

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_0 and characteristic energy E_0 is given by

$$\Delta H_i(J/g) = -\beta E_0(1 + \alpha T)\sqrt{\pi}W_0/2V_m \quad (1)$$

α being the expansion coefficient of the organic liquid and V_m its molar volume at $(T;p)$. The affinity coefficient β is a specific parameter of the adsorptive 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,

$$\begin{aligned} \Delta H_i(\text{exp}) &= \Delta H_i(\text{micropores}) + S_e \cdot h_i \\ &= -\beta E_0(1 + \alpha T)\sqrt{\pi}W_0/2V_m + S_e \cdot h_i \end{aligned} \quad (2)$$

h_i being the specific enthalpy in J/m^2 (see Table 1). Since $S_e \cdot h_i$ only represents a fraction of the total enthalpy of immersion, one may use with a good approximation the values of h_i 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_0 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_m and affinity coefficient β , provided that the accessibility of the micropore system corresponds to the volume W_0 accessible to the reference molecule.

If the experimental value of $\Delta H_i(T;p)$ 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

$$\Delta H_i(1)/\Delta H_i(2) = \beta_1(1 + \alpha_1 T)V_{m1}/\beta_2(1 + \alpha_2 T)V_{m2} \quad (3)$$

This relation does not contain parameters E_0 and W_0 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 triethylenediamine (1,4-diazabicyclo[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_3I , 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, $W_0 = 0.48$ cm³/g and $S_e = 90$ m²/g), on which vapours of CH_3I and CCl_4 were also adsorbed at 293 K, in order to determine their affinity coefficients: $\beta(\text{CH}_3\text{I}) = 0.70$ and $\beta(\text{CCl}_4) = 1.05$. Impregnation with TEDA was carried out from solutions in ethanol and corresponded to 1-11 in 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 $n\text{-C}_5\text{H}_{12}$, C_6H_6 , CH_3I 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 $\Delta H_i(\text{micropore})$ by using eqn (2) and the value of h_i given in Table 1. The non-specific contributions to the enthalpies of immersion of the reagents, CH_3I 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 immersions. The use of $n\text{-C}_5\text{H}_{12}$ or C_6H_6 takes into account possible modifications of the active carbon's properties on impregnation—essentially of the micropore volume W_0 and to a lesser extent of E_0 —which would introduce an error into the *a priori* calculations of ΔH_i . 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 per g of TEDA in CH_3I , and 680 ± 14 J per g of 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_3I leads to an enthalpy of 1433 ± 50 J/g.)

Table 1. Specific properties of the organic liquids used for immersion experiments at 293 K

Liquid	β	α [K ⁻¹]	$-h_i$ [mJ/m ²]	$V_m(293\text{ K})$ [cm ³ /mol]
C ₆ H ₆	1.00	1.24·10 ⁻³	114	88.91
n-C ₅ H ₁₂	1.15	1.62·10 ⁻³	110	115.22
CH ₃ I	0.70	1.24·10 ⁻³	93	62.28
CCl ₄	1.05	1.22·10 ⁻³	115	96.50

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 CCl₄.

The techniques described above can also be applied successfully to the case of other materials deposited on active carbons. In the case of CaCl₂, used as an *in situ* drying agent, the immersion technique with water leads to an enthalpy of solution of 746.6 J/g on the carbon, against 738.6 J/g for pure CaCl₂. In the case of water, however, one has to know the contribution to the enthalpy of immersion re-

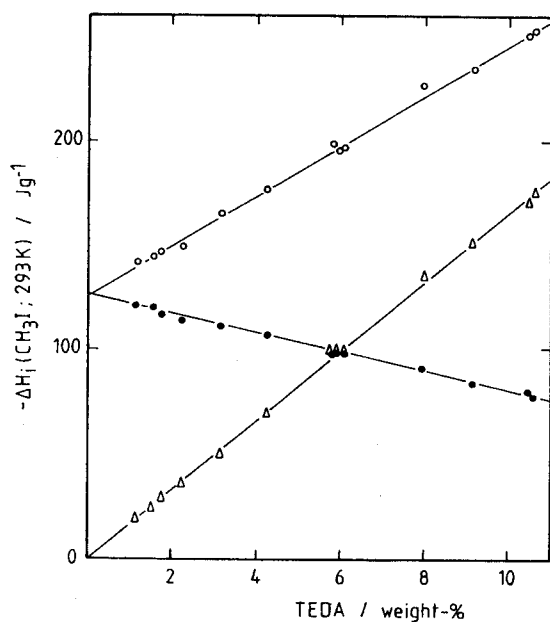


Fig. 1. The system (activated carbon + TEDA)/CH₃I at 293 K. Experimental (O) and calculated non-specific (●) enthalpies of immersion and the specific interactions (Δ). The calculated enthalpies are based on the data for *n*-pentane.

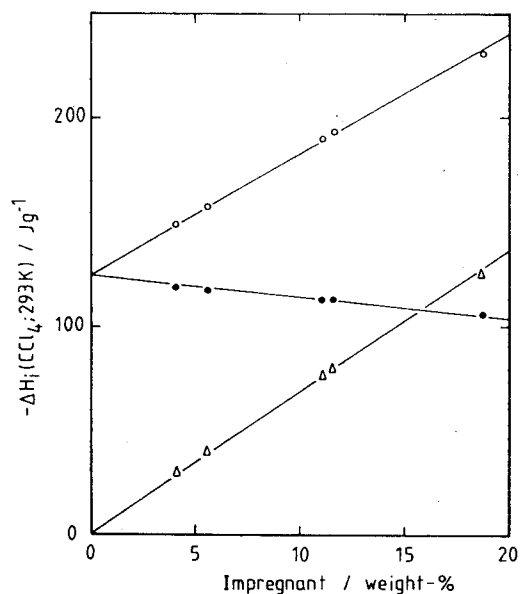


Fig. 2. The system (activated carbon + Cr/Cu salts)/CCl₄ at 293 K. Experimental (O) and calculated non-specific (●) enthalpies of immersion and the specific interactions (Δ) between the impregnant treated at 673 K and CCl₄. The calculated enthalpies are based on the data for benzene.

sulting from the specific interactions with hydrophilic centres on the carbon[2,7].

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

F. KRAEHENBUEHL
B. SCHMITTER
F. STOECKLI

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