Micellization and Solvation Properties of Newly Synthesized Imidazolium- and Aminium-Based Surfactants

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ABSTRACT: This work aimed to study the solvation properties of newly synthesized cationic surfactants: 1-hexyl-1-methyl-1H-imidazol-1-ium bromide (R6Im), 1-dodecyl-1-methyl-1H-imidazol-1-ium bromide (R12Im), N,N,N-tributylhexan-1-aminium bromide (R6N4), and N,N,N-tributyldodecan-1-aminium bromide (R12N4) in water and ethanol–water solvents with a 0.237 mole fraction of ethanol at 298.15 K using conductivity, refractive index, surface tension, and density measurements. Critical micelle concentration (CMC) for the synthesized surfactants was determined and discussed. Thermodynamic parameters including association constant, molal volume, and polarizability were calculated and discussed. Some surface properties of surfactants including excess surface concentration and minimum area per molecule were also calculated and discussed. A good agreement was found between the CMC values obtained from different techniques, such as conductivity, refractive index, and surface tension. Imidazolium surfactants had been proved to decrease the CMC and increase the association constant with the increase of ethanol mole fraction, while tributylamine had been proved to increase the CMC and decrease the association constant with the increase of ethanol mole fraction. Also, imidazolium surfactants had been proved to have higher CMC than tributylamine, which may be related to higher solvation of imidazolium surfactants than that of tributylamine. Both surfactants (R12Im) and (R12N4) were proved to have lesser CMC.

INTRODUCTION

Surfactants have vital importance in many industrial fields, especially cationic surfactants which play an effective role in food processing, oil recovery, delivery of genetic material, antimicrobial, cosmetics, and corrosion inhibitors.1–8 Imidazolium and tributyl cationic surfactants consist of a hydrophilic head which commonly depends on the amine or quaternary ammonium positive unit and a hydrophobic tail squeezed out of water due to the hydrogen bonds between water molecules. The surfactant in diluted concentration dispersed as individual molecules in solution. As the concentration increases, the properties of the solution change until reaching the concentration where individual molecules associate to form micelles. This concentration is called critical micelle concentration (CMC). CMC is a fingerprint of any surfactant at a given temperature and electrolyte concentration. The size and shape of micelles depend on factors including surfactant concentration, temperature, pH, and solvent properties.9 The variation of the CMC with chemical and physical parameters provides a perfect view for the nature of the surfactant self-association. Methods for CMC determination include conductivity, viscosity, surface tension, ion activity, dye incorporation, gel filtration spectrophotometrically, counterion magnetic resonance, and refractive index measurements.10–14 Solvation of different cationic surfactants in different solvents was investigated before,15–23 where CMC was measured with different methods. Also, density, refractive index, and UV spectra measurements of solutions are expected to shed some light on the solute–solvent interactions and configuration of their mixtures.26–29 Other thermodynamic properties including molal volume, ionic association, and polarizability were investigated for ionic liquids,24,25 especially for imidazolium ionic liquid surfactants.

The present work aims to study the synthesis and characterization of some cationic surfactants. Determination of accurate values of the CMC for the synthesized surfactants using different techniques, such as conductivity, refractive index, and surface tension was the second aim of the present study. Also, the present work aims to study the solvation thermodynamic

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parameters including molal volumes, refractive index, and UV–visible measurements of the synthesized surfactants in water and ethanol–water solvents with an ethanol mole fraction of 0.237.

## RESULTS AND DISCUSSION

### Structure Confirmation.
The chemical structure of the synthesized cationic surfactants was investigated using IR spectroscopy and $^1$H NMR spectroscopy.

**IR Spectroscopy Analysis.** The IR spectrum of R$_6$IM and R$_{12}$IM ionic liquids is represented in Figures 1 and 2. All vibration bands of functional groups are represented in Table 1. Both the parent compounds (R$_6$IM and R$_{12}$IM) are hydrophilic and show the presence of a large amount of water at 3444 and 3433 cm$^{-1}$, respectively, for R$_6$IM and R$_{12}$IM.

