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ORIGINAL ARTICLE

Synthesis and Surface Active Properties of Gemini Cationic Surfactants and Interaction with Anionic Azo Dye (AR52)

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Abstract A homologous series of new gemini cationic surfactants were synthesized and characterized using micro elemental analysis, FTIR, ^{1}H-NMR and mass spectra. The surface activities of these amphiphiles were determined based on the data of surface tension. Critical micelle concentration, effectiveness of the surface tension reduction, efficiency of adsorption, maximum surface excess, minimum surface area and critical packing parameter were evaluated. The effect of cationic micelles on solubilization of anionic azo dye, sulforhodamine B (Acid Red 52) in aqueous micellar solution of the synthesized gemini cationic surfactants was studied at pH 6.9 ± 0.5 and 25 °C. The results showed that the solubility of dye rose with increasing surfactant concentration as a consequence of some association between the dye and the micelles. It was also observed that the aggregation of surfactant and dye takes place at a surfactant concentration below the CMC of the individual surfactant. The partition coefficients between the bulk water and surfactant micelles as well as the Gibbs energies of distribution of dye between the bulk water and surfactant micelles were calculated using a pseudo-phase model. The effect of the hydrophobic chain length of Gemini cationic surfactants on the distribution parameters was also reported. The results show favorable solubilization of dye in cationic micelles.

Keywords Gemini cationic surfactant · Synthesis · Structure analysis · Surface activity · Acid Red 52 · Partition coefficient · Solubilization

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Introduction

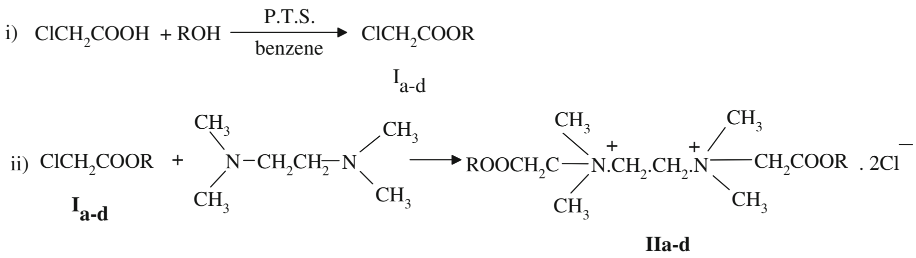
Gemini surfactants are a novel type of surfactant synthesized in recent years. Its advent has greatly broadened the perspective of interfacial science [1–3]. Compared with the conventional surfactants, gemini surfactants are more efficient in lowering surface tension and have a much lower critical micelle concentration (CMC). Despite their recent development, gemini surfactants are already a hot subject in colloids and surface science and are considered to be a type of surfactant that will be most widely used in the twenty-first century [4–6].

Gemini cationic surfactants have been extensively studied due to their easy preparation. This has also made them particularly interesting from an industrial point of view, and much of the published information concerning the solution properties of gemini surfactants is based on cationic species [7–9].

Surfactant–dye associations are subjects of numerous investigations [10–13]. Surfactants are used as auxiliaries in most textile finishing processes such as washing, wetting, dispersing, dyeing and finishing. Also, the interaction between dyes and surfactants have been studied to provide some insight into small molecule–macromolecule interactions, which is of major importance in biochemistry [14].

Many techniques have been used for qualitative and quantitative description of dye–surfactant interactions, i.e., potentiometry [15, 16], ordinary conductimetry [17, 18], or with ion selective electrodes [19, 20], but the most widely used are spectroscopical methods [21–26].

Surfactants are able to affect the electronic absorption spectra of many dyes. Consequently, in the presence of a surfactant, new bands in the electronic absorption spectra of many dyes can appear, and the stronger the mutual interaction between dye and surfactant is, the greater the



Scheme 1 Synthetic route for 1,2-bis-diquaternary ammonium gemini cationic surfactants. Where R: **a** = $-(CH_2)_9CH_3$, **b** = $-(CH_2)_{11}CH_3$, **c** = $-(CH_2)_{15}CH_3$, **d** = $-(CH_2)_{17}CH_3$

observed change [25]. In systems containing an ionic dye and an oppositely charged surfactant, electrostatic interactions appear. The thermodynamic process involving the transfer of the dye between micellar and bulk water phases is characterized by free energy changes and partition coefficients, respectively. The partition coefficient depends on the structure of the additive, the surfaces that constitute the micelles and other physicochemical variables such as the concentration and temperature. Among the various factors that contribute to the solubilization in micellar systems, hydrophobic contributions are quite significant [27].

