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Adsorption of a Gaseous Mixture of Ethane and Propane on a Carbon Molecular Sieve

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The adsorption of a binary gaseous mixture of ethane and propane on the carbon molecular sieve MSC•5A was measured at temperatures of 5, 30, and 50 °C and a pressure of 100 mmHg and at 30 °C and 300 mmHg. The amount of propane adsorbed was much higher than the value predicted by the method of Myers and Prausnitz. This preference for propane was greater at lower temperatures but did not change with pressure. Activity coefficients of the adsorbed phase calculated by the Myers–Prausnitz method showed that, at very high concentrations of propane, ethane dissolved in the adsorbed propane in the micropores rather than adsorbed on the surface of the adsorbent.

In a previous paper (*1*) we reported adsorption equilibrium data of pure light hydrocarbons on a hydrophobic microporous adsorbent, the carbon molecular sieve MCS•5A. Its physical and surface properties were reported in the same paper.

Since the adsorption of mixtures in the micropores deviates much from the value predicted by using the pure-component isotherms, it is necessary to generate experimental data for the development of correlations and predictions of mixture adsorption. In this paper we report the adsorption equilibrium data for the ethane–propane–MCS•5A system at 5, 30, and 50 °C and 100 mmHg, and also at 30 °C and 300 mmHg. The experimental data were compared with the values predicted by the method of Myers and Prausnitz (*2*) and of Cook and Basmadjian (*3*). The activity coefficients of ethane and propane in the adsorbed phase, which was obtained by the Myers–Prausnitz method, gave information about the behavior of the adsorbed phase in the micropores.

Experimental Section

The experimental apparatus was basically volumetric, but it has a spring balance in the adsorption tube in order to measure the weight of adsorbent after the degassing and to obtain the total weight of adsorption. The apparatus is shown in Figure 1. The volume of the adsorption tube including the capillary line was measured by helium and was found to be 668.70 (5 °C), 673.65 (30 °C), and 674.60 mL (50 °C). This size of volume was satisfactory for the equilibria not to be perturbed when 2 mL of the gas sample was taken 4 or 5 times for the gas-chromatographic analysis. In order to prepare the gas mixture, we measured propane in the gas buret whose temperature was held constant by circulating water. The gas was then let into the high-pressure gas cylinder which was cooled by the liquid nitrogen. Propane was thus frozen in the cylinder. The second component, ethane, was led into the same cylinder by the same procedure. The liquid-nitrogen bath was then removed and the cylinder was left at room temperature for 24 h to make the contents reevaporate and mix completely. The ~450 mg of adsorbent was degassed at 360 °C under high vacuum for 2 h. The weight of the sample was measured by deflection of a spring balance whose sensitivity was 0.023 97 cm/mg.

The preestimated gas mixture was introduced into the gas buret, and cock A was opened to let the gas into the adsorption tube, while the mercury level was elevated to adjust to the equilibrium pressure of ca. 100 mmHg. After the adsorption proceeded by 80~90% (20~30 min), the pressure was adjusted again to 100 mmHg. Cock A was then closed, and the remaining gas in the buret was evacuated. The mercury level was again elevated to the top line of the buret in order to minimize the volume. Since this minimum volume of the capillary tubing was 4.11 mL, no serious pressure change would occur when cock A was reopened. Ca. 24 h were necessary for the attainment of the adsorption and gas-phase equilibrium. The final equilibrium pressure was read by the manometer, and the total weight of adsorption was known by the spring balance. The gas composition was analyzed by gas chromatography, and the adsorption amount of each component was calculated from the material balance.

The total amounts of adsorption obtained by the material balance were greater than those obtained by the spring balance by 0~5%, depending on the temperature and the composition. Since this discrepancy could be attributed to the adsorption on the system, such as the lubricant of the stopcocks and the joints, and the inside surface of the apparatus, the total weight of adsorption measured by the spring balance was considered to be the true value. The adsorption of pure ethane and propane on the apparatus system was obtained at each temperature and at 100 mmHg. Since these values had rather a poor reproducibility because of the different behavior of lubricant at each run, the adsorbed weight ratios of propane to ethane on the apparatus were used; they were 2.3 (5 °C), 4.1 (30 °C), and 6.3 (50 °C). These values are close to the solubility ratio of propane to ethane in benzene, which is 3.90 at 20 °C (*4*).

