Description of equilibrium data of the adsorption of *n*-heptane on molecular sieve 5 A by an actual form of the Freundlich isotherm*

D. BOBOK, E. KOSSACZKÝ, and M. ŠEFČÍKOVÁ

Department of Chemical Engineering, Slovak Technical University,
880 37 Bratislava

Received 6 September 1974

In this paper a critical analysis of the semiempirical derivations of an actual form of the Freundlich equation of adsorption isotherm is presented. A statistical evaluation of the experimentally determined adsorption equilibria of *n*-heptane on molecular sieve 5 A showed that this equation fairly described the isothermal data over a relatively wide range of values. However, we did not succeed in establishing the relationship between the constants of this equation and temperature so that the calculated equilibrium data might conform to the statistical criteria.

В статье критически обсуждаются полуэмпирические выводы реального вида уравнения Фрейндлиха. Статистическая оценка экспериментально полученных адсорбционных равновесий *н*-гептана на молекулярном сите 5 А показала, что это уравнение хорошо описывает изотермические данные в довольно широком интервале значений. Не удалось, однако, определить простые зависимости констант этого уравнения от температуры с тем, чтобы обратным путем рассчитанные равновесные данные соответствовали статистическим требованиям.

In connection with the search for the distribution function of the energies of adsorption centres relative to the usual mathematical form of the equation of adsorption isotherm, *Sips* [1] has put forward the following actual form of the Freundlich adsorption isotherm

$$\Theta = \frac{a}{a_0} = \frac{b\,p^r}{1 + b\,p^r}, \tag{1}$$

where a is the concentration of adsorbate on adsorbent, p is the equilibrium pressure of adsorbate, Θ is the degree of covering of adsorbent by adsorbate or in the case of adsorption in volume the degree of packing of adsorbent by adsorbate, and a_0, b, r are constants while a_0 represents the maximum concentration of adsorbate in adsorbent. The procedure of Sips, who showed that the form of the distribution function of eqn (*1*) depended on the value of r and for $r = 0.5$ approximated the

---

* Presented at the 1st Czechoslovak Seminar on Adsorption, Bratislava, June 4—5, 1974.

Gaussian distribution function, was criticized in two respects [2]. The derivation is based on the assumption that the adsorption heat varies in the range from $-\infty$ to $+\infty$ and thus assumes also the negative values. The derived distribution function of the energies of adsorption centres is a function of temperature.

Supposing that each atom of adsorbate reacts with one active centre and assuming the chemisorption of diatomic molecule on the active centres of adsorbent, *Koble* and *Corrigan* [3] derived the concrete form of eqn (*1*) for $r = 0.5$.

From the description of the state behaviour of adsorbed phase as a two-dimensional gas and the Gibbs equation of adsorption isotherm *Kisarov* [4] derived an equation of adsorption isotherm which could be easily transformed into the form (*1*). This derivation is based on the following equation

$$\frac{\mathrm{d}S}{S - 2b_2} = r\frac{\mathrm{d}V}{V}, \tag{2}$$

where S is the surface of adsorbent covered by one mole of adsorbate, b_2 is a coefficient characterizing the correction with respect to the surface of the molecules adsorbed and is analogous to the coefficient b in the van der Waals equation of three-dimensional gas, and V is the volume of gaseous phase. In the cited paper it is pointed out that eqn (*2*) may be obtained from the Volmer considerations concerning the thermodynamics of the Langmuir equation if a correction for the cohesion ipressure in the adsorbed phase is introduced.

If we introduce a correction for the cohesion pressure into the Volmer state equation of two-dimensional gas [5]

$$F(S - b_2) = RT \tag{3}$$

n conformity with [4], we obtain

$$r\,F(S - b_2) = RT, \tag{4}$$

where F is the two-dimensional pressure of a two-dimensional gas. By differentiating eqn (*4*) at constant temperature and rearranging we obtain

$$\frac{\mathrm{d}F}{\mathrm{d}S} = -\frac{RT}{r(S - b_2)^2}. \tag{5}$$

If we express in the Gibbs equation of adsorption isotherm the increase in the concentration of adsorbate on the surface by means of S and substitute for RT from eqn (*5*) we obtain the following equation

$$\frac{1}{S} = -\frac{p}{r}\,\frac{1}{(S - b_2)^2}\,\frac{\mathrm{d}S}{\mathrm{d}p}. \tag{6}$$

Assuming that $b_2^2 \ll 2S\,b_2$ and replacing $\mathrm{d}p/p$ by the expression $-\mathrm{d}V/V$, eqn (*6*) may by transformed into eqn (*2*). In [4] it is also pointed out that the evaluation of a great amount of experimental data obtained by the investigation of equilibria on activated carbon, silica gels, and molecular sieves has shown the dependence of the constant r on the character and structure of adsorbent, properties of adsorbate and temperature, and equals to kT/β where k is a constant and β is the coefficient of affinity.

