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Thermochimica Acta 310 (1998) 217–222

thermochimica acta

Experimental study at the solid/liquid interface: Enthalpies of wetting of several liquids onto active carbon[1]

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Received 29 April 1997; received in revised form 13 June 1997; accepted 16 June 1997

Abstract

Enthalpies of wetting of several pure liquids onto active carbon were measured at 298.15 K with a quasi-isothermal microcalorimeter Setaram MS 80 II. New measuring cells with three independent cavities of about 15 cm^3 were created. The advantage of this new method is the high weight-in of active carbon and a reduced time per measurement for reaching a constant baseline. Experiments were carried out with *n*-alkanes, 1-alkanols, cyclohexane, 2,2,4-trimethyl-pentane (isooctane) and water. The experimental results for the enthalpy of wetting show a dependence of the geometric heterogeneity of the active carbon and the polarity of liquids. © 1998 Elsevier Science B.V.

Keywords: Enthalpies of wetting; Active carbon; Adsorption; Isothermal calorimetry

1. Introduction

Enthalpies of wetting give an insight into the interactions at the solid/liquid interface. Especially the examinations with pure liquids and the variation of their functional groups show the influence of specific electrostatic interactions with the solid surface. The calorimetric effect depends on the polarity, the size of the molecules and the energetic and geometric heterogeneity of the adsorbent. This paper is part of a project which examines enthalpies of wetting of pure liquids, enthalpies of displacement of binary liquid mixtures and the surface excess, i.e. the phase equilibrium of binary liquids on several active carbons. The aim of this project is the development of the Universal Group Contribution Model for liquid-phase adsorption (UGCMA), which predicts these thermodynamic properties (Friese et al. [1]).

This paper describes measurements of enthalpies of wetting $\Delta_w H$ of *n*-alkanes, 1-alkanols, cyclohexane, 2,2,4-trimethyl-pentane (isooctane) and water on a peat active carbon. Special attention was paid to the pretreatment of the active carbon. The granular active carbon was pulverized and the grain size distribution was measured. An activation procedure without oxidation was developed and a specially designed measuring cell for the calorimetric measurements was built.

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[1] Presented at the Twelfth Ulm-Freiberg Conference, Freiberg, Germany, 19–21 March 1997

PII S0040-6031(97)00399-7

2. Experimental

2.1. Materials

The reagents were used without further purification: methanol (purity 99.9% HPLC, Roth); ethanol (>99.8%, BfB); 1-butanol (>99.5%, Merck); 1-hexanol (>98%, Merck); 1-octanol (99.5%, Riedel-de-Haën); 1-decanol (>99%, Merck); *n*-hexane (99% p.a., Roth); 1-heptane (>99%, Roth); *n*-octane (99%, Merck); *n*-decane (99%, Aldrich); *n*-dodecane (99%, Merck); cyclohexane (99.8% p.a., Fluka); and 2,2,4-trimethyl-pentane (isooctane, 99.9% HPLC, Roth). The water content of the liquids were measured by Karl–Fischer titration. Especially the alkanols showed an unacceptable water content. Those liquids were dried with molecular sieve and degassed. Finally, the water content of all liquids was below 100 ppm.

The adsorbent used, active carbon from Roth (Karlsruhe, Germany), has the following properties (taken from the package label): raw material peat; bulk density 260 g/l; particle size 1–3 mm; BET 750 m^2/g; iodine number 800 mg/g; moisture 2%; and ash content 6%. Experimental results of surface excess measurements (Peel et al. [2]) show the necessity of a small grain size to reduce the time for getting equilibrium. Due to calculations with a diffusion model (Furusawa and Smith [3]) the diameter of active carbon particles should be below 20 μm. An agate ball mill was used to pulverize the active carbon. The grain size distribution for three different grinding times is shown in Fig. 1. For all calorimetric measurements, a 30 min grinding time was chosen because the pulverized active carbon showed a relatively narrow grain size distribution with the smallest mean value. Longer grinding times caused re-agglomeration of particles.

The carbon was activated in a vacuum oven at 1 Pa. The temperature and the duration of the activation procedure were varied. After 4 h, at 120°C, the mass loss was constant. At higher temperatures, a constant mass loss per time occurred due to a slight oxidation of carbon atoms. This activation method is similar to procedures given by several authors (Peel et al. [2], Joshi et al. [4]). Precise density measurements and a gas-chromatographic analysis of the condensed vapour phase showed only the existence of water on the surface and no organic vapours. The activation procedure was finished by cooling down the active carbon in a vacuum exsiccator. Then the calorimetric ampoule was filled at ambient pressure.

