

Study of the Microheterogeneous Environment of Reverse Micelles in Biocompatible Solvent

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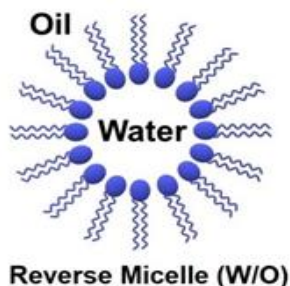
ABSTRACT

Reverse micelles are self-aggregated systems which are composed of amphiphilic surfactant molecules dispersed in hydrophobic medium. They are important for the synthesis of many types of nanoparticles as amphiphilic induced electrostatic interaction and H-bonding are considered to be the major stabilising factor operating at the interface by regulating radius of inner core. Therefore the study on the water/AOT/ dispersed phase type microemulsions with varying solvent and the effect of solvent on the structure of reverse micelle have been studied. In this case two non-protic ionic liquid [1-butyl-3-methylimidazolium (BMIM) chloride] and [1,1,3,3-Tetramethylguanidine (TMG) chloride] are seen their effect on the water intake capacity ω_0 which are revealed from water solubilisation method, conductance measurement and DLS method. [TMG][AOT] is found to be most conductive but lowest solubilisation capacity than others on RM systems in decane. Dynamic Light Scattering expresses the effect on size and size distribution of water droplets of AOT based reverse micelle. The whole work extends the scope of development of better reverse micelle formulation.

Key-words: amphiphilic, microemulsion, ionic liquid, DLS, reverse micelle

INTRODUCTION

When we think about aerosols, crude oil processing, or even biological systems, a common theme emerges: all rely on tiny water compartments surrounded by water-repelling environments [1–3]. The remarkable aspect is that amphiphilic molecules—the fundamental building blocks of these complex, self-organizing systems—offer a straightforward yet powerful way to control structure simply through molecular-level modifications [2]. Reverse micelles are a prime example of such amphiphilic assemblies [3]. These structures play a crucial role in daily life, providing benefits across diverse applications. Also known as water-in-oil (W/O)

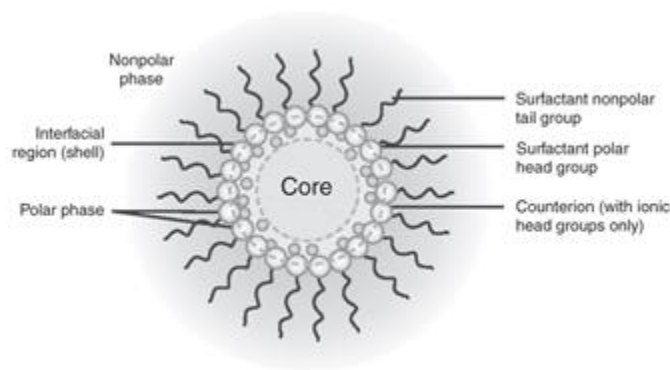


Scheme 1: Structure of a Reverse Micelle

microemulsions, reverse micelles are fascinating nanoscale aggregates of surfactant molecules formed in non-polar (organic) solvents. They are, in essence, the inverse of conventional micelles, which form in aqueous media. By compartmentalizing water-soluble species inside an organic phase and offering tunable size and internal environments, reverse micelles serve as versatile tools for scientific and industrial processes, particularly where controlled nanoscale reactions and separations are required [4]. Structurally, a reverse micelle consists of three main regions:

1. **A polar core**—formed by the inward-pointing hydrophilic head groups of surfactant molecules, which encapsulate water in a nanometer-sized space (unlike conventional micelles where hydrophobic tails face inward).
2. **A surfactant interfacial layer**—which shields the trapped water from the surrounding organic solvent.
3. **An organic continuous phase**—the bulk non-polar solvent.

The size of the inner aqueous core can be finely adjusted [2,8], primarily governed by the water-to-surfactant molar ratio ω_0 (i.e., $\omega_0 = [\text{water}]/[\text{surfactant}]$) [1,5]. Higher water content generally enlarges the aqueous pool, producing larger reverse micelles. Temperature, surfactant concentration, and solvent type also influence micellar size and stability.



Scheme 2: Reverse micelle core (filled with water)

Reverse micelles (scheme 2) form spontaneously when a surfactant dissolves in a non-polar solvent in the presence of a small amount of water [8,9]. Their amphiphilic nature drives this self-assembly, minimizing unfavorable interactions between polar water and non-polar solvents. Surfactant molecules orient so that their polar heads enclose water droplets, while hydrophobic tails remain in the organic medium. Some surfactants, such as sodium dioctyl sulfosuccinate (NaAOT) (Fig. 1), can form reverse micelles without co-surfactants [2]. Others, however, require a co-surfactant (e.g., alcohol) to enhance solubility or adjust interfacial curvature, thereby stabilizing the structure.

