isomerization reaction of compound 1 will be presented elsewhere.

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References

1. F. D. Lewis, A. M. Miller, and G. D. Salvi, *Inorg. Chem.*, 1995, **34**, 3173.
2. S. P. Babailov and Yu. G. Kriger, *Zh. Strukt. Khim.*, 1995, **36**, No. 4, 753 [*Russ. J. Struct. Chem.*, 1995, **36**, No. 4 (Engl. Transl.)].
3. S. P. Babajlov and Yu. H. Krieger, *The 28th Congress Ampere on Magnetic Resonance and Related Phenomena, Abstrs.*, Canterbury, 1996, 478.
4. P. J. W. Pouwels and R. Kaptein, *Appl. Magn. Reson.*, 1994, 7, 107.
5. J. Sandstrom, *Dynamic NMR Spectroscopy*, Academic Press, London, 1975.

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Surface tension of adsorbtive in the Hill equation for polymolecular adsorption

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A simple and fairly exact expression for the b constant in the Hill equation of polymolecular adsorption is proposed:

$$\ln(p_s/p) = b\theta^{-3}, \qquad (1)$$

where p is the equilibrium vapor pressure of an adsorbate; p_s is the saturation vapor pressure of a liquid at the temperature of the adsorbate; and θ is the adsorption in units of a dense monolayer. The expression for b is as follows:

$$b = 2.5\sigma_0 V_0/(RTd), \qquad (2)$$

where σ_0 and V_0 are the surface tension and molar volume of the adsorbate in the state of a normal liquid, respectively; d is the diameter of the molecules of the adsorbate; T is the temperature; and R is the universal gas constant.

In order to derive Eq. (2), let us compare two systems: I, the adsorption system consisting of an adsorption layer in the form of a liquid film on a planar surface of a solid adsorbent; and II, the "liquid" system that represents a bulk volume of a liquid with the planar liquid—vapor interface. In both systems, at the gas phase interface, a tangential pressure p_T exists that decreases when the distance (τ) from the boundary surface of zero thickness increases. Let us assume that the known equation[1] holds for both systems:

$$p_T = p + C\tau^{-3}, \qquad (3)$$

where C is the constant related to the parameters of interaction of the molecules of a liquid with each other and with the molecules of neighboring phases; p is an external pressure. Let us denote $C = C^I$ for the first system and $C = C^{II}$ for the second system. Previously,[2] the following expression was found for system I:

$$b = -3C^I V_0/(RTd^3). \qquad (4)$$

In order to estimate the C^{II} value for the second system, we assume that whole volume of a liquid, beginning from the boundary layer, is separated into layers one molecule thick that are parallel to the boundary layer. Let us denote the constant tangential pressure acting in the i layer and changing jumpwise from one layer to another as p_T. The tension of the i layer (σ_i), taking into account Eq. (3), is determined by the expression

$$\sigma_i = (p - p_{T,i})d = -C^{II}/(i^3 d^2),$$

where $\tau = id$. Apart from the critical temperature, it can be accepted with enough accuracy that the surface ten-

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sion of a liquid at the vapor interface is equal to the sum of σ_i:

$$\sigma_0 = \sum_{i=1}^{\infty}(p - p_{T,i})d = -(C^{II}/d^2)\left(1 + \frac{1}{2^3} + \frac{1}{3^3} + \ldots\right). \quad (5)$$

The sum in brackets that represents a convergent numerical series is approximately equal to 1.2. Then

$$C^{II} = -0.833\sigma_0 d^2. \quad (6)$$

Commonly, $C^I \neq C^{II}$, because the adsoption system, beginning already from the second layer, differs from a bulk liquid in the nature of its molecules. However, taking into account a fast decrease in the effect of lower molecular layers (see Eq. (5)), this difference can be neglected and it can be accepted that $C^I = C^{II}$. Inserting expression (6) into Eq. (4), we obtain the required Eq. (2), and hence, the equation of polymolecular adsorption takes the following form:

$$\ln(p_s/p) = 2.5\sigma_0 V_0/(RTd\theta^3). \quad (7)$$

The validity of assumptions made is confirmed by the experimental data. Figure 1 presents a dependence of θ^{-3} on $\ln(p_s/p)$ for two systems *A* and *B*: *A* is the nitrogen adsorbed on nonporous hydrated silica at 77 K; and *B* is the benzene adsorbed on graphitized thermal carbon black (GTC) at 293 K. Points are the experimental data obtained earlier for the *A* [3] and *B* [4] systems. The θ values are calculated according to the equation

$$\theta = a/a_m,$$

where *a* is the adsorption; a_m is the monolayer capacity determined on the basis of the BET equation for system *A* and from the value of molecular area of benzene (0.39 nm^2) and the known surface area of GTC for system *B*.

Solid lines in Fig. 1 are plotted on the basis of calculations according Eq. (7) with the use of the σ_0 and V_0 values taken from the handbook[5]: for nitrogen at 77 K $\sigma_0 = 8.85 \cdot 10^{-3}$ N m^{-1}, $V_0 = 34.63$ cm^3 mol^{-1}; for benzene at 293 K $\sigma_0 = 28.53 \cdot 10^{-3}$ N m^{-1}, $V_0 = 87.63$ cm^3 mol^{-1}. The diameter of the adsorbate molecules is determined from the expression $d = (V_0/N)^{1/3}$, where *N* is Avogadro's number.

As can be seen in Fig. 1, the calculation results agree with the experimental data. It should be noted that the ordinate of experimental points is very sensitive to the a_m value, because it appears in the third power. A small variation, within a few percent, makes it possible to obtain practically complete agreement between the theoretical calculation and experimental data. This makes it difficult to verify Eq. (7), because the accuracy of the a_m determination by the BET method does not exceed 10%.

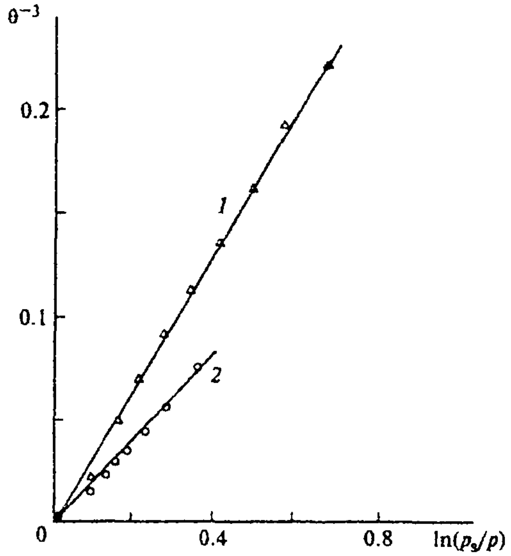

Fig. 1. Dependence of θ^{-3} on $\ln(p_s/p)$ for systems *A* (*1*) and *B* (*2*).

A correspondence between the calculated and experimental data allows one to consider Eq. (7) as a possible basis for an improved method for determining the specific surface area of nonporous adsorbents. In some cases, for example for the water—hydrocarbon adsorbent system, the calculations of a_m according to Eq. (7) are of special importance for the determination of the hydrophilic surface area.

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References

1. A. I. Rusanov, in *Fazovye ravnovesiya i poverkhnostnye yavleniya* [*Phase Equilibriums and Surface Phenomena*], Khimiya, Leningrad, 1967, 14 (in Russian).
2. G. I. Berezin, *Zh. Fiz. Khim.*, 1995, **69**, 304 [*Russ. J. Phys. Chem.*, 1995, **69** (Engl. Transl.)].
3. S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area, and Porosity*, Academic Press, London—New York, 1982.
4. A. A. Isirikyan and A. V. Kiselev, *J. Phys. Chem.*, 1961, **65**, 601.
5. N. B. Vargaftik, *Tables on the Thermophysical Properties of Liquids and Gases*, Hemisphere Publ., Washington, London, 2nd Ed., 1975, 755.

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