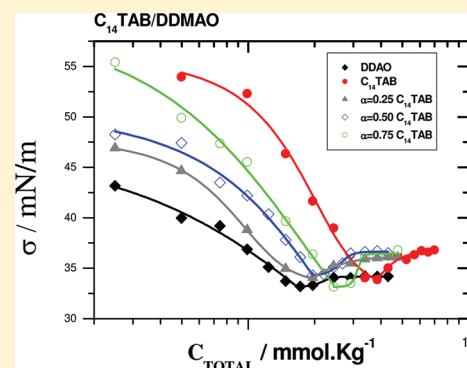


Micellar Parameters in Solutions with Cationic Surfactants and *N,N*-Dimethyldodecan-1-amine Oxide: Influence of Cationic Surfactant Chain Length

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ABSTRACT: The influence of chain length on the composition of mixed micelles in binary mixtures of *N,N*-dimethyldodecan-1-amine oxide (DDAO) and decyl-, dodecyl-, and tetradecyl-trimethyl-ammonium bromide surfactants (abbreviated as C_{10} TAB, C_{12} TAB, and C_{14} TAB, respectively) has been determined at 298 K. From the surface tension measurements, the critical micelle concentration (cmc) data were measured as a function of mixing composition. The cmc values were then analyzed according to regular solution model. The composition of mixed micelles, the interaction parameter (β), and the activity coefficients were evaluated from the regular solution model for all cationic–amphoteric mixed systems. The interaction parameter values indicated somehow a small deviation from ideality for the three mixed surfactant systems, for all investigated mole fractions. The strength of the interaction between the amphoteric surfactant and the alkyl-trimethyl-ammonium bromide surfactants in three mixed systems obeys the following order: (C_{10} TAB + DDAO) > (C_{12} TAB + DDAO) > (C_{14} TAB + DDAO) suggesting that the decrease in the length of cationic surfactant alkyl chain results in a stronger interaction with DDAO. Rheological measurements of these solutions in the presence of sodium salicylate, NaSal, for the three mixed systems were also measured. The viscosity data reveal a viscosity increasing trend of (C_{14} TAB + DDAO) > (C_{12} TAB + DDAO) > (C_{10} TAB + DDAO).



1. INTRODUCTION

Mixed surfactant solutions are encountered in nearly all practical life applications due to their unique properties that cannot be achieved by using single surfactant solutions.¹ Single solutions of amphoteric surfactants have the advantages of being less irritating to skin than many ionic surfactants, good solubility in water, low sensitivity to salts or temperature, high foam stability, low toxicity, broad isoelectric ranges, and resistance to degradation by oxidizing and reducing agents. Amphoteric surfactants have, on the other hand, higher production costs compared to cationic surfactants. A mixture of the two surfactants will reduce the production cost and keep the desired physical properties of the solution.^{2–4}

Some of the amphoteric surfactants are sensitive to change in pH. For example, alkyldimethylamine oxide amphoteric surfactant can form micelles with either protonated (cationic) or deprotonated (nonionic) head groups depending on pH.⁵ The charge variation of *N,N*-dimethyldodecan-1-amine oxide (DDAO) leads to changes in several physical properties such as surface tension, interfacial tension, and critical micelle concentration (cmc), and so forth. When a solution is prepared by mixing anionic surfactants with amphoteric surfactants, synergism was mainly observed due to the fact that anionic headgroup attracts the positively headgroup of the amphoteric molecule, and consequently mixed micelles were formed.^{1,6,7} Because of the synergism, the cmc values of the mixed system become lower than cmc values of unmixed surfactants.

The change in the value of cmc upon mixing two surfactants in aqueous solution was considered by Rubingh in his theory of regular solution,¹ and accordingly the synergism or antagonism was represented by a dimensionless parameter called the interaction parameter (abbreviated as β). If there is a type of attractive forces between the headgroups of the surfactants as in the case of (cationic + anionic) or (ionic + nonionic) mixed surfactant systems, synergism and a negative value of β were mainly obtained.⁸ The theory of regular solution was used to calculate the interaction parameter between polymer and zwitterionic surfactant² and between the bile salt and cationic surfactant.⁹

Although the values of interaction parameter β for several surfactant mixed systems are often reported in the literature, the amount of information regarding the interactions in mixed micelles is somehow limited.¹⁰ It is also worth noting that the literature data available on amphoteric surfactants (zwitterions) have been generally much less than other types of surfactants.

In this investigation, mixtures of (cationic + amphoteric) systems of decyl-, dodecyl-, and tetradecyl-trimethyl-ammonium bromide surfactants with an amphoteric surfactant *N,N*-dimethyldodecylamine oxide (DDAO) were prepared. The cmc values of the corresponding binary mixtures in the whole range of composition were obtained by the surface tension measure-

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ments, and then the results have been analyzed in terms of the interaction parameter, β , using Rubingh's regular solution theory. The influences of the cationic surfactants' tail length on the mixed micelle composition and the type of interactions in mixed micelles have been investigated. The results of viscosity in small micellar aggregates and in the rod-like micelle region for the three mixed systems are also presented and compared.

2. THEORY

Several theoretical models were proposed to explain the change in the physical properties of single surfactant solutions upon mixing with other surfactants. Typical models for treating mixed micellar systems are based on an equilibrium thermodynamic approach as an ideal mixing model that depends on the pseudo phase separation approach. This model deals with mixed micelles or other aggregates like a separate phase and assumes that the aggregation number approaches infinity.

The ideal mixing model predicts the values of cmc for a binary mixed system, cmc_{mix} according to the Clint equation:^{1,8,11,12}

$$1/\text{cmc}_{\text{mix}} = \alpha_1/\text{cmc}_1 + \alpha_2/\text{cmc}_2 \quad (1)$$

where cmc_{mix} is the critical micelle concentration of the mixed surfactant binary system, cmc_1 is the critical micelle concentration of the first surfactant, cmc_2 is the critical micelle concentration of the second surfactant, α_1 is the bulk mole fraction of the first surfactant, and α_2 is the bulk mole fraction of the second surfactant. The bulk mole fraction of the first surfactant, α_1 , is the actual mole fraction of the first surfactant that has been added to the solution which is directly calculated by dividing the number of moles for the first surfactant to the total number of moles, regardless of their forms (monomers or micellar form). However, many binary mixed surfactant systems do not follow the Clint equation and somehow deviate from ideality. Holland and Rubingh^{1,13,14} developed a new model to deal with nonideality, called the nonideal mixing model. Rubingh's model is based on the regular solution approximation and assumed that the excess entropy (S) during the mixing process equals zero. This assumption allows substitution of the excess enthalpy (H) in place of excess Gibbs free energy (G) so that $G = H - TS$ becomes $G = H$. Rubingh improved the Clint equation to:

$$1/\text{cmc}_{\text{mix}} = \alpha_1/f_1 \text{cmc}_1 + \alpha_2/f_2 \text{cmc}_2 \quad (2)$$

Here f_1 and f_2 are the activity coefficients, and they are equal to unity when the behavior is ideal. Rubingh suggested that some of the surfactants present in the bulk are involved in mixed micelles and proposed the other two symbols for the mole fractions in mixed micelles, namely, x_1 and x_2 , where x means the mole fraction of surfactant in the mixed micelle. The x value can be calculated by solving the following equation:

$$\frac{x_1^2 \ln[\text{cmc}_{\text{mix}}\alpha_1/\text{cmc}_1x_1]}{(1-x_1)^2 \ln[\text{cmc}_2(1-\alpha_1)/(1-x_1)\text{cmc}_2]} = 1 \quad (3)$$

