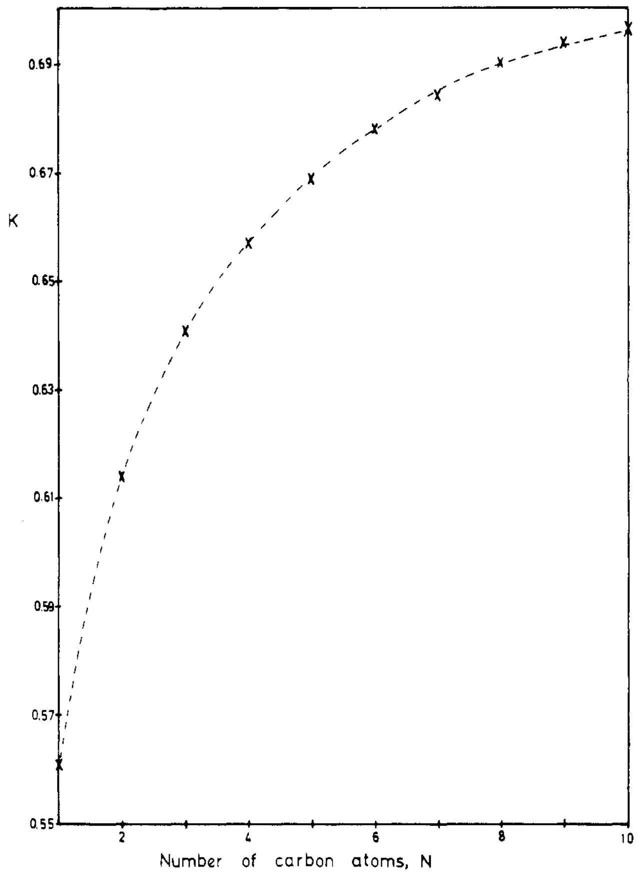

Figure 3. K values (eq 3) vs. number of carbon atoms, N.

refractive indices and higher than 0.998 for the densities. The empirical equation of Eykman (*1*, *3*), eq 3, offers an accurate

$$\frac{n_D^2 - 1}{n_D + 0.4}\,\frac{1}{\rho} = K \qquad (3)$$

way not only to check the accuracy of experimental densities and refractive indices but also to calculate one from the other. n_D is the refractive index, ρ the density at the same temperature, and K a constant. Eykman stated that the constant K is independent of temperature, and this fact was also observed in this work, the average deviation between the K values for any alcohol always being smaller than ±0.0004 unit. The values found for this constant at each temperature initialy increase faster than the number of carbon atoms (N) of the alcohol, and then more slowly than N increases. Figure 3 shows the representation of the K values vs. N, where it can be seen that the theoretical line joining the calculated points corresponds approximately to a logarithmic-type equation.

Glossary

a, b	parameters of eq 1
A, B	parameters of eq 2
K	constant of Eykman equation
N	number of carbon atoms
n_D	refractive index
t	temperature, °C
ρ	density, g cm^{-3}

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Adsorption of a Gaseous Mixture of Ethylene and Propylene on a Carbon Molecular Sieve

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The adsorption of a binary gaseous mixture of ethylene and propylene on the carbon molecular sieve MSC·5A was measured at temperatures of 1.7, 30, and 50 °C and at a pressure of 100 mmHg. The strong selectivity for propylene from mixtures was observed as in the case of the mixture of ethane and propane. The prediction calculation presented by Suwanayuen and Danner was applied to this system. The agreement between the experimental and calculated values was not satisfactory except for the total amount of adsorption.

The adsorption of a binary gaseous mixture on a microporous adsorbent often deviates from the predicted values that use the isotherms of pure components, as previously reported for the system of ethane–propane–carbon molecular sieve (MSC·5A) (*1*). In this paper, the adsorption equilibria for the system of ethylene–propylene–MSC·5A was measured at temperatures of 1.7, 30, and 50 °C at a pressure of 100 mmHg. The experimental results were compared with the predicted values from the Suwanayued–Danner method (*4*, *5*).

