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Adsorption Equilibria of O_2, N_2, and Ar on Carbon Molecular Sieve and Zeolites 10X, 13X, and LiX

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The adsorption equilibria of O_2, N_2, and Ar on carbon molecular sieve (CMS) and zeolites 10X, 13X, and LiX were measured by the gravimetric method. The equilibrium measurement was conducted at (293.15, 303.15, and 313.15) K and pressure up to 80 kPa. The experimental data were correlated by the Langmuir, Sips, and Toth equations. The Sips equation showed the smallest deviation from all the experimental data of adsorbents. The isosteric enthalpies of adsorption were calculated for O_2, N_2, and Ar on all the adsorbents.

Introduction

The separation and purification of O_2, N_2, and Ar from ambient air by using zeolite and carbon molecular sieve (CMS) are of considerable interest in the numerous chemical and petrochemical industries. Generally, various zeolites are used to produce O_2 from air while CMS is applied to produce N_2 of high purity.[1−4] A new development of the process and the quality of the adsorbent leads to an economically beneficial increase in the capacity of pressure swing adsorption (PSA) plants and a higher market share of oxygen or nitrogen from PSA units.[5] In addition, the field of application for oxygen and nitrogen generated in the PSA plants has widened considerably.[6] As a result, a number of numerous modified adsorption cycles were developed and have been vigorously studied until recently. In particular, it was reported that the vacuum swing adsorption (VSA) process produced oxygen with both high purity and high productivity.[2,7]

However, because air contains a small amount of Ar, which has physical properties similar to those of O_2, the product from zeolite bed contains a substantial amount of Ar as impurity.[8] Therefore, the upper limit of O_2 purity is restricted to less than 95 % in the equilibrium separation process using zeolite.

Recently, to overcome this purity limit and to produce high-purity O_2 (over 99 %), an adsorption process using CMS was developed as an additional purifier to remove minor impurities, such as N_2 and Ar, contained in oxygen-rich feed.[9] It was reported that the PSA process using CMS could purify the oxygen up to 99.8+ % purity, which is the standard oxygen purity in the semiconductor industries, if the purity of oxygen in the feed is higher than 90 %. Furthermore, a three-bed PVSA (pressure-vacuum swing adsorption) process, which combined two zeolite beds with one CMS bed, was reported to produce higher than 99 % purity O_2 directly from air.[10] The equilibrium and kinetic data on the CMS at elevated pressure were successfully applied to design the PSA processes.[11,12]

Prior to designing the cyclic adsorption process, understanding the adsorption equilibria of various adsorbents is crucial to achieve high working capacity for a given adsorbent and to improve process efficiency. Furthermore, it is important to select the proper adsorbent for the design of an efficient adsorption process.

Table 1. Physical Properties of the Adsorbents

property	CMS	zeolite 10X	zeolite 13X	zeolite LiX
bulk density ($g \cdot cm^{-3}$)	0.63	0.82	0.78	0.62
pore volume ($cm^3 \cdot g^{-1}$)	0.162[a]	0.260	0.250	0.248
micropore diameter (Å)	4.04[a]	8.00	8.40	4.90
BET surface area ($m^2 \cdot g^{-1}$)	523[a]	466	420	534
average pellet size (mm)	2.52	1.15	1.00	1.70
type	pellet	sphere	sphere	sphere

[a] Ref 11.

Table 2. Adsorption Isotherm Data on CMS

Ar		N_2		O_2	
P/kPa	*q*/mol·kg^{-1}	*P*/kPa	*q*/mol·kg^{-1}	*P*/kPa	*q*/mol·kg^{-1}
		293 K			
5.066	0.027	6.266	0.043	2.267	0.013
11.73	0.056	11.73	0.070	8.399	0.040
18.00	0.081	17.87	0.096	13.07	0.058
24.26	0.104	24.40	0.123	21.06	0.089
32.00	0.131	31.86	0.151	29.33	0.119
38.13	0.152	40.40	0.180	37.86	0.148
44.66	0.173	53.33	0.222	48.66	0.183
50.80	0.191	58.93	0.238	58.00	0.213
58.00	0.213	66.26	0.259	67.73	0.242
63.99	0.231			75.73	0.266
		303 K			
3.333	0.015	4.933	0.023	1.867	0.013
7.199	0.030	11.60	0.047	6.666	0.028
11.73	0.046	16.93	0.063	11.73	0.044
17.73	0.066	25.20	0.087	17.07	0.062
24.40	0.087	33.33	0.110	22.40	0.079
29.60	0.102	41.60	0.131	33.46	0.113
34.40	0.115	47.60	0.146	42.53	0.139
43.60	0.141	54.00	0.160	55.06	0.173
52.00	0.163	62.26	0.179	64.66	0.199
58.66	0.180			76.66	0.233
		313 K			
3.200	0.010	5.733	0.020	3.866	0.013
7.066	0.020	10.40	0.035	9.600	0.031
11.73	0.034	16.27	0.051	13.87	0.042
17.07	0.047	24.00	0.071	19.47	0.057
23.06	0.063	30.13	0.086	24.00	0.069
28.93	0.077	36.26	0.100	31.60	0.090
36.93	0.097	42.26	0.114	37.73	0.104
42.66	0.109	50.26	0.133	47.73	0.128
50.26	0.128	58.66	0.151	56.93	0.150
60.26	0.149	69.59	0.173	67.19	0.174

