Experimental study of adsorption equilibrium of n-alkanes vapour mixtures on synthetic zeolite

[a]J. LONGAUER, [b]J. ILAVSKÝ, and [b]A. BRUNOVSKÁ

[a]*Department of Chemical Engineering, Slovak Technical University,*
CS-812 37 Bratislava

[b]*Department of Organic Technology, Slovak Technical University,*
CS-812 37 Bratislava

Dedicated to Professor RNDr. J. Gašperík, founder of the Department of Organic Technology and of the Department of Chemical Technology of Plastics and Fibres of the Slovak Technical University on the occasion of the 40th anniversary of their foundation

In this paper experimental results of isothermal adsorption equilibrium of binary n-alkane vapour mixtures on synthetic zeolite Calsit 5A at a constant partial pressure ratio of adsorptive components (n-hexane, n-heptane) are presented. The experimental data obtained are analytically compared with those according to Langmuir, Dubinin, and Jovanović isotherms. The possibility of predicting mixture adsorption equilibrium on the basis of pure substance adsorption equilibrium is suggested.

В работе даны результаты экспериментального изучения адсорбционного равновесия двойных смесей н-алканов (н-гексан, н-гептан) на синтетическом цеолите Кальсит 5А при постоянном отношении парциальных давлений адсорбирующихся компонентов. Полученные экспериментальные данные были сравнены аналитически с данными согласно изотермам Лэнгмюра, Дубинина и Йовановича. Указывается на возможность прогноза адсорбционных равновесий смесей на основании адсорбционных равновесий чистых веществ.

The analytical description of mixture adsorption equilibrium in the case' of the adsorptive being a k-component gaseous mixture may be expressed by the function

$$F(a_1, a_2, \ldots, a_k, T, P_1, P_2, \ldots, P_k) = 0 \qquad (1)$$

where a_i is the relative mass fraction of the i-th adsorbate component on adsorbent (the mass of the i-th adsorbate component per mass adsorbent unit),

P_i is the partial pressure of the i-th adsorptive component.

For the adsorption of the binary mixture in addition to the temperature it is necessary to know the relative mass fractions of both the adsorbate components and their equilibrium partial pressures

$$f(a_1, a_2, T, P_1, P_2) = 0 \qquad (2)$$

In case of the partial pressure of one of the components being zero, the isotherm of mixture adsorption reduces to the isotherm of the pure second component.

The variable quantities can be combined in various ways, *e.g.* one can set the ratio of the partial pressures

$$Y_1 = \frac{P_1}{P_2} \qquad (3)$$

or to use the total pressure

$$P = P_1 + P_2 \qquad (4)$$

etc.

The equations of the mixture isotherms are, of course, much more complicated than those of pure substances. They are cumbersome for practical use in many cases [1—5]. The theoretical analysis of the experimental data of the mixture adsorption equilibrium can be simplified if one of the variable parameters is kept constant.

A number of measurements of the binary mixture adsorption isotherms have been made under constant total pressure of the adsorptive, *e.g.* [6—9] or under constant partial pressure of one of the components [10, 11]. Some of the papers [11—13] present the results of mixture adsorption under constant adsorbed amount of one of the components. In most cases one is interested in the permanent gases as the adsorptive components: nitrogen, oxygen, carbon monoxide, carbon dioxide, *etc.*, scarcely ever hydrocarbons in mixture with other gases, while the equilibrium adsorption data of n-alkane mixtures are very rare.

The experimental equilibrium adsorption data of binary mixtures of n-alkanes on synthetic zeolite presented in this paper have been measured in a laboratory isothermic rotating basket reactor. Its characteristics, in addition to the method of measurement and the properties of the adsorbent and adsorptive have been presented in a previous paper [14].

The following isotherms have been used in this paper for analytical expression of a mixture adsorption equilibrium:

— Langmuir isotherm (based on classical theory of adsorption),

— Dubinin isotherm (corresponding to the theory of volume filling of micropores),

— Jovanović isotherm (following the new ideas on the adsorption process).

The Langmuir isotherm of pure substances [15] has been extended also to mixture adsorption [6, 16, 17] preserving all assumptions of the validity of the original equation. For binary mixture it takes the form

$$a = a_m \frac{b_1 P_1 + b_2 P_2}{1 + b_1 P_1 + b_2 P_2} \tag{5}$$

where a is the equilibrium relative mass fraction of the adsorbate mixture on adsorbent,

a_m is the relative mass fraction of the adsorbate mixture on adsorbent in a case of monomolecular adsorbate layer formation,

b_i are the isotherm constants of the pure substances.

Under constant ratio of partial pressures of the adsorptive componets Y_1 (eqn (3)), eqn (5) simplifies to

$$a = A \frac{BP_2}{1 + BP_2} \tag{6}$$

where B is the mixture isotherm constant defined by means of the transformation

$$B = b_1 Y_1 + b_2 \tag{7}$$

The analytical expression of the isotherm of the binary mixture according to eqn (6) is particularly advantageous since it is a two-parameter isotherm as well, similarly to the isotherm of the pure substance.

