Photophysics of 3-hydroxyflavone in supercritical CO_2: a probe to study the microenvironment of SCF

Nitin Chattopadhyay [a,b,*], Monica Barroso [a], Carlos Serpa [a], M. Isilda Silva [a], Luis G. Arnaut [a,*], Sebastião J. Formosinho [a]

[a] *Department of Chemistry, Coimbra University, P-3004-535, Portugal*
[b] *Department of Chemistry, Jadavpur University, Calcutta 700 032, India*

Abstract

The excitation of 3-hydroxyflavone (3HF) to its second excited singlet state (S_2) gives rise to dual fluorescence in supercritical carbon dioxide. The ultraviolet fluorescence originated from the S_2 state of 3HF is well separated from the green emission emanating from the tautomeric form, produced via the excited state intramolecular proton transfer. The relative intensity of the S_2 to the tautomer fluorescence (S_2/T) has been studied as a function of pressure and temperature. It is shown that this ratio reflects the microheterogeneity of the supercritical CO_2, and confirms the value of fluorometric probes in disclosing the microscopic properties of supercritical fluids.
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Supercritical fluids (SCF) are getting enhanced attention in diverse fields, in view of their potential technological applications [1–5]. One of the most important properties of SCF is the local density effect on the solute molecules [6–8]. The density of a SCF is between that of a gas and a normal liquid, and can be easily tuned with a change in pressure under isothermal conditions. Consequently, medium properties can be continuously varied without a change in the molecular nature of the solvent. Because of its high sensitivity, fluorometric technique is gradually establishing its importance in characterising the SCF properties along with other techniques [9–13].

3-Hydroxyflavone (3HF) is known to exhibit excited state intramolecular proton transfer (ESIPT) reaction in solutions giving rise to dual fluorescence [14–21]. The ESIPT reaction of this fluorophore has been extensively studied since its discovery by Kasha and co-workers.

A recent work of Uchiyama et al. [22] where they have determined the solubility of the flavone and 3HF from the mass of solute trapped by decompressing and the volume of CO_2, has shown that 3HF is soluble in supercritical CO_2. In the preceding Letter [23], we reported that upon excitation of 3HF in sc-CO_2 to its second excited singlet state (S_2), a significant fluorescence emanating from the S_2 state is observed. In this Letter, we report the relative intensities of the S_2 to the tautomer fluorescence (S_2/T) as a function of the pressure and temperature of sc-CO_2. The present report establishes that 3HF can be used as a probe to monitor the microenvironment of sc-CO_2.

2. Experimental

3HF (Aldrich) was purified by repeated recrystallisation from ethanol. Trace of water was removed from the purified sample by putting it into an evacuator with occasional heating. Purity of the sample was checked through thin layer chromatography (with a 3:1 mixture of dichloromethane *n*-hexane as elluent) and spectroscopic measures. For preparation of the mother solution,

---

spectroscopic grade diethylether (Aldrich) was used after drying it further by distilling over metallic sodium. The dry ether was then stored over molecular sieves.

A Shimadzu UV-2001 spectrophotometer and a Spex Fluorolog 3 spectrofluorometer were used for the absorption and fluorescence measurements, respectively.

The supercritical cell with its accessories has been described in our previous article [9]. For spectroscopic measurements, the sample was prepared in the following way. A solution of 3HF (1×10^{-5} M) was made in diethylether and was loaded in the clean SCF cell. The solvent ether was then completely evaporated. The cell was evacuated and filled with CO_2 after thermostating at the experimental temperature. The pressure inside the supercritical cell was measured using a OMEGA DP20 digital pressure indicator ($\pm 0.25\%$) and temperature within the cell was controlled and measured using a OMEGA CN77000 series temperature controller (± 0.5 °C).

3. Results and discussion

It is known that 3HF undergoes ESIPT in solution phase as well as in jet cooled isolated condition. In hydrogen-bonding solvents, ESIPT gives rise to a dual fluorescence, the higher energy one corresponding to the molecular species (prior to ESIPT) and the lower energy one corresponding to the tautomer. To the best of our knowledge, there is no report where the photophysical properties of 3HF have been exploited to monitor the microenvironment of supercritical fluids.

