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Adsorption Equilibrium of Ethylene, Propane, Propylene, Carbon Dioxide, and Their Mixtures on 13X Zeolite

E. Costa, G. Calleja,* A. Jimenez, and J. Pau

Departamento de Ingenieria Quimica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040 Madrid, Spain

Equilibrium isotherms for the adsorption of ethylene, propane, propylene, and carbon dioxide on 13X zeolite have been obtained at 279, 293, and 308 K, in the pressure range 0–100 kPa. Experimental data were fitted to Langmuir, Prausnitz, and BET equations, showing the best results with Prausnitz isotherm. Binary adsorption isotherms for all binary systems were also obtained at 293 K and the same pressure range. Some displacement effects were observed for several systems at the adsorbed phase. Thus, propane is displaced by propylene for increasing pressures, showing a maximum in its individual adsorption isotherms.

Introduction

Adsorption is becoming more and more important as the basis of separation processes for gas mixtures, due to the development of useful continuous and batch techniques and the use of new synthetic adsorbents with molecular sieve properties.

New experimental and reliable equilibrium data are needed for gas mixture adsorption, to validate and compare existing theoretical models like ideal adsorbed solution (IAS) developed by Myers and Prausnitz (*1*), real adsorbed solution (RAS) developed by Costa et al. (*2–4*), and spreading pressure dependence (SPD) developed by Talu and Zwiebel (*5*), as well as to develop new equations for the reproduction and prediction of the adsorption equilibrium with a minimum number of empirical parameters.

The purpose of this work is to present new adsorption equilibrium data of the pure components and the binary mixtures of the system ethylene–propane–propylene–CO_2 on 13X zeolite, at 293 K. Data of pure components at two other temperatures are also given.

The analysis of these data with different theoretical models, including the highly nonideal behavior of some binary and higher mixtures, will be presented in a future publication.

Experimental Section

The experimental equipment used for the obtention of the adsorption isotherms was similar to the one used in previous works (*2*, *3*), but some new modifications were included to obtain a higher accuracy.

Basically, the equipment consists of a glass closed circuit, with an adsorption bed of 5.1-cm i.d. and 65-cm length, a stainless steel membrane compressor for circulating the gas mixture, and a bypass for homogenizing the mixture before the adsorption (Figure 1).

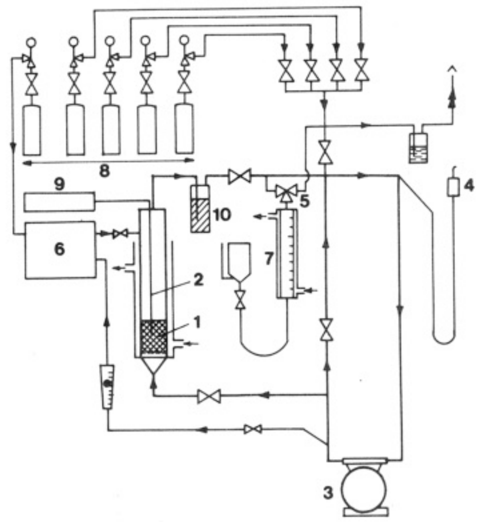

Figure 1. Experimental equipment for gas adsorption: (1) adsorption bed, (2) thermocouple, (3) compressor, (4) manometer, (5) three-way valve, (6) gas chromatograph, (7) gas buret, (8) gas containers, (9) temperature recorder, and (10) filter of gas spheres.

The modification introduced was a new three-way valve specially designed to reduce as much as possible the dead volume of gas retained during the charge of gases into the installation, so that a very accurate measurement of the gas introduced could be done, thus reducing the systematic experimental error to a minimum. A scheme of this valve is shown in Figure 2. With this modification, data dispersion was improved, and reproducibility and reliability of the experiments were even better.

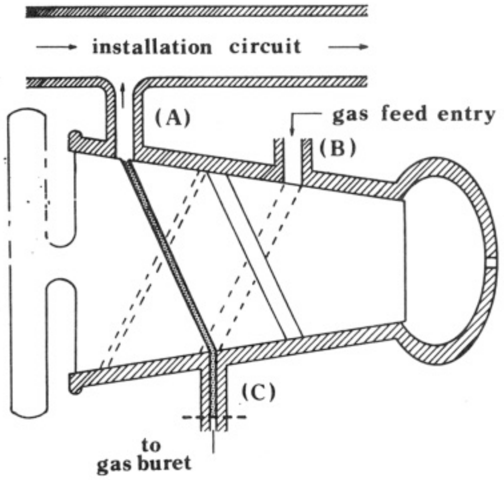

Figure 2. Scheme of the three-way high-vacuum valve (capillary opening C is 1 mm in diameter; openings A and B are 2 mm in diameter).

The analysis of the gaseous phase was made by gas chromatography (Hewlett-Packard Model 5840A with thermal conductivity detector) using a column of Porapak-Q of $^1/_8$-in. diameter and 2-m length. Partial pressures measured by GC techniques showed deviations due to experimental error of less than 5%. Measurement accuracy for temperature was ±0.1 °C. The composition of the adsorbed phase was calculated by mass balance.

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* To whom correspondence should be addressed.

