

Investigation of Relaxation Times of Alcohol-Water Mixtures by Time Domain NMR Technique

Cengiz OKAY¹

¹Department of Physics, Faculty of Science, Marmara University, İstanbul, Turkey

Sorumlu yazar e-posta: cokay@marmara.edu.tr ORCID ID: <http://orcid.org/0000-0001-9609-2912>

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Abstract

Nuclear magnetic resonance (NMR) is important technique to probe the molecular dynamics of alcohol-water mixtures by measuring their spin-lattice (T_1) and the spin-spin relaxation time (T_2). In this work, we used two different proton NMR devices to measure relaxation times: Bruker Minispec mq-20 time-domain NMR and 42MHz Magritek Spinsolve high-resolution NMR. T_1 and T_2 of the ethanol-water and methanol-water mixtures measured for changing concentrations from pure water to pure alcohol. The results obtained by both devices are similar with each other. The minimal values of both relaxation parameters are observed at volume fractions of ethanol-water and methanol-water mixtures 43% and 44%, respectively

Keywords

NMR; Spin-spin relaxation time; Spin-lattice relaxation time; Alcohol-water mixtures

Alkol-Su Karışımlarının Durulma Sürelerinin Zaman Boyutlu NMR Tekniği ile İncelenmesi

Öz

Nükleer manyetik rezonans (NMR), spin örgü (T_1) ve spin-spin (T_2) durulma zamanları ölçümleri sayesinde alkol-su karışımlarının moleküler dinamiği konusunda önemli bilgiler vermesinden dolayı önemli bir tekniktir. Bu çalışmada, durulma sürelerini ölçmek için iki farklı proton NMR cihazı kullanılmıştır: Bruker Minispec mq-20 zaman boyutlu NMR ve yüksek çözünürlüklü 42MHz'lik Magritek Spinsolve NMR. Etanol-su ve metanol-su karışımlarının T_1 ve T_2 değerleri, saf sudan saf alkole kadar değişen konsantrasyonlarda ölçülmüştür. Her iki cihaz tarafından elde edilen sonucun birbiriyle aynı eğilimde olduğu açıkça görülmektedir. Elde edilen etanol-su ve metanol-su karışımlarının hacimsel oranları sırasıyla 43% ve 44% olduğunda her iki tip durulma zamanlarında minimum gözlemlenmektedir.

Anahtar Kelimeler

NMR; Spin-spin durulma süresi; Spin-örgü durulma süresi; Alkol-su karışımları

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1. Introduction

Ethanol and other alcohols as well as their water mixture aqueous are used in many industrial applications. The most common alcohols used dissolved in water at room temperature are ethanol and methanol. Important property of alcohols is heterogeneity due to formation of alcohol-alcohol, water-water or alcohol-water clusters (Hayashi et al. 1990), (Nishikawa et al. 1993), (Tanaka et al. 1985), (Zhao et al. 2012). Alcohol-water mixtures have been investigated by molecular dynamics simulations (MDS), X-ray scattering, Infra-Red (IR), nuclear magnetic resonance (NMR) technique (Benmore et al. 2000), (Chizhik et al. 2016). It is very important both for safety (Rameev et al. 2012) and

for industrial applications (Jora et al. 2017), (Yoshida et al. 2006) to detect and distinguish various liquid substances and their mixtures (for example, alcohol-water mixtures). The NMR has many subtypes such as High Field Liquid (HF-NMR), Solid State (ss-NMR), Zero Field NMR, Earth Field NMR, Time Domain NMR (NMR Relaxometry). It is one of the most reliable method to determine all kinds of chemical structures of samples especially in liquids. Even though NMR spectroscopy knowing as high field (HF) NMR is very sensitive method for analyzing chemical structures, it needs to cryogenic system because containing of superconducting magnet system. In this case NMR spectroscopy is overpriced and difficult to use in practical application. On the

contrary, since TD-NMR is based on permanent magnet technology, it does not need a cryogenic system. Than it is cost-effective, easy to use and portable, it might be more preferable for quality control and security applications. Materials can be analyzed by measuring the relaxation times of samples instead of NMR spectrum in TD-NMR method. In TD-NMR method, two main parameters called as spin-spin (transverse, T_2) and spin-lattice (longitudinal, T_1) are measured. As it is known, the nuclear spins exposing to static magnetic field (B_0) localize in different energy level and the total magnetization (M) occur in the nucleus. Than, transitions consist between the energy levels by applied variable magnetic (RF) field (B_1). After the termination of B_1 , the nuclear spins try to come back to their previous positions. Therefore, to achieving thermal equilibrium, they transfer the energy to their surrounding spins and lattice. The time passing to transfer the energy to the neighbor spins is called as T_2 , and time passing to transfer the energy to the lattice is called as T_1 . Hence, each material has different relaxation times. Thus, it is a very important issue to conduct effective screening and analysis of various liquids according to TD-NMR parameters which are spin-lattice (T_1) and spin-spin relaxation time (T_2).

