CIENCIA, 2(1) (1994), 25-32
Maracaibo, Venezuela

Nuclear magnetic resonance of protons on DMSO-O_2-NaX Zeolite-system

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Recibido: 07-12-93 Aceptado: 02-03-94

Abstract

A DMSO-O_2-NaX-zeolite system was studied by pulsed protons NMR technique determining the T_1- and T_2- relaxation times, and FID at 10 MHz and 89.5 MHz in a temperature range between 125 K and 355 K. An isotropic rotation of the methyl group was proposed influenced by a coupling of the DMSO (dimethylsulphoxide) molecule with the zeolitic lattice for the microdinamic motion of this system.

Key words: NMR, zeolite, DMSO, oxygen, paramagnetic centers.

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Resumen

Se estudió el sistema DMSO-O_2-Zeolita NaX por medio de 4 técnica de RMN de protones, se midieron los tiempos de relajación T_1 (a 10 MHz) y T_2 y el FID (a 89,5 MHz) en un intervalo de temperaturas comprendida entre 125 K y 355 K. Se propone un estado de rotación isotrópica para el movimiento microdinámico del grupo metil, influenciado por un acoplamiento de la molécula de DMSO (dimetilsulfóxido) con la red zeolítica.

Palabras claves: RMN, zeolita, DMSO, oxígeno, centros paramagnéticos.

Introduction

In the study of molecules adsorbed on porous solids the pulsed NMR technique has been applied in the last decades (l) due to the fact that adsorbent-adsorbate interactions and microdynamic motions can be investigated. However, pulsed NMR measurements of protons, for instance, are usually limited to highly pure adsorption systems if magnetic relaxation time measurements *are* used, because paramagnetic impurities can disturb the signal response (2). Unfortunately, many industrial adsorption systems contain these impurities, this the use of protons NMR technique tends to *be* limited. Nevertheless, studies of adsorption systems with located paramagnetic impurities have been published (3). In this work an example is presented where information could be obtained about of protons relaxation in spite of the influence of paramagnetic centers (molecular oxygen) that produces a strong local magnetic field on dimethylsulfoxide (DMSO) adsorbed on pure porous adsorbent (NaX-Zeolite).

Materials and methods

Highly pure chemical reactants and NaX-zeolite were used for the preparation of the NMR sample. The zeolite was supplied by the Physics Department of the University of Torun, Poland. All substances showed EPR signals of paramagnetic impurities of the order of magnitude of 1 ppm. The zeolite was dehydrated in high vacuum at 260°C during one day. The DMSO was degassed in high vacuum and adsorbed both at room temperature and in vacuum. The sample was filtered and dried at atmospheric air (4). The concentration (determined by the EPR technique) of the molecular oxygen of the DMSO absorbed on the sample was $10^{19}/\text{cm}^3$. The NMR equipment worked at 10 MHz and 89.5 MHz and was built in our laboratory using modern electronic and a Bruker electromagnet supplied by the Volkswagenwerk Foundation of the GFR. The longitudinal and transversal relaxation times were determined using the π–τ–$\pi/2$ (inversion-recuperation) and $\pi/2$–τ–π (Hahn echo) sequences respectively. Furthermore, the free induction decay (FID) was measured taking its 1/e value.

Results and discussion

In Figure 1 the measured longitudinal and transversal times are shown as a function of sample temperature. For the longitudinal relaxation time the experimental data indicate a clear minimum near 35°C (308 K) of approximately 17 ms. The obvious oscillation in the transversal relaxation time is generally observed if paramagnetic centers are present (5). It was veryfied that this signal is caused by the paramagnetic oxygen molecules which are introduced in the zeolite sample during the preparation procedure. The signal was detected (with a structurelesss wide of $\Delta H = 1000\ G \pm 25\ G$) by an EPR (Electron Paramagnetic Resonance) technique and evaluated (4) with a formula reported by Poole (6). The rigid lattice behaviour of the FID at temperatures below -150°C is in relatively good agreement with the measured data of pure DMSO (7). From the T_2 rigid lattice of the order of 10^{-5}s (see Fig. 1), the second moment can be estimated by (8,9):

