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ON THE CHARACTERIZATION OF MICROPOROUS CARBONS BY IMMERSION CALORIMETRY ALONE

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Abstract—Immersion calorimetry is a useful tool for the characterization of solid surfaces in general, but in the case of microporous solids it usually requires complementary information, obtained from an adsorption isotherm. This article demonstrates the possibilities and the limitations of this technique when used alone. It appears that the use of a standard value for the enthalpy immersion does not always provide a reliable assessment of the total surface area.

Key Words—A. Activated carbon, C. adsorption, D. microporosity, D. surface area.

1. INTRODUCTION

The physical adsorption of vapours by typical microporous carbons is well described by the equation of Dubinin and Radushkevich (DR) [1,2]

$$N_a = N_{ao} \exp[-(A/\beta E_o)^2] \qquad (1)$$

where $A = RT\ln(p_s/p)$. The quantity N_a is the amount adsorbed at relative pressure p/p_s and N_{ao} is the limiting amount as p tends towards p_s. The latter is related to the total micropore volume $W_o = N_{ao}V_m$ accessible to the molecular probe, V_m being the molar volume of the liquid-like adsorbate. β is a scaling factor depending on the adsorbate and, by convention, $\beta(C_6H_6) = 1$. The quantity E_o, usually given in kJ mol^{-1}, is called the characteristic energy of the solid. It is related to the average micropore width L by [2–4]

$$L\,(\mathrm{nm}) = 10.8/(E_o - 11.4) \qquad (2)$$

For slit-shaped micropores the corresponding surface area S_{mi} is

$$S_{mi}\,(\mathrm{m^2\,g^{-1}}) = 2000\,W_o\,(\mathrm{cm^3\,g^{-1}})/L\,(\mathrm{nm}) \qquad (3)$$

A single adsorption isotherm therefore provides information on the microporous structure as perceived by the corresponding molecular probe. Molecular sieve effects can be detected by using probes of different sizes, but this may be time-consuming and difficult, since the vapour pressures of liquids with bulky molecules are often low. It is therefore convenient to use immersion calorimetry as a complementary technique. A thermodynamic consequence of Dubinin's theory is the equation for the enthalpy of immersion of a microporous carbon into a liquid, the vapour of which follows the DR equation (eqn (1)) [2]

$$-\Delta h_i\,(\mathrm{J\,g^{-1}}) = \beta E_o W_o(1+\alpha T)(\pi)^{1/2}/2V_m + h_i S_e \qquad (4)$$

where α is the thermal expansion coefficient of the liquid and $h_i S_e$ corresponds to the wetting of the external surface S_e.

As shown elsewhere [2,5,6], the combination of adsorption and immersion techniques leads to a detailed picture of the microporous structure of active carbons. In view of its simplicity, immersion calorimetry allows an important gain in time, in particular for the study of activation series [6]. However, it is important to assess how much information can be obtained from this technique alone. Therefore, its possibilities and its limitations must be pointed out.

2. THE ASSESSMENT OF MICROPOROSITY

We shall begin with the assessment of the micropore accessibility based on the enthalpies of immersion into liquids of various critical molecular sizes L_c [2], one of the liquids being taken as a reference. For convenience, this may be CH_2Cl_2 or benzene. Provided that $h_i S_e$ remains small, eqn (4) leads to

$$\Delta h_i(1)/\Delta h_i(2) = (E_{o1}W_{o1}/E_{o2}W_{o2})(\beta_1/\beta_2) \times (1+\alpha_1 T)V_m(2)/(1+\alpha_2 T)V_m(1) \qquad (5)$$

and it follows that

$$E_o W_o/E_{o\,\mathrm{ref}} W_{o\,\mathrm{ref}} = (\Delta h_i/\Delta h_{i\,\mathrm{ref}})[\beta_{\mathrm{ref}}(1+\alpha_{\mathrm{ref}}T)V_m /\beta(1+\alpha T)V_{m\,\mathrm{ref}}] \qquad (6)$$

This ratio can be calculated from the enthalpies of immersion and the specific parameters α, β and V_m of the liquids. If the accessibility of the pores is limited, either by gate effects or by the micropore distribution itself, the product $E_o W_o$ decreases as the size of the molecular probe increases.