Dubinin's idea of the adsorption of gases on microporous adsorbents, based on the theory of volume filling of micropores and formulated into an adsorption isotherm equation of pure substances, has been theoretically extended and adapted also to the mixture adsorption. The authors [18] developed an isotherm equation, which for a binary mixture can be expressed in the form

$$a = a_n \exp\left[-K \left(RT \ln \frac{P_{n12}}{P_{12}} \right)^2 \right] \tag{8}$$

where a_n is the relative mass fraction of the adsorbate mixture on adsorbent in saturation state at the temperature of adsorption,

K is a mixture isotherm constant,

P_{12} represents partial pressures sum of the adsorptive components: $P_{12} = P_1 + P_2$,

P_{n12} represents saturated vapour pressures sum of pure components at the temperature of adsorption: $P_{n12} = P_{n1} + P_{n2}$.

Among recent works on physical adsorption Jaroniec [19] proposes to use Jovanović isotherm [20] which for the adsorption of binary mixtures can be expressed in the form

$$a = A(1 - \exp[-(B_1 P_1 + B_2 P_2)]) \exp[C_1 P_1 + C_2 P_2] \tag{9}$$

where *A*   is the mixture isotherm constant,

B_i, C_i are the constants of the isotherms of pure substances.
Eqn (9) can be simplified provided the ratio of the partial pressures of the adsorptive components Y_1 (eqn (3)) is constant

$$a = A(1 - \exp[-BP_2]\exp)[CP_2] \qquad (10)$$

where *B*, *C* are the constants of the mixture isotherm, defined by means of the transformation

$$B = B_1 Y_1 + B_2$$
$$\qquad (11)$$
$$C = C_1 Y_1 + C_2$$

where B_i, C_i are the constants of the isotherms of pure substances.

Selected experimental data of isothermal adsorption equilibrium of the binary n-alkane vapour mixtures (n-hexane, n-heptane) on synthetic zeolite Calsit 5A at temperature 130 °C and in the presence of a carrier indifferent gas (nitrogen) are presented in Tables 1 and 2.

The equilibrium partial pressure values of the less volatile component of the adsorptive (n-heptane) P_2 are presented in column 1 while column 2 presents the experimental equilibrium values of the relative mass fraction of mixed adsorbate on the adsorbent a_{exp}.

Table 1

Adsorption equilibrium of the n-alkane vapour mixture (n-hexane (1) + n-heptane (2)) on synthetic zeolite Calsit 5A at 130 °C

Mixture 1, $P_1/P_2 = 1.97$

1	2	3	4	5	6	7	8	9
$\dfrac{P_2}{\text{Pa}}$	a_{exp} $\cdot 10^3$	a_{LANG} $\cdot 10^3$	$\cdot 10^3$	δ $\cdot 10^2$	a_{DUB} $\cdot 10^3$	a_{JOV} $\cdot 10^3$	$\cdot 10^3$	δ $\cdot 10^2$
0	0	0	0	0	0	0	0	0
141	66.1	68.5	78.0	13.9	75.9	62.8	79.2	26.1
249	80.8	81.4	83.8	2.9	82.9	80.7	82.4	2.1
312	86.2	85.7	85.5	−0.2	85.7	86.1	83.4	−3.1
425	91.0	90.6	87.4	−3.5	89.6	91.4	85.0	−7.0
587	94.9	94.8	88.8	−6.3	93.6	95.0	87.2	−8.2
801	98.0	98.0	89.9	−8.2	97.4	97.4	90.3	−7.3
1240	101.1	101.3	90.9	−10.2	102.7	101.3	97.0	−4.2

Table 2

Adsorption equilibrium of the n-alkane vapour mixture (n-hexane (1) + n-heptane (2)) on synthetic zeolite Calsit 5A at 130 °C

Mixture 2, $P_1/P_2 = 0.524$

1	2	3	4	5	6	7	8	9
$\dfrac{P_2}{Pa}$	a_{exp} $\cdot 10^3$	a_{LANG} $\cdot 10^3$	a_{LANG} $\cdot 10^3$	δ $\cdot 10^2$	a_{DUB} $\cdot 10^3$	a_{JOV} $\cdot 10^3$	a_{JOV} $\cdot 10^3$	δ $\cdot 10^2$
0	0	0	0	0	0	0	0	0
139	65.6	62.4	69.8	11.8	73.0	64.8	70.6	9.0
231	78.0	77.0	77.6	0.8	78.4	77.5	78.8	1.7
328	82.4	82.6	81.7	−1.1	82.1	83.1	81.7	−1.7
449	85.5	86.7	84.6	−2.4	85.5	86.2	83.3	−3.4
621	89.2	90.0	86.9	−3.4	88.9	88.7	85.1	−4.1
876	92.8	92.7	88.7	−4.3	92.5	91.7	87.6	−4.5
1296	96.0	94.9	90.2	−5.0	96.5	96.6	91.9	−4.9

