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APPLICATIONS OF IMMERSION CALORIMETRY IN DUBININ'S THEORY AND IN ELECTROCHEMISTRY

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Abstract. This study shows that immersion calorimetry is a useful technique which simplifies considerably the analysis of porosity and chemical nature of activated carbons.

The characterization of activated carbons in the general theoretical framework of Dubinin's theory with its extensions to calorimetry and adsorption from solutions allows the identification of some key parameters for the performance of these materials in electrochemical capacitors.

Keywords: activated carbon; immersion calorimetry; porosity; electrochemical capacitor

1. Introduction

Activated carbons can be characterized within the framework of Dubinin's theory. The basic relation is the Dubinin–Radushkevitch (DR) equation[1]

$$W = W_o \exp\left[-\left(\frac{A}{\beta E_0}\right)^2\right] \qquad (1)$$

where W represents the volume adsorbed at temperature T and relative pressure p/p_s, W_o is the limiting volume adsorbed in the micropores and

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A = RTln(p_s/p); β and E_o are specific parameters depending on the adsorptive and on the adsorbent. W_o and E_o are usually obtained from the adsorption of small molecular probe (typically CO_2, CH_2Cl_2, and C_6H_6) with critical dimensions around 0.33–0.40 nm, and unhindered by constrictions in the structure.

In view of its thermodynamic basis, the DR equation can easily be used in the context of immersion calorimetry.[1,2] Starting from the definition of the isosteric heat of adsorption of a vapour q^{st} (>0)

$$[\,\partial ln(p)/\partial T\,]_{Na} = q^{st}/RT^2 \tag{2}$$

The inversed DR equation leads to q^{st} as a decreasing function of the micropore filling

$$q^{st}(T;\theta) = \beta E_o\{\,[ln(1/\theta)]^{1/2} + (\alpha T/2)[\,ln(1/\theta)]^{-1/2}]\} + \Delta H_{vap} \tag{3}$$

where α is the thermal expansion coefficient of the adsorbate. On the other hand, the net heat of adsorption defined as

$$q^{net}\,(T;\,\theta) = q^{st} - \Delta H_{vap} \tag{4}$$

is related to the enthalpy of immersion of the solid into the corresponding liquid by

$$-\Delta_i H\,(T) = q^{net}\,d\theta + h_{LV}S_{LV} \tag{5}$$

Taking into account that there is practically no liquid–vapour interface in micropores, it follows that

$$-\Delta_i H_{mi}\left(Jg^{-1}\right) = \int q^{net} d\theta = \frac{\beta\, \mathrm{W_0 E_0} \sqrt{\pi}\left(1+\alpha T\right)}{2V_m} \tag{6}$$

Since active carbons often present an external (non-microporous) surface area, S_e, the experimental enthalpy of immersion will include an extra contribution, corresponding to the wetting of this surface and

$$-\Delta_i H\left(Jg^{-1}\right) = \frac{\beta\, \mathrm{W_0 E_0} \sqrt{\pi}\left(1+\alpha T\right)}{2V_m} - h_i S_e \tag{7}$$

It appears, as a thermodynamic consequence of Dubinin's theory, that the enthalpy of immersion of a microporous carbon into organic liquids is related to the parameters of the adsorption isotherm (W_o, E_o and S_e). This formal link between both approaches leads to a detailed picture of the porous structure and of the chemical nature of activated carbons.

The experimental set-up required for immersion calorimetry is relatively simple.[1] The sample is outgassed at 10^{-5} Torr and around 523 K in a glass bulb with a brittle end. The bulb is sealed, introduced into a cell containing around 5 cm^3 of the wetting liquid and placed inside the calorimeter. Once thermal equilibrium is achieved, the brittle end of the bulb is gently broken and the liquid wets the sample. The corresponding heat evolution through 180 thermocouples is monitored as a function of time and the integration of this signal leads, with the help of an electrical calibration, to the enthalpy of immersion $\Delta_i H$. A typical experiment lasts approximately 30–45 min, which allows an important gain in time, if compared with classical adsorption experiments.

