

Aggregation in Deep Eutectic Solvents (DESs): Formation of Polar DES-in-Nonpolar DES Microemulsions

Anushis Patra, Anjali, and Siddharth Pandey*

Cite This: *ACS Phys. Chem Au* 2024, 4, 531–535

Read Online

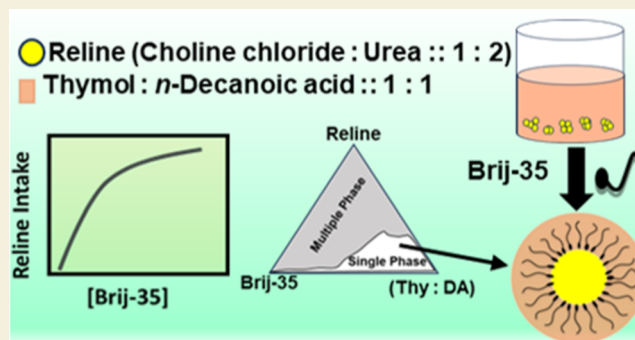
ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: The versatility of environmentally benign and inexpensive deep eutectic solvents (DESs) lies in their widely varying physicochemical properties. Depending on its constituents, a DES may be highly polar or nonpolar in nature. This offers an enticing possibility of formation of novel nonaqueous microemulsions (MEs). Evidence of the presence of polar DES-in-nonpolar DES MEs is presented with reline (formed by mixing choline chloride and urea in 1 : 2 mol ratio) as the polar DES forming the ME pools, Thy : DA [formed by mixing thymol (Thy) and *n*-decanoic acid (DA) in 1 : 1 mol ratio] nonpolar DES as the bulk oil phase and nonionic surfactant Brij-35 as the emulsifying agent. While only sparingly miscible in Thy : DA, as high as 2.5 M reline can be solubilized in this DES in the presence of 100 mM Brij-35; reline loading ($w_{\text{Rel}} = [\text{reline}]/[\text{Brij-35}]$) as high as 25 can be achieved. The ternary phase diagram of the Thy : DA/Brij-35/ reline system reveals a clear and transparent single-phase region where MEs may be forming. Dynamic light scattering confirms the presence of MEs of 2–10 nm size. Even as up to 2.5 M (ca. 0.35 mole fraction) reline, whose dynamic viscosity (η) and electrical conductivity (κ) are very high, is added to 100 mM Brij-35 solution of Thy : DA, the η and κ values of the solution increase insignificantly, thus conforming to the formation of MEs in the solution. Fourier transform infrared (FTIR) absorbance spectra and fluorescence probe responses further indicate that reline is not dispersed in the medium but rather forms polar pools of the MEs. These novel nonaqueous polar DES-in-nonpolar DES MEs will not only expand the application potential of DESs but also offer a new class of organized media with widespread potential.

KEYWORDS: aggregation, deep eutectic solvents (DESs), reline, nonaqueous microemulsions, hydrophobic DESs, fluorescence probing



INTRODUCTION

Microemulsions (MEs) are optically transparent thermodynamically stable compartmentalized dispersions usually consisting of two immiscible liquids (one polar and the other nonpolar) formed using an emulsifying agent, preferably a surfactant.^{1–3} Since their advent, such spontaneously formed aggregated assemblies have demonstrated applications in several areas, most notable being biochemistry, nanotechnology, synthesis, extraction, separation, oil recovery, polymerization, pharmaceutical, cosmetic, agrochemical, and food industries.^{4–8} The initial reports on MEs invariably involved water as the polar phase, and based on the relative amount of water, the MEs were characterized as oil-in-water (o/w) or water-in-oil (w/o) with mostly conventional organic solvent as the oil phase.⁹ The w/o MEs perhaps have garnered more attention due to the stabilization of water droplets within the bulk nonpolar “oil” using a surfactant offering plethora of applications.^{2,3} The water intake (or loading), which controls the crucial properties, such as size and shape of w/o MEs, is characterized in terms of $w_o = [\text{water}]/[\text{surfactant}]$.¹⁰

