

2008 Abstract of Master Thesis

Near Infrared and Attenuated Total Reflection - Infrared Studies of Phase Behavior of Ethylene Carbonate and Alcohol Binary Mixtures

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[Introduction] Phase behaviors of ethylene carbonate (EC) and alcohol binary mixtures have been investigated by Iwahashi *et al.* as results of density measurement and visual judgment¹⁾. They observed interesting behaviors, EC/1-propanol mixtures in liquid phase show a phase separation with an upper critical solution temperature (UCST), whereas EC/ethanol mixtures show only liquid one-phase. Spectroscopic analysis is necessary to understand the association structure of molecules in the liquid mixtures. Vibrational spectroscopy is one of the useful and appropriate methods to observe individual molecular interactions. Recently, Near-Infrared (NIR) spectroscopy has been applied to investigate the relationship between thermodynamic phase behavior and individual molecular interactions in triethylamin/water²⁾. The purposes of these studies are to investigate a relation between vibrational frequencies and phase behavior, and to elucidate the structure of EC and alcohol binary mixtures by use of NIR and ATR-IR spectroscopy.

[Experimental] EC/ethanol mixtures and EC/1-propanol mixtures were prepared at 50 °C showing a homogeneous one-phase with different molar fractions of EC ($x=0.00\sim1.00$) for prior NIR and ATR-IR spectral measurements. NIR spectra were measured during cooling process from 60 to 20 °C (cooling rate was about 1 °C / min) with a 2-mm quartz cell. ATR-IR spectra were obtained during cooling process from 60 to 30 °C. Commercial ATR kit of SeagullTM was arranged to set the planar reflection surface of a ZnSe hemispherical prism (12.7 mm radius) vertically. Solution samples were placed on the prism surface with a homemade batch cell.

[Results and Discussion] In chapter 1, the first overtone of C-H stretching and the first overtone of O-H stretching vibrations have been investigated. Most of C-H bands in the first overtone of C-H stretching vibration (6100-5600 cm⁻¹) are severely overlapping with each other except for CH₂ asymmetric stretching mode of EC (ν_{CH1}). The first overtone of the polymeric O-H stretching and the free terminal O-H stretching vibration of alcohol are found in the region of 7200-6100 cm⁻¹. The temperature-dependent wavenumber shifts of ν_{CH1} (Fig. 1(b)) and the polymeric O-H band of alcohol for EC/1-propanol mixtures have an obvious

shift at the critical concentration ($x=0.425$). It seems that the shifts indicate a precursor of phase separation from liquid one-phase to liquid two-phase. Moreover, the temperature-dependent ν_{CH_1} shift of EC/1-propanol mixture shows big skews around the critical concentration. The C-H band shift is possibly caused by density change of the mixtures²⁾. On the other hand, prominent difference of the shift could not be found in the first overtone of O-H stretching bands. This result supports the thermodynamic nature of phase separation, because no strong attractive force, such as hydrogen bonding, is required for UCST-type phase separation. The wavenumber shift of ν_{CH_1} is observed even in the EC/ethanol mixtures (Fig. 1(a)), which show only liquid one-

phase during cooling process. In chapter 2, the fundamental of O-H stretching, C=O stretching, C-H stretching, CH₂ stretching and ring vibration modes in the mid-infrared region (4000-650 cm⁻¹) have been investigated. The temperature-dependent wavenumber shifts of each the fundamental vibrations of EC/1-propanol mixtures and EC/ethanol mixtures have a certain similarity to the NIR study. The analysis of the concentration- and the temperature-dependents wavenumber shifts of the ATR-IR spectra suggest that strong dipole-dipole interaction of the self-association of EC molecules is weakened with addition of alcohol. As result of the steric limitation, intermolecular O---H-O interactions are probably formed between EC molecule (-C=O or -O-) and alcohol molecule (H-O-). These studies demonstrated potential of NIR and ATR-IR spectroscopy in investigating phase behavior and elucidating structure of binary mixtures.

[References]

- 1) Iwahashi *et al.* (unpublished data).
- 2) A. Ikehata, C. Hashimoto, Y. Mikami, Y. Ozaki, *Chem. Phys. Lett.* 2004, 393(4-6), 403.

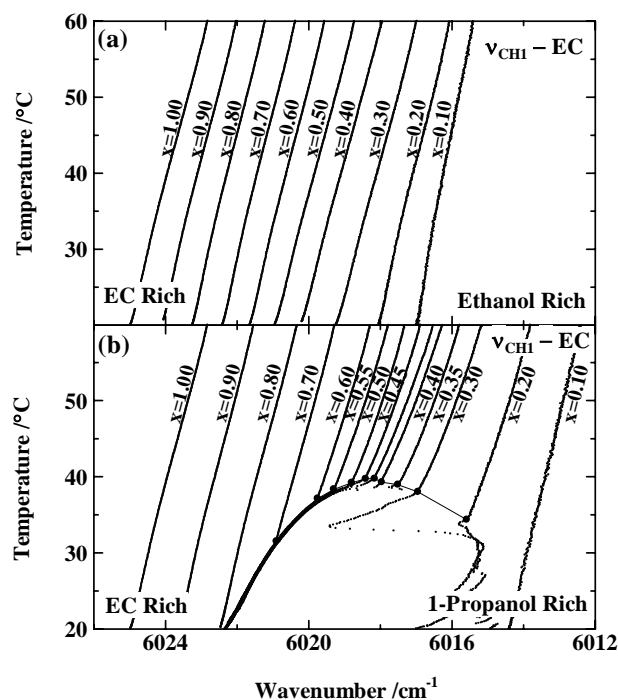


Fig 1. Plots of wavenumbers of the first overtone of CH₂ asymmetric stretching band (ν_{CH_1}) versus temperature for (a) EC/ethanol mixtures and (b) EC/1-propanol mixtures at various molar fractions