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J. Phys. Chem. B, Just Accepted Manuscript • DOI: 10.1021/acs.jpcb.7b07945 • Publication Date (Web): 27 Sep 2017

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The Journal of Physical Chemistry B is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Understanding Differential Interaction of Protic and Aprotic Ionic Liquids inside Molecular Confinement

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ABSTARCT

Considering the contemporary interests of water-free reverse micelles (RMs) in the field of organic reaction medium and potential drug delivery carrier, we synthesized two different classes of ionic liquids (ILs), protic N-methyl-2-pyrrolidonium hexanoate, [NMP][Hex] and aprotic choline hexanoate, [Chl][Hex] and subsequently incorporated in mixture of polyoxyethylene(20)sorbitan monooleate (Tween-80) and cyclohexane. In order to understand the differential nature of inter-interionic interaction of two ILs, we performed DFT calculations on pure ILs to correlate with experimental results. The formation of IL-inoil RMs was confirmed from phase behaviour and DLS studies. Interestingly, [NMP][Hex]based systems showed larger monophasic region and droplet size along with higher shear viscosity compared to [Ch1][Hex]-based systems. Stronger interaction between [NMP]⁺ and Tween-80 due to their protic nature might be the driving force for such observations which supported from the resonance stabilisation energy $[E^{(2)}]$ and charge population analysis by NBO calculation. Smaller $E^{(2)}$ values along with lesser NBO charges on atoms involved in Hbonding in pure [NMP][Hex] than [Chl][Hex] corroborated with the experimental observations. This primary hypothesis was further confirmed from FTIR and time-resolved fluorescence studies. These systems showed efficient thermal stability. Taken together the results, we anticipate that these RMs could use as efficient delivery systems and nanomaterial synthesis.

1. INTRODUCTION

Microemulsions or reverse micelles are formed when amphiphilic molecules self-aggregates in a nonpolar solvent leading to a transparent and thermodynamically stable system, often in combination with co-surfactant. Due to their unique properties such as low viscosity, very low interfacial tension, high solubilisation capacity *etc.*, microemulsions have been widely applied in different fields such as in pharmaceutical, cosmetic and agrochemical formulations and nanoreactors for nanomaterials synthesis.¹⁻³ Most of the studies on conventional microemulsions have used water as the polar component. However, in recent years, attempts were made to prepare and study waterless/non-aqueous reverse micelles (RMs), where other polar solvents like methanol, acetonitrile, glycerol, dimethylformamide (DMF), formamide, ethylene glycol etc. were exploited. The first study of non-aqueous RMs with ethylene glycol, lecithin and decane were reported by Friberg and Podzimek in 1984.⁴ Later, Laia et al., and Falcone *et al.* studied the properties of non-aqueous RMs using different polar solvents.^{5,6} These non-aqueous RMs have distinct advantages over aqueous ones such as: larger stable regions; large variety of surfactant usability and applicability as good reaction media, specifically for the reactants which react with water.⁷ These earlier studies soon attracted researchers attention towards the formulation of room temperature ionic liquids (RTILs) based non-aqueous RMs. Non-aqueous ionic liquid (IL) RMs provide hydrophobic or hydrophilic nano-domains and thus their applications can be extended to fields of reaction and separation or extraction media. For example, synthesis of polymer gels, nanoparticles, and open-cell porous materials have been reported surfactant IL-based RMs in some earlier studies.⁸ ILs are considered suitable solvents for various chemical processes due to their unique properties like negligible vapour pressure and tunability in structure by modifying cation and anion moieties. In addition, ILs exhibit excellent chemical and thermal stability, wide polarity and are recyclable.⁹⁻¹¹ They broadly divided in to protic (PILs) and aprotic (AILs) classes. Our group also involved in synthesis of different types of PILs and APILs.¹²⁻ ¹⁴ Despite of having many useful properties(arising from protic nature) and potential

applicability, literature on PILs are still scarce compared to their AIL counterparts.^{15,16} PILs are formed by the transfer of proton from acid to base and hence they consist of proton-donor and - acceptor sites which are responsible for building extended three dimensional hydrogen bond networks as in the case of water.¹⁷ In recent years, considerable progress in the structure-property relationships of ILs has been achieved with better understanding of the intermolecular forces. The elucidation of the difference between the interactions of PILs and those of AILs is important for understanding the unique properties of PILs. A number of

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reports were published on the differential behaviour on the interionic and ion-solvent interactions of protic and aprotic ILs with water both by theoretically and experimentally.¹⁸⁻²⁰ In the last few years, the use of both type of ILs has attracted a great deal of attention as suitable solvents for amphiphile self-assembly from the scientific community around the globe.

The effect of ILs on the aggregation properties, critical micellar concentration (cmc) and hydration behaviour of different kind of surfactants have been reported in several studies and found to be important for fine tuning the surfactant properties for specific applications.²¹⁻²³ Yue et al. had employed aprotic 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim]BF_4$) and protic ethylammonium nitrate (EAN) to investigate the aggregation behaviour of phytosterolethoxylate surfactant (BPS-10), which showed higher effectiveness of EAN over [Bmim]BF₄ in promoting non-ionic BPS-10 aggregation.²⁴ Later, the aggregation behaviour of the alkyl triphenylphosphonium bromides, CnTPB, in aprotic and protic ILs was also investigated, where a stronger solvophobic effect between C_nTPB and protic EAN evidenced than aprotic [Bmim][BF₄].²⁵ It can be inferred from these reports that higher protonation ability of EAN is the extra driving force for surfactant molecules to form ordered aggregates. However, this has to be further verified for different self-assembling systems. From this point of view, it is important to understand the nature of differential behaviour of PILs and APILs inside IL-in-oil RMs. A significant number of studies are already performed on the formation of AILs based RMs²⁶⁻²⁷, whereas PIL based RMs are scarcely reported. The use of PILs in RMs predominantly involved EAN and propylammonium nitrate (PAN) till now.²⁸⁻³¹ Very recently, Kusano et al. formulated water-in-IL RMs in an organic solvent-free system by employing a mixture of imidazolium-based AIL and PILs.³² However, still there is a scope to compare their differential nature of interactions inside the nanoscopic confinement of RMs through a systematic investigation, since this is an emerging field of research, where many issues are still unclear and highly debated.

