g)	BET constant C [-]
298.15	86.399	326.955
308.15	84.284	300.372
318.15	81.762	281.160
348.15	71.064	284.854
373.15	61.597	313.407

combination of the Langmuir and the Freundlich isotherms [Redrich and Peterson, 1958]. At a high partial pressure, this equation converges to the Freundlich form. At a very low partial pressure, it converges to a linear isotherm as the Langmuir equation.

$$Q = \frac{A \cdot P}{1 + B \cdot P^c} \tag{12}$$

In the Eq. (12), c lies between 0 and 1. If c is unity, then this becomes the familiar Langmuir equation. Because c is not greatly affected by the adsorption temperature, it was set to the average value, 0.85, obtained from the preliminary analysis at five different temperature levels. The Redrich-Peterson parameters, A and B, were obtained as Eq. (13) and Eq. (14) by nonlinear regression analysis using a modified Levenberg-Marquardt algorithm [Marquardt, 1963].

$$A = 1.175 \times 10^{-4} \cdot \exp\left(\frac{4715.30}{T}\right) \tag{13}$$

$$B = 9.0 \times 10^{-7} \cdot \exp\left(\frac{4000.11}{T}\right) \tag{14}$$

$$C = 0.85$$

1-5. The Langmuir-Freundlich Equation

The Langmuir-Freundlich equation expressed as Eq. (15) is a hybrid of the Langmuir equation and the Freundlich equation [Sips, 1958].

$$Q = \frac{Q_m B \cdot P^{(1/n)}}{1 + B \cdot P^{(1/n)}} \tag{15}$$

The temperature dependence of the Langmuir-Freundlich parameters was calculated by nonlinear regression analysis. The Q_m, B and n were obtained as Eq. (16), Eq. (17), and Eq. (18), respectively.

$$Q_m = 1123.50 \cdot \exp\left(\frac{441.09}{T}\right) \tag{16}$$

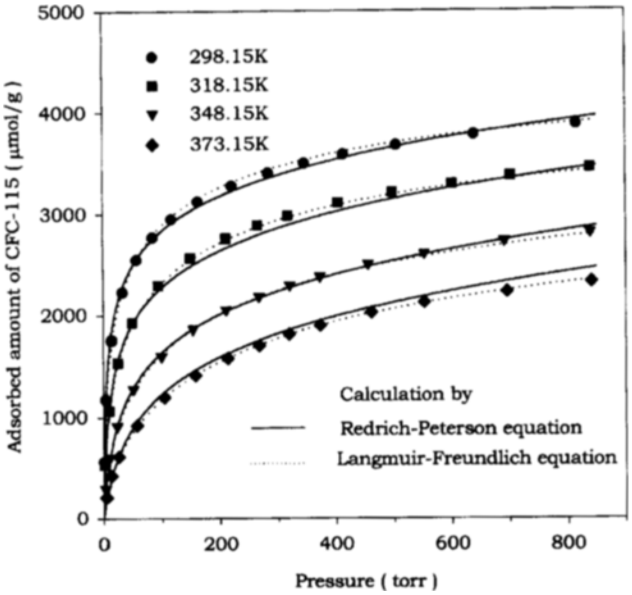


Fig. 5. The calculated isotherms by the Redrich-Peterson equation and the Langmuir-Freundlich equation.

$$B = 2.37 \times 10^{5} \cdot \exp\left(\frac{2644.82}{T}\right) \tag{17}$$

$$n = 5.439 \times 10^{-1} \cdot \exp\left(\frac{405.15}{T}\right) \tag{18}$$

Fig. 5 shows the calculated isotherms by the Redrich-Peterson equation and the Langmuir-Freundlich equation. The Langmuir-Freundlich equation gave better representation within 2 % absolute error than the Redrich-Peterson equation, where the absolute error was 6 %. The Langmuir-Freundlich equation has been widely used for design purposes for many years due to the reasonably good empirical correlation.

Considering the number of parameters, it is natural that three-parameter equations show better representation than two-parameter equations.

