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Adsorption Isotherms of Toluene and Gasoline Vapors on DAY Zeolite

Young-Ki Ryu,[†] Jay-Woo Chang,[‡] Sang-Yun Jung,[§] and Chang-Ha Lee*,[§]

Professional & Regulatory Service, ERD, Procter & Gamble Korea, Seoul 135-272, Korea,
SunKyung Engineering & Construction Limited, Seoul 110-300, Korea, and Department of Chemical Engineering, Yonsei University, Seoul 120-749, Korea

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The adsorption equilibria of toluene and gasoline vapors on DAY zeolite 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 2.5 kPa for toluene and 7.8 kPa for gasoline. The experimental data obtained were correlated by the Toth and UNILAN models, which are generally used for microporous adsorbents such as zeolite.

Introduction

In recent years, the recovery of volatile organic compounds (VOCs) emitted from gasoline storage or distillation facilities has attracted special interest as a means of protecting the environment from pollution and using energy resources efficiently. The amount of VOCs emitted from gasoline storage and distribution facilities was over 1.5% of the gasoline used in Korea. One of the most effective methods for the recovery of emitted VOCs is the adsorption process.[1−3]

Recently, interest has grown in the use of highly dealuminated Y zeolite (DAY) for adsorptive waste gas purification and the recovery of organic solvents.[4] Because of its known hydrophobic surface properties, this zeolite is successfully being substituted for activated carbon, which has been conventionally used for solvent recovery. Moreover, another attractive feature of DAY is that adsorbent ignition is inherently prevented because zeolites are nonflammable. In addition, its low water uptake reduces the energy required for treating high-humidity gas streams and allows the recovery of VOCs with low water contents.[4]

The design of adsorption facilities requires primarily knowledge of thermodynamic data on the adsorption equilibria over a broad range of temperatures.[5] However, relatively little information is available in the literature concerning the adsorption of toluene and gasoline on DAY zeolite at various temperatures. In this study, adsorption equilibrium data for toluene and gasoline on DAY zeolite 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 Toth and UNILAN models.

Experimental Section

Materials. Dealuminated Y (DAY) zeolite (DAY-20F, silicon-to-aluminum ratio = 20 to 1) was supplied in pellet type from Degussa AG, Hanau, Germany. 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 DAY zeolite are listed in Table 1. Prior to any measurements, the adsorbent was activated at 573 K for more than 12 h under dry vacuum conditions.

Table 1. Physical Properties of DAY Zeolite (DAY-20F)

property	value
bulk density (kg m^{-3})	500
solid density (kg m^{-3})	1550
BET surface area (m^2 g^{-1})	704
micropore area (m^2 g^{-1})	676
micropore volume (cm^3 g^{-1})	0.268
BJH desorption average pore diameter (nm)	1.40
average pore diameter by BET (nm)	2.17

Table 2. Properties of Gasoline

property	value
vapor pressure at 37.8 °C (kPa)	70
octane number	92.5
specific gravity at 15 °C	0.7208
distillation experiment	
distillation start point (°C)	32.4
10% distilled (°C)	51.5
50% distilled (°C)	83.3
90% distilled (°C)	149.4
distillation end point (°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)	0.0001
content of lead (g/L)	0.001
content of sulfur (mass ppm)	42.1

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 chemical properties are listed in Table 2. Because this commercial gasoline contains many chemical components, the gasoline vaporized at 298 K was assumed to be a pseudo-pure component in this study.

Apparatus and Procedure. The adsorption experiments were based on the static volumetric method, and a

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* To whom correspondence should be addressed. Tel.: +82-2-2123-2762. Fax: +82-2-2123-6401. E-mail: leech@yonsei.ac.kr.

[†] Procter & Gamble Korea.

[‡] SunKyung Engineering & Construction Limited.

[§] Yonsei University.

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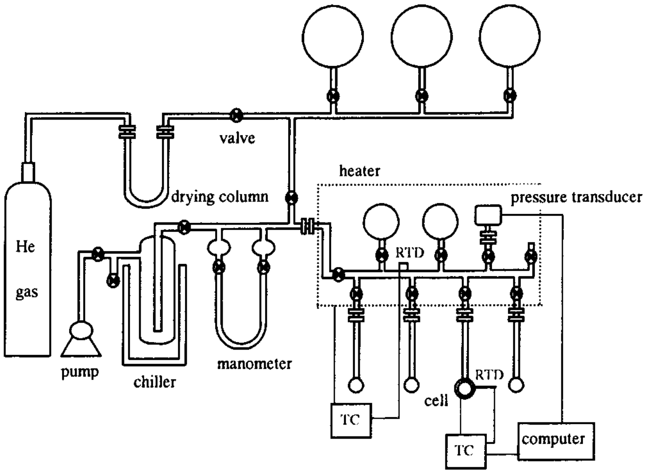

Figure 1. Adsorption equilibrium apparatus.

schematic diagram of the apparatus is shown in Figure 1. 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 0.01−110 kPa, and a 0.0015% resolution at full scale and a ±0.1% accuracy of measured value. During adsorption, the temperature of the adsorption cell and manifold were kept constant by two temperature controllers (Eurotherm type 2408). The adsorption cell temperature was measured by a RTD (Pt 100Ω) within ±0.05 K.