In view of this limited research on PIL-in-oil non-aqueous RMs compared to the conventional water and AIL-in-oil RMs, herein we investigated the formation and characterization of a series of PIL and APIL-in-oil RMs with following specific objectives. It is noteworthy to mention here that the two ILs, which we have used, bear the same anionic part, whereas the cationic part differs in presence of exchangeable protons (e.g., *N*-methyl-2-pyrrolidonium hexanoate, [NMP][Hex] and choline hexanoate, [Chl][Hex]). On the basis of this motivation, the [NMP][Hex] and [Chl][Hex] are employed as a replacement for water as

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the polar phase to explore their effects on aggregation behaviours of polyoxyethylene (20) sorbitan monooleate (Tween-80) in cyclohexane (Cy). As in most liquids, H-bonding leads to a preferred orientation among the nearest-neighbour species which in turn dictates important aspects of liquid behaviour such as solvation, dynamics and macroscopic physical properties.³³ We would like to demonstrate here that how the H-bond direction and strength of two different family of ILs can be related to macroscopic physicochemical properties of Tween-80-based RMs, which are generally regarded as non-toxic and non-irritant systems.³⁴ Considering the fact that research activities involving ILs in RMs have significant ambiguities regarding the mode of interaction between ILs and surfactant, it is essential to study this aspect by employing varieties of ILs. The majority of the studies in non-aqueous IL based RMs utilized Triton X-100 (TX-100) as the surfactant component.^{35–36} In this report, the microstructural, microenvironmental, and rheological properties along with the temperature dependent droplet sizes and viscosities of [NMP][Hex] and [Chl][Hex]-based RMs are examined and analyzed in light of our current understanding on hydrogen bonding and bulk liquid nanostructures in these liquids, which may give different perspective about the origins of macroscopic behaviour.

2. EXPERIMENTAL SECTION

2.1. *Materials:* Polyoxyethylene (20) sorbitan monooleate, Tween-80 (CAS No. 9005-65-6, *Sigma-Aldrich*), 8-Anilino-1-naphthalenesulfonic acid, ANS (\geq 97%, CAS No. 82-76-8, *Sigma-Aldrich*) and cyclohexane (Cy) were purchased from Sigma-Aldrich (anhydrous grade, 99.5 %, CAS No. 110-82-7) and used without further purification.

2.2. Synthesis and characterization of the ionic liquids (ILs): Analytical grade chemicals were used for all synthesis. N-methylpyrrolidinone (\geq 99%, CAS No. 872-50-4, Sigma-Aldrich), choline hydroxide solution (46 wt. % in H₂O, CAS No. 123-41-1, Aldrich), formic acid (\geq 95%, CAS No. 64-18-6, Sigma-Aldrich) and hexanoic acid (\geq 99%, CAS No. 142-62-1, Sigma-Aldrich) were used without further purification. The ILs was synthesized by adding equimolar amount of acid to neutralize the respective bases. For example, 11.616 g hexanoic acid (0.1 mol) was added drop wise from a pressure equalizing dropping funnel to 9.9 g of N-methyl-2-pyrrolidone (NMP) (0.1 mol) kept in a 250 mL single necked round bottomed flask in an ice bath with vigorous stirring. After complete addition, the ice bath was removed and stirring was continued for 12 h in room temperature (~27 °C). The obtained ILs were washed

several times with diethylether to remove any excess reactants. Then synthesised ILs were dried for 6 h under vacuum using a rotary evaporator. To minimise the water content the ILs were dried further in vacuum at 70 °C for 24 h. On the other hand, hexanoic acid (0.1 mol) was added drop wise into an aqueous solution of choline hydroxide (0.1 mol) with continuous stirring for 12 h at room temperature (~27 °C). Similar drying procedure as described above was followed. The synthesized ILs were characterized by ¹H NMR and ¹³C NMR spectroscopy recorded on a Bruker AM 500 spectrometer and shown in Supplementary Information (Figs. S1). ¹H-NMR (500 MHz, CDCl₃) for [NMP][For] δ (ppm): 2.32 (m, 4H) 2.93 (s, 3H) 3.34 (t, 2H) 6-8 (broad NH⁺ and HCOO⁻); for [NMP][Hex] δ (ppm): 0.89 (t, 3H) 1.31 (m, 4H) 1.63 (q, 2H) 2.01 (m, 2H) 2.35 (m, 4H) 2.83 (s, 3H) 3.38(t, 2H) (no broad peak for NH⁺); and ¹H-NMR (500 MHz, DMSO-d₆) of [Chl][Hex] δ (ppm): 0.74 (t, 3H) 1.15 (m, 4H) 1.41 (m, 2H) 1.92 (q, 2H) 3.2 (s, 9H) 3.52 (t, 2H) 3.91(s, 2H).

2.3. Experimental methods: The phase diagram of the ternary ILs/Tween-80/Cy mixture was determined by observing the physical states of the equilibrated mixture of synthesized ILs, Tween-80 and Cy. During the experiment, the IL was first mixed with the surfactant-oil solution at a series of weight ratios of Tween-80 and Cy, and then the mixtures were kept at 303 K for several minutes. After each addition of IL, the resulting mixture was thoroughly mixed with a vortex shaker through visual observation and equilibrated. The phase boundaries were taken when the mixture turned turbid from transparent condition and compositions of different components (wt %) of systems were evaluated. Anton Paar Lovis 2000ME instrument were used for viscosity measurements. The instrument measures the time taken by a rolling ball moving through a capillary filled with the sample to measure the viscosity. A built-in peltier device was used to maintain the temperature within accuracy of 0.02K. The sample to be measured (approx. 0.5ml) was filled in the capillary tube in bubble free condition. The calibration of the instrument were verified by measuring double distilled water (resistivity $18m\Omega \cdot m$) and atmospheric air and comparing their values with reported ones. A DLS instrument (Malvern Zetasizer nano-series) was employed to measure the hydrodynamic diameter of RM nanodroplets. This instrument is equipped with a thermostatted sample chamber and uses a 4 mW He-Ne laser ($\lambda = 632.8$ nm) for irradiation and collecting the scattered photons at 90° scattering angle. The software provided with the instrument were used to process the scattering intensity data to obtain the hydrodynamic diameter (d_h) and the size distribution of the scatterer. The d_h of the nano-droplet is estimated from the Stokes-Einstein equation, which is defined as;

$$d_{h} = \frac{k_{B}T}{3\pi\eta D}$$
(1)

