

ADSORPTION OF LIGHT HYDROCARBON MIXTURES ON MOLECULAR SIEVING CARBON MSC-5A

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Measurements of the adsorption of binary gaseous mixtures of methane-ethane, ethylene-propane, ethane-propane and propane-*n*-butane systems on molecular sieving carbon MSC-5A were carried out at a temperature of 303.15 K and pressures of 13.3 or 40 kPa. Experimental results are compared with the predictions of the two-dimensional fluid model which takes into account the interaction effect of the adsorbate. It is shown that the model predicts values which are close to the experimental results.

Introduction

Molecular sieving carbon MSC-5A is a nonpolar adsorbent with a particular surface structure which allows a molecular sieving effect.^{3,5)} Although many equilibrium data have been reported for pure gas adsorption on MSC-5A, the data for mixtures are limited to only a few systems.^{6,7)} In the present work, the adsorption equilibria of binary gaseous mixtures of light hydrocarbons were measured on MSC-5A.

1. Experimental Procedure

Experiments were carried out under constant total pressure in a volumetric apparatus. A schematic diagram of the apparatus is shown in Fig. 1. The main part consisted of the adsorption column and the first and second circulation chambers. All materials in contact with the gas phase were made of glass and Teflon. The apparatus was maintained at a temperature of 303.15 K (± 0.5 K) in an air bath.

Exactly weighed quantities of adsorbent pellets (Takeda Chemical Industries Co., Ltd.) in the range of 0.4 to 0.6 g were placed in the adsorption column and the volumes of the three sections were measured with helium. The volume of the adsorption column was 35 cm³ and those of the first and second chambers were, respectively, 400 and 250 cm³.

Experiments were conducted according to the following procedure. After total evacuation of the apparatus, both component gases of a binary system were introduced into the first and second chambers and were completely mixed by fans prior to their injection into the adsorption column. The composition of the mixture was analyzed by gas chromatog-

raphy. To bring the gaseous mixture of the first chamber into contact with the adsorbent, Cock A between the first and second chambers was closed and Cock B between the first chamber and the adsorption column was opened. Then the gaseous mixture in the second chamber was introduced slowly into the first chamber through Cock A up to a desired total pressure. When a constant pressure had been attained, the composition in the gas phase in the first chamber and that of the mixture remaining in the second chamber were measured by gas chromatography.*¹ The amount of each component adsorbed was determined from a material balance of P-V-T values and the compositions of the gaseous mixtures.

To check the attainment of adsorption equilibrium, the results of these experiments were compared with those obtained from experiments in which one component of a binary system was first introduced into the adsorption column before the introduction of the

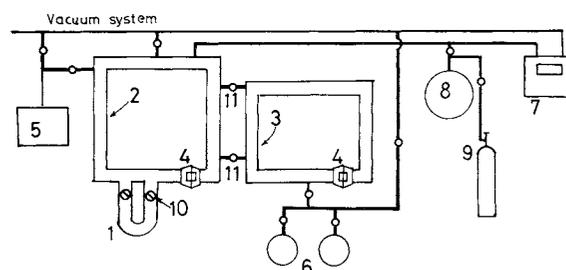


Fig. 1. Schematic diagram of apparatus. 1, adsorption column; 2, first circulation chamber; 3, second circulation chamber; 4, circulation fan; 5, gas chromatograph; 6, adsorption reservoir; 7, precision pressure gauge; 8, calibrated volume reservoir for helium gas; 9, helium gas cylinder; 10, cock B; 11, cock A.

