J. Chem. Eng. Data **2002,** *47,* 1237−1242

Adsorption Equilibria of CO_2 on Zeolite 13X and Zeolite X/Activated Carbon Composite

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The adsorption equilibria of CO_2 on zeolite 13X and zeolite X/activated carbon composite (Zeocarbon) were measured by a static volumetric method. The equilibrium experiments were conducted at (273.15, 293.15, 313.15, 333.15, and 353.15) K and at pressures up to 102.0 kPa for zeolite 13X and 99.7 kPa for Zeocarbon. The experimental data obtained were correlated by the Toth, UNILAN, and Sips models, which are generally used for microporous adsorbents such as zeolites and activated carbon. The isosteric enthalpies of adsorption were calculated for CO_2 on both adsorbents.

Introduction

The emission of CO_2 from power plants that burn fossil fuels is a major reason for the accumulation of CO_2 in the atmosphere, which causes long-term environmental problems.[1] Recently, much attention has been paid to the global warming effect caused by the excessive emission of CO_2 into the atmosphere.[2] Separation can play a key role in alleviating this problem, and 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. Therefore, adsorption is one of the most effective methods for the separation of emitted CO_2.

Information concerning the relevant adsorption equilibria is generally an essential requirement for the analysis and design of an adsorption separation process.[3] For practical applications, the adsorption equilibria must be known over a broad range of operation temperatures. Also, the isotherms of pure species are fundamental information for the dynamic simulation of adsorbers.[4] Furthermore, it is important to select the proper adsorbent for the design of an efficient adsorption process.

Whereas fossil resources are limited, biomass as an adsorbent is an inexpensive, renewable, and environmentally friendly additional resource that can be found readily all over the world.[5] Recently, a zeolite X/activated carbon composite (Zeocarbon) was synthesized from rice hulls that can be used in packed beds in pelletized form. However, little information is available in the literature concerning the adsorption of any components on Zeocarbon at various temperatures.

Zeocarbon was selected as an adsorbent in this study, and adsorption isotherms for CO_2 on Zeocarbon were measured and compared with those for CO_2 on zeolite 13X, which were measured previously.[6,7] In this study, commercial adsorbent pellets of zeolite 13X and Zeocarbon were used instead of crystals. The experimental data obtained at various temperatures were correlated with existing adsorption isotherm models such as the Toth, UNILAN, and Sips models.

Table 1. Physical Properties of Zeolite 13X and Zeocarbon

property	zeolite 13X	Zeocarbon
bulk density/($kg\cdot m^{-3}$)	689	500
BET surface area/($m^2\cdot g^{-1}$)	726	620
micropore area/($m^2\cdot g^{-1}$)	678	467
micropore volume/($cm^2\cdot g^{-1}$)	0.25	0.19
BJH desortion average pore diameter/nm	28	27
average pore diameter by BET/nm	23	28

Experimental Section

Materials. Spherical zeolite 13X and Zeocarbon pellets were supplied by Aldrich Co. and Zeobuilder Co., respectively. Zeocarbon synthesized from rice hull consists of the following components: 38.5 mass % zeolite X, 35 mass % activated carbon, 10 mass % inert silica, and 16.5 mass % zeolite A and P. The zeolite in Zeocarbon was exchanged with Ca ion by the supplier. Both adsorbent samples were crushed to 20−30 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 zeolite 13X and Zeocarbon samples are listed in Table 1. CO_2 with 99.9999 vol % purity was provided by Matheson Co.

Apparatus and Procedure. The adsorption experiments were based on the static volumetric method, and a schematic diagram of the apparatus is shown 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 (MKS, type 690A13TRA) with a high-accuracy signal conditioner (MKS, type 270D). Its pressure range is (0−133.33) kPa, and its reading uncertainty is ±0.05% within the usable measurement range. During experiments, the adsorption cell was put in a water bath, and the temperature was maintained constant to within ±0.02 K by a refrigerating circulator (Haake type F3).