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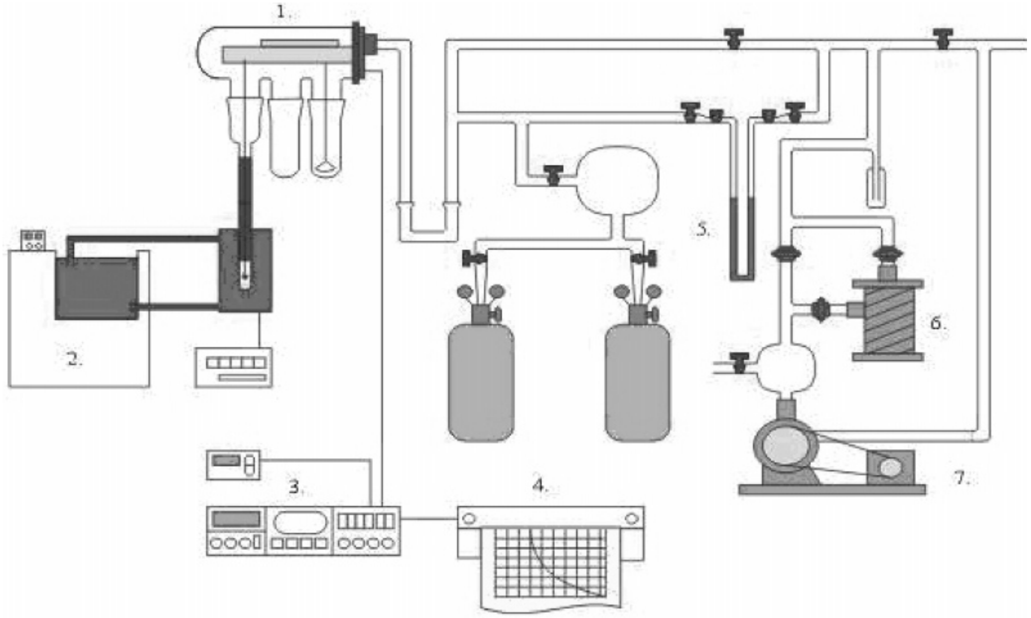

Figure 1. Adsorption equilibrium apparatus: 1, Cahn microbalance; 2, circulating water bath; 3, controller; 4, recorder; 5, manometer; 6, diffusion pump; 7, rotary vacuum pump.

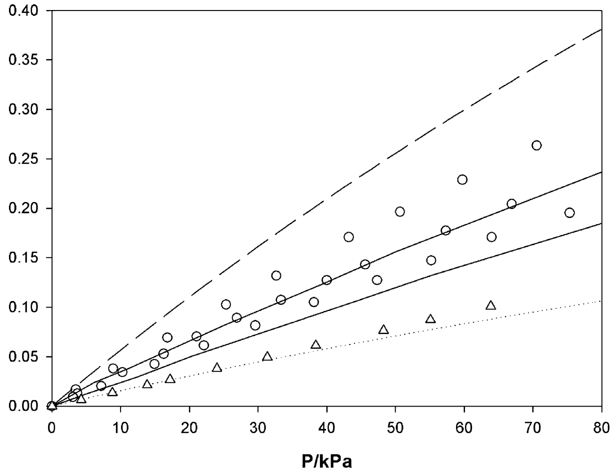

Figure 2. Comparison of isotherm data on zeolite 13X: ○, N_2 on 13X in this experiment at 293 K, 303 K, and 313 K; △, O_2 on 13X in this experiment at 293K; —, N_2 on 13X (CECA, France)[13] at 298 K and 308 K; - - -, N_2 on 13X (Linde)[14] at 295 K; · · ·, O_2 on 13X (Linde)[14] at 295 K.

Table 3. Adsorption Isotherm Data on Zeolite 10X

Ar		N_2		O_2	
P/kPa	*q*/mol·kg^{-1}	*P*/kPa	*q*/mol·kg^{-1}	*P*/kPa	*q*/mol·kg^{-1}
293 K					
4.533	0.007	6.266	0.032	7.466	0.010
10.40	0.015	12.00	0.054	12.00	0.016
14.40	0.021	18.53	0.079	18.53	0.024
20.00	0.027	24.26	0.097	24.80	0.031
28.40	0.037	32.00	0.119	32.66	0.040
35.06	0.045	40.00	0.142	38.66	0.047
42.53	0.053	49.73	0.168	43.73	0.052
50.53	0.061	56.00	0.185	51.06	0.060
62.13	0.072	62.66	0.202	59.86	0.068
71.73	0.082	68.39	0.216	69.46	0.077
303 K					
6.400	0.008	5.066	0.019	6.533	0.008
11.73	0.013	11.33	0.039	11.20	0.013
19.33	0.022	16.93	0.055	17.73	0.020
25.73	0.028	24.53	0.074	25.73	0.028
32.26	0.034	31.33	0.091	32.53	0.035
37.86	0.040	37.33	0.104	38.40	0.041
43.73	0.045	44.53	0.120	44.00	0.046
52.66	0.053	51.60	0.136	51.06	0.052
59.06	0.058	58.66	0.152	59.73	0.060
68.53	0.066	64.39	0.163	69.19	0.068
313 K					
6.666	0.006	4.933	0.014	6.000	0.006
12.00	0.011	9.999	0.027	13.33	0.013
17.33	0.016	14.40	0.037	20.40	0.020
24.40	0.022	20.27	0.050	28.93	0.028
32.00	0.028	25.33	0.060	36.00	0.034
39.33	0.034	33.60	0.076	43.46	0.041
44.40	0.038	42.66	0.092	55.20	0.051
52.80	0.045	49.06	0.104	59.60	0.054
59.03	0.049	57.46	0.119	65.06	0.059
68.53	0.056	65.33	0.133	72.26	0.064

This paper reports the single-component adsorption equilibria of Ar, N_2, and O_2 at (293.15, 303.15, and 313.15) K and at pressures up to 80 kPa onto the CMS, zeolite 10X, zeolite 13X and zeolite LiX pellets. Adsorption equilibria were measured using a gravimetric technique. The experimental data were correlated by the Langmuir, Sips, and Toth equations.

Experimental Section

Materials. CMS (Takeda Chem., 3A), zeolite 10X (Baylith, WE-G 639), zeolite 13X (Baylith, WE-G 652), and zeolite LiX (UOP Co., WE-J750) pellets were used as the adsorbents. Prior to the experimental runs, the zeolites 10X, 13X, and LiX were regenerated at 613 K overnight, and the CMS was regenerated at 423 K. The physical properties of the adsorbents are detailed in Table 1. The gases used as adsorbates were of high purity (> 99.9 %).