In this paper we offer a simple method for synthesizing gemini cationic surfactants based on 1,2-bis [*N*,*N*-dimethyl-*N*-carbalkoxy methyl ammonio] ethane dichloride (m-2-m; where m represents the hydrocarbon “tail” chain with a length of 10, 12, 16 and 18 carbon atoms). The surface tension and critical micelle concentration (CMC) of these surfactants were measured, and some of surface parameters were obtained on the basis of surface tension measurement. Their properties were compared with a monoalkyl quaternary ammonium salt (dodecyl trimethyl ammonium chloride DTAC) which has been presented in previous articles. Also, the solubilization and interaction of azo dye sulforhodamine B (Acid Red; AR52) with the synthesized surfactants were investigated by UV–visible spectroscopy measurements. Absorption spectrophotometry was used to quantify surfactant/water partition coefficients K_X- and K_S as well as the Gibbs energies of distribution of dye by applying the mathematical models that consider partitioning of the dye between the micellar and aqueous pseudophase. Schemes 1 describe the synthetic route of gemini cationic surfactants.

Experimental

Materials

N,*N*,*N*,*N*-tetramethyl 1,2-ethylene diamine and fatty alcohols (decyl, dodecyl, hexadecyl and octadecyl) were obtained from Sigma Co., and were used without purification. Chloroacetic acid and *p*-toluene sulfonic acid were obtained from Aldrich. All solvents were of high purity and used as purchased. Dye Acid Red 52 was obtained from Sigma. Triple-distilled water was used in all measurements. The characterization of dye is listed in Table 1.

Methods

Melting points were determined on a Reichert hot stage and were uncorrected. FT-IR spectra were recorded on a Perkin Elmer spectrometer in the 4,000–400 cm^{-1} range using KBr discs. ^{1}H-NMR spectra were recorded on a Joel-AX 500 MH_Z with TMS as an internal standard and mass spectra were recorded on a Joel- AX 500 (EI and FAB). Elemental analyses (C, H, N, Cl) were performed with a Varian elemental apparatus and in satisfactory agreement with the calculated values (Table 2). UV–visible spectra of AR52 solutions were recorded on Perkin Elmer-Lambda spectrophotometer model 201. Stock solutions of surfactants and dye used in this study were 1×10^{-1} and 1×10^{-2} $molL^{-1}$, respectively. The variation of absorbance of the dye solution by increasing surfactants concentrations was recorded at maximum absorption wavelength (λ_{max}) using water as a blank.

Synthesis

Synthesis of Alkyl Chloroacetate Esters ($I_{a–d}$)

Alkyl chloroacetates were prepared by refluxing chloroacetic acid (0.5 mol) with corresponding fatty alcohols (decyl, dodecyl, hexadecyl and octadecyl) in presence of *p*-toluene sulfonic acid (0.1%) and benzene (100 mL) as solvent, until the desired amount of water (0.1 mol, 1.8 mL) was removed. The mixture was extracted with two 50 portions of 25% sodium carbonate, and the benzene layer was dried over anhydrous sodium sulfate and the

Table 1 Characterization of AR 52

C.I	45100
Mol. formula	$C_{27}H_{29}N_2NaO_7S_2$
Formula weight	580.66
Appearance	Red brown powder
λ_{max}	554 nm

Table 2 Analytical and physical data of the synthesized 1,2-bis-diquaternary ammonium gemini cationic surfactants