Experimental Section

The apparatus for the measurement of adsorption is quite similar to the one previously reported (*1*) except for the fact that the pressure was measured by an electric pressure gage (Baratron 221A-1000) with a digital and analoge millivoltmeter

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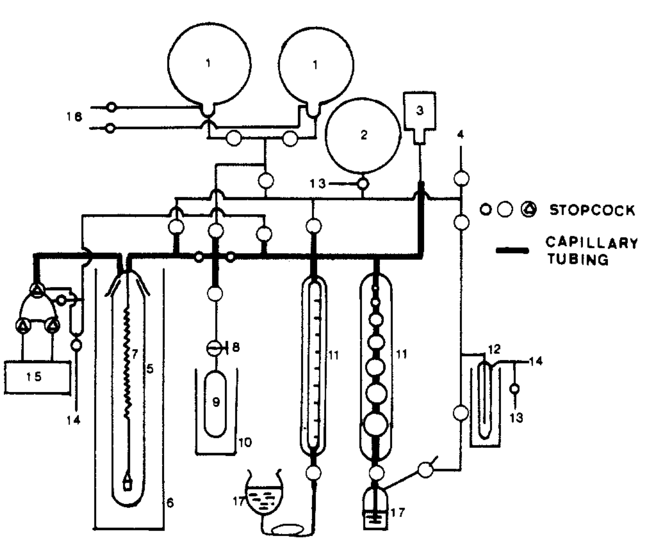

Figure 1. Experimental apparatus: (1) gas reservoir; (2) buffer tank; (3) electrical pressure gage; (4) Mcleod gage; (5) adsorption tube; (6) thermostat; (7) spring balance; (8) needle valve; (9) high-pressure gas cylinder; (10) liquid-nitrogen bath; (11) gas buret; (12) liquid-nitrogen trap; (13) vent; (14) vacuum pump; (15) gas chromatograph; (16) gas supply; (17) mercury reservoir.

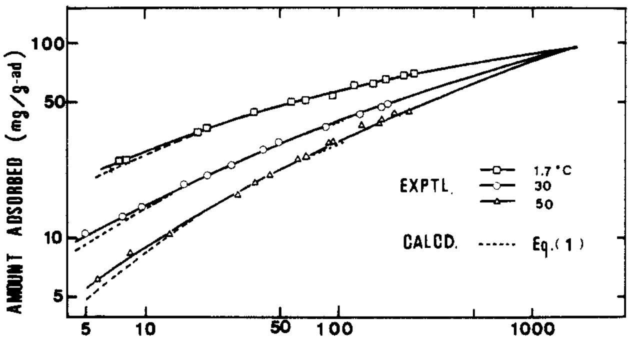

Figure 2. Adsorption isotherms of ethylene on MSC-5A.

(Figure 1). This pressure gage, which has an intrinsic dead volume of 20 mL, was connected to the adsorbtion tube with a capillary tube (i.d. = 2 mm) which was 80 cm long. The diffusing rate of gases through the capillary tube of this length was low. However, because of the considerable time (20 h) needed to obtain equilibrium, the diffused amount of gas could not be neglected. In order to avoid the heterogeneity of the gaseous mixture in the adsorption tube and in the gage, stopcock A was closed during the adsorption process and was opened only for the pressure reading. The composition in the dead volume of the gage and in the capillary tube of the right side of stopcock A was regarded as having the same composition as that of the inlet gas. It should be noted that the pressure appearing on the millivoltmeter decreased by 0.3 mmHg per 1 °C increase in temperature, because the transistors used in the Baratron gage have their own thermal characteristics.

The physical properties of the carbon molecular sieve MSC-5A used in this work were reported elsewhere (*2*). The adsorbent was renewed at each run. Since this carbon molecular sieve, after being crushed and sieved into 28–46 mesh, can be degraded in the open air, it was separated into small glass capsules for each usage. They were sealed under vacuum after being degassed. The purities of ethylene and propylene were both 99.7 mol %. The experimental and calculation methods for determining the adsorbed amount of each component were the same as those in the previous work (*1*). The adsorption isotherms for the pure components were measured with an electric balance (Cahn RG-HV), and the equilibrium pressure was read with a mercury manometer.

