Adsorption of Carbon Tetrachloride and Chloroform on Activated Carbon at (300.15, 310.15, 320.15, and 330.15) K

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The adsorption equilibria for carbon tetrachloride and chloroform vapors on activated carbon (Sorbonorit B4) were measured using a gravimetric method. The equilibrium data were obtained at (300.15, 310.15, 320.15, and 330.15) K with the pressure up to 7 kPa for carbon tetrachloride and 4.9 kPa for chloroform, respectively. The Toth and Dubinin-Astakov equations were successful in correlating the experimental isotherms. The Toth equation was used to determine thermodynamic properties such as the isosteric enthalpy of adsorption and Henry's constant. By using the Dubinin-Astakov isotherm equation, the total micropore volume of the adsorbent was determined

Introduction

VOCs (volatile organic compounds) have been used as dissolving and cleaning agents in many industrial processes such as printing, film coating, manufacturing of magnetic tapes and electronic chips, etc. The emission of vapors of the solvent from these industrial processes has not only caused severe air pollution but also great loss of valuable chemicals. One consequence of these manufacturing operations is that large amounts of organics are being emitted to the atmosphere each year. Accordingly, VOCs emission control is a major portion of environmental activities.

Carbon tetrachloride is used primarily as a chemical intermediate in the production of the refrigerants Freon 11 and 12. Also, it has been used as a general solvent in industrial degreasing operations and as an industrial solvent for cable and semiconductor manufacture. Chloroform is used in the production of dyes, pharmaceuticals, and pesticides. Most of the production of chloroform is used to produce fluorocarbon-22 which is used as a refrigerant and as an intermediate in the manufacture of tetrafluoroethene which then may be polymerized to give PTFE. They damage the liver and the kidneys, the central nervous system, and the heart. Therefore, the proper recovery of volatile solvent vapors from industries has multiple purposes such as the reduction of production cost, energy saving, and the environmental protection.[1,2]

Adsorption of VOCs from air has been studied for several decades. The adsorption method is an efficient and economic technology for recovering solvent vapors at low concentrations.[3] To design the adsorption facilities, thermodynamic data on adsorption equilibria is essential over a wide range of temperatures. However, there is a lack of information in previous studies concerning adsorption of carbon tetrachloride and chloroform on activated carbon at various temperatures. Hence, this study investigated the adsorption equilibrium of carbon tetrachloride and chloroform on activated carbon at (300.15, 310.15, 320.15, and 330.15) K.

Table 1. Physical Properties of Activated Carbons (Sorbonorit B4)

property	value
bulk density/kg · m^{-3}	430
pellet diameter/cm	0.37
Pellet length/cm	0.65
BET surface area/m^2 · g^{-1}	1170
micropore volume/cm^3 · kg^{-1}	450
mean pore size/Å	32.1

Experimental Section

Materials and Reagents. An activated carbon (Norit type Sorbonorit B4) was used as the adsorbent in this study. The physical properties of the activated carbon used are given in Table 1. Prior to use, the samples were kept in a drying vaccum oven at 423 K for more than 24 h to remove impurities. The adsorbates investigated were carbon tetrachloride and chloroform. The purity and manufacturer of each adsorbate are as follows: carbon tetrachloride, 99.5% (Junsei Chemical Co.); chloroform, 99.0% (Junsei Chemical Co.). All chemicals were used as received without further treatment.

Gravimetric Apparatus. The experimental apparatus made up of glass is shown in Figure 1. The solvent vapor was generated in a small chamber that was maintained at a constant temperature. The adsorbed amount of solvent vapors was measured by a quartz spring balance, which was placed in a closed glass system. A given amount of carbon particles were placed on the dish, which was attached to the end of quartz spring. This system was vacuumed for 15 h at 10^{-3} Pa and 523.15 K to remove volatile impurities from the carbon particles. A turbomolecular pump (Edward type EXT70) in combination with a rotary vacuum pump (Edward model RV5) was used to evacuate the system. A Pirani and Penning vacuum gauges (Edwards Series 1000) were used for the measurement of vacuum. The pressure of the system was measured using a Baratron absolute pressure transducer (MKS instru-

