

Solvation structure around 4-dimethylamino(benzonitrile) in a mixture of supercritical CO₂ and methanol

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 11437

(<http://iopscience.iop.org/0953-8984/14/44/496>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.97

The article was downloaded on 18/05/2010 at 17:20

Please note that [terms and conditions apply](#).

Solvation structure around 4-dimethylamino(benzonitrile) in a mixture of supercritical CO₂ and methanol

N Kometani, J Okamoto, K Asami and Y Yonezawa

Department of Applied Chemistry, Faculty of Engineering, Osaka City University,
Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585, Japan

E-mail: kometani@a-chem.eng.osaka-cu.ac.jp

Received 19 June 2002

Published 25 October 2002

Online at stacks.iop.org/JPhysCM/14/11437

Abstract

The fluorescence spectra of 4-dimethylamino(benzonitrile) (DMABN) have been measured for a mixture of supercritical CO₂ and methanol at high pressures up to 15.5 MPa at 318 K. It is found that the addition of a small amount of methanol can stabilize the intramolecular charge transfer (ICT) state of DMABN in the supercritical fluid mixture. The spectral shift of the ICT band has been analysed on the basis of Onsager reaction field theory; a significant increase of the local composition of methanol around the DMABN molecule in the ICT state is demonstrated.

1. Introduction

Supercritical CO₂ has received much attention due to its application in a variety of chemical processes as well as the increasing demand for environment-friendly solvents [1]. However, the solubility of polar solutes in supercritical CO₂ is usually very poor. To modify the solubility parameter of supercritical CO₂, a small amount of polar cosolvent such as methanol is often added to a solution. The increase in the solubility parameter has been interpreted in terms of the preferential solvation of cosolvent around the solute molecule. Thus, it is important to know the microscopic solvation structure around the solute molecule in the supercritical fluid mixture. The solvatochromic shifts of several probe compounds have been studied to examine the microscopic solvation structure in the cybotactic region of the solute molecule in supercritical fluid mixtures [2, 3]. 4-dimethylamino(benzonitrile) (DMABN) exhibits the formation of an intramolecular charge transfer (ICT) state in the excited state and shows dual fluorescence bands in polar solvents. Since the position and intensity of the ICT fluorescence band (ICT band) are very sensitive to the polarity of the surrounding media, DMABN would be suitable for probing for the preferential solvation of polar cosolvent. In this study, we have measured fluorescence spectra of DMABN in a mixture of supercritical CO₂ and methanol as

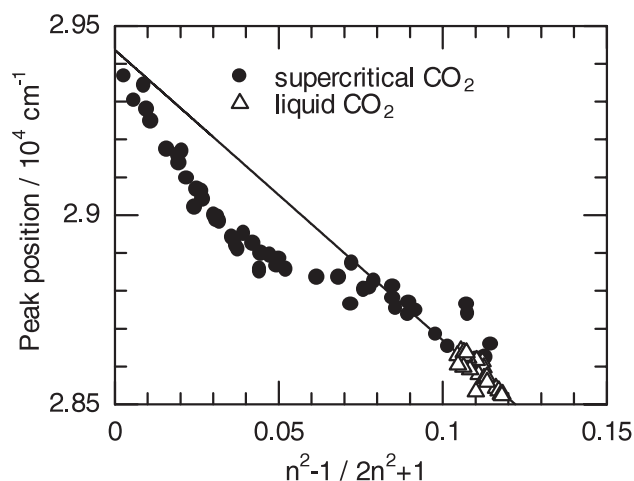


Figure 1. The plot of ν_{LE} as a function of $(n^2 - 1)/(2n^2 + 1)$. The solid circles represent the supercritical CO_2 and open triangles represent liquid CO_2 .

a function of pressure up to $P = 15.5$ MPa at 318 K. The spectral shift of the ICT band has been analysed on the basis of Onsager reaction field theory.

2. Results and discussion

We first measured the fluorescence spectra of DMABN in pure supercritical CO_2 . Experimental details have already been described elsewhere [4]. In the absence of polar cosolvent, only a locally excited (LE) band is observed around $\nu_{LE} = 29\,000\text{ cm}^{-1}$ due to the non-polarity of supercritical CO_2 . The position of the LE band is red-shifted with increasing pressure in the low- and high-pressure region while it is almost independent of pressure near the critical pressure, implying so-called local density augmentation of the solvent about the solute molecule near the critical point.

