Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Synthesis of two biofriendly anionic surfactants (N-*n*-decanoyl-L-valine and N-*n*-decanoyl-L leucine) and their mixed micellization with nonionic surfactant Mega-10 in tris-buffer medium at pH 9

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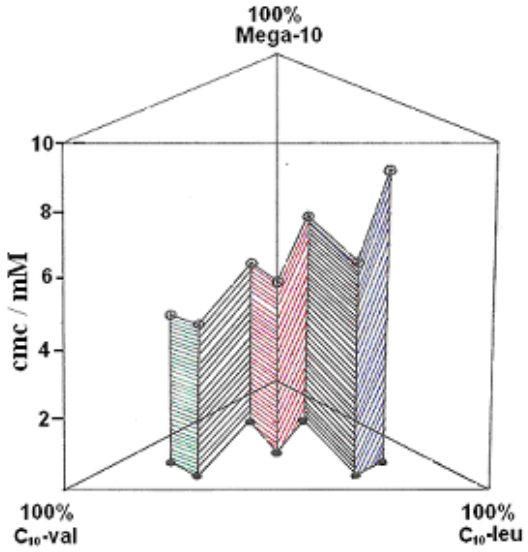

Figure S1. Composition dependent cmc values of C_{10}-val / C_{10}-leu / Mega-10 ternary mixtures

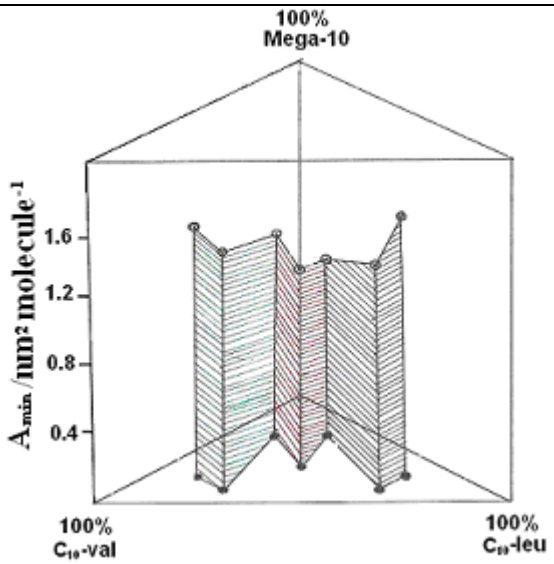

Figure S2. Composition dependent A_{min} values of C_{10}-val / C_{10}-leu / Mega-10 ternary mixtures

Table S1. Surface and thermodynamic properties of binary mixtures of C_{10}-leu / Mega-10 and C_{10}-val / C_{10}-leu in tris-buffer medium (pH = 9) at 298 K

$X_{C_{10}-val}$ / $X_{C_{10}-leu}$ /	cmc / (mM)	$10^6 \Gamma_{max}$ / mol m^{-2}	A_{min} / nm^2 molecule^{-1}	A^i_{min} / nm^2 molecule^{-1}	γ_{cmc} / mN m^{-1}	pC_{20}	$\frac{cmc}{C_{20}}$	Π_{cmc} / mN m^{-1}	$-\Delta G^0_m$ / kJ mol^{-1}	$-\Delta G^0_{ads}$ / kJ mol^{-1}
C_{10}-leu / Mega-10										
0	4.63	4.27	0.39	-	27.9	3.47	12.6	42.4	23.3	33.2
0.1	4.80	3.66	0.45	0.65	27.1	3.49	14.8	42.6	23.2	34.8
0.3	5.33	3.03	0.55	0.68	25.9	3.52	17.7	43.1	22.9	37.1
0.5	5.82	2.96	0.56	0.70	25.5	3.40	14.6	43.9	22.7	37.5
0.7	7.18	2.38	0.70	0.74	25.9	3.36	16.5	43.1	22.2	40.3
0.9	9.53	2.30	0.72	0.80	27.2	3.17	14.1	43.5	21.5	40.4
1	13.8	1.74	0.95	-	31.5	3.03	14.7	39.0	20.6	43.0
C_{10}-val / C_{10}-leu										
0	13.8	1.74	0.95	-	31.5	3.03	14.7	39.0	20.6	43.0
0.1	14.0	1.81	0.92	0.85	26.8	2.98	13.4	41.5	20.5	43.4
0.3	14.7	1.76	0.94	0.84	26.2	3.01	15.0	42.3	20.4	44.4
0.5	15.1	1.81	0.92	0.83	25.3	2.96	14.2	41.6	20.3	43.3
0.7	15.9	1.79	0.93	0.82	26.1	2.98	15.2	42.0	20.2	43.7
0.9	16.5	1.81	0.92	0.81	26.7	2.97	15.4	43.2	20.1	43.3
1	16.9	2.11	0.79	-	29.4	2.80	10.9	40.9	20.1	39.5