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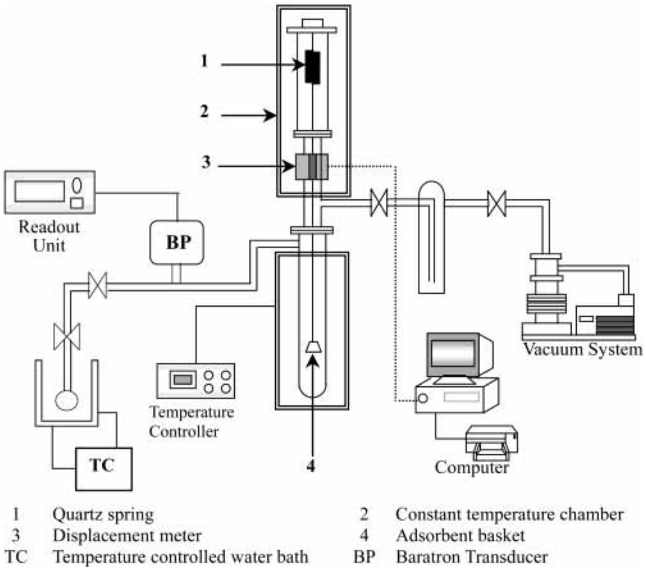

Figure 1. Schematic diagram of adsorption apparatus.

Table 2. Adsorption Isotherm Data for Carbon Tetrachloride on Sorbonorit B4

300.15 K		310.15 K		320.15 K		330.15 K	
P	*N*	*P*	*N*	*P*	*N*	*P*	*N*
kPa	mol·kg^{-1}	kPa	mol·kg^{-1}	kPa	mol·kg^{-1}	kPa	mol·kg^{-1}
0.015	0.399	0.011	0.218	0.012	0.127	0.020	0.188
0.047	0.915	0.033	0.532	0.025	0.323	0.051	0.544
0.071	1.257	0.052	0.790	0.045	0.627	0.093	0.990
0.132	1.936	0.082	1.155	0.075	0.992	0.155	1.469
0.241	2.673	0.111	1.515	0.121	1.464	0.290	2.026
0.373	3.030	0.152	1.903	0.252	2.165	0.498	2.421
0.581	3.347	0.370	2.751	0.445	2.578	1.132	2.845
1.182	3.695	0.605	3.052	0.843	2.918	2.409	3.179
2.729	3.957	1.110	3.344	1.548	3.196	3.469	3.335
4.404	4.060	1.999	3.580	2.479	3.381	4.969	3.463
5.748	4.110	2.979	3.721	3.499	3.530	5.968	3.530
6.643	4.148	4.189	3.807	4.669	3.611	6.968	3.553
		5.069	3.881	5.679	3.668		
		6.168	3.921	6.838	3.706		
		7.008	3.943				

ments type 127) and a power supply read out instrument (Type PDR−C-1C). The variation of mass was measured by a digital voltmeter that was connected to the spring sensor. The adsorption equilibrium was usually attained within 30−60 min. Equilibrium experiments were carried out at four temperatures of (300.15, 310.15, 320.15, and 330.15) K, respectively.

Results and Discussion

The adsorption equilibrium data of two chlorinated solvent vapors on activated carbon were obtained at (300.15, 310.15, 320.15, and 330.15) K with pressures up to 7 kPa for carbon tetrachloride and 4.9 kPa for chloroform. The adsorption isotherms obtained for carbon tetrachloride and chloroform on Sorbonorit B4 were found to be of Type I according to the IUPAC classification.[4] The experimental equilibrium data are presented in Tables 2 and 3. Figures 2 and 3 showed the adsorption equilibrium isotherms of carbon tetrachloride and chloroform on activated carbon at various temperatures.