$$M_{II_{r.l.}} = \langle \Delta H^2 \rangle_{r.l.} = \frac{\pi}{2\gamma_I^2 T_{2r.l.}^2} \approx 22.5\ G^2 \qquad [1]$$

which takes into account only the intramolecular interaction of the DMSO molecule (7,14). In our case, the second moment should be greater because of the additional contribution of the proton interaction with the paramagnetic center. Therefore:

$$\langle \Delta H^2 \rangle_{r.l.} = M_{II\text{rigid lattice}} + M_{IS\text{rigid lattice}} \qquad [2]$$

The total Hamiltonian operator which represents the interaction of a nuclear spin I with its surrounding is:

$$H = H_Z + H_{I-I} + H_{S-I} \qquad [3]$$

where H_Z is the Zeeman operator, H_{I-I} the dipolar operator between the nuclear spins and H_{S-I} in this study, the operator between the dipolar moment of the proton $\vec{\mu}_I = \gamma_I \hbar \vec{I}$ and the oxygen molecule $\vec{\mu}_S = \gamma_S \hbar \vec{S}$:

$$H_{S-I} = \sum_{i=1}^{6} \hbar^2 \gamma_I \gamma_S \left(\frac{\vec{I}_i \cdot \vec{S}}{r_i^3} - 3\frac{(\vec{I}_i \cdot \vec{r}_i)(\vec{S} \cdot \vec{r}_i)}{r_i^5} \right) \qquad [4]$$

where γ_i and r_i are the gyromagnetic factors and the distance proton-paramagnetic cen-