Apparatus. The adsorption equilibria was measured by the gravimetric method using an electrobalance (Cahn 2000). The schematic apparatus for the adsorption experiments is shown in Figure 1. About 350 mg of adsorbent was put into the basket in the hangdown tube of the electrobalance. The recording scale was set to 10 μg, and the uncertainty of the electrobalance was given as ± 0.1 μg. The basket was made of aluminum mesh in order to make it easy to emit the enthalpy of adsorption into the gas phase. A calibrated mercury manometer was used to measure the pressure of the adsorbate in the system. A circulating thermostat (Jeiotech Co., Rec-11) was set up to keep the temperature of the system constant to within ± 0.05 K. The isotherm of each component on zeolite 13X was measured two

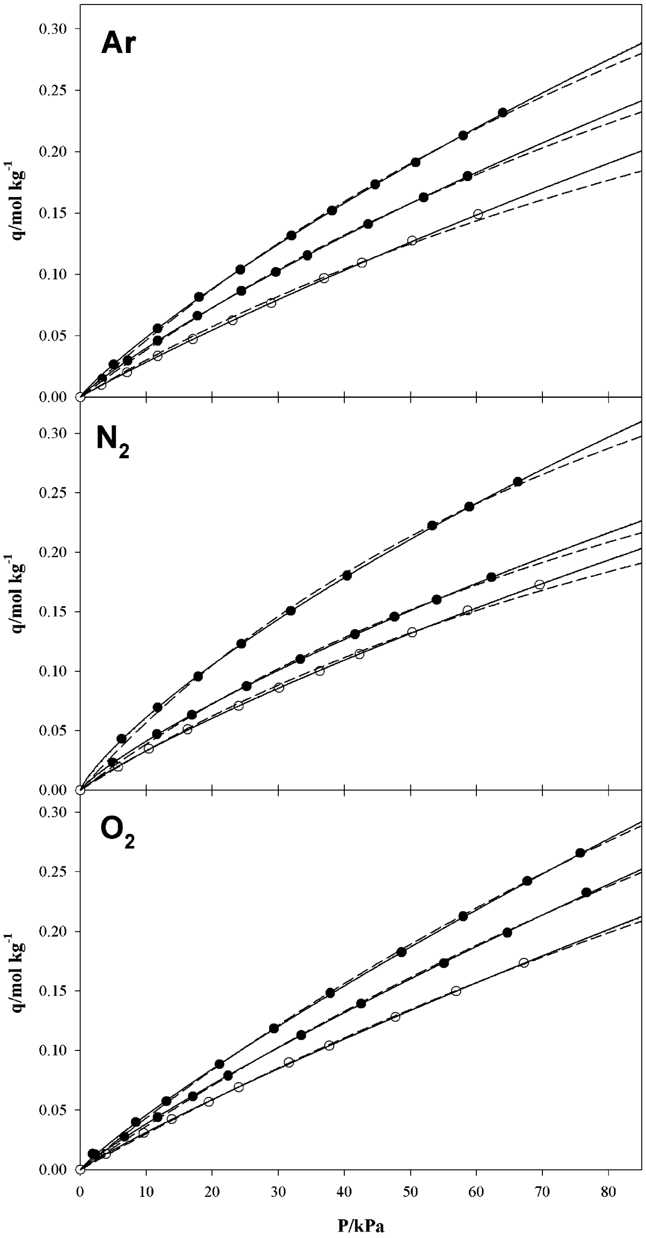

Figure 3. Adsorption isotherms on CMS: black, 293.15 K; gray, 303.15 K; white, 313.15 K; —, Sips; dashed line, Langmuir; - - -, Toth.

Table 4. Adsorption Isotherm Data on Zeolite 13X

Ar		N_2		O_2	
P/kPa	*q*/mol·kg^{-1}	*P*/kPa	*q*/mol·kg^{-1}	*P*/kPa	*q*/mol·kg^{-1}
293 K					
3.066	0.005	3.466	0.017	4.266	0.006
6.933	0.009	8.933	0.038	8.799	0.014
12.53	0.017	16.80	0.069	13.87	0.021
17.73	0.023	25.33	0.103	17.20	0.027
26.26	0.033	32.66	0.132	24.00	0.038
34.40	0.043	43.20	0.171	31.33	0.049
43.33	0.053	50.66	0.196	38.40	0.061
54.80	0.065	59.73	0.229	48.26	0.077
64.39	0.075	70.53	0.263	55.06	0.087
73.99	0.084			63.86	0.101
303 K					
3.733	0.004	3.733	0.013	3.066	0.004
10.93	0.012	10.27	0.034	8.27	0.012
16.40	0.018	16.27	0.053	14.67	0.021
22.26	0.024	21.06	0.070	21.33	0.031
28.13	0.031	26.93	0.089	28.40	0.041
35.20	0.038	33.33	0.107	35.06	0.051
44.40	0.047	40.00	0.127	40.26	0.059
53.33	0.055	45.60	0.143	45.73	0.067
62.53	0.064	57.33	0.178	57.73	0.084
71.06	0.072	66.93	0.204	65.33	0.095
313 K					
2.933	0.003	3.067	0.009	2.933	0.004
7.599	0.007	7.199	0.020	7.066	0.009
14.67	0.013	14.93	0.042	12.40	0.016
22.40	0.020	22.13	0.061	17.07	0.022
28.80	0.027	29.60	0.082	24.53	0.033
37.06	0.034	38.13	0.105	32.80	0.044
44.80	0.041	47.33	0.127	39.86	0.054
54.66	0.049	55.20	0.147	50.40	0.067
63.86	0.056	63.99	0.171	59.46	0.080
73.33	0.065	75.33	0.195	67.19	0.090