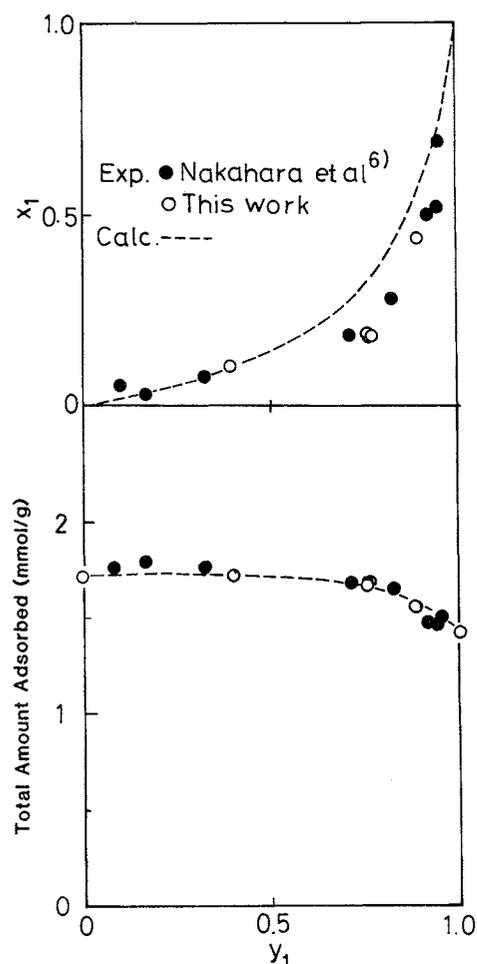
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*¹ After evacuation of the first chamber, the mixture from the second chamber was introduced into the first to analyse the composition.

Table 1. Experimental conditions

Adsorbent, MSC-5A; Temperature, 303.15 K

System	Total pressure [kPa]
Methane-Ethane	13.3, 40.0
Ethylene-Propane	13.3
Ethane-Propane	13.3, 40.0
Propane- <i>n</i> -Butane	13.3

**Fig. 2.** Comparison of experimental and calculated results of ethane(1)-propane(2) system ($P = 13.3$ kPa).

second component. Then similar experiments were repeated, changing the order in which the components were introduced. Each binary system was checked for consistency between the two types of results.

The experimental conditions are summarized in **Table 1**.

2. Results and Discussion

Adsorption equilibrium data for the ethane-propane system have also been reported by Nakahara *et al.*⁶⁾ The experimental results for this system of the present workers are compared with their results to examine the validity of the present measurement method. As shown in **Fig. 2**, there is a high degree of

Table 2. Adsorption equilibrium data

P (kPa)	y_1 [—]	x_1 [—]	Amount adsorbed [mmol/g]		
			N_t	N_1	N_2
Methane(1)-Ethane(2)					
13.3	0.170	0.000	1.390	0.000	1.390
13.4	0.575	0.000	1.167	0.000	1.167
13.3	0.665	0.022	1.031	0.023	1.008
13.3	0.677	0.029	1.067	0.031	1.036
13.3	0.747	0.095	1.011	0.096	0.915
13.3	0.815	0.072	0.896	0.065	0.831
13.5	0.876	0.143	0.801	0.115	0.686
13.3	0.914	0.198	0.691	0.137	0.554
13.3	0.952	0.309	0.566	0.175	0.391
13.3	0.981	0.476	0.437	0.208	0.229
39.9	0.522	0.082	1.620	0.133	1.487
40.0	0.680	0.061	1.422	0.088	1.354
40.0	0.756	0.105	1.338	0.140	1.198
40.0	0.807	0.100	1.326	0.133	1.193
40.0	0.852	0.194	1.234	0.239	0.995
40.6	0.877	0.239	1.195	0.286	0.909
40.0	0.911	0.276	1.090	0.301	0.789
40.0	0.949	0.547	0.882	0.482	0.400
Ethylene(1)-Propane(2)					
13.3	0.334	0.082	1.731	0.142	1.589
13.3	0.427	0.115	1.701	0.196	1.505
13.3	0.578	0.162	1.677	0.272	1.405
13.3	0.646	0.143	1.647	0.236	1.411
13.3	0.662	0.107	1.690	0.181	1.509
13.4	0.667	0.150	1.689	0.253	1.436
13.3	0.728	0.191	1.615	0.308	1.307
13.3	0.846	0.301	1.539	0.483	1.076
13.3	0.884	0.327	1.510	0.494	1.016
13.3	0.923	0.560	1.421	0.796	0.625
Ethane(1)-Propane(2)					
13.3	0.390	0.108	1.714	0.182	1.532
13.3	0.748	0.184	1.866	0.307	1.359
13.3	0.763	0.176	1.666	0.293	1.373
13.3	0.765	0.194	1.432	0.278	1.154
13.3	0.798	0.335	1.818	0.541	1.075
40.0	0.167	0.083	1.857	0.154	1.703
40.0	0.388	0.139	1.878	0.261	1.617
40.0	0.514	0.192	1.881	0.361	1.520
40.0	0.751	0.379	1.916	0.726	1.190
40.0	0.857	0.499	1.840	0.198	0.922
40.0	0.932	0.748	1.809	1.353	0.456
Propane(1)- <i>n</i> -Butane(2)					
13.4	0.225	0.046	1.720	0.079	1.641
13.5	0.429	0.133	1.726	0.229	1.497
13.4	0.626	0.203	1.741	0.353	1.389
13.3	0.673	0.208	1.673	0.349	1.324
13.4	0.735	0.266	1.709	0.455	1.234
13.3	0.888	0.413	1.674	0.691	0.983

