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Dynamical behavior of unfreezable molecules restricted in a frozen matrix

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Abstract

Broadband dielectric spectroscopy measurements performed around the freezing temperature showed two different dynamical behaviors for various mixtures of poly(vinyl pyrrolidone) (PVP)/water, poly(vinyl acetate)(PVAc)/benzene, PVP/poly(ethylene glycol) (PEG), and 4,4′-*n*-pentylcyanobiphenyl (5CB)/benzene. A discontinuous behavior of the temperature dependence of the relaxation time around the freezing temperature was observed for the processes due to water in PVP/water, PVP in PVP/PEG, and 5CB in 5CB/benzene mixtures, and a continuous behavior was observed for PVAc in PVAc/benzene and PEG in PVP/PEG mixtures. These behaviors are explained by a large volume effect from the large motional unit. PVP/*n*-alcohol mixtures support that the high hydrogen-bonding ability of water brings about the large volume effect also in PVP/water mixture.

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1. Introduction

Broadband dielectric spectroscopy (BDS) measurement is a useful experimental technique to investigate dynamical structures of molecular complex systems, which make it possible to precisely explain structures, various properties, and functions from the molecular mechanism [1,2]. For example, a Debye-type relaxation process due to reorientations of water molecules observed for pure water around 20 GHz at 25 °C is affected by solute molecules in the case of aqueous solutions. Solute molecules change the shape of the relaxation curves due to water and the peak frequency because of the intermolecular interactions. Though this interaction has been extensively investigated so far in various aqueous systems including biological systems [3], recent developments of dielectric spectroscopy bring more precise explanations of physicochemical properties and functions in terms of dynamical structures of molecular complex systems. Especially developments of dielectric spectroscopy in the microwave frequency region [4,5] and μHz frequency region [1,2] expand the techniques of BDS.

Freezing and/or melting processes have been extensively investigated by various experimental techniques such as thermal analysis [6]. Mixtures also indicate that there still exist mobile molecules even in the frozen state, and these unfreezable molecules affect dynamical structures of components included in the local liquid region [7,8]. Though a DSC study is very effective to investigate this molecular behavior of unfreezable molecules at the melting point, it is not easy to obtain the behaviors at any temperatures except the phase transition temperature. On the other hand, the BDS technique is available

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to investigate dynamical behaviors of unfreezable molecules at low temperatures [9,10]. Though the freezing process of mixture is quite complicated comparing with pure materials, various behaviors experimentally observed suggest more precise molecular interactions to determine the molecular mechanism and concept.

In the present work, mixtures of poly(vinyl pyrrolidone) (PVP)/water, poly(vinyl acetate) (PVAc)/benzene, PVP/poly(ethylene glycol) (PEG), and 4,4′-*n*-pentyl-cyanobiphenyl (5CB)/benzene were investigated by BDS for an interest in the dynamical behavior of molecules around the freezing temperatures. Furthermore PVP/*n*-alcohol mixtures were also observed at 25 °C to suggest molecular behaviors of water. These mixtures have been investigated by various experimental techniques as typical mixtures in each category of molecular complex systems, such as polymer/water, polymer/organic solvent, polymer/polymer, liquid crystal/solvent. Then it is expected that characteristic behaviors of the relaxation time observed by BDS measurements for these mixtures around respective freezing temperatures can be analyzed with data obtained so far. In the present paper, we focus our point to examine dynamical behaviors obtained as the temperature dependence of the relaxation time around the freezing temperature, and discuss which common concept of molecular mechanism leads to the characteristic behaviors.

2. Experimental procedures

PVP (weight-average molecular weight M_w: 10000; 40000) was purchased from Sigma Chemical Co. PEG (M_w: 400), PVAc (number-average molecular weight, M_n: 163400), and 5CB were obtained from Aldrich Chemical Co.

Alcohols and benzene with pure grades, that are available as commercial samples, were used without more purification. PVAc (M_n: 163400) was purified by reprecipitation under slow stirring in hexane from the benzene solution. PVAc thus obtained was dried under vacuum of 0.01 Torr for 3 days.

PVP (M_w: 10000)/water mixtures were prepared with MILI-Q water at desired concentrations for dielectric measurements. A 30 wt% PVP/PEG mixture was prepared with PVP (M_w: 40000) and PEG (M_w: 400) for BDS measurements. PVAc/benzene (5 wt%) and 10 wt% 5CB/benzene mixtures also were prepared for BDS measurements. PVP (M_w: 40000)/alcohols solutions were prepared in the concentration range of 0–40 wt%.

BDS measurements were usually performed by five sub-systems in each available frequency region of a whole range of 1 μHz to 20 GHz, i.e. time domain reflectometry (TDR: 10 MHz–20 GHz), Impedance/Material Analyzer (IMA: 1 MHz–1.8 GHz, Hewlett–Packard), LCR meter (20 Hz–1 MHz, Hewlett–Packard), AC phase analysis (ACPA: 1 mHz–100 Hz), and DC transient current method (DCTC: 1 μHz–100 mHz). TDR measuring system equipped a sampling head (Hewlett–Packard 54121 A) and a mainframe of digitizing oscilloscope (Hewlett–Packard 54121B), covered the frequency range from 10 MHz to 20 GHz. Details of TDR were described in former literatures [5,11–13]. IMA (Hewlett–Packard 4291A) and LCR meter (Hewlett–Packard 4284A) was utilized to cover the range of 1 MHz–1.8 GHz and 20 Hz–1 MHz, respectively. In the present work, TDR, IMA, and LCR meter systems were employed to perform BDS measurements between 20 Hz and 20 GHz. A semi-rigid cable (diameter of outer conductor: 2 mm; electric length: 0.15 mm; geometric capacitance: 0.0101 ± 0.0004 pF) was employed as an electrode especially for higher frequency region with electrodes usually employed in whole frequency range. Detailed measurement procedures in the lower temperature region were described in our former publications [2,9,10].

BDS measurements were performed below and above the freezing temperature for various mixtures except PVP/alcohol mixtures for which concentration dependences of dielectric relaxation processes were examined by BDS measurements only at 25 °C. The frequency range of BDS measurements varied from 3 to 16 decades according the temperature and concentration dependences of the relaxation time for various mixtures.

3. Results and discussion

Experimental results obtained in the present work are discussed for each mixture.

3.1. Dynamical behavior of solvent molecules in PVP/water mixture

Fig. 1 shows dielectric constant and loss for 20 wt% PVP/water mixture at various temperatures around the freezing temperature. The relaxation process observed in GHz region is due to dynamical clusters of water, and the peak frequency shifts to the lower frequency side with decreasing temperature. The relaxation process caused by chain dynamics of PVP must be observed in the lower frequency region. However in the case of aqueous polymer solutions, it is usually difficult to observe the relaxation process caused by the chain dynamics in MHz region, since the contribution of electric conductivity masks the process. The peak frequency and the relaxation strength clearly show a discontinuity at the freezing temperature already reported [9,10]. Below its freezing temperature, the relaxation process of water is still observed, since the part of water in the mixture remains in the liquid state. The relaxation time,