Since the values of cmc_1 , cmc_2 , cmc_{mix} , and α_1 are all known, the above equation can be solved using the iterative method to obtain the value of x_1 . It should be mentioned that the effect of the counterion was not taken into account in eq 3 and further details are reported elsewhere.¹⁵ The interaction parameter (β) in the theory of regular solution is then obtained from the relation between the micellar and bulk composition according

to the following equation.

$$\beta = \ln[\text{cmc}_{\text{mix}}\alpha_1/\text{cmc}_1x_1]/(1-x_1)^2 \quad (4)$$

where β is the interaction or dimensionless parameter that measures the extent of interaction between the surfactants and their deviation from the ideal behavior.⁸ The interaction parameter (β) takes a positive value in the case of demixing (antagonism), while it takes a negative value in the case of mixing (synergism). There is a mathematical relation between the activity coefficient in the Rubingh equation and the interaction parameter according to the following equations:⁵

$$f_1 = \exp \beta(1-x_1)^2 \quad (5)$$

$$f_1 = \exp \beta x_1^2 \quad (6)$$

If the interaction parameter (β) is zero, in this case the activity coefficients in Rubingh equation (eq 2) become equal to unity, and it will be converted into the Clint equation (eq 1) which represents the ideal behavior.

The interaction parameter β represents the molar interaction energies between the monocomponent micelles (β_{ii} or β_{jj}) and the molar interaction energies between the bicomponent micelles (β_{ij}) according to the relation:^{10,16}

$$\beta = [\beta_{ij} - (\beta_{ii} + \beta_{jj})/2]/RT \quad (7)$$

where R is the molar gas constant, and T is the absolute temperature. Here the physical interactions between the surfactants can lead to nonideal behavior on the properties of a mixed surfactant system, such as a significant decrease in the cmc and the interfacial tension compared to those of single surfactants.

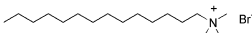
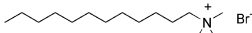
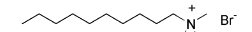
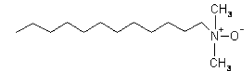
The negative value of β was found to be not the only limiting factor to describe the synergism between the surfactant molecules in the mixed micelle. An additional conditions for synergism have been derived mathematically by Hua and Rosen, according to which the synergism in binary mixed system is present only if (i) β is negative and (ii) the absolute value of interaction parameter $|\beta|$ must be greater than $\ln(\text{cmc}_1/\text{cmc}_2)$.¹⁷

3. EXPERIMENTAL SECTION

3.1. Materials Used. Decyl-trimethyl-ammonium bromide ($\text{C}_{13}\text{H}_{30}\text{NBr}$) with a purity (mass fraction, W_B) of $W_B = 99\%$ was supplied by ACROS; dodecyl-trimethyl-ammonium bromide ($\text{C}_{15}\text{H}_{34}\text{NBr}$) and tetradecyl-trimethyl-ammonium bromide ($\text{C}_{17}\text{H}_{38}\text{NBr}$) with a purity of $W_B = 99\%$ were from Sigma. DDAO was from Clariant. The surfactants were used without further treatment, to achieve the study from an application point of view. Sodium salicylate, NaSal, was from Merck with a purity $> W_B = 99.5\%$. Deionized doubly distilled water was used for the preparation of surfactant solutions at 298 K. The chemical structure, name, chemical formula, molecular weight (mol wt), and symbols for the studied surfactants are shown in Table 1.

3.2. Methods. **3.2.1. Surface Tension Measurements.** Surface tension measurements were determined at 298 K by the du Nouy ring method using a digital LAUDA tensiometer (TEIC). The instrument was calibrated against double-distilled water. According to the mode of this instrument, the number of measurements (at least seven measurements) and the required standard deviation, SD, are given as inputs. When the

Table 1. Chemical Structure, Nomenclature, Chemical Formula, Molecular Weight, $M/\text{mol}\cdot\text{kg}^{-1}$, and Symbols of the Surfactants Used in This Work

Chemical Structure Nomenclature	Chemical Formula	$M/\text{kg}\cdot\text{mol}^{-1}$	Symbols
 Br ⁻	$\text{C}_{17}\text{H}_{38}\text{NBr}$	0.3364	C_{14}TAB
Tetradecyl-trimethyl-ammonium bromide			
 Br ⁻	$\text{C}_{15}\text{H}_{34}\text{NBr}$	0.3083	C_{12}TAB
Dodecyl-trimethyl-ammonium bromide			
 Br ⁻	$\text{C}_{13}\text{H}_{30}\text{NBr}$	0.28028	C_{10}TAB ,
Decyl-trimethyl-ammonium bromide			
	$\text{CH}_3(\text{CH}_2)_{11}(\text{CH}_3)_2\text{N}^+\text{O}^-$	0.2295	DDAO
N,N-dimethyldodecan-1-amine oxide			

measurement is started, the instrument calculates the SD of the seven measured values, and if the resulting SD is higher than $0.1 \text{ mN}\cdot\text{m}^{-1}$, the instrument will automatically repeat the measurement through a new measuring cycle until having a value of SD less than $0.1 \text{ mN}\cdot\text{m}^{-1}$. Measurements were made at intervals of a few minutes until successive values agreed within standard deviation of $0.1 \text{ mN}\cdot\text{m}^{-1}$ or less. The cmc values were determined graphically as the intersection point between the decreasing and increasing/flat curves of the plot.

3.2.2. Viscosity Measurements. Viscosities were carried out using a Haake stress-controlled RS600 (RheoStress RS600) that works with the double gap method. The double gap (DG41 Titanium with gap 5.100 mm) is applicable for solutions of low viscosity. For double gap measurements a shear rate of $(0.50 \text{ to } 800.00) \text{ s}^{-1}$ was applied. The experimental conditions were kept the same for the whole solutions to get a reasonable comparison. For viscous solutions, oscillation measurements were made at the frequency range from (10 to 0.001) Hz at a constant deformation of 0.01 using the cone plate method. A sample cover provided with the instrument was used to minimize the change in sample composition by evaporation during the measurement. The experimental conditions were kept the same for the whole solutions to have reasonable comparison. The measurements were instrumentally performed, and the error was taken to be ± 0.5 of the last digit in the output values.

The experimental result of viscosity and complex viscosity for investigated systems are listed in Tables 2 and 3.

4. RESULTS AND DISCUSSION

The cmc values of the single cationic and amphoteric surfactants are listed in Table 4. The cmc values are in good agreement with those reported in the literature.^{18–21}

Increasing the tail length of cationic surfactant leads to a decrease in the cmc value due to the fact that increasing the tail length will increase surfactant hydrophobicity.²² The alkyl-trimethyl-ammonium bromide surfactants with a longer tail would combine at lower concentrations due to the increase in the van der Waals interactions between the alkyl chains, and thus a dramatic reduce in the solution cmc is obtained.

