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Medium effects on the fluorescence spectra of tertiary aliphatic amines in mixed solvents and supercritical fluids

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Abstract

Emission spectra of some tertiary amines were measured in cyclohexane (CH)–tetrahydrofuran (THF) mixtures and in supercritical fluids of CHF_3. The emission bands of these amines were found to show large successive red shifts with increasing concentration of polar solvent molecules. This finding was rationalized by considering the consecutive solvation of the polar molecules around the Rydberg excited state of the amine. In order to estimate the degree of solvation, the wavenumbers of the emission maxima were plotted as functions of the THF and CHF_3 concentrations. The changes in solvation number with increasing THF and CHF_3 concentrations were obtained from the spectral shifts by applying a calculation for the stepwise solvation model.

Keywords: Medium effect; Fluorescence spectra; Tertiary amines; Supercritical fluid; Mixed solvent; Stepwise solvation model

1. Introduction

Saturated tertiary amines are the most remarkable examples of aliphatic molecules exhibiting strong fluorescence emission in the vapor phase [1–3], as well as in solution [4,5]. The fluorescence quantum efficiencies of saturated tertiary amines in the vapor phase and in nonpolar solvents have been shown to be quite large. The amines are strongly emissive also in saturated ethers. There are large red shifts in the emission spectra of the tertiary amines in ethers relative to nonpolar solvents. The overall red shift upon going from cyclohexane (CH) ($\lambda_{max} = 285$ nm) to tetrahydrofuran (THF) ($\lambda_{max} = 344$ nm) is large.

Excitation of tertiary amines leads to Rydberg-type excited states characterized by an excited orbital of large spatial extension [6,7]. Such states are assumed to undergo strong perturbations resulting from interactions with the surrounding molecules, and this is demonstrated by efficient fluorescence quenching in polar solvents [8,9].

Muto et al. [8] observed large red shifts in the emission spectrum of 1,4-diaza-bicyclo[2,2,2]octane (DABCO) in ether solvents relative to nonpolar solvents. Similar large red shifts in the emission spectra of triethylamine (TEA) and *N*,*N*-diethylmethylamine (DEMA) in similar solvents were reported by van der Auweraer et al. [10] and Halpern [11]. Muto et al. explained the observation by the stabilization of the excited state of the amine by the ether solvents using the model of a solvated Rydberg state. Halpern also discussed the red shift in the emission spectrum of DEMA within the framework of universal and specific interactions between the excited amine and ether molecules, and discussed the exciplex formation. However, no evidence for the formation of intra and intermolecular 1:1 amine–ether exciplexes was found. He concluded that the original view of Muto et al. may account satisfactorily for the observation, though the possibility of the formation of higher associates remains [11].

Halpern et al. investigated the structural effects on photophysical processes and excimer formation in saturated amines [3,12,13], and also examined the fluorescence properties of members of the series ($(CH_3)_2N–(CH_2)_n–N(CH_3)_2$) and observed emission from excited monomer and an intramolecular

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excimer for $n = 3$ and 4 [14]. We observed broad and asymmetric emission spectra with some saturated diamines which have a primary and a tertiary amino group. These spectra were resolved into three component bands, and they were assigned to excited tertiary and primary amino group moieties and an intramolecular exciplex between an excited tertiary amino group and a ground state primary amino group [15,16].

Kohler studied the steady state and time-resolved fluorescence spectroscopy of triethylamine–ethanol and –deuterated ethanol mixtures and observed exciplex formation at low alcohol concentrations in hydrocarbon solution [17–19].

In amine–amine and amine–alcohol systems, the formation of excimer and exciplex was observed. As mentioned above, however, in amine–ether system the specific interaction between the excited amine and ether molecules was not observed.

Shang et al. studied solvent induced singlet (2p3s) Rydberg relaxation dynamics of DABCO in van der Waals clusters generated in a supersonic expansion. The singlet Rydberg state dynamics were found to depend upon cluster geometry, cluster size, and cluster vibrational energy. These results suggested that the Rydberg state is reactive and susceptible to environmental perturbation [20].

The examination of the dependence of the emission spectrum on the composition of the polar solvent in nonpolar–polar mixed solvents or that on the density of supercritical fluids of polar species can give more detailed information about the solvation of the excited tertiary amines. Solvation of polar solvent molecules is expected to occur stepwise by increasing the content of the polar solvent in CH–THF mixtures or by increasing the density in supercritical fluids of CHF_3.

In this study, the effects of the stepwise solvation of THF and CHF_3 molecules on the emission spectra of different types of tertiary amines have been examined in the CH–THF mixtures and in supercritical fluids of CHF_3.

