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Micellar and Surface Properties of Cationic-Cationic Binary Surfactant Mixtures: Synergistic Interactions and Solubility Enhancement of Anthracene

Elif Berna OLUTAS*[1]

Abstract

The micellar and surface behaviors of decylammonium chloride (DACl) in presence of L-alanine hydrochloride decylester (L-ADE) and L-alanine hydrochloride dodecylester (L-ADDE) at various mole fractions were investigated by conductivity and surface tension measurements. From the conductivity measurements, the critical micelle concentration (CMC), the degree of counter-ion ionization (α) and standard Gibbs energy of micellization (ΔG°_{mic}) were investigated for both pure and binary mixtures. The molecular interaction parameter (β) and the micellar mole fraction (X^{m}_{DACl}) for mixed micelle formation by DACl/L-ADE (C_{10}-C_{10}) and DACl/L-ADDE (C_{10}-C_{12}) were calculated using the regular solution equation proposed by Rubingh. The ideal values of CMC (CMC_{ideal}) and the micellar mole fraction ($X^{m}_{DACl(ideal)}$) were also obtained for mixed micelle according to the pseudo phase theoretical models. The negative β values showed that there were synergistic interactions for all compositions of DACl/L-ADE and DACl/L-ADDE mixed systems. From the surface tension measurements, adsorption parameters such as the surface excess concentration (Γ_{max}), minimum surface tension at the CMC, efficiency in the surface tension reduction (pC_{20}), standard Gibbs energy of adsorption (ΔG°_{ads}), and minimum area per head group of a molecule (A_{min}) in pure, mixed and their ideal values were also determined. The results indicated that the synergism and attractive interactions in the studied binary mixtures depend on the chain length of the cationic L-alanine ester and their mole fractions in the mixed system. The solubilization capacity of pure DACl and its mixed system with L-ADE and L-ADDE towards anthracene were determined and discussed in terms of molar solubilization ratio (MSR). Based on the MSR values, the solubility enhancement was found for anthracene in DACl/L-ADE and DACl/L-ADDE mixed systems.

Keywords: Surfactants, binary mixtures, micellization, synergistic interactions, solubilization.

1. INTRODUCTION

Surfactants, consist of both hydrophobic tail and hydrophilic head, are amphiphilic in nature and self-assemble in water to form aggregates called micelles. The micelles begin to form after a certain minimum concentration called the critical micelle concentration (CMC). Surfactants have important uses in detergent, food, medicine, cosmetics, and many other industries due to their

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unique properties [1,2], e.g., the formation of a micelle structure that can dissolve many substances that are not soluble in water.

The use of surfactants in different fields can be alone or as mixing systems consisting of different head groups (e.g., anionic, cationic, non-ionic and zwitterionic). In most case, the use of surfactant mixtures is preferred over single surfactant due to the better performance of the first one [3-6]. Mixing surfactants often leads to synergism that improves the properties and makes them suitable for their applications. Due to this synergism, surfactant mixtures show lower CMC values than those of pure surfactants. Many studies to understand the micelle formation, adsorption and solubilization phenomena of the surfactant mixtures have shown that physicochemical properties can be controlled by adjusting the compositions of these systems [7].

The hydrophilic head of cationic surfactants has a positive charge, so it adsorbs strongly onto most solid surfaces, that are usually negatively charged, and can give special properties to the substrate [1,8]. Therefore, they are widely used in many aspects, including anti-electrostatic, antibacterial, corrosion inhibitors for metals, dispersants for pigments, germicides for microorganisms, flotation agents for ores etc. [1,8]. The use of binary mixtures of cationic-cationic surfactants can also be improved the application properties. Therefore, the investigation of the micellar and surface properties of these kinds of mixed systems is important for new and effective formulations.

The solubilization is directly related to the micelle formation process and very important phenomenon in many areas such as detergency, oil recovery, dry cleaning, micellar catalysis, and pharmaceutical [1,9-12]. The solubility of organic substances, especially water-insoluble ones, increases by solubilization in the micelles formed by surfactants [9,10,13]. As well-known, polycyclic aromatic hydrocarbons (PAHs) contain fused aromatic rings with linear, cluster, or angular arrangements and contaminate the environment due to their stabilities, high toxicities, hard hydrophobicities, and low biodegradabilities. The low solubility of PAHs in water limits the degradation of these pollutants. One of the promising techniques that increase the aqueous solubility of PAHs is micellar solubilization [4,9,11,14]. In literature, it has been noted that surfactant mixtures not only improve the micellar properties of the system but also increase the solubilization power as well. In studies conducted in this field, it has been observed that especially the solubility of PAHs in water is increased by using mixed surfactant systems [3,4,14-21].

The objective of this study is first to investigate micellization and adsorption properties of pure and binary surfactant mixtures containing the cationic surfactant DACl, and amino acid-based cationic surfactants (L-ADE and L-ADDE) with different hydrophobic tails. Secondly, to reveal the properties of the mixed micelle, the interaction parameters in the micelle phase and at the air/water interface are determined using theoretical models. Finally, the solubility of anthracene that is a kind of PAH in the presence of pure DACl, and its equimolar binary mixture of L-ADE and L-ADDE in water were investigated and compared.

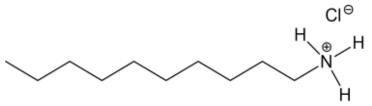
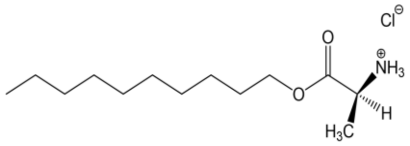
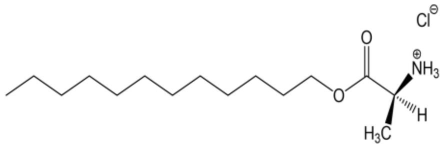
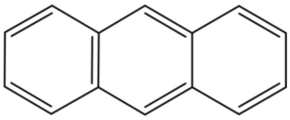
2. MATERIALS AND METHODS

2.1. Chemicals

L-alanine (purity, 99%), 1-decanol, 1-dodecanol (purity, 98%) decylamine (purity, 98%) and anthracene (purity, 98.5%) were obtained from Merck. They were used as received.

