

Investigation of the interaction of polyvinyl alcohol and tetraethoxysilane in dimethyl sulfoxide by NMR spectroscopy

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Introduction

The development of a competitive ion-conducting membrane material for a hydrogen-air solid polymer fuel cell (SPFC) is a fairly urgent task [1, 2]. Ion-conducting membranes for SPFC can be divided into three main groups: membranes based on perfluorinated sulfonated polymers, membranes based on polycondensation polymer systems and hybrid (organo-inorganic) membranes. The most interesting of them are hybrid membranes, which contain inorganic components in the polymer matrix, including those obtained by hydrolysis and condensation of tetraethoxysilane (TEOS), which contribute to an increase in moisture capacity, temperature and chemical stability of the membrane material [3]. Currently, a significant number of foreign and domestic scientific groups are engaged in the development of ion-conducting hybrid membranes based on various polymer materials – sulfonated or phosphorylated aromatic and aliphatic polymers [4]. As a rule, to achieve sufficient proton conductivity aromatic polymers require a high level of sulfation, which is due to the low acidity of the sulfogroups in the aromatic ring. Such a high level of sulfonation usually makes them excessively swollen and even soluble in water, which can lead to the loss of mechanical strength [5, 6]. Aliphatic polymers, on the contrary, are sulfated moderately. The ion-conducting membrane material based on a modified aliphatic polymer polyvinyl alcohol (PVA) is quite promising. Such material is technologically advanced and, after its modification, has high ionic conductivity, thermal stability and a fairly low cost.

The analysis of the literary data showed a limited number of scientific publications devoted to the production and study of hybrid membranes based on sulfonated PVA modified by TEOS in an aqueous medium [7, 8], and practically no scientific articles aimed at studying the interaction of PVA and TEOS in an organic medium – dimethyl sulfoxide (DMSO). The analysis of such systems is most carried out by using the methods of liquid-phase/solid-phase nuclear magnetic resonance (NMR) spectroscopy.

Previously, using the liquid-phase synthesis method, we obtained an ion-conducting hybrid membrane material based on furfural-crosslinked PVA modified by aminosulfonic acid (ASA) and TEOS and studied its composition and structure using ¹H NMR spectroscopy. However, due to the multicomponent nature of the system, it was not possible to determine exactly how the process of interaction between PVA and TEOS proceeded. Since this process underlies the synthesis of new ion-conducting hybrid membranes based on PVA, obtaining at

least qualitative or even semi-quantitative information about the mechanism of their interaction by NMR spectroscopy methods could provide additional useful information about possible ways to improve the performance of the finished membrane material.

The purpose of this work was to obtain and study the PVA-TEOS model system in DMSO- d_6 with and without distilled water using one-dimensional (^1H , ^{13}C) and two-dimensional (COSY, J-COSY and NOESY) liquid-phase NMR spectroscopy. Three the model systems with different ratio of components were selected (Table 1).

Table 1. Ratio of components of the PVA-TEOS model system

Sample 1	Sample 2	Sample 3
PVA 0.0022 g + TEOS 5 μl in DMSO- d_6	PVA 0.0022 g + TEOS 5 μl + H_2O 5 μl in DMSO- d_6	PVA 0.0023 g + TEOS 10 μl in DMSO- d_6

Experiments and results

Figure 1 shows the NMR (^1H and ^{13}C) and 2D spectrum J-COSY of the system PVA-TEOS (Sample 3) in DMSO- d_6 , obtained on a 400 MHz spectrometer at room temperature for 2 days after mixing the components. They indicate the presence of 3 types of OH group signals, which are designated by the letters “a”, “b” and “c” and belong to the PVA proton. Moreover, each of these groups consists of several overlapping doublet signals with the same values of the vicinal constants $^3J_{(\text{HO}-\text{CH})}$, but different for “a”-, “b”- and “c”- signals in the following sequence: $^3J_{(\text{HO}-\text{CH})}^{\text{a}} < ^3J_{(\text{HO}-\text{CH})}^{\text{b}} < ^3J_{(\text{HO}-\text{CH})}^{\text{c}}$ (Figure 1-1). This is clearly visible in a fragment of the J-COSY spectrum (Fig. 1-2), which shows the exact values of these constants from 3.9 to 6.0 Hz. The total intensity of all OH signals in the region of 4.7 – 4.1 ppm. is comparable with the intensity of the broadened O-CH- signal of PVA protons in the region of 3.9 – 3.7 ppm. and is 2 times less than the total intensity of the broadened signals in the region of 1.6 – 1.1 ppm, belonging to the protons of $-\text{CH}_2-$ groups of PVA.

