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Interactions between *N*-tetradecyl-*N*,*N*-dimethyl-*N*-(2,3-epoxypropyl) ammonium chloride and some surfactants

Jialin Zheng[a], Jing Zhao[a], Yan Li[a, *], Zhen Chen[b], Ling Wang[b], Xiaodeng Yang[a, *] & Guoqin Li[b]

[a]Key Laboratory of Fine Chemicals (Shandong Province), Qilu University of Technology,
Shandong Academy of Science, Ji'nan 250353, PR China

[b]The 1st Industrial Research Laboratory, Shandong Economy and Information Technology Institute,
Ji'nan 250013, PR China

Email: liyan2554666@163.com (YL)/ yangxiaodeng@qlu.edu.cn (XY)

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The interactions between the reactive cationic surfactant, *N*-tetradecyl-*N*,*N*-dimethyl-*N*-(2,3-epoxy propyl) ammonium chloride (TDEAC) and common surfactants, i.e., sodium dodecyl sulfate (SDS) sodium dodecyl sulfonate (AS), dodecyltrimethylammonium chloride (DTAC) and *N*, *N*-dimethyldodecylamine oxide (C_{12}DMAO) are studied through surface tension, conductivity, steady-state fluorescence and dynamic light scattering as well as Rubingh regular solution methods. The calculated values of cmc, γ_{cmc}, $p\mathrm{c}_{20}$, π_{cmc}, $\Gamma_{\max}$, and $A_{\min}$ indicate a strong synergistic effect between TDEAC and SDS (and AS) as compared with the relatively weak interaction of TDEAC with DTAC (and C_{12}DMAO). The cmcs of the mixed surfactant systems vary with temperature. Thermodynamic parameters calculated from conductivity data show that the micellization of TDEAC/SDS (AS) mixed systems is a spontaneous and exothermic process. Data from steady-state fluorescence, dynamic light scattering and Rubingh's regular solution approach, confirm the strong interaction between surfactants.

Keywords: Solution chemistry, Surface properties, Thermodynamic parameters, Surfactants, Cationic surfactants, Mixed surfactants

Cationic surfactants are a class of important amphiphilic molecules, with good bactericidal properties, adsorption capacity, water solubility, and chemical stability[1]. They are widely used in soil remediation[2,3], enhanced oil recovery[4], drug delivery[5,6], food industry[7], nanosized material preparation[8], and as micellar catalysts[9,10], etc. Surfactants, with special functional groups including ester[11], ether[12], epoxy[13], amino/amine[14], and amino acid[15], groups have attracted a great deal of attention, for their different physico-chemical properties.

The introduction of an ester group decreased the thermal stability of 3-methyl-1-alkyloxy-carbonylmethyl imidazolium bromides and 1-alkyloxy-carbonylmethyl pyridinium bromides, and enhanced their antibacterial activities as compared to their corresponding homologues[16]. The position and number of ester group also affect surfactant properties including solubility, aggregation behavior, micellization thermodynamic parameters, interface absorbing and their application[17,18]. Ester-functionalized surfactants could also interact with proteins, such as hen white egg lysozyme, bovine serum albumin and bovine milk xanthine oxidase, destroying their secondary structures through docking into their cavity[19,20].

The ether group increased the solubility and pH sensitivity of the solution, but decreased the surface activity[21]. N-Cetyl-N,N-dihydroxy-ethylammonium bromide formed denser molecular packing by forming multiple intermolecular hydrogen bonds with different aqueous pH, forming pH sensitive molecular self-assemblies[22]. Mao *et al.*[2] reported that macrocyclic compounds such as crown ether, cyclodextrin and calixarene-based surfactants had good washing performances on radionuclides-contaminated soils, radioactive waste, and superior selectivity of radioactive cesium compounds extraction.

Amine-based surfactants are reported to exhibit pH-responsivity, reversibility and high thermosensitivity[23]. Wu *et al.*[14] found that the amino group-terminated reductively cleavable surfactants showed selective cytotoxicity to cancerous cells and binding affinity on the surface of poly(D,L-lactide-coglycolide) nanoparticles. Amide functionalized piperazinium surfactant and *N*-alkylcaramoylmethyl-*N*-[2-(2-phenoxyacetamido)-ethyl]-*N*,*N*-dimethylammonium chloride possessed good DNA binding affinity, less cytotoxicity on C6 glioma cells and high antimicrobial activities[24-26]. These characteristics made amido-functionalized surfactants a potential sterilizing and targeted, safe and efficient chemotherapeutic candidate. Amino acid-based gemini surfactant derived from cysteine was also pH-sensitive and showed affinity to bovine serum albumin (BSA) through electrostatic interactions with specific sites, unfolding the secondary structure of BSA[15].

The epoxy group and epoxy-functionalized compounds have attracted much attention for decades for their high reactivity[27,28]. It was found that the epoxy group was a more suitable functional group for covalent bonding with hydroxyl or amino groups in the matrix and gave the compounds fascinating properties in potential utilization[29]. Epoxy-functionalized photochromic latex modified cellulose showed stimuli-responsibility[30,31]. Epoxy terminated polydimethylsiloxane modified gelatin improved the flexibility and hydrophobicity of gelatin-based materials[32-34]. However, the synthesis and physicochemical properties of epoxy-functionalized surfactants are scarcely reported.

In this study, the interactions between epoxy-functionalized cationic surfactant, N-tetradecyl-N,N-dimethyl-N-(2,3-epoxy propyl) ammonium chloride (TDEAC), and, dodecyltrimethylammonium chloride (DTAC), sodium dodecyl sulfate (SDS), sodium dodecyl sulfonate (AS), and N,N-dimethyl-dodecylamine oxide (C_{12}DMAO) were investigated by surface tension, conductivity, steady-state fluorescence, and dynamic light scattering methods. The surface activity, aggregation behavior and micellar thermodynamics of the mixed system were studied. The Rubingh regular solution model was used to predict the critical micelle concentration and the micelle composition of mixed system.

Materials and Methods

N-Tetradecyl-N,N-dimethyl-N-(2,3-epoxypropyl) ammonium chloride (TDEAC) was synthesized in our laboratory by literature method[35], and freeze-dried for 48 h before utilization. Sodium dodecyl sulfate (SDS), sodium dodecyl sulfonate (AS), and dodecyltrimethylammonium chloride (DTAC) (all A.R.) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). N,N-dimethyl-dodecylamine oxide (C_{12}DMAO) (30 wt% aqueous solution), purchased from Shandong Panze Chemical Technology Co. Ltd., was freeze-dried and then recrystallized three times with acetone. Triply distilled water was used for the experiments.