To eliminate any trace of pollutants, the zeolite 13X and Zeocarbon samples were kept in a drying oven at 543 K

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10.1021/je020050e CCC: $22.00 © 2002 American Chemical Society
Published on Web 06/26/2002

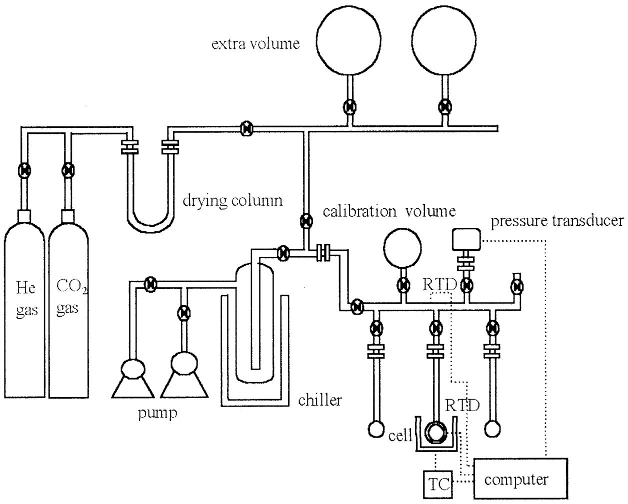

Figure 1. Adsorption equilibrium apparatus.

for 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 charged adsorbents were regenerated at 593 K under high vacuum for more than 12 h. An oil diffusion pump and a mechanical vacuum pump in combination (Edwards type Diffstak 63/150M) provided a vacuum down to 10^{-3} Pa, 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 measured by He were 583.03 and 23.62 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 CO_2 gas was supplied to the manifold controlled by a valve. When the adsorption cell reached the desired temperature, CO_2 gas was admitted into the adsorption cell. During the experiments, all of the temperatures and pressures were recorded automatically on an interfaced computer. The number of moles adsorbed were calculated from the measured pressure, temperature, and gas volume by using ideal gas law.

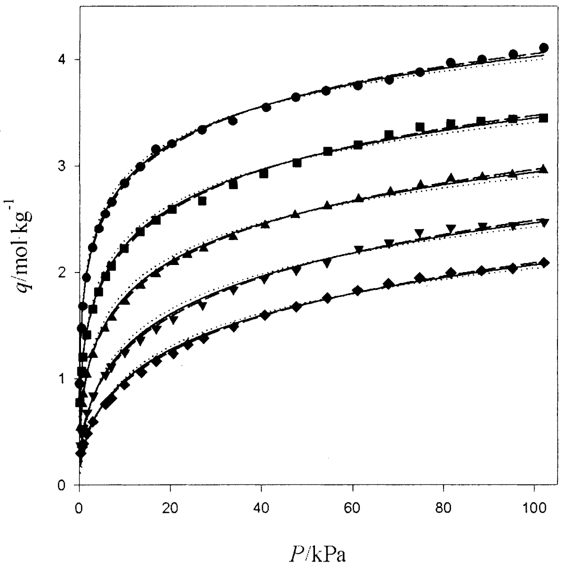

Figure 2. Experimental and correlated isotherms for CO_2 adsorption onto zeolite 13X at various temperatures: ●, 273 K; ■, 293 K; ▲, 313 K; ▼, 333 K; ◆, 353 K; —, Toth equation; · · ·, UNILAN equation; — — —, Sips equation.

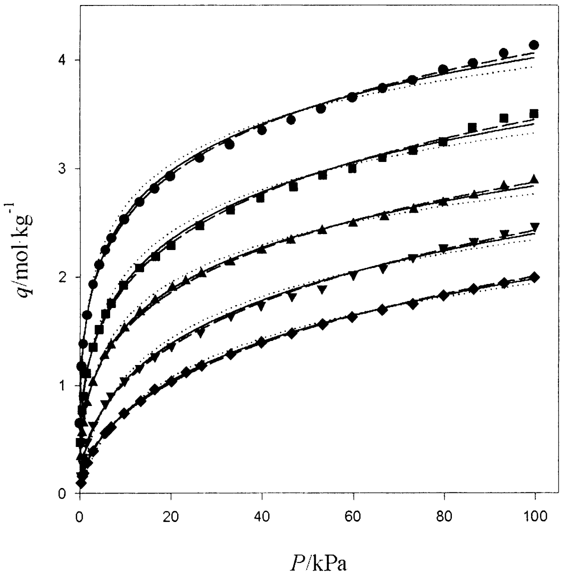

Figure 3. Experimental and correlated isotherms for CO_2 adsorption onto Zeocarbon at various temperatures: ●, 273 K; ■, 293 K; ▲, 313 K; ▼, 333 K; ◆, 353 K; —, Toth equation; · · ·, UNILAN equation; — — —, Sips equation.

