Pure and Multicomponent Adsorption Equilibrium of Carbon Dioxide, Ethylene, and Propane on ZSM-5 Zeolites with Different Si/Al Ratios

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Experimental adsorption isotherms of pure carbon dioxide, ethylene, and propane as well as their mixtures have been obtained on three samples of ZSM-5 zeolite of different atomic Si/Al ratios (15, 29, and 60) over the pressure range 0−100 kPa. The data are given at temperatures of 281, 293, and 308 K (pure data) and 293 K (binary and ternary data). Changes in the zeolite selectivity with its Si/Al ratio were observed for the pure components, with an increase in the loading of polar molecules, like carbon dioxide and ethylene, as the atomic Si/Al ratio decreases. The selectivity, however, was nearly constant for propane. The characteristic equilibrium curve was obtained for each adsorbent, and a good fit of the equilibrium data was obtained for all adsorbates at the three temperatures. Some equilibrium overadsorption and displacement effects with large deviations from the ideal behavior—including binary azeotropes—were found for the mixtures of polar and nonpolar compounds. Thus, ethylene and carbon dioxide are displaced by propane, showing a maximum in their individual adsorption isotherms in the binary mixtures. The Si/Al ratio of the zeolite was found to modify the azeotrope and overadsorption effects.

1. Introduction

The new advances in the field of adsorption and the development of new adsorbents have proved the usefulness of the adsorption as one of the most advantageous techniques for gas separation and purification. Adsorption is cleaner and less energy demanding than other separation techniques, like distillation and absorption, and as selective as them (Humprey, 1995; Keller, 1995). The design of industrial adsorption equipment requires the selection of the most beneficial adsorbent and also the availability of reliable equilibrium data and theoretical models for their accurate prediction. However, owing to the high number of adsorbents and gases, there is a lack of basic data, like mixture equilibrium data, required to design industrial equipment. Although there are many thermodynamic models to predict mixture adsorption equilibrium (Myers and Prausnitz, 1965; Costa et al., 1981; Cochran et al., 1985; Talu and Zwievel, 1986; Valenzuela et al., 1988), they still need pure and some of their binary equilibrium data to predict higher mixtures results. New methods based on molecular simulation (Allen and Tildesley, 1996), which do not need any experimental adsorption information, require a precise atomic description of both the adsorbate and the adsorbent and some physical information that is not always available or easy to determine. Hence, the experimental adsorption equilibrium data is essential, and moreover, it allows one to compare and validate the predictive models and to gain insights in the knowledge of the adsorption behavior depending on the adsorbate and adsorbent characteristics (geometry, chemical composition, etc.).

Despite the widespread use of the zeolites, there is no complete knowledge of the behavior of the adsorbate/zeolite systems. Therefore, it is of fundamental and practical importance to study new systems, which provide a clearer picture of adsorptive properties of the zeolites as a function of their structure, micropore size, chemical composition, and other properties.

In this paper, pure and multicomponent adsorption isotherms of carbon dioxide, ethylene and propane and their mixtures onto three samples of ZSM-5 zeolite (atomic Si/Al = 15, 29, and 60) were measured at temperatures of 281, 293, and 308 K (pure systems) and 293 K (binary and ternary systems) over a pressure range of 0−100 kPa. These components are frequently present in the refinery gas streams and usually have to be separated or purified. At the same time the three adsorbates have structures and properties different enough to exhibit a particular adsorption behavior, which is important for the comparison and validation of predictive and descriptive models, including the molecular simulation technique (Karavias and Myers, 1991; Myers et al., 1997). To complete the equilibrium picture, the so-called *characteristic equilibrium curve*, of each zeolite, has been obtained from the experimental equilibrium data, providing further information about the comparative behavior of adsorbents.

Table 1. Main Properties of the Synthesized Zeolites

Si/Al (atomic)	relative crystallinity (%)	particle size (μm)	crystal size (μm)
15	100	5.5	2
29	100	7.3	7
60	>99	12.0	12

2. Experimental Section

2.1. Materials. The three ZSM-5 zeolites with Si/Al ratio 15, 29, and 60 were obtained in the laboratory according to the procedure already established and previously published (Costa et al., 1987). Basically, the zeolites were prepared from a mixture of sodium silicate (27% SiO_2,

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Table 2. Adsorption Equilibrium Data of Pure Components on ZSM-5 (Si/Al = 15)

T = 281 K		T = 293 K		T = 309 K	
P/kPa	n/mol kg^{-1}	P/kPa	n/mol kg^{-1}	P/kPa	n/mol kg^{-1}
		Carbon Dioxide			
1.08	1.169	1.37	1.005	0.20	0.565
6.57	1.550	6.68	1.319	2.09	0.992
17.16	1.771	13.15	1.474	6.37	1.166
30.18	1.927	26.32	1.732	18.57	1.402
51.69	2.044	39.12	1.859	39.79	1.615
81.63	2.148	66.57	2.019	60.45	1.747
		91.02	2.114	88.75	1.869
		Ethylene			
0.73	1.068	0.18	0.738	2.79	0.965
7.41	1.521	3.46	1.149	7.00	1.140
16.03	1.698	8.56	1.323	12.75	1.275
32.82	1.849	14.06	1.423	24.49	1.445
51.44	1.944	41.06	1.730	44.52	1.588
81.15	2.035	53.63	1.808	68.14	1.741
		69.87	1.883	90.63	1.837
		92.30	1.990		
		Propane			
2.60	1.497	0.27	0.964	0.83	1.012
7.66	1.568	3.48	1.298	3.71	1.229
17.44	1.611	8.06	1.490	10.63	1.334
34.23	1.650	18.96	1.556	19.21	1.396
55.12	1.666	33.77	1.587	42.51	1.456
83.20	1.687	54.70	1.611	64.10	1.539
		71.51	1.626	90.37	1.605
		88.06	1.651		

Table 3. Adsorption Equilibrium Data of Pure Components on ZSM-5 (Si/Al = 30)

T = 281 K		T = 293 K		T = 309 K	
P/kPa	n/mol kg^{-1}	P/kPa	n/mol kg^{-1}	P/kPa	n/mol kg^{-1}
		Carbon Dioxide			
1.53	0.768	1.20	0.624	2.92	0.586
4.70	0.990	8.29	1.007	7.24	0.758
12.52	1.281	18.10	1.230	14.80	0.942
32.80	1.633	32.18	1.439	26.46	1.117
50.11	1.756	52.28	1.589	47.69	1.329
84.58	1.902	72.91	1.730	68.23	1.463
		94.94	1.832	92.33	1.602
		Ethylene			
1.32	0.779	2.07	0.727	2.14	0.613
4.83	1.083	5.17	0.936	5.87	0.804
12.40	1.385	11.23	1.165	14.68	1.053
31.79	1.663	21.31	1.382	26.69	1.241
56.22	1.796	42.81	1.587	39.10	1.379
82.19	1.899	62.77	1.733	61.55	1.531
		84.31	1.838	85.41	1.681
		Propane			
1.12	1.365	0.18	0.923	2.05	1.069
5.67	1.554	7.63	1.476	6.04	1.247
11.97	1.598	16.16	1.538	13.50	1.337
28.37	1.651	29.18	1.577	22.77	1.380
52.67	1.691	53.44	1.607	44.36	1.478
80.78	1.710	74.4	1.631	64.01	1.536
		91.20	1.665	87.24	1.594

8% Na_2O) and aluminum sulfate, using ethanol as promoter. Table 1 summarizes the main physical properties of the three zeolites. The Si/Al ratio of the samples was determined by both X-ray fluorescence (XRF) and atomic absorption spectroscopy (AA) measurements. Relative crystallinity of the adsorbents was obtained from X-ray diffraction (XRD) by comparing the intensity of the diffraction peak at $2\theta = 23.1°$ of the synthesized zeolites with a 100% crystalline pattern. Particle and crystal size and morphology of the powder zeolites were studied by Coulter counter and scanning electron microscopy (SEM). All the samples prepared showed similar properties to other ZSM-5 zeolite samples used in previous works (Calleja et al., 1995; Romero et al., 1996).