However, the presence of water turns out to be undesirable in several applications where it either reacts or degrades the chemical species under consideration.¹¹ Thus, the exploration of nonaqueous MEs has recently emerged as an important topic in academia.^{11,12} If water in w/o MEs is replaced with a polar organic compound, which is also immiscible with the bulk nonpolar “oil” phase, desired nonaqueous MEs could be formed.^{12,13} Certain polar organic solvents belonging to glycol, amide, and short-chain alcohol families as well as dimethyl sulfoxide, acetonitrile, and 2-pyrrolidinone, among others, have been utilized to prepare nonaqueous MEs, where analogous to w_o , $w_s = [\text{polar solvent}]/[\text{surfactant}]$ could be defined characterizing such MEs.¹² While some of the glycol and

Received: April 30, 2024

Revised: June 12, 2024

Accepted: June 12, 2024

Published: July 18, 2024



short-chain alcohol family polar solvents may be considered benign, many others have known adverse environmental effects.¹¹ More importantly, the majority of organic solvents that are used as the bulk “oil” phase predominantly belong to either alkane or chlorinated alkane or benzene-derived solvent family.¹⁴ These nonpolar solvents are highly volatile and toxic and cause detrimental effects to the environment and human health apart from offering a limited range in physicochemical properties. These have clearly imposed severe restrictions on the practical applications of such MEs. Thus, it is imperative to explore the formation of ecofriendly nonaqueous ME systems.

Deep eutectic solvents (DESs), in this context, offer enormous versatility as far as the preparation of such nonaqueous MEs are concerned.¹⁵ The major reason for this is that based on the constituents, the DESs can be highly nonpolar (or “hydrophobic”) or highly polar (or “hydrophilic”). DESs are environmentally benign and inexpensive alternatives to both polar and nonpolar organic solvents. Consequently, there have been investigations regarding the use of DESs in the formation of micelles,¹⁶ DES-in-oil¹⁷ and oil-in-DES¹⁵ MEs, where a polar DES has been used in lieu of water. The nonpolar DESs, however, offer an opportunity to replace toxic nonpolar organic solvents as the bulk “oil” phase of the MEs. Herein, we present evidence for the formation of unprecedented polar DES-in-nonpolar DES nonaqueous MEs as alternate compartmentalized media to the conventional water-in-oil (w/o) MEs. Specifically, the polar DES selected is reline [Rel, a prototypical hydrophilic DES, prepared by mixing choline chloride (ChCl) and urea (U) in 1 : 2 mol ratio], and the bulk nonpolar (or “oil”) DES that worked among many others investigated is Thy:DA [prepared by mixing thymol (Thy) with *n*-decanoic acid (DA) in 1 : 1 mol ratio]. The two sets of two individual constituents are all solid, whereas both the DESs are liquid under ambient conditions. Several emulsifying surfactants were investigated, and it was found that Brij-35 [polyoxyethylene (23) lauryl ether], a common nonionic surfactant, was the most effective among several others that were tried. Analogous to w_o and w_s , for our polar DES-in-nonpolar DES, i.e., reline-in-Thy:DA ME, we have defined w_{Rel} as equal to [reline]/[Brij-35].

EXPERIMENTAL SECTION

Materials

Thymol (Thy), *n*-decanoic acid (DA), choline chloride (ChCl), and urea (U) were chosen as the DES constituents and were obtained from Sigma-Aldrich and SRL Enterprises, respectively, within their highest purity $\geq 99\%$, while Brij-35 was purchased from Induschembio. Fluorescence probes 1,3-bis-(1-pyrenyl)propane [Py(3)Py] and 9-(2,2-dicyanovinyl)julolidine (DCVJ) [purity $\geq 97.0\%$ (HPLC)] were acquired from Molecular Probes and Sigma-Aldrich, respectively, and stored in a dried condition. All the chemicals were used as such without further purification.