Results and Discussion

Adsorption isotherms for CO_2 on zeolite 13X and Zeocarbon were obtained at (273.15, 293.15, 313.15, 333.15, and 353.15) K and at pressures up to 102.0 kPa on zeolite 13X and 99.7 kPa on Zeocarbon. The adsorption isotherms for CO_2 on zeolite 13X and Zeocarbon at the various temperatures are shown in Figures 2 and 3, respectively. The amount adsorbed on zeolite 13X was higher than that on Zeocarbon within the experimental range. However, the difference in the amounts adsorbed on the two adsorbents decreased with increasing pressure. The adsorption capacity, defined as the amount at the plateau of the isotherm, is higher for Zeocarbon than for zeolite 13X at higher pressures. The more favorable isotherms on zeolite 13X than on Zeocarbon at low pressure imply that the affinity of CO_2 is higher for zeolite 13X than for Zeocarbon because of the activated carbon in Zeocarbon. That is, the equilibrium adsorption capacities of zeolite 13X and Zeocarbon at 0.55 kPa and 293 K were 1.07 and 0.77 mol of CO_2/kg of the adsorbent, respectively, whereas those at 100 kPa and 293 K were both about 3.5 mol of CO_2/kg of the adsorbent. These values for zeolite 13X are similar to the results of a previous study.[6] However, the results for Zeocarbon as a zeolite X/activated carbon composite were higher than those for activated carbon, being about 0.2 mol of CO_2/kg of the adsorbent at 0.55 kPa and 297 K and 2.2 mol of CO_2/kg of the adsorbent at 100 kPa and 297 K.[8,9] This difference was due to the strong adsorption affinity of CO_2 on zeolite in the range of low pressures.

The experimental equilibrium data are presented in Tables 2 and 3, with the percent deviations DQ calculated by the following equation

$$\mathrm{DQ}/\% = 100\left[\frac{q_j^{\mathrm{exp}} - q_j^{\mathrm{cal}}}{q_j^{\mathrm{exp}}}\right] \qquad (1)$$

where q^{exp} and q^{cal} are the experimental and calculated numbers of moles adsorbed, respectively.