Table 4. Adsorption Equilibrium Data of Pure Components on ZSM-5 (Si/Al = 60)

T = 281 K		T = 293 K		T = 309 K	
p/kPa	n/mol kg^{-1}	p/kPa	n/mol kg^{-1}	p/kPa	n/mol kg^{-1}
		Carbon Dioxide			
1.39	0.329	0.18	0.150	1.86	0.207
4.41	0.521	0.67	0.225	6.33	0.656
10.30	0.735	1.96	0.340	14.00	0.512
17.92	0.903	4.29	0.443	22.00	0.658
25.94	1.060	8.69	0.580	30.29	0.799
37.02	1.231	16.07	0.731	39.70	0.914
52.54	1.375	22.04	0.835	49.60	1.017
		26.10	0.898	63.23	1.114
		32.99	0.984	73.92	1.196
		37.67	1.030	84.67	1.279
		50.33	1.139		
		57.95	1.200		
		63.16	1.241		
		78.97	1.360		
		81.44	1.377		
		Ethylene			
1.90	0.487	0.23	0.228	1.65	0.213
4.36	0.693	1.95	0.421	5.13	0.383
9.15	0.928	4.53	0.597	11.02	0.580
16.27	1.106	8.32	0.743	18.05	0.749
25.74	1.225	9.86	0.795	25.72	0.905
38.99	1.340	14.86	0.908	39.07	1.009
51.01	1.393	19.15	0.982	57.29	1.168
		22.99	1.036	83.17	1.313
		39.16	1.146		
		51.05	1.213		
		58.70	1.258		
		77.45	1.334		
		82.72	1.352		
		Propane			
0.18	0.630	0.10	0.387	0.68	0.495
0.88	0.980	0.37	0.614	3.07	0.863
4.27	1.172	0.76	0.753	8.96	1.062
12.17	1.243	1.35	0.904	19.05	1.164
21.67	1.275	2.83	1.012	33.90	1.238
35.01	1.307	6.25	1.106	49.70	1.290
51.69	1.335	7.73	1.135	65.87	1.328
		15.77	1.208	84.43	1.399
		40.18	1.294		
		69.44	1.349		
		86.03	1.369		

The powder zeolites were pelletized using a commercial bentonite (supplied by Minas de Gador, Almería, Spain) because of its low content of impurities. Final particles were nearly cylindrical with ca. 5 mm diameter, 3−6 mm length. The adsorbent bed diameter was 5.1 cm, the bed height 40.0 cm, the particle density 0.88 g/cm^{-3}, and the bed porosity 0.30. Pure gases were supplied by S.E.O. (Sociedad Española de Oxígeno) with purity higher than 99.5%. This purity was periodically checked in the laboratory by gas chromatography analysis.

2.2. Apparatus and Procedure. The volumetric apparatus used for obtaining the experimental isotherms has been described elsewhere (Costa et al., 1981; Costa et al., 1991). It consists of a glass closed circuit with a fixed bed of adsorbent, 5.1 cm i.d. and 65 cm length, a stainless steel compressor to recirculate the gas phase through the bed, a bypass to homogenize the mixture before the adsorption, and a volumetric system to introduce and measure the gases admitted in the circuit.

Prior to the adsorption runs, the adsorbent was previously weighed, placed in the adsorption bed, and regenerated at 270 °C under vacuum of 15 Pa for 12 h. The gas introduced, previously measured and homogenized (in the

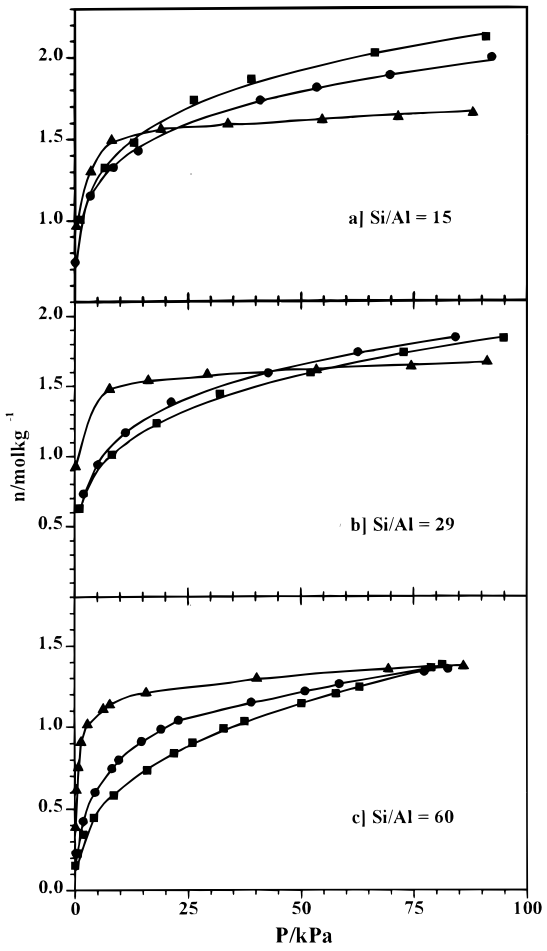

Figure 1. Adsorption isotherms of pure gases at 293 K on ZSM-5 zeolites: (a) Si/Al = 15, (b) Si/Al = 29, and (c) Si/Al = 60; (■) carbon dioxide, (●) ethylene, and (▲) propane.

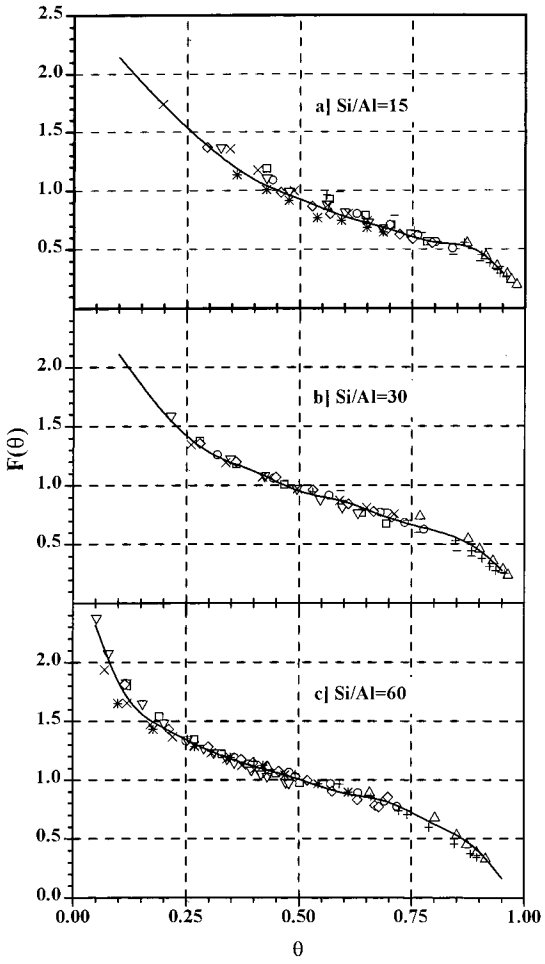

Figure 2. Characteristic equilibrium adsorption curves of ZSM-5 zeolites: (a) Si/Al = 15, (b) Si/Al = 29, and (c) Si/Al = 60; (□) carbon dioxide at 281 K, (○) ethylene at 281 K, (△) propane at 281 K, (▽) carbon dioxide at 293 K, (◇) ethylene at 293 K, (+) propane at 293 K, (×) carbon dioxide at 301 K, (*) ethylene at 301 K, (—) propane at 301 K.

case of a mixture), was circulated through the adsorbent bed until the equilibrium was reached, observing at this point constant values of pressure, temperature, and gas composition (for mixture isotherms). The amount adsorbed was calculated in each run by mass balance and P−V−T measurements using the virial gas equation of state.