consistency in the two sets of data.

All the data for the binary mixtures in this work are summarized in **Table 2**.

In the analysis of Nakahara *et al.*,⁶⁾ it was suggested that the nonideality of the adsorbed phase cannot be ignored in predicting the adsorption equilibrium for this adsorbent. The applicability of two-dimensional fluid models taking the interactions between adsorbed molecules into account has been suggested by some

Table 3. Value of parameters

Adsorbate	$a \times 10^{20}$ [kPa·g]	$b \times 10^{20}$ [g]	$c \times 10^{20}$ [g ^{1/2}]
Methane	10.6	0.0396	0.0062
Ethylene	5.43×10^{-1}	0.0498	0.0145
Ethane	4.00×10^{-1}	0.0535	0.0178
Propane	3.97×10^{-2}	0.0696	0.0226
<i>n</i> -Butane	7.27×10^{-3}	0.0769	0.0247

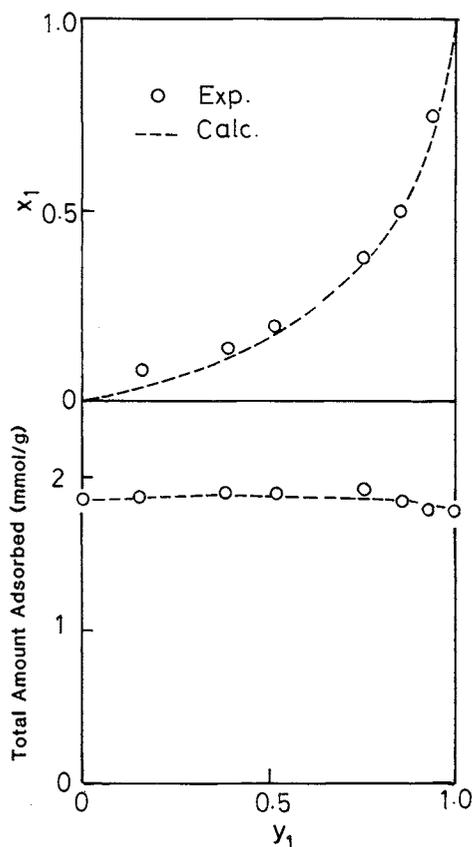


Fig. 3. Comparison of experimental and calculated results of ethane(1)-propane(2) system ($P = 40$ kPa).

investigators^{2,8,9)} for describing mixed gas adsorption. Thus, in this work a two-dimensional fluid model¹⁾ has been applied to investigate the equilibria over the adsorbent MSC-5A. The adsorption isotherm of component i in a binary system is then expressed as follows^{*2}:

$$Py_i = a_i \frac{N_i}{1 - (N_i b_i + N_j b_j)} \times \exp \left\{ -2(C_i^2 N_i + C_i C_j N_j) + \frac{(N_i + N_j) b_i}{1 - (N_i b_i + N_j b_j)} \right\} \quad (1)$$

where

*2 It is assumed in this model that the surface is energetically homogeneous and that no local correlation exist between adsorbed molecules. Some additional explanation can be found elsewhere.⁹⁾

