Full Articles

Analysis of adsorption isosteres of gas and vapor on microporous adsorbents

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The adsorption isosteres and isotherms of methane on the microporous carbon adsorbent PAU-10 were calculated using the Dubinin—Radushkevich equation taking into account nonideality of the gas phase. The conditions under which the adsorption isosteres are linear were outlined. The calculated and experimentally found adsorption isosteres were compared for the methane—PAU-10 system. The slope of the isosteres remains unchanged on going to the region of strong nonideality of the gas phase.

Key words: micropores, isostere, isotherm, adsorption, methane, adsorbent PAU-10, theory of volume micropore filling.

Adsorption isosteres, *i.e.*, curves describing the relation between the equilibrium pressure (p) and temperature (T) for a given amount adsorbed, are widely used to calculate adsorption processes. Based on them, one can analyze the thermodynamics of the adsorption process and determine temperature dependences of its energy characteristics.[1] This makes it possible to calculate adsorption processes using only physicochemical properties of the adsorbate and structural and energetic constants of the adsorbent. In addition, the property of linearity of adsorption isosteres allows one to calculate adsorption isotherms with high accuracy[2] in the region above critical temperatures and pressures, which needs, in the general case, very labor-and time-consuming calculations.

Adsorption isosteres in the coordinates $\ln p - 1/T$ are well approximated by straight lines in wide temperature and pressure intervals.[3—8] The properties of linearity of adsorption isosteres were examined[9] from the viewpoint of the theory of volume micropore filling (TVMF). This analysis is based on an assumption that an isostere is linear provided that the differential isosteric heat of adsorption is constant, *i.e.*, ignores the properties of real gases. A correction taking into account nonideality of the gas phase has later been introduced[10,11] into the expression for the differential isosteric heat of adsorption.

The purpose of the present work is to outline the conditions under which the adsorption isosteres are linear with allowance for the nonideality of the gas phase and to

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weigh a possibility of the linear extrapolation of the adsorption isosteres to the region of pressures and temperatures above critical.

Results and Discussion

Conditions of linearity of adsorption isosteres. Let us use the main equations of TVMF[12] to find the conditions under which adsorption isosteres are linear and clarify the factors affecting the deviation of the isosteres from linearity.

Using the Dubinin—Radushkevich equations, the equations for the limiting amount adsorbed, differential molar work of adsorption, and saturated vapor pressure,[12] and definition of the fugacity coefficient, we can calculate the partial derivative of the pressure logarithm with respect to the inverse temperature for a given amount adsorbed

$$\left(\frac{\partial \ln p}{\partial T^{-1}}\right)_a = \frac{\partial}{\partial T^{-1}}\left[\ln\left(\frac{\gamma_s}{\gamma}\right)\right] - N - \frac{E}{R}\frac{2\left[\ln\left(a_0^0/a\right) - \alpha(T-T_0)\right] + \alpha T}{2\sqrt{\ln\left(a_0^0/a\right) - \alpha(T-T_0)}}. \qquad (1)$$

Here p is the pressure; T is the temperature; γ_s is the fugacity coefficient at the saturated vapor pressure; γ is the fugacity coefficient at pressure p; N is the coefficient depending on the properties of the adsorptive[12]; E is the characteristic adsorption energy; R is the universal gas constant; $a^0{}_0$ is the limiting amount adsorbed at the boiling point T_0; a is the amount adsorbed at the pressure p and temperature T; α is the thermal coefficient of limiting adsorption.

The calculations show that the value of the first term of Eq. (1) $\ln(\gamma_s/\gamma)$ in a wide temperature range does not exceed several units. At the same time, the values of two other terms of Eq. (1) has an order of thousands. Therefore, the influence of the fugacity coefficient on the deviation of the adsorption isosteres from linearity can be neglected in the first approximation.

Then we have

$$\left(\frac{\partial \ln p}{\partial T^{-1}}\right)_a \approx -\frac{E}{R}\frac{2\left[\ln\left(a_0^0/a\right) - \alpha(T-T_0)\right] + \alpha T}{2\sqrt{\ln\left(a_0^0/a\right) - \alpha(T-T_0)}} - N. \qquad (2)$$

For the most part of substances it can be accepted in the first approximation that the coefficient N in Eq. (2) is constant. Therefore, the deviation of the isosteres from linearity is mainly affected by the first term of the equation, mainly, the temperature-coefficients $\alpha(T - T_0)$ and αT.

