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THERMODYNAMICS OF ADSORPTION ON MICROPOROUS FRACTAL SOLIDS

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Abstract

A new adsorption isotherm equation based on the extension of the potential theory of adsorption on microporous fractal solids and corresponding thermodynamic functions were formulated and applied for description of the experimental data of adsorption on a microporous carbon. The comparison of the obtained results with the original Dubinin–Astakhov equation is presented. In this paper the dependence of thermodynamic functions (the differential molar enthalpy of adsorption ΔH and the differential molar entropy of adsorption ΔS) on the fractal dimension D are discussed, as well.

Keywords: active carbon, adsorption, adsorption thermodynamics, fractal dimension, microporosity, pore diameter, potential theory

Introduction

In our previous papers the main properties of two new equations (fractal analog of Dubinin–Radushkevich (DR) and Dubinin–Astakhov (DA) equations) [1, 2] and their application to description of experimental adsorption data were presented [3]. It is well known that an adsorption isotherm measures an affinity between an adsorbate and a sorbent and, therefore, both the enthalpy and the entropy contribute to this affinity [4]. An agreement between a theoretical adsorption isotherm equation and experimental data is a necessary but not satisfactory condition of correctness of any assumption of a model. The fundamental satisfactory condition is, therefore, the agreement between experimental data and theoretical thermodynamic relations that can be derived from the proposed isotherm equation [5]. The aim of this paper is to present the thermodynamic relations describing adsorption on microporous fractal solids.

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Theory

According to the theory of adsorption on microporous materials, the experimental (overall) adsorption isotherm (Θ) [6, 7] is written as:

$$\Theta = \int_{x_{min}}^{x_{max}} \theta_l f_1(x) dx \quad (1)$$

where θ_l is the local adsorption isotherm and $f_1(x)$ is the micropore-size distribution function, where x [nm] is the slit-like micropore half-width, which is limited by x_{min} and x_{max} (the lower and the upper limit of a fine pore, respectively).

As it was proposed by Pfeifer and Avnir [8, 9], in the case of adsorption on a fractal microporous solid the fractal pore-size distribution associated with that solid is:

$$f_1(x) = \rho x^{2-D} \quad (x_{min} < x < x_{max}) \quad (2)$$

where x_{min} is the finest resolution at which fractality prevails and it is associated directly with the size of an adsorptive molecule (for example nitrogen) and x_{max} is the upper limit of fine pores in which adsorption occurs by a micropore filling mechanism (the upper limit of 'pore fractality' of an investigated object).

The micropore-size distribution should be normalised to unity:

$$\int_{x_{min}}^{x_{max}} f_1(x) dx = 1 \quad (3)$$

Normalisation of the function $f_1(x)$ given by Eq. (2) according to Eq. (3) gives the following expression for ρ (the normalisation factor) [10]:

$$\rho = \frac{3 - D}{x_{max}^{3-D} - x_{min}^{3-D}} \quad (4)$$

If the local adsorption isotherm (θ_l) in Eq. (1) is represented by the original DA equation [11] and $f_1(x)$ by Eq. (2), the overall adsorption isotherm Θ can be adequately represented by

$$\Theta = \int_{x_{min}}^{x_{max}} \exp(-\mu A^n x^n) \frac{3-D}{x_{max}^{3-D} - x_{min}^{3-D}} x^{2-D} dx \quad (5)$$

where $A = -\Delta G = RT \ln(p_s/p)$ [kJ mol^{-1}] is the adsorption potential defined as the change in the Gibbs' free energy taken with a negative sign; R [kJ mol^{-1}K^{-1}] is the gas constant; T [K] is temperature; p and p_s denote the equilibrium pressure

and the saturation vapour pressure of the adsorbate; $\mu=(\kappa\beta)^{-n}$, where κ [kJ nm mol^{-1}] is an empirical constant, which only slightly depends on the characteristic energy (E_o [kJ mol^{-1}]) [12, 13], β is the similarity coefficient, n is an equation parameter, μ depends on the adsorbate and the kind of a microporous structure.

