

Synergistic Interaction of Surfactant Blends in Aqueous Medium Reciprocates in Non-polar Medium with Improved Efficiency as Nano-reactor

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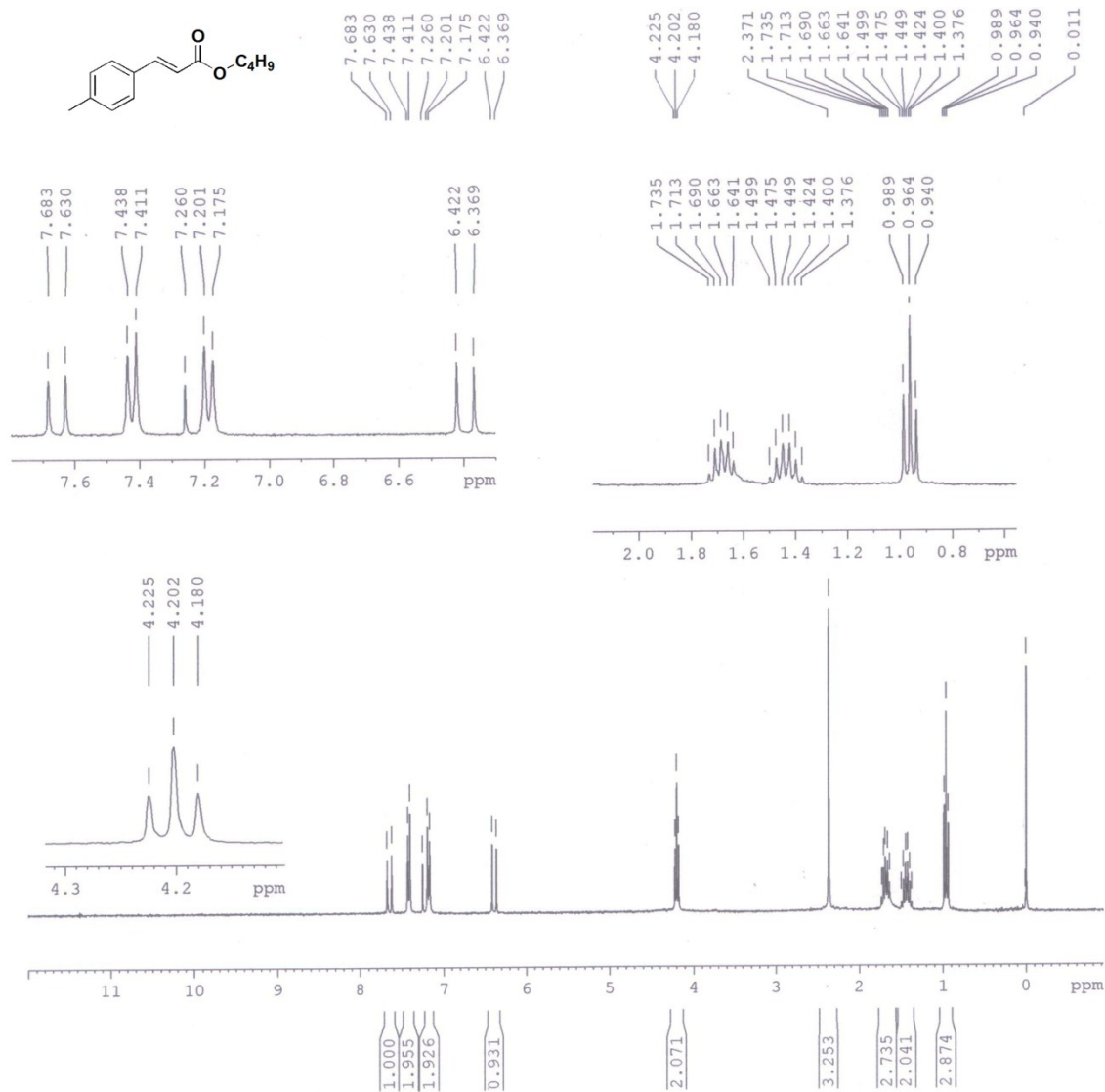
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Author Contributions: •S.B and K.K have contributed equally to this work.

