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Studies of Adsorption from Gaseous and Liquid Mixtures on Solids of Quasi-Gaussian Energy Distribution

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Previous research[6-9] has shown that the Tóth equation describes well the adsorption of hydrocarbons on carbon adsorbents, especially on Nuxit-Al charcoal. This fact is probably connected with the quasi-gaussian energy distribution function, which is related to Tóth's equation. In this paper, the parameters of the above mentioned equation have been discussed once again and recent results on this subject were taken into account. The modified Tóth equation has also been generalized for the case of adsorption from multicomponent gas and liquid mixtures on solids of quasi-gaussian energy distribution.

INTRODUCTION

The investigations of the physical adsorption of gases and liquids on solids are inseparably connected with the problem of heterogeneity of adsorbing surfaces. Many empirical and theoretical equations, describing the adsorption on heterogeneous surfaces have been proposed. One of them is Tóth equation[1]:

$$N(p) = N_c \left[\frac{p^m}{b^* + p^m} \right]^{1/m} \tag{1}$$

where $N(p)$ is the adsorbed amount when pressure of a gas in thermodynamic equilibrium with an adsorbate is equal to p, N_c is a constant connected with the monolayer capacity (both N and N_c are expressed in the units of mass or volume of an adsorbate per gram of an adsorbent), m is the heterogeneity parameter from the interval (0,1), and b^* is a constant connected with the characteristic adsorption energy. The exact definitions and physical meaning of the parameters appearing in eq. (1) will be given in section 2, where the modified form of the equation (1) will be discussed.

Up to now, this equation has been used to describe the monolayer[2-4] and multilayer[5] adsorption of single gases and the monolayer adsorption of binary gas mixtures[6-9], especially on charcoal. Our recent studies[10] have dealt with the description of the bilayer adsorption from binary gas mixtures using the Tóth equation.

In this paper we shall discuss the adsorption from multicomponent gaseous and liquid mixtures using the Tóth equation. In the case of mixed-gas adsorption we shall generalize the method proposed in Refs. (8, 9). However, application of the Tóth equation to adsorption from solutions in the whole concentration region will be discussed for the first time as the paper of Jossens et al.[11] deals with the adsorption from dilute solutions only. Additionally, we shall discuss once more the parameters b^* and m, by taking into consideration recent experimental and theoretical studies of this problem.

ADSORPTION OF SINGLE GASES

Starting from the theoretical discussion outlined in Ref. (2) we propose the slightly different form for Tóth adsorption isotherm (1), namely:

$$\vartheta^*(p) = N(p)/N_c = \left[\frac{p^m}{b^m + p^m}\right]^{1/m} \tag{2}$$

where $b^* = b^m$. Then, the constant b is analogous to the Langmuir constant and may be expressed by:

$$b = K \exp(-\varepsilon_0/RT) \tag{3}$$

where K is the function of temperature only and is defined by the ratio of the molecular partition functions corresponding to molecules in the bulk and adsorbed phases, whereas ε_0 is the characteristic adsorption energy (in the case of Langmuir equation, ε_0 is the adsorption energy of a homogeneous surface). The parameter N_c is expressed through the monolayer capacity, N_0, by the following equation[1]:

$$N_c = N_0 \left[\frac{b^m + p_0^m}{p_0^m}\right]^{1/m} \tag{4}$$

where p_0 is the value of p when the monolayer becomes completely filled up, so that $N(p_0) = N_0$. According to the above definition of the monolayer capacity, N_0, eq. 4 is equivalent to the statement that an infinite increase of the equilibrium pressure p is not required to fill up a monolayer. Thus, defining the relative coverage of the entire surface by:

$$\vartheta(p) = N(p)/N_0 \tag{5}$$

we obtain

$$\vartheta^*(p) = \vartheta(p) \left[\frac{b^m + p_0^m}{p_0^m}\right]^{1/m} \tag{6}$$

Eq. 6 leads us to the conclusion that $\vartheta^*(p)$ can vary in the interval

$$0 \leqslant \vartheta^*(p) \leqslant \left[\frac{p_0^m}{b^m + p_0^m}\right]^{1/m}$$

and since the expression on the right hand side of the above inequality is always smaller than unity, the surface coverage thus also becomes smaller than unity.

Now, let us discuss the heterogeneity effect connected with the Tóth equation. As was suggested earlier[2,8] the parameter m has a unique value for a given adsorbent which does not depend on the nature of the adsorbate and temperature. In the case $m = 1$, eq. 2 reduces to the ordinary Langmuir adsorption isotherm and it corresponds to a homogeneous surface, whereas m approaches zero as the heterogeneity of the adsorbent becomes higher.

Concluding this section we would like to emphasize one point. Namely, a very successful application of the Tóth equation to many adsorption systems can be easily understood when the form of the energy distribution function generated by this equation is considered. By definition, the energy distribution function (usually denoted by $\chi(\varepsilon)$) informs us what is the contribution of adsorption sites with the adsorption energy equal to ε. If Δ is the domain of ε, then the following condition must be fulfilled:

$$\int_{\Delta} \chi(\varepsilon)\, \mathrm{d}\varepsilon = 1$$

This equation ensures a proper normalization of $\chi(\varepsilon)$, for the summ of all contributions due to sites with adsorption energies from Δ must be equal to unity.

As it was pointed out by Tóth et al.[2], eq. 2 corresponds to a quasigaussian energy distribution:

$$\chi(\varepsilon) = (\pi RT)^{-1}\, \Lambda^{1/m} \sin\left[\frac{1}{m} \arcsin\left(\Lambda\, \lambda \sin(\pi m)\right)\right] \tag{7}$$

where

$$\Lambda = [\lambda^2 + 2\,\lambda \cos(m\pi) + 1]^{-1/2}$$

and

$$\lambda = \exp \frac{m\,(\varepsilon - \varepsilon_0)}{RT}\,; \qquad \varepsilon_0 = RT \ln(K/b)$$

There is a numerous group of adsorbents having gaussian-like energy distribution functions and charcoal adsorbents belong to this group. This fact is probably the main reason why the Tóth equation can describe well many adsorption systems.