Surface activity

Surface tensions of TDEAC, SDS, AS, DTAC, C_{12}DMAO, and TDEAC/SDS (AS, DTAC, C_{12}DMAO) mixed solutions with different molar ratios were measured using the single-measurement ring method on a Krüss K-100 tensiometer. After the solutions were equilibrated for 15 mins, the temperature was controlled with a HAAKE DC 30 thermostatic bath (Karlsruhe, Germany). Each measurement was repeated three times and the values were averaged.

Conductivity and aggregate size

Conductivity of TDEAC and its binary solutions were measured as a function of concentration with a low-frequency conductivity analyzer (DDS-307, Shanghai Precision and Scientific Instrument Co. Ltd.) at 25, 30, 35, 40 and 45 ºC. Each measurement was repeated three times and the results were averaged.

The aggregate size was determined using a Nano-Zeta Sizer 90 (ZEN3690, Malvern Instruments Limited). The scattering angle was 90º, equilibration time was 120 min, and measuring temperature was 25 ºC. All surfactant solutions were filtered with a 0.2 μm Millipore filter, and their concentrations were fixed at a value of three times their cmc.

Steady state fluorescence

The steady-state fluorescence measurements were made on a Hitachi F-4600 fluorescence spectrophotometer using a 1.0 cm quartz cell at room temperature. Pyrene was used as the fluorescence probe, and the concentration was fixed at 1.0×10^{-6} mol/L in all samples. The spectra of pyrene were recorded with a fixed excitation of 335 nm, while the emission spectra were collected from 355-500 nm, keeping both the excitation and emission slit widths as 2.5 nm. The intensity ratio of the peak at 373 nm (I_1) to that at 384 nm (I_3) showed the greatest solvent dependency, and so furnished a method to probe the micropolarity of surfactant aggregates and to obtain the cmc of the surfactant in aqueous solution[36].

Interaction between TDEAC and surfactants

The interaction parameter (β_{12}) between TDEAC and the surfactants SDS, AS, DTAC and C_{12}DMAO, molar fraction of the surfactants in mixed micelles (X_i) and cmc of the mixed system (cmc_{mix}) between TDEAC and the surfactants in mixed micelles were calculated by using Rubingh regular solution model,[37]

$$\frac{X_1^2 \ln(\alpha_1 cmc_{mix}/X_1 cmc_1)}{(1-X_1)^2 \ln[\frac{(1-\alpha_1)cmc_{mix}}{(1-X_1)cmc_2}]} = 1 \qquad \ldots (1)$$

$$\beta_{12} = \frac{\ln(\frac{\alpha_1 cmc_{mix}}{X_1 cmc_1})}{X_2^2} = \frac{\ln(\frac{\alpha_2 cmc_{mix}}{X_2 cmc_2})}{X_1^2} \qquad \ldots (2)$$

where, α_1 is the total molar fraction of surfactant 1 in the mixture, and cmc_1 and cmc_2 are the cmcs of surfactant 1 and surfactant 2.

Results and Discussion

Surface adsorption equilibrium

The surface tensions of TDEAC and mixed systems of TDEAC/SDS (AS, DTAC and C_{12}DMAO) were measured, and the plots of surface tension (γ) versus TDEAC concentration are shown in Fig. 1. With the increase in TDEAC concentration, the surface tension decreased for the adsorption of TDEAC molecules at the air/water interface until a turning point, after which the surface tension kept almost constant. The concentration corresponding to this point is critical micelle concentration (cmc), i.e., the micelles begin to form in aqueous solution and the surface tension (γ_{cmc}) is no longer dependent on DTEAC concentration[38]. The cmc and γ_{cmc} values decreased dramatically with the addition of even a small amount of SDS (or AS, e.g., c_{SDS} = 0.006 mmol/L for n_{SDS}/n_{TDEAC} = 0.2, and c_{SDS} = 0.002 mmol/L for other molar ratios; c_{SDS} = 0.002 mmol/L for all AS/TDEAC mixed systems), compared to the only TDEAC system (Table 1), and with further addition of SDS (or AS), both the values changed only slightly. This indicated the existence of a very strong electrostatic interaction and synergy between the two kind of oppositely charged surfactants[39]. In the binary system of TDEAC and SDS (or AS), double decomposition reaction takes place and the catanionic surfactant (abbreviated as TDEA-DS or TDEA-AS) was produced, which resisted the electrostatic repulsion among the molecules[40] and promoted the formation of