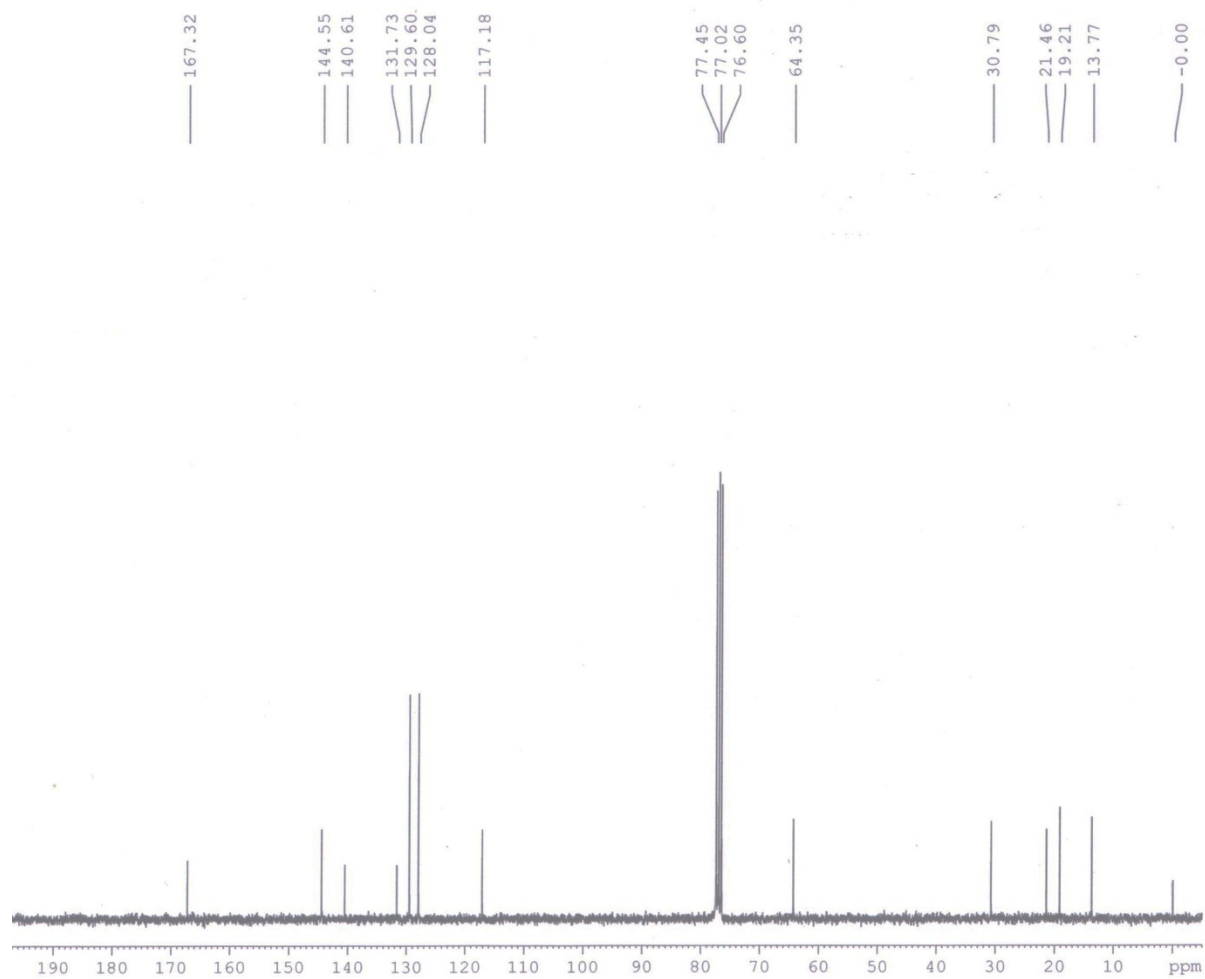
Analytical data for Heck Product (4-methyl butyl cinnamate):

$^1\text{H-NMR}$ (CDCl_3 , 300MHz) δ 0.96 (t, 3H, $J = 7.2$ Hz), 1.44 (m, 2H), 1.68 (m, 2H), 2.36 (s, 3H), 4.20 (t, 2H, $J = 6.6$ Hz), 6.39 (d, 1H, $J = 16.2$ Hz), 7.18 (d, 2H, $J = 7.8$ Hz), 7.42 (d, 2H, $J = 7.8$ Hz), 7.66 (d, 2H, $J = 16.2$ Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ 13.8, 19.2, 21.5, 30.8, 64.4, 117.2, 128.0, 129.6, 131.7, 140.6, 144.6, 167.3.

