Equilibrium Isotherms of Dichloromethane, Trichloroethylene, and 1,1,1-Trichloroethane on Activated Carbon Fiber

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The adsorption equilibrium isotherms of dichloromethane, trichloroethylene, and 1,1,1-trochloroethane on activated carbon fiber (KF-1500) were measured by a static volumetric technique. Equilibrium data were obtained at (298, 323, and 348) K and pressures up to 40 kPa for dichloromethane, 8 kPa for trichloroethylene, and 12 kPa for 1,1,1-trichloroethane, respectively. The Dubinin−Astakhov isotherm equation was found to provide an excellent fit to the experimental data.

Introduction

Adsorption is a surface phenomenon; therefore, the total surface area with respect to pore size and volume might be a criterion in determining its effectiveness in a particular application. Porous carbons can be manufactured from many carbonaceous starting materials such as wool, coconut shell, peat, bone char, petroleum, or rayon cloth. These materials in different forms play an important role in several industries, especially those with environmental concerns. Activated carbon fiber (ACF) is a carbonated fiber produced by using synthetic fibers as the base material. Although activated carbon fiber is not used as a structural reinforcement fiber, it uses the chemical properties of the carbon atom to provide a unique and effective filter material. Applications for activated carbon fiber are as varied as water filters in private homes to NBC (nuclear, chemical, and biological) suits used by the military (Chung, 1994).

In adsorption process for VOC (volatile organic compound) emission control, ACF is now being used as a promising adsorbent because of its attractive features. Feasible advantages are uniform pore sizes and dimensions, high electric conductivity, heat resistance and inflammability under 1000 °C, the flexible textile structure of the fiber, faster pore diffusion rates and better kinetics, higher adsorption amount than those of conventional granular activated carbon, lack of dust, and ease of handling (Chung, 1994; Takeuchi, 1991).

The present study has been performed to provide thermodynamic information in designing a solvent recovery process using ACF, as an adsorbent. In this paper, the adsorption equilibrium isotherms of three chlorinated hydrocarbons (dichloromethane, trichloroethylene, 1,1,1-trichloroethane) on commercially available ACF at (298, 323, and 348) K are presented. The Dubinin−Astakhov equation was used to correlate the experimental data.

Experimental Section

The activated carbon fiber (Toyobo type KF-1500), in felt type, was used as the adsorbent in this study. To characterize the sample, a BET experiment for adsorption and desorption of nitrogen was performed by a volumetric sorption analyzer (Micromeritics type ASAP-2000). From the nitrogen isotherms at 77 K, surface area and pore size distributions were calculated according to the BET theory and BJH method. The physical properties of the sample are listed in Table 1. Figure 1 shows the adsorption and desorption isotherms of nitrogen on KF-1500 at the normal boiling point of nitrogen and the desorption-pore distribution. As can be seen, the nitrogen isotherms show a negligible hysteresis between adsorption and desorption,

Table 1. Physical Properties of the Activated Carbon Fiber (KF-1500)

property	value
BET surface area, $m^2\ g^{-1}$	1530
micropore area, $m^2\ g^{-1}$	1110
micropore volume, $cm^3\ kg^{-1}$	620
average pore diameter, Å	17.1
solid density, $kg\ m^{-3}$	2300

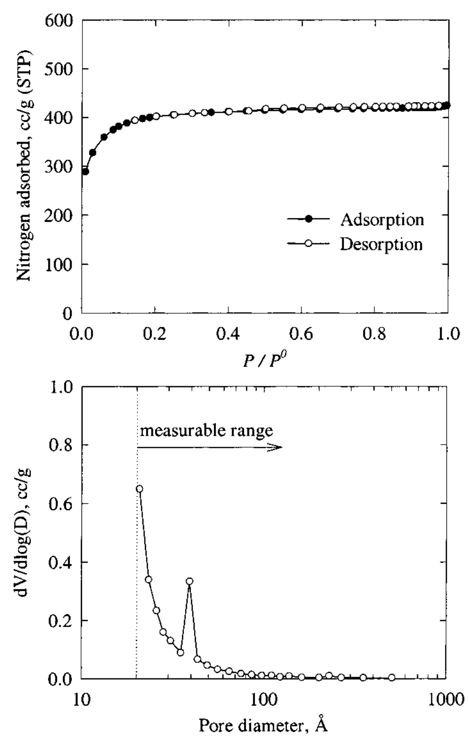

Figure 1. Equilibrium isotherms for nitrogen on activated carbon fiber at 77 K and BJH desorption pore size distribution.

