Adsorption Equilibria of Toluene, Dichloromethane, and Trichloroethylene onto Activated Carbon Fiber

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Adsorption equilibria of toluene, dichloromethane, and trichloroethylene onto the pitch-based activated carbon fiber were obtained by the static volumetric method. Equilibrium measurements were done at (298, 323, and 348) K and pressures up to 3 kPa for toluene, 12 kPa for dichloromethane, and 6 kPa for trichloroethylene, respectively. Among several isotherm models, the Toth equation agreed remarkably with the experiment data. For each adsorbate, characteristic and isosteric heat curves were derived from the equilibrium data. The isosteric heats of adsorption indicate that Nano-10 has an energetically heterogeneous surface.

Introduction

To date, activated carbon is the most universal adsorbent for volatile organic compounds (VOCs) control. However, some disadvantages for the application of activated carbon include its flammability, difficulty in regenerating high-boiling point solvents [caused polymerization or oxidation of some solvents to be toxic or insoluble materials], and requirement for humidity control.[1] On the positive side, activated carbon fiber (ACF) has uniform size and dimension, higher adsorption capacity, faster adsorption and desorption rates than activated carbon, and ease of handling.[2,3] These features obtain adsorptive system size reduction and added adsorbed vapor selectivity. In these respects, ACF, as an alternative to activated carbon inefficiencies, is an excellent micropore adsorbent. ACF is derived from raw materials as various as pitch, cellulose, polyacrylonitrile (PAN), and phenol resins. Several reports on cellulose fiber as a base material exist.[4,5] The adsorption characteristics of these ACF depend on the kinds of precursor selected. For instance, the pitch-based ACF has the highest carbon content and is suitable for organic solvent control.[6] Therefore, it is considered that the pitch-based ACF adsorbent is efficient for treating VOCs.

Adsorption equilibria of organic vapors have received much attention because of their practical importance in the fields of environmental issues. Knowledge of adsorption equilibria thermodynamic data is essential for adsorption facility design. This information obtains optimum conditions for operation temperature and pressure estimate ranges.[7]

The focus of this study is to measure adsorption equilibrium isotherms for VOCs onto ACF. Adsorption equilibria were obtained at temperatures of (298, 323, and 348) K for the adsorbates, toluene, dichloromethane (DCM), and trichloroethylene (TCE). Toluene is one of the major organic solvents, BTX (benzene, toluene, and *p*-xylene). DCM and TCE have been used widely in chlorinated hydrocarbons. Experimental data were correlated by the Toth equation.

Table 1. Physical Properties of the Activated Carbon Fiber

	Nano-10
BET surface area ($m^2 \cdot g^{-1}$)	764.3
total pore volume ($cm^3 \cdot g^{-1}$)	0.4096
mean pore diameter (Å)	21

Experimental Section

Materials. Pitch-based activated carbon fiber, Nano-10 (NanoTechnics Co., Korea),[8] was used as the adsorbent in this study. According to nitrogen adsorption isotherms, the characteristics of the activated carbon fiber are determined. Using adsorption of nitrogen, the BET surface area for Nano-10 was measured by an automatic sorption analyzer (Quantachrome Autosorb-1). The average pore diameter, total pore volume, and pore size distribution can be calculated by the DH method. The physical properties of the adsorbent are shown in Table 1. As can be seen in Figure 1, Nano-10 seems to be a Type I in that it has isotherms characterized by a quite horizontal plateau.[9] Moreover, Figure 2 shows that Nano-10 has a very large pore volume in the micropore range of pore diameters below 20 Å. Prior to the experiments, the sample was kept in a drying vacuum oven at 423 K for more than 12 h to remove impurities. The adsorbates, toluene, DCM, and TCE, were examined. The purity and the manufacturer of each material are as follows: Toluene, C_7H_8 (99.9%, J.T Baker); DCM, CH_2Cl_2 (98.5%, Junsei); TCE, C_2HCl_3 (99.0%, Oriental).

