

Experimental Selectivity Curves of Gaseous Binary Mixtures of Hydrocarbons and Carbon Dioxide on Activated Carbon and Silica Gel

Marie-Georges Olivier* and Roger Jadot

Faculté Polytechnique de Mons, Service de Thermodynamique, Boulevard Dolez, 31, 7000, Mons, Belgium

The selectivity curves of gaseous binary mixtures of ethane + ethylene, methane + carbon dioxide at 303 K and 700 kPa and butane + 2-methylpropane at 318 K and 200 kPa are determined on activated carbon and silica gel using an original apparatus. In this paper, a brief description of this apparatus is given. The difference in behavior of these two adsorbents is discussed.

Introduction

Data on the adsorption equilibria of gas mixtures are important both from a practical point of view for the design of gas adsorbers and from a theoretical basis for the understanding of the interactions between gases and solid surfaces.

The technology of adsorption is less advanced than that of other separation processes such as distillation, absorption, and extraction. Probably the major cause of this disparity is that adsorption phenomena are more complicated and not as well understood as the other techniques.

Compared to the voluminous data in the literature on pure gas adsorption, gas mixture data are extremely scarce. Various correlations for gas mixture adsorption have been developed, but they are inadequately tested owing to the paucity of the data (for example; Craknell and Nicholson (1995) and Kaul (1984)). Additionally mixture data are generally limited to the range of low pressures (inferior or equal to 100 kPa).

Multicomponent adsorption equilibria are usually obtained by modeling of pure component experimental data. A systematic study of the pure component adsorption equilibrium of ethane, ethylene, methane, carbon dioxide, butane, and 2-methylpropane on the same adsorbents and in the same range of pressure and temperature has been reported previously (Olivier et al., 1994; Olivier and Jadot, 1997).

To provide the data that are needed to validate the modeling of multicomponent adsorption equilibria, a volumetric apparatus for obtaining gas mixture adsorption data has been built. The apparatus determines the isothermal and isobaric selectivity curves of gaseous mixtures from measurements of volumes, pressures, and temperatures. The range of pressures and temperatures are from 150 kPa to 1000 kPa and from 298 K to 353 K, respectively.

The selectivity curves have been collected for the binary gaseous mixtures: ethane + ethylene and methane + carbon dioxide at 700 kPa and 303 K and for butane + 2-methylpropane at 200 kPa and 318 K on activated carbon and silica gel.

In the past, the methane + carbon dioxide binary mixture has been studied on BPL activated carbon at 101 kPa and 304 K by Wilson and Danner (1983). The equilibrium data for the ethane + ethylene mixture has been determined on Nuxit-al activated carbon at 100 kPa

and two temperatures: 293.15 K and 333.15 K (Szepezy and Illes, 1963a,b). Reich et al. (1980) give equilibrium data for this mixture at three temperatures: 212.15 K, 260.2 K and 301.4 K. These are ponctual experimental results and no selectivity curves. The selectivity of 2-methylpropane with regard to butane has never been obtained experimentally on activated carbon. The adsorption of the three mixtures has not been studied on silica gel.

Experimental Apparatus

This apparatus is based on a volumetric method. In this method, the total quantity of each gas admitted to the system and the amount of each gas in the vapor remaining after adsorption equilibrium are determined by appropriate P - V - T measurements and analyzed by a gas chromatograph. The adsorbed phase parameters are determined by subtraction between the quantities of admitted and remaining gases. A schematic diagram of the apparatus is shown in Figure 1.

The adsorption apparatus was maintained in an oven (E) regulated in temperature to within ± 0.4 K. The main part of the apparatus consists of a recycle loop and an adsorption cell (Cad). The recycle loop was constructed of 1/4-in. o.d. stainless steel tubing. A volumetric micrometer (MV) permitted accurate measurement and adjustment of the internal volume of the recycle loop and simple regulation of the system pressure. Its maximum internal volume is approximately of 500 cm³. This device is regulated in pressure by an electropneumatic system (RP). A hermetically sealed, magnetically coupled centrifugal pump (PC) provided circulation of gases. The adsorption cell was a stainless steel vessel in which the adsorbent was on a glass porous plate (S). This plate ensures an intimate contact between the adsorbates and the adsorbent. Two three-way valves (V1 and V2) allowed the isolation of the adsorption cell and the control over the direction of the flow of the gases either through the adsorption cell or through a bypass around the cell. A heating wire (RD) enabled the adsorbent sample to be regenerated in situ. Pressure measurements were made by a Druck PDCR 911 absolute pressure transducer (0–1000 kPa) (CP) of accuracy about $\pm 0.1\%$ of the scale. Temperature in the adsorption cell was measured using a thermocouple (T) with an accuracy of ± 0.1 K.

