NMR STUDIES ON GRAPHITE-METHANOL SYSTEM

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The nuclear magnetic relaxation times for protons of methanol on graphite have been studied. The perpendicular and the transversal magnetization as a function of temperature were measured. The results show that the presence of graphite slowed down the methanol movement compared with that in the pure alcohol, and that the methanol molecules are attached to the graphite surface via methyl groups.

1. Introduction

Considerable literature has accumulated over the years dealing with the thermo-dynamics of physical adsorption on surfaces [1, 2]. However less is known about the dynamics of adsorbed molecules, this in spite of the fact that from the early days of nuclear magnetic resonance it has been recognized [3] that NMR relaxation measurements are a powerful tool for the study of molecular dynamics.

Nuclear magnetic resonance free precession signals [4] are profoundly affected by molecular kinetic phenomena such as the motions of molecules, atoms or ions which either contain or exist near the observed nuclei. Consequently, motional phenomena of adsorbed molecules can be studied by NMR pulse experiments.

Nuclear magnetic resonance techniques appear to hold some promise as tools for investigating the interaction of adsorbed molecules with a substrate surface and with one another. A considerable amount of work has been done regarding the study of adsorption processes using nuclear magnetic resonance techniques [5–21]. However, the study of methanol on graphite by NMR has not been reported in literature, and it seems of interest, therefore, to study the methanol-graphite system and to throw some light on the behaviour of methanol molecules on graphite surface, since it is known [1, 2] that the graphitization

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process makes the surface homogeneous, regular and tends to remove [22] highly active centres. Moreover, Kiselev [23] has found from adsorption studies that, for the methanol adsorbed on graphitized carbon black, the molecules are usually less localized.

2. Experimental

Materials

The graphite used in this investigation is spectroscopic graphite of high purity, its surface area is $4 \text{ m}^2/\text{g}$. It was purchased from "Ringsdorf werk", Bad-Godesberg, West Germany, under the name of RWA and it contains less than 0.1 ppm paramagnetic ions. Deuterated methanols were obtained from Merk, Sharp and Dohme, Darmstadt, West Germany.

Preparation of samples

A certain weight of graphite was taken in a constricted pyrex tube and evacuated at 200°C for three hours. The ultimate vacuum was not less than 10^{-5} torr as measured with a calibrated McLeod gauge. A certain amount of methanol was also weighed and evacuated until it was completely free from air. The transfer of methanol on graphite was then undertaken. After this, the tube was sealed off. Three samples of different methanol--graphite mass ratios were prepared for CH_3OD and CD_3OH. In the case of CH_3OD the ratios were 0.4, 0.7 and 1.0, these samples are designated A_1, A_2 and A_3, respectively. In the case of CD_3OH the mass ratios were 1.0, 1.6 and 2.2 for samples designated B_1 B_2 and B_3, respectively. Some other diluted samples were prepared by diluting CH_3OD, with CD_3OD (25% or 50%, by weight).

Measurements[1]

The spin lattice relaxation times reported here were all measured by a standard 90°, 90° pulse sequence [24]. The recovery of the magnetization to equilibrium could in all cases be a single exponential with constant T_1. T_2^* effective transversal relaxation time has been measured from the logarithmic plot of the free induction decay. T_2^* is considered as a qualitative measurement of T_2 transversal relaxation time, since these samples were found experimentally to exhibit a steady simple exponential decay.

Temperature control

The temperature was adjusted from −90°C up to 25°C by circulating thermostated water through the probe head. For low temperatures a stream of nitrogen gas was passed through a copper coil immersed in liquid nitrogen. The cold stream of nitrogen was passed around the probe head. This stream was usually heated to the required temperature by means of a heating coil. The temperature was measured by means of a thermocouple placed in the gas stream, and was controlled to within 1°C by means of an electronic regulator (Artromix-Model 5301 E).

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[1] The proton relaxation times were measured by using a conventional NMR spectrometer operating at 60 MHz.