We showed in the preceding Letter that excitation of 3HF in sc-CO_2 at 291 nm gives a S_2 fluorescence band in the region 300–350 nm together with the Stokes' shifted fluorescence from the tautomeric species peaking at 520 nm (Fig. 1 of [23]). The different excitation spectra of these bands suggested that two ground-state precursors should be present in sc-CO_2 and it was proposed that they differ in their solvation environment. Thus, it is expected that a change in the local molecular density in the supercritical media should lead to a modification in the relative S_2 to the tautomer fluorescence (S_2/T).

Fig. 1 shows that the relative amplitude of S_2/T in Sc-CO_2 has a characteristic pressure dependence. Since the two emission bands are widely separated, the absolute heights of the maxima of the individual emissions corresponding to the two (S_2 and T) bands were used for the calculation of the relative intensity (S_2/T). The fluorescence spectra represented in Fig. 1 were normalised at the tautomer emission maximum of 3HF, and reflect the variation of the emission behaviour with pressure at 314 K. Fig. 2 plots S_2/T against pressure at different temperatures. At any particular temperature over the range studied, an increase in pressure leads to a decrease in S_2/T until a certain pressure (P_{min}) is
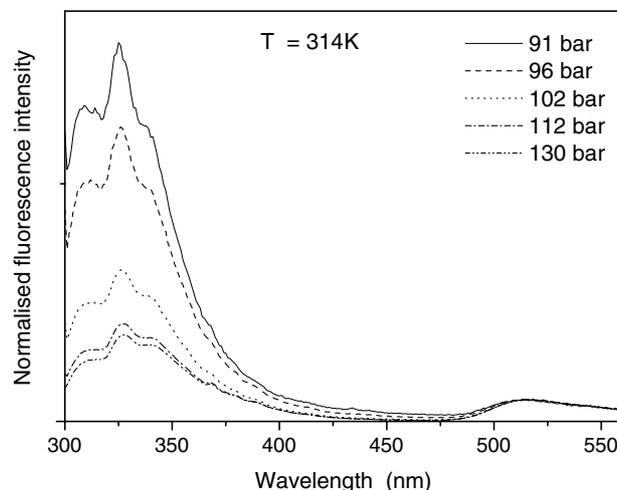
Fig. 1. Fluorescence spectra of 3HF in sc-CO_2 at different pressures at 314 K. The spectra are normalised at the maximum of the tautomer fluorescence band.
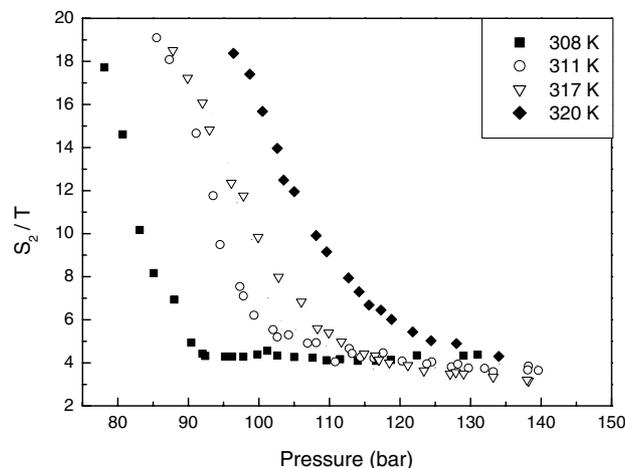
Fig. 2. Plot of S_2/T fluorescence ratio of 3HF in sc-CO_2 as a function of pressure at different temperatures. The temperatures are given in the inset. Plot of the data at 314 K has been dropped for the clarity of the figure.

reached. For pressures higher than P_{min}, we did not observe any further decrease of S_2/T. This gives rise to a break point (P_{min}) indicating a change in the organisation of the environment around the fluorophore. With an increase in the temperature, P_{min} shifts towards higher pressures with a concomitant reduction in the sharpness of the break point. These observations are very similar to those of our previous experimental study with benzil [9] and to the theoretical work of Bartle et al. [24], that were correlated with the kinematic behaviour of sc-CO_2. Thus, the S_2/T fluorescence ratio of 3HF can also be used to monitor the kinematic behaviour of sc-CO_2.