Mataga and Kubota [5] have derived an expression for the solvatochromic shift of the solute fluorescence band on the basis of Onsager reaction field theory:

$$\Delta\nu = \frac{\mu_g^2 - \mu_e^2}{a^3} \left[\frac{2\mu_e}{\mu_g + \mu_e} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + \frac{n^2 - 1}{2n^2 + 1} \right] \quad (1)$$

where μ_g and μ_e refer to the dipole moments of the ground and excited states, ε denotes the solvent permittivity, n denotes the solvent refractive index, and a is the Onsager cavity radius. The first and second terms of equation (1) represent the contributions of the interaction between solute–solvent dipole moments and the interaction between solute dipole and solvent-induced dipole moments, respectively. In the case of pure CO_2 , the first term vanishes due to the absence of a solvent dipole moment. Therefore, the spectral shift is simply proportional to $(n^2 - 1)/(2n^2 + 1)$. This expression is known to apply successfully to the spectral shift in the liquid-phase solution. In figure 1, the peak position of the LE band in supercritical and liquid CO_2 is plotted against $(n^2 - 1)/(2n^2 + 1)$. As seen in this figure, the peak position in the liquid CO_2 is almost proportional to $(n^2 - 1)/(2n^2 + 1)$ and the straight line can be obtained by least-squares fitting (solid line in figure 1). On the other hand, there is a significant deviation from the straight line in the supercritical region. We have estimated the local density augmentation around solute molecules from the difference between the observed shift and the fitted line; the result is a maximum enhancement of about 1.8 with respect to the bulk density at $\rho = 0.35\text{--}0.4\text{ g cm}^{-3}$.

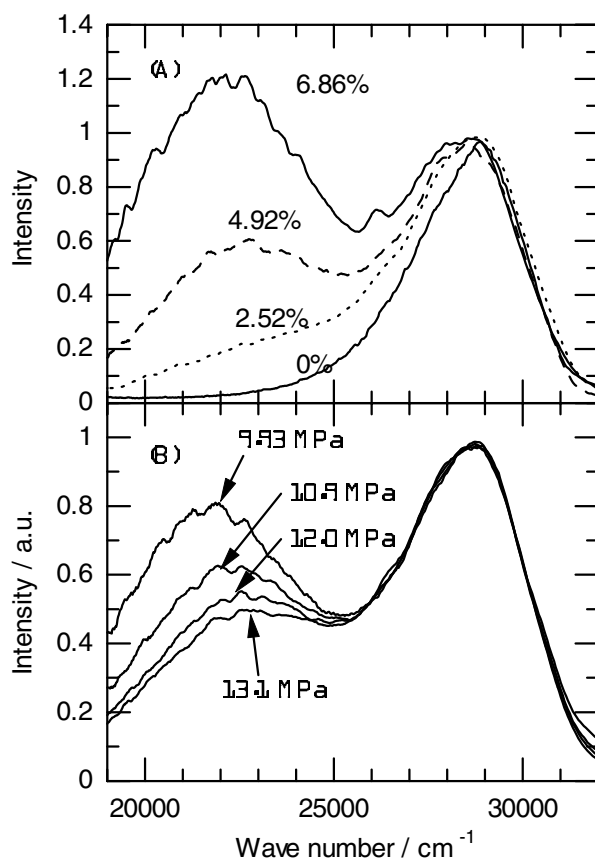


Figure 2. Fluorescence spectra of DMABN in a mixture of supercritical CO₂ and methanol (A) for various values of [methanol] at constant pressure ($P = 11$ MPa) and temperature ($T = 318$ K), (B) for various pressures at constant temperature ($T = 318$ K) and [methanol] (5 mol%). The intensities are normalized to the maximum of the LE band.

We next examined the solvation structure around DMABN in a mixture of supercritical CO₂ and methanol. It has been confirmed that the mixture forms a single phase at the pressure and temperature where we carried out the experiments. In figure 2 we show typical fluorescence spectra of DMABN for various values of [methanol] at constant pressure (11 MPa) and temperature (318 K). In the presence of methanol above 2.5 mol%, one can see a broad fluorescence peak at about $\nu_{ICT} = 22\,500$ cm⁻¹, which is attributed to the fluorescence from the ICT state (ICT band). It is interesting that the addition of such a small amount of methanol is enough to stabilize the ICT state of DMABN. The relative intensity of the ICT band increases and ν_{ICT} is substantially red-shifted with increasing [methanol], indicating that the polarity of the solvent around the solute molecules increases with increasing [methanol].

