19F NMR DIFFUSION STUDIES OF MOLECULES ADSORBED ON ZEOLITES

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SUMMARY

    The 19F nmr pulsed field gradient technique is applied to study
molecular self-diffusion of fluorine containing molecules adsorbed on
zeolites. Most favourable conditions for the nmr self-diffusion
measurements are provided by the X type zeolites. In this case, self-
diffusion coefficients at both single-component (SF_6, CF_4, CHF_2Cl and C_6F_6)
and two-component (C_6F_6/C_6H_6) adsorption are determined. In A type
zeolites, molecular diffusion is dramatically reduced due to the smaller
diameter of the windows between the micropores of the zeolite crystallites.
The diffusion coefficients of the fluorocarbons investigated are compared
with those previously obtained for the corresponding hydrogen-containing
compounds.

INTRODUCTION

    Zeolites are aluminosilicates whose framework structures have pores of
molecular dimensions [1,2]. Following Barrer's invention of the possibility
of their synthesis in the laboratory [1], today zeolites are produced
industrially on a large scale [2,3,4]. The crystallite diameters of
synthetic zeolites are typically of the order of a few micrometers. The
commercial relevance of the zeolites results from three different ways of
their application, which are correlated with different aspects of zeolite
structure chemistry [5]: As a d s o r b e n t s and m o l e c u l a r
s i e v e s zeolites offer hydrophilic or (in the case of siliceous
materials) hydrophobic micropores with well-defined dimensions allowing the
access of molecules only up to a certain critical diameter [6]. It has been
found that micropore adsorption (e.g. of organic fluorocarbons [7]) may
take place up to Lennard-Jones critical molecular diameters slightly
exceeding the diameters of the windows of the zeolite micropores. The
application as c a t a l y s t s is based on the existence of active
sites within the zeolite structure [4,8] in combination with shape-
selective constraints. Finally, zeolites may be applied as i o n
e x c h a n g e r s [9] owing to the existence of mobile nonframework
cations within the zeolite structure.

    In all cases of application, the rate of the considered processes may
significantly depend on the velocity of molecular transport within the

zeolite framework. In gas phase adsorption, the traditional way to
determine intracrystalline molecular mass transfer is to follow molecular
uptake in response to a change of the pressure of the surrounding adsorbate
[6,10,11]. Corresponding experiments with adsorption from the liquid phase
necessitate an analysis of the time dependence of molecular concentration
in the liquid phase [12].

It is the main advantage of the nmr pulsed field gradient technique
[13,14] that it allows the 'in-situ' observation of molecular migration.
The quantity directly measured is the molecular mean square displacement
$\langle[r(\Delta)-r(0.)]^2\rangle$ during an observation time Δ of typically some
milliseconds. Using Einstein's relation

$$\langle[r(\Delta)-r(0)]^2\rangle/6\Delta = D, \tag{1}$$

the mean square displacements may be straightforwardly transferred into the
respective self-diffusion coefficients D. For root mean square
displacements $\langle[r(\Delta)-r(0)]^2\rangle^{1/2}$ much less than the mean crystallite
diameters, the thus determined self-diffusion coefficients exclusively
refer to migration in the intracrystalline space and are termed as
coefficients of intracrystalline self-diffusion. It is this quantity which
we shall consider in the present study.

The nmr pulsed field gradient technique is based on the observation of
an nmr signal ("spin echo") following a sequence of appropriately chosen rf
pulses. Under the influence of additionally applied pulsed magnetic field
gradients, the nmr signal is found to be damped following the relation

$$\psi(\delta g,\Delta) = \exp\{-\gamma^2\delta^2g^2\langle[r(\Delta)-r(0)]^2\rangle/6\}, \tag{2}$$

with δ, g and Δ denoting respectively the width, intensity and separation
of the magnetic field gradient pulses. γ is a characteristic constant, the
"gyromagnetic ratio", of the nuclear species under consideration, which is
equal to $2.68 \times 10^8 T^{-1}s^{-1}$ for protons, and to $2.52 \times 10^8 T^{-1}s^{-1}$ for
fluorine, respectively.

