13C and 1H NMR measurements to investigate the kinetics and the mechanism of acetic acid (CH3CO2H) ionization as a model for organic acid dissociation dynamics for polymeric membrane water filtration

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A B S T R A C T

The formation of ionic charge carriers and their transport in acetic acid (CH_3COOH): water mixtures have been investigated by ^{13}C and ^1H NMR. The obtained dissociation constant from the NMR measurements is close to $pK_a = 4.70$ in a highly diluted system which is in full agreement with literature values. The maximum molar concentration of ions (H_3O^+ and CH_3COO^-) is found at a water mole fraction around 0.5 to 0.6. Remarkably, minima in the molecular diffusion coefficients and ionic mobility are observed at this concentration. Ionic concentrations, ionic strength and the pH curve were obtained for any water content based on the ^{13}C and ^{-1}H NMR as well as pH measurements and the numerical calculations. The data is relevant for the understanding and optimization of the properties of polymeric nanofiltration membranes for organic ion removal. They provide interesting insight into the water dependence of the viscoelastic and kinematic properties, the charge formation mechanism and the dissociation limit, especially for highly diluted systems simulating the case of ionic pollutants.

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1. Introduction

The separation of ions from aqueous solutions is of huge relevance to numerous fields both of science and for industrial applications [1]. Polymeric membrane filtration such as microfiltration, ultrafiltration, nanofiltration (NF) and reverse osmosis (RO) for water treatment is being used widely to convert brackish or seawater to clean water and to purify wastewater, additionally, it is used to recover dissolved salts and heavy metals from industrial processes. The applications of organic solvent nanofiltration (OSN) in the pharmaceutical, chemical and petrochemical industries has led to an increased demand for high performance polymeric filtration membranes [2] which are mechanically and chemically stable in extreme pH conditions [3], high ionic concentration and for strong hydrogen bonded networks. Polymeric membrane separations are promising technologies for separation of neutral and charged solutes in aqueous solutions [4,5]. The charge of the polymeric membranes applied can be either negative, positive or neutral depending on the pH and the ionic strength of the solution to be treated [6].

Dilute organic acid waste streams are produced in large quantities by many petrochemical processes and fine chemical industries which are using organic acid as a chemical reagent for the production of many chemical compounds in the manufacture of purified chemicals such as terephthalic acid, polyethylene terephthalate, vinyl acetate monomer and acetic anhydride.

Acetic acid is an important organic acid for industrial, chemical and biochemical applications and it is one of the major organic acid pollutants. Understanding the kinetics and the dissociation mechanism of acetic acid is essential to evaluate the impact of acetic acid on many chemical and biological processes. The dissociation constant (pK_a), ionic strength and ionic concentrations at different degrees of hydration were the subject of numerous theoretical and experimental studies for weak and organic acids [7–9].

Many of the calculations showed that the dissociation of acetic acid is not only driven by breaking of H-bonds, but can also be triggered by a solvent reorganization around the proton-accepting water [10]. The structure of acetic acid has been studied by low frequency Raman spectroscopy and ab initio calculations [11]. The investigation showed that acetic acid molecules form a chain structure by intermolecular hydrogen bonds between the hydroxyl hydrogen atom and the carboxyl oxygen one. Moreover, X-ray diffraction techniques [12] suggested that acetic acid molecules cannot form cyclic dimers but can form chain structures by hydrogen bonds. Neutron diffraction experiments on a single crystal of acetic acid revealed an infinite chain structure in the solid state [13,14]. Large angle X-ray scattering and NMR proved a strong relationship between the mole fraction of the acid and the structural change of the mixture [15].

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In the current study, acetic acid serves as a model system for understanding the dissociation, the ionic charge formation, the hydrogen-bonded complexes, the microviscosity and the intramolecular kinetics of organic acid hydrations in aqueous solution. For this purpose, ^{13}C and ^1H NMR chemical shifts, spin lattice relaxation times, self-diffusion coefficients and the densities of the acetic acid/water binary system have been experimentally investigated. Investigations were also done at temperatures above room temperature, as the polymeric membrane filtration process is operated at slightly elevated temperatures.

2. Experimental and sample preparation

All measurements have been performed on acetic acid/water mixtures. The acetic acid (p.a.) was purchased from Sigma Aldrich and was used without any further purification. Acetic acid was diluted in de-ionized water resulting in ten molar fractions of acetic acid from 100% to 0%. For density determination of each fraction, 0.5 mL acidic water solution was directly weighed several times. The water mole fractions were prepared by weighing acetic acid and water as required for water mole fraction X_{H_2O}. The samples have been prepared within the range $0 < X_{H_2O} < 1$, where $X_{H_2O} = 0$ corresponds to the pure acid and $X_{H_2O} = 1$ to pure water. More explanation and data about the sample preparation are listed in Table 1 and shown in Fig. 1.

Table 1 The parameters of the prepared acetic acid/water binary system mixtures. X_{H_2O} represents the added (initial) water mole fraction.

The ^{13}C and ^1H NMR measurements were carried out at 600 MHz for ^1H and 150 MHz for ^{13}C on a Bruker AVANCE III NMR spectrometer equipped with a high resolution multi-channel cryoprobe and a room temperature PABBO 5 mm inverse probe. A cryoprobe was used to measure ^{13}C signal at extremely low acid concentrations while ^1H NMR measurements were done with a room temperature (Bruker PABBO 5 mm inverse probe) head to avoid the radiation damping effect. ^{13}C NMR spin lattice relaxation times were measured using the inversion recovery pulse sequence. No lock was used, and trimethylsilylpropionic acid (TSP) was employed for referencing of ^1H and ^{13}C spectra. 1D and 3D gradient shimming and additional manual shimming, if required, was used. NMR data were acquired and processed with Bruker Topspin V3.2. Analysis and plots were done with ACD labs V9.0 and OriginLab V9.5.