From eqn (*4*) it follows that the coefficient r characterizing the correction for the cohesion pressure is greater than one. On the basis of analysis of the experimentally determined equilibrium data for the adsorption of benzene on activated carbon, *Kisarov* [4] found the values of the constant r to be $r < 1$. By testing the equilibrium data of the adsorption of methane, ethane, propane, butane, ethylene, propylene, and carbon dioxide on activated carbon at 20—90°C by means of eqn (*1*), *Szepesy*, *Illés*, and *Fáy* [6] found too, that the values of the constant r to be $r < 1$. In this respect, the derivation of eqn (*1*) presented by *Kisarov* [4] cannot be considered to be physically justified.

Ginoux and *Bonnetain* [7, 8] refer to eqn (*1*) as to a semiempirical *Cohen* equation which was derived on the basis of the *Polanyi* theory under the assumption that the equation of characteristic curve had the form [9]

$$\Theta = \frac{1}{1 + \exp\left(\frac{\varepsilon - \varepsilon_{\mathrm{M}}}{A}\right)}, \tag{7}$$

where ε is the adsorption potential defined by the equation

$$\varepsilon = RT \log \frac{p_0}{p}\cdot \tag{8}$$

ε_{M} and A are constants depending only on the properties of the system and independent on temperature, and p_0 is the pressure of the saturated vapour of adsorbate. If we insert for ε from eqn (*8*) into eqn (*7*) and introduce the subsequent constants

$$r = \frac{RT}{A}$$

and

$$b = \exp\left(\frac{\varepsilon_{\mathrm{M}} - RT \log p_0}{A}\right) \tag{9}$$

eqn (*7*) may be rearranged into eqn (*1*). Thus eqn (*1*) may be regarded as a semiempirical equation which contains three constants and therefore is usable for the description of adsorption equilibria with sufficient accuracy over a relatively wide range of values.

Discussion

The experimentally determined equilibrium data for n-heptane and molecular sieve Calsit 5 are shown in Fig. 1. They were tested by means of eqn (*1*). The best values of the constants in eqn (*1*) were calculated from the equilibrium data using a combined method [10]. The calculated values of the constants together with statistical quantities, *i.e.* variance

$$s^2 = \frac{\sum\limits_{i=1}^{n} (a_i - a_{vi})^2}{n - 2}, \tag{10}$$

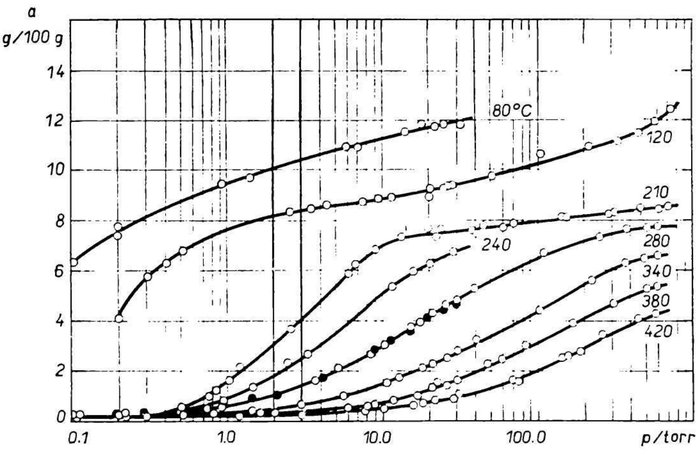

Fig. 1. Adsorption isotherms of the system *n*-heptane—molecular sieve Calsit 5.