ISOSTERIC HEAT OF ADSORPTION

The energy distribution functions can be temperature dependent. However, as was shown by Misra[12,13] there exists a self-compensation effect which gives practically temperature independent functions. Thus, the isosteric heat of adsorption on heterogeneous surfaces may be evaluated by using the approximate formula proposed by van Dongen and Broekhoff[14]:

$$Q^{st}(p, T) = \frac{\int_{\Delta} q^{st}(p, T, \varepsilon) \left[\dfrac{\partial\, \Theta(p, T, \varepsilon)}{\partial \ln p}\right]_T \chi(\varepsilon)\, \mathrm{d}\varepsilon}{\int_{\Delta} \left[\dfrac{\partial\, \Theta(p, T, \varepsilon)}{\partial \ln p}\right]_T \chi(\varepsilon)\, \mathrm{d}\varepsilon} \tag{8}$$

where Q^{st} and q^{st} are isosteric heats of adsorption for heterogeneous and homogeneous surfaces respectively, and Θ is the relative coverage for homogeneous surface.

On the other hand, the isosteric heat of adsorption, Q^{st}, may be calculated directly from the equation of the overall adsorption isotherm[15]:

$$Q^{st}(p, T) = RT^2 \left[\frac{\partial \ln p}{\partial T}\right]_{\vartheta} \tag{9}$$

Let now assume that the overall adsorption isotherm $\vartheta(p)$ is described by the Tóth equation 2 (in the further discussion the superscript »*« at the symbol ϑ wil be omitted), i. e., we shall calculate the isosteric heat of adsorption Q^{st} in a similar way as in the case of the Langmuir equation; (see Appendix I) and the function $\chi(\varepsilon)$ is given by eq. 7. From eq. 2 we obtain

$$\ln p = \ln b + \ln \vartheta - (1/m) \ln (1 - \vartheta^m) \tag{10}$$

As it was hitherto assumed the heterogeneity parameter m is temperature invariant, however, this is not completely true. Recent papers of Jaroniec and Tóth[8] on the adsorption of hydrocarbons on charcoal »Nuxit-Al« have shown that the parameter m changes with temperature; with increasing temperature the parameter m slowly increases too. This result is easy to understand because with increasing temperature a smaller heterogeneity of the adsorbent surface is expected.

Differentiation of eq. 10 with respect to temperature T leads to the expression for the overall isosteric heat of adsorption:

$$Q^{st}(p, T) = RT^2 \left[\frac{\partial \ln b}{\partial T}\right]_{\vartheta} + RT^2 \left[\frac{\partial m}{\partial T}\right]_{\vartheta} F(\vartheta) \tag{11}$$

where

$$RT^2 \left[\frac{\partial \ln b}{\partial T}\right]_{\vartheta} = RT^2 \left[\frac{\partial \ln K}{\partial T}\right]_{\vartheta} + \varepsilon_0 \tag{12}$$

and

$$F(\vartheta) = m^{-2} \ln (1 - \vartheta^m) + \frac{\vartheta^m \ln \vartheta}{m(1 - \vartheta^m)} \tag{13}$$

The first term on the right hand side of eq. 11 (eq. 12) is expressed by means of characteristic adsorption energy, which is somewhat greater for the Tóth distribution than the average adsorption energy[8] and is constant in the whole region of the relative surface coverage. The second term on the right hand side of eq. 11 depends upon the relative surface coverage and is still negative. In the limit $\vartheta \rightarrow 0$ it increases to zero, while when the relative surface coverage approaches unity it decreases. The derivative $(\partial m/\partial T) > 0$ because with increasing temperature the parameter m slowly increases too. Let us assume that $m(T)$ is a linear function, then $(\partial m/\partial T) = \eta = \text{const.}$ and

$$Q^{st} = RT^2 \left[\frac{\partial \ln b}{\partial T}\right]_{\vartheta} + RT^2 \eta F(\vartheta) \tag{14}$$

Figure 1 presents the function $F(\vartheta)$ calculated for different values of the parameter m. Thus, the dependence Q^{st} vs. ϑ is a decreasing function.

It appears from the above discussion that introduction of the temperature dependent parameter m must lead to taking into consideration the temperature dependence of the energy distribution function (7). This being so, the eq. 8 is not longer valid since it was derived for temperature independent energy distribution. Therefore, we will generalize the van Dongen and Broek-

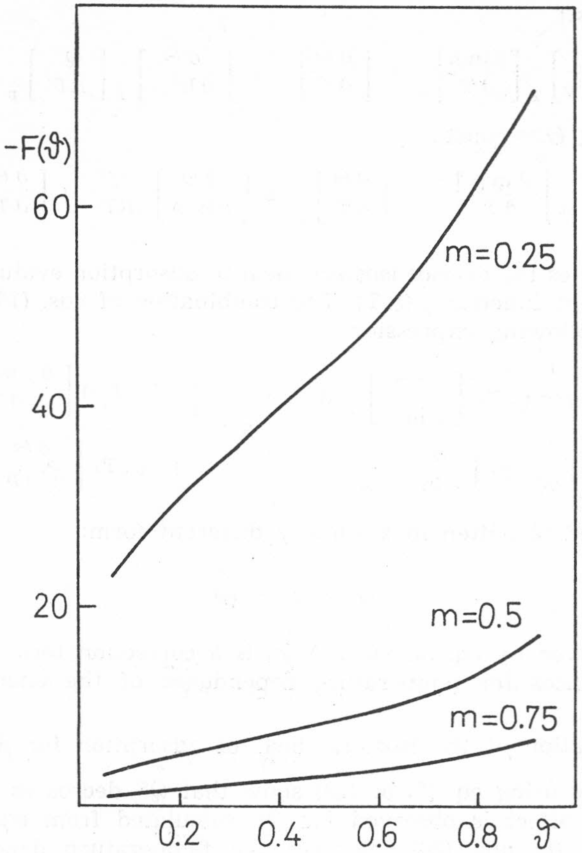

Figure 1. Function $F(\vartheta)$ calculated according to eq. (13) for different values of the parameter m.