The IR spectrum of R$_6$N$_4$ and R$_{12}$N$_4$ ionic liquids is represented in Figures 3 and 4. All vibration bands of functional groups are represented in Table 2. Both the parent compounds (R$_6$N$_4$ and R$_{12}$N$_4$) are hydrophilic and show the presence of a large amount of water at 3444 and 3433 cm$^{-1}$, respectively, for R$_6$N$_4$ and R$_{12}$N$_4$.

**$^1$H NMR Analysis.** The general structure of R$_6$IM and R$_{12}$IM with position numbers (a–h) corresponding to different shifts is shown in Scheme 1. Resonance signals corresponding to the presence of functional groups at different positions are shown in Figures 5 and 6 and represented in Table 3, where the composition of the imidazolium ring and alkyl chain for both surfactants was explained because of their chemical shifts.$^{30–32}$

![Figure 1. IR spectra for the R$_6$IM surfactant.](image1)

![Figure 2. IR spectra for the R$_{12}$IM surfactant.](image2)

| Table 1. IR Bands of R$_6$IM and R$_{12}$IM Surfactants with Their Vibration Names |
|-------------------------------------------------|----------------|-----------------|-----------------|
| wavenumber (cm$^{-1}$) | R$_6$IM | R$_{12}$IM | Vibration |
|-----------------|-----------------|-----------------|-----------------|
| 523             | 523             | C–Br (halogen group) |
| 621             | 622             | imidazole C$_2$–N$_1$–C$_3$ bending |
| 757             | 749             | out-of-plane C–H bending of the imidazole ring |
| 844             | 860             | C–N stretching vibration |
| 1167            | 1170            | imidazole H–C–C and H–C–N bending |
| 1463            | 1464            | asymmetrical bending vibration of the methyl group (C–H bond) |
| 1570            | 1570            | ring stretching vibration of the imidazole group |
| 1628            | 1631            | O–H bending (physically adsorbed water) |
| 2861            | 2854            | stretching vibrations of aliphatic (C–H) sym |
| 2930            | 2924            | stretching vibrations of aliphatic (C–H) asym |
| 3087            | 3085            | stretching vibrations of alkyl groups at the (N) atom of the imidazolium ring |
| 3146            | 3149            | stretching vibrations of alkyl groups at the (N) atom of the imidazolium ring |
| 3444            | 3433            | stretching of N–H bond water |

Figures 5 and 6 and represented in Table 3, where the composition of the imidazolium ring and alkyl chain for both surfactants was explained because of their chemical shifts.$^{30–32}$

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The general structure of R₆N₄ and R₁₂N₄ with position numbers (a–e) corresponding to different shifts is shown in Scheme 2. Resonance signals corresponding to the presence of functional groups at different positions are shown in Figures 7 and 8 and represented in Table 4, where the composition of alkyl chain and tributylamine of both surfactants was explained because of their chemical shifts.²¹–³³

Micellization and Solvation Studies. CMC Measurements. The CMC of synthesized surfactants was determined by using different techniques including conductivity, refractive index, and surface tension.

First, using conductivity measurements, the conductivity for surfactants in water and ethanol–water mixed solvents with a 0.237 ethanol mole fraction has been measured at 298.15 K, as described before in the Experimental Section. By plotting the concentration in (mol L⁻¹) against specific conductance in (μS/cm) as shown in Figures 9–12, the CMC of surfactants in water and ethanol–water mixed solvents was estimated.

Second, using refractive index measurements, the refractive indices for the surfactant solution in water and ethanol–water mixed solvents with a 0.237 ethanol mole fraction have been measured at 298.15 K, as mentioned in the Experimental Section. By plotting the concentration in (mol L⁻¹) against...
refractive indices as shown in Figures 13−15, the CMC has been estimated. Finally, using surface tension measurements, the surface tension of surfactants in water was measured, as mentioned in the Experimental Section. By plotting the concentration (mol L\(^{-1}\)) against surface tension as shown in Figure 16, the CMC for surfactants in water solvent was estimated at 298.15 K.

The CMC values for surfactants (R\(_6\)Im) and (R\(_{12}\)Im) in water and ethanol−water mixed solvents with a 0.237 ethanol mole fraction as estimated from different techniques (conductivity, refractive index, and surface tension) are summarized in Table 5.