The different models have been used to correlate experimental equilibrium data of carbon tetrachloride and chloroform on activated carbon. In this study, two kinds of adsorption equilibrium models were used.

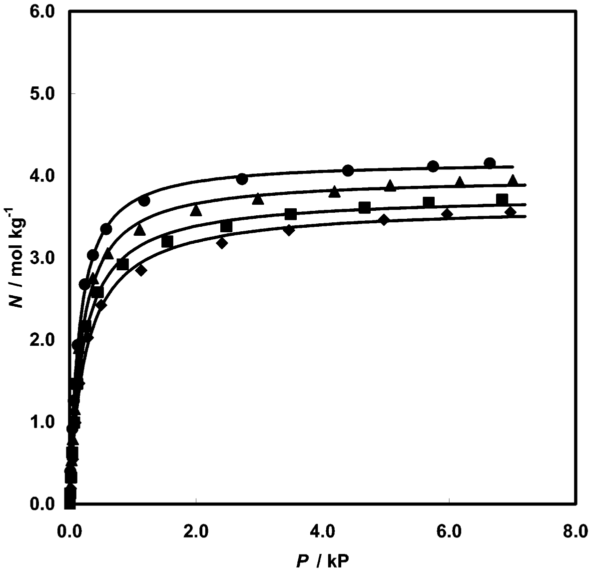

Figure 2. Adsorption equilibrium isotherm of carbontetrachloride on Sorbonorit B4 at various temperatures: (●, 300.15 K; ▲, 310.15 K; ■, 320.15 K; ◆, 330.15 K; −, Toth equation).

Table 3. Adsorption Isotherm Data for Chloroform on Sorbonorit B4

300.15 K		310.15 K		320.15 K		330.15 K	
P	*N*	*P*	*N*	*P*	*N*	*P*	*N*
kPa	mol·kg^{-1}	kPa	mol·kg^{-1}	kPa	mol·kg^{-1}	kPa	mol·kg^{-1}
0.024	0.404	0.011	0.152	0.011	0.093	0.019	0.127
0.043	0.686	0.025	0.297	0.021	0.184	0.038	0.342
0.080	1.117	0.043	0.498	0.052	0.502	0.071	0.632
0.121	1.520	0.060	0.739	0.102	1.003	0.112	1.012
0.193	2.265	0.082	0.923	0.171	1.511	0.129	1.143
0.240	2.506	0.104	1.138	0.229	1.757	0.181	1.385
0.295	2.742	0.121	1.352	0.341	2.181	0.241	1.599
0.352	3.012	0.168	1.773	0.429	2.394	0.299	1.730
0.461	3.350	0.219	2.057	0.515	2.629	0.392	2.055
0.618	3.634	0.292	2.395	0.704	2.933	0.488	2.253
0.682	3.697	0.349	2.623	0.955	3.175	0.672	2.500
0.829	3.869	0.432	2.879	1.235	3.430	0.951	2.900
1.072	4.070	0.499	3.121	2.299	3.900	1.241	3.128
1.334	4.217	0.701	3.390	3.449	4.149	1.944	3.508
2.519	4.558	0.848	3.522	4.509	4.292	2.679	3.722
3.914	4.730	1.080	3.729	5.788	4.409	3.399	3.888
5.414	4.847	1.398	3.923			4.439	4.012
		1.899	4.137			5.448	4.116
		2.629	4.330			6.958	4.275
		3.669	4.489				
		4.559	4.579				
		5.658	4.655				

Because of its simplicity in form and its correct behavior at low and high pressures, the Toth equation is popularly used for heterogeneous adsorbents such as activated carbon.[5]

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

where P is the equilibrium pressure and N is the moles adsorbed. m, b, and t are the parameters. When the parameter t is unity, the Toth equation reduces to the Langmuir equation. Therefore, the parameter t depends on the lateral interaction and the heterogeneity of the systems.

