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Comparative study of micellization and surface properties of cationic and anionic surfactants in acetonitrile–water mixed media

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Abstract: A comparative study was conducted to investigate the micellization behaviour, surface properties and wettability of the cationic surfactant cetyltrimethylammonium bromide (CTAB) and the anionic surfactant sodium dodecyl sulfate (SDS) in acetonitrile–water (ACN–water) mixed media. Surface tension and contact angle measurements were performed in pure water and ACN–water mixtures (0.10, 0.20 and 0.40 volume fractions of ACN) at 298.15 K to determine the critical micelle concentration (CMC), surface excess concentration (Γ_{max}), minimum surface area per molecule (A_{min}), micellar surface pressure (π_{CMC}) and packing parameter (P). Contact angle measurements were used to assess wettability on borosilicate glass surfaces. Results indicate that increasing ACN content leads to an increase in CMC , suggesting reduced micellization feasibility in less polar media. Surface excess concentration decreases with higher ACN fractions, while minimum surface area per molecule increases, indicating looser molecular packing at the air/solution interface. Contact angle measurements reveal a decrease in wettability with higher ACN content, demonstrating enhanced surfactant adsorption at the solid-liquid interface. Additionally, micellar surface pressure and packing parameter decline with increasing ACN concentration. These findings underscore the critical role of solvent composition in modifying surfactant aggregation and interfacial behaviour.

Keywords: surface tension; surfactant; contact angle; acetonitrile.

INTRODUCTION

Surfactants, a class of amphiphilic organic compounds, play a critical role in various industrial and scientific applications due to their ability to form micelles in solution, which significantly alter the properties of the medium. Amphiphilicity is a property of an organic molecule that possesses both hydrophilic, identified as head and hydrophobic, identified as tail. This dual nature allows them to interact

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with both polar (aqueous) and non-polar (organic) environments, making them crucial in a variety of chemical and biological processes. Surfactants exhibit unique behaviour when dissolved in a solvent, especially in aqueous media. At low concentrations, these molecules tend to arrange themselves at the interface between water and air, reducing the surface tension. However, when their concentration exceeds a critical threshold, known as the critical micelle concentration (*CMC*), these molecules spontaneously form micelles.¹ In these micelles, the hydrophobic tails aggregate inward to avoid water (being hydrophobic), while hydrophilic heads face outward, interacting with the aqueous environment. This self-assembly process is driven by the system's tendency to minimize free energy and is fundamental to many industrial and biological applications.^{2–6}

Aqueous–organic mixed solvents play a crucial role in influencing the micellization behaviour of surfactants due to the unique interplay of polar and non-polar interactions in these media. In such systems, the combination of water- and water-soluble organic solvents like alcohol, acetone creates a versatile environment where the solvation properties, hydrophobic effects and surfactant aggregation dynamics can be finely tuned.^{7–11}

Ionescu *et al.*¹² studied the development of micelles of CTAB in water–dimethyl sulfoxide (DMSO) mixtures, observing that DMSO has a variable effect on CTAB micellization. Shah *et al.*¹⁰ investigated the influence of methanol on the micellar properties of dodecyltrimethylammonium bromide (DTAB) and found that *CMC* increased with increasing methanol content, suggesting that the addition of organic co-solvents disrupts micelle formation. Niraula *et al.*¹³ similarly showed that the *CMC* of SDS rises with methanol content, supporting the general observation that polar organic solvents reduce the feasibility of micelle formation. Bielawska *et al.*¹⁴ explored the effect of short-chain alcohol on CTAB micellization and observed that alcohols significantly alter *CMC* values. Das *et al.*¹⁵ reported that the presence of cosolvents increases the *CMC* and decreases the aggregation number for cationic, anionic and nonionic surfactants.

In the context of acetonitrile (ACN), Misra *et al.*¹⁶ examined CTAB and SDS micellization in ACN–water and tetrahydrofuran (THF)–water mixtures and observed a consistent increase in *CMC* with rising ACN mole fraction. The increase was more pronounced for CTAB than for SDS, indicating stronger disruption of cationic surfactant self-assembly by ACN. Šteflová *et al.*¹⁷ found that low ACN concentration (up to 0.10 by volume fraction) reduces *CMC* of SDS, whereas higher ACN volume fraction increases it, indicating a biphasic effect. Jalali and Gerandaneh¹⁸ observed that the *CMC* of CTAB increases linearly with ACN content due to weakened solvophobic effects in the medium. Ležaić *et al.*¹⁹ further reported a simultaneous rise in *CMC* and decline in aggregation number for CTAB in ACN–water, reflecting reduced micellar stability. Banjare *et al.*²⁰ confirmed

these trends and showed decreased surface excess and increased minimum area per molecule (A_{\min}) in CTAB–ACN–water systems.

