

# The Study of Micro phase behavior for the binary system of [bmim][PF<sub>6</sub>] and ethanol by dielectric spectroscopy

Liyan Ma, Kongshuang Zhao\*

College of Chemistry, Beijing Normal University, Beijing 100875, China,

\*Corresponding author: zhaoks@bnu.edu.cn

**Abstract:** Dielectric spectra of mixtures containing ionic liquid [bmim][PF<sub>6</sub>] (IL) and ethanol with different ethanol mass fraction are measured over a frequency range from 10MHz to 20GHz at a constant temperature. The spectra could be satisfactorily fitted by assuming only two relaxation modes: Cole-Cole process at lower frequencies and a Debye process at higher frequencies. Detailed analysis indicates that both the two relaxation processes contain additional modes respectively and all dielectric parameters have a turning point at the ethanol mass fraction of 20%.

**Keywords:** Dielectric spectra, binary system, turning point, micro-structure, macroscopic phase separation.

## 1. Introduction

To aid in the development of ionic liquids for reactions and separations, many researches on phase equilibrium of ionic liquids(IL) mixture have been reported<sup>1,2</sup>. Nevertheless, the micro-structure data of the mixture is still lacking, this limits the further application of IL. In addition, few studies about room-temperature ionic liquids RTIL/cosolvent mixtures by dielectric spectroscopy have been reported. The aim of present work is to clear the microstructure of the mixture and modes of interaction between the IL and alcohol through analysis of dielectric parameters. On this basis, the interpretation to macroscopic phase behavior of IL mixture is also attempted.

## 2. Experimental and method

The dielectric measurements were carried out with an Agilent E8362B PNA series network analyzer, equipped with an Agilent 85070E open-ended coaxial probe, covers the frequency ranges from 100 MHz to 20 GHz, at 21 ± 0.1 °C. All dielectric parameters can be obtained by fitting the experimental data with the Cole–Cole equation. The Cavell equation<sup>3</sup> describing the relation between dielectric increment  $\Delta\varepsilon_i$  of a relaxation process and effective dipole moment  $\mu_{eff,i}$  of the species responsible for that process was used.

$$\frac{2\varepsilon_i + 1}{\varepsilon_i} \Delta\varepsilon_i = \frac{N_A c_i}{k_B T \varepsilon_0} \cdot \mu_{eff,i}^2$$

Where  $i$  is the number of the dielectric relaxation,  $\varepsilon_i$  is static permittivity,  $\Delta\varepsilon_i$  is the dielectric increment for each mode  $i$ ,  $N_A$  and  $k_B$  are the Avogadro and Boltzmann constants respectively,  $T$  the thermodynamic temperature, and  $c_i$  the molar concentration of the species  $i$ .

## 3. Results and discussion

Fig.1(a) shows a dielectric spectroscopy with two relaxation processes. The low-frequency process is mainly due to the reorientation of the dipolar [bmim]<sup>+</sup> and ion pairs and cooperative dynamics of the H-bond system.

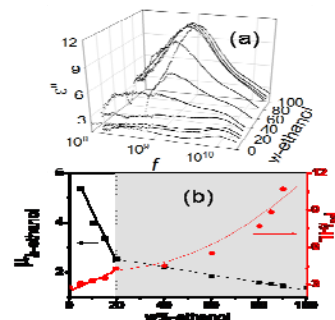
The high-frequency mode is a composite of the inter-ion distance motions of ion-pairs formed between cationic and anionic species originating from the IL and the motion of singly H-bonded ethanol monomers at the ends of the ethanol chain structure. A turning point appears at the ethanol mass fraction of 20% for all parameters (eg.  $\Delta\varepsilon$ ,  $\mu$ ,  $\kappa_i$ ), Fig.1(b) shows the dependence of micro-dipole moment  $\mu_h$  of high-frequency for constituent phase of mixture on the concentration of ethanol. The dielectric analysis indicates there are crucial differences in micro-structure before and after 20%, being consistent of Macro phase diagram<sup>4</sup>.

## 4. Conclusions

The relaxation mechanism and micro-phase behavior before and after  $W_{et} = 20\%$  ethanol content are explained based on dielectric parameters and micro-dipole moment. When  $W_{et} \leq 20\%$ , large IL super-molecular structure intersperses with a few ethanol molecules by hydrogen bonding, IL keeps its characteristics (one phase in macro sense). When  $W_{et} \geq 20\%$ , with  $W_{et}$  increases, IL super-molecular structure are succeeded in turn by contact ion pairs (CIPs), solvent-shared ion pairs (SIPs) while ethanol molecules form chain-like hydrogen bonding structure with only a spot of CIP and SIP fluctuating around, the system keeps the characteristics of both IL and ethanol molecules, respectively, which shows two phase in macro sense. The results provide some available information for the applications of IL in separation.

## References

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**Fig.1(a)** 3-D representation for the frequency dependencies of dielectric loss  $\varepsilon''$  of the [bmim][PF<sub>6</sub>]/ethanol with different ethanol mass fraction. **(b)** The dependence of micro-dipole moment  $\mu_h$  of various relaxation species of high-frequency on the concentration of ethanol.