In general, the thermodynamic consistency test of the isotherm equation used is very important. Although the Toth equation is an empirical equation, it has the Henry

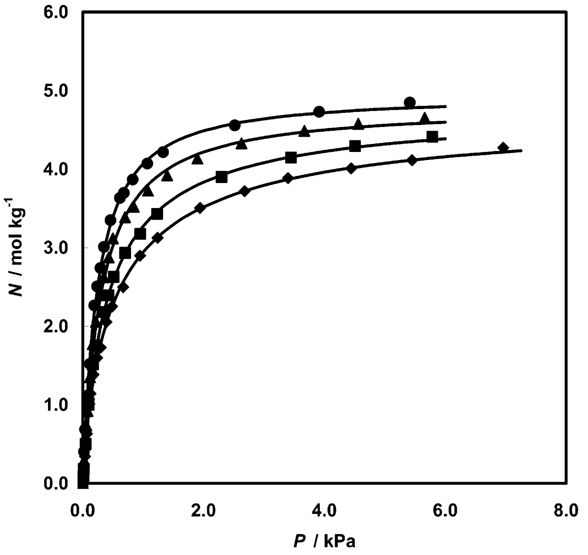

Figure 3. Adsorption equilibrium isotherm of chloroform on Sorbonorit B4 at various temperatures: (●, 300.15 K; ▲, 310.15 K; ■, 320.15 K; ◆, 330.15 K; −, Toth equation).

Table 4. Toth Equation Parameters for Carbon Tetrachloride and Chloroform

adsorbate	T K	m mol·kg^{-1}	b kPa	t	SOR
carbon tetrachloride	300.15	4.1716	0.1445	1.0815	0.0102
	310.15	3.9734	0.1816	1.0322	0.0273
	320.15	3.7658	0.2099	0.9611	0.0327
	330.15	3.6509	0.2532	0.9391	0.0275
chloroform	300.15	4.9454	0.2394	1.0952	0.0192
	310.15	4.7973	0.3028	1.0567	0.0328
	320.15	4.8153	0.3979	0.8667	0.0152
	330.15	4.8010	0.4512	0.7605	0.0203

constant at low pressures and approaches the saturation limit at high pressures.[5,6]

$$H = \lim_{P\to 0}\frac{N}{P} = \lim_{P\to 0}\frac{dN}{dP} = \frac{m}{b^{1/t}} \tag{2}$$

$$\lim_{P\to\infty} N = m \tag{3}$$

The Dubinin-Astakov (DA) equation applied so far works reasonably well in describing adsorption equilibria of many vapors and gases such as organic vapors onto microporous activated carbon. DA adsorption equation can be described using the following form:[7,8]

$$W = W_0 \exp\left[-\left(\frac{\epsilon}{\beta E^0}\right)^r\right],\quad W = NV^0,\quad \epsilon = RT\ln\left(\frac{P^*}{P}\right) \tag{4}$$

where W is the adsorbate condensed in micropores at temperature T and relative pressure P^*/P, W^0 is the total volume of the microporous system, β is the affinity coefficient (where $\beta = 1$ for the reference vapor), $E°$ is the characteristic adsorption energy for a reference vapor, r describes the surface heterogeneity, ϵ is the adsorption potential, N is the moles adsorbed at equilibrium, and V^0 is the liquid molar volume. In this study, carbon tetrachloride was chosen as the reference vapor because it has a polarity similar to that of chloroform. The liquid molar volume was calculated using the modified Rackett equation. [9]

