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Adsorption Equilibria of Water Vapor on Activated Carbon and DAY Zeolite

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The adsorption equilibria of water vapor on activated carbon and DAY zeolite were measured by a static volumetric method. The equilibrium experiments were conducted at (293, 313, 333, 353, and 373) K and pressures up to 3.4 kPa for activated carbon and 1.9 kPa for DAY zeolite. According to the classification of isotherms, the experimental data are correlated by the Dubinin−Serpinsky and Sips models for activated carbon as well as the Toth, UNILAN, and Sips models for DAY zeolite.

Introduction

The adsorption of gases and vapors by microporous solids has attracted much attention because of its great practical importance in the fields of gas separation, gas purification, and environmental problems. Information concerning adsorption equilibria is used to calculate the operation time of a specific bulk concentration level and to derive the optimum size of adsorbers and operating conditions.[1]

An issue that has come under increasing scrutiny in recent years is the interaction between water vapor and adsorbents.[2,3] In addition, the adsorption of water vapor has been encountered in applications such as volatile organic compound (VOC) removal from humid air streams and the steam regeneration process.

To estimate practical or dynamic adsorption capacity, however, it is essential to have information on adsorption equilibrium. Furthermore, it is important to select the proper adsorbent for the design of an efficient adsorption process. The selection of a proper adsorbent for a given separation is a complicated problem. The predominant scientific basis for absorbents is the equilibrium isotherm,[1] and the thermodynamic data of adsorption equilibria must be known over a wide range of temperatures.

Recently, there is a growing interest in the use of highly dealuminated Y (DAY) zeolite for the purification of adsorptive waste gas 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]

In this study, adsorption equilibrium data for water vapor on activated carbon and DAY zeolite at (293, 313, 333, 353, and 373) K are reported. The experimental data obtained are correlated with existing adsorption isotherms such as the Dubinin−Serpinsky and Sips models for activated carbon and the Toth, UNILAN, and Sips models for DAY zeolite.

Table 1. Physical Properties of Activated Carbon (BPL) and DAY Zeolite (DAY-20F)[5,6]

property	activated carbon	DAY zeolite
bulk density/kg m^{-3}	480	500
BET surface area/m^2 g^{-1}	993	704
micropore area/m^2 g^{-1}	956	676
micropore volume/cm^3 g^{-1}	0.414	0.268
BJH desorption average pore diameter/nm	1.40	1.40
average pore diameter by BET/nm	2.00	2.17

Experimental Section

Materials. Dealuminated Y (DAY) zeolite (DAY-20F, silicon-to-aluminum ratio 20:1) in pellet type and bituminous-based activated carbon (BPL 4−10 mesh) in granular type were supplied from Degussa AG (Germany) and Calgon Carbon Co. (U.S.A.), respectively. Both adsorbent samples were crushed into 12−30 mesh. The BET surface areas, micropore volumes, and pore diameters of the adsorbents 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 and the activated carbon are listed in Table 1.

Apparatus and Procedure. The adsorption experiments were based on the static volumetric method, and a schematic diagram of the apparatus is shown in Figure 1. In the method, the total quantity of gas admitted into the system and the amount of gas in the vapor phase remaining after 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, a 0.0015% resolution at full scale, and a ±0.1% accuracy of measured value. To prevent the water vapor from turning into condensation during adsorption, the temperature of the adsorption cell and manifold were maintained constant by two temperature controllers (Eurotherm type 2408). In addition, the experiments were performed in the range lower than the saturated vapor

