Adsorption of gas mixtures on homogeneous surfaces Extension of Jovanović equation on adsorption from gaseous mixtures

M. JARONIEC

Department of Physical Chemistry, Institute of Chemistry, University of M. Curie-Skłodowska, 200 31 Lublin, Poland

Received 20 September 1974

Accepted for publication 31 January 1975

The Jovanović equation of monolayer adsorption isotherm on homogeneous surfaces is extended on a case of adsorption from gaseous mixtures.

Уравнение Йовановитя для однослойной адсорбционной изотермы на гомогенных поверхностях было приспособлено и для случая адсорбции из газообразных смесей.

In the development of the theory of physical adsorption of gases a very important part is played by an extension of studies on multicomponent systems, *i.e.*, extension of pure-gas equations on the adsorption from gaseous mixtures. Then the multicomponent adsorption isotherms are derived in terms of parameters of the pure-gas isotherms.

As a typical example the mixed-gas Langmuir equation of *Markham* and *Benton* [1] may be considered.

Recently *Jovanović* [2] reexamined the Langmuir adsorption model, and proved that a more rigorous treatment of this model leads to new isotherm equation for monolayer adsorption of pure gas on homogeneous surfaces.

Jovanović [3] demonstrated on numerous adsorption systems that his equation fits experimental data better than the Langmuir equation. Since, the Jovanović equation has been adopted by *Misra* [4], *Rudziński* and *Jaroniec* [5] for developing the description formalism for adsorption on heterogeneous surfaces. The statistical interpretation of Jovanović equation was discussed by *Jaroniec* [6].

The adsorption model considered by Jovanović is essentially the same as that of Langmuir, except for two new types of collisions taken into account. In addition to the two types of surface-molecule collisions considered by Langmuir, two new types of collisions between bulk and adsorbed molecules are considered by Jovanović. In the language of statistical mechanics it means that the considerations of Jovanović take into account the mechanical contact between adsorbed and bulk phase [5—7].

The adsorption mechanism assumed by *Jovanović* leads (after some complicated kinetic derivation) to the following isotherm equation [2]

$$N = N_m[1 - \exp(-ap)], \tag{1}$$

where N is the adsorbed amount and N_m is the monolayer capacity. The constant a stands for the expression

$$a = (1/K)\exp(E/RT), \tag{2}$$

where $K(T)$ is the temperature-dependent constant (the constant K is analogous to the one in the Langmuir isotherm) and E is the adsorption energy. For $p \to 0$, eqn (*1*) is reduced to the Langmuir pure-gas adsorption isotherm

$$N = N_m \, a \, p/(a \, p + 1). \tag{3}$$

On basis of *Jovanović* model [2] we proposed for a total adsorption isotherm from gaseous mixtures the equation

$$N = N_m \left[1 - \exp\left(- \sum_{i=1}^{n} a_i \, p_i \right) \right], \tag{4}$$

where p_i is the partial pressure of the i-th gas, a_i is the constant from eqn (*1*) for the i-th gas, and n denotes the number of components in the gas mixture.

The eqn (*4*) can be derived by applying the *Jovanović* procedure based on a detailed analysis of molecular collisions in the adsorbed phase [2]. Jovanović assumed that the surface of adsorbent is characterized by an adsorption energy E which is correlated to the average time of settling of one molecule on the surface τ by the well-known equation

$$\tau = \tau_0 \exp(E/RT). \tag{5}$$

Since the average value of τ includes all settling times from 0 to τ_{max}, he assumed that each molecule which arrives to the surface is adsorbed. When the state of equilibrium is attained, all the adsorbed molecules must evaporate within τ, but they will not evaporate simultaneously. Jovanović examined minutely a very small fraction of the adsorbed phase. For this purpose, he divided τ into m time intervals $\Delta\tau_i$ (where $m \to \infty$ and $\Delta\tau_i \to 0$) considering that within such a minuscule period an instantaneous evaporation of adsorbed molecules will occur. The starting point in Jovanović derivation is the expression for number of molecules contained in each $\Delta\tau_i$ interval. This number is directly proportional to the expression

$$(2\pi \, M \, R \, T)^{-1/2} \, p \, \sigma \, \Delta\tau_i = p \, \varphi \, \Delta\tau_i.$$

(The symbols having their conventional meaning.) However, in the case of adsorption from binary gas mixtures this proportionality factor equals $(p_1 \varphi_1 + p_2 \varphi_2) \Delta\tau_i$. Further derivation of eqn (*4*) is identical with the Jovanović equation (*2*).