The similarity between the representation of the S_2/T ratio as a function of pressure and temperature with the

corresponding plot in our previous study [9], corroborates our earlier study and invites a similar interpretation for all the observations. They can be interpreted on the basis of a microscopic view of sc-CO_2, considering the microenvironment around the fluorophore at various pressures.

An increase in pressure induces the CO_2 molecules to rearrange around the fluorophore and form a solvent shell around the probe [9]. Once a first solvation shell is formed, further increase in pressure is expected to have a rather modest effect on the probe. Thus, a saturation effect is expected at higher pressures. The break point (P_{min}) in the plot indicates a saturation of the inner solvent shell. The inner shell solvation can approximately be described by Langmuir equilibrium model [25]. With a further increase in pressure, the solvent molecules assemble in the secondary solvation shell. We argued in the preceding article [23] that the precursors of the S_2 normal emission and tautomer emission differ in the size of their solvation shell. At lower pressures, CO_2 clusters of different sizes may be formed around the solute molecules and co-exist in rapid equilibrium. At higher pressures, such clusters merge into a more homogeneous microscopic structure. The decrease of the S_2/T ratio with the pressure indicates that the normal S_2 emission is favoured by incomplete solvation shells. Considering that the tautomer is formed by ESIPT and that it is perturbed by external hydrogen bonding to the solvent molecules, the high intensity of the normal S_2 emission at lower pressures suggests that CO_2 forms stronger hydrogen bonds in incomplete solvation shells. In fact, we expect to find a larger energy stabilisation in the association of an isolated CO_2 molecule to a hydroxyl group, than when such association has to be made at the cost of the interaction of that CO_2 molecule with others of the same kind. Clearly, sc-CO_2 makes a microheterogeneous environment rather than a homogeneous one around the fluorophore. The concept of microheterogeneity of the supercritical environments has already been adopted for different SCFs including sc-CO_2 [4,9,26–29].

With an increase in the temperature, the kinetic energy of the solvent molecules increases, thereby requiring a higher pressure to form large clusters. This is consistent with the observed shift of the P_{min} towards higher pressure at elevated temperature. Moreover, the increased molecular velocities at high temperatures make onset of the saturation less precise, leading to a reduction of the sharpness of the change of S_2/T value near the break point, as shown in Fig. 2. Fig. 3 shows that P_{min} is a linear function of the temperature. The P_{min} values at different temperatures determined in this work are in good agreement with those reported in our earlier work [9], although the two systems differ in their photophysics. The similarity between these results suggests that, at least for fluorophores of comparable
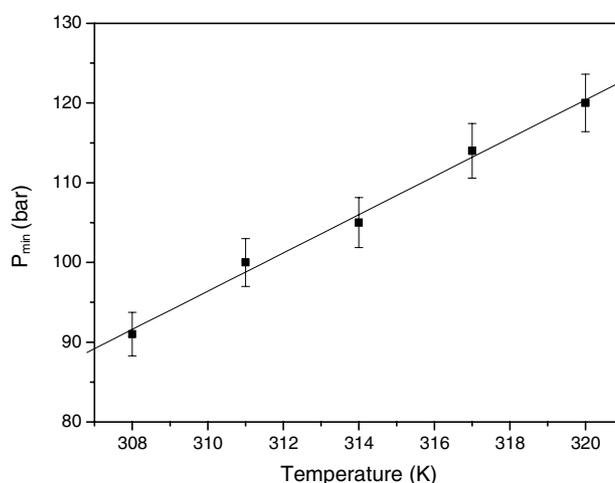
Fig. 3. Variation of P_{min} against temperature.

dimensions (the molecular lengths of 3HF and *trans*-benzil are 11.25 and 11.65 Å, respectively), P_{min} is independent of the fluorophore and reflects the microscopic properties of sc-CO_2.

4. Conclusion

The present work, in conjunction with our earlier work [9], establishes the value of spectroscopic/fluorometric probes in disclosing the microscopic properties of supercritical fluids. With an increase in pressure, sc-CO_2 evolves from an ensemble of clusters of different sizes surrounding the probe molecule, to a solvent shell that encloses the probe molecule. This change modifies the fluorometric behaviour of the probe, and provides information on the microheterogeneous environment created by sc-CO_2.