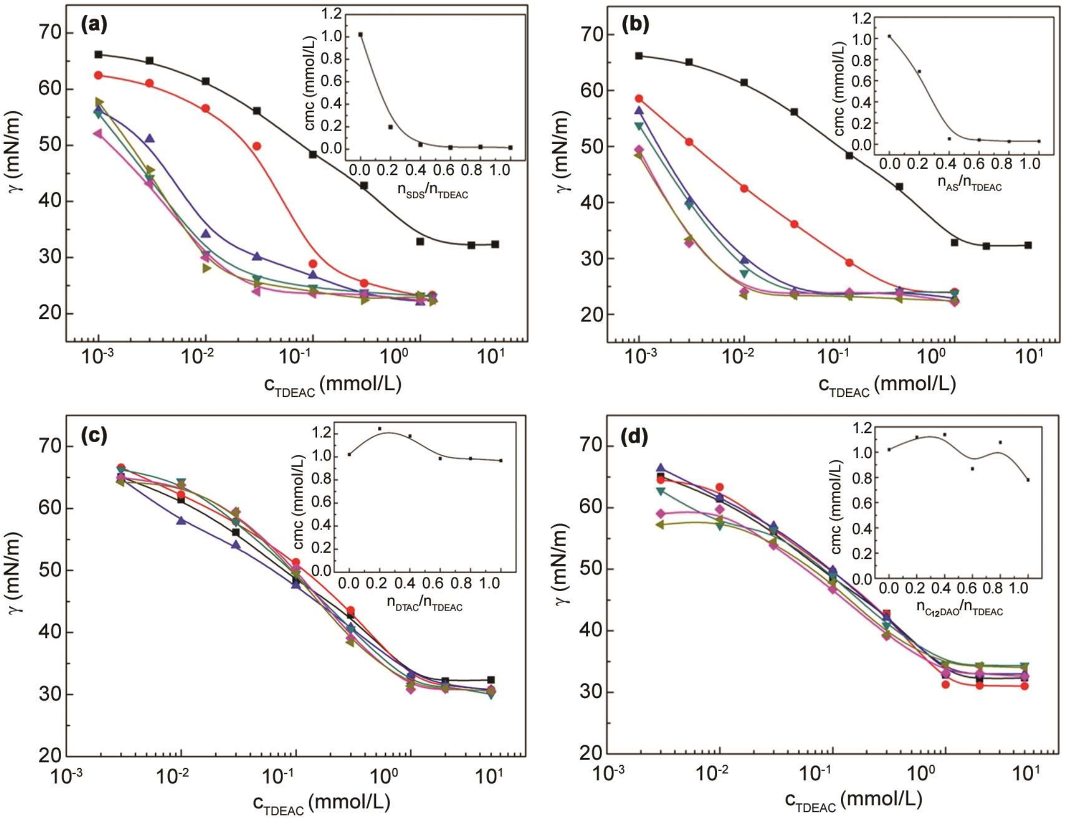

Fig. 1 — Plots of surface tension versus c_{TDEAC} for TDEAC/SDS (AS, DTAC, C_{12}DMAO) mixed systems with molar ratio of 0, 0.2, 0.4, 0.6, 0.8, and 1.0 at 25 ºC. [The insets are the plots of cmc versus molar ratios of surfactants].

Table 1 — Surface properties of TDEAC/SDS (AS, DTAC, C_{12}DMAO) mixed systems with varying molar ratios

Molar ratio	cmc (mmol/L)	γ_{cmc} (mN/m)	π_{cmc} (mN/m)	pc_{20}	Γ_{max} (μmol/m^2)	A_{min} (nm^2)
SDS/TDEAC						
0	1.021±0. 01	33.29±0. 3	37.26±0. 4	1.154±0. 01	3.450±0. 04	0.481±0. 005
0.2	0.197±0.002	25.72±0. 3	41.59±0. 4	1.481±0. 02	1.015±0. 01	1.636±0. 02
0.4	0.040±0.0004	28.08±0. 3	36.19±0. 4	2.328±0. 02	12.51±0. 1	0.133±0. 001
0.6	0.015±0.0002	26.08±0. 3	40.43±0. 4	2.553±0. 03	36.34±0. 4	0.005±0.0005
0.8	0.020±0.0002	24.28±0. 2	41.68±0. 4	2.620±0. 03	44.82±0. 5	0.004±0.0004
1.0	0.014±0.0001	25.56±0. 3	45.41±0. 5	2.638±0. 03	34.88±0. 4	0.005±0.0005
AS/TDEAC						
0.2	0.688±0.007	23.66±0.2	46.94±0.5	1.991±0.02	2.23±0.02	0.744±0.007
0.4	0.051±0.0005	24.46±0.2	46.20±0.5	2.328±0.02	12.66±0.1	0.131±0.001
0.6	0.041±0.0004	23.98±0.2	46.69±0.5	2.409±0.02	92.86±0.9	0.002±0.0002
0.8	0.027±0.0003	24.30±0.2	46.55±0.5	2.569±0.03	56.48±0.6	0.003±0.0003
1.0	0.028±0.0003	23.36±0.2	47.61±0.5	2.620±0.03	58.05±0.6	0.003±0.0003
DTAC/TDEAC						
0.2	1.245±0.01	32.14±0.3	38.13±0.4	0.945±0.01	4.366±0.04	0.380±0.004
0.4	1.180±0.01	32.28±0.3	38.05±0.4	1.226±0.01	3.725±0.04	0.446±0.004
0.6	0.986±0.01	32.72±0.3	37.66±0.4	1.070±0.01	3.478±0.04	0.477±0.005
0.8	0.986±0.01	31.42±0.3	39.08±0.4	1.032±0.01	3.535±0.04	0.470±0.005
1.0	0.967±0.01	31.56±0.3	38.81±0.4	1.055±0.01	3.408±0.03	0.487±0.005
C_{12}DMAO/TDEAC						
0.2	1.118±0.01	31.99±0.3	39.03±0.4	1.109±0.01	3.749±0.04	0.443±0.004
0.4	1.139±0.01	33.01±0.3	37.99±0.4	1.086±0.01	3.740±0.04	0.444±0.004
0.6	0.868±0.009	35.17±0.4	35.82±0.4	1.141±0.01	2.432±0.02	0.683±0.007
0.8	1.077±0.01	32.42±0.3	38.55±0.4	1.298±0.01	2.993±0.03	0.555±0.006
1.0	0.780±0.008	34.44±0.3	36.54±0.4	1.250±0.01	2.067±0.02	0.803±0.008

dense adsorption layer at the air/water interface. With increasing SDS (or AS) concentration, a large amount of TDEA-DS (or TDEA-AS) was produced and the steric hindrance dominated the arrangement of their molecules at the air/water interface, and hence, the γ_{cmc} and cmc were almost constant. Contrarily to the strong synergy between TDEAC and SDS (or AS), DTAC and C_{12}DMAO showed very little impact on the surface tensions of both TDEAC and SDS (or AS) mixed systems.

Surface excess (Γ_{max}), minimum cross-sectional area (A_{min}), calculated from Gibbs ($\Gamma_{max} = -\frac{1}{2RT} \times \frac{d\gamma}{dlnc}$) and derivative equations ($A_{\min} = \frac{10^{24}}{N_A \cdot \Gamma_{\max}}$) are listed in Table 1. Two factors influence the adsorption of catanionic surfactant at the air/water interface: (i) electrically neutral interface principle, i.e., the catanionic surfactant is adsorbed at the air/water interface according to the symmetry principle with equal molar ratio; and, (ii) surfactant with high surface activity is preferentially adsorbed, resulting in asymmetric adsorption of surfactants with different surface activity. The first factor dominates the adsorption at a high surfactant concentration, while the second one plays a major role at a low surfactant concentration[39]. The surface activity of TDEA-DS (or TDEA-AS) is higher than that of TDEAC, and therefore, TDEA-DS (or TDEA-AS) is preferentially adsorbed at the air/water interface and its Γ_{max} is larger than that for TDEAC. The TDEA-DS (or TDEA-AS) occupied a larger sectional area than TDEAC due to steric hindrance among the double hydrocarbon chains. Therefore, the Γ_{max} and A_{min} for catanionic surfactant of TDEA-DS (or TDEA-AS) increase. The Γ_{max} and A_{min} values of TDEAC/DTAC (or C_{12}DMAO) systems are almost consistent with that of TDEAC, indicating weak interaction between the two surfactant molecules.