These findings are further supported by our recent study²¹ that compared the effects of 10 % by volume of DMSO, ACN and 1-propanol on SDS, DTAB and CPC. The data showed that ACN significantly increases the *CMC* and decreases the aggregation number and surface excess concentration (Γ_{\max}), indicating reduced micellar compactness and lower interfacial adsorption. The overall trend of co-solvent strength was found to be: 1-propanol > ACN > DMSO in terms of disrupting micellization.

Overall, these studies underscore the pivotal role of solvent polarity and specific interactions in modulating micelle formation and interfacial behaviour of ionic surfactants. In particular, ACN emerges as a moderately polar aprotic solvent that weakens hydrophobic interactions and reduces surfactant packing, thus significantly altering micellization and adsorption dynamics.

Studying both SDS (anionic) and CTAB (cationic) surfactants in ACN–water mixtures is particularly relevant due to their contrasting ionic head groups, which interact differently with polar aprotic co-solvents like acetonitrile. SDS carries a negatively charged sulfate group, while CTAB contains a positively charged quaternary ammonium head. These differences influence not only micelle formation and *CMC* values but also interfacial adsorption, counterion binding and solvation dynamics in mixed solvent environments. A comparative analysis provides insights into how solvent polarity modulates electrostatic and hydrophobic contributions to micellization, enabling a broader understanding of surfactant behaviour in non-aqueous or mixed-phase systems relevant to colloidal formulation, extraction and drug delivery applications.

The wetting behaviour of surfactants is significantly influenced by the composition of the solvent system,²² as the balance between hydrophilic and hydrophobic interactions dictates surfactant adsorption at interfaces. In mixed solvent systems, such as water–organic mixtures, the presence of co-solvents alters surface tension, interfacial interactions and contact angle, thereby modifying wettability. Polar solvents like short-chain alcohols disrupt the structured hydrogen-bonding network, weakening surfactant adsorption at the solid–liquid interface and increasing the contact angle, leading to reduced spreading.²³

The objective of this study is to investigate the micellization and surface properties of CTAB and SDS in ACN–water mixed media, focusing on their surface properties and wetting behaviour. By analysing *CMC*, surface tension, contact angle and related parameters, this work aims to provide an understanding of how solvent composition influences surfactant aggregation and wettability. While several earlier studies have examined the micellization behaviour of ionic surfactants in ACN–water mixed solvent systems, including CTAB¹⁶ and SDS,¹⁷ most have focused primarily on micellization behaviour in the bulk phase using

classical techniques such as conductometry or fluorescence. In contrast, the present study incorporates surface and wetting property analysis – especially surface tension and contact angle measurements evaluate the interfacial behaviour of both cationic (CTAB) and anionic (SDS) surfactants in ACN–water mixtures. This dual focus enables the exploration of how co-solvent-modified polarity affects not only micelle formation but also surfactant adsorption and spreading behaviour on a solid surface.

EXPERIMENTAL

Materials

CTAB (99.0 % pure) and SDS (99.0 % pure) were purchased from Loba Chemie Pvt. Ltd., Mumbai, India. These surfactants were used without further purification. They were heated in an oven at 100 °C for 1 h prior to use. Acetonitrile (ACN, 99.0 % pure) was obtained from E. Merk, India. All the solvent mixtures and solutions were prepared in double-distilled water (specific conductance < 0.6 $\mu\text{S cm}^{-1}$ at 298.15 K).

Methods

The surface tension of a freshly prepared solution was measured by an Easydyne K20 force tensiometer (Kruss, Germany) equipped with a du Nouy's ring. The ring was cleaned by dipping it in ethyl alcohol and then heated until red-hot in the blue flame of a Bunsen burner. Double-distilled water was used to calibrate; the value obtained was 72.30 mN m^{-1} at 298.15 K. The temperature was controlled by a circulatory water bath (Orbit, RS10S) with an accuracy of ± 0.1 K.