Table 2. Adsorption Isotherm Data for CO_2 on Zeolite 13X

P	q	DQ %			P	q	DQ %		
kPa	mol·kg^{-1}	Toth	UNILAN	Sips	kPa	mol·kg^{-1}	Toth	UNILAN	Sips
273.15 K									
0.067	0.95	11.6	32.6	1.87	26.92	3.33	−1.61	−1.05	−0.28
0.468	1.47	−1.23	1.42	−1.63	33.68	3.42	−2.30	−1.52	−1.16
0.829	1.68	−2.30	−1.94	−1.26	40.95	3.54	−1.67	−0.72	−0.72
1.598	1.95	−2.70	−3.60	−0.68	47.43	3.64	−0.95	0.12	−0.15
2.980	2.23	−2.64	−3.82	−0.23	54.08	3.70	−1.13	0.04	−0.45
4.336	2.41	−2.39	−3.46	0.05	61.08	3.75	−1.45	−0.18	−0.88
5.748	2.55	−2.15	−3.04	0.24	67.95	3.80	−1.56	−0.20	−1.07
7.071	2.66	−1.76	−2.50	0.54	74.67	3.88	−0.71	0.70	−0.31
9.960	2.83	−1.68	−2.12	0.44	81.49	3.96	0.20	1.65	0.52
13.41	2.99	−1.26	−1.40	0.65	88.31	3.99	−0.08	1.43	0.17
16.80	3.15	0.25	0.33	1.95	95.16	4.05	0.46	2.00	0.65
20.35	3.20	−1.25	−0.98	0.32	101.9	4.11	1.07	2.64	1.20
293.15 K									
0.147	0.77	17.5	37.7	6.17	26.91	2.67	−2.88	−3.91	−2.64
0.569	1.07	3.54	8.35	−0.22	33.74	2.82	−1.59	−2.24	−1.58
0.882	1.20	1.14	2.57	−0.88	40.46	2.92	−1.37	−1.73	−1.55
1.626	1.41	−0.87	−2.42	−1.16	47.78	3.03	−0.58	−0.68	−0.93
2.946	1.65	−1.39	−4.23	−0.71	54.47	3.14	0.74	0.84	0.26
4.264	1.82	−1.02	−4.06	−0.05	61.12	3.20	0.70	0.97	0.10
5.771	1.96	−0.97	−3.95	0.09	67.90	3.30	2.02	2.44	1.33
7.045	2.06	0.67	−3.51	0.38	74.72	3.37	2.56	3.09	1.77
9.792	2.22	−0.63	−3.13	0.34	81.47	3.40	2.07	2.72	1.20
13.41	2.38	−0.44	−2.52	0.37	88.13	3.42	1.43	2.19	0.48
16.90	2.49	−0.70	−2.45	−0.06	95.10	3.44	0.83	1.69	−0.20
20.43	2.59	−0.56	−2.01	−0.08	101.9	3.45	0.06	1.01	−1.04
313.15 K									
0.226	0.54	14.5	37.9	0.87	27.23	2.23	−1.02	−2.44	−0.43
0.625	0.76	7.21	16.5	1.44	33.70	2.33	−1.38	−2.34	−1.04
0.892	0.85	4.77	10.1	0.99	40.73	2.44	−0.83	−1.38	−0.74
1.706	1.04	1.16	1.17	0.14	47.33	2.54	0.05	−0.17	−0.05
2.997	1.23	−0.76	−3.29	−0.28	54.32	2.63	0.73	0.80	0.44
5.629	1.47	−2.14	−5.67	−0.85	61.26	2.69	0.58	0.90	0.15
7.084	1.57	−2.11	−5.63	−0.73	68.21	2.75	0.69	1.22	0.11
10.02	1.73	−1.87	−5.10	−0.49	74.85	2.82	1.41	2.12	0.72
13.50	1.88	−1.28	−4.07	−0.05	81.49	2.88	1.89	2.77	1.10
16.83	1.99	−1.08	−3.48	−0.01	88.43	2.90	1.07	2.11	0.17
20.70	2.10	−0.68	−2.67	0.20	95.10	2.92	0.43	1.61	−0.57
23.66	2.16	−0.99	−2.71	−0.25	101.9	2.96	0.53	1.84	−0.55
333.15 K									
0.318	0.37	26.3	51.8	10.8	33.78	1.84	−1.55	−3.24	−0.59
0.682	0.48	14.7	32.0	5.64	40.53	1.94	−1.26	−2.45	−0.62
0.912	0.54	11.9	25.4	5.15	47.52	2.02	−1.47	−2.21	−1.11
1.746	0.68	6.08	11.7	3.56	54.26	2.09	−1.50	−1.86	−1.40
3.086	0.84	2.39	2.81	2.42	61.28	2.22	1.44	1.44	1.32
5.775	1.03	−1.84	−4.67	−0.20	67.92	2.28	1.47	1.75	1.16
7.043	1.11	−1.71	−5.03	0.17	74.63	2.38	3.50	4.04	3.03
10.04	1.25	−2.43	−6.11	−0.33	81.53	2.42	3.06	3.84	2.43
13.44	1.36	−3.85	−7.46	−1.78	88.45	2.44	1.99	3.00	1.21
16.94	1.47	−3.52	−6.81	−1.61	95.22	2.45	0.71	1.93	−0.22
20.61	1.56	−3.67	−6.60	−1.96	102.1	2.47	−0.07	1.35	−1.14
27.00	1.69	−3.71	−6.03	−2.37					
353.15 K									
0.353	0.30	38.3	51.8	22.4	27.31	1.38	−2.23	−9.30	−1.20
0.712	0.36	22.4	29.3	11.3	33.87	1.49	−1.55	−7.41	−0.86
0.922	0.39	16.9	20.6	7.70	40.69	1.60	−0.16	−4.95	0.20
1.758	0.48	6.92	2.55	2.31	47.55	1.68	−0.02	−3.96	0.06
3.060	0.59	0.66	−8.81	−0.85	54.38	1.76	0.66	−2.52	0.48
5.839	0.76	−3.41	−15.5	−2.63	61.05	1.83	1.21	−1.35	0.81
7.075	0.81	−4.81	−17.0	−3.63	67.79	1.89	1.47	−0.54	0.87
9.949	0.94	−3.83	−15.4	−2.26	74.66	1.95	1.91	0.41	1.12
13.67	1.06	−4.32	−14.9	−2.67	81.51	1.99	1.55	0.49	0.59
16.94	1.17	−2.24	−11.7	−0.71	88.30	2.01	0.41	−0.26	−0.72
20.65	1.23	−4.31	−13.0	−2.92	95.13	2.04	−0.07	−0.37	−1.35
23.85	1.32	−2.13	−9.91	−0.93	102.0	2.09	0.53	0.57	−0.88