Comp no.	Empirical formula	Formula wt.	M.P. (°C)	Yield (%)	Calc./found			
					C	H	N	Cl
II_a	$C_{30}H_{62}N_2O_4Cl_2$	585.25	80–82	85	61.57	10.59	4.79	12.12
					61.21	10.32	4.51	11.90
II_b	$C_{34}H_{70}N_2O_4Cl_2$	641.29	118–120	87	63.68	10.92	4.37	11.06
					63.39	10.66	4.12	10.86
II_c	$C_{42}H_{86}N_2O_4Cl_2$	753.38	124–126	92	66.96	11.42	3.72	9.41
					66.60	11.19	3.48	9.19
II_d	$C_{46}H_{94}N_2O_4Cl_2$	809.42	140–142	96	68.26	11.61	3.46	9.01
					68.01	11.48	3.29	8.90

solvent distilled off afterward. The esters of chloroacetic acid were obtained with a yield high as 95–97%. Decyl and dodecyl esters were obtained as liquids, while hexadecyl and octadecyl esters were solid. M.P. 30–32 and 37–39 °C, respectively. ^{1}H NMR for C_{12} ($CDCl_3$, TMS): δ 0.86(t,3H); δ 1.18-1.35(m,18H); δ 1.64(m,2H) and δ 3.81(s,2H); δ 4.10 (t,2H).

*Synthesis of 1, 2-Bis[N,N-Dimethyl-N-Carbalkoxymethyl Ammonio] Ethane Dichloride (**$II_{a–d}$**)*

Sodium hydroxide (0.05 mol) was added into alkyl chloroacetates (0.2 mol) in 50 mL ethanol. Afterwards, *N*,*N*,*N*,*N*,-tetramethyl ethylene diamine (0.1 mol) and 1 g KI were added to the solution. The mixture was refluxed for 8 h, then cooled to room temperature and filtered to remove insoluble materials. The filtrate was evaporated then the residue was recrystallized twice from ethyl acetate giving **$II_{a–d}$** (*m*-2-*m*, *m* = 10, 12, 16 and 18) as a highly hygroscopic white solid (Table 2). A typical IR spectra for C_{12}: 2,919 cm^{-1} for CH–stretching, υ C=O at 1,628, υ CH at 1,485 cm^{-1} υ C–O at 1,467 cm^{-1} and $\underset{\upsilon}{}-\overset{+}{N}\!\!<$ at 3,050 cm^{-1}. ^{1}H NMR($CDCl_3$, TMS): δ 0.87 (t, 6H, $2CH_3$), 1.26 (m, 36H, 2 $(CH_2)_8$; δ1.62 (m, 4H, $2(CH_2)_9\,\underline{CH_2}$); δ3.35 (s, 12H, $4CH_3$); δ 4.20 (t, 4H, $OC\underline{CH_2}C$); δ 4.34 (s, 4H, $2COO\underline{CH_2}N^+$) and δ 4.60 (s,4H,H, $\overset{+}{N}CH_2CH_2\overset{+}{N}$). EI/FAB$^+$ (m/z: 640 (M^+–1) (1.13%) and the following abundant peaks: 86(23.69%) for $[CH_3(CH_2)_5]^{+,}$ 116 (16.19%) for $[(Me)_2NCH_2CH_2N(Me)_2]^{+,}$ 142(100%) for $[CH_3(CH_2)_9]^+$ and 144(10.37%) for $[CH_3(Me)_2NCH_2CH_2N\ (Me)_2\ CH_2]^+$; Fig. 1.