Where, k_B is the Boltzmann constant, η is the viscosity (as obtained from viscometer), D is the translational diffusion coefficient, and T is the temperature. DLS experiments were performed three times for each samples with at least 15 runs per measurement. Prior to measurement, to remove possible dust particles, the RM solutions were filtered through a 0.22 µm pore size membrane (MILLEX(R)-GP. Fourier transform infrared (FTIR) spectra were recorded in a JASCO FT/IR-4100 spectrometer (transmission mode) in the 400-4000 cm^{-1} window using CaF₂ window with 100 number scans and 4 cm⁻¹ spectral resolution. For the experiments performed on the different IR modes, the cyclohexane spectrum was used as the background. The steady-state fluorescence spectra were performed in a Fluoromax-4 spectrofluorimeter. During recording the emission spectra, excitation wavelength was fixed at 360 nm and the excitation/emission slit widths was maintained at 2/2 nm. Water was circulated through a jacketed cuvette holder from a JULABO refrigerated bath (JULABO, Germany) to maintain proper temperature. Fluorescence lifetime measurements were performed using a Horiba Jobin-Yvon time correlated single-photon counting (TCSPC) lifetime instrument. For excitation source, a 370 nm nano-LED was used. The instrumental full width half-maximum of the 370 nm LED was ~ 1.1 ns, including the detector response. The photomultiplier tube (PMT) voltage was set as 950V. The pulse repetition rate was set to 1 MHz. The instrument response function was collected using Ludox AS40 colloidal silica. IBH (DAS-6) software was used to analyze the decay data. The fitting is considered to be good when the symmetrical distribution of the residuals gives a value of χ^2 , $0.99 \le \chi^2 \le 1.2$. The average fluorescence lifetime (τ_{avg}) values were calculated by following equation:

$$\tau_{\text{avg}} = \left(\sum_{i=1}^{n} \alpha_i \tau_i^2\right) / \left(\sum_{i=1}^{n} \alpha_i \tau_i\right)$$
⁽²⁾

Rheological measurement of RM samples was executed by Anton Paar's MCR (Modular Compact Rheometer) 102, with a CP 40 Cone and Plate configuration (radius 40 mm and angle = 1°) in dynamic mode. To measure rheological properties, a small portion of sample was placed on the smooth plate of rheometer and the cone-plate geometry was allowed to compress slowly to the set truncation gap (0.08 mm). The temperature of system was controlled to 303 K using P-PTD 200/AIR Plate-Peltier temperature device. Equilibrium process runs for 10 minutes before the experiment starts. The storage and loss modulus measurements were performed from 1 to 100 rad s⁻¹ frequency sweeps with 50% strain. Steady-shear experiments were performed in the range of shear rate from 100 to 1000 s⁻¹. The

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viscosity curve was extrapolated to the vertical coordinate to obtain the zero shear viscosity. Prior to rheological measurements, all samples were equilibriated at the experimental temperature for at least 15 min. The surfactant solution was fixed at a concentration of 0.1 mol dm⁻³ for all the experiments if not mentioned otherwise.

2.4. Computational details: Gaussian 09 program was used for all theoretical calculations containing the ion-pairs of ILs of interest.³⁷ Stable optimized structures of ILs were deadlocked at B3LYP/6-311+G(d,p) theoretical level.^{38,39} Herein, NBO5.G code⁴⁰ was employed to compute the natural bond orbital (NBO) charges of discrete atoms of optimized ILs due to its more reliability compared to the estimation of Mulliken charges.⁴¹

3. RESULTS AND DISCUSSION

In the present report, two important class of newly synthesized ILs, namely aprotic [Chl][Hex] and protic [NMP][Hex], were used instead of water as polar phase to form a nonaqueous RMs stabilized by the non-ionic Tween-80 in cyclohexane (Cy). We have specifically focused on the determination of different degree of H-bonding interaction between the ion pairs of two ILs (protic and aprotic) theoretically, which believed to be the primary governing factor in controlling the microstructure of the formulated IL-based RMs. In view of these, we optimized the structures of two ILs considering all possible configurations using the B3LYP method in conjunction with 6-311+G(d,p) basis set, which have been shown in Fig. 1. The interioric interactions between the ion pairs of [NMP][Hex] and [Chl][Hex] could be characterized by intermolecular hydrogen bonds of O···H-N and O. H-O type that formed mainly between the electronegative oxygen atoms of the carboxylate anion and the N-H and O-H bonds of the [NMP]⁺ and [Chl]⁺, respectively. In both ILs, two O atoms of [Hex]⁻ act as proton acceptors, whereas the N-H bonds of [NMP]⁺ and O-H bonds of [Chl]⁺ act as proton donors. It is clearly evident from the Fig. 1 that the interionic distance is much shorter in [Chl][Hex] (O.H-O = 1.733 Å) compared to [NMP][Hex] ($O \cdots H - N = 1.824$ Å). The H-bonds are the explicit structural features in these ion pairs. Along with these structural features, we also determined the resonance stabilisation energy, $E^{(2)}$ from second-order perturbation theory analysis obtained after the NBO calculations. The stabilization energy was measured using the following equation:⁴²

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_i - \varepsilon_j}$$
(3)

where, q_i , ε_i , ε_j and F_{ij} are designated as the occupancy of the donor orbital, energies of the orbitals and the off diagonal NBO Fock matrix element, respectively. Therefore, the estimated energy is interrelated to the degree of covalency, and subsequently with H-bonding strength.⁴² Earlier, Weinhold and co-workers have shown a direct relation between the NBO charge transfer from acceptor to donor and the H-bond interaction strength,⁴² which can further be connected to the energies of the charged H-bonded complex.⁴³ The $E^{(2)}$ values for major H-bonds in two ILs are listed in Table 1, which mainly involve an oxygen lone-pair of electrons n(O) and nitrogen-hydrogen or oxygen-hydrogen anti-bond $\sigma^*(N-H \text{ or } O-H)$ that are important in stabilizing these ILs. The NBO analysis suggest strong orbital

Table 1. Second order perturbation theory analysis of Fock matrix in NBO basis of ionicliquids calculated by B3LYP/6-311+G(d,p) level of theory.