Table 5. Adsorption Isotherm Data on Zeolite LiX

Ar		N_2		O_2	
P/kPa	*q*/mol·kg^{-1}	*P*/kPa	*q*/mol·kg^{-1}	*P*/kPa	*q*/mol·kg^{-1}
293 K					
3.600	0.004	3.466	0.037	3.066	0.004
8.533	0.010	8.799	0.090	8.533	0.010
15.33	0.017	14.93	0.141	15.60	0.019
22.80	0.025	24.26	0.209	23.60	0.028
31.33	0.034	33.86	0.270	32.26	0.038
38.40	0.041	43.46	0.326	43.33	0.051
48.00	0.050	53.46	0.378	50.26	0.059
56.66	0.058	60.40	0.418	59.73	0.069
		70.53	0.454	68.39	0.079
		78.26	0.485	77.86	0.087
303 K					
3.466	0.003	3.333	0.030	3.466	0.004
10.00	0.010	8.276	0.058	9.866	0.010
16.67	0.016	13.33	0.099	18.00	0.020
24.53	0.023	20.53	0.150	24.40	0.026
31.73	0.030	26.93	0.180	32.00	0.034
38.50	0.036	35.33	0.230	43.46	0.046
47.20	0.044	44.93	0.280	50.66	0.054
56.44	0.052	55.60	0.330	59.06	0.063
		64.53	0.365	66.53	0.069
				74.13	0.077
313 K					
2.267	0.002	3.600	0.025	3.200	0.003
5.733	0.005	8.666	0.058	10.27	0.010
11.60	0.010	15.20	0.096	18.40	0.018
16.67	0.014	23.33	0.141	29.06	0.028
22.93	0.019	30.66	0.180	33.46	0.032
27.60	0.023	36.80	0.209	43.06	0.041
33.46	0.028	46.00	0.248	52.93	0.051
38.93	0.033	55.73	0.285	60.26	0.058
46.61	0.039	65.06	0.320	69.86	0.066
55.73	0.046	73.59	0.351	79.33	0.074

to three times at the same condition. The reproducibility was shown at less than ± 2 % deviation.

Experimental Procedure. The adsorbents in the basket were regenerated for more than 7 h at 613 K for zeolites 10X, 13X, and LiX and at 423 K for CMS in a vacuum conditions. The system was evacuated to the extent of less than 1.33×10^{-2} Pa by the vacuum pump and diffusion pump before the experiment. The adsorbate was supplied to the system through a fine valve during a short time (less than 0.5 s). The pressure of the adsorbate was increased in a stepwise manner from 0 to 80 kPa. To prevent the system from being contaminated by the pollutant, the system was flushed with He for more than 2 h after finishing each experiment.

Results and Discussion

Equilibrium data for oxygen, nitrogen, and argon onto CMS, zeolite 10X, zeolite 13X, and zeolite LiX were obtained at (293.15, 303.15, and 313.15) K at pressure up to 80 kPa.

The experimental data were compared with the previous published data in Figure 2. In the case of the N_2 on zeolite 13X, the experimental data were compared with the results on zeolite 13X (CECA, France) at 298 K and 308 K.[13] And, the equilibria of the O_2 on zeolite 13X were compared with the adsorption of oxygen on zeolite 13X (Linde) at 295 K.[14] Considering the

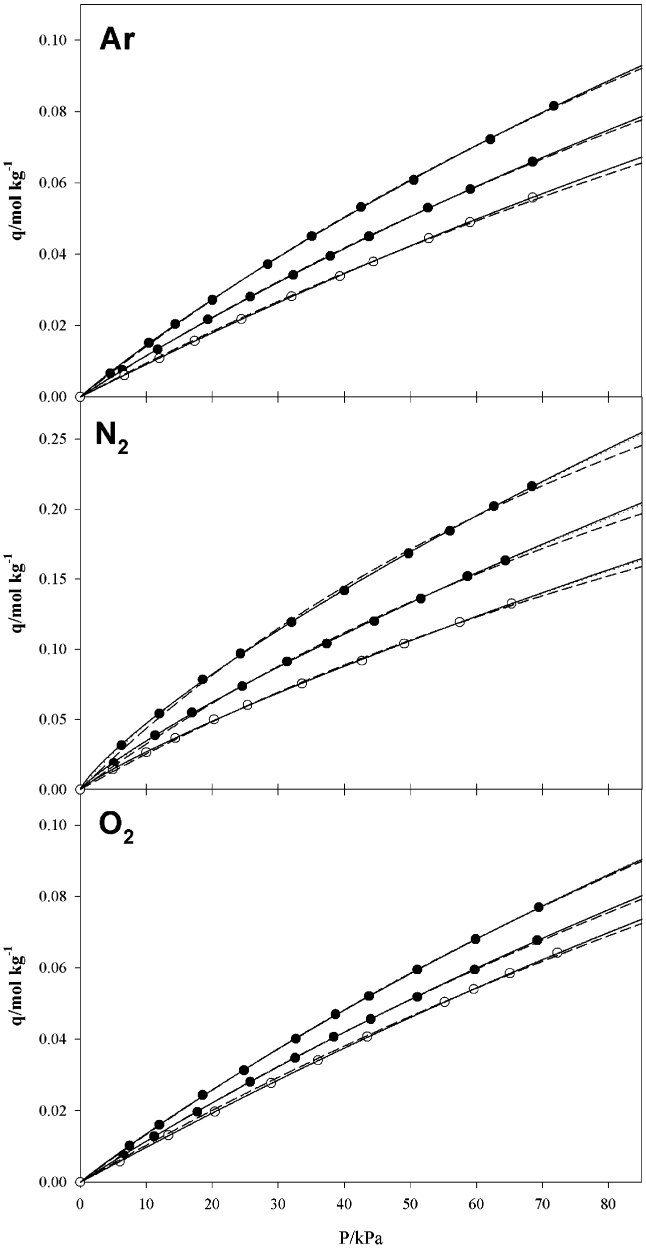

Figure 4. Adsorption isotherms on zeolite 10X: black, 293.15 K; gray, 303.15 K; white, 313.15 K; —, Sips; - - -, Langmuir; • • •, Toth.