The adsorption on the apparatus from the mixture was regarded as the mole fraction linear average. The amounts of each component adsorbed on the apparatus a_i are therefore expressed by eq 1 and 2, where L is the adsorbed weight ratio

$$a_1 \text{ (ethane)} = \Delta W Y_1/(Y_1 + Y_2 L) \qquad (1)$$

$$a_2 \text{ (propane)} = \Delta W Y_2 L/(Y_1 + Y_2 L) \qquad (2)$$

of propane to ethane, the values of which are given above, and

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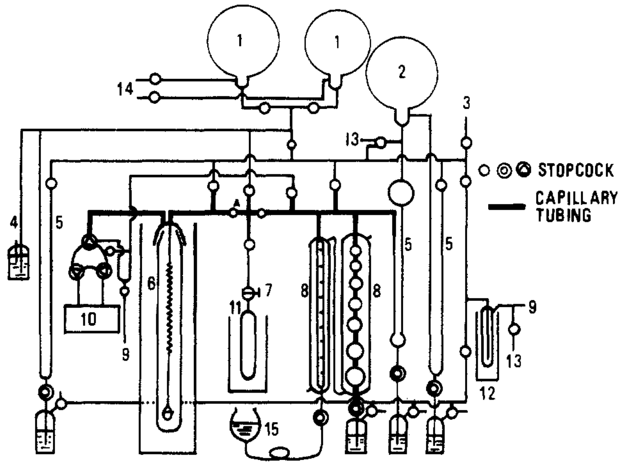

Figure 1. Experimental apparatus: (1) gas reservior; (2) buffer tank; (3) Mcleod gage; (4) mercury safety; (5) manometer; (6) adsorption tube; (7) needle valve; (8) gas buret; (9) vacuum pump; (10) gas chromatograph; (11) high-pressure glass cylinder; (12) liquid-nitrogen trap; (13) vent; (14) gas supply.

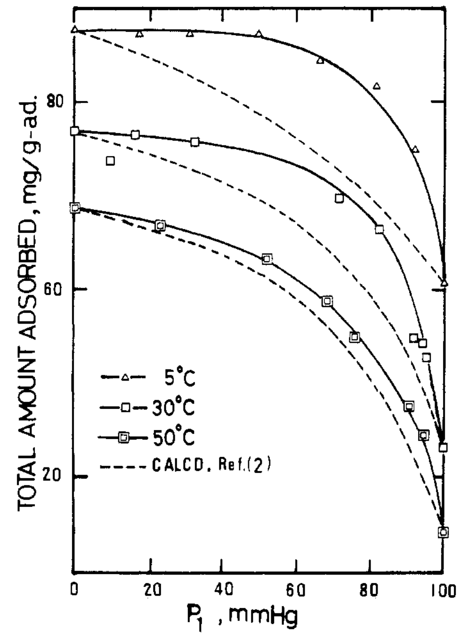

Figure 2. Total amount of adsorption for ethane-propane-MSC·5A system.

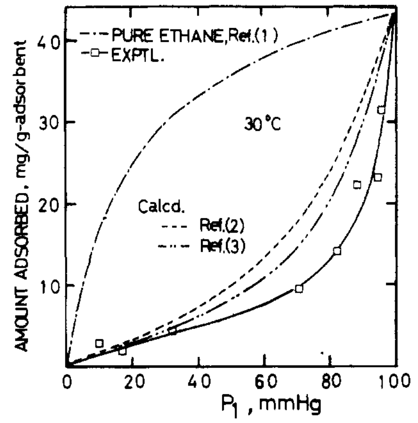

Figure 3. Adsorbed amount of ethane.