The analysis of the gas phase was made by gas chromatography using a Porapack-Q column ($^1/_8$ in. diameter) and a thermal conductivity detector. The partial pressures determined by this technique showed deviations smaller than 3%. The temperature was kept constant within ±0.5 °C, and the deviation errors in the pressure and volumetric measurements were less than 0.015 kPa and 0.1 cm^3, respectively. To check the accuracy of the experiments, several runs were repeated in identical conditions, obtaining in all cases a good reproducibility, with deviations of the amount adsorbed smaller than 5%, which are typical errors found for the volumetric method technique (Olivier and Jadot, 1997; Berlier and Frère, 1997).

3. Results

3.1. Pure Components. Previous experiments confirmed that the three adsorbates show physical adsorption on these zeolites since the adsorption and desorption isotherms were practically coincident during several adsorption−desorption cycles. It was also observed that the bentonite does not show adsorption properties in the conditions studied, compared to the zeolites.

Tables 2, 3, and 4 show the adsorption equilibrium isotherms for the three compounds (carbon dioxide, ethylene, and propane) at three temperatures (281, 293, and 308 K). As shown, the loading of all the adsorbates are of the same order of magnitude, which means that there is no molecular sieve effect for these gases on the channels of the ZSM-5 zeolite. On the other hand, the increase of the loading with decreasing temperature shows that the adsorption process is exothermic, as expected. All the isotherms correspond to type I, according to the classification proposed by IUPAC.

It is interesting to observe the effect of the Si/Al ratio of the adsorbent on the selectivity. As shown in Figure 1, there is a change in the relative adsorption capacity of the zeolites with the Si/Al ratio, the loading of carbon dioxide and ethylene being increased for lower Si/Al ratios, whereas the loading of propane remains nearly constant. This effect is even more important for carbon dioxide than for ethylene. The explanation is related to the chemical structure of both the adsorbates and the adsorbent. The substitution of Si^{4+} for Al^{3+} into the ZSM-5 lattice generates a charge default in the zeolite that is compensated by other cations, so that there are more charged sites on the surface as the Si/Al ratio of the zeolite decreases. On the other hand, carbon dioxide and ethylene are molecules with a large quadrupole moment (-1.43×10^{13} and -1.31×10^{13} C m^2, respectively), and thus the interaction with the electric field inside the micropores of the zeolite is higher. This effect is larger for the carbon dioxide molecule, which has a

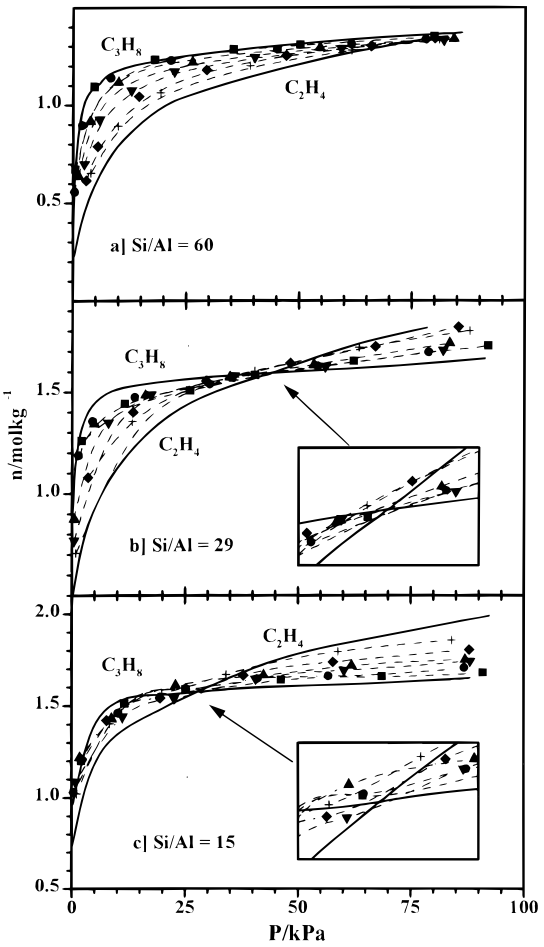

Figure 3. Experimental adsorption isotherms of binary mixtures of ethylene (1) and propane (2) in ZSM-5 zeolites (Si/Al ratio = 60, 29, and 15) at 293 K. Solid lines; pure data; dashed lines; mixture data. Initial volumetric ratios, v_1/v_2: (■) 1/8; (●) 1/4; (▲) 1/2; (▼) 1/1; (◆) 2/1; (+) 4/1. (a) Si/Al = 60, (b) Si/Al = 29, and (c) Si/Al = 15.

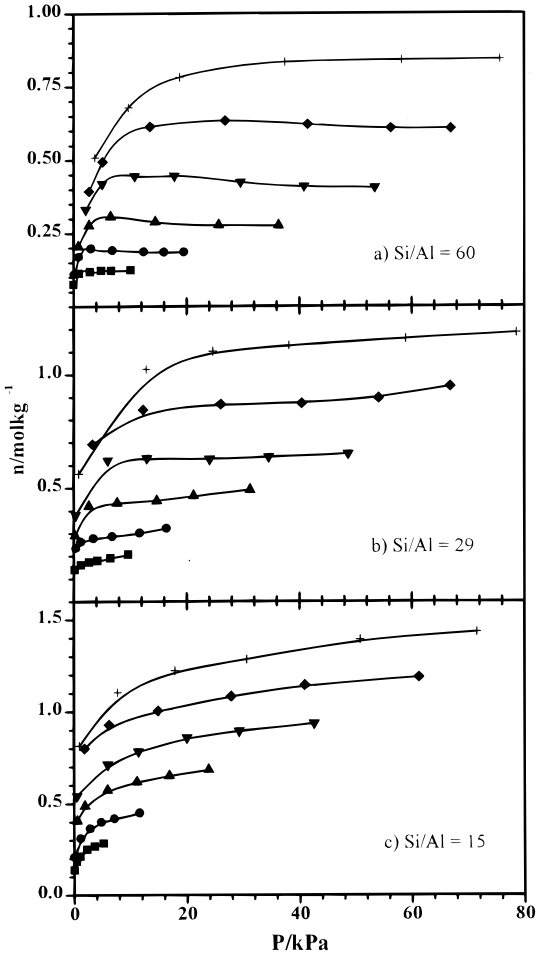

Figure 4. Experimental individual adsorption isotherms of ethylene in the mixture of ethylene (1) + propane (2) in ZSM-5 zeolites (Si/Al ratio = 60, 29, and 15) at 293 K. Initial volumetric ratios, v_1/v_2: (■) 1/8; (●) 1/4; (▲) 1/2; (▼) 1/1; (◆) 2/1; (+) 4/1. (a) Si/Al = 60, (b) Si/Al = 29, and (c) Si/Al = 15.

quadrupole moment higher than that for the ethylene molecule, dispersion forces becoming dominant as the Si/Al ratio of ZSM-5 increases. A similar behavior was found in previous works (Dunne et al., 1996; Calleja et al., 1994, Costa et al., 1991).