2. Isosteric Heat of Adsorption

The heat of adsorption is an important property for the characterization of the type of adsorption and the degree of heterogeneity of the surface. The isosteric heat of adsorption of CFC-115 on the activated carbon powder was determined using the Clausis-Clapeyron equation:

$$q_{iso} = -R\left[\frac{(\partial \ln P)}{\partial(1/T)}\right]_{\theta} \tag{19}$$

where R is gas constant and subscription θ means the constant surface coverage. The result is shown in Table 3. The isosteric heat of adsorption increased with the increase of the surface coverage (θ), which was rather unusual since the heat of adsorption is generally known to decrease with the increase of surface coverage. A similar behavior was observed in the adsorption of CFC-113 on the activated carbon pellet and the activated carbon felt [Cho and Lee, 1995]. Other similar results were reported in the adsorption of CFC-11, CFC-12, CFC-13, and CFC-113 on NaY, KY, and CsY zeolite [Kobayashi, 1994]. Kobayashi et al. [1994] suggested that this phenomenon

Table 3. The isosteric heat of adsorption for CFC-115 on activated carbon powder estimated from the BET isotherm

Temperature (K)	Surface coverage θ	Isosteric heat of adsorption q_{iso} (kcal/mol)
298	0.0463	5.963
	0.1389	6.128
	0.3241	6.615
	0.5093	7.670
	0.6945	8.067

The heat of condensation, q_{con}=3.494 kcal/mol at 298 K [Ichigawa, 1990]

θ=V/V$_m$ at 298 K

could be interpreted by terms of Hill's nonlocalized equation [Hills, 1946] related to the interaction between the adsorbed molecules.

Since the isosteric heat of adsorption of CFC-115 was approximately the same order of magnitude with the heat of condensation, the adsorption of CFC-115 on the activated carbon powder was thought to be primarily due to physical forces.

CONCLUSION

An equilibrium study on the adsorption of chloropentafluoroethane (CFC-115, CF_3CF_2Cl) on activated carbon powder was performed in the relative pressure range of $0.0001<P/P_0<0.12$ at five different temperature levels between 298.15 K and 373.15 K.

The Freundlich isotherm was well fitted compared to the Langmuir isotherm. Among the two-parameter isotherm equations, the BET equation gave the best result. When the entire relative pressure range was divided into two regions at $P/P_0=0.002$, a better result was obtained by applying the Langmuir equation in the low pressure range and the BET equation in the high pressure range. The absolute error was less than 4 % in both regions. Among the three-parameter isotherm equations, the Langmuir-Freundlich equation represented the equilibrium data fairly well within 2 % absolute error. The Redrich-Peterson isotherms gave a larger deviation of 6 % absolute error. The isosteric heat of adsorption of CFC-115 was approximately the same order of magnitude as the heat of condensation, indicating that the adsorption was primarily due to physical forces.

NOMENCLATURE

A : Redrich-Peterson parameter [μmol/g/torr]
B : Langmuir parameter [Torr^{-1}], Redrich-Peterson parameter [Torr^{c}], and Langmuir-Freundlich parameter [Torr^{n}]
C : BET constant
c : Redrich-Peterson parameter
K : Freundlich constant, [μmol/g·torr^{n}]
N : number of data points
n : Freundlich parameter, and Langmuir-Freundlich parameter
P : partial pressure of adsorbate [Pa]
P_o : vapor pressure at saturation [Pa]
Q : amount of gas adsorbed per unit weight of adsorbent [μmol/g]
Q_m : monolayer uptake [μmol/g]
q_{iso} : isosteric heat of adsorption [kcal/mol]
q_{con} : heat of condensation [kcal/mol]
R : gas constant [kcal/mol·K]
T : absolute temperature [K]
T_c : critical temperature [K]
V : amount of gas adsorbed per unit weight of adsorbent [cc/g, at STP].
V_m : monolayer uptake per unit weight of adsorbent [cc/g, at STP]

Greek Letter

θ : surface coverage [V/V$_m$]

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