Figure 1 illustrates the case of carbon CMS, the reference liquid being C_6H_6. By assuming that $E_o/E_{o\,\mathrm{ref}} = 1$, a first and good approximation can be

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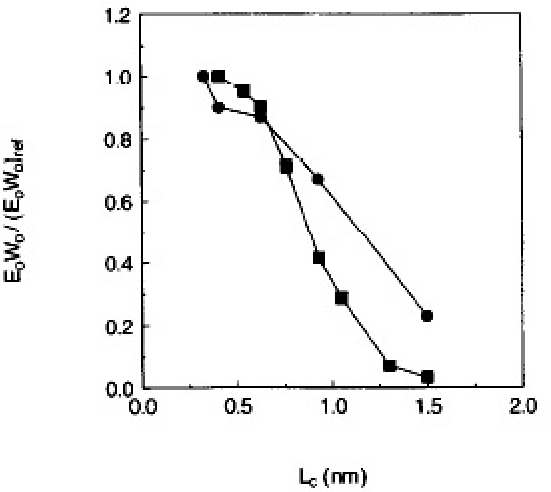

Fig. 1. Plot of $W_0E_0/(E_0W_0)_{ref}$ calculated using eqn (6), as a function of the critical molecular size L_c of the probes. Carbons CMS (■) and L4BC-A (●). The liquids used as references are respectively C_6H_6 and CH_2Cl_2 at 293 K.

obtained for the micropore distribution $\Delta W/\Delta L$ (Fig. 2). The average micropore width is 0.92 nm, which corresponds to $E_{o\ ref}=23.1$ kJ mol^{-1} versus 26.1 kJ mol^{-1} from the adsorption isotherm. From the histogram, it is possible to calculate the average micropore width of the space filled by the various probes and to estimate the values of E_o with the help of eqn (2). In the present case, they vary from 23.1 (benzene) to 18 kJ mol^{-1} (tri-2,4-xylyl phosphate, the largest molecule considered here). However, it appears that this procedure does not change the original histogram significantly.

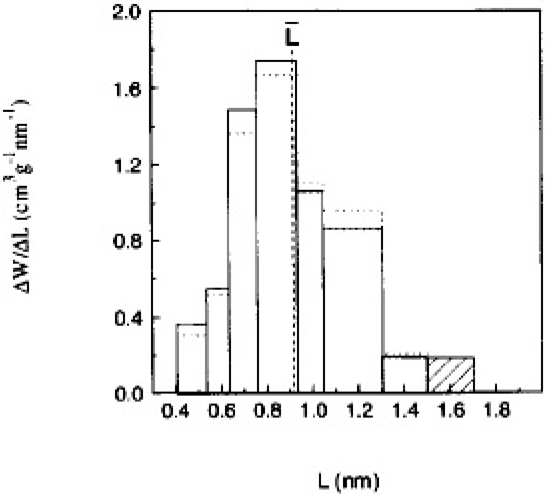

Fig. 2. Micropore size distribution of carbon CMS derived from eqn (6) (see also Fig. 1). The average micropore width L is 0.9 nm versus 0.7 nm derived from adsorption data. The dashed lines correspond to the improved histogram using individual E_o values.

With $E_{o\ ref}=23.1$ kJ mol^{-1}, eqn (4) leads to a micropore volume of $W_o=0.29$ cm^3 g^{-1}, which is in good agreement with the real value of 0.25 cm^3 g^{-1} (the external surface area, not considered in this approach, is 25 m^2 g^{-1}).