$^1\text{H NMR}$



¹³C NMR



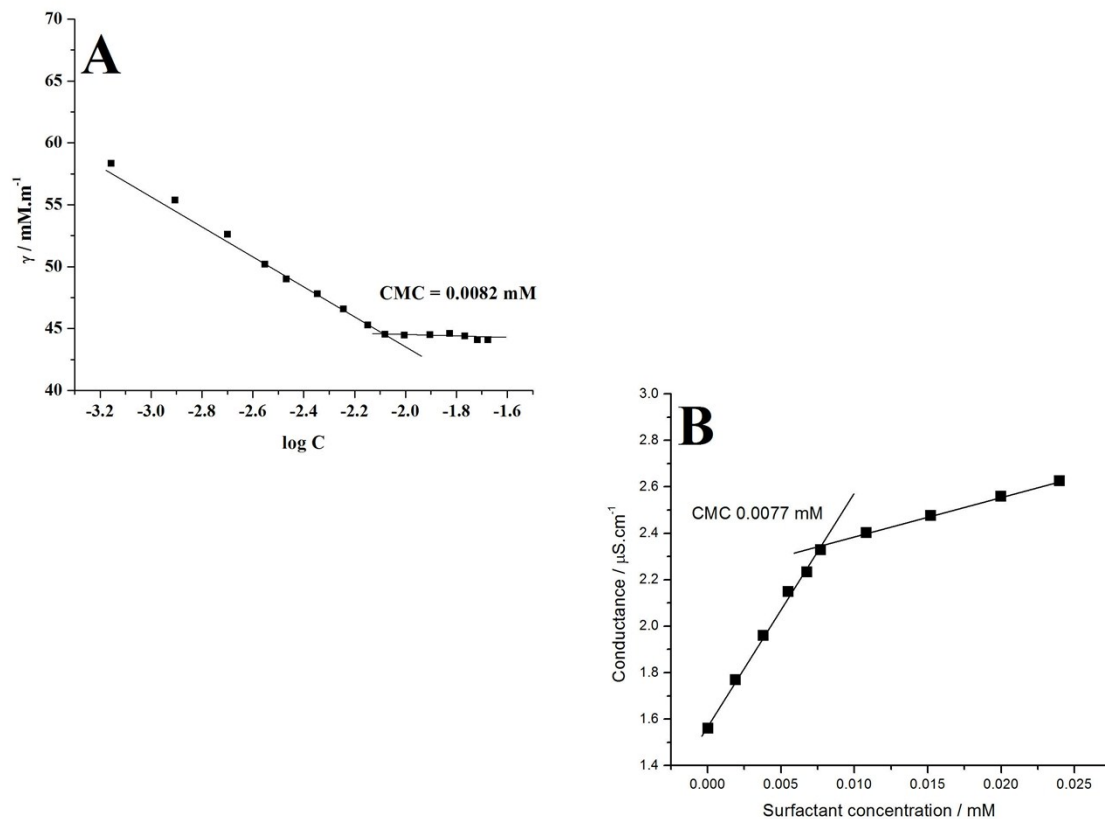


Fig. S1. Tensiometric (A) and conductometric (B) determination of critical micellar concentration (CMC) for single $C_{16}E_{20}$ surfactant system at a fixed temperature (303K).

Table S1. Micellar parameters: experimental CMC values obtained from surface tension and conductivity techniques at 303K, literature CMC (CMC_{lit}) and ideal CMC (CMC_{ideal}) of binary mixture of cationic CTAB with non-ionic $C_{16}E_{20}$.