Table 6, we can note that there is good agreement between the CMC values obtained using three different methods (conductivity, refractive index, and surface tension). This indicates that the suitable value of CMC for surfactants under study is reported in Table 5. In the solvation and micellization processes, we can see that as the hydrophilic nature increases, solvation increases and micellization decreases, and thus, high concentration is needed, that is, high CMC and vice versa. Based on this, the CMC of surfactants (R\(_6\)Im) and (R\(_{12}\)Im) was found to decrease with the increase of ethanol mole fraction, indicating more micellization and less solvation, which may be related to the increase of hydrogen bond formation in ethanol−water mixed solvent. On comparing the CMC of both surfactants, it was found that the CMC of (R\(_6\)Im) in both water and ethanol−water mixed solvents is more than the CMC of (R\(_{12}\)Im), indicating an
increase in micellization (low CMC) with an increase in hydrocarbon chain.\textsuperscript{35}

On the other hand, the CMC of surfactants (R\textsubscript{6}N\textsubscript{4}) and (R\textsubscript{12}N\textsubscript{4}) was found to increase with the increase of ethanol mole fraction, indicating less micellization and more solvation compared with that of (R\textsubscript{6}Im) and (R\textsubscript{12}Im), which may be due to the dissociation of the inter- and intrahydrogen bonds.\textsuperscript{36}

On comparing the CMC of both surfactants, it was found that the CMC of (R\textsubscript{6}N\textsubscript{4}) in both water and ethanol–water mixed solvents is more than the CMC of (R\textsubscript{12}N\textsubscript{4}), indicating an
increase in micellization (low CMC) with an increase in hydrocarbon chain.\textsuperscript{37}

**Thermodynamic Parameters. Concentration Dependence of Conductivity.** Degree of ionization ($\alpha$) and counterion binding, $\beta = (1 - \alpha)$, for surfactants under study in water and ethanol–water mixed solvents with a 0.237 ethanol mole fraction at 298.15 K were estimated from eqs 1 and 2 ever and represented in Table 6.

\[
\alpha = \frac{S_2}{S_1} \tag{1}
\]

\[
\beta = (1 - \alpha) \tag{2}
\]

where $S_2/S_1$ is the ratio between the slope of post- and premicelle regions. The Gibbs free energy of micellization was estimated from the following equation

\[
\Delta G_{mic} = (2 - \alpha)RT \ln[\text{CMC}] \tag{3}
\]

where $\alpha$ is the degree of ionization, $R$ is the universal gas constant, and $T$ is the absolute temperature. The values of the standard free energy change of micellization ($\Delta G_{mic}$) are represented in Table 6.

**Association Constant.** Equivalent conductance ($\Lambda$) of surfactants in water and ethanol–water mixed solvents with a 0.237 ethanol mole fraction at 298.15 K has been calculated from the conductivity measurements before the CMC value by using eq 4.

\[
\Lambda = \frac{1000 \times K_c}{C} \tag{4}
\]

By plotting $\Lambda$ against $\sqrt{C}$ in eq 5, the intercept which is the limiting equivalent conductance ($\Lambda_\infty$) has been estimated.

\[
\Lambda = \Lambda_\infty - B\sqrt{C} \tag{5}
\]

Conductivity data were used to calculate the value of association constant for the surfactant under study in water.
and ethanol—water mixed solvents with a 0.237 ethanol mole fraction at 298.15 K according to the Shedlovsky extrapolation (eq 6).\(^3\)\(^9\)

\[
\gamma \Lambda = \gamma \Lambda^0 + \gamma \Lambda^0 \frac{S_z}{K_a S_z^1} \\
(6)
\]

where \(S_z\) is the Shedlovsky function, which can be calculated from following equation

\[
S_z = \left( \frac{Z}{2} + \sqrt{1 + \left( \frac{Z}{2} \right)^2} \right)^2 \\
(7)
\]

where \(K_a\) is the association constant and \(\gamma\) is the activity coefficient estimated from the Debye–Hückel limiting law as modified by Robinson and Stokes.

The standard free energy change of association at 298.15 K can be calculated using following equation

\[
\Delta G_a = -2.303RT \log K_a \\
(8)
\]

The values of the association constant \((K_a)\) and the standard free energy change of association \((\Delta G_a)\) are represented in Table 6.

