

## THE ENTHALPIES OF IMMERSION OF ACTIVE CARBONS, IN RELATION TO THE DUBININ THEORY FOR THE VOLUME FILLING OF MICROPORES

H. F. STOECKLI† and F. KRAEHNBUHL

Chemistry Department of the University, Av. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

**Abstract**—It is shown that an exact expression can be derived from Dubinin's theory, for the enthalpy of immersion of active carbons. It appears that for a given liquid, the specific enthalpy of immersion is a function of the characteristic energy  $\beta E_0$  of the Dubinin-Astakhov equation. The new relation is illustrated by data obtained for 10 different carbons immersed into benzene and *n*-heptane at 34°C. Simultaneously, results are presented for the immersion into water, not described by Dubinin's theory, but providing useful complementary information about the chemical state of the surface.

### 1. INTRODUCTION

Adsorption by microporous carbons is described by Dubinin's theory of micropore volume filling (TVFM)[1]. In its present formulation, the adsorption isotherm is given by the equation of Dubinin-Astakhov[2]

$$W = W_0 \exp\{-(A/\beta E_0)^n\} \quad (1)$$

where  $A = RT \ln(p_0/p)$ ,  $E_0$  is the characteristic free energy for the adsorption of a reference vapour,  $W$  is the volume of micropores filled at temperature  $T$  and relative pressure  $p/p_0$ , and  $W_0$  is the total volume of the micropores. Parameter  $\beta$  (the affinity coefficient), is a shifting factor depending on the adsorptive. By convention, benzene is taken as the reference vapour and  $\beta(\text{C}_6\text{H}_6) = 1$ .

When exponent  $n = 2$ , the D-A eqn (1) reduces to the classical equation of Dubinin and Radushkevich which is commonly used in the case of active carbons,

$$W = W_0 \exp\{-B(T/\beta)^2 \log^2(p_0/p)\}. \quad (2)$$

The so-called structural constant  $B$  is related to  $E_0$  through

$$E_0 = 0.01915/B^{1/2}. \quad (3)$$

According to Dubinin and Stoekli[3], these parameters are related to an average micropore dimension. This property, and the observation that eqn (2) is well followed in the case of adsorption by carbons with molecular sieve properties, has lead to the generalization of eqn (2) for adsorption by heterogeneous carbons[3-5],

$$W = W_0 \exp\{-B_0 y\} \exp\{y^2 \Delta^2/2\} \cdot [1 - \text{erf}(x)]/2 \quad (4)$$

where  $y = (T/\beta)^2 \log^2(p_0/p)$  is a generalized coordinate,

†Author to whom communications should be addressed.

$x = (y - B_0/\Delta^2)\Delta\sqrt{2}$  and  $\Delta$  is a measure of the spread  $f(B)$  of  $B$  round  $B_0$ . The generalized eqn (4), put forward by Stoekli[4], has been discussed by Huber and Stoekli[5] and by Dubinin and Stoekli[3]. The latter authors showed that eqn (4) is compatible with the case where  $1 < n < 2$  in eqn (1). The work of János and Stoekli[6], based on the small angle scattering of X-rays, also confirms the basic assumptions on which eqn (4) rests. Furthermore, it has been shown recently by Stoekli *et al.*[7], by combining adsorption data and enthalpies of immersion, that the adsorption of bulky molecules could induce modifications in the microporous structure of active carbons. These findings are an indication for possible deviations from Dubinin's theory and for limitations in the case of adsorption of large molecules.

Although eqn (2) has been adapted to the case of adsorption from solutions, it is interesting to point out that the consequences of Dubinin's theory have not been worked out for the case of immersion of microporous carbons (or other solids) into simple liquids. The purpose of the present work is to establish formally the link between the enthalpy of immersion  $\Delta H_i$  and the parameters of TVFM, and to present experimental results obtained with a range of microporous carbons. The experimental conditions were such, that modifications of the structure[7], did not occur and the study could take place within the framework of Dubinin's theory.