3. *Results and conclusion*

Figs 1 and 2 show the results of measurements of longitudinal relaxation time T_1 as a function of temperature for the CH_3OD-graphite system, the CD_3OH-graphite system as well as those of the corresponding pure alcohols. The results for pure alcohol, for example, CH_3OD (cf. Fig. 1) compares satisfactorily with those obtained by O'Reilly [25]
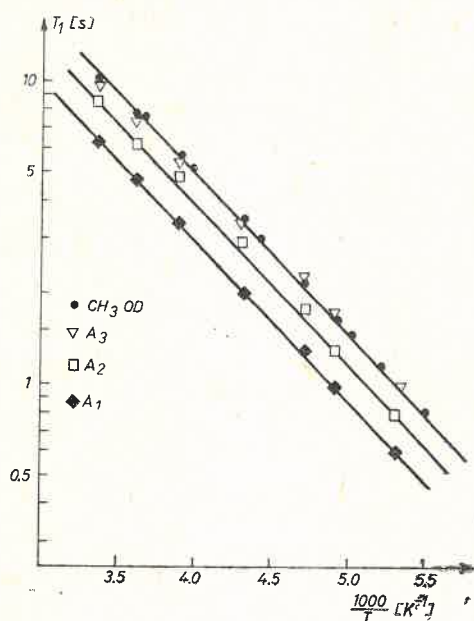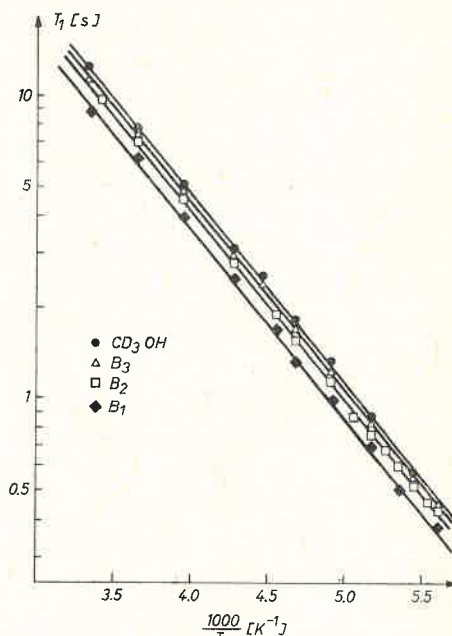

Fig. 1

Fig. 2

who found the average value of activation energy E_a of this alcohol in the temperature range 145 – 335°K to be 2.62 ± 0.15 Kcal/mole. O'Reilly also found that the value of E_a is usually smaller in the high temperature range. In this investigation the value of E_a equals 2.4 ± 0.2 Kcal/mole, since it was determined in the temperature range 183 — 298°K. The value of Ea for CD_3OH in the same temperature range was found to be 2.9 ± 0.2 Kcal/mole. From Figs 1 and 2, it is clear that T_1 for the alcohol-graphite samples are temperature dependent in a similar manner as T_1 for pure alcohols. Increasing the graphite content leads to a decrease in the proton relaxation time with a negligible change in the activation energy of the system. Thus, the presence of graphite is, in fact, slowing down the alcohol movement. However, this occurs without the appearance of a dispersion minimum [14, 21] in the temperature range investigated.

At such a minimum of the relaxation time, the relation $\omega T_c \approx 1$ holds and as a consequence of not finding the minimum, at −90°C the molecular motion is still comparatively fast, i.e. $T_c \leqslant 2.5 \times 10^{-9}$ sec.

The relation between $1/T_1$ and the mole fraction of the proton-containing species in the system $CH_3OD - CD_3OD$-graphite was also investigated. From the intercept of the

straight line $(1/T_1)$intra, the intramolecular relaxation rate has been determined and was found to be equal to 4.7×10^{-2} sec^{-1} for the three samples A_1, A_2 and A_3. This is the same value obtained by Zeidler [26] for the pure alcohol at the same temperature.

