

Anthracene Adsorbed at the Solid/Liquid Interface. A ^2H -NMR Study of the Dynamics and Structure

G. Neue

Lehrstuhl für Physikalische Chemie II, Universität Dortmund

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^2H -NMR relaxation time studies were performed on the adsorption system anthracene + cyclohexane/graphite at 295.2 K. Translational and rotational diffusion coefficients are determined for adsorbed anthracene molecules. No trace of rotational anisotropy with respect to the surface was found rendering the term orientation meaningless for a description of the structure of the adsorbed layer. Instead, a model is proposed viewing the solvent as the primary component forming a foam-like hollow structure on top of the solid, where each cavity contains an anthracene molecule which performs almost isotropic rotational diffusion.

1. Introduction

PAH* carbon systems are of special interest because they are produced by combustion processes as soots [1] and PAHs are well-known carcinogenic substances [2]. Much work is aimed to elucidate the hazards caused by the inhalation of soots (mainly diesel soots) [3]. Soots are small carbon particles coated by tar-like substances which contain a large number of different PAHs in variable composition. These systems have to be regarded as solutions in contact with a solid surface. As a simple example of this kind the present work uses the system anthracene + cyclohexane/graphite as a model system because thermodynamic data are available [4].

The liquid/solid interface is much less studied than the gas/solid interface. There are several reasons for this situation. Usually the gas phase is easily described by theoretical expressions. Due to strong lateral interactions combined with mobility, molecules in liquid phases are much less easily described. In the case of a solution in contact with solid surfaces the mixed phase complicates the situation even more. Non-ideal behaviour is common in such systems [5]. Moreover, the ratio substance (adsorbed)/substance (bulk) usually is much smaller when a liquid is adsorbed. Hence, any method using bulk properties requires extreme precisions to detect the small changes accompanying the adsorption process.

NMR is a very promising tool to study liquid/solid interfaces. In principle, selecting a certain nucleus (e.g. ^1H , ^{13}C , ^2H , ^{15}N) the investigator monitors molecules, groups or specific atoms. NMR is very sensitive to motion [6]. Isotropic motion of a molecule within a liquid averages the linewidth of the NMR signal by about six orders of magnitude as compared to a rigidly adsorbed molecule. Anisotropic or hindered motions therefore are easily detected and quantified. The theory of the influence of molecular motions upon NMR parameters is extremely well developed [6–8]. Any detailed model can be checked against experimental data.

Inherent to this approach there is a disadvantage. As there is an infinite number of possible motions but only a certain number of experimental points, other methods and/or physical arguments have to be used in advance to reduce the possible models to a few alternatives. As the present work is aimed at gaining first insight to the dynamics within a liquid/solid adsorption system another approach is taken. The specific details of rotational motions only change the values of relaxation rates by a few ten percents [2] whereas the speed of the overall rotation determines by far the NMR parameters as illustrated by the above example. Therefore, in some cases simple models will be used to characterize the motion.

2. Theory

The ^2H nucleus is ideally suited to study the rotational molecular dynamics. Its low natural abundance of 0.015% makes it a specific probe when deuterated

* PAH = polycyclic aromatic hydrocarbon.

Reprint requests to Dr. G. Neue, Lehrstuhl für Physikalische Chemie II, Universität Dortmund, Otto-Hahn-Straße, D-4600 Dortmund 50, Germany.

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compounds are used. Relaxation of the spin ($I = 1$) is by far dominated by fluctuations of electric field gradients interacting with the quadrupolar nucleus. The field gradients are characteristic of specific bonds [9] and can be regarded as constant in magnitude. Hence, the only cause for fluctuations are rotations of the field gradient because of rotations of the molecule.

The relaxation rates are linear combinations of spectral densities of correlation functions of second order spherical harmonics describing the orientation of the electric field gradient with respect to the external magnetic field [7]:

$$\frac{1}{T_i} = \sum_{n=0}^2 c_{ni} J_n(n\omega), \quad i = 1, 2. \quad (1)$$

If the motion is a fast isotropic rotational diffusion, T_1 and T_2 are simply given by

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{2} \pi^2 (\text{QCC})^2 \tau_c, \quad (2)$$

where QCC is the quadrupole coupling constant and τ_c is the correlation time of the rotational diffusion. In (2) it has been assumed that the asymmetry parameter η of the electric field gradient is negligible [9]. T_2 is related to the linewidth Δv by [7]

$$T_2 = (\pi \Delta v)^{-1}. \quad (3)$$

In the presence of surfaces it is advisable to perform a transformation from the laboratory frame (magnetic field) to a crystal frame where the correlation functions are referenced to for having a simple possibility to include surface induced asymmetries of the motion. Then [6],

$$\frac{1}{T_i} = \sum_n c_{ni} \sum_m D_{nm}^{(2)*} D_{nm}^{(2)} J_m. \quad (4)$$

T_2 computed with the aid of (4) is meaningless if the frequency of the motion is slow as compared to the width of the solid state spectra [7], which in this case are observed. Spin alignment methods [10] can be used then to deduce the type of motion as well as rotational diffusion coefficients.

