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Strikingly different miscibility of *n*-octanol in highly-confined and quasi-confined water

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1. Experimental Details

1.1. ***Materials used.*** 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS, pyranine), sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and *n*-octanol were purchased from Sigma-Aldrich Chemicals. HPLC grade *n*-heptane and ethanol were purchased from Spectrochem India. Water (resistivity 18.2 MΩ cm) was obtained from a Millipore system.

1.2. ***Instruments and detection methods.*** The absorption and emission spectra were recorded in a Perkin-Elmer Lamda-750 spectrophotometer and Jobin-Yvon Fluromax4 spectroflurometer, respectively. Dynamic light scattering (DLS) measurements were recorded using Malvern Nano ZS90 instrument. The He-Ne Laser ($\lambda = 632.8$ nm) was used as excitation source. The scattering was collected at a fixed angle of 90^o. The solutions were filtered with PTFE syringe filters having 0.2 μm pore size prior to DLS measurements. All measurements were performed at 298 K. For the DLS measurement, we estimated the viscosity of the continuous phase comprising of the mixtures of *n*-heptane (η = 0.386 cp) and the alcohol (ethanol (η = 1.084 cp) or *n*-octanol (η = 7.24 cp) using the equation[1]

$$\eta = (\eta_1^{1/3} X_1 + \eta_2^{1/3} X_2)^3 \qquad \text{(S1)}$$

where η, η_2 stand for viscosities and X_1, X_2 for mole fractions of *n*-heptane and the alcohol (ethanol or *n*-octanol), respectively.

In the calculation, partitioning of alcohol (ethanol or octanol) into the reverse micelle (in the core and/or interface) is neglected. Such partitioning is expected to be small compared to the octanol partition into n-heptane due to their high mutual miscibility. Note, *n*-heptane and octanol are completely miscible at all mole fractions.

1.3 Preparation of Reverse Micelle Solutions. The reverse micelle solutions at w_0 = 5 and 10 were prepared by adding a requisite amount of water (using the relation, $w_0 = [H_2O]/[\text{Surfactant}]$) into 0.09 M AOT solution in *n*-heptane. To incorporate the probe into the reverse micelle (RM) solution, a required amount of a stock solution of HPTS in water were injected into the reverse micelle solution. In all experiments, the overall concentration of the HPTS was kept at ~12 μM. From the absorption spectrum of HPTS, the local pH within the water pool was initially slightly basic (pH~7-8) with considerable absorbance band centered around 450 nm. The measured pH of the reverse micelle without any pH adjustment was 7.8. However, the reverse micelle solution was made slightly acidic (pH ~5) by adding 2 μL of 1.2 M HCl into 2.5 ml of the reverse micelle solution to ensure that only the protonated form of dye remains in the ground state. Bulk pH measurement revealed a pH of 5.3 after this adjustment. Thereafter, n-octanol (stock concentration ~ 6.29 M) was added gradually up to alcohol/ water mole ratio of 1.79 and

0.23 in w_0 = 5 and 10, respectively. Similarly, ethanol (stock concentration ~ 16.95 M) was added gradually up to alcohol/ water mole ratio 1.79 and 0.44 in w_0 = 5 and 10, respectively.

1.4 pH dependence of HPTS absorption spectrum

A stock solution of sodium dihydrogen phosphate (Na_2HPO_4) was prepared by dissolving 0.7g in 25 ml Millipore water and 1.33 g of disodium hydrogen phosphate (NaH_2PO_4) in 25 ml Millipore water. The buffer solution is made by mixing 10 ml of sodium dihydrogen phosphate and 15ml of disodium hydrogen phosphate solutions. The volume was made up to 50 ml with distilled water. This gives a phosphate buffer strength of 0.2 M.

A pH meter (Jenway, 3510 p^H meter) was standardized with standard buffers. The electrode was washed with distilled water and introduced into the phosphate buffer. The pH was observed to be 7.4. Then, different buffer solutions of varying pH (2- 10) were obtained by titration with 1N HCl or 5N NaOH solutions.

Absorption spectrum of HPTS was measured in the buffer solutions of different pH (figure S1). Note that the below pH = 5, the absorbance solely arises from the protonated form of HPTS and the de-protonated absorption band gradually appears with increase of pH. Thus, by comparing the absorption spectrum at different pH we can estimate the pH of an unknown solution (in this case water pool of reverse micelle).