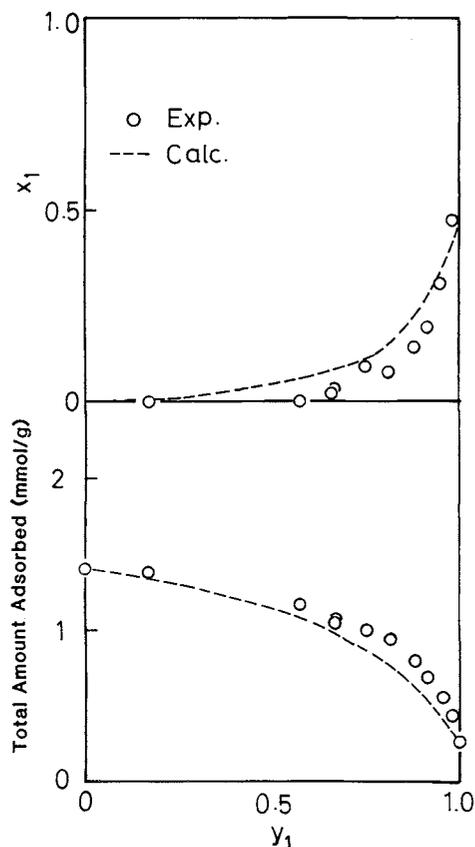


Fig. 4. Comparison of experimental and calculated results of methane(1)-ethane(2) system ($P = 13.3$ kPa).

$$a_i = \frac{kT}{A} \left(\frac{2\pi m_i kT}{h^2} \right)^{1/2} \exp \left(-\frac{\phi_i}{kT} \right) \quad (2)$$

$$b_i = \frac{\pi d_i^2}{4 A} \quad (3)$$

$$c_i = \left(\frac{\alpha_i}{AkT} \right)^{1/2} \quad (4)$$

The values of the parameters a_i , b_i and c_i for each component were determined by fitting the data of pure gas adsorption reported in the literature.⁵⁾ The parameter values determined are summarized in Table 3. It was confirmed that Eq. (1) fits well the adsorption equilibria for pure-component systems.

Using the values of the parameters, the adsorption equilibria of the mixtures were calculated. The results are presented in Figs. 2-7. In Figs. 3, 5 and 6 the calculated results are in good agreement with the experimental results. On the other hand, in Figs. 2, 4 and 7 it is found that, although the model predicts values close to the measurements, there are minor discrepancies between the experimental and the calculated results. Although it might be considered that the discrepancies were caused by failure to estimate the interaction effect of the adsorbate accurately in the model or by the invalidity of the assumption of uniform adsorption energy,⁴⁾ there is insufficient evi-

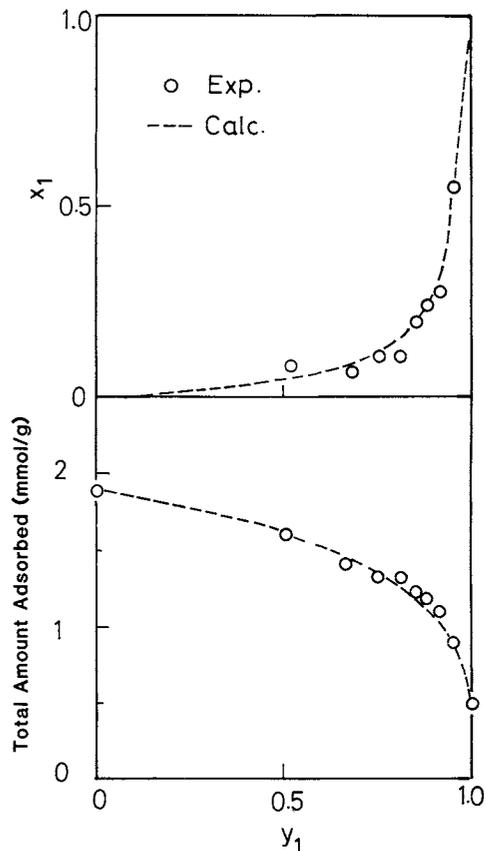


Fig. 5. Comparison of experimental and calculated results of methane(1)-ethane(2) system ($P=40$ kPa).