This example shows that it is possible, in principle at least, to obtain a first assessment of the micropore distribution from immersion calorimetry alone, but this may not always be the case. Experience shows that a number of carbons may display a gate effect, either at an early stage of activation, or following specific treatments. This effect is only revealed by comparison of the average micropore size obtained from the adsorption isotherm of a small molecule and the unusually low values for the enthalpies of immersion into liquids which should be accessible to them. In the case of carbon L4BC-A (Fig. 1), the *D–R* plot of the CH_2Cl_2 isotherm even shows two linear sections, which indicate the presence of two micropore systems [6]. The first has an average width of 0.3–0.5 nm (E_{o1} near 40 kJ mol^{-1}) and a small volume ($W_{o1}=0.03$ cm^3 g^{-1}). The second system consists of supermicropores ($E_{o2}=13$ kJ mol^{-1}) with a much larger volume ($W_{o2}=0.43$ cm^3 g^{-1}). This system should accommodate molecules such as tetrabutylurea (0.93 nm) and tri-2,4-xylyl phosphate (1.5 nm), but only 67 and 23% of the pores are filled by these liquids. This means that a large proportion of the large pores are only accessible through the first system, which acts as a gate. In the present case, the determination of a histogram based on calorimetry alone would lead to the wrong conclusions.

These examples show that it is difficult to distinguish between open porosity and gate effects without the knowledge of E_o for a small probe, obtained from the corresponding adsorption isotherm and indicating the real average micropore size. As a consequence, one may reach the wrong conclusions. On the other hand, in the case of activation series, immersion calorimetry can be used to follow the development of microporosity with an appreciable gain in time over the measurement based exclusively on adsorption isotherms.

3. IMMERSION CALORIMETRY AND SURFACE AREAS

It has been suggested on several occasions that immersion calorimetry could be used to determine the surface area of microporous carbons with the help of a specific enthalpy of immersion h_i, by analogy with non-porous materials, where $S=\Delta h_i/h_i$. However, a more rigorous approach shows that h_i is not constant. The combination of eqns (2)–(4) leads to

$$-\Delta h_i/S_{mi}\ (\mathrm{J\ m^{-2}})=\beta(10.8+11.4L) \times(1+\alpha T)(\pi)^{1/2}/4V_m \qquad (7)$$

which shows that the specific enthalpy of immersion depends on L. Theoretically, in the range $0.4<L<1.5$ nm, h_i should vary from 0.098 to

0.117 J m^{-2} for CH_2Cl_2 and from 0.104 to 0.190 J m^{-2} for benzene. However, h_i is a formal value, because the liquid fills a confined space and all the molecules change their energy during the process of immersion. Therefore, h_i also includes the contribution of the bulk of the liquid in the pores and not necessarily in contact with the walls.

The enhancement of the adsorption energy in a micropore and its relation to the pore width have been described by Everett and Powl [7] and by Stoeckli et al. [8,9]. The model shows that the influence of the opposite walls decreases as the width of the pore increases, in agreement with the initial differential heats of adsorption determined calorimetrically for active carbons with different pore widths [10]. It appears that, even for supermicropores, the heat of adsorption, and consequently Δh_i, remain important. On the other hand, for larger pores ($L > 2.5$–3 nm) one may expect a standard value for h_i, close to that found with open surfaces. For benzene on graphitized carbon blacks, the average value is $h_i = -0.114$ J m^{-2} [2–4].

This point can be illustrated by three examples taken from Table 1. In the case of carbon CEP-22, where $L = 0.40$ nm and $W_o = 0.20$ cm^3 g^{-1}, the micropore surface area calculated from eqn (3) is 1000 m^2 g^{-1}. On the other hand, the monolayer equivalent of W_o is only 563 m^2 g^{-1}, which indicates the presence of a single layer facing the two walls of the slit-shaped micropore. The enthalpy of immersion of this layer, facing both walls, is $-101/563 = -0.179$ J m^{-2} (a correction of 3 J g^{-1} is made to the experimental value of Δh_i for the wetting of the external surface area, $S_e = 25$ m^2 g^{-1}). On the other hand, if one considers a micropore surface area of 1000 m^2 g^{-1}, one obtains a value of $-101/1000 = -0.101$ J m^{-2}. The two values have different meanings in the case of a single layer.