Surface tension measurements and *CMC* determination were conducted for SDS and CTAB solutions. For SDS (0.0004–0.08 M) in distilled water and ACN–water mixtures (0.10, 0.20, 0.40 volume fractions of ACN), a 50 mL vessel was filled with 30 mL of solution. Surface tension was measured using a platinum ring and a tensiometer after stirring and resting for 2 min. Similarly, CTAB (0.0006–0.001 M) solutions were analysed following the same procedure.

The *CMC* was determined from a surface tension (γ) *versus* logarithm of surfactant concentration ($\log C/M$) plot. The data were fitted with linear regression corresponding to the pre-micellar region. In the pre-micellar region, γ decreases linearly with increasing $\log C/M$ as surfactant molecules accumulate at the air/solution interface. Beyond *CMC*, γ remains almost constant or changes very slightly. The interaction point of these pre- and post-micellar regions is commonly depicted as *CMC*.²⁴

Contact angles of freshly prepared solutions were measured using a drop shape analyzer (DSA25E, Kruss, Germany) by the sessile drop method on a borosilicate glass surface. For SDS (0.08–0.0004 M) in distilled water and ACN–water mixtures (0.10, 0.20, 0.40 volume fractions of ACN), a 3 μL drop was placed at 2.57 $\mu\text{L/s}$ and contact angles were recorded from both sides, averaging thirty replicates. The syringe was calibrated and cleaned before use. Similarly, CTAB (0.0006–0.001 M) solutions were analysed following the same procedure. Eight readings were recorded for each case.

RESULTS AND DISCUSSION

Surface tension and surface properties

Surface tension (γ) of CTAB and SDS solutions was measured in water, 0.10, 0.20 and 0.40 volume fractions of ACN–water mixed solvent media at 298.15 K.

A graph is plotted between γ and the logarithm of concentration ($\log C$) for each solution, as shown in Fig. 1. The break point of the graph represents CMC . The slope of the graph $\partial\gamma/\partial(\log C)$ is utilized to calculate surface properties. One of the surface properties is the maximum surface excess concentration (Γ_{\max}) given as:²⁵

$$\Gamma_{\max} = -\frac{1}{2.303nRT} \left(\frac{\partial\gamma}{\partial \log C} \right)_{T,p} \quad (1)$$

R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) denotes the gas constant, T indicates the absolute temperature and C indicates the concentration of surfactant. The value of n taken as the constant pre-factor, is assumed to be 2 for the normal ionic surfactant. T is the absolute temperature, C is the concentration of surfactant, $(\partial\gamma/\partial \log C)$ is the slope of the γ versus $\log (C/M)$ plot just below the CMC at constant temperature.

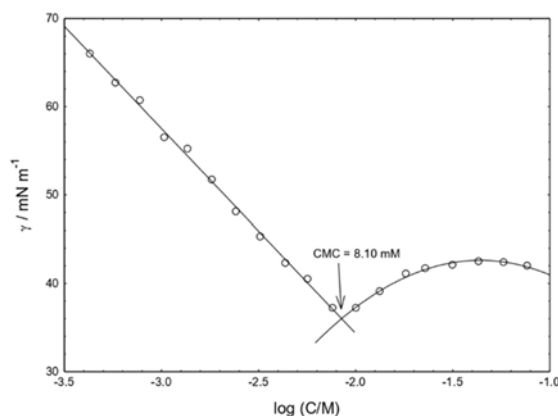


Fig. 1. Plot of surface tension (γ) against the logarithm of SDS concentration ($\log C/M$) in water at 298.15 K; the critical micelle concentration (CMC) is indicated by an arrow.

The minimum area per molecule (A_{\min}) of surfactant at the air–water interface, *i.e.*, the area covered by a surfactant molecule on the solution/air interface, is given as:

$$A_{\min} = \frac{1}{N_A \Gamma_{\max}} \quad (2)$$

where N_A denotes Avogadro number ($6.022 \times 10^{23} \text{ mol}^{-1}$).

The surface pressure (π_{CMC}) is a measure of how efficiently a surfactant lowers the surface tension of a solution at CMC . It can be calculated using:

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad (3)$$

where γ_0 and γ_{CMC} are surface tensions (in mN m^{-1}) of solvent and CMC , respectively.

A_{\min} can be utilized to calculate the packing parameter (P) that predicts the shape of aggregated micelle:²⁶

$$P = \frac{V_0}{A_{\min} l_C} \quad (4)$$

where V_0 denotes the volume of exclusion per monomer during aggregation, as explained in Tanford's formula:²⁷ $V_0 = (27.4 + 26.9n_C) \text{ \AA}^3$ and $l_C = (1.54 + 1.26n_C) \text{ \AA}$ shows the maximum chain length and n_C denotes the total number of carbon atoms present in the alkyl chain.