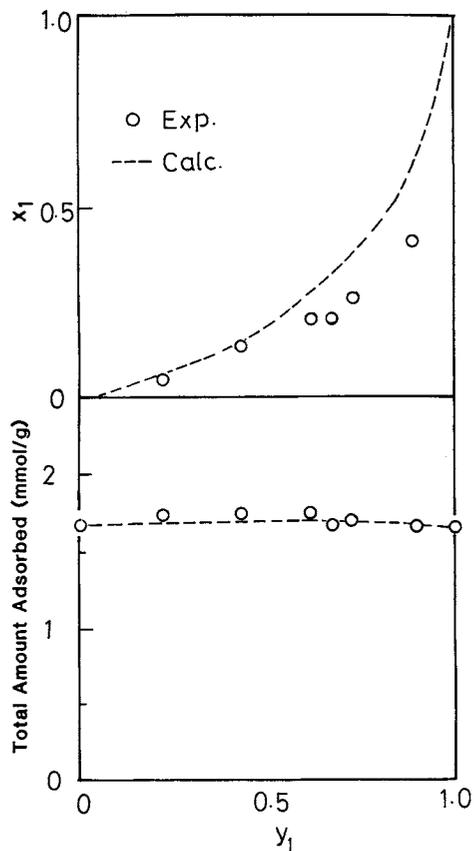


Fig. 7. Comparison of experimental and calculated results of propane(1)-*n*-butane(2) system ($P=13.3$ kPa).

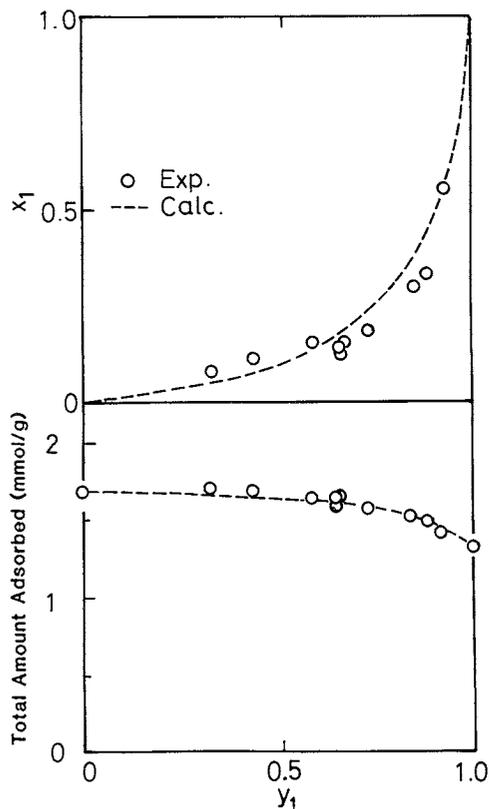


Fig. 6. Comparison of experimental and calculated results of ethylene(1)-propane(2) system ($P=13.3$ kPa).

dence for either hypothesis to be adopted.

Conclusions

Binary adsorption equilibria were measured under the condition of constant total pressure in adsorption of nonpolar light hydrocarbons by the adsorbent MSC-5A. Experimental results were compared with those calculated from a two-dimensional fluid model. Relatively good agreement was obtained between experimental and theoretical adsorption isotherms.