Decylammonium chloride (DACl) was obtained by neutralizing the decylamine with dilute hydrochloric acid in ethanol [22]. The esters of L-alanine, L-alanine hydrochloride decylester (L-ADE), and L-alanine hydrochloride dodecylester (L-ADDE), were synthesized using the corresponding alcohols and L-alanine, as described previously [23]. The structures and chemical formulas of DACl, L-ADE, L-ADDE and anthracene are listed in Table 1.

Table 1 The structures and chemical formulas of DACl, L-ADE, L-ADDE and anthracene, respectively.

DACl	
	$C_{10}H_{24}ClN$
L-ADE	
	$C_{13}H_{28}ClNO_2$
L-ADDE	
	$C_{15}H_{32}ClNO_2$
Anthracene	
	$C_{14}H_{10}$

2.2. Preparation of solutions

The stock solutions of surfactants were prepared in distilled water (Milli-Q water purification system) using an analytical balance (±0.00001 g). The concentration of stock solutions was chosen at a concentration well above the CMC values of single surfactants. The stock solutions were then homogenized with the aid of a magnetic stirrer. To prepare the mixed systems with different compositions, stock solutions of pure surfactants were mixed with a proper volume of each pure solution. For instance, for the binary system of DACl/L-ADE (or L-ADDE), 5.0 mL DACl and 5.0 mL L-ADE (or L-ADDE) stock solutions with the same concentrations were mixed to get desired mole fraction of 0.50/0.50. For all other binary mixtures of DACl/L-ADE (or L-ADDE) were prepared with the stock solutions of pure surfactants. The composition of the mixed systems was stated as a mole fraction of cationic surfactant α(DACl).

$$\alpha_{(\mathrm{DACl})}=\frac{n_{(\mathrm{DACl})}}{n_{(\mathrm{DACl})}+n_{(\text{L-ADE or L-ADDE})}} \qquad (1)$$

where n_{DACl} and n_{L-ADE} (or L-ADDE) are the moles of the cationic surfactants DACl and L-ADE (or L-ADDE) in the binary mixture, respectively. The temperature was kept at 25 °C for all measurements.

2.3. Conductivity measurements

A Cyberscan PC 510 digital conductivity meter (Oakton Instruments, cell constant 1.03cm^{-1}) was used to perform measurements. Firstly, the conductance of a known amount of distilled water in the conductivity cell was measured. Then, a certain volume of the stock solution consisting of pure or binary solutions was progressively added to the cell with a micropipette. The conductance was recorded after mixing well and equilibration of the temperature.

2.4. Surface tension measurements

Surface tension measurements were done by a du Noüy ring digital tensiometer (KSV Sigma 702). The accuracy of the tensiometer was within ± 0.01 mN.m^{-1}. The du Noüy ring was cleaned thoroughly and dried before use. The calibration of the tensiometer was done by measuring the surface tension of distilled water. Firstly, a known amount of water was placed into the vessel and the surface tension of the water was recorded. Then, a certain volume of the stock solution was progressively added to the vessel with a micropipette. After thorough mixing and temperature equilibration processes, the surface tension of the pure or mixed system was measured.

2.5. UV-Vis measurements

A UV–Vis double-beam spectrophotometer (Hitachi U-2900) was used for the determination of apparent solubility of anthracene in micellar solutions of DACl and its equimolar binary mixture of L-ADDE in water above their CMCs. Anthracene was added in an excess amount to surfactant solutions with different concentrations. Then, the surfactant solutions containing anthracene were mixed at 25 °C for 24 h. The solutions were centrifuged at 10000 rpm to remove undissolved anthracene. To eliminate the effect of surfactants, the concentration of pure and binary mixture of surfactants was kept the same both in reference and experimental quartz cells having 1 cm of path length. Since anthracene has very low solubility in water (2.53x10^{-7} M), a known amount of anthracene was dissolved in methanol to construct a calibration curve [20,24]. Then, the concentration of anthracene in surfactant solutions was determined from the absorbance data using the standard curve. Therefore, each aliquot of the supernatant and its corresponding surfactant solution in reference cell was diluted with appropriate volume of methanol while measuring their absorbances as stated in the literature [21,24,25,26].

3. RESULTS AND DISCUSSION

3.1. Micellization properties

The conductivity measurements are frequently used method to determine the value of CMC. The conductivity of surfactants increases linearly with the concentration. This increase in conductivity is greater due to the counter ions and charged head groups of free surfactant monomers below the CMC, whereas above the CMC, it is low due to the lower ionic mobility of the micelle in proportion to free surfactant monomers [27]. Therefore, a break is observed at the intersection point of the two straight lines obtained from the conductivity (κ) versus total surfactant concentration (C) graph. This point is taken as the CMC. Representative plots of the κ versus C of single surfactant DACl, and its binary mixtures, DACl/L-ADE and DACl/L-ADDE, with mole fraction of 0.50 in aqueous solution are shown in Figure 1.

