Pure & Appl. Chem., Vol. 65, No. 8, pp. 1713–1716, 1993.
Printed in Great Britain.

Experimental probes of excited state character in supercritical fluids

Marye Anne Fox* and Ya-Ping Sun

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, USA

Abstract Solute-solute and solute-solvent clustering of N,N-dimethylaminobenzonitrile and ethyl N,N-dimethylaminobenzoate in supercritical fluoroform, supercritical carbon dioxide, and supercritical fluoroform-carbon dioxide mixtures are quantitatively evaluated from the dependence of the relative contributions of the locally excited (LE) state and the twisted intramolecular charge transfer (TICT) emissions on supercritical fluid composition and pressure. Microscopic and macroscopic solvation in these mixtures can be rationalized with an Onsager reaction field model. Photophysical measurements on the singlet excited state of tetraphenylethylene (^{1}p* state) in supercritical fluid mixtures similarly indicate high local polarity with inhomogeneous clustering about a dipolar excited state. Fluorescence lifetimes of 9-cyanoanthracene in the low and near-critical density regions of a supercritical fluid show that the relationship between the emissive radiative rate constant and the solvent refractive index in supercritical fluid mixtures differs appreciably from that observed in liquid solvents.

INTRODUCTION

Supercitical fluids provide a unique medium for characterizing condensed phase solute-solute and solute-solvent interactions at a fundamental level.[1,2] In the highly compressible region near the supercritical point, significant deviations from solvation, as predicted by dielectric continuum theory, are indicative of enhanced local solvent density associated with macroscopic clustering. Although the nature of the local interaction is specific for a particular solvent-solute couple, three separate regions with varying degrees of clustering can often be characterized experimentally. These include a low density gas-like region in which a discrete stoichiometric ratio characterizes the solute-solvent association; an intermediate region in which the solute-solvent and solvent-solvent interactions are comparably important; and a high density region in which the solvation behavior corresponds to a classical dielectric interaction, thus mirroring the interactions observed in typical liquid solutions.

Fluorescence spectroscopy has proven to be particularly useful in characterizing local density, local composition, and solute-solvent interactions. For example, detailed investigations of bimolecular photochemical reactions have provided evidence for solute-solute[3] and solute-co-solvent[4] clustering on excited state surfaces. A particularly sensitive probe for local interactions would be available in molecules in which relatively polar and non-polar emissive excited states are formed after the initial excitation event. For example, N,N-dimethylaminobenzonitrile and ethyl N,N-dimethylaminobenzoate both form two emissive states which can be easily resolved spectroscopically. These involve a locally excited state and a twisted intramolecular charge transfer (TICT) state, in which the relative population of the two states is significantly influenced by medium properties.[5,6]

We have previously shown that this same sensitivity to the immediate solvent shell can be used to probe local interactions of these molecules in supercritical carbon dioxide or supercritical fluoroform.[7,8] We describe in this paper how similar spectroscopic and kinetics studies in supercritical fluid mixtures can provide valuable information on weak, local intermolecular associations and how an appropriate modeling for this local clustering about the probe solute molecule can provide a unique corollary description of the excited state polarity of included probe. We have studied two molecules known to form TICT states (N,N-dimethylaminobenzonitrile and ethyl N,N-dimethylaminobenzoate) and one molecule (tetraphenylethylene) in which a highly polarized TICT state has been suggested, but not yet completely unambiguously demonstrated. We also describe the dependence of the fluorescence lifetime of 9-cyanoanthracene in supercritical ethane on local solvent refractive index in the low and near-critical density regions. This molecule was chosen as a probe for molecules in which geometric distortion cannot produce a TICT state.

EXPERIMENTAL PROCEDURE

A high pressure spectrosocopic cell equipped with thick quartz or sapphire windows was used for these studies.[8-10] Pressure, as controlled with an external syringe pump, was monitored with an internally positioned gauge. Cell temperature was maintained with a resistive heater and internal temperature was measured with a thermocouple. Steady state absorption spectra were measured on a Varian 2300 spectrometer at 40^0 C. Fluorescence spectra were obtained on a computer-interfaced SLM Aminco SPF-500C emission spectrophotometer equipped with a 300 W xenon lamp. Fluorescence lifetimes were measured on a time-correlated single photon counting spectrometer at the Center for Fast Kinetics Research (CFKR) at the University of Texas. Picosecond transient absorption measurements were also conducted at CFKR. In these measurements, the excitation source was the third harmonic (355 nm, 30 ps pulse) of a Quantel YG 402 mode-locked Nd:YAG laser, from which part of the fundamental (1064 nm) was focused onto a cell containing a solution of phosphoric acid in deuterated water. Each spectrum was obtained as an average of 80 - 150 laser shots.

