

学 位 論 文 要 旨

A Fundamental Study of Self-association Behavior of Highly Polar Molecules in Solution

(溶液中における高極性分子の自己会合挙動に関する基礎研究)

環境資源共生科学専攻 森林資源物質科学大講座

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Intermolecular association behavior is often observed in solutions of various kinds of highly polar compounds. As the concentration of solute molecule increases, dimers and other higher order intermolecular associations may form in the solution. The association phenomena are strongly influenced by physicochemical characteristics of the solute compounds. In the self-association processes, the effect resulted from dipole-dipole interaction has not been gathered enough attention as intermolecular interaction caused by hydrogen bonding. The essence of the dipole-dipole interactions leading to intermolecular association phenomena still remains as open questions, which should be solved for full understanding of physics and chemistry of liquid state materials.

In this thesis, the formation of anti-parallel dimers, in the configuration of electric dipole moments, was quantitatively discussed and the dynamics controlling the self-association processes was also elucidated clearly. Specifically, The formation of anti-parallel dimers of liquid crystal forming 4-cyano-4'-alkyl biphenyls (n CB, $n = 5$ and 8) and of not forming ones ($n = 3$ and 4) was confirmed in an isotropic cyclohexane solution. Dielectric relaxation (DR) and fluorescence emission (FE) experiments were carried out to investigate the molecular dynamics of the n CB molecules in detail. The DR spectra of solutions at intermediate to high concentrations were comprised of two dynamic processes. A fast mode with the relaxation time of *ca.* 90 ps was assigned to the free rotations of monomeric n CB molecules. The slow mode with the relaxation time of *ca.* 400 ps was attributed to the dissociation process of the anti-parallel dimers ($(n$ CB)₂). The Kirkwood

factor (g_K), a measure of the orientational correlation between the dipole moments of the cyano groups, was markedly less than unity for the slow mode, which demonstrated the formation of anti-parallel dimers, $(nCB)_2$. The equilibrium constant for anti-parallel dimer formation in the isotropic solution evaluated *via* the DR data increased with increasing the concentration. At the moderate to high concentrations excimer emission was clearly observed. The relative intensity of the excimer emission to the monomer emission significantly increased with increasing the concentration. Moreover, the equilibrium constant for the excimer formation reasonably agreed with that for the anti-parallel dimer formation evaluated by the DR data, strongly suggesting that the excimers of nCB and the $(nCB)_2$ dimers were identical chemical species. Since the lifetime of the excimer was determined to be *ca.* 40 ns *via* the results of time-resolved FE measurements, it is likely that the lifetime of the anti-parallel dimer in the excited state is considerably longer than that of dimers in the ground state.

Ethylene carbonate (EC) has been widely used as a typical chemical component in electrolyte liquids of many commercial lithium ion secondary batteries. The equilibrium constants for the anti-parallel dimer formation of EC in solutions of pure solvents, *i.e.*, benzene (Bz) and dimethyl carbonate (DMC), were quantitatively determined at room temperature (25 °C) and various concentrations using Raman scattering (RS) and DR experiments. In RS measurements, the strong C=O stretching vibrational band of EC observed at approximately 1800 cm^{-1} split into a monomeric EC signal, and signals assigned to anti-parallel dimers $((EC)_2)$ in the examined solutions. From the concentration dependence of the C=O stretching vibrational signal intensities, equilibrium constants of the formation of $(EC)_2$ in the solutions were determined assuming a chemical process, $2EC \leftrightarrow (EC)_2$. In DR measurements, two major dielectric processes were identified in both Bz and DMC solutions. The relaxation times were *ca.* 8 and *ca.* 20 ps in Bz, and *ca.* 20 and *ca.* 40 ps in DMC solution for the two relaxation processes, respectively. The population of monomeric EC was evaluated from the strength of the faster relaxation mode assigned to the rotational mode of monomeric EC. The libration of EC molecules was observed as a sharper resonance signal at *ca.* $1.5 \times 10^{13}\text{ s}^{-1}$ when they existed as monomeric EC rather than in the form of $(EC)_2$ in Bz, whereas the signal was not so sharp in DMC. The fact that the determined equilibrium constants *via* DR measurements depended on the solvent; $3\text{--}7\text{ M}^{-1}$ in Bz and $0.05\text{--}0.1\text{ M}^{-1}$ in DMC, reveals that the choice of solvent governs the efficiency of $(EC)_2$ formation. The equilibrium constants obtained by the DR experiments showed reasonable agreement with that determined in the RS experiments. Moreover, the fact that the equilibrium constants substantially depend on the species in the solvent and on the EC composition strongly manifests that the choice of a solvent effectively governs the anti-parallel dimer formation, and consequently influences the performance of lithium ion secondary batteries.