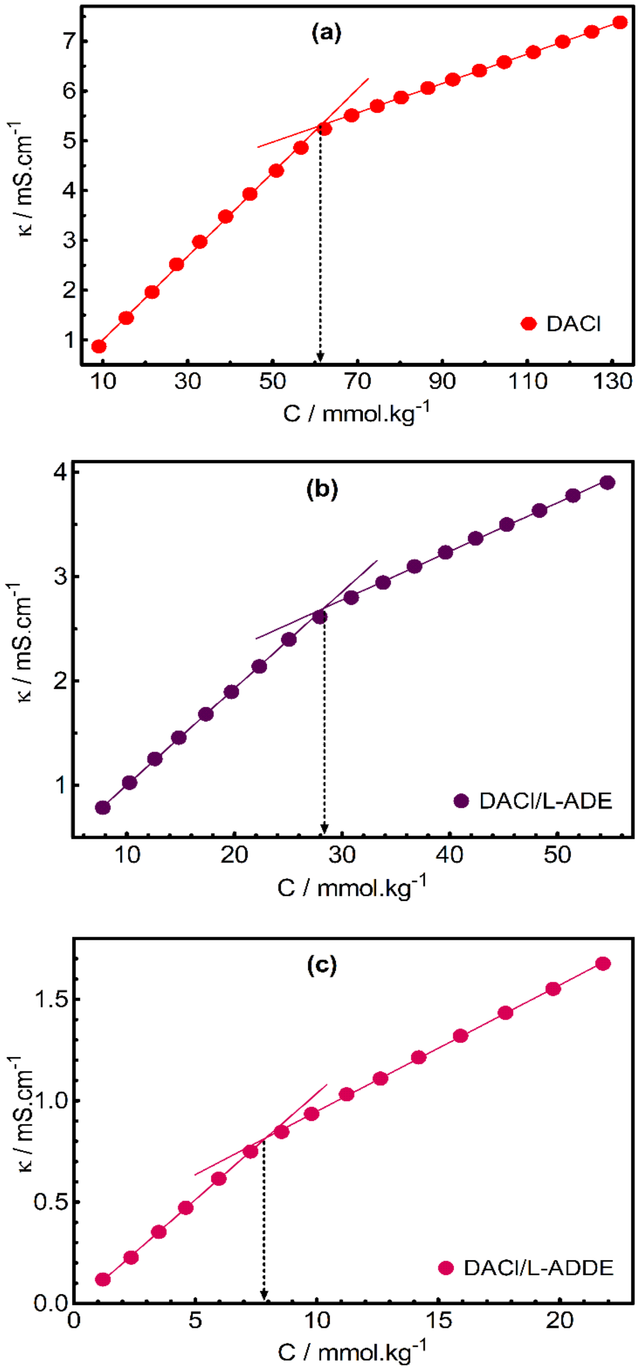


Figure 1 Plot of conductivity (κ) versus concentration (C) for (a) pure DACl, and binary mixtures of (b) DACl/L-ADE, and (c) DACl/L-ADDE with mole fraction of 0.50 in water at 25 °C. The CMC is indicated by the dashed arrow.

Similar behavior was also obtained for the single surfactants L-ADE and L-ADDE, and the binary mixtures of DACl/L-ADE (C_{10}-C_{10}) and DACl/L-ADDE (C_{10}-C_{12}) with different mole fractions. The parameter obtained from the ratio of the slopes of the curves above and below the CMC is the degree of counterion dissociation of the micelle (α). The α values for both single and binary mixtures of the surfactants under study were also calculated. It was found that the α values of the mixed systems increased due to the addition of the second surfactant. In addition to that, the standard Gibbs energy of micellization for all systems was estimated using CMC and α values according to the pseudo-phase separation model [11,28]

$$\Delta G^{\circ}_{mic} = (2-\alpha) RT\, ln X_{CMC} \qquad (2)$$

where X_{CMC}, R and T are the CMC value in terms of mole fraction, the ideal gas constant, and the absolute temperature, respectively. The results have been tabulated in Table 2.

It was observed that the CMC value of DACl is in good agreement with the literature [29,30]. From Table 2, it was also seen that the CMC value of L-ADDE was significantly lower than that of L-ADE despite having the same hydrophilic group. As expected, this difference is due to two additional methylene groups that of L-ADDE has. In the literature, there is a general rule that the CMC of ionic surfactants is halved by adding a methylene group to a straight chain hydrophobic group [1]. The CMC values of mixed systems are generally between those of pure ones [4,31-34]. For our systems, it was found that the CMC values of binary surfactant mixtures were lower than the CMC of DACl and higher than L-ADE or L-ADDE, i.e., they were also between the pure surfactant CMC's, Table 2. Here, it was shown a schematic representation of the micelle consisting of an equimolar (0.50:0.50) binary mixture of DACl/L-ADE to give an idea for studied systems, Figure 2. In general, the studied systems are expected to have aggregates of two different sizes, mostly in the micellar region (below ~10 nm) as previously ones [35].

In addition, the values of ΔG^{o}_{mic} were calculated using Eq. (2) for all systems. As seen from Table 2, ΔG^{o}_{mic} values are all negative indicating the micelle formation is spontaneous process and favored for both pure and mixed surfactant systems.

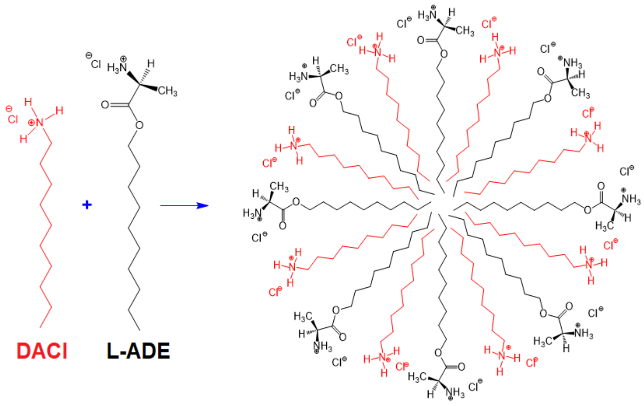


Figure 2 Representive structure of mixed micelle for DACl/L-ADE with 0.50:0.50 mole fraction.