Methods

Hydrophobic DES Thy:DA was prepared by simply mixing their constituents in a molar ratio of 1 : 1 under gentle heating and constant stirring at 50°C until the mixture become clear and homogeneous. Similarly, hydrophilic DES reline was prepared by mixing ChCl and U in a molar ratio of 1 : 2 under heating at 80°C until a homogeneous and colorless liquid was formed and which was then stored in an airtight container under an inert atmosphere. Prior to usage, the obtained DESs were subjected to vacuum drying for approximately 5 h. A Karl Fischer titrator was employed to estimate the water content, and in every measurement, the water content was found to be <100 ppm. The surfactant solutions of the desired

concentrations were freshly prepared in Thy:DA DES. The maximal reline intake was determined by visual cloud point observation, and consequently, a phase diagram was constructed. Each observation was repeated at least thrice.

The electrical conductivity of 100 mM Brij-35-added Thy:DA system was measured at different amounts of reline intake or w_{Rel} at $T = 298$ K using a conductivity cell (CC-03B) purchased from Elico Ltd., India, and CM-183 μp -based EC-TDS analyzer with an ATC probe. The particle size distribution of ME was measured at 298 K using a Malvern Nano ZSU3200-Pro Blue instrument. Samples were also characterized through attenuated total reflectance-Fourier transform infrared (ATR-FTIR) absorbance data, which were acquired on a double-beam spectrophotometer (Agilent Technologies Cary 660 ATR) from 4000 to 400 cm^{-1} . Stock solutions of probes were prepared by dissolving a precalculated amount of the respective probe in ethanol and stored at $4 \pm 1^\circ\text{C}$ in precleaned brown amber glass vials. A Mettler-Toledo AB104-S balance was used to weigh the proper amount of probe with an accuracy of ± 0.0001 g. A prerequisite amount of the prepared stock solution was taken in a 1 cm^2 quartz cuvette, and high-purity nitrogen gas was used to evaporate ethanol. A precalculated volume of DES was transferred to the cuvette to make the required concentration of the probe. Dissolution of the probes in DESs was confirmed using the linearity of the absorbance versus the concentration plot. The steady-state fluorescence spectra were obtained using an FLS1000 spectrometer with emission monochromators (STGM325-M) and grating excitation (STGM325-X) containing a 450 W xenon arc lamp as the radiation source, a red PMT detector, and a temperature-controller (Quantum Northwest Luma 40). The spectrometer was bought from Edinburgh Instruments, Ltd. Appropriate blank was subtracted from the emission and excitation spectra before analysis.

RESULTS AND DISCUSSION

Under ambient conditions, the solubility of reline in Thy:DA is only ca. 0.07 M. However, in the presence of surfactant Brij-35, the intake of reline increases drastically. For 100 mM Brij-35 (the maximum [Brij-35] investigated) in Thy:DA, the intake of reline is found to become as high as 2.5 M corresponding to $w_{\text{Rel}} = 25$. Other DA-based DESs, citronellol : DA :: 1 : 1 and geraniol : DA :: 1 : 1, do not exhibit any appreciable intake of reline in the presence of 100 mM Brij-35; in the presence of 100 mM of other nonionic surfactants, Triton X-100 and Tergitol, respectively, also, no increase in reline intake is observed. Reline was found to be immiscible in Thy-based DES, Thy : camphor :: 1 : 1, in the presence of 100 mM Brij-35, Triton X-100, Tergitol, and Aerosol OT (anionic surfactant), respectively; only ca. 0.14 M reline could be solubilized in Thy : menthol :: 1 : 1 DES in the presence of 100 mM Brij-35. Another nonpolar DES, lactic acid : menthol :: 1 : 1, exhibited reline intakes of 0.96 and 0.84 M, respectively, in the presence of Brij-35 and Aerosol OT with no miscibility in the presence of Triton X-100 and Tergitol. Based on the aforementioned observations, a system composed of reline in Thy:DA DES in the presence of surfactant Brij-35 was investigated further for nonaqueous ME formation.