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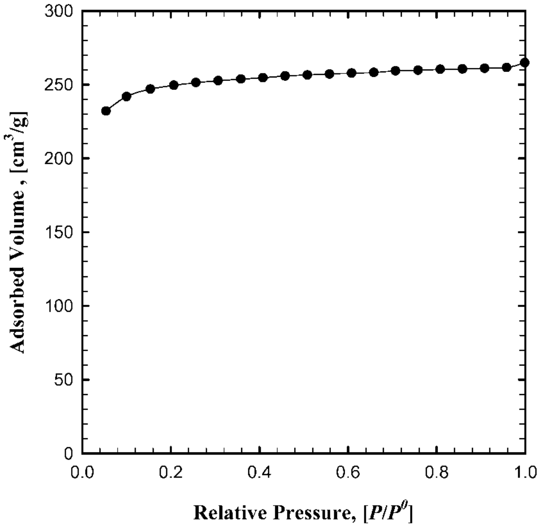

Figure 1. Equilibrium isotherms for nitrogen onto Nano-10.

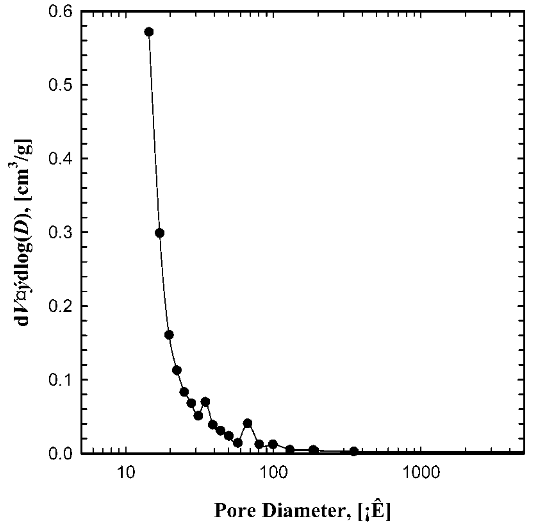

Figure 2. Adsorption pore size distribution.

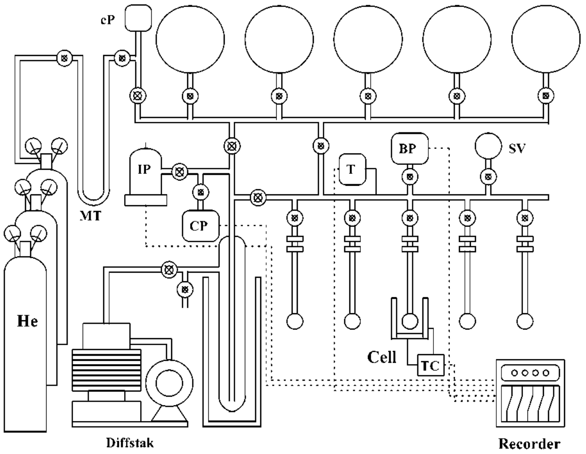

Figure 3. Adsorption equilibrium apparatus: (BP) Baratron transducer; (CP) convectron gauge; (cP) compound gauge; (IP) ion gauge; (MT) moisture trap; (SV) standard volume; (T) thermocouple; (TC) temperature controller.

Table 2. Experimental Isotherm Data for Toluene onto Activated Carbon Fiber

298.15 K		323.15 K		348.15 K	
P	N	P	N	P	N
kPa	mmol·g^{-1}	kPa	mmol·g^{-1}	kPa	mmol·g^{-1}
0.010	0.314	0.010	0.307	0.011	0.396
0.010	0.320	0.011	0.327	0.012	0.428
0.025	1.142	0.016	0.521	0.023	0.829
0.051	2.266	0.021	0.777	0.048	1.504
0.073	2.679	0.023	0.840	0.058	1.621
0.331	3.183	0.040	1.546	0.114	2.018
0.493	3.227	0.101	2.396	0.177	2.255
1.471	3.385	0.320	2.908	0.531	2.655
1.539	3.394	0.782	3.013	0.943	2.808
2.315	3.518	1.407	3.144	1.459	2.913
		2.196	3.242	1.832	2.959
		2.500	3.260	2.308	3.040
				2.312	3.044

Table 3. Experimental Isotherm Data for Dichloromethane onto Activated Carbon Fiber