Table S2. Aggregation number, Stern-Volmer constant, micropolarity, hydrodynamic diameter and diffusion coefficients of binary mixtures of C_{10}-val / Mega-10 and C_{10}-val / C_{10}-leu in tris-buffer medium (pH = 9) at 298 K

$X_{C_{10}-val} / X_{C_{10}-leu}$	$N_{agg}^{obs} / N_{agg}^{cal}$	$10^4 \times K_{SV}$ / L mol^{-1}	I_1 / I_3	D_h / nm (PDI)	$D_0 \times 10^{11}$ m^2 / s
C_{10}-val / Mega-10					
0	91	2.35	0.84	6.3 0(0.28)	7.78
0.1	94/90	2.56	0.83	3.71 (0.26)	13.2
0.3	83/89	2.20	0.81	2.72 (0.31)	18.1
0.5	82/88	2.17	0.80	2.67 (0.27)	18.4
0.7	89/86	2.50	0.78	2.67 (0.22)	18.4
0.9	87/85	2.54	0.77	2.56 (0.34)	19.2
1	84	2.43	0.76	2.33 (0.37)	21.1
C_{10}-val / C_{10}-leu					
0	52	1.67	0.72	2.60 (0.21)	18.9
0.1	57/55	1.73	0.73	2.33 (0.34)	21.1
0.3	65/62	1.89	0.73	2.33(0.31)	21.1
0.5	69/68	2.11	0.74	2.33 (0.20)	21.1
0.7	72/74	2.21	0.75	2.43 (0.29)	20.2
0.9	75/81	2.36	0.76	2.33 (0.24)	21.1
1	84	2.43	0.76	2.33 (0.37)	21.1

Table S3. Micellar compositions ($X_{\mathrm{M}} / X_{\mathrm{R}} / X_{\mathrm{I}}^{\sigma}$), interaction parameters ($\beta_{\mathrm{R}} / \beta^{\sigma}$), activity coefficients (f_{R}) and cmc's of binary mixtures at 298 K by Motomura, Rubingh and Rosen methods at different stoichiometric compositions (X_i) of C_{10}-leu / Mega-10 and C_{10}-val/ C_{10}-leu.

C_{10}-leu / Mega-10					
$X_{\mathrm{C_{10}-leu}}$	$X_{\mathrm{M}} / X_{\mathrm{R}} / X_{\mathrm{I}}^{\sigma}$	$\beta_{\mathrm{R}} / \beta^{\sigma}$	$f_{\mathrm{R}}^{\mathrm{C_{10}-leu}}$	$f_{\mathrm{R}}^{\text{Mega-10}}$	cmc / mM Obsd/Clint
0.1	0.01/0.06/0.46	-0.70/-8.99	0.54	1.00	4.80/4.96
0.3	0.20/0.18/0.52	-0.63/-6.42	0.65	0.98	5.33/5.78
0.5	0.27/0.32/0.56	-0.75/-5.18	0.71	0.93	5.82/6.91
0.7	0.41/0.46/0.63	-0.85/-3.86	0.78	0.83	7.18/8.64
0.9	0.81/0.68/0.74	-0.92/-2.60	0.91	0.65	9.53/11.5
C_{10}-val/ C_{10}-leu					
$X_{\mathrm{C_{10}-val}}$	$X_{\mathrm{M}} / X_{\mathrm{R}} / X_{\mathrm{I}}^{\sigma}$	$\beta_{\mathrm{R}} / \beta^{\sigma}$	$f_{\mathrm{R}}^{\mathrm{C_{10}-val}}$	$f_{\mathrm{R}}^{\mathrm{C_{10}-leu}}$	cmc / mM Obsd/Clint
0.1	0.08/0.08/0.60	0.006/-12.65	1.00	1.00	14.0/14.0
0.3	0.26/0.26/0.67	0.025/-8.50	1.01	1.00	14.7/14.6
0.5	0.45/0.45/0.72	-0.028/-6.13	0.99	0.99	15.1/15.2
0.7	0.65/0.66/0.79	0.011/-3.96	1.00	1.00	15.9/15.8
0.9	0.88/0.88/0.89	-0.021/-1.64	1.00	0.98	16.5/16.6