The Toth, UNILAN, and Sips models were used to correlate the experimental adsorption data for CO_2 on zeolite 13X and Zeocarbon.

Toth Isotherm. The Toth isotherm[10] 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 used in many applications as the isotherm equation for fitting data for many adsorbates on activated carbon as well as zeolites.[11] It is a three-parameter model

Table 3. Adsorption Isotherm Data for CO_2 on Zeocarbon

P	q	DQ			P	q	DQ		
		%					%		
kPa	mol·kg^{-1}	Toth	UNILAN	Sips	kPa	mol·kg^{-1}	Toth	UNILAN	Sips
273.15 K									
0.065	0.65	8.19	52.5	−9.86	26.31	3.09	−2.73	−3.15	−0.25
0.457	1.17	1.42	12.9	−1.85	32.93	3.22	−3.01	−2.87	−0.81
0.811	1.38	0.86	5.86	0.14	40.02	3.34	−3.08	−2.43	−1.15
1.562	1.65	0.39	0.70	1.72	46.36	3.44	−2.88	−1.83	−1.18
2.913	1.93	−0.24	−2.21	2.28	52.87	3.55	−2.14	−0.74	−0.65
4.239	2.11	−0.64	−3.18	2.31	59.71	3.65	−1.56	0.16	−0.28
5.619	2.25	−0.97	−3.63	2.16	66.42	3.74	−1.03	0.98	0.07
6.912	2.36	−1.02	−3.64	2.16	73.00	3.81	−0.85	1.41	0.10
9.736	2.53	−1.83	−4.16	1.37	79.65	3.90	−0.03	2.44	0.75
13.11	2.69	−2.20	−4.09	0.88	86.33	3.97	0.35	3.03	0.99
16.42	2.81	−2.62	−4.10	0.33	93.02	4.06	1.30	4.15	1.80
19.89	2.93	−2.40	−3.47	0.37	99.63	4.13	1.83	4.85	2.21
293.15 K									
0.144	0.47	9.89	52.0	−10.2	26.30	2.47	−2.20	−3.90	−0.07
0.556	0.77	3.13	21.7	−3.94	32.98	2.62	−1.83	−2.83	−0.02
0.863	0.90	2.24	13.7	−1.84	39.55	2.72	−2.42	−2.82	−0.89
1.589	1.11	0.89	4.71	−0.07	46.71	2.83	−2.33	−2.15	−1.09
2.879	1.35	0.51	−0.37	1.59	53.24	2.94	−1.49	−0.85	−0.51
4.168	1.52	0.62	−1.93	2.52	59.75	3.00	−2.07	−1.04	−1.31
5.641	1.66	0.19	−3.12	2.54	66.37	3.10	−1.09	0.33	−0.56
6.886	1.76	0.13	−3.43	2.67	73.04	3.17	−0.96	0.82	−0.61
9.572	1.92	−0.63	−4.24	2.08	79.63	3.24	−0.63	1.45	−0.47
13.11	2.08	−1.32	−4.62	1.38	86.15	3.38	1.90	4.20	1.89
16.52	2.19	−2.35	−5.26	0.25	92.96	3.46	2.62	5.17	2.45
19.97	2.29	−2.83	−5.31	−0.37	99.63	3.50	2.32	5.13	2.01
313.15 K									
0.221	0.34	−3.65	40.4	−26.1	26.62	2.03	−0.19	−2.95	0.89
0.611	0.56	1.78	22.8	−7.91	32.94	2.13	−1.10	−3.16	−0.29
0.872	0.65	1.84	16.3	−4.98	39.82	2.24	−1.02	−2.37	−0.50