Micellar System	CMC_{exp} (mM)		CMC_{lit} (mM)	CMC_{ideal} (mM)
	Surface Tension	Conductance		
	CTAB	0.9301	-	0.92 ^a , 0.871 ^b
$C_{16}E_{20}$	0.0077	-	0.0080 ^c	-
CTAB/ $C_{16}E_{20}$ (1:1)	0.0105	0.0109	-	0.0150

^{a,c}Ref.¹ ^bRef.²

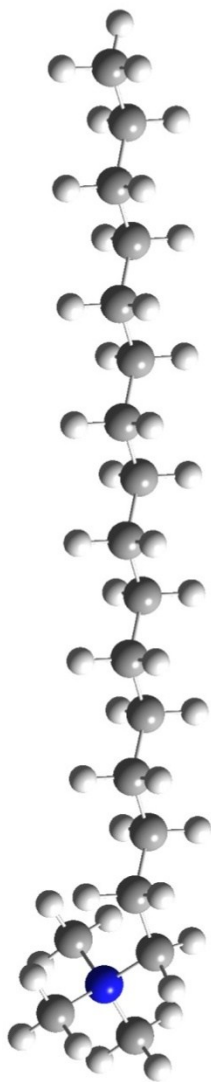


Fig. S2A. Optimized geometry at the B3LYP/6-31G level for isolated CTAB. Color code for atoms: blue, nitrogen; dark gray, carbon; and light gray, hydrogen.

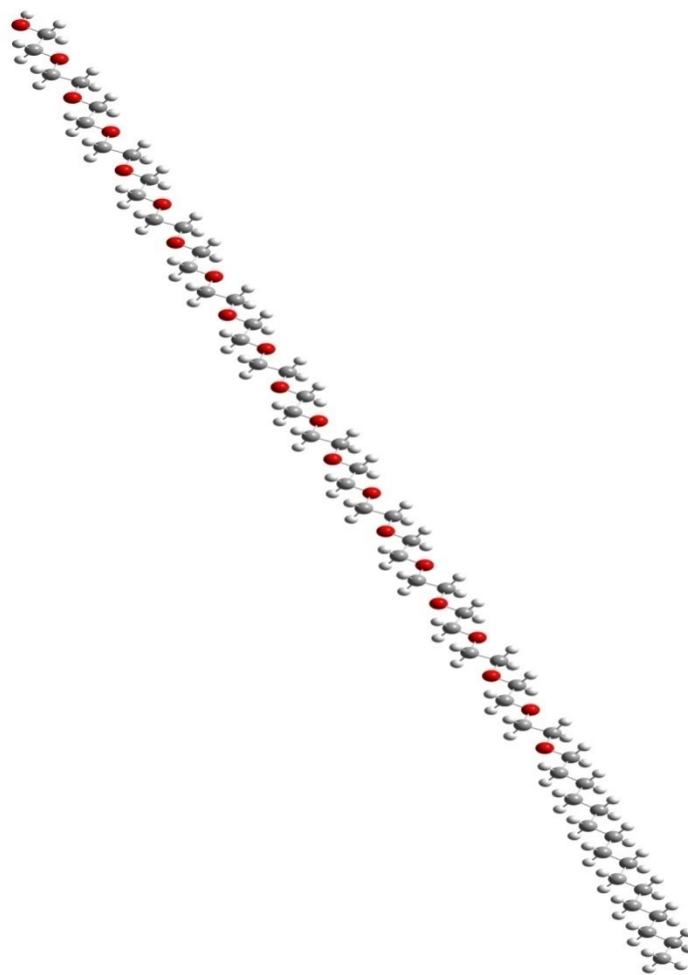
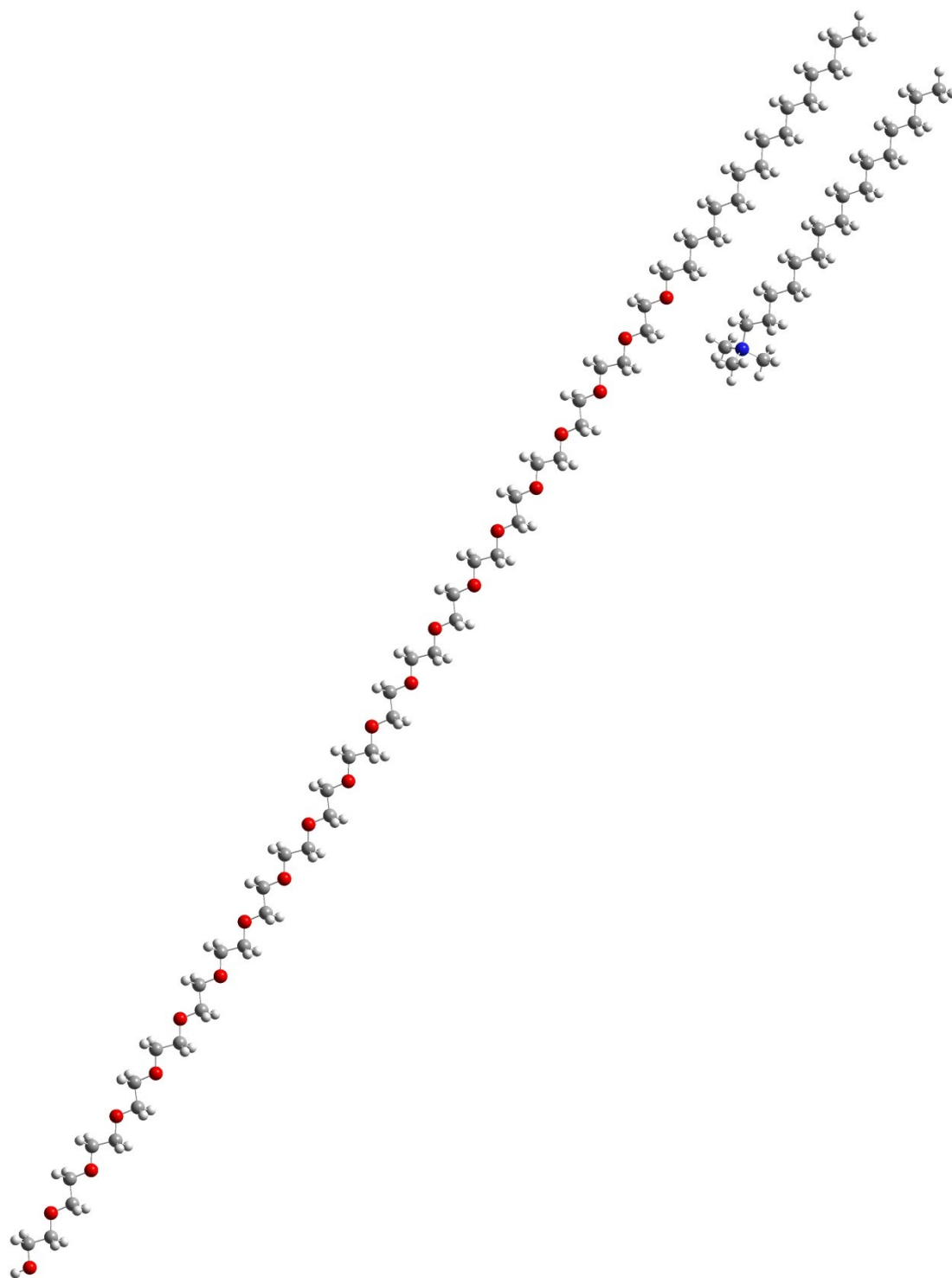