Donor NBO (i)	Acceptor NBO (j)	<i>E(2)</i> [kcal mol ⁻¹] [NMP][Hex]	<i>E(2)</i> [kcal mol ⁻¹] [Chl][Hex]
LP(1) O19	BD*(1) N10-H15	2.03	-
LP(2) O19	BD*(1) N10-H15	6.38	-
LP(2) O20	BD*(1) C3-H8	0.07	-
LP(1) O23	BD*(1) O8-H9	-	6.51
LP(2) O23	BD*(1) O8-H9	-	6.37
LP(1) O24	BD*(1) C18-H21	-	3.24
LP(2) O24	BD*(1) C1-H2	-	1.35
LP(2) O24	BD*(1) C18-H21	-	6.01

interactions between the anti-bonding orbital of the proton donor $\sigma^*(O-H \text{ or } N-H)$, and the lone pairs of the proton acceptor, n(O), which is supported by the increased electron density and the increased second-order interaction energies in the related localized anti-bonding orbital. The increase of the electron density in $\sigma^*(N-H \text{ or } O-H)$ is a consequence of the charge transfer from *LP*(O19) to mainly $\sigma^*(N10-H15)$ or from *LP*(O23) to mainly $\sigma^*(O8-H9)$ in [NMP][Hex] and [Chl][Hex], respectively. The stabilization energy *E*(2) associated with hyperconjugative interactions for $LP1(O19) \rightarrow \sigma^*(N10\text{-}H15)$ and $LP2(O19) \rightarrow \sigma^*(N10\text{-}H15)$ of [NMP][Hex] are 2.03 and 6.38 kcal/mol. Whereas, for $LP1(O23) \rightarrow \sigma^*(O8\text{-}H9)$ and $LP2(O23) \rightarrow \sigma^*(O8\text{-}H9)$ of [Chl][Hex], the E(2) values are 6.51 and 6.37 kcal/mol. These results point out that the hydrogen bond in [Chl][Hex] is much stronger than that of [NMP][Hex]. This assumption is further strengthen by looking at the O…H-C distance in these two ILs (Fig. 1) along with the value of related to $E^{(2)}$ for $n(O) \rightarrow \sigma^*(C-H)$ (Table 1). Considering the proximity of donor-acceptor atoms, the obtained stabilization energies falls under the nominal H-bond range (5-40 kJ mol⁻¹),⁴⁴ which indicates a significant H-bonding interactions in case of these ILs.



FIG. 1. The optimized molecular structures with interionic distances and NBO charges for ionic liquids (ILs).

Since the formation of hydrogen bonds is followed by charge redistributions, we further examined the NBO charge distribution of these ILs to gain more insight into the problem. It is evident that the hydrogen atoms involved in H-bonds gain more positive charges, while the oxygen atoms acting as electron acceptor have more negative charges. Indeed, the charge of H15 in [NMP][Hex] is +0.473, while it is +0.508 on H9 of [Chl][Hex]. Consequently, the NBO charges of O19 and O20 in [NMP][Hex] are -0.490 and -0.348, respectively while it is -0.836 and -0.785, respectively on O23 and O24 in [Chl][Hex]. Thus, the NBO charges of hydrogen and oxygen atoms involved in H-bonds in [Chl][Hex] are larger than the corresponding values obtained for [NMP][Hex]. These results are consistent with our

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prediction in second-order perturbation energy E(2) and confirm that interionic hydrogen bond in [Chl][Hex] is stronger than that of [NMP][Hex].⁴⁵

Our next objective is to correlate the computed parameters for two ILs with various physical properties observed for IL-based non-aqueous RMs. The knowledge of the phase behaviour is important to ensure an optimal microemulsion system for chemical reaction and separation processes. The ternary phase diagrams of [NMP][Hex or [Chl][Hex]/Tween-80/Cy systems at 303 K are shown in Fig. 2A. Two different regions were observed, namely single phase and biphasic, which marked as "1 Φ " and "2 Φ ", respectively. Admittedly, the overall "1 Φ " microemulsion region for [NMP][Hex]-based system was monitored to be larger than that in the [Chl][Hex]-based system. This could be attributed to the differential interaction strength between the electropositive cationic counterpart of ILs and the electronegative oxygen atoms of polyoxyethylene (POE) units (Tween-80), leading to the effective solubilisation of ILs inside the core of the surfactant aggregates and alters rigidity of interfacial layer.⁴⁶



FIG. 2. Phase diagrams of the ILs/Tween-80/cyclohexane ternary systems at 303 K, where ILs are **(A)** [NMP][Hex] or [Chl][Hex], and **(B)** [NMP][For].

To further investigate the influence of chain length of the RTIL anion in formation of the non-aqueous microemulsion, the phase behaviour was investigated using [NMP][For] as polar phase. Fig. 2B shows the phase diagram of [NMP][For]/Tween-80/Cy ternary system at 303 K. The area of single phase region was found to follow the trend; [NMP][Hex] > [NMP][For]. This may be due to the difference in strength of interaction, which arises due to

the presence of formyl and hexyl chain in [NMP][For] and [NMP][Hex], respectively. Longer chain length of [Hex]⁻ may be responsible for more pronounced penetration because it aids in aligning the anion of IL with the tail part of Tween-80.⁴⁶ This results in more rigid oil/IL interfacial layer in case of [NMP][Hex]-based system, which further increases solubilization capacity of RTIL as well as the single-phase region.³⁶ Although the formation of RTIL/Tween-80/Cy microemulsion is indicated by the phase behaviour study, we need to confirm whether the surfactant molecules are effectively entrapping the RTIL molecules or not. In view of this, we have conducted DLS measurement to confirm the formation of IL-inoil (IL/O) microemulsions or RMs. Earlier studies using DLS have shown that the size of droplets increased regularly up to a certain level with increase in R values (where, R is defined as the molar ratio of RTILs to Tween-80) when the IL encapsulated to form IL/O systems.^{47,48} The size distribution and variation of size with increasing R for [NMP][Hex] or [Chl][Hex]/Tween-80/Cy systems are shown in Fig. S2 and Fig. 3, respectively. In all these systems, an increase in the droplets size was evidenced with increase in IL content (i.e., R), which implies that the both ILs are sequestrated by the surfactants constructing IL-in-Cy RMs. This clearly shows that the RM media consist of discrete spherical and non-interacting droplets of ILs stabilized by the Tween-80,³⁵ which is further confirmed from the monomodal size distributions of droplets (Fig. S2). In this study, maximum droplet sizes were observed in the order of 100 nm for these RMs, which are much larger than common traditional aqueous RMs of droplet sizes less than 40 nm. The larger droplet size may be related to the unique formation mechanism of non-ionic surfactant based IL/O RMs. The effective area of electrostatic attraction for POE chains of Tween-80 with ILs is significantly higher compared to water, which leads to a much extended conformation resulting in an increased size of IL RMs.⁴⁸ It is interesting to mention that although both systems show a linear tendency, the droplet sizes at studied range of R were quite different for two ILs. For example, at R = 0.3and 0.7 the droplet size is \Box 50 and 63 nm, respectively for [Chl][Hex]-based and \Box 70 and 108 nm, respectively for [NMP][Hex]-based RMs. Moreover, the different slopes of the droplet size's plot in Fig. 3 could also indicate a differential interaction between ILs and surfactant in these systems. Due to comparatively weaker H-bonding interaction between ionpairs of [NMP][Hex] compared to [Chl][Hex] (as revealed from theoretical NBO calculations), we might consider the stronger interaction between [NMP]⁺ and Tween-80 at the palisade layer of IL/O system. However, this assumption could not be confirmed due to the lack of enough evidence at this point. In the subsequent paragraph, we will show how the rheological properties of such nanostructures are affected after incorporation of ILs through