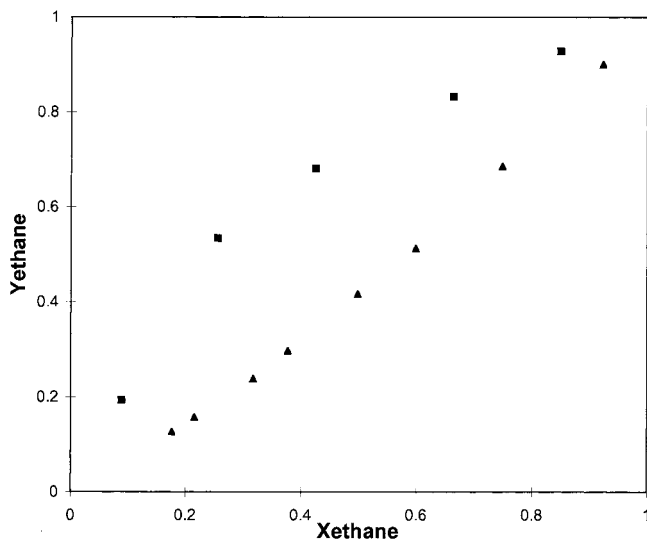


Figure 2. Selectivity curves of ethane + ethylene at 700 kPa and 303 K on activated carbon (▲) and on silica gel (■).

Table 2. Main Characteristics of Activated Carbon F30/470 and Silica Gel KC as Adsorbents

	activated carbon F30/470	silica gel KC
specific surface	1100 m ² /g	750 m ² /g
apparent density	800 kg/m ³	460 ± 20 kg/m ³
particle size	>2.0 mm	2–5 mm
mean diameter of pores		20 Å
volume of pores total	0.9 cm ³ /g	0.35 cm ³ /g
0–2 nm	0.4 cm ³ /g	
2–30 nm	0.1 cm ³ /g	

pressure of 150 kPa, this error is equal to 0.7%, and for a maximal consigned pressure, this error is about 0.1%), and the error obtained for the gas chromatograph analysis (<1%). This results in a relative error in the moles adsorbed of 2%. Such experimental errors are common for the volumetric method in which the moles adsorbed are not directly measured.

Materials

The adsorbents used in this study are type F30/470 AC supplied by Chemviron Carbon and type KC silica gel supplied by Kalie Chemie. The surface areas are 1100 m² g⁻¹ and 750 m² g⁻¹, respectively. The main characteristics of these adsorbents are given in Table 2.

The structure of activated carbon consists of elementary microcrystallites of graphite, but these microcrystallites are stacked together in random orientation and it is the spaces between the crystals that form the micropores. The pore size distribution is typically trimodal. The surface of carbon is essentially nonpolar. Carbon adsorbents tend to be hydrophobic and organophilic.

Silica gel is a partially dehydrated form of polymeric colloidal silicic acid. The chemical composition can be expressed as SiO₂·*n*H₂O. The water content, which is present mainly in the form of chemically bound hydroxyl groups, amounts typically to about 5 mass %. The pore size shows generally a unimodal distribution (20 Å).

The methane, ethane, ethylene, butane, 2-methylpropane, and carbon dioxide were obtained from Air Liquide Belgium with a purity of 99.5%, respectively.