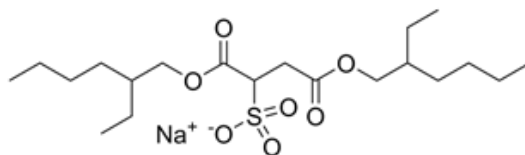


Fig 1: Sodium 1,4- bis-2-ethylhexylsulfosuccinate

Because reverse micelles cannot be understood without surfactants, it is important to note that surfactants—or "surface-active agents"—reduce surface tension at the interface between two immiscible phases (like oil and water) [7]. They achieve this due to their amphiphilic nature, possessing both hydrophilic and hydrophobic components [8]. In this study, we focus on three AOT-based surfactants: sodium 1,4-bis-2-ethylhexylsulfosuccinate (NaAOT), 1-butyl-3-methylimidazolium 1,4-bis-2-ethylhexylsulfosuccinate ([BMIM][AOT]), and 1,1,3,3-tetramethylguanidinium 1,4-bis-2-ethylhexylsulfosuccinate ([TMG][AOT]). These surfactants are employed to explore the formation and characterization of reverse micelles.

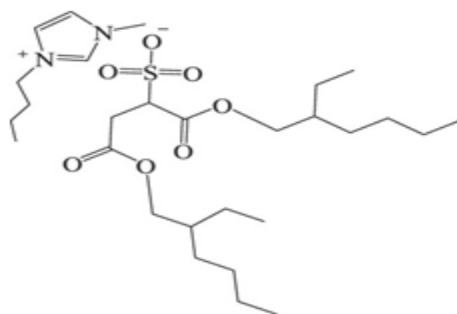


Fig 2: 1-butyl-3-methylimidazolium 1,4-bis-2-ethylhexylsulfosuccinate

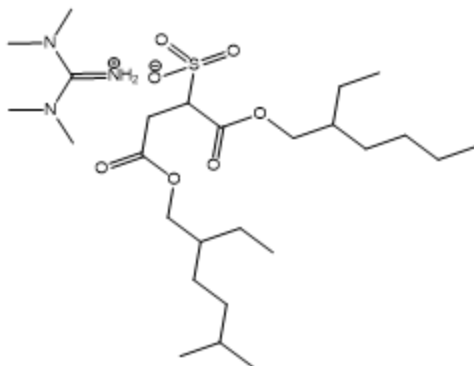


Fig 3: 1,1,3,3-tetramethylguanidinium 1,4- bis-2-ethylhexylsulfosuccinate

Over the past decades, significant advances have been made in applying reverse micelles to medicine, everyday products, and scientific research. One striking physical feature of W/O microemulsions is conductance percolation [6,15,16,20]. As temperature approaches a critical point, electrical conductivity can increase by two to three orders of magnitude. Similarly, Dynamic Light Scattering (DLS) has proven effective in determining microemulsion sizes and distributions down to sub-nanometer scales, provided sufficient scattering contrast exists [1,2,17]. Comparative studies reveal notable differences between sodium AOT and [BMIM][AOT] systems. Sodium AOT forms stable reverse micelles with strong hydrogen-bonding interactions at low hydration ($\omega_0 \leq 6$) [2,3], stabilizing the interface but restricting water mobility due to the tight binding of Na^+ ions. At higher hydration ($\omega_0 = 7$), these interactions weaken, reflecting structural transitions [10]. In contrast, [BMIM][AOT]—with its bulky, lower-



Scheme 3: Functioning of Reverse Micelles in drug delivery system

charge-density BMIM⁺ cation—creates more fluid interfaces. Water molecules exhibit dynamics closer to bulk water, enhancing interfacial reactivity and ionic conductivity. Thus, sodium AOT emphasizes stability, while [BMIM][AOT] favors flexibility and reactivity [11,12,18]. These distinctions underscore the importance of counterion selection for tailoring reverse micelles to specific needs, from nanoreactors demanding high reactivity to drug delivery systems requiring controlled release. Building on this, it was investigated the solubility and characterization of NaAOT, [BMIM][AOT], and [TMG][AOT]. Comparative studies included determining percolation thresholds, water-holding capacities (ω_0), and the effects of added salts on micellar behavior in two non-polar solvents: isopropyl myristate (IPM), a biocompatible oil, and decane (DEC). Conductivity measurements revealed percolation points, while Nuclear Magnetic Resonance (NMR) analysis provided structural insights into the newly synthesized [TMG][AOT], developed in collaboration with the Tata Institute of Fundamental Research (TIFR), Mumbai [1]. Additionally, Dynamic Light Scattering (DLS) was used to assess the influence of salts and ionic liquids on particle size. The interplay between hydrogen bonding, ion mobility, and interfacial fluidity in these systems exemplifies how molecular-level interactions dictate macroscopic functionality in nanoconfined environments [1-9,15, 20, 21].



Fig 4: Structure of solvents: (A) n-Decane ; (B) iso-propyl myristate (IPM)

In this context, I examined various characterization and solubility tests, along with a comparative study of three surfactants - NaAOT, [BMIM][AOT], and [TMG][AOT]. The investigation focused on their percolation points, water-holding capacities (ω_0) at room temperature, and the effects of adding salts at different concentrations to identify salting effects and the role of hydrogen bonding in the presence and absence of salts in two distinct non-polar organic solvents [5]. The solvents used were iso-propyl myristate (IPM), a biocompatible oil, and decane (DEC) (Fig. 4). For each surfactant system, specific conductance was measured with incremental water addition until the percolation points were reached [2, 21]. Additionally, Nuclear Magnetic Resonance (NMR) data for the synthesized [TMG][AOT] surfactant—provided by the Tata Institute of Fundamental Research (TIFR), Mumbai—were analyzed [1]. To further assess the influence of ionic salts and ionic liquids on particle size, Dynamic Light Scattering (DLS) measurements were carried out on samples with varying concentrations.