Equation (5) can be solved analytically and finally we obtain the fractal analog of DA equation (FRDA) [14]:

$$\Theta = \frac{\rho}{n}(\mu A^n)^{(D-3)/n}\left[\gamma\left(\frac{3-D}{n}, x_{\max}^n \mu A^n\right) \quad \gamma\left(\frac{3-D}{n}, x_{\min}^n \mu A^n\right)\right] \tag{6}$$

where Θ is the degree of pore filling and γ is an incomplete gamma function. Assuming n=2, we obtain the fractal analog of DR equation (FRDR) [15].

If was shown elsewhere [16] that the differential enthalpy of adsorption ΔH and the differential entropy of adsorption ΔS, which characterise micropore filling, can be expressed as follows:

$$\Delta H = \left(\frac{\partial A}{\partial T}\right)_\Theta + \alpha T\left(\frac{\partial A}{\partial \ln a}\right)_T - A \tag{7}$$

$$\Delta S = \left(\frac{\partial A}{\partial T}\right)_\Theta + \alpha\left(\frac{\partial A}{\partial \ln a}\right)_T \tag{8}$$

where a is the amount adsorbed under the equilibrium pressure p and at temperature T; α is the coefficient of the adsorbate thermal expansion given by $\alpha=(\partial \ln V/\partial T)_A$, where V is a molar volume and $\Theta=W/W_0$ (W – the volume of a liquid-like adsorbate present in micropores, W_0 – the limiting volume of the adsorption space or the micropore volume).

The relationship between the adsorption potential A and Θ is not trivial because the incomplete gamma function is dependent on the relative pressure (p/p_s) [3].

The differential adsorption potential distribution $F(A)$ can be written as follows [17]:

$$F(A) = -\frac{d\Theta(A)}{dA} \tag{9}$$

We can replace the derivative in Eqs (7) and (8) by the following expression:

$$\left(\frac{\partial A}{\partial \ln a}\right)_T = a\left(\frac{\partial A}{\partial a}\right)_T = \Theta\left(\frac{\partial A}{\partial \Theta}\right)_T = -\frac{\Theta}{F(A)} \tag{10}$$

Assuming the fulfilment of the main condition of the potential theory [16] (first of all the temperature invariance condition $(\partial A/\partial T)_\Theta=0$) and combining Eqs (7–10), we obtain:

$$\Delta H = -A - \alpha T\frac{\Theta}{F(A)} \tag{11}$$

$$\Delta S = -\alpha\Theta/F(A) \tag{12}$$

The 'pure' enthalpy of adsorption (q^{st}–L) is given by:

$$q_{st} - L = -\Delta H = A + \alpha T\frac{\Theta}{F(A)} \tag{13}$$

where L is the enthalpy of an adsorbate condensation.

Equation (9) allows the calculation of the differential potential distribution $F(A)$ associated with the fractal analog of DA equation (6):

$$-F(A) = \frac{\rho}{n}(\mu A^n)^{(D-3)/n}\left(\frac{A^{n-1}n\mu x_{max}^n(A^n\mu x_{max}^n)^{(3-D-n)/n}}{\exp[A^n\mu x_{max}^n]} - \frac{A^{n-1}n\mu x_{min}^n(A^n\mu x_{min}^n)^{(3-D-n)/n}}{\exp[A^n\mu x_{min}^n]}\right) +$$

$$+\frac{\rho}{n}A^{n-1}\mu(D-3)(\mu A^n)^{(D-3-n)/n}\left[\gamma\left(\frac{3-D}{n},x_{max}^n\mu A^n\right) - \gamma\left(\frac{3-D}{n},x_{min}^n\mu A^n\right)\right] \tag{14}$$

The substitution Eq. (14) into Eqs (12) and (13), gives the differential molar entropy and the differential 'pure' molar enthalpy of adsorption on a fractal microporous solid.

