

Adsorption Equilibrium of the System Methane–Ethane–Silica Gel at High Pressures and Ambient Temperatures

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The adsorption of eight methane-ethane mixtures, ranging from pure methane to pure ethane, on silica gel at 5°, 15°, 25°, and 35° C. up to a maximum pressure of 1400 p.s.i.a. was studied by chromatography combined with the tracer perturbation technique. The hypothetical perfect gas approach was used to determine the free gas phase volume in the column. No previous data have been reported for the full composition range of the system. The amount of adsorption was determined for three different definitions: absolute adsorption, Gibbs adsorption, and Gibbs adsorption taking into account molecular size. The difference among the definitions were significant at these ambient temperatures. The partition *K*-values for methane and ethane between gas and adsorbed phase were calculated and plotted as functions of pressure and composition of the gas phase. Continuity exists between the *K*-values for adsorption and *K*-values for vapor-liquid equilibrium for the same mixture at 5° C.

THE adsorption behavior of methane and ethane mixtures on silica gel has been determined from 5° to 35° C. The data are reported for the entire composition range and for three definitions of adsorption.

EXPERIMENTAL

Fundamental Equations. Three definitions for the amount of adsorption (3) are:

$$N^A(i) = [v_R(i) - (v_1 + v_d)] c_1(i) \quad (1)$$

$$N^G(i) = [v_R(i) - v_R(PG)] c_1(i) \quad (2)$$

$$N^{GM}(i) = [v_R(i) - (v_1 + v_d + v_2)] c_1(i) \quad (3)$$

The partition *K*-value for adsorption of component *i* is

$$K(i) = y(i)/x^A(i) \quad (4)$$

Experimental System. Detailed descriptions of the apparatus and method have been given elsewhere (3). Table I gives the compositions of the eight gas mixtures of methane and ethane. The adsorbent was silica gel (Davison Chemical, Grade 15) with a specific surface area of 803.5 sq. meters per gram. The adsorbent sample for the experimental runs was 2.048 grams; the adsorbent for the correction runs was 2.013 grams. Temperatures were 5.00°, 15.00°, 25.00°, and 35.00° ± 0.03° C. The maximum pressure ranged from 400 to 1400 p.s.i.a. as given in Table I. The adsorbed phase was assumed to be 8.0 Å. thick. The sum (*v*₁ + *v*_d) was 2.60 ml.

Correction for Degradation of Adsorbent. During the 5-month course of the experimental studies, some degradation of the adsorbent was found. The effect of the degradation was a slight lowering of the retention volume with a maximum of 4.9% *V*_R^o (C₂H₆)/*P* and 3.3% *V*_R^o (CH₄)/*P* for elution gas No. 8 near atmospheric pressure at 25° C. The effect on the amount of adsorption was slightly greater. In general, the effect was larger at lower pressure, at lower temperature, and for the heavier component.

The correction was determined by the following procedure: After the entire series of experimental runs had

been made, the original 2.048 grams sample of adsorbent was replaced by a fresh silica gel sample of 2.013 grams.

A second series of experimental runs was made for the eight gas mixtures and four temperatures at two pressures each, corresponding to ¼ and ½ of the maximum pressure studied for that composition.

The new retention volume data was multiplied by the factor (2.048/2.013) to convert it to the original data basis. This process was justified because the retention volumes for methane and ethane were large compared with the free gas phase volume in the column. All of the experimental retention volume data from both series were converted to standard conditions, *V*_R^o (*i*), by the gas law. The compressibility factors used were reported in an earlier paper (3).

The resulting *V*_R^o (*i*) were plotted on large graph paper.

The difference between the two points of the second series and the original data for each temperature-composition set was expressed by the exponential equation

$$\Delta V_R^o(i)/P = a \exp(-bP) \quad (5)$$

The complete series was corrected by the appropriate correction, Equation 5.

The retention data at zero pressure were not corrected, since they were determined at the first stage of the experimental runs before degradation of the adsorbent set in.

