

## NUCLEAR MAGNETIC RESONANCE APPARATUS FOR MEASURING THE SPIN LATTICE RELAXATION TIME

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**Abstract.** The construction of a simple nuclear magnetic resonance (NMR) apparatus for measuring the spin lattice relaxation time  $T_1$  is described. The changes of  $T_1$  in the micellar phase of the system Triton X-114-water are investigated. Information about the structure and dynamics of the aggregates of this phase is obtained.

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### 1. Introduction

The nuclear magnetic resonance (NMR) spin lattice relaxation time  $T_1$  gives certain information about intramolecular and supramolecular motions of the studied systems. The simplest methods of measurement of  $T_1$  are based on the adiabatic fast passage through resonance. The method of Chiarotti et al. [1] uses an asymmetric modulation of the magnetic field  $H$  around its resonance value. In this case the signals are grouped in pairs with amplitudes

$$M_1 = M_0 \frac{1 - 2 \exp\left(-\frac{\tau_2}{T_1}\right) + \exp\left(-\frac{\tau_1 + \tau_2}{T_1}\right)}{1 - \exp\left(-\frac{\tau_1 + \tau_2}{T_1}\right)} \quad (1)$$

$$M_2 = M_0 \frac{-1 + 2 \exp\left(-\frac{\tau_1}{T_1}\right) - \exp\left(-\frac{\tau_2}{T_1}\right)}{1 - \exp\left(-\frac{\tau_1 + \tau_2}{T_1}\right)} \quad (2)$$

where  $\tau_1$  and  $\tau_2$  are the times during which the field  $H$  is lower and higher than the resonance value. One can adjust the times  $\tau_1$  and  $\tau_2$  so that the second signal is zero

and then from Eq. (2) it follows:

$$1 - 2 \exp\left(-\frac{\tau_1}{T_1}\right) + \exp\left(-\frac{\tau_2}{T_1}\right) = 0. \quad (3)$$

$T_1$  can be calculated from this equation at a given  $\tau_1$  and  $\tau_2$ . The determination of the moment of time where the second signal is zero and the measurement of the times  $\tau_1$  and  $\tau_2$  leads to some unaccuracy of the value of  $T_1$ .

Derzhanski *et al.* [2] proposed a method which eliminates some shortcomings of the method of Chiarotti *et al.* [1]. According to [2] the ratio  $\tau_1/\tau_2$  is kept constant when the modulation period is changed. The authors [2] obtained that

$$T_1 = 0.42(\tau_1 + \tau_2) \quad (4)$$

if  $\tau_2 = 3\tau_1$ .

## 2. The NMR Apparatus

We constructed a NMR apparatus for measuring of  $T_1$  according to the method in [2]. Its scheme is shown in Fig. 1. As a spin detector we use the autogenerator (AU) (1, Fig. 1). The AU operating frequency is 20.56 MHz which corresponds to the resonance frequency of the hydrogen nuclei in the magnetic field about 0.5 T. The electromagnet with its supply and current stabilization and also the probe temperature regulator device are not shown in the Fig. 1.

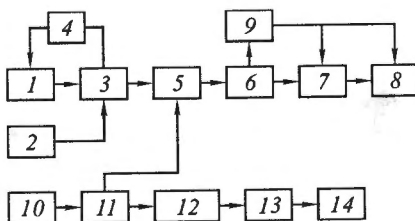


Fig. 1. Scheme of the NMR apparatus

The frequency response of the AU is used as a detector of the NMR dispersion. The frequency modulated signal of the AU (because of the passage through the resonance) is mixed with the signal of quartz stabilized generator (QG) (2, Fig. 1) in the mixer (3, Fig. 1). The difference of the frequencies of the AU and QG is obtained at the output of the mixer. The feed-back control (4, Fig. 1) ensures a constant AU frequency when the magnetic field  $H$  is out of its resonance value. The converter (5, Fig. 1) transforms the amplitude to TTL labels (0-5 V). This is necessary for operating of the devices 6, 7, 8 and 9 which are built on the basis of the TTL microschemes. The electronic circuit-breaker 6 (Fig. 1) forms two pulse sequences — the first, when the resonance appears, and second, when the resonance is absent. The differences between the number of pulses of these two sequences are calculated by the counter 7 (Fig. 1) and it is collected with the own sign in the storage of the managing device 9 (Fig. 1).

After every 10 passages through the resonance (in order to decrease the error) the sum of these differences is displayed on the indicator 8 (Fig. 1).

The magnetic field modulation is realized by the devices presented in the bottom of Fig. 1 (10-14). The generator 10 (Fig. 1) produces rectangular pulses which period can be changed from 0.08 to 2s. The device 11 (Fig. 1) changes the duty ratio of these pulses from 0.5 to 0.25. This device also controls the electronic switch in order to assure feeds of the two above mentioned pulse sequences. The change of the magnetic field  $\frac{dH}{dt}$  must fulfill the inequality

$$\frac{1}{T_1} \ll \frac{1}{H_1} \frac{dH_0}{dt} \ll \gamma H_1 \quad (5)$$

in order to obtain a fast passage through the resonance. This means that it must modify the slope of the change of the magnetic field  $H$ . The device 12 (Fig. 1) transforms the rectangular pulse to trapezium-shaped one and we can change the slope of the pulse fronts in order to obtain the optimum conditions for fast passage through the resonance. The amplifier (13, Fig. 1) amplifies the modulation circuit. The device 14 (Fig. 1) is the modulation coils on the magnet poles.

### 3. An Investigation of the Spin-lattice Relaxation of the System Triton X-114-Water

Triton X-114 is a surfactant which is widely used at the manufacturing of soap powders.