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Table I. Adsorption Isotherms of Pure Components

T = 279 K		T = 293 K		T = 308 K		T = 279 K		T = 293 K		T = 308 K	
P, kPa	n, mol/kg	P, kPa	n, mol/kg	P, kPa	n, mol/kg	P, kPa	n, mol/kg	P, kPa	n, mol/kg	P, kPa	n, mol/kg
Ethylene											
0.74	0.8450	0.23	0.1583	1.48	0.4599	32.88	2.6245	13.52	2.0186	50.99	2.3022
1.52	1.2606	1.47	0.7082	3.69	0.8261	53.04	2.6973	20.57	2.2204	71.67	2.4527
2.62	1.5910	2.24	0.9576	6.56	1.1739			38.26	2.4964		
5.37	1.9757	3.33	1.1866	10.88	1.5050			62.56	2.6031		
11.71	2.2975	6.85	1.6298	18.26	1.8655			86.38	2.6415		
20.21	2.4761	9.56	1.8345	31.96	2.1294						
Propane											
0.32	0.8403	0.25	0.2216	1.11	0.5423			9.46	1.8571		
0.84	1.4291	0.57	0.5174	2.07	0.9284			9.91	1.8811		
2.00	1.7494	1.01	0.8845	3.16	1.2210			24.36	2.0162		
7.00	2.0134	1.26	1.0596	4.79	1.4395			24.68	2.0258		
19.42	2.1428	1.53	1.1769	11.49	1.7311			33.46	2.0817		
35.87	2.2127	2.63	1.4762	24.96	1.9152			52.82	2.1269		
65.86	2.2309	3.26	1.5687	48.15	2.0340			68.78	2.1644		
		4.15	1.6736	73.94	2.1005			92.21	2.1957		
CO_2											
0.62	0.9911	0.20	0.2921	1.09	0.5386	63.03	4.0303	24.07	2.9818	73.94	3.3293
1.54	1.4815	0.82	0.6516	2.07	0.9845			33.68	3.2317		
2.84	1.9693	2.08	1.0780	3.16	1.4091			39.35	3.3611		
4.93	2.4550	4.56	1.6342	4.79	1.7477			65.51	3.6365		
9.56	2.9693	5.52	1.7871	11.49	2.1443			74.66	3.7085		
18.59	3.4951	8.96	2.1610	24.97	2.4974			91.41	3.7916		
37.53	3.8542	14.81	2.6050	48.15	2.9805						
Propylene											
0.04	1.2525	0.02	0.8322	0.17	1.0292	32.31	2.5204	10.16	2.2394	37.99	2.3466
0.17	1.8358	0.19	1.4104	0.62	1.4995	56.30	2.5453	28.32	2.3613	54.91	2.3937
1.62	2.1380	0.38	1.6529	2.37	1.8729			50.03	2.4257	72.13	2.4444
6.26	2.3196	1.05	1.8908	7.79	2.1011			71.77	2.4728		
16.22	2.4488	3.44	2.1005	22.79	2.2611						

Table II. Values of Parameters of Equilibrium Adsorption Equations Fitted to Experimental Data of Pure Components and Average Deviation Errors

Langmuir

component	T, K	n_s	K	ϵ, %	component	T, K	n_s	K	ϵ, %
ethylene	279	2.7286	0.0725	3.3	CO_2	279	4.0979	0.0449	6.5
	293	2.7601	0.0293	2.2		293	3.9580	0.0198	5.3
	308	2.7054	0.0159	1.7		308	3.7087	0.0131	5.0
propane	279	2.2155	0.2614	2.5	propylene	279	2.4028	3.3659	6.6
	293	2.1850	0.0934	3.7		293	2.2855	1.3205	10.5
	308	2.1578	0.0496	3.0		308	2.3083	0.4626	6.5

Prausnitz

component	T, K	A	B	β	ϵ, %	component	T, K	A	B	β	ϵ, %
ethylene	279	0.2426	2.0494	0.0515	0.7	CO_2	279	0.2773	2.2788	0.1002	3.0
	293	0.0923	2.1387	0.0414	1.3		293	0.1246	1.7615	0.1267	2.5
	308	0.0466	2.1359	0.0377	1.5		308	0.0802	1.2068	0.1767	2.0
propane	279	0.6307	2.0520	0.0144	1.9	propylene	279	13.806	1.9869	0.0421	1.3
	293	0.2015	2.2283	−0.003	3.7		293	11.710	1.6375	0.0681	2.9
	308	0.1031	2.3169	−0.012	3.2		308	2.0156	1.6408	0.0637	0.5

BET

component	T, K	n_m	b	p_s	ϵ, %	component	T, K	n_m	b	p_s	ϵ, %
ethylene	279	2.5704	0.0413	4950	1.6	CO_2	279	3.6864	217.44	3793	4.4
	293	2.6366	382.26	11831	1.7		293	3.4504	126.72	4763	3.8
	308	2.5669	197.33	11338	1.6		308	2.9897	58.526	3000	3.3
propane	279	2.1677	3437.1	12361	1.9	propylene	279	2.2744	13523	3336	3.7
	293	2.1541	2516.3	26030	3.6		293	2.0550	7014	2743	7.7
	308	2.1447	3468.0	69051	3.2		308	2.1112	2200	2200	3.2

The adsorbent used was commercial 13X zeolite from Union Carbide International Co., having a 20% binder. Particles were cylindrical, 1.66-mm diameter and 2–5-mm length. Pure gases were supplied by SEO (Sociedad Española de Oxigeno) with a purity higher than 99% in all cases. This purity was periodically checked in the laboratory.