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Table 2. Experimental Isotherm Data for Dichloromethane on Activated Carbon Fiber

298.15 K		323.15 K		348.15 K	
P/kPa	N/mmol g^{-1}	P/kPa	N/mmol g^{-1}	P/kPa	N/mmol g^{-1}
0.0229	0.411	0.0409	0.323	0.0615	0.232
0.0509	0.807	0.0493	0.373	0.0677	0.254
0.1195	1.449	0.1800	0.904	0.1655	0.448
0.2413	2.337	0.1923	0.950	0.1953	0.512
0.4039	3.017	0.2879	1.254	0.2947	0.639
0.5267	3.435	0.3773	1.449	0.3591	0.733
0.6701	3.852	0.4467	1.583	0.5204	0.894
0.9683	4.553	0.6125	1.871	0.6137	0.995
1.3453	5.221	0.6992	2.004	0.8415	1.185
1.9947	6.056	0.9671	2.378	1.0193	1.310
2.8733	6.842	0.9731	2.382	1.1507	1.409
5.2427	8.080	1.3139	2.785	1.6107	1.702
8.4133	8.916	1.5973	3.085	1.9080	1.860
10.348	9.245	1.9853	3.438	2.0867	1.963
13.163	9.678	2.6667	3.978	3.7440	2.707
18.893	10.02	3.4373	4.461	3.8067	2.724
		4.3413	4.952	5.9413	3.450
		5.6587	5.503	6.9413	3.738
		6.8840	5.941	9.3253	4.331
		8.9906	6.516	12.943	5.004
		9.2666	6.614	16.133	5.503
		12.300	7.271	20.507	6.043
		15.747	7.752	26.947	6.638
		18.480	8.222	33.533	7.123
		22.627	8.572	34.867	7.275
		24.640	8.818	44.720	7.841
		27.080	8.940		
		33.000	9.192		
		33.067	9.213		

and the shapes seem to be a Type I, which is a type representative of microporous solids. In addition, KF-1500 has a pore structure in which the micropore volume is very large, according to the BJH pore distribution report.

Before use, the sample was kept in a drying vacuum oven at 423 K for more than 24 h to remove impurities. The chlorinated hydrocarbons examined were dichloromethane (DCM), 1,1,1-trichloroethane (1,1,1-TCE), and trichloroethylene (TCE). The purity and the manufacturer of each adsorbate are as follows: dichloromethane, 99.0% (Junsei Chemical Co.); 1,1,1-trichloroethane, 99.0% (Aldrich Chemical Co.); trichloroethylene, 98.5% (Oriental Chemical Industry).

In this study, the isotherm measurements were performed using a static volumetric apparatus. In the method, the amount adsorbed at an equilibrium pressure can be determined by appropriate $P-V-T$ measurements. The mass of activated carbon fiber sample was determined with an accuracy of $\pm 10\ \mu$g and introduced into the adsorption cell. Prior to each measurement, the charged activated carbon fiber was regenerated at 473 K under high vacuum of 10^{-3} Pa for 12 h. Details of the equipment and the operating procedures used are described in the previous publication of Yun et al. (1998a).

Results and Discussion

The pure adsorption equilibrium data of three chlorinated hydrocarbons on activated carbon fiber were obtained. Measurements were done at (298.15, 323.15, and 348.15) K and pressures up to 40 kPa for DCM, 8 kPa for TCE, and 12 kPa for 1,1,1-TCE, respectively. The experimental equilibrium data are presented in Tables 2−4. Figure 2 shows the adsorption equilibrium isotherms of DCM, TCE, and 1,1,1-TCE on activated carbon fiber at 323 K. Apparently, the order of adsorption affinities for these hydrocarbons on activated carbon fiber is 1,1,1-TCE > TCE > DCM. For maximum adsorption capacities, however, the order is DCM > TCE > 1,1,1-TCE in the experimental range.