298.15 K		323.15 K		348.15 K	
P	N	P	N	P	N
kPa	mmol·g^{-1}	kPa	mmol·g^{-1}	kPa	mmol·g^{-1}
0.017	0.551	0.046	0.505	0.121	0.440
0.066	1.247	0.113	0.834	0.187	0.513
0.133	1.804	0.115	0.818	0.464	0.884
0.321	2.713	0.216	1.187	0.694	1.130
0.461	3.157	0.406	1.622	1.292	1.464
0.716	3.724	0.737	2.153	2.443	2.133
1.412	4.365	1.212	2.663	3.596	2.578
1.709	4.565	1.923	3.236	5.613	3.092
2.027	4.761	2.880	3.807	7.012	3.452
2.847	5.085	5.765	4.634	12.638	4.213
4.124	5.395	7.456	4.999		
		8.598	5.192		

Apparatus and Procedure. The isotherm measurement apparatus in Figure 3 is based on the static volumetric method. In this method, the total amount of vapor introduced and recovered in the system after equilibrium is determined and recovered by appropriate pressure, volume, and temperature measurements. The pressure was recorded using a Baratron absolute pressure transducer (MKS-type 270D) ranging from (0 to 133.00) kPa with an accuracy of 0.05%.

During adsorption, the adsorbent cell was placed in a water bath and maintained constantly by a refrigeration circulator (Haake-type F3) with a precision of ±0.02 K. Prior to the introduction in the adsorbent cell, the mass of the adsorbent was determined with an accuracy of ±10 μg after regeneration at 473 K at high vacuum for 12 h. An oil diffusion pump coupled to a mechanical vacuum pump (Edward-type Diffustak 63/150M) provided vacuum to 10^{-3} Pa. The pressure was monitored by a convectron gauge with a vacuum gauge controller (Granville-Philips-type 307). The volume of the adsorbent cell was determined by expansion of helium gas.

Results and Discussion

The adsorption equilibrium data of various adsorbates onto Nano-10 were obtained at (298, 323, and 348) K and pressures up to 3 kPa for toluene, 12 kPa for DCM, and 6 kPa for TCE, respectively, as presented in Tables 2−4. The adsorbed moles of adsorbates per unit mass of activated carbon fiber versus equilibrium pressure for each adsorbate are shown in Figure 4. As seen, the adsorptivity of DCM is higher than toluene and TCE at low- and high-pressure ranges, implying that the adsorption affinity for DCM is higher than toluene and TCE; also, the DCM adsorption capacity is superior to other vapors in the experimental range.

Table 4. Experimental Isotherm Data for Trichloroethylene onto Activated Carbon Fiber

298.15 K		323.15 K		348.15 K	
P	*N*	*P*	*N*	*P*	*N*
kPa	mmol·g^{-1}	kPa	mmol·g^{-1}	kPa	mmol·g^{-1}
0.041	2.347	0.086	2.255	0.175	1.987
0.080	3.131	0.395	3.277	0.954	2.978
0.300	3.677	0.539	3.421	2.107	3.330
0.459	3.811	1.162	3.664	2.672	3.445
0.650	3.919	1.531	3.790	2.824	3.484
0.859	3.957	2.400	3.899	6.391	3.834
1.267	4.053	4.225	4.078		
1.593	4.077	7.082	4.272		
2.063	4.134				
2.776	4.206				
3.799	4.378				
5.148	4.536				

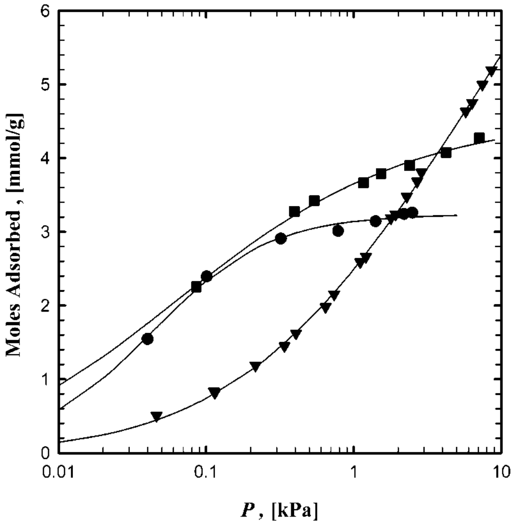

Figure 4. Measured and fitted isotherms for toluene, dichloromethane, and trichloroethylene onto activated carbon fiber at 323 K: (●) toluene; (▼) dichloromethane; (■) trichloroethylene; (—) Toth equation.