In the association, solvation, and micellization processes, we can see that as the hydrophilic nature increases, solvation increases, micellization decreases (high CMC), and association increases. Based on this, the values of the association constant for both \((R_{6Im})\) and \((R_{12Im})\) were found to increase with the increase of ethanol mole fraction, as indicated from the decrease in CMC with the increase of ethanol mole fraction, which may be related to the decrease in the dielectric constant of ethanol than that of water and thus decrease in solvation.\(^3\)\(^8\)\(^-\)\(^4\)\(^1\) The association constant values of both surfactants in water and ethanol—water mixed solvents with a 0.237 ethanol mole fraction increase with an increase in hydrocarbon chain length, as indicated from more micellization (low solvation and low CMC) of \((R_{12Im})\) than that of the \((R_{6Im})\) surfactant. Negative values of standard free energy of micellization and association processes indicate spontaneous nature of micellization and association processes. More negative \(\Delta G_{mic}\) and \((\Delta G_a)\) have more tendencies to form micelles and to associate.\(^4\)\(^2\)

On the other hand, it was found that the values of association constant for \((R_{6N4})\) and \((R_{12N4})\) surfactants decrease with the increase of ethanol mole fraction, which can be related to the

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**Table 5. CMC Values of the Surfactants under Study in Water and Ethanol—Water Mixed Solvents at 298.15 K**

| surfactant | ethanol mole fraction | from conductivity | from refractive index | from surface tension |
|------------|-----------------------|-------------------|----------------------|---------------------|
| \(R_{6Im}\) | Water                 | 0.0220            | 0.0195               | 0.0210              |
|            | 0.237                 | 0.0088            | 0.0085               |                     |
| \(R_{12Im}\)| Water                | 0.0122            | 0.0124               | 0.0120              |
|            | 0.237                 | 0.0075            | 0.0090               |                     |
| \(R_{6N4}\) | Water                 | 0.0035            | 0.0031               | 0.0029              |
|            | 0.237                 | 0.0082            | 0.0075               |                     |
| \(R_{12N4}\)| Water                | 0.0018            | 0.0019               | 0.0019              |
|            | 0.237                 | 0.0022            | 0.0022               |                     |

*Standard uncertainties, \(u\), of CMC are \(u(CMC) = 0.0002\) mol L\(^{-1}\).*
increase in CMC of both surfactants with the increase of ethanol mole fraction.43,44 The association constant values of both surfactants in water and ethanol—water mixed solvents with a 0.237 ethanol mole fraction increase with an increase in hydrocarbon chain length, as indicated from more micellization of (R12N4) than that of (R6N4) surfactant. Negative values of standard free energy indicate spontaneous nature of micellization and association processes.

Solution Surface Properties. According to the measurement of surface tension of the surfactant under study in water at 298.15 K, some surface properties such as maximum surface concentration, minimum area per molecules, and effectiveness of reduction of surface areas were calculated as follows:

The effectiveness of surface tension reduction was calculated by using the following equation 45

$$\pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}}$$  \hspace{1cm} (9)

where $\gamma_0$ is the surface tension of pure water at the appropriate temperature and $\gamma_{\text{CMC}}$ is the surface tension of the solution at the CMC.

Maximum surface excess concentration ($\Gamma_{\text{max}}$)46 considered effective adsorption of the surfactant on the air—water interface. This is defined as the concentration of surfactant molecules in a surface plane, relative to that at a similar plane in the bulk which can be calculated by using the Gibbs adsorption (eq 10)

$$\Gamma_{\text{max}} = -\left(\frac{1}{2.303RT}\right)\left(\frac{\partial \gamma}{\partial \log C}\right)_{\text{max}, T, p}$$  \hspace{1cm} (10)

where $R$ is the universal gas constant, $T$ is the absolute temperature, and $(\partial \gamma/\partial \log C)$ is the ratio between surface tension values at CMC to concentration at CMC.

The minimum surface area of surfactant molecules at air—water solution interfaces ($A_{\text{min}}$)$^{11}$ can be calculated from the following 11

$$A_{\text{min}} = \frac{1}{N \Gamma_{\text{max}}}$$  \hspace{1cm} (11)

where $N$ is the Avogadro number. The values of effectiveness, excess surface concentration, and minimum surface area are summarized in Table 7.