Table I. Compositions of Elution Gas Mixtures as Analyzed by Mass Spectrometry and the Maximum Pressure Studied for Each Elution Gas

Elution Gas No.	Methane, Mole %	Ethane, Mole %	Air and Others, Mole %	<i>P</i> max., P.S.I.A.
1	99.98	0.02	...	1400
2	98.56	1.44	...	1300
3	94.27	5.58	0.15	1200
4	89.42	10.58	...	1100
5	79.49	20.51	...	1000
6	60.07	39.79	0.14	800
7	33.60	66.40	...	500
8	0.00	99.94	0.06	400

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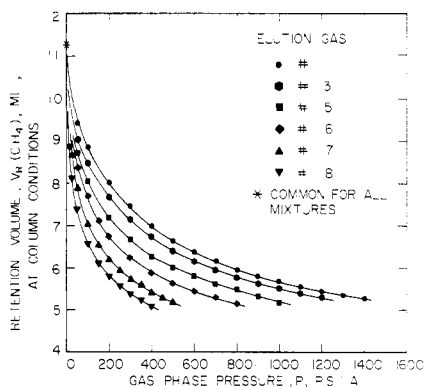


Figure 1. Corrected retention volume for methane through a column packed with 2.048 grams of silica gel (area = 1645 sq. meters), free gas phase volume = 2.60 ml.

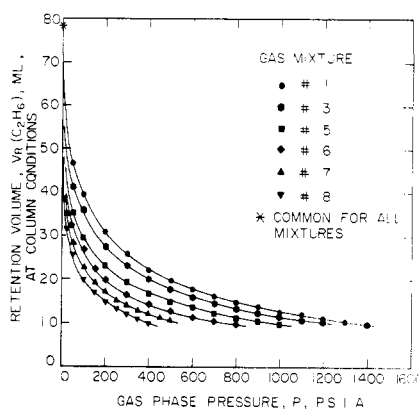
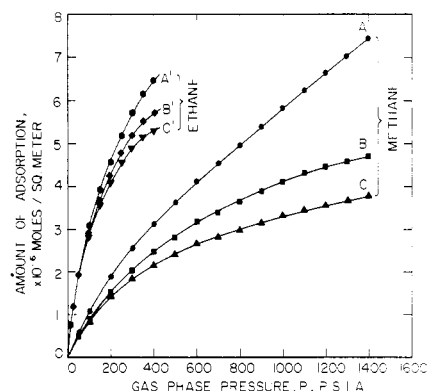


Figure 2. Corrected retention volumes for ethane through a column packed with 2.048 grams of silica gel (area = 1645 sq. meters), free gas phase volume = 2.60 ml.



A, A' ABSOLUTE ADSORPTION
B, B' GIBBS ADSORPTION
C, C' GIBBS ADSORPTION TAKING INTO ACCOUNT MOLECULAR SIZE

Figure 3. Comparison of three definitions of adsorption for methane and ethane on silica gel at 25°C.

DISCUSSION OF RESULTS

As an example of the results, Figures 1 and 2 show the corrected retention volumes at 25°C. for some mixtures. The entire series formed a regular sequence; some mixtures have been omitted only for clarity. The retention volume at zero pressure is unique for the species, the adsorbent, and the temperature; but it is common for all compositions.

Some results [complete tables for all temperatures and all gases may be obtained from University Microfilm, S. Masukawa, Monograph, Rice University (1967) or from the American Documentation Institute] of this study for 25°C. are given in Table II as the amount of adsorption according to the three definitions in Equations 1, 2, and 3. Table II includes the limiting values at zero pressure and infinite dilution. Absolute adsorption is used for the development of a correlation (2). Gibbs adsorption taking into account molecular size is used to calculate the spreading pressure of the adsorbed phase (1). Figure 3 illustrates the differences among the three definitions of adsorption.

Figures 4 and 5 show K -values calculated by Equation 4 at the temperature limits, 5° and 35°C. In Figure 4,

Table II. Absolute Adsorption, Gibbs Adsorption, and Gibbs Molecular Adsorption of Methane (1) and Ethane (2) on Silica Gel from Their Mixtures at 25.00°C. for Elution Gas No. 1^a

