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Adsorption Equilibria of Toluene and Gasoline Vapors on Activated Carbon

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The adsorption equilibria of toluene and gasoline vapors on activated carbon were measured by a static volumetric method. The equilibrium experiments were conducted at (298.15, 318.15, 338.15, 358.15, and 378.15) K and pressures up to 3.1 kPa for toluene and 8.0 kPa for gasoline. The experimental data obtained were correlated by the UNILAN and Sips models, which are generally used for microporous adsorbents such as activated carbon. The Henry constant was calculated to characterize interactions between adsorptive and adsorbent.

Introduction

Volatile organic compounds (VOCs) are the most common air pollutants emitted from chemical, petrochemical, and allied industries. Increasing environmental awareness has led to stringent regulations to control VOCs emissions. The amount of VOCs emitted from gasoline storage and distribution facilities was over 1.5% of the gasoline used in Korea. As a result, the recovery of VOCs emitted from gasoline storage and distillation facilities has attracted special interest as a means of protecting the environment from pollution and for using energy resources efficiently. An adsorption process is one of the most effective methods for the recovery of emitted VOCs.[1,2]

The design of adsorption facilities requires primarily knowledge of thermodynamic data on the adsorption equilibria.[3] For practical applications, the adsorption equilibria must be known over a broad range of operation temperatures. The information is used to calculate the operation time of a specific concentration level and to derive the optimum size of adsorbers and operating conditions.[4] However, little information is available in the literature concerning the adsorption of gasoline vapor on activated carbon at various temperatures even though various adsorption processes for the recovery of emitted VOCs from gasoline had been commercialized. Because each type of coals presents different adsorption forces, it is necessary to measure the adsorption isotherm for various adsorbate−adsorbent couples. The adsorption of toluene on various activated carbons has been measured by a few authors.[5−7]

In this study, adsorption equilibrium data for toluene and gasoline on activated carbon at (298.15, 318.15, 338.15, 358.15, and 378.15) K are reported. The experimental data obtained are correlated with existing adsorption isotherms such as the UNILAN and Sips models.

Experimental Section

Materials. Bituminous-based activated carbon (BPL 4 × 10) in granular type was supplied from Calgon Carbon Co., USA. The samples were crushed into 12−30 meshes. The BET surface area, micropore volume, and pore diameter of the adsorbent were measured with an automatic volumetric sorption analyzer (Micromeritics, ASAP-2010) using nitrogen adsorption at 77 K. The measured and supplied physical properties of the activated carbon are listed in Table 1.

Table 1. Physical Properties of Activated Carbon (BPL) and Gasoline

property	value
Activated Carbon	
bulk density/kg·m^{-3}	480
real density by He displacement/kg·m^{-3}	2100
BET surface area/m^2·g^{-1}	993
micropore area/m^2·g^{-1}	956
micropore volume/cm^3·g^{-1}	0.414
BJH desortion average pore diameter/nm	1.40
average pore diameter by BET/nm	2.00
Gasoline[8]	
vapor pressure at 37.8 °C/kPa	70
octane number	92.5
specific gravity at 15 °C	0.7208
distillation experiment	
distillation start point T/°C	32.4
10% distilled T/°C	51.5
50% distilled T/°C	83.3
90% distilled T/°C	149.4
distillation end point T/°C	182.1
residues/(vol %)	1.0
content of aromatics/(vol %)	18.07
content of benzene/(vol %)	0.43
content of olefin/(vol %)	17.71
content of oxygen/(mass %)	1.6
content of phosphate/g·L^{-1}	0.0001
content of lead/g·L^{-1}	0.001
content of sulfur/(mass ppm)	42.1

The toluene was obtained from Yakuri Pure Chemicals Co. (Osaka, Japan), and its purity was over 99.5%. The gasoline used in this study was a commercial sample obtained from a gas station in Korea, and its detailed chemical properties are listed in Table 1. Because this commercial gasoline contains many chemical components, the gasoline vaporized at 298 K was assumed to be a pseudopure component in this study.

