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ADSORPTION ON HETEROGENEOUS SURFACES: ANALOGY BETWEEN ADSORPTION FROM GASES AND SOLUTIONS

By

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Abstract

The analogy in the mathematical description between adsorption from liquids and adsorption from gases on heterogeneous surfaces is considered. This analogy makes the development of an identical method for determining the distribution function of adsorption energy in both cases possible.

MYERS and SIRCAR¹⁾ have recently published an important paper concerning the analogy between adsorption from liquids and adsorption from vapors on homogeneous surfaces. In both cases, on assuming idealness of volume phases, the adsorption isotherm is expressed

$$\Theta(x_i, \varepsilon_i) = \left[1 + \frac{K_i}{x_i} \exp\left(\frac{-\varepsilon_i}{RT}\right) \right]^{-1} \quad \text{for } i = g, s \quad (1)$$

where the subscripts (*g*) and (*s*) denote gas and liquid adsorption, respectively. In the case of adsorption from gases, x_g is the pressure of adsorbate, ε_g is the adsorption energy, and K_g is the constant connected with the molecular partition function of adsorbed molecules.^{2,3)} However, in the case of adsorption from solutions, $x_s = x_1/(1-x_1)$, x_1 is a molar fraction of the component "1" in the volume phase, $\varepsilon_s = \varepsilon_{g1} - \varepsilon_{g2}$, ε_{g1} and ε_{g2} being adsorption energies of components "1" and "2", and K_s is the constant connected with ratio of the molecular partition functions of the adsorbed molecules of the components "1" and "2".^{1,4)} In both cases x_i varies in the range $(0, \infty)$, and $\lim_{x_i \rightarrow \infty} \Theta(x_i, \varepsilon_i) = 1$.

Also on the basis of the patch model of heterogeneous surface we obtain an analogous expression for the overall (real) adsorption isotherm

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$v(x_i)$ in both cases (*i.e.* for adsorption from gases and solutions)^{5,6)}

$$v(x_i) = \int_{\Delta_i} \Theta(x_i, \varepsilon_i) \chi(\varepsilon_i) d\varepsilon_i \quad i = g, s \quad (2)$$

where Δ_i is the variation range of ε_i , in the case of adsorption from gases $\Delta_g = (0, \infty)$, whereas in the case of adsorption from solutions $\Delta_s = (-\infty, \infty)$, $\chi(\varepsilon_i)$ is the distribution function of ε_i , normalized to unity. The formal analogy in the mathematical description of adsorption from solutions and gases expressed in eqs. (1) and (2) makes the development of an equal method for determining the distribution function $\chi(\varepsilon_i)$ in both cases possible. This method we shall construct, on the basis of approximation of the local adsorption isotherm by means of the step-function and approximation of experimental overall adsorption isotherm by the equation

$$v(x_i) = \begin{cases} \exp \left[\sum_{n=1}^N B_{in} \left(RT \ln \frac{x_i}{x_{i0}} \right)^n \right] & \text{for } x_i \leq x_{i0} \\ 1 & \text{for } x_i > x_{i0} \end{cases} \quad (3)$$

where x_{i0} is the value at which the plateau $v(x_i)$ is obtained and B_{in} ($n=1, 2, \dots, N$) are analogous to parameter B in the Dubinin-Radushkevich (DR) isotherm equation. Equation (3) is a generalization of the DR isotherm equation in the case of gas adsorption. Our studies showed that eq. (3) is very convenient for numerical calculations, because it is restricted to approximation of the value $\ln v(x_i)$ of the polynomial (approximation of this type is very accurate).⁷⁾