Experimental Results

The selectivity curves of following binary mixtures are been determined on activated carbon and silica gel: ethane

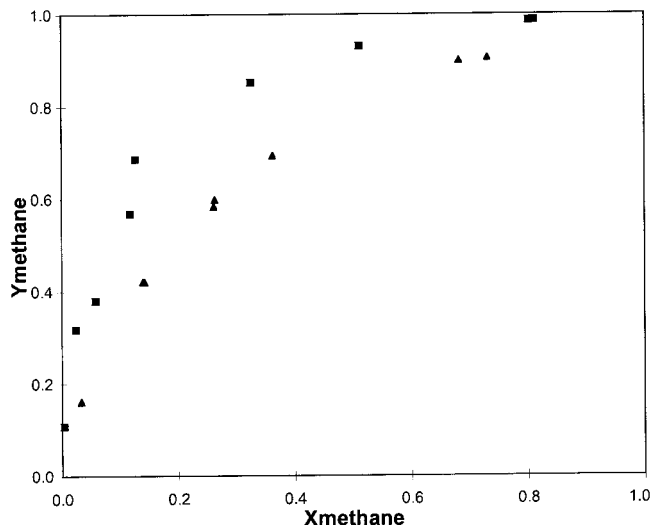


Figure 3. Selectivity curves of methane + carbon dioxide at 700 kPa and 303 K on activated carbon (▲) and on silica gel (■).

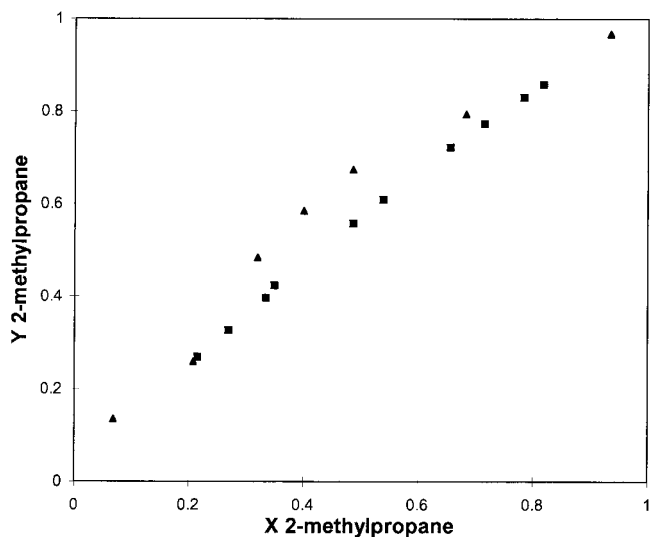


Figure 4. Selectivity curves of butane + 2-methylpropane at 200 kPa and 318 K on activated carbon (▲) and on silica gel (■).

+ ethylene (Figure 2) and methane + carbon dioxide (Figure 3) at 700 kPa and 303 K and butane + 2-methylpropane (Figure 4) at 200 kPa and 318 K.

The quantity used to determine if an adsorptive separation of binary gaseous mixture is viable is the separation factor called the selectivity of component *i* with regard to component *j* which is given by

$$S_{ij} = x_i y_j / x_j y_i$$

where x_i and y_i are the adsorbed phase and bulk gas phase mole fraction respectively of component *i*, and x_j and y_j are the same quantities related to component *j*.

The experimental results are given in Tables 3–8.

Discussion

On microporous media, the selectivity of a component 1 with regard to a component 2 is given qualitatively by

$$S_{1/2} = \frac{x_1 y_2}{x_2 y_1} = \frac{f_2^{\text{Int}_2} [\text{Geo}_1]}{f_1^{\text{Int}_1} [\text{Geo}_2]}$$

where $f_1^{\text{Int}_1}$ and $f_2^{\text{Int}_2}$ are the standard fugacities of component 1 and component 2, respectively. For the subcritical com-

Table 3. Ethane (1) + Ethylene (2) on Activated Carbon F30/470 at 700 kPa and 303 K

x_1	y_1	$S_{1/2}$	$N_1/\text{mol kg}^{-1}$	$N_2/\text{mol kg}^{-1}$
0.176	0.128	1.46	0.901	4.220
0.215	0.158	1.45	1.104	4.033
0.317	0.239	1.48	1.604	3.457
0.377	0.298	1.42	1.891	3.124
0.498	0.417	1.39	2.579	2.599
0.598	0.513	1.37	3.193	2.146
0.748	0.687	1.35	3.344	1.126
0.923	0.901	1.32	4.456	0.372

Table 4. Ethane (1) + Ethylene (2) on Silica Gel KC at 700 kPa and 303 K

x_1	y_1	$S_{1/2}$	$N_1/\text{mol kg}^{-1}$	$N_2/\text{mol kg}^{-1}$
0.088	0.194	0.40	0.108	1.125
0.255	0.535	0.30	0.325	0.948
0.425	0.682	0.34	0.408	0.553
0.663	0.833	0.39	0.741	0.377
0.633	0.710	0.41	0.821	0.476
0.849	0.929	0.43	1.182	0.210