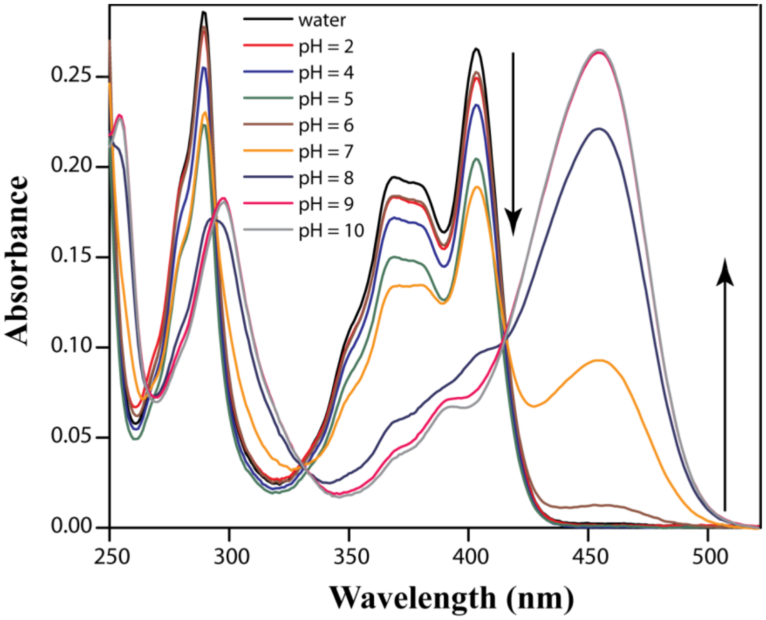

Figure S1 Effect of pH variation on the absorption spectrum of HPTS. At lower pH the absorption of the protonated form (absorption maximum ~ 405 nm) dominates but at higher pH the absorption of the de-protonated form (absorption maximum ~ 450 nm) becomes gradually prominent.

1.5 Approximate number of octanol present inside the water pool

The equilibrium mole fraction of water soluble in *n*-octanol at 25 °C is 7.03×10^{-5}.[2]

At $w_0 = 5$, the diameter of RM is 5.6 nm

Considering the interface is ~ 1 nm thick, the radius of water pool is ~ 1.8 nm.

Thus the volume of water pool is $\frac{4}{3}\pi(1.8)^3$ = 24.43 nm^3.

Molecular volume of water is ~ 0.03 nm^3

Thus, at $w_0 = 5$, water pool should contain ~810 molecules.

Similarly, at $w_0 = 10$, water pool should contain ~4160 molecules

Considering the solubility of octanol in the water pool is similar to bulk water, at $w_0 = 5$ and 10, water pool should contain 0.06 molecules and 0.3 molecules.of n-octanol Thus, if the bulk solubility applies for water pool, then presence of octanol in the core can be effectively neglected.

2. Results

2.1. Absorption spectra of HPTS in different systems.

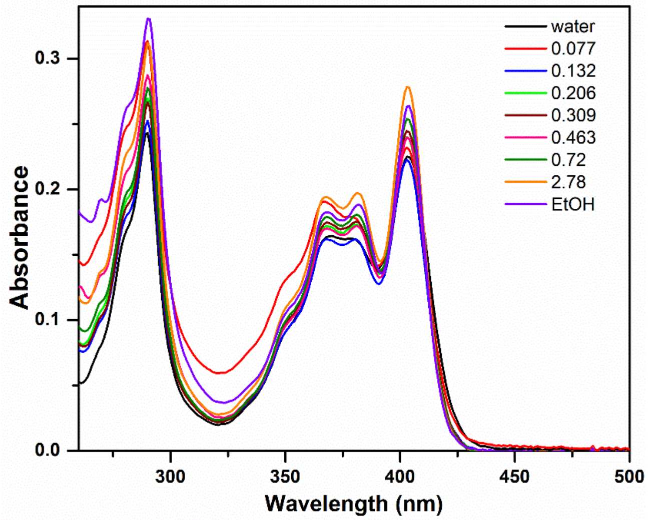

Figure S2 Absorption spectra of HPTS in ethanol-water mixtures at various alcohol/water mole ratios. Absorption spectrum of HPTS in neat water and ethanol are also included for comparison.