References

[1] T. Clifford, Fundamentals of Supercritical Fluids, Oxford University Press, London, 1999.
[2] J.L. Kendall, D.A. Canelas, J.L. Young, J.M. DeSimone, Chem. Rev. 99 (1999) 543.
[3] A. Baiker, Chem. Rev. 99 (1999) 453.
[4] S.C. Tucker, Chem. Rev. 99 (1999) 391.
[5] A.J. Mesiano, E.J. Beckman, A.J. Russell, Chem. Rev. 99 (1999) 623.

[6] P.G. Debenedetti, R.S. Mohamed, J. Chem. Phys. 90 (1989) 4528.

[7] K.S. Shing, S.T. Chung, J. Phys. Chem. 91 (1987) 1674.

[8] C.A. Eckert, D.H. Ziger, K.P. Johnston, S. Kim, J. Phys. Chem. 90 (1986) 2738.

[9] N. Chattopadhyay, C. Serpa, M.I. Silva, L.G. Arnaut, S.J. Formosinho, Chem. Phys. Lett. 347 (2001) 361.

[10] M. Poliakoff, S.M. Howdle, S.G. Kazarian, Angew. Chem. Int. Ed. Eng. 34 (1995) 1275.

[11] M.P. Heitz, F.V. Bright, J. Phys. Chem. 100 (1996) 6889.

[12] T.A. Betts, F.V. Bright, Appl. Spectrosc. 44 (1990) 1203.

[13] A. Kordikowski, D.G. Robertson, M. Poliakoff, T.D. DiNoia, M. McHugh, A. Aguiar-Ricardo, J. Phys. Chem. B 101 (1997) 5853.

[14] A.J.G. Strandjord, P.F. Barbara, Chem. Phys. Lett. 98 (1983) 21.

[15] P.K. Sengupta, M. Kasha, Chem. Phys. Lett. 68 (1979) 382.

[16] D. McMorrow, M. Kasha, J. Phys. Chem. 88 (1984) 2235.

[17] P.F. Barbara, P.K. Walsh, L.E. Brus, J. Phys. Chem. 93 (1989) 29.

[18] S.J. Formosinho, L.G. Arnaut, J. Photochem. Photobiol. A 75 (1993) 21.

[19] A. Mühlpfordt, T. Bultmann, N.P. Ernsting, B. Dick, Chem. Phys. 181 (1994) 447.

[20] S. AmeerBeg, S.M. Ormson, R.G. Brown, P. Matousek, M. Towrie, E.T.J. Nibbering, P. Foggi, F.V.R. Neuwahl, J. Phys. Chem. A 105 (2001) 3709.

[21] J. Guharay, R. Chaudhuri, A. Chakrabarti, P.K. Sengupta, Spectrochim. Acta A 53 (1997) 457.

[22] H. Uchiyama, K. Mishima, S. Oka, M. Ezawa, M. Ide, J. Chem. Eng. Data 42 (1997) 570.

[23] N. Chattopadhyay, M. Barroso, C. Serpa, J. Seixas de Melo, L.G. Arnaut, S.J. Formosinho, Chem. Phys. Lett. 387 (2004) 258.

[24] K.D. Bartle, T. Boddington, A.A. Clifford, G.F. Shiltone, J. Chromatogr. A 471 (1989) 347.

[25] A. Morita, O. Kajimoto, J. Phys. Chem. 94 (1990) 6420.

[26] J.F. Brennecke, D.L. Tomasko, J. Peshkin, C.A. Eckert, Ind. Eng. Chem. Res. 29 (1990) 1682.

[27] Y.P. Sun, G. Bennett, K.P. Johnston, M.A. Fox, J. Phys. Chem. 96 (1992) 10001.

[28] Y.P. Sun, M.A. Fox, K.P. Johnston, J. Am. Chem. Soc. 114 (1992) 1187.

[29] Y.P. Sun, C.E. Bunker, N.B. Hamilton, Chem. Phys. Lett. 210 (1993) 111.