Table 3. Experimental Isotherm Data for Trichloroethylene on Activated Carbon Fiber

298.15 K		323.15 K		348.15 K	
P/kPa	N/mmol g^{-1}	P/kPa	N/mmol g^{-1}	P/kPa	N/mmol g^{-1}
0.0151	2.363	0.0141	1.301	0.0116	0.545
0.0368	3.377	0.0341	1.926	0.0308	0.937
0.0687	4.091	0.0767	2.635	0.0655	1.404
0.1303	4.822	0.1527	3.307	0.1345	1.938
0.2237	5.427	0.2441	3.798	0.2080	2.308
0.3727	5.949	0.4115	4.373	0.3653	2.842
0.5725	6.299	0.6811	4.934	0.5951	3.342
0.7283	6.376	0.9295	5.261	0.8351	3.705
0.9903	6.574	1.1677	5.529	1.2339	4.143
1.1293	6.616	1.2668	5.608	1.8080	4.573
1.5387	6.732	1.8680	5.989	2.5307	4.965
1.6160	6.741	1.9600	6.033	3.4400	5.322
1.8693	6.800	2.7307	6.293	4.2533	5.562
2.4053	6.938	3.2947	6.389	5.4747	5.869
2.4507	6.952	3.9480	6.528	6.9573	6.134
3.6707	7.162	4.6160	6.608	8.4733	6.315
		5.8693	6.806		

Table 4. Experimental Isotherm Data for 1,1,1-Trichloroethane on Activated Carbon Fiber

298.15 K		323.15 K		348.15 K	
P/kPa	N/mmol g^{-1}	P/kPa	N/mmol g^{-1}	P/kPa	N/mmol g^{-1}
0.0013	0.742	0.0037	0.477	0.0115	0.281
0.0023	0.969	0.0231	1.297	0.0369	0.631
0.0067	1.601	0.0659	2.010	0.1101	1.209
0.0120	2.027	0.1381	2.559	0.2424	1.701
0.0196	2.365	0.2503	3.121	0.4501	2.314
0.0343	2.873	0.4411	3.681	0.8479	2.901
0.0603	3.371	0.7099	4.105	1.4533	3.416
0.1024	3.821	1.2609	4.543	2.3280	3.973
0.2055	4.379	2.0520	4.895	3.7360	4.363
0.2301	4.452	3.4693	5.229	5.1053	4.609
0.3765	4.806	5.1187	5.409	7.4880	4.891
0.4055	4.872	5.1453	5.419	10.156	5.094
0.5760	5.111	6.9533	5.522	12.755	5.217
0.6177	5.138	7.7840	5.569		
1.0624	5.435	9.2560	5.611		
1.0652	5.457	10.439	5.665		
1.8920	5.636	11.995	5.695		
2.1667	5.694				
2.9640	5.749				
3.5507	5.818				
4.6653	5.859				
5.2853	5.919				
7.4773	6.009				
8.5773	6.017				
9.9573	6.104				
11.431	6.131				

For practical utility, adsorption equilibrium data should be correlated by a mathematical equation. It has been reported that the Dubinin−Astakhov equation is appropriate for interpreting adsorption by capillary condensation or pore filling (Stoeckli et al., 1982; Agarwal and Schwarz, 1988; Yun et al., 1998b).

$$W = W^\circ \exp\left[-\left(\frac{\epsilon}{\beta E^\circ}\right)^r\right], \quad W = NV^\circ \tag{1}$$

where W is the specific volume of adsorbate condensed in micropores at temperature T and relative pressure P/P° (P° is the equilibrium saturation vapor pressure at T), W° is the limiting specific volume of the adsorbed space, which equals the micropore volume, N is the moles adsorbed per unit mass of fiber at equilibrium, $\epsilon = \Delta G = RT \ln(P^\circ/P)$, β is the affinity coefficient, V° is the saturated liquid molar volume, and r and E° are the specific parameters of the