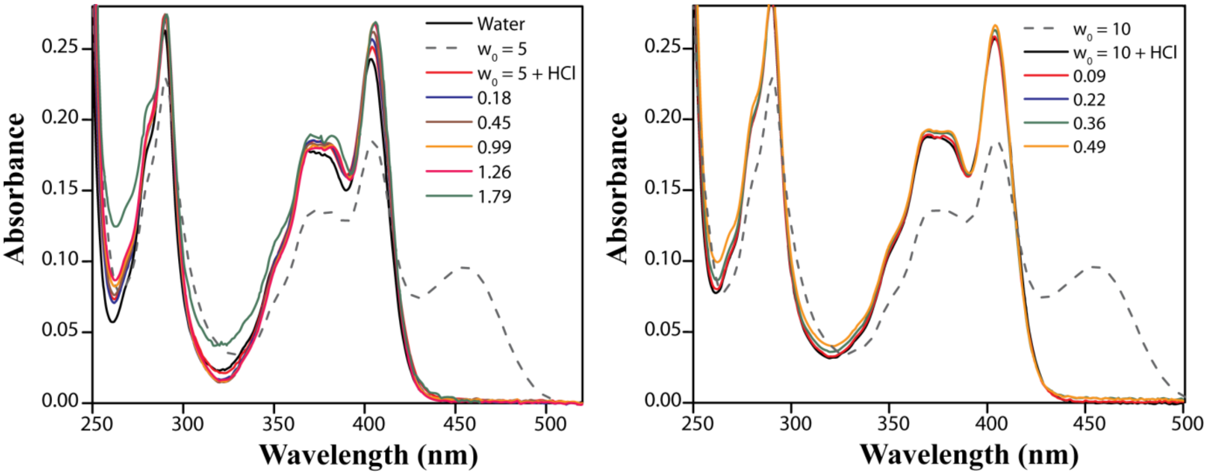

Figure S3 Absorption spectra of HPTS in the water/ AOT/ *n*-heptane reverse micelle for (a) w_0 = 5 and (b) w_0 = 10 at various ethanol/water mole ratios. The dotted line represents the absorption spectra of HPTS inside the reverse micelle after addition of neutral Millipore water without any pH adjustment. The water pool was made slightly acidic (pH ~5-6) to suppress the de-protonated absorption. Addition of ethanol was performed after this pH adjustment.

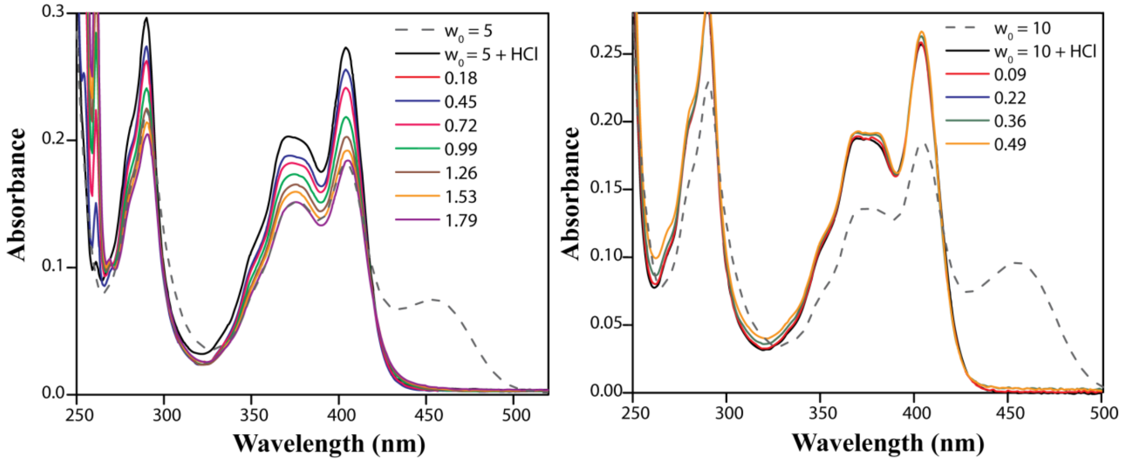

Figure S4 Absorption spectra of HPTS in the water/ AOT/ *n*-heptane reverse micelle for (a) w_0 = 5 and (b) w_0 = 10 at various alcohol/water mole ratios. The overall absorption decreases slightly upon octanol addition at w_0 = 5 but no change occurs at w_0 = 10. The dotted line represents the absorption spectra of HPTS inside the reverse micelle after addition of neutral Millipore water without any pH adjustment. The water wool was made slightly acidic (pH ~5-6) to suppress the de-protonated absorption. Addition of octanol was performed after this pH adjustment.