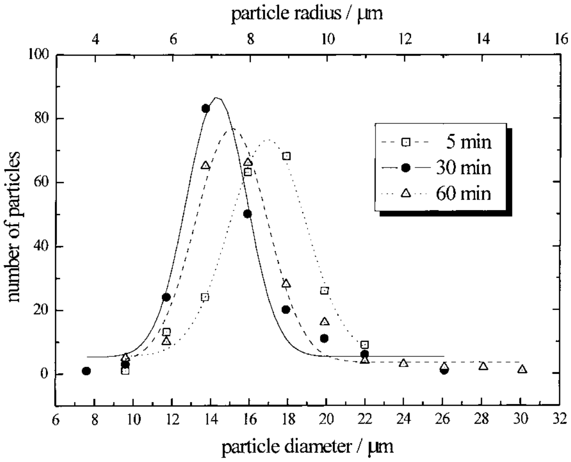

Fig. 1. Grain size distribution of the pulverized active carbon.

The surface characteristic was studied by selective stepwise titrations in order to determine the part of the acidic (phenolic: 0.1889 mmol/g, lactonic: 0.0000 mmol/g and carboxylic: 0.0000 mmol/g) and basic (chromenic and pyronic: 0.5993 mmol/g) functional groups. The iodine and methylene blue number were determined to be 940 and 220 mg/g, respectively. The pore size distribution was calculated from nitrogen adsorption isotherm data using the density-functional theory (Fig. 2).

2.2. Calorimeter

We started the measurement of heats of wetting using a quasi-isothermal microcalorimeter SETARAM MS 80 II. Special measuring cups were developed as shown in Fig. 3. The activated adsorbent is given into the inner cylinders, which are closed by sinter plates at the top. The sinter plates have a mean pore diameter of 3 μm and a height of 3 μm, i.e. the wetting area can be assumed as being free of vapour of the wetting liquid at the beginning of an experiment. Each cell can be calibrated electrically by using the built-in 50 Ω resistors.

After reaching a constant baseline (5 to 8 h), an electrical calibration with a Knick precision DC power

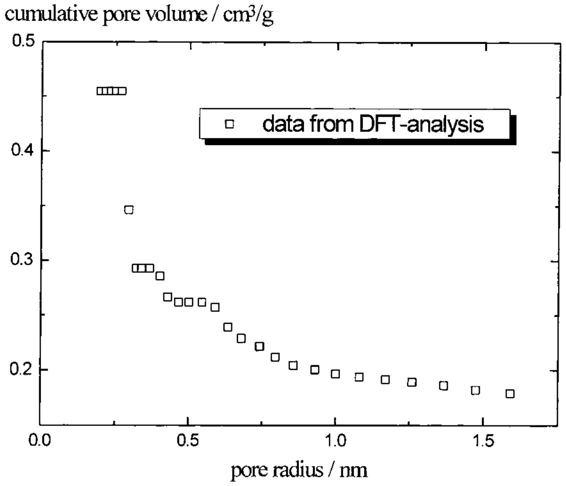

Fig. 2. Pore size distribution.

source driven by a time switch begins (4 h). Then liquid is delivered by $\dot{V} = 0.05$ ml/min for 5 h through the inlet tube into the inner cylinder (Fig. 4) by an HPLC pump. The pressure drop due to the sinter plate can be neglected. In order to guarantee complete wetting, the pump is driven until the liquid is delivered into the waste bottles. Afterwards, an electrical calibration (4 h) is carried out. The whole procedure