Table 5. Dubinin–Astakhov Parameters and Physical Properties of Dichloromethane, Trichloroethylene, and 1,1,1-Trichloroethane on Activated Carbon Fiber

	T/K	$W°$/cm^3 kg^{-1}	E/kJ mol^{-1}	r	β	$P°$/kPa	$V°$/cm^3 mol^{-1}	100D
DCM	298.15	662.8	10.97	2.064	0.692	56.56	62.12	0.69
	323.15	734.3	10.35	1.693	0.697	139.7	64.44	1.06
	348.15	878.7	9.212	1.417	0.703	298.6	67.10	1.44
TCE	298.15	618.5	15.37	2.606	0.976	9.235	87.59	0.59
	323.15	653.8	15.73	2.090	0.975	27.82	90.13	0.37
	348.15	674.0	15.68	2.009	0.974	69.01	92.96	0.72
1,1,1-TCE	298.15	606.4	17.62	2.264	1.118	16.28	100.3	0.60
	323.15	611.8	17.37	2.165	1.120	44.51	103.5	0.57
	348.15	617.1	16.63	2.320	1.122	102.9	107.1	0.90

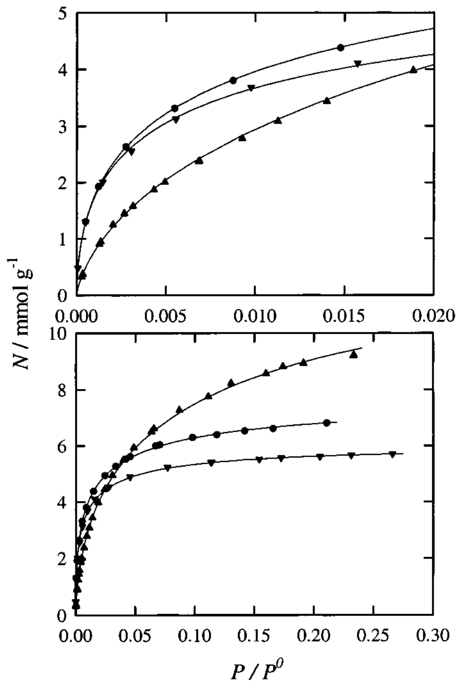

Figure 2. Adsorption isotherms for three chlorinated hydrocarbons on activated carbon fiber at 323 K: ▲, DCM; ●, TCE; ▼, 1,1,1-TCE; —, Dubinin–Astakhov equation.

system investigated. The definition of affinity coefficient can be found elsewhere (Noll et al., 1989; Yun et al., 1998a).

The parameters of the Dubinin–Astakhov equation were determined from the best fit of the experimental data, and they are summarized in Table 5 along with the average absolute deviation parameter D.

$$D = \frac{1}{k}\sum_{i=1}^{k}\left|\frac{N_i^{\text{obs}} - N_i^{\text{cal}}}{N_i^{\text{obs}}}\right|, \quad k = \text{number of data} \tag{2}$$

The solid lines in Figure 2 denote the calculated isotherms from the Dubinin–Astakhov equation. As can be seen, the Dubinin–Astakhov equation is in good agreement with the experimental data for all species.

In adsorption studies, the isosteric enthalpy of adsorption, which is a measure of the interactions between adsorbate molecules and adsorbent lattice atoms, may be used as an indicator of the degree of energetic heterogeneity of a surface. Furthermore, the limiting quantity of isosteric enthalpy can be regarded as a criterion of adsorption affinity. In this study, the isosteric enthalpies of adsorption were calculated by the Clausius–Clapeyron equation (Hill, 1949):

$$\frac{q_{\text{st}}}{RT^2} = \left[\frac{\partial \ln P}{\partial T}\right]_N \tag{3}$$