MATERIALS

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) (Sigma-Aldrich, >97% purity, CAS No. 577-11-7), 1-butyl-3-methylimidazolium chloride (Sigma-Aldrich, >98% purity, CAS No. 79917-90-1), 1,1,3,3-Tetramethylguanidine chloride (Sigma-Aldrich, >99% purity, CAS No. 80-70-6), Sodium Chloride (Sigma-Aldrich, CAS No. 7647-14-5), n-Decane (Sigma-Aldrich, CAS No. 124-18-5) were purchased from Sigma-Aldrich, USA. Iso-Propyl Myristate (Loba Chemie, Extra Pure, >95% purity, CAS No. 110-27-0) was purchased from Loba Chemie, Mumbai, India.

METHODOLOGY

Nuclear Magnetic Resonance:

Nuclear Magnetic Resonance (NMR) spectroscopy exploits the magnetic properties of atomic nuclei to reveal molecular structure. The core of an NMR instrument is a powerful superconducting magnet, generating a very strong and uniform magnetic field. This field aligns the tiny magnetic moments of specific nuclei (like hydrogen or carbon-13) in the sample. The surfactants [BMIM][AOT] and [TMG][AOT] were synthesized at TIFR, Mumbai following a previously described procedure [1]. Characterizations of the obtained SAILs have been done by ^1H NMR and ^{13}C NMR spectroscopy (Bruker AM500 spectrometer), and the measured data are shown in Figure 5 and 6.

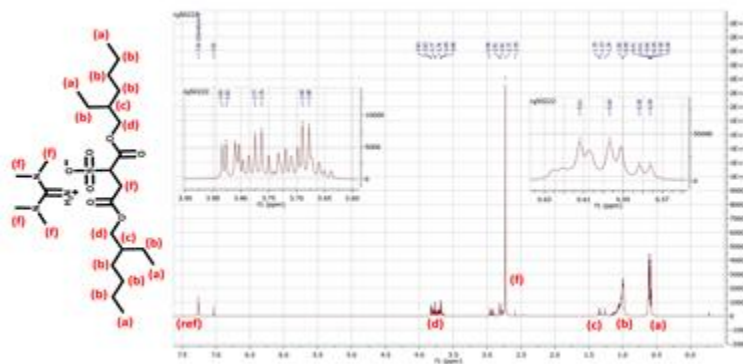


Fig 5: ^1H NMR spectra of [TMG][AOT]

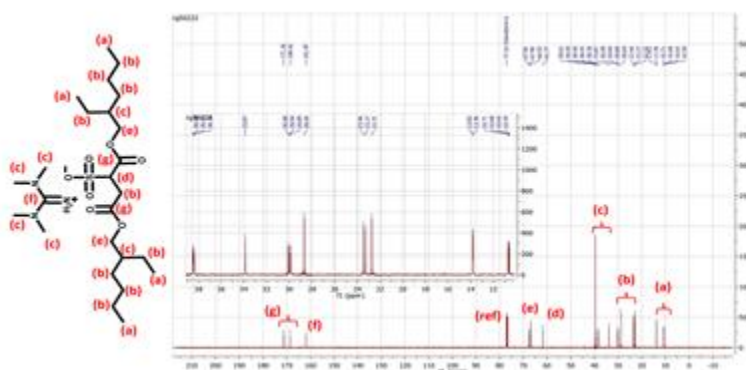


Fig 6: ^{13}C NMR spectra of [TMG][AOT]

Water Solubilization:

A fixed concentration of surfactant(s) (0.1 mol dm^{-3}) was prepared in 2 mL of organic solvent (oil) was continuously stirred at room temperature, using a vortex shaker. Water—or aqueous NaCl solutions of varying concentrations—was then incrementally added using a micropipette (Thermo Scientific, India). The maximum solubilization of water, or NaCl at each surfactant blend composition was determined by the onset of permanent turbidity, marking the titration's endpoint. The maximum water uptake capacity of the reverse micelles, expressed as the molar ratio of water to surfactant (ω_0) [1,2], was then measured by gradually adding double distilled water (or aqueous NaCl solution) with constant stirring.

$$\omega_0 = \frac{\text{number of moles of water}}{\text{number of moles of surfactant}}$$

The ω_0 values are studied by adding water and NaCl solutions of varying concentrations to water/AOT/hydrocarbon systems taking different solvents. Also, it has been prepared 0.01 mol dm^{-3} , 0.05 mol dm^{-3} and 0.1 mol dm^{-3} NaCl solutions. Each experiment was replicated 2-3 times to obtain mean results.

Electrical Conductivity Measurement:

Electrical conductivity measurements were conducted using a calibrated conductivity meter (Deluxe Conductivity Meter; Model number 610; Electronics India) equipped with a cell having a constant of 1.0 cm^{-1} . The experimental temperature was maintained at 298 K through a thermostated water bath. Double-distilled water (or NaCl salt solutions of various concentrations) was incrementally added into 6 mL of surfactant solution in a non-polar solvent (used throughout the experiment) using a micropipette (Thermoscientific, India). After each aliquot addition, the mixture was thoroughly mixed before measuring the stabilized specific conductance (κ). Three independent measurements were performed for each concentration, with averaged specific conductance values showing a maximum deviation of 2%.