3. Results and discussion

3.1. ^{13}C NMR for acetic acid-water mixtures

Fig. 2 shows the high resolution ^{13}C NMR spectra for pure acetic acid and the acetic acid/water mixtures at various water mole fractions X_{H_2O}. In these spectra selected molar fractions of the acetic acid/water

Table 1
shows the parameters of the mixture such as water mole fraction, densities of the mixture and the difference between densities as they have been measured experimentally and calculated theoretically. Fig. 1a shows the initial water mole fraction versus density of the mixture and Fig. 1b represents the difference of the densities versus the water mole fraction; as seen in Fig. 1b the maximum difference can be seen around $X_{H_2O} = 0.5 - 0.6$ due to dissociation and the formation of hydrogen bonds with increasing water content.

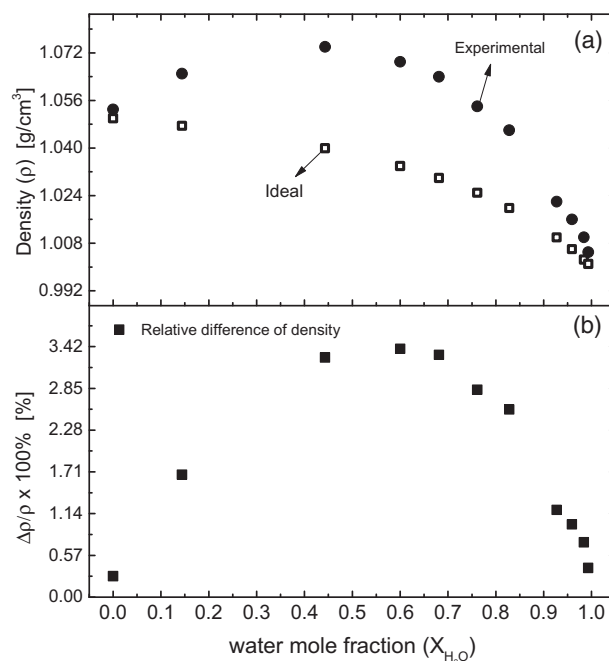| Sample	Water mole fraction X_{H_2O}	Experimental Density [g/ml]	Theoretical Density [g/m]	Density difference [g/ml]
1	0.000	1.053	1.043	0.010
2	0.144	1.065	1.039	0.026
3	0.443	1.074	1.037	0.037
4	0.681	1.064	1.024	0.040
5	0.761	1.054	1.021	0.033
6	0.828	1.046	1.014	0.032
7	0.927	1.022	1.008	0.014
8	0.959	1.016	1.003	0.013
9	0.984	1.015	0.998	0.017
10	0.993	1.001	0.997	0.004

Fig. 1. (a) The ideal$^{(*)}$ and the experimental densities of acetic acid - water binary system mixtures, and (b) the relative difference between ideal and experimental densities versus water mole fraction $X_{H_2O} = 1$ at $T = 298$ K. $^{(*)}$ Ideal density is the linear combination of the species densities taking into account their mole fractions.

mixture were chosen to facilitate the comparison. The ^{13}C NMR spectra of the acetic acid/water mixtures show two resonances with chemical shifts of 178.03 ppm and 20.00 ppm, corresponding to the signals of COOH and CH_3 groups, respectively.

According to the dissociation of acetic acid given by Equation (1)

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \tag{1}$$
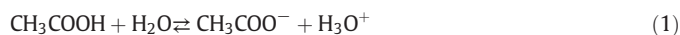
the two lines observed in the ^{13}C NMR spectra of the acetic acid/water mixtures show that the carboxyl carbons in COOH and COO^- groups rapidly exchange which leads to a single line based on the NMR time scale. This single line shifts strongly corresponding to the change of the acetic acid/water ratio.

Fig. 3 (a and b) shows the ^{13}C NMR chemical shifts for the carboxyl (−COOH) and methyl (−CH_3) groups as a function of the water mole fraction X_{H_2O} for different temperatures. The chemical shifts of the carboxyl group decrease (change toward high field) with X_{H_2O} between 0 and 0.6 and then increase (change toward low field) again with X_{H_2O}. The minimum of the ^{13}C NMR chemical shifts for the carboxyl group of acetic acid molecules at $X_{H_2O} \approx 0.6$ can be explained as follows. The high-field shift with decreasing X_{H_2O} from 1 to 0.6 originates from hydrogen bonds between acid-water, water-water and acid-water-hydronium ion molecules in weak acids [16,17]. By ionic dissociation of acetic acid, the electrons of the methyl group partly move to the carboxyl group by hydrogen bonding with water molecules, leading to the higher electron density on the carboxyl carbon atoms. With further increasing X_{H_2O} above 0.6 the dissociation of acetic acid molecules is enhanced (Fig. 3). Hence, the electron density for the carbon atoms of carboxylate decreases because a negative charge spreads on the resonance structure of the carboxylate. Consequently, the ^{13}C NMR chemical shifts for the carboxyl group increase again with increasing X_{H_2O}.

In the case of the methyl group in the acetic acid molecule, the chemical shift values increase with X_{H_2O}. The absolute change of COOH chemical shift values is much more pronounced than the change in CH_3 shifts (Fig. 3). The hydrogen bond networks and the hydrogen bonded complexes in acetic acid/water binary mixtures have previously been studied by density functional theory and ab initio calculations [18],