hoff[14] equation by taking into account the temperature dependence of the energy distribution function. If the relative surface coverage is held constant, then the differentiation of the integral adsorption isotherm

$$\vartheta\,(p, T) = \int_{\Delta} \Theta\,(p, T, \varepsilon)\, \chi\,(\varepsilon, T)\, \mathrm{d}\,\varepsilon \tag{15}$$

with respect to the temperature gives:

$$0 = \int_{\Delta} \left[\frac{\partial\, \Theta\,(p, T, \varepsilon)}{\partial\, T} \right]_{\vartheta} \chi\,(\varepsilon, T)\, \mathrm{d}\,\varepsilon + \int_{\Delta} \Theta\,(p,T, \varepsilon) \left[\frac{\partial\, \chi\,(\varepsilon, T)}{\partial\, T} \right]_{\vartheta} \mathrm{d}\,\varepsilon \tag{16}$$

In the above, $\chi\,(\varepsilon, T)$ is essentially given by eq. 7, however the parameter m appearing in this equation is now a function of the temperature.

The following relationship, true for a local adsorption isotherm $\Theta\,(p, T, \varepsilon)$:

$$\mathrm{d}\,\Theta = \left[\frac{\partial\, \Theta}{\partial \ln p} \right]_{T} \mathrm{d} \ln p + \left[\frac{\partial\, \Theta}{\partial\, T} \right]_{p} \mathrm{d}\, T \tag{17}$$

gives (ϑ = const)

$$\left[\frac{\partial \Theta}{\partial T}\right]_{\vartheta} = \left[\frac{\partial \Theta}{\partial \ln p}\right]_{T} \left[\frac{\partial \ln p}{\partial T}\right]_{\vartheta} + \left[\frac{\partial \Theta}{\partial T}\right]_{p} = \left[\frac{\partial \Theta}{\partial \ln p}\right]_{T} \left[\frac{Q^{st}}{RT^{2}}\right]_{p} + \left[\frac{\partial \Theta}{\partial T}\right] \tag{18}$$

and by putting Θ = const.:

$$\left[\frac{\partial \Theta}{\partial \ln p}\right]_{T} \left[\frac{\partial \ln p}{\partial T}\right]_{\Theta} + \left[\frac{\partial \Theta}{\partial T}\right]_{p} = \left[\frac{\partial \Theta}{\partial \ln p}\right] \frac{q^{st}}{RT^{2}} + \left[\frac{\partial \Theta}{\partial T}\right]_{p} = 0 \tag{19}$$

where $\hat{Q}^{st}$ denotes the overall isosteric heat of adsorption evaluated for temperature dependent function $\chi(\varepsilon, T)$. The combination of eqs. (18), (19), and (16) leads to the following expression

$$\hat{Q}^{st} = \frac{\int_{\Delta} q^{st} \chi(\varepsilon, T) \left[\frac{\partial \Theta}{\partial \ln p}\right]_{T} \mathrm{d}\varepsilon}{\int_{\Delta} \chi(\varepsilon, T) \left[\frac{\partial \Theta}{\partial \ln p}\right]_{T} \mathrm{d}\varepsilon} - RT^{2} \frac{\int_{\Delta} \Theta(p, T, \varepsilon) \left[\frac{\partial \chi(\varepsilon, T)}{\partial T}\right] \mathrm{d}\varepsilon}{\int_{\Delta} \chi(\varepsilon, T) \left[\frac{\partial \Theta}{\partial \ln p}\right]_{T} \mathrm{d}\varepsilon} \tag{20}$$

Eq. (20) may be rewritten in a slightly different form:

$$\hat{Q}^{st} = Q^{st} - \Delta\hat{Q}^{st} \tag{21}$$

where Q^{st} is given by eq. (8) vhile $\Delta \hat{Q}^{st}$ is a correction term associated with making allowances for temperature dependence of the energy distribution function.

The calculation of the isosteric heat of adsorption for different energy distributions by using eq. (8) or (20) show that $\hat{Q}^{st}$ decreases with increasing ϑ[16]. The same effect is observed for Q^{st} calculated from eq. (1). The comparison of eq. (8) and (20) indicates the temperature dependence of the parameter m.

THE GENERALIZED TÓTH EQUATION FOR ADSORPTION OF MULTICOMPONENT GAS MIXTURES

For the purpose of generalization of the Tóth equation (2) for the adsorption of multicomponent gas mixtures, we shall use the method reported for the first time in Ref. (17). This method is based on the simplified integral equation, which can be obtained from the generalized integral equation[10,18] if the functional relationship between adsorption energies of the components is known. For a great number of mixed-gas adsorption systems, this relationship assumes the following linear form:

$$\varepsilon_i - \varepsilon_1 = \varepsilon_{i1} = \varkappa_{i1} \quad \text{and} \quad i = 2, 3, \ldots, n \tag{22}$$

The quantity $\varkappa_{i1}$ is constant for all homogeneous surface patches[8]. In the above equation ε_i is the adsorption energy of the i-th component, and n is the number of components in the gas mixture. The parameter $\varkappa_{i1}$ is constant if the heterogeneity parameters of i-th and 1-st component are identical; as it has been already mentioned in the introduction, such a condition is satisfactory for many mixed-gas adsorption systems[1,8,9]. Taking into account the condition (22) in the Langmuir adsorption isotherm of gas mixtures, we obtain

$$\Theta_{(n)}(\mathbf{p}, \varepsilon_1) = \frac{a_1 z_1}{1 + a_1 z_1} \tag{23}$$

where

$$z_1 = p_1 + \sum_{i=2}^{n} r_{i1} p_i \tag{24}$$

and

$$r_{i1} = a_i/a_1 = \frac{K_1}{K_i} \exp[(\varepsilon_i - \varepsilon_1)/RT] \equiv \frac{K_1}{K_i} \exp(\varkappa_{i1}/RT) \tag{25}$$