2.2. Emission spectra of HPTS in water/ AOT/ n-heptane reverse micelle at w_0 = 5 and 10 upon addition of ethanol.

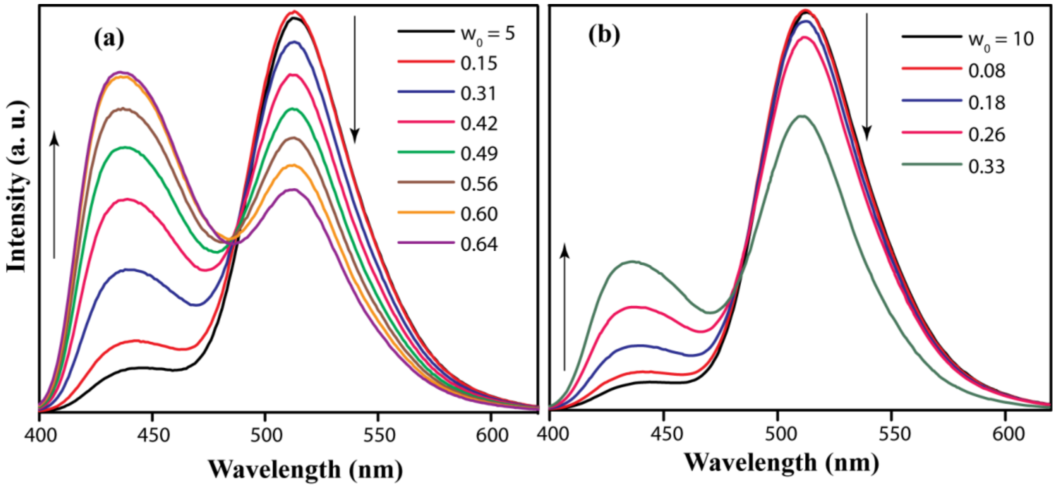

Figure S5 Emission spectra of HPTS in water/ AOT/ n-heptane reverse micelle at w_0 = 5 and 10 with gradual addition of ethanol.

2.3. Comparison of effect of alcohol in the reverse micelle and ethanol water mixtures.

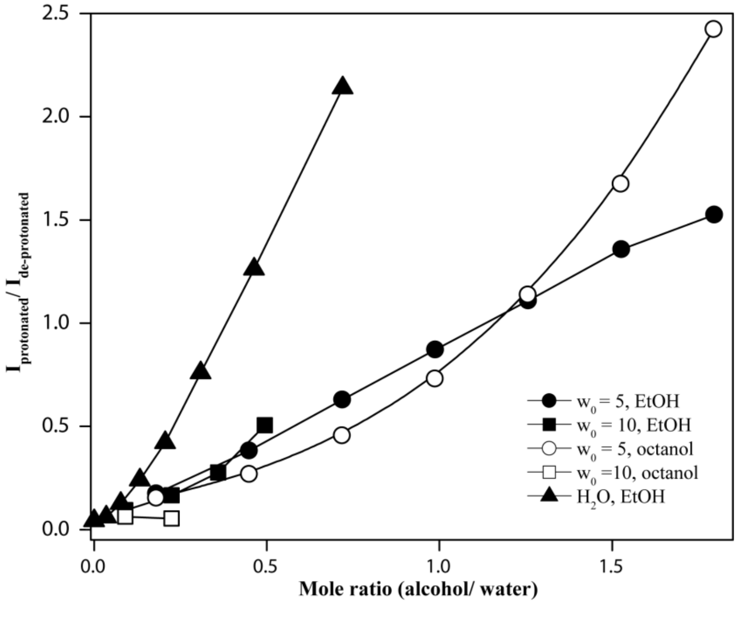

Figure S6 Comparison of the extent of HPTS intensity modulation (ratio of Iprotonated/ Ide-protonated) upon alcohol (ethanol or octanol) addition in different systems. The full intensity ratio graph for ethanol and water mixture is provided in the manuscript in figure 1 (b).