To gain important information about the interactions between mixed surfactants, it is important to investigate the relationship between the CMCs and the composition of the surfactants. The pseudo-phase separation model was utilized to understand how the micellization behavior of DACl/L-ADE and DACl/L-ADDE mixtures deviate from the ideal mixing [36]. Firstly, the ideal CMC values (CMC_{ideal}) of the ideal binary surfactant mixture that has no net interactions between the monomers were obtained by using Clint's equation [2,6,17,27,31,34,37],

$$\frac{1}{CMC_{ideal}} = \frac{\alpha_{DACl}}{CMC_{DACl}} + \frac{(1-\alpha_{DACl})}{CMC_{L-ADE}} \qquad (3)$$

in which CMC_{DACl} and $CMC_{L\text{-}ADE}$ represents the critical micelle concentrations of pure DACl and pure L-ADE (or L-ADDE). The α_{DACl} is the mole fraction of DACl in the binary mixture. The experimental and ideal CMC values (CMC_{exp} and CMC_{ideal}) with a mole fraction of added DACl to L-ADE and L-ADDE are depicted in Figure 3. The experimentally determined CMC values (CMC_{exp}) for DACl/L-ADE and DACl/L-ADDE mixed systems were found to be lower than the CMC_{ideal} values calculated from the individual DACl, L-ADE and L-ADDE surfactant molecules using Equation (3). As it is well known that any deviation of CMC_{exp} from CMC_{ideal} would indicate mutual interactions among surfactants. A positive deviation from ideality ($CMC_{ideal} < CMC_{exp}$) represents antagonism, whereas a negative deviation ($CMC_{ideal} > CMC_{exp}$) shows synergism in the system. It was clear that there were synergistic interactions characterized by a reduction in CMC data for both binary mixtures, Table 2, and Figure 3.

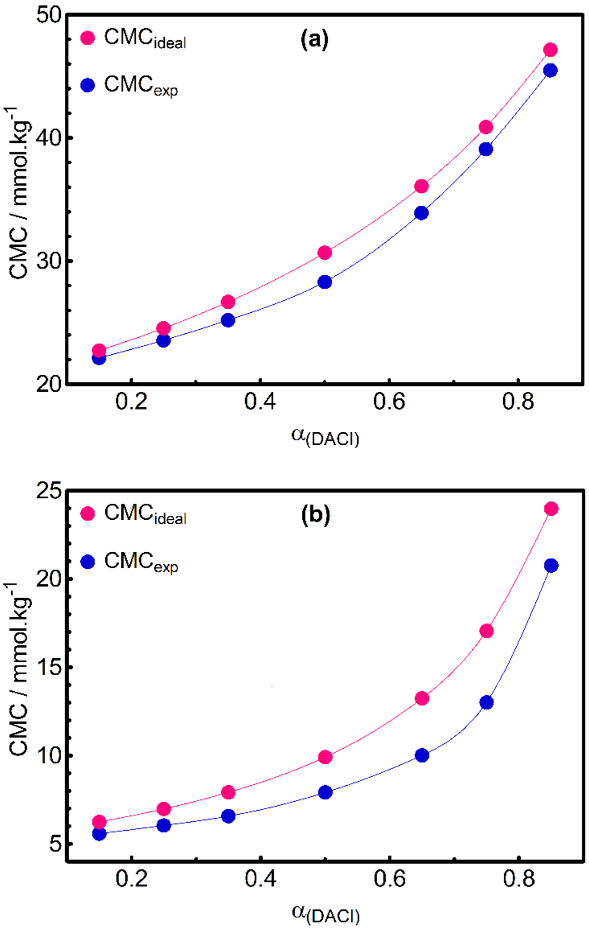


Figure 3 Plots of CMC values (experimental, CMC$_{exp}$ and ideal, CMC$_{ideal}$) versus mole fraction of DACl, $\alpha_{(DACl)}$, for binary mixtures (a) DACl/L-ADE (C_{10}-C_{10}), and (b) DACl/L-ADDE (C_{10}-C_{12}), respectively. The solid lines are a guide for the eye.

Another important parameter that represents the nature and the strength of the interactions between the surfactant monomers in a mixed micelle is the interaction parameter (β^m), i.e., any deviation from the ideality indicating the existence of attractive (synergistic) or repulsive (antagonistic) interactions [3,4]. The negative magnitude of β^m shows synergism, whereas the positive one implies antagonism between the surfactant molecules in the mixed micelles [1,15,16,17]. The composition of mixed micelles, i.e., micellar mole fraction (X^m_{DACl}) and β^m are obtained from the CMC values and the equations of Rubingh's model [6,18,19,31,34.37,38],

$$\frac{X^{m2}_{DACl}\ln(\alpha_{DACl}CMC_{exp}/X^m_{DACl}CMC_{DACl})}{(1-X^m_{DACl})^2\ln[(1-\alpha_{DACl})CMC_{exp}/(1-X^m_{DACl})CMC_{L\text{-}ADE}]}=1 \qquad (4)$$

$$\beta^m=\frac{\ln(\alpha_{DACl}CMC_{exp}/X^m_{DACl}CMC_{DACl})}{(1-X^m_{DACl})^2} \qquad (5)$$

Besides, the micellar mole fraction of DACl in the mixed micelles at an ideal state ($X^m_{DACl(ideal)}$) was determined using the following equation [6,31,34,39],

$$X^m_{DACl(ideal)} = \frac{\alpha_{DACl}CMC_{L\text{-}ADE}}{\alpha_{DACl}CMC_{L\text{-}ADE}+(1-\alpha_{DACl})CMC_{DACl}} \qquad (6)$$