For adsorption of binary gas mixtures the eqn (*4*) can be simplified

$$N = N_m[1 - \exp(-a_1 \, p_1 - a_2 \, p_2)]. \tag{6}$$

Evidently, for $p_i \to 0$ $(i = 1,2)$ the eqn (*6*) is reduced to the Langmuir equation

$$N = N_m(a_1 \, p_1 + a_2 \, p_2)/(1 + a_1 \, p_1 + a_2 \, p_2). \tag{7}$$

However, for $p_1 = 0$ and $p_2 \neq 0$ (or $p_2 = 0$ and $p_1 \neq 0$), the eqn (*6*) is reduced to the adsorption isotherm of the 2-nd pure gas (or 1-st pure gas), *i.e.* it is reduced to eqn (*1*).

Let us assume that a great number of measurements of the total adsorption isotherm from gaseous mixtures is performed at a constant total pressure $p = p_1 + p_2$. Then the total adsorption isotherm from eqn (*6*) can be written as

$$N = N_m[1 - \exp(A - B \, p_1)], \tag{8}$$

where

$$A = -a_2 p \quad \text{and} \quad B = a_1 - a_2. \tag{9}$$

The eqn (*8*) is analogous to the Langmuir equation

$$N = N_m(-A + B p_1)/(1 - A + B p_1). \tag{10}$$

The numerical calculations for a series of adsorption systems (the following systems were examined: $Ar-O_2$ and $CO-N_2$ on CsI [8], $Xe-CO_2$ on Al_2O_3 [9], $CO_2-C_2H_2$ on charcoal [10]; beside, the data concerning the adsorption of hydrocarbons on Nuxit-Al presented by *Szepesy* and *Illés* [11—13] were utilized), have proved that the Jovanović eqns (*6*) and (*8*) fits better the experimental data than the Langmuir eqns (*7*) and (*10*).

In order to illustrate the above considerations, we compared the eqn (*8*) with the Langmuir eqn (*10*) for adsorption from a mixture of carbon dioxide and acetylene on charcoal Nuxit-Al at 273 and 293 K. This adsorption system was investigated experimentally by *Schay*, *Székely*, and *Szigetváry* [10]. First, the adsorption isotherms for pure gases will be discussed. In order to determine the parameters of Jovanović eqn (*1*) and Langmuir eqn (*3*) we performed the well-known linear plots of these equations. The parameters of eqns (*1*) and (*3*) are summarized in Table 1. Subsequently, the equations of adsorption isotherms from gas mixtures are discussed. For this purpose, we have rewritten the eqns (*8*) and (*10*) into a linear form

$$\ln(1 - \Theta) = A - B p_1 \tag{11}$$

Table 1

Parameters of Jovanović and Langmuir equations for adsorption of CO_2 and C_2H_2 on charcoal Nuxit-Al

Adsorbate	T K	N_m 10^6 m^3	$a \cdot 10^5$ m$^2/N$	$a \cdot 10^5$ m$^2/N$	$\Delta a \cdot 10^5$ m$^2/N$
Langmuir parameters		Pure-gas adsorption eqn (*3*)		Mixed adsorption eqn (*10*)	
C_2H_2	273	109.7	2.82	3.48	−0.66
CO_2	273	86.8	1.80	1.24	0.56
C_2H_2	293	110.7	1.36	1.64	−0.28
CO_2	293	83.6	1.00	0.88	0.12
Jovanović parameters		Pure-gas adsorption eqn (*1*)		Mixed adsorption eqn (*8*)	
C_2H_2	273	84.5	2.97	3.20	−0.23
CO_2	273	69.5	0.95	1.10	−0.15
C_2H_2	293	57.5	1.82	2.05	−0.23
CO_2	293	75.5	1.34	1.15	0.19

and

$$\Theta/(1 - \Theta) = - A + B p_1, \qquad (12)$$

where $\Theta = N/N_m$ denotes the relative coverage.