In the above $\Theta_{(n)}(\mathbf{p}, \varepsilon_1)$ is the relative monalayer coverage on homogeneous surface for n-component gas mixture defined as a summ of the coverages corresponding to all components; a_i is the Langmuir constant of the i-th gas and in the case of homogeneous surface it is equal to $1/b_i$ (see eq. (3)); K_i is the constant of the i-th component and defined as described earlier (see the discussion following eq. (3)); and the symbols **n**, **p**, are n-dimensional vectors:

$$\mathbf{n} = (1, 2, \ldots, n)$$

$$\mathbf{p} = (p_1, p_2, \ldots, p_n)$$

Thus, the overall adsorption isotherm for n-component gas mixture on a heterogeneous surface, $\vartheta_{(n)}$, may be represented by the following integral (for derivation of this equation see Appendix II):

$$\vartheta_{(n)} = \int_{\Delta_1} \frac{a_1 z_1}{1 + a_1 z_1} \chi_1(\varepsilon_1)\, d\varepsilon_1 \tag{26}$$

Using the Tóth distribution for $\chi_1(\varepsilon_1)$ we get

$$\vartheta_{(n)} = \left[\frac{z_1^m}{b_1^m + z_1^m}\right]^{1/m} \tag{27}$$

Now, let us consider the adsorption of binary gas mixtures. Then, z_1 is the function of p_1 and p_2 only. Thus, $\vartheta_{(1,2)}$ may be presented graphically in the three-dimensional space. Now, if the experimental isotherms are measured at selected constant parameters, then $\vartheta_{(1,2)}$ may be presented in the two-dimensional space, because z_1 depends only upon one variable:

$$z_1 = P(y_1 + r_{21} y_2) = \alpha P \quad \text{for} \quad y_1, y_2 = \text{constant} \tag{28a}$$

$$z_1 = p_1(1 - r_{21}) + r_{21} P = \alpha^* p_1 + \beta^* \quad \text{for} \quad P = \text{constant} \tag{28b}$$

$$z_1 = p_1 + r_{21} p_2 = p_1 + \beta \quad \text{for} \quad p_2 = \text{constant} \tag{28c}$$

In the above $y_i = p_i/P$ is the mole fraction of i-th component in the gas phase, $P = p_1 + p_2 + \ldots + p_n$ is the total pressure, and in the present case $P = p_1 + p_2$, for we are considering two-component gas mixtures. In practical calculations, the parameter r_{21} may be evaluated by using pure-gas adsorption parameters:

$$r_{21} = a_2/a_1 \quad \text{ratio of Langmuir's constants} \tag{29a}$$

$$r_{21} = b_1/b_2 \quad \text{ratio of Tóth's constants} \tag{29b}$$

For the purpose of illustration we shall present numerical results obtained for adsorption of hydrocarbons on charcoal »Nuxit-Al«[19] In Table I the pure-gas adsorption parameters b_1 and N_c, calculated for the 1-st component according to eq. 2, have been compared with the adsorption parameters b_1 and N_c obtained from the mixed-gas adsorption data. The parameter r_{21} was calculated by means of the Langmuir parameters (eq. (29a)) and the Tóth parameters (eq. (29b)). Both equations give very similar results and may be used to calculate r_{21}. In Figure 2 the linear dependences $N^{-m}_{(1,2)}$ vs. z_1^{-m} for

TABLE I

Comparison of Tóth's Parameters Evaluated from the Pure-gas and Mixed-gas Adsorption Isotherms of Hydrocarbons on Charcoal »Nuxit-Al« by Using $m = 0.38$

Adsorption system		Temp.	Pure-gas adsorption parameters of eq. 2			Mixed-gas adsorption parameters of eq. 27 for z_1 defined by eq. 28b		
1-st component	2-nd component	K	b_1/Torr	N_c/cm^3 g^{-1}		r_{21}	b_1/Torr	N_c/ cm^3 g^{-1}
C_3H_6	C_2H_4	293	1.91	145.0	i	0.142	2.727	178.8
					ii	0.097	1.972	151.8
C_3H_8	C_2H_6	293	1.435	117.3	i	0.090	1.022	119.1
					ii	0.046	0.756	111.9

i — parameters obtained using r_{21} from eq. 29a
ii — parameters obtained for r_{21} defined by eq. 29b

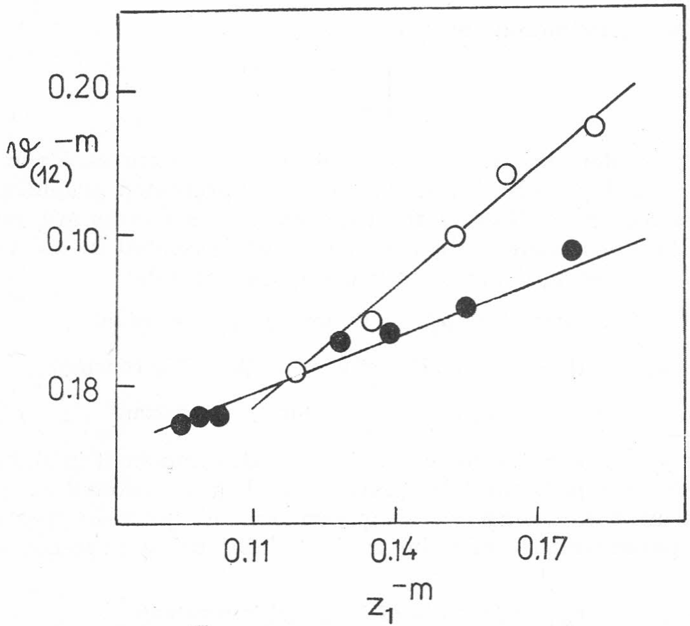

Figure 2. Linear dependences $\vartheta^{-m}_{(1,2)}$ vs z_1^{-m} for adsorption isotherms (27): (●) C_3H_8-C_{26} at 293 K, (○) C_3H_6-C_2H_4 at 293 K on charcoal »Nuxit-Al«. r_{21} has been calculated from eq. (29b).

adsorption isotherm (27) are presented; these lines have been calculated by using r_{21} from eq. (29b). Figure 2 that equation (27) describes well the investigated adsorption systems.