The results show an increase in minimum area per molecule of surfactants (R12Im) and (R12N4) than that of (R6Im) and (R6N4), respectively. This may be related to the increase in hydrocarbon chain length and thus increase in the effectiveness of surface tension reduction. This may be related to the increase in the adsorption of the surfactant (R12Im) than that of (R6Im) at the air—water interface, which orients themselves away from the water, leading to a decrease in maximum surface excess concentration. This indicates an increase in the efficiency of reducing surface tension solution of the surfactant with an increase in hydrocarbon chain length.46

Molar Volumes. The density of surfactants in molal concentration in water and water—ethanol with a 0.237 mole fraction of ethanol was measured at 298.15 K. Molar volumes ($V_w$) of the surfactant under study were then calculated from the following 12 46

$$V_w = \frac{M}{\rho} - \frac{1000}{m} \left[\frac{1}{\rho^o} - \frac{1}{\rho}\right]$$  \hspace{1cm} (12)

where $M$ is the molecular weight of the surfactant; $m$ is the molar concentration of the surfactant in solution; and $\rho$ and $\rho^o$ are the densities of solution and solvent, respectively.

The packing density ($P$) (the relation between the van der Waals volume and the molar volume of relatively large molecules) was found to be constant.47,48 Therefore, van der Waals volumes ($V_w$) of the surfactants can be calculated by using 13 following equation 49

$$V_w = V_w - V_w = 0.661 \pm 0.017$$  \hspace{1cm} (13)

Electrostriction volume which indicated the volume compressed by the solvent can be calculated from 14 following equation 50

$$V_E = V_w - V_w$$  \hspace{1cm} (14)

The values of density ($\rho$), molar volume ($V_w$), electrostriction volume ($V_E$), and van der Waals volume ($V_w$) of the surfactants under study in water and ethanol—water mixed solvent with a 0.237 ethanol mole fraction at 298.15 K are reported in Table 8.

The densities of all surfactants under study were found to decrease with the increase of ethanol mole fraction. Also, molar volume was found to increase with the increase of ethanol mole fraction.

Table 6. Degree of Ionization ($\alpha$), Counterion Binding Constant ($\beta$), Free Energy Change of Micellization ($\Delta G_{\text{mic}}$), Limiting Molar Conductance ($\Lambda_e$), Association Constant ($K_a$), and Free Energy Change of Association ($\Delta G_a$) for the Surfactants under Study in Water and Ethanol—Water Mixed Solvents with a 0.237 Ethanol Mole Fraction at 298.15 K

| surfactant | ethanol mole fraction | $\alpha$ | $\beta$ | $\Delta G_{\text{mic}}$ (kJ/mol) | $\Lambda_e$ (S cm$^2$ mol$^{-1}$) | $K_a$ (L mol$^{-1}$) | $\Delta G_a$ (kJ/mol) |
|------------|----------------------|---------|--------|-----------------------------|-----------------|----------------|-----------------|
| R6Im       | Water                | 0.1027  | 0.9820 | -14.2285                    | 135.73          | 80.280         | -10.87          |
|            | 0.237                | 0.0152  | 0.9848 | -17.6842                    | 61.980          | 199.13         | -13.12          |
| R12Im      | Water                | 0.79112 | 0.2088 | -10.0276                    | 117.36          | 112.02         | -11.69          |
|            | 0.237                | 0.13421 | 0.8658 | -17.1856                    | 66.640          | 498.35         | -15.39          |
| R6N4       | Water                | 0.9972  | 0.0028 | -14.057                      | 102.51          | 138.82         | -12.22          |
|            | 0.237                | 0.8393  | 0.1607 | -13.821                      | 37.770          | 33.820         | -8.725          |
| R12N4      | Water                | 0.6613  | 0.3387 | -20.971                      | 104.22          | 664.93         | -16.11          |
|            | 0.237                | 0.6238  | 0.3962 | -20.875                      | 85.14           | 99.9           | -11.41          |

“Standard uncertainties, $u$, are $u(\alpha) = 0.0005$, $u(\beta) = 0.0004$, $u(\Delta G_{\text{mic}}) = 0.1$, $u(\Delta G_a) = 0.01$, $u(K_a) = 0.18$, and $u(\Delta G_a) = 0.13$.