Effect of ACN on CMC

The *CMC*, which is the concentration of surfactants at which micelles start to form, is extremely sensitive to solvent composition. In purely aqueous solutions, the hydrophobic effect is the primary driving force for micelle formation, with water molecules tending to "squeeze out" the non-polar tails of surfactants, forcing them to aggregate into micelles to minimize free energy. As ACN is added to water, the solvent becomes less polar and the hydrophobic effect is weakened. This means that surfactants require a higher concentration to reach the point where micelles can form. The *CMC* thus increases with ACN content. This effect is seen in both SDS and CTAB cases, where the *CMC* of SDS and CTAB increases with the increase in volume fraction of ACN.

The effect of ACN addition on the micellization of CTAB has been reported by several studies at 298.15 K, using different analytical techniques. Across all reports, the *CMC* increases with rising ACN content, attributed to the reduced polarity and weakened hydrophobic interactions in the solvent mixture. Misra *et al.*¹⁶ employed spectroscopic and conductometric methods to determine the *CMC* of CTAB in ACN–water mixtures at 298.15 K. The *CMC* increased from 0.42 mM in pure water to 0.78 mM at an ACN mole fraction of 0.141. Jalali and Gerandaneh¹⁸ used conductivity measurements and found the *CMC* to rise from 0.96 mM in water to 1.63 mM at 0.20 volume fraction of ACN and further to 3.19 mM at 0.40 volume fraction of ACN, all measured at 298.15 K. Ležaić *et al.*¹⁹ determined the *CMC* using conductometry and fluorescence techniques, reporting a value of 0.98 mM in pure water and 3.50 mM at 0.40 volume fraction of ACN at 298.15 K. Banjare *et al.*²⁰ applied surface tension measurements, reporting *CMC* values increasing from 1.0 mM in water to 1.5 mM at 0.005 volume fraction of ACN, 2.5 mM at 0.01 volume fraction of ACN and 3.0 mM at 0.03 volume fraction of ACN. This indicates that the presence of ACN affects the micellization behaviour of CTAB. Similarly, Šteflová *et al.*¹⁷ observed that the *CMC* of SDS increases progressively with higher ACN content, from 4.8 mM at no ACN to 22 mM at 0.35 volume fraction of ACN, indicating reduced micelle stability in ACN-rich environments.

Effect of ACN on surface properties

Figs. 2 and 3 represent combined plots of γ and $\log C$ for SDS and CTAB in different volume fractions of ACN–water mixed solvent media at 298.15 K. The regression analysis is provided in Table I. The fits demonstrate good linearity ($r^2 \geq 0.90$), confirming the reliability of the surface tension data. The premicellar slopes derived from the plot of γ against the logarithm of SDS concentration ($\log C/M$) (Table I) provide insight into the efficiency of surfactant adsorption at the air/solution interface prior to micelle formation. In both SDS and CTAB systems, the magnitude of the slope decreased (became less negative) with increasing ACN content. This trend suggests that the presence of ACN reduces the surface activity of the surfactants in the premicellar region, likely due to weaker hydrophobic interactions and decreased interfacial packing efficiency. The steeper slope in pure water indicates stronger adsorption, consistent with the structured hydrogen-bonding network of water supporting micellization. Our group has previously reported similar trends in mixed solvent systems. In a recent study,²⁴ we demonstrated that the premicellar slope of TX100 decreased systematically with increasing concentrations of methanol, ethanol and 1-propanol, highlighting the weakening of surfactant adsorption and interfacial cohesion in less polar media. CMC and surface properties (Γ_{\max} , A_{\min} , π_{CMC} and P) of SDS and CTAB solutions in water and in 0.10, 0.20 and 0.40 volume fractions of ACN are presented in Tables II and III, respectively.