To characterize the behavior of a given adsorbent, it is also useful to reduce all isotherms of the different adsorbates at various temperatures to a single equilibrium curve, characteristic of the adsorbent. Such a curve, called the characteristic equilibrium curve, $F(\theta)$, was deduced by Myers and Sircar (1985) for heterogeneous adsorbents and is expressed in terms of the reduced amount adsorbed, θ, defined as the ratio of the amount adsorbed at a given pressure, n, and the amount adsorbed at saturation, n_s

$$F(\theta) = \frac{n_s RT \ln\left(\frac{p}{p_s}\right)}{\Delta G_i} = \frac{n_s}{\Delta G_i}(-\epsilon) \qquad (1)$$

where p is the pressure, T the temperature, ΔG_i the free energy of immersion, and ϵ the adsorption potential of Polanyi. The free energy of immersion is expressed by the following equation:

$$\Delta G_i = RT\int_0^n \ln\frac{p}{p_s}\,\mathrm{d}n \qquad (2)$$

It can be shown that $F(\theta)$ is related to the adsorption potential of Polanyi but the term $n_s/\Delta G_i$ transforms it into a dimensionless function that should be the same for different adsorbates on the same adsorbent at any temperature.

The experimental data shown in Tables 2−4 were used to calculate the characteristic equilibrium adsorption function, $F(\theta)$, for all the adsorbates at the three temperatures studied, for every individual zeolite. For this calculation, the saturation capacity, n_s, was estimated by means of Gurvitsch's rule, being the detailed calculation procedure described earlier (Costa et al., 1984). Figure 2 shows the results obtained with a good fitting of the equilibrium data. It is also observed that the characteristic equilibrium curves for the three adsorbents are almost coincident, although the isotherms of the polar sorbates showed significant differences with the Si/Al ratio. Therefore, a unique characteristic curve could be proposed for the zeolite, regardless of the Si/Al ratio, but taking into account that its accuracy decreases for low relative coverage values. These results confirm the validity of the characteristic equilibrium curve, which provides a useful way to predict approximate values of adsorption equilibrium data of any adsorbate at any temperature for a given adsorbent, provided that no significant extrapolation is done (Costa et al., 1984).

3.2. Binary Mixtures. The adsorption isotherms of the binary systems carbon dioxide + ethylene, carbon dioxide

Table 5. Binary Adsorption Equilibrium Data on ZSM-5 (Si/Al = 15) at 293 K

$(v_1/v_2)_0$	p_1/kPa	p_2/kPa	n_1/mol kg^{-1}	n_2/mol kg^{-1}	$(v_1/v_2)_0$	p_1/kPa	p_2/kPa	n_1/mol kg^{-1}	n_2/mol kg^{-1}
				Carbon Dioxide (1) + Ethylene (2)					
1/8	0.81	3.44	0.121	1.025	1/1	1.40	0.55	0.522	0.538
	1.70	8.55	0.139	1.203		5.83	3.00	0.645	0.698
	2.94	16.22	0.155	1.382		10.23	5.91	0.700	0.781
	5.21	31.13	0.171	1.579		18.42	12.16	0.802	0.926
	8.40	54.11	0.180	1.698		30.78	22.71	0.863	1.025
	10.86	73.08	0.186	1.763		49.84	49.86	0.917	1.132
1/4	0.70	1.17	0.190	0.791	2/1	3.63	0.43	0.798	0.418
	2.96	7.07	0.250	1.091		8.37	2.09	0.920	0.499
	5.41	14.49	0.281	1.266		15.61	4.39	1.014	0.566
	8.42	23.98	0.306	1.419		27.39	8.83	1.136	0.664
	14.06	45.72	0.323	1.547		46.19	16.86	1.225	0.736
	20.04	67.11	0.346	1.645		69.55	26.48	1.281	0.807
1/2	1.94	1.79	0.377	0.792	4/1	1.84	0.15	0.843	0.217
	4.62	5.13	0.430	0.936		9.74	1.17	1.134	0.307
	8.36	10.47	0.472	1.061		19.02	2.66	1.289	0.363
	14.18	19.75	0.534	1.241		30.22	4.64	1.395	0.406
	23.90	36.42	0.563	1.352		48.94	8.55	1.504	0.449
	33.34	54.36	0.594	1.431		73.07	14.32	1.603	0.504
				Carbon Dioxide (1) + Propane (2)					
1/8	0.40	1.70	0.131	1.078	1/1	1.41	0.48	0.567	0.584
	1.49	9.60	0.163	1.348		4.21	1.79	0.639	0.682
	2.81	21.95	0.175	1.405		12.59	7.48	0.733	0.829
	4.83	42.01	0.189	1.443		21.98	15.93	0.791	0.907
	6.93	62.55	0.201	1.459		33.95	29.09	0.837	0.930
	8.99	82.84	0.221	1.469		47.44	42.31	0.856	0.953
1/4	0.23	0.37	0.204	0.826	2/1	0.96	0.08	0.801	0.205
	1.38	3.32	0.252	1.049		3.75	0.41	0.988	0.254
	4.04	13.34	0.294	1.231		10.40	0.83	1.157	0.321
	8.39	32.76	0.332	1.342		32.31	4.09	1.350	0.411
	12.32	52.26	0.359	1.372		59.13	9.26	1.424	0.560
	17.35	75.69	0.377	1.385		79.63	12.72	1.442	0.588
1/2	0.87	0.72	0.365	0.747	4/1	1.40	0.05	0.898	0.114
	3.53	3.97	0.452	0.961		7.37	0.24	1.287	0.174
	9.45	14.29	0.511	1.111		20.03	0.78	1.416	0.209
	15.45	27.45	0.532	1.128		36.55	1.71	1.510	0.241
	21.44	40.85	0.555	1.148		63.92	4.02	1.659	0.284
	30.34	62.54	0.586	1.143		83.44	5.46	1.710	0.310
				Ethylene (1) + Propane (2)					
1/8	0.11	2.20	0.136	1.062	1/1	0.45	0.37	0.542	0.544
	0.53	11.27	0.184	1.327		5.99	5.21	0.713	0.727
	1.17	24.05	0.210	1.376		11.41	11.22	0.784	0.756
	2.40	44.01	0.247	1.391		19.95	20.72	0.858	0.786
	3.70	65.14	0.265	1.391		29.25	31.00	0.893	0.799
	5.28	85.74	0.281	1.395		42.61	45.55	0.935	0.807
1/4	0.07	0.45	0.206	0.820	2/1	1.83	0.47	0.801	0.409
	1.21	9.12	0.309	1.150		6.18	1.54	0.928	0.493
	2.89	22.42	0.363	1.228		14.87	4.65	1.004	0.539
	4.88	36.29	0.397	1.246		27.83	10.14	1.083	0.582
	7.16	49.77	0.416	1.242		40.97	16.83	1.145	0.592
	11.62	75.33	0.447	1.257		61.23	26.74	1.188	0.615
1/2	0.52	1.23	0.407	0.810	4/1	0.95	0.11	0.814	0.206
	1.93	6.90	0.487	0.942		7.74	0.64	1.104	0.300
	5.89	17.05	0.573	1.307		17.85	2.01	1.223	0.344
	11.14	31.25	0.616	1.049		30.65	3.48	1.284	0.386
	16.87	45.11	0.650	1.067		50.78	8.14	1.391	0.402
	23.87	63.20	0.683	1.068		71.56	12.50	1.433	0.424

+ propane, and ethylene + propane in the three ZSM-5 zeolites were obtained at 293 K over the total pressure range 0−100 kPa. For each binary system, six different initial volumetric ratios of the two components were studied: $(v_1/v_2)_0$ = 1/8, 1/4, 1/2, 1/1, 2/1, and 4/1. These results are given in Tables 5−7.