If the surface has a symmetry equal to or higher than threefold, then the $D_{nm}^{(2)}$ depend only on β , the angle between the surface normal and the direction of the magnetic field.

As stated in the introduction, relaxation rates can be expected to be different for molecules within a liquid described by (1) and adsorbed molecules (4). The

very existence of an adsorption equilibrium means that there is an exchange between the solution and the adsorption layer. The effective relaxation rates resulting from a two site exchange are studied by Winkler [11].

The most extreme case is the so-called fast exchange. It is realized when the mean life-time of a molecule within a certain phase is short as compared to the relaxation times. In this case a single relaxation rate for both phases is observed:

$$\frac{1}{T_i} = \frac{P_1}{T_{i,1}} + \frac{P_2}{T_{i,2}}, \quad (5)$$

where the P_m denote the probabilities to find the molecule within phases m and are related to the total number of molecules within the respective phases,

$$P_m = N_m / (N_1 + N_2). \quad (6)$$

As is evident from (6), even in the limit of fast exchange it is possible to shift the observed value of the relaxation rate towards the rate of the pure adsorbed layer as the surface area/liquid volume ratio is increased.

Graphites produce local variations of the magnetic field mainly due to their extreme anisotropic magnetic susceptibility [12] leading to inhomogeneous asymmetric line shapes which can be observed in solid Xe layers on graphite where other interactions are small [13]. In such a case Hahn echoes [14] can be used to measure a true T_2 .

Complications arise if there is a considerable translational diffusion carrying the molecules through different magnetic fields. This, too, represents a case of exchange. But now it is not possible to reduce the problem to a simple two-site model because there is a continuous distribution. Even more worse, nothing is known about the magnetic field strength as a function of the distance travelled by a molecule. But there is a way around this problem. The line narrowing of the inhomogeneous part of the signal should not depend on a specific molecule but only on its translational diffusion coefficient. If the line-width is known as a function of the diffusion coefficient for a particular substance the same relationship should be valid for any other substance provided the adsorbent is the same. To become independent of the external field strength, linewidths are to be given in ppm. Fortunately, in one case the inhomogeneous linewidths and diffusion coefficients are known from independent measurements [12, 15] of the temperature dependence

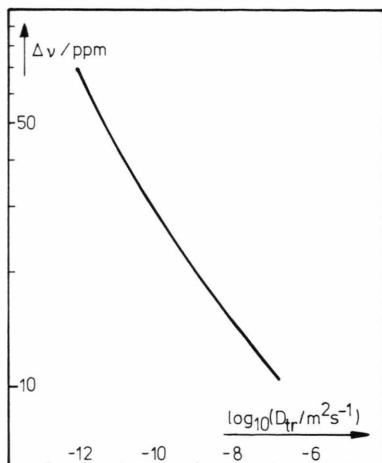


Fig. 1. Magnetic line broadening Δv of ^2H spectra caused by Graphon surfaces as a function of the translational diffusion coefficient D_{tr} of molecules adsorbed on top of the surfaces.

of both quantities. Combining the two sets of data of n-butane adsorbed on Graphon gives the required functional dependence shown in Figure 1.

3. Experimental

The graphites used for this investigation are Graphon (Cabot, Boston, Mass., USA), a graphitized carbon black and Grafoil (Union Carbide, USA), a foil consisting of very thin parallel sheets of graphite. Because of its narrow distribution of the graphitic surface normals in space, Grafoil can be used to study orientations of adsorbed molecules. The specific surfaces are determined by the BET-method to be $80 \text{ m}^2 \text{ g}^{-1}$, and $30 \text{ m}^2 \text{ g}^{-1}$, respectively. The geometries of both materials are shown schematically in Figure 2.