The variations of X^m_{DACl} and $X^m_{DACl(ideal)}$ with $\alpha_{(DACl)}$ for DACl/L-ADE and DACl/L-ADDE mixed systems are given in Figure 4. For the studied binary surfactant mixtures, the values of X^m_{DACl}, $X^m_{DACl(ideal)}$and β^m are also summarized in Table 2. As seen from Table 2, the values of α_{DACl} are greater than X^m_{DACl} and $X^m_{DACl(ideal)}$ for all cases. Therefore, it can be concluded that the contribution of DACl in mixed micelles (X^m_{DACl}) is less than the mixing ratios (α_{DACl}), indicating the priority of formation of mixed micelles are mainly governed by L-ADE or L-ADDE. This shows that the surfactant composition in mixed micelles is different from the composition in solution. The $X^m_{DACl(ideal)}$ values for all mixed systems, except α_{DACl} = 0.85, are lower than X^m_{DACl} values indicating more DACl prefers to settle into mixed micelles when compared with the ideal state. The synergistic (attractive) interactions were observed among DACl and L-ADE (or L-ADDE) monomers in the mixed micelles indicating negative β^m at all mole fractions. As known, the higher the negative magnitude of β^m, the stronger is the synergism between the surfactants. The values β^m are larger for L-ADDE as compared to L-ADE. Even though L-ADE and L-ADDE have the same head group, this difference probably arises from the interactions between the dissimilar hydrophobic tails of DACl (C_{10}) and L-ADDE (C_{12}) that affect the CMC values.

Table 2 Physical parameters of the pure and binary (cationic-cationic) mixed systems as a function of the initial mole fraction of DACl ($\alpha_{(DACl)}$) from conductivity measurements at 25 °C.

(a) DACl/L-ADE (C_{10}-C_{10}) system

$\alpha_{(DACl)}$	CMC /mmol.kg^{-1}	CMC$_{ideal}$ /mmol.kg^{-1}	α	ΔG^o_{mic} /kJ.mol^{-1}	X^m_{DACl}	$X^m_{DACl(ideal)}$	β^m
1	61.28	61.28	0.35	–27.8	–	–	–
0.85	45.49	47.16	0.48	–26.8	0.6438	0.6542	–0.16
0.75	39.09	40.89	0.49	–27.2	0.5004	0.5004	–0.18
0.65	33.92	36.08	0.50	–27.5	0.3957	0.3828	–0.26
0.50	28.31	30.68	0.50	–28.1	0.2848	0.2503	–0.41
0.35	25.21	26.68	0.47	–29.1	0.1877	0.1524	–0.40
0.25	23.57	24.55	0.45	–29.8	0.1301	0.1002	–0.40
0.15	22.14	22.73	0.44	–30.3	0.0778	0.0556	–0.43
0	20.46 [a]	20.46 [a]	0.41 [a]	–31.2 [a]	–	–	–

(b) DACl/L-ADDE (C_{10}-C_{12}) system

$\alpha_{(DACl)}$	CMC /mmol.kg^{-1}	CMC$_{ideal}$ /mmol.kg^{-1}	α	ΔG^o_{mic} /kJ.mol^{-1}	X^m_{DACl}	$X^m_{DACl(ideal)}$	β^m
1	61.28	–	0.35	–27.8	–	–	–
0.85	20.76	23.98	0.70	–25.5	0.3700	0.3326	–0.63
0.75	13.01	17.06	0.66	–27.7	0.3099	0.2088	–1.40
0.65	10.01	13.24	0.64	–29.0	0.2663	0.1404	–1.71
0.50	7.91	9.91	0.59	–30.9	0.2063	0.0809	–1.84
0.35	6.57	7.92	0.54	–32.8	0.1626	0.0452	–2.09
0.25	6.04	6.98	0.50	–33.9	0.1287	0.0285	–2.18
0.15	5.58	6.24	0.46	–35.2	0.0988	0.0153	–2.44
0	5.39 [b]	–	0.37 [b]	–37.3 [b]	–	–	–

[a,b] Values are taken from [28] and [40], respectively.

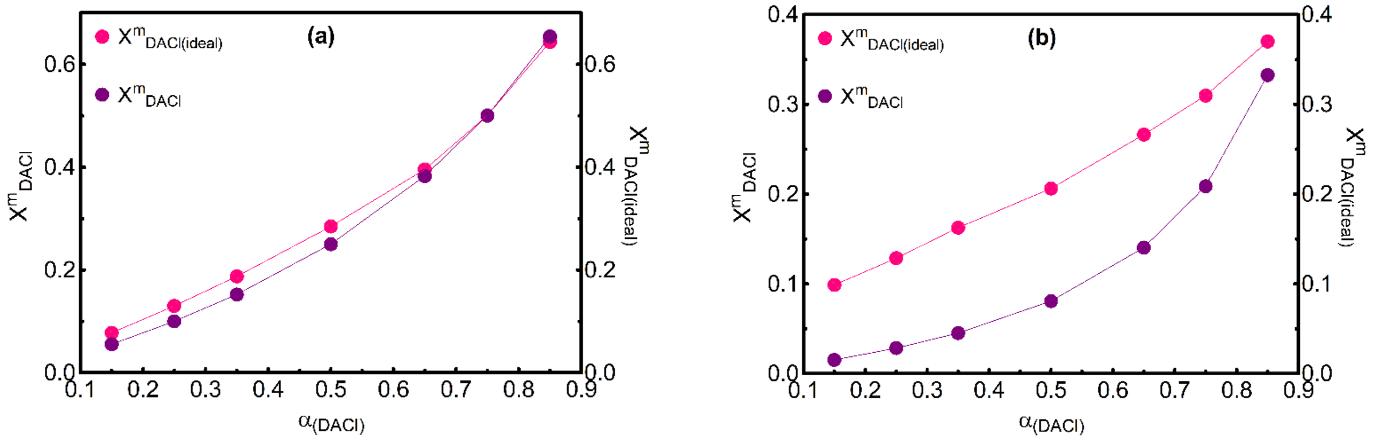


Figure 4 Variations of X^m_{DACl} and $X^m_{DACl(ideal)}$ versus mole fraction of DACl, $\alpha_{(DACl)}$, in systems (a) DACl/L-ADE (C_{10}-C_{10}), and (b) DACl/L-ADDE (C_{10}-C_{12}), respectively. The solid lines are a guide for the eye.

