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Diffusive Transport of Micelles and Monomeric Solutes in Supercritical CO_2

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A wide variety of applications, including separations, enzymatic reactions, and catalytic reactions utilize water-in-CO_2 microemulsions.[1] Over the past several years, much progress has been made toward understanding these media in terms of their phase equilibria, structure, and micellar interactions.[2] The general picture is a surfactant micelle with an internal water pool (of radius 2 nm for example[2a]), floating in the supercritical CO_2 medium. There is less understanding of the diffusive mobilities of such micellar structures and of small molecules not sequestered by the micelles but diffusing solely in the CO_2 phase. This report describes quantitative microelectrode-based voltammetry[3] that delineates these widely differing mobilities.

The strategy is to select (a) an ionic surfactant whose water-in-CO_2 microemulsion exhibits ionic conductivity sufficient to support voltammetric measurements and (b) electroactive solutes that partition either into the micellar water pool or remain in the CO_2 phase. Niehaus et al.[4] and Ohde et al.[5] have shown that (a) is possible, although we introduce here a voltammetrically better behaved system, namely[6] $H_2O/PFPECO_2^-NH_4^+/CO_2$. The electroactive probes chosen are ferrocene (Fc), which is very soluble in CO_2 but not in water,[7] and the water-soluble salts trimethyl (ferrocenylmethyl)ammonium trifluoromethanesulfonate and potassium iodide, whose electroactive components $Fc\text{-}N^+$ and I^- should prefer the micellar water pool, as cartooned in Figure 1. The Fc diffusion coefficient should (ideally) represent transport in the CO_2 phase whereas those of $Fc\text{-}N^+$ and I^- should measure the diffusivity of the micelle itself. This strategy represents a limiting case of the micellar-partition tactics used[8] by McIntire, Rusling, and others to measure micellar binding and diffusion coefficients in more conventional media. For completeness, Figure 1 also indicates other possible transport mechanisms, namely association of a neutral probe with the surfactant phase and partitioning of an ionic probe as an ion-pair into the CO_2 phase. These and an additional transport mode, probe hopping between micelles, will be discussed, and dismissed, below.

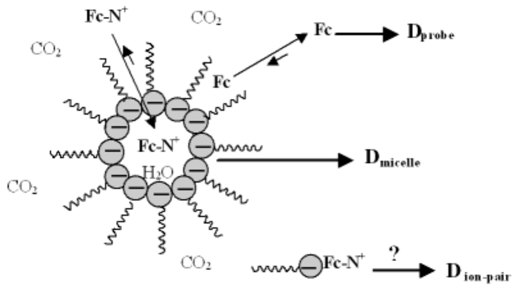

Figure 1. Cartoon showing possible partitioning and diffusion behavior of Fc and $Fc\text{-}N^+$ in water-in-CO_2 microemulsions.

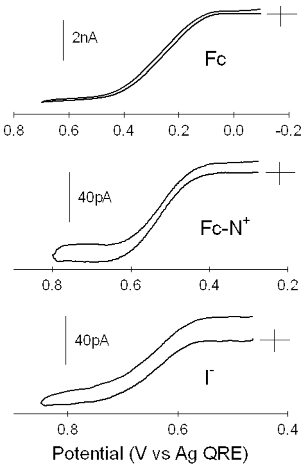

Figure 2. Cyclic voltammograms of 150 μM Fc, 110 μM $Fc\text{-}N^+$, and 90 μM I^- in water-in-CO_2 microemulsions (32 °C, 4080 psi, and $\phi = 0.29$) at a 12.5 μm radius Pt electrode and a scan rate of 5 mV s^{-1}.

Microdisk electrode voltammetry of the probes[9] Fc, $Fc\text{-}N^+$, and I^- in $H_2O/PFPECO_2^-NH_4^+/CO_2$ microemulsions[6] is shown in Figure 2. The electrode reactions are well behaved and show no signs of previously observed problems of adsorption,[5] product precipitation,[4] and limiting currents not proportional to concentration.[5] Figure 2 yields experimental diffusion coefficients (D_{APP})[10] equal to 4.8×10^{-5}, 1.1×10^{-6}, and 1.0×10^{-6} cm^2/s, for Fc, $Fc\text{-}N^+$, and I^-, respectively. The D_{APP} for $Fc\text{-}N^+$ and I^- are essentially identical even though the former is a counterion, and the latter, a co-ion of the anionic surfactant. This result argues that both $Fc\text{-}N^+$ and I^- (and their respective salt counterions) reside predominantly within the micellar water pool and that

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[1] (a) Jacobson, G. B.; Lee, C. T., Jr.; Johnston, K. P. *J. Org. Chem.* **1999**, *64*, 1201. (b) Holmes, J. D.; Steytler, D. C.; Rees, G. D.; Robinson, B. H. *Langmuir* **1998**, *14*, 6371. (c) Kane, M. A.; Baker, G. A.; Pandey, S.; Bright, F. V. *Langmuir* **2000**, *16*, 4901. (d) Clarke, M. J.; Harrison, K. L.; Johnston, K. P.; Howdle, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 6399. (e) Ji, M.; Chen, X.; Wai, C. M.; Fulton, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2631.