standard deviation

$$\delta = \sqrt{\frac{\sum\limits_{i=1}^{n}\left(\frac{a_i - a_{vi}}{a_i}\right)^2}{n-2}} \tag{11}$$

and correlation coefficient [11]

$$\varrho = \frac{\sum\limits_{i=1}^{n}(a_i - \bar{a})\,(a_{vi} - \bar{a}_v)}{\sqrt{\sum\limits_{i=1}^{n}(a_i - \bar{a})^2 \sum\limits_{i=1}^{n}(a_{vi} - \bar{a}_v)^2}} \tag{12}$$

are assembled in Table 1. In eqns (*10*), (*11*), and (*12*) a_{vi} is the adsorbed amount calculated from eqn (*1*), $\bar{a}$ and $\bar{a}_v$ are the arithmetic means of the values a_i or a_{vi}, respectively. From Table 1 it is obvious that the data obtained at all temperatures but 210°C show a relatively small values of the variance. Except the data obtained at 80 and 120°C, the values of standard deviation are relatively high which is due to a higher relative inaccuracy of the equilibrium data obtained at lower pressures of adsorbate. The values of correlation coefficients are, however, very high which demonstrates that it is possible to use eqn (*1*) for the description of the equilibrium data of *n*-heptane on molecular sieve Calsit 5 in a relatively wide range of values.

On the basis of the calculated values of the constants in eqn (*1*) we tried to find out the dependence of these constants on temperature. Here, the relationships $a_0 = \mathrm{f}(T)$, $a_0 = \mathrm{f}(1/T)$, and $\log a_0 = \mathrm{f}(1/T)$ were considered and it was ascertained that the values of the constants a_0 and b listed in Table 1 fitted best the last of these expressions. A graphical representation of the relationship between the constants a_0 and b and temperature expressed by this relationship is given in Figs. 2 and 3, respectively. The corresponding numerical relationships between these constants and temperature calculated by the least-squares method are

Table 1

Calculated values of the constants in eqn (*1*)

t °C	Quantity					
	a_0 g/100 g	$b \cdot 10^2$ torr^{-r}		$s^2 \cdot 10^2$ g/100 g^2	$\delta \cdot 10^2$	ϱ
80	12.856	271.57	0.4326	2.22	1.72	0.998
120	14.261	91.80	0.2500	2.21	8.33	0.973
210	8.143	22.88	1.3472	5.25	26.79	0.997
240	7.643	12.85	1.1837	0.63	20.50	1.000
280	8.202	8.21	0.8286	0.37	11.09	1.000
340	7.845	3.61	0.7769	0.63	13.11	1.000
380	6.128	1.20	0.9780	1.05	26.73	0.998
420	7.296	1.05	0.7741	0.59	29.57	0.999

$$\log a_0 = 232.6777 \frac{1}{T} + 0.47970,$$

$$\log b = 1713.0156 \frac{1}{T} - 4.33092. \qquad (13)$$

The values of r from Table 1 plotted as a function of temperature are presented in Fig. 4. The points of the plot in Fig. 4 exhibit a relatively high variance, but they show that there is a maximum in the relationship between r and T (line *1*). A more thorough examination of Fig. 4 points out a falling tendency of the dependence r *vs.* T for the temperatures of adsorption above 210°C. The linear approxi-

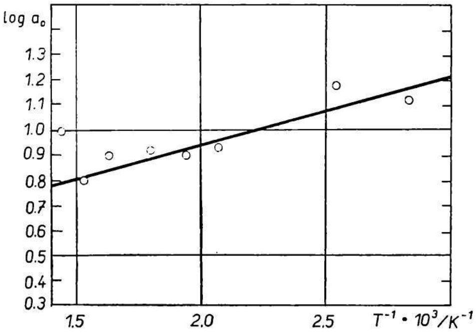

Fig. 2. Values of a_0 calculated from experimental equilibrium data and expressed as a function $\log a_0 = f(1/T)$.

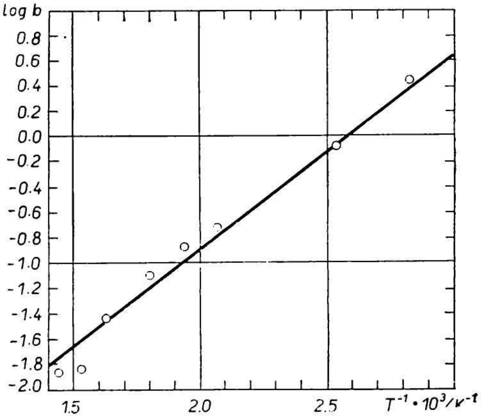

Fig. 3. Values of b calculated from experimental equilibrium data and expressed as a function $\log b = f(1/T)$.

