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# CALORIMETRIC INVESTIGATION OF ADSORPTION OF ORGANIC COMPOUNDS BY ACTIVE CARBONS

*P. Ulbig, Surya-Lukito, S. Schulz and J. Seippel*

Universität Dortmund, Lehrstuhl für Thermodynamik, D-44221 Dortmund, Germany

## Abstract

Enthalpies of wetting of two active carbons and one brown coal coke by several pure liquids (mainly homologous series) were measured at 298.15 K with two quasi-isothermal microcalorimeters. Different measuring cells with cavities of about 0.5 and 15 $cm^3$ were used. The advantage of the larger measuring cell with three independent 15 $cm^3$ cavities is the higher mass of active carbon, leading to a high reproducibility with standard deviations below 1% and a reduced measuring time. Experiments were carried out with *n*-alkanes, 1-alkanols, cycloalkanes and isomers thereof, i.e. 2-propanol, methylcyclohexane, 2,2,4-trimethylpentane (isooctane and 2-ethyl-1-hexanol, and water. Like the polarity, the size and the three-dimensional expansion of the molecules, the energetic and geometric heterogeneity of the adsorbent influences the enthalpy of wetting.

**Keywords:** active carbon, adsorption, enthalpies of wetting, isothermal calorimetry

## Introduction

Enthalpies of wetting give an insight into interactions at solid/liquid interfaces. In particular, examinations with pure liquids and the variation of their functional groups reveal 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. The work reported in this paper is part of a project which examines enthalpies of wetting by pure liquids, enthalpies of displacement of binary liquid mixtures and the surface excesses, i.e. the phase equilibria of binary liquids on 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 [1].

This paper describes measurements of enthalpies of wetting $\Delta_w H$ for *n*-alkanes, 1-alkanols, cycloalkanes and isomers thereof, i.e. 2-propanol, methylcyclohexane, 2,2,4-trimethylpentane (*iso*-octane) and 2-ethyl-1-hexanol, and water on the active carbon from Roth, the active carbon CPL from Elf Atochem and the non-activated brown coal coke Lusorb BR from Lurgi.

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Special attention was paid to the pretreatment of the active carbons. The granulated active carbon from Roth was pulverized in order to guarantee a small particle size. An activation procedure was used for the carbons without oxidation [2] and specially designed measuring cells were built for the calorimetric measurements.

## Experimental

### *Materials*

The following reagents were used: methanol (purity 99.9%, Roth), ethanol (99.8%, BfB), 1-propanol (99.5%, Roth), 2-propanol (99.9%, Roth), 1-butanol (99.5%, Merck), 1-pentanol (amylalcohol, 99%, Merck), 1-hexanol (98%, Merck), 1-heptanol (99%, Merck), 1-octanol (99.5%, Riedel-de-Haën), 1-decanol (99%, Merck), *n*-hexane (99% Roth), *n*-heptane (99%, Roth) *n*-octane (99%, Merck), *n*-decane (99%, Aldrich), *n*-dodecane (99%, Lancaster), cyclopentane (99%, Fluka), cyclohexane (99.8%, Fluka), cyclooctane (99%, Aldrich), 2-ethyl-1-hexanol (99%, Merck), methylcyclohexane (98%, Merck) and 2,2,4-trimethylpentane (*iso*-octane, 99.9%, Roth). The water contents of the liquids were measured by Karl-Fischer titration. Especially the alkanols had an unacceptable water content. These liquids were dried with molecular sieve and degassed. Finally, the water content of all liquids was below 100 ppm.

Experimental results of surface excess measurements [3] demonstrated the necessity of a small grain size to reduce the time for reaching equilibrium. Calculations with a diffusion model [4] have shown, that the diameter of active carbon particles should be below 20 µm. Therefore, an agate ball mill was used to pulverize the granulated active carbon from Roth. The grain size distribution and pore size distribution were reported earlier [2]. The other coals were distributed as powdered carbons ($d_{70}$ approximately 40 µm) and used without further pulverization. Some of the technical data on the carbons are shown in Table 1.