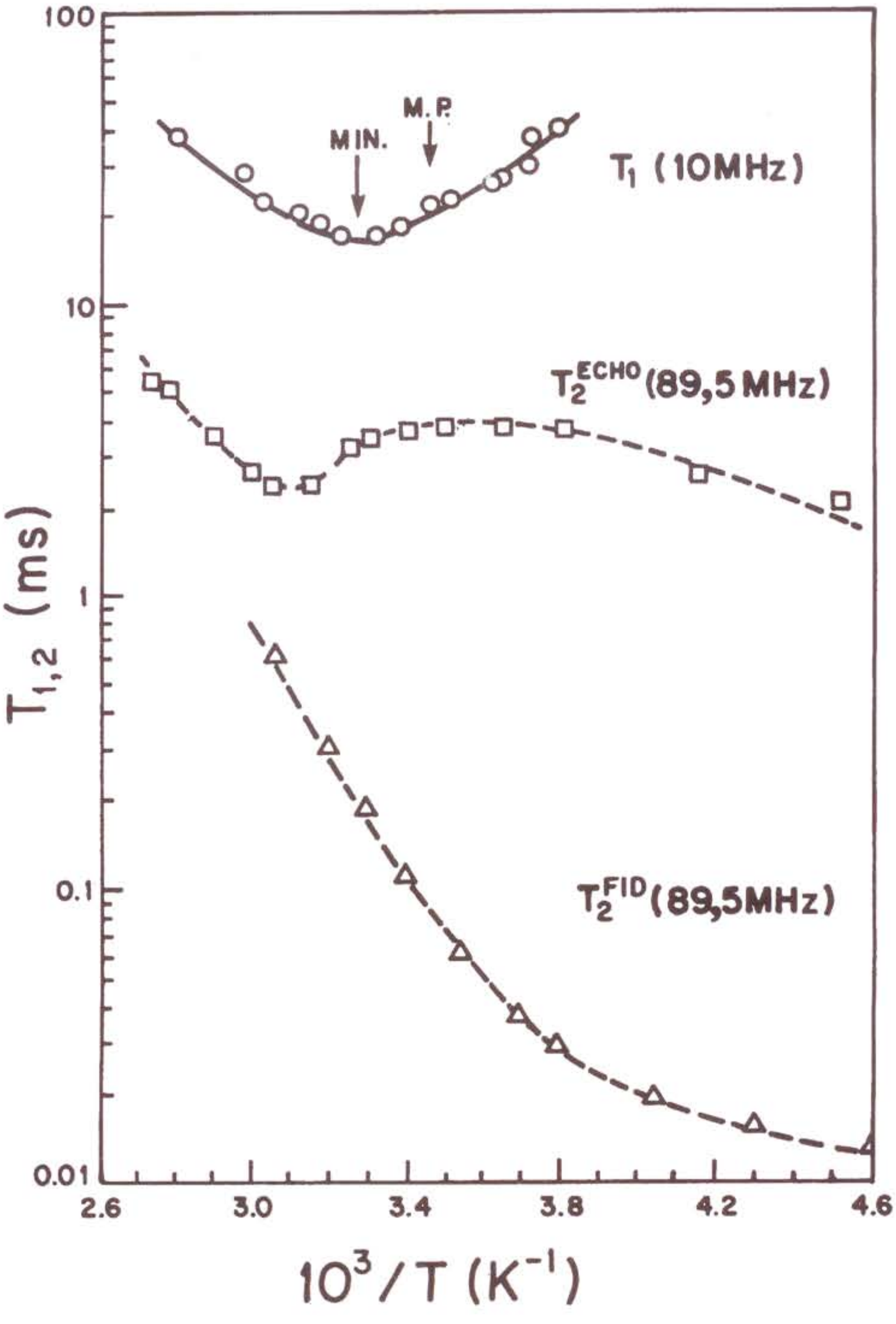

Figure 1. The experimental longitudinal (0) and transversal relaxation times (❐) and the free induction decay (Δ) of protons on *DMSO*-O_2-NaX-Zeolite system as a function of the sample temperature. The continuous line in the T_1 graphic is a theoretical fitness using the equation 16. MP: Melting Point.

ter respectively. It is assumed that the DMSO molecule interacts only with one paramagnetic center and the dipolar moment of the oxygen molecule is punctual. The dipolar field of the paramagnetic center has its instantaneous relaxation effect on the methylprotons only in a small region around the paramagnetic center defined by the barrier radius (which is the distance where the magnetic field of the proton is equal to the magnetic field of the paramagnetic centre (11)):

$$b = \left(\frac{<\mu_S^2> H_0}{\mu_I KT}\right)^{1/3}.a \qquad [5]$$

with "a" the interprotonic distance of 1.78 Å (10) and Ho the external magnetic field where $<\mu s^2>$ is the mean quadratic value of the moment of the paramagnetic centre and the dynamic effects are considered in the factor $<\mu s^2>Ho/KT$ which equals to the averaged moment of the paramagnetic centre which finds the nucleus in rapid reorientation ($\tau \ll T_2$). In our case, this radius is approximately 2 Å at 300 K and

$$<\mu s^2\ (O_2)> = \gamma_s^2\ \hbar^2 S(S+1)$$
$$= 6.73x10^{-40}\ (ergs/G^2) \qquad [6]$$

where we have supposed isotropy for the "g" factor of Landé ($\gamma_s\ \hbar = g.\beta$) and the molecule of oxygen is in the fundamental state. The relaxation effect of the most nuclei is caused by nuclei transport (hopping) or nuclear magnetization transport (molecular or spin diffusion) to the paramagnetic relaxation sink. Both effects are considered by the differential equation:

$$(\delta M\ (r,t)/\delta t)_{total} =$$
$$(\delta M(r,t)/\delta t)_{paramagn.} + (\delta M(r,t)/\delta t)_{trans} \qquad [7]$$