Such a hydrogen-deuterium dilution plot (cf. Fig. 3) shows that really the magnetic dipole-dipole interaction between the alcohol protons causes the relaxation rate and not paramagnetic centres on the graphite surface. Furthermore, the plot in connection with the fact that the intramolecular relaxation rate is unchanged in the alcohol system indicates
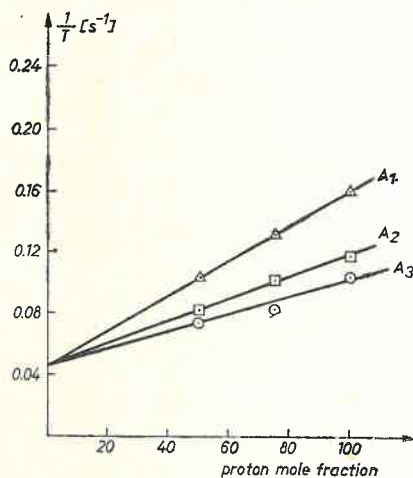

Fig. 3

that the relative translational motion causing the intermolecular relaxation rate is slowed down on the graphite surface in comparison with the pure liquid methanol. The rotational motion of the methyl group which dominates the intramolecular relaxation rate is virtually unchanged.

Fig. 4 shows T_2^* (effective transversal relaxation time) as a function of temperature which has been obtained from the logarithmic plot of the free induction decay. The study of T_2^* may be considered as a qualitative measurement of T_2 transversal relaxation time since for the samples investigated it was experimentally found that the free induction exhibits a steady simple exponential decay. It may be seen that the value of T_2 changes only slightly with temperature, whereas the variation of T_1 with temperature is much stronger (cf. Figs 1 and 2). The value of T_2 of CH_3OD-graphite and CD_3OH-graphite samples show a different temperaure dependence, but for both alcohol-graphite samples, the value of T_2 increases with increasing methanol content. The values of T_2 are more strongly influenced by the methanol concentration than T_1. For both pure alcohols the values of T_2 is ≈ 1 ms — and the free induction decay is not exponential. It is clear that the value of T_2 of the alcohol-graphite samples differ definitely from T_2 of pure alcohols. It is also well known from the BPP theory [27] in magnetic dipole relaxing liquids, over a large range of temperature and frequency that $T_1 = T_2$. Generally, paramagnetic impurities can change this relation and then one will get $T_1 > T_2$. This was explained by Bloem-

bergen [28, 29]. Resing [14, 16, 17] in his work especially in Ref. [16] proposed another explanation. The main idea of this work is that there exists a distribution of correlation time when the molecules on the surface and molecules in the liquid are considered.
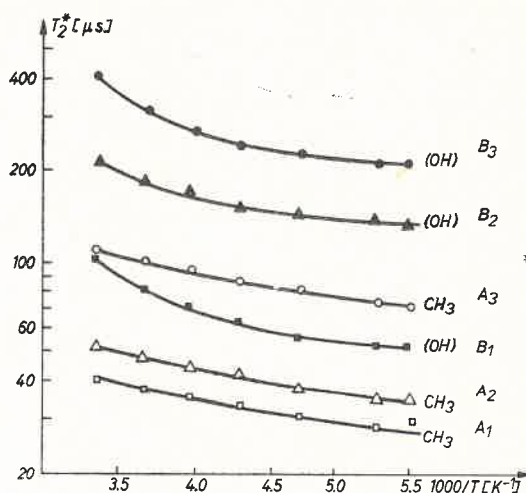

Fig. 4

Since the graphite under investigation has a high degree of purity, i.e. has no paramagnetic centers on the surface, as was also evidenced by the measurement of intramolecular relaxation rates, the scalar interaction between the paramagnetic centres and the alcohol protons must be completely excluded.