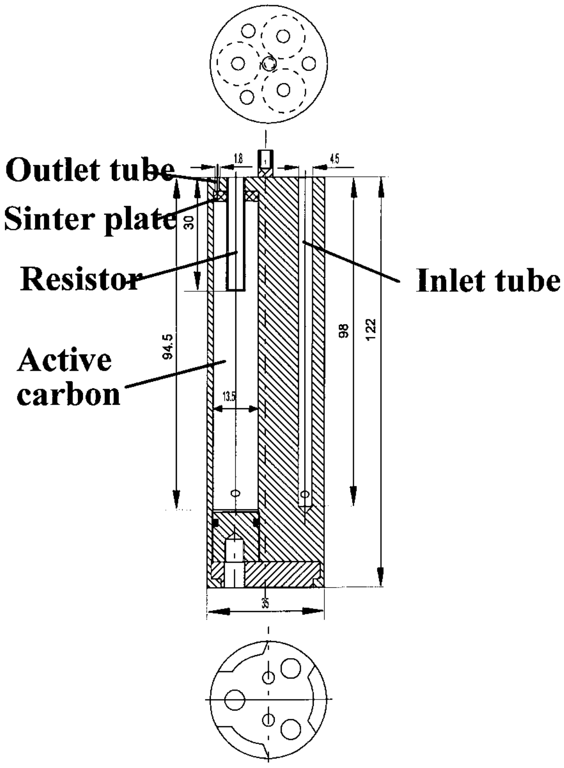

Fig. 3. Semi-batch measuring cup for heats of wetting.

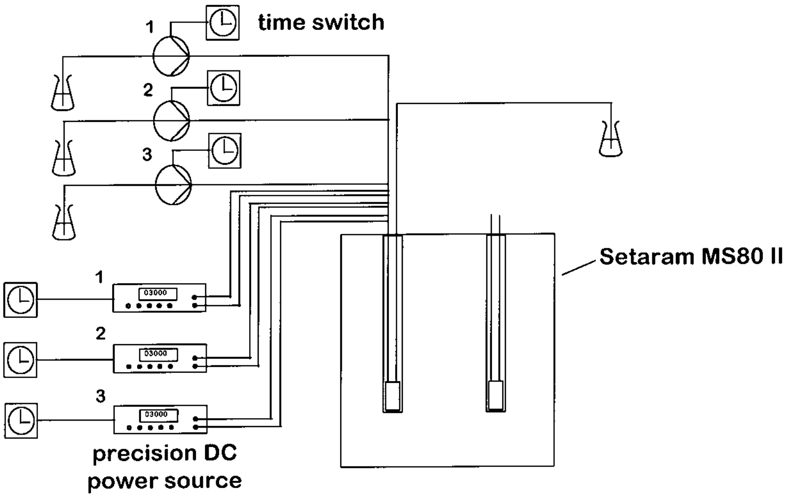

Fig. 4. Calorimetric setup.

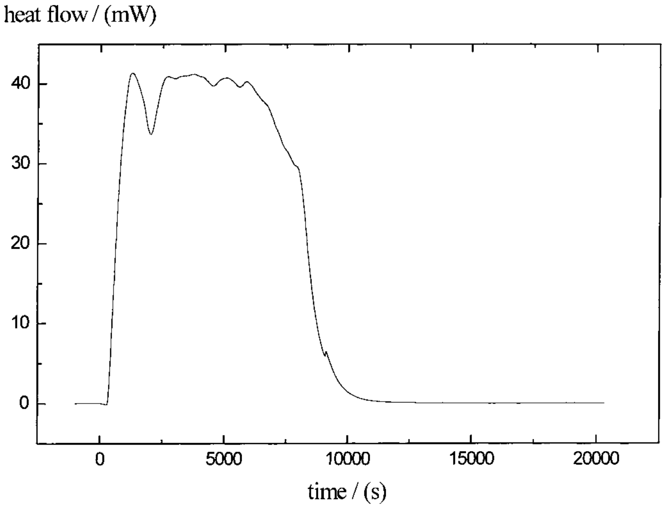

Fig. 5. Adsorption of liquid 1-butanol on active carbon (typical curve).

repeats itself with the next measuring cylinder, beginning with the first electrical calibration. The experiments were carried out at 298.15 K.

Fig. 5 shows a complete measurement curve for 1-butanol on active carbon. There is a sufficient heat exchange between the liquid and calorimeter cylinder before entering the measuring cylinder. Convectious heat losses through the outlet tube can be neglected. There is a small vapourisation effect when the liquid enters the measuring cylinder.

3. Results

The pure liquids were chosen with regard to the examination of the effect of increasing chain lengths in homologue alkanes and alkanols on the heat of wetting because in these systems the steric and polar influences become significant. Our results are shown in Fig. 6 and Table 1, respectively. Standard deviations were in the range 0.5–2.0%.

4. Discussion

The absolute value of the heat of wetting of water is much lower than those of the organic liquids. Thus, the active carbon surface is proved to be relatively non-polar compared with the high-polar water molecule. On the other hand, the surface is not completely non-polar (see Section 2.1) because the *n*-alkanols yield larger absolute heats of wetting than the *n*-alkanes at the same number of C-atoms. This was also found by Clint et al. [5].

