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Propane–Carbon Dioxide and Propylene–Carbon Dioxide Mixture Adsorption in 5A Molecular Sieves

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Measurements of the adsorption on 5A molecular sieves have established that, at 1 atm and 24.0 °C, both systems, propane–carbon dioxide and propylene–carbon dioxide, form ideal solution adsorbed phases. Total mass adsorbed ranges from 112 to 207 mg/g of sorbent for propane–carbon dioxide and from 130 to 207 mg/g of sorbent for propylene–carbon dioxide.

Introduction

Meyers and Praunsnitz (*1*) have pointed out that the concept of an adsorbed phase clarifies the meaning of an ideal solution behavior among components adsorbed at low coverages on adsorbents such as molecular series. The ideal adsorbed solution theory (IAST) (*1*,*2*) assumes that components in adsorbed mixtures have the same thermodynamic state as the pure adsorbed components at the same temperature and spreading pressure. Accordingly, many adsorbed systems are ideal as verified by Friedrich and Mullins (*3*). Further discussions of systems and suggestions about methods for calculation of the spreading pressure were presented by Kidnay and Meyers (*4*).

Recently, Glessner has measured the adsorption of binary mixtures of ethane and *n*-butane, and ethane and carbon dioxide, and surveyed the literature on molecular sieves (*5*). He found that the first system was ideal but that the second gave indications for nonideality.

Interest in molecular sieves for separations of propylene–propane mixtures was revived by Grossmann and Schirmer (*6*), and the attractiveness of carbon dioxide as a displacement medium for removing the adsorbed separated hydrocarbon indicates that the energy required to regenerate would be lower than that required for pure hydrocarbon desorption. The data required to test the ideal adsorbed solution theory includes the pure-component isotherms and the mixture isotherms.

Experimental Section

Materials. Linde molecular sieve type 5A was the sorbent supplied as 8/12 mesh pellets by the Fisher Scientific Co. (Fair Lawn, NJ). For all experiments, the weight of sieves used was ~100 mg.

Propane and propylene were research-grade gases obtained from Phillips Petroleum Co. and certified by Phillips to be 99.99% pure. The certification indicated that the most probable impurity in the propane cylinder was ethane and that in the propylene cylinder was propane. Nitrogen was obtained from Airco Co. (NY) and carbon dioxide from Acetylene Gas Co. (St. Louis, MO).

Apparatus and Procedure. The quartz spring apparatus for all experiments was made of glass and designed to use volumetric data to check gravimetric sorption results (*7*). The isotherms were obtained by degassing the sorbent at less than 0.01 mmHg and 296 °C for 12 h. Gas was added to the sorption chamber, and the pressure was recorded as a function of time. Forty minutes later the pressure in the sorption chamber, the temperature of the sorbent, the spring elongation, and the gas composition (by gas–liquid chromatography) were measured. The amount of gas adsorbed was calculated from both spring elongation and the total volume of sample gases added to the system. The remainder of an isotherm was obtained by successive sorptions and desorptions. Gas compositions, needed for adsorbed mixture compositions, were determined by gas–liquid chromatography to 1%.

Table I. Propane–Carbon Dioxide Mixture Data (at 24.0 °C)[a]

(1)	P	n_A	n_B	n_{Aa}	n_{Ba}	y_A	x_A
CO_2	726.0	50.42	7.483	3.282	4.152	0.934	0.441
CO_2	727.0	48.74	9.172	2.150	5.230	0.922	0.291
C_3H_8	727.0	47.74	10.40	2.511	5.097	0.895	0.330
CO_2	732.0	45.58	13.20	1.620	6.276	0.864	0.205
CO_2	736.0	43.68	15.78	1.320	6.978	0.828	0.159
CO_2	743.0	39.55	20.74	0.819	7.824	0.750	0.095
CO_2	741.5	42.77	17.04	0.842	7.457	0.814	0.101
CO_2	728.0	37.22	22.37	0.788	8.198	0.720	0.088

[a] (1) Component contacted first with the sorbent; P, equilibrium pressure in mmHg; n_A, amount of propane present in cm^3(STP)/0.1 g; n_B, amount of propane adsorbed in cm^3(STP)/0.1 g; n_{Aa}, amount of propane adsorbed in cm^3(STP)/0.1 g; n_{Ba}, amount of CO_2 adsorbed in cm^3(STP)/0.1 g; y_A, mole fraction of propane in gas phase; x_A, mole fraction of propane in sorbed phase.

