Adsorption Isotherms of Benzene and Methylbenzene Vapors on Activated Carbon

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The adsorption isotherms of benzene and methylbenzene vapors on activated carbon were obtained by a static volumetric apparatus. The measurements were done at 303.15, 313.15, 323.15, 333.15, and 343.15 K and pressures up to 7 kPa for benzene and 2 kPa for methylbenzene, respectively. The experimental data obtained were correlated by the UNILAN equation, which is generally used for heterogeneous adsorbents such as activated carbon.

Introduction

In recent years, the adsorption process of removing and recovering organic solvents in trace levels from air has attracted special interest as a means of protecting the environment from air pollution. As useful solvents, benzene and methylbenzene have been widely used in chemical plants including those that make or use inks, paints, and adhesives. However, it has been reported that benzene derivatives that leaked out during operation are harmful to the environment and human health (Macek, 1991; Ruhl, 1993). With its high surface area, activated carbon has been widely used as an adsorbent for such applications (Macek, 1991; Ruddy and Carroll, 1993; Ruhl, 1993). In order to design the adsorption facilities, thermodynamic data on the adsorption equilibria must be known over a broad range of temperature (Yang, 1987). However, there appears to be relatively little information in the literature concerning adsorption of benzene and methylbenzene on activated carbon at various temperatures. In this paper, we report the adsorption equilibrium data of benzene and methylbenzene on activated carbon at (303.15, 313.15, 323.15, 333.15, and 343.15) K.

Experimental Section

Materials. The activated carbon (Norit type Sorbonorit B4) was employed as an adsorbent in this study. Samples were crushed into 20–30 mesh, which originally consisted of cylindrical particles, 0.37 cm in diameter and 0.65 cm in length. The specific surface area was measured by an automatic volumetric sorption analyzer (Quantachrome, Autosorb-1) using nitrogen adsorption at 77 K.

The measured and supplied properties of activated carbon used are tabulated in Table 1. The benzene and methylbenzene were obtained from J. T. Baker, and the purity of these materials was 99.99%.

Apparatus and Procedure. The adsorption apparatus is based on the static volumetric method, and a schematic diagram of apparatus is shown in Figure 1. In the method, the total quantity of vapor admitted to the system and the amount of vapor in the gas phase at equilibrium are determined by appropriate P-V-T measurements. The system pressure measurements are made by a baratron absolute pressure transducer (MKS type 690A13TRA) with a high-accuracy signal conditioner (MKS type 270D). Its pressure range is from 0 to 133.33 kPa, and its reading accuracy is 0.05%, within the usable measurement range.

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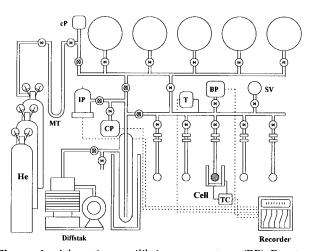


Figure 1. Adsorption equilibrium apparatus: (BP) Baratron transducer; (CP) convectron gauge; (cP) compound gauge; (IP) ion gauge; (MT) moisture trap; (SV) standard volume; (T) thermocouple; (TC) temperature controller.

 Table 1. Physical Properties of Activated Carbon

 (Sorbonorit B4)

property	value	
bulk density, kg m ⁻³	429	
pellet diameter, cm	0.37	
pellet length, cm	0.65	
specific surface area, m ² /g pore distribution, %	826	
micropore (<1 nm)	45.16	
transition pore $(1-100 \text{ nm})$	9.68	
macropore (>100 nm)	45.16	

During the adsorption, the adsorption cell was placed in a water bath and the temperature was maintained constant within ± 0.02 K by the refrigerating circulator (Haake type F3).

To eliminate any trace of pollutants, the activated carbon is kept in a drying oven of 423 K for 24 h. Its mass was determined with an accuracy of $\pm 10 \ \mu$ g, and it was introduced into the adsorption cell. Prior to each isotherm measurement, the charged activated carbon was regenerated at 473 K under a high vacuum for 12 h. An oil diffusion pump and a mechanical vacuum pump in combination (Edward type Diffstak 63/150M) provided a vacuum down to 10^{-3} Pa, and the evacuation was monitored by both an ion gauge and a convectron gauge with a vacuum gauge controller (Granville-Phillips type 307). The volume of the adsorption cell is determined by expansion of helium gas at the experimental temperature.