The transversal magnetization decay (M_{xy}) and the longitudinal magnetization decay (M_z) are given by equation-1 and 2.

$$M_{xy}(t) = M(0)e^{\left(-\frac{t}{T_2}\right)} \quad (1)$$

$$M_z(t) = M(0)[1 - 2e^{\left(-\frac{t}{T_1}\right)}] \quad (2)$$

Here $M_{xy}(t)$ and $M_z(t)$ are magnetization amplitude and $M(0)$ is initial magnetization amplitude.

In this study, T_1 and T_2 relaxation times of ethanol-water and methanol-water mixtures have been measured by using two different commercial devices (Bruker Minispec mq20 (20MHz) and Magritek Spinsolve 42MHz) and consistency of the results have been compared to emphasize the availability of TD-NMR methods in security application.

2. Material and Method

2.1. Experimental Procedures

Methanol and ethanol liquids have been provided from Sigma-Aldrich® (%99). Ethanol-water and methanol-water mixtures have been prepared by using deionized water (Milli-Q, 18.2 M Ω) with

different molar fractions and stored at room temperature. A set of samples with various alcohol concentration of alcohol-water mixtures have been measured by using of two types of commercial devices (**Figure 1-2**).



Figure 1. Photo of Bruker Minispec mq20 TD-NMR device(20MHz)



Figure 2. Photo of Magritek Spinsolve NMR spectrometer (42MHz)

The samples have been placed in the tubes of 10 mm diameter for Bruker Minispec mq20 TD-NMR and 5 mm diameter for Magritek Spinsolve NMR device. Before each measurement, the samples have been placed in the NMR device for at least 10 minutes to keep the thermal equilibrium. T_2 relaxation time has been measured with use of Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence. T_1 relaxation time have been obtained using inversion recovery (IR) protocol.

3. Results and Discussion

The measurement parameters (number of scans) for these commercial devices are 4 and 2 for CPMG (T_2) and IR (T_1) sequences, respectively. T_1 and T_2 relaxation curves of each samples have been showed in **Figure 3** (only Magritek Spinsolve NMR device). To calculate the T_1 and T_2 values, the exponential fitting has been applied to relaxation time curves of each samples and the T_1 and T_2 versus

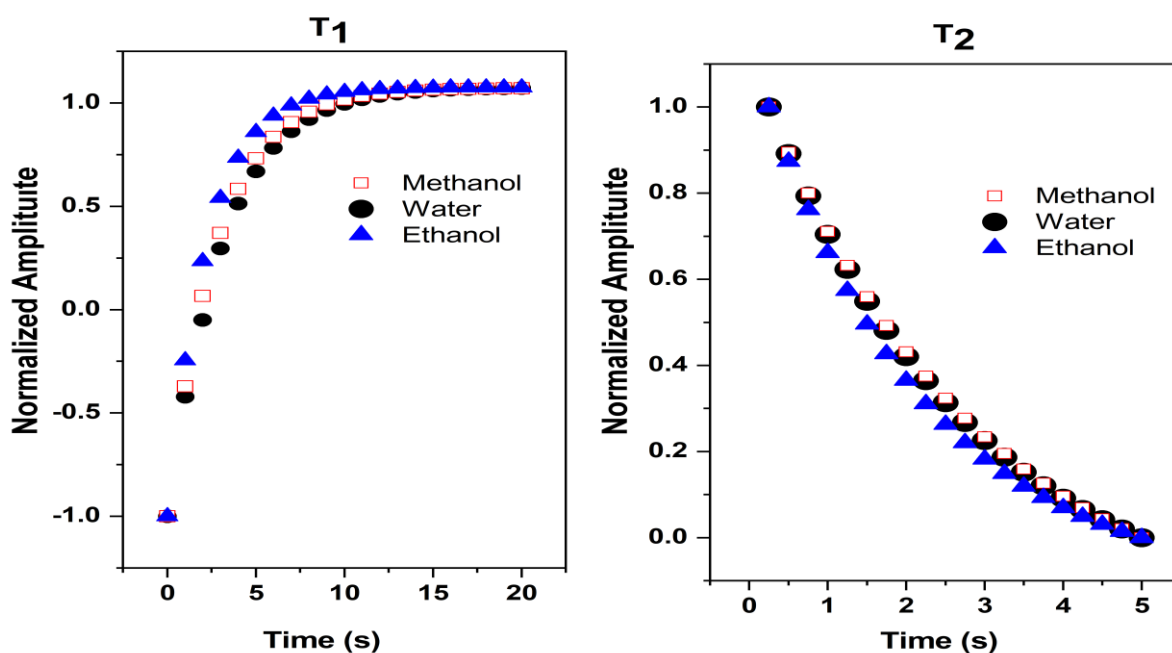


Figure 3. Spin-lattice (T_1) and spin-spin relaxation times (T_2) spectra for pure water, methanol and ethanol.