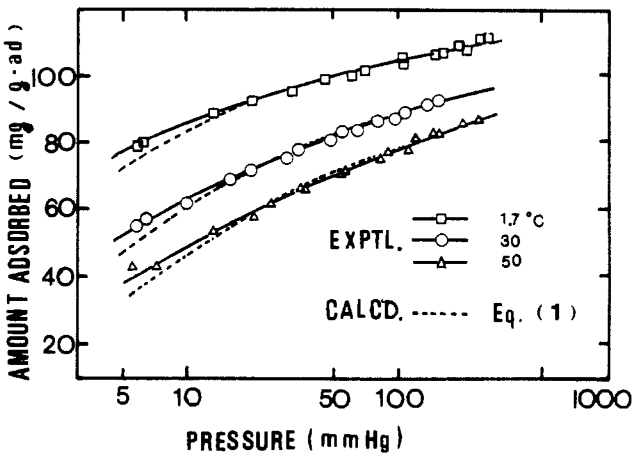

Figure 3. Adsorption isotherms of propylene on MSC-5A.

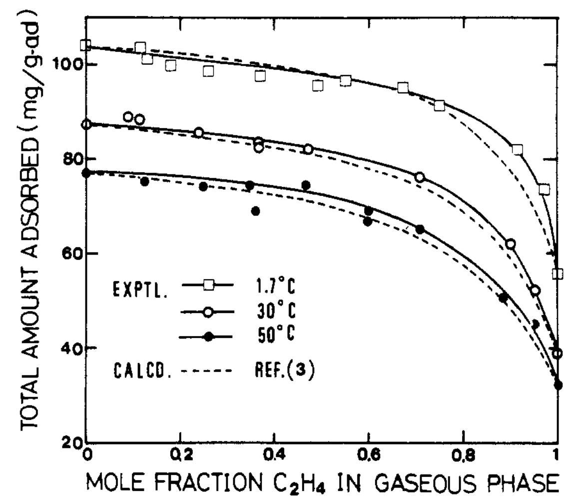

Figure 4. Total amount adsorbed for ethylene–propylene–MSC-5A.

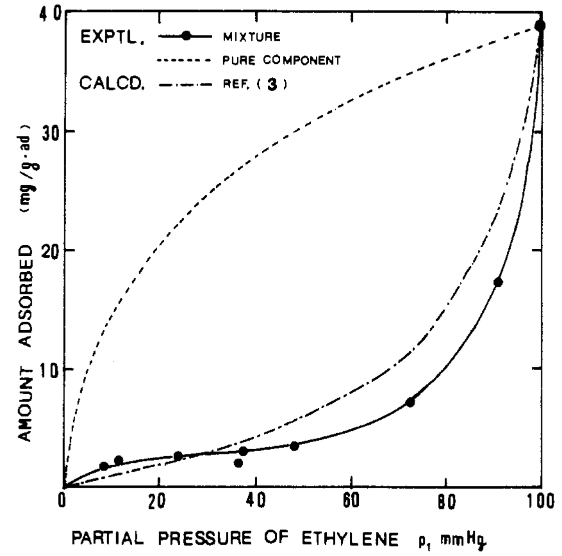

Figure 5. Adsorbed amount of ethylene at 30 °C.