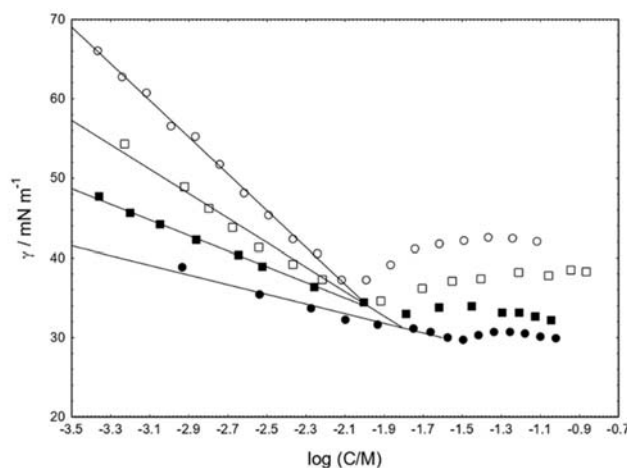


Fig. 2. Plot of surface tension (γ) against the logarithm of SDS concentration ($\log C/M$) in 0.10 (\square), 0.20 (\blacksquare) and 0.40 (\bullet) ACN volume fractions in ACN–water mixtures at 298.15 K.

Surface excess concentration (Γ_{\max}) is a measure of how much surfactant accumulates at the surface compared to the bulk solution. In an aqueous solution, surfactants migrate to the air/water interface to minimise the system's free energy.

The surfactant molecules arrange themselves such that the hydrophobic tails are oriented away from the water, while the hydrophilic heads remain in contact with it. The addition of a polar organic solvent into aqueous solutions of surfactants significantly alters the surface and interfacial properties, including Γ_{\max} , A_{\min} , π_{CMC} and P . The effect primarily arises from its ability to reduce the overall polarity of the solvent and disrupt the structured hydrogen-bonding network of water.

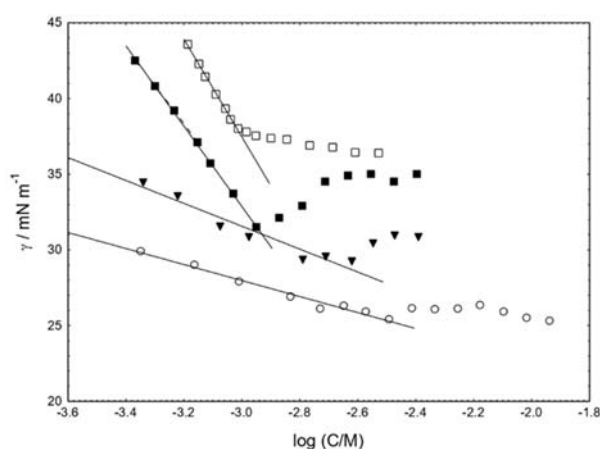


Fig. 3. Plot of surface tension (γ) against the logarithm of CTAB concentration ($\log C/M$) in water (\square) and 0.10 (\blacksquare), 0.20 (\blacktriangledown) and 0.40 (\circ) ACN volume fractions in ACN–water mixtures at 298.15 K.

TABLE I. Regression summary of the plot of surface tension (γ) against the logarithm of concentration ($\log C/M$) related to Figs. 2 and 3

Volume fraction of ACN	$(\partial\gamma/\partial\log C)$	r^2
SDS		
0.00	-23.2	0.99
0.10	-15.4	0.97
0.20	-9.79	0.99
CTAB		
0.00	-32.3	0.99
0.10	-26.5	0.99
0.20	-7.56	0.94
0.40	-5.29	0.98
0.00	-32.3	0.99

ACN, being less polar than water, interacts more favourably with the hydrophobic tails of surfactants, reducing the driving force for their accumulation at the interface. This weakens the hydrophobic effect, resulting in fewer surfactant

TABLE II. CMC by surface tension (ST) and contact angle (CA) methods; Γ_{\max} , A_{\min} , π_{CMC} and P of SDS in different volume fractions of ACN at 298.15 K

Volume fraction of ACN	CMC (mM)		$\Gamma_{\max} \times 10^6$ mol m ⁻²	A_{\min} Å molecule ⁻¹	π_{CMC} mN m ⁻¹	P
	ST	CA				
0.00	8.10	7.90	2.02	82.07	33.97	0.26
0.10	12.09	12.12	1.34	123.11	25.50	0.17
0.20	16.32	15.33	0.85	193.66	15.20	0.10
0.40	31.99	32.42	0.53	312.31	8.30	0.07

TABLE III. CMC by surface tension (ST) and contact angle (CA) methods, Γ_{\max} , A_{\min} , π_{CMC} and P of CTAB in different volume fractions of ACN at 298.15 K