In Fig. 1 the experimental adsorption data for adsorption system CO_2—C_2H_2—charcoal calculated according to eqn (*11*) (open circles and solid line) and eqn

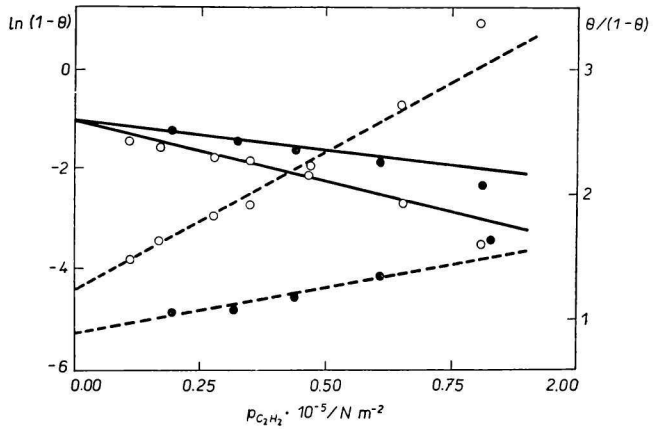

Fig. 1. The mixed adsorption of carbon dioxide and acetylene on charcoal at 273 K (○) and 293 K (●).
The solid lines refer to the Jovanović equation (*11*) for both temperatures and the dashed lines refer to the Langmuir equation (*12*).

(*12*) (open circles and dashed line) are presented. The experimental values were measured at 273 K; for monolayer capacity, however, the arithmetical mean of the monolayer capacities for pure-gas adsorption was assumed: for Jovanović eqn (*11*) — 77.0×10^{-6} m^3 (normal conditions) and for Langmuir eqn (*12*) — $98.2 \times \times 10^{-6}$ m^3 (normal conditions). Similar diagrams for the same adsorption system at 293 K are presented in Fig. 1 (black circles). The calculations were performed using monolayer capacities: for Jovanović eqn (*11*) — 66.5×10^{-6} m^3 and for Langmuir eqn (*12*) — 97.1×10^{-6} m^3. Parameters of the straight lines from Fig. 1 were used in the calculations of parameters a_1 and a_2 (for this purpose the relations (*9*) were used). From a comparison of the parameters a_1 and a_2 obtained from pure-gas adsorption isotherms with those evaluated from the linear plots (Fig. 1) it follows that Jovanović parameters a_1 and a_2 calculated by means of eqn (*11*) are closer to those calculated from pure-gas isotherm (*1*) than it was in the case where Langmuir eqns (*3*) and (*12*) were used. This indicates that Jovanović eqn (*8*) fits the experimental data better than the Langmuir eqn (*10*).

References

1. Markham, E. C. and Benton, A. F., *J. Amer. Chem. Soc.* ***53***, 497 (1931).
2. Jovanović, D. S., *Kolloid-Z. Z. Polym.* ***235***, 1203 (1970).

3. Jovanović, D. S., *Kolloid-Z. Z. Polym.* ***235***, 1214 (1970).
4. Misra, D. N., J. *Colloid Interface Sci.* ***43***, 85 (1973).
5. Rudziński, W. and Jaroniec, M., *Surface Sci.* ***42***, 552 (1974).
6. Jaroniec, M., *Kolloid-Z. Z. Polym.*, in press.
7. Rudziński, W. and Jaroniec, M., *Ann. Chim. Soc. Polonorum* ***49***, 165 (1975).
8. Tompkins, F. C. and Young, D. M., *Trans. Faraday Soc.* ***47***, 88 (1951).
9. Lasoń, M. and Nodzeński, A., *Ann. Chim. Soc. Polonorum* ***47***, 591 (1973).
10. Schay, G., Székely, G., and Szigetváry, G., *Acta Chim. Acad. Sci. Hung.* ***12***, 309 (1957).
11. Szepesy, L. and Illés, V., *Acta Chim. Acad. Sci. Hung.* ***35***, 37 (1963).
12. Szepesy, L. and Illés, V., *Acta Chim. Acad. Sci. Hung.* ***35***, 53 (1963).
13. Szepesy, L. and Illés, V., *Acta Chim. Acad. Sci. Hung.* ***35***, 245 (1963).