2. Application of Immersion Calorimetry for Structural and Chemical Characterization of Activated Carbons

2.1. STRUCTURAL ASPECTS OF IMMERSION CALORIMETRY

2.1.1. *Calorimetric studies of selective adsorption from aqueous solutions: determination of specific surface areas*

This section shows how the enthalpy of immersion of carbons into aqueous solution of caffeine (0.1 M) or phenol (0.4 M) becomes another source of information for the determination of specific surface area of carbons.[1,3–6]

Some years ago, a calorimetric approach[3] showed that the enthalpy of immersion of carbon blacks into aqueous solutions of caffeine is a linear function of the mass of carbon. The comparison of $\Delta_i H$ (J g^{-1}) with the S_{BET} (m^2 g^{-1}) of the materials led to an average specific enthalpy h_i of $-(0.112 \pm 0.015)$ J m^{-2}. This correlation, confirmed by the corresponding adsorption isotherm from the solution, implies that adsorption is limited to a single layer. This is also true for microporous carbons, where no volume filling process takes place, as opposed to adsorption from the vapour phase. It follows that for both porous and non-porous carbons the total surface area can be determined with a good accuracy from the enthalpy of immersion into an aqueous solution of caffeine with the help of the simple relation[1,3]

$$S_{total}\left(m^2 g^{-1}\right) = \frac{\Delta_i H_{caffeine}\,(J g^{-1})}{0.112\ (J m^{-2})} \tag{8}$$

Since the caffeine molecule cannot penetrate into micropores of less than approximately 0.6 nm, this procedure provides an estimate of the total surface area in carbons with pores wider than 0.6–0.7 nm.[1,3,4]

Subsequently, this technique has been used successfully with diluted aqueous solutions of phenol (0.4 M) and the study of carbon blacks and active carbons[5,6] suggested a process similar to that observed for caffeine. Phenol appears to form a monolayer, which provides information on the surface area of pores above approximately 0.45 nm. In this case, the specific enthalpies h_i corresponded to $-(0.109 \pm 0.003)$ J m^{-2} and

$$S_{total}\left(m^2 g^{-1}\right) = \frac{\Delta_i H_{phenol}\,(J g^{-1})}{0.109\,(J m^{-2})} \tag{9}$$

It should be pointed out that the enthalpy of immersion into aqueous solution of phenol is affected by the surface acidity of the carbon since water is adsorbed preferentially by the oxygen-containing surface groups.[5,6] The reduction in specific surface area has been estimated to be around 70 m^2 per mmol of surface oxygen, but due to a compensation effect, Eq. (9) still provides a good assessment of S_{total} in the case of oxidized carbons.

On the other hand, it appears that the enthalpies of immersion of the microporous carbons into concentrated solutions are generally larger than observed for the dilute solution. This increase confirms that the adsorption of phenol from concentrated aqueous solutions corresponds to a process of micropore filling and that it is not limited to the coating of the micropore walls, as observed for dilute solutions.[6]

2.1.2. *The assessment of micropore size distribution of carbons*

Equation (7) can be used to evaluate, on the basis of the experimental enthalpies of immersion, the volumes $W(L_c)$ filled by a molecular probe of critical dimension L_c,[1]

$$W(L_c) = -\frac{[\Delta_i H - h_i S_e]\,2V_m}{\beta E_o \sqrt{\pi}\,(1+\alpha T)} \tag{10}$$

E_o is the characteristic energy obtained from the reference isotherm of a small adsorbate (CH_2Cl_2, C_6H_6, CO_2, etc.) and L_c is the smallest micropore width accessible to the molecules of the liquid.

The use of a series of liquids of known molecular dimensions (i.e. dichloromethane [0.33 nm], benzene [0.41 nm], cyclohexane [0.54 nm], carbon tetrachloride [0.63 nm], cyclododeca-1,5,9-triene [0.76 nm], tri-2,4-xylyl phosphate [1.5 nm]) leads to the micropore size distribution.[1,7–9]

However, this technique reflects the true pore size distribution only as long as the entry into wider pores is not limited by constrictions smaller than their actual size. If such "gate" effects are present, one obtains an apparent pore size distribution.[8,9] The difference between the apparent and the real pore size distributions can been illustrated if one uses the approach based on the modelling of CO_2 adsorption, a molecule which is small enough to bypass gate effects.[9] The two techniques are therefore complementary and provide a refined picture of the porous structure.