1.668	0.84	1.25	6.09	−1.63	46.27	2.34	−0.48	−1.24	−0.22
2.930	1.03	1.04	0.33	0.46	53.09	2.43	−0.16	−0.35	−0.14
5.503	1.27	0.34	−3.60	1.28	59.88	2.49	−0.68	−0.39	−0.90
6.925	1.37	0.42	−4.03	1.67	66.68	2.55	−0.91	−0.17	−1.34
9.795	1.53	0.53	−4.13	2.05	73.17	2.62	−0.42	0.71	−1.04
13.19	1.68	0.87	−3.54	2.41	79.66	2.68	−0.17	1.32	−0.96
16.45	1.79	0.73	−3.30	2.21	86.45	2.75	0.49	2.32	−0.46
20.24	1.90	0.78	−2.77	2.12	92.96	2.84	2.02	4.12	0.92
23.13	1.96	0.16	−3.03	1.39	99.58	2.89	2.18	4.57	0.95
333.15 K									
0.311	0.17	1.09	48.9	−29.6	33.02	1.64	−1.56	−3.85	0.19
0.667	0.28	4.43	38.1	−12.0	39.62	1.74	−2.09	−3.75	−0.66
0.892	0.34	6.22	34.2	−6.12	46.46	1.82	−3.10	−4.14	−1.99
1.706	0.48	6.78	23.4	1.03	53.04	1.89	−3.81	−4.27	−2.99
3.017	0.64	5.87	13.9	3.99	59.91	2.02	−1.11	−1.00	−0.61
5.645	0.83	2.79	4.00	3.62	66.40	2.08	−1.62	−1.02	−1.37
6.885	0.91	2.53	2.21	3.93	72.96	2.18	0.18	1.22	0.18
9.812	1.05	1.40	−0.86	3.48	79.70	2.27	1.43	2.90	1.21
13.14	1.16	−0.83	−3.98	1.55	86.46	2.33	1.52	3.38	1.08
16.56	1.27	−1.08	−4.49	1.33	93.08	2.40	2.20	4.42	1.58
20.14	1.36	−1.91	−5.26	0.45	99.76	2.47	2.96	5.51	2.16
26.39	1.49	−3.02	−5.96	−0.90					
353.15 K									
0.345	0.10	−0.33	48.8	−40.4	26.70	1.18	−0.366	−2.88	1.57
0.696	0.16	−0.50	38.7	−24.7	33.11	1.29	−0.62	−2.82	1.04
0.901	0.19	−1.15	34.1	−20.8	39.78	1.40	−0.02	−1.74	1.30
1.718	0.28	0.50	24.3	−9.73	46.48	1.48	−0.73	−1.93	0.28
2.991	0.39	0.32	14.9	−4.42	53.16	1.56	−0.74	−1.42	−0.06
5.708	0.56	−0.05	5.51	−0.62	59.68	1.63	−0.81	−0.99	−0.43
6.916	0.61	−1.84	1.65	−1.57	66.26	1.69	−1.15	−0.84	−1.06
9.726	0.74	0.06	0.52	1.40	72.98	1.75	−1.25	−0.47	−1.45
13.37	0.86	−0.48	−1.87	1.44	79.67	1.83	0.01	1.23	−0.44
16.56	0.97	1.46	−0.64	3.51	86.31	1.89	0.35	1.98	−0.34
20.18	1.04	−0.62	−3.12	1.50	92.99	1.94	0.30	2.33	−0.62
23.31	1.12	0.36	−2.20	2.39	99.72	2.00	0.89	3.28	−0.25

usually written in the form

$$q = \frac{q_s P}{(b + P^t)^{1/t}} \qquad (2)$$

where P is the equilibrium pressure; q is the number of moles adsorbed; 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 experi-

