

Comparison of electrochemical- and nuclear magnetic resonance spectroscopy methods for determination of diffusion coefficients in gel environment



Bożena Adrjan, Marcin Karbarz*, Wiktor Koźmiński, Zbigniew Stojek¹

Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

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ABSTRACT

Two advanced methods: one based on chronoamperometry in solution of any ionic strength and the second one related to nuclear magnetic resonance spectroscopy (NMR) were used to determine the diffusion coefficients of the selected species in complex polymeric gels. For this purpose a series of polyacrylamide gels with different content of monomer and crosslinker were synthesized. Rod shaped samples of polymers were swelled with solutions of either 1,1'-ferrocenedimethanol, or 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt or *cis*-dichlorobis(2,2'-bipyridine) ruthenium (II) in D₂O. These compounds were good probes for examining the transport in the gel medium due to electrochemical reaction and well-defined signals in ¹H NMR spectroscopy. The values of diffusion coefficients obtained by both methods were compared and the limitations of the methods were discussed. The measurements were done at three temperatures: 25, 35 and 45 °C.

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1. Introduction

The polymeric hydrogels consist of cross-linked hydrophilic polymer networks filled with an aqueous solution. The unique structure and environmental sensitivity make these gels useful materials in drug delivery systems, separation techniques and construction of sensors [1–14]. The content of water in the hydrogels is usually very high, so in the microscopic scale the gels exhibit the properties of liquids. As a consequence the soluble species are transported there by diffusion. In the characterization of hydrogels the knowledge of the values of diffusion coefficients of molecules and ions in these materials is of great importance.

Several methods are used for the determination of diffusion coefficients in gels: light scattering spectroscopy [15,16], fluorescence correlation spectroscopy [17], pulsed-field-gradient spin-echo NMR spectroscopy [18–20] and electrochemistry [21,22]. However, each of these techniques has either some limitations or inconvenient requirements.

The NMR method is a potential technique for the determination of diffusion coefficients. The fact that molecular diffusion can be

measured by NMR methods was realized in the early days of NMR spectroscopy [23]. Pulsed field gradient NMR experiments are often associated with diffusion-ordered spectroscopy (DOSY) experiments. The first practical pulse sequence for measuring diffusion coefficients by NMR spectroscopy was introduced in 1965 by Stejskal-Tanner (see equation 1) [24].

$$S = S_0 e^{-D\gamma^2 \delta^2 g \Delta'} \quad (1)$$

where S is spin or stimulated echo signal amplitude, S_0 is amplitude in absence of diffusion, γ is magnetogyric ratio, g is gradient amplitude, and Δ' is diffusion time corrected for effects of δ , finite gradient pulse width. Diffusion NMR measurements have increasingly been used since 1965. In principle, the diffusion coefficient of a molecular species dissolved in a given solvent depends on molecular weight, size and shape of the species and temperature. Diffusion coefficients may reflect the intermolecular interactions that play an important role in chemistry and biology and was successfully used for molecular recognition. Diffusion NMR measurements are used in different disciplines including medical sciences [25] and material sciences [26]. The reports on theoretical and practical aspects of gradient NMR spectroscopy can be found in the literature [19,27]. More specific reviews are focused on diffusion in polymers [28], zeolites and porous systems [29], surfactants [30] and liquid crystals and membranes [31]. Comparing to electrochemistry, the NMR method can be

* Corresponding author.

E-mail address: karbarz@chem.uw.edu.pl (M. Karbarz).

¹ ISE member.

particularly useful in the cases where electrochemistry is useless. These cases involve diffusion of electroinactive species and the molecules of the solvent [32].

The electroanalytical methods provide fast, inexpensive and accurate approaches to determination of diffusion coefficients of electroactive species in various media including gels. We have already shown that the steady-state voltammetry at micro-electrodes is a very convenient technique for the determination of some important parameters characterizing the transport properties in the polymeric gels [3,33]. However, this method requires that the probe concentration is known. Sometimes it is not possible to meet this condition. Fortunately, a combination of the steady-state microelectrode response with another experiment obtained in the transient time regime can overcome this limitation. Such an approach and its modifications appeared useful in complex matrices and for any level of concentration of supporting electrolyte [34–36]. The other troublesome situation in electrochemical methods is the fact that after immersing the electrode into a gel the polymer chains block the surface area to some degree. It is not clear what the contribution of that blocking to the drop in the obtained diffusion coefficient compared to regular solutions is.

In this paper we describe the results of determination of diffusion coefficients of uncharged 1,1'-ferrocenedimethanol ($\text{Fc}(\text{MeOH})_2$), as the main probe, and two ions (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt and *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II)), as the support probes, at different temperatures and in demanding polyacrylamide gels by the electrochemical method developed in our group for any level of ionic strength [37] and by NMR methods. The gels differed in crosslinker % concentration, C was in the range 1–10%, and in total percentage of monomers, $T=2.5$ –15%. We also discuss the applicability and limitations of the methods used.