2.2. CHEMICAL ASPECTS OF IMMERSION CALORIMETRY

2.2.1. *Detection of surface oxygen from immersion into water*

As opposed to organic liquids and vapours, where the volume filling of micropores and adsorption on the external surface area S_e are the fundamental processes, water interacts strongly with functional groups of carbon surface. An interesting consequence is the possibility to estimate the number of surface groups from the experimental enthalpies of immersion of active carbons into water and into benzene at 293 K and taking into account the chemistry of the surface through an excess enthalpy of immersion, $\Delta_i H\ (H_2O)_{excess}$. As reported earlier,[10,11] water interacts in a similar fashion with surface functionalities containing mainly oxygen (–12.1 J $mmol^{-1}$) and with basic groups (–10.3 J $mmol^{-1}$). The latter are characterized by their equivalents of HCl and it appears that most of them do not contain oxygen. An overall assessment for a large variety of activated carbons led to[10]

$$\Delta_i H\ (H_2O)\ (J\ g^{-1}) = 0.210\ \Delta_i H\ (C_6H_6) - 9.9\ (J\ mmol^{-1})\ [O + HCl] \quad (11)$$

with average specific interactions around –(9.9 ± 0.7) J $mmol^{-1}$ of oxygen or HCl mequivalents of basic sites. As the concentration of the basic sites of typical carbons is not high, the bulk of the specific interactions is related to oxygen atoms.

2.2.2. *Determination of acidic and basic groups on carbon surface*

The correlation between the net enthalpy of neutralization into 2N aqueous solution of NaOH

$$\Delta_i H(NaOH)_{net} = \Delta_i H(NaOH) - \Delta_i H(H_2O) \quad (12)$$

and the number of equivalents of acid obtained from direct titration leads to a net enthalpy of neutralization of –(41.1 ± 1.8) kJ eq^{-1} for acidic sites. A similar approach for the net enthalpy of neutralization into 2N HCl

$$\Delta_i H(HCl)_{net} = \Delta_i H(HCl) - \Delta_i H(H_2O) \quad (13)$$

leads to a neutralization energy of –(52.3 ± 2.0) kJ eq^{-1} for basic sites.[12]

Further calorimetric experiments with 1N aqueous solutions of $NaHCO_3$ allow a clear distinction between carboxylic sites the other acidic sites. Selective neutralization of carboxylic groups reported a value of $-(39.7 \pm 1.7)$ kJ eq^{-1} which is close to the result obtained with NaOH for the bulk of the acidic groups.[12]

3. Application of Immersion Calorimetry to the Characterization of Carbons Used in Electric Double Layer Capacitors

Electrochemical capacitors have generated wide interest in recent years for high power applications where high efficiency and long cycle life are required. At the present, most commercial devices correspond to those referred to as electrical double layer capacitors (EDLCs) which perform by an electrostatic attraction between electric charges accumulated on the electrode surface and ions of opposite charge in the electrolyte side.[13]

Activated carbons are widely used as electrodes in EDLCs systems, as far as their high surface areas provide large interfaces for the formation of the electric double layer.[14] The reliable characterization of activated carbons in the general theoretical framework of Dubinin's theory, with its extensions to calorimetry and adsorption from solutions, leads to the identification of key parameters for high performance in electrochemical capacitors.[15–17] In this context, the determination of the real surface of the carbons is of prime importance and immersion calorimetry plays a major role, as illustrated below. Useful information can only be gained from several independent techniques, including the technique based on aqueous phenol solutions (see Section 2.1). As discussed in detail elsewhere, S_{BET}, is often too large[18] and leads to erroneous surface related properties.[15,17] As a consequence, it is difficult to establish reliable correlations.

In the case of 2M H_2SO_4 aqueous electrolyte, the study of a large variety of activated carbons showed that the specific capacitance at low current density (1 mA cm^{-2}), C_o, depends on standard contributions from the total surface area and from the surface groups which desorb as CO in Thermally Programmed Desorption (TPD)[15]:

$$C_o[H_2SO_4]\,(F\,g^{-1}) = 0.081\,(F\,m^{-2})\,S_{tot} + 63\,(F\,mmol^{-1})[CO](mmol\,g^{-1}) \quad (14)$$

This approach reflects the important role played by both the surface area S_{tot} and its chemical nature in the overall capacitance of activated carbons. It also establishes the origin of a pseudocapacitive process (via redox reactions involving CO-desorbing groups) which should be added to the purely EDLC mechanism. Furthermore, this approach explains the important scatter for the values of surface-related capacitance in (F m^{-2})

quoted in the literature with no clear linear correlation between the specific capacitance and the specific surface area of activated carbons.