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Table 2. Adsorption Isotherm Data for Toluene on Activated Carbon

P/kPa	q/mol·kg^{-1}	P/kPa	q/mol·kg^{-1}
	298.15 K		
0.01	0.695	1.87	2.835
0.03	1.361	2.17	2.915
0.16	1.885	2.54	2.946
0.52	2.394	2.84	2.976
1.02	2.625	3.15	3.002
1.50	2.731		
	318.15 K		
0.01	0.399	1.99	2.282
0.05	1.046	2.31	2.307
0.25	1.688	2.58	2.333
0.80	2.021	2.87	2.363
1.35	2.162	3.38	2.380
1.65	2.260		
	338.15 K		
0.03	0.504	1.44	1.719
0.13	0.951	1.75	1.765
0.37	1.240	2.04	1.819
0.65	1.443	2.34	1.854
0.97	1.583	2.64	1.894
1.25	1.642	3.01	1.915
	358.15 K		
0.03	0.467	1.62	1.453
0.22	0.838	1.92	1.536
0.47	1.060	2.30	1.583
0.72	1.174	2.57	1.624
0.96	1.273	2.84	1.641
1.28	1.369	3.09	1.656
	378.15 K		
0.07	0.434	1.59	1.218
0.37	0.743	1.90	1.281
0.67	0.904	2.26	1.346
0.92	0.998	2.57	1.366
1.16	1.105	2.94	1.398
1.35	1.157		

Apparatus and Procedure. The adsorption experiments were based on the static volumetric method. In the method, the total quantity of vapor admitted into the system, as well as the amount of vapor in the gas phase under adsorption equilibrium, were determined by appropriate $P-V-T$ measurements. The system pressure was measured by an absolute pressure transducer (Balzers AG, CMR261) with a vacuum measurement and control unit (Balzers AG, TPG251A). The transducer has a measurable pressure range of (0.01 to 110) kPa and a 0.0015% resolution at full scale and a ±0.1% accuracy of the measured value. During adsorption, the temperatures of the adsorption cell and manifold were kept constant by two temperature controllers (Eurotherm type 2408). The adsorption cell temperature was measured by RTD (Pt 100Ω) within ±0.05 K.

To eliminate any trace of pollutants, the activated carbon was kept in a drying oven at 423 K for more than 24 h. Its mass was determined with an accuracy of ±100 μg, and the activated carbon was introduced into the adsorption cell. Prior to each isotherm measurement, the charged activated carbon in the adsorption cell was regenerated at 453 K under a high vacuum for more than 12 h. A mechanical vacuum pump (Edwards High Vacuum International, Sussex, U.K., RV 5) provided the vacuum, and the evacuation was monitored with a pressure indicator. The volumes of the manifold and adsorption cell in the adsorption system were determined by expansion of helium gas at the experimental temperature. Details of the equipment and the operating procedures used are described in the previous work by Ryu et al.[8]

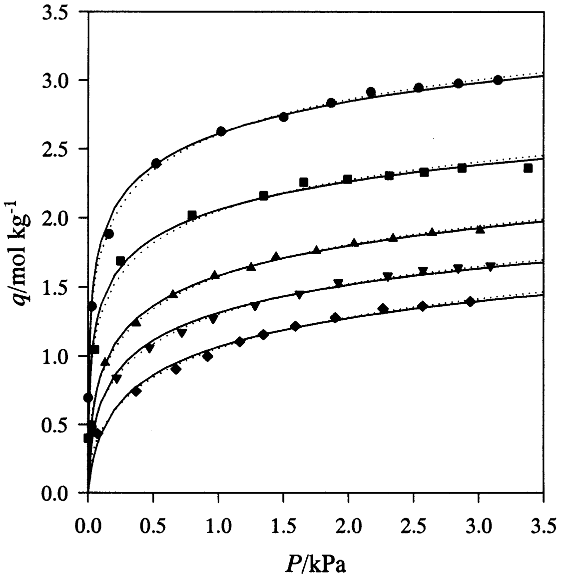

Figure 1. Experimental and correlated isotherms for toluene adsorption onto activated carbon at various temperatures: ●, 298.15 K; ■, 318.15 K; ▲, 338.15 K; ▼, 358.15 K; ◆, 378.15 K; —, UNILAN equation; ···, Sips equation.

Table 3. Adsorption Isotherm Data for Gasoline on Activated Carbon

P/kPa	q/mol·kg^{-1}	P/kPa	q/mol·kg^{-1}
	298.15 K		
0.28	1.015	4.53	1.835
0.66	1.281	5.45	1.902
1.47	1.529	6.88	1.993
2.53	1.673	8.07	2.079
3.56	1.746		
	318.15 K		
0.29	0.671	4.84	1.740
1.00	1.165	5.85	1.840
1.73	1.371	6.75	1.897
2.57	1.496	7.92	1.973
3.58	1.633		
	338.15 K		
0.31	0.522	4.42	1.592
0.75	0.861	5.45	1.681
1.35	1.096	6.84	1.807
2.38	1.316	8.46	1.909
3.60	1.473		
	358.15 K		
0.37	0.440	4.50	1.381
0.87	0.745	5.62	1.484
1.53	0.919	6.81	1.585
2.47	1.100	8.10	1.705
3.54	1.259		
	378.15 K		
0.31	0.322	4.64	1.261
0.94	0.619	5.72	1.331
1.67	0.806	6.80	1.401
2.59	0.999	7.86	1.515
3.63	1.145		