The reline intake and the corresponding w_{Rel} as a function of [Brij-35] are presented in Figure 1. It is interesting to note, however, that for increasing [Brij-35] of 10, 25, 50, and 75 mM, while the reline intake increases monotonically, w_{Rel} decreases to 140, 67, 37, and 29, respectively (vide infra). A ternary phase diagram of the Thy:DA/Brij-35/reline system was constructed via visual observation. Reline was added to the various desired mass ratios of Thy:DA and Brij-35 (1 : 0 to 0 : 1 with 0.1 mass ratio difference) until the mixture was clear and transparent (Figure 2). While the dark shaded area in the phase diagram represents the multiphase region which is turbid

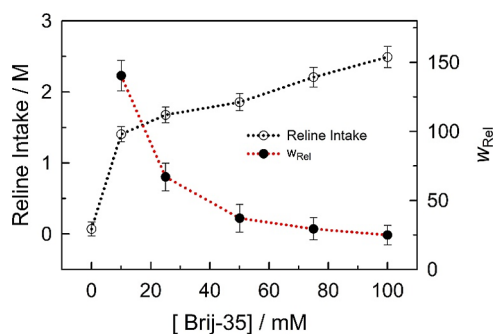


Figure 1. Reline intake and reline loading (w_{Rel}) within the Brij-35-added Thy:DA system at various concentrations of Brij-35 under ambient conditions.

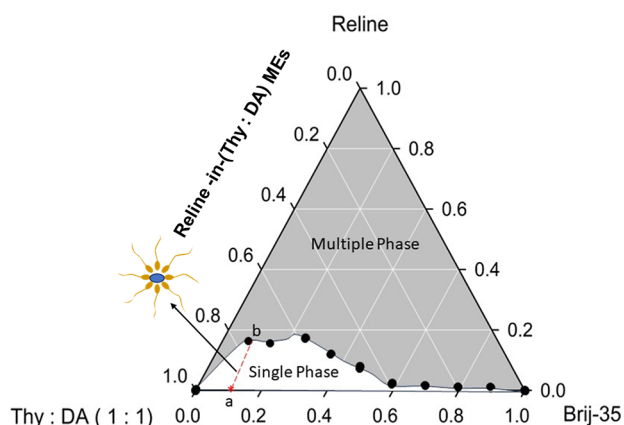


Figure 2. Ternary phase diagram of the system consisting of Thy:DA DES, Brij-35, and reline under ambient conditions. Components are expressed in mass fractions. The system is explored through the dotted line a...b.

and also shows some crystal formation, the nonshaded area is the single-phase region which is clear/transparent and homogeneous. The area under the multiphase region and the single-phase region is calculated from the procedure mentioned in the literature¹⁸ and found to be 86% and 14%, respectively. The system has been further explored along the dotted line a...b, where “a” corresponds to 100 mM Brij-35 dissolved in Thy:DA and “b” corresponds to 2.5 M reline in 100 mM Brij-35 solution of Thy:DA. The nonaqueous MEs—polar DES-in-nonpolar DES, i.e., [reline-in-Thy:DA]—are proposed to be formed in this single-phase region.

The initial evidence of the presence of polar DES-in-nonpolar DES MEs formed by Brij-35 is afforded by dynamic light scattering (DLS) data (Figure 3A). By increasing [reline] in 100 mM Brij-35 solution in Thy:DA, the data show the presence of aggregates. The DLS data are characterized by bimodal curves that possibly indicate the presence of smaller aggregates with size < 2 nm and of bigger aggregates with size in the 2–10 nm range. The characterization of smaller aggregates is under further investigation currently; we tentatively attribute them as being the reverse micelles with smaller size. Importantly, the bigger aggregates are assigned to the reline-in-Thy:DA MEs formed due to the presence of Brij-35, with the reline pool size increasing with increasing [reline] (Figure 3B). The formation of Brij-35 assisted nonaqueous MEs with polar DES pools and nonpolar DES as the bulk phase is corroborated nonetheless.