Via eq.(1), eq.(2) may be transformed into

$$\psi(\delta g,\Delta) = \exp\{-\gamma^2\delta^2g^2D\Delta\}. \tag{3}$$

Thus the self-diffusion coefficient may be straightforwardly determined by
comparing the slope of a $\ln\psi$ - vs - $(\delta g)^2$ plot for the investigated sample
with that of a standard liquid with a known self-diffusion coefficient.

As yet, owing to the optimum measuring conditions, nmr self-diffusion
measurements of adsorbate-adsorbent systems have mainly been carried out
using the proton magnetic resonance signal. However, measurement of the
nuclear magnetic resonance signal of other nuclei clearly offers the
possibility to study a larger variety of adsorbate molecules. In the
following, the first results of nmr self-diffusion studies of fluorine
containing molecules adsorbed on zeolites will be presented.

EXPERIMENTAL

In order to guarantee well-defined conditions, under which molecular migration in the interior of the zeolite crystallites is studied, at first the adsorbent was activated. For this purpose, it was spread over an area of about 300 mm² up to a bed height of about 3 mm and activated at a heating rate of 10 K/h under continuous pumping ("shallow bed" conditions [15]). At the final temperature of 400°C, the adsorbent was kept until the pressure was lower than 10^{-2}Pa. Then the activated adsorbent was loaded with the adsorbate via vacuum distillation. The amount of adsorbed molecules was controlled both volumetrically and gravimetrically, and afterwards checked by measuring the intensity of the nmr signal [16]. After loading, the material was transferred under vacuum into 8 mm glass ampoules up to a filling height of about 20 mm. Afterwards, the ampoules were sealed by flame.

The nmr self-diffusion measurements have been carried out by means of the home-built nmr pulse spectrometer FEGRIS [17] at a resonance frequency of 60 MHz, corresponding to a magnetic field of 1.4 T for protons and of 1.5 T for fluorine. Generally, the nmr signal was observed after two rf pulses (primary echo). Only in the case of larger observation times $\Delta > 10$ ms also the stimulated echo (nmr signal after three rf pulses) has been measured. Intensity, width and separation of the magnetic field gradient pulses were typically of the order of $g < 10$ T/m, $\delta = 0.2...0.3$ ms and $\Delta = 2...200$ ms, respectively [17].

The zeolite specimens of type NaCaA and NaX, with mean crystallite diameters of about 15 and 30 μm, respectively, have been synthesized by S.P.Shdanov and N.N.Feokistova in Leningrad [18]. In the zeolite NaCaA, about 70 % of the amount of sodium cations originally contained in the specimen has been exchanged by Ca^{2+}. As fluorine containing molecules we have chosen CF_4, CHF_2Cl, SF_6 and C_6F_6 with a purity of higher than 98 %.