Fig. S2B. Optimized geometry at the B3LYP/6-31G level for isolated C₁₆E₂₀. Color code for atoms: red, oxygen; dark gray, carbon; and light gray, hydrogen.



Color code for atoms:

Table S2. Optimization of C-C cross coupling Heck reaction in micelles and w/o mixed microemulsion media at 303K.^a

Entry	Solvent	Water content (ω)	Yield (%)^d
1.	Water	-	07
2.	CTAB ^b	-	57

3.	C ₁₆ E ₂₀ ^b	-	44
4.	CTAB/ C ₁₆ E ₂₀ ^b	-	66
5.	Heptane (Hp)	-	37
6.	Decane (Dc)	-	15
7.	Hp/1-pentanol (Pn) (1:2, wt%)	-	40
8.	Dc/Pn (1:2, wt%)	-	19
9.	Water/CTAB/ C ₁₆ E ₂₀ /Pn/Hp ^c	10	79
10.	Water/CTAB/ C ₁₆ E ₂₀ /Pn/Hp ^c	20	70
11.	Water/CTAB/ C ₁₆ E ₂₀ /Pn/Hp ^c	30	59
12.	Water/CTAB/ C ₁₆ E ₂₀ /Pn/Hp ^c	40	56
13.	Water/CTAB/ C ₁₆ E ₂₀ /Pn/Hp ^c	50	54

