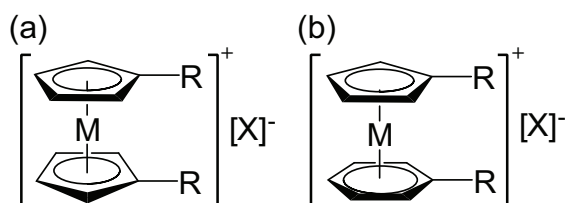


## Low-frequency spectra of metallocenium ionic liquids studied by terahertz time-domain spectroscopy

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**Introduction:** In recent years a number of theoretical and experimental studies on dynamics of ionic liquids (ILs) have been reported by several groups.<sup>1-2</sup> In most of the studies, ILs used contain imidazolium cations. We have recently developed unconventional ionic liquids containing metallocenium cations (Figure 1). These materials can be regarded as functional liquids containing metal ions, which exhibit unusual physical properties. The metallocenium ILs are characterized by their bulky molecular shape and charge localization inside the cation, which make contrast with imidazolium-based conventional ILs. Therefore, the molecular motions as well as intermolecular interactions in these liquids are of great interest. To characterize the dynamical aspect of ILs in the far IR region, we have applied terahertz (THz) time-domain spectroscopy. Prior to this work, there are very few reports on the THz spectroscopy study on ionic liquids.<sup>3-4</sup> Since the low frequency dynamics is governed by both the intra and collective inter molecular motions, so by varying the cation part with suitable metal and by varying anion, we would like to understand the exact dynamics playing crucial role in the low frequency region.



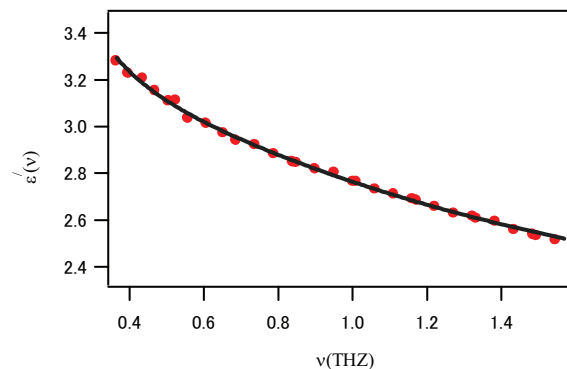
**Figure 1.** Structural formula of metallocenium ionic liquids. (a) M = Co, R = Et, X = N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>, b) M = Fe, R = Et, X = N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>.

**Experiment:** The THz time-domain measurement was done on two ionic liquids (1a and 1b in Fig.1) using two different methods; one is based on electro-optic sampling, and other method uses the photoconductive antenna (PC) system. The frequency range covered in the experiments is from 10 to 80 cm<sup>-1</sup>.

**Results and Discussion:** The dielectric response is well fitted to a two-term Debye model according to following equation

$$\hat{\epsilon} = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_2}{1 + i\omega\tau_1} + \frac{\epsilon_2 - \epsilon_{\infty}}{1 + i\omega\tau_2},$$

where  $\epsilon_{\infty}$  and  $\epsilon_s$  are the optical and static dielectric constant, respectively,  $\epsilon_2$  is the intermediate dielectric constant, and  $\tau_1$  and  $\tau_2$  are the first and second Debye relaxation time, respectively. A representative fit of the real part of the dielectric constant following this Debye model is shown in Figure 2.



**Figure 2.** Real part of dielectric response of ferrocenium IL (IL in Figure 1(b))

Thus, the time constants obtained from the fitting are 2.01 ps and 0.121 ps for the ferrocenium ionic liquid and 1.65 ps and 0.10 ps for cobaltocenium ionic liquid. In all the cases, the  $\epsilon_s$  and  $\epsilon_{\infty}$  as obtained from fitting are found to be 10 and 2.1. The intermediate frequency was 3.065 for ferrocenium ionic liquid and 3.45 for cobaltocenium ionic liquid. This result is similar to the relaxation of imazolium ionic liquid reported earlier.<sup>3-4</sup> Yamamoto et al.<sup>3</sup> reported a three term Debye type model to ionic liquid. However, in the present study, the use of the three-term Debye model function does not add any improvement to the fitting.

The important observation is that unlike short chain alcohol there is a structured line shape in the imaginary dielectric constant part of both the ionic liquids. Thus, the dielectric response spectra beyond the region  $50 \text{ cm}^{-1}$  could not be fitted to a multi Debye relaxation. This observation is consistent to the early study in ionic liquid.<sup>3</sup>

The two ionic liquids have the same anions but differ only in the cationic part. Almost same relaxation times indicate that in low frequency region the dynamics is not solely governed by the motions of any single ions. Since the intramolecular vibration of the anions occurs in much higher frequency range, we thus conclude that low frequency spectra in  $0 - 80 \text{ cm}^{-1}$  arises from cooperative intermolecular vibration dynamics involving both the cations and the anions. The OKE-RIKES studies also support this conjecture.  
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