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systematic variation in the structure and H-bonding capacity of the constituents, such as IL ions and polar head of Tween-80.

In principle, rheological measurements contain information regarding the inter-droplet interactions to monitor microstructural changes in RMs.⁴⁹ To investigate the effect of molecular architecture of protic and aprotic ILs on the formation of IL/O RMs, samples were prepared by adding different amounts of ILs ([Chl][Hex] and[NMP][Hex]) to Tween-80/Cy solution with a fixed surfactant concentration.



FIG. 3. Hydrodynamic diameter of the droplets of [NMP][Hex] or [Chl][Hex]/Tween-80/cyclohexane RMs as a function of molar ratio of IL to surfactant (R) at fixed surfactant concentration of 0.1 mol dm⁻³ and at 303 K.

The steady-shear measurements were carried out for two non-aqueous IL-based RMs at different R (= 0.3 and 0.7). The shear rate curve in Fig. 4A shows the change in shear viscosity (η) as a function of shear rate (γ) for four investigated systems. Overall, the solution viscosity is found to be independent of the shear rate, and thus shows a typical Newtonian fluid behaviour.⁵⁰ This indicate that in the given shear rate, the three dimensional network structures formed by the IL droplets were apparently intact. This network structure is not static like a synthetic polymer, instead, a transparent network which repeatedly collapse and reforms itself. Further, to estimate the rheological characteristics of the two non-aqueous RMs more specifically, the apparent viscosity (η_a) was estimated from the Herschel-Bulkely

equation.⁵¹ This equation, though empirical and does not have theoretical corroboration, is useful for estimation of apparent viscosity of similar sample, which can be defined as;⁵²

$$\tau = \tau_a + \eta_a (\frac{d\gamma}{dt})^n \tag{4}$$

Where, τ , τ_a , $(d\gamma/dt)$ and *n* are the shear stress, apparent yield stress, shear rate, and H-B index, respectively. Herein, the value of n is considered to be 1. However, the "apparent viscosity" (η_a) term used here is clearly different from "viscosity" and also have different dimensions. The systems showed good proportionality between the shear stress and rate (with R^2 values ≥ 0.98) and the apparent viscosity was obtained from the slopes of the shear stress vs. shear rate plots (Fig. 4B). The η_a values were found to be 3.36 and 4.64 mPa.s for [Chl][Hex]-based RMs and 4.29 and 9.50 mPa.s for [NMP][Hex]-based RMs at R = 0.3 and 0.7, respectively. The increase of the shear viscosity for both systems with increasing IL content (R) can be correlated with the enlarged droplet size and/or droplet-droplet interactions.⁵³ It is also worth noticing the subtle differences present between the RMs containing [Chl][Hex] and [NMP][Hex], which appear to be even more compelling. Very similar to the DLS results, the η_a of the [NMP][Hex]/Tween-80/Cy system found to be higher than that containing [Chl][Hex]. This implies that a stronger network and more steady internal structure of the inverted micelle is developed for [NMP][Hex] based systems, which increases the droplet-droplet interactions, causing the droplets to be packed more closely. Thus, these fluids can resist shear more strongly.⁵⁴ Similar flow behaviour was earlier reported for RMs composed of water/polysorbate 80/soybean lecithin/IPM and water/medium-chain glyceride/polysorbate 80/IPM.55,56



FIG. 4. Variation of **(A)** viscosity (η) and **(B)** shear stress (τ) versus steady shear rate (γ) plots for [NMP][Hex] or [Chl][Hex]/Tween-80/cyclohexane RMs at different molar ratio of IL to surfactant (R) and at 303 K. The filled spheres and solid lines in **(B)** denote experimental data and linear fits to the Herschel-Bulkely equation, respectively. View in color for best clarity.

Oscillatory shear (frequency sweep) measurements were also performed to further investigate viscoelastic properties of these solutions in addition to steady-shear measurements. The variations of the storage modulus (G'), the loss modulus (G''), and the complex viscosity $(|n^*|)$ versus oscillation frequency (ω) of the RMs at different R values are shown in Figs. S3A-S3D (Supporting Information). Essential information regarding the fluidity and rigidity of viscoelastic samples can be obtained from dynamic rheological studies. Two key parameters are G', which corresponds to the ability of the deformed materials to store energy, and G", which represents the flow behaviour of the material under applied stress.⁵⁷ All these systems show a liquid-like behaviour normally observed in RMs, indicating the loss modulus is greater than the storage modulus ($G' \leq G''$) at any tested frequency. Also, a differences between the shear (n) and the dynamic $(|n^*|)$ viscosity was observed. The dynamic viscosity exceeds the shear viscosity, especially at higher frequencies. This variation can be attributed to intermolecular interactions.⁵⁸ The $|n^*|$ values also found to be higher for [NMP][Hex]based systems compared to [Chl][Hex]-based RMs. The molecular architectures of constituents ions of ILs in addition to the strength of intermolecular H-bonding network of ILs and surfactant have a significant impact on viscosity.³³ In this study, two ILs have common anionic counterpart (Hex]⁻) but different cation ([NMP]⁺ and [Chl]⁺), in which

[NMP]⁺ is protic in nature. These two ILs (protic and aprotic) primarily differs from each other in the proficiency of donation and acceptance of proton. The protic IL can build up H-bonding network like water, whereas the aprotic IL cannot.¹⁵ As a result, higher viscosity (both apparent as well as complex) obtained for [NMP][Hex]-based system compared to [Chl][Hex]-based system. Next, we resorted to FTIR measurement in the subsequent section to confirm these postulates.