According to these data, Figure 3 shows the experimental adsorption isotherms of the whole mixture ethylene (1) + propane (2) on the three zeolites and the isotherms of the pure components included as a reference. As observed, the collection of global isotherms in the ZSM-5 of Si/Al = 60 lies always between the isotherms of the pure components, as expected. However, this is not the case for the other zeolites (Si/Al = 29 and 15), where the amount adsorbed of the binary mixture can be larger than the amount adsorbed of the pure component more readily adsorbed, as shown in the pressure range around the crossing point of the curves. In this situation, there is no single crossing point of all binary isotherms, the pressure range where the scattering takes place being slightly larger for smaller Si/Al ratios. It was checked that this effect is not merely the result of experimental data dispersion but actually the consequence of the overadsorption phenomena previously mentioned.

The overadsorption effect shown by the ethylene + propane mixtures, which also occurs with the carbon dioxide + propane mixtures, does not appear, however, in the mixture of carbon dioxide + ethylene, where both molecules are polar. This type of behavior was already found in other systems (Costa et al., 1991) and indicates a

Table 6. Binary Adsorption Equilibrium Data on ZSM-5 (Si/Al = 29) at 293 K

$(v_1/v_2)_0$	p_1/kPa	p_2/kPa	n_1/mol kg^{-1}	n_2/mol kg^{-1}	$(v_1/v_2)_0$	p_1/kPa	p_2/kPa	n_1/mol kg^{-1}	n_2/mol kg^{-1}
				Carbon Dioxide (1) + Ethylene (2)					
1/8	0.90	3.82	0.095	0.806	1/1	1.47	0.58	0.345	0.355
	1.60	8.05	0.112	0.988		4.85	2.40	0.467	0.522
	3.07	17.35	0.135	1.217		9.44	5.40	0.545	0.656
	5.29	31.43	0.151	1.396		20.28	13.39	0.673	0.809
	8.66	54.16	0.166	1.565		31.11	22.99	0.711	0.927
	11.07	73.48	0.174	1.660		49.20	38.88	0.779	1.046
1/4	0.67	1.12	0.140	0.581	2/1	3.61	0.45	0.544	0.293
	2.07	4.55	0.187	0.803		8.18	2.11	0.675	0.395
	3.80	9.31	0.208	0.987		15.64	4.40	0.808	0.483
	7.77	22.11	0.262	1.217		27.05	9.01	0.923	0.563
	14.45	45.76	0.294	1.404		46.47	16.97	1.026	0.671
	19.95	66.78	0.317	1.513		67.61	25.74	1.096	0.735
1/2	2.23	2.06	0.281	0.592	4/1	2.45	0.23	0.584	0.156
	4.39	4.87	0.338	0.735		9.78	1.18	0.833	0.235
	8.88	11.12	0.407	0.915		18.90	2.65	1.002	0.298
	15.14	20.90	0.458	1.062		28.75	4.41	1.112	0.343
	21.38	31.94	0.479	1.161		50.35	8.51	1.239	0.413
	33.34	52.92	0.498	1.327		78.82	14.50	1.349	0.477
				Carbon Dioxide (1) + Propane (2)					
1/8	0.87	1.25	0.121	1.119	1/1	0.15	0.07	0.480	0.483
	2.74	8.13	0.119	1.322		7.04	1.11	0.587	0.746
	4.95	19.25	0.110	1.417		17.86	4.86	0.590	0.936
	6.84	32.34	0.107	1.452		29.59	10.69	0.569	1.069
	9.52	52.05	0.108	1.506		41.20	19.80	0.551	1.118
	11.98	71.19	0.115	1.575		58.64	35.18	0.572	1.192
1/4	1.20	0.67	0.211	0.953	2/1	9.35	0.18	0.908	0.284
	6.93	10.19	0.206	1.285		13.65	0.35	0.986	0.328
	9.01	15.76	0.199	1.330		30.33	1.16	1.121	0.449
	14.68	35.71	0.194	1.384		51.42	2.49	1.143	0.600
	18.20	48.17	0.199	1.444		80.80	5.71	1.131	0.667
	23.22	68.12	0.211	1.501					
1/2	1.75	0.17	0.343	0.773	4/1	4.00	0.18	0.662	0.380
	5.65	2.22	0.385	1.010		12.62	0.92	0.819	0.552
	14.00	10.25	0.361	1.188		25.56	2.37	0.857	0.704
	21.73	22.32	0.351	1.257		40.67	5.34	0.841	0.817
	28.92	35.22	0.355	1.305		55.79	10.00	0.820	0.883
	35.72	46.98	0.368	1.379		70.25	15.43	0.822	0.932
				Ethylene (1) + Propane (2)					
1/8	0.29	1.87	0.138	1.118	1/1	0.36	0.07	0.380	0.388
	1.35	10.36	0.158	1.282		6.01	1.94	0.620	0.728
	2.76	23.32	0.170	1.336		12.92	4.42	0.630	0.857
	4.29	36.23	0.178	1.381		24.08	11.69	0.624	0.955
	6.59	55.65	0.190	1.451		34.57	21.38	0.636	0.989
	9.70	92.33	0.205	1.520		48.70	33.34	0.648	1.058
1/4	0.44	1.03	0.233	0.953	2/1	3.31	0.19	0.693	0.386
	1.30	3.26	0.260	1.093		12.23	1.14	0.845	0.556
	3.49	10.41	0.275	1.197		25.98	3.59	0.869	0.686
	6.81	23.64	0.285	1.235		40.44	7.74	0.872	0.771
	11.70	42.57	0.300	1.317		54.14	12.96	0.896	0.827
	16.47	62.46	0.320	1.373		66.83	18.59	0.948	0.873
1/2	0.21	0.19	0.289	0.584	4/1	0.86	0.02	0.562	0.145
	2.67	2.19	0.419	0.923		12.81	0.43	1.025	0.330
	7.63	8.44	0.434	1.051		24.56	1.07	1.102	0.411
	14.70	20.11	0.441	1.132		38.17	2.11	1.128	0.474
	21.17	32.24	0.464	1.170		58.96	4.49	1.158	0.562
	31.20	52.31	0.489	1.249		80.03	7.86	1.182	0.618

nonideal behavior of the mixture. It can be explained by a synergetic effect due to the adsorbate−adsorbate interactions over the adsorbent surface, which can take place between molecules of very different nature. Carbon dioxide and ethylene are both polar molecules and have a nonzero quadrupole moment so that they interact with the electric field inside the zeolite pores, which is higher for low Si/Al ratios. The presence of another adsorbate of different nature in their mixtures can modify the attractive and repulsive forces with the adsorbent and enhance its affinity for the mixture. The electrostatic interactions between the adsorbate and the adsorbent are expected to be negligible for the zeolite of higher Si/Al ratio (lower aluminum content and therefore weaker electric field) and much more appreciable for lower Si/Al ratios. Carbon dioxide and ethylene molecules, being more similar in polarity, do not show the same synergetic effect in their binary mixtures, and therefore no overadsorption effect is shown.