RESULTS AND DISCUSSION

SF_6 in NaX

X type zeolites consist of a system of cavities with a volume of about 0.8 nm³, arranged in tetrahedral coordination and separated from each other by windows with a mean diameter of 0.8 nm [1,2]. Since the molecular diameter of SF_6 is of the order of 0.6 nm [19], there is no steric hindrance for molecular passage from one cavity to an adjacent one. Moreover, as a highly symmetric molecule, SF_6 is not subjected to a pronounced interaction with adsorption sites within the zeolite structure. It has been found that in this case the molecular self-diffusion coefficient may be expected to decrease monotonically with increasing sorbate concentration (type 1 concentration dependence of the self-diffusion coefficient [20]). In ref.[21] this behaviour was attributed to the decrease in the molecular free volume with increasing sorbate concentration. As demonstrated in Fig. 1, the measured self-diffusion coefficients are in complete agreement with this model. It is noteworthy that irrespective of the differences in the absolute values, for all sorbate concentrations the same activation energy of (12 ± 2.5) kJ mol^{-1} is found. This is just the behaviour observed for n-paraffins in NaX [21].
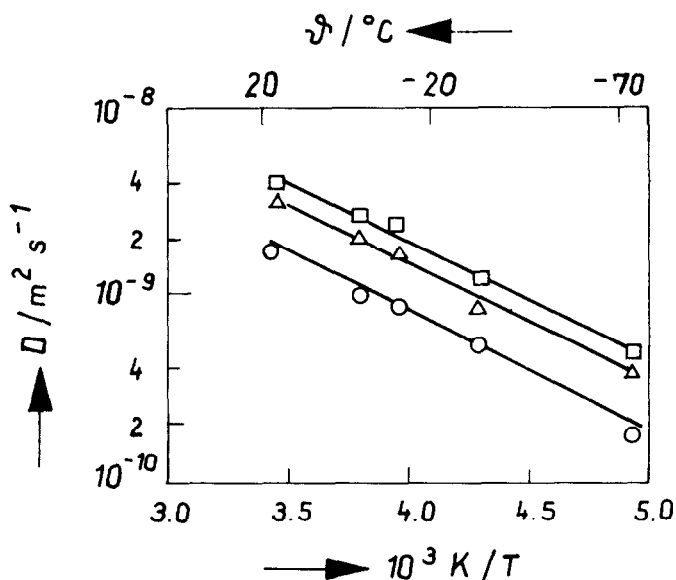
Fig. 1. Temperature dependence of the self-diffusion coefficient of SF$_6$ in zeolite NaX at a sorbate concentration of 1.2 ($\square$), 3 ($\triangle$) and 5 ($\bigcirc$) molecules per cavity.

Previous investigations of molecular transport of SF$_6$ in NaX were based on uptake measurements [22] and on an analysis of the temperature dependence of the nuclear magnetic relaxation times [23]. The diffusivities derived from the uptake measurements were found to be by a factor of 10^3 smaller than the values calculated from the relaxation data. One must have in mind, however, that nuclear magnetic relaxation is controlled by the elementary steps of molecular motion. Hence the diffusivities calculated in this way must be based on model considerations whose validity cannot be proved directly. On the other hand, in view of the numerous processes possibly influencing molecular uptake, also this method cannot be considered to be a direct one for diffusion measurement. With the present investigations it could be clarified that the self-diffusion coefficients determined from the relaxation studies (e.g. 10^{-9} m^{2}s^{-1} for 2 molecules per cavity at 300 K [23]) are of the correct order of magnitude, while the uptake measurements [22] provide diffusivity data, which are in fact by 3 orders of magnitude below the correct values. It is remarkable that there is also a satisfactory agreement between our activation energies and the values determined in ref.[23]. As has been shown in subsequent studies [24] it is most likely that the diffusivity data formally derived from the uptake experiments have been determined by the finite rate of adsorption heat release rather than by the rate of intracrystalline diffusion.

CF₄ and CHF₂Cl in NaX

Fig. 2 presents the self-diffusion coefficients of CF₄ and CHF₂Cl in NaX. Comparison of the data for CF₄ with those of SF₆ provide the same type 1 concentration dependence. The higher mobility of CF₄ is straightforwardly explained by its smaller size and molecular weight.

Both the lower mobility and the higher activation energy of CHF₂Cl in comparison with CF₄ indicate a stronger interaction of these molecules with the zeolite lattice, which may be straightforwardly explained by the large value of the electric dipole moment of CHF₂Cl (1.42 D [25]).