**Table 1** Specifications of the carbons used

| Name | Raw material | Activation procedure | BET surface/ m$^2$ g$^{-1}$ | pH value | Acidic groups/ | Alkaline groups/ |
|---|---|---|---|---|---|---|
| | | | | | m$^2$ m$^{-2}$ | |
| Lusorb BR | brown coal | none (coke) | 250 | 13 | 0.5% | 17% |
| Roth | peat | physically activated (steam) | 750 | 9–10 | 0.1% | 4% |
| CPL | pine wood | chemically activated ($H_3PO_4$), acid-washed | 1700 | 4–7 | 0.1% | 0.3% |

The carbon was activated in a vacuum oven at 1 hPa. The temperature and the duration of the activation procedure were varied. After 4 h at 120°C, the mass loss was constant. This activation method is similar to procedures known from the literature [3, 5]. Precise density measurements and gas chromatographic analysis of the condensed vapour phase showed only the existence of water on the surface and no organic vapour was detected. The activation procedure was finished by cooling down the active carbon in a vacuum desiccator. The calorimetric ampoule was then filled quickly at ambient pressure and installed in the calorimeter.

The polar surface characteristics were studied by selective stepwise titration in order to determine the acidic (phenolic, lactonic and carboxylic) and basic (chromenic and pyronic) functional groups (Table 1). The absolute molar values were converted by using the mean specific surface areas of the functional groups and the BET surface areas.

## *Calorimeter*

We started the measurement of heats of wetting with a quasi-isothermal microcalorimeter Thermometric TAM 2277, with measuring cells similar to those described in Ref. [6] for the same calorimeter type. The cell is shown in Fig. 1. The activated adsorbent is placed in the inner cylinder, which is closed by sinter

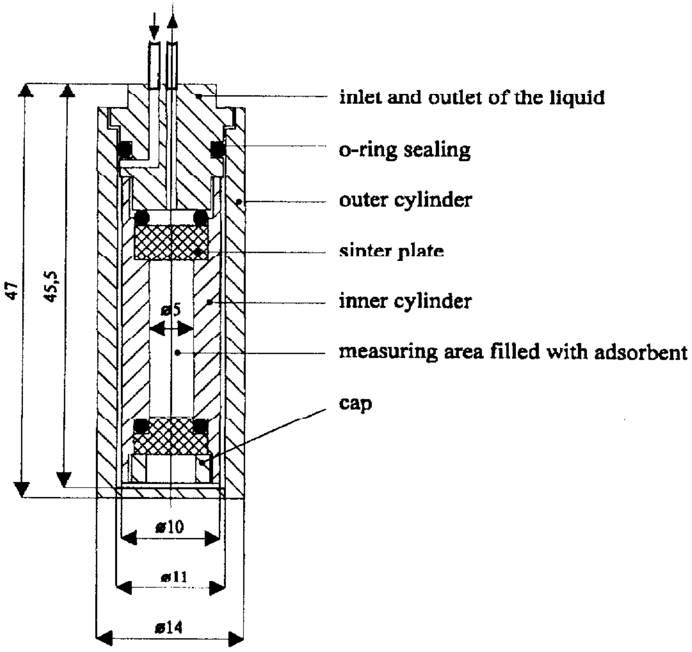

**Fig. 1** Semi-batch measuring cup for heats of wetting with the Thermometric TAM 2277

plates at the top and at the bottom. The sinter plates have a mean pore diameter of 3 μm and a height of 3 mm, i.e. the wetting area can be assumed to be free from vapour of the wetting liquid at the beginning of an experiment. By using the twin principle of the calorimeter and two measuring cells, the noise of the baseline can be reduced. Each cell can be calibrated electrically by using the internal built-in electrical calibration. After a constant baseline is reached (3 to 4 h), electrical calibration begins (1 h). Liquid is then delivered at a rate of 0.01 cm$^3$ min$^{-1}$ (1 h) through the inlet tube into the outer cylinder by a HPLC pump.

The pressure drop due to the sinter plates can be neglected. When the wetting area is completely filled by liquid, the pump is stopped in order to avoid convectional heat losses through the outlet tube. Afterwards, electrical calibration (1 h) is carried out. The whole procedure is repeated with the second measuring cylinder, beginning with the first electrical calibration.

Further measurements were carried out with a Setaram MS 80 II calorimeter. Special measuring cups with three independent cavities were developed, as

