Molecular self-diffusion in active carbons

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Abstract - Self-diffusion of water and organic compounds absorbed on active carbons of different microporous structure is studied by means of the nmr pulsed field gradient technique. In all cases considered, molecular translational motion is found to be controlled by the laws of ordinary diffusion, so that the coefficient of self-diffusion may be indeed understood as a genuine measure of mass transfer on a microscopic scale. The observed transport properties of the adsorbate molecules may be adequately interpreted on the basis of their adsorption behaviour in combination with the data on the mean pore widths of the adsorbents as deduced from an analysis of the adsorption isotherms by the theory of volume filling of micropores.

INTRODUCTION

In many cases, the efficiency of the application of active carbons as molecular sieves or adsorbents decisively depends on the transport properties of the adsorbed molecules. However, the determination of the kinetic parameters by means of traditional uptake methods necessitates the application of more or less approximative assumptions on the adsorbent structure. With active carbons, the application of uptake measurements is complicated by the non-regular adsorbent structure which, e.g., is in sharp contrast to the situation encountered with zeolitic adsorbents. A direct observation of mass transfer in adsorbate-adsorbent systems has become possible by X ray monitoring (ref. 1) or by nmr spin mapping ("dynamic zeugmatography", ref. 2). These techniques, however, require molecular displacements of the order of at least micrometers and are insensitive, therefore, to molecular transport on a microscopic scale.

In the last ten years, the nmr pulsed field gradient technique (refs. 3 - 6) has become a most effective tool for the study of diffusion processes in adsorbate-adsorbent systems. This method allows a direct determination of molecular mean square displacements \( \langle r^2(t) \rangle \) during a time interval \( t \) of a few milliseconds, and hence via Einstein's relation

\[
D = \frac{\langle r^2(t) \rangle}{6t}
\]  

of the self-diffusion coefficient \( D \). In our communication, we present first results of an application of this nmr method to diffusion studies in active carbons. By considering various adsorbate molecules at different temperatures and different concentrations, the transport characteristics thus determined shall be shown to contribute to a better understanding of the nature of molecular adsorption by active carbons.
EXPERIMENTAL

All self-diffusion measurements have been carried out at a proton resonance frequency of 60 MHz by means of the nmr pulse spectrometer FEGRIS built at the Physics Department of the Karl Marx University Leipzig. The device allows the application of pulsed field gradients up to 20 T/m with rise and fall times of the order of 10 μs.

For sample preparation, the active carbon has been introduced into glass tubes with an outer diameter of about 7.53 mm up to a filling height of about 20 mm, and evacuated at a pressure of 10⁻⁴ Pa and a temperature of 673 K over 3 hrs. Afterwards, the adsorbate has been introduced into the activated adsorbent by chilling from a well-defined volume. After fusing the sample tube, the amount adsorbed was checked gravimetrically. The relative pore filling factors which have been introduced to characterize the sorbate concentrations are determined as the ratio of the respective volumes of the adsorbate and of the pore system by assuming that the molecular density of the adsorbate coincides with that of the free liquid. During the self-diffusion measurements within the probe of the spectrometer, the samples were permanently cooled by a stream of evaporating nitrogen or heated by a stream of preheated air, respectively, in order to keep them at the desired temperature with an accuracy of about 1 K. The nmr diffusion measurements have been carried out by applying either the primary or the stimulated echo technique (ref. 5), with typical observation times t of 1 to 3 ms, and of 3 to more than 100 ms, respectively. In the calculations, we have in general applied the medium diffusion coefficients provided by the stimulated echo technique, i.e. for observation times t>3 ms. The self-diffusion coefficients have been determined by comparing the decay of the nmr signal in dependence on the width of the applied field gradient pulses with that of a standard liquid. For this purpose, we have chosen n-propanol with a self-diffusion coefficient of 7.5×10⁻⁹ m²/s at room temperature. The accuracy of the measurements is indicated by typical error bars in the representations of the self-diffusion coefficients.

The pore structure parameters (W₀ and E₀) and the half widths x of the slitlike pore model as indicated in Table 1, have been determined from the adsorption isotherm of benzene at 293 K and of nitrogen at 77 K, respectively, by applying the theory of volume filling of micropores (ref. 8).

The pore structure parameters (W₀ and E₀) and the half widths x of the slitlike model for the active carbons considered

