Molecular self-diffusion in active carbons

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Abstract - Self-diffusion of water and organic compounds ad-
sorbed 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
self-diffusion coefficients are measured over a large variety
of pore sizes, pore filling factors and sorbate species. The
observed transport properties of the adsorbate molecules may be
adequately interpreted on the basis of their adsorption beha-
viour 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 efficency 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 adsor-
bent 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

$$D = \langle r^2(t) \rangle / 6t \tag{1}$$

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 mole-
cular 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 7.5 mm up to a filling height of about 20 mm, and evacuated at a pressure of 10^{-3} 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^{-10} $m^2 s^{-1}$ 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 (W_o and E_o) 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).

TABLE 1.   Structure parameters W_o and E_o and half widths x of
           the slitlike model for the active carbons considered

Active carbon	W_o cm^3/g	E_o kJ/mol	x nm	Active carbon	W_o cm^3/g	E_o kJ/mol	x nm
AC-11[a]	0.12	-	0.2	AC-63	0.51	22.6	0.54
AC-14[a]	0.09	-	0.2	AC-65	0.47	21.8	0.55
AC-15	0.20	32.4	0.31	AC-72	0.45	21.0	0.59
AC-2	0.48	30.3	0.35	AC-1	0.32	20.0	0.62
AC-16	0.25	29.9	0.36	AC-10	0.28	19.0	0.66
AC-13	0.15	26.9	0.43	AC-66	0.82	17.8	0.67
AC-61	0.43	25.6	0.46	AC-67	0.69	17.1	0.70
AC-7[b]	0.40	24.4	0.49	AC-42[c]	0.40	16.7	0.73
AC-8[b]	0.40	24.4	0.49	AC-71[c]	1.44	-	0.77

[a] There is practically no adsorption of nitrogen and benzene by AC-11 and AC-14, the value of W_o has been calculated, therefore, from the adsorption isotherm at p/p_s=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, Brunauer and Bodor (ref. 9), leading to a specific surface area of 1870 m^2/g, W_o has been determined at p/p_s=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)

$$\langle r^2(t)\rangle = \propto t^x, \tag{2}$$

with $\propto$ 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 μm) no deviations from ordinary diffusion are visible. On the other hand, it cannot be excluded that for displacements below 1 μm 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, at present 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.
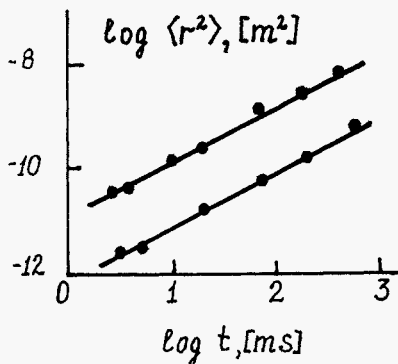

Fig. 1. Molecular mean square displacement of n-hexane in AC-72 at a temperature of 223 K (1) and 343 K (2),in dependence on the observation time
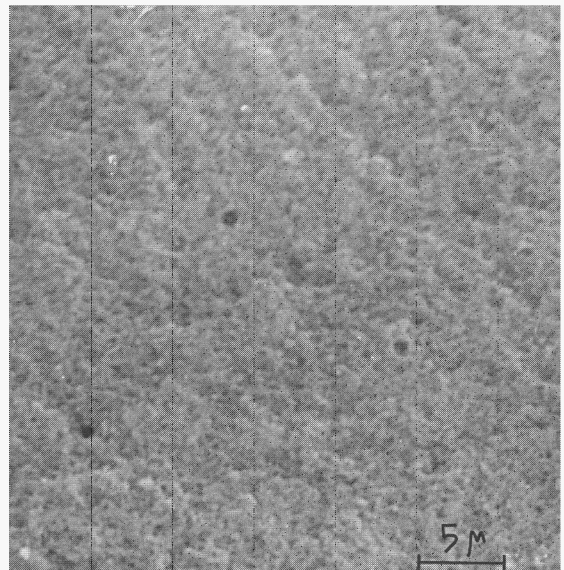

Fig. 2. Electron micrograph of AC-72

Concentration dependence

Figure 3 shows the concentration dependence of the water diffusivities in active carbons with different characteristic pore widths x. The observed dependences 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