The columns 3, 6, 7 present calculated values of the relative mass fraction of mixed adsorbate on the adsorbent based on the isotherms: Langmuir (6), Dubinin (8), and Jovanović (10). The values of the constants of the isotherms have been estimated numerically by means of simplex method [21]. The function to be minimized is

$$F = \sum_{j=1}^{n} (a_j - a_{vj})^2 \qquad (12)$$

where a_j, a_{vj} are the relative mass fractions of mixed adsorbate on the adsorbent
— experimental (a_j), calculated (a_{vj}),
n is the number of the equilibrium data.

The results presented in the tables indicate that all three isotherms relatively satisfactorily approximate the experimental values in the given region of adsorptive pressures. Larger deviations appear only at the lowest value of the partial pressure of the second adsorptive component P_2, which can be explained by the steep slope of the isotherm in this region.

The values in columns 4 and 8 offer the possibility to predict mixture adsorption equilibrium based on the adsorption equilibrium of pure substances. The relative mass fractions of the mixed adsorbate on adsorbent have been calculated on the basis of the isotherms (6) and (10) in this case as well but the constants of the isotherms have been estimated by means of the transformations (7) and (11) using the constants of the pure substance isotherms. These pure substance isotherm

constants have been obtained from the experimental adsorption equilibrium data of pure vapour n-hexane and n-heptane at the same temperature after applying the above-mentioned method of minimization of the function (12). The columns 5 and 9 present the relative deviations of the equilibrium relative mass fractions of mixed adsorbate on adsorbent calculated from the adsorption equilibrium data of pure substances and mixtures.

The results obtained from the study of isothermal adsorption equilibrium of mixtures allow to accept the possibility of a prediction of the mixture adsorption equilibrium based on the adsorption equilibrium of pure substances with good results particularly for chemical engineering practice. As it is obvious from the tables, this conclusion concerns the case of binary n-alkane vapour mixture adsorption on synthetic zeolite in a region of adsorptive partial pressures to 5 kPa.

We regard the Jovanović isotherm (10) as the most convenient one for an analytical expression of mixture adsorption equilibrium in accordance with the results of this paper. It is particularly significant that all three constants of this multilayer adsorption isotherm are physically unambiguously defined [20] and they can be used for the calculation of the heat of adsorption as well as for the estimation of the average time of the accommodation of the molecules on the adsorbent surface.

Good agreement of the Langmuir monolayer adsorption isotherm (6) with the experimental adsorption equilibrium data is connected with the low values of adsorptive partial pressures used. This is due to the formation of "low number of adsorbed molecules layers" on the adsorbent surface as it is in the case of adsorption in the intracrystalline cavities where only some of the molecules of the adsorbate can be accommodated. According to the Langmuir isotherm the total adsorbate mass on the adsorbent surface seemingly corresponds to the continuing formation of the adsorption monolayer. Here one can look for the explanation of the comparatively good description of experimental data by the Langmuir isotherm in spite of the fact that the conditions for its validity are practically never fulfilled.

Symbols

a equilibrium relative mass fraction of the adsorbate mixture on adsorbent (the mass of the adsorbate mixture per mass adsorbent unit)

a_i relative mass fraction of the i-th adsorbate component on adsorbent

a_m relative mass fraction of the adsorbate mixture on adsorbent in a case of monomolecular adsorbate layer formation

a_n relative mass fraction of the adsorbate mixture on adsorbent in saturation state at the temperature of adsorption

a_{LANG} relative mass fraction of the adsorbate mixture on adsorbent, calculated from Langmuir isotherm (in tables)

a_{DUB} relative mass fraction of the adsorbate mixture on adsorbent, calculated from Dubinin isotherm

a_{JOV} relative mass fraction of the adsorbate mixture on adsorbent, calculated from Jovanović isotherm

A mixture isotherm constant in eqns (6), (9), (10)

b_i pure i-th component isotherm constant

B mixture isotherm constant in eqns (6) and (10)

B_i pure i-th component isotherm constant in eqn (9)

C mixture isotherm constant in eqn (10)

C_i pure i-th component isotherm constant in eqn (9)

K mixture isotherm constant in eqn (8)

n number of experimental equilibrium data

P adsorptive pressure

P_i i-th adsorptive component partial pressure

P_{12} partial pressures sum of the adsorptive components

P_{ni} saturated vapour pressure of pure i-th component at a temperature of adsorption

P_{n12} saturated vapour pressures sum of pure components

R universal gas constant

T thermodynamic temperature

Y_1 partial pressures ratio of the adsorptive components

δ relative deviation

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