[2] (a) Zielinski, R. G.; Kline, S. R.; Kaler, E. W.; Rosov, N. *Langmuir* **1997**, *13*, 3934. (b) See Supporting Information for further references.

[3] (a) The microelectrode assembly was prepared as previously described[3b−d] except for being potted in 0.25 in of 316 stainless steel tubing. High-pressure fittings (Swagelok) sealed the electrode assembly into the variable-volume stainless steel view cell. For safety information regarding handling of high-pressure apparatus, see for example: Sullenberger, E. F.; Michael, A. C. *Anal. Chem.* **1993**, *65*, 2304. (b) Wightman, R. M.; Wipf, D. O. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1989; Vol. 15, pp 267−353. (c) Geng, L.; Reed, R. A.; Longmire, M.; Murray, R. W. *J. Phys. Chem.* **1987**, *91*, 2908. (d) Niehaus, D. E.; Wightman, R. M. *Anal. Chem.* **1991**, *63*, 1728.

[4] (a) Niehaus, D.; Philips, M.; Michael, A.; Wightman, R. M. *J. Phys. Chem.* **1989**, *93*, 6232. (b) D_{APP} is reported[4a] in moist CO_2 as 2.9×10^{-4} cm^2/s, at 80 °C and 1300 psi. The 6-fold increase over the 4.8×10^{-5} cm^2/s result (at 32 °C) is reasonably attributed to the large temperature difference.

[5] Ohde, H.; Hunt, F.; Kihara, S.; Wai, C. M. *Anal. Chem.* **2000**, *72*, 4738.

[6] Perfluoropolyether carboxylic acid, ammonium salt; ($PFPECO_2^-NH_4^+$) of general structure: $CF_3O(CF_2CF(CF_3)O)_3CF_2CO_2^-NH_4^+$ was used as a surfactant. The microemulsion water-to-surfactant ratio (corrected for the solubility of water in CO_2)[3d] was 12.6 ± 0.3 throughout. Micellar volume fraction (ϕ) was changed by varying the cell volume at constant pressure (4080 ± 20 psi) and temperature (32 ± 0.1 °C). Additional experimental details, including ruling out of potential measurement artifacts, are described in Supporting Information.

[7] (a) Solubility of Fc in CO_2[7b] at 38 °C, 2940 psi is 0.055 M and ca. 5×10^{-5} M in water[8d] at ambient temperature and pressure. (b) Hunt, F.; Ohde, H.; Wai, C. M. *Rev. Sci. Instrum.* **1999**, *70*, 4661.

[8] (a) McIntire, G. L.; Chiappardi, D. M.; Casselberry, R. L.; Blount, H. N. *J. Phys. Chem.* **1982**, *86*, 2632. (b) Rusling, J. F.; Shi, C. N.; Kumosinski, T. F. *Anal. Chem.* **1988**, *60*, 1260. (c) Rusling, J. F. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1994; Vol. 18, pp 1−88. (d) Georges, J.; Desmettre, S. *Electrochim. Acta* **1984**, *29*, 521. (e) Kaifer, A. E.; Bard, A. J. *J. Phys. Chem.* **1985**, *89*, 4876. (f) Zana, R.; Mackay, R. A. *Langmuir* **1986**, *2*, 109.

[9] The $Fc\text{-}N^+CF_3SO_3^-$ salt was prepared from the iodide (K&K Laboratories) by ion exchange. KI (Aldrich, 99.998%) was used as received and Fc purified by sublimation.

[10] D_{APP} was calculated from $i_{LIM} = 4nFrD_{APP}C$, where r is electrode radius, C is concentration, and the other terms have their usual meaning.[3b]

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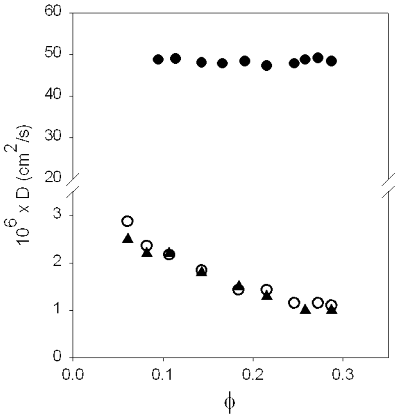

Figure 3. Dependence of D_{APP} on ϕ for Fc (filled circles), Fc-N$^+$ (open circles), and I$^-$ (triangles) in water-in-CO$_2$ microemulsions (32 °C, 4080 psi).

escape of Fc-N$^+$ either singly or as an ion-pair with monomeric surfactant (Figure 1) is negligible. The diffusion coefficient of micelles in this particular water-in-CO$_2$ microemulsion is therefore 1×10^{-6} cm^2/s at 32 °C and 4080 psi.

