Thermodynamics of Vapour Adsorption on Heterogeneous Microporous Adsorbents

MICHAŁ ROZWADOWSKI and ROMAN WOJSZ*
Institute of Chemistry, Nicholas Copernicus University, 87–100 Toruń, Poland

Abstract. Fundamental thermodynamic functions have been derived for equations of adsorption isotherms including structural heterogeneity connected with micropore dimensions. Good agreement has been achieved between values of the differential molar enthalpy of adsorption and values of the isosteric adsorption heats obtained experimentally.

Key words. Adsorption, microporous adsorbents, active carbons, thermodynamic functions of adsorption.

1. Introduction

Theoretical studies [1–4] showed that adsorption on microporous solids is distinguishable thermodynamically from adsorption on nonporous surfaces, and it requires the formulation of a separate description. There are many papers [5–10] reporting experimental and theoretical studies on the physical adsorption of gases and vapours on microporous solids.

An agreement between theoretical considerations and experimental adsorption isotherms is a necessary but not satisfactory condition of correctness for any assumption of every theory. The fundamental satisfactory condition is the agreement between experiment and thermodynamic dependence which can be derived from a given isotherm equation.

Bering *et al.* [2] determined the differential molar entropy of adsorption in the case of the theory of volume filling of micropores (TVFM) [11, 12] as

$$\Delta S = \left(\frac{\partial A}{\partial T}\right)_{\theta} + \alpha \left(\frac{\partial A}{\partial \ln a}\right)_T \tag{1}$$

where A is the Gibbs free energy ΔG taken with a minus sign; a is the amount adsorbed under equilibrium pressure p and at temperature T; α is the thermal coefficient of the limiting adsorption a_0 and

$$\theta = a/a_0. \tag{2}$$

The differential molar enthalpy is defined as [4]

$$\Delta H = -A + T\left(\frac{\partial A}{\partial T}\right)_{\theta} + \alpha T\left(\frac{\partial A}{\partial \ln a}\right)_T. \tag{3}$$

Equations (1) and (3) can be simplified in accordance with the theory of volume

* Author for correspondence.

filling of micropores [11], on the assumption that the temperature invariance of characteristic curve θ (A) is:

$$\left(\frac{\partial A}{\partial T}\right)_{\theta} = 0. \tag{4}$$

Wojsz and Rozwadowski succeeded in directly differentiating their modified DRS [10, 13, 14] equation in respect to $(\partial/\partial \ln a)_T$ and thus they obtained expressions for ΔS and ΔH [3] as a development of the TVFM.

The aims of this paper are to fill the gaps occurring in the investigations of adsorption on microporous solids by applying the thermodynamic considerations and deriving equations for the fundamental thermodynamic functions on the basis of adsorption isotherms, including the structural heterogeneity [15–19] connected with micropore dimensions. This way, we would like additionally to explain the correctness of the adsorption isotherm equations derived earlier by us [16–19] as a modification of the generalized adsorption isotherm (GAI) [20] on the basis of the TVFM.

2. Experimental

The investigations have been carried out on active carbon prepared from chemically pure saccharose activated with carbon dioxide (sample B) and by so-called chemical activation (samples D, E) using $ZnCl_2$ as the activator. The details of preparation and the texture parameters for the carbons studied have been given previously [21]. The adsorption isotherms for spectrally pure aliphatic alcohols (MeOH, EtOH) have been measured within the temperature range of 298.2–322.7 K and up to a relative pressure of about 0.2 [22, 23] in a vacuum device equipped with a MacBain balance.

3. Discussion of Results

The important condition in order to obtain the correct value of the parameter W_0 is to select a correct function for the micropore volume distribution. This distribution would satisfy the necessary condition

$$\frac{1}{W_0} \int_{k_{min}}^{k_{max}} f(k) \, dk = 1, \tag{5}$$

where k is the structural parameter and W_0 is the limiting volume of the adsorption space or the micropore volume. As shown in paper [10] only the micropores of dimensions $x_{min} < x < x_{max} \Leftrightarrow 0.25 < x < 1.6$ nm have any physical meaning.