The object of our investigation is the  $T_1$  of the micellar phase of the system Triton X-114-water. By this way an information about the structure and dynamics of the aggregates of this phase should be obtained.

The spin-lattice relaxation times  $T_1$  of two samples with Triton's concentrations 55 and 70 wt. % in the temperature region 40-60 °C have been measured. The results are shown in Figs 2 and 3, where the experimental data are approximated by a linear function.

In the above mentioned concentration and temperature regions the investigated by us system forms a micellar phase with spheric (or close to spheric) aggregates. The relation between the spin-lattice relaxation time  $T_1$  and rotational correlation time  $\tau_c$  of such aggregates is [3]

$$\frac{1}{T_1} = \text{const} \left( \frac{\tau_c}{1 + \omega^2 \tau_c^2} \frac{2\tau_c}{1 + 4\omega^2 \tau_c^2} \right) \quad (6)$$

The correlation times in the liquid crystal systems are of the order of  $10^{-5}$  s. On the other hand the resonance frequency of our NMR apparatus is about  $10^7$  Hz. In this case we obtain

$$\frac{1}{T_1} \sim \frac{1}{\tau_c} \quad (7)$$

The correlation time  $\tau_c$  can be expressed by

$$\tau_c = \tau_{c0} \exp\left(\frac{E}{kT}\right). \quad (8)$$

After substitution of Eq. (8) in Eq. (7) it is possible to obtain

$$\ln T_1 \sim \frac{1}{T}. \quad (9)$$

The approximation of the data from Figs 2 and 3 with a linear function gives us the next results:

$$\ln T_1 = -17.34 + 4782 \left(\frac{1}{T}\right) \quad (10)$$

for the sample with 55 wt. % Triton X-114 and

$$\ln T_1 = -8.38 + 1960 \left(\frac{1}{T}\right) \quad (11)$$

for the sample with 70 wt. % Triton X-114.

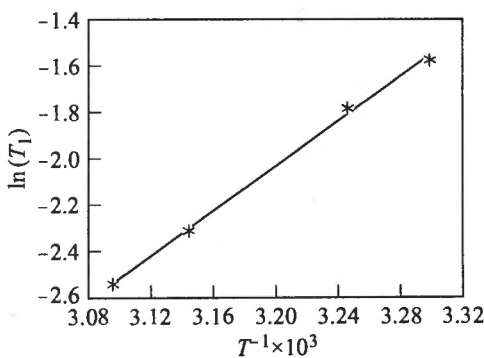


Fig. 2. The spin-lattice relaxation time of the sample with 55 wt Triton X-114 as a function of the temperature

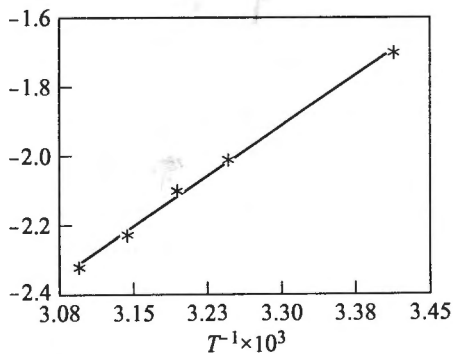


Fig. 3. The spin-lattice relaxation time of the sample with 70 wt. % Triton X-114 as a function of the temperature

The slopes of the lines described by the last two equations are  $\delta_{55} = -0.0036$  and  $\delta_{70} = -0.0042$ .

Let us examine the temperature laws of changing of the water and octan viscosity. We choose the octan because of its similarity (in the hydrocarbon length) with the Triton X-114. The viscosity of the liquids  $\eta$  is changed according to an exponential law

$$\eta = \eta_0 \exp\left(\frac{E}{kT}\right), \quad (12)$$

therefore

$$\ln \eta \sim \frac{1}{T}. \quad (13)$$

We approximated the data for  $\ln \eta$  of the water and octan as a function of the reciprocal temperature and obtained that

$$\ln \eta_{\text{H}_2\text{O}} = -5.94 + 1730 \left( \frac{1}{T} \right) \quad (14)$$

for the water and

$$\ln \eta_{\text{octan}} = -4.19 + 1047 \left( \frac{1}{T} \right) \quad (15)$$

for the octan.

The line slopes are  $\delta_{\text{H}_2\text{O}} = -0.00343$  for the water and  $\delta_{\text{octan}} = -0.004$  for the octan. It can be seen that the  $T_1$  change of the sample with 55 wt. % Triton X-114 is similar to the change of the water viscosity. On the other hand, the octan viscosity is changed according to a law which is likely to the changing of the relaxation time of the sample with 70 wt. % Triton X-114.

In what way can be interpret our results? The NMR correlation time  $\tau_c$  is accepted to be 1/3 of the Debye's correlation time [3]

$$\tau_c = \frac{4\pi\eta a^3}{3kT}. \quad (16)$$

In the last equation is accepted that the molecules are spheres with radius  $a$ . From the Eq. (16) follows that the correlation time  $\tau_c$  is proportional to the viscosity  $\eta$ . On the other hand, the  $T_1$  is proportional to the correlation time. Consequently, the  $T_1$  should be proportional to the viscosity. In this way our interpretation of the experimental data is as follows:

1. At lower Triton's concentration the system is in normal micellar phase. The surfactant forms micelles, swimming in a continuous water medium. The micelle motion is determined mainly by the friction in the water because the hydrated water molecules form water layer which is in contact with the surrounding water. The observed temperature dependence of  $T_1$  can be explained by the change of the water viscosity.
2. An inverted micellar phase is formed at the higher Triton's concentration. The hydrocarbon chains form a continuous medium. The changes of the viscosity of this hydrocarbon medium lead to the observed relaxation time changes.

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