DDAO surfactant, on the other hand, has a lower cmc value in comparison with alkyl-trimethyl-ammonium bromide due to lower repulsion forces between the headgroups. For the

Table 2. Experimental Results of Viscosity, $\eta/\text{Pa}\cdot\text{s}$, Obtained from Shear Rate Measurements ($200.7 \text{ to } 800$) s^{-1} for Solutions with $100 \text{ mmol}\cdot\text{kg}^{-1}$ C_nTAB ($n = 10, 12,$ and 14) and Different Concentrations of DDAO in Water at 298 K

$(\text{C}_{10}\text{TAB} + \text{DDAO})$ in water at 298 K		
$[\text{C}_{10}\text{TAB}]$	$[\text{DDAO}]$	η
$\text{mmol}\cdot\text{kg}^{-1}$	$\text{mmol}\cdot\text{kg}^{-1}$	$\text{Pa}\cdot\text{s}$
100	93	0.00101 ± 0.000005
100	185	0.00124 ± 0.000005
100	262	0.00139 ± 0.000005
100	359	0.00167 ± 0.000005
$(\text{C}_{12}\text{TAB} + \text{DDAO})$ in water at 298 K		
$[\text{C}_{12}\text{TAB}]$	$[\text{DDAO}]$	η
$\text{mmol}\cdot\text{kg}^{-1}$	$\text{mmol}\cdot\text{kg}^{-1}$	$\text{Pa}\cdot\text{s}$
100	180	0.00128 ± 0.000005
100	263	0.00136 ± 0.000005
100	355	0.00160 ± 0.000005
100	443	0.00172 ± 0.000005
$(\text{C}_{14}\text{TAB} + \text{DDAO})$ in water at 298 K.		
$[\text{C}_{14}\text{TAB}]$	$[\text{DDAO}]$	η
$\text{mmol}\cdot\text{kg}^{-1}$	$\text{mmol}\cdot\text{kg}^{-1}$	$\text{Pa}\cdot\text{s}$
100	94	0.00115 ± 0.000005
100	190	0.00125 ± 0.000005
100	262	0.00138 ± 0.000005
100	363	0.00138 ± 0.000005

Table 3. Experimental Results of Complex Viscosity, η^* , Obtained from Oscillation Measurements ($1.00 \text{ to } 0.01$) Hz for Aqueous Solutions with $100 \text{ mmol}\cdot\text{kg}^{-1}$ C_nTAB ($n = 10, 12,$ and 14), $360 \text{ mmol}\cdot\text{kg}^{-1}$ DDAO, and $200 \text{ mmol}\cdot\text{kg}^{-1}$ NaSal at 298 K

$(\text{C}_n\text{TAB} + \text{DDAO} + \text{NaSal})$ in water at 298 K.	
composition	$\eta^*/\text{Pa}\cdot\text{s}$
$100 \text{ mmol}\cdot\text{kg}^{-1}$ of $\text{C}_{10}\text{TAB} + 360 \text{ mmol}\cdot\text{kg}^{-1}$ of DDAO + $200 \text{ mmol}\cdot\text{kg}^{-1}$ of NaSal	0.01604 ± 0.000005
$100 \text{ mmol}\cdot\text{kg}^{-1}$ of $\text{C}_{12}\text{TAB} + 360 \text{ mmol}\cdot\text{kg}^{-1}$ of DDAO + $200 \text{ mmol}\cdot\text{kg}^{-1}$ of NaSal	0.08929 ± 0.000005
$100 \text{ mmol}\cdot\text{kg}^{-1}$ of $\text{C}_{14}\text{TAB} + 360 \text{ mmol}\cdot\text{kg}^{-1}$ of DDAO + $200 \text{ mmol}\cdot\text{kg}^{-1}$ of NaSal	0.134 ± 0.0005

Table 4. Critical Micelle Concentration Values, cmc, of Single Surfactants at 298 K^a

surfactant	cmc/ $\text{mmol}\cdot\text{kg}^{-1}$	
	this work	literature value (ref no.)
C_{10}TAB	60	64 [18]
C_{12}TAB	13	15 [19]
C_{14}TAB	3.5	3.5 [20]
DDAO	1.72	1.7 [21]

^acmc, critical micelle concentration; C_{14}TAB , tetradecyl-trimethyl-ammonium bromide; C_{12}TAB , dodecyl-trimethyl-ammonium bromide; C_{10}TAB , decyl-trimethyl-ammonium bromide; DDAO, N,N -dimethyldodecan-1-amine oxide.

cationic surfactants, the higher concentration is essential to overcome the electrostatic repulsive forces between negatively charged headgroups to form micelles. This explains the high cmc values for ionic surfactants.²³

The surface tension data measured in aqueous solutions containing different amounts of alkyl-trimethyl-ammonium

Table 5. Concentration, $C/\text{mmol}\cdot\text{kg}^{-1}$, and Surface Tension \pm Standard Deviation ($\sigma \pm \text{SD}$)/ $\text{mN}\cdot\text{m}^{-1}$ for All Investigated Single and Mixed Surfactant Systems