Prior to the adsorption runs, degasification and preliminary preparation of the installation were carried out as usual (*2–4*). Reproducibility of the experiments was checked by repeating some experiments in identical conditions and confirming that a good replication was obtained, with experimental deviations of less than 5%.

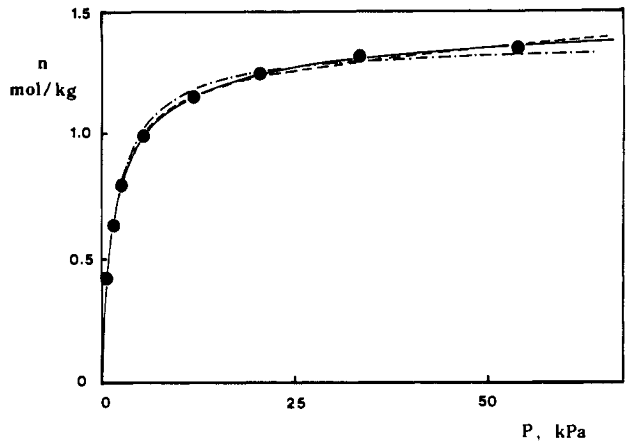

Figure 3. Adsorption isotherm of pure ethylene in 13X zeolite at 279 K: (●) experimental result, (—) Prausnitz equation, (-·-) BET equation, and (--) Langmuir equation.

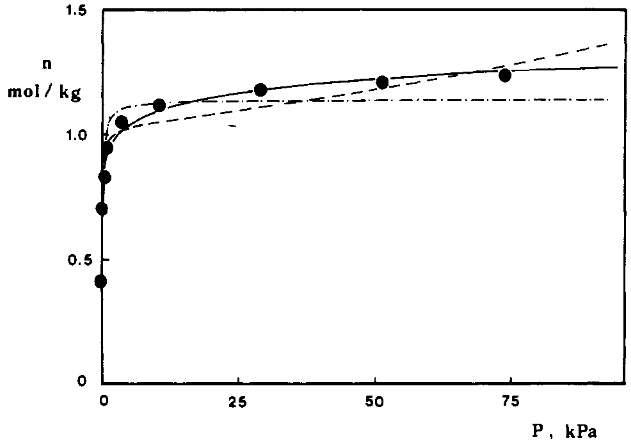

Figure 4. Adsorption isotherm of pure propylene in 13X zeolite at 279 K: (●) experimental result, (—) Prausnitz equation, (--) BET equation, and (-·-) Langmuir equation.

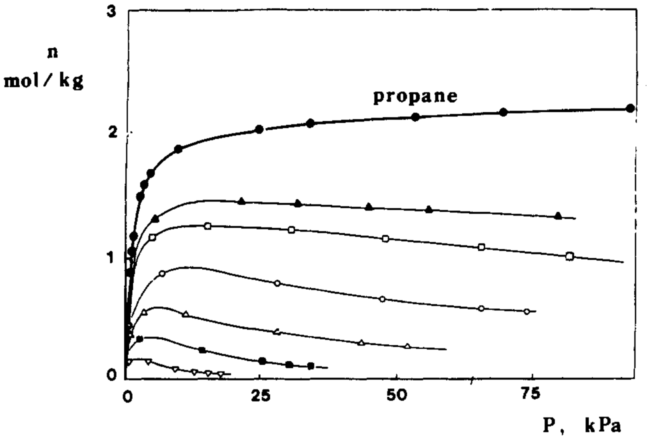

Figure 5. Individual adsorption isotherms of propane from binary mixtures propane (1)–propylene (2) on 13X zeolite at 293 K. Initial volumetric ratios (V_1/V_2): (▲) 3/1, (□) 2/1, (○) 1/1, (△) 1/2, (■) 1/4, (▽) 1/9; (●) pure propane.

Results

1. Pure Components. Table I shows the adsorption equilibrium isotherms of the pure components, ethylene, propane, propylene, and carbon dioxide, at three temperatures, 279, 293, and 308 K. These data are similar to other results available in the literature (*5*, *6*). An increase of adsorption, with decreasing temperature, can be observed, as expected.