Dynamic Light Scattering (DLS):

The hydrodynamic diameter (D_h) of the reverse micelle (RM) droplets was measured using a Zetasizer Nano ZS-90 (Malvern, UK) equipped with the dynamic light scattering (DLS) technique. Prior to measurement, the RM solutions were equilibrated for 2–3 hours and subsequently filtered through a $0.22 \mu\text{m}$ Millipore membrane. The samples were then transferred to a 1 cm path length quartz cuvette and irradiated with a He–Ne laser at a wavelength of 632.8 nm and a scattering angle of 90° . The diffusion coefficient (D), obtained from the intensity correlation function, was analyzed using the Stokes–Einstein equation to calculate D_h [17]. The Stokes–Einstein equation, which is the working formula of Dynamic Light Scattering can be written as follows

$$D_h = \frac{kT}{3\pi\eta D}$$

Where, k = Boltzmann Constant, η = coefficient of viscosity, D = Diffusion Coefficient, T = absolute temperature

RESULTS AND DISCUSSION

Water Solubilization

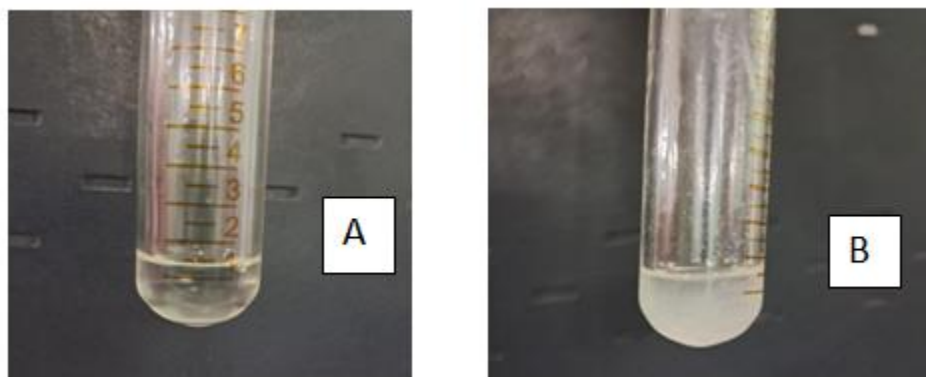


Fig 7: [TMG][AOT] Reverse Micelles in IPM medium with water in core, (A) before ω_0 is reached, and (B) beyond ω_0

It was measured the maximum water solubilization capacity (ω_0) of water/AOT/hydrocarbon reverse micelles a function of water-to-surfactant molar ratio in presence of NaCl of varying concentrations. The differential effects of the ions on droplet size and water solubilisation capacity require some molecular- level explanation. It has been observed, for a single solvent, like taking example of Decane (which is a very non-polar solvent), with addition of 0.01M NaCl, water holding capacity (ω_0) increases by quite a margin when compared to addition of double distilled water only. However, when the concentration of NaCl solution is increased further, I see significant drop in water holding capacity (ω_0). The more concentrated the NaCl solution becomes, ω_0 drops even more in decane. Similar trend is also observed when the solvent is changed to a more polar solvent iso-propyl myristate (IPM), a bio-compatible solvent. IPM (Isopropyl Myristate) is a type of oil that is not as oily as n-decane. This is because IPM has special connections in its structure called ester linkages, that make it a bit more like water [18]. Addition of a small amount of salt (like 0.01M NaCl) can screen the electrostatic repulsion between the negatively charged AOT head groups. This allows the surfactant molecules to pack more efficiently at the interface, leading to a more stable interface that can encapsulate *more* water. The reduction in interfacial tension and increased packing density initially enhances the water solubilization [2]. When there's a lot of salt, things get a bit crowded. The salt makes the water inside the tiny water drops (micelles) want to leave [1,3,5].

Table 1: Water solubilization capacities (ω_0) of NaAOT, [BMIM][AOT] and [TMG][AOT] surfactants in decane solvent

	Pure water	0.01M NaCl	0.05M NaCl	0.1M NaCl
NaAOT	58.34	74.99	80.55	36.11
[BMIM][AOT]	49.99	66.67	36.11	24.99
[TMG][AOT]	19.44	33.33	13.89	8.32