Fitted data of adsorption isotherm data, using several pure species equilibrium models, is essential to practical adsorption process operation. Isotherm equations used in this study were Langmuir, Freundlich, Sips, Toth, Unilan,[10] Dubinin−Astakov (D−A), and Dubinin−Radushkevitch (D−R).[11]

Langmuir

$$N = \frac{mbP}{1 + bP} \tag{1}$$

Freundlich

$$N = kP^{1/t} \tag{2}$$

Sips

$$N = \frac{mbP^{1/t}}{1 + bP^{1/t}} \tag{3}$$

Toth

$$N = \frac{mP}{(b + P^t)^{1/t}} \tag{4}$$

Unilan

$$N = \frac{m}{2s}\ln\left[\frac{c + Pe^{+s}}{c + Pe^{-s}}\right] \tag{5}$$

Table 5. Toth Equation Parameters of Each Adsorbate onto Activated Carbon Fiber

adsorbate	*T* K	*m* mmol·g^{-1}	*b* kPa	*t*	100·*D*
toluene	298.15	3.507	0.033	0.849	1.800
	323.15	3.240	0.035	0.756	1.748
	348.15	3.292	0.094	0.620	0.766
dichloromethane	298.15	7.520	0.374	0.506	1.499
	323.15	12.483	0.747	0.346	1.795
	348.15	22.739	1.144	0.271	2.645
trichloroethylene	298.15	4.595	0.070	0.532	2.023
	323.15	4.595	0.123	0.505	1.162
	348.15	5.079	0.216	0.365	0.421

D−A

$$W = W^0 \exp\left[-\left(\frac{\epsilon}{E}\right)^r\right] \tag{6}$$

D−R

$$W = W^0 \exp\left[-\left(\frac{\epsilon}{E}\right)^2\right] \tag{7}$$

where *N* is the amount adsorbed, *P* is the equilibrium pressure, and *m*, *b*, *c*, *s*, and *t* are the isotherm parameters.

Because correlation by the Toth equation obtained the minimum value of the average deviation parameter (*D*) among the several models, the Toth equation was employed. The deviation parameter (*D*) was employed to compare the correlation results with the experiment data.

$$D = \frac{1}{k}\sum_i^k \left|\frac{N_i^{\text{obs}} - N_i^{\text{cal}}}{N_i^{\text{obs}}}\right|, \quad k = \text{the number of data} \tag{8}$$

In Figure 4, experimental data at 323 K are represented as symbols and fitted data using the Toth equation as solid lines. Isotherm parameters of the Toth equation are tabulated in Table 5. In eq 4, *N* is the specific amount adsorbed, *P* is the equilibrium pressure, *m* is the maximum adsorbed amount with respect to the complete monolayer coverage, and *b* is related to the adsorption affinity. Also, *t* refers to the heterogeneity of the system, when $t = 1$; the system is homogeneous.[10] To derive these parameters for each adsorbate, the Nelder−Mead simplex pattern search algorithm was applied as the parameter estimation technique.[12]

The objective functions used is as follows:

$$\min \sum_i (N_i^{\text{obs}} - N_i^{\text{cal}})^2 \tag{9}$$

The characteristic curve has been accepted in that it represents a unique temperature-independent relationship between the adsorption potential and the amounts of vapor adsorbed for a given adsorbent−adsorbate system. It can be a significant means of summarizing equilibrium data over a wide range of temperatures and pressures.[13] The characteristic curves of each adsorbate are represented in Figure 5. These figures were plotted by the Methods of Plotting the Characteristic Curve for the Toth equation.[7] According to this method, these characteristic curves are given a specific temperature-independent tendency for each adsorbate.