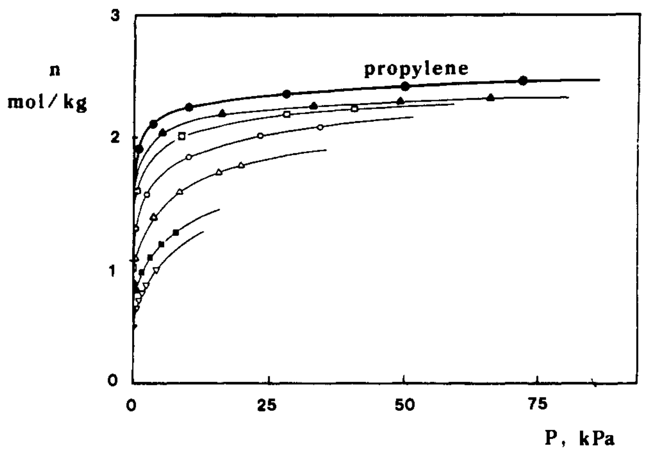

Figure 6. Individual adsortion isotherms of propylene from binary mixtures propane (1)–propylene (2) on 13X zeolite at 293 K. Initial volumetric ratios (V_1/V_2): (▽) 3/1, (■) 2/1, (△) 1/1, (○) 1/2, (□) 1/4, (▲) 1/9; (●) pure propylene.

From Table I we observe the adsorption isotherms of the four components at 293 K. The curve corresponding to the ethylene isotherm shows the smaller slope at low coverages (lower Henry's constant), due to its lowest molecular weight. Propane and propylene, however, have larger slopes at the low concentration range and tend to reach saturation at a lower pressure, showing isotherm curves closer to a step pattern. Crossing of isotherm curves for propane–ethylene and propylene–ethylene occurs at pressures close to 15 and 25 kPa, respectively. Propylene adsorbs more than propane, for all pressures, probably due to the polarizability of the propylene molecule and the existence of acid sites at the surface of the zeolite, where additional electrostatic adsorbate–adsorbent forces develop, contributing to the preferential adsorption of olefins compared to paraffins of similar molecular weight. Carbon dioxide is adsorbed in more extension than the hydrocarbons at pressures higher than 7 kPa, due to both effects: high molecular weight and polarizability.

Experimental data of all pure components were fitted to different equilibrium models. The following theoretical equations were used in this work:

(a) Langmuir (*8*)

$$\theta = n/n_s = KP/(1 + KP) \tag{1}$$

(b) Prausnitz (*9*)

$$1/n = 1/AP + 1/BP^{\beta} \tag{2}$$

(c) BET (*10*)

$$n/n_m = \frac{b(P/p_s)}{(1 - P/p_s)(1 - P/p_s + bP/p_s)} \tag{3}$$

Fitting of experimental data was done with use of a nonlinear regression method based on Marquardt's algorithm (*11*). Table II shows the values of the different parameters involved in the three adsorption equations, as well as the average errors in the fitting for each model, defined as $\epsilon = 100\sigma/n$, where the typical deviation σ is expressed by:

$$\sigma = \frac{\sum(n_i^{\text{exp}} - n_i^{\text{rep}})^2}{N - 1} \tag{4}$$

It is observed from Table II that the Prausnitz equation gives the best results, reproducing the experimental data of all pure

Table III. Adsorption Isotherms of the Binary Mixtures Ethylene (1)–Propane (2) at 293 K

V_1/V_2	P_1, kPa	P_2, kPa	n_1, mol/kg	n_2, mol/kg	V_1/V_2	P_1, kPa	P_2, kPa	n_1, mol/kg	n_2, mol/kg
4/1	1.22	0.21	0.6070	0.1533	1/2	0.33	0.60	0.2233	0.4478
	3.22	0.45	1.0478	0.2670		0.90	1.18	0.4052	0.8197
	7.71	0.96	1.4480	0.3764		1.98	2.44	0.5418	1.1062
	14.36	1.91	1.6609	0.4403		5.14	6.92	0.6469	1.3439
	25.51	3.72	1.8068	0.4913		11.55	18.32	0.7054	1.4779
	44.14	7.49	1.9183	0.5326		19.48	35.22	0.7371	1.5303
	65.62	12.37	1.9891	0.5574		27.22	52.09	0.7630	1.5610
2/1	0.80	0.31	0.4491	0.2258	1/4	0.15	0.60	0.1346	0.5389
	2.58	0.76	0.8809	0.4484		0.51	1.37	0.2466	0.9968
	5.30	1.40	1.1467	0.5918		1.49	4.22	0.3469	1.4176
	11.75	3.17	1.3572	0.7189		3.52	11.54	0.3956	1.6203
	23.81	7.68	1.4836	0.8049		6.85	25.59	0.4238	1.7229
	39.38	14.53	1.5586	0.8563		10.68	43.44	0.4448	1.7680
	57.04	22.84	1.6014	0.8856		14.77	63.24	0.4617	1.7844
1/1	0.42	0.36	0.2988	0.2995	1/9	0.10	0.80	0.0762	0.6872
	1.12	0.76	0.5177	0.5228		0.22	1.46	0.1174	1.0641
	2.25	1.31	0.7300	0.7440		0.51	3.07	0.1565	1.4260
	5.08	2.73	0.9167	0.9517		1.18	9.59	0.1887	1.7131
	12.16	7.85	1.0392	1.1039		2.28	21.71	0.2065	1.8402
	23.10	17.29	1.1046	1.1917		4.15	42.89	0.2217	1.9127
	38.82	33.32	1.1533	1.2356		6.56	71.12	0.2373	1.9559

Table IV. Adsorption Isotherms of the Binary Mixtures Ethylene (1)–CO_2 (2) at 293 K

