

Ion Exchange Membranes by NMR

Subjects: Others

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An ion-exchange membrane lets pass certain ions while blocking other ions or neutral molecules. Nuclear Magnetic Resonance (NMR) spectroscopy is a technique for determining the content, purity, and molecular structure of a sample. NMR methods provide the unique possibility of acquiring detailed information on the state of molecules and ions, the local molecular and ionic mobility, and the diffusion on the spatial scale from several tenths of nanometer to several millimeters.

Keywords: ion exchange membranes ; hydration ; protein association ; red blood cells ; chemical shift ; spin-relaxation ; pulsed field gradient NMR

1. Overview

The results of NMR, and especially pulsed field gradient NMR (PFG NMR) investigations, are summarized. Pulsed field gradient NMR technique makes it possible to investigate directly the partial self-diffusion processes in spatial scales from tenth micron to millimeters. Modern NMR spectrometer diffusive units enable to measure self-diffusion coefficients from 10^{-13} m²/s to 10^{-8} m²/s in different materials on ¹H, ²H, ⁷Li, ¹³C, ¹⁹F, ²³Na, ³¹P, ¹³³Cs nuclei. PFG NMR became the method of choice for reveals of transport mechanism in polymeric electrolytes for lithium batteries and fuel cells. Second wide field of application this technique is the exchange processes and lateral diffusion in biological cells as well as molecular association of proteins. In this case a permeability, cell size, and associate lifetime could be estimated. The authors have presented the review of their research carried out in Karpov Institute of Physical Chemistry, Moscow, Russia; Institute of Problems of Chemical Physics RAS, Chernogolovka, Russia; Kazan Federal University, Kazan, Russia; Korea University, Seoul, South Korea; Yokohama National University, Yokohama, Japan. The results of water molecule and Li⁺, Na⁺, Cs⁺ cation self-diffusion in Nafion membranes and membranes based on sulfonated polystyrene, water (and water soluble) fullerene derivative permeability in RBC, casein molecule association have being discussed.

2. Cation-Exchange Membranes. Structure, Hydration, Ionic, and Molecular Mobility

Ion-exchange membranes are widely applied for modern electrochemical technologies and separation processes. New materials design requires an electro mass transfer investigation. This research is mainly concerned about macroscopic transport processes [1][2][3][4][5][6][7]. However, ion and molecular translation microscopic mobilities have to be investigated for membrane selectivity mechanism understanding.

Of most interest is the relationship between the following fundamentally important characteristics that determine the ion and molecular transport:

- The nanoscale structure of ion transport channels. The structure and dynamics of polymer matrix at the submicro level from several tenths of nanometer (sizes of solvated ions and molecules) to several nanometers or several tens of nanometers (characteristic lateral dimensions and lengths of ionic channels), determine the selective ion transport because these structural units form transport path for ion transfer by macroscopic distances. Studying the nanostructure opens up the prospects for targeted synthesis of ion exchange polymer, insofar as their preparation is accompanied by the formation of the nanostructure.
- The type of interaction of mobile ions and hydration water molecules with functional groups. Data on the structure of ionic complexes and on the mechanisms of interaction of ions and water molecules with the polymer matrix are necessary for understanding the mechanisms of selectivity of ion-exchange membranes and elementary steps of the diffusion transport of ions.
- The elementary steps of diffusion of ions and molecules, which can be characterized by the lifetime of a species on functional group, the time of translational displacement, the partial diffusion coefficient on various spatial scales (if

diffusion occurs in a heterogeneous medium).

The problem of elementary diffusion jumps logically follows from the aforesaid. Evidently, the time of elementary jump and the height of the potential barrier overcome by a moving species are largely determined by the geometry of diffusion channels and the structure of hydrate ionic complexes. This information is necessary for both the elaboration of adequate transport models and the targeted synthesis of high-performance ion exchange polymers.

The knowledge of structure and dynamics in a different spatial scale and in a broad band of molecular motion frequencies may be obtained by NMR directly.

NMR spectroscopy The most popular method is ^1H NMR, which was used to study Dowex 50 W, CU-2 sulfonate cation exchanger resin and the corresponding membranes MC-40, cation exchange membranes based on polyethylene and sulfonated grafted polystyrene MSC [8][9][10][11][12][13][14][15][16][17] and perfluorinated cation-exchange membranes [18][19][20][21][22][23][24][25][26]. To date, techniques have been developed for recording high-resolution NMR spectra and the main factors that determine the chemical shift of water protons in granulated sulfonate cation-exchangers and ion-exchange membranes have been elucidated. The required information can also be obtained from the solid-state high-resolution NMR spectroscopy data [23][24]. Information on hydration of ionic channels in membranes is of fundamental importance for understanding the mechanism of migration of cations and water molecules.

Alkaline metal cations of lithium, sodium, and cesium were studied by NMR on ^7Li , ^{23}Na and ^{133}Cs nuclei in cation-exchange membranes [16][17][20][21][27][28][29][30][31][32] and in sulfonated polystyrene salts [33][34]. Some qualitative data about ionogenic group-cation interaction and cation motion were obtained.

Pulse NMR methods NMR relaxation techniques were for the first time applied for local cationic and water molecules mobility characterization in polymeric electrolytes more than 50 years ago [10]. Spin-lattice and spin-spin relaxation times measurements on ^1H , ^7Li , ^{19}F NMR nuclei were performed in Nafion and MF-4SC (Russian Nafion type membrane) membranes [35][36][37][38][39][40][41]. Unfortunately, the numerical calculation of correlation times is hard work because of wide molecular motion frequency distribution.