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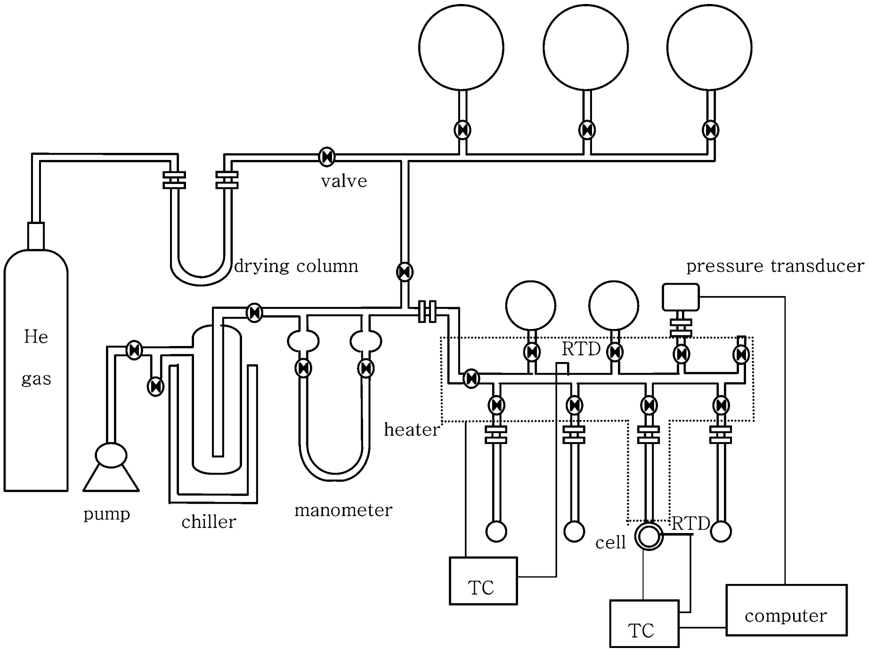

Figure 1. Adsorption equilibrium apparatus.

pressure of water at the experimental temperature, that is, $P/P_s < 0.8$. A resistance temperature detector (RTD, Pt 100Ω) was installed inside the adsorption cell, and the temperature was measured within ±0.05 K. The volumes of the manifold and adsorption cell in the adsorption system were determined by the expansion of helium gas at the experimental temperature. In this study, the horizontal manifold in Figure 1 was used as a loading cell. The total volumes of the manifold and adsorption cell were 209.8 and 38.5 cm^3, respectively. The volume of the adsorption cell included the volume of the valve connected to the adsorption cell.

To eliminate any trace of pollutants, the DAY zeolite and the activated carbon samples were kept in a drying oven at 573 K and 423 K, respectively, for more than 24 h. After the mass of adsorbent was determined by a microbalance with an accuracy of ±10 μg, the samples were introduced into the adsorption cell. Prior to each isotherm measurement, the adsorption system was flushed with helium gas three times and evacuated with a vacuum pump. The charged DAY zeolite and activated carbon samples were regenerated at 573 K and 423 K, respectively, 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. 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. Details of the equipment and the operating procedures used are described in the previous work.[5,6]

Results and Discussion

Adsorption isotherms for water vapor on activated carbon and DAY zeolite were obtained at (293, 313, 333, 353, and 373) K and pressures up to 3.4 kPa for activated carbon and 1.9 kPa for DAY zeolite. The adsorption isotherms for water vapor on activated carbon and DAY zeolite at various temperatures are shown in Figures 2 and 3, respectively, and the experimental data are presented in Tables 2 and 3.

Water is known to have an extremely low affinity toward the graphitic surface, and its adsorption mechanism is due to the quasi-chemisorption of water with some specific surface functional groups on the carbon surface.[7,8] Once water molecules adsorb onto the specific groups, they themselves act as secondary sites for further water adsorption through a hydrogen bonding mechanism. Due to the finiteness of the volume space within the carbon particle, the more water adsorption occurs, the lesser is the availability of these secondary sites.

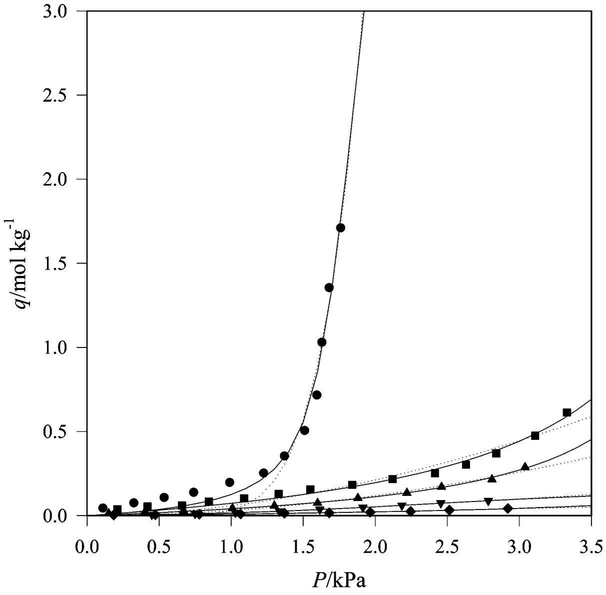

Figure 2. Experimental and correlated isotherms for water vapor adsorption onto activated carbon at various temperatures: ●, 293 K; ■, 313 K; ▲, 333 K; ▼, 353 K; ◆, 373 K; —, D−S equation; · · ·, Sips equation.

