

Electronic Supplementary Information

Micellar and Bicontinuous Microemulsion Structures Show Different Solute-Solvent

Interaction: A Case Study by Ultrafast Nonlinear Infrared Spectroscopy

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1 FTIR Spectra of AOT in Different Solutions

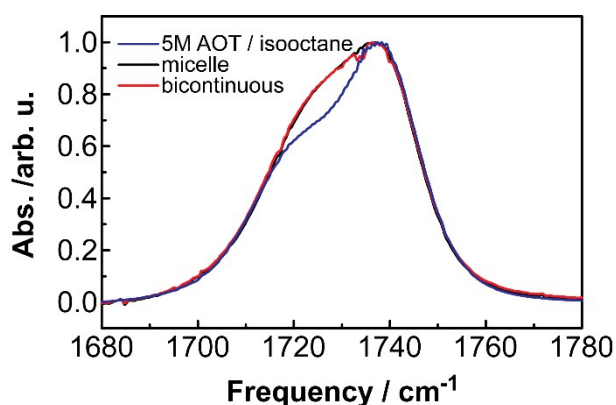


Fig. S1 FTIR spectra of the ester carbonyl stretching vibrations of AOT in different solution environments.

We measured the FTIR spectra of the carbonyl stretching vibrational mode of AOT in different media (see Fig. S1). There are two components in the spectra and their peak positions are around 1720 cm⁻¹ and 1740 cm⁻¹. These two components are due to the C=O stretching mode of the AOT molecules associated with the acyl C-C rotational isomerization.^{1,2} The 1740-cm⁻¹ component is the *trans* conformation and the 1720-cm⁻¹ component is the *gauche* conformation. In 5 M AOT / isooctane solution, there are more AOT molecules in the *trans* conformation, which indicates that the AOT is more likely to exist in the *trans* conformation in the disordered arrangement. However, in the micellar and bicontinuous structures, water molecules make the arrangement of AOT molecules regular. In this case, the AOT is more likely to exist in the *gauche* conformation, which is the most amphiphilic shape of the AOT molecule.¹ This increases the population of the 1720-cm⁻¹ component. This result shows that water molecules can change the conformation of AOT, which is consistent with the vibrational dynamical results presented in this work that the AOT molecules are ordered in

the presence of water molecules.

2 FTIR Spectra of the Probe Molecule in Different Solutions

The overall linear IR spectra of the $C\equiv N^-$ absorption profiles are quite similar in two microemulsion structures. However, subtle differences do exist. Fig. S2 shows the enlarged FTIR spectra of the $C\equiv N^-$ stretching mode of ferrocyanide in three different aqueous media.

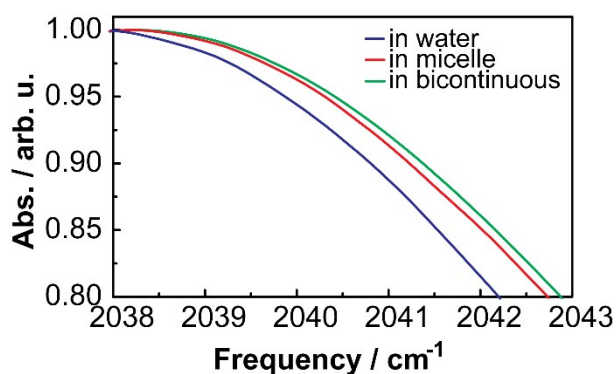


Fig. S2 The enlarged FTIR spectra of the $C\equiv N^-$ stretching mode of ferrocyanide in three different aqueous media.

3 The Dynamical Effects on the Spectral Line Width

The effect of vibrational and rotational dynamics on the spectral line width^{3,4} can be evaluated.

The total homogeneous dephasing time T_2 is given by:

$$\frac{1}{T_2} = \frac{1}{T_2^*} + \frac{1}{2T_1} + \frac{1}{3T_{or}}, \quad (1)$$

where T_2^* is the pure dephasing time, T_1 is the vibrational life time, and T_{or} is the anisotropy

relaxation time constant. The total homogeneous linewidth can be computed using T_2 :

$$\Delta\nu = \frac{1}{\pi c T_2}. \quad (2)$$

Substituting our data into Eqs. (1) and (2) yields the contribution of vibrational relaxation and rotational dynamics to the homogeneous linewidth, which is only 0.35 cm^{-1} , in the case of bicontinuous, and a very similar value in micelle.

4 Harmonic Frequency Calculations

Table S1 Harmonic vibrational transition frequency (ω) and Infrared intensity (I) of certain normal modes of $\text{W}(\text{CO})_6$ and isooctane.

$\text{W}(\text{CO})_6$			Isooctane		
Mode	ω / cm^{-1}	I / $\text{km}\cdot\text{mol}^{-1}$	Mode	ω / cm^{-1}	I / $\text{km}\cdot\text{mol}^{-1}$
A_{1g}	2184.5	0	A	1529.1	20.5
E_g	2082.8	0	A	1518.9	14.0
T_{1u}	2058.4	2232.4	A	1408.0	14.5
T_{1u}	606.0	85.7	A	1405.7	8.0
T_{2u}	539.9	0	A	1268.2	6.5
T_{1u}	384.3	57.8	A	1186.6	4.6

Table S2 Harmonic vibrational transition frequency (ω) and Infrared intensity (I) of certain normal modes of AOT in two different conformations.

AOT (trans)			AOT (gauche)		
Mode	ω / cm^{-1}	I / $\text{km}\cdot\text{mol}^{-1}$	Mode	ω / cm^{-1}	I / $\text{km}\cdot\text{mol}^{-1}$
A	1794.1	260.4	A	1800.3	294.9
A	1777.0	332.3	A	1784.4	294.1
A	1238.3	196.6	A	1291.6	343.9
A	1260.4	285.8	A	1281.1	308.6
A	1240.4	181.6	A	1278.2	103.2
A	1229.5	309.0	A	1244.9	205.6
A	1187.0	119.4	A	1221.5	220.8
A	1105.2	326.5	A	1067.4	146.9
A	609.4	86.1	A	972.1	180.3

References

1. D. J. Christopher, J. Yarwood, P. S. Belton and B. P. Hills, *J. Colloid Interface Sci.*, 1992, **152**, 465-472.
2. Z. L. Lai and P. Y. Wu, *J. Mol. Struct.*, 2008, **883**, 236-241.
3. A. Tokmakoff and M. D. Fayer, *J. Chem. Phys.*, 1995, **103**, 2810-2826.
4. A. Tokmakoff, R. S. Urdahl, D. Zimdars, R. S. Francis, A. S. Kwok and M. D. Fayer, *J. Chem. Phys.*, 1995, **102**, 3919-3931.