The isosteric heat of adsorption can be calculated by the Clausius−Clapeyron equation,[14]

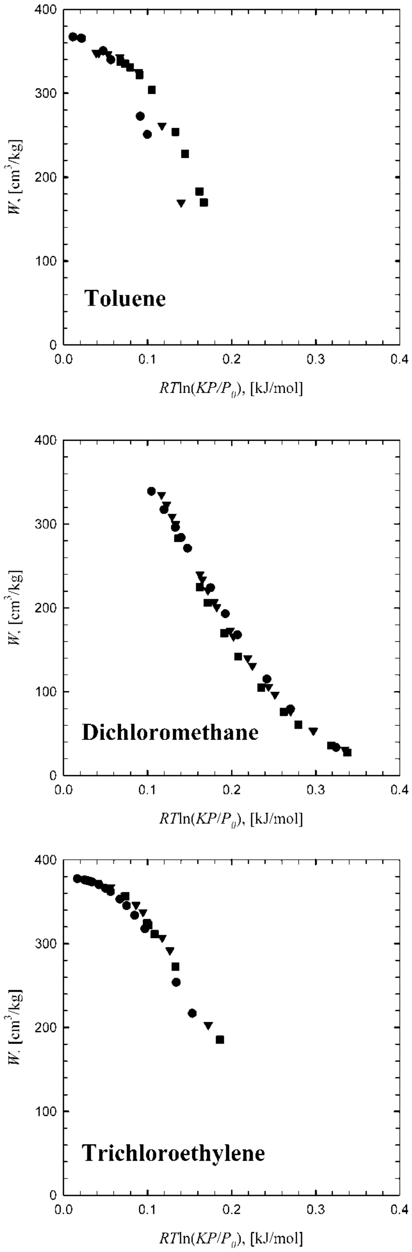

Figure 5. Characteristic curve of toluene, dichloromethane, and trichloroethylene: (●) 298 K; (▼) 323 K; (■) 348 K.

$$\frac{q_{\mathrm{st}}}{RT^2} = \left[\frac{\partial \ln P}{\partial T}\right]_N \qquad (10)$$

where P is the pressure, T is the temperature, and R is the gas constant. The isosteric heat curves are represented in the plot of the isosteric heat versus moles adsorbed of adsorbate per adsorbent mass and may be used as the criterion of the energetic heterogeneity of the adsorbent surface. As shown in Figure 6, the isosteric heat is varied with respect to loading. These patterns indicate the heterogeneity of adsorbent, as a property of the surface, and are assumed to be independent of the adsorbate used.[15] That Nano-10 has an energetically heterogeneous surface is reflected through the variation of the isosteric heat as in Figure 6.

Conclusions

The adsorption equilibrium data of toluene, dichloromethane, and trichloroethylene onto Nano-10 were ob-

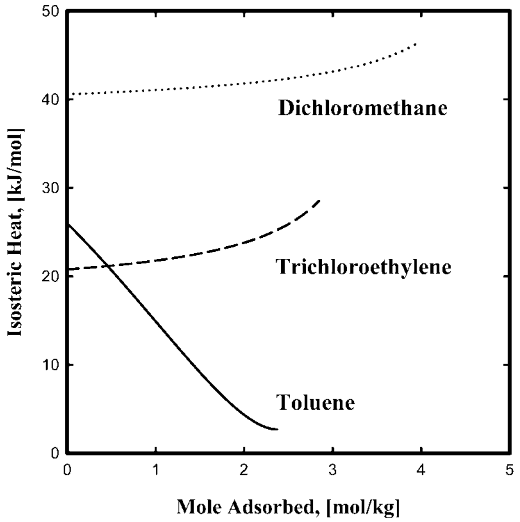

Figure 6. Isosteric heat of adsorption for toluene, dichloromenthane, and trichloroethylene.

tained at (298, 323, and 348) K and pressures up to 3 kPa for toluene, 12 kPa for dichloromethane, and 6 kPa for trichloroethylene. The correlations by the Toth equation were in remarkable agreement with the experiment data. Also, the Toth equation obtained characteristic curves according to the relationship of the adsorbent−adsorbate. The isosteric heats of adsorption derived from the Clausius−Clapeyron equation indicate that Nano-10 has an energetically heterogeneous surface.

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