$C_{14}\text{TMBr}$		$C_{12}\text{TMBr}$		$C_{10}\text{TMBr}$	
[C]	$\sigma \pm \text{SD}$	[C]	$\sigma \pm \text{SD}$	[C]	$\sigma \pm \text{SD}$
$\text{mmol}\cdot\text{kg}^{-1}$	$\text{mN}\cdot\text{m}^{-1}$	$\text{mmol}\cdot\text{kg}^{-1}$	$\text{mN}\cdot\text{m}^{-1}$	$\text{mmol}\cdot\text{kg}^{-1}$	$\text{mN}\cdot\text{m}^{-1}$
0.50	53.96 \pm 0.09	0.50	55.13 \pm 0.10	11.8	54.43 \pm 0.10
0.99	52.31 \pm 0.07	0.99	55.56 \pm 0.09	21.1	48.37 \pm 0.09
1.48	46.35 \pm 0.10	1.48	53.67 \pm 0.08	28.6	45.75 \pm 0.10
1.96	41.65 \pm 0.10	1.96	53.93 \pm 0.09	34.8	42.87 \pm 0.09
2.44	39.00 \pm 0.04	2.44	53.53 \pm 0.09	40	40.18 \pm 0.08
2.91	36.35 \pm 0.08	2.91	52.630.10	44.4	37.98 \pm 0.08
3.38	34.05 \pm 0.09	3.38	52.13 \pm 0.08	46.4	37.19 \pm 0.05
3.85	33.87 \pm 0.05	4.76	49.16 \pm 0.08	48.3	36.21 \pm 0.05
4.31	35.02 \pm 0.10	6.54	45.20 \pm 0.10	50	36.15 \pm 0.05
4.76	36.24 \pm 0.05	8.26	42.32 \pm 0.09	51.6	36.47 \pm 0.04
5.21	35.86 \pm 0.10	9.91	39.41 \pm 0.08	53.1	35.98 \pm 0.05
5.66	36.33 \pm 0.06	11.5	36.77 \pm 0.10	54.5	35.88 \pm 0.06
6.10	36.74 \pm 0.04	13.0	34.09 \pm 0.09	55.9	36.19 \pm 0.06
6.54	36.60 \pm 0.06	13.8	34.98 \pm 0.08	57.1	36.31 \pm 0.05
6.98	36.81 \pm 0.05	14.5	37.44 \pm 0.08	$C_{10}\text{TMBr}/\text{DDAO}$ (0.25:0.75)	
$C_{14}\text{TMBr}/\text{DDAO}$ (0.25:0.75)		15.3	37.98 \pm 0.10	0.25	40.49 \pm 0.09
0.25	46.91 \pm 0.10	16.0	38.33 \pm 0.10	0.74	37.47 \pm 0.08
0.50	44.66 \pm 0.06	16.7	38.47 \pm 0.07	1.48	35.39 \pm 0.09
0.99	38.81 \pm 0.08	17.7	38.69 \pm 0.06	1.96	32.95 \pm 0.10
1.48	34.96 \pm 0.09	18.4	38.46 \pm 0.01	2.44	32.80 \pm 0.09
1.96	34.05 \pm 0.06	$C_{12}\text{TMBr}/\text{DDAO}$ (0.25:0.75)		2.91	33.35 \pm 0.09
2.44	35.24 \pm 0.06	0.50	40.19 \pm 0.10	3.38	33.91 \pm 0.07
2.91	35.50 \pm 0.05	0.99	36.64 \pm 0.09	3.85	33.75 \pm 0.03
3.38	35.92 \pm 0.04	1.48	36.12 \pm 0.08	4.31	33.20 \pm 0.08
3.85	36.01 \pm 0.04	1.96	33.2 \pm 0.05	4.76	33.97 \pm 0.08
4.31	36.11 \pm 0.03	2.44	33.71 \pm 0.10	$C_{10}\text{TMBr}/\text{DDAO}$ (0.50:0.50)	
4.76	36.08 \pm 0.04	2.91	34.08 \pm 0.08	0.50	40.67 \pm 0.09
$C_{14}\text{TMBr}/\text{DDAO}$ (0.50:0.50)		3.38	34.64 \pm 0.08	0.74	39.79 \pm 0.10
0.25	48.3 \pm 0.09	3.85	34.24 \pm 0.05	1.48	38.02 \pm 0.06
0.5	47.42 \pm 0.05	4.31	34.68 \pm 0.06	1.72	37.77 \pm 0.08
0.74	43.48 \pm 0.09	4.76	34.88 \pm 0.04	2.44	35.18 \pm 0.10
0.99	42.20 \pm 0.08	$C_{12}\text{TMBr}/\text{DDAO}$ (0.50:0.50)		2.91	31.84 \pm 0.09
1.23	40.36 \pm 0.08	0.50	49.59 \pm 0.08	3.38	32.24 \pm 0.10
1.48	37.81 \pm 0.06	0.99	43.78 \pm 0.09	3.85	32.7 \pm 0.09
1.72	36.09 \pm 0.06	1.48	39.73 \pm 0.06	4.31	32.91 \pm 0.04
1.96	34.30 \pm 0.09	1.96	37.75 \pm 0.09	4.76	33.47 \pm 0.04
2.2	34.41 \pm 0.10	2.44	35.19 \pm 0.08	5.21	33.1 \pm 0.07
2.44	35.11 \pm 0.08	2.91	33.28 \pm 0.05	5.66	33.55 \pm 0.06
2.68	35.47 \pm 0.08	3.38	33.75 \pm 0.07	$C_{12}\text{TMBr}/\text{DDAO}$ (0.25:0.75)	
2.91	36.46 \pm 0.04	3.85	34.21 \pm 0.10	1.96	43.18 \pm 0.10
3.38	36.62 \pm 0.05	4.31	34.63 \pm 0.08	2.91	40.74 \pm 0.08
3.85	36.71 \pm 0.05	4.76	34.45 \pm 0.10	3.85	37.13 \pm 0.10
4.31	36.50 \pm 0.05	5.21	34.89 \pm 0.05	4.31	36.46 \pm 0.10
$C_{14}\text{TMBr}/\text{DDAO}$ (0.75:0.25)		5.66	35.26 \pm 0.04	4.76	35.74 \pm 0.08
0.25	55.42 \pm 0.07	6.10	35.18 \pm 0.05	5.21	34.4 \pm 0.10
0.5	49.92 \pm 0.10	6.54	35.55 \pm 0.05	5.66	33.42 \pm 0.08
0.74	47.37 \pm 0.10	6.98	35.84 \pm 0.05	6.1	33.43 \pm 0.08
0.99	45.54 \pm 0.08	$C_{12}\text{TMBr}/\text{DDAO}$ (0.75:0.25)		6.54	33.61 \pm 0.05
1.48	39.66 \pm 0.09	0.50	52.4 \pm 0.10	6.98	33.82 \pm 0.07
1.96	36.39 \pm 0.08	0.99	49.21 \pm 0.09	DDAO	
2.44	33.16 \pm 0.09	1.48	47.42 \pm 0.05	0.25	43.18 \pm 0.07
2.91	33.50 \pm 0.08	1.96	43 \pm 0.08	0.50	39.98 \pm 0.05
3.38	36.21 \pm 0.07	2.44	41.6 \pm 0.08	0.74	39.20 \pm 0.09
3.85	36.33 \pm 0.05	2.91	39.91 \pm 0.10	0.99	36.87 \pm 0.05
4.31	36.21 \pm 0.10	3.38	38.19 \pm 0.09	1.23	35.11 \pm 0.05
4.76	36.79 \pm 0.04	3.85	36.4 \pm 0.05	1.48	33.73 \pm 0.09
		4.31	35.02 \pm 0.06	1.72	33.19 \pm 0.07

Table 5. continued

C ₁₄ TMBr		C ₁₂ TMBr		C ₁₀ TMBr	
[C]	$\sigma \pm \text{SD}$	[C]	$\sigma \pm \text{SD}$	[C]	$\sigma \pm \text{SD}$
mmol·kg ⁻¹	mN·m ⁻¹	mmol·kg ⁻¹	mN·m ⁻¹	mmol·kg ⁻¹	mN·m ⁻¹
		4.76	34.57 ± 0.05	1.96	33.32 ± 0.05
		5.21	34.6 ± 0.10	2.44	34.06 ± 0.10
		5.66	35.38 ± 0.09	2.91	34.05 ± 0.05
		6.10	35.69 ± 0.08	3.38	34.22 ± 0.07
		6.54	35.66 ± 0.05	3.85	34.14 ± 0.05
		6.98	35.76 ± 0.08	4.31	34.17 ± 0.08

bromide cationic surfactants and amphoteric surfactants DDAO are listed in Table 5 and presented in Figure 1a–c that shows surface tension, σ , as a function of concentration, C , for mixtures of C₁₄TAB, C₁₂TAB, and C₁₀TAB with DDAO at 0.00, 0.25, 0.50, 0.75, and 1.00 mole fractions at 298 K. Figure 1a–c shows that the surface tension decreases rapidly with increasing concentration and each curve has a distinct point at the concentration corresponding to the cmc then takes almost constant value at high concentrations.

Figure 1a–c shows that the cmc values and surface tension at cmc, σ_{cmc} , of the surfactant mixture are between values of individual surfactant and more close to surfactant with lower cmc (i.e., DDAO). The interaction between the DDAO and C_nTAB surfactants screens the repulsion between the head-groups of the cationic surfactants, and consequently the cmc of the binary mixed system decreases compared to the cmc of individual cationic surfactants. When the amounts of cationic surfactants in the solution are further increased, the cmc continues to increase slightly. This trend can be explained by the fact that increasing the mole fraction of cationic surfactants increases the repulsion between the positively charged headgroups, and consequently an increase in the cmc values is obtained.