Press., P.S.I.A.	N^A (1) $\times 10^{-6}$ Moles/Sq. Meter	N^A (2) $\times 10^{-6}$ Moles/Sq. Meter	N^G (1) $\times 10^{-6}$ Moles/Sq. Meter	N^G (2) $\times 10^{-6}$ Moles/Sq. Meter	N^{GM} (1) $\times 10^{-6}$ Moles/Sq. Meter	N^{GM} (2) $\times 10^{-6}$ Moles/Sq. Meter
0	0.0146P	0.1274Py	0.0127P	0.1254Py	0.0123P	0.1252Py
50	0.580	3.74y	0.487	3.66y	0.467	3.62y
100	1.068	6.32y	0.890	6.13y	0.843	6.10y
200	1.874	9.80y	1.539	9.46y	1.417	9.34y
300	2.545	12.27y	2.060	11.80y	1.851	11.58y
400	3.106	14.01y	2.475	13.38y	2.170	13.07y
500	3.607	15.30y	2.820	14.51y	2.423	14.12y
600	4.112	16.41y	3.164	15.47y	2.674	14.98y
700	4.515	17.40y	3.397	16.30y	2.819	15.70y
800	4.950	18.12y	3.658	17.04y	2.987	16.16y
900	5.378	18.78y	3.886	17.23y	3.146	16.53y
1000	5.815	19.00y	4.104	17.28y	3.312	16.50y
1100	6.238	19.33y	4.303	17.40y	3.454	16.55y
1200	6.642	19.80y	4.447	17.63y	3.566	16.73y
1300	7.030	19.78y	4.578	17.36y	3.669	16.43y
1400	7.435	19.86y	4.696	17.16y	3.794	16.23y

^ay in the column is infinitely close to zero.

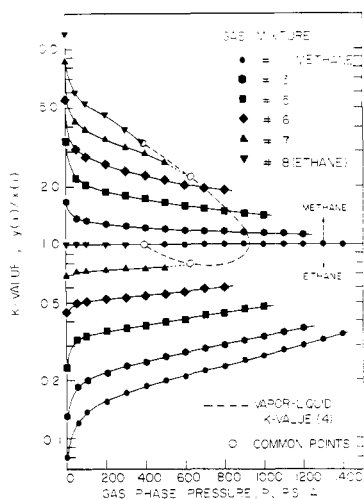


Figure 4. K -values for methane-ethane adsorption on silica gel as functions of gas phase pressure and composition, and their continuity to methane-ethane vapor-liquid K -values at 5°C .

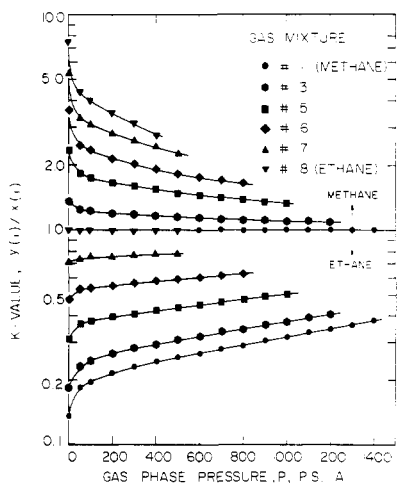


Figure 5. K -values for methane-ethane adsorption on silica gel as functions of gas phase pressure and composition at 35°C .

vapor-liquid K -values obtained by interpolation of the data of Price and Kobayashi (4) are shown as a dashed line. In both figures, it was necessary to omit some of the mixtures for clarity. At 5°C . (Figure 4) only mixtures No. 7 and No. 8 condense at higher pressures. Although the vapor-solid curves end before they reach their dew points, the intersections of the smooth extension of the

vapor-solid curves with the vapor-liquid curve define common points at the dew points. This is not only a justification for the idea of continuity of K -values between vapor-solid and vapor-liquid systems but, also, an evidence of the consistency and correctness of the results obtained in the neighborhood of the dew points.

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NOMENCLATURE

- a, b = constants in Equation 5
- $c_1(i)$ = molecular concentration of species i in the free gas phase 1 at column conditions
- $K(i)$ = partition coefficient defined by Equation 4
- $N^A(i)$ = absolute adsorption, total number of molecules of species i in the adsorbed phase
- $N^G(i)$ = Gibbs adsorption, net increase in the number of molecules of species i in the adsorbed phase
- $N^{GM}(i)$ = Gibbs (G) adsorption taking into account molecular (M) size corresponding to the thermodynamic version of Gibbs adsorption
- P = pressure
- v_1 = free gas phase volume in the column
- v_2 = adsorbed phase volume in the column
- v_d = uncompensated dead space in tubing and connections
- $v_R(i)$ = retention volume for species i at column conditions
- $V_R^{\circ}(i)$ = retention volume for species i at standard conditions, 14.696 p.s.i.a. and 25.00°C .
- $v_R(PG)$ = retention volume for the hypothetical perfect gas obtained by energy extrapolation of retention volumes of a set of real gases
- $x^A(i)$ = mole fraction of species i in the adsorbed phase
- $y(i)$ = mole fraction of species i in the free gas phase

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