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NaCl interaction with interfacially polymerized polyamide films of reverse osmosis membranes: A solid-state ^{23}Na NMR study

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Abstract

^{23}Na nuclear magnetic resonance (NMR) spectroscopy of NaCl-exchanged polyamide (PA) films comparable to those of the active skin layer of many reverse osmosis (RO) membranes provides novel insight into the structural environments and dynamical behavior of Na^+ in such films. Unsupported PA films were synthesized via interfacial polymerization of trimesoyl chloride in hexane and *m*-phenylenediamine in aqueous solution, and SEM, FT-IR, and ^{13}C NMR data demonstrate successful thin film polymerization. Compositional data confirm this conclusion and demonstrate equal Na and Cl incorporation during NaCl exchange from aqueous solution. The ^{23}Na NMR spectra for freshly made polymer samples exchanged in 1 M NaCl solution show significant relative humidity (RH) dependence. At near 0% RH, there are resonances for crystalline NaCl and rigidly held Na^+ in the PA. With increasing RH, a resonance for solution-like dynamically averaged Na^+ appears and above 51% RH is the only signal observed. The slightly negative chemical shift of this resonance suggests a dominantly hydrous environment with some atomic-scale coordination by atoms of the polymer. The greatly reduced ^{23}Na T_1 relaxation rates for this resonance relative to bulk solution and crystalline NaCl confirm close association with the polymer. Variable temperature ^{23}Na NMR spectra for a sample equilibrated at 97% RH obtained from −80 to 20 °C show the presence of rigidly held Na^+ in a hydrated environment at low temperatures and replacement of this resonance by the dynamically averaged signal at temperatures above about −20 °C. The results provide support for the solution–diffusion model for RO membranes transport and demonstrate the capabilities of multi-nuclear NMR methods to investigate molecular-scale structure and dynamics of the interactions between dissolved species and RO membranes.

Keywords: Polyamide films; ^{23}Na NMR; T_1 relaxation; Interfacial polymerization; Reverse osmosis; Sodium chloride; FT-IR spectrum

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1. Introduction

Thin film composite (TFC) reverse osmosis (RO) membranes are used worldwide for desalination of brackish and sea water [1–6], but little is known about how they function at the molecular level. These membranes are typically formed by depositing a thin layer of polyamide polymer on a microporous polysulfone support layer, and current technology is well developed. Most previous, published research on transport across these membranes has focused on measurement of permeate flux and solute rejection ratio and has interpreted the results in terms of macroscopic diffusion and convection models, including the effects of membrane defects and foulants [1,2,4,7–10]. More recently, scanning electron microscopy, atomic force microscopy and spectroscopic methods including ^{1}H nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy have provided increased understanding of the microstructure, polymer structure, and water dynamics in these membranes [11–13]. ^{1}H NMR, for instance, has shown a positive correlation between the rate of water diffusion in thin film polyamide materials and polymer chain mobility, as measured by the $T_1\rho$. [11]. Molecular dynamics (MD) computer simulations of the structure and diffusion of water, Na^+, and Cl^- in polyamide membranes have suggested that H_2O transport occurs by a jump-diffusion process with each jump ~3 Å in length, that the experimentally and computationally observed decrease in water permeability is due to molecular-scale interaction with the ions in the membrane, and that the high observed salt rejection is due to large differences in the

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water and salt diffusivities in the discriminating membrane layer [14,15].

Development of advanced membranes with enhanced water flux and salt rejection will require more comprehensive understanding of the molecular-scale mechanisms of salt and water transport in the active layer. Here we present ^{23}Na nuclear magnetic resonance (NMR) chemical shift, line shape, and T_1 relaxation data for Na^+ dissolved in polyamide polymer that provide direct, molecular-scale insight into the Na^+ environments and dynamical behavior of dissolved species in these materials. The results demonstrate the potential of multi-nuclear NMR in membrane science. Potential applications include, for instance, understanding of the effects of active layer composition and synthesis on the structural environments and dynamics of water and a wide range of organic and inorganic ions, understanding of the relationships between molecular-scale structure and dynamics and the separation properties of the polymers, and understanding the molecular-scale origin of degradation and fouling of these membranes.