At temperatures close to the boiling point T_0 the main effect on the deviation of the adsorption isosteres from linearity is exerted by the coefficient αT. In this case, the $\alpha(T_0 - T)$ coefficient is low, and the αT value leads to increasing deviations of the adsorption isosteres. However, since the α coefficient has an order of magnitude of 10^{-3}, the deviation of the isosteres from linearity is low.

With increasing temperature the influence of the $\alpha(T_0 - T)$ coefficients on the deviation of the isosteres from linearity becomes stronger but a noticeable effect is exerted only for far extrapolation.

Thus, the conclusion about linearity of the adsorption isotherms from the viewpoint of the TVMF (see Ref. 9) is confirmed taking into account the nonideality of the gas phase as well. The nonlinearity is ~10^{-3} K^{-1}.

Comparison of adsorption isosteres in the region of temperatures below critical. To check the condition of linearity of the isosteres, we calculated the isosteres of methane adsorption[13] on the microporous carbon adsorbent PAU-10. The following constants were used for the calculations[2]: micropore volume $W_0 = 0.44$ cm^3 g^{-1}; characteristic energy with respect to benzene $E_0 = 29.3$ kJ mol^{-1}; similarity constant $\beta = 0.35$; average effective micropore radius $x_0 = 0.41$ nm.

Comparison of the isosteres calculated by the main TVMF equations and obtained from the experimental data[2] showed good linearity and satisfactory agreement between the calculation and experiment in the temperature intervals from the boiling point to the critical temperature (Fig. 1).

As follows from the data in Fig. 1, for an amount adsorbed of 1 mmol g^{-1} the experimental data systematically exceed the calculated data. The experimental isostere is linear; however, the both coefficients in the equation of this straight line differ from the calculated values. This deviation appears because the TVMF is an unsuitable model at such a low value of the amount adsorbed. The filling of micropores is 0.1. At the same time, is has

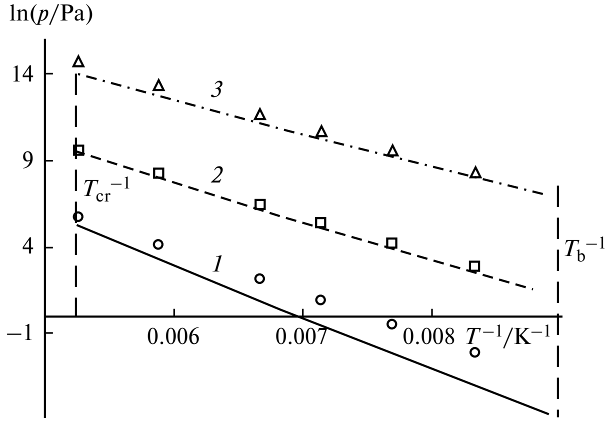

Fig. 1. Isosteres of methane adsorption on PAU-10 in the temperature interval from the boiling point (T_b) to the critical temperature (T_{cr}) at the amounts adsorbed a = 1 (*1*), 5 (*2*), and 10 mmol g^{-1} (*3*).

been shown previously[12] that the lower boundary of applicability of the TVMF corresponds to a filling of 0.15—0.2.

For an amount adsorbed of 5 mmol g^{-1}, the calculated and experimentally found isosteres agree well (see Fig. 1). This value of the amount adsorbed corresponds to the micropore filling $\theta = 0.4$. In this case, the TVMF is applicable for the description of the adsorption system and, as follows from the data in Fig. 1, its use makes it possible to perform the linear extrapolation of isosteres with rather high accuracy.

At high fillings when the amount adsorbed is 10 mmol g^{-1}, the angular coefficient of the experimental isostere exceeds slightly that of the calculated isostere. In the methane—PAU-10 system at the amount adsorbed 10 mmol g^{-1} and temperature 190 K, the micropore filling is $\theta = 0.97$. At this micropore filling, the TVMF indicates departure of the calculated heat of adsorption from the experimentally measured value.[12] Therefore, in the first approximation it seems mostly reasonable to use the linear extrapolation of the isosteres at the micropore fillings lower 0.90—0.95.[12]

Based on the calculated isosteres, we plotted the adsorption isotherms in the temperature interval from the boiling point to the critical temperature (Fig. 2) and compared them with experiment at 120—190 K.