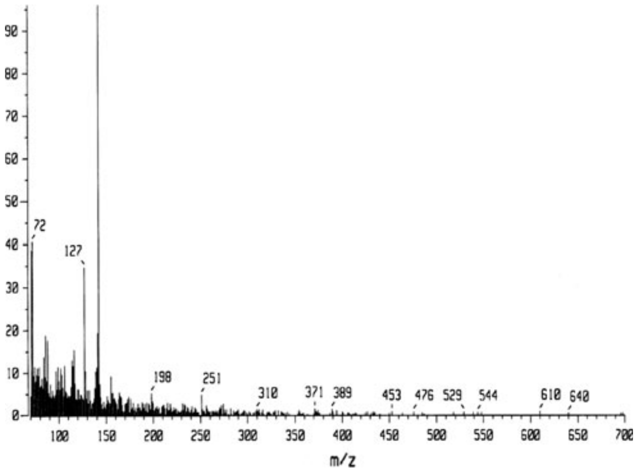


Fig. 1 Mass spectra of II_b

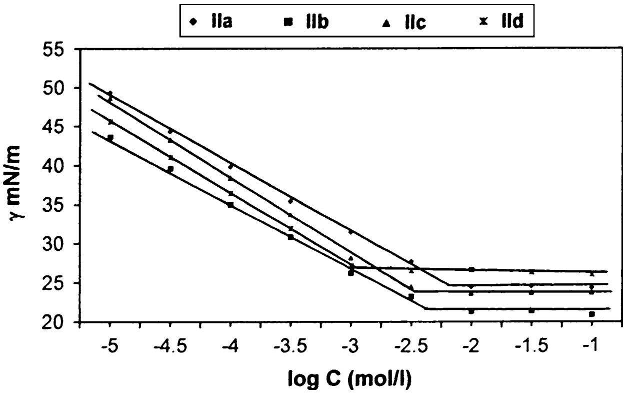


Fig. 2 Surface tension versus log C of 1,2-bis-diquaternary ammonium gemini cationic surfactants at 25 °C

Surface Tension Measurements

Surface tension measurements were performed for freshly prepared solutions of surfactants in the concentration ranges of 10^{-1}–10^{-5} mol L^{-1} using Du-Nouy tensiometer at 25 °C. The tensiometer was calibrated against triple distilled water. The platinum ring was thoroughly cleaned and dried before each measurement. Each experiment was repeated several times until good reproducibility was achieved. The results was accurate within ±0.1 mNm^{-1}; Fig. 2.

Table 3 Surface properties of 1,2-bis-diquaternary ammonium gemini cationic surfactants at 25 °C and monododecyl trimethylammonium chloride for comparison

Comp	CMC $molL^{-1}$	γ_{CMC} mN/m	π_{CMC} mN/m	$\Gamma_{max} \times 10^{-6}$ mol/m^2	$A_{min} \times 10^2$ nm^2	pc_{20}	CMC/C_{20}	CPP
II_a	6.31×10^{-3}	25.0	47.0	3.97	41.81	2.20	1.12	0.50
II_b	4.47×10^{-3}	22.0	50.0	4.43	37.47	2.75	2.51	0.56
II_c	2.81×10^{-3}	26.0	46.0	5.42	30.63	2.85	1.99	0.69
II_d	9.55×10^{-4}	28.5	43.5	5.55	29.91	2.90	0.76	0.70
DTAC	1.20×10^{-2a}	39.0^a	33.0^b	3.42^c	49.00^a	2.60^c	3.16^b	0.43^b

DTAC Dodecyl trimethyl ammonium chloride

See references a [41], b [calculated]; c [42]

Micelle/Water Partition Coefficients (K_s and K_x)

K_s and K_x were determined from the absorbance of a series of solution containing a fixed concentration of dye (C_{dye}; 30 µmolL^{-1}) and the surfactants concentration were changed in the range of 10^{-1}–10^{-5} molL^{-1} in CMC scale. All tests were conducted at 25 °C and pH 6.9 ± 0.0.5.

Results and Discussion

Surface Properties

Surface Tension γ and Critical Micelle Concentration (CMC)

The surface tension of aqueous solutions of gemini surfactants were measured at 25 °C. The results of surface tension measurements decrease with increasing concentration, and then reached to constant values within the narrow concentrations. The break points in Fig. 2 are taken as CMC. The values of CMC of each gemini surfactant are shown in Table 3. Conventional surfactant dodecyl trimethyl ammonium chloride (DTAC) was used as a control compound. According to Table 3, CMC values of gemini $\mathbf{II_{a-d}}$ are 6.31×10^{-3}, 4.47×10^{-3}, 2.81×10^{-3} and 9.55×10^{-4} molL^{-1}, respectively, while for the conventional surfactant DTAC it is 1.20×10^{-2} molL^{-1}. As expected from recent publications, the CMCs of these gemini surfactants are lower than that of DTAC, because the two cationic head groups are connected by a spacer and the electrostatic repulsion between head groups is hindered.

It also can be seen from Table 3 and Fig. 3 that the CMC values of prepared gemini surfactant decrease with an increase in the hydrophobic carbon chain from 10 to 18 as for common surfactants in a homologous series [28]. Gemini surfactants have a greater tendency to form micelles with ethylene as spacer compared to the rigid spacer [29].