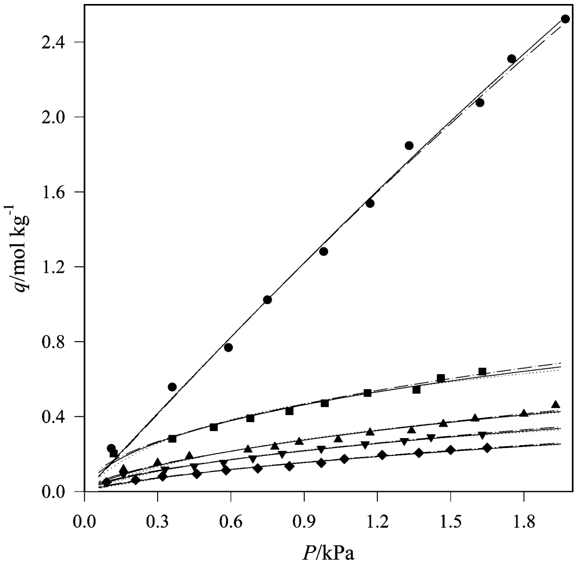

Figure 3. Experimental and correlated isotherms for water vapor adsorption onto DAY zeolite at various temperatures: ●, 293 K; ■, 313 K; ▲, 333 K; ▼, 353 K; ◆, 373 K; —, Toth equation; · · ·, UNILAN equation; - - -, Sips equation.

Table 2. Adsorption Isotherm Data for Water Vapor onto Activated Carbon

P/kPa	*q*/mol·kg^{-1}	*P*/kPa	*q*/mol·kg^{-1}
	293 K		
0.1100	0.0447	1.3700	0.3545
0.3250	0.0759	1.5100	0.5052
0.5350	0.1080	1.5950	0.7166
0.7400	0.1382	1.6300	1.0303
0.9900	0.1972	1.6800	1.3550
1.2250	0.2532	1.7600	1.7102
	313 K		
0.2100	0.0377	1.8400	0.1826
0.4200	0.0545	2.1200	0.2170
0.6600	0.0599	2.4150	0.2524
0.8450	0.0840	2.6300	0.3034
1.0900	0.1026	2.8400	0.3699
1.3300	0.1285	3.1100	0.4749
1.5500	0.1562	3.3300	0.6137
	333 K		
0.1500	0.0134	1.8800	0.1043
0.4000	0.0191	2.2200	0.1342
0.6700	0.0293	2.4600	0.1703
1.0100	0.0436	2.8100	0.2149
1.3000	0.0585	3.0400	0.2879
1.6000	0.0749		
	353 K		
0.1850	3.086×10^{-3}	1.6150	0.0367
0.4500	5.675×10^{-3}	1.9150	0.0485
0.7500	0.0108	2.1850	0.0609
1.0300	0.0179	2.4550	0.0746
1.3350	0.0261	2.7850	0.0886
	373 K		
0.1850	4.365×10^{-3}	1.6800	0.0163
0.4750	5.735×10^{-3}	1.9650	0.0209
0.7800	8.725×10^{-3}	2.2450	0.0248
1.0650	0.0105	2.5150	0.0324
1.3700	0.0139	2.9200	0.0421