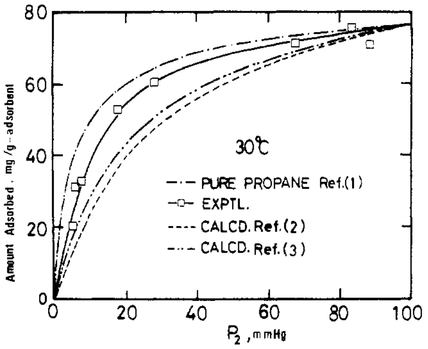

Figure 4. Adsorbed amount of propane.

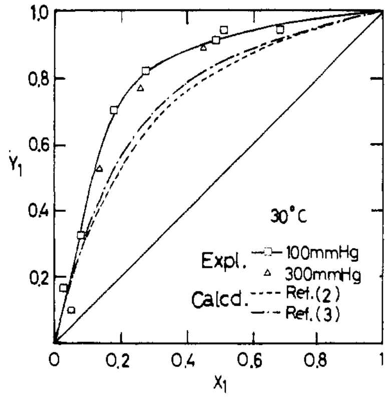

Figure 5. $X-Y$ diagram for ethane-propane-MSC·5A system.

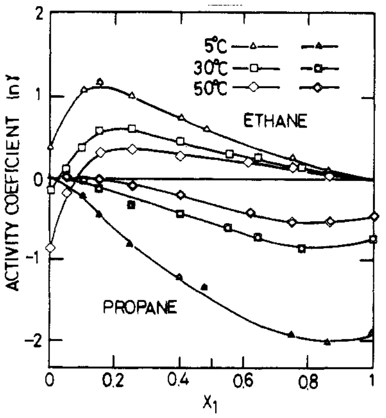

Figure 6. Activity coefficient of ethane and propane in adsorbed phase.

ΔW is the difference between the total weight adsorbed on MSC·5A obtained by the volumetric method and by the spring balance. The corrected adsorbed amount of each component on MSC·5A, W'_i, is calculated by eq 3, where W_i(VM) is the

$$W'_i = W_i(\mathrm{VM}) - a_i \tag{3}$$

uncorrected amount of adsorption on MSC·5A measured by the volumetric method.

Results

The adsorption equilibrium data are listed in Table I. The adsorption isotherms for pure ethane and propane were reported elsewhere (*1*). The total adsorption amounts are plotted in Figure 2. The adsorption amounts of each component are plotted against the partial pressures in Figures 3 and 4 at 30 °C. For the adsorption isotherms of pure components in these figures, the partial pressure means the equilibrium pressure. The adsorption of ethane was very inhibited by the existence of propane. Figure 5 shows the $X-Y$ diagram at 30 °C, 100 and 300 mmHg. No evident difference was observed between those two pressures.

The predicted values by Myers and Prausnitz (*2*) are shown in Figures 2–5. In this method it is necessary to know the