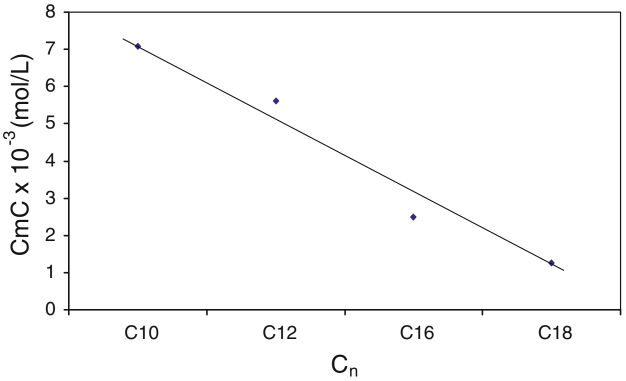


Fig. 3 Critical micelle concentration of the homologous series of 1,2-bis-diquaternary ammonium gemini cationic surfactants versus there number of carbon atoms in the alkyl substituent (R)

Surface Excess Concentration (Maximum Surface Excess) $\mathbf{\Gamma}_{max}$ and Minimum Surface Area; $\boldsymbol{A}_{min}$

The maximum surface excess of the diquaternary amphiphiles (Table 3) was calculated using Gibbs adsorption isotherm [30, 31].

$$\Gamma_{max} = -1/2.303\, nRT\, (\partial\gamma/\partial \log C)_T \tag{1}$$

According to Zana [32, 33], the constant n takes a value of 2 for an ionic surfactant when the surfactant ion and the counterion are univalent, and a value of 3 for a dimeric surfactant made up of a divalent surfactant ion and two univalent counterions, in the absence of a swamping electrolyte. In order to extract the minimum surface area occupied by a surfactant molecule, A_{min} (nm^2), at the air–water interface when the surface adsorption was saturated, Eq. 2 was used:

$$A = 10^{16}/N.\Gamma_{max} \tag{2}$$

where N is the Avogadro number, $R = 8.314$ J $mol^{-1}k^{-1}$, T is absolute temperature and ($\partial\gamma/\partial \log C$) is the slope of the γ versus log C plot at 25 °C.

A substance which lowers the surface tension is thus present in excess at or near the surface, i.e. when the surface tension decreases with increasing the activity of the surfactants, $\Gamma_{\max}$ is positive. The results given in Table 3 indicate that increasing of the hydrophobic chain length led to a decrease in $A_{\min}$ values. Crowding occurred at the interface as a result of increasing $\Gamma_{\max}$, which consequently decreased the area occupied by surfactant molecules at the interface. Also, comparing the values of $A_{\min}$ for all investigated surfactants and DTAC which are listed in Table 3, we can see that all compounds have a smaller $A_{\min}$ value than monomeric surfactant DTAC.

Surface Tension Reduction γ_{CMC}

The effectiveness of surface tension reduction γ_{CMC} for all investigated compounds is smaller than that (39.0 mN/m) of DTAC. This is in line with previous work showing that the presence of two hydrophobic groups in the gemini molecule leads to greater surface activity [31, 34]. Comparing the values of γ_{CMC} for all investigated compounds with other gemini surfactants, we can find that these salts produce a larger decrease in surface tension at the air–water interface than the other Gemini surfactant [35, 36].

Efficiency of Adsorption PC_{20}

The values of efficiency of the prepared surfactants are shown in Table 3, where the efficiency is slightly increased with increasing molar ration of methylene units. This is due to the fact that the efficiency of adsorption at interfaces increases linearly with an increase in the carbon atoms of hydrophobic group [37, 38]. Moreover, the bis-alkyl quaternary ammonium salts in this investigation adsorb more efficiently at the interface than do the monoalkyl quaternary ammonium salt DTAC.

The ratio $\mathrm{CMC/C_{20}}$ value is a measure of the surfactant preference for adsorption relative to micellization. The value of this $\mathrm{CMC/C_{20}}$ ratio determined for the studied gemini surfactants indicates that this surfactant shows a great preference for adsorption at the interface.

Effectiveness of the Surface Tension Reduction π_{CMC}

π_{CMC} is the difference between the surface tension of the pure water γ_{o} and the surface tension of the surfactant solution γ at CMC (see Table 3). The most efficient surfactant is the C_{12} one which results in the largest reduction of the surface tension at CMC.