Now let us return to the problem of approximation of the local adsorption isotherm $\Theta(x_i, \varepsilon_i)$ by means of the step-function. Thus, we shall replace in eq. (2) the true kernel Θ from eq. (1), by the step-function which suddenly rises from zero to unity, generally depending on the adsorption energy ε_i . If we define $E_i(x_i)$ as the last energy for which, at x_i , the step-function is equal to unity, eq. (2) becomes

$$v(x_i) = \int_{E_i(x_i)}^{\infty} \chi_c(\varepsilon_i) d\varepsilon_i \quad (4)$$

where $\chi_c(\varepsilon_i)$ is the approximate energy distribution function. The value x_i for which the step-function is equal to unity, is conveniently chosen to minimize the distance between eq. (1) and the step-function. This value x_i we get from the CEROFOLINI^{8,9)} general results ($\Theta(x_i, \varepsilon_i) = 1/2$) and for eq. (1) this relation between energy and x_i can be written in the form

$$E_i = RT \ln \frac{K_i}{x_i} \quad (5)$$

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Expressing, by means of the equation (5), x_i as a function E_i and differentiating both members of eq. (4) with respect to E_i we obtain

$$\chi_c(E_i) = -(d/dE_i) \tilde{v}(E_i) \quad (6)$$

where $\tilde{v}(E_i) = v[x_i(E_i)]$. From eqs. (3) and (5) we get

$$\tilde{v}(E_i) = \begin{cases} \exp \left[\sum_{n=1}^N B_{in} (E_{i_0} - E_i)^n \right] & \text{for } E_i \geq E_{i_0} \\ 1 & \text{for } E_i < E_{i_0} \end{cases} \quad (7)$$

where

$$E_{i_0} = RT \ln \frac{K_i}{x_{i_0}} \quad (8)$$

Thus the distribution function from eqs. (6) will be expressed by the following equation

$$\chi_c(E_i) = \begin{cases} \sum_{n=1}^N n B_{in} (E_{i_0} - E_i)^{n-1} \exp \left[\sum_{n=1}^N B_{in} (E_{i_0} - E_i)^n \right] & E_i \geq E_{i_0} \\ 0 & E_i < E_{i_0} \end{cases} \quad (9)$$

The determination of the function $\chi_c(E_i)$ has been reduced to the following numerical operations: (i) computation of the coefficients B_{in} of the eq. (3) by using the polynomial approximation to the experimental data according to the following equation

$$y_i = \sum_{n=1}^N B'_{in} z_i^n \quad (10)$$

where

$$y_i = \ln N_i(x_i), \quad z_i = \ln(x_i/x_{i_0}) \quad (11)$$

$$B'_{in} = B_{in} \cdot (RT)^n \text{ and } v(x_i) = N_i(x_i)/N_{i_0}$$

($N_{i_0} = \exp(B_{i_0})$ is the monolayer capacity), and (ii) calculation of the function $\chi_c(E_i)$ according to the formula (9).

The purpose of the numerical calculations was to examine the adsorption of benzene and cyclohexane on silica gel. For the numerical calculations the experimental data were taken of MYERS and SIRCAR concerning adsorption from the gas phase (benzene-silica gel, cyclohexane-silica gel) and adsorption from solutions (benzene-cyclohexane-silica gel) measured at 303°K.^{10,11} Firstly, functions of energy distribution $\chi_c(E_g)$ for adsorption systems from gases were calculated. They are presented in Fig. 1. The

strongly dashed line on Fig. 1 denotes the function $\chi_c(E_g)$ for cyclohexane on silica gel, whereas the weakly dashed line denotes $\chi_c(E_g)$ for benzene on silica gel. The parameters defining the above functions $\chi_c(E_g)$ are given in Table I. The constant K_v was determined according to the relation proposed by ADAMSON¹²⁾