The relationship between k and x found from experimental investigations of benzene adsorption on microporous carbons is [10]

$$x = \text{const} \sqrt{k} \tag{6}$$

Then a value of 0.25 for x yields the defined value of k_{min} as 0.000789 mol^2/kJ^2 and a value of 1.6 for x gives the value of k_{max} as 0.0151 mol^2/kJ^2. For these cases, we presented previously [17] the following modified DRS equation:

$$W = \frac{W_0 \exp\left(\frac{\Delta^2 Y^2}{2} - k_0 Y\right)\left[\operatorname{erf}\left(\frac{k_0 - k_{\min}}{\Delta\sqrt{2}} - \frac{\Delta Y}{\sqrt{2}}\right) + \operatorname{erf}\left(\frac{\Delta Y}{\sqrt{2}} + \frac{k_{\max} - k_0}{\Delta\sqrt{2}}\right)\right]}{\operatorname{erf}\left(\frac{k_0 - k_{\min}}{\Delta\sqrt{2}}\right) + \operatorname{erf}\left(\frac{k_{\max} - k_0}{\Delta\sqrt{2}}\right)} \qquad (7)$$

where W is the volume of the liquid-like adsorbate present in the micropores at temperature T and under relative pressure p/p_s; $Y = (A/\beta)^n$; A is the Gibbs free energy taken with a minus sign; β is the similarity factor reflecting the nature of the adsorbate; k_0 and Δ represent the maximum and the half-width of the distribution function $f(k)$, respectively; erf and erfc are an error function and an error function complement, respectively.

In the case of Equation (7), when the dependence [4] is satisfied we obtained expressions for ΔS and ΔH, which describe adsorption on heterogeneous microporous solids characterized by the Gaussian distribution.

$$\Delta S = \alpha a V \left\{ \frac{aVnA^{n-1}}{\beta^{2n}} (\Delta^2 A^n - k_0 \beta^n) \right.$$

$$+ \sqrt{\frac{2}{\pi}} \frac{W_0 n \Delta A^{n-1}}{v\beta^n} \left\langle \exp\left[-\frac{k_{\max} A^n}{\beta^n} - \frac{(k_{\max} - k_0)^2}{2\Delta^2} \right] \right.$$

$$\left. \left. - \exp\left[-\frac{k_{\min} A^n}{\beta^n} - \frac{(k_{\min} - k_0)^2}{2\Delta^2} \right] \right\rangle \right\}^{-1}, \qquad (8)$$

where

$$v = \operatorname{erfc}\left(\frac{k_{\min} - k_0}{\Delta\sqrt{2}}\right) - \operatorname{erfc}\left(\frac{k_{\max} - k_0}{\Delta\sqrt{2}}\right)$$

and V is the molar volume of liquid adsorbate,

$$\Delta H = \alpha T a V \left\{ \frac{aVnA^{n-1}}{\beta^{2n}} (\Delta^2 A^n - k_0 \beta^n) \right.$$

$$+ \sqrt{\frac{2}{\pi}} \frac{W_0 n \Delta A^{n-1}}{v\beta^n} \left\langle \exp\left[-\frac{k_{\max} A^n}{\beta^n} - \frac{(k_{\max} - k_0)^2}{2\Delta^2} \right] \right.$$

$$\left. \left. - \exp\left[-\frac{k_{\min} A^n}{\beta^n} - \frac{(k_{\min} - k_0)^2}{2\Delta^2} \right] \right\rangle \right\}^{-1} - A. \qquad (9)$$

Recently [24], Dubinin proposed a modification of the DRS equation, assuming a slit-like micropore model and a normal Gaussian distribution of the micropore volumes according to their characteristic dimension x. In this case, the slit half-width x is approximately proportional to the radii of inertia of the slits R_i [10]. Following that, we have derived [18, 19] a more general equation containing the accepted real range of the variability of parameter x. The equation can be applied to all microporous solids – also to those with $n > 2$ in the DA equation.