2. Experimental

All the reagents were obtained from commercial sources. TEA (extra pure grade) was used after drying with potassium hydroxide and a trap-to-trap distillation. 1-Azabicyclo [2,2,2]octane (ABCO) was used as supplied. Trioctylamine (TOA) was used after drying with potassium hydroxide and filtration. CH, THF and diethyl ether (DEE) were of spectroscopic grade and were used as available. Diisopropyl ether (DIPE; extra pure grade) was used after drying with calcium hydride and distillation. CHF_3 gas was of high-purity.

The steady-state fluorescence spectra of amines in CH, THF, DEE, DIPE and CH–THF mixtures were measured by using a Shimadzu spectrofluorophotometer, model RF-5300PC (band pass typically 10 nm) at room temperature. The concentrations of amines were 3.0×10^{-4} mol dm^{-3}. The solutions were degassed by four freeze–pump–thaw cycles immediately prior to measurement. Excitation was effected at 245 nm in each case.

The optical cell for the supercritical fluid experiments was made of stainless steel (SUS 304) with three quartz windows of 15 mm diameter. The cell was evacuated and sample gases were introduced using a vacuum line. Supercritical CHF_3 was fed to the cell with an HPLC pump (JASCO, SCF-Get). The pressure in the cell was changed by adding CHF_3 successively, and the pressure was monitored with a strain pressure gauge (Kyowa, PGM-200KH). The temperature of the cell was monitored with a K-type thermocouple and maintained at 35.0 ± 0.2 °C by circulating hot water from the thermostated water bath (Tokyo Rika Co. UA-100G) through the cell. The fluorescence spectra of TEA and ABCO in supercritical CHF_3 were obtained with a Shimadzu spectrofluorophotometer, model RF-5300PC) using the high-pressure cell. The pressure was monitored with a piezo gauge and the density was calculated from the P-V-T data for CHF_3 [21].

3. Results and discussion

According to the model postulated by Muto et al. the stabilization energy (ΔE) of the excited amine was expressed approximately as follows:

$$\Delta E = E_{\text{ex}} - E_{\text{ep}} - E_{\text{op}} \qquad (1)$$

where E_{ex} is a repulsive exchange energy between the Rydberg electron and solvent molecules, and E_{ep} and E_{op} are electronic and orientational polarization energies, respectively. They estimated the quantity ($E_{\text{ex}} - E_{\text{ep}}$) from the energy of blue shift of the Rydberg absorption band, and E_{op} from the ion–dipole interaction energy. They could obtain an explanation for the observation of a shift of the emission band of DABCO by using a model in which several polar solvent molecules are solvated to the Rydberg state of the amine.

In order to examine the solvent polarity dependence of the emission band using the successive solvation model in more detail, the emission spectra of TEA were measured in CH, THF and several CH–THF mixtures. The results are shown in Fig. 1. The observed spectra show large successive bathochromic shifts with increasing THF content. Similar spectral shifts in CH–THF mixtures were observed for ABCO and TOA. Fig. 2 shows the wavenumbers of the emission peak of TEA as a function of the relative permittivity of CH–THF mixtures and some neat solvents. As shown in Fig. 2, the shifts of the emission band in

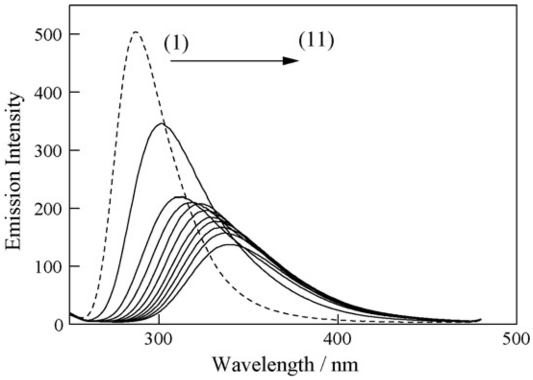

Fig. 1. Emission spectra of TEA in CH/THF mixtures with different concentrations of THF. (1) [THF] = 0 mol dm^{-3}, (2) 1.23 mol dm^{-3}, (3) 2.47 mol dm^{-3}, (4) 3.70 mol dm^{-3}, (5) 4.93 mol dm^{-3}, (6) 6.17 mol dm^{-3}, (7) 7.40 mol dm^{-3}, (8) 8.63 mol dm^{-3}, (9) 9.86 mol dm^{-3}, (10) 11.10 mol dm^{-3} and (11) 12.33 mol dm^{-3}.