where $\vec{M}\,(\vec{r},t)$ represents the nuclear magnetization vector. Lowe and Tse (12) solved this equation for spin diffusion at low temperatures calculating the T_1 relaxation time. Combined with hopping precesses; Richards (5) reported a expanded solution. The relaxation times of nuclear spins relaxed by paramagnetic centers were considered by La Mar *et al.* (2), taking into account the correlation times of the paramagnetic centers and of the molecular diffusion of the protons but without spin diffusion:

$$\frac{1}{T_{1IS}} = \frac{1}{2}\gamma_I^2 M_{IS}\Big(\frac{\tau_c}{1+(\omega_I-\omega_s)^2\,\tau_c^2}$$
$$+\frac{6\tau_c}{1+(\omega_I+\omega_S)^2\,\tau_c^2}+\frac{3\tau_c}{1+\omega_I^2\,\tau_c^2}\Big) \qquad [8]$$

$$\frac{1}{T_{2IS}} = \frac{1}{4}\gamma_I^2 M_{IS}\Big(4\tau_c+\frac{\tau_c}{1+(\omega_I-\omega_S)^2\,\tau_c^2}+$$
$$\frac{3\tau_c}{1+\omega_I^2\,\tau_c^2}+\frac{6\tau_c}{1+\omega_s^2\,\tau_c^2}+\frac{6\tau_c}{1+(\omega_I+\omega_S)^2\,\tau_c^2}\Big) \qquad [9]$$

where γ_I, M_{IS}, ω_I, ω_S and τ_c are the gyromagnetic factor, the second moment of the proton-center interaction, the Larmor frecuencies of the proton and the paramagnetic center and finally the correlation time of the paramagnetic center-proton interaction in the diluted system:

$$\tau_c^{-1} = \tau_{cm}^{-1} + \tau_{cs}^{-1} + \tau_{chemical\ exchange}^{-1} \qquad [10]$$

where τ_{cm} is the correlation time of the translation and/or rotation of the *DMSO* molecule, $\tau_{\text{chemical exchange}}$ the correlation time of the proton exchange and τ_{cs} the correlation time of the spin of the paramagnetic center which fulfills the condition:

$$\tau_{cs} = T_{1s} = T_{2s} \qquad [11]$$

in a dilute system. At sufficient high temperatures (and unknown the chemical exchange of the protons in the *DMSO* due to the high stability of the CH_3 group) the molecular diffusion is more effective than the spin diffusion and modulate the field of the paramagnetic center (9). In this temperature range:

$$\tau_{cm} << \tau_{cs} \qquad [12]$$

where the correlation time τ_{cs} is of the order of 10^{-6}s. The total longitudinal relaxation time rate of the *DMSO* proton is:

$$1/T_1 = 1/T_{1II} + 1/T_{1IS} + 1/T_{1HF} \qquad [13]$$

Here T_{1II}, T_{1IS} and T_{1HF} are the relaxation times of the proton-proton interaction, proton-paramagnetic center interaction and the Fermi contact contribution respectively. Equation [13] can be simplified because of the insignificant contribution of the second moment of the order of some milligauss of the magnetic proton-proton interaction in the measured temperature range, predominantly above the *DMSO* melting point, and of the insignificant superposition of the electronic wave functions between the oxygen molecule and the methyl protons caused by their generally great distance. Therefore,

$$1/T_1 = 1/T_{1IS} \qquad [14]$$

Considering furthermore that $\omega_S >> \omega_I$, i.e. $\omega_S = 660\ \omega_I$, the relaxation times T_1 and T_2 of a proton-paramagnetic center interaction in a diluted paramagnetic system with an average distance of the paramagnetic centers of:

$$R = (3/4\pi N)^{1/3} = 30\ \text{Å} \qquad [15]$$

is:

$$\frac{1}{T_{1IS}} = \frac{1}{2}\gamma_I^2 M_{IS}\left(7\frac{\tau_c}{1+\omega_S^2\tau_c^2} + 3\frac{\tau_c}{1+\omega_I^2\tau_c^2}\right) \qquad [16]$$

$$\frac{1}{T_{2IS}} = \frac{1}{4}\gamma_I^2 M_{IS}\left(4\tau_c + 13\frac{\tau_c}{1+\omega_S^2\tau_c^2} + 3\frac{\tau_c}{1+\omega_I^2\tau_c^2}\right) \quad [17]$$