V_1/V_2	P_1, kPa	P_2, kPa	n_1, mol/kg	n_2, mol/kg	V_1/V_2	P_1, kPa	P_2, kPa	n_1, mol/kg	n_2, mol/kg
4/1	0.54	0.02	0.2862	0.0734	1/2	0.37	0.24	0.1401	0.2874
	2.59	0.21	0.8429	0.2172		1.23	1.17	0.3473	0.7136
	5.22	0.51	1.2427	0.3223		2.46	2.69	0.5471	1.1270
	9.36	1.06	1.6219	0.4244		5.13	6.15	0.7259	1.5125
	18.85	2.09	1.9173	0.5181		10.42	12.41	0.8653	1.8552
	35.41	3.78	2.1211	0.6055		20.26	23.53	0.9341	2.1187
	57.10	6.19	2.2160	0.6727		30.78	34.96	0.9544	2.2994
	70.30	7.73	2.2391	0.7043		42.54	48.49	0.9619	2.4614
	83.20	9.27	2.2664	0.7358	1/4	0.30	0.57	0.1044	0.4260
2/1	0.67	0.06	0.2784	0.1429		0.75	1.48	0.2051	0.8425
	2.35	0.47	0.6905	0.3555		1.63	3.85	0.3351	1.3794
	5.07	1.24	1.0872	0.5626		3.47	8.55	0.4516	1.8849
	11.27	2.70	1.4233	0.7545		7.13	17.75	0.5435	2.3223
	18.45	4.43	1.6120	0.8764		13.65	32.89	0.5912	2.6840
	36.78	8.82	1.7732	1.0269		19.05	45.57	0.6002	2.8512
	61.36	14.84	1.8458	1.1566		26.64	64.23	0.5961	3.0071
	74.54	18.31	1.8845	1.2231	1/9	0.16	0.52	0.0537	0.4972
1/1	0.38	0.09	0.1412	0.1455		0.48	2.37	0.1241	1.1458
	1.81	0.80	0.4867	0.5016		1.01	5.75	0.1899	1.7592
	4.16	2.24	0.8168	0.8452		1.27	7.57	0.2108	1.9537
	10.97	6.11	1.1494	1.2207		2.05	12.46	0.2483	2.3217
	23.48	12.83	1.3334	1.4910		2.85	16.26	0.2611	2.4882
	39.65	22.31	1.3863	1.6426		4.38	25.38	0.2867	2.7862
	59.23	33.68	1.3885	1.7662					

Table V. Adsorption Isotherms of the Binary Mixtures Ethylene (1)–Propylene (2) at 293 K

V_1/V_2	P_1, kPa	P_2, kPa	n_1, mol/kg	n_2, mol/kg	V_1/V_2	P_1, kPa	P_2, kPa	n_1, mol/kg	n_2, mol/kg
2/1	4.52	0.08	1.0377	0.5697	1/4	0.68	0.10	0.2343	0.9989
	9.45	0.24	1.2424	0.7557		2.21	0.42	0.3223	1.4854
	18.92	0.62	1.3446	0.8772		5.60	1.66	0.3278	1.7969
	32.26	1.41	1.3635	1.0310		14.67	9.45	0.2404	2.1106
	45.99	2.66	1.3567	1.1589		22.29	24.43	0.1881	2.2661
	72.40	5.85	1.2427	1.3367		30.78	48.56	0.1564	2.3658
1/1	1.32	0.02	0.5432	0.5734	1/6	0.45	0.10	0.1552	0.9925
	6.50	0.33	0.9157	1.0587		1.29	0.37	0.2185	1.4830
	15.19	1.12	0.9598	1.2862		4.80	2.56	0.2160	1.9290
	27.76	2.99	0.9113	1.4831		11.50	12.99	0.1464	2.1818
	41.74	6.38	0.8361	1.6561		16.64	29.28	0.1101	2.3106
	59.83	13.28	0.7472	1.8265		22.78	56.44	0.0909	2.4187
1/2	1.19	0.08	0.3933	0.8414	1/10	0.42	0.17	0.1141	1.2344
	4.24	0.42	0.5675	1.3253		3.26	2.86	0.1315	2.0070
	11.25	1.79	0.5706	1.6315		9.42	24.89	0.0707	2.3204
	22.36	5.96	0.4761	1.8707		12.05	42.82	0.0591	2.3961
	32.32	13.08	0.4097	2.0446		14.03	57.99	0.0544	2.4370
	46.55	28.55	0.3248	2.1885		15.62	70.90	0.0507	2.4756

components with the smallest error, always less than 4%. Higher deviations of Langmuir and BET equations can be attributed to the limitations of their respective hypotheses (saturated monolayer and constant energy of adsorption in the

Table VI. Adsorption Isotherms of the Binary Mixtures Propane (1)–CO_2 (2) at 293 K