### 2. THEORETICAL

It can be shown[8-10] that in the case of microporous solids without external surface area the enthalpy of immersion  $\Delta H_i$  is related to the isotheric heat of adsorption  $q^{\text{st}}$  by a simple expression,

$$-\Delta H_i(T) = \int_0^1 q^{\text{st}}(T; \theta) d\theta - \Delta H_{\text{vap}}(T) \quad (5)$$

where  $\theta$  is the degree of micropore filling  $W/W_0$ . The

minus sign is due to the fact that  $q^{st}$  is conventionally defined as a positive quantity, whereas the calorimetric quantity  $\Delta H_i$  is negative.

As shown by Dubinin[1], the net differential heat of adsorption

$$q^{net} = q^{st} - \Delta H_{vap} \quad (6)$$

can be derived exactly from eqns (1) or (2).

For  $n = 2$ , one obtains

$$q^{net}(T; \theta) = \beta E_0 [(\ln 1/\theta)^{1/2} + (\alpha T/2)(\ln 1/\theta)^{-1/2}] \quad (7)$$

where  $\alpha$  is the thermal expansion coefficient of the adsorbate at temperature  $T$ . The combination of eqns (5) and (7), followed by integration[11], leads to the formal relation

$$-\Delta H_i(T) = \beta E_0 \left( \frac{\sqrt{\pi}}{2} \right) [1 + \alpha T]. \quad (8)$$

Owing to the dimensions of  $E_0$ , the calculated enthalpy of immersion  $\Delta H_i$  in eqn (8) is given in kJ or J/mole of adsorptive. This corresponds to the filling of a volume of micropores equal to the molar volume of the adsorbate. It is reasonable to assume that this quantity is equal to the molar volume of the pure liquid  $V_m(T; p)$ , if the temperature is near or below the normal boiling point of the adsorptive[1].

It follows that the calculated enthalpy of immersion, conveniently expressed in J/cm<sup>3</sup> of micropores, can be obtained by dividing the r.h.s. of eqn (8) by  $V_m$  (cm<sup>3</sup>/mole),  $E_0$  being itself in J/mole,

$$-\Delta H_i(\text{J/cm}^3) = \beta E_0 (1 + \alpha T) \sqrt{\pi} / 2 V_m. \quad (9)$$

For the comparison with earlier data found in the literature and given in mJ/m<sup>2</sup>, the conversion factor in eqn (8) involves the surface occupied by one mole of ad-

sorbate, in the form of a monolayer[8] ( $2.47 \times 10^5$  m<sup>2</sup>/mole of benzene, for example).

Eqns (8) and (9) apply strictly to the case where the adsorbate follows eqns (1) and (2) for the adsorption from the gas phase. However, it is also valid for the case of heterogeneous carbons following the generalized eqn (4), which assumes a spread  $f(B)$  or  $f(E)$  of  $B$  and  $E_0$  around their average values. The weighting of eqn (8) with symmetrical or nearly symmetrical functions  $f(B)$  or  $f(E_0)$  leaves the result unchanged.

Equation (8) shows further that the enthalpy of immersion is a function of the adsorptive (parameters  $\alpha$  and  $\beta$ ) and of the micropore system, since  $E_0$  is related to an average pore size[3].

### 3. EXPERIMENTAL

The enthalpies of adsorption were measured at 34°C with a relatively simple calorimeter of the CALVET type[8]. It was designed specifically for the immersion of active carbons, which have relatively large equivalent surface areas (500–1300 m<sup>2</sup>/g). The calorimeter has 200 copper–constantan thermocouples (total sensitivity of 4300  $\mu$ V/K) placed between the immersion cell and the surrounding block of copper.

The equipment was calibrated with an electric resistance, and also by measuring the enthalpies of immersion of carbon black Vulcan 3[12] and of CABOSIL grade M5 in benzene[13]. The results obtained from the integration of the thermocouple response versus time showed an agreement which was within the overall accuracy and reproducibility of our calorimeter ( $\leq 1\%$ ).