$$D \sim <\ell^2>/6\tau \qquad\qquad (3)$$

correlating the diffusivities with the mean square jump length $<\ell^2>$ 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 τ 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.
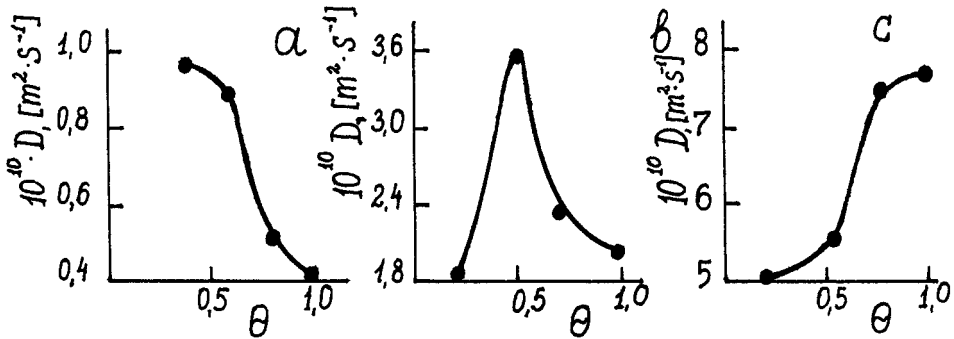

Fig. 3.   Concentration dependence of the self-diffusion coefficient of water at 293 K for AC-15 (a), AC-10 (b) and AC-71 (c), with the respective mean half pore widths x = 0.31nm, 0.66nm and 0.77nm

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
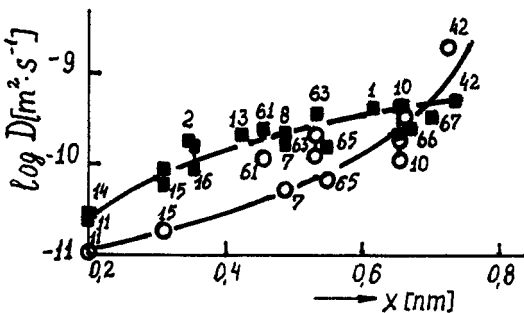

Fig. 4. Self-diffusion coefficient of water (full symbols) and of methanol (open symbols) in dependence on the mean half pore width x

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 mole-
cules. 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).
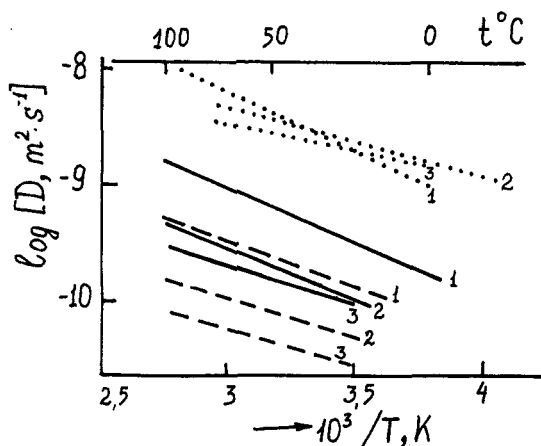

Fig. 5. Temperature dependence of
the self-diffusion coefficients
of water (1), methanol (2) and
benzene (3) in AC-7 (broken line)
and AC-10 (full line) in comparison
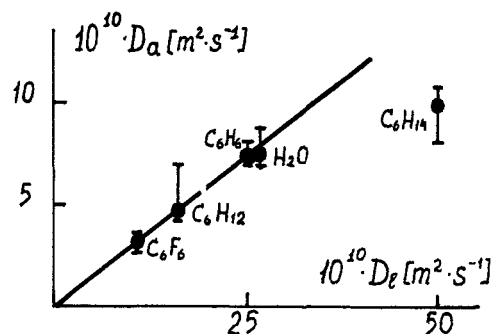with that of the neat liquid
(dotted line)

Fig. 6. Comparison of the self-
diffusion coefficients in the neat
liquids (D_l) with those of the same
compound adsorbed on AC-71 (D_a)
at 298 K

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 coeffi-
cients of various C_6 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 mole-
cules 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 inves-
tigated the diffusion properties of water-hexafluorobenzene mixtures adsorbed
on active carbons, which allows the simultaneous observation of the diffusivi-
ties of both components by applying either proton or fluorine nuclear magnetic
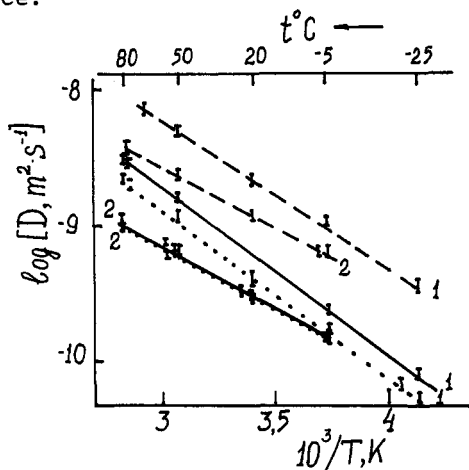resonance.

Fig. 7. Temperature dependence
of the self-diffusion coeffi-
cient of water (1) and of
hexafluorobenzene (2) adsorbed
on active carbons either in
the mixture (dotted lines) or
at single-component adsorption
(full lines) and comparison
with the diffusivities in the
neat liquids

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 hexafluoroben-
zene 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.

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