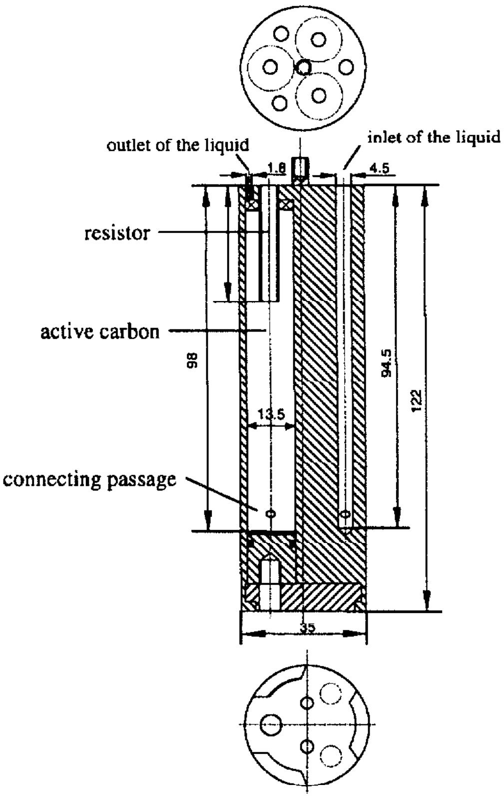

**Fig. 2** Semi-batch measuring cup for heats of wetting (Setaram MS 80 II)

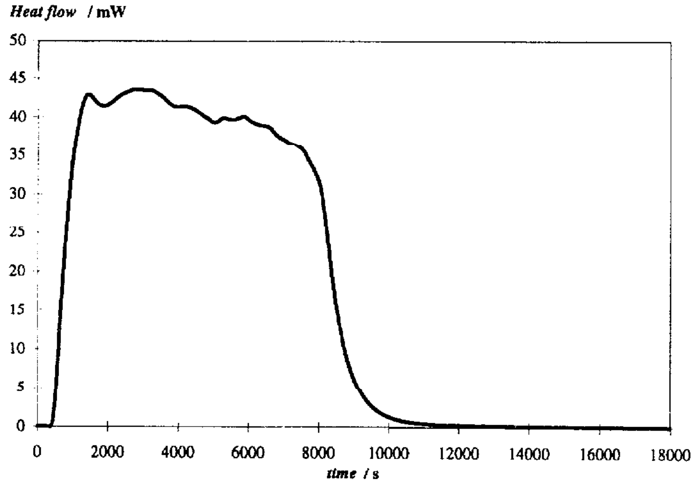

**Fig. 3** Calorimetric curve of wetting of 3.4475 g active carbon from Roth with 1-pentanol at 25°C (Setaram MS 80 II)

shown in Fig. 2. The activated adsorbent is placed in the inner cylinders, which are closed by sinter plates at the top. The sinter plates have the same characteristics as those used with the Thermometric calorimeter. After a constant baseline is reached (6 h), the liquid is delivered at a rate of 0.05 $cm^3$ $min^{-1}$ (4.5 h) through the inlet tube into the inner cylinder by a HPLC pump. When the wetting area is completely filled by liquid, the pump is stopped while monitoring of the calorimeter signal is continued (0.5 h). The whole procedure is repeated with the next measuring cylinder. Each cell can be calibrated electrically by using the built-in 50 ohm resistors. Due to the limited time on working days, the electrical calibration was carried out at weekends only with a Knick precision DC power source (10 mA for 2 h). It could be shown that this is sufficient for monitoring the inertia characteristics of the measuring cells. All parts of the experiment were automated, i.e. pumps and power sources were driven by time switches. Figure 3 illustrates a calorimetric curve of wetting for the active carbon from Roth with 1-pentanol.

With both calorimeters, the experiments were carried out at 298.15 K.

## Results

The results of the adsorption of ethanol on the active carbon from Roth are shown in Fig. 4. It can be seen that the results of the measurements with the Thermometric calorimeter are scattered and a much smaller average could be estimated. The mass of active carbon for the different measuring cells differs by a factor of 22 (0.6 $cm^3$ Thermometric to 13 $cm^3$ Setaram). Obviously, only with the larger measuring cell is it possible to prepare a sufficiently random sample,

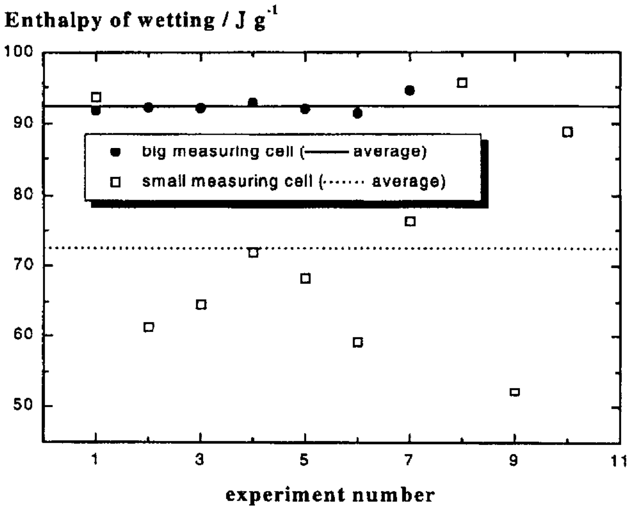

**Fig. 4** Enthalpies of wetting of active carbon from Roth with ethanol with different measuring cells

which leads to a reduced scattering of the calorimetric results. After these first results, all further experiments were carried out with the measuring cells in the Setaram calorimeter.