The experiments were performed with a series of well characterized active carbons, used in the present laboratory[3]. The solids, prepared from polymers (1–3), vegetable materials (4, 9, 10) and from anthracite (5–8) are characterized by a low ash content and a small external surface area. Samples of 0.3–0.4 g were out-gassed under standard conditions and sealed under vacuum in the ampoules used for immersion (about 5 ml

Table 1. Experimental enthalpies of immersion of microporous carbons into benzene, *n*-heptane and water, at 307K (Values of  $\Delta H_i$  in J/cm<sup>3</sup> of micropores)

Carbon	$W_0$ (cm <sup>3</sup> /g)	$B(10^{-6} \text{K}^{-2})$	$E_0(10^3 \text{J/mole})$	$\Delta H_i(\text{C}_6\text{H}_6)$	$\Delta H_i(\text{n-C}_7\text{H}_{16})$	$\Delta H_i(\text{H}_2\text{O})$
1	0.16	0.50	27.1	394	-	146
2	0.19	0.50	27.1	377	355	90
3	0.44	0.57	25.4	366	346	39
4	0.49	0.66	23.6	349	321	110
5	0.40	0.87	20.5	295	293	42
6	0.43	0.92	20.0	287	267	68
7	0.43	0.92	20.0	284	-	76
8	0.43	0.92	20.0	273	276	65
9	0.64	1.03	18.9	265	256	79
10	0.62	1.30	16.8	232	242	73

Samples 6–8 have been submitted to various physico-chemical treatments [7].

of benzene, *n*-heptane or deionized water). The initial immersion data, in J/g, were corrected for the external surface area of the solids (meso and macropores). We used the values of  $\Delta H_i$  quoted for graphitized carbons [8, 10, 12],  $-107 \text{ mJ/m}^2$  (benzene) and  $111 \text{ mJ/m}^2$  (*n*-heptane). The experimental enthalpies of immersion, corresponding to the micropores only, were obtained by using the micropore volumes  $W_0$  derived from vapour adsorption experiments [3]. The corresponding values are given in Table 1. In the case of MSC-5, before and after reduction in  $\text{H}_2$  at  $650^\circ\text{C}$  (samples 1 and 2, respectively), the adsorption isotherms of water and benzene vapours were determined gravimetrically at  $20^\circ\text{C}$ .

#### 4. RESULTS AND DISCUSSION

The data obtained for the immersion of 10 different active carbons in benzene and in *n*-heptane (Table 1) show that eqns (8) and (9) are followed in a satisfactory way. It is found that the proportionality constants between the experimental values of  $\Delta H_i$  and the values calculated with eqn (9) are 1.05 for benzene and 1.02 for heptane. In the case of *n*-heptane, we used the value of  $\beta = 1.62$ , suggested by the comparison of static adsorption of  $\text{C}_6\text{H}_6$  and *n*- $\text{C}_7\text{H}_{16}$  vapours at  $298\text{K}$ , on two different carbons.

Similar correlations for  $\Delta H_i$  have also been obtained for experiments on a limited number of carbons, of the same series, immersed into  $\text{CCl}_4$  and toluene. Figure 1 illustrates the proportionality which exists, according to eqn (8), between the experimental enthalpy of immersion  $\Delta H_i$  ( $\text{J/cm}^3$ ) and the characteristic energy  $E_0$  of the corresponding carbon. For the sake of clarity, the results for *n*-heptane are not shown.

Our examples illustrate the validity of eqns (8) and (9) in the case of benzene and *n*-heptane, two typical adsorbates following the basic equation of TVFM. Our values for benzene vary from  $-230$  to  $-396 \text{ J/cm}^3$ , the latter being in agreement with the values quoted by

different authors [9, 14, 15]. It appears, however, that the value of  $-505 \text{ mJ/m}^2$  proposed by Maggs *et al.* [16] is definitely too high.

The present study summed up by eqns (8) and (9), shows that it is not possible, in the case of active carbons, to use a standard value for  $\Delta H_i$  to calculate directly the micropore volumes  $W_0$  from enthalpies of immersion alone. According to eqns (8) and (9), the enthalpy of immersion for a given liquid is also a function of  $E_0$  and consequently of the micropore system.