Table 7. Maximum Surface Excess Concentration ($\Gamma_{\text{max}}$), Minimum Surface Area ($A_{\text{min}}$), and Effectiveness of Reduction of Surface ($\pi_{\text{CMC}}$) in Water Solvent at 298.15 K

| surfactant | $\Gamma_{\text{max}}$ x 10$^7$ cm$^2$/molecule | $A_{\text{min}}$ x 10$^{10}$ nm$^2$/molecule | $\pi_{\text{CMC}}$ dyne/cm |
|------------|-----------------------------------------------|---------------------------------------------|---------------------------|
| R6Im       | 7.33                                         | 2.27                                        | 1.30                      |
| R12Im      | 3.01                                         | 5.52                                        | 39.0                      |
| R6N4       | 4.11                                         | 4.04                                        | 13.0                      |
| R12N4      | 3.09                                         | 5.37                                        | 24.2                      |
molecular weight of the R12 surfactant than that of R6. The molar volume of all surfactants under study was found to increase with the increase of ethanol mole fraction, which may be related to the higher density of water than that of ethanol. The molal volume of all surfactants under study was found to increase with the increase of ethanol mole fraction, which may be related to the higher density of water than that of ethanol. The molal volume of (R12N4), which may be related to the higher density of the R12 surfactant than that of R6. The molal volume of (R6N4) and (R12N4) were found to be greater than those of (R6Im) and (R12Im), respectively. This may be related to the higher density of the R12 surfactant than that of R6.

The molar volumes of (R6N4) and (R12N4) were found to be greater than those of (R6Im) and (R12Im), respectively. This may be related to the higher density of the R12 surfactant than that of R6.

**Refractive Index.** Refractive index of surfactants under study in water and ethanol—water solvent with different ethanol mole fractions (x1 = 0.0 to x1 = 0.42) were found to be greater than those of (R6Im) and (R12Im), respectively. This may be related to the closer proximity of the hydrocarbon chains of the surfactants in water mixed solvent with different ethanol mole fractions (x1 = 0.0 to x1 = 0.42) were measured and are represented in Figures 17–20. The values of the absorbance and the wavelength of surfactants are collected in Tables 10 and 11.

For R6Im and R12Im surfactants in ethanol—water solvent, a decrease in UV absorbance (peak 1) was noted with an increase in ethanol mole fraction from x1 = 0.018 to x1 = 0.421. The increase in the apparent molar volume of the two surfactants with the increase in the mole fraction of ethanol.

The molar refraction and polarizability of (R6Im) and (R12N4) are found to be greater than those of (R6Im) and (R12N4), respectively, in water and ethanol—water solvent with a 0.237 mole fraction of ethanol. This may be related to the increase in hydrocarbon chain length which increases the micellization and decreases the solvation.

The refractive index, molar refraction, and polarizability of (R6Im) and (R12Im) are found to be greater than those of (R6N4) and (R12N4), respectively. This may be related to the higher molar volumes of (R6N4) and (R12N4) than those of (R6Im) and (R12Im), respectively.

**UV–Visible Spectra.** The UV–visible spectra of all surfactants under study with concentration (0.001 M) in water and ethanol—water mixed solvents with different ethanol mole fractions (x1 = 0.0 to x1 = 0.42) are represented in Figures 17–20. The values of the absorbance and the wavelength of surfactants are collected in Tables 10 and 11.

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The refractive index, molar refraction, and polarizability of (R6N4) and (R12N4) are found to be greater than those of (R6Im) and (R12Im), respectively. This may be related to the higher molar volumes of (R6N4) and (R12N4) than those of (R6Im) and (R12Im), respectively.

The increase in the apparent molar volume of the two surfactants with the increase in the mole fraction of ethanol.