Comparison of the obtained results (see Fig. 2) showed that the isotherms calculated from the condition of linearity of isosteres rather well correspond to the experimental isotherms. The divergence of the calculated and experimental isotherms in the region of low amounts adsorbed is caused, as already mentioned, by inapplicability of the TVMF to so low fillings.

Comparison of adsorption isosteres in the region above critical temperatures. The standard values of the saturated vapor pressure p_s and limiting amount adsorbed a_0 are used in the TVMF in the temperature interval from the boiling point to the critical temperature. However, this is impossible at the temperatures higher than the critical temperature because of the absence of the phase transition of the first order: the idea of p_s is inapplicable.

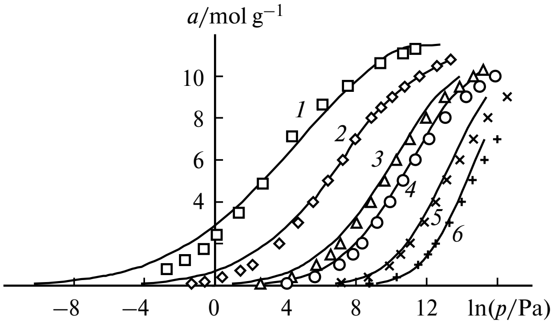

Fig. 2. Methane adsorption on the microporous carbon adsorbent PAU-10 at temperatures 120 (*1*), 150 (*2*), 190 (*3*), 210 (*4*), 273 (*5*), and 330 K (*6*). Calculation based on the condition of linearity of the isosteres is shown by solid lines; symbols are experiment.[12]

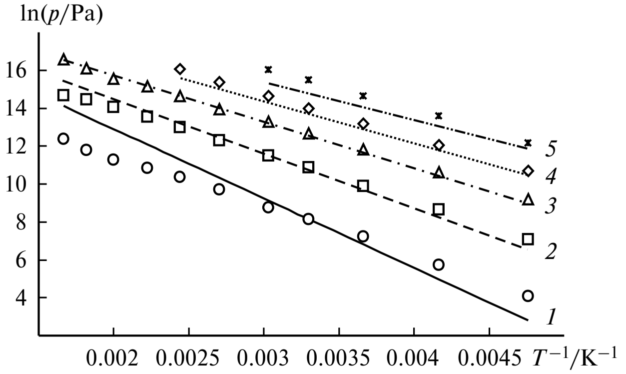

Fig. 3. Isosteres of methane adsorption on PAU-10 in the region above critical temperatures at the amounts adsorbed a = 0.1 (*1*), 1 (*2*), 3 (*3*), 5 (*4*), and 7 mmol g^{-1} (*5*).

To calculate adsorption isotherms in the region of temperatures above critical, one can use the property of linearity of the isosteres constructed in the region below critical values extending this property to the region of temperatures above critical. For this purpose, the isotherms of methane adsorption calculated at T = 190 and 120 K were used. The isosteres plotted from these isotherms were extrapolated to the region of temperatures above critical. The results of calculations and their comparison with experiment are presented in Fig. 3.

At an amount adsorbed of 0.1 mmol g^{-1}, the calculated and experimental data agree weakly (see Fig. 3), because the TVMF is inapplicable at so low fillings.[12] However, it can be seen from the data in Fig. 3 that the isostere plotted on the basis of the experimental data is virtually linear and its angular coefficient remains unchanged on going to the region of sharp nonideality of the gas phase. The isostere corresponding to an amount adsorbed of 1 mmol g^{-1} has a similar shape (see Fig. 3).

The angular coefficient of the calculated isosteres exceeds the experimental angular coefficient, because at so low fillings the heats of adsorption calculated by the TVMF exceed the real heats of adsorption. The difference between the heats increases with a decrease in the micropore filling (see Fig. 3). For example, at the amount adsorbed a = 0.1 mmol g^{-1} the angular coefficients of the calculated and experimental isosteres differ appreciably, whereas for an amount adsorbed of 1 mmol g^{-1} departure is substantially less.

For an amount adsorbed of 3 mmol g^{-1} the experimental and calculated isosteres are in good accord (see Fig. 3). The calculated isostere agrees well with the experimental isostere up to 600 K. This confirms the assumption on a possibility of linear extrapolation of the adsorption isosteres to the region of temperatures and pressures above critical on the basis of the TVMF.