To complete this picture, Figure 4 shows the individual isotherms of ethylene in the mixture ethylene (1) + propane (2) for the three ZSM-5 zeolites and for different initial volumetric ratios of both components. Most of the individual isotherms of ethylene show a slight maximum at low partial pressures when the Si/Al ratio of the zeolite is high, but the maximum vanishes for low Si/Al ratios. This means that ethylene is displaced by propane when the electrostatic field of the zeolite is weak, and as a consequence the polarity of the molecule does not play an important role. However, when the aluminum content increases (smaller Si/Al ratios) and the dispersion forces

Table 7. Binary Adsorption Equilibrium Data on ZSM-5 (Si/Al = 60) at 293 K

$(v_1/v_2)_0$	p_1/kPa	p_2/kPa	n_1/mol kg^{-1}	n_2/mol kg^{-1}	$(v_1/v_2)_0$	p_1/kPa	p_2/kPa	n_1/mol kg^{-1}	n_2/mol kg^{-1}
				Carbon Dioxide (1) + Ethylene (2)					
1/8	1.01	4.15	0.055	0.526	1/1	2.07	0.88	0.182	0.208
	1.95	9.41	0.073	0.721		5.08	2.73	0.268	0.319
	3.47	17.31	0.085	0.905		9.25	5.24	0.330	0.416
	5.38	30.10	0.097	1.039		18.25	11.89	0.438	0.575
	7.68	45.73	0.102	1.136		26.17	18.50	0.495	0.660
	9.28	57.23	0.106	1.200		35.40	26.43	0.529	0.722
	11.19	71.31	0.111	1.258		49.08	36.48	0.535	0.806
1/4	1.29	2.56	0.087	0.402	2/1	2.60	0.50	0.250	0.142
	3.07	6.96	0.124	0.611		7.19	1.86	0.380	0.228
	5.30	13.62	0.152	0.772		13.31	3.62	0.478	0.304
	5.30	13.62	0.152	0.772		13.31	3.62	0.478	0.304
	9.40	26.74	0.178	0.945		22.30	6.92	0.591	0.387
	12.35	36.86	0.190	1.029		32.34	11.00	0.679	0.451
	15.47	47.96	0.198	1.092		44.73	15.12	0.717	0.515
	19.41	62.64	0.207	1.152		59.85	21.42	0.773	0.570
1/2	2.95	3.08	0.165	0.391	4/1	4.70	0.52	0.357	0.103
	6.78	8.26	0.234	0.583		11.67	1.56	0.510	0.157
	11.85	15.70	0.277	0.728		19.66	2.92	0.642	0.204
	17.36	24.67	0.311	0.838		33.50	5.36	0.801	0.265
	23.29	35.07	0.334	0.917		50.35	8.06	0.893	0.321
	31.99	51.07	0.363	1.001		67.50	11.63	0.980	0.358
				Carbon Dioxide (1) + Propane (2)					
1/8	0.53	0.63	0.066	0.603	1/1	4.92	0.47	0.340	0.432
	2.28	4.01	0.085	0.990		9.59	1.04	0.390	0.568
	4.59	14.83	0.083	1.138		19.43	3.19	0.406	0.744
	7.03	33.07	0.082	1.205		30.76	8.09	0.390	0.862
	9.46	49.31	0.083	1.232		42.12	15.34	0.373	0.930
	11.95	68.81	0.086	1.269		54.54	25.22	0.370	0.978
1/4	1.30	0.63	0.126	0.602	2/1	3.92	0.18	0.363	0.218
	3.83	2.50	0.148	0.867		8.74	0.38	0.483	0.324
	7.60	8.62	0.143	1.045		16.28	0.79	0.548	0.426
	11.61	18.93	0.133	1.127		28.07	1.78	0.596	0.551
	15.30	31.27	0.129	1.164		42.59	3.90	0.591	0.655
	18.77	44.11	0.131	1.191		57.27	7.22	0.577	0.730
	22.97	60.26	0.136	1.225		71.45	11.49	0.578	0.788
1/2	1.50	0.35	0.190	0.436	4/1	7.06	0.12	0.444	0.145
	5.51	1.49	0.255	0.710		15.02	0.28	0.573	0.215
	12.75	5.99	0.251	0.910		26.58	0.53	0.700	0.302
	20.41	15.11	0.239	1.014		41.41	1.07	0.761	0.383
	27.53	26.79	0.238	1.065		57.77	1.96	0.787	0.456
	37.75	45.48	0.246	1.118		74.53	3.26	0.804	0.519
				Ethylene (1) + Propane (2)					
1/8	0.09	0.48	0.074	0.595	1/1	2.12	0.35	0.331	0.368
	0.99	3.87	0.112	0.980		5.01	0.82	0.419	0.507
	2.95	15.16	0.117	1.113		10.78	2.11	0.446	0.628
	4.93	30.64	0.121	1.160		17.84	4.49	0.445	0.725
	6.69	43.56	0.121	1.184		29.53	10.62	0.423	0.819
	10.16	69.85	0.123	1.226		40.86	18.46	0.409	0.878
						53.45	28.63	0.406	0.924
1/4	0.15	0.30	0.110	0.445	2/1	2.72	0.18	0.394	0.222
	0.94	1.17	0.168	0.728		5.07	0.32	0.495	0.294
	3.14	5.22	0.196	0.940		13.54	0.94	0.613	0.430
	6.94	14.75	0.190	1.034		26.83	2.60	0.632	0.545
	12.43	32.77	0.184	1.097		41.52	5.52	0.620	0.632
	16.04	45.69	0.183	1.123		56.32	9.70	0.607	0.693
	19.57	58.60	0.184	1.149		66.97	13.03	0.606	0.734
1/2	0.78	0.37	0.204	0.433	4/1	3.75	0.12	0.509	0.144
	2.68	1.12	0.276	0.640		9.66	0.27	0.678	0.214
	6.50	3.53	0.306	0.809		18.74	0.58	0.781	0.280
	14.45	11.87	0.288	0.929		37.49	1.62	0.831	0.368
	25.64	28.99	0.276	1.014		58.26	3.41	0.839	0.441
	36.33	47.90	0.274	1.061		75.64	5.38	0.842	0.490

dominate owing to the high electrostatic field inside the pores of the zeolite, the adsorption of ethylene is favored. Similar changes in selectivity were found in the mixtures of carbon dioxide and propane, the carbon dioxide in this case showing a similar behavior to the ethylene.

The displacement effect of an adsorbate in a mixture with another gas of different polarity when using adsorbents that exhibit significant charge distributions in their structure, like the 13X and 5A zeolites, has been previously reported, whereas it was not observed in other neutral adsorbents such as the carbon molecular sieves (Costa et al., 1991; Calleja et al., 1994, 1996). In all cases, the stronger affinity of the adsorbent for some molecules is explained by taking into account the structure and the electric nature of the adsorbent surface and the physicochemical properties of the adsorbate molecule.