MICROSCOPIC SOLVATION OF TICT STATES

Solute-solute and solute-solvent clustering of N,N-dimethylaminobenzonitrile and ethyl N,N-dimethylaminobenzoate in supercritical fluoroform, supercritical carbon dioxide, and supercritical fluoroform-carbon dioxide mixtures can be described by quantitatively evaluating the dependence of the relative contributions of the locally excited (LE) state and the twisted intramolecular charge transfer (TICT) emissions on supercritical fluid composition and pressure.[9] For a quantitative description of these contributions, it has proved necessary to resolve the dual fluorescence spectra of these probe molecules through a principal component analysis spectral resolution.[10] This spectral resolution was necessary because the LE and TICT bands severely overlap, making determination of spectral shifts a challenging task.

Dual fluorescence spectral for localized and highly polar excited states depend strongly on the composition and total pressure of a supercritical mixture. By using a combination of principal component analysis- self modeling and non-linear least squares spectral resolution, we have established boundary conditions for the spectral properties of these probe molecules in supercritical fluid mixtures. With this method, we have shown that the average density dependence of the local solvation of the mixtures is similar to that observed in the pure component fluids.

The magnitude of the bathochromic shift of the fluorescence spectra of both probe molecules increases with increasing fluid density. The shifts are large with modest density changes in the low-density region, reaching a plateau in the medium denity region and then increasing more slowly in the high density region. This result is obtained irrespective of whether the mixture is formed by adding the probe solute to a pre-formed mixture of the solvents or if the solute is pre-equilibrated in one solvent with the second solvent being titrated into the resulting mixture to attain the desired net composition. This result is obstained even though the composition of the first solvent shell depends on the method by which the mixture is formed. Greater inhomogenity exists in the system in which carbon dioxide is added to a known amount of CHF_3: the polarity of the medium decreases with the increasing fraction of the non-polar CO_2, but increases because of the concomitantly increasing total pressure and density. The polar CHF_3 clusters preferentially with the solute, with the size of the solute-solvent cluster depending on the total pressure. As in pure supercritical fluoroform, no evidence for specific hydrogen bonding with the molecular probe could be seen in the CHF_3-CO_2 mixtures.

Both microscopic and macroscopic solvation in these mixtures can be rationalized with an Onsager reaction field model.[11,12] As a macroscopic descriptor of medium polarity and polarizability, this theory predicts a competition between these opposing effects, apparently resulting in a reversal of their relative importance with varying solvent composition. Thus, two separate regions are observed upon varying the ratio of solvents present: in the first, Df decreases with additional CO_2 and in the second it increases. In the first region, the fractional contribution of both the TICT emission and the observed spectral shifts are nearly identical to those observed in pure CHF_3. The excess of the polar component of a solvent mixture about a polar solute molecules has also been described in binary liquids, but this preference seems to be enhanced in the low density region where local composition is dominated by preferred dipolar interactions between solute and solvent. In any case, these results clearly indicate that the bulk and local (microscopic) solvent compositions in supercritical fluids are substantially different.

SUPERCRITICAL FLUIDS AS PROBES OF EXCITED STATE POLARITY

With this model of local solvation, it is also possible to employ supercritical fluid mixtures as a chemically invariant probe for excited state character. It is well known that many olefins undergo geometric photoisomerization through an intermediate $^1p^*$ state in which the termini of the double bond have been twisted to an orthogonal geometry. In ethylene, the $^1p^*$ state is zwitterionic as a result of "sudden polarization", which reflects the highly polar character of the lowest excited singlet state. Whether analogous zwitterionic character is equally important in conjugated polyenes or in aryl-substituted ethylenes remains unclear, however. A determination of the polarity of the excited state of stilbene, for example, has proved to be difficult because of the very short lifetime of the perpendicular state.[13]

Schilling and Hilinski have reported that the observed dependence of the lifetime of the singlet excited state of tetraphenylethylene is consistent with a highly polar $^1p^*$ state, with the shorter lifetime in polar solvents being attributed to a decreased energy gap deriving from solvent stabilization of a highly polarized state.[14] This conclusion was also supported by a recent photoacoustic calorimetry study.[15] Photophysical measurements in supercritical fluid mixtures similarly indicate high local polarity with inhomogeneous clustering of a polar component about the dipolar excited state.