2.4 Time-resolved fluorescence

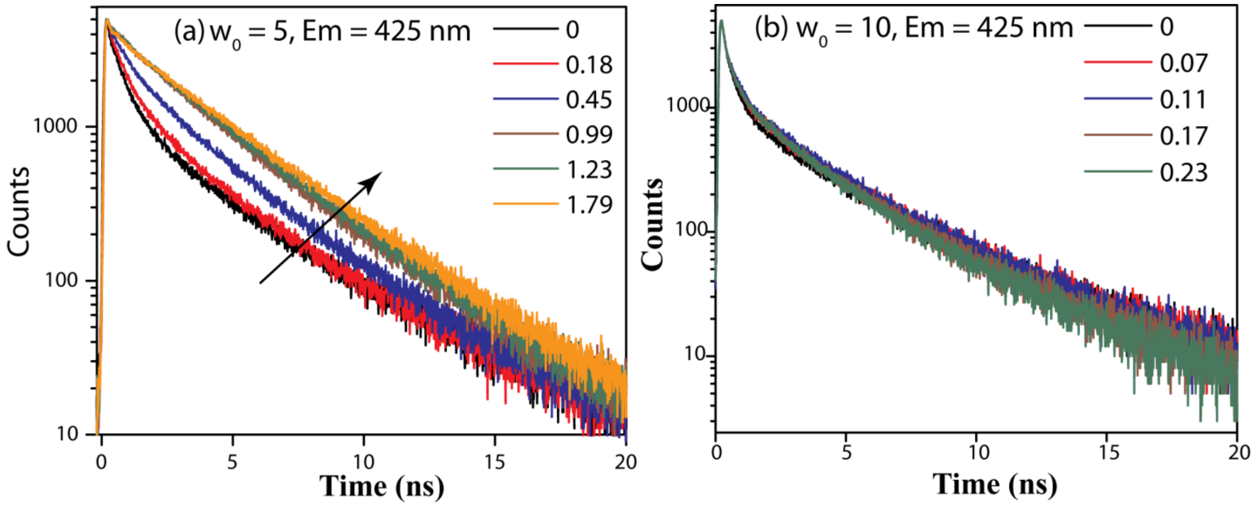

Figure S7 The effect of octanol on the fluorescence transients of HPTS (at emission wavelength of 425 nm) inside the water/AOT/*n*-heptane reverse micelle at w_0 = 5 and w_0 = 10. A dramatic slowing down of the fluorescence decay was observed upon octanol addition at w_0 = 5 but almost no change is noticed among the transients at w_0 = 10.

2.5. Dynamic light scattering (DLS) measurements.

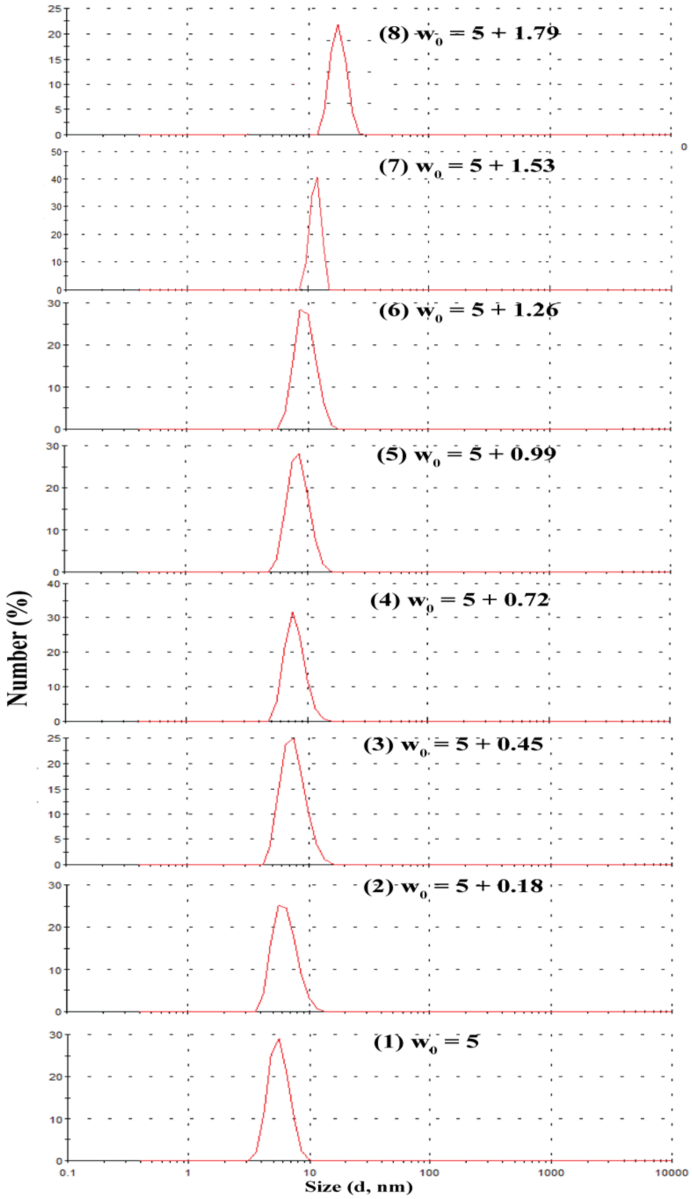

Figure S8 Effect of ethanol on the size distribution of water/AOT/n-heptane reverse micelles at w_0 = 5 obtained from dynamics light scattering (DLS). The size of reverse micelle increases gradually upon addition of ethanol supporting its incorporation into the water pool.