3.2. Surface properties

Adsorption properties of the studied systems were obtained by surface tension measurements. The values of surface tension (γ) were used to determine both CMC and γ_{CMC} values from the break-points of the curves of γ versus lnC, Figure 5. The surface tension values decrease with increasing concentration (C) of the surfactants, and in the range of above CMC, the variation is almost constant. As in the conductivity measurements, the CMC values of the binary mixtures were found to be between the CMC values of pure surfactants. In addition, the γ_{CMC} value of DACl/L-ADE system was between the γ_{CMC} values of pure surfactants, whereas the γ_{CMC}

values of DACl/L-ADDE system were slightly higher than the pure ones. All results were summarized in Table 3.

The maximum surface excess concentration (Γ_{max}) at the air/water interface, which is the number of moles of surfactant molecule adsorbed at the air/water interface per unit area, is evaluated from the surface tension plots using the Gibbs adsorption isotherm equation [5,40,41],

$$\Gamma_{max}=-\frac{1}{nRT}\left(\frac{\partial\gamma}{\partial lnC}\right)_{T,P} \qquad (7)$$

in which R and T are the ideal gas constant in $J.mol^{-1}.K^{-1}$ and the temperature in Kelvin, respectively. Here, n denotes the number of ionic species in solution, which depends on the type and structure of the surfactant and the presence of extra solutes. It was found that Γ_{max} decreases with $\alpha_{(DACl)}$ for both mixed systems, Table 3.

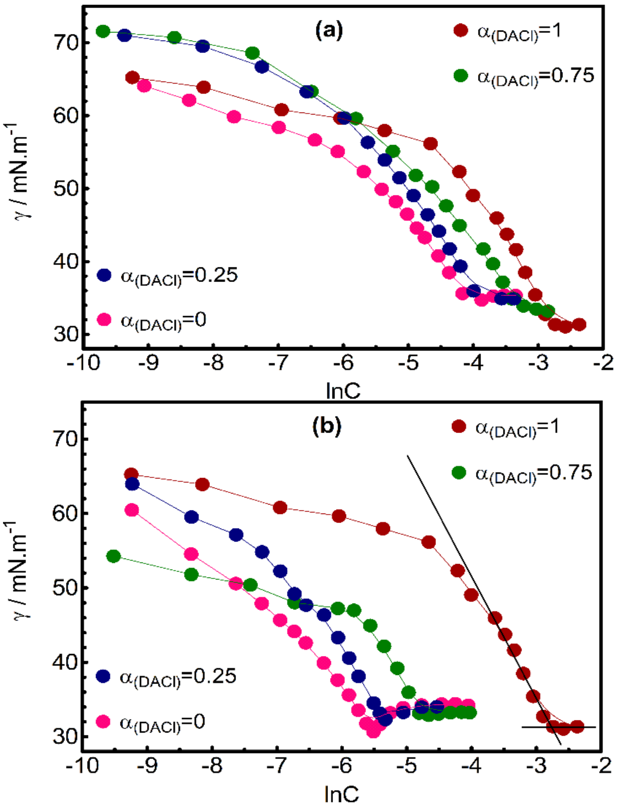


Figure 5 Surface tension versus lnC for (a) DACl/L-ADE (C_{10}-C_{10}), and (b) DACl/L-ADDE (C_{10}-C_{12}) mixed systems with mole fractions of $\alpha_{(DACl)}$=1, 0.75, 0.25 and 0 (pure L-ADE or L-ADDE), respectively. The solid lines are a guide for the eye. The intersection point is used for the determination of CMC and γ_{CMC} values.

The minimum surface area per head group of the surfactant molecule (A_{min}) occupied at the air/water interface was determined using the Γ_{max} values according to equation below [1,11,15,28,29,39,40]:

$$A_{min}=\frac{10^{16}}{N_A\Gamma_{max}} \qquad (8)$$

in which N_A is the is the Avogadro's number and the value of A_{min} in nm^2.

For ideal mixing, the values of A_{min}^{ideal} were calculated from the following expression [42,43]:

$$A_{min}^{ideal}=\alpha_{DACl}A_{min}^{DACl}+(1-\alpha_{DACl})A_{min}^{L-ADE} \qquad (9)$$

where A_{min}^{DACl} and A_{min}^{L-ADE} are the minimum surface area per head group of DACl and L-ADE (or L-ADDE), respectively. It was seen that the experimentally obtained values deviate from those obtained for ideal mixing, i.e., the A_{min} values are smaller than the corresponding A_{min}^{ideal} ones, Table 3, and Figure 6. These results indicate synergistic interactions between the mixed surfactant systems, DACl/L-ADE and DACl/L-ADDE.