Picosecond transient absorption spectra and decay kinetics for the twisted excited state of tetraphenylethylene in supercritical fluid - cosolvent mixtures reveal microscopic solvation of a highly polar state: the observed lifetime of the $^1p^*$ state depends on solvent composition of supercritical CHF_3 - n-hexane mixtures.[16] This conclusion is supported by the shortened singlet state lifetime observed as greater amounts of the polar co-solvent fluoroform is added to the cell. In liquid solvents, the lifetime of the $^1p^*$ state is shortened with increasing quantities of the more polar component, apparently because of dipolar solute-solvent interactions. In relatively non-polar supercritical CO_2- tetrahydrofuran mixtures, in contrast, much smaller changes with varying solvent composition are observed, presumably reflecting a decrease in medium polarity with the presence of greater quantities of the non-polar CO_2 being partially offset by an increase in total pressure. In both mixtures, parallel dependence of both the bathochromic spectral shift and the relative quantum yield of emission on solvent composition was observed for ethyl N,N-dimethylaminobenzoate, which is known to form a TICT state, and for tetraphenylethylene.

Radiationless relaxation theories predict a linear relationship between the rate constant for radiationless relaxation and the energy gap separating the states. Upward deviation from an Onsager reaction field model in single component supercritical fluids has been ascribed to the larger local filed experienced by the solute compared with that expected from bulk dielectric and refractive index. Similar upward deviations are also observed in the supercritical fluid mixtures, either as pre-mixed solutions or as titration mixtures. As in the TICT studies of N,N-dimethylaminobenzonitrile and ethyl N,N-dimethylaminobenzoate, the local density and composition reflect substantial development of local charge in the excited state of tetraphenylethylene. We conclude that solvent effects on the radiationless decay rate of the perpendicular excited state of tetraphenylethylene are related to the solvent-induced alteration of the $^1p^*$ - ^1p energy gap, as expected from standard theories of radationless relaxation. The $^1p^*$ state is thus similar in polarity to the highly polar TICT state of ethyl N,N-dimethylaminobenzoate.

LOCAL SOLVATION FROM FLUORESCENCE LIFETIMES

9-Cyanoanthracene is a highly fluorescent molecule in which no geometric isomerization occurs on the excited state manifold. Its photophysical properties were therefore probed as a control for characterizing local microscopic solvation in supercritical fluids without the possibility of geometrically enforced sudden polarization. Because this molecule has no polar TICT state for measurement of perturbation of microscopic polarity, the lifetime of a highly fluorescent probe can provide important information regarding the local solvation in such complex mixtures. Fluorescence radiative rate constants vary with solvent refractive index,[17] and the lifetime of 9-cyanoanthracene in a supersonic jet expansion[18] is co-linear with the observed dependence of its fluorescence lifetime with the refractive index of a series of solvents.[19] Such a system is thus amenable to study in supercritical fluids and supercritical fluid mixtures.

The variation of pressure in a cell filled with supercritical ethane at 50^o induces a variation in the medium's refractive index which can be calculated from the Lorentz-Lorenz equation. When 9-cyanoanthracene is charged into such a fluid-filled cell, strong wavelength-independent fluorescence is observed, in which the decay can be fit to a single exponential.[20] A plot of the dependence of the reciprocal of the fluorescence lifetime on the square of the fluid's calculated refractive index shows pronounced upward curvature from the predicted linearity. For example, a much shorter fluorescence lifetime is observed in low density supercritical ethane than in liquid hexane. We interpret such effects as indicative of local density aggregation to produce solvent-solute clustering differing markedly from that expected from a homogeneous bulk fluid. In a weakly polar excited state, bathochromic shifts in the absorption spectrum are to be anticipated as the solvent polarization coefficient increases. This value can be measured directly from changes in the refractive index $\{(n^2-1)/(n^2+2)\}$. In accord with this rationalization, upward curvature is also observed in a plot of the dependence of the observed bathochromic absorption shift for the probe on the solvent polarization coefficient.[21] Thus, the expected linear dependence of the fluorescence rate constant on the square of the dielectric constant is not observed in the low and near-critical density regions of supercritical fluids and mixtures. Local density effects cannot quantitatively account for these deviations and a new model for excited state solvation in this environment is required.