The pure liquids were chosen with regard to the examination of the effect of increasing chain length in homologue *n*-alkanes, cycloalkanes, and 1-alkanols on the enthalpy of wetting, for in these systems the steric and polar influences are particularly significant. In order to increase these effects, some branched isomers were chosen. The results are shown in Figs 5 to 7, and Table 2.

The standard deviations of the different experimental runs were approximately 1%, indicating the high reproducibility of our results. At the present state, we cannot give details as concerns the differences between the enthalpies of wetting presented in this work and the enthalpies of immersion obtained from immersion calorimetry as described in, for example, Ref. [7]. Generally speaking, a systematic error occurs in wetting experiments due to the presence of air. The air has to be displaced by the liquid, giving a negative heat of desorption. Furthermore, the air cannot be completely displaced from small micropores. According to Ref. [8], a correlation can be achieved between the enthalpies of immersion and the enthalpies of wetting obtained by flow calorimetry, which is one objective of our ongoing project.

## Discussion

The experimental results can be understood as a superimposition of several adsorption effects due to the interaction between adsorbate and adsorbent, which are summarized as follows:

## *Arrangement*

The results for the *n*-alkanes in all cases reveal an increasing enthalpy of wetting with increasing chain length (Figs 4 to 6).

For example, *n*-dodecane always gives higher values than those for *n*-hexane. Obviously, the arrangement of one *n*-dodecane molecule within the surface layer is much more effective than the arrangement of two *n*-hexane molecules. The ar-