<table>
<thead>
<tr>
<th>Active carbon</th>
<th>W₀ cm/g</th>
<th>E₀ kJ/mol</th>
<th>x nm</th>
<th>Active carbon</th>
<th>W₀ cm/g</th>
<th>E₀ kJ/mol</th>
<th>x nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-11 a)</td>
<td>0.12</td>
<td>-</td>
<td>0.2</td>
<td>AC-63</td>
<td>0.51</td>
<td>22.6</td>
<td>0.54</td>
</tr>
<tr>
<td>AC-14 a)</td>
<td>0.09</td>
<td>-</td>
<td>0.2</td>
<td>AC-65</td>
<td>0.47</td>
<td>21.8</td>
<td>0.55</td>
</tr>
<tr>
<td>AC-15</td>
<td>0.20</td>
<td>32.4</td>
<td>0.31</td>
<td>AC-72</td>
<td>0.45</td>
<td>21.0</td>
<td>0.59</td>
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<tr>
<td>AC-2</td>
<td>0.48</td>
<td>30.3</td>
<td>0.35</td>
<td>AC-1</td>
<td>0.32</td>
<td>20.0</td>
<td>0.62</td>
</tr>
<tr>
<td>AC-16</td>
<td>0.25</td>
<td>29.9</td>
<td>0.36</td>
<td>AC-10</td>
<td>0.28</td>
<td>19.0</td>
<td>0.66</td>
</tr>
<tr>
<td>AC-13</td>
<td>0.15</td>
<td>26.9</td>
<td>0.43</td>
<td>AC-66</td>
<td>0.82</td>
<td>17.8</td>
<td>0.67</td>
</tr>
<tr>
<td>AC-61</td>
<td>0.43</td>
<td>25.6</td>
<td>0.46</td>
<td>AC-67</td>
<td>0.69</td>
<td>17.1</td>
<td>0.70</td>
</tr>
<tr>
<td>AC-7 b)</td>
<td>0.40</td>
<td>24.4</td>
<td>0.49</td>
<td>AC-42 c)</td>
<td>0.40</td>
<td>16.7</td>
<td>0.73</td>
</tr>
<tr>
<td>AC-8</td>
<td>0.40</td>
<td>24.4</td>
<td>0.49</td>
<td>AC-71</td>
<td>1.44</td>
<td>-</td>
<td>0.77</td>
</tr>
</tbody>
</table>

a) There is practically no adsorption of nitrogen and benzene by AC-11 and AC-14, the value of W₀ has been calculated, therefore, from the adsorption isotherm at p/p₀=1.

b) AC-8 has been produced by subjecting AC-7 to a stream of humid air at 623 K.

c) The parameters of the large-pore AC-71 have been calculated following the method by Mikhail, Bruqauer and Bodor (ref. 9), leading to a specific surface area of 1870 m²/g, W₀ has been determined at p/p₀=1.
RESULTS AND DISCUSSION

Influence of the observation time

A study of the dependence of the self-diffusion coefficient on the observation time may provide unique information about the degree of homogeneity of the sample. According to Einstein's relation (equ. 1), any time dependence of the self-diffusion coefficient indicates a deviation from the linear interdependence between the mean square displacement and the observation time. This might be brought about by transport resistances (barriers) as well as by the existence of zones of high molecular mobility at low population densities. Diffusion in fractal networks is characterized by the expression (ref. 10)

\[ \langle r^2(t) \rangle = \alpha t^x, \tag{2} \]

with \( \alpha \) and \( x \) denoting, respectively, a factor of proportionality, independent of the observation time, and a scaling parameter, in general \(< 1\). For curvilinear diffusion along entangled channels, one has, e.g., \( x = 0.5 \) (ref.11). If the time dependence of the self-diffusion coefficient is caused by the adsorbent structure, deviations from constancy should be observed independent of the nature of the adsorbate and of the temperature of the experiment. However, in no experiment we could observe a reliable indication of such deviations from ordinary diffusion. As an example, Figure 1 presents the mean square displacements for molecular diffusion of \( n \)-hexane in AC (active carbon) - 72. The obtained results indicate that in the range of displacements followed in the experiments (about 1 to 100 \( \mu m \)) no deviations from ordinary diffusion are visible. On the other hand, it cannot be excluded that for displacements below 1 \( \mu m \) fractal properties may appear. It should be mentioned, however, that deviations from a linear relation between the mean square displacement and the observation time may as well be caused by reasons, which are in no way related to a possible fractal nature of the adsorbent, such as e.g. the influence of restricted diffusion (ref. 11). In view of the fact, that with decreasing observation times the accuracy of the nmr self-diffusion measurements as well decreases, a final decision on the existence or non-existence of fractal transport properties in active carbons for sufficiently small molecular displacements is not possible. The electron micrograph of AC-72 as presented in Figure 2 shows the existence of quasi-homogeneous microporous regions of large extend, which is in complete agreement with the experimental finding of ordinary diffusion.
Concentration dependence

Figure 3 shows the concentration dependence of the water diffusivities in active carbons with different characteristic pore widths \( x \). The observed dependencies are found to follow quite different patterns, showing in the various samples both increase and decrease of the mobilities with increasing pore filling factors. By adopting the model of activated jumps, from a microscopic point of view the concentration dependence of molecular mobilities may be analysed on the basis of the relation

\[ D \sim <l^2>/6\tau \]

(3)

correlating the diffusivities with the mean square jump length \(<l^2>\) and the mean life time between two succeeding jumps. According to the established model of water adsorption on active carbons (ref. 12), at small water concentrations water adsorption occurs most likely at the primary adsorption sites. The degree of localization steadily decreases with increasing amounts adsorbed, which leads to a decrease of the mean life times \( \tau \) and hence, according to equation (3), to increasing mobilities. An increase in the amounts adsorbed leads, on the other hand, to a decrease in the free space and with it most probably to a decrease in the mean jump lengths, which, vice versa, tends to enhance the diffusivities. The overall effect is decisively determined by the geometry of the micropores and the concentration of the primary adsorption sites. The experimental data show that, in general, for active carbons with relatively narrow micropores the water diffusivities decrease with increasing pore filling factors, while for large pore active carbons the water diffusivities increase. In some cases, the diffusivities are found to pass through a maximum.