14.	Water/CTAB/ C ₁₆ E ₂₀ /Pn/Dc ^c	10	68
15.	Water/CTAB/ C ₁₆ E ₂₀ /Pn/Dc ^c	20	57
16.	Water/CTAB/ C ₁₆ E ₂₀ /Pn/Dc ^c	30	45
17.	Water/CTAB/ C ₁₆ E ₂₀ /Pn/Dc ^c	40	44
18.	Water/CTAB/ C ₁₆ E ₂₀ /Pn/Dc ^c	50	41

^a Reaction condition: 4-iodo toluene (0.5 mmol), n-butyl acrylate (0.6 mmol), Triethylamine (1.0 mmol), Pd(OAc)₂ (0.02 mmol, 4 mol%), temperature; 303K, ^b Micellar system, [CTAB]= 0.9301 mM, [C₁₆E₂₀] = 0.0077 mM, [CTAB]:[C₁₆E₂₀] (1:1) = 0.0105 mM, ^c w/o mixed microemulsion; [water/CTAB/C₁₆E₂₀/Pn/oil, [CTAB]:[C₁₆E₂₀] (1:1); S:CS = 1:2 wt.%], ^d HPLC yield of the Heck product.

Table S3. Interfacial composition and thermodynamic parameters of CTAB/C₁₆E₂₀/1-pentanol/*n*-heptane (or *n*-decane)/water microemulsion at 303K with varying water content (ω).

ω	10	20	30	40	50
10⁴ n_aⁱ/mol	15.30 (10.12) ^c	9.90 (7.42)	7.39 (5.92)	6.60 (5.45)	5.69 (4.68)
10⁴ n_a⁰/mol	10.29 (23.29)	20.59 (26.73)	28.50 (31.75)	33.34 (37.67)	42.48 (49.96)
K_d	20.65 (13.25)	10.46 (8.77)	5.24 (5.03)	4.07 (3.86)	3.54 (3.26)

$-\Delta G_t^0/\text{KJ mol}^{-1}$	7.62 (6.50)	5.91 (5.47)	4.17 (4.07)	3.53 (3.40)	3.18 (2.98)
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^aAll the mixed microemulsion systems are formed using constant amount of mixed surfactant (0.5 mmol) and oil (14.0 mmol).

^bThe average errors in K_d and ΔG_t^0 were within ± 5 and $\pm 3\%$, respectively.

^cThe values in parentheses indicate parameters for *n*-decane (Dc) stabilized system.

Evaluation of interfacial and bulk composition of cosurfactant from thermodynamic point of view by the dilution method

W/o microemulsion consists of dispersion of water droplets in Hp or Dc continuum wherein the mixed surfactants (CTAB and C₁₆E₂₀ at equimolar composition) were considered to populate at the oil/water interface in partial association with the cosurfactant (Pn), which remained distributed between the interface and the bulk oil, because of its negligible solubility in water.³ Thus, at a fixed [surfactant(s)], a critical concentration of Pn is required for the stabilization of the mixed microemulsions. Addition of extra oil (Hp or Dc) extracts Pn from the interface to destabilize the

system, which can be stabilized by the addition of extra cosurfactant in the system. This is the fundamental basis of oil dilution experiment (the dilution method). The following equations are helpful to rationalize the distribution vis-à-vis transfer process of Pn from the continuous oil phase to the interfacial region:

$$k_o = \frac{n_a^o}{n_o} \quad (S1)$$

$$\frac{n_a}{n_s} = \frac{n_a^i}{n_s} + k_o \frac{n_o}{n_s} \quad (S2)$$

$$K_d = \frac{X_a^i}{X_a^o} = \frac{\frac{n_a^i}{n_a^i + n_s}}{\frac{n_a^o}{n_a^o + n_o}} = \frac{n_a^i(n_a^o + n_o)}{n_a^o(n_a^i + n_s)} \quad (S3)$$

$$\Delta G_t^0 = -RT \ln K_d = -RT \ln \frac{X_a^i}{X_a^o} = -RT \ln \frac{I(1+S)}{S(1+I)} \quad (S4)$$