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For R6Im and R12Im surfactants in ethanol—water solvent, a decrease in UV absorbance (peak 1) was noted with an increase in ethanol mole fraction from x1 = 0.018 to x1 = 0.421. The increase in the apparent molar volume of the two surfactants with the increase in the mole fraction of ethanol.
decrease in the absorption of UV light is called a hypochromic effect. On the other hand, an increase in UV absorbance was noted (peak 2) with an increase in ethanol mole fraction from $x_1 = 0.118$ to $x_1 = 0.421$ in ethanol–water mixed solvent. Increase in the absorption of UV light is called a hyperchromic effect. These effects may be due to the disruption of the hydrogen bonds between the surfactant molecules as a result of the interaction with ethanol than that with water molecules as a result of change in the dielectric properties of the solvent.

For R$_6$N$_4$ and R$_{12}$N$_4$ surfactants in ethanol–water solvent, an increase in UV absorbance was noted (peaks 1 and 2) with an increase in ethanol mole fraction from $x_1 = 0.118$ to $x_1 = 0.421$ in ethanol–water mixed solvent. This effect may be due to the disruption of the hydrogen bonds between the surfactant molecules as a result of change in the dielectric properties of the solvent.

With respect to the wavelength shift, no shift was found for all surfactants under study.

**CONCLUSIONS**

This study is concerned with the synthesis and characterization of some cationic surfactants: 1-hexyl-1-methyl-1H-imidazol-1-ium bromide (R$_6$Im), 1-dodecyl-1-methyl-1H-imidazol-1-ium bromide (R$_{12}$Im), N$_3$N$_3$N-tributylhexan-1-aminium bromide (R$_6$N$_4$), and N$_3$N$_3$N-tributyldodecan-1-aminium bromide (R$_{12}$N$_4$). By using different techniques such as conductivity, refractive index, and surface tension, thermodynamic parame-
ters in water and ethanol-water solvents at 298.15 K were measured, calculated, and discussed. A good agreement was found between the CMC values obtained from different techniques, such as conductivity, refractive index, and surface tension. Imidazolium surfactants had been proved to decrease the CMC and increase the association constant with the increase of ethanol mole fraction, while tributylamine had been proved to increase the CMC and decrease the association constant with the increase of ethanol mole fraction. Also, imidazolium surfactants had been proved to have higher CMC than tributylamine, which may be related to the higher solvation of imidazolium surfactants than that of tributylamine. Both surfactants (R12Im) and (R12N4) were proved to have fewer CMC values than (R6Im) and (R6N4), respectively, indicating the effect of hydrocarbon chain length, which means the longer the chain length, the more the micellization and the less the solvation.

**EXPERIMENTAL SECTION**

**Materials.** The chemical compounds used in this study were purchased from different international companies with high-purity grade, as shown in Table 12.

**Synthesis of Cationic Surfactants.**

**Synthesis of Cationic Surfactants Based on 1-Methylimidazole.** Cationic surfactants based on 1-methylimidazole were synthesized, as illustrated in Scheme 3. This process was carried out by using the quaternization reaction. 1-Methylimidazole (50 mM) and 1-bromoalkanes, namely, 1-bromohexane and 1-bromododecane, were charged individually in a 250 mL round flask in the presence of acetone (100 mL) as a solvent. The reaction mixture was refluxed under stirring for 18 h, and then the reaction mixture was cooled to room temperature. The brown precipitate was filtered, washed twice with diethyl ether, and then recrystallized from acetone to afford the white crystal products of the cationic surfactants. The yields of the brown crystal products ranged between 74 and 83%. The obtained products of quaternary ammonium cationic surfactants were designated as (R6Im) for 1-hexyl-1-methyl-1H-imidazol-1-ium bromide and (R12Im) for 1-dodecyl-1-methyl-1H-imidazol-1-ium bromide.

**Synthesis of Cationic Surfactants Based on Tri-n-butyl Amine.** Cationic surfactants based on tri-n-butyl amine were synthesized, as illustrated in Scheme 4. This process was carried out by using the quaternization reaction. Tri-n-butyl amine (50 mM) and 1-bromoalkanes, namely, 1-bromohexane and 1-bromododecane, were charged individually in a 250 mL round flask in the presence of acetone (100 mL) as a solvent. The reaction mixture was refluxed under stirring for 18 h, and then the reaction mixture was cooled to room temperature. The brown precipitate was filtered, washed twice with diethyl ether, and then recrystallized from acetone to afford the white crystal products of the cationic surfactants. The yields of the brown crystal products ranged between 78 and 86%. The obtained products of quaternary ammonium cationic surfactants were designated as (R6N4) for N,N,N,tri-n-butylhexan-1-aminium bromide and (R12N4) for N,N,N-tri-n-butyldecan-1-aminium bromide.