From surface tension isotherms, we can obtain the surface tension reducing efficiency of a surfactant (pc_{20}, $pc_{20}= -\log c_{20}$) and the surface tension reducing ability of surfactant (π_{cmc}, $\pi_{cmc}=\gamma_0-\gamma_{cmc}$). The higher the two parameters, stronger is the adsorption efficiency and higher is the surface tension reduction effectiveness of the surfactant[41]. The parameters in Table 1 confirm the strong electrostatic interaction and synergy between TDEAC and SDS (or AS), and the weak interaction between TDEAC and DTAC (or C_{12}DMAO).

Conductivity

The conductivity of TDEAC and TDEAC/SDS (AS, C_{12}DMAO) mixed solutions measured at five different temperatures as a function of TDEAC concentration is plotted in Fig. 2. Each curve is composed of two straight lines with two different slopes. The breakpoint corresponds to the cmc. The conductivity below the cmc is due to the contributions of the free ions, while the conductivity above the cmc is due to the micelles, the concentration of which increases slowly with the increase of surfactant concentration due to the binding of some counter ions to the micelles. The cmc values of TDEAC and TDEAC/SDS (AS) mixed systems decrease with increasing temperature and then increase, showing a U-shape (inset in Fig. 2(a), and Fig. 2(b) and 2(c)). The temperature corresponding to the minimum value of cmc increases from ~28 ºC to ~36 ºC with increasing n_{SDS}/n_{TDEAC} from 0.2 to 0.8 (Fig. 2(b)). The temperature corresponding to the minimum cmc value of AS/TDEAC system with molar ratio of 0.6 (~31 ºC) is lower than that of SDS/TDEAC with the same molar ratio (~33 ºC). In contrast to the TDEAC/SDS (AS) system, the cmc value of TDEAC/C_{12}DMAO system increases linearly from 0.0189 mmol/L to 0.0218 mmol/L (R^2 = 0.98) with increasing temperature (Fig. 2(c)).

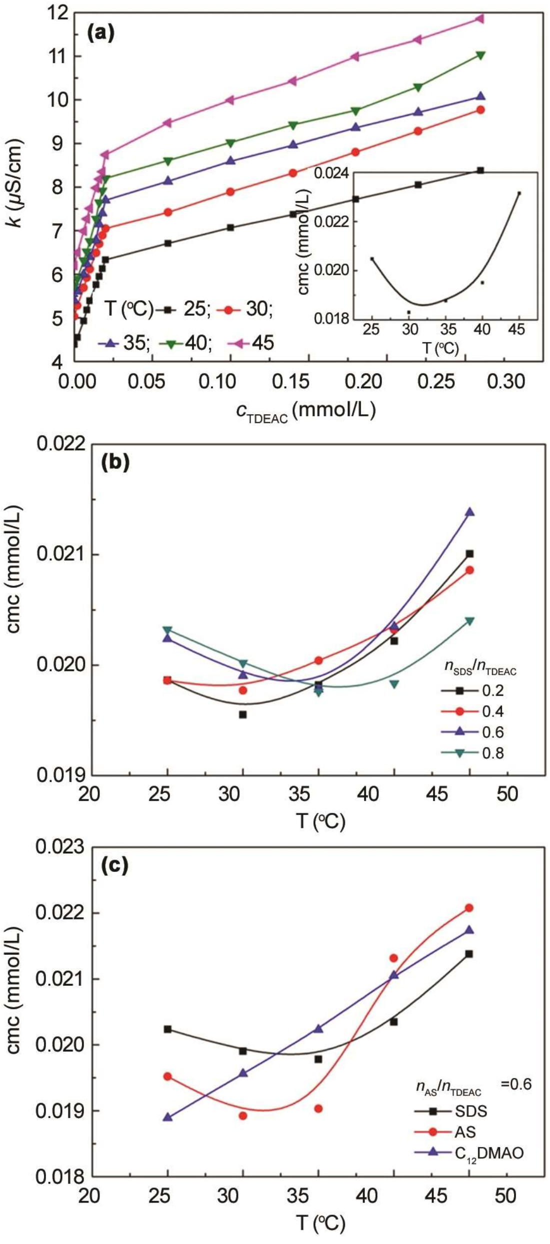

Fig. 2 — (a) Plots of electrical conductivity, *κ*, against c_{TDEAC} at different temperatures. Plots of cmc against temperature for (b) SDS/TDEAC mixed solutions at various molar ratio, and, (c) AS (or C_{12}DMAO)/TDEAC mixed solutions with molar ratio of 0.6.

Usually, temperature influences the cmc of ionic surfactants from two aspects[42]. One is that high temperature reduces the hydration degree of the hydrophilic group, promoting micelle formation. The other is that high temperature destroys the water structures surrounding the hydrophobic chains, hindering micelle formation. It is notable that both the aspects influence the TDEAC/SDS (AS) micellization formation, while the second aspect plays a key role in TDEAC/C_{12}DMAO micellization formation. With increasing temperature, the effect on TDEAC is weaker than that on C_{12}DMAO, inhibiting the formation of TDEAC/C_{12}DMAO micelles.

Thermodynamic parameters

The degree of counter-ion binding to micelles, β, can be obtained from (1-α), where α is the degree of counter-ion dissociation and calculated from the ratio of the slopes of the plots above and below the cmc. The values of β are listed in Table 2. The β values of TDEAC/SDS (AS, C_{12}DMAO) mixed systems are much larger than that of TDEAC due to the strong electrostatic interaction between cationic surfactant and anionic surfactant(s). There are two lone pairs in C_{12}DMAO, therefore, an electrostatic interaction between the two types of molecules could also exist.