Volume fraction of ACN	CMC (mM)		$\Gamma_{\max} \times 10^6$ mol m ⁻²	A_{\min} Å molecule ⁻¹	π_{CMC} mN m ⁻¹	P
	ST	CA				
0.00	0.96	0.89	2.82	58.69	37.02	0.35
0.10	1.12	1.01	2.32	71.74	34.60	0.29
0.20	1.63	1.72	0.66	250.78	32.96	0.08
0.40	3.19	3.22	0.46	358.40	29.68	0.05

molecules migrating to the interface. Consequently, the surface excess concentration decreases as the ACN content increases. As the ACN content in the solution increases, the interactions between surfactant head groups and the solvent become weaker. ACN's lower polarity compared to water reduces the effectiveness of the hydrophilic head group's interaction with the surrounding solvent molecules. This leads to less efficient packing of surfactant molecules at the surface, resulting in a larger minimum area per molecule A_{\min} . The larger value of A_{\min} indicates that surfactant molecules are spaced farther apart at the interface in ACN-rich mixtures than in purely aqueous solutions. Surface pressure (π_{CMC}) represents the pressure exerted by surfactants at the interface once micelles start forming in the bulk solution. A higher π_{CMC} value indicates stronger surface activity of the surfactant because it means that the surfactant has significantly reduced the surface tension. It is seen from the data (Tables II and III) that the presence of ACN decreases π_{CMC} values for both SDS and CTAB. The packing parameter (P) describes the morphology of micelles. $P \approx 1/3$ corresponds to spherical micelles. The lower values of P in the presence of ACN indicate that the size of the micelles changes from spherical to worm-like structures. To contextualize the present findings, surface properties such as Γ_{\max} and A_{\min} for CTAB and SDS were compared with literature values in binary solvent systems. Recently, our group observed that the addition of co-solvents (DMSO, ACN, 1-propanol) to surfactants SDS, DTAB and CPC reduced adsorption (lower Γ_{\max}), increased molecular packing area (A_{\min}) and decreased surface pressure (π_{CMC}). 1-Propanol showed the strongest impact due to its amphiphilic nature and its disruption of water's hydrogen bonding network.²¹ The surface properties of Triton X-100 (TX100) change significantly with increasing alcohol volume

fractions. π_{CMC} decreases, Γ_{max} declines and A_{min} increases, reflecting reduced adsorption efficiency and disrupted surfactant packing due to alcohol–surfactant interactions and weakened hydrophobic effects.²⁴ The study reveals that adding 2-propanol to surfactant solutions significantly reduces γ , increases the CMC and alters adsorption properties by decreasing Γ_{max} while increasing A_{min} .²³ The surface properties of sodium dodecyl sulfate (SDS) in water–acetamide mixtures show that the limiting surface tension at the CMC remains constant regardless of acetamide concentration. Γ_{max} decreases with increasing acetamide content, stabilizing beyond 30 % acetamide due to changes in solvophobicity and mixed water–acetamide structures.²⁸

Contact angle

The spreading of a liquid on a solid surface is known as wettability, which is quantitatively measured by the contact angle (θ). Geometrically, contact angle (θ) is defined as the angle formed between the liquid drop and the solid surface where the solid, liquid and gas phases intersect each other. The Young's equation is commonly used to establish the relationship between θ and γ :

$$\cos \theta = \frac{\gamma_{S-V} - \gamma_{S-L}}{\gamma_{L-V}} \quad (5)$$

where γ_{S-V} is the solid/vapor interfacial tension, γ_{S-L} is the solid/liquid interfacial tension and γ_{L-V} is the liquid/vapor interfacial tension.

The contact angle (θ) *versus* concentration of SDS and CTAB in different volume fractions of ACN–water mixtures at 298.15 K is represented in Figs. 4 and 5. The obtained results showed that θ increases with an increase in surfactant concentration (for surfactant concentrations smaller than CMC) and then decreases

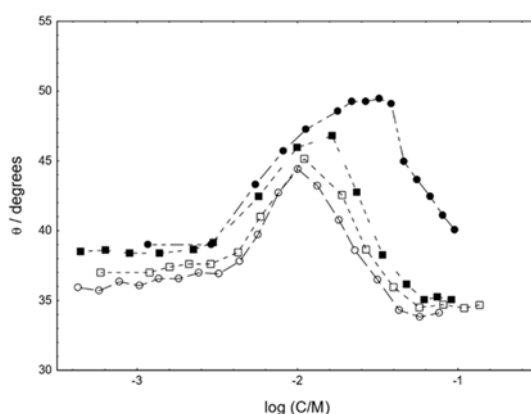


Fig. 4. Plot of contact angle (θ) against the logarithm of SDS concentration ($\log C/M$) in water (o) and 0.10 (□), 0.20 (■) and 0.40 (●) ACN volume fractions of ACN–water mixtures at 298.15 K.