This is because the water molecules become more attracted to the salt particles around them. So, the water molecules get busy clinging to the salt instead of staying inside the micelle. Because of this, the amount of water inside the micelles gets smaller, and eventually, the micelles can't hold water anymore [8]. Also, all that salt outside the micelle creates pressure that helps push the water out too. At high concentration, the water in the micelle's core starts to move out. This causes the water pool to get smaller. Eventually, the micelles can't hold water anymore and become unstable. The extra push from the salt (called osmotic pressure) also helps to force water out of the micelle [1-5,11,13, 22]. For almost all conditions and surfactant types, the water holding capacity in decane is significantly higher than in IPM. This can be explained by the difference in polarity and solvent penetration in Reverse Micellar systems. n-Decane is a very nonpolar, aliphatic hydrocarbon. This leads to a relatively high interfacial tension between the water core and the decane solvent. A higher interfacial tension means there's a stronger driving force for the AOT molecules to form a tight, well-defined interface around the water pool to minimize the water-oil contact [9]. This strong interface makes the micelles less prone to structural fluctuations and fusion. IPM, on the other hand, is an ester, and while still considered a nonpolar solvent, it is significantly more polar than n-decane due to the presence of ester linkages. This increased polarity allows for a greater degree of interaction between the IPM molecules and the polar head groups of the AOT surfactant at the interface, and potentially with the water molecules themselves. Decane, being much less polar than IPM, leads to a higher interfacial tension between the water pool and the decane solvent. A higher interfacial tension drives the [AOT]⁻ surfactant to form a tighter, more stable interface around the water, maximizing the water solubilization capacity by minimizing unfavourable water-oil contact. IPM, being more polar (due to its ester groups), interacts more strongly with the polar head groups of [AOT]⁻, potentially "softening" or "disordering" the interface [5]. This reduced interfacial tension might lead to less effective water encapsulation.

Table 2: Water solubilization capacities (ω_0) of NaAOT, [BMIM][AOT] and [TMG][AOT] surfactants in IPM solvent

	Pure Water	0.01M NaCl	0.05M NaCl	0.1M NaCl
NaAOT	22.23	30.55	27.78	24.99
[BMIM][AOT]	16.67	27.78	19.44	13.88
[TMG][AOT]	16.67	22.23	8.33	5.56

The reduction in interfacial tension renders micelles less rigid and more flexible, which can result in larger and more stable aggregates. However, paradoxically, this flexibility leads to less efficient percolation. The reason is that the more “spread out” or “fluid” interface reduces the likelihood of transient connections forming between water pools—connections that are crucial for percolation, often detected as an increase in conductivity [9,17]. When examining different solvents, an interesting trend emerges: although the overall pattern remains consistent across all solvents, the specific behavior varies significantly for each surfactant. Experimental results clearly show that [BMIM][AOT] exhibits the lowest water-holding capacity in both solvents. In contrast, NaAOT demonstrates the highest capacity, while [TMG][AOT] falls between the two when ω_0 is considered. This difference can be explained by the nature of the counter ions. Sodium (Na^+) is a small, monovalent cation, allowing AOT head groups to pack tightly and efficiently at the water/oil interface. The minimal steric hindrance between Na^+ , the AOT head groups, and water molecules in the micellar core promotes a compact, stable interface capable of solubilizing a substantial amount of water, thereby yielding a high ω_0 . In the case of [BMIM][AOT], the counter ion (BMIM^+) is significantly larger and structurally more complex than Na^+ . Being a bulky organic cation, BMIM^+ introduces considerable steric hindrance at the interface, which prevents the AOT head groups from packing as efficiently.

This looser arrangement leads to a less stable interface and reduces the efficiency of water encapsulation [5]. Consequently, the water holding capacity (ω_0) for [BMIM][AOT] is generally lower than that of NaAOT under similar conditions. When talking about [TMG][AOT], it is important to note down the huge size of the cation and steric hindrances, and the charge delocalisation tendencies of the molecule. The $[\text{TMG}]^+$ cation is considerably larger and bulkier than both the small, spherical Na^+ ion and even the less spherical, but still relatively compact, BMIM^+ ion. Efficient packing of surfactant molecules is fundamental for forming stable and large reverse micelles. If the packing is severely disrupted, the interfacial layer becomes less stable, less curved, and thus less capable of enclosing a significant volume of water [18]. This directly leads to very low water solubilization capacities (ω_0). Additionally, inefficient charge screening also contributes to the lower ω_0 values. The optimal formation of reverse micelles (water-in-oil) relies on the surfactant having a preferred negative curvature [5]. This is influenced by the packing parameter, which depends on the head group area, tail volume, and effective length.

Electrical Conductivity Analysis

Conductance of AOT based RM systems are primarily pertained due to the transfer of Na^+ ions from one droplet to another droplet during inter droplet collision [2]. It is already evident from the above discussions that water holding capacity of every surfactant is much more in decane than IPM. However, the results from the electrical conductivity analysis gives us evidence regarding mobility of the system. Here the conductance of NaAOT, [BMIM][AOT] and [TMG][AOT] containing RMs are studied as function of water domain (ω_0).

Effect of SAIL and surfactant For individual surfactants, I observe a significant difference in each of these surfactants in terms of electrical conductivity. With increase in ω_0 , the curves show an interesting change in each surfactant. NaAOT shows a sharp increase in conductivity up to the point of percolation, beyond which, water molecule clustering takes place. As a result, a slight drop in conductivity with increase in ω_0 is observed. The curve shows a slight drop in conductivity towards the percolation point by the end [6]. Conductance in the RM systems originate due to the migration of charged droplets under an external electric field. Here the conductivities (κ) of $[\text{Na}][\text{AOT}]^-$ and $[\text{BMIM}][\text{AOT}]^-$ based RMs are also studied as a function of water content (ω_0) at room temperature. At low water content, the water molecules are dispersed as nanometer-sized domains in the IPM continuous phase and are involved in hydrating the Na^+ cations and $[\text{AOT}]^-$ anions. Such a type of noninteracting spherical droplets in $[\text{Na}][\text{AOT}]^-$ based RM system was also evident from the DLS. In case of $[\text{BMIM}][\text{AOT}]^-$, we observe a very different trend. Percolation point is non-existent, as a result, conductivity increases very sharply, but after a point of saturation, it drops hard, almost to a minimum.