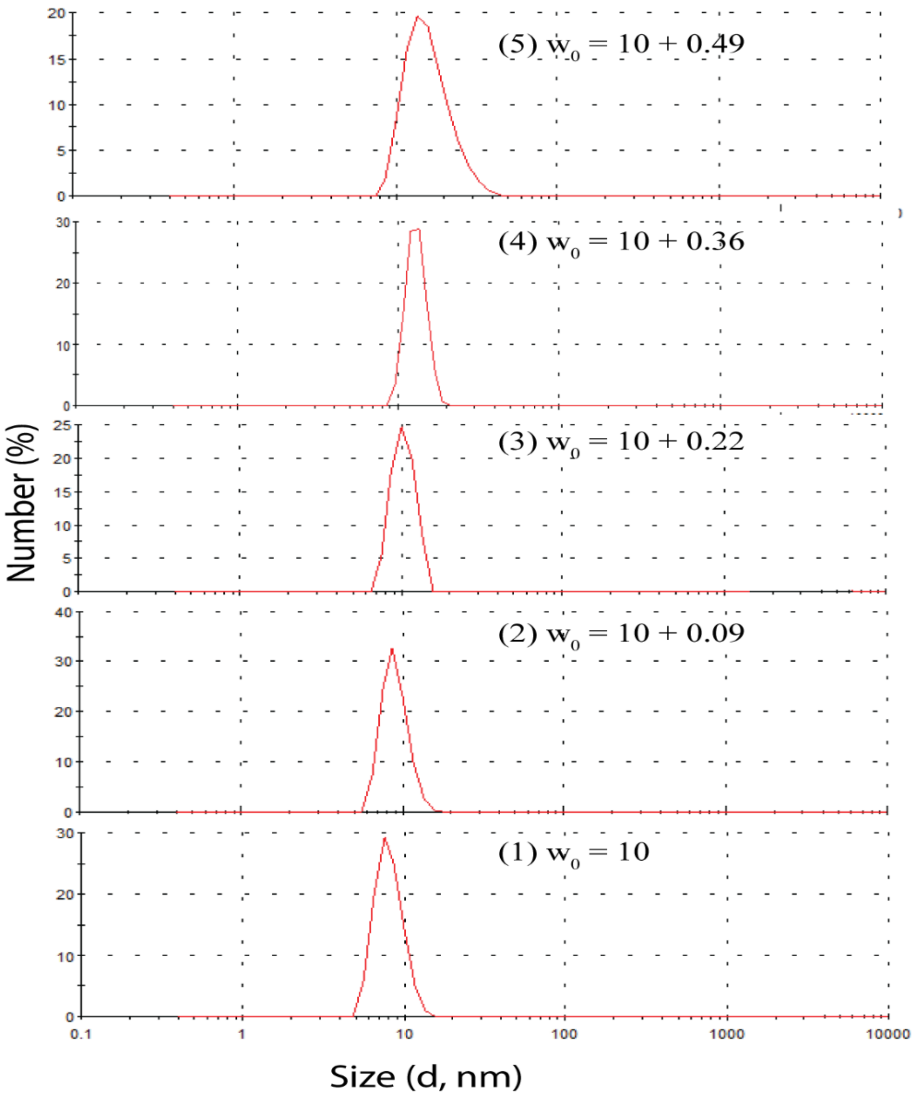

Figure S9 Effect of ethanol on the size distribution of water/AOT/n-heptane reverse micelles at w_0 = 10 obtained from dynamics light scattering (DLS). The size of reverse micelle increases gradually upon addition of ethanol supporting its incorporation into the water pool.