Prior to each isotherm measurement, the charged DAY zeolite in the adsorption cell was regenerated at 573 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. The total volumes of the manifold and adsorption cell were 209.8 and 38.5 cm^3, respectively. Before the experiment, the adsorption system was flushed with helium gas three times and evacuated with a vacuum pump. Then, the desired amount of vapor was supplied to the manifold controlled by a valve. When the adsorption cell reached the desired temperature, the vapor was admitted into the adsorption cell. During the experiment, the temperatures and pressures were recorded automatically on a computer. By using the pressure, temperature, and gaseous volume before and after each adsorption step, the number of moles adsorbed could be calculated. In this study, the ideal gas law was used for the calculation of the number of moles of gas.

Table 3. Adsorption Isotherm Data for Toluene on DAY Zeolite

P (kPa)	q (mol kg^{-1})	P (kPa)	q (mol kg^{-1})
298.15 K			
0.03	0.823	1.22	1.476
0.12	1.156	1.58	1.524
0.34	1.304	1.99	1.593
0.60	1.387	2.25	1.662
0.91	1.430		
318.15 K			
0.09	0.688	1.07	1.207
0.12	0.846	1.41	1.249
0.24	1.014	1.73	1.308
0.47	1.101	2.16	1.363
0.75	1.153	2.49	1.407
338.15 K			
0.20	0.352	1.24	0.943
0.37	0.558	1.69	1.027
0.54	0.741	2.22	1.060
0.86	0.876	2.56	1.088
358.15 K			
0.28	0.201	1.32	0.603
0.50	0.303	1.72	0.644
0.74	0.402	2.15	0.713
1.00	0.524	2.54	0.771
378.15 K			
0.16	0.051	1.34	0.278
0.37	0.106	1.69	0.318
0.75	0.171	2.04	0.368
1.04	0.228	2.46	0.390

Table 4. Adsorption Isotherm Data for Gasoline on DAY Zeolite

P (kPa)	q (mol kg^{-1})	P (kPa)	q (mol kg^{-1})
298.15 K			
0.21	0.734	4.10	1.201
0.81	0.966	5.09	1.256
1.71	1.045	6.21	1.327
2.95	1.135	7.59	1.372
318.15 K			
0.36	0.376	3.93	0.971
0.72	0.580	5.08	1.016
1.50	0.784	6.25	1.047
2.48	0.880	7.19	1.077
338.15 K			
0.43	0.209	3.59	0.763
0.93	0.338	5.06	0.856
1.72	0.491	6.42	0.911
2.53	0.616	7.80	0.963
358.15 K			
0.33	0.071	3.92	0.547
0.94	0.171	5.20	0.640
1.74	0.287	6.47	0.727
2.83	0.409	7.82	0.802
378.15 K			
0.25	0.030	3.85	0.345
0.78	0.091	5.20	0.444
1.61	0.172	6.34	0.534
2.69	0.252	7.72	0.633

Results and Discussion

Adsorption isotherms for toluene and gasoline on DAY zeolite were obtained at (298.15, 318.15, 338.15, 358.15, and 378.15) K and pressures up to 2.5 kPa for toluene and 7.8 kPa for gasoline. The experimental equilibrium data are presented in Tables 3 and 4. The adsorption isotherms for toluene and gasoline on DAY zeolite at the various temperatures are displayed in Figures 2 and 3, respectively. As shown, the adsorption amount of gasoline vapor is smaller than that of toluene for 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. Moreover, the adsorption isotherm of gasoline vapor showed a nearly linear increase over 1−2 kPa at all temperatures, whereas that of toluene approached saturation at the lower temperatures.

The experimental equilibrium data are presented in Tables 3 and 4. The Toth and UNILAN models were used to correlate the experimental adsorption data for toluene and gasoline.

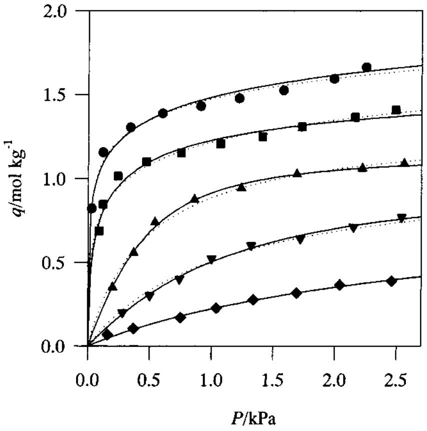

Figure 2. Experimental and correlated isotherms for toluene adsorption onto DAY zeolite at various temperatures. ●, 298 K; ■, 318 K; ▲, 338 K; ▼, 358 K; ◆, 378 K; —, Toth equation; ···, UNILAN equation.