On the other hand, surface oxide related pseudocapacitance contributions in the aprotic electrolyte 1M $(C_2H_5)_4NBF_4$ in acetonitrile are much weaker (9 F mmol^{-1} of CO generated in TPD, for the best performing carbons) than in the H_2SO_4 electrolyte (63 F mmol^{-1} of CO).[16] As illustrated by Figure 1, the specific capacitance at low current density, C_o, increases linearly with the total specific surface area, following the approximate correlation

$$C_o[(C_2H_5)_4NBF_4]\ (Fg^{-1}) = 0.09\ (Fm^{-2})\ S_{tot}\ (m^2g^{-1}) \qquad (15)$$

The deviation observed for some carbons is attributed to exclusion effects in the aprotic electrolyte. The fact that these materials display average micropore sizes or "gate" effects around 0.5–0.6 nm[16] limits the internal surface area accessible to ions $(C_2H_5)_4N^+$ with critical dimension around 0.69 nm.

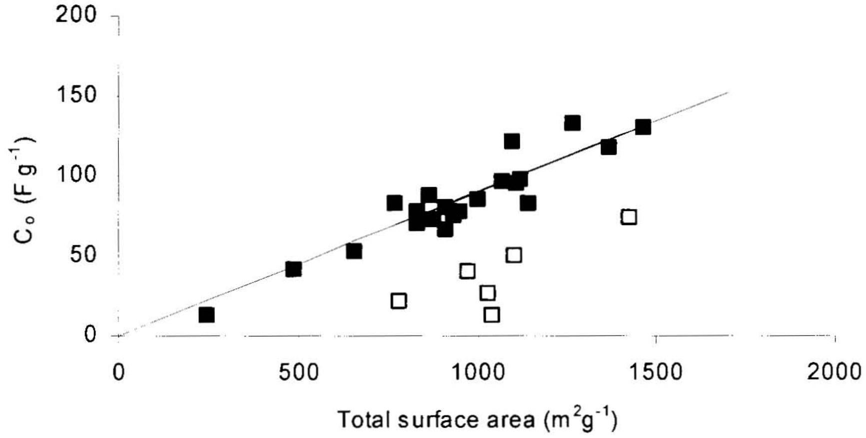

Figure 1. Variation of the specific capacitance (1 mA cm^{-2}) of activated carbons with the total surface area in 1M $(C_2H_5)_4NBF_4$/acetonitrile. The deviation for some carbons (□) reflects exclusion effects in the aprotic electrolyte.

Finally, the present work confirms the possibilities of immersion calorimetry used alone for the prediction of the specific capacitance at low current density of unknown activated carbons in the aprotic electrolyte 1M $(C_2H_5)_4NBF_4$ in CH_3CN (Figure 2). As far as the specific capacitance and the enthalpy of immersion into benzene, $-\Delta_iH[C_6H_6]$, are surface-related properties of the materials, one obtains a relatively good correlation between both parameters

$$C_o[(C_2H_5)_4NBF_4]\ (F\,g^{-1}) = -0.57\ (F\,J^{-1})\ \Delta_iH[C_6H_6]\ (J\,g^{-1}) \qquad (16)$$

As suggested by recent calorimetric tests,[17] the micropore system of typical activated carbons where the average micropore size is above 0.8 nm displays a similar accessibility to $(C_2H_5)_4NBF_4$/acetonitrile and to benzene. The deviations observed in Figure 2 (□) confirm the limited accessibility of the aprotic electrolyte into micropores of less than 0.7 nm.