Table 4. Toth Equation Parameters for CO_2 on Zeolite 13X and Zeocarbon

T	q_s	b	t	Δq
K	$mol \cdot kg^{-1}$	kPa		%
		zeolite 13X		
273.15	9.01	0.311	0.168	1.85
293.15	8.28	0.436	0.190	1.93
313.15	7.51	0.591	0.213	2.05
333.15	6.94	0.936	0.250	4.35
353.15	6.44	1.19	0.265	5.09
		Zeocarbon		
273.15	14.9	0.395	0.143	1.81
293.15	13.5	0.575	0.170	1.94
313.15	12.1	0.670	0.178	0.97
333.15	11.0	1.27	0.235	2.59
353.15	10.0	1.83	0.266	0.62

Table 5. UNILAN Equation Parameters for CO_2 on Zeolite 13X and Zeocarbon

T	q_s	c	s	Δq
K	$mol \cdot kg^{-1}$	kPa		%
		zeolite 13X		
273.15	8.03	104.8	8.39	2.89
293.15	7.07	130.7	7.33	4.18
313.15	6.29	169.3	6.65	4.92
333.15	5.76	252.7	5.85	8.41
353.15	5.12	307.0	5.81	10.1
		Zeocarbon		
273.15	8.19	134.0	7.33	5.35
293.15	7.26	171.9	6.37	6.29
313.15	6.23	200.8	6.09	5.58
333.15	5.92	292.2	5.00	9.59
353.15	5.19	314.9	4.38	8.26

Table 6. Sips Equation Parameters for CO_2 on Zeolite 13X and Zeocarbon

T	q_s	b	n	Δq
K	$mol \cdot kg^{-1}$	kPa		%
		zeolite 13X		
273.15	7.55	0.307	3.47	0.72
293.15	6.82	0.225	3.01	0.98
313.15	6.13	0.167	2.67	0.52
333.15	5.60	0.104	2.26	2.18
353.15	5.02	0.0792	2.09	2.89
		Zeocarbon		
273.15	11.9	0.139	3.52	1.49
293.15	10.6	0.100	2.94	1.72
313.15	9.05	0.0863	2.74	2.62
333.15	7.84	0.0503	2.11	3.57
353.15	7.17	0.0340	1.89	5.05

mental data are summarized in Table 4, with the average percent deviations Δq calculated by the equation

$$\Delta q/\% = \frac{100}{k}\sum_{j=1}^{k}\left|\frac{q_j^{\exp} - q_j^{\mathrm{cal}}}{q_j^{\exp}}\right| \tag{3}$$

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 moles adsorbed, 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 for both zeolite 13X and Zeocarbon. The Toth equation provided a better fit for Zeocarbon than for zeolite 13X at higher temperatures (333 and 353 K).

UNILAN Equation. The UNILAN equation is another empirical relation obtained by assuming a patchwise topography on the surface, in which each patch is ideal so that the local Langmuir isotherm is applicable on each patch. The distribution of energy on the surface is assumed to be uniform.[11,12] The following UNILAN equation is also frequently used to correlate the adsorption equilibrium data of many solids, such as activated carbon and zeolites[11]

$$q = \frac{q_s}{2s}\ln\left(\frac{c + Pe^{+s}}{c + Pe^{-s}}\right) \tag{4}$$

where q_s, c, and s are isotherm parameters. The parameters and average percent deviations calculated by eqs 3 and 4 are summarized in Table 5. 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 deviations for both zeolite 13X and Zeocarbon in the UNILAN equation became larger at high temperatures (333 and 353 K).