Nomenclature

A	= surface area of adsorbent	$[\text{m}^2/\text{g}]$
a	= model parameter defined by Eq. (2)	$[\text{Pa} \cdot \text{g}]$
b	= model parameter defined by Eq. (3)	$[\text{g}]$
c	= model parameter defined by Eq. (4)	$[\text{g}^{1/2}]$
d	= molecular size	$[\text{m}]$
h	= Planck constant	$[\text{J} \cdot \text{s}]$
k	= Boltzmann constant	$[\text{J} \cdot \text{K}^{-1}]$
m	= molecular mass	$[\text{g}]$
N	= number of adsorbed molecules per unit mass of adsorbent	$[\text{g}^{-1}]$
P	= total pressure	$[\text{Pa}]$
T	= absolute temperature	$[\text{K}]$
x	= mole fraction in adsorbed phase	$[-]$
y	= mole fraction in gas phase	$[-]$
α	= interaction parameter of adsorbate	$[\text{K} \cdot \text{m}^2]$
ϕ	= adsorption energy	$[\text{J}]$

<Subscripts>

i, j = component

Literature Cited

- 1) de Boer, J. H.: "The Dynamical Character of Adsorption," Clarendon Press Oxford (1953).
- 2) Danner, R. P. and E. C. F. Choi: *Ind. Eng. Chem. Fundam.*, **17**, 248 (1978).
- 3) Eguchi, Y. and K. Itoga: *Hyomen*, **10**, 521 (1972).
- 4) Konno, M., M. Terabayashi, Y. Takako, K. Arai and S. Saito: *Chem. Eng. Japan Symposium Series No. 2*, p. 90 (1983).
- 5) Nakahara, T., M. Hirata and T. Omori: *J. Chem. Eng. Data*, **19**, 310 (1974).
- 6) Nakahara, T., M. Hirata and S. Komatsu: *J. Chem. Eng. Data*, **26**, 161 (1981).
- 7) Nakahara, T., M. Hirata and H. Mori: *J. Chem. Eng. Data*, **27**, 317 (1982).
- 8) Patrykiewicz, A., M. Jaronic and W. Rudzinski: *Chem. Eng. J.*, **15**, 147 (1978).
- 9) Saito, S.: "Heiko Bussei Suzan no Kiso," Baifukan (1983).

ADSORPTION EQUILIBRIA OF HYDROCARBON GASEOUS MIXTURES CONTAINING POLAR COMPONENTS

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Key Words: Gas Adsorption, Phase Equilibrium, Polar Hydrocarbon, Nonpolar Hydrocarbon, Two-Dimensional Fluid Model, Local Molecular Concentration, Adsorption Energy Distribution

Adsorption equilibria were measured for binary systems of hydrocarbon gaseous mixtures containing polar components. Three different adsorbents were used: molecular sieve 13X, activated carbon G-2X and molecular sieving carbon MSC-5A. The experimental results were compared with results calculated according to two currently adopted prediction methods: the ideal adsorbed solution model and the two-dimensional fluid model.

The adsorption equilibria of molecular sieve 13X were in good agreement with the predictions from both models. However, neither model was found to give a good fit with the adsorption equilibria obtained with the other adsorbents.

It is shown that the adsorption equilibria of activated carbon G-2X can be well predicted by a modified two-dimensional fluid model which takes into account the distribution of the local molecular concentration. The experimental results obtained from molecular sieving carbon MSC-5A are considered to be accounted for by the nonuniformity of the adsorption energy.

Introduction

Gas adsorption phenomena have been widely utilized in separation processes. Knowledge of the adsorption equilibria is essential for the design of these processes.

To explain adsorption equilibria, a number of models have been proposed. However, lack of experimental data has made it difficult both to develop a model and to evaluate models in the literature. This deficiency is particularly conspicuous in the adsorption of multi-component systems.

Experimental work in the past has mainly used mixtures of inorganic substances with low molecular weight or of nonpolar light hydrocarbons. There has

been only a little work done on mixtures of polar and nonpolar components. In these systems, the interaction of the components in the adsorbate might be expected to cause non-ideality of the adsorbed phase. This would have a significant effect compared with that exerted on the adsorption equilibrium by the adsorbate-adsorbent interaction, which has been insufficiently investigated.

Another area of difficulty lies in the nonuniformity of adsorption energy, which arises from its dependency on the adsorbent employed. Furthermore, it should be kept in mind that the non-ideality of the adsorbed phase also depends upon the adsorbent. Therefore, it seems important to obtain experimental data for different types of adsorbents.

In the present work, adsorption equilibria have been measured, using three different types of adsorbents for binary systems of hydrocarbon mixtures

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