V_1/V_2	P_1, kPa	P_2, kPa	n_1, mol/kg	n_2, mol/kg	V_1/V_2	P_1, kPa	P_2, kPa	n_1, mol/kg	n_2, mol/kg
4/1	0.40	0.01	0.2988	0.0760	1/2	0.21	0.18	0.1491	0.3009
	0.73	0.06	0.6000	0.1519		0.53	0.96	0.3664	0.7343
	1.53	0.19	1.0465	0.2644		1.02	2.45	0.5857	1.1654
	2.49	0.36	1.3373	0.3382		2.51	7.18	0.8064	1.5806
	6.31	0.75	1.5837	0.4082		7.59	15.93	0.9224	1.8335
	32.14	2.62	1.8032	0.5310		17.91	29.25	0.9577	2.0124
	58.84	4.78	1.8569	0.6176		27.30	39.86	0.9733	2.1649
	83.96	7.25	1.8558	0.6682		39.44	53.99	0.9470	2.2626
2/1	0.40	0.06	0.2987	0.1514	1/4	0.14	0.18	0.0742	0.3022
	1.00	0.33	0.7469	0.3759		0.25	0.63	0.1486	0.6002
	2.55	1.02	1.1798	0.5936		0.38	1.75	0.2602	1.0375
	8.51	2.45	1.4077	0.7305		0.66	3.71	0.3701	1.4647
	22.42	5.38	1.5058	0.8390		1.23	7.59	0.4740	1.8568
	40.93	9.32	1.5386	0.9338		2.02	11.93	0.5379	2.0953
	56.93	12.78	1.5327	0.9975		4.61	23.05	0.6104	2.3739
	78.29	17.93	1.5232	1.0742		11.05	41.70	0.6477	2.8028
1/1	0.31	0.11	0.2219	0.2247	1/9	0.11	0.60	0.0724	0.5829
	0.84	0.68	0.5941	0.5963		0.22	2.17	0.1455	1.1579
	2.01	2.17	0.9591	0.9564		0.40	5.02	0.2184	1.7207
	5.51	4.83	1.2019	1.2118		0.67	9.02	0.2722	2.1240
	17.72	11.77	1.3279	1.4155		1.24	15.88	0.3185	2.4604
	39.96	23.93	1.3192	1.5568		3.21	34.81	0.3682	2.8110
	59.49	34.34	1.3063	1.6793		5.93	51.50	0.3832	3.0051
						10.12	75.20	0.3871	3.1823

Table VII. Adsorption Isotherms of the Binary Mixtures Propane (1)–Propylene (2) at 293 K

V_1/V_2	P_1, kPa	P_2, kPa	n_1, mol/kg	n_2, mol/kg	V_1/V_2	P_1, kPa	P_2, kPa	n_1, mol/kg	n_2, mol/kg
3/1	5.32	0.04	1.3125	0.4763	1/2	0.56	0.07	0.3831	0.7899
	21.22	0.66	1.4319	0.6211		3.05	0.54	0.5662	1.2570
	31.31	1.17	1.4159	0.6884		10.74	2.43	0.5514	1.5288
	44.21	1.86	1.3802	0.7471		27.57	10.19	0.4114	1.8281
	55.11	2.57	1.3731	0.8103		42.81	23.51	0.3074	2.0041
	78.91	4.53	1.3173	0.9248		51.30	33.33	0.2762	2.0801
2/1	4.70	0.13	1.1583	0.6289	1/4	0.33	0.06	0.2279	0.9403
	14.78	0.67	1.2413	0.7697		2.21	0.76	0.3428	1.5520
	30.07	1.74	1.2198	0.9061		13.74	8.93	0.2414	1.9972
	47.38	3.42	1.1461	1.0253		24.77	28.36	0.1523	2.1911
	64.64	5.45	1.0714	1.1350		29.92	40.64	0.1150	2.2304
	81.09	8.10	1.0128	1.2281		33.62	51.95	0.1110	2.2918
1/1	0.60	0.04	0.4616	0.4741	1/9	0.39	0.25	0.1497	1.4195
	6.42	0.59	0.8847	1.0153		3.88	5.24	0.1512	2.0256
	27.59	3.85	0.8056	1.3372		8.70	16.25	0.0874	2.1727
	46.71	8.72	0.6912	1.5414		12.32	33.36	0.0580	2.2534
	64.65	15.91	0.6038	1.6954		14.89	49.12	0.0445	2.2920
	72.96	20.01	0.5736	1.7595		17.23	65.55	0.0357	2.3162

Table VIII. Adsorption Isotherms of the Binary Mixtures CO_2 (1)–Propylene (2) at 293 K

V_1/V_2	P_1, kPa	P_2, kPa	n_1, mol/kg	n_2, mol/kg	V_1/V_2	P_1, kPa	P_2, kPa	n_1, mol/kg	n_2, mol/kg
4/1	5.22	0.09	1.5588	0.4090	1/2	0.60	0.05	0.4037	0.8260
	8.61	0.16	1.8731	0.4896		2.13	0.38	0.6277	1.3180
	13.98	0.34	2.0688	0.5676		5.83	1.76	0.7348	1.6292
	22.26	0.63	2.2548	0.6426		14.39	8.92	0.7503	1.8107
	46.12	2.07	2.4486	0.7636		23.74	22.47	0.7625	1.9233
	75.63	5.19	2.5470	0.8564		32.74	39.16	0.7854	1.9925
2/1	1.78	0.01	0.9576	0.4929	1/4	0.26	0.07	0.2435	0.9896
	5.49	0.18	1.3910	0.7367		1.52	0.80	0.3882	1.6372
	11.05	0.49	1.6248	0.8936		4.07	4.27	0.4289	1.9087
	21.56	1.47	1.7815	1.0406		8.38	15.48	0.4412	2.0549
	37.97	4.00	1.8458	1.1642		12.56	31.19	0.4554	2.1288
	66.21	11.28	1.8844	1.2937		16.57	48.96	0.4740	2.1763
1/1	0.85	0.04	0.5637	0.5769		19.43	61.94	0.4878	2.2061
	3.02	0.22	0.9436	0.9885	1/9	0.13	0.12	0.1353	1.2350
	9.20	1.11	1.1667	1.2984		1.05	2.18	0.2021	1.9363
	25.22	6.39	1.2395	1.5417		3.53	19.98	0.2243	2.2083
	45.20	18.70	1.2431	1.6682		5.55	40.57	0.2365	2.2803
	54.20	26.25	1.2635	1.7117		7.16	58.67	0.2470	2.3158
						8.25	71.76	0.2572	2.3556