Herein, the formation mechanism of the ILs/Tween-80/Cy microemulsions was studied by employing FTIR techniques after monitoring the change in vibrations of the bonds of surfactant head groups that are particularly involved in the interactions with ILs at the droplet interface. Thus, we focused on the O-H stretching frequency of the terminal hydroxyl group of Tween-80. Figs. 5A and 5B reveal the C-H and O-H stretching modes of Tween-80 in [NMP][Hex] and [Chl][Hex]-based RMs, respectively as a function of various amounts of ILs (indicated by R values) at 303 K. The FTIR spectra of pure [NMP][Hex] and [Ch1][Hex] were subtracted from the spectra of RMs to eliminate the contribution of vibrational bands of pure ILs. It can be noted that the O-H bands are progressively blue-shifted with increasing R for [NMP][Hex]-based RMs, whereas no noticeable changes are observed for [Chl][Hex]based systems. This behaviour can be rationalized by hypothesizing that in pure Tween-80/Cy RMs, the terminal hydroxyl of Tween-80 is H-bonded with the oxygen atoms of POE units or terminal hydroxyl groups of other Tween-80 molecules. Conversely, when [NMP][Hex] is added to this, the electronegative oxygen atoms of the POE units bind to the electropositive [NMP]⁺ ring by weakening the hydrogen-bond interaction between the POE groups of Tween-80. This leads to the appearance of O-H stretching band in the highfrequency region of the IR spectrum.⁵⁹ Similar behaviour were also observed earlier for the bmimBF₄-in-*p*-xylene RMs.⁶⁰ So far, it is observed that the microstructures of formulated non-aqueous RMs differ drastically for two ILs upon confinement and show a considerable degree of inhomogeneity due to disruption in their hydrogen bonding network. To acquire a full panorama for these non-ionic IL/O RMs, we further attempt to examine the microenvironment that the both ILs and Tween-80 molecules experience inside the RM droplets and to improve the basic understanding about the polarity and H-bond interactions between the constituents.



FIG. 5. FTIR spectra of -CH and -OH stretching bands of Tween-80 in ILs/Tween-80/cyclohexane RMs as a function of R at 303 K, where ILs are **(A)** [NMP][Hex] and **(B)** [Chl][Hex]. View in color for best clarity.

In view of this, we have performed steady-state fluorescence measurement using ANS as a probe molecule, which is well-known to extract information of microheterogeneous systems.⁶¹ The ANS concentration remains constant ($\sim 10^{-6}$ mol dm⁻³) throughout the spectroscopic measurements. The emission spectra of [NMP][Hex] or [Chl][Hex]/Tween-80/Cy RMs as a function of R (= 0.3 and 0.7) at 303 K are presented Fig. 6. ANS exhibits emission maxima at 430, 494 and 489 nm in Cy, [NMP][Hex] and [Chl][Hex], respectively at excitation wavelength (λ_{exi}) of 360 nm (Figs. S4-S5). On addition of Tween-80 to a solution of ANS in Cy, the emission maximum of ANS exhibits a marked red shift from 430 to 460 nm, which indicates transfer of the ANS molecules from bulk Cy to the interior of Tween-80 RMs. The blue shift of probe in IL-in-oil RMs compared to neat ILs indicates that the polarity of the RMs is much lower compared to that of bulk ILs. The emission maximum of ANS displays red shift from 465 to 471 nm and 470 to 472 nm for [Chl][Hex] and [NMP][Hex]-based RMs, respectively with increase in R (Table 2). These results suggest that a significant portion of the probe molecules moved towards the polar IL core of the RMs. At comparable R, the more red-shifted emission maxima for [NMP][Hex]-based RMs compared to [Chl][Hex]-based system indicates that the polarity of the microenvironment of [NMP][Hex]-based RMs is superior compared to [Chl][Hex]-based system. This may be due to effective penetration of [NMP][Hex] near surfactant head group for its protic nature.⁶² Thus, it can be concluded that the microenvironment experienced by ANS in the

[NMP][Hex]-based system is different from the [Chl][Hex]-based system. So far, we have gathered information regarding location of the probe molecule (ANS) inside the [NMP][Hex] or [Chl][Hex]/Tween-80/Cy RMs. It will therefore be fascinating to find out how the H-bonding interactions between the constituents and droplet size influence the dynamics of the solute in the nanopools of RMs.



FIG. 6. Emission spectra of ANS in ILs/Tween-80/cyclohexane RMs at different R values and at 303 K.

In order to understand the diffusional dynamics of the ANS in presence of encapsulated ILs and to get an in-depth knowledge on the influences of the local H-bonding environment on excited state behaviour, we performed time-resolved fluorescence study. It was reported that the difference in the lifetime of the fluorophore arises due to differential degrees of solvent relaxation around the fluorophore and/or the distribution of fluorophore in different distinct regions of a confined environment.⁶³ The time-resolved decay profiles of ANS ($\lambda_{ex} = 360 \text{ nm}$) with varying R in these RMs at their corresponding maxima are illustrated in Figs. 7A and 7B, and the decay parameters are summarized in Table 2. ANS shows bi-exponential decay in neat ILs, whereas tri-exponential decay evidenced inside IL-based RMs. Several distinct features of dynamics of probe in RTIL should be discussed before explaining the behaviour of solvent relaxations in [NMP][Hex] or [Chl][Hex]/Tween-80/Cy RMs.