Results and Discussion

Adsorption isotherms for toluene and gasoline on activated carbon were obtained at (298.15, 318.15, 338.15, 358.15, and 378.15) K and pressures up to 3.1 kPa for toluene and 8.0 kPa for gasoline. The experimental equilibrium data are presented in Tables 2 and 3. The adsorption isotherms for toluene and gasoline on activated carbon at various temperatures are shown in Figures 1 and 2, respectively. As shown, both isotherms of toluene and gasoline on the activated carbon are type-I adsorption

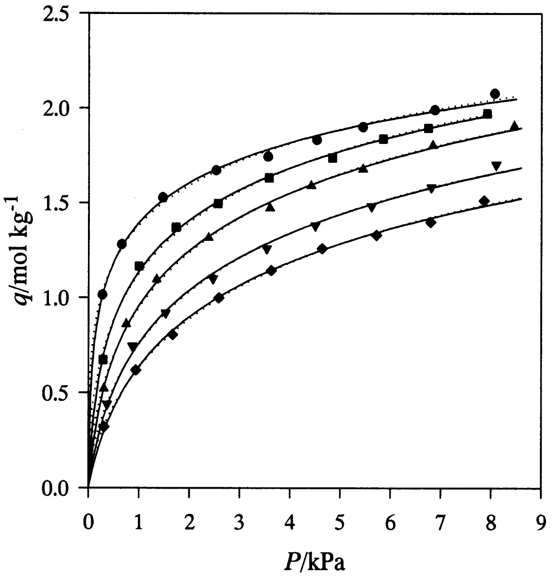

Figure 2. Experimental and correlated isotherms for gasoline adsorption onto activated carbon at various temperatures: ●, 298.15 K; ■, 318.15 K; ▲, 338.15 K; ▼, 358.15 K; ◆, 378.15 K; —, UNILAN equation; ···, Sips equation.

isotherms (Brunauer classification) in the experimental range studied. As shown in the figures, the adsorption amount of toluene is larger than that of gasoline vapor at the same experimental conditions. This implies that the adsorption affinity of gasoline vapor vaporized at 298.15 K is lower than that of toluene. Also, it is assumed that the average molecular weight of the main components in the gasoline vapor is less than that of toluene. However, the adsorption amount of toluene on the activated carbon approached the saturation amount within the experimental pressure range while that of gasoline continuously increased with an increase in pressure.

The UNILAN and Sips models were used to correlate the experimental adsorption data for toluene and gasoline.

UNILAN Equation. The UNILAN equation is an empirical relation obtained by assuming a patchwise topography on the surface, with each patch being ideal such that the local Langmuir isotherm is applicable on each patch.[9,10] The following UNILAN equation is also frequently used to correlate the adsorption equilibrium data of many solids, such as activated carbon and zeolites:[9]

$$q = \frac{q_s}{2s}\ln\left[\frac{c + Pe^{+s}}{c + Pe^{-s}}\right] \qquad (1)$$

where P is the adsorption pressure; q is the number of adsorbed moles; and q_s, c, and s are isotherm parameters that are determined numerically. In this study, a nonlinear curve-fitting procedure was used to determine q_s, c, and s. The parameters obtained from the best fit to experimental data are summarized in Table 4, with the average percent deviations Δq calculated according to

$$\Delta q/\% = \frac{100}{k}\sum_{j=1}^{k}\left|\frac{q_j^{\mathrm{exp}} - q_j^{\mathrm{cal}}}{q_j^{\mathrm{exp}}}\right| \qquad (2)$$

where k is the number of data points at a given temperature and q^{exp} and q^{cal} are the experimental and calculated numbers of adsorbed moles, respectively. The solid lines in Figures 1 and 2 denote the adsorption isotherms calculated according to the UNILAN equation. The experimental data were well fitted by the calculated isotherm. The UNILAN equation provided a better fit for gasoline consisting of multiple components than that for toluene.