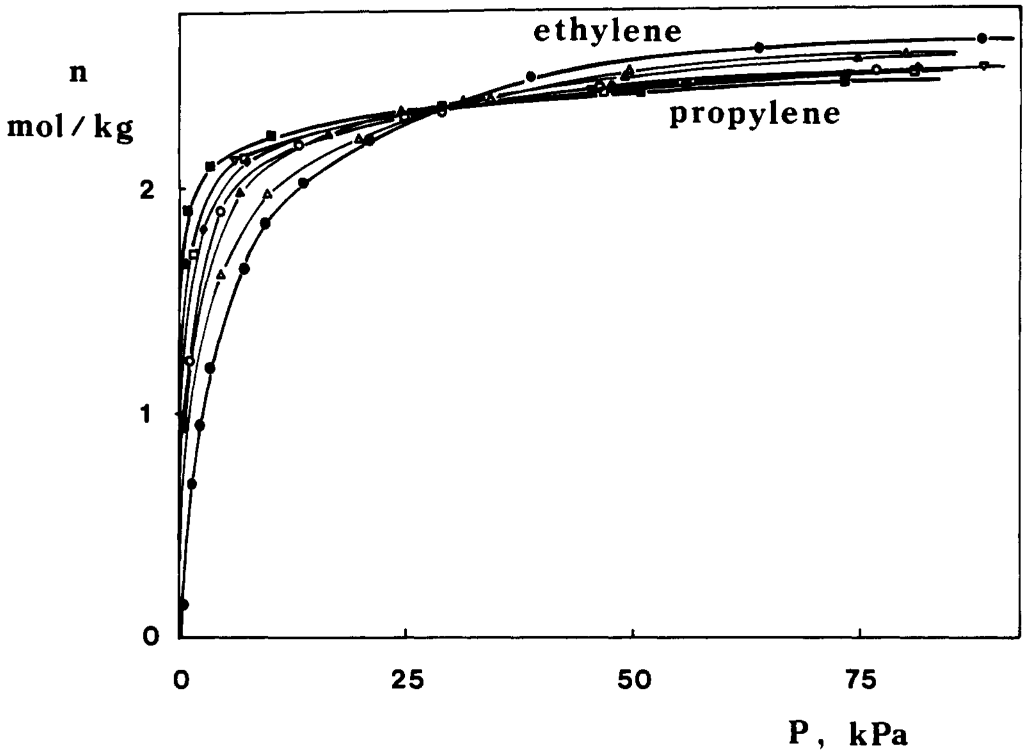

Figure 7. Global adsorption isotherms of mixtures ethylene (1)–propylene (2) on 13X zeolite at 293 K. Initial volumetric ratios (V_1/V_2): (▽) 1/10, (□) 1/6, (◆) 1/4, (○) 1/2, (▲) 1/1, (△) 2/1; (■) pure propylene, (●) pure ethylene.