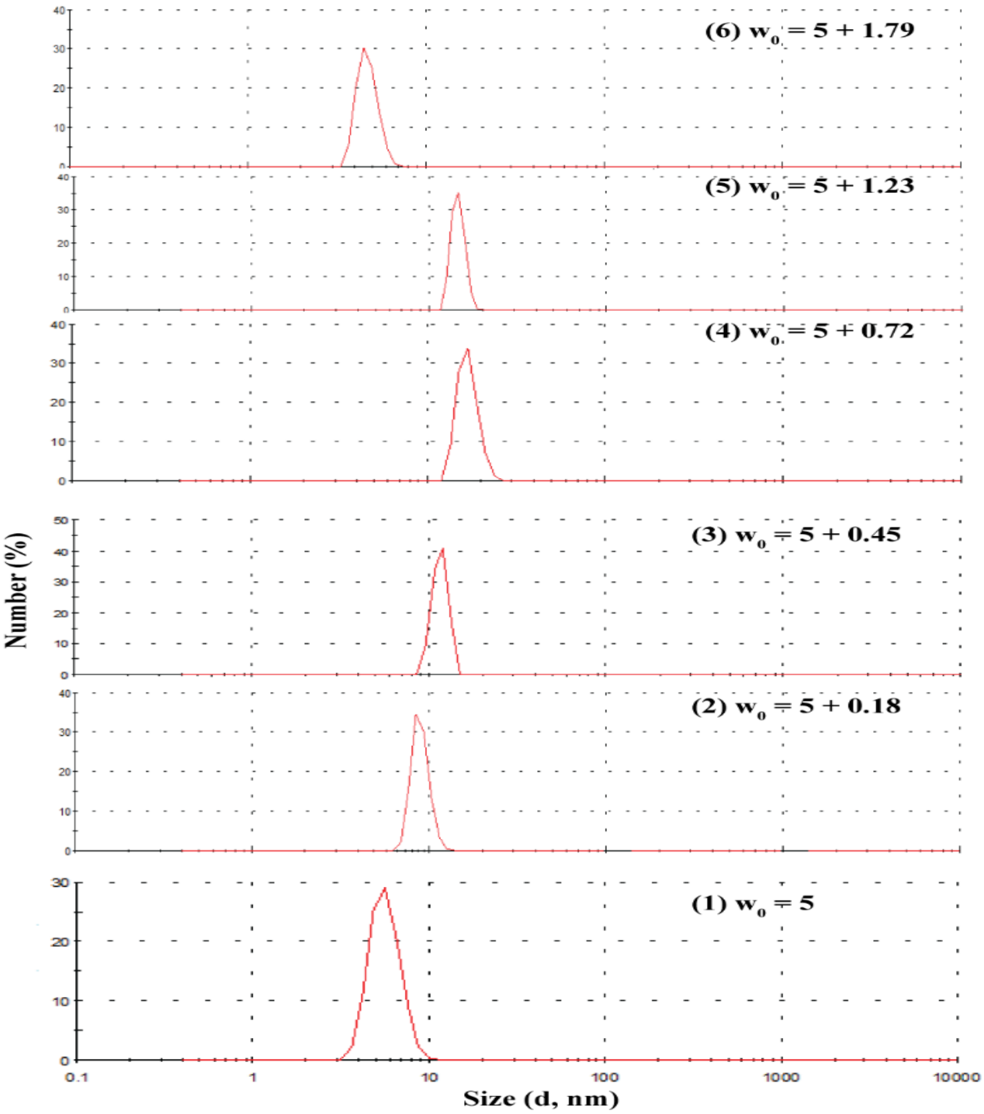

Figure S10 Effect of octanol on the size distribution of water/AOT/n-heptane reverse micelles at $w_0 = 5$ obtained from dynamics light scattering (DLS). The size of reverse micelle first increases upon addition of *n*-octanol up to octanol/water mole ratio of 0.72 but then the size decreases upon further addition. The octanol may preferentially partition into the core at $w_0 = 5$ at lower octanol content but interface-partitioning dominates at higher amount of octanol resulting in shrinking of the reverse micelle.

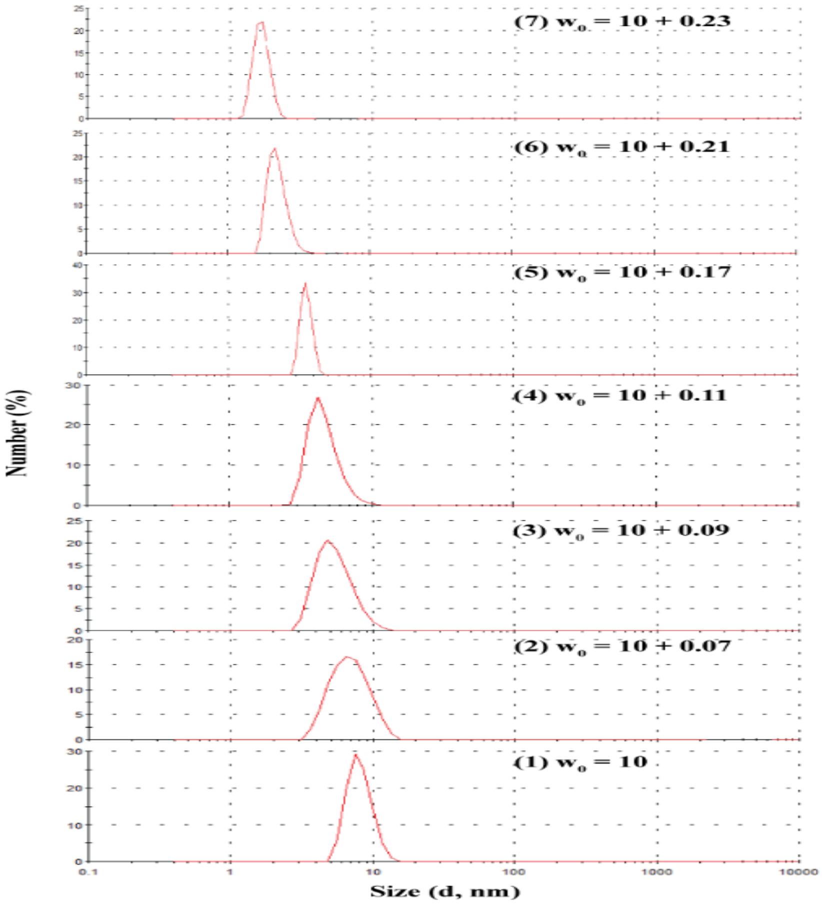

Figure S11. Effect of octanol on the size distribution of water/AOT/n-heptane reverse micelles at w_0 = 10 obtained from dynamics light scattering (DLS). The size of reverse micelle gradually decreases upon addition of n-octanol. The shrinking of reverse micelle is consistent with the interface partitioning of octanol at this w_0.