The parameters obtained from Eqs (6), (13) and (14) can be used for the characterisation of porosity and for the calculation of average pore diameters of adsorbents using the equation of the average value of x [7, 18]:

$$\bar{x} = \int_{x_{min}}^{x_{max}} x f_1(x)\mathrm{d}x \tag{15}$$

which leads to:

$$\bar{x} = x_{min}\left(\frac{3-D}{4-D}\right)\left(\frac{r^{4-D}-1}{r^{3-D}-1}\right) \tag{16}$$

where

$$r = \frac{x_{max}}{x_{min}} \tag{17}$$

It can be compared with the average pore diameters, obtained from the parameter E_o (the characteristic energy) of the original DA equation using the relation proposed by McEnaney [19]:

$$2\bar{x} = 6.6 - 1.79 \ln E_o \tag{18}$$

The properties of the isotherm of adsorption, the enthalpy of adsorption and the entropy of adsorption equations

The main properties of Eqs (6), (12) and (13), for n=2 were investigated assuming benzene as an adsorbate (κ=12 kJ nm mol^{-1}, β=1, α=0.00128 K^{-1}) and taking temperature as 298.15 K. The adsorbent (an activated carbon) was modelled to be a microporous solid characterised by the fractal dimension D. The values of x_{min} and x_{max} were assumed as equal to 0.25 nm [12] and 1 nm [20], respectively.

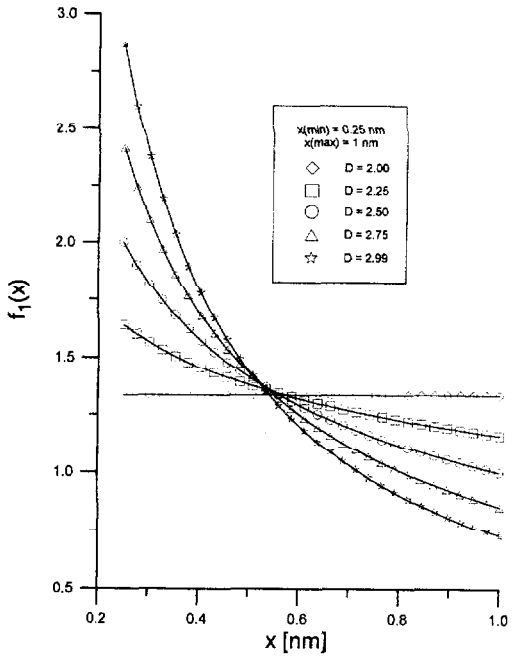

Fig. 1 Micropore-size distributions (Eq. (2)) for D=2.00; 2.25; 2.50; 2.75 and 2.99. In this case adsorbent was assumed to be microporous (x_{min}=0.25 and x_{max}=1 nm, respectively)

Figures 1–4 present the micropore-size distribution (Eq. (2)), the benzene adsorption isotherm (Eq. (6)), the differential entropy of adsorption (Eq. (12)) and the 'pure' enthalpy of adsorption (Eq. (13)) for different D values (2.00; 2.25; 2.50; 2.75 and 2.99).

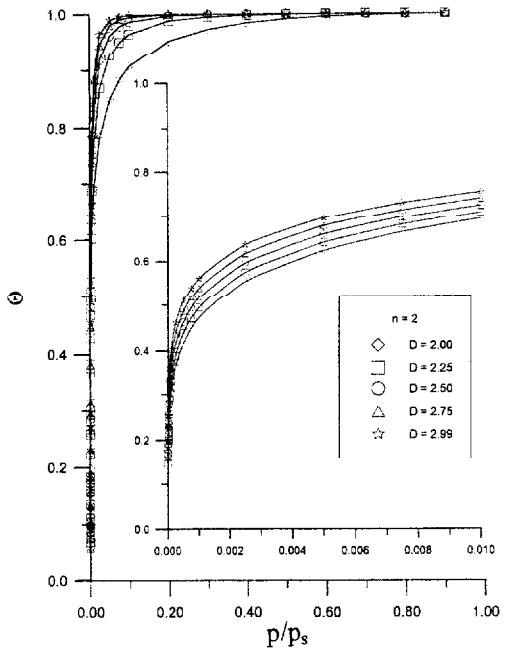

Fig. 2 Isotherms of benzene adsorption (T=298.15 K) generated by Eq. (6) for n=2 (symbols as in Fig. 1)

It was assumed [21] that Polanyi's adsorption potential A in micropores is related to pore sizes and those pores are filled gradually from the smallest to the largest in order of decreasing A values. The behaviour of benzene adsorption isotherms, 'pure' enthalpies of adsorption and differential entropies of adsorption for a microporous solid characterised by different values of the fractal dimension ($D \in <2, 3$) should be associated with the dependence of the micropore-size distribution $f_1(x)$ on D (Fig. 1). The function $f_1(x)$ for D=2 is constant (the homogeneous distribution) and for the range of the fractal dimension 2–3 it was a fragment of hyperbolic function. From Fig. 1 it is seen that the fraction of small micropores (close to x_{min}) increases as D increases and the fraction of micropores with larger diameters decreases.