For sample CEP-69, $L = 0.78$ nm, $S_{mi} = 1436$ m^2 g^{-1} and the monolayer equivalent of W_o is 1576 m^2 g^{-1}. This confirms that there are approximately two layers of benzene in the micropores and $h_i = -191/1436 = -0.133$ J m^{-2}. This value is higher than for an open surface. Finally, in the case of sample FTCB-30, the average micropore width is 1.12 and $S_{mi} = 393$ m^2 g^{-1}. The equivalent monolayer corresponds to 619 m^2 g^{-1}, which indicates the presence of approximately three layers in the average micropore of this carbon (one for each wall of 196 m^2 g^{-1} and a third between them). The specific enthalpy of immersion for the two layers in contact with the walls, a formal quantity, is $-57.7/393 = -0.147$ J m^{-2}. This is higher than for sample CEP-69, in spite of the fact that the influence of the opposite walls decreases. The reason for this is the presence of the middle layer, also subjected to the influence of both walls. It contributes to Δh_i and therefore to the apparent h_i value for the two layers in contact with the micropore walls.

It follows that no standard value of h_i can be proposed to determine S_{mi} (for example, -0.114 mJ m^{-2} in the case of benzene). Moreover, the experimental enthalpy of immersion also contains a contribution from the external surface area S_e, for which, on the other hand, the value of 0.114 J m^{-2} applies. This means that the quantity $S_{tot}(h_i) = \Delta h_i / h_i$ will not necessarily be compatible with the total surface area $S_{tot} = S_{mi} + S_e$ derived from the DR approach and confirmed by other techniques [2,3]. In the case of carbon FTCB-30, for example, $-\Delta h_i/0.114$ leads to an apparent total surface area of 646 m^2 g^{-1} instead of 496 m^2 g^{-1}, obtained through eqns (1)–(4). This point is illustrated in Fig. 3, which shows the ratio of the apparent surface areas $S_{tot}(h_i) = \Delta h_i(C_6H_6)/0.114$ to the total surface area $S_{mi} + S_e$ as a function of the average micropore size L. The data correspond to more than 40 active carbons investigated in our laboratory. It appears that the ratio between the two areas increases with the micropore size L, which confirms the predictions of eqn (7). This means that the total surface area of an unknown active carbon cannot be assessed from immersion calorimetry by using a standard value of h_i. Similar results would be obtained with other organic probes.

4. IMMERSION INTO WATER

Finally, we wish to discuss the case of the enthalpy of immersion of active carbons into water, $\Delta h_i(H_2O)$, which gives interesting and complementary information. As opposed to organic liquids, where the volume filling of micropores is the funda-

Table 1. Data for typical active carbons with micropore widths in the range $0.4 < L < 2$ nm. The quantities h_i are equal to the experimental enthalpies of immersion divided by S_{tot}

Carbon	W_o (cm^3 g^{-1})	E_o (kJ mol^{-1})	L (nm)	S_{tot} (m^2 g^{-1})	$-h_i(C_6H_6)$ (J m^{-2})	$-h_i(H_2O)$ (J m^{-2})
CEP-22	0.20	38.1	0.40	1025	0.101	0.035
CEP-52	0.33	31.8	0.52	1312	0.112	0.036
CMS	0.25	26.1	0.73	710	0.134	0.038
CEP-69	0.56	25.2	0.78	1463	0.132	0.047
CCA-25	0.43	22.7	0.95	893	0.152	0.033
FTCB30	0.22	21.0	1.12	496	0.148	0.041
LD43DA	0.43	20.2	1.22	785	0.145	0.059
CHEM V	0.45	19.0	1.42	718	0.178	0.052
BTH	0.43	18.1	1.61	677	0.171	0.059
N-125	0.64	16.6	2.08	715	0.242	0.044