Table 2

Statistical data for the correlation of the constants in eqn (*1*)

t °C	From expression (*13*)		r determined from Fig. 4 for line											
			1				*2*				*3*			
	a_0 g/100 g	$b \cdot 10^2$ torr^{-r}		$s^2 \cdot 10^2$ (g/100 g)^2	$\delta \cdot 10^2$	ϱ		$s^2 \cdot 10^2$ (g/100 g)^2	$\delta \cdot 10^2$	ϱ		$s^2 \cdot 10^2$ (g/100 g)^2	$\delta \cdot 10^2$	ϱ
80	13.7676	332.57	0.187	233.81	19.98	0.995	—	—	—	—	0.3508	157.86	14.40	0.997
120	11.7964	106.62	0.425	54.89	9.41	0.963	—	—	—	—	0.4187	55.45	9.39	0.963
210	9.1594	16.43	0.899	74.63	32.31	0.933	1.2033	48.03	24.54	0.992	0.5714	402.73	64.59	0.911
240	8.5756	10.19	0.973	23.13	29.48	0.993	1.1414	4.09	20.72	0.999	0.6223	326.45	56.62	0.995
280	7.9516	5.84	0.939	2.43	17.02	0.999	1.0520	14.19	19.60	0.995	0.6920	153.14	33.34	0.982
340	7.2322	2.91	0.910	3.08	15.51	0.998	0.9177	4.22	15.84	0.998	0.7920	24.27	20.85	0.999
380	6.8553	1.96	0.859	7.57	37.36	0.937	0.8233	2.96	32.03	0.973	0.8599	7.76	37.53	0.967
420	6.5382	1.38	0.800	6.09	32.38	0.993	0.7388	2.60	27.88	0.997	0.9278	85.40	61.10	0.987

mation of this relationship performed by the least-squares method is shown in Fig. 4 and denoted by number *2*. If the relationship between r and T should comply with the ideas of *Kisarov* [4] and *Cohen* [9], the values of r obtained at 210 and 240°C must not be considered. The linear approximation of the dependence r *vs.* T established by the least-squares method from the values thus adapted is in Fig. 4 denoted by number *3*. The decision on the general tendency (rising or falling) of the relationship between r and T in the investigated range of values may be seized from the pertinent statistical quantities on the assumption that the values of the constants as individual temperatures were calculated from a sufficiently wide range of the values of equilibrium data. As a criterion for the determination of equilibrium data required for the computation of the constants of eqn (*1*), the postulate should be applied that the range of equilibrium data must be large enough to find out the course of the whole distribution function of the energies of adsorption centres. According to [2, 12] the distribution function of the energies of adsorption centres is given by the expression

$$h(q) = -\left(\frac{\partial a}{\partial q}\right)_T = \frac{1}{RT}\left(\frac{\partial a}{\partial \ln p}\right)_T, \qquad (14)$$

where q is the energy of adsorption centres and R is gas constant. The corresponding distribution functions are represented in Fig. 5. Here, it can be seen that the range of the values of equilibrium data experimentally determined at 80 and 120°C is not adequate. By omitting these values we obtain a falling relationship between r

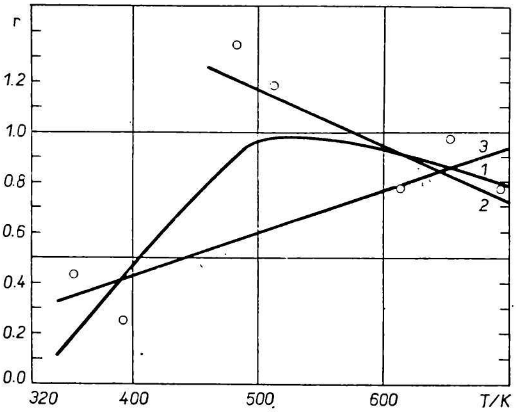

Fig. 4. Values of r calculated from experimental equilibrium data as a function of T.
1. All points are considered; *2.* only the points at $T \geqslant 483$ K are considered; *3.* the points at 483 and 513 K are omitted.

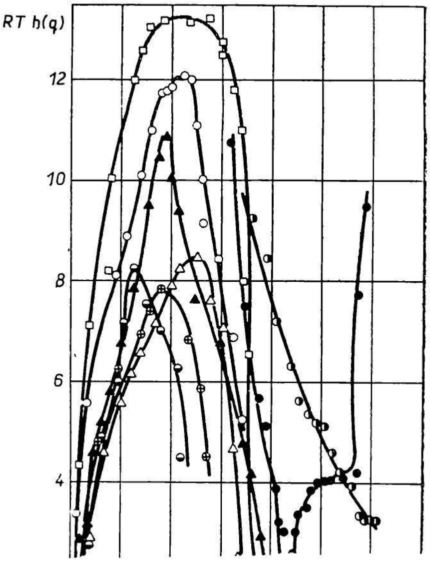

Fig. 5. Relationship $RT\,h(q) = f(a)$.
◑ 80°C; ● 120°C; □ 210°C; ○ 240°C; ▲ 280°C; △ 340°C; ⊕ 380°C; ◒ 420°C.

and T (Fig. 4, line *2*) which is in contradiction with the definition of the constant r according to eqn (*9*) as well as with the considerations of *Kisarov* [4] on the properties of the constant r. From this point of view it is not possible to consider the derivations of eqn (*1*) published beforehand to be physically justified for the description of physical adsorption.