Prior to sample preparations Graphon was baked under vacuum at 400 K for 24 hours to remove physisorbed molecules (mainly water). Grafoil proved to be much more contaminated with organic materials. Extraction with cyclohexane (Uvasol, Merck, Darmstadt) was carried out for 96 h within a Soxhlet apparatus. Cyclohexane was added until the samples appeared wet. Also added was a precalculated amount of anthracene-d₁₀ (Merck, Sharp, and Dohme, Canada) to produce $\theta = 0.36$. The necessary adsorption data were taken from [4]. Immediately after filling the tubes were closed by plugs to prevent evaporation of the solvent. The samples were left for two days until the

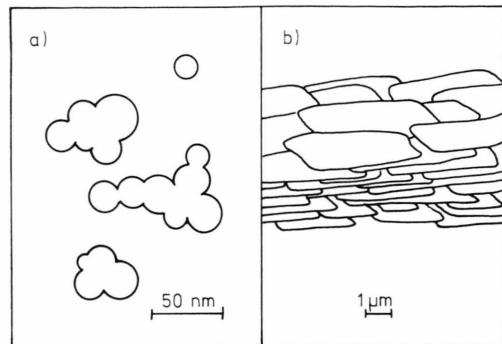


Fig. 2. Schematic representation of the geometries of Graphon (a) and Grafoil (b) surfaces. All surfaces accessible to molecules are graphitic basal planes.

anthracene crystals disappeared completely. The addition of solid anthracene was necessary because the amount needed exceeded the solubility limit [4] by about a factor of ten. Prior to NMR measurements the samples were left overnight within the probe head at 295.2 K to assure thermodynamic equilibrium.

The ^2H -NMR measurements were carried out with a CXP 100 spectrometer (Bruker Physik, Karlsruhe) supplemented by a cryomagnet (Oxford Instruments, Oxford, England) at 52.72 MHz.

4. Results and Discussion

As was described in the experimental section, almost 90% of all molecules belong to the surface layer. Relaxation times T_1 and T_2 of the solution were observed to be about 200 ms, i.e. much longer than the corresponding times for the system solution + graphite. According to (5) it can be concluded that the observed relaxation rates reflect almost exclusively the motional behaviour of molecules of the adsorption layer irrespective of the simultaneous presence of the solution. Shown in Fig. 3 is the ^2H spectrum of anthracene-d₁₀ adsorbed on graphon. The signal possesses a Lorentzian lineshape except for a small shoulder at lower field. This shoulder is readily identified from its relaxation behaviour as due to molecules far from any surface and most probably results from a small excess of liquid. It contributes much less than 1% to the signal. The linewidth Δv of the main signal was observed to be 2950 Hz (66 ppm). As can be proved by application of a Hahn-echo pulse sequence, the line is mainly determined by magnetic field inhomogeneities of Graphon. Therefore, the line-

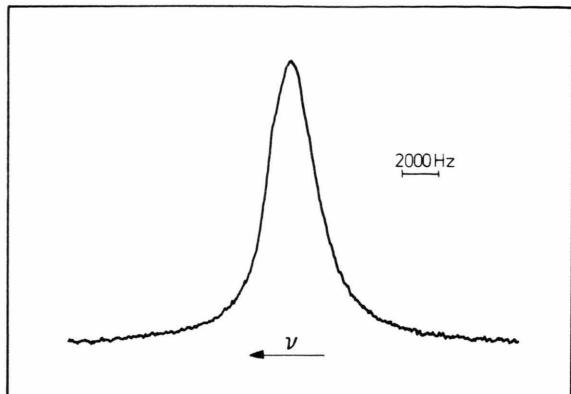


Fig. 3. ^2H -spectrum of anthracene adsorbed on Graphon (with cyclohexane as solvent).

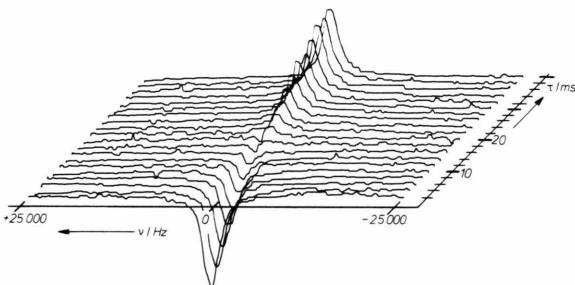


Fig. 4. Inversion recovery spectra of anthracene adsorbed on Graphon. The time interval τ for which the longitudinal magnetization was allowed to relax is indicated.

width reflects the averaging of the different magnetic fields by translation of the adsorbed molecules along the graphitic surface. Using Fig. 1 as explained above, the translational diffusion coefficient is estimated to be $D_{tr} = 9 \cdot 10^{-13} \text{ m}^2 \text{ s}^{-1}$, which is much slower than that expected for a molecule within a liquid. Obviously, the surface slows down the translational mobility of anthracene molecules by four or five orders of magnitude.

To obtain T_2 of the quadrupolar interaction free from the stochastic averaging process of the translational diffusion a sample containing Grafoil has been used. The large planar sheets of Grafoil produce only large scale variations of the magnetic field, which render the line shapes meaningless. In this case no averaging occurs, and Hahn echoes can be used to measure the true T_2 of the quadrupolar interaction.