The volumetric data were used to check the consistency of the experiments. From the record of pressure vs. time, the initial pressure was obtained from a semilogarithmic plot of pressure extrapolated to zero time (*8*). The amount of gas adsorbed and its composition were calculated by assuming ideal gas, and an experiment was accepted when this value agreed with that from the spring elongation within 2%. Only Danner and Choi (*9*) seem to have recognized the value of combining gas-composition measurements with both gravimetric and volumetric data to ensure experimental accuracy.

Results and Discussion

Pure-Component Isotherms. Pure-component isotherms at two temperatures were obtained gravimetrically for carbon dioxide, propane, propylene, and nitrogen in type 5A molecular sieves. The amount adsorbed increases from propane to propylene to carbon dioxide. The desorption points agree with the sorption points within experimental error.

Values for carbon dioxide at 24.0 °C from 5 to 400 mmHg are a little lower than those from the Linde Data Sheet No. 24 (*10*) at 25 °C and a little higher in a range from 400 to 700 mmHg but agree within 2%. Values for propane at 24.0 °C are ca. 5% higher than the Linde Data Sheet No. 141 at 25.0 °C from 5 to 200 mmHg and ca. 2% higher from 200 to 700 mmHg. Therefore, these are not reported here.

Values for heats of adsorption implied by the two isotherms were calculated from plots of the logarithm of the equilibrium pressure as a function of reciprocal absolute temperature (*11*) with an absolute scatter of 0.25 kcal/mol. For carbon dioxide, the initial heat of sorption is 11.51 kcal/mol compared to 11.50 kcal/mol reported by Barrer and Gibbons (*12*) and 11.39 kcal/mol calculated from the Linde Date Sheet No. 22. The initial heat of sorption of propane is 12.67 kcal/mol compared to 11.90 kcal/mol reported by Barrer and Sutherland (*13*). The values for propylene were 14.52 kcal/mol (initial) and 12.7 kcal/mol (1 atm).

Binary-Mixtures Isotherms. Mixture sorption isotherms at 24.0 °C were obtained for the binary mixtures of propane and

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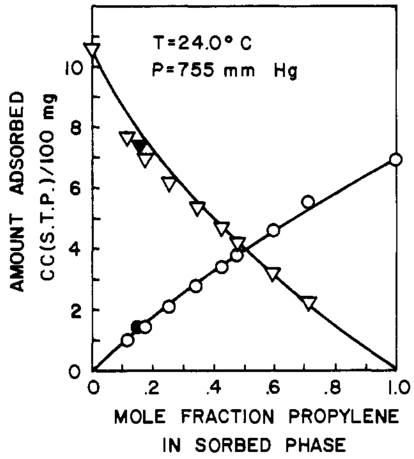

Figure 1. Propane–carbon dioxide mixture: (○,▽) CO_2 contacted first; (●,▼) C_3H_8 contacted first; ideal adsorbed solution theory.

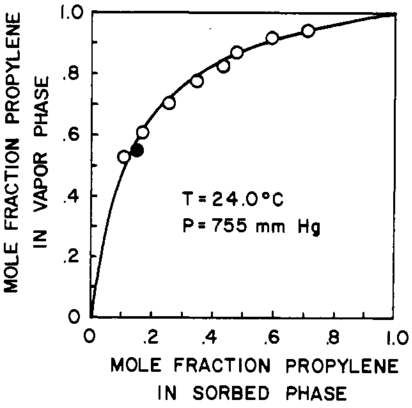

Figure 2. Propane–carbon dioxide mixture: (○,▽) CO_2 contacted first; (●,▼) C_3H_8 contacted first; ideal adsorbed solution theory.