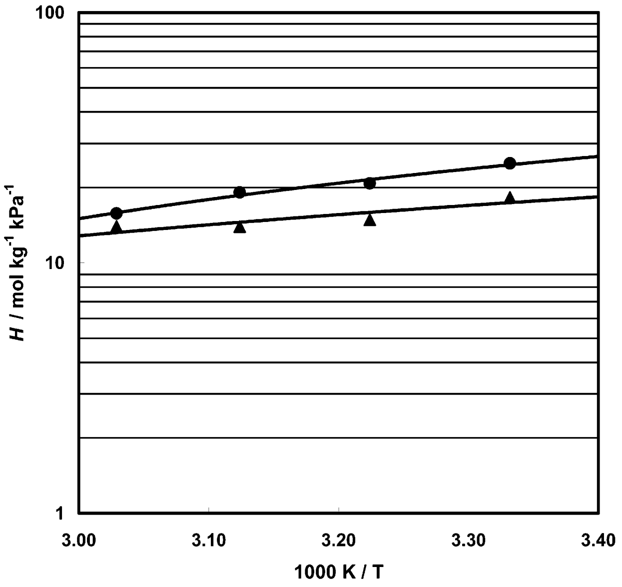

Figure 4. Henry's constant of adsorption for various temperatures: ●, carbontetrachloride; ▲, chloroform.

The isotherm parameters for each adsorption were determined using a pattern search algorithm namely "Nelder-Mead simplex method".[10] The comparison of fit of data by the models was based on the square of residuals (SOR), defined as follows:

$$SOR = \frac{1}{2}\sum (N_{\text{exp}} - N_{\text{cal}})^2 \tag{5}$$

where N_{cal} and N_{exp} are the calculated and experimental amounts adsorbed, respectively. The SOR is an absolute value, the magnitude of which is dependent on the accuracy of fit as well as the number of experimental data. The parameters of the Toth and DA equations as well as SOR are listed in Tables 4 and 5.

It is valuable to evaluate the Henry's constant because it has been used as a criterion of the adsorption affinity. By using the Toth isotherm equation, the Henry's constants were calculated and plotted in Figure 4. Although the calculated Henry's constants were extrapolations based on the isotherm used, this procedure could be used to discuss the adsorption affinity. As shown in Figure 4, the adsorp-

Table 5. Dubinin−Astakov Parameters for Carbon Tetrachloride and Chloroform

adsorbate	T K	W^0 cm^3 · mol^{-1}	E kJ · mol^{-1}	r	β	V^0 cm^3 · mol^{-1}	SOR
carbon tetrachloride	300.15	399.692	13.167	3.496	1.000	97.342	0.0216
	310.15	383.603	14.216	3.623	1.000	98.496	0.0298
	320.15	365.939	15.475	3.691	1.000	99.699	0.0224
	330.15	358.648	16.419	3.779	1.000	100.954	0.0187
chloroform	300.15	400.744	13.328	3.603	0.8449	82.242	0.0241
	310.15	393.195	14.283	3.661	0.8455	83.280	0.0244
	320.15	390.550	15.052	3.332	0.8462	84.365	0.0051
	330.15	390.448	15.929	3.144	0.8469	85.501	0.0120

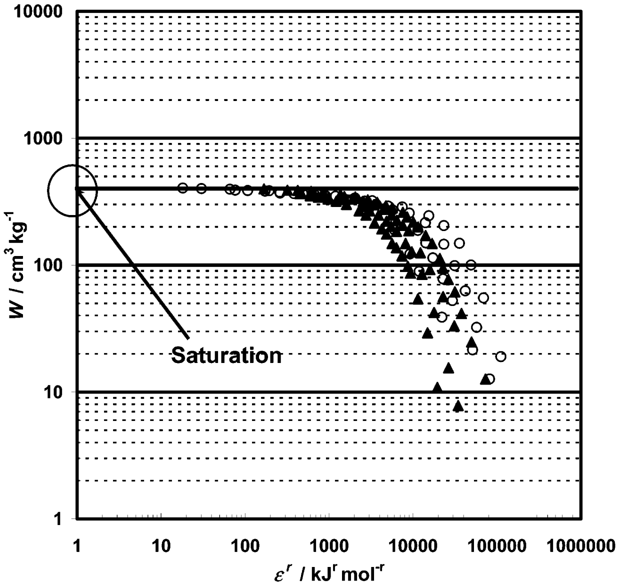

Figure 5. Dubinin–Astakov plot for determing the saturation capacity of Sorbonorit B4: ○, carbontetrachloride; ▲, chloroform.