Results

Table I and Figures 2 and 3 show the adsorption isotherms for ethylene and propylene on MSC-5A at 1.7, 30, and 50 °C. Table II shows the adsorption equilibrium data for a binary

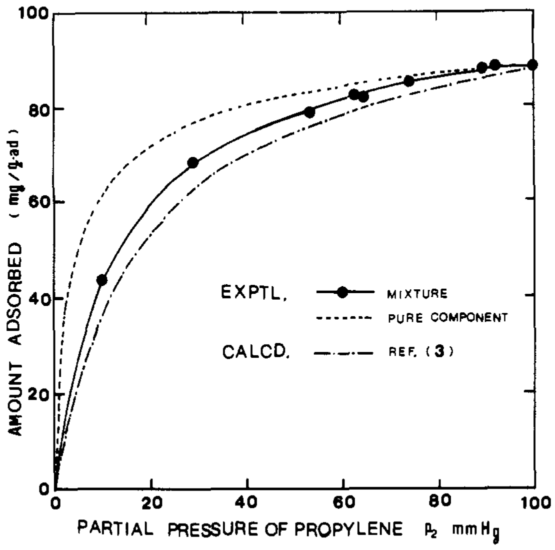

Figure 6. Adsorbed amount of propylene at 30 °C.

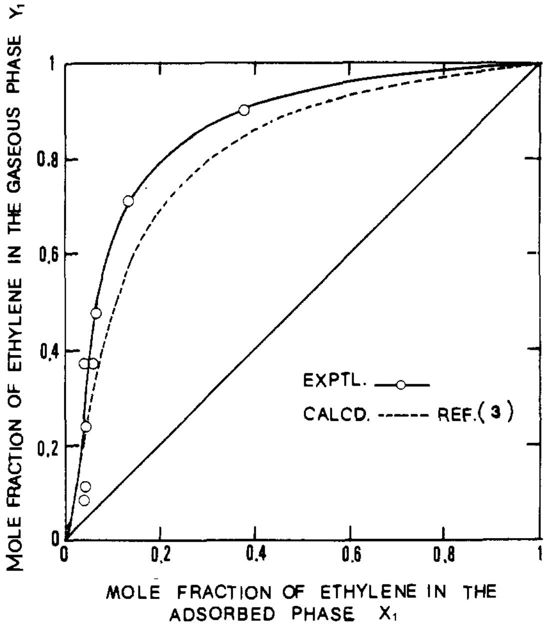

Figure 7. X–Y diagram for ethylene–propylene–MSC-5A at 30 °C.

gaseous mixture of ethylene and propylene on MSC-5A. The total amount of adsorption at 30 °C was plotted against the mole fraction of ethylene in the gaseous phase (Figure 4). The adsorption amounts of each component at 30 °C shown in Figures 5 and 6, together with the isotherms of the pure components. Figure 7 shows the X–Y diagram at 30 °C.

The prediction calculation presented by Suwanayuen and Danner (*4*, *5*) requires the isotherms of pure components to be represented by Margules' two-suffix equation or by Wilson's equation. We applied the former, which is expressed by eq 1.

$$P = \frac{n_i^\infty}{b_i}\,\frac{\theta_i}{1-\theta_i}\exp\left(\frac{-2W_{i3}}{RT}\theta_i\right) \tag{1}$$

The three constants b_i, n_i^∞, and W_{i3} in this equation can be obtained from the experimental data. Henry's constant b_i was obtained by the definition $b_i \equiv \lim_{P\to0}(n_i^\infty/P)$ using the graphical method. The amount adsorbed at infinite pressure was considered to be independent of the temperature as Suwanayuen and Danner have suggested. This hypothesis was true in the case of the adsorption of ethylene where the surface coverages θ_i at 1.7, 30, and 50 °C at 100 mmHg were quite low at 0.590, 0.405, and 0.323, respectively. In these cases the amount adsorbed at $P = \infty$ was not sensitive to the isotherm. The value of n_i^∞ for ethylene was therefore obtained from the crossing point of the three isotherms as shown in Figure 2. The surface coverages of propylene at 1.7, 30, and 50 °C at a pressure of 100 mmHg were as much as 0.89 ~ 0.95. Therefore, the small difference of n_i^∞ caused the large error in the calculated isotherm. The value of n_i^∞ could be considered as a temperature-dependent value like liquid density according to the volume-filling theory which states that the adsorbed gases or vapors in the micropores condense like liquids. The saturation adsorption for propylene was therefore defined for each temperature, and this improved considerably the agreement between the calculated and experimental isotherms. The ratios of n_i^∞ of propylene at 30 and 50 °C to the one at 1.7 °C were 0.87 and 0.80, respectively. These values were quite close to the ratios of the saturated-liquid densities of propylene at the same temperatures, which were 0.90 and 0.82, respectively. The liquid densities used here were calculated by the Gunn–Yamada method (*3*).