Table 3. Adsorption Isotherm Data for Water Vapor onto DAY Zeolite

P/kPa	*q*/mol·kg^{-1}	*P*/kPa	*q*/mol·kg^{-1}
		293 K	
0.1100	0.2294	1.1700	1.5379
0.3600	0.5573	1.3300	1.8465
0.5900	0.7683	1.6200	2.0754
0.7500	1.0229	1.7500	2.3102
0.9800	1.2808	1.9700	2.5228
		313 K	
0.1200	0.2026	0.9850	0.4708
0.3600	0.2814	1.1600	0.5253
0.5300	0.3433	1.3600	0.5434
0.6800	0.3914	1.4600	0.6051
0.8400	0.4285	1.6300	0.6404
		333 K	
0.1600	0.1182	1.1700	0.3141
0.3000	0.1533	1.3400	0.3245
0.4300	0.1886	1.4700	0.3603
0.6700	0.2227	1.6000	0.3889
0.7800	0.2382	1.8000	0.4134
0.8800	0.2641	1.9300	0.4606
1.0400	0.2768		
		353 K	
0.1600	0.0928	0.9700	0.2285
0.3300	0.1176	1.1500	0.2522
0.4500	0.1356	1.3100	0.2711
0.5700	0.1541	1.4200	0.2905
0.6900	0.1776	1.6300	0.3046
0.8100	0.2025		
		373 K	
0.0900	0.0490	0.9700	0.1526
0.2100	0.0611	1.0650	0.1736
0.3200	0.0809	1.2200	0.1949
0.4600	0.0941	1.3700	0.2062
0.5800	0.1131	1.5000	0.2217
0.7100	0.1235	1.6500	0.2326
0.8400	0.1349		

Figure 2 shows that the isotherms of water vapor on the activated carbon are type-III isotherms at a temperature range of 293−333 K and linear isotherms at a temperature range of 353−373 K in viewpoint of the Brunauer classification. Since the experiments were performed in the range of low relative pressure, an inflection point of type-V isotherm in the activated carbon and water system was not observed in the experimental range.[1,2] It is noted that the adsorbed amount of water on the activated carbon is significantly decreased from 293 K to 313 K in comparison with other temperature differences. In Figures 2 and 3, such a significant decrease in the adsorption amount from 293 K to 313 K on both adsorbents stemmed from the change in the saturated pressure of water. Because an increase in temperature results in a steep increase in the saturated vapor pressure of water, the experimental range of relative pressure, P/P_0, decreases rapidly as the temperature of isotherm changes from 293 K to 373 K. The adsorption is unfavorable at low pressure because of the hydrophobic nature of the activated carbon. At sufficiently high pressures, the adsorption is due to the capillary condensation. Although activated carbon is an excellent adsorbent for organic vapors, it is not effective for the adsorption of hydrophilic molecules.[9,10] Therefore, the weak interaction of a water molecule with the graphitic surface is the reason the adsorption of water on the activated carbon exhibits an unfavorable-type isotherm at the low-pressure range.

The isotherms of water on the DAY zeolite exhibit a slightly favorable type-I isotherm in the experimental range studied, as shown in Figure 3. Like the water-vapor-activated carbon system, the adsorbed amount of water on the DAY zeolite is significantly decreased from 293 K to 313 K. In addition, the adsorbed amount of water on the DAY zeolite is higher than that on the activated carbon under the same conditions.

In this study, to correlate the experimental adsorption data of water vapor the Dubinin−Serpinsky (D−S) and Sips models were used for the activated carbon, and the Toth, UNILAN, and Sips models were used for the DAY

Table 4. Isotherm Parameters Estimated for Water Vapor onto Activated Carbon

		temperature/K				
		293	313	333	353	373
D−S	q_p/mol·kg^{-1}	0.0884	0.2917	0.1477	0.0742	0.0482
	r	1.381	1.482	4.295	9.483	16.03
	k/kg·mol^{-1}	4.819×10^{-2}	6.690×10^{-9}	1.316×10^{-10}	1.315×10^{-13}	2.809×10^{-7}
	Δq_1/%	30.89	18.45	11.90	10.24	15.32
	Δq_2/%	1.8839	0.4266	0.0793	0.0559	0.0328
Sips	q_m/mol·kg^{-1}	35.48	28.75	13.61	0.7521	0.6324
	b/kPa	9.066×10^{-4}	2.052×10^{-3}	2.271×10^{-3}	2.261×10^{-2}	1.410×10^{-2}
	n	0.1405	0.5396	0.5119	0.5761	0.6917
	Δq_1/%	49.38	29.09	26.28	11.29	20.75
	Δq_2/%	5.1762	1.0939	0.3456	0.0204	0.0595