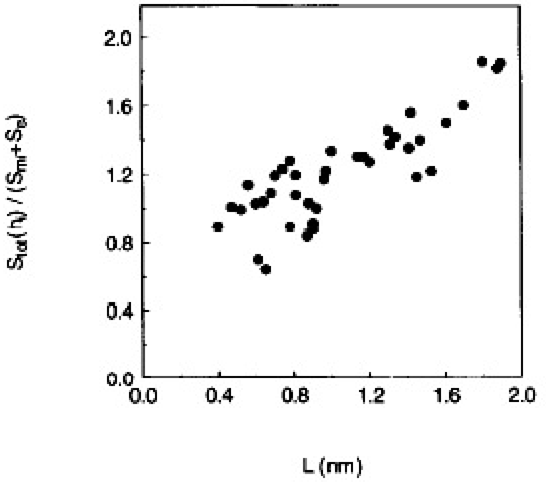

Fig. 3. Ratio of the apparent surface area $S_{tot}(h_i)=\Delta h_i(C_6H_6)/0.114\ J\ m^{-2}$ to $(S_{mi}+S_e)$ as a function of the average micropore width L. Data based on 45 active carbons.

mental process, water interacts strongly with so-called primary hydrophillic centres found on the surface [11,12]. The enthalpy of immersion reflects both contributions, as summed by the empirical relation [2,11]

$$-\Delta h_i(H_2O)\ (J\ g^{-1})=25a_o+0.6(a_s-a_o) \quad (8)$$

where a_o denotes the number of primary centres of the Dubinin–Serpinski equation [2,11,12] and a_s is the total amount of water adsorbed in the micropores (a supplementary term may be added for the wetting of the external surface area). For typical and untreated active carbons, it is found that a_o/a_s varies from 2 to 6%, which confirms that in eqn (8) the specific interactions are more important than the filling of the micropores. It also appears that the density of the primary centres a_o/S_{tot} is of the order of 1×10^{-3} mmol m^{-2} [11,13]. These observations suggest that the enthalpy of immersion is related, to some extent, to the total surface area S_t.

A statistical analysis of 40 typical active carbons, not subjected to any particular oxidizing treatment, shows that the specific enthalpy $h_i(H_2O)=\Delta h_i/S_{tot}$ varies from -0.035 to $-0.060\ J\ m^{-2}$. One obtains an average of $-0.048\ J\ m^{-2}$ and a standard deviation $\sigma=\pm0.010\ J\ m^{-2}$. The latter is relatively important, but it is found that within activation series the specific enthalpies are often similar. This is illustrated in Fig. 4, relating $\Delta h_i(H_2O)$ to S_{tot} for six active carbons prepared under similar conditions, from bituminous coal and anthracite [6]. In this case, the best fit corresponds to $h_i(H_2O)=-0.045\ J\ m^{-2}$. As opposed to organic liquids such as benzene, the enthalpy of immersion into water could therefore provide a first estimate of the total surface area for other carbons in a given activation series.

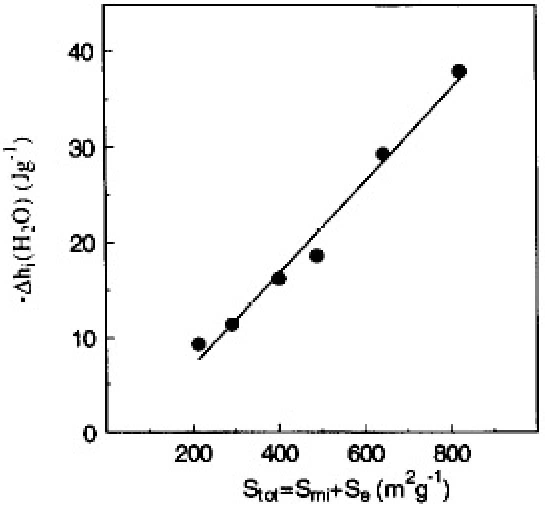

Fig. 4. Relation between $-\Delta h_i(H_2O)$ and $S_{tot}=S_{mi}+S_e$ for active carbons prepared from bituminous coals and anthracites [6]. The best fit corresponds to $h_i(H_2O)=-0.045\ J\ m^{-2}$.

In conclusion, the present paper illustrates the possibilities and limitations of immersion calorimetry used alone for the characterization of microporous carbons. It appears that a reliable assessment based on this technique still requires the knowledge of at least one isotherm to remove uncertainties. We believe that the adsorption of CH_2Cl_2 or C_6H_6 vapour near 293–298 K is a convenient choice, since it provides more reliable information than N_2(77 K) and/or CO_2 between 273 and 298 K.

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