Dynamic light scattering studies (Fig. 3) show that there are two types of aggregates in the TDEAC solution, corresponding to the diameters, ~4 nm and

~180 nm. It is similar to the aggregates of dodecyl dimethylammonium bromide in water, which is ascribed to the accumulation of small micelles[43]. The diameters of TDEAC/SDS mixed systems are much larger than that of pure TDEAC due to the reduced electrostatic repulsion between the charged head groups, which results in the accommodation of more surfactant molecules[44]. With $n_{\mathrm{SDS}}/n_{\mathrm{TDEAC}}$ (or $n_{\mathrm{SDS}}/n_{\mathrm{TDEAC}}$) system increasing to 0.4, the large number of accumulated micelles are reflected by one large peak. The diameters of mixed systems with $n_{\mathrm{SDS}}/n_{\mathrm{TDEAC}}$ = 0.4, 0.6 and 0.8 are 295, 342 and 460 nm respectively, which are much larger than those of $n_{\mathrm{SDS}}/n_{\mathrm{TDEAC}}$ = 0.2 system. For $n_{\mathrm{SDS}}/n_{\mathrm{TDEAC}}$ = 0.2,

Table 2 — Micellization parameters for TDEAC/SDS (AS, C_{12}DMAO) mixed systems with different molar ratios

T (ºC)	β	ΔG^0_{m} (kJ/mol)	ΔH^0_{m} (kJ/mol)	$T\Delta S^0_{\mathrm{m}}$ (kJ/mol)
		TDEAC		
25	0.4368±0.004	-32.25±0.3	9.76±0.1	42.01±0.4
30	0.4502±0.005	-33.03±0.3	-13.39±0.1	19.64±0.2
35	0.4675±0.005	-37.14±0.4	-33.31±0.3	3.83±0.04
40	0.4438±0.004	-35.06±0.4	-34.06±0.3	1.00±0.01
45	0.4015±0.004	-34.36±0.3	-35.37±0.4	-1.01±0.01
		$n_{\mathrm{SDS}}/n_{\mathrm{TDEAC}}$ = 0.2		
25	0.7044±0.007	-62.72±0.6	1.81±0.02	64.53±0.6
30	0.6786±0.007	-62.85±0.6	-6.15±0.0	56.70±0.6
35	0.7249±0.007	-65.30±0.7	-7.34±0.0	57.96±0.6
40	0.7204±0.007	-66.34±0.7	-8.40±0.08	57.94±0.6
45	0.6879±0.007	-65.91±0.7	-9.53±0.1	56.38±0.6
		$n_{\mathrm{SDS}}/n_{\mathrm{TDEAC}}$ = 0.4		
25	0.8112±0.008	-63.65±0.6	1.31±0.01	64.96±0.6
30	0.8197±0.008	-64.46±0.6	-3.13±0.03	61.33±0.6
35	0.8035±0.008	-65.21±0.7	-5.82±0.06	59.39±0.6
40	0.7981±0.008	-66.23±0.7	-10.06±0.1	56.17±0.6
45	0.7866±0.008	-66.04±0.7	-10.75±0.1	55.29±0.6
		$n_{\mathrm{SDS}}/n_{\mathrm{TDEAC}}$ = 0.6		
25	0.9078±0.009	-65.11±0.7	0.82±0.008	64.96±0.6
30	0.8979±0.009	-67.06±0.7	-6.46±0.06	61.33±0.6
35	0.9076±0.009	-68.74±0.7	-9.77±0.1	59.39±0.6
40	0.8995±0.009	-69.26±0.7	-10.04±0.1	56.17±0.6
45	0.9281±0.009	-70.48±0.7	-12.97±0.1	55.29±0.6
		$n_{\mathrm{SDS}}/n_{\mathrm{TDEAC}}$ = 0.8		
25	0.9004±0.009	-69.81±0.7	-1.83±0.02	67.98±0.7
30	0.9207±0.009	-70.50±0.7	-2.30±0.02	68.20±0.7
35	0.9120±0.009	-70.36±0.7	-2.33±0.02	68.03±0.7
40	0.9096±0.009	-70.22±0.7	-3.31±0.03	66.91±0.7
45	0.8973±0.009	-69.65±0.7	-4.67±0.05	64.98±0.6
		$n_{\mathrm{AS}}/n_{\mathrm{TDEAC}}$ = 0.6		
25	0.9110±0.009	-70.39±0.7	4.94±0.05	75.33±0.8
30	0.9177±0.009	-70.78±0.7	2.02±0.02	72.80±0.7
35	0.9152±0.009	-70.65±0.7	-10.14±0.1	60.51±0.6
40	0.9350±0.009	-70.85±0.7	-12.90±0.1	57.95±0.6
45	0.9251±0.009	-70.31±0.7	-16.59±0.2	53.72±0.5
		$n_{\mathrm{C12DMAO}}/n_{\mathrm{TDEAC}}$ = 0.6		
25	0.8725±0.009	-69.12±0.7	-5.81±0.06	63.31±0.6
30	0.9216±0.009	-70.76±0.7	-5.73±0.06	65.03±0.7
35	0.9119±0.009	-70.25±0.7	-11.00±0.1	59.25±0.6
40	0.9228±0.009	-70.20±0.7	-12.14±0.1	58.06±0.6
45	0.9039±0.009	-69.84±0.7	-12.71±0.1	57.13±0.6

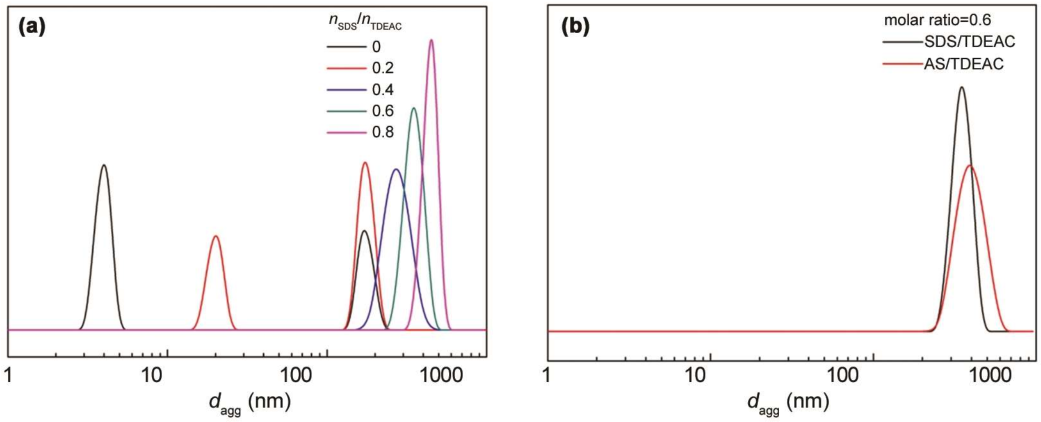

Fig. 3 — (a) Diameter of TDEAC/SDS (AS) aggregates at different molar ratios at 25 ºC, and, (b) diameter of SDS/TDEAC and AS/TDEAC mixed systems at molar ratio of 0.6.