Critical Packing Parameter (CPP)

It can provide a good idea of the shape of aggregates spontaneously forming [39] through the following equation:

$$CPP = \frac{V_H}{a_o x L_C} \tag{3}$$

where V_H is the volume occupied by a saturated hydrocarbon chain containing n_{c} carbon atoms and L_{C} is the length of hydrocarbon groups in the micelle core. At saturation, a_{o} can be replaced by A and V_H and L_{C} can be calculated by the following relation [40]:

$$V_H = 27.4 + 26.9\,n_c$$

$$L_C = 1.5 + 1.26\,n_c$$

The packing parameter calculated for the gemini surfactant is less than 1, indicating the probable formation of lamellar vesicles.

Interaction of Acid Red 52 with Gemini Cationic Surfactants

Figure 4 is shown as an example for studying the effect of different concentration of the Gemini surfactant on the absorption spectrum of AR 52. From Fig. 4, it can be seen that the addition of gemini surfactant (12-2-12) at concentration below CMC caused a bathochromic shift of about 20–30 nm with the appearance of a short peak at 400 nm. This hyperchromic shift is characteristic of AR52 bound to cationic micelles of surfactant and the intensity of the maximum absorption band increased with increasing surfactant concentration after the CMC [43]. In submicellar regions, the dye formed a sparingly soluble precipitate which became soluble as the gemini (12-2-12) concentration reached its CMC. The loss of absorption band in the dye solution is due to this precipitate. The electrostatic forces between positive charges of cationic surfactants and anionic sulfonate groups of the dye and hydrophobic forces cause the formation of the dye-surfactant complex. An interesting and most likely explanation involves the formation of dye aggregates in parallel orientation, the so, called H-aggregates [25, 44, 45].

Further addition of the Gemini (12-2-12) led to a bathochromic shift of about 20–30 nm [43]. This hyperchromic peak is characteristic of AR52 bound to cationic surfactant micelles. The intensity of the maximum absorption band increased with increasing surfactant concentration beyond the CMC. Figure 4, also indicates that the solubility of the dye in the micellar medium increases with increasing surfactant concentration, probably because of the penetration of dye molecules into the micelles. This result is in good agreement with the findings of Ali R. et al. [11]. The effect of alkyl chain length on the interaction between AR52 and gemini cationic surfactants was examined and all the curves obtained are similar to those obtained in the case of the gemini (12-2-12); hence, the spectra of gemini (12-2-12) was used only as an example in this work to explain