where, n_a , (n_a^i) and Gibbs free energy ($-\Delta G_t^0$), n_a^o , n_o , n_s denote the total number of moles of cosurfactant, its number at the interface, in the oil phase, the total number of moles of oil and the total number of moles of surfactant, respectively. A plot of n_a/n_s against n_o/n_s (Fig. S3) according to Eq. (S2) yields the values of the slope (S) and the intercept (I). Slope (S) is actually k_o and n_a^o can be determined from Eq. (S1). On the other hand, n_a^i can be calculated from the intercept (I), which is equal to n_a^i/n_s . The partition of cosurfactant between the continuous oil phase and the interface of the droplet can be expressed in terms of the distribution constant, which is represented by K_d . X_a^i and X_a^o are the mole fraction of alkanol in the interfacial layer and in the oil, respectively. ΔG_t^0 represents standard Gibbs free energy change of transfer of cosurfactant from oil to the interface.

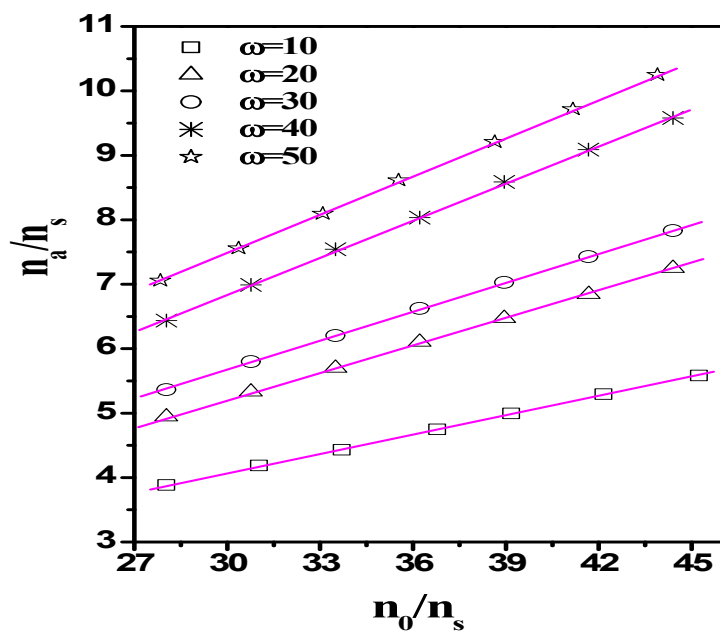


Fig. S3. Plot of n_a/n_s against n_0/n_s for systems comprising equimolar (1:1) mixed surfactant (CTAB and $C_{16}E_{20}$) (0.5mmol) and n-decane (14.0 mmol) stabilized by 1-Pn with different ω (10→50) at a constant temperature (303K).

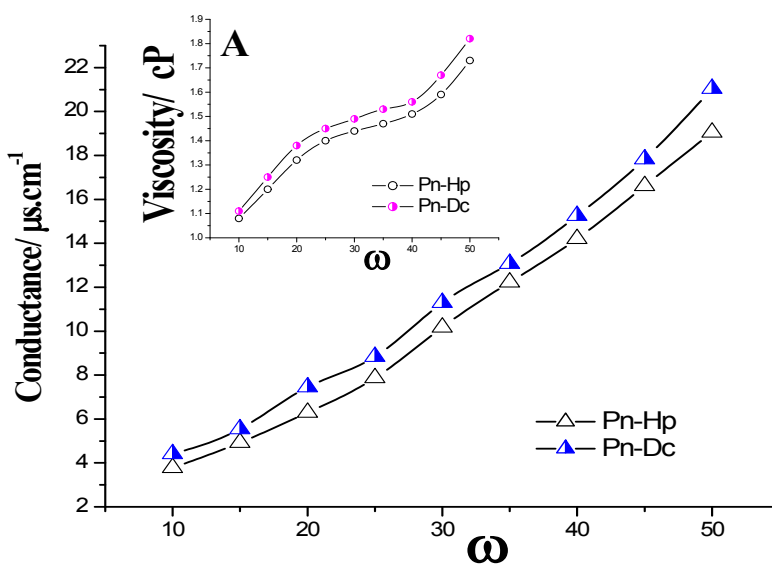


Fig. S4. Dependence of conductance value on water content (ω) for CTAB/C₁₆E₂₀ (1:1)/Pn/Hp (Dc)/water microemulsions at 303K. **Inset A:** Dependence of viscosity on water content (ω) for the same systems of similar composition at 303K.