Figure 2 shows typical fluorescence spectra of DMABN measured under various pressures at constant [methanol] (5 mol%) and temperature (318 K). At constant [methanol], the position of the LE band is almost independent of pressure. In contrast, the position of the ICT band is blue-shifted and the relative intensity decreases with increasing pressure, reflecting the fact that the stabilization of the ICT state is very sensitive to change of the solvent polarity around the solute molecule. The remarkable feature of this result is that the ICT state is destabilized with increasing solvent density, indicating decrease of the solvent polarity around the solute

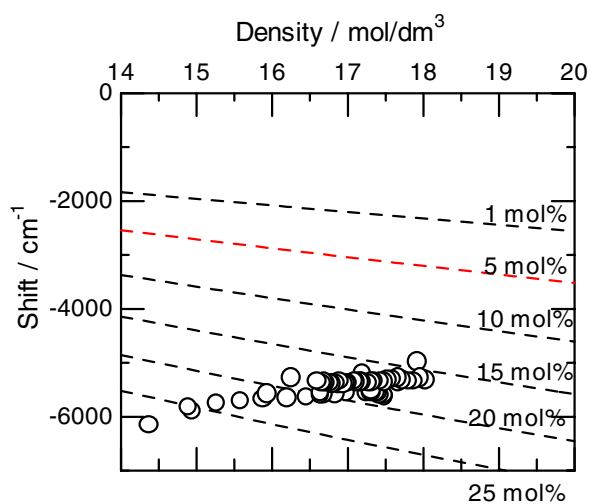


Figure 3. The spectral shift of the ICT band as a function of solvent density in a mixture of supercritical CO₂ and methanol. The dashed curves represent the calculated shift for [methanol] = 1, 5, 10, 15, 20, and 25 mol%.

(This figure is in colour only in the electronic version)

molecule. We have again used equation (1) to interpret these results. To calculate the spectral shift of the ICT band using equation (1), the parameters $\mu_g = 7.6$ D, $\mu_e = 16.1$ D, and $a = 4 \times 10^{-8}$ cm have been used for DMABN. The solvent permittivity, ϵ , of the supercritical fluid mixture was determined from the equation of Böttcher given in [6]:

$$\frac{\epsilon - 1}{12\pi\epsilon} = \frac{x_n(\epsilon_n - 1)M_n}{4\pi(2\epsilon + \epsilon_n)v\rho_n} + \frac{x_p(\epsilon_p - 1)M_p}{4\pi(2\epsilon + \epsilon_p)v\rho_p} + \frac{(2\epsilon + 1)(\epsilon_p + 2)^2 x_p N_A}{27kT(2\epsilon + \epsilon_p)^2 v} g\mu^2 \quad (2)$$

where v is the molar volume, and x_i , M_i , and ρ_i are the mole fraction, molecular weight, and density of the non-polar (subscript n) and polar (subscript p) components, respectively. μ denotes the dipole moment of methanol. g is the Kirkwood correlation parameter and takes the value of 1.3 in this study [7]. ϵ_n and ϵ_p were calculated from the Clausius–Mossotti relation. The density of the mixture was calculated using the equation of state proposed by Patel and Teja [8]. To estimate the refractive index of the supercritical fluid mixture, the well-known Lorentz–Lorenz law was used.

The spectral shift of the ICT band in the mixture of supercritical CO₂ and methanol can be calculated with these parameters. Figure 3 shows the plot of $\Delta\nu$ for the ICT band as a function of density at 318 K, [methanol] = 5 mol%. It is found in this figure that the observed spectral shift is considerably smaller than that calculated at [methanol] = 5 mol% and consistent with one calculated at [methanol] = 15–25 mol%. This suggests that the local composition in methanol around DMABN in the ICT state is much higher than that in the bulk solution, reflecting the attractive interaction between DMABN and methanol being much stronger than that between DMABN and CO₂. The enrichment of the local composition becomes less evident and approaches the bulk composition with increasing solvent density, resulting in a blue-shift of the ICT band with increasing pressure as seen in figure 2. Egorov *et al* [9] have recently demonstrated that the attractive interaction governs the solvation structure around a solute molecule in the low-density region, whereas the repulsive interaction becomes operative in the high-density region. Considering this, it is not unreasonable that the local composition of

attractive cosolvent around DMABN approaches the bulk composition with increasing solvent density.

References

- [1] Kiran E and Brennecke J F (ed) 1993 *Supercritical Fluid Engineering Science (ACS Symp. Ser. No 154)* (Washington, DC: American Chemical Society)
- [2] Sun Y-P, Bennett G, Johnston K P and Fox M A 1992 *J. Phys. Chem.* **96** 10 001
- [3] Schulte R D and Kauffman J F 1994 *J. Phys. Chem.* **98** 8793
- [4] Kometani N, Toyoda Y, Asami K and Yonezawa Y 2000 *Chem. Lett.* 682
- [5] Mataga N and Kubota T 1970 *Molecular Interactions and Electronic Spectra* (New York: Dekker)
- [6] Böttcher C F J 1973 *Theory of Electric Polarization* vol 1 (Amsterdam: Elsevier)
- [7] Dombro R A Jr, McHugh M A, Prentice G A and Westgate C R 1991 *Fluid Phase Equilib.* **61** 227
- [8] Patel N C and Teja A S 1982 *Chem. Eng. Sci.* **37** 463
- [9] Egorov S A, Yethiraj A and Skinner J L 2000 *Chem. Phys. Lett.* **317** 558