CHF₂Cl allows the application of both ¹H and ¹⁹F nuclear magnetic resonance. As to be expected, in both cases coinciding diffusivities have been obtained.
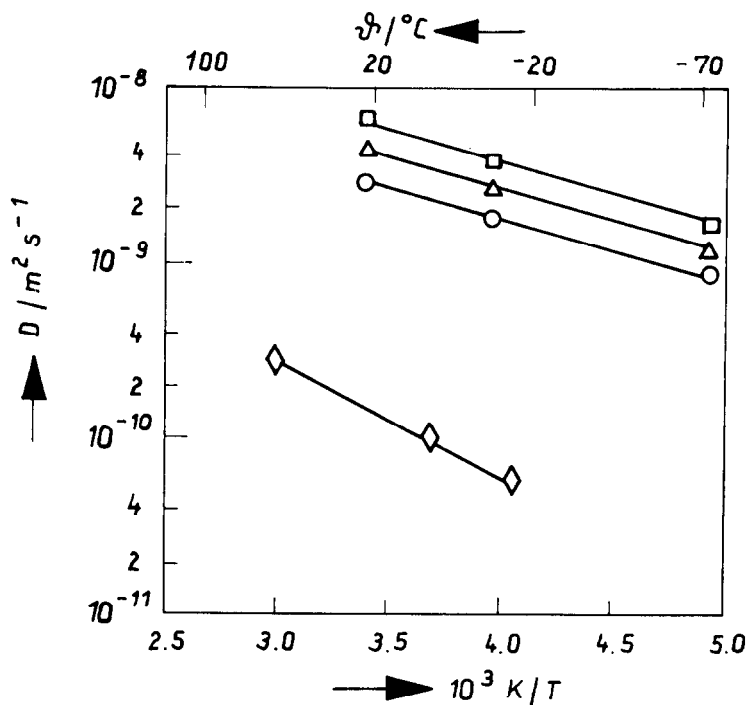

Fig. 2. Temperature dependence of the self-diffusion coefficient of CF₄ at a sorbate concentration of 2 (□), 4 (△) and 6 (○) molecules per cavity and of CHF₂Cl at a sorbate concentration of 5 (◇) molecules per cavity in zeolite NaX.
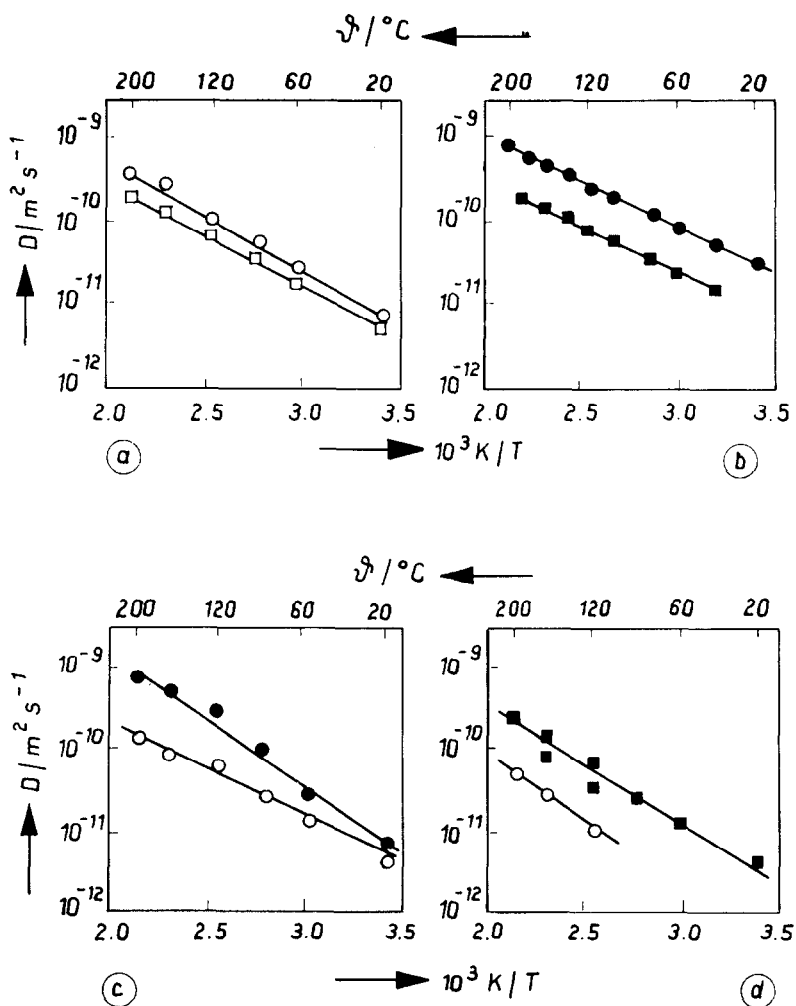
Fig.3. Temperature dependence of the self-diffusion coefficients of C_6F_6 and C_6H_6 in zeolite NaX:
a) single-component adsorption of C_6F_6, with 1 (○) and 3.5 (□) molecules per cavity;
b) single-component adsorption of C_6H_6, with 1.8 (●) and 3.8 (■) molecules per cavity;
c) two-component adsorption with 1 molecule C_6F_6 (○) and 1 molecule C_6H_6 (●) per cavity;
d) two-component adsorption with 1.3 molecules C_6F_6 (○) and 2.6 molecules C_6H_6 per cavity (■).