$$
W = \frac{W_0 \exp\left(-\dfrac{m^{n/2}x_0^n A^n}{c^2}\right)\left[\mathrm{erf}\left(\dfrac{x_0^{n/2}}{\delta^{n/2}\sqrt{2}c} - \dfrac{x_{\min}^{n/2}c}{\delta^{n/2}\sqrt{2}}\right) + \mathrm{erf}\left(\dfrac{x_{\max}^{n/2}c}{\delta^{n/2}\sqrt{2}} - \dfrac{x_0^{n/2}}{\delta^{n/2}\sqrt{2}c}\right)\right]}{c\left[\mathrm{erf}\left(\dfrac{x_0^{n/2} - x_{\min}^{n/2}}{\delta^{n/2}\sqrt{2}}\right) + \mathrm{erf}\left(\dfrac{x_{\max}^{n/2} - x_0^{n/2}}{\delta^{n/2}\sqrt{2}}\right)\right]}
\tag{10}
$$

where $m = (\beta\kappa)^{-2}$; $\kappa = xE_0$ (E_0 is the characteristic energy of adsorption from the DA equation [12]); x_0 is the micropore half-width at the distribution curve maximum; δ is the dispersion and $c = \sqrt{1 + 2m^{n/2}\delta^n A^n}$. In accordance with the procedure described above, the expressions for ΔS and ΔH corresponding to Equation (10) have the forms:

$$
\Delta S = \alpha a V \left\{ -\frac{aVm^{n/2}x_0^n nA^{n-1}}{c^4} - \frac{aVm^{n/2}\delta^n nA^{n-1}}{c^2} \right.
$$

$$
+ \frac{2W_0 m^{n/2}\delta^n nA^{n-1}\exp\left(-\dfrac{m^{n/2}x_0^n A^n}{c^2}\right)}{vc^2\sqrt{\pi}} \cdot \left\langle \left(\frac{x_{\max}^{n/2}}{\delta^{n/2}\sqrt{2}} + \frac{x_0^{n/2}}{\delta^{n/2}c^2\sqrt{2}}\right) \right.
$$

$$
\cdot \exp\left[-\left(\frac{x_{\max}^{n/2}c}{\delta^{n/2}\sqrt{2}} - \frac{x_0^{n/2}}{\delta^{n/2}c\sqrt{2}}\right)^2\right] - \left(\frac{x_0^{n/2}}{\delta^{n/2}c^2\sqrt{2}} + \frac{x_{\min}^{n/2}}{\delta^{n/2}\sqrt{2}}\right)
$$

$$
\left. \left. \cdot \exp\left[-\left(\frac{x_0^{n/2}}{\delta^{n/2}c\sqrt{2}} - \frac{x_{\min}^{n/2}c}{\delta^{n/2}\sqrt{2}}\right)^2\right]\right\rangle \right\}^{-1}
\tag{11}
$$

where

$$
v = \mathrm{erf}\left(\frac{x_0^{n/2} - x_{\min}^{n/2}}{\delta^{n/2}\sqrt{2}}\right) + \mathrm{erf}\left(\frac{x_{\max}^{n/2} - x_0^{n/2}}{\delta^{n/2}\sqrt{2}}\right)
$$

$$
\Delta H = \alpha TaV \left\{ -\frac{aVm^{n/2}x_0^n nA^{n-1}}{c^4} - \frac{naVm^{n/2}\delta^n A^{n-1}}{c^2} \right.
$$

$$
+ \frac{2W_0 m^{n/2}\delta^n nA^{n-1}\exp\left(-\dfrac{m^{n/2}x_0^n A^n}{c^2}\right)}{vc^2\sqrt{\pi}}
$$

$$
\cdot \left\langle \left(\frac{x_{\max}^{n/2}}{\delta^{n/2}\sqrt{2}} + \frac{x_0^{n/2}}{\delta^{n/2}c^2\sqrt{2}}\right)\exp\left[-\left(\frac{x_{\max}^{n/2}c}{\delta^{n/2}\sqrt{2}} - \frac{x_0^{n/2}}{\delta^{n/2}c\sqrt{2}}\right)^2\right]\right.
$$

$$
\left. \left. -\left(\frac{x_0^{n/2}}{\delta^{n/2}c^2\sqrt{2}} + \frac{x_{\min}^{n/2}}{\delta^{n/2}\sqrt{2}}\right)\exp\left[-\left(\frac{x_0^{n/2}}{\delta^{n/2}c\sqrt{2}} - \frac{x_{\min}^{n/2}c}{\delta^{n/2}\sqrt{2}}\right)^2\right]\right\rangle \right\}^{-1} - A
\tag{12}
$$