The statistical data for the values of a_0 and b obtained from expressions (*13*) and the values of r from Fig. 4 for linear and curved course are given in Table 2. It is obvious that the values of the variance of standard deviation and correlation coefficient are in all cases worse than those for the data in Table 1. In order to assess which values from the set of the constants in eqn (*1*) in Table 2 conform to the measured data with a sufficient accuracy we may use the F test for the values of the variance while the data in Table 1 will serve as minimum values of the variance. For the significance level $\alpha = 0.05$ it may be found out from tables [13] that for the satisfactory values of the constants in eqn (*1*) it must hold $s^2 < 3s^2_{\min}$. In spite of relatively high values of the correlation coefficient only the constants at 380°C in Table 2 corresponding to line *2* comply with this postulate. Hence, the form of eqn (*1*) complies with the experimental equilibrium data of the adsorption of *n*-heptane on molecular sieve 5 A. We have not succeeded in finding out simple relationships between the constants of this equation and temperature. This is mainly due to the properties of eqn (*1*) which so far has not been derived in a physically justified manner for the description of the equilibrium of substances adsorbed physically as well as to the fact that the experimental equilibrium data have not been ascertained at all temperatures in an adequate range of values.

Symbols

a	concentration of adsorbate on adsorbent
	arithmetic mean of the experimental values of the concentration of adsorbate on adsorbent
	arithmetic mean of the calculated values of the concentration of adsorbate on adsorbent
a_0	maximum concentration of adsorbate on adsorbent
A	constant in eqns (*7*) and (*9*)
b	constant in eqn (*1*)
b_2	coefficient characterizing the correction for the surface of adsorbed molecules
F	two-dimensional pressure of a two-dimensional gas
$h(q)$	distribution function of the energies of adsorption centres
k	constant
p	pressure of adsorbate
q	energy of adsorption centres
r	constant in eqn (*1*)
R	gas constant
s^2	variance
S	surface of adsorbent covered with one mole of adsorbate
T	temperature of adsorption
δ	standard deviation
Θ	degree of covering of adsorbent by adsorbate
ϱ	correlation coefficient

References

1. Sips, R., J. *Chem. Phys.* ***16***, 490 (1948).
2. Young, D. M. and Crowell, A. D., *Physical Adsorption of Gases.* Butterworths, London, 1962.
3. Koble, R. A. and Corrigan, T. E., *Ind. Eng. Chem.* ***44***, 383 (1952).
4. Kisarov, V. M., *Zh. Fiz. Khim.* ***43***, 1037 (1969).
5. de Boer, J. H., *The Dynamical Character of Adsorption*, Sec. Ed. Clarendon Press, Oxford, 1968.
6. Szepesy, L., Illés, V., and Fáy, L., *Acta Chim. Acad. Sci. Hung.* ***37***, 71 (1963).
7. Ginoux, J. L. and Bonnetain, L., *C. R. Acad. Sci.* (Paris), *Ser. C*, ***272***, 879 (1971).
8. Ginoux, J. L. and Bonnetain, L., *C. R. Acad. Sci.* (Paris), *Ser. C*, ***272***, 1067 (1971).
9. Cohen, G., *Thesis.* Grenoble, 1967; cited in [5, 6].
10. Bobok, D., Havalda, I., Kossaczký, E., and Šefčíková, M., *Ropa a Uhlie* ***15***, 539 (1973).
11. Yule, G. V and Kendall, M. G., *Teoriya statistiki.* (Theory of Statistics; Russian translation.) Gosstatizdat, Moscow, 1960.
12. Ponec, V., Knor, Z., and Černý, S., *Adsorpce na tuhých látkách.* (Adsorption on Solids.) Státní nakladatelství technické literatury. (State Publishing House of Technical Literature.) Prague, 1968.
13. Garaj, I. and Krišťák, M., *Teória pravdepodobnosti a matematická štatistika.* (Theory of Probability and Mathematical Statistics.) Slovak Technical University, Bratislava, 1970.

Translated by R. Domanský