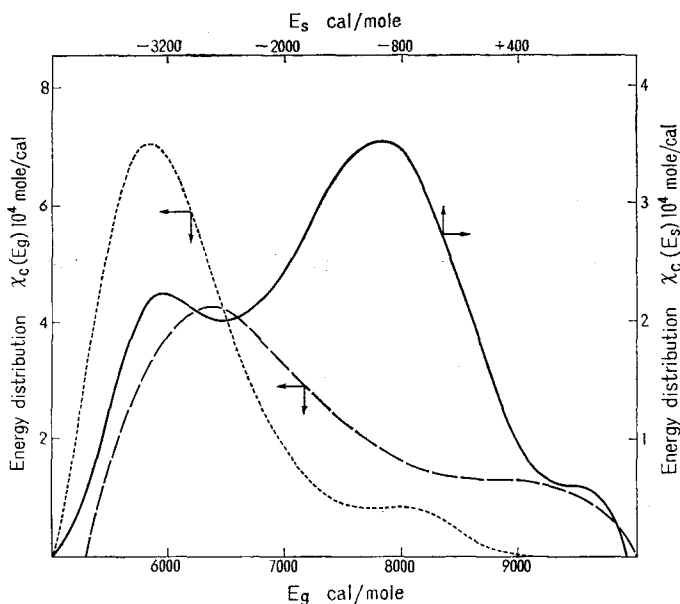


Fig. 1. The energy distribution functions for the adsorption from the gas phase: the strongly dashed line denotes the function for cyclohexane on silica gel at 30°C, the weakly dashed line for benzene on silica gel at 30°C, and the energy distribution function for adsorption from solutions: the solid line denotes the function $\chi_c(E_s)$ for adsorption system benzene-cyclohexane on silica gel at 30°C.

TABLE I

The adsorption system	K_i	x_{i0}	N_{i0} mmole/g	N_{i0}^* mmole/g	S_i	E_{i0}	N
benzene-silica gel at 30°C	$4.94 \cdot 10^5$ torr	121 torr	3.79	3.91	0.029	5.3	5
cyclohexane-silica gel at 30°C	$2.82 \cdot 10^5$ torr	123 torr	2.97	3.06	0.026	4.9	5
benzene-cyclohexane on silica gel at 30°C	1.0	17	2.88	3.24	0.031	0.6	4

* These values N_{i0} were evaluated by SIRCAR and MYERS.^{10,11)}

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$$K_{\theta} = x_{gs} \exp(E_{g\theta}/RT) \quad (12)$$

where x_{gs} is the pressure of saturated vapour and $E_{g\theta}$ is the condensation energy. The results obtained indicate that the surface of silica gel shows a great heterogeneity in relation to benzene and cyclohexane molecules. The range of adsorption energy in both cases is high: it is 5000 cal/mole for benzene, whereas for cyclohexane it is about 4500 cal/mole. The difference of minimal adsorption energies $E_{g\theta}$ of benzene and cyclohexane is about 400 cal/mole. It can be concluded from the shape of the functions $\chi_n(E_{\theta})$ that two kinds of adsorption centers exist on the surface of silica gel. The above results coincide with the studies of many authors.^{7,13-15} The distribution functions $\chi_n(E_{\theta})$ from Fig. 1 for benzene and cyclohexane on silica gel were used for calculations of theoretical adsorption isotherm $N_t(x_{\theta})$. Fig. 2 presents theoretical adsorption isotherm $N_t(x_{\theta})$ of benzene (the solid line) and cyclohexane (the dashed line) in comparison with the experimental points (white and black circles). In the Table I the sums S_i of squares of deviations of theoretical isotherm from experimental ones are given.

The calculations for benzene adsorption from cyclohexane on silica gel were indentially carried out. The function $\chi_n(E_s)$ for this system is defined