The sample was measured with the three different orientations of the surface normal with respect to the external field. T_2 values obtained were 12, 15, and

14 ms \pm 5 ms for orientations of 0°, 60°, and 90°, respectively. Any anisotropy is smaller than the errors, and the differences in T_2 as a function of the orientation are not considered to be real. The magnitude of the uncertainty results from the high electric conductivity of Grafoil which damps the NMR receiver circuit to such an extent that the signal to noise ratio becomes extremely poor. If a mean value of $T_2 = 14 \text{ ms}$ is adopted and $\text{QCC} = 181 \text{ kHz}$ [16] is used, (2) predicts $\tau_c = 1.5 \cdot 10^{-10} \text{ s}$, which is roughly equal to the time needed for a full rotation of the anthracene molecule. In line with this interpretation is the value of $T_1 = 23 \text{ ms}$, which has been determined from the inversion recovery of the spectra of anthracene adsorbed on Graphon (Figure 4). The similarity of T_1 and T_2 , as well as the orientational independence of T_2 lead to the conclusion that the rotational motion is rather isotropic with respect to the graphitic surface, so that the application of (2) to determine τ_c is justified, and thus this quantity should be reliable to the extent to which T_2 is known exactly. The important question of anisotropy can be discussed with much higher precision regarding the magnitude of T_2 itself. According to (3) it corresponds to a linewidth of $\Delta\nu = 23 \text{ Hz}$, which is a factor of 5000 smaller than that expected for a molecule without rotational motion. Keeping in mind that the orientational dependence of the spectra is given by $D_{00}^{(2)} = \frac{1}{2}(3 \cos^2 \theta - 1)$, the small linewidth implies that the weighted mean of $D_{00}^{(2)}$ taken over a time of the order of T_2 is zero to within 0.02%. This is exceedingly close to perfect isotropy.

In [4] it is stated that adsorption of anthracene from cyclohexane by Graphon reaches saturation when the coverage is $\theta = 0.4$. This value was based on a theoretical monolayer of close packed motionless anthracene molecules oriented flat with respect to the surface. This finding may be interpreted in a new way when combined with the dynamical information of the present work. The rotation of the molecules is much faster than the translation. It is easily computed that within 1 ns the anthracene molecule has completed several rotations while simultaneously it has been translated by only 40 pm. Viewing the adsorption layer as a close-packed arrangement of spheres there is a radius of 0.82 nm for each of the spheres. As estimated from van der Waals diameters an anthracene molecule rotating in place will use a radius of 0.53 nm for its motion. The difference may just be enough allowing for a single shell of solvent molecules.

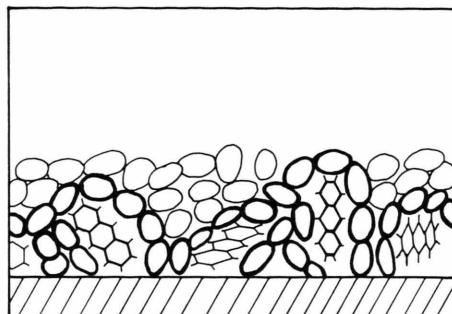


Fig. 5. Schematic picture of the dynamic cage model of the adsorbed layer compatible with the NMR data. Ellipses represent cyclohexane molecules which dominate the structure and dynamics of the liquid/solid interface.

Another detail should not go unnoticed. If the rotational correlation time τ_c is converted to a hypothetical translational diffusion coefficient for a motion around the spherical volume of a rotating anthracene molecule, this quantity is of the order of $1 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$. This is remarkably close to translational self-diffusion coefficients of liquids.

From the above considerations the following structure model is proposed to account for the dynamical behaviour of the adsorbed anthracene molecules. The solvent is the active component within the adsorption layer. At the surface cyclohexane forms a network around anthracene providing cavities where rotational diffusion takes place. This rotation is generated by the translation of cyclohexane molecules next to anthracene explaining the apparently perfect isotropy of the rotation with respect to the surface. Translation

appears as a simple by-product of the ever changing shape of the cavity. The structure model is depicted schematically in Figure 5.

5. Conclusions

The present paper showed that deuteron NMR is able to elucidate the dynamical behaviour of molecules adsorbed at the liquid/solid interface. Based on the dynamics found, a structure model for the layer adjacent to the solid is developed, where the solvent molecules play the most important role. They form shells around anthracene, forcing it to rotate when they diffuse by.

The question of how the solute is oriented with respect to the surface is proved to be obsolete in this system. The first question to be asked appears to be: are there any asymmetries of the rotational motion of the adsorbed solute molecules with respect to the surface?

It is hoped that this work will stimulate further investigations using different techniques in order to confirm or disprove the dynamic structure model of the interfacial region.

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