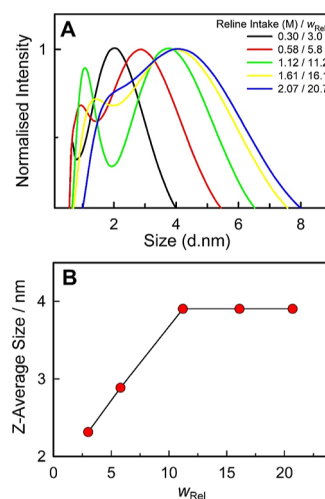


Figure 3. Representative DLS spectra (A) and average size (B) of MEs within 100 mM Brij-35-added Thy:DA system at different amounts of reline under ambient conditions.

Dynamic viscosity (η) has been a key property to characterize MEs, especially, the w/o type.^{12,19} The experimentally obtained η values (at 298 K) of 100 mM Brij-35 solution of Thy:DA in the absence and presence of up to 2.5 M reline are presented in Figure 4A. While the η value of 100 mM Brij-35 in Thy:DA is measured to be only 26.34 mPa.s, that of neat reline is reported to be 1398 mPa.s at 298 K.²⁰ A careful examination of the experimental η data reveals, however, that the addition of up to 2.5 M reline (corresponding to ca. 0.35 mole fraction of reline in the solution) results in only a very gradual increase in η (η increases to only 43.06 mPa.s). With a considerably high η of reline in comparison, one would expect the η value to be much higher as reline is added [η_{ideal} values are estimated using the equation $\ln \eta_{\text{ideal}} = \chi_1 \ln \eta_1 + \chi_2 \ln \eta_2$,²¹ where χ_1 , χ_2 and η_1 , η_2 are the mole fractions and viscosities of 100 mM Brij-35 added Thy:DA and reline, respectively, and are presented in Figure 4A along with the experimental values], and the experimental η values are considerably lower, indicating the formation of reline-in-Thy:DA MEs within the system. It is stated that one of the conditions of the presence of MEs in such solutions is that η of the ME solution should not be very different from that of η of the bulk solvent.¹² The presence of reline-in-Thy:DA MEs is clearly supported by the η data. Similarly, the electrical conductivity (κ) data of the aforementioned system also support the presence of reline-in-Thy:DA MEs within the system (Figure 4B). With κ of reline being fairly high ($400 \mu\text{S cm}^{-1}$)²⁰ and that of 100 mM Brij-35 in Thy:DA being fairly low ($0 \mu\text{S cm}^{-1}$), one would expect κ to increase dramatically as up to 2.5 M reline (ca. 0.35 mole fraction) is added. However, the increase in κ is miniscule ($1.4 \mu\text{S cm}^{-1}$) in comparison, implying that reline is not dispersed but rather present in ME pools only. The FTIR absorbance of Thy:DA, 100 mM Brij-35 in Thy:DA with and without reline, and reline alone indicates no emergence of the reline spectral feature (3200 cm^{-1}) as up to 2.5 M reline added to 100 mM Brij-35 solution of Thy:DA implies reline to be not present in the dispersed phase (Figure 4C). The possibility that reline is predominantly located in ME pools is further supported.