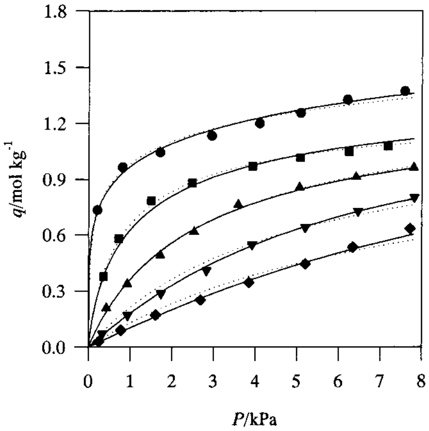

Figure 3. Experimental and correlated isotherms for gasoline adsorption onto DAY zeolite at various temperatures. ●, 298 K; ■, 318 K; ▲, 338 K; ▼, 358 K; ◆, 378 K; —, Toth equation; ···, UNILAN equation.

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

adsorbate	T (K)	q_s (mol kg^{-1})	b (kPa)	t	Δq (%)
toluene	298.15	2.452	0.1235	0.2301	0.34
	318.15	1.796	0.1595	0.3890	3.16
	338.15	1.139	0.4117	1.581	1.47
	358.15	0.9879	1.445	1.333	2.87
	378.15	0.9259	2.644	0.8925	3.08
gasoline	298.15	3.509	0.2133	0.1508	2.08
	318.15	1.493	0.7163	0.6246	2.72
	338.15	1.347	2.237	0.8966	2.87
	358.15	1.313	9.767	1.201	2.72
	378.15	1.291	29.80	1.360	5.43

Table 6. UNILAN Equation Parameters for Toluene (1) + Gasoline (2)

adsorbate	T (K)	q_s (mol kg^{-1})	c (kPa)	s	Δq (%)
toluene	298.15	2.483	0.2670	7.051	2.18
	318.15	2.197	0.5369	5.782	3.10
	338.15	1.302	0.4682	0.0150	3.36
	358.15	1.057	1.085	0.0078	4.70
	378.15	0.8532	2.838	0.3696	3.41
gasoline	298.15	2.377	3.282	6.907	2.24
	318.15	1.263	0.9147	1.524	1.84
	338.15	1.371	3.027	0.9790	2.80
	358.15	1.227	4.775	0.0019	8.08
	378.15	1.155	7.959	0.0003	10.69

Toth Isotherm. The Toth isotherm[6] is a semiempirical expression that effectively describes many systems with submonolayer coverage. Because of its simplicity in form and its correct behavior at low and high pressures, the Toth equation is recommended as the first choice of an isotherm equation for fitting the data of many adsorbates on activated carbon as well as zeolites.[7] It is a three-parameter model usually written in the form

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

where P is the equilibrium pressure; q is the number of adsorbed moles; and q_s, b, and t are isotherm parameters that are determined numerically. In this study, a nonlinear curve-fitting procedure was used to determine q_s, b, and t. The parameters obtained from the best fit to the experimental data are summarized in Table 5, with the average percent deviations Δq calculated according to

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

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 2 and 3 denote the adsorption isotherms calculated according to the Toth equation. The experimental data were well-fitted by the calculated isotherm. The Toth equation provided a better fit for toluene than for gasoline consisting of maultiple components. Because the t values were very different from unity, it can be concluded that the Langmuir model is not appropriate for the system.

UNILAN Equation. The UNILAN equation is another 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. The distribution of energy on the surface is assumed to be uniform.[7,8] The following UNILAN equation is also frequently used to correlate the adsorption equilibrium data of many solids, such as activated carbon and zeolites[7]

$$q = \frac{q_s}{2s}\ln\left[\frac{c + Pe^{+s}}{c + Pe^{-s}}\right] \tag{3}$$

where q_s, c, and s are isotherm parameters. The parameters and average percent deviations calculated by eqs 2 and 3 are summarized in Table 6. The dotted lines in Figures 2 and 3 denote the isotherms calculated according to the UNILAN equation. The deviation in the UNILAN equation was slightly larger than that in the Toth equation. In particular, the UNILAN equation was not appropriate for the correlation of the experimental gasoline adsorption data at high temperatures (358 and 378 K).

Conclusions

The adsorption equilibria for toluene and gasoline on DAY zeolite were measured at (298, 318, 338, 358, and 378) K and at pressures up to 2.5 kPa for toluene and 7.8 kPa for gasoline. The experimental data were correlated with the Toth and UNILAN equations, which are generally used for zeolite. The experimental equilibrium data for toluene and gasoline vapors on DAY zeolite were satisfactorily correlated with the Toth equation. However, the correlation of the adsorption equilibrium of gasoline vapor at high temperatures (358 and 378 K) by the UNILAN equation was not satisfactory.

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