A suppressed or shifted percolation due to the bulkier BMIM^+ ion's steric hindrance and lower mobility [2,5,6], the conductivity curve of the water/ [BMIM][AOT]/IPM system can be divided in three distinct regions: (i) At a low water content, the gradual increase in conductivity with water content is due to the motion of non-interacting charged droplets, similar to the parent $[\text{Na}][\text{AOT}]^-$ system. (ii) As the water content increases, the counterions ($[\text{BMIM}]^+$) exchange and redistribute readily during the process of droplet collision and transient fusion. (iii) A further increase in water content results in a gradual decrease in conductivity, which indicates restricted ion migration at higher water content. Notably, DLS results suggest the structural transition and the formation of cylindrical droplets at a higher ω_0 . As the $[\text{BMIM}]^+$ cations get entrapped in the narrow core of such a cylindrical structure, the exchange of $[\text{BMIM}]^+$ cations become hindered. Hence, the conductivity of the water/[BMIM]-[AOT]/IPM system decreases with increased ω_0 [5].

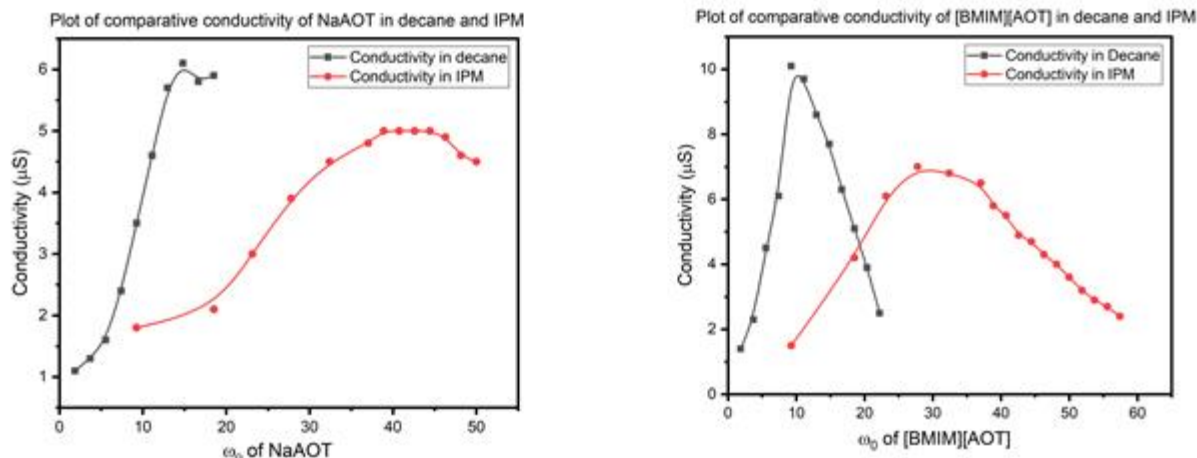


Fig 8: Comparative Electrical conductivity of (A) NaAOT and (B) [BMIM][AOT] in both Decane and IPM mediums

[TMG][AOT] on the other hand has the highest conductivity of them all. It has a persistent increase in electrical conductivity at a range of very low ω_0 , showing a consistent percolation trend. ([TMG][AOT]) shows the highest percolation conductivity compared to NaAOT and [BMIM][AOT], despite having the lowest water solubilization capacity (ω_0) and a bulky counterion, it points to a very specific and likely non-conventional mechanism of charge transport [10]. The graph shows no drop by the end point and conductivity shows a simple increasing curve. This can be explained by delocalised charge and proton transfer, low critical percolation point, and flexibility of counter-ion. The guanidinium group is known for its highly delocalized positive charge and its ability to participate in proton transfer mechanisms. While

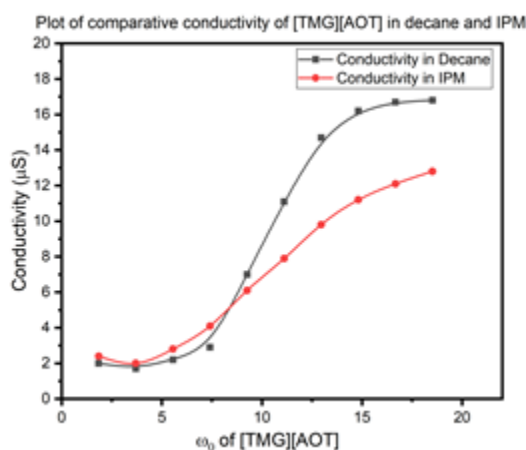


Fig 9: Comparative Electrical conductivity of [TMG][AOT] in both Decane and IPM mediums

[AOT]⁻ is anionic, and the [TMG]⁺ is the counter ion, the unique electronic structure of the guanidinium group at the interface could facilitate a very efficient charge transfer process. The counter ion, despite its huge size, has a very high mobility within the interface. The bulky counterion can make the interface more fluid or dynamically unstable, leading to very frequent fusion/fission events. If these events are rapid and numerous, and the charge transfer during each event is efficient, it could lead to high overall conductivity, even with smaller water pools. It could induce a specific interfacial structure that promotes charge transfer across the interface directly, rather than through the bulk water [1,2,5]. This explains the high conductivity of [TMG][AOT] surfactant in both decane and IPM mediums, despite having a very low ω_0 values. The high percolation in [TMG][AOT], despite low ω_0 , strongly suggests that the unique chemical and electronic properties of the 1,1,3,3-tetramethylguanidinium counterion enable a highly efficient, possibly interfacial, charge transport mechanism that bypasses the need for large, continuous water channels, which are typical for other AOT reverse micelle systems.