Finally, the solvatochromic spectral responses of two fluorescence probes further corroborate the presence of reline-in-Thy:DA MEs in our system. Intramolecular excimer formation by the probe 1,3-bis-(1-pyrenyl)propane [Py(3)Py]

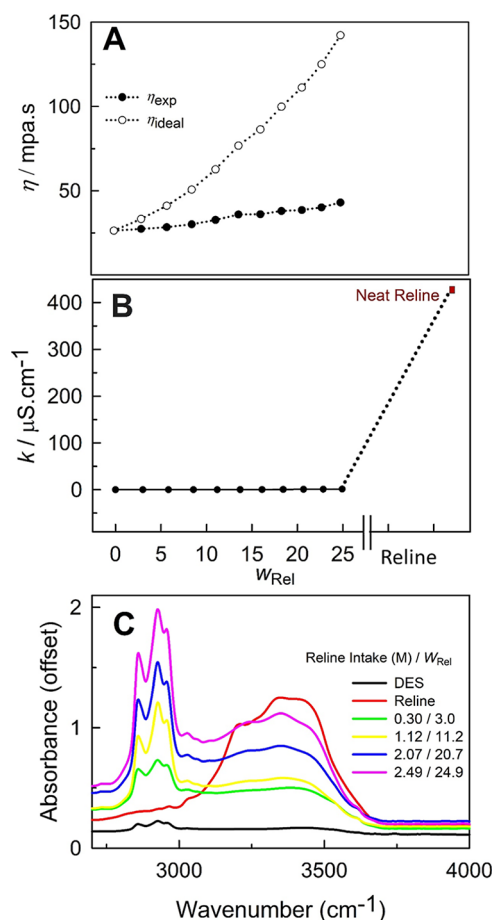


Figure 4. Experimentally determined viscosity (η_{exp}) and theoretically estimated viscosity (η_{ideal}) (A), electrical conductivity (κ) (B), and FTIR absorbance spectra (C) of 100 mM Brij-35-added Thy:DA system at different amounts of reline under ambient conditions.

is manifested via fluorescence emission spectra of the probe in Figure 5A. While the high-energy structured spectral features characterize fluorescence emission from pyrenyl moieties, the low-energy broad structureless band is due to the formation of intramolecular excimers.²² It is clear that up to 2.5 M addition of reline to 100 mM Brij-35 solution of Thy:DA, the intramolecular excimer band maxima are more or less constant at 500 ± 3 nm, with no appreciable change in the band broadness; a much broader band for [Py(3)Py] is clearly seen in reline with the excimer band maxima shifted bathochromically to 513 nm. No shift in excimer band maxima combined with no change in band shape and/or broadness implies that the [Py(3)Py] cybotactic region undergoes no change as reline is added to 100 mM Brij-35 solution of Thy:DA. Being nonpolar in nature, [Py(3)Py] is preferentially solvated in the nonpolar bulk region constituted predominantly of Thy:DA and that no dispersed reline is present within the system; dispersed reline would result in changes in the band shape and excimer band maxima. Another fluorescence probe DCVJ also exhibits a similar behavior [Figure 5B presents the fluorescence emission spectra of DCVJ in reline added to 100 mM solution of Brij-35 in Thy:DA and reline alone]. Similar to that observed for [Py(3)Py], the fluorescence emission maxima of DCVJ also do not change statistically (emission maxima at 497 ± 3 nm) as reline is added to Thy:DA solution containing Brij-35; however, in reline alone, the band maximum is at a

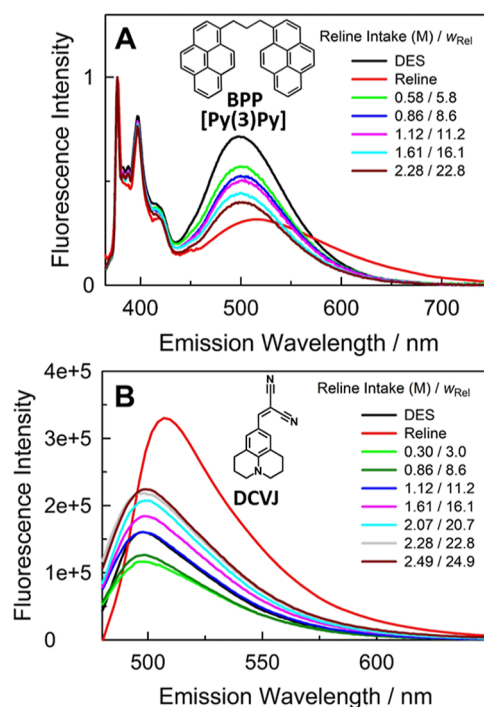


Figure 5. Fluorescence emission spectra of [Py(3)Py] [25 μM , $\lambda_{ex} = 344$ nm (A)] and DCVJ [25 μM , $\lambda_{ex} = 472$ nm (B)] in DES, reline, and 100 mM Brij-35-added Thy:DA system at different amounts of reline under ambient conditions.