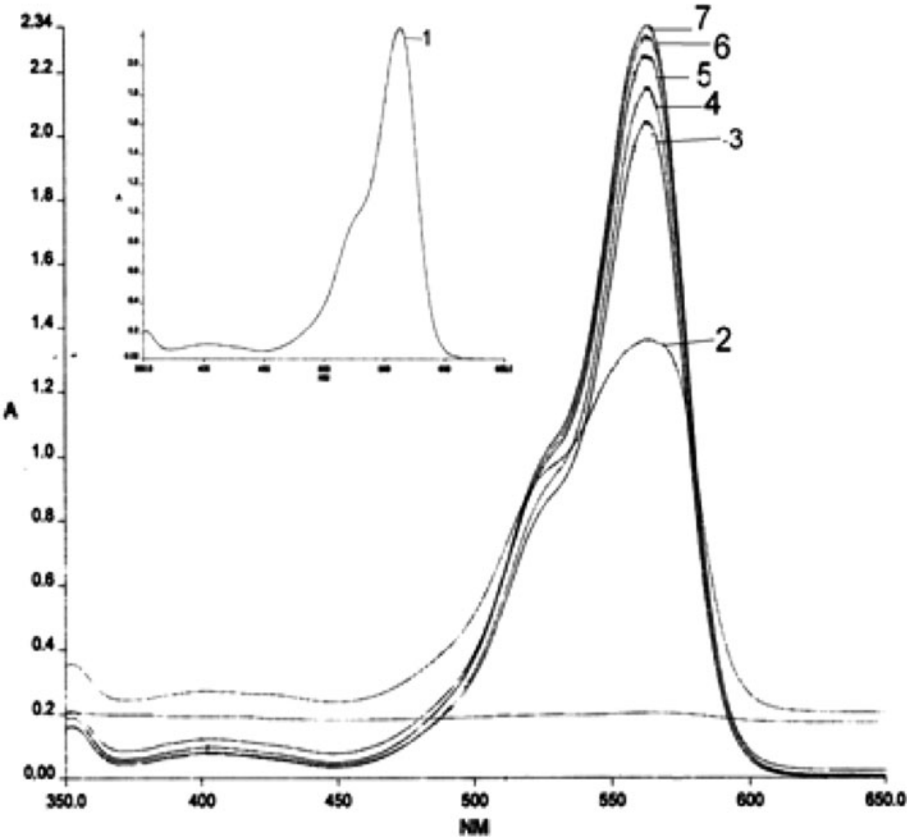


Fig. 4 Influence of Gemini 12-2-12 on absorption spectra of "AR"52 30 μmolL^{-1}: (1) 0 molL^{-1}; (2) 5 × 10^{-5}; (3) 1 × 10^{-4}; (4) 5 × 10^{-4}; (5) 5 × 10^{-3}; (6) 1 × 10^{-3}; (7) 1 × 10^{-2} molL^{-1} at 25 °C, pH 6.9 ± 0.5

such effect and the data which were obtained from the spectra of the other surfactants are recorded in Table 4. By comparing the spectra of AR52 in the presence of varying amounts of gemini surfactant with different alkyl chains length, i.e. C10, 12, 16 and 18, it was found that the intensities of the absorption bands at 554 and 400 nm increase with increasing alkyl chain length from gemini C10 to C18. This indicates an increase in the strength of the interactions with the increase of the alkyl chain length, as observed in reference [43].

Determination of the Partition Coefficients (K_x, K_s)

Absorbance values obtained at $\lambda_{\max}$ 554 nm can be also used for the calculation of partition coefficient, K_x, defined according to the pseudo-phase model as:

Table 4 The values of the partition coefficient and reacted Gibbs energies for interaction and solubilization of AR 52 (30 μmolL^{-1}) with different 1,2-bis-diquaternary ammonium gemini cationic surfactants at 25 °C

Surfactant	$K_s \times 10^2$	ΔG^o_S	$K_x \times 10^2$	ΔG^o_X
10-2-10	23.23	−19.15	12.89	−17.71
12-2-12	25.23	−19.35	14.00	−17.92
16-2-16	28.83	−19.70	16.00	−18.25
18-2-18	31.00	−19.88	17.70	−18.50

$$K_x = \frac{X^m_{Dye}}{X^w_{Dye}} \tag{4}$$

where X^m_{Dye} and X^w_{Dye} are the mole fractions of dye in micellar and aqueous phase, respectively. They are related with concentration of species in the solubilization system:

$$X^m_{Dye} = \frac{C^m_{Dye}}{C^m_{Dye} + C^m_{surfactant}} \tag{5}$$

$$X^w_{Dye} = \frac{C^w_{Dye}}{C^w_{Dye} + C^w_{surfactant} + n_w} \tag{6}$$

where $C^m_{surfactant}$ and $C^w_{surfactant}$ represent concentrations of surfactant in micellar and monomeric states, and $n_w = 55.5$ mol dm^{-3} is the molarity of water. Under the present experimental conditions $C^m_{Dye} + C^w_{surfactant} \ll n_w$, if we express K_s/n_w, we get the equation:

$$K_s = \frac{C^m_{Dye}/\left(C^m_{Dye} + C^m_{surfactant}\right)}{C^w_{Dye}} \tag{7}$$

The fraction f of the associated dye may be defined as:

$$f = \frac{C^m_{Dye}}{C_{Dye}} \tag{8}$$

At a certain C_{Dye}, f is equal to zero in the non-micellar region up to. CMC and increases with increasing the concentration of surfactant above CMC. As $C_{\mathrm{surfactant}}$ increases up to infinity, f approaches unity, since all added dye should be solubilized in micelles.

The fraction f can be directly calculated from the experimental data using the following equation:

$$f = \frac{\Delta A}{\Delta A^{\infty}} \tag{9}$$

where $\Delta A = A - A_{\mathrm{w}}$ and $\Delta A^{\infty} = A^{\infty} - A_{\mathrm{w}}$, A^{∞} being the absorbance of dye completely bounded to surfactant.