Table 5. Methane (1) + Carbon Dioxide (2) on Activated Carbon F30/470 at 700 kPa and 303 K

x_1	y_1	$S_{1/2}$	$N_1/\text{mol kg}^{-1}$	$N_2/\text{mol kg}^{-1}$
0.033	0.162	0.173	0.165	4.848
0.139	0.422	0.221	0.610	3.781
0.142	0.421	0.227	0.635	3.834
0.261	0.584	0.252	1.084	3.070
0.263	0.599	0.239	1.041	2.919
0.362	0.695	0.249	1.347	2.373
0.682	0.900	0.239	2.030	0.946
0.731	0.906	0.281	2.168	0.798

Table 6. Methane (1) + Carbon Dioxide (2) on Silica Gel KC at 700 kPa and 303 K

x_1	y_1	$S_{1/2}$	$N_1/\text{mol kg}^{-1}$	$N_2/\text{mol kg}^{-1}$
0.003	0.109	0.02	0.007	2.556
0.024	0.318	0.05	0.054	2.178
0.058	0.380	0.10	0.122	1.984
0.117	0.569	0.10	0.214	1.609
0.127	0.687	0.07	0.179	1.235
0.325	0.853	0.08	0.360	0.747
0.511	0.932	0.08	0.421	0.403
0.802	0.987	0.05	0.436	0.107
0.811	0.988	0.05	0.430	0.100

Table 7. 2-Methylpropane (1) + Butane (2) on Activated Carbon F30/470 at 200 kPa and 303 K

x_1	y_1	$S_{1/2}$	$N_1/\text{mol kg}^{-1}$	$N_2/\text{mol kg}^{-1}$
0.068	0.136	0.461	0.225	3.080
0.208	0.260	0.467	0.706	2.687
0.320	0.485	0.498	1.110	2.359
0.400	0.585	0.472	1.317	1.975
0.486	0.675	0.455	1.589	1.680
0.682	0.795	0.552	2.222	1.036
0.934	0.968	0.466	2.967	0.210

pounds, they are equal to the vapor pressure at low pressure and for the supercritical compounds, they are given by hypothetical fugacities (Prausnitz et al., 1986). The ratio of fugacities depends only on properties of pure gas.

$[\text{Int}_i]$ is an interactive parameter (generally represented by the activity coefficients). It takes into account the interactions between the adsorbent and the gas i . If the interaction between adsorbate i and adsorbent is strong, $[\text{Int}_i]$ is near 0, but if this interaction is weak, $[\text{Int}_i]$ is near unity.

$[\text{Geo}_i]$ is a geometrical parameter. It represents the possibility for a molecule of i to enter ($[\text{Geo}_i] \cong 1$) or not ($[\text{Geo}_i] \cong 0$) in the adsorbent pores.

Table 8. 2-Methylpropane (1) + Butane (2) on Silica Gel KC at 200 kPa and 303 K

x_1	y_1	$S_{1/2}$	$N_1/\text{mol kg}^{-1}$	$N_2/\text{mol kg}^{-1}$
0.215	0.270	0.74	0.594	2.167
0.269	0.328	0.76	0.693	1.885
0.334	0.398	0.76	0.827	1.648
0.349	0.424	0.73	0.960	1.792
0.486	0.559	0.75	1.178	1.245
0.538	0.610	0.74	1.340	1.151
0.655	0.723	0.73	1.552	0.817
0.714	0.774	0.73	1.699	0.681
0.783	0.831	0.74	1.903	0.614
0.817	0.859	0.73	1.976	0.443

The selectivity of ethane with regard to ethylene is opposite when the selectivity curves of ethane + ethylene mixture are determined in the same operative conditions on activated carbon and on silica gel (Figure 2). On activated carbon, $S_{\text{ethane+ethylene}}$ is greater than 1 and has an average value of 1.4. Therefore the adsorption of ethane is preferential on this adsorbent. At 303 K, ethane is subcritical while ethylene is supercritical. The main parameter in favor of ethane adsorption is the ratio of the fugacities ethylene + ethane ($\cong 1.2$) on a nonpolar adsorbent such as the activated carbon. On silica gel, $S_{\text{ethane+ethylene}}$ is less than 1 and has an average value of 0.4. The ratio of fugacities is greater than 1 and the adsorption of ethylene is preferential. The presence of hydroxyl groups imparts a degree of polarity to the surface of silica gel so that molecules such as unsaturated hydrocarbons (which can form π -complexes) are adsorbed in preference to nonpolar molecules such as saturated hydrocarbons ($[\text{Int}_{\text{ethylene}}] \ll [\text{Int}_{\text{ethane}}]$).

