Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 1011-1020

EMPIRICAL RELATIONSHIPS DESCRIBING ENERGETICS OF ADSORPTION AT LOW COVERAGES ON MICROPOROUS CARBONS

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Abstract

The fundamental empirical relationships that correlate the adsorption energy with physicochemical parameters of adsorbates are discussed. Based on the experimental data of the adsorption enthalpy of different organic adsorbates on microporous activated carbons some new correlations between adsorption enthalpy and entropy at zero surface coverage and physicochemical parameters of adsorbed molecules are proposed. It is shown that they can be applied for the calculation of carbon porosity. The influence of carbon surface oxidation on its energetic heterogeneity is also discussed.

Keywords: adsorption, adsorption calorimetry, microporous carbon, porosity

Introduction

Empirical relationships play an important role in the investigation of adsorption processes. First of all they can be applied for the determination of the nature of adsorbate-adsorbent interaction. For example, it was shown by Cordona-Martinez and Dumesic that differential enthalpy of adsorption of different bases on Al_2O_3/SiO_2 can be correlated with acid-base properties of adsorbates [1]. The method developed by Berezin and Buriak [2, 3], in which the linearity of the enthalpy of adsorption at low coverages *vs.* critical parameters of adsorbates is investigated, yields the information on the degree of solid homogeneity. Using the reference plot evaluated by Ticknor and Saluja [4] and knowing the enthalpy of adsorption of *n*-butanol the BET surface area of low-surface area materials can be easily calculated. Avgul and co-workers [5] showed that for some adsorbents the enthalpy of adsorption at zero coverage can be correlated with adsorbate polarizability and Kiselev [6] evaluated similar correlation between enthalpy of adsorption of benzene, *n*-hexane and diethyl ether and changes in stretching vibrations of silica OH surface groups.

* Presented at CETTA'97, Zakopane, Poland.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

In this paper we present an application of the calorimetric enthalpy of adsorption for the evaluation of different correlations that provide important information on the nature of the interphase boundary in the system: adsorbate–microporous activated carbon.

Experimental

The adsorption isotherms and the enthalpy of adsorption of methane, methanol, ethanol, carbon di- and tetrachloride at 308 K were measured on two microporous carbons obtained from polyfurfuryl alcohol (unoxidized – called A, and oxidized with concentrated nitric acid – called B). The detailed procedure of the carbon preparation and the carbon characteristics were given previously [7–10]. The differential enthalpy of adsorption was determined with the accuracy of ±1.5% using a Tian-Calvet microcalorimeter [11].

Results and discussion

The correlation between the enthalpy of adsorption and physicochemical constants of adsorbed molecules

Based on the results of measurements of the differential enthalpy of adsorption on the two carbons, integral molar enthalpy of adsorption was calculated using numerical integration [11]. The initial integral enthalpies of adsorption (up to a=0.15 mol kg^{-1}) were linearized to obtain the enthalpies of adsorption at zero coverage (Q^0). In Figs 1 and 2 (where the data, published previously, for another adsorbates are also included [7]) it is shown that they can be correlated with adsorbate polarizability (α) (adsorption on the carbon A) or dielectric constant (ε) (adsorption on the carbon B). From Fig. 1 it can be noticed that the experimental points can be divided into two groups. For the first of them i.e. for the non-specific adsorbates, that is for the molecules without any dipole moment (μ=0 – methane, carbon dioxide and carbon tetrachloride), the linear relationship between the enthalpy of adsorption and the adsorbate polarizability (α) is observed, and can be fitted with Eq. (1)

$$Q^{0A}(\mu = 0) = 13.02 + 4.86(\alpha) \quad (1)$$

The same (i.e. linear) relation between these values was observed for the adsorption of non-specific molecules on graphitized carbon black [5] and for adsorption in some microporous systems [12–14] and it characterises the dispersive adsorbate – adsorbent interactions.