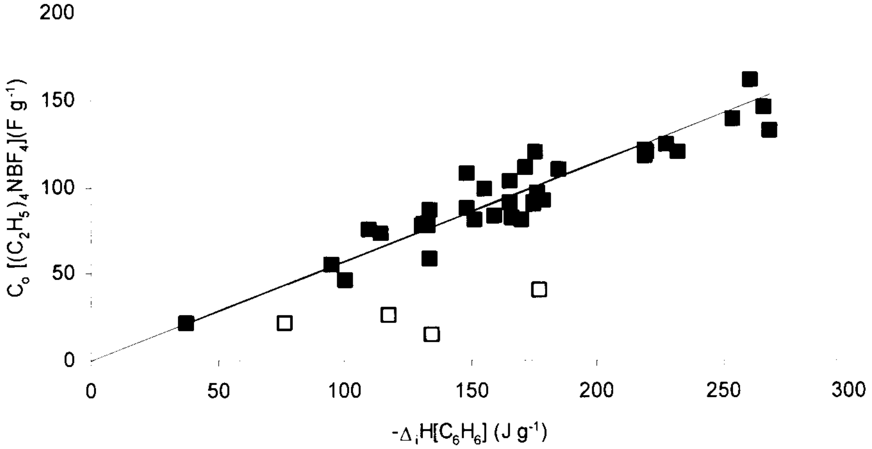

Figure 2. Correlation between the specific capacitance (1 mA cm^{-2}) of different activated carbons in the aprotic electrolyte, C_o $[(C_2H_5)_4NBF_4]$, and the enthalpy of immersion of carbons into benzene, $-\Delta_iH(C_6H_6)$. (□) Carbons with micropore widths below 0.7 nm.

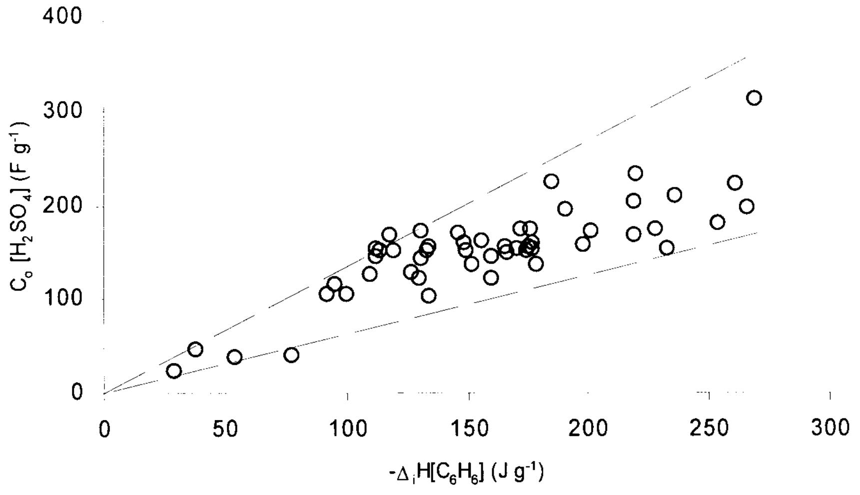

Figure 3. Evolution of the specific capacitance (1 mA cm^{-2}) of different activated carbons in H_2SO_4 aqueous electrolyte, C_o $[H_2SO_4]$, and the enthalpy of immersion of carbons into benzene, $-\Delta_iH(C_6H_6)$.

On the other hand, Figure 3 shows the limitations of this technique to assess, with a good accuracy, the suitability of a carbon to be used in H_2SO_4 aqueous capacitors. It is not surprising, in view of the significant influence of the CO-generating surface groups on the capacitance in H_2SO_4 aqueous medium (see Eq. (14)) whereas the enthalpy of immersion into a non-specific liquid such as benzene does not depend on the presence of oxygen.

4. Conclusions

Immersion calorimetry provides complementary information to the adsorption isotherms and simplifies considerably the assessment of porosity and chemical nature of activated carbons.

The assessment of activated carbons in the framework of Dubinin's theory with its extensions to calorimetry and adsorption from solutions led to the identification of key parameters for the performance of these materials in electrochemical capacitors. For 2M H_2SO_4 aqueous electrolyte, the limiting capacitance of activated carbons at low current densities depends essentially on the total surface area and on the surface groups which generate CO in TPD. In the case of the aprotic electrolyte 1M $(C_2H_5)_4NBF_4$ in acetonitrile, the specific capacitance increases linearly with the total specific surface area, the contribution from surface oxygen groups being less significant.

Micropore widths or "gate" effects of less than 0.7 nm notably reduce the internal surface area accessible to ions $(C_2H_5)_4N^+$ of the aprotic electrolyte, as opposed to the SO_4^{2-} ion of the aqueous medium.

This work confirms the possibilities of immersion calorimetry used alone for the prediction of the specific capacitance of carbons in 1M $(C_2H_5)_4NBF_4$ in CH_3CN, but it also shows the limitations of this technique to assess, with a good accuracy, the suitability of a carbon to be used as electrodes in H_2SO_4 aqueous capacitors.

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