Examples of curves for the differential molar enthalpy of adsorption ($-\Delta H + L$) corresponding to the Dubinin–Radushkevich (DR) Equation (16) [3] and the modified DRS Equation (19) [3], and obtained from Equations (9) and (12) for the cases studied are shown in Figure 1. The differential molar entropies of adsorption corresponding to these curves [Equations (15) [3], (18) [3], (8), and (11)] are presented in Figure 2.
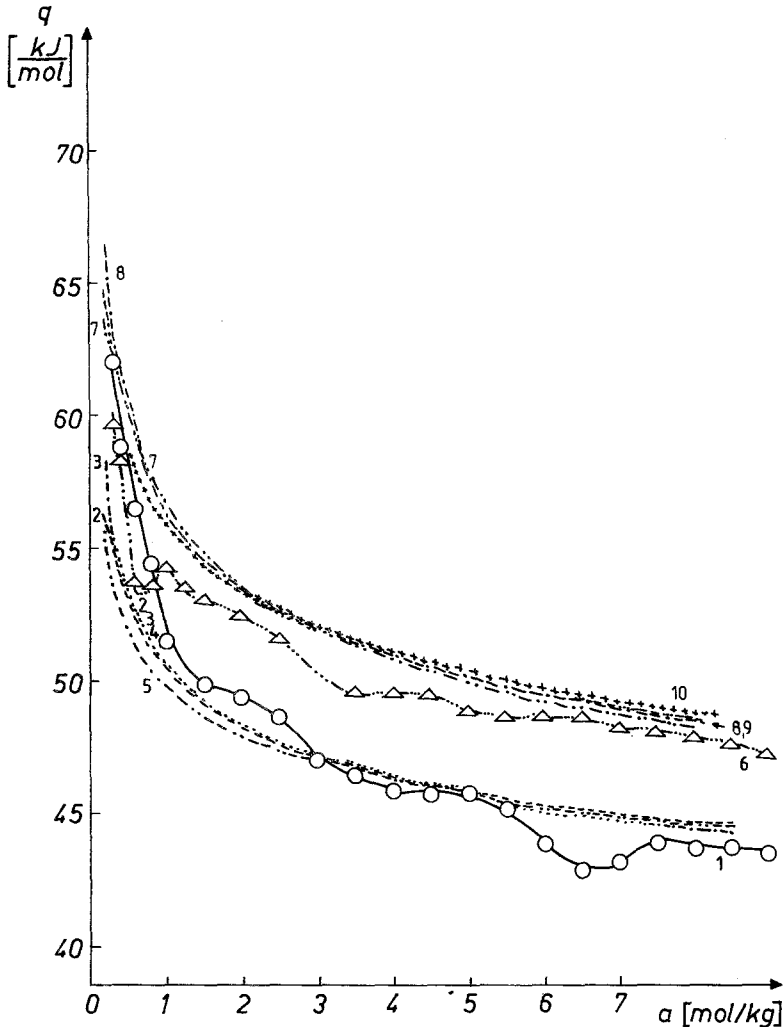
Fig. 1. The dependence of the isosteric heat of adsorption on the amount of MeOH and EtOH adsorbed on carbon E within the temperature range 298.2–322.7 K. 1 – experimental points for MeOH adsorption; 2 – resulting from Equation (16) [3] for MeOH; 3 – resulting from Equation (19) [3] for MeOH; 4 – resulting from Equation (9) for MeOH; 5 – resulting from Equation (12) for MeOH; 6 – experimental points for EtOH adsorption; 7 – resulting from Equation (16) [3] for EtOH; 8 – resulting from Equation (19) [3] for EtOH; 9 – resulting from Equation (9) for EtOH; 10 – resulting from Equation (12) for EtOH.