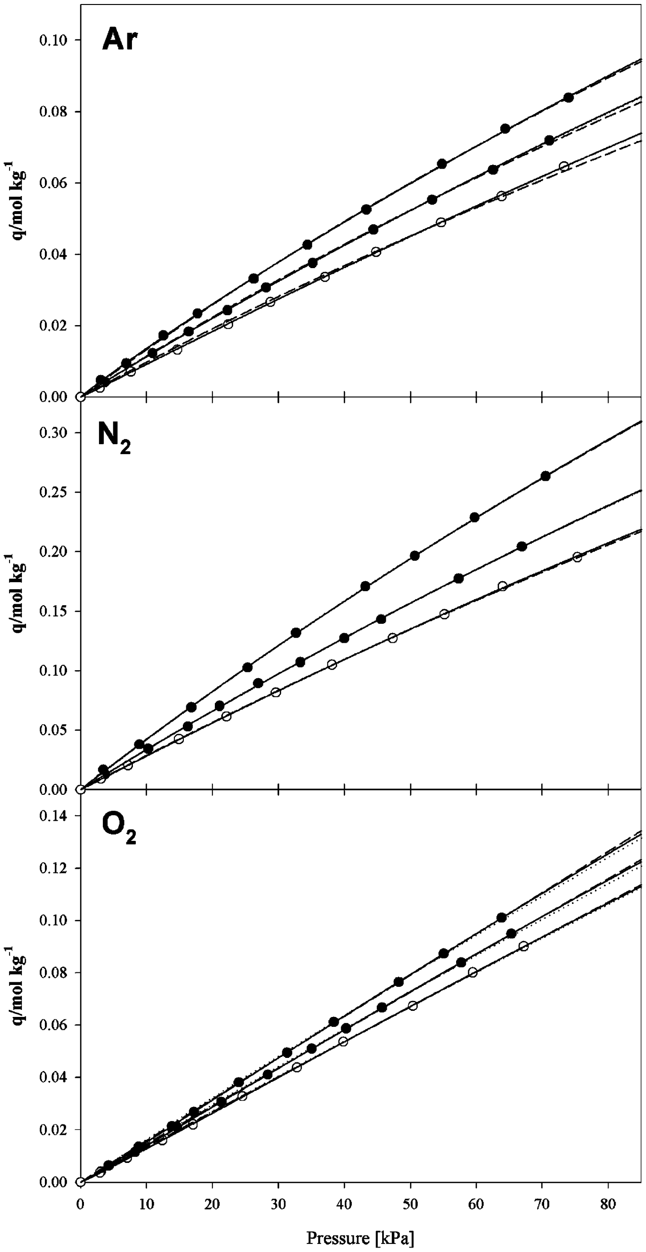

Figure 5. Adsorption isotherms on zeolite 13X: black, 293.15 K; gray, 303.15 K; white, 313.15 K; —, Sips; - - -, Langmuir; • • •, Toth.

difference in the adsorbent's manufacturers and experimental conditions {zeolite 13X from Baylith at (293.15, 303.15, and 313.15) K}, the experimental method and results were reasonable. In the case of the CMS, the experimental data are also similar to the published data measured at a low-pressure range.[15,16] However, in the case of different manufacturing companies of CMS,[8] the difference in the adsorbed amounts of O_2 and Ar was 16 % and 15 % from ours.

Experimental data are summarized in Tables 2 to 5 and presented graphically in Figures 3 to 6. All the isotherms on CMS show slightly convex curvature (favorable) as shown in Figure 3, and the difference in the adsorbed amount among adsorbates was not much. In the case of zeolites, the isotherm of O_2 was linear and that of Ar was almost linear (Figures 4 to 6). However, owing to slightly strong adsorption affinity of N_2, its isotherm was more favorable than those. Also, compared to other adsorbates, in cases of zeolites, N_2 shows higher temperature dependency.

For each set of equilibrium data, rigorous assessments were performed and correlated by several pure-species equilibrium models. In Figures 3 to 6, the experimental data were fitted by the following Langmuir, Sips, and Toth equations.[17]

Langmuir Isotherm. The Langmuir equation is widely used for physical adsorption from either gas or liquid solution. This expression is obtained from the rate expressions of both adsorption and desorption. The mathematical form of model is

$$q = \frac{q_m bP}{1 + bP} \tag{1}$$

where q is the amount adsorbed, P is the equilibrium pressure, and q_m and b are isotherm parameters.

Sips Isotherm. Recognizing the problem of the continuing increase in the amount adsorbed at increasing in pressure in the Freundlich equation, Sips proposed an equation similar in form to the Freundlich equation, but it has a finite limit when

Table 6. Isotherm Parameters Estimated for Ar

	CMS			zeolite 13X			zeolite 10X			zeolite LiX		
	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K
						Langmuir						
q_m/mol·kg^{-1}	0.856	0.714	0.573	0.493	0.480	0.465	0.345	0.328	0.310	0.486	0.449	0.421
$b \times 10^{-3}$/Pa	5.719	5.682	5.578	2.775	2.447	2.150	4.278	3.649	3.164	2.394	2.270	2.160
100 Δq	1.917	2.459	3.366	2.097	1.081	3.445	0.825	0.619	1.932	1.000	3.604	4.235
						Sips						
q_m/mol·kg^{-1}	2.088	1.895	1.769	0.793	0.747	0.677	0.476	0.430	0.391	0.470	0.454	0.401
$b \times 10^{-3}$/Pa	3.088	2.748	1.803	1.930	1.585	1.306	3.488	2.920	2.345	2.456	1.945	1.770
n	0.889	0.894	0.960	0.957	0.986	1.022	0.954	0.976	1.009	1.003	1.038	1.068
100 Δq	0.408	0.372	0.704	1.432	0.560	0.806	0.970	0.406	0.359	0.966	1.248	2.111
						Toth						
q_m/mol·kg^{-1}	30.89	18.67	5.309	1.364	0.959	0.603	0.768	0.664	0.391	0.451	0.385	0.359
b/kPa	15.02	17.98	80.13	107.4	304.9	2426	75.33	125.1	531.1	467.0	633.4	971.8
t	0.325	0.356	0.588	0.683	0.851	1.204	0.699	0.767	1.040	1.031	1.085	1.146
100 Δq	0.286	0.299	0.861	1.700	0.459	1.041	0.832	0.441	0.428	0.986	3.302	3.375