At temperatures sufficiently above the *DMSO* melting point (291.6 K) and below of 355 K, the correlation time is influenced principally by the fluctuation of the molecular rotation, i.e. isotropical diffusion:

$$1/\tau_{c\ mol.\ diff.} = 1/\tau_{c\ rot.\ DMSO.} \qquad [18]$$

In the equation [16] and[17] the second moment M_{IS} can be calculated by the formula reported by Pfeifer (l):

$$M_{IS} = <\Delta H^2>_{motion} = \frac{1}{3}\gamma_S^2\hbar^2 S(S+1)\ N_I^{-1}\sum_i^{N_I}$$

$$<(1 - 3\cos^2\Theta_{is})^2 r_{is}^{-6}> \qquad [19]$$

where r_{is} is the proton-paramagnetic center distance and Θ_{is} the angle between r_{is} and the external magnetic field. In this expresion [19] it has taken into account the influence of one single paramagnetic center (R > b) about the protons inside the spherical radius R. By requiring in equation [16] the condition for the T_1 minimum, i.e. $\omega_I\tau_c = 1$, we obtain for the second moment:

$$M_{IS} = \frac{4}{3}\left(\frac{\omega_I}{\gamma_I^2 T_{1min}}\right) \approx 7G^2 \qquad [20]$$

at the T_1 minimum temperature (308 K), what means that $M_{IS\ r.1}$ should be greater than this value. Assuming in equation [19] an isotropic molecular diffusion:

$$<(1 - 3\cos^2\Theta_{is})^2>_{isotropic} = 12/15 \qquad [21]$$

the radius of the first coordination sphere rcs can be estimated by:

$$r_{CS} = \left[\frac{4\gamma_S^2\hbar^2 S(S+1)}{15M_{IS}}\right]^{1/6} = 17\ \text{Å} \qquad [22]$$

Table 1

The correlation time (τ_c) at 291.6 K and its value at infinite high temperature (τ_o), the rotational viscosity constant (η), the rotational diffusion constant (D), the activation entropy (S) and the moment of inertia (I) of pure DMSO and DMSO-O_2-NaX-zeolite system

Sample	τ_c[s]	τ_o[s]	η[cp]	D[cm^2/s]	S[KJ/mol.K]	I[gr.cm^2]
DMSO-O_2-NaX zeolite	2.7×10^{-8}	8×10^{-13}	908	6.7×10^{-9}	-0.019	3.0×10^{-39}
DMSO pure (14)	1.9×10^{-10}	5.4×10^{-13}	6.4	0.95×10^{-6}	-0.016	1.4×10^{-39}
Parameter ratio	142	1.48	142	1/142	1.19	$(1.48)^2$

This result means that it is sufficient to extend the radius r_{IS} up to this value.

In a study published before (15), where all the sites of adsorption were dynamicaly equivalents for the *DMSO* on the zeolitic surface, but in the case discuss here the aim was to adjust the experimental T_1 value with a distribution of the time of correlation because the adsorption of the O_2 molecules in the sample depend simultaneously of the *DMSO* and the zeolitic surface (4). Therefore, the O_2 molecule can couple not only with the *DMSO* but also with the zeolitic surface. The coupling sites with the zeolitic lattice can be no-equivalents dinamically and can wait for a distribution of the correlation times. With this goal, the formula:

$$\frac{1}{T_1} = \overset{\infty}{\underset{0}{S}} p(\tau_c)(\frac{1}{T_1(\tau_c)} d\tau_c) \qquad [23]$$