The values of the isosteric heat of adsorption (curves 1 and 6 in Figure 1) as well as those of the differential molar entropy of adsorption (curves 1 and 6 in Figure 2) corresponding to the systems investigated show a relatively good agreement with the data obtained theoretically. It is especially concerned with the course of changes in the isosteric heats for the systems studied (Figure 1). This demonstrates the wide applicability of the derived equations describing the adsorption on microporous carbon adsorbents. The fact that the theoretical differential molar enthalpies of
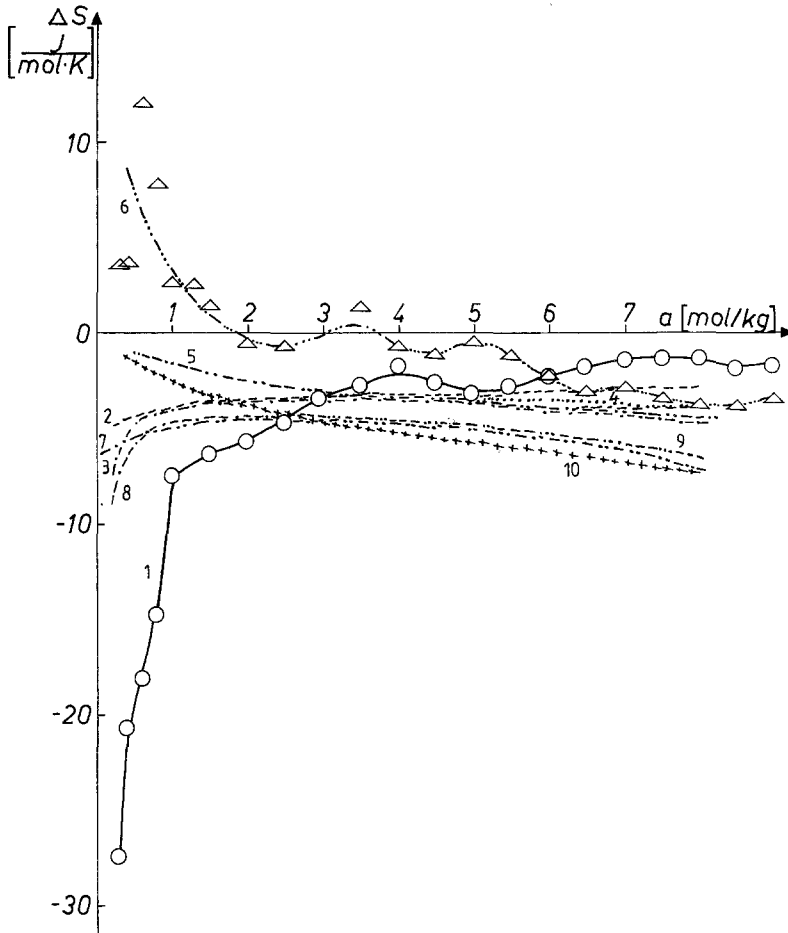
Fig. 2. The dependence of the differential molar entropy of adsorption on the amount of MeOH and EtOH adsorbed on carbon E within the temperature range 298.2–322.7 K. 1 – experimental points for MeOH adsorption; 2 – resulting from Equation (15) [3] for MeOH; 3 – resulting from Equation (18) [3] for MeOH; 4 – resulting from Equation (8) for MeOH; 5 – resulting from Equation (11) for MeOH; 6 – experimental points for EtOH adsorption; 7 – resulting from Equation (15) [3] for EtOH; 8 – resulting from Equation (18) [3] for EtOH; 9 – resulting from Equation (8) for EtOH; 10 – resulting from Equation (11) for EtOH.

adsorption are in agreement with experimental ones over a whole range of values, and that the entropies of adsorption are in agreement for different equations of adsorption isotherms confirms the versatility of the Polanyi–Dubinin potential theory model in describing adsorption on microporous carbon adsorbents.

Acknowledgement

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