(for surfactant concentrations higher than CMC), forming one maximum (peak); this maximum corresponds to the value of the CMC .

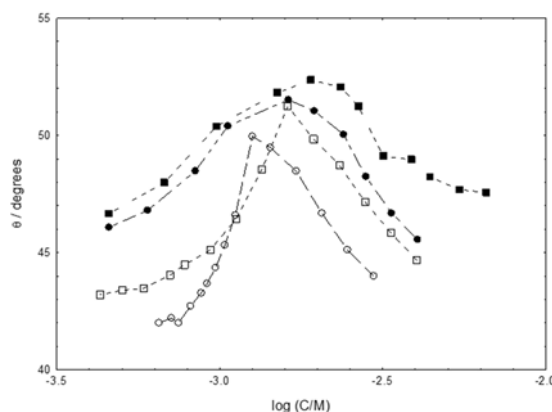


Fig. 5. Plot of contact angle (θ) against the logarithm of CTAB concentration ($\log C/M$) in water (o) and 0.10 (\square), 0.20 (\blacksquare) and 0.40 (\bullet) ACN volume fractions of ACN–water mixtures at 298.15 K.

The Lucassen–Reynolds²⁹ equation describes the relationship between surface excess concentrations at three interfaces and their respective interfacial tensions, expressed as:

$$\frac{\Gamma_{S-V} - \Gamma_{S-L}}{\Gamma_{L-V}} = \frac{d(\gamma_{S-V} - \gamma_{S-L})}{d\gamma_{L-V}} = \frac{d\gamma_{S-G} \cos \theta}{d\gamma_{L-G}} \quad (6)$$

Assuming $\Gamma_{S-V} = 0$, the ratio of Γ_{S-L} to Γ_{L-V} can be determined from the slope of a plot of $d\gamma_{L-G} \cos \theta$ (also referred to as the adhesion tension, A_T) against $d\gamma_{L-G}$.

The work of adhesion (W_A) is defined as the reversible work required to separate a unit area of liquid from a solid surface. It quantifies the interactive forces between the solid and liquid phases and can be determined from the contact angle using the following equation:

$$W_A = \gamma_{L-G} (1 + \cos \theta) \quad (7)$$

For $\theta = 0^\circ$, $W_A = 2\gamma_{L-G}$, indicating that the attraction between the liquid and solid is at least as strong as the cohesive forces within the liquid itself.²²

In this study, the wettability of CTAB and SDS on a hydrophilic glass surface was evaluated by measuring the contact angle in various volume fractions of acetonitrile.

Fig. 6 represents the variation of the work of adhesion with the concentration of CTAB in the premicellar region in different volume fractions of ACN. The trend clearly demonstrates that increasing ACN volume fractions results in enhancement

of surfactant adsorption, thereby increasing the interactive forces between the liquid and solid surfaces. The trend is more pronounced for SDS, highlighting its stronger affinity for the glass surface compared to CTAB.

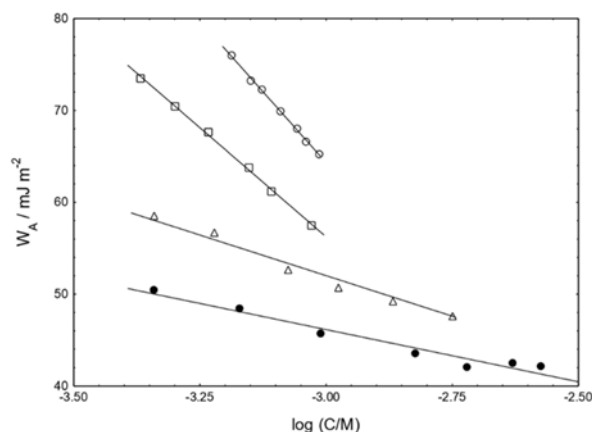


Fig. 6. Variation of W_A with concentration of CTAB in water (o) and several volume fractions of ACN (0.10 (\square), 0.20 (Δ) and 0.40 (\bullet)).