To reduce the signal to noise ratio, the CPMG and IR measurement protocols have been replicated three times for each samples and the average of these three relaxation times curve have been obtained. The relaxation delay between these measurements was chosen to be approximately 5 times longer than the observed values of T_1 and T_2 to be sure that samples have fully relaxed between the measurements. In this manner, the signal intensity curves for CPMG and inversion recovery measurements the T_1 and T_2 parameters have been obtained. It should be note that various echo-times have been tested to check the effect of self-diffusion. For minimization of contribution of the diffusion term, the echo-time was fixed to be 0.5 ms.

alcohol concentration percentages graphs have been demonstrated in **Figure 4**. According to results, for all substance the T_1 values are always somewhat larger than the T_2 ones, as expected for liquids. As mentioned in the previous section, the origin of relaxation times is related with transferring of the energy between spin-lattice for T_1 and spin-spin for T_2 . Because, the space between the spin lattice is higher that the space between two spins, it is expected that the T_1 should be longer than T_2 . Consequently, the measurement completed in this study are consistent with the theory (Jiang et al. 2017), (Jora et al. 2017).

The trends observed in the T_1 and T_2 values for various concentrations of water-methanol and water-ethanol mixtures are similar. It is obvious that the results obtained by both commercial devices are in agreement with each other. The maximal difference, observed at high alcohol concentrations, does not exceed 7%. The differences are obviously related to various operating frequencies of these

devices. The operating frequency of the Magritek Spinsolve high-resolution NMR device is 42MHz, which is two times bigger than that of the Bruker Minispec mq-20 (20MHz).

$$\frac{1}{T_{2eff}} = \frac{1}{T_2} + \frac{1}{3}\gamma^2 G^2 D\tau^2 \quad (3)$$

It is known that the relaxation time of materials under the inhomogeneous magnetic field is defined as (Bloch, 1946).

Magritek Spinsolve devices 145ppm and 36ppm, respectively. As a result of these values, the inhomogeneity of the Magritek Spinsolve device is much better with respect to the Bruker Minispec TD NMR. The cases which have been explained above shows that the different relaxation times which have been measured for different devices.

As we mentioned above, the trend in the dependence of relaxation times vs concentration is very similar for both types of alcohols. The only