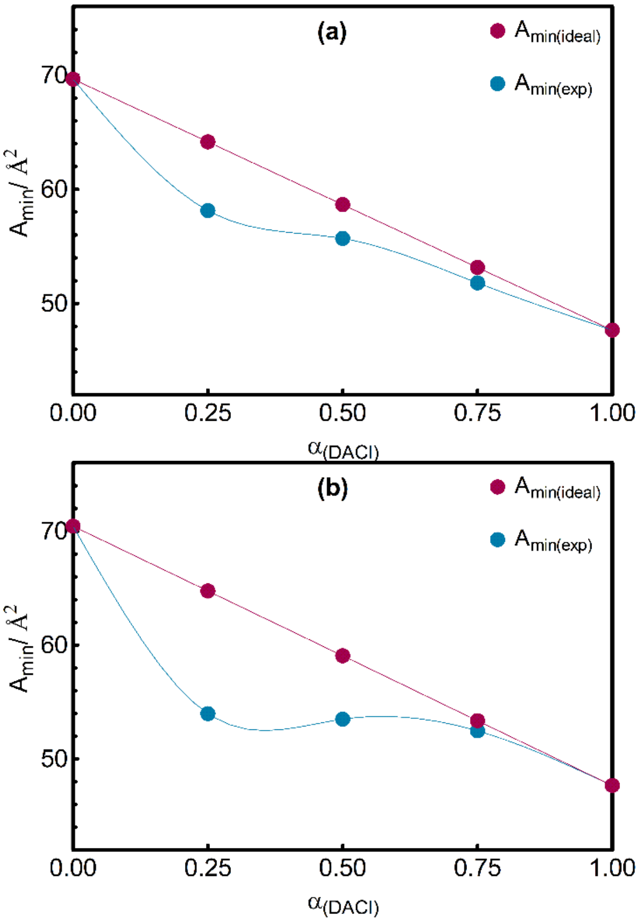


Figure 6 Variations of $A_{min(exp)}$ and $A_{min(ideal)}$ versus mole fraction of DACl, $\alpha_{(DACl)}$, in systems (a) DACl/L-ADE (C_{10}-C_{10}), and (b) DACl/L-ADDE (C_{10}-C_{12}), respectively. The solid lines are a guide for the eye.

Table 3 Physical parameters of the pure and binary (cationic-cationic) mixed systems as a function of the initial mole fraction of DACl from surface tension measurements at 25 °C.

(a) DACl/L-ADE (C_{10}-C_{10}) system

$\alpha_{(DACl)}$	CMC /mmol.kg^{-1}	γ_{CMC} /mN.m^{-1}	Γ_{max} /x10^{-10}mol.cm^{-2}	A_{min} /Å^2	A_{min}^{ideal} /Å^2	pC_{20}	ΔG^o_{ads} /kJ.mol^{-1}
1	62.56	31.23	3.48	47.67	–	1.8	–39.5
0.75	35.28	33.86	3.21	51.81	53.16	2.1	–39.1
0.50	29.13	33.89	2.98	55.70	58.66	2.1	–40.9
0.25	20.38	34.88	2.86	58.14	64.16	2.3	–42.8
0	17.08	35.16	2.38	69.65	–	2.5	–46.4

(b) DACl/L-ADDE (C_{10}-C_{12}) system

$\alpha_{(DACl)}$	CMC /mmol.kg^{-1}	γ_{CMC} /mN.m^{-1}	Γ_{max} /x10^{-10}mol.cm^{-2}	A_{min} /Å^2	A_{min}^{ideal} / Å^2	pC_{20}	ΔG^o_{ads} /kJ.mol^{-1}
1	62.56	31.23	3.48	47.67	–	1.8	–39.5
0.75	8.40	33.02	3.16	52.47	53.36	3.6	–40.0
0.50	5.99	32.91	3.10	53.49	59.06	3.2	–43.2
0.25	4.72	32.41	3.08	53.98	64.75	3.0	–46.8
0	4.50 [a]	31.82 [a]	2.36 [a]	70.44 [a]	–	3.4 [a]	–54.6 [a]

[a] Values are taken from [40].

The efficiency of adsorption (pC_{20}) is the negative logarithm of the surfactant concentration required to produce a 20 $mN.m^{-1}$ drop at the surface tension (C_{20}) for a given solvent and obtained by the given relation [1,8,28,40,44],

$$pC_{20} = -\log C_{20} \tag{10}$$

The greater the pC_{20} value of a surfactant, the more it tends to adsorb at the air-water interface, thus reducing the surface tension more efficiently. The pC_{20} values of mixed systems are greater than DACl, Table 3. This shows that the mixed systems are superior in their efficiency at reducing surface tension. Finally, the standard Gibbs energy of adsorption (ΔG°_{ads}) is calculated using the equation below [11,28,39,41],

$$\Delta G^{\circ}_{ads} = \Delta G^{\circ}_{mic} - \pi_{CMC} / \Gamma_{max} \tag{11}$$

in which π_{CMC} indicates the surface pressure at the CMC (the difference between the surface tension of the pure water and γ_{CMC} value) and is related to the effectiveness of a surfactant. The ΔG°_{ads} values, Table 3, were found to be all negative indicating the adsorption of pure and mixed systems at air/water interface is also spontaneous as in the case of the micellization process.

3.3. Solubilization properties

In addition to finding the micellization and surface properties of pure DACl and their binary mixtures with L-ADE and L-ADDE, it was also aimed to investigate the solubilization of anthracene using mixed systems. Investigating this phenomenon in the systems containing more than one surfactant would be of interest and importance from both practical and academic perspectives.

To find the molar solubility of anthracene in surfactant solutions, firstly, the absorbance of a series of anthracene solutions was measured, Figure 7(a). Then, a standard curve (R^2=0.9999) satisfying the Beer-Lambert law was obtained by plotting the absorbance versus the concentration, Figure 7 (b). The molar extinction coefficient (ε) of anthracene was determined as $7.28\times10^{3}\ M^{-1}cm^{-1}$ at the maximum absorption wavelength λ_{max}=355nm from the slope of the Figure 7 (b). The value ε, which tallied well with the literature value, was then used to determine the total molar solubility of anthracene (S) for the studied systems using the Beer-Lambert law [20].