two diameters at ~20 and ~180 nm are observed. According to the equation proposed by Evans and Ninham[45], the effective packing parameters (p_{eff}) of the mixed systems are in the range of 0.15–0.28, which is smaller than the p_{eff} (= 0.386) of 70 mol% SDS + 30 mol% CTAB mixture[46]. At $p_{\text{eff}} < 1/3$, the SDS/TDEAC aggregates are all spherical micelles. The absence of the cross flower (not shown) from polarized optical microscopy confirms the formation of micelles. The results are similar to those reported by Geng *et al.*[47] obtained from TEM morphology.

Based on the phase separation model, the thermodynamic parameters including the standard Gibbs free energy of micellization (ΔG_m^0, $\Delta G_m^0 = (1+\beta)RTlnX_{cmc}$), the standard enthalpy change (ΔH_m^0, $\Delta H_m^0 = -RT^2(0.5+\beta)\frac{lnX_{cmc}}{dT}$) and the standard entropy (ΔS_m^0, $T\Delta S_m^0 = \Delta H_m^0 - \Delta G_m^0$) of micellization were calculated[35] (Table 2). The values of ΔG_m^0 are all negative, indicating that the formation of micelles is spontaneous. The ΔG_m^0 values of TDEAC/SDS (AS, C_{12}DMAO) are much smaller than those of TDEAC, showing a greater tendency for forming micelles. The ΔH_m^0 values of TDEAC and SDS(AS)/TDEAC mixed systems with molar ratios of 0.2, 0.4 and 0.6 are positive at 25 ºC, while those of other systems are all negative. This means that the micellization process is exothermic at 25 ºC, and endothermic process at other temperatures. It is reported that ΔH_m^0 originates in the hydrophobic, repulsive electrostatic and electrostatic interactions. During micellization, the surfactants aggregate by releasing solvated water around the hydrocarbon chains and by subsequent hydrophobic interaction between the hydrocarbon chains. The process of aggregation is exothermic. On the other hand, the attractive electrostatic interaction is endothermic[48]. Considering this viewpoint and the values of β, it is proposed that the hydrophobic interaction governs the micellization of TDEAC and mixed systems at temperature higher than 25 ºC. The values of ΔG_m^0 are mainly contributed by $T\Delta S$, indicating that the micellization is an entropy-driven process.

Microenvironment of micelles

The micellization of TDEAC and TDEAC/SDS (AS, C_{12}DMAO) systems were also studied by steady-state fluorescence method using pyrene as a probe. Pyrene, a strongly hydrophobic probe, exhibits a characteristic emission spectrum with 5 bands within 370 and 400 nm (Figure not shown). In polar media, there are five vibronic peaks, and the intensity of the first to the third vibronic peak (I_1/I_3) can be used to estimate the polarity of the environment[49]. During the formation of micelles, pyrene molecules are prone to incorporate into the micro-hydrophobic reservoir of the micelles, causing a sharp decrease of the I_1/I_3 ratio[36]. The relationship between TDEAC concentration for TDEAC and TDEAC/SDS (AS, C_{12}DMAO) systems with different molar ratios and the variation of I_1/I_3 ratio are shown in Fig. 4. The concentration of surfactant corresponding to the sharp decrease of I_1/I_3 ratio is the cmc. The cmc values are 0.67 (TDEAC), 0.072 ($n_{SDS}/n_{TDEAC} = 0.2$), 0.076 ($n_{SDS}/n_{TDEAC} = 0.4$), 0.041 ($n_{SDS}/n_{TDEAC} = 0.6$), 0.017 ($n_{SDS}/n_{TDEAC} = 0.8$), and 0.01 ($n_{AS}/n_{TDEAC} = 0.6$), 0.079 mmol/L ($n_{C12DMAO}/n_{TDEAC} = 0.6$). These values are consistent with those obtained from surface tension and conductivity methods.

At a concentration higher than cmc, a low I_1/I_3 ratio indicates the solubilization of pyrene in the palisade layer adjacent to the polar head groups[36]. For the TDEAC/SDS systems, the I_1/I_3 value decreases with the increase in molar ratio of SDS to TDEAC (Fig. 4(a)). At a fixed molar ratio, the order of the I_1/I_3 value is TDEAC/AS < TDEAC/SDS < TDEAC/C_{12}DMAO (Fig. 4(b)). The small I_1/I_3 value is ascribed to the tight packing of the micelle palisade layer and the existence of pyrene in a more non-polar microenvironment[50]. The strong electrostatic interaction between TDEAC and SDS (AS, C_{12}DMAO) is responsible for the tight packing in the micelles.

Interaction parameters between TDEAC and surfactants

In the mixture of TDEAC and SDS (AS, DTAC and C_{12}DMAO), the binary surfactants adsorbed on the surface and formed micelles. The cmc values of the four mixed systems have been obtained from surface tension (Table 1) and conductivity (Fig. 2) data, which are in agreement with each other. The interaction parameter, β_{12}, between TDEAC (2) and SDS (AS, DTAC and C_{12}DMAO) (1) for various molar ratios are calculated and are listed in Table 3. The β_{12} values are in the range of –11 to –15 for the TDEAC/SDS system, –8 to –12 for the TDEAC/AS system, 7 to 10 for the TDEAC/DTAC system and ~7.5 for the TDEAC/C_{12}DMAO system. Generally, a negative β_{12} value implies the existence of strong attraction or weak repulsion between different surfactant molecules, and a positive one shows the