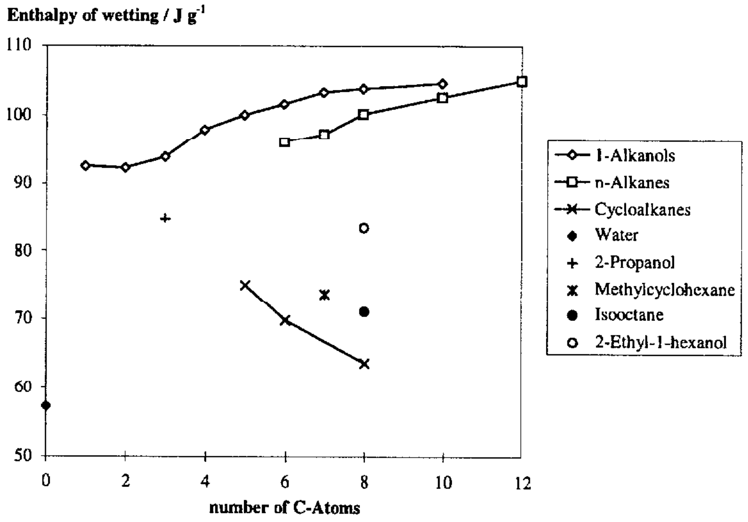

**Fig. 5** Enthalpies of wetting of active carbon from Roth at 25°C

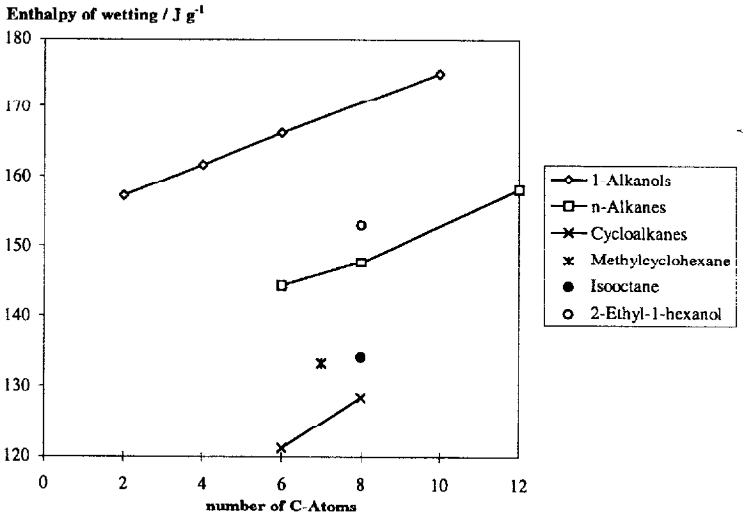

**Fig. 6** Enthalpies of wetting of active carbon from CPL Elf at 25°C

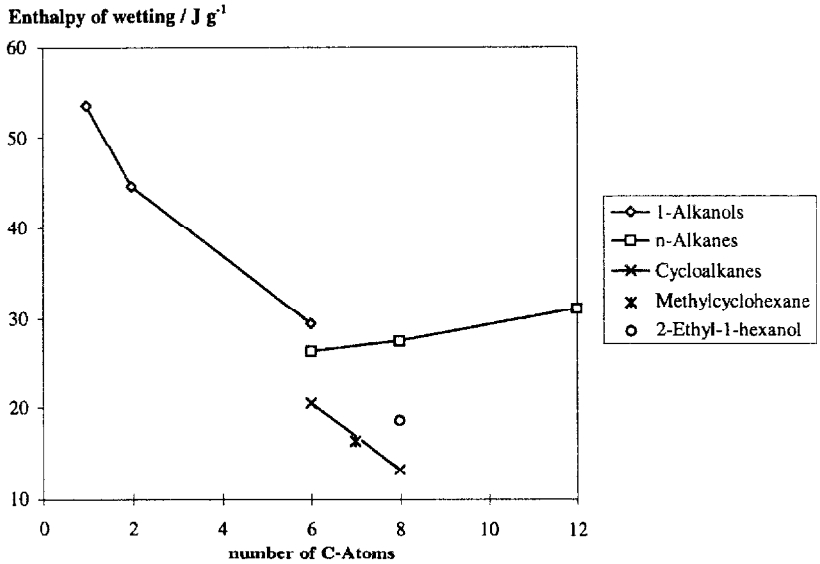

**Fig. 7** Enthalpies of wetting of brown coal coke Lusorb BR at 25°C

rangement ability determines the surface capacity, which can be obtained from the saturation point of gas adsorption isotherms.

## *Polarity*

Polar functional groups (in this work the hydroxy group) give an additional adsorption effect. This leads to higher enthalpies of wetting for the 1-alkanols relative to the *n*-alkanes, as far as the same numbers of C atoms are concerned, e.g. Fig. 4.

A decreasing fraction of polar groups within a molecule can produce a decrease in the enthalpy of wetting on highly polar adsorbent surfaces. This can be seen by the adsorption of 1-alkanols on Lusorb BR (Fig. 6). The fraction of the hydroxy group decreases with increasing chain length.

## *Geometry*

The shape and the three-dimensional expansion of the molecules, together with the pore size distribution, determine the accessible pore volume.

A comparison of the *n*-alkanes with the cycloalkanes indicates generally smaller enthalpies of wetting for the cycloalkanes.

Similar behaviour is observed when *n*-octane is compared with *iso*-octane, or 1-octanol is compared with 2-ethyl-1-hexanol (Fig. 4).

**Table 2** Enthalpies of wetting $\Delta_w H$ /J g$^{-1}$ on different adsorbents at 25°C

| Substance | Roth | Elf CPL | Lusorb BR |
|---|---|---|---|
| Water | 57.25 | | |
| Methanol | 92.42 | | 53.53 |
| Ethanol | 92.19 | 157.18 | 44.54 |
| 1-Propanol | 93.80 | | |
| 1-Butanol | 97.83 | 161.67 | |
| 1-Pentanol | 99.95 | | |
| 1-Hexanol | 101.47 | 166.39 | 29.53 |
| 1-Heptanol | 103.15 | | |
| 1-Octanol | 103.58 | | |
| 1-Decanol | 104.36 | 175.1 | |
| *n*-Hexane | 95.91 | 141.39 | 26.49 |
| *n*-Heptane | 97.10 | | |
| *n*-Octane | 100.06 | 147.77 | 27.67 |
| *n*-Decane | 102.38 | | |
| *n*-Dodecane | 104.75 | 158.30 | 31.20 |
| Cyclopentane | 75.08 | | |
| Cyclohexane | 69.82 | 121.26 | 20.54 |
| Cyclooctane | 63.67 | 128.48 | 13.27 |
| 2-Propanol | 84.80 | | |
| 2-Ethyl-1-hexanol | 83.28 | 153.07 | 18.64 |
| Methylcyclohexane | 73.75 | 133.30 | 16.37 |
| Isooctane | 71.07 | 134.13 | |

## Conclusions

Interactions at solid/liquid interfaces can be studied by wetting experiments. The thermal 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 do the polarity, the size and the three-dimensional expansion of the molecules. The examination of these interactions is necessary in order to describe phase equilibria between the bulk and surface phases of binary or multicomponent liquid-phase adsorption processes. The calorimetric method described yields enthalpies of wetting for pure liquids with deviations of 1%. In consequence of the high sample mass and the use of pulverized active carbon, the scattering of the experimental results could be reduced. These experimental results will be used as basis for the theoretical part of this project.

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