Now consider the isosteric heat of adsorption for a given component of the binary mixture. From eq. (27) we obtain

$$\ln z_1 (p_1) = \ln b_1 + \ln \vartheta_{(1,2)} - (1/m) \ln (1 - \vartheta_{(1,2)}{}^{m}) \tag{30}$$

Differentiation of eq. 30 with respect to temperature gives

$$\left(\frac{\partial \ln z_1}{\partial T}\right)_{\vartheta_{(1,2)}} = \left(\frac{\partial \ln b_1}{\partial T}\right) + \frac{\partial m}{\partial T} m^{-2} \ln (1 - \vartheta^{m}_{(1,2)}) + \left(\frac{\partial m}{\partial T}\right) \frac{\vartheta^{m}_{(1,2)} \ln \vartheta_{(1,2)}}{m (1 - \vartheta^{m}_{(1,2)})} \tag{31}$$

where

$$\left(\frac{\partial \ln z_1}{\partial T}\right)_{\vartheta_{(1,2)}} = \begin{cases} \dfrac{1}{\alpha^* p_1 + \beta^*} \left[p_1 \left(\dfrac{\partial \ln p_1}{\partial T}\right)_{\vartheta_{(1,2)}} + p_1 \left(\dfrac{\partial \alpha^*}{\partial T}\right) + \left(\dfrac{\partial \beta^*}{\partial T}\right)\right], \ P = \text{const.} & \text{(32a)} \\[2ex] \dfrac{1}{p_1 + \beta} \left[p_1 \left(\dfrac{\partial \ln p_1}{\partial T}\right)_{\vartheta_{(1,2)}} - \left(\dfrac{\partial \beta}{\partial T}\right)\right], \ p_2 = \text{const.} & \text{(32b)} \end{cases}$$

Applying definition of the isosteric heat of adsorption for the first component, i. e.,

$$Q^{\text{st}}_{1(1,2)} = RT^2 \left[\frac{\partial \ln p_1}{\partial T}\right]_{\vartheta_{(1,2)}} \tag{33}$$

and combining eqs. (30), (31) and (32), we get

$$Q^{\text{st}}_{1(1,2)} = RT^2 \frac{\alpha^* p_1 + \beta^*}{p_1} \left\{ \left[\frac{\partial \ln b_1}{\partial T}\right] + \left(\frac{\partial m}{\partial T}\right) \left[\frac{1}{m^2} \ln (1 - \vartheta^{m}_{(1,2)}) + \frac{\vartheta^{m}_{(1,2)} \ln \vartheta_{(1,2)}}{m (1 - \vartheta^{m}_{(1,2)})}\right] \right.$$
$$\left. - \frac{1}{\alpha^* p_1 + \beta^*} \left(\frac{\partial \beta^*}{\partial T}\right) - p_1 \left(\frac{\partial \alpha^*}{\partial T}\right) \right\}, \ P = \text{const.} \tag{34a}$$

$$Q^{\text{st}}_{1(1,2)} = RT^2 \frac{p_1 + \beta}{p_1} \left\{ \left(\frac{\partial \ln b_1}{\partial T}\right) + \left(\frac{\partial m}{\partial T}\right) \left[\frac{1}{m} \ln (1 - \vartheta^{m}_{(1,2)}) \right.\right.$$
$$\left.\left. + \frac{\vartheta^{m}_{(1,2)} \ln \vartheta_{(1,2)}}{m (1 - \vartheta^{m}_{(1,2)})} \right] - \frac{1}{p_1 + \beta} \left(\frac{\partial \beta}{\partial T}\right) \right\}, \ p_2 = \text{const.} \tag{34b}$$

$$p_1 = p_1 (\vartheta_{(1,2)}) = \begin{cases} \dfrac{1}{\alpha^*} \dfrac{b_1 \vartheta_{(1,2)}}{(1 - \vartheta^{m}_{(1,2)})} - \dfrac{\alpha^*}{\beta^*} \ \text{for } P = \text{const.} & \text{(35a)} \\[2ex] \dfrac{b_1 \vartheta_{(1,2)}}{1 - \vartheta^{m}_{(1,2)}} - \beta \ \text{for } p_2 = \text{const.} & \text{(35b)} \end{cases}$$

and

$$\frac{\partial \alpha^*}{\partial T} = - \frac{\partial r_{21}}{\partial T} \ ; \quad \frac{\partial \beta^*}{\partial T} = P \frac{\partial r_{21}}{\partial T} \ ; \quad \frac{\partial \beta}{\partial T} = p_2 \frac{\partial r_{21}}{\partial T} \tag{36}$$

The parameter r_{21} is defined by eq. (25). Assuming that temperature dependences of the constants K_1 and K_i are identical, we get

$$\frac{\partial r_{21}}{\partial T} = - \frac{\varkappa_{i1}}{RT^2} r_{21} \tag{37}$$

The above assumption is based on the fact, that K's are expressed by the molecular partition functions and therefore for molecules characterized by the same set of degrees of freedom their molecular partition functions assume the same analytical form. Next, when the differences in numerical values of parameters characterizing components of the mixture are not big, and the ratio K_1/K_2 is close to unity, then eq. (37) becomes

$$\frac{\partial r_{21}}{\partial T} = \frac{r_{21}}{T} \ln (1/r_{21}) \tag{38}$$

The relationship (38) should be a good approximation in the case of adsorption of hydrocarbons with a similar carbon chain lenght. Instead, the relationship (37) has a more general significance. It does not work when the components have a different chemical structure and therefore are characterized by different sets of degrees of freedom. It doesn't mean, however, that the equations for the isosteric heat of adsorption derived in this section have a limited validity. The parameter r_{21} is defined by eq. (25) and when the analytical expressions for all K's are available we can obtain the expression for $(\partial r_{21}/\partial T)$.

