The Use of Immersion Calorimetry for the Quantitative Analysis of Impregnating Agents on Active Carbons

It has been shown that enthalpies of immersion into organic liquids can be used to characterize the micropore system[1–2] and the external surface[3] of active carbon. In the case of liquids whose vapours are adsorbed according to the Dubinin–Radushkevich equation[2], the enthalpy of immersion for the micropore system of volume \( W_m \) and characteristic energy \( E_0 \) is given by

\[
\Delta H(I_{\text{g}}) = -\beta E_0 (1 + \alpha T)^{\frac{1}{\alpha}} W_m/2V_a \tag{1}
\]

\( \alpha \) being the expansion coefficient of the organic liquid and \( V_a \), its molar volume at \( (T_P) \). The affinity coefficient \( \beta \) is a specific parameter of the adsorbate relative to benzene, for which \( \beta = 1 \) by convention.

If a non-negligible external surface \( S_e \) is also present in the solid, the experimental enthalpy of immersion also contains a contribution due to the wetting of this surface,

\[
\Delta H(\text{exp}) = \Delta H(\text{micropores}) + S_e \cdot h
\]

\[
= -\beta E_0 (1 + \alpha T)^{\frac{1}{\alpha}} W_m/2V_a + S_e \cdot h \tag{2}
\]

\( h \), being the specific enthalpy in J/m\(^2\) (see Table 1). Since \( S_e \cdot h \) only represents a fraction of the total enthalpy of immersion, one may use with a good approximation the values of \( h \) corresponding to the immersion of graphitized carbon blacks into organic liquids[4]. As shown earlier[3], there exists a good correlation between various techniques used for the determination of the external (or non-microporous) area.

If the specific parameters \( E_0 \), \( W_m \) and \( S_e \) of a given active carbon are known, it is possible to compute the expected enthalpy of immersion into an organic liquid of molar volume \( V_a \) and affinity coefficient \( \beta \), provided that the accessibility of the micropore system corresponds to the volume \( W_m \) accessible to the reference molecule.

If the experimental value of \( \Delta H(T_P) \) is smaller than that calculated from eqn (2), molecular sieve effects are present and consequently micropore distributions can be obtained from these experiments[5]. It can be seen from eqn (1) that for organic liquids with similar molecular sizes, the ratio of the enthalpies of immersion in the micropore system is given by

\[
\Delta H(1)/\Delta H(2) = \beta_1 (1 + \alpha_1 T)V_{\text{ad}}/\beta_2 (1 + \alpha_2 T)V_{\text{ad}}. \tag{3}
\]

This relation does not contain parameters \( E_0 \) and \( W_m \) and therefore the enthalpy of immersion of the micropores into a given liquid can be calculated on the basis of an experiment performed with a reference liquid.

The enthalpy of immersion given by eqns (1), (2) corresponds to non-specific interactions, i.e., to a physical process, as opposed to specific and chemical interactions which can also take place. In the case of active carbons containing impregnating agents such as triethylene diamine (1,4-diaza-dicyclo[2.2.2]octane: TEDA)[6] or a standard mixture of inorganic salts, the enthalpies of immersion into specific liquids will correspond to contributions from the physical and chemical interactions. TEDA will react with CH\(_3\)J, whereas standard mixtures of copper and chromium salts react strongly with CCl\(_4\), after heating under vacuum at 673 K.

As found experimentally, if the impregnants represent a few percent (1–15) in weight of the activated carbon, the contributions from physical or chemical interactions on immersion are of the same order of magnitude. Since the non-specific component of the enthalpy of immersion can be calculated beforehand with eqn (2), it follows that immersion calorimetry can lead to a quantitative assessment of the impregnants on the basis of their specific interactions.

This technique is described below.

The experiments were performed with a well-defined activated carbon (\( E_0 = 17.7 \) kJ/mol, \( W_a = 0.48 \) cm\(^3\)/g and \( S_e = 90 \) m\(^2\)/g), on which vapours of CH\(_3\)J and CCl\(_4\) were also adsorbed at 293 K, in order to determine their affinity coefficients: \( \beta(\text{CH}_3\text{J}) = 0.70 \) and \( \beta(\text{CCl}_4) = 1.05 \). Impregnation with TEDA was carried out from solutions in ethanol and corresponded to 1–11 percent by weight of dry carbon. The Cr/Cu salts were deposited by soaking the carbon at 293 K with aqueous ammonia solutions of various concentrations. The amounts of impregnants, expressed in weight percent of dry carbon, were determined by weighing the materials after drying to 383 K.