From Figure 1a–c, it is evident that DDAO and C_nTAB surfactants show a minimum in the surface tension at the intersection point of the two curves. This type of minimum is believed to be due to some impurities in the surfactant.²⁴ However, this minimum is ignored, and the cmc is calculated to be the point of intersection between the decreasing and increasing/flat curves as indicated for the CMC of C₁₄TAB in Figure 1a. The presence of the impurity decreases the surface tension at cmc point, but it has no significant influence on cmc value itself as it can be seen from Table 2 that the literature values of cmc are in good agreement with those obtained in this work. Additionally, Sierra and Svensson reported the cmc values for alkylglycosides nonionic surfactants mixed for the first time with unrecrystallized sodium dodecyl sulfate (SDS); in the second time with crystallized SDS it shows no minimum at cmc, and they found that the differences in the cmc values for the two mixed system were negligible.²⁵

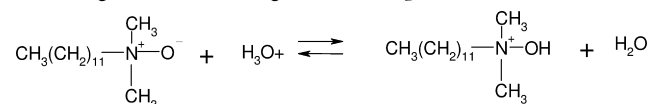
With the experimentally determined cmcs and according to eqs 3 and 4, the mole fraction of the cationic surfactant in the mixed micelles, x_1 , and the interaction parameter, β , were calculated for each bulk mole fraction, α , as listed in Table 6

The variation of cmc as a function of bulk mole fraction (α) is depicted in Figure 2a–c for the three mixed systems. Figure 2a–c shows that the experimental cmc's are lower than ideal behavior as described by eq 1 and that the three systems exhibit small negative deviations from ideal behavior.

The shape of the curves in Figure 2c is typical of mixed systems where the cmc values of pure surfactant are very different.

According to results in Table 6, the β values become mainly less negative as the mole fraction of cationic surfactant increases. From Table 6, one could notice that β -values are not constant for a given system, and their values vary as the content of cationic surfactant increases in the mixed system. As the content of cationic surfactant increases, the repulsion between head will increase, leading to less interaction between the heads and hence higher β values. The average β -values for (C₁₄TAB + DDAO), (C₁₂TAB + DDAO), and (C₁₀TAB + DDAO) mixed systems are -0.49 , -0.71 , and -1.55 respectively. For each system, the variation in the interaction parameter could also indicate an interaction that depends on relative arrangement of the monomers or the packing structure of the monomers in the mixed micelle.¹⁹

The values of β are negative for all systems, suggesting an attraction between the monomers of both surfactants. Such attractive interaction is related to the property of the amphoteric surfactants DDAO that can exist in aqueous solutions as either nonionic or cationic form, depending on pH.^{10,26} The DDAO is capable of accepting a proton and acting as a cationic surfactant. Using zeta potential measurements, evidence was provided by Alargova et al.²⁷ indicating that the positive charge of DDAO head-groups was increasing with the decrease in pH. In acidic pH, DDAO exists as a cationic (protonated form), and as nonionic surfactant at basic pH according to the following chemical equation:



Furthermore, it was reported that DDAO is completely cationic (protonated) at low pH (pH < 3 approximately) and completely nonionic at high pH (pH > 9 approximately). When the pH is in the range of 3 to 9 at concentrations higher than cmc (cmc \approx 1.72 mmol·kg⁻¹), DDAO forms partially protonated micelles containing both cationic and nonionic types of surfactants.^{28,29}

In the present work, the solutions were prepared in almost neutral medium (slightly basic; pH = 7.4), and thus the DDAO is expected to form partially protonated micelles consisting of cationic and nonionic monomers.³⁰

Having some of the DDAO surfactants in the nonionic form allows DDAO surfactant to interact more strongly with the alkyl-trimethyl-ammonium surfactants due to formation of dipole–ion interaction between the ionic surfactants and the nonionic form of DDAO.³¹ The formation of such mixed micelle does not only stabilize the resultant micelles due to

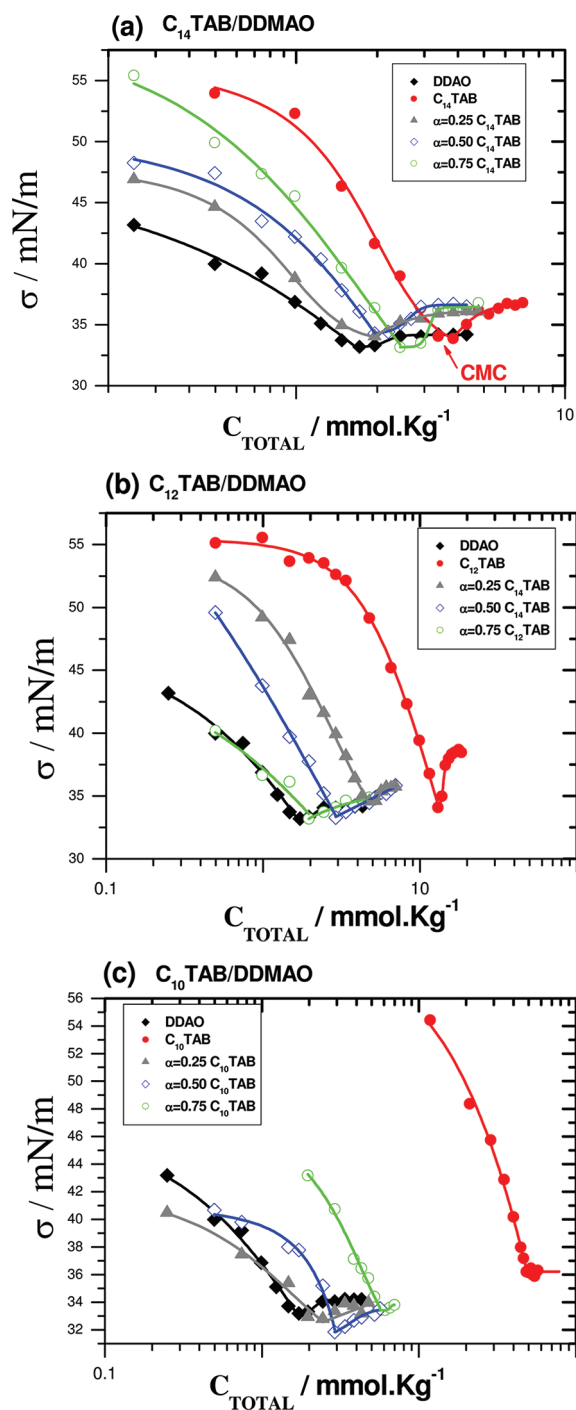


Figure 1. Plots of surface tension (σ) vs total concentration (C) for the (a) ($C_{14}\text{TAB} + \text{DDAO}$), (b) ($C_{12}\text{TAB} + \text{DDAO}$), and (c) ($C_{10}\text{TAB} + \text{DDAO}$) systems at 298 K for different mole fractions, α , of $C_n\text{TAB}$, where $\alpha = \bullet$, 1.0; \blacktriangle , 0.25; \diamond , 0.50; \circ , 0.75; and \blacklozenge , 0.0. The cmc was calculated to be the point of intersection between the decreasing and the increasing/flat curve for each plot in the figure. $C_{14}\text{TAB}$, tetradecyl-trimethyl-ammonium bromide; DDAO, N,N -dimethyldodecan-1-amine oxide; $C_{12}\text{TAB}$, dodecyl-trimethyl-ammonium bromide; $C_{10}\text{TAB}$, decyl-trimethyl-ammonium bromide.

physical interaction between the heads but also due to the reduction of electrostatic free energy at the interface.¹⁰

According to Hua and Rosen,¹⁷ synergism in binary mixed system is present only if (i) β is negative and (ii) the absolute value of interaction parameter $|\beta|$ must be greater than $\ln(\text{cmc}_1/$