In decane, the conditions (lower polarity, higher interfacial tension, lower viscosity) are more conducive to strong micelle-micelle attractions and efficient, short-lived fusion events that facilitate rapid ion exchange and the formation of

conducting clusters, leading to a distinct percolation threshold. In decane, a highly nonpolar solvent, stronger attractive interactions occur between AOT reverse micelles. Such interactions drive the micelles to collide and fuse more readily, thereby creating transient conductive pathways. Furthermore, the high interfacial tension between water and decane forces AOT molecules to pack tightly, resulting in a relatively rigid and well-defined interface [6,10,13]. In contrast, iso-propyl myristate (IPM) behaves differently.

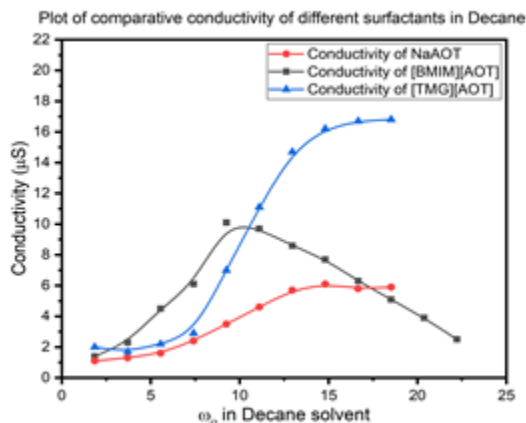


Fig 10: Electrical conductivity of NaAOT, [BMIM][AOT] and [TMG][AOT] based RMs in Decane

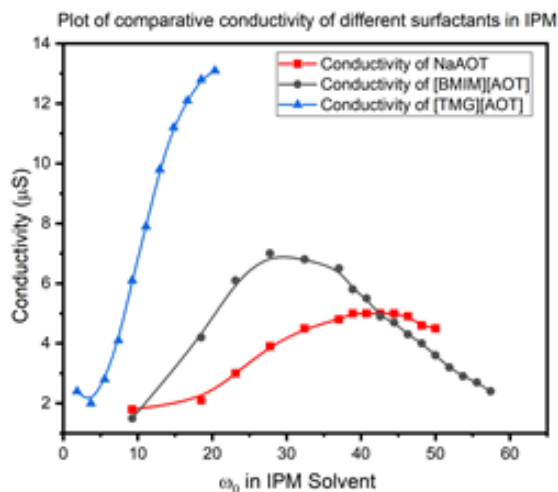


Fig 11: Electrical conductivity of NaAOT, [BMIM][AOT] and [TMG][AOT] based RMs in IPM.

Its higher polarity and viscosity, combined with its stronger potential to interact with the AOT interface, disrupt the optimal conditions needed for efficient micellar collision and connectivity. Although individual micelles may still form and encapsulate water, their capacity to exchange ions and establish continuous charge-transport pathways is significantly reduced. Consequently, conductivity decreases and the percolation phenomenon is either suppressed or entirely absent [3,5,6].

Dynamic Light Scattering (DLS) data analysis:

Dynamic Light Scattering (DLS) gives us an idea about determine the size distribution profile of small particles suspended or dissolved in a liquid [1]. In this case, we have prepared reverse micellar systems in both IPM and Decane solvent systems using surfactants NaAOT, [BMIM][AOT] and [TMG][AOT]; and evidently observed some fascinating results. We will divide our observations in two sections, accordingly as in effects of solvents, and effects of SAIL and surfactants, and later on will also discuss our findings in molecular distribution. Using $5 \omega_0$ NaAOT as a standard surfactant, it has observed the particle sizes (D_h) using DLS method and found a very interesting observation. The size of particles is almost similar in both cases, with IPM showing slightly larger particle sizes in major concentrations. In decane, the particle size turns out to be around $D_h = 4.25\text{nm}$, whereas in case of IPM, it's around $D_h = 4.35\text{ nm}$.

Effects of SAIL and Surfactants

This technique works on the principle of swelling law, which provides us with the valuable information regarding evidence of an entrapped polar domain in a continuous apolar phase [17]. According to the swelling law, encapsulated polar phase in a RM system should result in linear increase of droplet size with increasing concentration of polar phase. It is evident that in presence of SAIL, discrete spherical nanodroplets do exist. Any deviation from the linearity would result in droplet aggregation at higher ω_0 and structural transition, which seems to be the case of [BMIM][AOT] based RM system at $\omega_0 > 10$.