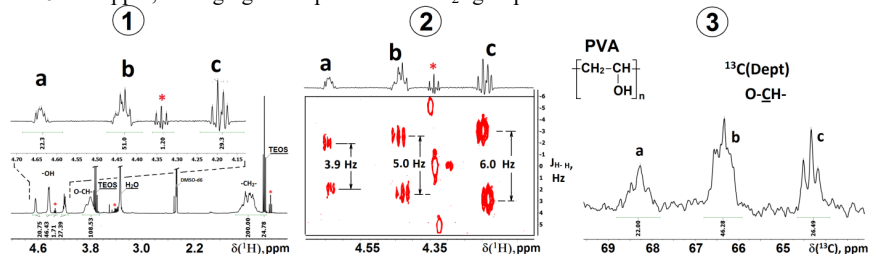


Figure 1. ^1H NMR spectrum (1), fragments of the J-COSY (2) and ^{13}C (DEPT-135) (3) spectra of the PVA-TEOS system in DMSO- d_6 , recorded during the first two days after the preparation of sample 3 (ethanol (EtOH) is formed by the reaction of PVA with TEOS and in spectra its signals are depicted by red asterisk)

In the ^{13}C NMR spectrum in the region of 69 – 63 ppm, which contains carbon signals of O-CH groups, as well as in the proton spectrum, three signals with a complex structure are observed at 68, 66 and 64 ppm. Based on this, we can conclude that PVA is a structurally heterogeneous polymer. This can be explained by the fact that in dimethyl sulfoxide strong hydrogen bonds arise between PVA and the solvent, which significantly slow down the rate of OH-proton exchange and the vicinal constants $^3J_{\text{OH}-\text{CH}}$ are observed in the form of doublets. In addition, hydrogen bonds apparently cause a downfield shift of the OH group proton signal by 0.5 ppm. and a decrease in the vicinal constant $^3J_{\text{OH}-\text{CH}}$ by approximately 2 Hz while going from stereoisomer “c” to “a”.

Good resolution of the signals of OH protons of stereoisomers “a” – “c” made it possible to determine the position of the signals of O-CH- and -CH₂- groups in the overlapping regions of 4.7 – 4.1 (Fig. 2-1) and 1.6 – 1.1 ppm. (Fig. 2-2), respectively, with the help of COSY method. In the EXSY-NOESY spectrum, along with exchange cross-peaks between the signals of OH-protons (including water), NOE cross-peaks of the same positive polarity as the exchange cross-peaks are observed between the signals of OH-protons and the signals of O-CH- and -CH₂- group. The coincidence of the sign of the exchange and NOE cross-peaks indicates the negative Overhauser effects and the polymeric nature of PVA existing under conditions of the spin diffusion limit ($\omega_0\tau_c > 1$) [9].

NMR analysis of the PVA-TEOS system also showed that the process of their interaction includes the formation of one (or more) intermediate products and proceeds depending on the ratio of these components with different rates. To prove this, experimental dependences of the composition of the PVA-TEOS system on time were obtained for all three samples, which lasted for six months (Fig. 2-4 and 2-5).

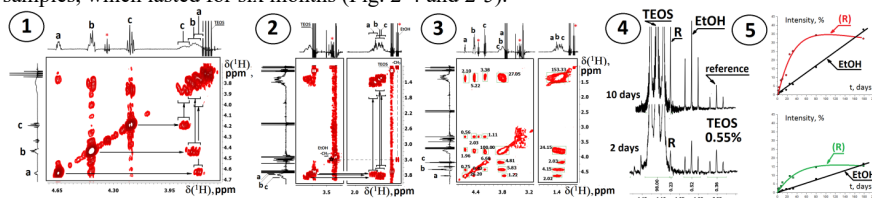


Figure 2. Fragments of COSY (1 and 2) and EXSY-NOESY (3) spectra of PVA-TEOS system in DMSO-*d*₆, recorded during the first two days after the preparation of the sample 3. High-field part of ¹H NMR spectrum of the sample 1 after two and ten days (4) and (5) – dependences of triplet intensities on the time for intermediate R and product EtOH measured relatively to ¹³C_α-satellite triplet of TEOS for sample 1 (high) and sample 2 (low)

Conclusion

In the PVA-TEOS system in DMSO-*d*₆ the multiplet structure of the signals of hydroxyl protons was discovered and studied using NMR methods, which made it possible to identify the overlapping signals of the corresponding methine and methylene protons of PVA. The formation of the intermediate (R) with low molecular weight and the final (EtOH) product of the interaction of PVA with TEOS in DMSO-*d*₆ was discovered and their complete NMR identification was carried out.

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