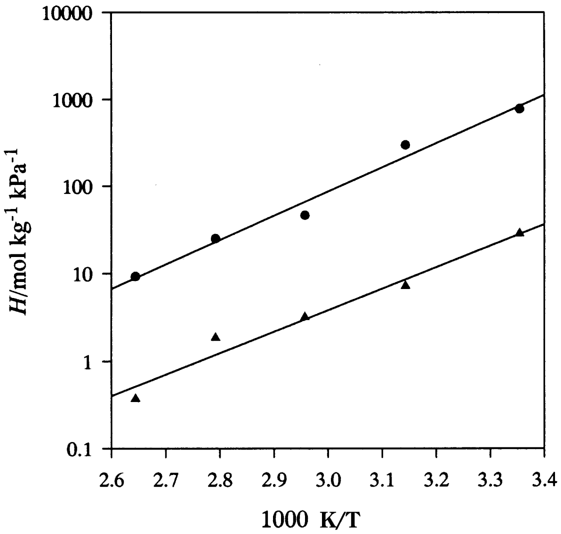

Figure 3. Henry's constant of adsorption for various temperatures: ●, toluene; ▲, gasoline.

Table 4. UNILAN Equation Parameters for Toluene (1) + Gasoline (2)

adsorbate	T/K	q_s/mol·kg^{-1}	c/kPa	s	Δq/%
toluene	298.15	4.896	0.6149	7.262	2.87
	318.15	3.901	0.6923	6.546	3.64
	338.15	3.402	1.451	5.356	0.89
	358.15	3.017	1.930	5.100	3.65
	378.15	2.687	2.482	4.302	3.33
gasoline	298.15	4.919	32.25	8.012	0.98
	318.15	4.733	21.54	5.975	1.10
	338.15	4.502	18.68	4.860	1.16
	358.15	4.021	17.29	4.220	1.99
	378.15	3.560	15.13	3.768	1.75

The UNILAN equation reduces to Henry's law at pressures approaching zero. Thus, it provides a good fit for adsorption data at low pressure[4,10]

$$H = \lim_{P\to 0}\frac{q}{P} = \lim_{P\to 0}\frac{\mathrm{d}q}{\mathrm{d}P} = \frac{m}{c}\,\frac{\sinh(s)}{s} \qquad (3)$$

where H is the Henry's constant. The Henry's constant has been used as a criterion of the adsorption affinity. By using eq 3, the Henry's constants were calculated and plotted in Figure 3. The adsorption affinity of toluene was higher than that of gasoline. It should be noted that these values are extrapolations based on the UNILAN equation.

Sips Equation. Recognizing the problem of the continuing increase in the adsorbed amount with an increase in pressure (concentration) in the Freundlich equation, Sips proposed an equation similar in form to the Freundlich equation, but it has a finite limit when the pressure is sufficiently high.[9] In form, this equation resembles that of the Langmuir equation, as follows

$$q = \frac{q_s b P^{1/n}}{1 + bP^{1/n}} \qquad (4)$$

where q_s, b, and n are isotherm parameters. The parameters and average percent deviations calculated are summarized in Table 5. The dotted lines in Figures 1 and 3 denote the isotherms calculated according to the Sips

Table 5. Sips Equation Parameters for Toluene (1) + Gasoline (2)

adsorbate	T/K	q_s/mol·kg^{-1}	b/kPa	n	Δq/%
toluene	298.15	4.732	1.225	3.148	0.72
	318.15	3.837	1.147	2.877	3.17
	338.15	3.212	0.9620	2.366	1.36
	358.15	2.835	0.8513	2.222	1.78
	378.15	2.617	0.6757	1.967	1.93
gasoline	298.15	4.177	0.4945	3.142	1.25
	318.15	3.422	0.4892	2.030	1.73
	338.15	3.072	0.4444	1.664	1.83
	358.15	2.783	0.3711	1.511	1.79
	378.15	2.682	0.3077	1.470	1.12

equation. The deviation in the Sips equation was slightly smaller for toluene than that in the UNILAN equation.

Conclusions

The adsorption equilibria for toluene and gasoline on activated carbon were measured at (298.15, 318.15, 338.15, 358.15, and 378.15) K and pressures up to 3.1 kPa for toluene and 8.0 kPa for gasoline. The experimental data were correlated with the UNILAN and Sips equations, which are generally used for activated carbon. The experimental equilibrium data for toluene and gasoline vapors on activated carbon were satisfactorily correlated with the UNILAN and Sips equations. According to the Henry's constants based on the UNILAN equation, the adsorption affinity of toluene was higher than that of gasoline.

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