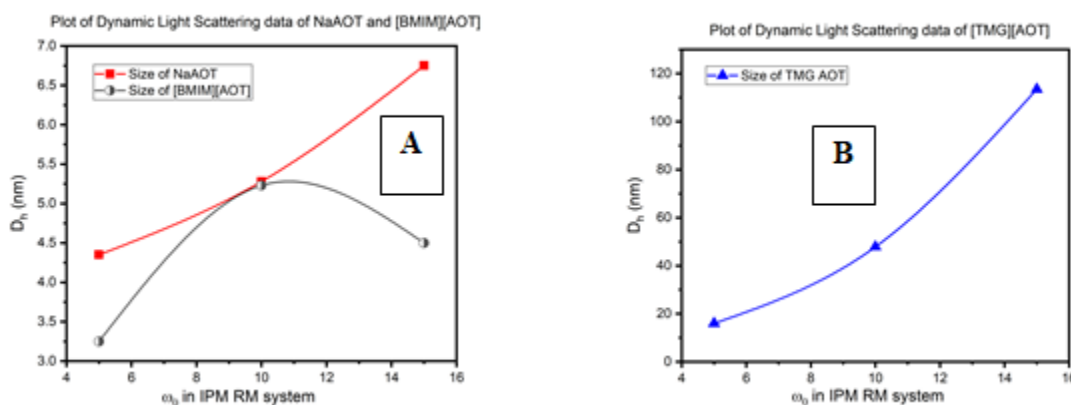


Fig 12: Dynamic light scattering measurement data of the water/NaAOT/IPM and water/[BMIM][AOT]/IPM RM systems (A), and water/[TMG][AOT]/IPM RM system (B) at different water-to-surfactant mole ratios.

Table 3: Dynamic light scattering measurement data of water/AOT/IPM microemulsions at different water-to-surfactant molar ratios for NaAOT, [BMIM][AOT] and [TMG][AOT]

	5 ω_0	10 ω_0	15 ω_0
NaAOT	4.35	5.28	6.75
[BMIM][AOT]	3.25	5.23	4.5
[TMG][AOT]	15.95	47.85	113.44

From the table, we can observe some fascinating trends. Both NaAOT and [TMG][AOT] based RM systems show a linear curvature with increased concentration of neat water content, whereas in case of [BMIM][AOT], when the system is at $\omega_0 > 10$, we see a sudden drop of size of particles, as shown in Figure 6 (a). The more distinctive observation is the size of particles in [TMG][AOT] based RM system. The system displays an absurd increase in size of particles, which increases with increase in water solubilisation, as displayed in Figure 6 (b). The strange behaviour for [BMIM][AOT]/IPM RM system in terms size with change in water solubilization capacity can be explained by the influence of counterions on the shape of RMs, which has been extensively studied [12], and the result might be due to shape transition of the water/[BMIM][AOT]IPM RM droplets from ellipsoidal to spherical from their DLS measurements, which showed a decreasing hydrodynamic diameter at lower ω_0 . In this RM system, we observed a reverse trend of linearly increasing diameter at low water content until $\omega_0 \sim 10$ and then a declining trend from $\omega_0 > 10$. This bell-shaped nature of D_h as a function of ω_0 indicates the possibility of shape change of the RM droplets from spherical to cylindrical/elliptical in the water/[BMIM][AOT]/IPM system. This indicates that the smaller droplets in [BMIM][AOT] are a consequence of a less-structured W/O interface due to weaker interactions between the surfactant headgroups and the bulky [BMIM]⁺ cations [1]. In case of water/[TMG][AOT]/IPM system, the size of the particles is immensely high when compared to NaAOT or [BMIM][AOT] systems, for example at $\omega_0 = 10$, D_h of NaAOT and [BMIM][AOT] systems are around 5.28 nm and 5.23 nm respectively, but the same of [TMG][AOT] system is 47.85 nm, which is almost 9 times that of previous two RM systems.

CONCLUSION

This study was carried out with combined experimental techniques, including water solubilization, electrical conductance and DLS, to investigate AOT/IPM and SAIL/IPM reverse micelles. It was demonstrated that the presence of [BMIM]⁺ and [TMG]⁺ counter ions significantly improved the water uptake capacity and stability of these biocompatible reverse micelles. Specifically, the nanodroplets formed with [TMG][AOT] were remarkably larger than any previously reformulated water-in-oil reverse micelle systems supplemented with ionic liquid counterions or additives. We found that the [TMG][AOT] system outperformed both NaAOT and [BMIM][AOT] based reverse micelle systems. This superior

performance is attributed to an extended hydrogen-bonding network, triggered by the proton-donating ability of the [TMG]⁺ counterions to the water core. It has been successfully produced significantly large and stable biocompatible water-in-oil reverse micelles using SAILs. The comprehensive study unequivocally is demonstrated the superiority of [TMG][AOT] in reverse micelle formulation compared to both [BMIM][AOT] and NaAOT; and I have also done in-depth measurements using conductivity and DLS providing a crucial insight into the mechanism behind this improved formulation. The findings suggest that SAIL-based reverse micelles, with their tuneable droplet size, hold significant promise as templates for various reverse micelle-based applications. Given the expanding landscape of ionic liquids, further rigorous research into this novel class of molecules is warranted to develop even better reverse micelle formulations.

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