Since the adsorption of water vapour by active carbons does not follow the basic eqn of TVFM [1], the new relations (8) and (9) do not apply to the immersion into this liquid. This is also confirmed by our results, where no trend is observed. However,  $\Delta H_i$  in water seems to provide useful and complementary information to the results obtained within the framework of TVFM.

In view of the low value of the non-specific interactions between carbon and water, and of the high value for specific interactions with surface groups containing oxygen [17], the enthalpy of immersion technique can be used to characterize specifically these groups. In the case of MSC-5, before and after reduction in  $\text{H}_2$  ( $650^\circ\text{C}$  for 3 hr), the specific enthalpy of immersion into benzene varies relatively less than for water (Table 1 and Fig. 1).

The large change observed for the immersion into  $\text{H}_2\text{O}$  reflects the modification observed in the displacement of the water adsorption isotherm towards higher values of ( $p/p_0$ ) after reduction (Fig. 2).

Our values for the enthalpies of immersion into water can be compared with those found in the literature. According to the data of Youssef [15],  $-\Delta H_i(\text{H}_2\text{O}; 307\text{K})$  varies from  $115$  to  $46 \text{ mJ/m}^2$  ( $323$ – $129 \text{ J/cm}^3$ ) for microporous wood charcoals prepared between  $500$  and  $1200^\circ\text{C}$ . In the case of graphitic carbons [9, 17], on the other hand, this enthalpy varies from  $-90$  to  $-30 \text{ mJ/m}^2$ , depending on the origin and the treatment of the solid. At

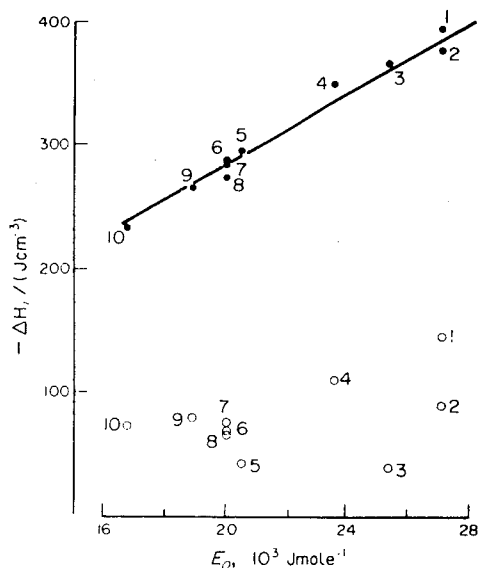


Fig. 1. Enthalpies of immersion of microporous carbons 1 to 10 into benzene (●) and water (○) at  $307\text{K}$ .

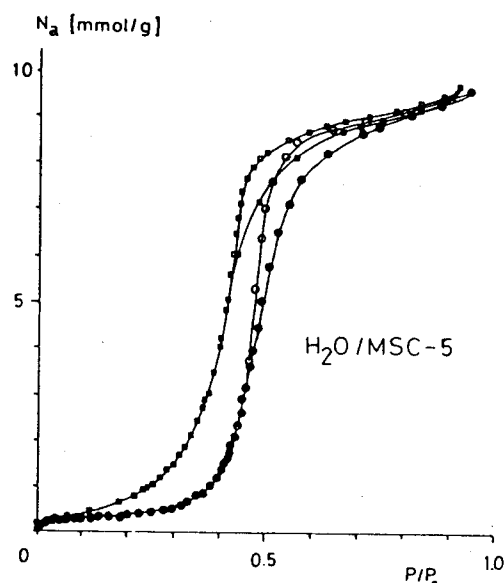


Fig. 2. Water adsorption by MSC-5 before (■) and after (●) treatment in  $\text{H}_2(650^\circ\text{C}; 3 \text{ hr})$ . Closed and open symbols refer to adsorption and desorption, respectively, at  $293\text{K}$ .

the present time, no explanation can be offered for the cases where the enthalpies of immersion of active carbons into water and benzene are smaller than the limiting values on graphitized carbon blacks.

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