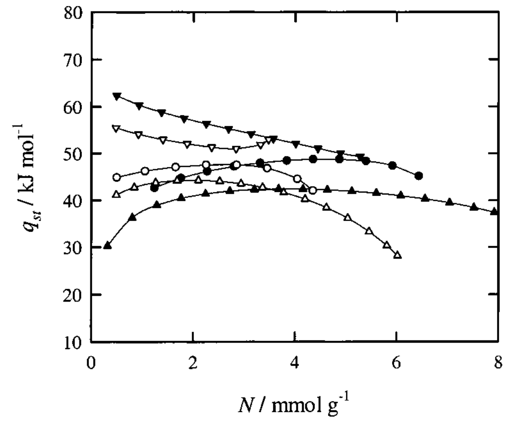

Figure 3. Isosteric heat data for three chlorinated hydrocarbons by activated carbon fiber (ACF, Toyobo KF-1500) and by activated carbon (AC, Calgon Xtrusorb-600): ▲, DCM-ACF; ●, TCE-ACF; ▼, 1,1,1-TCE-ACF; △, DCM-AC; ○, TCE-AC; ▽, 1,1,1-TCE-AC.

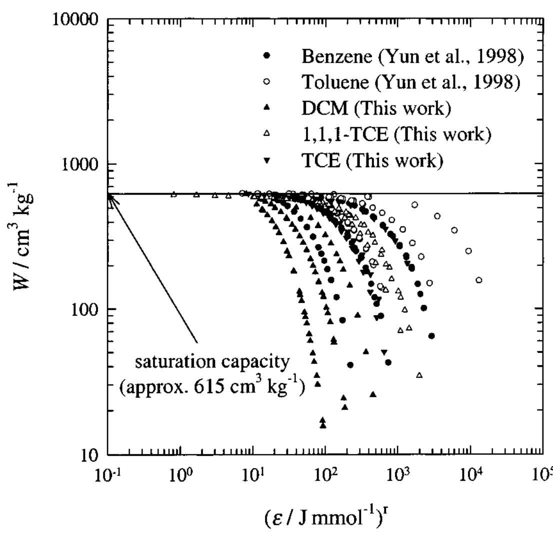

Figure 4. Dubinin–Astakhov plot for determining the saturation capacity of activated carbon fiber (KF-1500).

q_{st} in eq 3 is the differential enthalpy of vaporization, which is commonly called the isosteric enthalpy. The resulting isosteric enthalpy data for DCM, TCE, and 1,1,1-TCE on activated carbon fiber are plotted in Figure 3 along with the isosteric enthalpy data for the same adsorbates on activated carbon reported by Yun et al. (1998a). As shown in Figure 3, the isosteric enthalpy varied with the surface loading for all adsorbates, suggesting that the activated carbon fiber possesses an energetically heterogeneous surface. In addition, the activated carbon fiber (Figure 3, black icons) exhibits a similar order of adsorption affinity (1,1,1-TCE > TCE > DCM) to those of activated carbon (Figure 3, clear icons). However, the absolute values of the limiting quantities appear to differ from those of activated carbon and do not appear to follow a particular trend.

The correlation by the Dubinin−Astakhov equation has a great utility in that it can provide a determination of the total micropore volume of the adsorbent. In Figure 4, a useful plot is given to determine the effective saturation capacity of the activated carbon fiber. As can be seen, the effective saturation volume is approximately 615 $cm^3\ kg^{-1}$.

Conclusion

The adsorption equilibria for dichloromethane, trichloroethylene, and 1,1,1-trichloroethane at 298, 323, and 348 K were measured on a commercially available activated carbon fiber at pressures up to 40 kPa for dichloromethane, 8 kPa for trichloroethylene, and 12 kPa for 1,1,1-trichloroethane, respectively. The experimental equilibrium data were satisfactorily correlated using the Dubinin−Astakhov equation, which is a fundamental theoretical relation for describing the filling of micropores. The isosteric enthalpies of adsorption were evaluated, and the resulting curves imply that the activated carbon fiber used has an energetically heterogeneous surface. In addition, the Dubinin−Astakhov equation gives the determination of the total micropore volume of the activated carbon fiber.

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