For the second group the relationship between the enthalpy of adsorption and polarizability is more complicated, because as it was shown previously based on the detailed mechanisms of adsorption [15] the specific adsorbate – adsorbate in-

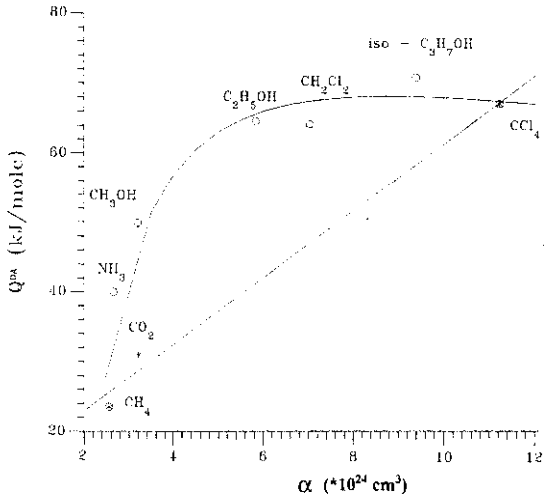

Fig. 1 The dependence of the enthalpy of adsorption on carbon A on adsorbate polarizability. Points – experimental data, linear relationship – plotted using Eq. (1), dashed curve – plotted using Eq. (2)

teractions contribute to the enthalpy of adsorption at low coverages for these molecules (using the Eq. (1), and knowing the adsorption enthalpy value, and, moreover, assuming the additivity of specific and non-specific interactions, one is able to separate the enthalpy of adsorption into the contributions of the two kinds of energy to this enthalpy). These relationships can be fitted using different models and among them we choose Eq. (2)

$$Q^{0A}(\mu \neq 0) = 80.39 + (-0.91)(\alpha) + ((-315.27)/(\alpha)^2) \quad (2)$$

It is interesting to admit that the enthalpy of adsorption at zero coverage on the oxidized carbon (carbon B) can be described by the similar relation for the all investigated adsorbates:

$$Q^{0B}(\mu = 0 \text{ and } \mu \neq 0) = 73.54 + 0.07(\varepsilon) + ((-115.78)/(\varepsilon)^2) \quad (3)$$

This suggests that for the oxidized carbon the specific adsorbate – adsorbent interactions predominate during adsorption in carbon micropores.

Based on Eqs (1)–(3) the enthalpy of adsorption on the investigated carbons can be calculated for an arbitrary chosen adsorbate.

The contributions of functional groups of an adsorbate to the enthalpy of adsorption on carbon black and on microporous carbon

On the other hand, based on the method proposed by Avgul and co-workers [16] the enthalpy of adsorption at zero coverage can be separated into various

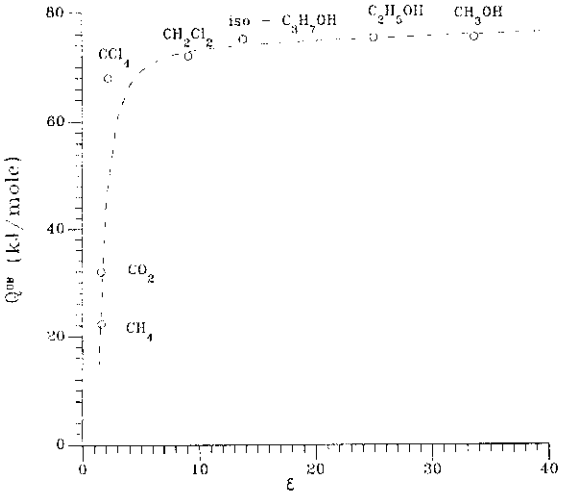

Fig. 2 The dependence of the enthalpy of adsorption on carbon B on adsorbate dielectric constant. Points – experimental data; dashed curve – plotted using Eq. (3)

contributions, assuming the additivity of dispersive interactions of all functional groups of an adsorbate molecule with a surface. The application of such a procedure leads, for example, for the adsorption enthalpy of methanol ($Q^0_{CH_3OH}$) to the following equation:

$$Q^0_{(CH_3OH)} = Q^0_{(CH_3)} + Q^0_{(OH)} \tag{4}$$

It can be easily deduced that the enthalpy of adsorption of the (CH_2) group can be obtained from the subtraction:

$$Q^0_{(C_2H_5OH)} - Q^0_{(CH_3OH)} = Q^0_{(CH_2)} \tag{5}$$

Knowing this energy together with the enthalpy of adsorption of methane and carbon tetrachloride, one can calculate the energy of interaction between other atoms or functional groups of an adsorbate and a surface:

$$Q^0_{(CH_4)} = Q^0_{(C)} + 4Q^0_{(H)} \tag{6}$$

$$Q^0_{(H)} = [Q^0_{(CH_4)} - Q^0_{(CH_2)}]/2 \tag{7}$$

$$Q^0_{(C)} = Q^0_{(CH_4)} - 4Q^0_{(H)} \tag{8}$$

Using the data of methane, methanol, ethanol and carbon tetrachloride adsorption on Sterling MT 3000 graphitized carbon black, published by Avgul and

co-workers [5], together with Eqs (1)–(8), we calculated the contributions of adsorbate functional groups to the adsorption enthalpy at zero – coverage on the carbon black. The same procedure was applied for the data of the enthalpy of adsorption on the carbon A. The results are presented in Table 1 and on Fig. 3 where the contributions of functional groups to the enthalpy of adsorption in carbon micropores are compared with those for adsorption on the homogeneous surface of graphitized carbon. It can be noticed that the obtained correlation has a linear form and:

$$Q^0_{(\text{microp. carbon})} = 5.78 + 0.795\,Q^0_{(\text{graph. carbon})} \tag{9}$$

Knowing the contribution of some chosen surface groups to the enthalpy of adsorption on the carbon black (Table 1) and using Eq. (9), the enthalpy of adsorption of these groups can be calculated; and, afterwards, by a simple addition, one obtains the approximate value of enthalpy of adsorption of a molecule in carbon micropores.

Table 1 The contributions of adsorbate functional groups to the enthalpy of adsorption at low coverages on graphitized carbon black and on microporous carbon A

An adsorbate functionality	$Q^0_{(\text{graph. carbon})}$ / kJ mol^{-1}	$Q^0_{(\text{microp. carbon})}$ / kJ mol^{-1}
	1.73	6.10
	6.81	14.80
–H	2.54	4.35
–OH	32.65	30.75
–Cl	9.62	15.30

The verification of Eqs (1)–(9) is presented in Table 2, where are given calculated, using the procedure described above, the enthalpies of adsorption for a few arbitrary chosen adsorbates on carbon black and in investigated carbon micropores and then compared the obtained results with the experimental data.

The enhancement of the adsorption potential in carbon micropores

The integral molar adsorption energies on the carbon A can be compared with the enthalpies of adsorption of the same molecules on graphitized carbon black, and the enhancement of the adsorption potential in micropores (Q^a) can be calculated. If we assume that the adsorption enthalpy at zero coverage is equivalent to

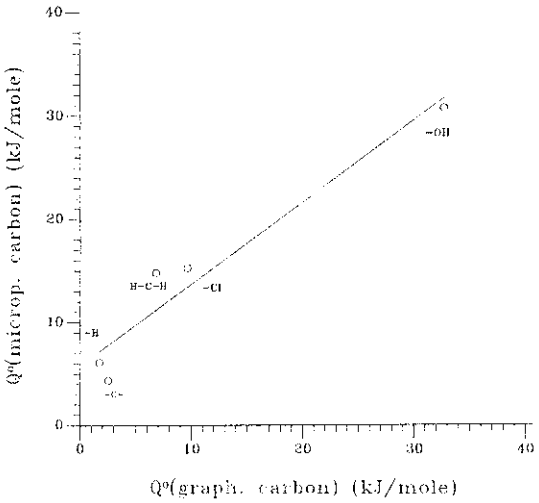

Fig. 3 The comparison of contributions of functional groups to the enthalpy of adsorption on carbon A with those for adsorption on the homogeneous surface of graphitized carbon. Solid line – plotted using Eq. (9)

Table 2 The enthalpies of adsorption of a few arbitrary chosen adsorbates on carbon black and on microporous carbon A calculated with the use of procedure described in the text and compared to the experimental data

Adsorbate	Q^{0calc} (using Table 1)/ kJ mol^{-1}	Q^{0exp} [5, 7, 15]/ kJ mol^{-1}	Q^{0calc}/Q^{0exp}
	graphitized carbon black		
CH_2Cl_2	26.04	23.90	1.09
$CHCl_3$	33.11	28.90	1.14
C_2H_6	18.69	17.33	1.08
C_3H_7Cl	32.57	28.15	1.16
	microporous carbon A		
CH_2Cl_2	45.4	64.3	0.71
iso-C_3H_7OH	69.05	71.02	0.97

the energy of adsorbate – adsorbent interactions, the value of this enhancement is strictly related to the pore diameter (L) and simply:

$$Q_a = cd/L \tag{10}$$

where c is a constant, and d is the adsorbate diameter.