Fig. 7 illustrates the relationship between adhesion tension and surface tension for CTAB solutions containing different volume fractions of ACN. It shows a linear relationship between adhesion tension and surface tension for CTAB in all volume fractions of ACN. The evaluated slopes are all positive (+0.83 in water) and slightly increase with volume fractions of ACN, indicating unequal adsorption at the solid/liquid and liquid/gas interfaces. Similar observations were found in our previous study.²³

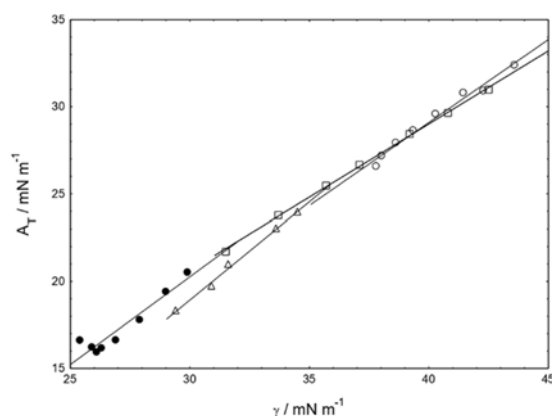


Fig. 7. Variation of A_T with γ of CTAB in water (o) and several volume fractions of ACN (0.10 (\square), 0.20 (Δ) and 0.40 (\bullet)).

CONCLUSION

In this study we elucidated how solvent polarity modulates the interfacial and self-assembly behaviour of anionic (SDS) and cationic (CTAB) surfactants in 0.10, 0.20 and 0.40 volume fractions of acetonitrile–water (ACN–water) mixtures at 298.15 K. By measuring surface tension and contact angles, we showed that the presence of ACN systematically increases the *CMC* and reduces the surface excess concentration (Γ_{\max}), while enlarging the minimum area per molecule (A_{\min}), lowering the micellar surface pressure (π_{CMC}) and the packing parameter (P). These trends reflect the weakening of hydrophobic and electrostatic interactions in less-polar media, leading to looser packing of surfactant molecules. The contact angle data reveal that higher ACN volume fraction produces larger θ values on borosilicate glass, indicating diminished wettability and weaker surfactant adsorption at the solid–liquid interface. Importantly, *CMC* values derived from contact angle measurements align with those obtained from surface tension data, confirming the reliability of the dual-method approach. Overall, these findings show that adjusting the acetonitrile content in the solvent directly influences surfactant adsorption, wetting and aggregation behaviour. The comparative analysis of SDS and CTAB also suggests that anionic and cationic surfactants respond differently to polarity changes, with SDS showing larger shifts in contact angle, hinting at differing adsorption mechanisms. Future work could extend this approach to other co-solvents, explore the influence of temperature or ionic strength and examine a wider range of substrates to build a more general framework for controlling surfactant-mediated processes.

ИЗВОД

УПОРЕДНА СТУДИЈА МИЦЕЛИЗАЦИЈЕ И ПОВРШИНСКИХ СВОЈСТАВА
КАТЈОНСКИХ И АНЈОНСКИХ СУРФАКТАНАТА У МЕШАНОМ РАСТВОРАЧУ
АЦЕТОНИТРИЛ–ВОДА

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Сprovedена је упоредна студија ради испитивања способности мицелизације, површинских својстава и кvasивости катјонског сурфактаната цетилтриметиламонијум-бромида (СТАВ) и анјонског сурфактаната натријум-додецил-сулфата (SDS) у мешаном растварачу ацетонитрил–вода (ACN–вода). Мерења површинског напона и контактнoг угла извршена су у чистој води и смешама ACN–вода (0,10, 0,20 и 0,40 запреминских удела ACN) на 298,15 K ради одређивања критичне мицеларне концентрације (*CMC*), површинског вишка концентрације (Γ_{\max}), минималне површине по молекулу (A_{\min}), мицеларног површинског притиска (π_{CMC}) и параметра паковања (P). Мерења контактнoг угла коришћена су за процену кvasивости на површинама боросиликатног стакла. Резултати показују да повећање садржаја ACN доводи до повећања *CMC*, што указује на смањену мицелизацију у мање поларним срединама. Површински вишак концентрације се смањује са вишим фракцијама ACN, док се минимална површина по молекулу пове-

ћава, што указује на лабавије молекулско паковање на граници ваздух/раствор. Мерења контактнoг угла показују смањење квазивости са вишим садржајем ACN, што значи побољшану адсорпцију сурфактанта на граници чврста супстанца–течност. Поред тога, мицеларни површински притисак и параметар паковања опадају са повећањем концентрације ACN. Ови резултати истичу критичну улогу састава растварача у модификовању агрегације сурфактанта и понашања на граници фаза.

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