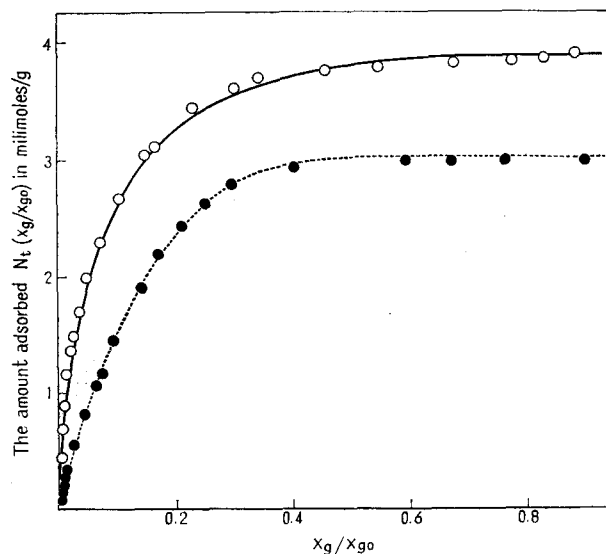


Fig. 2. The theoretical adsorption isotherms $N_t(x_g/x_{g0})$ of benzene (the solid line) and cyclohexane (the dashed line) on silica gel at 30°C in comparison with the experimental points (white and black circles).

by continuous line in Fig. 1. Constant K_s in this case was assumed to be unity by reference to the results^{1,6}). The distribution function $\chi_c(E_s)$ for the above system is determined in the interval of energy E_s from -4400 cal/mole to 600 cal/mole. The minimal difference of adsorption energy E_{s_0} with regard to the absolute value is approximate to the difference of minimal adsorption energy E_g of benzene and cyclohexane from gases. A considerable part of the function diagram $\chi_c(E_s)$ is in the interval of negative adsorption energies, which accounts for positive adsorption of benzene from cyclohexane on silica gel. Also in the case of adsorption from solution, two groups of adsorption centers are distinctly visible on the energy distribution function (Fig. 1—solid line). The distribution function calculated for benzene adsorption from cyclohexane served for cyclohexane served for calculation, according to the equation,

$$\Omega_1 = N_{s_0} v(x_1) - N_{s_0} x_1 \quad (13)$$

the theoretical excess adsorption isotherm Ω_1 .

The theoretical isotherm Ω_1 (solid line in Fig. 3) was compared with the theoretical isotherm calculated by SIRCAR and MYERS¹¹), on assuming a homogeneous surface (dashed line in Fig. 3), and with the experimental

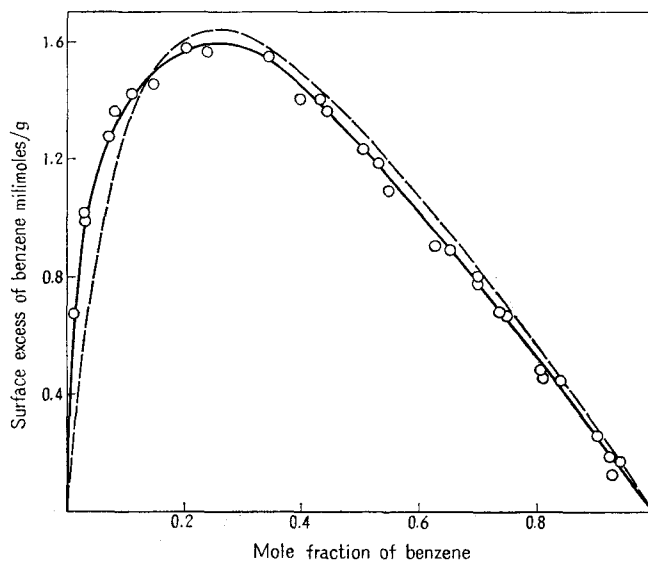


Fig. 3. Adsorption system benzene-cyclohexane on silica gel at 35°C . The circles represent experimental points of SIRCAR and MYERS. The solid line represents our theoretical isotherm, whereas the dashed line is the theoretical curve of SIRCAR and MYERS.

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data (circles, Fig. 3). The sum of the squares of the differences between calculated and observed surface excess one points to a better coincidence of our isotherm (the standard deviation of our isotherm is $S_s=0.0309$, whereas for that of SIRCAR and MYERS $S_s=0.5267$).

In conclusion it can be stated that the study of gas adsorption system, taking into consideration the model of heterogeneous surface, gives valuable information as regards analogical systems from solutions.

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