However, as it was shown above, in the carbon A micropores specific adsorbate – adsorbate interactions enlarge the enthalpy of adsorption of molecules

with dipole moments at low coverages. Fortunately, using the Eq. (1), the energy of adsorbate – adsorbent interactions can be calculated and the energy of specific interactions can be subtracted from the enthalpy of adsorption. Knowing the value of potential enery enhancement and using Everett and Powl's theoretical results [17], the carbon A pore diameters (L) can be calculated for the two potential models and for each adsorbate molecule. They are shown in Fig. 4 together with the pore diameters calculated using different models of porosity determination and based on low-temperature nitrogen adsorption data (published previously [9]). In this case micropore diameters were calculated from empirical relations between nitrogen characteristic adsorption energy at 77.5 K and a pore diameter, or from pore size distributions (equations used for this purpose were published previously [18]). We can write the general relations between L and d for the (10:4) potential:

$$L = 2.056d + 0.224 \tag{11}$$

and for the (9:3) potential:

$$L = 1.960d + 0.170 \tag{12}$$

The correlation between pore diameters calculated from the potential energy enhancement and from nitrogen adsorption data is not satisfactory only for the equation of McEnaney. This can be caused by the existence of closed porosity in polyfurfuryl alcohol carbon [19].

The new equations can be used for the verification of the applicability of the methods proposed for the determination of an active carbon micropore diameter.

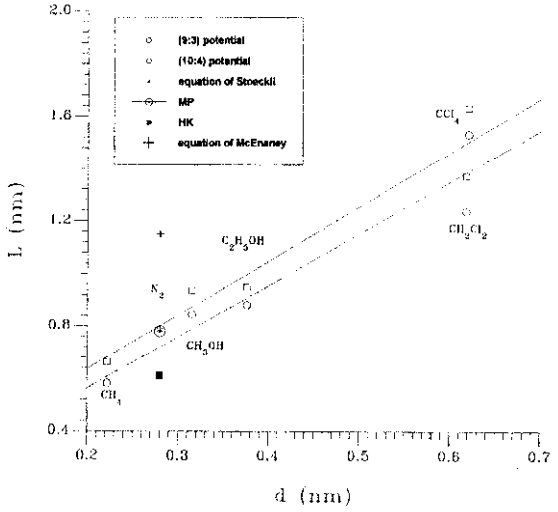

Fig. 4 Carbon A pore diameters calculated from the enhancement of adsorption potential in micropores (and theoretical data of Everett and Powl) and low temperature nitrogen adsorption data

Empirical relationships describing the changes in adsorption entropy

The empirical equations describing the change of the entropy of adsorption at 'zero-coverage' can be developed. However, in this case the correlations between entropy changes and physicochemical parameters of adsorbates, like to those shown in Figs 1 or 2, do not exist. The entropy changes can be approximately calculated using the following empirical equations:

$$\Delta S^{A} = ((T_b/(10\sigma)) + \mu\alpha r)(L/r) \tag{13}$$

$$\Delta S^{B} = ((T_b/(10\sigma)) + \mu\alpha r)(L/r) + (\varepsilon\alpha/r) \tag{14}$$

where $\Delta S^{A/B}$ are the changes in differential molar entropy of adsorption on the carbon A or B (J (mol K)$^{-1}$), assuming the ideal gas at the pressure of 101325 Pa as a reference state, T_b is the adsorbate boiling point (K), σ is the (6–12) Lennard-Jones potential parameter (nm), μ is the dipole moment (D).