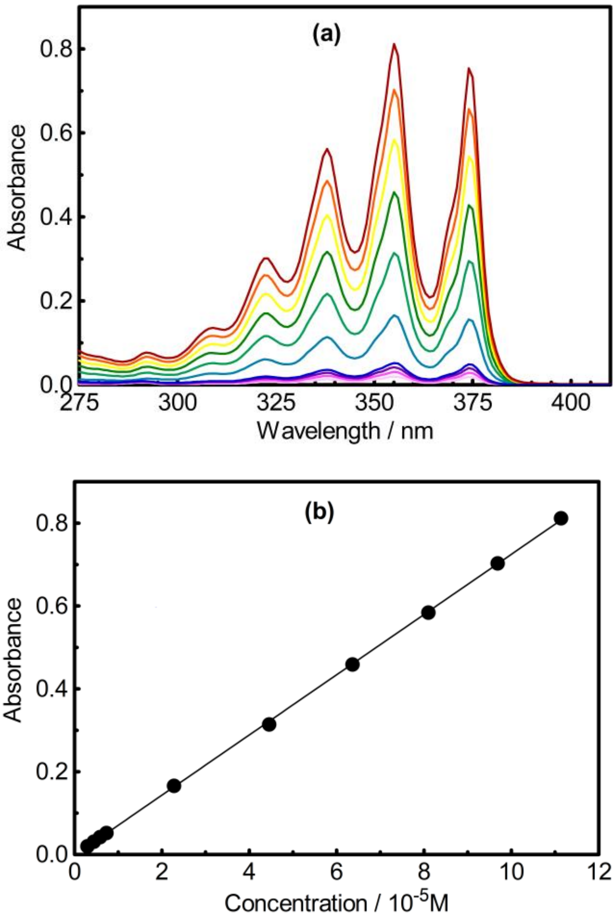


Figure 7 (a) Absorption spectra of anthracene in methanol at different concentrations. (b)Variations of maximum absorbance at 355 nm with anthracene concentration.

The solubilization capacity of a surfactant is expressed in terms of the molar solubilization ratio (MSR). The value of MSR can be calculated with the following expression [4,11,14-21]

$$MSR = \frac{(S_t - S_{CMC})}{(C_t - C_{CMC})} \tag{12}$$

in which S_t and S_{CMC} represent the total molar solubility of anthracene in the pure/mixed surfactant solutions at a particular total concentration (C_t) and CMC, respectively.

The change of anthracene solubility as a function of the concentration of pure DACl and its equimolar binary mixtures with L-ADE and L-

ADDE is shown in Figure 8. The values of MSR obtained from the slope of the plots for studied systems herein are given in Table 4. It was seen that the solubility of anthracene increased linearly with the concentration of single and mixed surfactants. This was related to solubilization of anthracene within single and mixed surfactant micelles. The solubilization capacity of mixed systems was found to be greater than that of the single one for anthracene in line with the literature [4,15,16,21,24,45]. This has been demonstrated the advantage of using a mixture rather than a single surfactant. Among the mixed systems, DACl/L-ADDE showed better solubilization capacity (higher MSR value) for anthracene than that of DACl/L-ADE, Table 4. This was related to the more hydrophobic environment of DACl/L-ADDE (C_{10}-C_{12}) mixed micelles where more solubilization occurred [24].

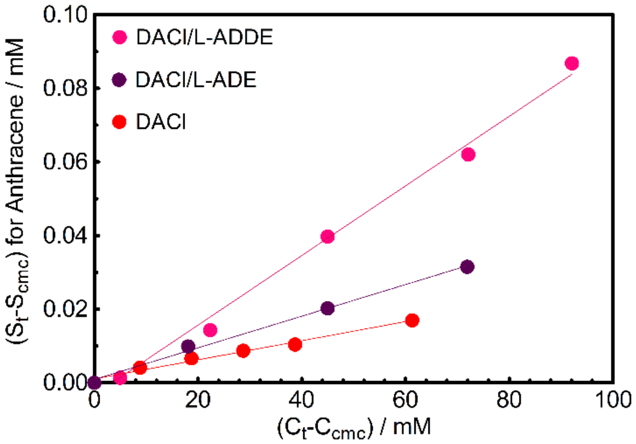


Figure 8 Variations of solubility of Anthracene with surfactant concentration in pure DACl and equimolar (0.50:0.50) binary mixtures with L-ADE and L-ADDE.

Table 4. Molar solubilization ratio (MSR) values pure and equimolar binary (cationic-cationic) mixed systems for anthracene at 25 °C.

	DACl	DACl/L-ADE	DACl/L-ADDE
MSR	0.00026	0.00043	0.00095

4. CONCLUSION

Mixed micelle formations in two systems consisting of cationic surfactants, DACl/L-ADE (C_{10}-C_{10}) and DACl/L-ADDE (C_{10}-C_{12}), were studied using conductivity and surface tension methods. It was found that synergism and attractive interactions between surfactants dominate micellization at all mole fractions of DACl. These synergistic interactions in surfactant mixtures are important in reducing the amount of surfactant required for certain applications, thus contributing to reduced cost and environmental impact. The effect of pure DACl and its equimolar binary mixture of L-ADE and L-ADDE on the solubilization of anthracene was studied. It was reported that the solubility of anthracene in water increases with the use of pure and mixed surfactants. This increase is more in mixed systems than in the single one. The results show that experiments can be extended to increase the solubility of other hydrophobic materials, such as dyes and drugs, and shed light on future studies.

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The Declaration of Conflict of Interest/ Common Interest

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The Declaration of Ethics Committee Approval

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The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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