Table 7. Isotherm Parameters Estimated for N_2

	CMS			zeolite 13X			zeolite 10X			zeolite LiX		
	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K
						Langmuir						
q_m/mol·kg^{-1}	0.681	0.555	0.520	2.017	1.860	1.701	0.643	0.604	0.535	1.188	1.160	1.113
$b \times 10^{-3}$/Pa	9.119	7.522	6.827	2.135	1.840	1.722	7.267	5.695	4.982	8.800	7.068	6.231
100 Δq	2.893	2.803	1.867	1.670	0.748	0.947	2.717	2.504	2.538	1.601	3.278	0.855
						Sips						
q_m/mol·kg^{-1}	2.573	1.992	1.919	2.292	1.927	1.757	3.198	2.916	2.636	1.407	1.334	1.165
$b \times 10^{-3}$/Pa	3.825	3.052	2.259	1.933	1.788	1.596	2.268	1.677	1.378	8.552	6.169	6.141
n	0.806	0.842	0.891	0.989	0.997	1.010	0.820	0.856	0.873	0.946	0.988	0.988
100 Δq	0.405	0.331	0.814	1.515	0.724	0.922	0.699	0.802	0.742	0.919	3.078	0.648
						Toth						
q_m/mol·kg^{-1}	116.7	85.66	32.90	1.607	1.344	1.144	26.20	24.49	21.33	1.769	1.370	1.192
b/kPa	6.460	8.734	16.69	694.3	919.5	1996	10.16	14.44	17.59	46.14	131.8	134.6
t	0.212	0.236	0.319	1.103	1.141	1.267	0.289	0.316	0.332	0.761	0.951	0.955
100 Δq	0.588	0.522	0.760	1.732	0.793	0.874	0.595	0.683	0.694	0.751	3.142	0.752

Table 8. Isotherm Parameters Estimated for O_2

	CMS			zeolite 13X			zeolite 10X			zeolite LiX		
	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K
						Langmuir						
q_m/mol·kg^{-1}	1.167	1.129	0.976	24.97	23.39	21.68	0.382	0.372	0.363	0.983	0.963	0.939
$b \times 10^{-3}$/Pa	3.866	3.339	3.196	0.064	0.062	0.062	3.623	3.195	2.936	1.262	1.163	1.078
100 Δq	3.585	6.818	2.146	1.606	2.039	2.033	0.606	0.473	2.388	1.587	2.284	2.509
						Sips						
q_m/mol·kg^{-1}	4.066	3.739	3.515	1.396	1.317	1.223	0.482	0.449	0.423	0.585	0.578	0.533
$b \times 10^{-3}$/Pa	1.464	1.300	1.091	0.986	0.947	0.928	3.105	2.687	2.245	1.884	1.607	1.538
n	0.894	0.905	0.918	1.051	1.054	1.058	0.970	0.989	1.023	1.042	1.058	1.064
100 Δq	0.798	4.356	0.538	0.415	0.146	1.056	0.361	0.280	0.366	1.944	2.478	1.385
						Toth						
q_m/mol·kg^{-1}	86.20	49.71	21.01	2.531	2.283	1.945	0.797	0.625	0.308	19.11	7.184	6.926
b/kPa	18.72	24.45	35.70	1349	1551	6073	101.0	187.1	1604	177.2	481.0	669.2
t	0.308	0.347	0.413	0.982	1.003	1.199	0.732	0.836	1.286	0.497	0.703	0.735
100 Δq	1.420	4.926	1.050	2.920	3.282	2.703	0.310	0.283	0.485	1.597	1.968	1.666

the pressure is sufficiently high:[18]

$$q = \frac{q_m b P^n}{1 + bP^n} \tag{2}$$

where q_m, b, and n are isotherm parameters.

Toth Isotherm. The Toth isotherm[19] is a semiempirical expression that effectively describes many systems with submonolayer coverage. It is a three-parameter model usually written in the form:

$$q = \frac{q_m P}{(b + P^t)^{1/t}} \tag{3}$$

where P is equilibrium pressure; q is the number of adsorbed moles; and q_m, b, and t are isotherm parameters that are determined numerically. In this study, a nonlinear curve-fitting procedure was used to determine q_m, b, and t.

The parameters obtained from the best fit to the experimental data are summarized in Tables 6 to 8, with the average percent deviations Δq calculated according to

$$\Delta q = \frac{1}{k}\sum_{j=1}^{k}\left|\frac{q_j^{\mathrm{exp}} - q_j^{\mathrm{cal}}}{q_j^{\mathrm{exp}}}\right| \tag{4}$$

where k is the number of data points at a given temperature and q^{exp} and q^{cal} are the experimental and calculated values of adsorbed moles, respectively.