APPLICATION OF THE TÓTH EQUATION TO THE ADSORPTION FROM IDEAL LIQUID MIXTURES

Let us consider adsorption of the component »1« from a binary ideal liquid mixture »1—2« on a homogeneous surface; then, the relative surface excess of the component »1«, defined in terms of Gibbs' theory of adsorption[20], is equal to:

$$\tilde{\Theta}^{e}_{1(1,2)} = \tilde{\Theta}_{1(1,2)} - x_1 \tag{39}$$

where $\tilde{\Theta}_{1(1,2)}$ is the relative coverage of the homogeneous surface formed by molecules of the component »1«, x_1 is the mole fraction of the component »1« in the bulk phase, and the superscript »$\sim$« refers to adsorption from liquid mixtures. As it is known[20], the relative coverage $\tilde{\Theta}_{1(1,2)}$ may be expressed as:

$$\tilde{\Theta}_{1(1,2)} = \frac{\tilde{a}_{12} x_{12}}{1 + \tilde{a}_{12} x_{12}} \tag{40}$$

where $\tilde{a}_{12}$ is a constant, and $x_{12} = x_1/(1 - x_1) = x_1/x_2$. The constant $\tilde{a}_{12}$ has similar physical meaning as the one used in the case of mixed-gas adsorption $(a_{12} = a_1/a_2)$, and it may be expressed in the form:

$$\tilde{a}_{12} = \frac{\tilde{K}_2}{\tilde{\varkappa}} \exp [(\tilde{\varepsilon}_1 - \tilde{\varepsilon}_2)/RT] = 1/\tilde{K}_{12} \exp (\tilde{\varepsilon}_{12}/RT) \tag{41}$$

where $\tilde{\varepsilon}_{12}$ is the difference of adsorption energies $\tilde{\varepsilon}_1$ and $\tilde{\varepsilon}_2$.

According to Refs. (21) and (22) the relative coverage $\tilde{\vartheta}_{1(1,2)}$ on a heterogeneous surface may be defined by the following integral:

$$\tilde{\vartheta}_{1(1,2)}(x_{12}) = \int_{\Omega_{12}} \tilde{\Theta}_{1(1,2)}(x_{12}, \tilde{\varepsilon}_{12})\, \varphi(\tilde{\varepsilon}_{12})\, d\tilde{\varepsilon}_{12} \tag{42}$$

where $\varphi(\tilde{\varepsilon}_{12})$ is the distribution function of $\tilde{\varepsilon}_{12}$ normalized to unity, and Ω_{12} is the integration region for $\tilde{\varepsilon}_{12}$. Using the Tóth energy distribution function in eq. (42) which in the case of adsorption from binary liquid mixtures takes the form (see Appendix III)

$$\tilde{\varphi}(\varepsilon_{12}) = (\pi RT)^{-1}\, \tilde{\Lambda}^{1/\tilde{m}} \sin[(1/\tilde{m}) \arcsin(\tilde{\Lambda}\tilde{\lambda} \sin(\pi \tilde{m}))] \tag{43}$$

with

$$\tilde{\Lambda} = [\tilde{\lambda}^2 + 2\tilde{\lambda}\cos(\tilde{m}\pi) + 1]^{-1/2}; \quad \tilde{\lambda} = \exp\left[\frac{\tilde{m}(\tilde{\varepsilon}_{12} - \tilde{\varepsilon}^0{}_{12})}{RT}\right]$$

$$\tilde{\varepsilon}^0{}_{12} = RT \ln(\tilde{K}_{12}/\tilde{b}_{12})$$

and from eq. (40) for $\tilde{\Theta}_{1(1,2)}$ we get

$$\tilde{\vartheta}_{1(1,2)} = \left[\frac{x_{12}^{\tilde{m}}}{q_{12}^{\tilde{m}} + x_{12}^{\tilde{m}}}\right]^{1/\tilde{m}} \tag{44}$$

or

$$\tilde{\vartheta}^{e}_{1(1,2)} = \left[\frac{x_{12}^{\tilde{m}}}{b_{12}^{\tilde{m}} + x_{12}^{\tilde{m}}}\right]^{1/\tilde{m}} - x_1 \tag{45}$$

where $\tilde{m}$ and $\tilde{b}_{12}$ are constants analogous to the constants m and b in the case of gas adsorption. The differential adsorption heat

$$\tilde{Q}_{12} = RT^2 \left(\frac{\partial \ln x_{12}}{\partial T}\right)_{\tilde{\vartheta}_{1(1,2)}} \tag{46}$$

corresponding to the Tóth isotherm (43) is equal to:

$$\tilde{Q}_{12} = RT^2 \left(\frac{\partial \ln \tilde{b}_{12}}{\partial T}\right) + RT^2 \left(\frac{\partial \tilde{m}}{\partial T}\right) \left[\tilde{m}^{-2} \ln(1 - \tilde{\vartheta}^{\tilde{m}}_{1(1,2)}) + \frac{\tilde{\vartheta}^{\tilde{m}}_{1(1,2)} \ln \tilde{\vartheta}_{1(1,2)}}{\tilde{m}(1 - \tilde{\vartheta}^{\tilde{m}}_{1(1,2)})}\right] \tag{47}$$

Eq. (47) is formally analogous to the eq. (11).