In Fig. 2 benzene adsorption isotherms generated by Eq. (6) are presented for two ranges of relative pressure (p/p_s) $1 \cdot 10^{-7}$–0.1 and $1 \cdot 10^{-7}$–0.9. For all the values of the fractal dimension (for D=2, also) these adsorption isotherms belong to type 1 of IUPAC classification (i.e. Langmuir) [20]. A general tendency in Fig. 2 that for a fixed value of the degree of pore filling (Θ), p/p_s decreases with D, especially for the first of the relative pressure ranges mentioned above. In the other words, for two microporous solids with different values of D, the same fraction (Θ) of the filled micropores occurs at a lower value of p/p_s for a solid with a higher D.

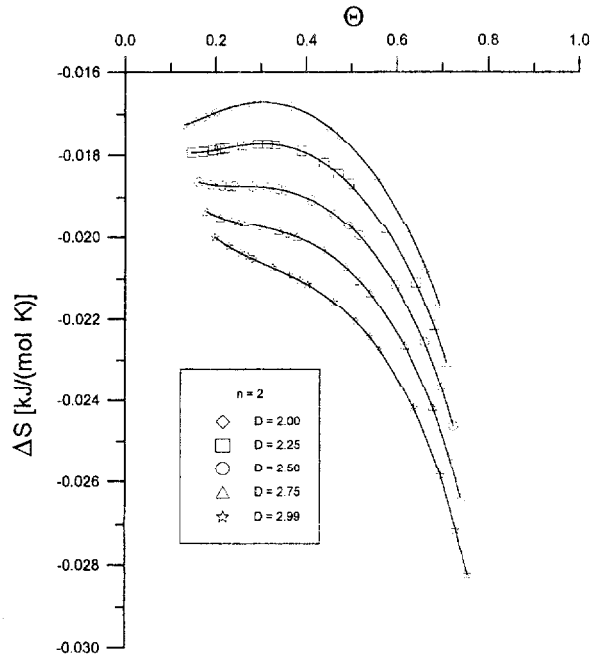

Fig. 3 The differential entropies of adsorption, calculated on the basis of Eq. (12), for adsorption isotherms from Fig. 2 (symbols as in Fig. 1)

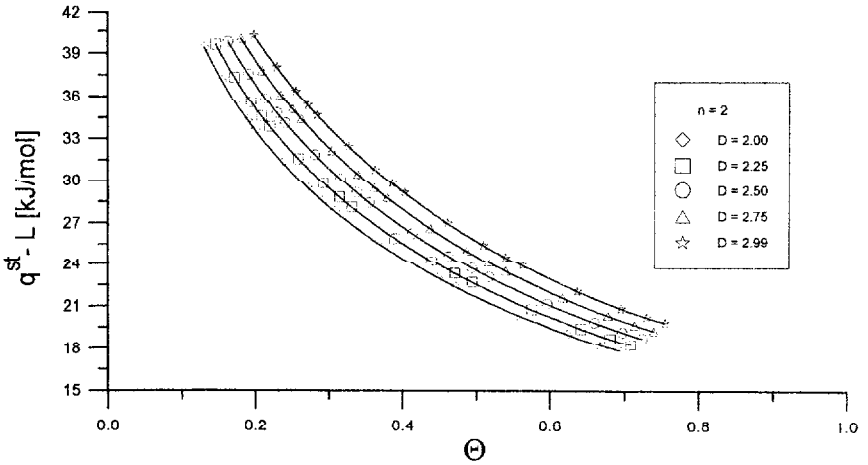

Fig. 4 'Pure' enthalpies of adsorption, calculated on the basis of Eq. (13), for adsorption isotherms from Fig. 2 (symbols as in Fig. 1). The error of isosteric enthalpy is marked by error bars

Figure 3 presents the changes of the differential molar entropy of adsorption (Eq. (12)). The entire ΔS curves lie in the negative zone of the ΔS axis, as was expected [16]. It is associated with transition from a disordered gaseous state to a more ordered adsorbed state. For a fixed Θ the differential entropy of adsorption decreases when D increases. It is possible that in the very narrow micropores (close to x_{min}) only one molecule can be adsorbed, because the distance from wall to wall is slightly greater than the diameter of a molecule of an adsorptive. In this case, the adsorption system possesses a more ordered configuration than for wider pores that can accommodate more molecules.