As follows from the data in Fig. 3, at an amount adsorbed of 5 mmol g^{-1} the calculated and experimental data still agree satisfactorily. However, for the amount adsorbed 7 mmol g^{-1} this agreement is substantially violated. The divergence increases at high micropore fillings with the temperature rise because of the difference in angular coefficients and factors affecting the deviation of the isosteres from linearity. The difference between the calculated and experimental data increases with an increase in the amount adsorbed.

The isotherms plotted from the condition of linearity of the isosteres (see Fig. 2) satisfactorily correspond to the experimental isotherms. However, the region for which the calculated and experimental data agree satisfactorily decreases with increasing temperature. For instance, for the system considered, when the critical temperature is exceeded by 120 K, satisfactory agreement is observed only to an amount adsorbed of ~4.5 mmol g^{-1}.

Comparison of the obtained results showed that the adsorption isosteres have no jumpwise transitions but remain linear on going to the region of critical pressures and temperatures. However, the region in which the calculated and experimental data agree well decreases sharply when the temperature increases.

The isotherms calculated from the conditions of linearity of the isosteres rather well correspond to the experimental data (see Fig. 2). The divergence of the calculated and experimental isotherms in the region of high amount adsorbed is caused by inapplicability of the TVMF to high fillings of micropores. The upper boundary of applicability becomes lower with the temperature rise.

Thus, the adsorption isosteres in the TVMF calculated taking into account nonideality of the gas phase are well approximated by linear dependence in a wide range of temperatures and pressures, The nonlinearity is ~10^{-3} K^{-1}.

The slope of the isosteres remains unchanged on going to the region of sharp nonideality of the gas phase.

To calculate the amount adsorbed of gases and vapors on microporous adsorbents under the conditions of precritical and supercritical temperatures, one can make use of the structural and energetic characteristics of the adsorbent, which are determined using the TVMF, and the property of linearity of adsorption isosteres.

References

1. A. A. Fomkin, *Adsorption*, 2005, **11**, No. 3/4, 425.
2. E. V. Chkhaidze, A. A. Fomkin, V. V. Serpinskii, G. V. Tsitsishvili, and M. M. Dubinin, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1988, 2640 [*Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1988, **37**, No. 11 (Engl. Transl.)].
3. T. Shibata, K. Kyaw, F. Watanabe, H. Matsuda, and M. Hasatani, *J. Chem. Eng. Jpn*, 1996, **29**, 830.
4. V. V. Zhukov, Ph. D. (Phys.-Math.) Thesis, Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow, 1974, 145 pp. (in Russian).
5. A. A. Fomkin, V. V. Serpinskii, and K. Fidler, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1982, 1207 [*Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1982, **31**, No. 6 (Engl. Transl.)].
6. B. P. Bering, V. V. Serpinskii, and A. A. Fomkin, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1974, 2111 [*Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1974, **23** (Engl. Transl.)].
7. D. Shen and M. Bulow, *Microporous, Mesoporous Materials*, 1998, **22**, 237.
8. R. M. Barrer and J. W. Sutherland, *Proc. Roy. Soc.*, 1956, **A237**, 439.
9. B. P. Bering, M. M. Dubinin, and V. V. Serpinskii, *Dokl. Akad. Nauk SSSR*, 1961, **138**, 1373 [*Dokl. Chem.*, 1961 (Engl. Transl.)].
10. V. A. Bakaev, Doct. Sci. (Phys.-Math.) Thesis, Moscow State University, Moscow, 1989, 348 pp. (in Russian).
11. L. G. Shekhovtsova and A. A. Fomkin, *Izv. Akad. Nauk*, *Ser. Khim.*, 1992, 19 [*Bull. Russ. Acad. Sci.*, *Div. Chem. Sci.*, 1992, **41**, No. 1 (Engl. Transl.)].
12. M. M. Dubinin, *Adsorbtsiya i poristost´* [*Adsorption and Porosity*], Izd. Voennoi Akademii Khim. Zashchity, Moscow, 1972, 127 pp. (in Russian).
13. V. V. Sychev, A. A. Vasserman, V. A. Zagoruchenko, A. D. Kozlov, G. A. Spiridonov, and V. A. Tsymarnyi, *Termodinamicheskie svoistva metana* [*Thermodynamic Properties of Methane*], Izd. Standartov, Moscow, 1979, 348 pp. (in Russian).

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