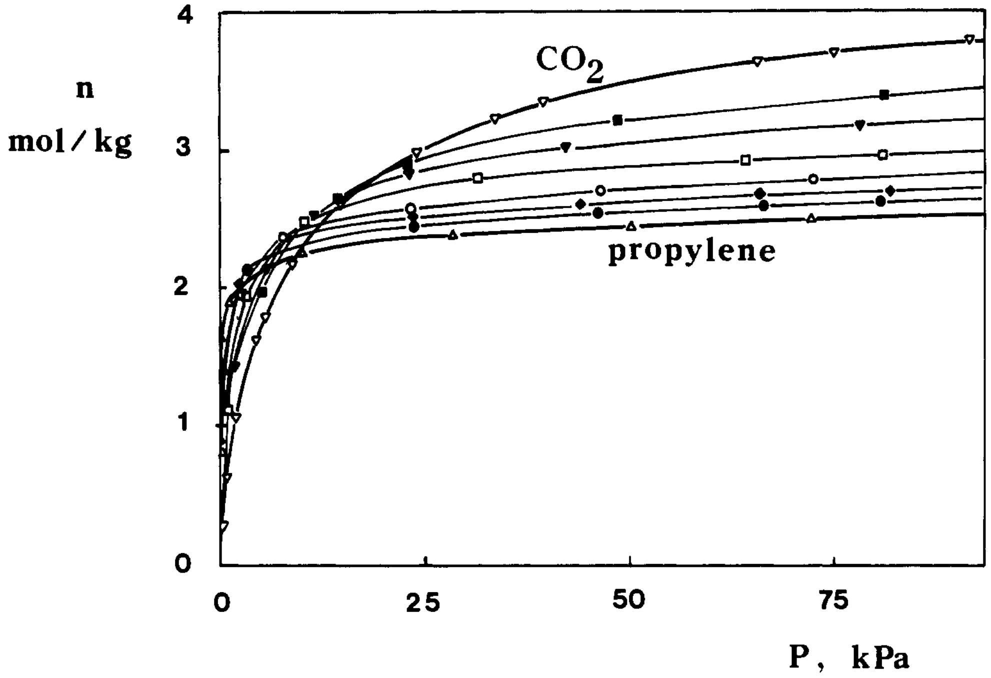

Figure 8. Global adsorption isotherms of mixtures CO_2 (1)–propylene (2) on 13X zeolite at 293 K. Initial volumetric ratios (V_1/V_2): (●) 1/9, (◆) 1/4, (○) 1/2, (□) 1/1, (▼) 2/1, (■) 4/1; (▽) pure CO_2, (△) pure ethylene.

Langmuir model; adsorbate behavior similar to that of a saturated liquid from the first layer in the BET model).

As an example, Figures 3 and 4 show the equilibrium data, experimental and reproduced, by the three models, for ethylene at 279 K and propane at 293 K, respectively. The best fitting is obtained with the Prausnitz equation, as commented.

*2. **Binary Mixtures.*** Binary data of all systems (ethylene–propane, ethylene–CO_2, ethylene–propylene, propane–CO_2, propane–propylene, and CO_2–propylene) at 293 K are presented in Tables III–VIII. Individual isotherms of each component of the binary mixture, n_i vs P_i, are given for different initial volumetric ratios V_1/V_2 in the gas phase. These data can be easily represented to obtain the individual adsorption isotherms, n_i–P_i.

Thus, Figure 5 shows the individual isotherms of propane in the mixture propane–propylene, together with the isotherm of pure propane, and Figure 6 shows the corresponding isotherms of propylene in the same mixture, together with the isotherm of pure propylene. It is observed that all the isotherms of propane show a maximum, located in the low-pressure region, from which the amount adsorbed for higher partial pressures decreases smoothly. This is not the case, however, with the propylene curves (Figure 6), where a continuous growth is always observed. This situation, which has been also observed in the system ethylene–propylene (Table V), is due to the displacement effect shown by propylene molecules that are adsorbed preferentially compared to ethylene and propane molecules. This stronger "affinity" of the adsorbent for propylene molecules can be explained by taking into account the structure of the adsorbent, the electrical nature of its surface, where the distribution of electrical charges contributes to create stronger interactions with some adsorbates (i.e. polarized molecules), and the chemical nature of the adsorbate molecules, particularly the presence of double bonds.

This effect is not observed in the mixture ethylene–propane (Table III), probably because the larger molecular weight of propane compensates for the presence of the double bond of ethylene.

Finally, Figures 7 and 8 show the global isotherms (total amount adsorbed of the mixture) of two binary mixtures, ethylene–propylene and CO_2–propylene, respectively, at 293 K. The different curves correspond again to different initial volumetric ratios V_1/V_2. The isotherms of pure components are also included as a reference in both figures.

In the first case, Figure 7, the collection of global isotherms of the system ethylene–propylene lies always between the isotherms of the pure components, as expected, and all curves cross at the same point. However, in the case of CO_2–propylene, Figure 8, there is a range of pressures where the amount adsorbed of some binary mixtures is larger than that of the pure component more readily adsorbed at that pressure, and therefore no single crossing point of all isotherms appears. This result of adsorption beyond the expected limit is probably due to an effect of molecule "association", which can occur between molecules of very different nature, so that the pressure of one type of molecule adsorbed on the surface facilitates or contributes to further adsorption of the other type of molecule of the mixture, following a kind of sinergetic effect. The electromagnetic changes produced by the presence of the two different molecules closely adsorbed in the zeolite surface could probably be the reason of the variation of the attraction forces that result in a larger extent of adsorption of the mixture.

Glossary

A	Prausnitz's constant
B	Prausnitz's constant
b	BET equation's constant
n	total amount adsorbed (mol of adsorbate/kg of adsorbent)
n_i	amount adsorbed of component i (mol/kg of adsorbent)
n_s	saturation amount adsorbed (mol/kg of adsorbent)
n_m	monolayer saturation amount adsorbed (mol/kg of adsorbent)
N	number of experimental points
K	Langmuir's constant
P	equilibrium pressure (kPa)
P_i	partial pressure of component i in the gas phase (kPa)
p_s	saturation pressure (kPa)
T	temperature (K)
V_i	initial volume of component i in the gas phase (m^3)
β	Prausnitz's constant
ϵ	average error
σ	typical deviation
θ	reduced amount adsorbed

Registry No. CO_2, 124-38-9; ethylene, 74-85-1; propane, 74-98-6; propylene, 115-07-1.

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