Spontaneous Formation of Nano Cubic Particles and Spherical Vesicles in Catanionic Mixtures of Ester-containing Gemini Surfactants and Sodium Dodecyl Sulfate in Presence of Electrolyte

Hasti Aghdastinat[a] , Soheila Javadian*,[a] , Alireza Tehrani-Bagha[b,c] , Hussein Gharibi [a]

[a] Department of Physical Chemistry, Tarbiat Modares University, P.O. Box 14115-117, Tehran, Iran.

[b] Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden.

[c] Institute for Color Science and Technology, Tehran, Iran.

* **Corresponding author**: Soheila Javadian, Department of Physical Chemistry, Tarbiat Modares University, P.O. Box 14115-117, Tehran, Iran. Tel: 98 21 82883477, Fax: 98 21 82883455, email: javadian_s@modares.ac.ir.

S1. Theory

The surface excess concentration (Γ_{max}, mol.m^{-2}) of a surfactant is a measure of adsorption at the air/water interface. The surface excess (Γ_{max}) and the minimum area per molecule (A_{min}) were calculated using the Gibbs adsorption equation:

$$\Gamma_{max} / mol.m^{-2} = \frac{-1}{2.303\, nR\, T} \left(\frac{d\gamma}{d\, log\, C} \right)_{T,P} \tag{1}$$

and

$$A_{min}/nm^2.molecule^{-1} = \frac{10^{18}}{N_A \Gamma_{max}} \tag{2}$$

Where R, T, C, and N_A are the gas constant, absolute temperature, surfactant concentration and Avogadro's constant, respectively. n is the number of species formed in the solution by the dissociation of the surfactant molecules. For mixture of two different surfactants, the value of n for the mixture, $n_{mix} = n_1 Z_1 + n_2 Z_2$, where n_1 and n_2 are the values for individual surfactants 1 and 2 and Z_1 and Z_2 are their respective mole fractions at the interface.[1]

The surface activity, pC_{20}, is an index of surface tension reduction efficiency:

$$pC_{20} = -log\, C_{20} \tag{3}$$

C_{20} is the molar concentration of surfactant required to reduce the surface tension of the solvent by 20 mN.m^{-1}.

The surface pressures π_{CMC} were calculated from

$$\pi_{CMC} = \gamma_\circ - \gamma_{CMC} \tag{4}$$

Where $\gamma_\circ$ is the surface tension of the solvent (i.e. here water) and γ_{CMC} is the surface tension of the solution at CMC.

Applying the mass action law, the Gibbs free energy of micellization has been derived for the gemini surfactants as follows:

$$\Delta G°_{mic} /(kJ.mol^{-1}) = RT\, (1.5 - \alpha_{diss})\, \ln X_{CMC} \tag{5}$$

Where X_{CMC} is the CMC value on the mole fraction scale and α_{diss} is the degree of counterion dissociation.

The standard free energy of adsorption ($\Delta G°_{ads}$) for surfactants at the air/solution interface was also calculated by the equation (6):

$$\Delta G°_{ads}/(kJ.mol^{-1}) = \Delta G°_{mic} - \left(\frac{\Pi_{CMC}}{\Gamma_{max}}\right) \tag{6}$$

The nature and the strength of the interactions between two surfactants in binary systems can be determined by calculating interaction parameter, β, which can be obtained using the regular solution model developed by Rubingh et al.[2-3]

The interaction parameter for mixed micelle in an aqueous medium, β^M, is calculated using the following equations:

$$\frac{(X_1)^2 \ln(\alpha_1 C_{12}^M / X_1 C_1^M)}{(1-X_1)^2 \ln\left[(1-\alpha_1)\right]C_{12}^M /(1-X_1)C_2^M} = 1 \tag{7}$$

$$\beta^M = \frac{\ln\left[\alpha_1 C_{12}^M / X_1 C_1^M\right]}{(1-X_1)^2} \tag{8}$$

Where X_1 is the mole fraction of SDS in the mixed micelle and C_1^M, C_2^M and C_{12}^M are the CMCs for surfactant 1, surfactant 2 and their mixture, respectively, at the mole fraction α_1.