was used witr the distribution function of the correlation times $p(\tau_c)$, while $T_1(\tau_c)$ was given by the formula [16]. For $p(\tau_c)$, the different distribution functions -reported in (13)- were used, but the result was unsuccessful. The distribution of Cole-Davidson was rejected because of the asymmetry and the symmetrical ones (Gaussian, log-gaussianic, Cole-Cole, Fuoss-Kirkwood and Fang) require distribution parameters which are not in the range of validy and/or require activation energies which differ substantially from the experimental value ($\Delta E > 30\%$) and/or the theoretical minimum of the distribution presents important displacement with regarded experimental position ($\Delta(1000/T) > 30\%$).

In accordance with these results the longitudinal relaxation time defined by equation [16] was fitted with least-square method (using a Pascal program running in a PC-XT Computer) to the experimental T_1 measuring points assuming a single thermal activation energy of Arrhenius type (continuous line in the top of the Fig. 1):

$$\tau_c = \tau_0 exp(E/KT) \qquad [24]$$

The parameters determined are the activacion energy (E) and the pre-exponential factor (τ_0). The first was found to 25.2 kJ/mol and the last to 8×10^{-13}s. The obtained energy has approximately the double value of the one for pure *DMSO* (14). Furthermore, the minimum of the T_1 relaxation time of the DMSO-O_2-NaX-zeolite sample was measured at a higher temperature (at 308 K at 10 MHz) than those from of the pure *DMSO* sample (at 216 K and 163 K at 25 MHz) (14) while the melting point of the dimethylsulfoxide (at 291.5 K) lies between these two minimum temperatures. From these facts one must suppose that the microdynamic motions of the methyl group are not the same in both samples. It is known that the motion of the pure *DMSO* below the melting point is characterized by a solid-like state (7,14), this means, principally by an anisotropic rotation of the methyl group around its axis with a jump frequency $(1/\tau_0)$ of $1,85\text{x}10^{12}$Hz ($\tau_0 = 5,4x10^{-13}$s), see Table 1.

In contrast the model above mentioned we stated for the saturated DMSO-O_2-NaX-zeolite system a more liquid like state at least above 291.6 K. For this reason, we assume as a possible microdynamic model a nearly isotropic rotation of the methyl group caused by the collisions between the *DMSO* molecules in the NaX-zeolite cages with a jump frequency, in this case of $1.25\text{x}10^{12}$ Hz ($\tau_0 = 8x10^{-13}$s). This means a small reduction due to the coupling with the zeolitic lattice and in lesser degree with the paramagnetic center.

The two minima found at purified dimethylsulfoxide (14) could not be observed in the DMSO-O_2-NaX-zeolite system. The presence of an single T_1 minimum may be attributed, however, to the coupling of the DMSO with the zeolitic lattice which perturbs obviously the original unequal S-C bond lengths of the pure DMSO molecule (10). This supposition is confirmed by experimental results of adsorbed dimethylsulfoxide on NaX-zeolite without oxygen molecules (15) and of pure dimethysulfone (14) with equal S-C bond lengths, where in both cases only one T_1 minimum was found.

In Table 1 some characteristic data of the pure dimethylsulfoxide and adsorbed in a O_2-NaX-zeolite are compared. In order to obtain these values, the DMSO volume was used determined by X-ray diffraction (120Å^3). For the determination of the radius of 3.06 Å, the DMSO molecule was supposed spherical. Furthermore, a classical rotor was assumed (16) to estimate the moment of inertia. As it can be seen, the obviously notable differences caused in the examples compared here by the correlation time ratio or its logarithmic or square value at infinite temperature (τ_0).

Acknowledgments

This work was supported by the "Consejo de Desarrollo Científico y Humanístico" of the Universidad Central de Venezuela and the Volkswagenwerk Foundation of Germany.

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