The change of T_2 with a change of the graphite content of the samples can be explained by the alcohol molecules being attached to the graphite surface for a fairly short time. At the surface the molecular motion is strongly anisotropic. This leads to a loss of phase coherence of the spins in the molecules at the surface and the exchange between the attached state and free methanol then causes the observed rapid decay of the transversal magnetisation of the alcohol-graphite samples. The smaller values of T_2 for the methyl group in CH_3OD as compared with those of CD_3OH indicates that the anisotropic motion in the attached state has a greater influence on the CH_3 relaxation which contains an intramolecular contribution. This may even be taken as an evidence that weak attachement of the alcohol on the graphite surface occurs via the methyl groups.

REFERENCES

[1] W. A. Steele, *Adv. Colloid Interface Sci.* **1**, 3. (1961)
[2] N. N. Avgul, U. Kiselev, *Chem. Phys. Carbon* **6**, 1 (1970).
[3] N. Bloembergen, E. M. Purcell, R. V. Pound, *Phys. Rev.* **73**, 679 (1948).
[4] E. L. Hahn, *Phys. Rev.* **80**, 580 (1950)

[5] J. R. Zimmerman, B. G. Holmes, J. A. Lansater, *J. Phys. Chem.* **60**, 1157 (1956).

[6] J. R. Zimmerman, W. P. Brittin, *J. Phys. Chem.* **61**, 1328 (1957).

[7] J. R. Zimmerman, J. A. Lansater, *J. Phys. Chem.* **62**, 1157 (1958).

[8] H. Winkler, *Z. Naturforsch.* **16a**, 780 (1961).

[9] D. E. Woessner, *J. Chem. Phys.* **35**, 41 (1961).

[10] H. Kimmel, *Z. Naturforsch.* **16a**, 1058 (1961).

[11] D. E. Woessner, J. R. Zimmerman, *J. Phys. Chem.* **67**, 1590 (1963).

[12] D. E. Woessner, *J. Chem. Phys.* **39**, 2783 (1963).

[13] W. S. Brey Jr, K. D. Lawson, *J. Phys. Chem.* **68**, 1474 (1964).

[14] H. A. Resing, J. K. Thompson, J. J. Krebs, *J. Phys. Chem.* **68**, 1621 (1964).

[15] S. Reball, H. Winkler, *Z. Naturforsch.* **19a**, 861 (1964).

[16] H. A. Resing, *J. Chem. Phys.* **43**, 669 (1965).

[17] J. K. Thompson, J. J. Krebs, H. A. Resing, *J. Chem. Phys.* **43**, 3853 (1965).

[18] D. Michel, *Z. Naturforsch.* **21a**, 366 (1966).

[19] J. Reuben, D. Fiat, M. Folman, *J. Chem. Phys.* **45**, 311 (1966).

[20] J. Reuben, D. Fiat, *J. Chem. Phys.* **46**, 4453 (1967).

[21] J. W. Riehl, K. Koch, *J. Chem. Phys.* **57**, 2199 (1972).

[22] R. A. Beebe, J. Biscoe, W. R. Smith, C. B. Wendell, *J. Am. Chem. Soc.* **69**, 95 (1947).

[23] A. V. Kiselev, A. I. Lygina, *Kolloidnyi Zh.* **23**, 369 (1961).

[24] T. C. Farrer, E. D. Becker, *Pulse and Fourier Transformation NMR*, Academic Press, Oxford 1971.

[25] D. E. O'Reilly, E. M. Peterson, *J. Chem. Phys.* **55**, 2155 (1971).

[26] E. V. Goldammer, M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.* **73**, 4 (1969).

[27] N. Bloembergen, E. M. Purcell, R. V. Pozund, *Phys. Rev.* **73**, 579 (1967).

[28] N. Bloembergen, *J. Chem. Phys.* **27**, 572 (1957).

[29] N. Bloembergen, *J. Chem. Phys.* **27**, 595 (1957).