Table 6. Mole Fraction of Cationic Surfactant, $\alpha_{\text{cationic surf.}}$, Critical Micelle Concentration of the Mixed System (cmc_{mix}), Mole Fraction of the Cationic Surfactant in Mixed Micelles ($X_{\text{cationic surf.}}$), and Interaction Parameter (β) of ($C_n\text{TAB} + \text{DDAO}$) Binary Mixed Systems in Water at 298 K

$\alpha_{\text{cationic surf.}}$	cmc_{mix}		$X_{\text{cationic surf.}}$	β
	$\text{mmol}\cdot\text{kg}^{-1}$			
0.0 $C_{14}\text{TAB}$	1.72			
0.25 $C_{14}\text{TAB}$	1.8		0.195	-0.647
0.50 $C_{14}\text{TAB}$	2		0.367	-0.627
0.75 $C_{14}\text{TAB}$	2.65		0.587	-0.199
1.0 $C_{14}\text{TAB}$	3.5			
			average β	-0.49
0.00 $C_{12}\text{TAB}$	1.72			
0.25 $C_{12}\text{TAB}$	1.92		0.136	-1.74
0.50 $C_{12}\text{TAB}$	2.95		0.138	-0.26
0.75 $C_{12}\text{TAB}$	4.8		0.295	-0.13
1.00 $C_{12}\text{TAB}$	13			
			average β	-0.71
0.0 $C_{10}\text{TAB}$	1.72			
0.25 $C_{10}\text{TAB}$	2.2		$3.85\cdot 10^{-2}$	-1.55
0.5 $C_{10}\text{TAB}$	2.8		0.143	-2.48
0.75 $C_{10}\text{TAB}$	6		0.120	-0.61
1.0 $C_{10}\text{TAB}$	60			
			average β	-1.55

$\text{cmc}_2]$. The calculations according to the Hua and Rosen second condition are presented in Table 7.

Depending on the results in Table 7, it is clear that the two conditions for synergism are not satisfied over the entire mole fraction range. β -values are negative, but the absolute values of β are less than the $\ln(\text{cmc}_1/\text{cmc}_2)$. Therefore, the three mixed systems do not fulfill all conditions of Hua and Rosen for synergism.

The calculated values of the mole fraction of cationic surfactant in the mixed micelle (x_1) at different mole fractions in the bulk (α) are listed in Table 6 and presented graphically in Figure 3. These results reflect a deviation from the ideal behavior for the three mixed systems. Plots of x_1 versus α show a deviation from ideal behavior that increases with decreasing chain length. From the x - α curves in Figure 3, one could notice that the mole fractions of cationic surfactant in the mixed micelles are less than those added to the bulk. Adding higher amounts of $C_n\text{TAB}$ to the mixed micelles will increase the repulsion between the heads. Additionally, the amount of cationic surfactant in the mixed micelle, x_{cationic} , generally decreases with decreasing surfactant chain length. This effect can be explained by the fact that the solubility of surfactant monomers increases with decreasing surfactant chain length.

The activity coefficient values f_1 and f_2 describe the effect and the contribution of individual component in the mixed micelles, and consequently it is necessary to calculate them. f_1 and f_2 were calculated using eqs 6 and 7. The values of f_1 and f_2 are listed in Table 8.

Since there is a direct relation between f_1 or f_2 and the mole fraction of the cationic surfactants in the mixed micelle, x_1 , as can be notified in eqs 5 and 6, the much lower mole fraction (x_1) of cationic surfactant is reflected by its small activity coefficient (f_1) values. The f_1 -values vary slightly among the three mixed systems and are not consistent as can be seen for f_2 -values. The f_2 values suggest somehow similar interaction between the two surfactants.

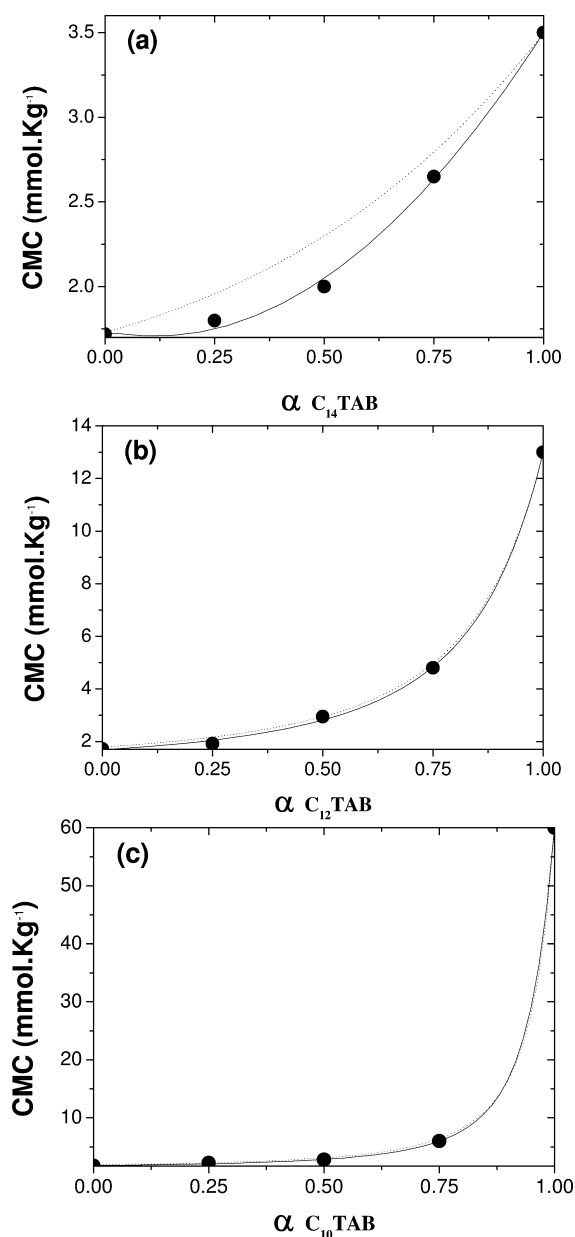


Figure 2. Variation of critical micelle concentration (cmc) with mole fraction (α) of (a) C_{14} TAB in (C_{14} TAB + DDAO), (b) C_{12} TAB in (C_{12} TAB + DDAO), and (c) C_{10} TAB in (C_{10} TAB + DDAO) mixed systems in water at 298 K. The dashed line (----) refers to ideal behavior calculated from equ.1, while the solid line (—) represents the real behavior according to the experimentally determined values of cmc. C_{14} TAB, tetradecyl-trimethyl-ammonium bromide; DDAO, *N,N*-dimethyldodecan-1-amine oxide; C_{12} TAB, dodecyl-trimethyl-ammonium bromide; C_{10} TAB, decyl-trimethyl-ammonium bromide.

It seems that f_2 represents the interaction between the headgroups that should be the same for all mixed micelles. The deviation in f_1 values, on the other hand, is related to hydrophobic interaction between surfactant alkyl chains.

Figure 4 shows the average value of interaction parameter β as a function of number of carbon atoms in the alkyl chain.