NMR is a sensitive and versatile probe of molecular-scale structure and dynamics in solids and liquids and at solid–liquid interfaces. It has been widely used in chemistry, materials and polymer science and geochemistry [11,16–25]. Chung et al. [25] provide a short review of the NMR principles relevant to quadrupolar nuclei such as ^{23}Na in polymer materials. There are several NMR parameters used in the study presented here. The NMR chemical shift is the difference between the resonance frequency of the observed nucleus and a standard and is a highly sensitive measure of the local (nearest and next nearest atomic neighbor) chemical bonding environment. The NMR line shape is sensitive to the symmetry of the local bonding environment and to molecular-scale dynamics at frequencies of the order of the observed static peak width, which are typically in the kHz to 100 kHz range for hydrated materials. The T_1 NMR time constant describes the rate at which an excited nuclear spin system relaxes to equilibrium and is very sensitive to molecular-scale dynamics near the Larmor (resonance) frequency, which is 79.38 MHz in this study. T_1 values for bulk aqueous solutions and in rigid solids are often quite long (slow relaxation). In situations in which the rate of motion is intermediate between these two situations, however, the measured T_1 values are normally much shorter. This is often the case for interaction with surfaces and polymers.

Most NMR studies of polymer materials have used ^{1}H and ^{13}C to probe the structure and dynamics of the polymer itself, but there have been several recent studies investigating the behavior of alkali cations [25–31]. Most of these studies have focused on application of polymers as fast ion conductors, and few have investigated hydrated materials that are relevant to RO membranes under operating conditions. Minato and Satoh [26] showed that the ^{23}Na NMR chemical shift of Na poly(acrylate) gel in water/organic solutions become more shielded (more negative) with increasing fraction of organic species in the solvent and propose that this is due to increasing Na^+ ion pairing with the carboxylic groups of the polymer. Asaro et al. [28] show that increased ^{23}Na NMR T_1 relaxation rates can be used to assess aggregation of poly(vinyl pyrrolidone) and poly(ethylene oxide) in surfactant-polymer solutions. Mauritz et al. [29] evaluated the effects of hydration on Na poly(styrene-b-isobutylene-b-styrene) block copolymer ionomers. For as-cast and dried samples, they observe a narrow resonance near 10 ppm, which they attribute to isolated $Na^+SO_4{}^-$ ion pairs, and a broader peak with a maximum near −20 ppm, which they attribute to aggregated $Na^+SO_4{}^-$ ion pairs. In contrast, a sample hydrated by immersion in water yields only one narrow resonance at a slightly negative chemical shift (value not given), which they attribute to dissociated and hydrated Na^+. These results demonstrate that hydration causes dynamical averaging and a single solution-like resonance for the hydrated sample that represents “solvent-separated” Na^+ ions.

Incorporation of ions in hydrated RO polymer materials occurs in confined nano-spaces, and the results of ^{6,7}Li, ^{23}Na, and ^{133}Cs NMR studies of alkali cations confined in hydrated clays and zeolites are directly relevant to interpreting the results here [16,17,32–38]. For instance, ^{133}Cs variable-temperature (VT) MAS NMR has shown that Cs^+ adsorbed on hydrated smectite clays occurs on multiple structural sites and undergoes dynamical exchange between the interlayer sites at frequencies greater than $\sim 10^4$ Hz at temperatures $\gtrsim -40\,^{\circ}\mathrm{C}$ [16]. ^{23}Na and ^{133}Cs NMR results demonstrate that Na and Cs occupy different surface adsorption sites (outer sphere and inner sphere, respectively) on the sheet silicate mineral illite [32]. ^{23}Na and ^{133}Cs NMR T_1 studies of the interactions of alkali cations with the surfaces of illite demonstrate large increases in the relaxation rate (decreases in measured T_1 values) relative to bulk solution due to their interaction with the surface [17].

2. Materials and experimental methods

2.1. PA film preparation

Unsupported PA films for the NMR experiments were synthesized via interfacial polymerization by rapidly adding 0.1% (w/v) trimesoyl chloride (TMC, Acros Organics) hexane solution into an equal volume of 2% (w/v) aqueous *m*-phenylenediamine (MPD, Alfa Aesar) solution without stirring or agitation [4,13]. The PA thin films grew instantaneously, and growth became self-limiting. Fig. 1 illustrates the reaction thought to dominate the polymerization [12]. The films formed at the solution interface were retrieved, dried at 95 °C for 210 s, and neutralized with 0.2 wt.% sodium carbonate solution. The films were suction-filtered from this solution and then washed extensively with deionized water and methanol to remove unreacted monomer and occluded salt. Part of the PA was then stored in a desiccator over P_2O_5 (∼0% relative humidity) for one week prior to further characterization. The rest was used for ion exchange experiments.

2.2. Ion-exchange experiments

For ion exchange, freshly made PA films were immersed in 1 M aqueous NaCl solution with magnetic stirring for 16 h. The NaCl-exchanged films were suction-filtered from the solution and a portion was washed twice using deionized water to