2. Experimental

2.1. Chemicals

Polymer network constituents: acrylamide (AM, 99%), *N,N'*-methylenebisacrylamide (BIS, 99%) and ammonium persulfate (APS, 99.99%) were purchased from Aldrich. The deuterium oxide (D_2O , 99.99% atom D) and electroactive probes: 1,1'-ferrocenedimethanol ($\text{Fc}(\text{MeOH})_2$, 98%), 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS, 98%) and *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II) ($(\text{bpy})_2\text{RuCl}_2$, 97%) were also purchased from Aldrich. *N, N, N', N'*-tetramethylethylenediamine (TEMED, 99%) was provided by ACROS ORGANICS. Potassium chloride (KCl, 99%, Aldrich) was chosen as the supporting electrolyte. All chemicals were used as received except for NIPA, which was recrystallized twice from the benzene/hexane mixture (90:10 v/v). All solutions were prepared using high purity water obtained from a Milli-Q Plus/Millipore purification system (conductivity of water: 0.056 mS cm^{-1}).

2.2. Gel synthesis

A series of polyacrylamide gels with different total concentrations of monomers (T_{mon}) and percent of cross-linker (C_{link}) were obtained by free-radical polymerization. T_{mon} and C_{link} are defined as follows:

$$T_{\text{mon}} = \frac{(m_{\text{AM}} + m_{\text{BIS}})}{V} \times 100\% \quad (2)$$

$$C_{\text{link}} = \frac{m_{\text{BIS}}}{(m_{\text{AM}} + m_{\text{BIS}})} \times 100\% \quad (3)$$

were m_{AM} is mass of acrylamide, m_{BIS} denotes mass of *N,N'*-methylenebisacrylamide and V is volume of water.

Two series of gel, one with total concentration of monomers in the range from 2.5% to 15% and with constant percent of cross-linker equal to 2% (denoted *a*–*h*) and another one with the percent of cross-linker from 1% to 10% and constant total concentration of monomers equal to 5% (denoted *i*–*n*), were obtained.

The solutions were prepared by dissolving appropriated amounts of monomers in 5 mL of water and were degassed. The polymerization was initiated and accelerated by adding 25 μL of degassed 10% solution of APS and 5 μL of TEMED. Then the reaction mixture was transferred into glass tubes with inner diameter 4.2 mm. The reaction mixture was kept at 5 °C for 24 hours and after that time the obtained gels were mechanically removed. Then the gels were immersed into a large amount of deionized water for 1 week to wash away the excess of residual chemicals. During the washing time, water was exchanged several times. After

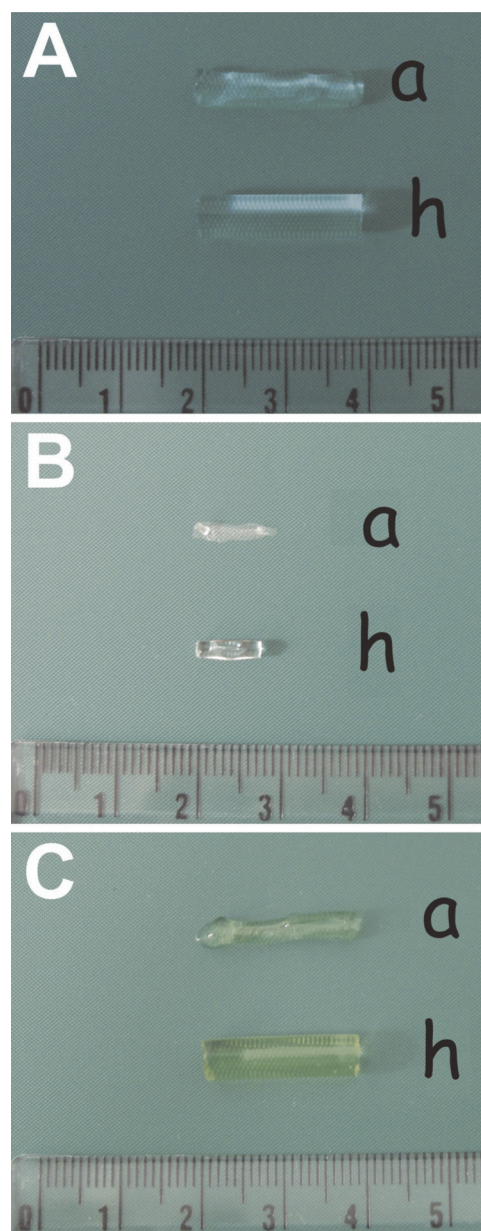


Fig. 1. Size of gel samples; a) $C_{\text{link}}=2\%$, $T_{\text{mon}}=2.5\%$ and h) $C_{\text{link}}=2\%$, $T_{\text{mon}}=15\%$. (A) swollen gels in water, (B) dried gels, (C) gels swollen in solution of 1,1'-ferrocenedimethanol (8 mM, D_2O).

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