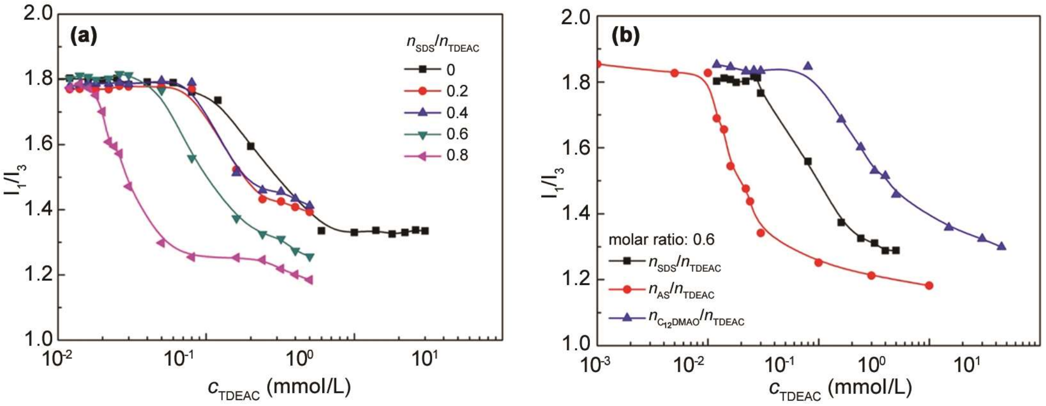

Fig. 4 — Variation of I_1/I_3 ratio of pyrene in TDEAC and TDEAC/SDS (AS, C_{12}DMAO) solutions with increasing c_{TDEAC} at 25 ºC.

Table 3 — Interaction parameters of TDEAC/SDS (AS, DTAC and C_{12}DMAO) mixed systems calculated from Rubingh regular solution model

Molar ratio	cmc[a] (mmol/L)	cmc_{mix} (mmol/L)	β_{12}	X_1
		SDS/TDEAC		
0.2	0.197±0.002	0.079±0.0008	-11.32±0.1	0.31±0.003
0.4	0.040±0.0004	0.047±0.0005	-13.23±0.1	0.36±0.004
0.6	0.015±0.0002	0.037±0.0004	-14.28±0.1	0.38±0.004
0.8	0.020±0.0002	0.031±0.0003	-15.00±0.2	0.39±0.004
		AS/TDEAC		
0.2	0.688±0.007	0.148±0.001	-8.39±0.08	0.26±0.003
0.4	0.051±0.0005	0.092±0.0009	-10.47±0.1	0.32±0.003
0.6	0.041±0.0004	0.070±0.0007	-11.57±0.1	0.35±0.004
0.8	0.027±0.0003	0.061±0.0006	-12.32±0.1	0.37±0.004
		DTAC/TDEAC		
0.2	1.245±0.01	0.997±0.01	10.46±0.1	0.50±0.005
0.4	1.180±0.01	0.992±0.01	9.23±0.09	0.42±0.004
0.6	0.986±0.01	0.989±0.01	8.33±0.08	0.39±0.004
0.8	0.986±0.01	0.987±0.01	7.79±0.8	0.36±0.004
		C_{12}DMAO/TDEAC		
0.2	1.118±0.01	1.311±0.01	7.55±0.08	0.52±0.005
0.4	1.139±0.01	1.195±0.01	7.93±0.08	0.46±0.005
0.6	0.868±0.009	1.121±0.01	7.86±0.08	0.43±0.004
0.8	1.077±0.01	1.069±0.01	7.67±0.08	0.40±0.004

[a]Values were calculated from surface tension isotherms.

existence of weak attraction or strong repulsion. A β_{12} value near to 0 indicates the absence of any remarkable interaction between the surfactant molecules[51]. For TDEAC/SDS (AS) mixed systems, the negative β_{12} values may be due to both, the depressed repulsion among TDEAC molecules as well as the increscent interaction amongst the molecules. The strong attraction between TDEAC and SDS (AS) molecules induces the formation of TDEA-DS (TDEA-AS), which shows enhanced hydrophobic effect. The β_{12} values decrease with increasing molar ratio of SDS (AS) to TDEAC.

For the mixed systems of TDEAC/SDS (AS), their cmcs calculated from Rubingh regular solution model are higher than those obtained from surface tension and conductivity methods, indicating non-ideal mixing behavior and demonstrating favorable synergistic effect between the oppositely charged surfactants in the mixed micelles[3]. The cmcs of TDEAC/DTAC and TDEAC/C_{12}DMAO systems calculated from Rubingh regular solution model are approximately equal to their corresponding experimental results, indicating that no synergistic effect occur in these systems[47]. The electrostatic repulsion between the TDEAC and DTAC molecules results in the cmc remaining almost unchanged. Both electrostatic repulsion (positively charged nitrogen atoms) and electrostatic interaction (positively charged nitrogen atom and oxygen atom with lone pair) coexist between the TDEAC and C_{12}DMAO molecules. The results obtained from surface tension and conductivity methods and Rubingh regular solution model, show that the electrostatic repulsion between positively charged nitrogen atoms of TDEAC/C_{12}DMAO molecules dominate the interaction.

Conclusions

The interactions between TDEAC and SDS (AS, DTAC and C_{12}DMAO) have been studied through surface tension, conductivity, steady-state fluorescence and dynamic scattering and Rubingh regular methods. Both surface tension and cmc of TDEAC/SDS (AS) decrease with the increase in SDS (AS)/TDEAC molar ratio, as compared with those of DTAC/TDEAC and C_{12}DMAO/TDEAC systems. The surface tension reducing efficiency and surface tension reducing ability of SDS (AS)/TDEAC systems are larger than those of DTAC (C_{12}DMAO)/TDEAC systems. This phenomenon is attributed to the strong electrostatic interaction between the two oppositely charged surfactants, as compared with the relatively weak interaction between DTAC (C_{12}DMAO) and TDEAC. The hydrophobic interaction between SDS (AS) and TDEAC governs their micellization. The cmc of SDS (AS)/TDEAC solutions decreases with increasing temperature initially, and then increases, as temperature influences both, the hydration degree of the hydrophilic group and the water structure around hydrophobic chains. A strong interaction between SDS (AS) and TDEAC results in the tight packing of micelle palisade layer. The parameters calculated from Rubingh regular solution model confirm the strong interaction between the oppositely charged surfactants.