Table S1. The variation of hydrodynamic diameter of water/AOT/*n*-heptane reverse micelle upon addition of ethanol obtained from dynamics light scattering (DLS) measurements at $w_0 = 5$ and 10. The estimated viscosities of the continuous phase are also included.

System	overall concentration of ethanol, M	ethanol/water mole ratio	Viscosity of continuous phase (cp)	Hydrodynamic diameter (d, nm)
$w_0 = 5$	0	0	0.386 (pure n-heptane)	5.6
	0.08	0.18	0.3914	6.5
	0.2	0.45	0.3997	7.7
	0.32	0.72	0.4078	8.0
	0.44	0.99	0.4157	8.6
	0.56	1.26	0.4235	9.7
	0.68	1.53	0.4311	11.6
	0.8	1.79	0.4386	15.0
$w_0 = 10$	0	0	0.386 (pure n-heptane)	8.2
	0.08	0.09	0.3914	9.0
	0.2	0.22	0.3997	10.4
	0.32	0.36	0.4078	12.4
	0.44	0.49	0.4157	15.9

Table S2. The hydrodynamic diameters of water/AOT/n-heptane reverse micelles with addition of *n*-octanol obtained from dynamics light scattering (DLS) at $w_0 = 5$ and 10. The estimated viscosities of the continuous phase are also included.

System	overall concentration of octanol, M	*n*-octanol/water mole ratio	Viscosity of continuous phase (cp)	Hydrodynamic diameter (d, nm)
$\mathbf{w_0 = 5}$	0	0	0.386 (pure n-heptane)	5.6
	0.08	0.18	0.409	7.7
	0.2	0.45	0.444	11.6
	0.32	0.72	0.480	16.9
	0.56	1.26	0.551	14.7
	0.8	1.79	0.625	4.5
$\mathbf{w_0 = 10}$	0	0	0.386 (pure n-heptane)	8.2
	0.06	0.07	0.403	7.1
	0.08	0.09	0.409	6.2
	0.09	0.11	0.412	5.5
	0.15	0.17	0.430	3.5
	0.18	0.21	0.439	2.4
	0.2	0.23	0.445	1.7

2.6 Approximate dimension of the reverse micelle systems

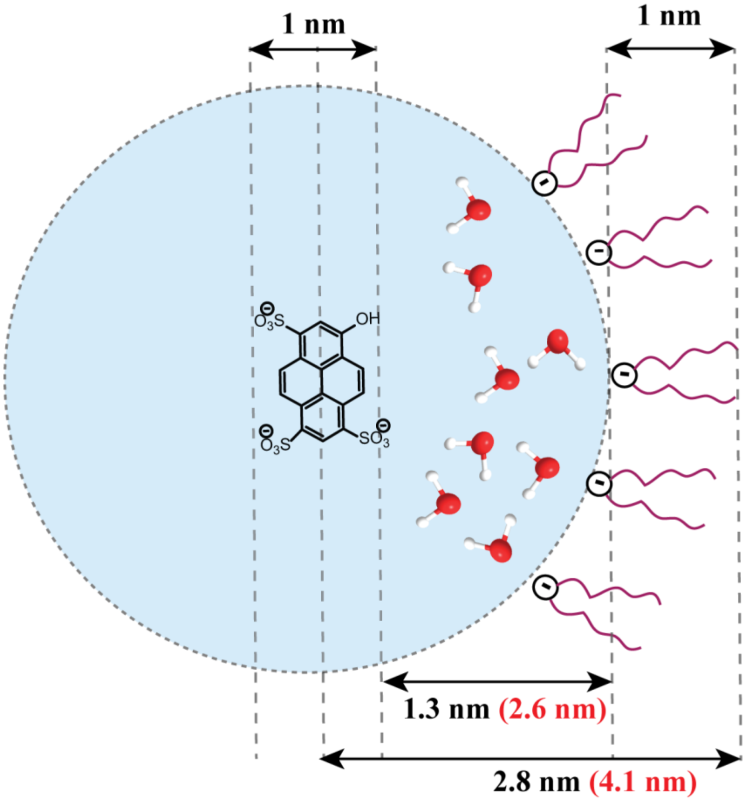

Figure S12 A scheme showing approximate dimension of the reverse micelle systems at $w_0 = 5$ and 10 containing HPTS in the core

References

1. H. Iloukhani, M. Rezaei-Sameti and J. Basiri-Parsa, *J. Chem. Thermodyn.*, 2006, 38, 975-982.
2. J. Sangster, *J. Phys. Chem. Ref. Data*, 1989, 18, 1111-1229.