Motomura theory for the calculation of micellar mole fraction of a surfactant in the mixed micelle (X_M)

The basic equation has the following form[31]

$$X_M = \hat{X}_1 - (\hat{X}_1 \hat{X}_2 / \hat{C}_{\mathrm{m}}) \left(\frac{\partial \hat{C}_{\mathrm{m}}}{\partial \hat{X}_1} \right)_{\mathrm{P,T}} \qquad (1)$$

where, $\hat{X}_1 = \dfrac{v_2 X_1}{v_1 X_1 + v_2 X_2}$

and $\hat{C}_{\mathrm{m}} = (v_1 X_1 + v_2 X_2) C_{\mathrm{m}}$

The subscripts 1 and 2 denote surfactants 1 and 2 respectively; X_i denotes the stoichiometric mole fraction; v represents the number of ions dissociated by a surfactant; X_M presents the mole fraction of a surfactant in the mixed micelle and $\hat{C}_{\mathrm{m}}$ is the cmc of the mixture. Then the determination of $\left(\frac{\partial \hat{C}_m}{\partial \hat{X}_1}\right)$ from the plot of $\hat{C}_{\mathrm{m}}$ vs $\hat{X}_1$, leads to the evaluation of X_M.

Maeda theory for the calculation of excess free energy of the ionic-nonionic mixed micelle (g^{ex})

$X_{\mathrm{m_I}}$ can be calculated from the plot of $\ln C_{\mathrm{m}}$ vs X_{I} using the equation

$$X_{\mathrm{m_I}} = \frac{X_{\mathrm{I}}[1-(1-X_{\mathrm{I}})(d\ln C_{\mathrm{m}}/dX_{\mathrm{I}})]}{[1+v(1-X_{\mathrm{I}})\{X_{\mathrm{I}}(d\ln C_{\mathrm{m}}/dX_{\mathrm{I}})+1\}]} \quad (2)$$

Due to the presence of excess amount of salt, the degree of counterion binding (v) is negligible in our study. Then equation 2 becomes

$$X_{\mathrm{m_I}(v=0)} = X_{\mathrm{I}}[1-(1-X_{\mathrm{I}})(d\ln C_{\mathrm{m}}/dX_{\mathrm{I}})] \quad (3)$$

The activity coefficients of the ionic and nonionic surfactants are given by

$$X_{\mathrm{I}} = X_{\mathrm{m_I}} f_{\mathrm{I}} = X_{\mathrm{I}} \frac{C_{\mathrm{m}}}{C_{\mathrm{N}}}$$

and

$$X_{\mathrm{N}} = (1-X_{\mathrm{m_I}})\, f_{\mathrm{N}} = (1-X_{\mathrm{I}}) \frac{C_{\mathrm{m}}}{C_{\mathrm{N}}}$$

Nagarajan's theory for the calculation of cmc and different free energy contributions to the total free energy

The total free energy of transfer $\left(\frac{\Delta\mu_g^0}{kT}\right)_{\mathrm{T}}$ is the sum of transfer free energy for the methyl and methylene group in the surfactant tail from solution to the aggregate core.