In Fig. 4 the typical plots of the 'pure' isosteric enthalpy of adsorption (q^{st}–L) changes (Eq. (13)) are shown. The enthalpy of adsorption decreases with increasing Θ. For a fixed Θ it increases when D increases and this trend is associated with a micropore-size distribution (narrow micropores generate higher values of the adsorption potential than wider do).

Approximation of the experimental data

The experimental data of adsorption and isosteric enthalpy of adsorption cyclohexane at 353.15 K on the carbon SA, published by Dubinin and Polstyanov [22–24] were approximated. The correlation coefficients of adsorption isotherm (CC_p), enthalpy of adsorption (CC_q) and entropy of adsorption (CC_s) were calculated basing on Eqs (6), (12) and (13) for two ranges of relative pressures, p/p_s: $1\cdot10^{-6}$–0.1 [25] and $1\cdot10^{-6}$–0.01 [26] (Table 1) because there are different opinions of the range of use of the DA equation. The same procedure was used for FRDA adsorption isotherms and thermodynamic functions based on this equation (Table 1).

Table 1 The correlation coefficients for two relative pressure ranges ($1\cdot10^{-6}$–0.01 and $1\cdot10^{-6}$–0.1, respectively) between theoretical and experimental data of adsorption isotherm (CC_p), heat of adsorption (CC_q) and entropy of adsorption (CC_s) for DA and FRDA equations

p/p_s	DA			FRDA		
	CC_p	CC_q	CC_s	CC_p	CC_q	CC_s
$1\cdot10^{-6}$–0.01	0.9903	0.9954	0.9745	0.9900	0.9898	0.9296
$1\cdot10^{-6}$–0.1	0.9925	0.9954	0.9745	0.9909	0.9898	0.9296

The optimization method used in this paper was analogous to Ref. [3]. The functional $(1-(CC_pCC_q)^2)$ was minimized. The numerical programs in FORTRAN 77, published previously [3, 14, 15] were modified and used for this purpose. The comparison of experimental and theoretical isotherms, enthalpies and entropies of adsorption is presented in Figs 5–7. The obtained parameters of the DA equation and its fractal analog (FRDA) are shown in Table 2.

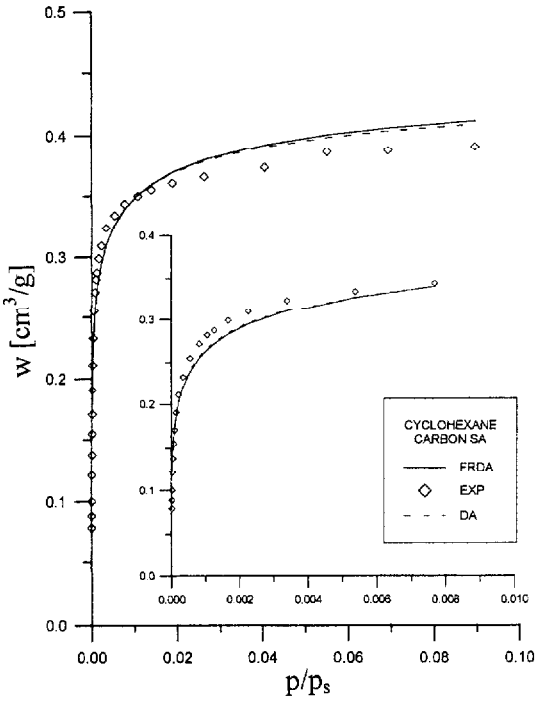

Fig. 5 The comparison of experimental (points) and theoretical (lines) adsorption isotherms for the system: cyclohexane–carbon SA at 353.15 K. FRDA – fractal analogue of DA equation, DA – original DA equation