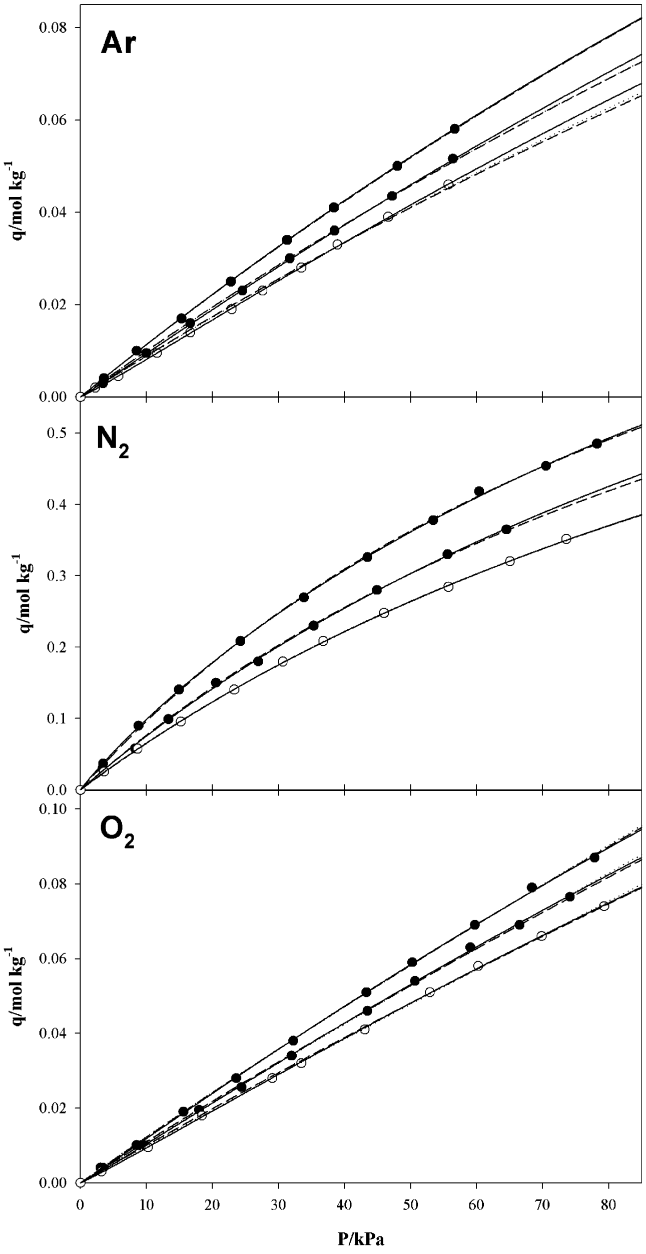

Figure 6. Adsorption isotherms on zeolite LiX: black, 293.15 K; gray, 303.15 K; white, 313.15 K; solid line, Sips; - - -, Langmuir; • • •, Toth.

Table 9. Overall Average Deviation (100 Δ*q*) of Each Equilibrium Isotherm Model: Langmuir, Sips and Toth

	CMS	zeolite 10X	zeolite 13X	zeolite LiX
		Langmuir		
Ar	2.58	1.13	2.21	2.95
N_2	2.52	2.59	1.12	1.91
O_2	4.18	1.16	1.89	2.13
average	3.10	1.62	1.74	2.33
		Sips		
Ar	0.48	0.58	0.93	1.44
N_2	0.52	0.75	1.05	1.55
O_2	1.90	0.34	0.54	1.94
average	0.97	0.56	0.84	1.64
		Toth		
Ar	0.48	0.57	1.07	2.55
N_2	0.62	0.66	1.13	1.55
O_2	2.47	0.36	2.97	1.74
average	1.19	0.53	1.71	1.95

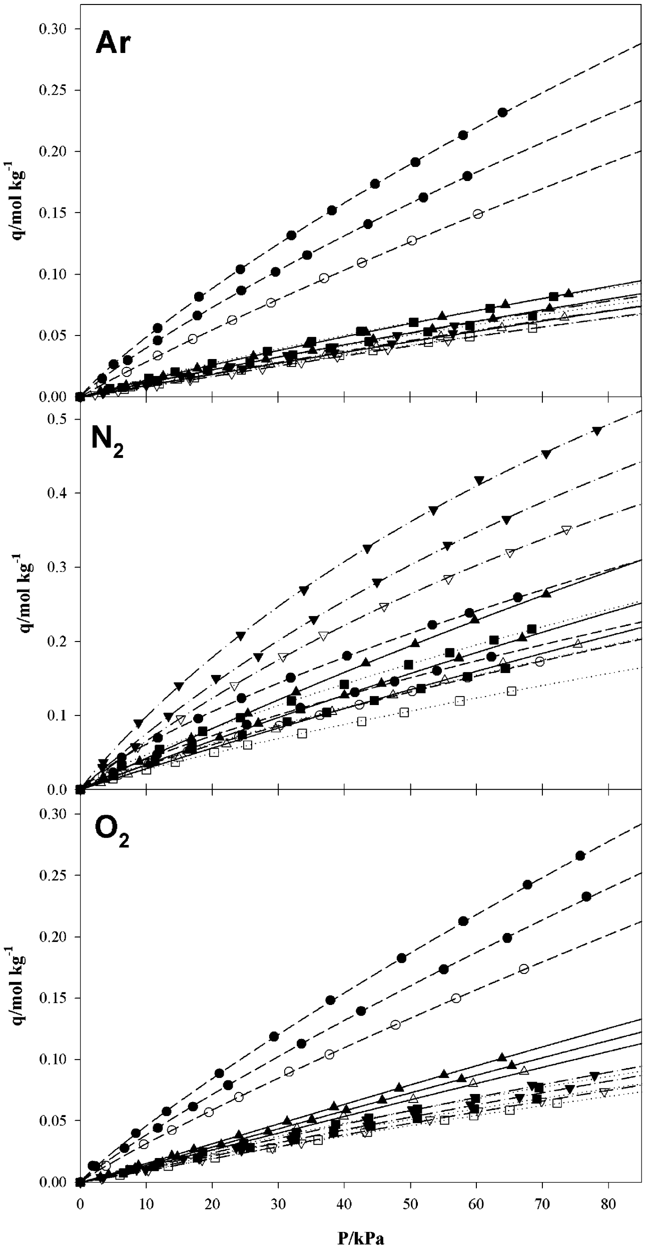

Figure 7. Adsorption isotherm of Ar, N_2, and O_2; ○, CMS; □, zeolite 10X; △, zeolite 13X; ▽, zeolite LiX; - - -, CMS; • • •, 10X; —, 13X; - • -, LiX; black, 293.15 K; gray, 303.15 K; white, 313.15 K.

In Tables 6 to 8, the parameters for each isotherm model were presented. All the isotherms agreed well with the experimental data. Especially, the Sips and Toth equations provided a better fit than Langmuir equation. In addition, Ar and N_2 show better agreement than O_2. Overall average deviations (100 Δ*q*) of each equilibrium isotherm model are detailed in Table 9.