Table 3 The comparison of experimental [20, 21] and calculated values using Eqs (13) and (14) for different adsorbate – adsorbent systems

Adsorbate	ΔS^{calc}/J mol^{-1} K^{-1}	ΔS^{exp}/J mol^{-1} K^{-1}	$\Delta S^{exp}/\Delta S^{calc}$
Adsorption on microporous carbon A – unoxidised (Eq. (13))			
CH_3OH	85	101	1.19
C_2H_5OH	96	143	1.49
CCl_4	60	65	1.08
CH_2Cl_2	156	136	0.87
CO_2	53	45	0.85
NH_3	67	74	1.10
Adsorption on microporous carbon B – oxidised (Eq. (14))			
CH_3OH	119	141	1.18
C_2H_5OH	130	150	1.15
CCl_4	64	145	2.26
CH_2Cl_2	166	166	1.00
CO_2	54	51	0.94
NH_3	107	124	1.16
Adsorption on microporous carbon CHT – unoxidised (Eq. (13))			
CH_3OH	20	21	1.05
CH_3CN	86	60	0.70
CH_3NO_2	62	60	0.97
CH_2Cl_2	50	130	2.60
Adsorption on carbon COX – oxidised (Eq. (14))			
CH_3OH	55	64	1.16

The comparison of experimental and calculated data, using Eqs (13) and (14), is shown in Table 3, where are also given calculated entropy changes for the adsorption on other carbons and compared with the experimental data published previously [20, 21].

The energetic homogeneity of the adsorbent

Berezin and Buriak [2, 3] showed that for the adsorption on a homogeneous surface:

$$Q^0 = DT_c/(p_c)^{1/2} \tag{15}$$

where D is a constant, T_c and p_c are an adsorbent critical temperature and pressure.

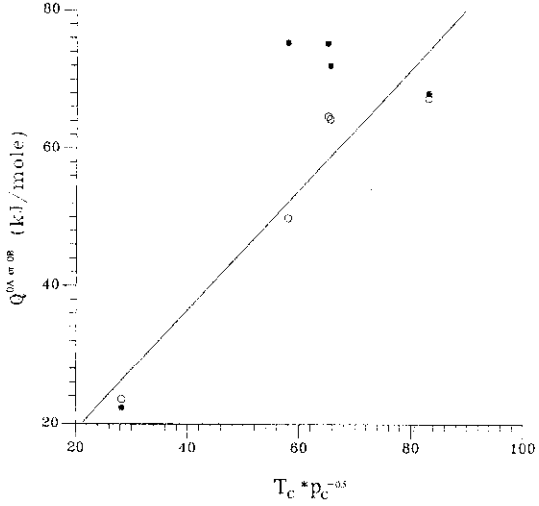

Fig. 5 The enthalpy of adsorption data (for carbon A we used linear approximation) on two carbons plotted in the coordinates of Eq. (15). Open symbols – carbon A; closed symbols – carbon B

It means that the adsorbent homogeneity can be evaluated using Eq. (15). Stach and co-workers [22] showed the applicability of Eq. (15) for the adsorption of *n*-alkanes in micropores of some zeolites and on silica gel, and for other systems [23]. From Fig. 5 it can be noticed that among the investigated carbons the carbon A is the most homogeneous, and surface oxidation leads to the increase of the carbon energetic heterogeneity.

Conclusions

The empirical relations play an important role in adsorption. It is shown that they can be applied for the calculation of the enthalpy of adsorption of an arbi-

trary chosen molecule on the investigated carbons, with the use of the proposed relations between the enthalpy of adsorption and physicochemical constants of adsorbed molecules. The enthalpy of adsorption can also be calculated using the equation which relates the enthalpy of adsorption of adsorbate functional groups in carbon micropores to those on graphitized carbon black. The application of the proposed correlation is presented for the calculation of porosity of the investigated carbon. It is shown that the obtained carbon pore diameters are different for different adsorbates, though, they obey the general linear relationship for the both applied potential models. Moreover, the pore diameters calculated from the nitrogen adsorption isotherm measurements fall close to this line.

The empirical equations describing the low coverage adsorption entropy changes on the two carbons are presented, and it is shown that they can be used for the approximate calculation of this value for the adsorption of other adsorbates on different carbons. Finally, based on the empirical relationship proposed by Buriak and co-workers, it is demonstrated that an unoxidized microporous carbon is more homogeneous energetically than an oxidized one.

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