The absolute heat of wetting, within the homologue row of the 1-alkanols increases with increasing chain length. For small alcohols, a competition between polar and geometric effects occurs. On one side, the smaller pores become more and more inaccessible, therefore, the larger the molecules the more homogeneous the surface is. On the other side, polar functional groups give a higher contribution to the heat of wetting than non-polar groups. For very long molecules the polarity becomes more and more irrelevant. Therefore, the shape of the curve of the enthalpies of wetting for 1-alkanols approaches the one of the *n*-alkanes with increasing chain length.

The absolute heat of wetting of cyclohexane in comparison to *n*-hexane, and of Isooctane in comparison to *n*-octane, respectively, is smaller. This effect is also proved by Fernandez-Colinas et al. [6] as being independent of the surface porosity of different active carbons. It is rather due to the difference between the molecule shapes, which influences the orientation of the molecules in higher adsorption layers, i.e. the number of molecules, which are involved with regard to the range of adsorption forces.

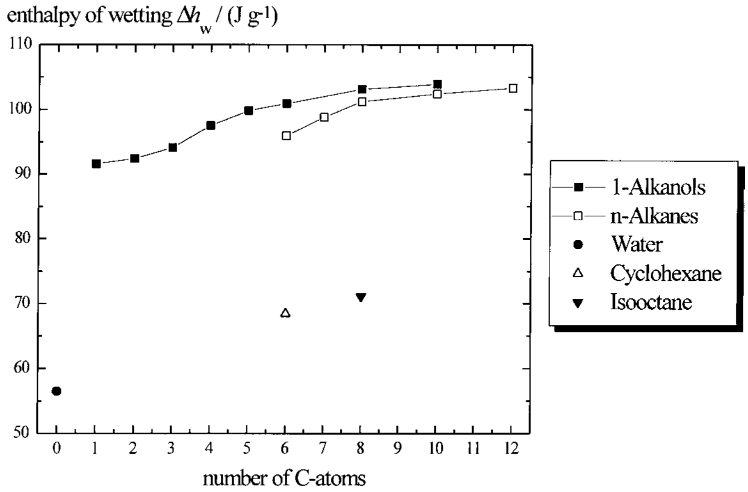

Fig. 6. Enthalpies of wetting on active carbon at 25°C.

Table 1
Enthalpies of wetting on active carbon at 25°C

Substance	$\Delta_w H$ (J g^{-1})
Water	56.6
Methanol	91.6
Ethanol	92.4
1-Propanol	94.1
1-Butanol	97.5
1-Pentanol	99.8
1-Hexanol	100.9
1-Octanol	103.1
1-Decanol	103.9
n-Hexane	96.0
n-Heptane	99.9
n-Octane	102.2
n-Decane	102.7
n-Dodecane	103.3
Cyclohexane	68.4
2,2,4-Trimethyl-pentane (isooctane)	71.1

Our results confirm those given by Clint [5], Bikerman [7], Widyani [8] and can be summarized as follows:

- Polar functional groups on the surface have an important influence with regard to the enthalpy of wetting of small molecules.
- The heat contribution of large non-polar molecules is influenced rather by the geometric surface structure, than by its polarity.
- An increasing chain length of the molecules, on the one hand, leads to a decrease of the enthalpy of wetting at porous adsorbents since small pores become inaccessible, and, on the other hand, to an increase of the enthalpy of wetting at non-porous surfaces due to the orientation effect of molecules within higher layers.

5. Conclusions

Interactions at the solid/liquid interface can be studied by wetting experiments. The caloric effect depends on the interactions between the functional groups of the liquid and the surface of the solid. The energetic and geometric heterogeneity of the adsorbent influences the enthalpy of wetting, as well as the polarity, size, and three-dimensional expansion of the molecules. The examination of these interactions is necessary in order to describe phase equilibrium between bulk and surface phases of binary or of multicomponent liquid-phase adsorption processes. The calorimetric method described yields enthalpies of wetting of pure liquids with deviations smaller than 2%. Due to a high weight-in and the use of pulverized and activated active carbon the scatter of the experimental results could be reduced. These experimental results will be used as a basis for the theoretical part of this project.

Acknowledgements

The authors thank the DFG (Deutsche Forschungsgemeinschaft) for the financial aid which supported these studies and Dr. M. Heuchel and K. Koch from the University of Leipzig, Institute of Physical and Theoretical Chemistry for the help with the pore size distributions and the DFT analysis.

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