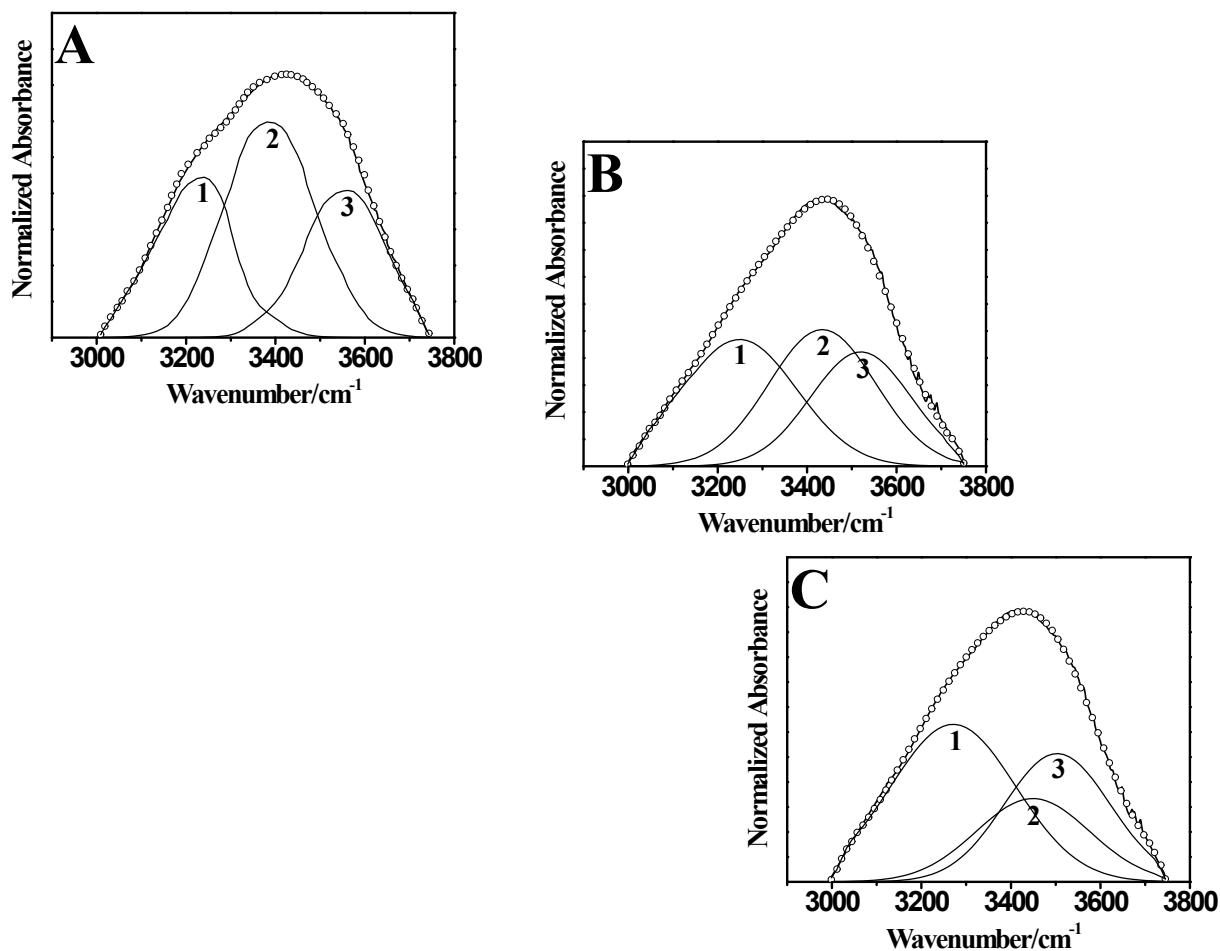


Fig. S5. Representative FTIR spectra of O-H band for w/o mixed surfactant microemulsions, CTAB/C₁₆E₂₀/Pn/Hp/water at equimolar composition (1:1) as a function water content (ω) at fixed surfactant and cosurfactant mass ratio (1:2) and temperature (303K) [A: $\omega = 10$; B: $\omega = 30$; and, C: $\omega = 50$ (Specification: experimental spectra, overall fitted curve (open circle) and deconvoluted curves (1: free water; 2: bound water; 3: trapped water)].

Reference:

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