The process of solvation in neat RTIL is much different from the solvation process occurring in conventional polar solvents like methanol or acetonitrile.⁶⁴ The solvation time in neat RTILs is much larger (0.1-10 ns) compared to the solvation time for most conventional solvents (1-10 ps).⁶⁵ As shown by Chapman and Maroncelli the ionic solvation is slower compared to the pure solvent.⁶⁶ The solvation in neat RTILs are controlled by motion of the cations and anions around the photoexcited dipolar molecules. On the other hand, in case of polar solvents, the solvation happens as a result of reorientation of solvent molecules around the excited dye. The average life-times of ANS along with different components in neat ILs are tabulated in Table 2. The τ_{avg} of ANS in neat [NMP][Hex] was found to be 3.63 ns with time constants of 0.81 and 3.87 ns along with relative contribution of the fast and slow components being 29 and 71%, respectively. Whereas, the values for neat [Chl][Hex] were 2.39 ns with time constants of 0.40 and 2.60 ns along with relative contribution of the fast and slow components being 40 and 60%, respectively. The diverse features of the dynamics of bulk [NMP][Hex] and [Chl][Hex] would arise from the variable interionic and ion-solvent interactions of two ILs, as observed earlier from computational study. Several reports are available which describes the biphasic nature of solvation process in RTIL.67-69

Table 2. Steady-State Emission Maxima and Lifetimes of ANS in neat ionic liquids (ILs),

and ILs/Tween-80/cyclohexane RMs at 303 K.								
Syste	em	λ _{max} (nm)	$\tau_1/ns(\alpha_1)$	$\tau_2/ns(\alpha_2)$	$\tau_3/ns(\alpha_3)$	$ au_{avg}/ns$	χ²	

[Chl][Hex]	489	2.60 (0.60)	0.40 (0.40)		2.39	1.01
R=0.3_[Chl][Hex]	465	0.96 (0.38)	2.95 (0.30)	10.79 (0.29)	8.39	1.01
R=0.7_[Chl][Hex]	468	0.74 (0.42)	3.05 (0.32)	10.46 (0.24)	7.76	1.08
R=1.1_[Chl][Hex]	471	0.66 (0.45)	2.92 (0.35)	9.85 (0.20)	6.87	1.09
[NMP][Hex]	494	3.87 (0.71)	0.81 (0.29)		3.63	1.06
R=0.3_[NMP][Hex]	470	1.29 (0.37)	3.18 (0.15)	12.82 (0.46)	11.70	1.10
R=0.7_[NMP][Hex]	472	0.97 (0.40)	3.41 (0.16)	13.19 (0.44)	11.34	1.05



FIG. 7. Time-resolved fluorescence intensity decay of ANS in ILs/Tween-80/cyclohexane RMs at different R values and at 303 K; where **(A)** [NMP][Hex], and **(B)** [Chl][Hex] (inset shows comparative decay profile for two ILs in RMs at identical R = 0.30). The sharp profiles in black are the instrument response functions. View in color for best clarity.

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The tri-exponential nature of solvation dynamics in IL-based RMs with increased time constants compared to that of neat ILs originates from the presence of different environments of IL molecules inside the RMs, such as near and apart from surfactants head group. RTILs in the core of RMs experience less restricted environment as compared to those present near the head group, i.e., at the interfacial regions. As a result slow life-time component arises due to the presence of RTIL near surfactant head group or at the interfacial region. On the other hand, the fast component of solvation dynamics implies the presence of RTIL in the nano IL-pool. At lower R values, most of the RTIL molecules are involved in interacting with other ILs and surfactant head group through ion-dipole interactions and mainly in solvating surfactant molecules. As the concentration of RTIL in the system increases, they forms a bulk like pool where they have less restricted movement as compared to the interfacial region.⁷² At higher R values, proportion of IL present at the core of RMs increases and subsequent proportion at interfacial regions decreases. As a consequence, diffusional motion of ions increases and values of slow and fast components of the solvation dynamics decreases leading to reduction in the average life-time.

In the present context, it is desirable to make comparison between the changes in τ_{avg} on going from [NMP][Hex]-in-Cy to [Chl][Hex]-in-Cy RMs at comparable compositions. In former system, the average life-time is 11.70 ns with time constants of 1.29 ns (37%), 3.18 (15%) and 12.82 ns (46%) at R = 0.30. However, at this R value, the average life-time becomes 8.39 ns with time constants 0.96 ns (38%), 2.95 (30%) and 10.79 ns (29%) for the latter one. Similar trend is also evidenced at R value of 0.70. This shows that the interactions between the protic [NMP][Hex] with the polar head group of Tween-80 and with other [NMP][Hex] molecules are stronger than the case of [Chl][Hex]. Therefore, a reduction in the mobility of [NMP][Hex] molecules at the proximity of reverse micellar cavity surface is expected due to strong interaction. Earlier, Shirota et al.⁶² was observed similar type of behaviour in the solvation dynamics of protic formamide (FA) and aprotic dimethylformamide (DMF) in AOT/*n*-heptane RMs.



FIG. 8. Hydrodynamic diameter of the droplets of ILs/Tween-80/cyclohexane RMs as a function of molar ratio of IL to surfactant (R) at different temperatures, where ILs are (A) [NMP][Hex] and (B) [Chl][Hex]. View in color for best clarity.

In order to scrutinize the effects of the ILs on the thermal stability of formulated IL-in-oil RMs more directly, we examined the droplet size and viscosity of formulated systems in the temperature range of 298-313 K. However, to our knowledge, the influence of temperature on IL entrapped RMs scarcely reported.^{46,48,72} Therefore, it would be very interesting and of utmost prominence to investigate their microstructural change of RM droplets based on nonionic surfactant with temperature. Figs. 8A and B show the temperature-dependent size variation of IL-in-Cy RMs through DLS measurement. The corresponding size distribution plots are provided in Supporting Information (Figs. S6-S7). It is evident from the DLS measurements that the IL based RMs are monodisperse in nature, where the size of droplets decreases with increase in temperature in all cases. For example, increasing temperature from 298 to 313 K, the droplet sizes decreases from 135 to 75 nm and 52 to 45 nm for [NMP][Hex] and [Chl][Hex]-based RMs at constant R of 0.70, respectively. This shows that the RMs retain their structural integrity across the temperature range studied. Most notable observation is that the RMs was not destroyed even after further rise in temperature. Rather single phase transparent RMs was observed even as the temperature approaches the boiling point of Cy (347 K). Reports are scarce for such a stable non-ionic surfactant supported RMs.

We have also measured the viscosity of [NMP][Hex] or [Chl][Hex]/Tween-80/Cy RMs at the similar temperature range used in DLS measurement. The temperature dependence of viscosity of these systems as a function of R is illustrated in Figs. 9A and B. With gradual

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increasing of temperature, the viscosity of the RMs gradually decreases. Strong electrostatic interaction between the [NMP]⁺ or [Chl]⁺ and POE of Tween-80 decreases with gradual increase in temperature and as consequence viscosity decreases.