Table 2.	Adsorption	Isotherm	Data	for	Benzene	on
Activate	d Carbon					

 Table 3. Adsorption Isotherm Data for Methylbenzene

 on Activated Carbon

clivated Carbon					
<i>P</i> /kPa	$N/mol \ kg^{-1}$	P/kPa	Nmol kg ⁻¹		
303.15 K					
0.0345	3.323	0.8804	4.388		
0.0403	3.355	1.3320	4.526		
0.0845	3.482	2.0679	4.654		
0.1696	3.671	2.9266	4.758		
0.3141	3.986	4.1119	4.869		
0.5560	4.210	5.6119	4.977		
	313.	15 K			
0.0264	2.934	0.4209	3.699		
0.0293	2.975	0.7414	3.957		
0.0393	3.030	1.3432	4.220		
0.0577	3.088	2.0159	4.381		
0.0793	3.146	2.7453	4.489		
0.1067	3.228	3.8119	4.595		
0.1593	3.339	5.1799	4.708		
0.2495	3.490	6.7505	4.812		
	323.	15 K			
0.0360	2.776	0.5337	3.538		
0.0696	2.879	1.0746	3.864		
0.1101	2.980	1.8186	4.110		
0.1537	3.071	3.0399	4.340		
0.2015	3.158	5.2919	4.550		
0.2915	3.291	7.1012	4.675		
	333.	15 K			
0.0689	2.550	0.5020	3.166		
0.0865	2.591	0.9128	3.455		
0.1080	2.636	1.9426	3.845		
0.1352	2.690	3.4786	4.135		
0.1819	2.775	5.5639	4.352		
0.2805	2.919	6.7025	4.435		
	343.	15 K			
0.0859	2.294	0.5348	2.883		
0.1040	2.332	0.8720	3.115		
0.1233	2.373	1.3030	3.313		
0.1608	2.437	2.5519	3.659		
0.2067	2.510	4.0092	3.888		
0.2856	2.620	5.4505	4.050		
0.3908	2.745	6.8398	4.154		

The operating procedure for the adsorption isotherm determination is to admit the vapor into the manifold, to measure its temperature and pressure, to expand the vapor into the adsorption cell, and finally to record the equilibrium temperature and pressure. During the procedure, all of temperatures and pressures were recorded automatically. The time for reaching equilibria changes from 30 to 240 min depending on the temperature, pressure, and adsorbate. It takes a longer time when the temperature is lower, the pressure is higher, and the molecular weight is higher. The knowledge of the pressure, temperature, and gaseous volume before and after each step of adsorption gives the moles of gas before and after adsorption and, by difference, the moles adsorbed. In this study, the virial gas equation of state was employed for the calculation of gaseous moles (Reid et al., 1988).

Results and Discussion

Equilibrium Data. Adsorption isotherms for benzene and methylbenzene on activated carbon at (303, 313, 323, 333, and 343) K are obtained at pressures up to 7 kPa for benzene and 2 kPa for methylbenzene, respectively. The experimental equilibrium data are presented in Tables 2 and 3. The adsorption isotherms for benzene and methylbenzene on activated carbon at 303 and 343 K are shown in Figures 2 and 3. The adsorption capacity, defined as the amount of plateau of the isotherm, is higher for benzene compared with methylbenzene. At low pressure, however, the amount adsorbed is higher for methylbenzene compared with benzene, implying that the affinity of adsorption is higher for methylbenzene compared with benzene.

Activated Carbon				
<i>P</i> /kPa	<i>N</i> /mol kg⁻	-1 <i>P</i> /kPa	<i>N</i> ∕mol kg ^{−1}	
		303.15 K		
0.0296	3.387	0.5413	3.846	
0.0671	3.492	0.8133	3.913	
0.1180	3.588	1.0754	3.972	
0.1861	3.670	1.3440	4.025	
0.3160	3.755	1.6226	4.074	
		313.15 K		
0.0463	3.352	0.3973	3.681	
0.0945	3.435	0.5408	3.743	
0.1493	3.502	0.7978	3.825	
0.2109	3.562	1.1230	3.903	
0.2873	3.619	1.6253	3.982	
		323.15 K		
0.0816	3.264	0.5120	3.614	
0.1009	3.297	0.6511	3.666	
0.1495	3.359	0.8605	3.726	
0.2063	3.419	1.1318	3.786	
0.3017	3.497	1.4626	3.846	
0.3980	3.557	1.8706	3.904	
0.0000	01001		01001	
0.0357	2.966	333.15 K 0.3076	3.335	
0.0524	3.004	0.3078	3.432	
0.0324	3.004	0.6816	3.549	
0.0780	3.113	1.0364	3.663	
0.1523	3.113	1.4013	3.740	
0.2120	3.244	1.4013	3.810	
0.2120	0.211	343.15 K	0.010	
0.0241	2.695	0.3337	3.126	
0.0241	2.095	0.3337	3.238	
0.0435	2.804	0.6730	3.337	
0.1019	2.858	0.9453	3.440	
0.1573	2.838	1.4346	3.562	
0.2356	3.034	1.9040	3.643	
0.2000	0.001	1.0010	0.010	
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-1 Moles Adsorbed / mol kg				
Σ	1		-	