Figure 7 shows the comparison of adsorption isotherm among the adsobents. Owing to comparatively larger surface area and more complex pore structure of CMS; the adsorbed amounts of Ar and O_2 were much larger than them on zeolites 10X, 13X, and LiX (Table 1). However, the adsorbed amount of N_2 on CMS was much smaller than that on zeolite LiX. In the case of zeolite LiX with smaller pore radius and larger surface area (Table 1), the adsorbed amount of N_2 and O_2 was larger than those on the other zeolites, but the difference in the adsorbed Ar amount among the zeolites was relatively small. Comparatively larger adsorption capacity in LiX is the result of the smaller ionic radius of Li^+ (0.68 Å) as compared to those of Na^+ (0.97 Å) and Ca^{2+} (0.99 Å).[20] Also the surface area, pore

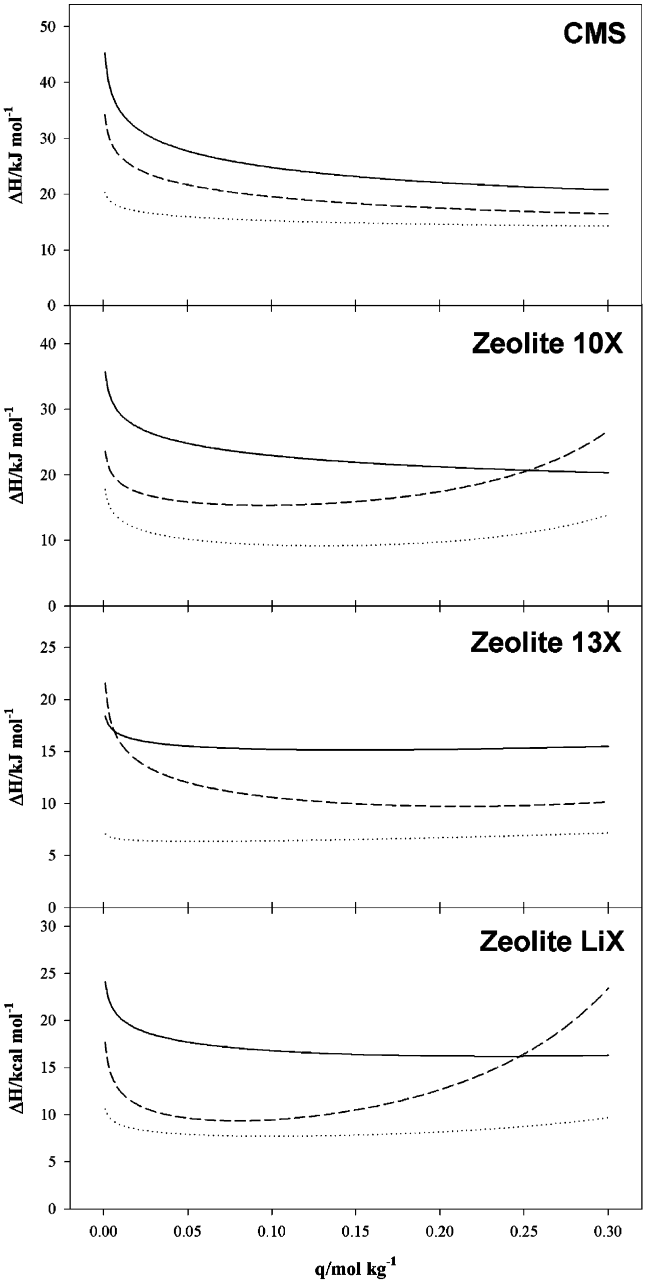

Figure 8. Isosteric enthalpy of adsorption with respect to surface loading: - - -, Ar; —, N_2; • • •, O_2.

volume, and pore radius structured by exchanging positive ion are the very important factors to determine the adsorption characteristics.[20] In addition, properties of adsorbate, such as quadrupole moment, dipole moment, polarizability (in this paper, Ar, N_2, and O_2 shows similar value), and molecular structure, greatly affect the affinities and capacities on each adsorbent. In ion exchange zeolite, such as 10X, 13X, and LiX, N_2 interacts strongly with the positive ion, such as Ca^{2+}, Na^{+}, and Li^{+}, to a significantly higher electric field gradient potential. Therefore, the adsorption affinity of N_2 on ion-exchanged zeolite increased because the relatively large quadrupole moment of N_2 leads to more favoable adsorption than Ar and O_2 on zeolites.[11,20]

Isosteric Enthalpies of Adsorption. Isosteric enthalpies of adsorption (q_{st})[21,22] could be calculated from the temperature dependence of the equilibrium capacity using the Clausius−Claypeyron equation (eq 5)[21] along with the Sips isotherm:

$$\frac{q_{st}}{RT^2} = \left(\frac{\partial \ln P}{\partial T}\right)_N \tag{5}$$

where q_{st} is the isosteric enthalpy of adsorption, P is the pressure, T is the temperature, and R is the gas constant.

When the surfaces are energetically homogeneous and there is no interaction between the adsorbed molecules, the isosteric enthalpy of adsorption is independent of the amount adsorbed.[21] However, if different levels of surface energy exist and the interactions between the adsorbed molecules cannot be neglected, then the isosteric heat of adsorption varies with the surface coverage. As shown in Figure 8, the isosteric enthalpy of each adsorbate on CMS was higher than that of the corresponding adsorbate on all the zeolites. In addition, the isosteric enthalpy of O_2 adsorption was almost constant and lower than others regardless of the adsorbents. And the average isosteric enthalpy of N_2 adsorption was highest at each adsorbent. The isosteric enthalpy of N_2 adsorption on CMS and zeolite 10X slightly decreased with an increase in the adsorbed amount, while that on zeolite 13X and zeolite LiX was almost constant after decreasing steeply in an infinite dilute region. In the case of Ar, zeolite 10X and zeolite LiX showed an increase in the isosteric enthalpy with the adsorbed amount.

Conclusions

The adsorption equilibria of the pure gases, such as argon, nitrogen, and oxygen, onto CMS, zeolite 10X, zeolite 13X, and zeolite LiX were measured in the pressure range of 0 to 80 kPa at (293.15, 303.15, and 313.15) K using a gravimetric method. The adsorbed amounts of Ar and O_2 on CMS were much larger than those on zeolite 10X, zeolite 13X, and zeolite LiX. However, the adsorbed amount of N_2 on CMS was much smaller than those on zeolite LiX and similar to that on zeolite 10X and zeolite 13X. In the case of zeolite LiX, the adsorbed amount of O_2 was larger than those on other zeolites, which was different from the Ar adsorption in the zeolites. The isosteric enthalpy of each adsorbate on CMS was higher than that of the corresponding adsorbate on all the zeolites. In addition, the isosteric enthalpy of O_2 adsorption was almost constant and lower than others regardless of the adsorbent. And the average isosteric enthalpy of N_2 adsorption was highest at each adsorbent. In the case of Ar, zeolite 10X and zeolite LiX showed an increase in the isosteric enthalpy with the adsorbed amount.

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