### Table 12. Reg. CAS Number, the Supplier, the Purity, and the Purification Methods for Chemicals throughout the Investigation

| Component          | Reg. CAS Number | Supplier     | Purity before purification % | Purification Methods | Purity after purification % |
|--------------------|-----------------|--------------|------------------------------|----------------------|-----------------------------|
| 1-bromohexane      | 111-25-1        | Alfa Aesar, Germany | 99.00                       | the components were used without further purification | 99.00                     |
| 1-bromododecane    | 143-15-7        | Alfa Aesar, Germany | 98.00                       |                       | 98.00                     |
| 1-methylimidazole  | 616-47-7        | Alfa Aesar, Germany | 99.00                       |                       | 99.00                     |
| Acetone            | 67-64-1         | Aldrich, USA   | 99.90                       |                       | 99.90                     |
| Ethanol            | 64-17-5         | Perfect, Egypt | 99.90                       |                       | 99.90                     |
| Water              | 7732-18         | Bi-distilled   |                              |                       |                            |

**Scheme 3. Synthetic Route of the Cationic Surfactants Based on 1-Methylimidazole**

**Scheme 4. Synthetic Route of the Cationic Surfactants Based on Tributylamine**

\[\text{Tri-n-butyl amine} \rightarrow \text{Acetone} \rightarrow \text{Reflux 18 hrs} \rightarrow \text{Brown precipitate} \rightarrow \text{Filter, wash twice, recrystallize from acetone} \rightarrow \text{White crystal products} \]

\[\text{n=2: } N,N,N,\text{tri-n-butylhexan-1-aminium bromide (R6N4)}\]

\[\text{n=8: } N,N,N,\text{tri-n-butyldecan-1-aminium bromide (R12N4)}\]
Characterization of the Synthesized Cationic Surfactants.

The synthesized surfactants (R₁;IM) and (R₂;IM) were characterized by using a Thermo Fisher Nicolet iS10 IR spectroscope in the range of 400–4000 cm⁻¹ and with a resolution of 4 cm⁻¹. The solid (R₂;IM) was mixed with KBr pellets. The wavelength of the peaks was proved particular functional groups according to the synthesized surfactant structures. Then, both surfactants were characterized using ¹H NMR spectroscopy. Samples were prepared using D₂O as a solvent and then recorded by using a JNM-ECA Series FT NMR spectrometer with a frequency of 500 MHz. Chemical shifts of samples were expressed in parts per million according to their structures.

Solvation Studies of the Synthesized Cationic Surfactants.

The conductivity measurements were carried out using a Jenway conductivity bridge of certainty (±0.025 µS cm⁻¹). The conductivity bridge was calibrated by the determination of the cell constant, Kcell using different standard potassium chloride solutions. To avoid errors, the concentration of the surfactant solution increased by adding 0.1 mL from the prepared surfactant solution having concentrations of 0.1 M (mol L⁻¹) and 0.01 (mol L⁻¹) to 10 mL of pure solvent placed in a double Jacket glass cell at a constant temperature of 298.15 ± 0.1 K using an ultrathermostat of type MLW 3230 (Germany). After each addition, the solution was stirred to maintain homogeneity of the mixer, and then the conductivity of the solution was measured in µS cm⁻¹. Conductivity measurement was used to calculate different thermodynamic parameters. Density measurements with a weight of 1 mL of the pure solvent including water and a 0.237 ethanol mole fraction solvent and surfactant solution in the same solvents with a concentration of 0.01 (mol L⁻¹) were carried out. Refractive indices were measured for 0.01 (mol L⁻¹) solutions of surfactants in both water and ethanol mole fraction solvents by putting one drop of the solution under a Digital refractometer (DR101-60-A. KRÜSS Optronic GmbH, Germany). Surface tension measurements were achieved for the surfactant solution in water solvent by using a ring method with a digital tensiometer K9.

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Notes
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