C_6F_6/C_6H_6 mixtures in NaX

In zeolite application for both molecular sieving and catalytic reactions one has to do with at least two adsorbate components. Diffusion studies under the condition of multicomponent adsorption are therefore of special practical relevance. Due to its sensitivity to a certain nucleus, nuclear magnetic resonance provides favourable conditions for the measurement of the self-diffusion coefficient of one component in multicomponent mixtures. To date it has been performed in the case of ^{1}H nmr by the use of perdeuterated molecules, leaving only one hydrogen-containing compound in the samples [20,26]. Then it was exactly the self-diffusion coefficient of this molecular species which was determined by ^{1}H nmr. The measurement of any other species necessitated a further sample preparation with a corresponding change in the application of perdeuterated and hydrogen containing components. With the application of both ^{1}H and ^{19}F nmr, in the present study for the first time a separate determination of the self-diffusion coefficients of both adsorbate components using the same sample has become possible.

Fig. 3 provides a comparison of the self-diffusion coefficients of C_6F_6 and C_6H_6 in NaX. For small concentrations the self-diffusion coefficients in the mixture are found to be of the order of the values for single component adsorption. This may be explained by the fact that the mutual interaction of the adsorbate molecules is still negligibly small. Also at higher concentrations, benzene diffusion proceeds at a rate similar to single-component adsorption, whereas the mobility of C_6F_6 is found to be more restricted by molecules of the second species (C_6H_6) than by the C_6F_6 molecules themselves.

CF_4 in NaCaA

Zeolites A contain cavities of nearly the same volume as zeolites X. However, the diameters of the windows between the cavities are much smaller, being of the order of 0.5 nm for the investigated zeolite NaCaA. One has to expect, therefore, that in zeolite NaCaA molecular migration of CF_4 with a molecular diameter of 0.53 nm [19] proceeds at a much lower rate than in NaX. This could in fact be found in the experiments, which provided an upper limit of the self-diffusion coefficient of $3 \times 10^{-12} m^2 s^{-1}$ at a temperature of 473 K and sorbate concentrations of 1...3 molecules per cavity. According to both uptake measurements and calculations on the basis of the absolute rate theory by Ruthven [27], the intracrystalline diffusivities at the given temperature should be expected to be of the order of $10^{-14} m^2 s^{-1}$, which is not in contrast to the nmr result.

Previous self-diffusion measurements of methane in zeolite NaCaA at 473 K led to values of about $10^{-9} m^2 s^{-1}$ [28]. It is remarkable that the increase in the van-der-Waals diameters from 0.4 nm for methane to 0.53 nm for CF_4 leads to such a dramatic decrease in the mobilities. This is clearly due to the similarity in the diameters of the molecules and the windows. In zeolite NaX the diameters of the windows are distinctly above these molecular diameters. Consequently, there is only an order-of-magnitude difference between the self-diffusion coefficients of methane ($\approx 10^{-8} m^2 s^{-1}$ at 250 K [21]) and CF_4 as presented above.

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