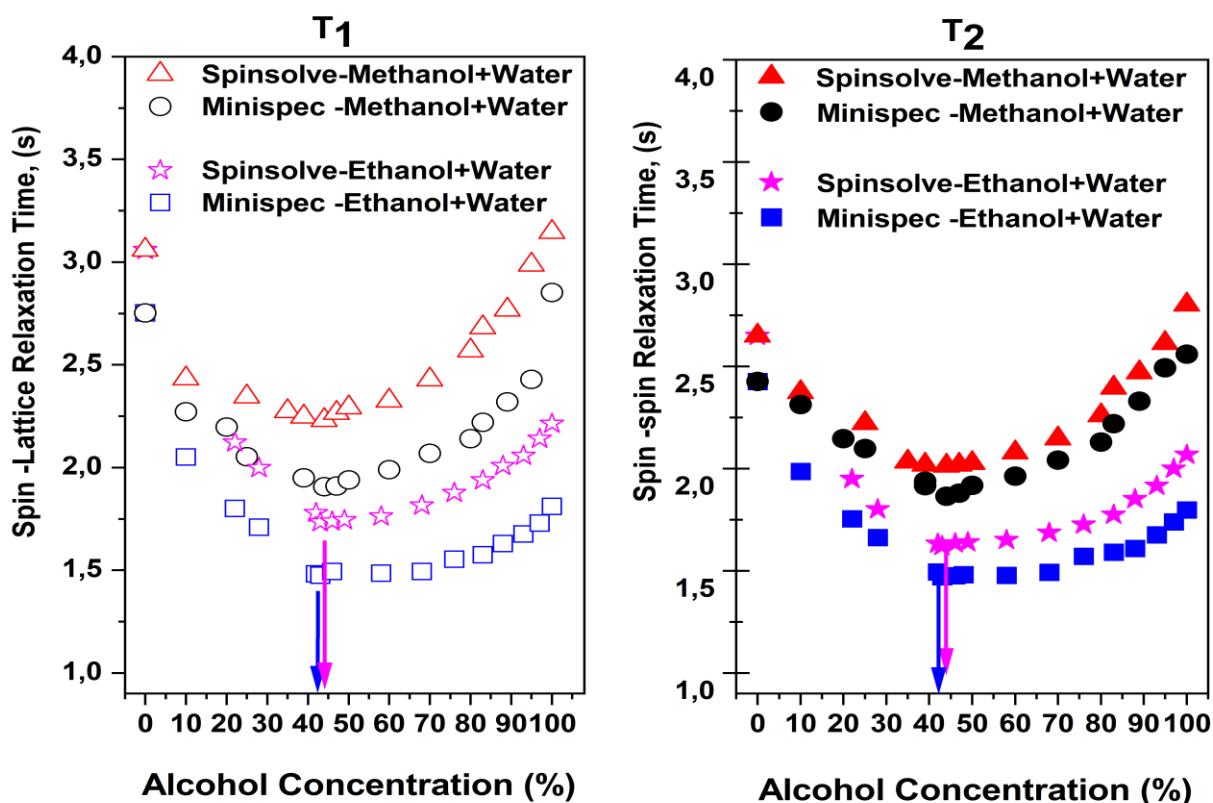


Figure 4. Spin-lattice and spin-spin relaxation times for alcohol-water mixture.

Where in T_{2eff} is characteristic spin-spin relaxation time under the CPMG pulse sequence, G is magnetic field gradient, D is diffusion coefficient, γ is the gyromagnetic ratio of proton and τ is echo time. To obtain the inhomogeneity-the magnetic field gradient (G) following procedure have been used: (a) pure alcohol, (b) T_2 values for different τ , (c) T_2 versus τ^2 graph, (d) slope of this graph, (e) $\gamma=267 \times 10^6 \text{ s}^{-1}\text{T}^{-1}$ and $D=0.85 \times 10^{-9} \text{ m}^2\text{s}$ (Vitalij, 1995a) [Vitalij, 1995]. According to our calculations by using equation 3 contribution of field non-uniformity in T_{2eff} is negligibly small for two devices. The magnetic field gradient (G) have been calculated (equation 3) for Bruker Minispec and

difference is turnover (breaking) points in T_1 and T_2 values. Arrows are given as references to mark special volume (breaking) points in T_1 and T_2 values. Arrows are given as references to mark special volume concentrations: %43 for ethanol, %44 for methanol. In the molar fractions of ethanol and methanol-water mixtures, these values correspond to $x_{et} \approx 0.20$ and $x_{met} \approx 0.26$, respectively. This breaking point is related to the change in the transition structure of alcohol-water clusters. It also depends on the formation of hydrogen bonds between water-alcohol molecules. This clumping phenomenon affects both rotational and translational motion of water and molecules. A several research group (Burikov et al. 2010), (Matsugami et al. 2016), (Nasten, 1972), (Takamuku

et al. 2001), (Takamuku et al. 2004) have investigated the hydrogen-bonding properties of alcohol-water system by using various techniques. Based on literature data we explained the observed concentration dependence in the following manner. It is known that the molecules of a pure water even in liquid state prefer a tetrahedral arrangement, i.e., in average, neighbor molecules oriented to each other in such manner that they form for some time the tetrahedral water clusters (in a near range). Adding alcohol in a small amount does not affect this dynamic arrangement initially, but further increase of alcohol concentration starts to alter the near-range arrangement of water molecules. In the middle concentration range, tetrahedral-like arrangement is broken (at volume concentrations of %43 for ethanol and %44 for methanol), because alcohol-water clusters rather than water-water clusters are formed in the mixtures. This results in slower molecular dynamics and shortening the T_1 and T_2 values. Further rising the alcohol concentration beyond of turnover concentrations results in a decrease of the ratio of alcohol-water clusters and increase of the number of chain-like clusters of alcohols molecules with higher T_1 and T_2 values (Burikov et al. 2010), (Takamuku et al. 2004).

4. Conclusion

In this study, two commercial NMR devices, Bruker Minispec mq series 20MHz TD-NMR and Magritek Spinsolve 42MHz NMR device have been used to measure the spin-lattice and spin-spin relaxation times of ethanol-water and methanol-water mixtures. The consistency in the results obtained using various devices have been observed. The same trend in the concentration dependence of the relaxation times have observed for both type of alcohols. Firstly, both T_1 and T_2 decrease with increase of concentration toward to turnover points. After that both T_1 and T_2 values increase at higher alcohol fractions towards to pure alcohol liquid. Inhomogeneity-the magnetic field gradient (G) of the Magritek Spinsolve NMR has been obtained better than the Bruker Minispec device. And also, values of the T_1 and T_2 for the Magritek Spinsolve NMR has been observed longer than the Bruker Minispec device. The qualitative explanation of the observed behavior is presented.

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