Margules' two-suffix parameter W_{i3} was calculated by the regression analysis of the experimental isotherm. The caluclated constants are listed in Table III, and the calculated isotherms using these values are shownn in Figures 2 and 3. The prediction calculations for adsorption equilibria with these values were done following the procedure presented by Suwanayuen

Table I. Adsorption Isotherms for Pure Ethylene and Propylene

1.7 °C		30.0 °C		50.0 °C	
press., mmHg	amount adsorbed, mg/(g of ad)[a]	press., mmHg	amount adsorbed, mg/(g of ad)	press., mmHg	amount adsorbed, mg/(g of ad
		Ethylene, Run 1			
7.8	25.28	5.0	10.39	5.7	6.04
21.1	36.93	10.0	14.70	13.6	10.21
41.3	39.57	21.7	21.16	30.2	16.76
69.7	48.98	42.3	28.46	44.8	21.09
122.0	60.89	88.8	37.45	65.2	25.18
187.8	65.07	171.5	46.71	93.9	30.12
240.8	68.37			175.6	38.02
				244.1	42.91
		Ethylene, Run 2			
7.4	23.84	7.9	12.95	8.7	8.36
19.2	34.80	16.5	18.90	20.4	14.07
36.9	43.08	29.3	23.91	37.3	19.02
58.7	48.97	50.9	31.47	68.0	25.76
94.6	55.69	89.4	37.33	98.1	30.41
155.0	61.77	135.1	43.66	139.9	36.67
227.3	66.10	180.1	47.06	175.7	40.18
250.1	67.94			208.3	42.74
		Propylene, Run 1			
5.7	78.14	6.6	56.62	7.2	42.57
13.8	87.33	11.3	63.78	21.7	57.92
32.6	94.76	16.9	68.50	38.8	65.13
62.5	99.84	35.1	77.24	58.1	70.60
111.5	104.42	58.1	82.66	82.7	74.20
163.7	106.16	85.3	86.06	115.4	77.58
227.6	107.64	113.2	88.77	164.5	82.34
259.3	110.73	166.7	91.92	255.3	86.42
		Propylene, Run 2			
6.0	79.28	6.0	54.06	5.5	42.44
20.6	91.95	10.3	60.93	13.6	53.12
46.2	98.83	20.8	70.03	25.7	61.44
71.4	101.67	30.6	74.47	36.3	66.28
113.4	105.38	50.3	79.63	55.4	70.75
174.9	106.69	68.3	82.96	93.0	76.33
211.3	108.99	104.8	86.60	127.1	80.43
287.2	117.17	148.8	89.73	158.0	82.66
		172.8	91.05	211.0	85.14

[a] ad = adsorbent.

Table II. Adsorption Equilibrium Data for the Ethylene (1)-Propylene (2)-MSC·5A System