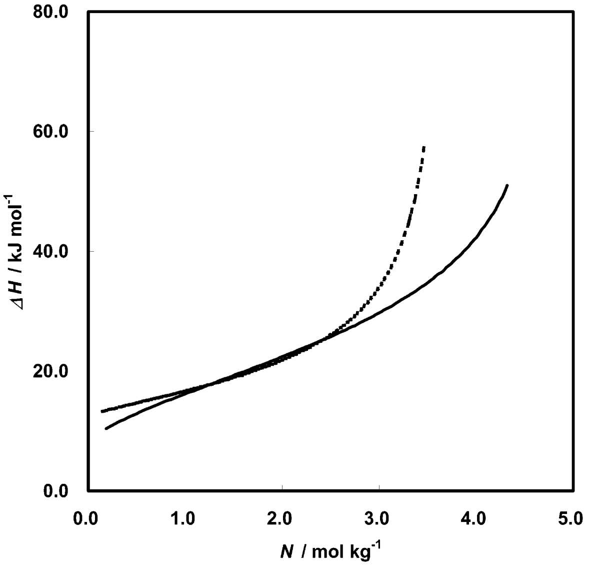

Figure 6. Isosteric enthalpy of adsorption with respect to surface loading: ..., carbontetrachloride; –, chloroform.

tion affinity of carbon tetrachloride is higher than that of chloroform, and this result is identical with the order of the isosteric enthalpy values at zero coverage for each adsorbate.

By the DA equation, the total micropore volume of adsorbent, W^0, was determined. Figure 5 indicates the effective saturation capacity of the activated carbon. The effective saturation volume was approximately 385 cm^3/kg. It was noted that the value found using the DA equation is comparable in the case of using BET equation.[6]

In general, when an adsorbent adsorbs one or more adsorbates, the adsorption heat is usually generated because all adsorption processes are exothermic. Eventually, the heat evolved affects the adsorption performance considerably. If the adsorption system were very ideal which follows the Langmuir isotherm, the heat of adsorption would be independent of the amount adsorbed. However, it would not be true for most adsorption processes because adsorbents have energetically heterogeneous surfaces.

As a useful thermodynamic property, the isosteric enthalpy of adsorption has been generally applied to characterize the adsorbent surface. The isosteric enthalpy of adsorption is evaluated simply by applying the Clausius–Clapeyron equation if one has a good set of adsorption equilibrium data obtained at several temperatures:[4,11]

$$\frac{q_{\mathrm{st}}}{RT^2} = \left[\frac{\partial \ln P}{\partial T}\right]_N \tag{6}$$

where q_{st} is the isosteric enthalpy of adsorption, R is the gas constant, and N is the moles adsorbed. In Figure 6, the isosteric enthalpies of adsorption for two vapors studied are plotted as a function of the moles adsorbed. Because of the joint effects of the energetic nonuniformity of the adsorbent surface and the interaction of adsorbate molecules in the adsorbed film itself, the heat of adsorption in general varies significantly with the amount adsorbed. Figure 6 shows that the isosteric enthalpy curves vary with the surface loading for each adsorbate. This result implies that the activated carbon used has energetically heterogeneous surfaces.

Conclusion

The adsorption equilibrium data were obtained for pure vapors at (300.15, 310.15, 320.15, and 330.15) K with pressures up to 7 kPa for carbon tetrachloride and 4.9 kPa for chloroform, respectively. In the analysis, the Toth equation was used to determine Henry's constants and the Clasius–Clapeyron equation to determine the isosteric enthalpy of adsorption. By calculating the Henry's constant, it was found that the adsorption affinity of carbon tetrachloride is carbon tetrachloride higher than that of chloroform. In this study, the Dubinin–Astakov equation was useful to estimate the total micropore volume of the activated carbon from the experimental results. The values of isosteric enthalpy of adsorption vary with surface coverage, and this result implies that the activated carbon used has energetically heterogeneous surfaces.

Acknowledgment

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