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References

1 Darsh T W, Martin E G & Shah D O, *Surfactants in Chemical/Process Engineering,* (Marcel Dekker, New York) 1998.

2 Mao X, Jiang R, Xiao W & Yu J, *J Hazard Mater*, 285 (2015) 419.

3 Yadav S K, Parikh K & Kumar S, *Colloids Surf A*, 522 (2017) 105.

4 Kamal M S, *J Surfact Deterg*, 19 (2016) 223.

5 Honary S & Zahir F, *Trop J Pharm Res*, 12 (2013) 255.

6 Honary S & Zahir F, *Trop J Pharm Res*, 12 (2013) 265.

7 Chang Y, McLandsborough L & McClements D J, *Food Chem*, 172 (2015) 298.

8 Xin B & Hao J, *RSC Adv*, 2 (2012) 5141.

9 Khan M N & Ismail E, *J Chem Soc Perkin Trans*, 8 (2001) 1346.

10 Mirgorodskaya A B, Bogdanova L R, Kudryavtseva L A, Lukashenko S S & Konovalov A I, *Russ J Gen Chem*, 78 (2008) 163.

11 Tehrani-Bagha A R, Singh R G & Holmberg K, *J Colloid Interf Sci*, 376 (2012) 112.

12 Frank C, Frielinghaus H, Allgaier J & Prast H, *Langmuir*, 23 (2007) 6526.

13 Zhang X, Hao L, Sun H, Chen X, Jiang W, Wu J, Xu M & Pan Q, *J Macromol Sci A*, 52 (2015) 168.

14 Wu J, Zhang J, Deng C, Meng F & Zhong Z, *Biomacromolecules*, 17 (2016) 2367.

15 Branco M A, Pinheiro L & Faustino C, *Colloids Surf A*, 480 (2015) 105.

16 Garcia M T, Ribosa I, Perez L, Manresa A & Comelles F, *Langmuir*, 29 (2013) 2536.

17 Akram M, Anwar S, Ansari F, Bhat I A & Kabir ud D, *RSC Adv*, 6 (2016) 21697.

18 Chauhan V, Kamboj R, Singh Rana S P, Kaur T, Kaur G, Singh S & Kang T S, *J Colloid Interf Sci*, 446 (2015) 263.

19 Akram M, Bhat I A, Bhat W F & Kabir ud D, *Spectrochim Acta A*, 150 (2015) 440.

20 Patel R, Mir M U H, Maurya J K, Singh U K, Maurya N, Parray M u d, Khan A B & Ali A, *Luminescence*, 30 (2015) 1233.

21 Dong Z, Wang X, Liu Z, Xu B & Zhao J, *Colloids Surf A*, 419 (2013) 233.

22 Zhao L, Wang K, Xu L, Liu Y, Zhang S, Li Z, Yan Y & Huang J, *Soft Matter*, 8 (2012) 9079.

23 Feng Y & Chu Z, *Soft Matter*, 11 (2015) 4614.

24 Shaban S M, Fouda A S, Elmorsi M A, Fayed T & Azazy O, *J Mol Liq*, 216 (2016) 284.

25 Cao G, Guo X, Jia L & Tian X, *RSC Adv*, 5 (2015) 27197.

26 Chauhan V, Singh S, Mishra R & Kaur G, *J Colloid Interf Sci*, 436 (2014) 122.

27 Sydlik S A, Lee J H, Walish J J, Thomas E L & Swager T M, *Carbon*, 59 (2013) 109.

28 Adrar S, Habi A, Ajji A & Grohens Y, *Appl Clay Sci*, 146 (2017) 306.

29 Florea N M, Lungu A, Badica P, Craciun L, Enculescu M, Ghita D G, Ionescu C, Zgirian R G & Iovu H, *Compos Part B-Eng*, 75 (2015) 226.

30 Abdollahi A, Rad J K & Mahdavian A R, *Carbohyd Polym*, 150 (2016) 131.

31 Abdollahi A, Mahdavian A R & Salehi-Mobarakeh H, *Langmuir*, 31 (2015) 10672.

32 Hao C, Cui Y, Yang P, Zhang H, Mao D, Cui X & Li J, *Colloids Surf B*, 128 (2015) 528.

33 Xu J, Xia Y, Qiao C D, Zhu W, Wang Y & Li T D, *Colloids Surf B*, 123 (2014) 945.

34 Xu J, Li T D, Jiang Q W, Qiao C D & Cheng J Y, *Colloids Surf B*, 103 (2013) 375.

35 Liu Y, Yang X, Li Y, Chen Y, Zhou X & Li T, *Colloids Surf A*, 498 (2016) 248.

36 Kalyanasundaram K & Thomas J K, *J Am Chem Soc*, 99 (1977) 2039.

37 Holland P M & Rubingh D N, *J Phys Chem*, 87 (1983) 1984.

38 Oliviero C, Coppola L, La Mesa C, Ranieri G A & Terenzi M, *Colloids Surf A*, 201 (2002) 247.

39 Wang T F, Shang Y H, Peng C J & Liu H, *Acta Chim Sin*, 67 (2009) 1159.

40 Hao J & Hoffmann H, *Curr Opin Colloid In*, 9 (2004) 279.

41 Rosen M J & Kunjappu J T, *Surfactants and Interfacial Phenomena*, 4th Edn, (John Wiley, New Jersey, USA) 2012.

42 Hunter R J, *Foundations of Colloid Science,* Vol 1, 2nd Edn, (Oxford University Press, New York), 2001.

43 Zhang Q, Li S, Zhang F, Wei X, Liu M, Liu J & Sun D, *J Surfact Deterg*, 20 (2017) 1281.

44 Kundu K, Das A, Bardhan S, Chakraborty G, Ghosh D, Kar B, Saha S K, Senapati S, Mitra R K & Paul B K, *Colloids Surf A*, 504 (2016) 331.

45 Evans D F & Ninham B W, *J Phys Chem*, 90 (1986) 226.

46 Rajkhowa S, Mahiuddin S, Dey J, Kumar S, Aswal V K, Biswas R, Kohlbrecher J & Ismail K, *Soft Matter*, 13 (2017) 3556.

47 Geng T, Zhang C Q, Jiang Y J, Ju H B & Wang Y K, *J Mol Liq*, 232 (2017) 36.

48 Shimizu S, Pires P A R & El Seoud O A, *Langmuir*, 20 (2004) 9551.

49 Zana R, In M, Lévy H & Duportail G, *Langmuir*, 13 (1997) 5552.

50 Ao M, Huang P, Xu G, Yang X & Wang Y, *Colloids Polym Sci*, 287 (2008) 395.

51 Bakshi M S, Singh J, Singh K & Kaur G, *Colloids Surf A*, 237 (2004) 61.