For the methane + carbon dioxide binary mixture, the adsorption of carbon dioxide is preferential on the two studied adsorbents (Figure 3). On activated carbon, the main parameter in favor of the adsorption of carbon dioxide is the ratio of fugacities methane + carbon dioxide. Indeed, the two adsorbates are nonpolar and have the same polarizability, and the activated carbon may be considered as a nonpolar adsorbent. On this adsorbent, $S_{\text{methane+carbon dioxide}}$ has an average value of 0.24 and the ratio of fugacities (real for carbon dioxide and hypothetical for methane) is equal to 0.27 at this temperature. On silica gel, considered as a polar adsorbent of which the active surface is formed by hydroxylic groups $-\text{OH}$, $S_{\text{methane+carbon dioxide}}$ has an average value of 0.07. In this case, the hydrophilic behavior of carbon dioxide, shown by its reactions with water and other oxides and its higher solubility in water [a ratio equal to 30 in favor of carbon dioxide at 1 atm and 25 °C (Hildebrand and Scott, 1964)] enhances the selectivity of carbon dioxide with regard to methane by a factor of 3.5.

The selectivity of 2-methylpropane with regard to butane has an average value of 0.48 on activated carbon and 0.74 on silica gel. The ratio of fugacities of these compounds at 318 K is equal to 0.69. The preferential adsorption of butane is more important on activated carbon than on silica gel (Figure 4). These compounds are isomers. They have the same chemical composition but are distinguishable by their geometrical structure: butane is linear, and 2-methylpropane is branched. The pure isotherms of 2-methylpropane and butane are obtained on activated carbon (Olivier et al., 1994); we have shown that for the same relative pressure (P/P_s), the amount adsorbed on this activated carbon decreases for the branched compound. This phenomenon is due certainly to the trimodal pore size distribution on activated carbon. Being linear, the butane has access to micropores having a smaller diameter than

the average diameter of a 2-methylpropane molecule ($[Geo_{\text{methylpropane}}] < [Geo_{\text{butane}}]$). On silica gel, the pore size distribution is unimodal and this average value is equal to 20 Å. This size is much greater than the average diameter of 2-methylpropane and butane molecules. The adsorption phenomenon on silica gel is governed principally by the chemical nature of the adsorbent surface; the difference of chemical nature between these two compounds is the main factor which determines the difference of selectivity. These compounds being similar chemically, its selectivity on silica gel is near to the ratio of fugacities.

Conclusion

An experimental apparatus has been built to determine the selectivity curves of binary gaseous mixtures. Data have been obtained at constant pressure and constant temperature at pressures greater than the atmospheric pressure. From adsorption selectivity curves of following binary mixtures: ethane + ethylene, methane + carbon dioxide and butane + 2-methylpropane on activated carbon and silica gel, a difference of behavior in these two adsorbents can be observed.

On activated carbon, the difference of properties of pure gas between the two components and the adsorbent microporosity are very important parameters, while on silica gel, the chemical nature of the adsorbent surface is the principal factor that determines the selectivity of one component with regard to another component.

Silica gel is a better adsorbent than activated carbon for the separation of carbon dioxide from methane. Being polar, it adsorbs also preferentially the component having one or several double bonds. Its main disadvantage is that it reacts chemically with several unsaturated compounds contained in the natural gas (Olivier and Jadot, 1997), for example, with propylene, 2-methylpropene, and 1,3-butadiene.

As shown, activated carbon gives a better selectivity for the 2-methylpropane + butane separation than silica gel. However, this selectivity is very weak. For the separation of these isomers, it is possible to prepare carbon adsorbents with a very narrow distribution of micropore size and which

therefore behave as molecular sieves. The micropore size distribution of such sieves is much narrower than in a typical activated carbon, and the porosity and therefore the adsorptive capacity are generally very much smaller.

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