Prior to immersion, the solids impregnated with TEDA were outgassed at 373 K for 10–15 hours. Those containing the Cr/Cu salts were heated to 673 K for 12–16 hours, under vacuum, in order to achieve a reproducible treatment. Thermogravimetric experiments carried out with the impregnated carbons, reveal an irreversible and exothermic transformation between 170 and 204°C, with a total loss in weight of 23% between 100 and 400°C. This reaction, not observed for the pure mixture of impregnating agents, probably leads to the active form reacting with CCl\(_4\).

The enthalpies of adsorption in n-C\(_3\)H\(_7\), n-C\(_4\)H\(_8\), CH\(_3\)I, and CCl\(_4\) were determined at 293 K, as described previously[1], with a reproducibility of 1%.

In the case of impregnated carbons of known external surface area \( S_e \), the enthalpy of immersion into an inert liquid such as n-pentane or benzene, leads to \( \Delta H(\text{micropore}) \) by using eqn (2) and the value of \( E_0 \), given in Table 1. The non-specific contributions to the enthalpies of immersion of the reagents, CH\(_3\)I or CCl\(_4\), can be calculated from eqns (3) and (2) and the specific interactions are obtained as the differences with the experimental enthalpies of immersion.

The use of n-C\(_3\)H\(_7\) or n-C\(_4\)H\(_8\) takes into account possible modifications of the active carbon's properties on impregnation—essentially of the micropore volume \( W_m \), and to a lesser extent of \( E_0 \)—which would introduce an error into the \( a \ priori \) calculations of \( \Delta H(1) \). This effect is illustrated in the figures by the slight decrease in the non-specific interactions (closed circles), resulting from the blocking of some micropores.

The results for the carbons impregnated either with TEDA or with the Cr/Cu salts, are shown in Figs. 1 and 2. The specific contributions to the enthalpies of immersion are 1650 ± 50 J/g for TEDA in CH\(_3\)I, and 680 ± 14 J/g for the original Cr/Cu salt, reacting with CCl\(_4\), after the heat treatment described above. (It is interesting to note that the reaction of pure TEDA with CH\(_3\)I leads to an enthalpy of 1433 ± 50 J/g.)
Table 1. Specific properties of the organic liquids used for immersion experiments at 293 K

<table>
<thead>
<tr>
<th>Liquid</th>
<th>β</th>
<th>α</th>
<th>(\Delta h_1)</th>
<th>(V_m(293 K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_6H_6)</td>
<td>1.00</td>
<td>1.24 \times 10^{-3}</td>
<td>114</td>
<td>88.91</td>
</tr>
<tr>
<td>n-C_3H_12</td>
<td>1.15</td>
<td>1.62 \times 10^{-3}</td>
<td>110</td>
<td>115.22</td>
</tr>
<tr>
<td>CH_3I</td>
<td>0.70</td>
<td>1.24 \times 10^{-3}</td>
<td>93</td>
<td>62.28</td>
</tr>
<tr>
<td>CCl_4</td>
<td>1.05</td>
<td>1.22 \times 10^{-3}</td>
<td>115</td>
<td>96.50</td>
</tr>
</tbody>
</table>

It also appeared that in the case of impregnation with both materials, TEDA and the Cr/Cu salts, only the former could be characterized reliably, as the heat treatment to 673 K in the presence of TEDA leads to spurious results for the immersion into CCl_4.

The techniques described above can also be applied successfully to the case of other materials deposited on active carbons. In the case of CaCl_2, used as an in situ drying agent, the immersion technique with water leads to an enthalpy of solution of 746.6 \text{J/g} on the carbon, against 738.6 \text{J/g} for pure CaCl_2. In the case of water, however, one has to know the contribution to the enthalpy of immersion resulting from the specific interactions with hydrophilic centres on the carbon.[2,7].

Fig. 1. The system (activated carbon + Cr/Cu salts)/CCl_4 at 293 K. Experimental (○) and calculated non-specific (●) enthalpies of immersion and the specific interactions (Δ) between the impregnant treated at 673 K and CCl_4. The calculated enthalpies are based on the data for benzene.

Fig. 2. The system (activated carbon + Cr/Cu salts)/CCl_4 at 293 K. Experimental (○) and calculated non-specific (●) enthalpies of immersion and the specific interactions (Δ) between the impregnant treated at 673 K and CCl_4. The calculated enthalpies are based on the data for benzene.

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REFERENCES