By combining Eqs. 6, 7 and 8, a linear form can be written:

$$\frac{1}{\Delta A} = \frac{1}{\Delta A^{\infty}} + \frac{1}{K_{\mathrm{s}} \Delta A^{\infty} (C_{Dye} + C_{surf.} - CMC)} \tag{10}$$

K_{s} and K_{x} ($K_{\mathrm{s}} = K_{\mathrm{x}}/n_{\mathrm{w}}$) were obtained from the slope of the plot of $\frac{1}{\Delta A}$ versus $1/(C_{Dye} + C_{surf.} - CMC)$, Fig. 5, Table 4.

The Gibbs energy of solubilization of the dye surfactant micelles is given by [46]:

$$\Delta G_{S}^{o} = -RT \ln K_{\mathrm{s}} \tag{11}$$

The standard free energy change for the transfer of dye from the bulk water phase to the micellar phase is given by [43, 47].

$$\Delta G_{x}^{o} = -RT \ln K_{\mathrm{x}} \tag{12}$$

A conclusion that can be drawn from Table 4 is that the solubilization constant K_{s} increase from C_{10} to C_{18}. Also, by comparing the values of K_{x} for the synthesized gemini cationic surfactants with different alkyl chain lengths, it is found that the solubilization constant K_{x} increases with the alkyl chain. This confirms that the increase in hydrophobicity strengthens the dye-gemini cationic surfactant interactions and the solubilization of AR 52 in the micelles of these compounds.

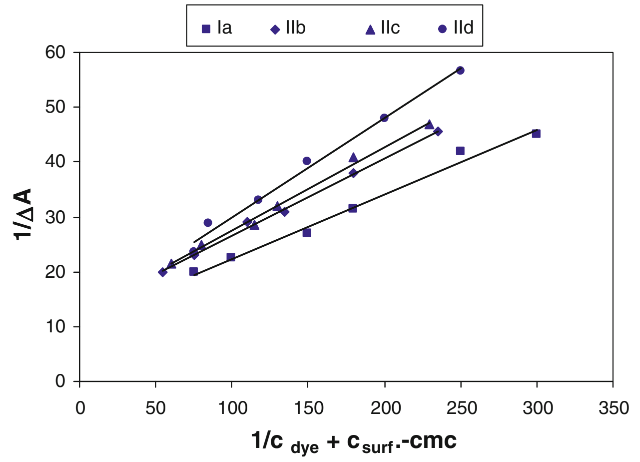


Fig. 5 Plot of $1/\Delta A$ versus ($1/c_{dye} + c_{surf.}$ − CMC) for "AR" 52(30 μmolL^{-1}) with different 1,2-bis-diquaternary ammonium gemini cationic surfactants

The free energy of solubilization (ΔG_{s}^{o}) and the free energy to change from bulk aqueous phase to micellar phase (ΔG_{x}^{o}) were negative and their magnitudes increased with increasing the hydrophobicity of the gemini surfactant.

It was observed that the power of solubility of the Gemini surfactant increased as the hydrophobicity of surfactant increased.

It seems that electrostatic and hydrophobic interactions between the molecules of dye and the surfactant micelles play a major role in the penetration of the dye into the micelles and the solubilization, as well as on the distribution of dye molecules between aqueous and micellar phases. A proposed mechanism of this interaction was similar to that previously mentioned [48].

According to these results, the surfactant which contained longer hydrophobic chain had a stronger tendency to solubilize the dye; the solubilization constants were higher than those measured for the surfactant with the shorter hydrophobic chain.

Conclusions

The reported results show that the aggregation of the synthesized surfactant and anionic azo dye takes place at surfactant concentrations far below the critical micelle concentration of the individual surfactants; their $\lambda_{\max}$ have considerable hypsochromic shift along with a decrease in their intensities which strongly depend on combination of bulk hydrophobic and electrostatic interaction. By increasing cationic surfactants concentration bathochromic shift occurs due to the increase in the solubility of AR52 in cationic micelles. The partition coefficient and free energy charge determined from spectroscopy measurements indicate the incorporation of dye into cationic micelles.

The increase in the alkyl chain length of the gemini surfactant lead to greater hydrophobic interactions and consequently enhanced solubility of the dye in the cationic micelles.

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