According to results in Figure 4, it is clear that the decrease in the chain length of the cationic surfactants leads to a stronger interaction between the surfactants and the degree of interaction is higher when the hydrophobicity of cationic surfactant is lower. This result was explained by the fact that, as

Table 7. Calculations According to Hua and Rosen Conditions^a

$\alpha_{\text{cationic surf.}}$	$ \beta > \ln(\text{cmc}_1/\text{cmc}_2)$ must be satisfied
0.25 C_{14} TAB	$ -0.647 < \ln(3.5/1.72) = 0.710$
0.50 C_{14} TAB	$ -0.627 < \ln(3.5/1.72) = 0.710$
0.75 C_{14} TAB	$ -0.199 < \ln(3.5/1.72) = 0.710$
0.25 C_{12} TAB	$ -1.740 < \ln(13/1.72) = 2.02$
0.50 C_{12} TAB	$ -0.260 < \ln(13/1.72) = 2.02$
0.75 C_{12} TAB	$ -0.130 < \ln(13/1.72) = 2.02$
0.25 C_{10} TAB	$ -1.550 < \ln(60/1.72) = 3.55$
0.5 C_{10} TAB	$ -2.480 < \ln(60/1.72) = 3.55$
0.75 C_{10} TAB	$ -0.610 < \ln(60/1.72) = 3.55$

^a $\alpha_{\text{cationic surf.}}$ is the bulk mole fraction of the cationic surfactant; β is the interaction parameter; cmc_1 is the critical micelle concentration of cationic surfactant, and cmc_2 is the critical micelle concentration of amphoteric surfactant.

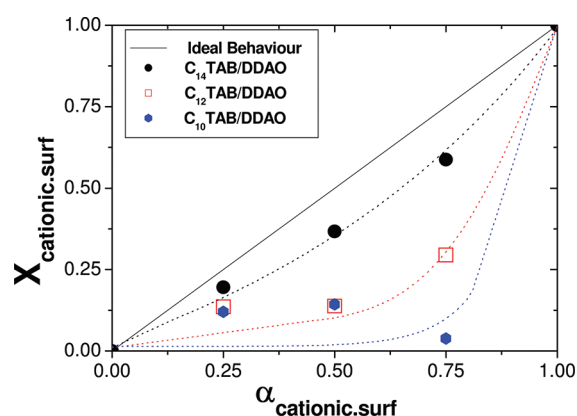


Figure 3. Plot of mole fraction of C_n TAB ($n = 14, 12,$ and 10) in (C_n TAB + DDAO) mixed micelle (X_1) versus mole fraction in the bulk (α) at 298 K. —, ideal behavior, ---, real behavior.

Table 8. Mole Fractions of Cationic Surfactant in Mixed Micelle, $x_{\text{cationic surf.}}$, the Activity Coefficients (f_1 and f_2) for the Three Mixed Systems of (C_{14} TAB + DDAO), (C_{12} TAB + DDAO), and (C_{10} TAB + DDAO)

α	$x_{\text{cationic surf.}}$	f_1	f_2
0.25 C_{14} TAB	0.195	0.881	0.98
0.50 C_{14} TAB	0.367	0.794	0.92
0.75 C_{14} TAB	0.587	0.890	0.93
0.25 C_{12} TAB	0.136	0.789	0.97
0.50 C_{12} TAB	0.138	0.965	1.00
0.75 C_{12} TAB	0.295	0.962	0.99
0.25 C_{10} TAB	$3.85 \cdot 10^{-2}$	0.942	1.00
0.5 C_{10} TAB	0.143	0.701	0.95
0.75 C_{10} TAB	0.120	0.929	0.99

the tail group of cationic surfactant becomes longer, the steric hindrance would also increase and lead to lower interaction.

Since there is no difference between the head groups of C_{10} TAB, C_{12} TAB, and C_{14} TAB, the distinct behavior of the three mixed systems is then attributed to the difference in the interaction between the tails that was mathematically described by the f_1 -values. The positive charge center of cationic surfactant cannot overlap with the amphoteric surfactant which is surrounded by two methyl group induces (steric hindrances) unless a special type of packing is created; there is a type of mutual incompatibility between the hydrophobic tails in

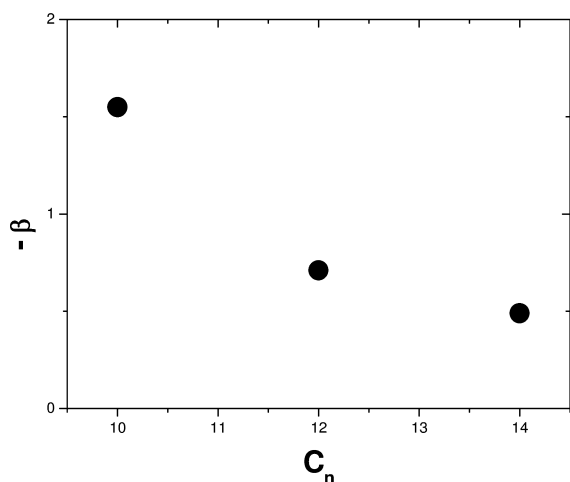


Figure 4. Interaction parameter, β , as a function of the number of carbon atom C_n in the alkyl chain for the mixtures alkyl-trimethylammonium bromide and DDAO surfactants.

the mixed micelles. When the tail is long, a type of distortion in the micelle core would result. Such type of distortion will influence the tail packing in the micelle core and decrease the interaction between them.

Similar results were also obtained by Kakehashi et al. for the mixed system of sodium oleate NaOl and alkylglucoside surfactants C_nG . It was found that the interaction parameter for (NaOl + C_8G) mixed system is more negative than that for (NaOl + $C_{10}G$) mixed system.³¹ Bakshi et al.³² obtained also a similar result for a mixed system of cationic and nonionic surfactants. It was found that, when increasing the chain length of nonionic surfactant from octaethyleneglycolmono-decylether $C_{10}EO_8$ to octaethyleneglycolmono-tetradecylether $C_{14}EO_8$, the nature of the mixed micelles starts shifting from synergistic to antagonistic mixing. The authors concluded that increasing the hydrophobicity of the nonionic component along with that of the cationic component induces steric hindrances in the course of mutual arrangement of longer hydrophobic tails of the unlike components in the mixed state.

Figure 5 shows the variation in the viscosity, η , for solution with $100 \text{ mmol}\cdot\text{kg}^{-1}$ $C_{10}\text{TAB}$, $C_{12}\text{TAB}$, or $C_{14}\text{TAB}$ as a function of shear rate at different DDAO concentrations (≈ 100 to 400) $\text{mmol}\cdot\text{kg}^{-1}$ at 298 K .

Figure 5a–c shows that the change in the viscosities of $C_n\text{TAB}$ surfactant at different DDAO concentrations at 298 K is insensitive to surfactant chain length, and consequently no direct relation can be established between the interaction parameter and the viscosity. The results obtained are also contrary to the reported research studies that correlate the increase in the viscosity to interaction parameters.⁹

Such small viscosity values are characteristics for micelles that consist of small aggregates (spherical or globular shape). The theoretical basis for the viscosity of such aggregates follows Einstein's law as described by the equation according to which the viscosity is linearly increasing with the volume fraction ϕ of the particles:³³

$$\eta = \eta_s(1 + 2.5\phi) \quad (8)$$

In the present study, it was found that the viscosities of these solutions can significantly be enhanced by adding hydrophobic salts like sodium salicylate, NaSal. Adding enough amounts of NaSal to hexadecyl-trimethyl-ammonium bromide, CTAB