Table I. Adsorption Equilibrium Data for Ethane (1)–Propane (2)–MSC·5A System

		adsorbed amount of ethane		adsorbed amount of propane		total amount adsorbed			
temp, °C	press., mmHg	mmol/(g ad)	mg/(g ad)	mmol/(g ad)	mg/(g ad)	mmol/(g ad)	mg/(g ad)	adsorbate mole fraction, X_1	gas-phase mole fraction, Y_1
5.0	102.0	0.000	0.00	1.990	87.78	1.990	87.78	0.000	0.000
	100.4	0.128	3.86	1.890	83.35	2.018	87.21	0.064	0.204
	98.9	0.186	5.61	1.853	81.70	2.039	87.31	0.091	0.363
	99.5	0.242	7.27	1.816	80.08	2.058	87.35	0.119	0.495
	99.4	0.352	10.59	1.673	73.76	2.025	87.35	0.174	0.666
	99.8	0.542	16.29	1.485	65.48	2.017	81.77	0.267	0.815
	99.3	0.838	25.21	1.129	49.80	1.967	75.01	0.426	0.926
	98.9	2.622	60.80	0.000	0.000	2.622	60.80	1.000	1.000
30.0	100.9	0.000	0.00	1.741	76.80	1.741	76.80	0.000	0.000
	98.9	0.094	2.83	1.610	71.00	1.704	73.83	0.031	0.101
	100.4	0.057	1.70	1.695	74.74	1.752	76.74	0.055	0.168
	99.5	0.142	4.26	1.623	71.58	1.765	75.84	0.080	0.325
	99.3	0.314	9.44	1.367	60.28	1.681	69.72	0.187	0.715
	100.0	0.468	14.06	1.188	52.40	1.656	66.46	0.282	0.823
	96.6	0.734	22.08	0.746	32.88	1.480	54.96	0.496	0.910
	101.4	0.766	23.03	0.710	31.29	1.476	54.32	0.519	0.947
	101.1	1.036	31.14	0.467	20.58	1.503	51.72	0.689	0.952
	100.4	1.457	43.80	0.000	0.00	1.457	43.80	1.000	1.000
	300.0	0.000	0.00	1.859	82.00	1.859	82.00	0.000	0.000
	301.9	0.258	7.76	1.605	70.78	1.859	78.54	0.139	0.526
	303.6	0.494	14.84	1.341	59.14	1.835	73.98	0.269	0.776
	300.4	0.829	24.92	1.021	45.03	1.850	69.95	0.448	0.884
	301.0	1.929	58.00	0.000	0.00	1.929	58.00	1.000	1.000
50.0	100.0	0.000	0.00	1.558	68.70	1.558	68.70	0.000	0.000
	101.6	0.090	2.72	1.454	64.11	1.554	66.83	0.058	0.232
	102.6	0.179	5.38	1.397	61.59	1.576	66.94	0.144	0.371
	99.8	0.186	5.58	1.305	57.53	1.481	63.41	0.131	0.520
	101.0	0.214	6.42	1.188	52.39	1.402	58.81	0.153	0.680
	101.5	0.354	10.64	1.012	44.64	1.366	55.28	0.258	0.807
	100.7	0.528	15.88	0.722	31.82	1.300	47.70	0.423	0.903
	102.5	0.705	21.20	0.533	23.50	1.238	44.70	0.570	0.949
	100.0	1.141	34.30	0.000	0.00	1.141	34.30	1.000	1.000

isotherms of ethane up to the pressures of 300 (5 °C), 450 (30 °C), and 520 mmHg (50 °C).

The activity coefficient γ_i is calculated by eq 4, where $P_i(\pi)$

$$PY_i = P_i(\pi)\gamma_i X_i \tag{4}$$

is the equilibrium pressure for the pure component corresponding to the spreading pressure which has been defined by Myers et al. As shown in Figure 6, activity coefficients of propane are less than unity in the whole range X_1. Activity coefficients of ethane are larger than unity at most of the compositions except at a very high composition of propane, where it should be considered that ethane dissolves in the adsorbed propane rather than adsorbs on the surface of the adsorbent. The maximum activity coefficients of ethane appear at the compositions where propane just covers the whole surface of the adsorbent, inhibiting the direct adsorption of ethane on the surface but not being enough to make ethane dissolve in propane.

The prediction method proposed by Cook and Basmadjian (*3*) was also applied in this work. The results are shown in Figures 3–5. Data for the adsorption isotherms of ethane were necessary to pressures of 180, 220, and 250 mmHg at temperatures of 5, 30, and 50 °C, respectively.

Glossary

a_i	adsorption of component i from the mixture on the apparatus (g)
L	adsorption ratio of pure propane to pure ethane on the apparatus
P	total pressure (mmHg)
P_i	partial pressure of component i (mmHg)
$P_i(\pi)$	equilibrium pressure of pure component i corresponding to the spreading pressure, definedby Myers and Prausnitz (mmHg)
ΔW	difference of total adsorption weight measured by the spring balance and by the volumetric method (g)
W_i(VM)	adsorbed amount of component i measured by the volumetric method (g)
X_i	mole fraction of component i in the adsorbed phase
Y_i	mole fraction of component i in the gaseous phase
γ_i	activity coefficient of component i in the adsorbed phase

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