CONCLUSIONS

Supercritical fluids constitute an important reaction medium for probing contrasting microscopic and macroscopic solvation. In the region of high compressibility, a minor perturbation in the externally applied pressure on a supercritical fluid or solution affords a large change in the density-dependent bulk solvent properties, such as dielectric constant and viscosity. This permits characterization of local solvation, and its alteration, without a change of bulk solvent composition. Molecules which form TICT states upon photochemical excitation uniquely sample the local environmental perturbation induced by rapid polarity changes in a solute immersed within either a single component or a solvent mixture of supercritical fluids. When local solute-solvent clustering in such media can be quantitatively described, excited state polarity changes in other molecules can be defined as a function of the expected local clustering. Deviations from normal excited state relaxation rates are also to be expected in supercritical fluids when microscopic inhomogeneity occurs.

Acknowledgements

This work was generaously supported by the National Science Foundation. We are grateful to Dr. Stephen J. Atherton for assistance with the lifetime measurements which were made at the Center for Fast Kinetics Research, a facility jointly supported by the Biotechnology Branch of the Division of Reserach Resources of the National Institutes of Health and by the University of Texas at Austin.

REFERENCES

1. Paulaitis, M.E.; Krukonis, V.J.; Kurnik, R.T.; Reid, R.C., Eds. Amer. Chem. Soc. Sympos. Ser., Vol. 488 (1992).
2. Shaw, R.W.; Brill, T.B.; Clifford, A.A.; Eckert, C.A. Chem. Engin. News 69, 26 (1991).
3. Combes, J.R.; Johnston, K.P.; O'Shea, K.E.; Fox, M.A. Amer. Chem. Soc. Sympos. Ser. 488, 166 (1992).
4. Chateauneuf, J.E.; Roberts, C.B.; Brennecke, J. F. Amer. Chem. Soc. Sympos. Ser. 488, 106 (1992).
5. Rettig, W. Angew. Chem. Internat. Ed. Engl. 25, 971 (1986).
6. Lippert, E.; Rettig, W.; Bonacic- Koutecky, V.; Heisel,, F.; Miehe, J.A.; Adv. Chem. Phys. 68, 1 (1987).
7. Hrnjez, B.; Yahzdi, P.; Fox, M.A.; Johnston, K.P. J. Amer. Chem. Soc. 111, 1915 (1988).
8. Sun, Y.P.; Fox, M.A.; Johnston, K.P. J. Amer. Chem. Soc. 114, 1187 (1992).
9. Sun, Y.P.; Bennett, G.; Johnston, K.P.; Fox, M.A. J. Phys. Chem. in press (1992).
10. Sun, Y.P.; Bennett, G.; Johnston, K.P.; Fox, M.A. Anal. Chem. 64, 1763 (1992).
11. Lippert, E. Ber. Bunsenges. Phys. Chem. 61, 962 (1957).
12. Mataga, N.; Kiafu, Y.; Loizumi, M. Bull. Chem. Soc. Jpn. 29, 115, 465 (1956).
13. Repinec, S.T.; Sension, R.J.; Szarka, A.Z.; Hochstrasser, R.M. J. Phys. Chem. 95, 10380 (1991).
14. Schilling, C.L.; Hilinski, E.F. J. Amer. Chem. Soc. 110, 2296 (1987).
15. Morais, J.; Ma, J.; Zimmt, M.B. J. Phys.Chem. 95, 3885 (1991).
16. Sun, Y.P.; Bennett, G.; Johnston, K.P.; Fox, M.A. J. Amer. Chem. Soc. 114, in press (1992).
17. Strickler, S.J.; Berg, R.A. J. Chem. Phys. 37, 814 (1962).
18. Hirayama, S.; Shobatake, K.; Tabayahi, K. Chem. Phys. Lett. 121, 228 (1985).
19. Hirayama, S.; Yasuda, H.; Okamoto, M.; Tanaka, F. J. Phys. Chem. 95, 2971 (1991).
20. Sun, Y.P.; Fox, M.A. J. Phys. Chem., submitted for publication (1992).
21. Hudson, B.S.; Kohler, B.E.; Schulten, K. Excited States 6, 1 (1982).