		adsorbed amount of ethylene		adsorbed amount of propylene		total amount adsorbed			
temp, °C	press., mmHg	mmol/ (g of ad)[a]	mg/ (g of ad)	mmol/ (g of ad)	mg/ (g of ad)	mmol/ (g of ad)	mg/ (g of ad)	X_1	Y_1
1.7	97.6	0.062	1.75	2.412	101.29	2.474	103.04	0.025	0.114
	101.3	0.098	2.73	2.365	99.35	2.463	101.08	0.040	0.128
	99.3	0.138	3.86	2.279	95.71	2.417	99.57	0.057	0.181
	97.7	0.114	3.19	2.264	95.10	2.378	98.29	0.048	0.259
	100.8	0.111	3.09	2.244	94.25	2.355	97.34	0.047	0.369
	99.9	0.139	3.89	2.180	91.55	2.319	95.44	0.060	0.494
	100.6	0.165	4.63	2.190	91.98	2.355	96.61	0.070	0.549
	100.2	0.257	7.19	1.966	82.56	2.222	89.75	0.116	0.670
	99.9	0.251	7.01	2.007	84.31	2.258	91.32	0.111	0.745
	99.7	0.522	14.62	1.606	67.44	2.128	82.02	0.245	0.915
	103.6	1.588	44.49	0.576	24.16	2.164	68.65	0.734	0.976
30.0	101.0	0.071	1.99	2.075	87.75	2.146	89.74	0.033	0.088
	102.2	0.086	2.42	2.049	86.05	2.135	88.47	0.040	0.112
	97.8	0.093	2.61	1.988	83.48	2.081	86.09	0.045	0.242
	99.9	0.076	2.12	1.931	81.10	2.001	83.22	0.038	0.367
	101.5	0.115	3.21	1.901	79.83	2.016	83.04	0.056	0.368
	101.2	0.130	3.61	1.873	78.66	2.003	82.30	0.065	0.476
	101.7	0.259	7.24	1.641	68.94	1.900	76.18	0.136	0.710
	100.6	0.629	17.62	1.041	43.72	1.670	61.83	0.377	0.901
50.0	100.7	0.018	1.50	1.758	73.83	1.786	75.34	0.010	0.124
	101.3	0.052	1.44	1.723	72.36	1.775	73.80	0.029	0.245
	101.2	0.093	2.59	1.714	71.97	1.806	74.56	0.051	0.345
	100.4	0.043	1.20	1.616	67.86	1.658	69.06	0.026	0.360
	100.9	0.126	3.52	1.707	68.69	1.833	72.21	0.069	0.467
	105.1	0.168	4.70	1.539	64.64	1.707	69.34	0.098	0.595
	100.8	0.167	4.68	1.478	62.09	1.645	66.77	0.102	0.594
	103.9	0.192	5.38	1.431	60.12	1.623	65.50	0.118	0.708
	103.2	0.431	12.06	0.921	38.68	1.352	50.72	0.319	0.883
	100.6	0.653	18.28	0.642	26.97	1.295	45.25	0.504	0.954

[a] nd = adsorbent.

Table III. Parameters of Adsorption Isotherm of Eq 1

temp, °C	gas	b_i, mg/ (g of ad· mmHg)[a]	n_i, mg/ (g of ad)	$-W_{i3}$, L· atm/ (g-mol)
1.7	ethylene	9.75	96.0	37.95
	propylene	110.0	109.0	19.02
30.0	ethylene	3.15	96.0	48.45
	propylene	37.0	95.0	17.35
50.0	ethylene	1.33	96.0	45.11
	propylene	17.0	87.0	14.27

[a] ad = adsorbent.

et al., assuming the interaction parameter between the adsorbates of the adsorbed phase, W_{12}, to be zero. The results at 30 °C are shown in Figures 4–7, where the agreements between estimated and experimental values are not satisfactory except for the total amount adsorbed in Figure 4. Putting either the appropriate negative or positive values into the interaction parameter W_{12} skewed the $X-Y$ curve but did not improve the agreement with the experimental values.

Glossary

b_i	Henry's constant defined by $b_i \equiv \lim_{P\to 0}(n_i^\infty/P)$, mg/(g of adsorbent·mmHg)
n_i^∞	saturated amount adsorbed at infinite pressure, mg/(g of adsorbent)
P	equilibrium pressure, mmHg
R	gas constant, 0.082 06 L·atm/(g-mol·K)
T	temperature, K
W_{i3}	Margules' two-suffix parameter between the gas (i) and the adsorbent (3) in the adsorbed phase, L·atm/g-mol
X_i	mole fraction of component i in the adsorbed phase
Y_i	mole fraction of component i in the gaseous phase
θ_i	surface coverage

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