Table 5. Isotherm Parameters Estimated for Water Vapor onto DAY Zeolite

		temperature/K				
		293	313	333	353	373
UNILAN	q_m/mol·kg^{-1}	56.88	3.987	3.482	2.599	2.477
	c/kPa	79.14	350.3	489.7	470.6	574.1
	s	2.159	7.557	7.031	7.104	6.753
	Δq_1/%	6.17	6.86	8.28	5.40	9.20
	Δq_2/%	0.3886	0.3148	0.2262	0.1049	0.1556
Toth	q_m/mol·kg^{-1}	13.27	11.59	10.62	8.974	8.342
	b/kPa	20.96	0.9370	1.426	1.421	1.963
	n	1.352	0.2086	0.2467	0.2415	0.2769
	Δq_1/%	6.30	5.14	6.26	4.09	7.40
	Δq_2/%	0.4058	0.1583	0.1292	0.0583	0.0970
Sips	q_m/mol·kg^{-1}	15.37	13.41	11.39	9.891	3.248
	b/kPa	0.0965	0.0374	0.0261	0.0238	0.0534
	n	0.9628	1.918	1.631	1.628	1.418
	Δq_1/%	6.66	4.24	5.29	3.55	6.46
	Δq_2/%	0.4526	0.1079	0.0947	0.0412	0.0730

zeolite. The mathematical forms of these models are as follows:[1,7,11]

Dubinin−Serpinsky

$$q = \frac{-\frac{1}{k}\left(\frac{1}{rP_r} + kq_p - 1\right) + \sqrt{\frac{1}{k^2}\left(\frac{1}{rP_r} + kq_p - 1\right)^2 + \frac{4q_p}{k}}}{2} \quad (1)$$

Sips

$$q = \frac{q_m b P^{1/n}}{1 + bP^{1/n}} \quad (2)$$

UNILAN

$$q = \frac{q_m}{2s} \ln\left[\frac{c + Pe^{+s}}{c + Pe^{-s}}\right] \quad (3)$$

Toth

$$q = \frac{q_m P}{(b + P^n)^{1/n}} \quad (4)$$

where q is the amount adsorbed, P is the equilibrium pressure, P_r is the relative pressure, and q_p, r, k, q_m, b, n, s, and c are isotherm parameters.

To determine the isotherm parameters for each adsorption system, a nonlinear curve-fitting procedure was used. The model parameters obtained form the best fit to experimental data are summarized in Tables 4 and 5 with the average percent deviations, Δq_1, and the degree of dispersion, Δq_2, calculated by the following equations.

$$\Delta q_1/\% = \frac{100}{n}\sum_{j=1}^{n}\left|\frac{q_j^{\text{exptl}} - q_j^{\text{calcd}}}{q_j^{\text{exptl}}}\right| \quad (5)$$

$$\Delta q_2/\% = \frac{100}{n}\sum_{j=1}^{n}\frac{[q_j^{\text{exptl}} - q_j^{\text{calcd}}]^2}{q_j^{\text{exptl}}} \quad (6)$$

where n is the number of data points at a given temperature and q^{exptl} and q^{calcd} are the experimental and calculated numbers of adsorbed moles, respectively. The lines in Figures 2 and 3 denote the calculated adsorption isotherms from the models.

As shown in Figure 2 and Table 4, to predict the adsorption of water on the activated carbon, the Dubinin−Serpinsky equation provided a better isotherm fit in all of the temperature range than the Sips equation. Moreover, the Sips equation was not appropriate for the prediction of the water vapor adsorption at 293 K, which was highly unfavorable. The major deviation of both the isotherm equations came from the lower-pressure range. From a mathematical viewpoint, the deviation between the experiments and the D−S equation in the low-pressure range seems to originate from the form of an equation. In other words, because the D−S equation is a quadratic equation in terms of the amount adsorbed, q, the hyperbolic behavior of the D−S equation could lead to some errors. On the contrary, in the case of the DAY zeolite in Figure 3 and Table 5, the Sips equation provided a better isotherm fit than the other isotherm models, but the difference among them was small.

Conclusions

The adsorption equilibria of water vapor were measured at (293, 313, 333, 353, and 373) K and pressures up to 3.4 kPa for activated carbon and 1.9 kPa for DAY zeolite. The adsorption isotherms on the activated carbon were type-III isotherms in the experimental range, and these experimental data were correlated with the Dubinin−Serpinsky and Sips equations. However, since the isotherms on the DAY zeolite were type-I, the data were correlated with the Sips, Toth, and UNILAN equations. In view of the results based on the correlation used, the experimental equilibrium data of water vapor on the DAY zeolite were satisfactorily correlated with the Toth, UNILAN, and Sips equations. The Dubinin−Serpinsky equation showed a more reasonable fit for water adsorption on the activated carbon than the Sips equation.

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