Table II. Propylene–Carbon Dioxide Mixture Data (at 24.0 °C)

(1)	P	n_A	n_B	n_{Aa}	n_{Ba}	y_A	x_A
CO_2	775.0	34.17	28.06	1.418	6.945	0.608	0.170
CO_2	743.5	38.52	21.41	2.089	6.164	0.705	0.253
CO_2	798.0	46.12	16.48	2.802	5.336	0.781	0.344
CO_2	733.5	45.99	13.16	3.469	4.697	0.834	0.425
CO_2	753.5	49.36	10.96	3.798	4.154	0.870	0.478
CO_2	725.5	51.01	7.180	4.612	3.146	0.920	0.594
CO_2	758.5	52.02	8.502	2.250	5.550	0.944	0.712
CO_2	758.5	28.68	32.73	1.002	7.686	0.525	0.115
C_3H_6	750.0	29.91	31.09	1.448	7.418	0.546	0.153

[a] (1) Component contacted first with the sorbent; P, equilibrium pressure in mmHg; n_A, amount of propane present in cm^3(STP)/0.1 g; n_B, amount of CO_2 present in cm^3(STP)/0.1 g; n_{Aa}, amount of propane adsorbed in cm^3(STP)/0.1 g; n_{Ba}, amount of CO_2 adsorbed in cm^3(STP)/0.1 g; y_A, mole fraction of propane in gas phase; x_A, mole fraction of propane in sorbed phase.

carbon dioxide and for propylene and carbon dioxide on type 5A molecular sieves.

For the propane–carbon dioxide mixture data in Table I, the expermental points were obtained for a range of propane mole fractions, in the sorbed phase, from 0.08 to 0.44. Beyond that range, the ratio of propane mole fraction to carbon dioxide mole fraction in the gas phase was too high (greater than 15) to be analyzed by the gas chromatograph. The experimental results are plotted in Figures 1 and 2. The relative volatility suggested in Figure 2 is 19 at 50% of mole fraction in the sorbed phase.

For the propylene–carbon dioxide, data are tabulated in Table II and plotted in Figures 3 and 4 with a range of propylene mole fractions, in the sorbed phase, from 0.11 to 0.71. Figure 4 suggests that the relative volatility is 6.7 at 50% of mole fraction in the sorbed phase. Both adsorption and desorption approaches to equilibrium yield the same compositions within 2%.

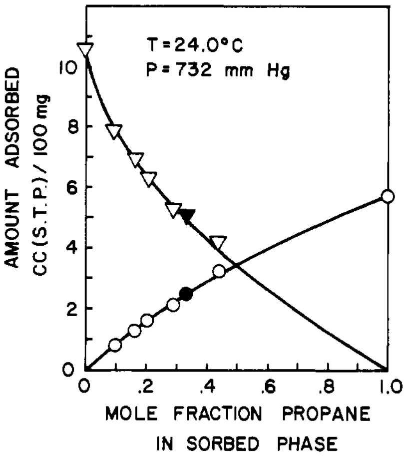

Figure 3. Propylene–carbon dioxide mixture: (○,▽) CO_2 contacted first; (●,▼) C_3H_6 contacted first; ideal adsorbed solution theory.

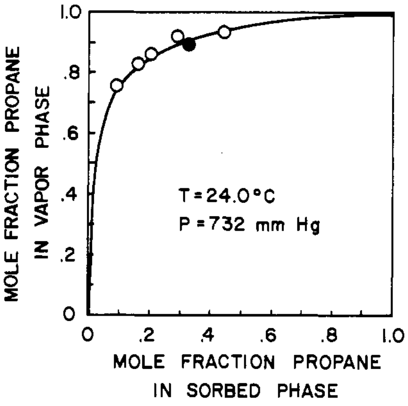

Figure 4. Propylene–carbon dioxide mixture: (○,▽) CO_2 contacted first; (●,▼) C_3H_6 contacted first; ideal adsorbed solution theory.

The prediction of ideal adsorbed solution theory of ref 1 and 2 for a mixture was made for the mean constant total pressure (732 mmHg for propane–carbon dioxide and 755 mmHg for propylene–carbon dioxide). The equilibrium total pressures of the experimental data varied within 2% from the mean for the propane–carbon dioxide mixture and 5% for propylene–carbon dioxide mixture, and the possible error caused by those differences is negligible. Both systems can be considered ideal.

Conclusions

Both systems, propane–carbon dioxide and propylene–carbon dioxide, may be considered to form ideal sorbed phases on 5A molecular sieves at 24.0 °C and 1 atm. Total mass adsorbed ranges from 112 to 207 mg/g of sorbent for propane–carbon dioxide and from 130 to 207 mg/g of sorbent for propylene–carbon dioxide.

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