In the similar way as for mixed-gas adsorption, eq. (43) may be generalized to the adsorption of multicomponent ideal liquid mixtures. Then, $\tilde{\Theta}_{1(n)}$ is given by the expression[23]:

$$\tilde{\Theta}_{1(n)} = \frac{\tilde{a}_{1n} x_{1n}}{1 + \mathbf{a}_n \mathbf{x}_n} \tag{48}$$

where $\mathbf{a}_n = (\tilde{a}_{1n}, \tilde{a}_{2n}, \ldots, \tilde{a}_{(n-1)n})$ and $\mathbf{x}_n = (x_{1n}, x_{2n}, \ldots, x_{(n-1)n})$. Let $\tilde{\varepsilon}_{in} - \tilde{\varepsilon}_{1n} = \tilde{\varepsilon}_{i1} = \tilde{\varkappa}_{i1}$ for $i = 2, 3, \ldots, n - 1$ be constant for the whole adsorbent surface, then

$$\tilde{\Theta}_{1(n)} = \frac{\tilde{a}_{1n} x_{1n}}{1 + \tilde{a}_{1n} \tilde{z}_1} \tag{49}$$

where

$$\tilde{z}_1 = x_{1n} \left(1 + \sum_{i=2}^{n-1} \tilde{r}_{i1} x_{i1}\right) = \gamma x_{1n} \tag{50}$$

and

$$\tilde{r}_{i1} = \tilde{a}_{in}/\tilde{a}_{1n} = (K_1/K_i) \exp(\tilde{\varepsilon}_{i1}/RT) = \tilde{K}_{i1} \exp(\tilde{\varkappa}_{i1}/RT) \tag{51}$$

The overall adsorption isotherm $\tilde{\vartheta}_{1(n)}$ may be expressed by the equation similar to eq. (26):

$$\tilde{\vartheta}_{1(n)}(x_{1n}) = \int_{\Omega_{1n}} \frac{\tilde{a}_{1n} x_{1n}}{1 + \tilde{a}_{1n} x_{1n} \gamma} \tilde{\varphi}(\varepsilon_{1n}) \, d\tilde{\varepsilon}_{1n} \tag{52}$$

Using the Tóth distribution for $\varphi(\tilde{\varepsilon}_{1n})$ we get

$$\tilde{\vartheta}_{1(n)} = \frac{x_{1n}}{[\tilde{b}_{1n}^{\tilde{m}} + (\gamma x_{1n})^{\tilde{m}}]^{1/\tilde{m}}} \tag{53}$$

Generalizing the above considerations it can be stated that the heterogeneity of adsorbing surface in the case of adsorption from n-component liquid mixtures may be taken into account in the similar way as in the adsorption of $(n - 1)$-component gas mixtures.

For the purpose of examination of eq. (43) the linear dependences

$$\tilde{N}_{1(1,2)}^{\tilde{m}} = (\tilde{N}_c x_{12}/\tilde{b}_{12})^{-\tilde{m}} + \tilde{N}_c^{-\tilde{m}} \tag{54}$$

have been calculated for adsorption of benzene from isooctane and benzene from CCl_4 on aerosil. These adsorption systems were investigated experimentally by Larionov[24]. For small values of x_1 values of the surface excess $\tilde{N}_{1(1,2)}^{e}$ are approximately equal to $\tilde{N}_{1(1,2)}$, and they may be used to calculate the parameter $\tilde{m}$, $\tilde{N}_c$ and $\tilde{b}_{12}$ (where $\tilde{N}_c = \tilde{N}_{1(1,2)} + \tilde{N}_{2(1,2)}$). Figure 3 shows

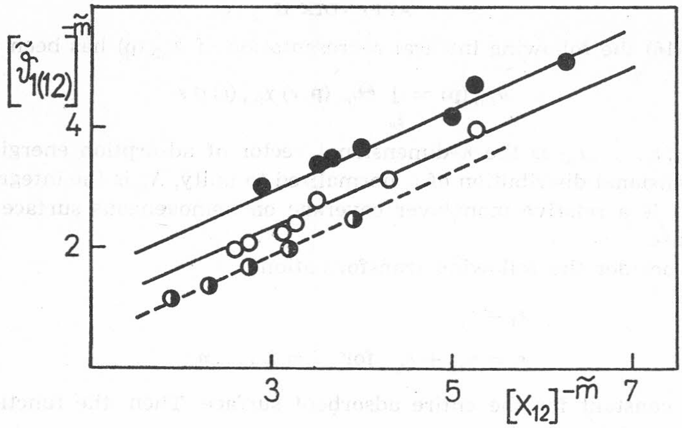

Figure 3. Linear dependences $\tilde{\vartheta}_{1(1,2)}^{-\tilde{m}}$ vs. $x_{12}^{-\tilde{m}}$ for binary liquid mixtures on aerosil: (1) benzene-(2)isooctane at 303 K (dashed line): $m = 0.45$, and (1) benzene-(2)CCl_4 at 303 K (solid line -○); $m = 0.45$, and 338 K (solid line -●); $m = 0.50$.

that the experimental values of $[\tilde{N}^{e}_{1(1,2)}]^{-\tilde{m}}$ for $x_1 \leqslant 0.1$ lie on straight lines. Thus, the adsorption data measured below $x_1 \leqslant 0.1$ may be used for preliminary calculation of $\tilde{N}_c$, $\tilde{m}$, and $\tilde{b}_{12}$; these parameters may be used as starting ones in the bestfit procedure optimizing the adjustable eq. (44), to the experimental data from the whole concentration region.