Sips Equation. Recognizing the problem of the continuing increase in the amount adsorbed at increasing pressure (concentration) in the Freundlich equation, Sips proposed an equation similar in form to the Freundlich equation but with a finite limit when the pressure is sufficiently high.[11] The resulting equation, which resembles the Langmuir equation in form, is given by

$$q = \frac{q_s b P^{1/n}}{1 + bP^{1/n}} \tag{5}$$

where q_s, b, and n are isotherm parameters. The parameters and average percent deviations calculated are summarized in Table 6. The dashed lines in Figures 2 and 3 denote the isotherms calculated according to the Sips equation. The Sips equation provides a better fit for zeolite 13X than for Zeocarbon at all temperatures.

Isosteric Enthalpies of Adsorption. Isosteric enthalpies of adsorption (q_{st}) can be calculated by the Clausius–Clapeyron equation for adsorption[12]

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

where P is the pressure, T is the temperature, and R is the gas constant. The isosteric enthalpies are a measure of the interaction between the adsorbate molecules and the adsorbent lattice atoms and can be used as a measure of the energetic heterogeneity of a solid surface. Usually, the isosteric enthalpy curve varies with the surface loading. This phenomenon has been understood as indicating that the adsorbent for adsorptive separation usually has an energetically heterogeneous surface.[10] According to the ideal Langmuir model, the enthalpies of adsorption should be independent of coverage, but this requirement is seldom fulfilled in real systems because the effects of surface heterogeneity and adsorbate–adsorbent interactions are generally significant. Knowledge of the magnitude of the enthalpy of adsorption and its variation with coverage can provide useful information concerning the nature of the surface and the adsorbed phase.[3]

As shown in Figure 4, the isosteric enthalpy of adsorption on Zeocarbon increases with increasing surface loading of CO_2. In contrast, the isosteric enthalpy of adsorption in zeolite 13X is almost constant near 40 kJ/mol.

Conclusions

The adsorption equilibria for CO_2 were measured at (273, 293, 313, 333, and 353) K and at pressures up to 102.0 kPa

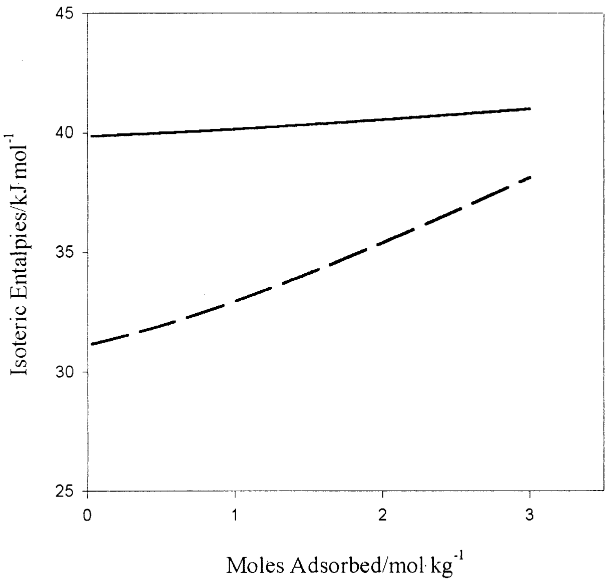

Figure 4. Isoteric enthalpies of adsorption with respect to surface loading: —, zeolite 13X; — — —, Zeocarbon.

for zeolite 13X and 99.7 kPa for Zeocarbon. The adsorption of CO_2 on zeolite 13X showed a more favorable isotherm than that on Zeocarbon. However, the amounts adsorbed on the two adsorbents became similar as the pressure increased. The experimental equilibrium data of CO_2 on zeolite 13X and Zeocarbon were satisfactorily correlated with the Toth, UNILAN, and Sips equations. The Toth and Sips equations showed the smallest deviations for zeoltie 13X and Zeocarbon, respectively. The isosteric enthalpy of adsorption on Zeocarbon increased with pressure, whereas that on zeolite 13X was almost constant.

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Received for review March 13, 2002. Accepted May 15, 2002.

JE020050E