The D_{APP} of Fc (4.8×10^{-5} cm^2/s) is 50-fold larger than that of the micelles, from which we infer that Fc resides exclusively in the supercritical CO$_2$ phase.[4b] The results in Figure 3 verify this inference by showing that D_{APP} of Fc is *independent* of the volume fraction (ϕ)[11] of the micelle. Application of the Stokes–Einstein equation[12] to this D_{APP} value gives a microscopic viscosity for the CO$_2$ phase of 0.13 cP, which is similar to literature value of pure CO$_2$.[13] Partitioning in supercritical CO$_2$ microemulsions may vary with the surfactant; a previous study[5] with a different surfactant claimed strong association of Fc with the micellar fraction.

Figure 3 shows that (unlike Fc) the D_{APP} values for Fc-N$^+$ and I$^-$, while *remaining identical*, decrease with increasing micelle volume fraction. This behavior is consistent with these probes being entirely associated with the micelles, so that the D_{APP} values measure the micelle's diffusion. The hydrodynamic radius of Fc (0.36 nm)[12b] is ca. 6-fold smaller than the micellar water pool radius (2.0 nm)[2a] determined by small-angle neutron scattering (SANS), so that D_{APP} is expected to be smaller for a micelle-sequestered probe (e.g., Fc-N$^+$). The observed 20∼50-fold D_{APP} difference (Figure 3) is much larger than the ratio of the hydrodynamic radii, and the volume fraction dependence of the micelle diffusion coefficient is not easily rationalized solely on the basis of size. Decreases in D_{APP} with increasing micelle volume fraction in nonsupercritical microemulsion systems have been attributed to intermicellar interactions.[14] The changes in micellar D_{APP} values in Figure 3 suggest some kind of attractive interactions between micelles that increase with ϕ, as has been observed in conductivity measurements with H$_2$O/PFPECO$_2$$^-$-NH$_4$$^+$/CO$_2$ microemulsion systems.[11b] Furthermore, recent SANS experiments[15] showed the invariance of micelle size with ϕ. Thus, micellization of the ionic redox probes may combine with attractive intermicellar interactions to decrease D_{APP} values with increasing ϕ.

The possibility of attractive micellar interactions raises the possibility of yet another transport mode in water-in-CO$_2$ microemulsions, namely intermicellar hopping of redox probes. The coupling of micelle physical diffusion with the hopping of probes between micelles can be described by theory[16] applied to the analogous situation of electron hopping in redox polymers. The theory predicts an increase in D_{APP} with concentration of the putative hopping entity; experimentally, however, the D_{APP} of Fc-N$^+$ is essentially concentration-independent over a 50-fold change.[17] On the basis of a 2.0 nm water pool size,[2a] at the highest concentration of Fc-N$^+$ (5.4 mM) and $\phi = 0.29$, each micelle contains on average one Fc-N$^+$ molecule. Since at lower probe and micelle concentrations D_{APP} is invariant, we conclude that intermicellar hopping of redox probes is not an important transport mode (in this system) and, again, that the measured D_{APP} is effectively that of the micelle.

These results show that diffusion of small molecules and micelles in a supercritical fluid microemulsion can be quantified by a judicious choice of the microemulsion surfactant and the partitioning characteristics of redox probe. Furthermore, the detection of intermicellar interactions may permit an improved understanding of distinction between microscopic and macroscopic mobility and viscosity in microemulsions. The use of voltammetric methods in measuring diffusion coefficients and viscosity may furthermore prove useful in designing and monitoring reactions in microemulsion media and in designing real-time sensors for emerging CO$_2$ process technologies in microelectronics and precision cleaning operations.

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Supporting Information Available: Further references of ref 2 and experimental details (ref 6) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] (a) Volume fraction ϕ is the volume ratio (water + surfactant)/(water + surfactant + CO$_2$), using values of 1 and 1.8 g/mL for water and surfactant densities, respectively.[11b] (b) Lee, C. T., Jr.; Bhargava, P.; Johnston, K. P. *J. Phys. Chem. B* **2000**, *104*, 4448.

[12] (a) $\eta = kT/6\pi DR_H$, where η is viscosity and R_H hydrodynamic radius of ferrocene.[12b] (b) Armstrong, N. R.; Quinn, R. K.; Vanderborgh, N. E. *Anal. Chem.* **1974**, *46*, 1759.

[13] Herreman, W.; Grevendonk, W.; De Bock, A. *J. Chem. Phys.* **1970**, *53*, 185.

[14] Cebula, D. J.; Ottewill, R. H.; Ralston, J.; Pusey, P. N. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2585.

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[16] (a) $D_{APP} = D_{PHYS} + k_{EX}\delta^2 C/6$, where D_{PHYS} is physical diffusivity, k_{EX} the hopping rate constant, C the probe concentration, and δ the average hop distance. (b) Majda, M., In *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; John Wiley & Sons: New York, 1992; pp 159–206.

[17] D_{APP} is 1.1×10^{-6}, 1.1×10^{-6} and 1.3×10^{-6} cm^2/s at $\phi = 0.29$ for the Fc-N$^+$ concentration of 0.1, 0.6, and 5.4 mM, respectively.