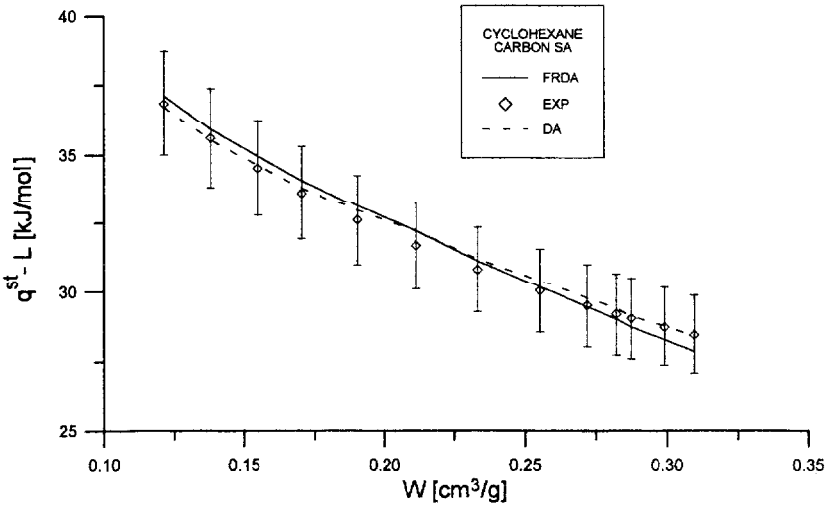

Fig. 6 The comparison of experimental and theoretical heat of adsorption data for the system from Fig. 5

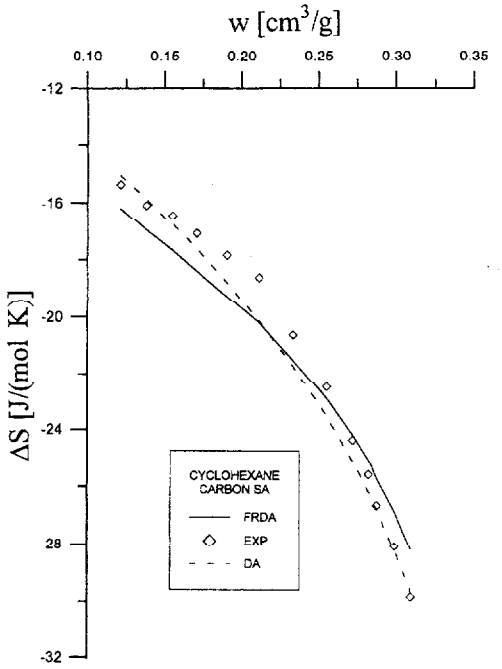

Fig. 7 The comparison of experimental and theoretical entropy of adsorption data for the system from Fig. 5

Table 2 The parameters of DA and FRDA equations obtained from simultaneous description of the adsorption and the adsorption enthalpy data

DA					
W_0/cm^3 g^{-1}	n	E_0/kJ mol^{-1}	(Eq. 18)		
0.4324	2.0349	27.0965	0.425		
FRDA					
W_0/cm^3 g^{-1}	n	x_{min}/nm	x_{max}/nm	D	(Eq. (16))
0.4368	1.9882	0.461	0.500	2.915	0.480

Conclusions

The fundamental thermodynamic functions were derived for the equation of adsorption isotherm (Eq. (6)) in which the structural heterogeneity of solid connected with micropore dimension (the micropore-size distribution (Eq. (2) is a function of the fractal dimension) was included. The values of the adsorption, of

the isosteric enthalpy of adsorption (Fig. 6) and of the differential molar entropy of adsorption (Fig. 7) corresponding to the investigated system show a good agreement with the data obtained theoretically (Table 1). The average pore diameters calculated from the obtained values of the fractal dimension and minimal and maximal pore widths are similar to those obtained using the equation of McEnaney, developed from the analysis of SAXS data [3]. This confirms the correctness of equations based on the Polanyi-Dubinin potential theory describing the adsorption on microporous fractal carbon adsorbents. This theory is not a universal one, and our model, as a version of this theory should describe the same cases for which the DA equation is valid.

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