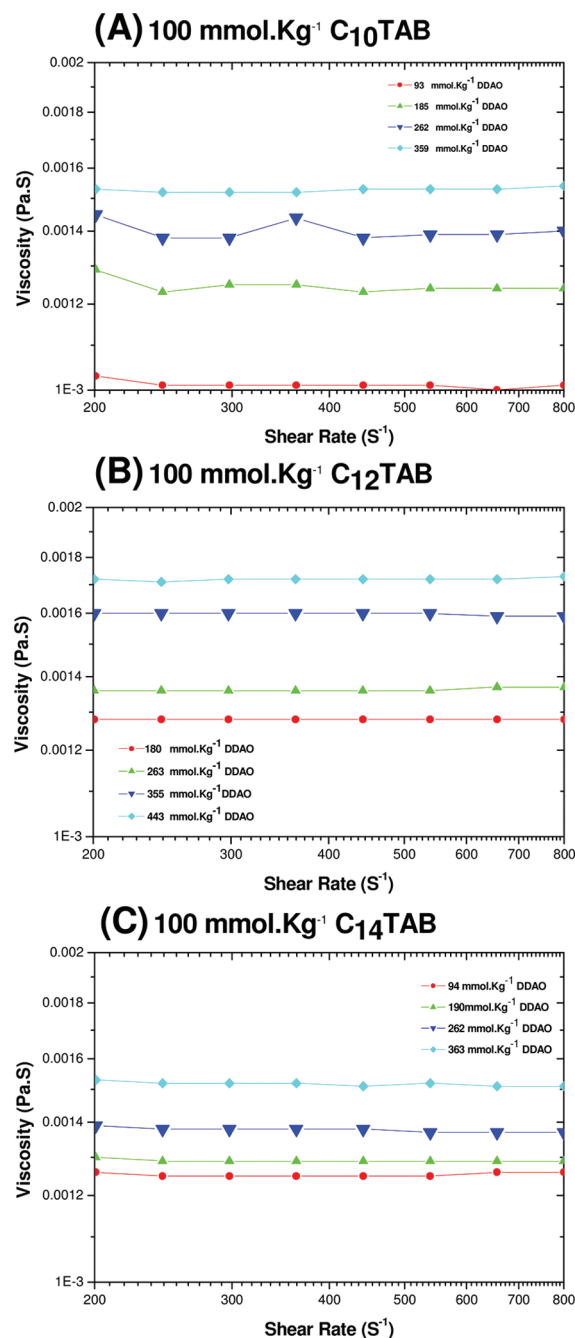


Figure 5. Variation in the viscosity, η (Pa·s), for (A) $C_{10}\text{TAB}$, (B) $C_{12}\text{TAB}$, and (C) $C_{14}\text{TAB}$ ($100 \text{ mmol}\cdot\text{kg}^{-1}$) as a function of shear rate at different DDAO concentrations (≈ 100 to 400) $\text{mmol}\cdot\text{kg}^{-1}$ at 298 K .

surfactant solutions results in the formation of viscoelastic rod-like micelles.³⁴

Figure 6a shows the dependence of loss modulus, G'' , and complex viscosity, η^* , on angular frequency (ω) for solutions with $100 \text{ mmol}\cdot\text{kg}^{-1}$ $C_n\text{TAB}$ ($n = 14, 12,$ and 10), $360 \text{ mmol}\cdot\text{kg}^{-1}$ DDAO, and $200 \text{ mmol}\cdot\text{kg}^{-1}$ NaSal at 298 K . The loss modulus, G'' , gives an idea about the viscous character of the viscoelastic solution. As can be noticed from Figure 6a, the magnitude of G'' increases with surfactant chain length, indicating an increase in the viscous character of the solutions. The complex viscosity, η^* , increases with chain length and is independent of applied frequency, which is equivalent to

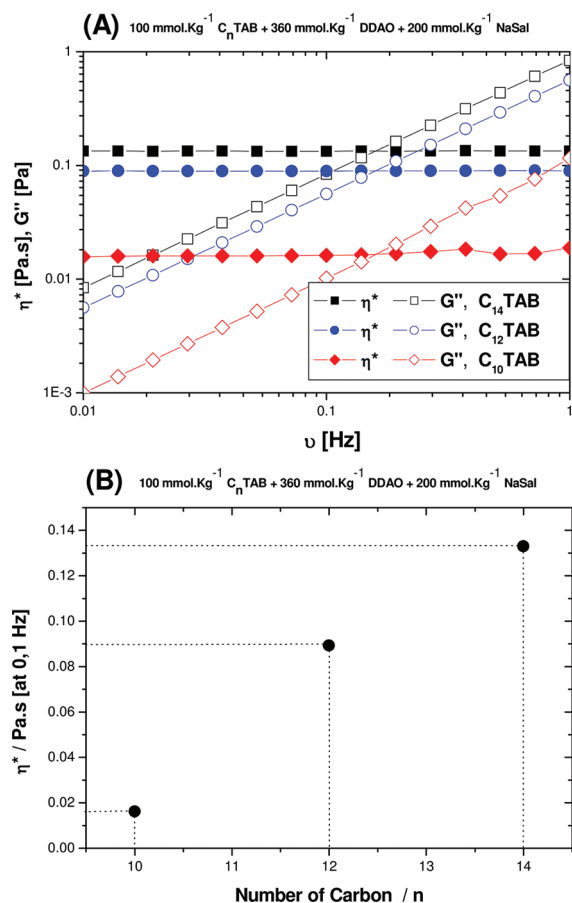


Figure 6. (a) Variation of the complex viscosity, η^* , loss modulus G'' vs frequency, ν , for solutions with 100 mmol.kg⁻¹ C_nTAB ($n = 14, 12,$ and 10), 360 mmol.kg⁻¹ DDAO, and 200 mmol.kg⁻¹ NaSal at 298 K. Part b demonstrates an increase in the viscosity with the increase in cationic surfactant chain length.

dynamic viscosity, η . Figure 6b demonstrates that the viscosity at 0.1 Hz increases as the chain length of the surfactant increases.

It is evident from the results in Figure 6 that the chain length is therefore an important factor for the viscosity and the long chain surfactants would form viscous micellar aggregate.

However, it has to be mentioned that the pK_a value for salicylic acid is 2.78.³⁵ Therefore, the experiments carried out in the presence of NaSal (sodium salicylate) will increase the basicity of the solution ($pH \approx 8.04$) enhancing the nonionic character of the partially protonated micelles.^{28,29} Under this situation, no direct comparison between the data in Figures 5 and 6 can be obtained.

By comparing the results in Figures 4 and 6 it seems that the interaction parameter calculated according to Rubingh's theory reversed the influence on the resultant viscosity of (alkyl-trimethyl-ammonium bromide + DDAO) mixed systems.

5. CONCLUSION

The following conclusions could be drawn from this article:

- (1) The binary surfactant systems of DDAO and alkyl-trimethyl-ammonium bromide surfactants of alkyl chain length, 10, 12, and 14 carbon atoms show somehow small deviation from ideal behavior as indicated by the values of interaction parameters.

- (2) The nonionic heads of DDAO surfactant form dipole-ion bonding with the heads of alkyl-trimethyl-ammonium surfactants.
- (3) The activity coefficients of the components in the mixed systems are not far from ideal behavior (unity), suggesting an ideal behavior.
- (4) The origin of decreasing β with respect to increase in chain length of the cationic surfactants could be due to the improper packing of the surfactant with longer hydrophobic tails in the mixed micelle.
- (5) It seems that the interaction parameter calculated according to Rubingh's theory has no direct influence on the resultant viscosity of (alkyl-trimethyl-ammonium bromide + DDAO) mixed systems.

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Notes

The authors declare no competing financial interest.

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