The activity coefficients of SDS (f_1) and gemini surfactant (f_2) within micelles were calculated by following equations using the micelle mole fraction, X_1, obtained by the Rubingh method:

$$f_1 = \exp[\beta(1-X_1)^2] \tag{9}$$

$$f_2 = \exp[\beta(X_1)^2] \tag{10}$$

The interaction parameter for mixed monolayer at the aqueous solution/air interface, β^σ, is calculated using the following equations:

$$\frac{Z_1^2 \ln(\alpha_1 C_{12} Z_1 C_1^0)}{(1-Z_1)^2 \ln\left[(1-\alpha_1)\right]C_{12} /(1-Z_1)C_2^0} = 1 \tag{11}$$

$$\beta^\sigma = \frac{\ln(\alpha_1 C_{12} / Z_1 C_1^0)}{(1-Z_1)^2} \tag{12}$$

Where Z_1 is the mole fraction of surfactant 1 in the total mixed monolayer (on a surfactant-only basis); and C_1^0, C_2^0 and C_{12} are the molar concentrations of surfactant 1, surfactant 2, and their mixture, respectively, in the solution phases required to produce a given surface tension value at the mole fraction α_1 of surfactant 1. Equation (11) is solved numerically for Z_1, which is then substituted into equation (12) to calculate β^σ.

The ideal mixing minimum area per molecule, A_{ideal}, calculated from the equation:

$$A_{ideal} = Z_1 A_1 + (1 - Z_1) A_2 \tag{13}$$

Where Z_1 is the mole fraction of SDS in the mixed monolayer, and A_1 and A_2 are the minimum area per molecule of SDS and geminis, respectively.

The G_{mic}^{ex} values have been estimated using equation (14) and the values of activity coefficients, f_1 and f_2 calculated using equations (9) and (10), respectively.

$$G_{mic}^{ex} = RT[X_1 \ln f_1 + (1 - X_1) \ln f_2] \tag{14}$$

The experimental G_{mic}^{ex} values have also been calculated from:

$$G_{mic}^{ex} = \Delta G_{mic,mix}^0 - [X_1 \Delta G_{mic,1}^0 + (1 - X_1) \Delta G_{mic,2}^0] \tag{15}$$

Where $\Delta G_{mic,1}^0$ and $\Delta G_{mic,2}^0$ are the micellization Gibbs free energy of surfactant1 and 2, respectively.

In CV, the peak current i_{pa} for a redox-active reversible system is given by the Randles–Sevcik equation:

$$i_{pa} = 0.4463 \, FACn \, (\frac{nF \nu D_{agg}}{RT})^{\frac{1}{2}} \tag{16}$$

Where n is the number of electrons involved in oxidation or reduction, F is Faraday's constant, A is the area of the electrode, D_{agg} is the diffusion coefficient of the ferrocene probe, C is the concentration of the ferrocene in the solution, R is the gas constant, T is the absolute temperature, and ν is the scan rate.

At concentrations above but not far from the CMC, aggregates mutually interact; consequently, the calculated values for diffusion coefficients are lower than those at the CMC. The linear interaction theory was used to calculate the interparticle interaction parameter, k_d:

$$D_{agg} = D_{agg}^0 [1 - k_d (C_s - CMC)] \tag{17}$$

Where D_{agg}^0 is the self-diffusion coefficient in the absence of particle interaction (infinite dilution), and C_s is the surfactant concentration.

In CV measurements, the mean hydrodynamic radius (R_h), was determined by the Stokes–Einstein equation:

$$R_h = \frac{kT}{6\pi\eta D_{agg}} \tag{18}$$

Where k, T and η are the Boltzmann constant, absolute temperature and viscosity of medium, respectively.

The packing parameter, p, is:[1]

$$p = V_H / l_c a_0 \tag{19}$$

Where V_H is the volume occupied by the hydrophobic portion of the surfactant in the micellar core, l_c is the length of its hydrophobic portion in the core, and a_0 is the cross-sectional area occupied by its hydrophilic portion at the micelle-solution interface.