FIG. 9. (A) Three dimensional representation of viscosity as a function of R and temperature (T) for [NMP][Hex]/Tween-80/cyclohexane RMs. **(B)** Temperature-dependent viscosity profile for [NMP][Hex] or [Chl][Hex]/Tween-80/cyclohexane RMs at different values of R. View in color for best clarity.

Activation energies (E_a) associated with these processes can be calculated from analysis of temperature dependency of viscosity. From an Arrhenius plot the E_a , can be calculated by;

$$\eta = A e^{\frac{E_a}{RT}} \tag{4}$$

Where, R is the universal gas constant, and A is the pre-exponential factor. The energy required to move individual droplets in an environment of surrounding RMs is given by interactions between individual aggregates, known as the activation energy.⁷³ The values of E_a were evaluated from the slope of the logarithmic plot of $1/\eta$ against 1/T, which illustrated in Fig. 10 for [NMP][Hex] or [Chl][Hex]/Tween-80/Cy RMs at different R values. The E_a obtained for [NMP][Hex]-based systems are 26.52 and 26.77 kJ/mol at R of 0.30 and 0.70, respectively. Whereas, these values are 25.96 and 26.19 kJ/mol at R of 0.30 and 0.70, respectively for [Chl][Hex]-based systems. Similar values for RMs are reported in literature but were obtained using different approach.^{72,74} The E_a value for [NMP][Hex]-based system is higher compared to [Chl][Hex]-based system. Generally, E_a value depends on the structure of RTILs and it is the energy barrier for the ions to move past each other. Thus the larger E_a

of [NMP][Hex] systems may be due to the stronger hydrogen bonding environment in [NMP][Hex]/Tween-80/Cy system, and as a result its orientational motion is hindered.⁷⁴



FIG. 10. Arrhenius plots of variation of viscosity in logarithmic function with inverse of temperature for [NMP][Hex] or [Chl][Hex]/Tween-80/cyclohexane RMs at different values of R. View in color for best clarity.

4. OVERALL COMPREHENSION

A series of protic and aprotic ILs such as, [NMP][For], [NMP][Hex] and [Chl][Hex] were synthesized and subsequently entrapped within Tween-80/Cy RM nanocage in order to understand the basic difference between the nature of interionic as well as IL-surfactant interactions. The phase behaviour of the ternary ILs/Tween-80/Cy mixture showed large monophasic transparent region, which varied with the nature of cation (protic [NMP]⁺ or aprotic [Chl]⁺) and alkyl chain length of anion ([For]⁻ and [Hex]⁻) of ILs. Swelling behaviour of these ILs confirmed the formation of IL/O RM droplets, which found to be larger for [NMP][Hex]-based systems compared to [Chl][Hex]. The higher shear viscosity for [NMP][Hex]-based systems than [Chl][Hex] correlated with the fact that a stronger network structure developed for the former system, due to increase in droplet-droplet interactions, which causes the more closely packed RM droplets at comparable IL content (R) compared to latter system. All these microstructural information actually offers a clue that the incorporation of [NMP][Hex] in Tween-80/Cy RMs creates stronger electrostatic or H-

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bonding interaction with POE chains of Tween-80. Also, this primary hypothesis supports the gas phase theoretical calculations which shows weaker H-bonding interaction in ion-pair of [NMP][Hex] compared to [Chl][Hex]. Thus, [NMP]⁺ is more prone to interact with Tween-80 when entrapped in RM confinement. The basic difference between two types of ILs used herein ([NMP][Hex] and [Chl][Hex]) is the presence of exchangeable proton in [NMP][Hex], which can form extended H-bonding network with Tween-80. In order to strengthen the understanding of formation mechanism of non-aqueous RMs with these two different classes of ILs, we performed both FTIR and dynamic fluorescence studies. Both of these measurements revealed stronger binding of the electronegative oxygen atoms of the POE units with electropositive [NMP]⁺ ring by weakening the hydrogen-bond interaction between POE groups of Tween. This results in more blue shifting of O-H stretching modes of Tween-80 and higher average life-time of fluorophore inside [NMP][Hex]-based RMs compared to [Chl][Hex]-based systems. Finally, the temperature-dependent DLS and viscosity measurements confirmed the decrease in droplet size and viscosity due to weakening of the electrostatic or H-bonding interactions between the ILs and surfactant without any phase separation. Thus, these systems retain their structural integrity across the whole temperature range studied. The thermal stability of two different IL RMs based on non-ionic Tween-80 opens up the possibility of application of non-aqueous RMs at high temperature.

5. SUMMARY

In this report, we have investigated the significant difference observed in flexibility or internal rigidity of RMs, dictated by the nature of the polar ILs- [NMP][Hex] and [Chl][Hex], and analyzed by independent methods such as: phase diagram study, DLS, FTIR, rheology, and fluorescence measurements. The results show that by simply changing the cationic part of the IL, remarkable changes in the oil/IL interface and microstructures of RMs, such as modification of the hydrogen bonding ability of the ILs with surfactant molecules can be achieved. This findings are very important from the viewpoint of formulating the shape- and size-controlled reverse micelle systems with critical applications, for examples, in nano-bio architectonics, where strategic design of nanostructure materials is crucial.⁶⁸ It is interesting that the use of ILs in RM systems can widen their field of application by eliminating the problems of using pure ILs: viz. low solubility of some chemical compounds and high viscosity. Furthermore, compared to conventional microemulsion systems, the studied systems are much less expensive due to their low IL content, and also easier to synthesize.

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properties by varying the type and amount of additives; and will also escalate research on similar filed.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Plots of ¹H NMR and ¹³C NMR spectra of synthesized ILs; Size distribution of [Chl][Hex] and [NMP][Hex] ; Variation of the storage modulus (G'), loss modulus (G'')and complex viscosity ($|\eta^*|$) relative to the angular frequency (ω) of microemulsion systems; Emission spectra of ANS in cyclohexane (Cy); Emission spectra of ANS in neat ionic liquids (ILs); Size distribution plots [NMP][Hex]-based RMs as a function of temperature; Size distribution plots [Chl][Hex]-based RMs as a function of temperature (PDF).

Acknowledgments

The authors are grateful to IIT Madras for financial support, through Institute Research and Development Award (IRDA): CHY/15-16/833/RFIR/RAME. We would like to thank Mr. Prashant Kumar and Sophisticated Analytical Instruments Facility (SAIF), IIT Madras, for the fluorescence life-time measurement and the computer resource of Computer Centre, IIT Madras is gratefully acknowledged.

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TOC Graphic