Both effects, overadsorption and displacement, are related and suggest a nonideal behavior of the corresponding mixtures. This is confirmed by the isobaric equilibrium $x-y$ diagrams, obtained from the binary isotherm data at

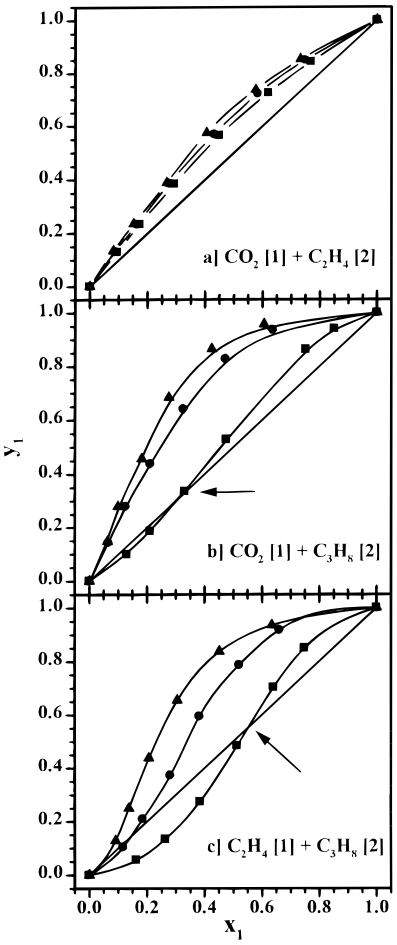

Figure 5. Isobaric equilibrium $x-y$ diagrams for binary mixtures of carbon dioxide, ethylene and propane in ZSM-5 zeolites at 293 K and 80 kPa. Zeolite Si/Al ratios: (▲) 60; (●) 29; (■) 15. (a) carbon dioxide (1) + ethylene (2), (b) carbon dioxide (1) + propane (2), and (c) ethylene (1) + propane (2).

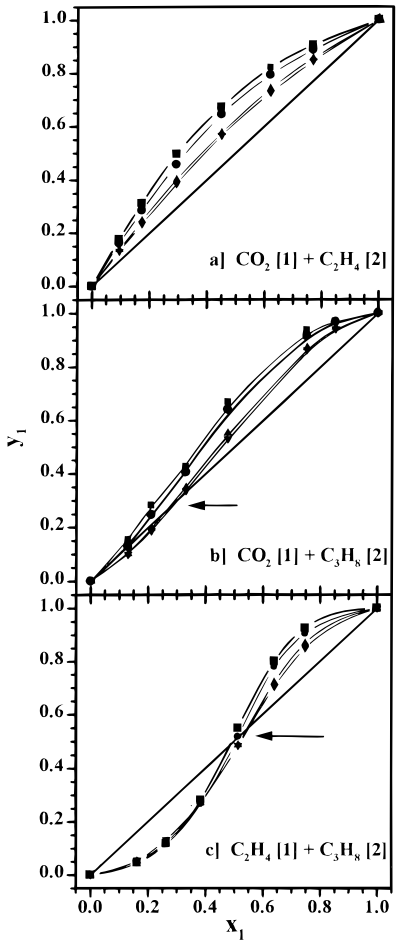

Figure 6. Isobaric equilibrium $x-y$ diagrams for binary mixtures of carbon dioxide, ethylene and propane in ZSM-5 zeolites (Si/Al = 15) at 293 K. Total pressure: (▼) 80 kPa; (▲) 53.3 kPa; (●) 13.3 kPa; (■) 6.6 kPa. (a) carbon dioxide (1) + ethylene (2), (b) carbon dioxide (1) + propane (2), and (c) ethylene (1) + propane (2).

constant pressure. Thus, $x-y$ diagrams for carbon dioxide + propane and ethylene + propane at 6.6, 13.3, 53.3, and 80 kPa showed significant deviations from ideality, as shown in Figure 5 for 80 kPa. These deviations are very much dependent on the Si/Al ratio of the zeolite, as observed in Figure 5b,c. The change in selectivity with the Si/Al ratio is clearly observed for both binary mixtures, carbon dioxide + propane and ethylene + propane, and the strong deviations from ideality can even show an azeotrope. In these two binary mixtures, selectivity for propane is clearly much higher when the zeolite Si/Al ratio is high, the $x-y$ curve being far from the diagonal. But the situation changes when the Si/Al ratio decreases, and then in addition to the decrease of selectivity for propane a much stronger nonideal behavior is shown and the appearance of an azeotrope is produced. On the other hand, the isobaric diagrams corresponding to the mixture carbon dioxide + ethylene shown in Figure 5a correspond to rather ideal binary mixtures, with no significant differences in the selectivity, which is small. All these results are in agreement with the results and discussions presented with the isotherms.

Finally, Figure 6 shows the effect of total pressure on the $x-y$ diagrams of the three mixtures with the zeolite of Si/Al ratio = 15. As observed, this effect is not so important and does not change the shape of the curves, but anyway the increase of pressure produces a slight decrease of the selectivity since the surface coverage is higher.

3.3. Ternary Mixtures. The adsorption isotherms of ternary mixtures of carbon dioxide + ethylene + ethane with two zeolites (Si/Al ratio = 60 and 15) were obtained at 293 K and over the total pressure range 0−100 kPa. Tables 8 and 9 summarize the experimental data in a similar way than for binary data. The overadsorption and displacement effects found in some of the binary mixtures were not appreciable in the ternary isotherms, probably because they are unnoticed with the higher dilution.

The isobaric equilibrium $x-y$ data were obtained at 6.6, 13.3, 53.3, and 80 kPa by following a similar procedure to that used for binary mixtures. Figure 7 shows two isobaric equilibrium diagrams of the ternary mixture at 293 K, corresponding to zeolites of Si/Al = 60 and 15. In this type of representation, the pure component and the binary and ternary compositions correspond to the vertex, sides, and interior points of the triangle diagram, respectively. The equilibrium composition of the gaseous phase (y_i) and of the adsorbed phase (x_i) are shown by solid and open symbols, respectively, joined each other by a straight line, whose length is a measure of the selectivity. The compositions of the binary azeotropes are also shown in the triangle sides.

There are some remarkable differences between both systems in these diagrams. First, it is to be noted for the zeolite of higher Si/Al ratio (Figure 7a) that the selectivity is quite high, as denoted by the large distance between the adsorbed and the gas phase compositions, in comparison

Table 8. Ternary Adsorption Equilibrium Data of Carbon Dioxide (1) + Ethylene (2) + Propane (3) Mixtures on ZSM-5 (Si/Al = 15) at 293 K

$(v_1/v_2/v_3)_0$	p_1/kPa	p_2/kPa	p_3/kPa	n_1/mol kg^{-1}	n_2/mol kg^{-1}	n_3/mol kg^{-1}
1/1/1	0.19	0.04	0.05	0.255	0.259	0.258
	4.34	1.85	1.24	0.418	0.476	0.490
	15.10	9.12	7.68	0.447	0.594	0.630
	18.67	12.04	10.37	0.451	0.614	0.654
	25.33	18.06	17.28	0.464	0.642	0.660
	34.80	27.05	27.27	0.485	0.668	0.662
1/1/8	0.20	0.02	0.49	0.104	0.108	0.853
	1.94	0.69	12.06	0.141	0.173	1.212
	3.41	1.48	25.51	0.153	0.204	1.268
	5.00	2.47	39.36	0.157	0.223	1.270
	6.50	3.54	52.22	0.160	0.235	1.273
	8.68	5.24	72.72	0.167	0.251	1.285
1/2/4	0.55	0.32	0.64	0.146	0.308	0.616
	2.53	2.19	5.28	0.183	0.436	0.849
	5.10	5.55	14.59	0.196	0.511	0.932
	7.57	9.58	24.11	0.200	0.540	0.954
	9.93	13.79	33.97	0.207	0.564	0.967
	13.02	19.56	47.58	0.213	0.581	0.977
1/6/4	0.38	0.82	0.26	0.095	0.600	0.406
	2.47	9.16	4.38	0.113	0.809	0.579
	5.10	22.94	14.04	0.127	0.955	0.667
	6.79	32.47	20.58	0.129	0.989	0.685
	8.43	41.85	27.07	0.132	1.014	0.695
	9.53	48.06	31.43	0.133	1.029	0.700
3/1/3	1.44	0.09	0.27	0.462	0.163	0.488
	8.57	1.12	3.99	0.581	0.235	0.689
	18.68	3.10	12.11	0.638	0.292	0.802
	28.76	5.55	22.60	0.683	0.333	0.849
	33.62	6.93	27.66	0.704	0.348	0.860
	40.48	8.83	34.14	0.713	0.360	0.877