The transfer free energy for the methyl and methylene group in the surfactant tail as a function of temperature can be written as

$$\left(\frac{\Delta\mu_g^0}{kT}\right)_{tr} = 5.85\ln T + \frac{896}{T} - 36.15 - 0.0056T \quad \text{for} \quad -CH_2 \quad \text{group and} \tag{4}$$

$$\left(\frac{\Delta\mu_g^0}{kT}\right)_{tr} = 3.38\ln T + \frac{4064}{T} - 44.13 - 0.02595T \quad \text{for } -CH_3 \text{ group.} \tag{5}$$

The interfacial $\left(\frac{\Delta\mu_g^0}{kT}\right)_I$ and head group $\left(\frac{\Delta\mu_g^0}{kT}\right)_H$ contributions were calculated by following Tanford's rationale[1]

$$\left(\frac{\Delta\mu_g^0}{kT}\right)_I = \left(\frac{\sigma_{agg}}{kT}\right)a_e \tag{6}$$

and

$$\left(\frac{\Delta\mu_g^0}{kT}\right)_H = \left(\frac{\alpha}{kT}\right)\frac{1}{a_e} \tag{7}$$

where, σ_{agg} is the aggregate core-water interfacial tension, a_e is the area per surfactant monomer at the interface of the aggregate core and α is the head group repulsion parameter ($\alpha = \sigma_{agg}\, a_e^2$), which accounts for the electrostatic interaction between the ionic head groups. σ_{agg} is calculated from the surface tension of surfactant tail (σ_S) and water (σ_W). The expressions of σ_{agg}, σ_S and σ_W are given below

$$\sigma_{agg} = \sigma_S + \sigma_W - 2\psi(\sigma_S\sigma_W)^{1/2} \tag{8}$$

$$\sigma_S = 35.0 - 325M^{-2/3} - 0.098(T - 298) \tag{9}$$

$$\text{and } \sigma_W = 72.0 - 0.16(T - 298) \tag{10}$$

where, ψ is constant with a value of 0.55 for water, M is the molecular weight of the surfactant tail and T is in Kelvin.

The expression of a_e is given by

$$a_e = \left[\frac{2\pi e^2 d}{\varepsilon \sigma_{agg}} \frac{1}{1+\kappa l_0} \right]^{1/2} \tag{11}$$

where, e is the electronic charge (4.8×10^{-10} esu), d is the capacitor thickness in the double layer model, ε is the dielectric constant of the solvent medium (78.21 for water at 298 K), κ^{-1} is the Debye length depending on the ionic strength of the solution and l_0 is the extended tail length per surfactant monomer and is obtained from Tanford's equation,

$$l_0 \le l_{max} \approx (0.154 + 0.1265\, n_c) \tag{12}$$

where, n_c is the number of carbon atom in the surfactant tail.

According to Israelachvili,[2] the geometry of the micellar aggregate can be predicted from the packing parameter, P which can be expressed as

$$P = \frac{v_0}{a_e l_0} \tag{13}$$

where, v_0 is the volume of exclusion per surfactant molecule in the aggregate and is given by Tanford's equation as

$$v_0 \approx (0.0274 + 0.0269\, n_c) \tag{14}$$

The structure of the aggregate will be spherical when $P < 1/3$, non spherical when $1/3 < P < 1/2$, vesicles or bilayers when $1/2 < P < 1$ or inverted structures when $P > 1$.

Assuming the tail to deform nonuniformly,[3] the packing free energy can be calculated from

$$\left(\frac{\Delta\mu_g^0}{kT} \right)_P = \frac{Q}{a_e'^2} \tag{15}$$

with $Q_{sph} = \left(\frac{27}{8}\right) v_0 L$, $Q_{cyl} = \left(\frac{20}{8}\right) v_0 L$, $Q_{bilayer} = \left(\frac{10}{8}\right) v_0 L$ and a_e' is given by

$$a_e' = \left(\frac{\alpha}{\sigma_{agg}} + \frac{2Q/a_e}{\sigma_{agg}/kT} \right)^{1/2} \tag{16}$$

where, Q is used to denote the coefficient of $1/a_e'^2$ in the free energy expression and it stands for Q_{sph}, Q_{cyl} and $Q_{bilayer}$ depending upon the aggregate shape. L is the length per unit segment and its value is 4.6Å.

References

1. C. Tanford *in* "The Hydrophobic Effect: Formation of Micelles and Biological Membranes", Wiley and Sons: New York, 1980.

2. J. N. Israelachvili. Intermolecular and surface force; Academic Press: London, second edition, 1991, Chapter 17, p.370.

3. A. N. Semenov, *Soviet Phys. JETP*, 1985, **61**, 733.