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3.   Schulz, P. C.; Rodríguez, J. L.; Minardi, R. M.; Sierra, M. B.; Morini, M. A., Are the mixtures of homologous surfactants ideal? *J. Colloid Interface Sci.* **2006,** *303*, 264-271.
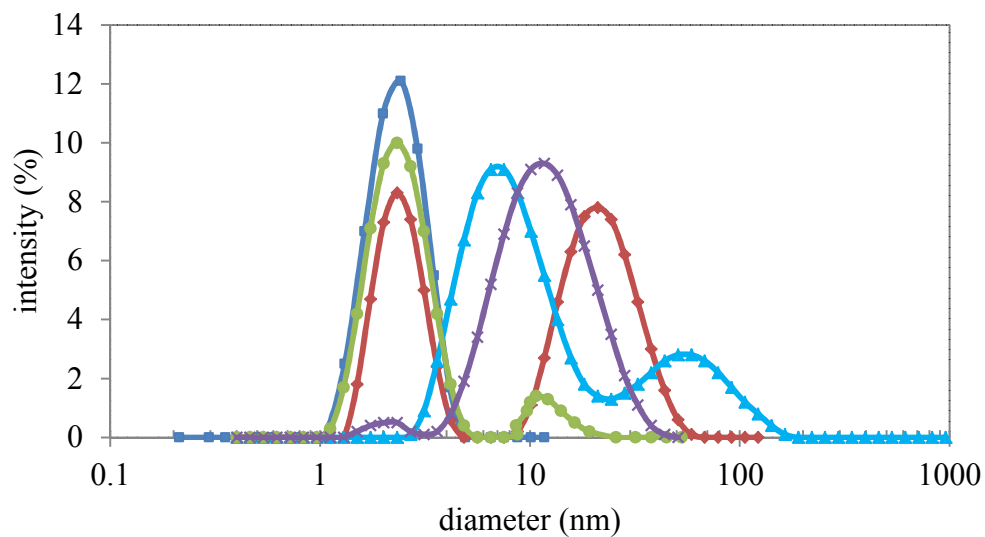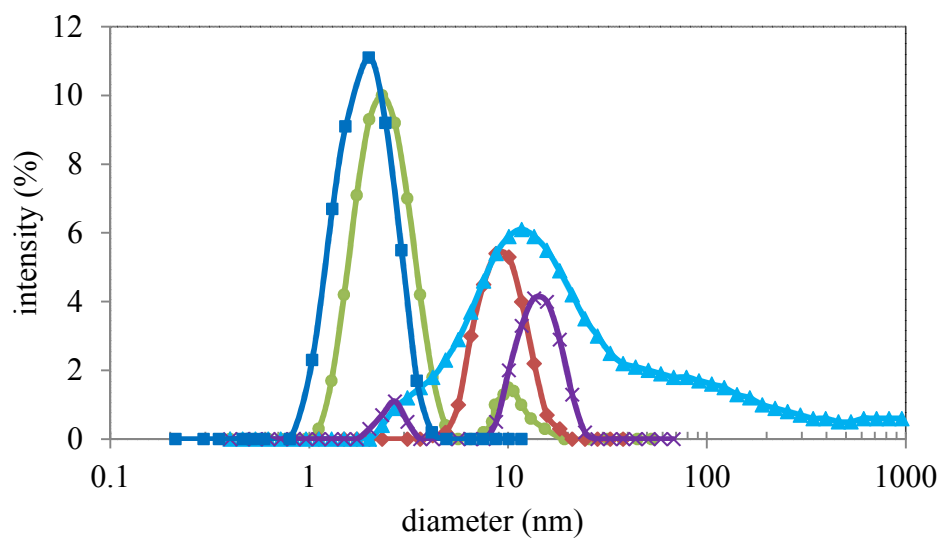
(a)

(b)

Figure S1: Phase behavior of (a) esterquat gemini and (b) betainate gemini at various mole fractions of SDS.

(a)

(b)

Figure S2: Size distribution of gemini surfactants and mixed systems in the absence of KCl at: (a) [C_{tot}]= 15 mM, (b) [C_{tot}]= 5 mM (■) pure esterquat gemini, (◆) esterquat gemini/SDS (α_{SDS}=0.1), (▲) esterquat gemini/SDS (α_{SDS}=0.2), (● pure betainate gemini, (×) betainate gemini/SDS (α_{SDS}=0.1).

Table S1. The Viscosity of solutions in the presence of 0.05 M KCl and at 298K.

[C_{tot}] (mM)	System	Viscosity (cP)
5	esterquat gemini	1.27
15	esterquat gemini	1.31
5	betainate gemini	1.11
20	betainate gemini	2.82
5	esterquat gemini/SDS α_{SDS}=0.1	1.31
15	esterquat gemini/SDS α_{SDS}=0.1	1.93
5	betainate gemini/SDS α_{SDS}=0.1	1.22
15	betainate gemini/SDS α_{SDS}=0.1	2.11