The study of the metal ion mobility is associated with even more serious complications. The most serious obstacle is the absence of theoretical works to serve as the base for studying the region of diffusion motion with the characteristic correlation times longer than ω_0^{-1} (where ω_0 is the NMR frequency, usually, $\sim 10^9$ Hz). To date, ^7Li and ^{23}Na NMR relaxation works have been performed dealing with the mobilities of lithium and sodium cations in the CU-2 type sulfonate cation exchangers and the corresponding membranes, perfluorinated sulfonate cation-exchange membranes [31][32][33][34][39][40][41].

The pulsed field gradient NMR method, [42][43] which makes it possible to directly measure the diffusion coefficients of protons and other ions in heterogeneous media, is free from these drawbacks. The number of studies of this type substantially increased in recent decades, [5][6][19][38][39][40][41][44][45][46][47][48][49][50][51][52][53][54][55][56][57][58][59][60][61][62][63][64][65][66][67][68][69][70][71][72][73][74][75][76][77][78][79][80][81][82][83] which was associated with the increased interest in the problems of ionic mobility in polyelectrolytes.

To summarize the foregoing, the following points should be underlined. The magnetic resonance techniques and, especially, NMR methods provide the unique possibility of acquiring detailed information on the state of molecules and ions, the local molecular and ionic mobility, and the diffusion on the spatial scale from several tenths of nanometer to several millimeters. The advantages of NMR spectroscopy also involve the possibility of studying one and the same sample under conditions resembling the service conditions by several methods simultaneously, which makes it possible to compare the results of different measurements and unambiguously interpret them. For these studies to be performed the experimental procedures should be worked out and the problems associated with theoretical quantitative description of data should be solved.

The NMR methods are especially attractive for acquiring detailed information on the ion and molecular transport in polymer electrolytes. The modern level of experimental research instruments allows one to study both elementary processes and macroscopic transfer under the service conditions of electrochemical systems. The successful introduction of NMR methods into the research and technological practice is limited by the lack of publications devoted, first of all, to demonstration of the potential of experimental NMR techniques in this research field.

Despite the considerable number of NMR studies of polymer electrolytes, the reviews on this subject are scarce. In the present review, the experimental results obtained by NMR methods on the ion and water molecular transport in polymer

ion exchangers carried out in Russia and abroad are analyzed and generalized. From our point of view, such an analysis will demonstrate the potential of modern NMR methods and help to reveal some fundamental features of ion and molecular transport in ion exchange membranes at the molecular level.

The main results of NMR studies in ion-exchange membranes are discussed. Attention is focused on the potential of NMR techniques in solving particular problems in relation to the most widely known ion exchangers. The most thorough studies were carried out for perfluorinated membranes. Using these membranes as examples, an attempt is made to find the relationship between the polymer matrix structure, the ion hydration details, and the diffusion mobility of ions and molecules on different spatial scales and then to apply this information for revealing details of the ion transport mechanism in ion-exchange membranes.

3. Conclusions

Nowadays, chemical power sources, based on sulfocation exchange membranes find wide application. The principal part of these systems is formed by a polymer ion exchange membrane that should have high ionic conductivity. The problem of revealing the mechanism of ion transport in these membranes becomes quite challenging. The last decade was characterized by active studies of the state and mobility of cations and molecules in ion-exchange membranes of various types by using the methods of NMR and pulsed field gradient NMR on various nuclei.

Therefore, the review of NMR technique applications is a problem of today. In this review paper the results of cation-exchange membrane investigation obtained by hetero nuclear high resolution NMR spectroscopy, NMR relaxation, pulsed field gradient NMR are discussed.

The main attention is given to interconnection of membrane diffusion channel nanostructure, cation hydration and water molecule and cation mobility in different spatial scales. NMR self-diffusion data are compared with ionic conductivity measurements.

The main parts of NMR investigations were carried out in Nafion (or Russian Nafion analog) MF-4SC sulfonate perfluorinated membranes. These membranes are most studied by different physical techniques and could be a model system for a wide set of ion-exchangers.

The comparison of local water molecule and Li^+ cation mobility calculated from ^1H and ^7Li spin relaxation data with water and lithium cation self-diffusion coefficients measured by PFG NMR shows that macroscopic transfer is controlled by ion and molecular jumping near sulfonate groups. This result is conformed to Nafion channel structure model in [Figure 3](#). Therefore, a cation hydration governs by ionic motion.

Hydration numbers of alkaline and alkaline–earth metal cations were calculated from water molecule ^1H chemical shift temperature dependences. For Li^+ , Na^+ , Cs^+ counter ions, the relative part of contact pairs cation-charge group dependently on humidity was measured by ^7Li , ^{23}Na , ^{133}Cs NMR. Some conclusions about membrane selectivity mechanism to these ions were proposed.

It was definitely shown that in sulfonate cation–exchangers in acid ionic form the least hydration number is equal two and at low water content hydrated cation $[\text{H}_5\text{O}_2]^+$ is formed.

In opposite to conception based on DSC data about water freezing in membranes below 0°C it was shown that amount of mobile water molecules does not change at temperature variation in spite of DSC peak observing. On the basis of ^1H spin–relaxation data it was supposed that at freezing temperature water molecules form mobile associates, but not ice phase. This assumption explains water and cation self-diffusion and ion conductivity temperature dependences.

A comparison of ion conductivity calculated from cation self-diffusion coefficients with experimental values confirms the cluster-channel structural model for membranes based on sulfonated polystyrene and channel structural model for Nafion membranes.

From our opinion these NMR results give opportunity to understand mechanism of ionic and molecular transport in ion-exchange membranes more deeply.

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