Table 9. Ternary Adsorption Equilibrium Data of Carbon Dioxide (1) + Ethylene (2) + Propane (3) Mixtures on ZSM-5 (Si/Al = 60) at 293 K

$(v_1/v_2/v_3)_0$	p_1/kPa	p_2/kPa	p_3/kPa	n_1/mol kg^{-1}	n_2/mol kg^{-1}	n_3/mol kg^{-1}
1/2/8	0.91	0.72	0.72	0.058	0.139	0.602
	2.52	2.83	3.28	0.061	0.170	0.856
	4.44	6.39	11.28	0.058	0.170	0.989
	5.72	11.11	25.17	0.059	0.165	1.074
	8.34	14.73	37.74	0.061	0.164	1.113
	10.48	19.26	53.98	0.063	0.162	1.148
1/2/2	1.98	1.83	0.29	0.111	0.268	0.302
	4.16	4.51	0.68	0.140	0.364	0.448
	7.53	9.92	1.75	0.144	0.400	0.578
	13.04	20.44	5.26	0.139	0.401	0.732
	18.58	32.34	11.81	0.133	0.371	0.818
	23.52	43.38	19.85	0.140	0.360	0.874
1/1/1	2.58	1.12	0.18	0.173	0.205	0.225
	6.88	3.54	0.52	0.234	0.306	0.371
	13.15	8.46	1.41	0.251	0.352	0.504
	20.11	14.81	3.13	0.254	0.368	0.620
	27.36	22.28	6.20	0.249	0.359	0.706
	36.39	31.69	11.55	0.245	0.347	0.781
1/6/4	1.18	3.53	0.33	0.053	0.392	0.306
	2.46	9.24	0.85	0.064	0.502	0.451
	4.08	18.57	2.19	0.067	0.533	0.577
	6.91	35.78	6.80	0.064	0.509	0.711
	8.74	47.19	11.29	0.063	0.493	0.769
	10.50	58.31	16.58	0.064	0.485	0.810
2/1/8	1.73	0.28	0.71	0.118	0.071	0.605
	4.74	1.19	3.06	0.130	0.091	0.864
	8.90	2.93	10.63	0.118	0.092	1.008
	13.62	5.04	24.64	0.112	0.094	1.093
	17.19	6.97	37.44	0.112	0.092	1.124
	20.70	8.99	50.27	0.114	0.086	1.157
3/1/3	4.14	0.59	0.32	0.254	0.102	0.337
	8.82	1.49	0.74	0.306	0.133	0.481
	18.80	3.73	2.53	0.319	0.161	0.670
	30.05	7.32	6.93	0.306	0.160	0.805
	42.94	10.42	13.72	0.257	0.169	0.887
	51.99	13.28	20.43	0.253	0.172	0.934

with the diagram in the zeolite of lower Si/Al ratio (Figure 7b). Besides, this selectivity remains constant for the whole diagram in the first case, whereas it decreases in the second one, becoming even smaller with the proximity to the ethylene−propane binary azeotropic point. Second, the direction of the joining lines clearly indicates that the

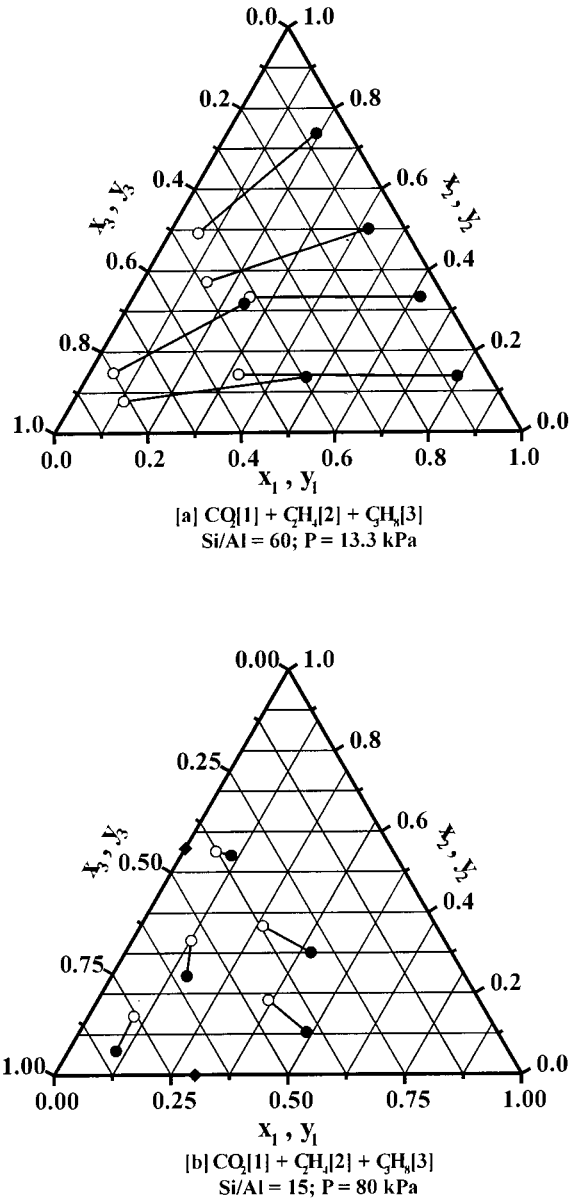

Figure 7. Ternary equilibrium $x-y$ diagrams for the systems (a) carbon dioxide (1) + ethylene (2) + propane (3) in ZSM-5 (Si/Al = 60) at 293 K and 13.3 kPa total pressure and (b) carbon dioxide (1) + ethylene (2) + propane (3) in ZSM-5 (Si/Al = 15) at 293 K and 80.0 kPa. (○) adsorbed phase (x), (●) gas phase (y), and (◆) binary azeotropes.

selectivity of the zeolite of Si/Al = 60 is toward propane (Figure 7a), whereas for the zeolite of lower Si/Al the selectivity is for the ethylene−propane binary azeotropic composition. These results confirm the above-mentioned influence of the Si/Al ratio on the zeolite adsorptive properties: as the Si/Al ratio decreases the selectivity changes from propane to polar compounds, being more pronounced for ethylene than for carbon dioxide.

4. Conclusions

The adsorption capacity of the ZSM-5 zeolites varies with their Si/Al ratio. The preference of the adsorbent for polar molecules increases as the Si/Al ratio decreases owing to the higher surface heterogeneity and the stronger electrostatic field inside the pores of the zeolite. This effect is more pronounced for molecules of high quadrupolar moment, like carbon dioxide and ethylene. The validity of the characteristic equilibrium curve proposed by Myers and Sircar (1985) is confirmed since it can describe the whole collection of isotherms on a given adsorbent with a single reduced curve.

The influence of the Si/Al ratio is also found in the adsorption of mixtures, where the changes in selectivity can even give rise to some overadsorption and displacement effects, as well as the appearance of azeotropes. Mixtures of molecules with similar polarity show an ideal behavior whereas mixtures of polar and nonpolar molecules deviate significantly from the ideal behavior as the Si/Al ratio decreases.

These results show the important role of the adsorbate polarity and adsorbent surface heterogeneity in the adsorption equilibrium, particularly on selectivity and ideal/nonideal behavior.

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