APPENDIX I

Consider the problem of calculation of the isosteric heat of adsorption for equations, which predict filling up a monolayer at finite adsorbate pressure. For the Tóth equation we can write

$$\left(\frac{p^m}{b^m + p^m}\right)^{1/m} = \vartheta \cdot h\,(b, p_o, m) \tag{AI-1}$$

where

$$\vartheta = N\,(p)/N_o$$

and

$$h\,(b, p_o, m) = \left(\frac{p_o{}^m}{b^m + p_o{}^m}\right)^{1/m}$$

Thus

$$\ln p = \ln \vartheta + \ln b - (1/m) \ln\,[f\,(b, p_o, m) - \vartheta^m] \tag{AI-2}$$

with

$$f\,(b, p_o, m) = [h\,(b, p_o, m)]^{-m}$$

Equations (9) and (AI-2) give

$$Q_o^{st} = RT^2\left(\frac{\partial \ln b}{\partial T}\right) + RT^2\left(\frac{\partial m}{\partial T}\right)\left[m^{-2}\ln\,[f\,(b, p_o, m) - \vartheta^m] + \frac{\vartheta^m \ln \vartheta}{m\,(f\,(b, p_o, m) - \vartheta^m)}\right]$$

$$- \left(\frac{\partial f\,(b, p_o, m)}{\partial T}\right)[m\,(f\,(b, p_o, m) - \vartheta^m)]^{-1} \tag{AI-3}$$

For $p_o \rightarrow \infty$ the function $f\,(b, p_o, m) \rightarrow 1$, and Q^{st} calculated from eq. (AI-3) tends to the isosteric heat of adsorption calculated from eq. (11).

APPENDIX II

In Ref. (18) the following integral representation of $\vartheta_{(n)}(\mathbf{p})$ has been derived:

$$\vartheta_{(n)}(\mathbf{p}) = \int_{\Delta_n} \Theta_{(n)}(\mathbf{p}, \varepsilon)\, \chi_{(n)}(\varepsilon)\, d\, \varepsilon \qquad \text{(AII-1)}$$

where $\varepsilon = (\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_n)$ is the n-dimensional vector of adsorption energies ε_i, $\varkappa_{(n)}(\varepsilon)$ is the n-dimensional distribution of ε, normalized to unity, Λ_n is the integration region of ε, and $\Theta_{(n)}$ is a relative monalayer coverage on homogeneous surface for n-component mixture.

Let us consider the following transformation:

$$\begin{aligned} \varepsilon_i &= \varepsilon_1 \\ \varepsilon_i &= \varkappa_{i1} + \varepsilon_1 \quad \text{for} \quad i = 2, \ldots, n \end{aligned} \qquad \text{(AII-2)}$$

where $\varkappa_{i1}$ is constant for the entire adsorbent surface. Then, the function $\Theta_{(n)}(\mathbf{p}, \varepsilon)$ depends on $\mathbf{p}$ and ε_1 only, i. e.,

$$\Theta_{(n)}(\mathbf{p}, \varepsilon) = \Theta_{(n)}(\mathbf{p}, \varepsilon_1, \varkappa_{21} + \varepsilon_1, \ldots, \varkappa_{n1} + \varepsilon_1) \qquad \text{(AII-3)}$$

Inserting eq. (AII-3) into eq. (AII-1) we obtain

$$\vartheta_{(n)}(\mathbf{p}) = \int_{\Delta_1} \Theta_{(n)}(\mathbf{p}, \varepsilon_1, \varkappa_{21} + \varepsilon_1 \ldots, \varkappa_{n1} + \varepsilon_1) \cdot \left(\int \chi(\varepsilon)\, d\, \varepsilon_2\, d\, \varepsilon_3, \ldots, d\varepsilon_n\right) d\, \varepsilon_1 \qquad \text{(AII-4)}$$

Denoting the expression

$$\int \varkappa_{(n)}(\varepsilon)\, d\, \varepsilon_2\, d\, \varepsilon_3, \ldots, d\, \varepsilon_n$$

by $\chi_1(\varepsilon_1)$ and putting eq. (23) for $\Theta_{(n)}$, eq. (AII-4) gives eq. (26).

APPENDIX III

It has been shown in Ref. (21) that equations describing adsorption of single gases on solids are formally identical with those for adsorption of binary liquid mixtures on solids. For example: the adsorption of gas »1« on a homogeneous surface can be described by Langmuir's equation:

$$\Theta_1(p_1) = \frac{a_1 p_1}{1 + a_1 p_1} \qquad \text{(AIII-1)}$$

However, the adsorption from an ideal binary liquid mixture on a homogeneous surface is described by Everett's equation (40). Eqs. (AIII-1) and (40) are formally identical. The same is observed for the integrals (15) and (42), describing the adsorption of single gases and binary liquid mixtures on heterogeneous surfaces. Thus, from the viewpoint of mathematics, the functions (7) and (43) /appearing in the integrals (15) and (42)/ have the same properties. However, the physical meaning of these two functions is slightly different; the function (7) depends on adsorption energy ε, whereas, the function (43) depends on the difference of adsorption energies of both components. It results from different definitions of surface heterogeneity in gas and liquid adsorption. In the case of gas adsorption the surface is heterogeneous when adsorption sites have different values of ε, whereas, in the case of liquid adsorption the surface is heterogeneous when sites have different values of ε_{12}.

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SAŽETAK

Studij adsorpcije iz plinskih i tekućih smjesa na čvrstim tijelima s kvazi-Gaussovom raspodjelom energije

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Ranija istraživanja su pokazala da Tóthova jednadžba dobro opisuje adsorpciju ugljikovodika na ugljikovim adsorbentima a posebno na Nuxit-Al ugljenu. Ta činjenica vjerojatno je povezana s kvazi-Gaussovom raspodjelom energije koja je povezana s Tóthovom jednadžbom. U ovom radu razmatrani su ponovno parametri spomenute jednadžbe uzimajući u obzir nove podatke. Modificirana Tóthova jednadžba je poopćena za slučaj adsorpcije iz višekomponentnih plinskih i tekućih smjesa na čvrstim tijelima s kvazi-Gaussovom raspodjelom energije.

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