Molecular mobility in dependence on the micropore structure

Figure 4 shows the self-diffusion coefficients of water and methanol in various active carbons in dependence on the pore half width \( x \). It appears from this representation, that irrespective of the different nature or way of preparation of the active carbons, there is a general tendency of increasing mobility with increasing pore diameters. The same behaviour has as well been observed with adsorbed benzene. This tendency is most obviously visible in the series AC-11, 14, 15 and 16, where in the small pore active carbons AC-11 and AC-14 the
water diffusivities are found to be by about 100 times smaller than in the neat liquid. Such a decrease should be referred to the influence of the rigid lattice of the adsorbent, which becomes most pronounced for the smallest pore diameters. In ref. 4, this "stabilization effect" has been demonstrated to be a quite general peculiarity of adsorbate-adsorbent systems. It is interesting to note that for the smallest pore widths the diffusivities of methanol are found to be below those for water, while the situation is reversed for medium and higher pore diameters. This experimental finding may be understood by realizing that in the small pores the mobility of the larger methanol molecules may be assumed to be considerably more reduced than that of the smaller water molecules. For larger pore widths, the sequence in the mobility of the adsorbed species will be the same as in the liquid state, where, at the temperature of the experiments, the methanol mobility is higher than that of water (Figure 5).

Comparison of the different adsorbates

It has been demonstrated by the experimental data for water and methanol, as presented in Figure 4, that for the small pore active carbons the mobility decreases with increasing molecular diameter. This tendency is confirmed by including the molecular diffusivities observed for benzene. Figure 5 provides a summary of the temperature dependence of the diffusivities in small pore active carbons and in the liquid state, respectively. It is worthwhile to note that the sequence in the activation energies, viz. water > methanol > benzene, as observed for the neat liquids, is as well preserved in the adsorbed state.

Figure 6 shows the results of a systematic study of the self-diffusion coefficients of various C₆ hydrocarbons and of water in large pore active carbons. They are represented in dependence on the diffusivities in the neat liquids. It may be deduced from the observed behaviour that in the given case the mobility of the adsorbed molecules is determined by the mobility in the liquid state rather than by the molecular size. Thus it turns out, e.g., that the adsorbed benzene molecules are much more mobile than the cyclohexane molecules, which are of the same molecular volume. In fact, their mobility is found to be comparable with that of the much smaller water molecules. For all probe molecules the mobility in the adsorbed state is found to be reduced by a factor of about 3.5 in comparison to the neat liquid. This reduction indicates the effect of the adsorbent tortuosity. The deviation from a linear dependence between the diffusivities in the free and adsorbed state as observed for n-hexane seems to indicate that the stated correlation should only be expected for sufficiently small and rigid molecules. The reduction of the self-diffusion coefficient of n-hexane in the adsorbed state in comparison to the liquid phase should be explained, therefore, by motional hindrance due to the more extended molecular size, acting in addition to the influence of tortuosity.
For comparing the diffusivities of the different adsorbates, we have applied data obtained at a pore filling factor of 0.5. It should be noted that the observed correlation is not essentially changed by considering the respective concentration dependences. The vertical lines in Figure 6 indicate the region of diffusivities observed with varying concentrations.

Diffusion measurements at two-component adsorption

Being sensitive to a certain nuclear species, the nmr pulsed field gradient technique provides promising prospects for the investigation of the molecular mobility of the individual components in multicomponent systems. In contrast to previous experiments, in which two-component diffusion has been observed by applying the respective adsorbate molecules alternatively in the hydrogen- and in the deuterium-containing form (ref. 13), in the present study we have investigated the diffusion properties of water-hexafluorobenzene mixtures adsorbed on active carbons, which allows the simultaneous observation of the diffusivities of both components by applying either proton or fluorine nuclear magnetic resonance.

Figure 7 shows the temperature dependence of the self-diffusion coefficients of water and hexafluorobenzene at single- and two-component adsorption in an active carbon with a relatively large mean pore width, in comparison with the data for the free liquid. In all cases the total pore filling factor amounts to 0.5. In the mixtures, equal volume fractions of the two components have been applied. As mentioned above in connection with Figure 6, at room temperature the diffusivities of the single components are by a factor of about 3.5 smaller than in the liquids. Replacing a part of the water molecules by hexafluorobenzene leads to a reduction of the mobility of the remaining water molecules, while the mobility of the hexafluorobenzene molecules remains essentially unchanged after water replacement. A more detailed study of the concentration dependences and of their correlation with the liquid state will be the subject of further investigation.

REFERENCES

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