P / kPa

4.5

7.5

6.0

Figure 2. Adsorption isotherms for benzene on activated carbon at 303 and 343 K: ●, 303 K; ▲, 343 K; −, Unilan equation.

3.0

0

0.0

1.5

Correlation. The correlation of the experimental data allows one to obtain physical parameters of a model over a wide range of pressures and temperatures. In this regard, the correlation of the results using either a theoretical or empirical equation is essential to practical adsorption operation (Yun *et al.*, 1996). In the present study, the UNILAN equation, which is based on a uniform distribution of energies of adsorption with the Langmuir equation for the local isotherm, was employed to describe the experimental data (Valenzuela *et al.*, 1989)

$$N = \frac{m}{2\sigma} \ln \left[\frac{c + P e^{+\sigma}}{c + P e^{-\sigma}} \right]$$
(1)

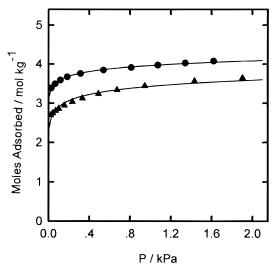


Figure 3. Adsorption isotherms for methylbenzene on activated carbon at 303 and 343 K: ●, 303 K; ▲ 343 K; –, Unilan equation.

Table 4. UNILAN Equation Parameters for Benzene and Methylbenzene

adsorbate	<i>T</i> /K	<i>m</i> /mol kg ⁻¹	c∕kPa	σ	100 <i>D</i>
benzene	303.15	9.997	5.923	14.72	0.991
	313.15	9.617	7.591	13.68	1.840
	323.15	9.512	10.11	12.33	2.026
	333.15	9.316	12.76	10.86	1.991
	343.15	8.929	16.05	10.16	2.106
methylbenzene	303.15	8.337	3.319	24.35	0.347
·	313.15	8.156	3.222	22.47	0.497
	323.15	7.928	2.697	19.19	0.286
	333.15	7.666	2.417	17.15	0.950
	343.15	7.256	2.388	15.88	1.583

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

The correlation by the UNILAN equation has two aims (Valenzuela et al., 1989). The first one is that the UNILAN equation is for heterogeneous adsorbents such as activated carbon, contains only three parameters, and gives analytical expressions for the amount adsorbed. Secondly, this model reduces to Henry's law at pressures approaching zero; thus, it provides a good fit for adsorption data at low pressure

$$H = \lim_{P \to 0} \frac{N}{P} = \lim_{P \to 0} \frac{\mathrm{d}N}{\mathrm{d}P} = \frac{m}{c} \frac{\sinh(\sigma)}{\sigma}$$
(2)

where *H* is Henry's constant.

The parameters of the UNILAN equation obtained for all systems, together with the average deviation parameter, D, are tabulated in Table 4.

$$\delta D = \frac{1}{k_{i=1}^{k}} \left| \frac{N_i^{\text{obs}} - N_i^{\text{cal}}}{N_i^{\text{obs}}} \right|, \quad k = \text{number of data} \quad (3)$$

Conclusion

The adsorption equilibria for benzene and methylbenzene at (303, 313, 323, 333, and 343) K were measured on activated carbon at pressures up to 7 kPa for benzene and 2 kPa for methylbenzene, respectively. The maximum adsorption capacity of benzene on activated carbon is higher than that of methylbenzene. The adsorption equilibria were correlated by the UNILAN equation, which is generally used for heterogeneous adsorbents such as activated carbon.

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