considerably lower energy (507 nm). This also implies that reline is not dispersed in the system; rather, it forms ME pools.

CONCLUSIONS

Depending on its constituents, a DES may be highly polar or highly nonpolar in nature. Polar DES-in-nonpolar DES nonaqueous MEs are formed using nonionic surfactant Brij-35 as the emulsifying agent, with polar DES reline forming the ME pools and nonpolar DES Thy:DA constituting the bulk oil phase. Reline loading (w_{Rel}) as high as 25 is achieved. Ternary phase diagram, DLS, dynamic viscosity, electrical conductivity, FTIR absorbance, and fluorescence probe responses corroborate and characterize these MEs. These nonaqueous environmentally benign MEs may open new application avenues from drug delivery to nanomaterial synthesis.

AUTHOR INFORMATION

Corresponding Author

Siddharth Pandey – Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India; orcid.org/0000-0003-3175-5353; Phone: +91-11-26596503; Email: sipandey@chemistry.iitd.ac.in; Fax: +91-11-26581102

Authors

Anushis Patra – Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India
Anjali – Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsphyschemau.4c00031>

Author Contributions

CRedit: **Anushis Patra** data curation, formal analysis, investigation, methodology, validation, visualization, writing-review & editing; **Anjali** formal analysis, methodology, writing-original draft; **Siddharth Pandey** conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, software, supervision, validation, visualization, writing-original draft, writing-review & editing.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was generously funded by the Council of Scientific & Industrial Research, EMR-II (CSIR-EMR-II), GoI through a grant to S.P. [grant number 01(3043)/21/EMR-II]. The authors gratefully acknowledge Science and Engineering Research Board (SERB), GoI for providing funding [grant no. CRG/2021/000602] for the Malvern Nano ZSU3200-Pro Blue instrument. The authors also thank the Central Research Facility at IIT Delhi, for FTIR. A.P. and Anjali thank the Indian Institute of Technology, Delhi for the doctoral fellowship.

REFERENCES

- (1) Luisi, P. L.; Straube, B. E. *Reverse Micelles*; Plenum Press: New York, 1984.
- (2) Moulík, S. P.; Paul, B. K. Structure, Dynamics and Transport Properties of Microemulsions. *Adv. Colloid Interface Sci.* **1998**, *78*, 99–195.
- (3) Langevin, D. Microemulsions. *Acc. Chem. Res.* **1988**, *21*, 255–260.
- (4) Van Horn, W. D.; Ogilvie, M. E.; Flynn, P. F. Reverse Micelle Encapsulation as a Model for Intracellular Crowding. *J. Am. Chem. Soc.* **2009**, *131*, 8030–8039.
- (5) Paul, B. K.; Moulík, S. P. Uses and Applications of Microemulsions. *Curr. Sci.* **2001**, *80*, 990–1001.
- (6) Misra, A.; Florence, K.; Lalan, M.; Shah, T. Surfactants and Block Copolymers in Drug Delivery. *Colloids Drug Delivery* **2010**, *20100581*, 1–53.
- (7) Zhou, J.; Wei, C.; Jia, G.; Wang, X.; Feng, Z.; Li, C. Formation and Stabilization of G-Quadruplex in Nanosized Water Pools. *Chem. Commun.* **2010**, *46*, 1700–1702.
- (8) Eastoe, J.; Gold, S.; Rogers, S. E.; Paul, A.; Welton, T.; Heenan, R. K.; Grillo, I. Ionic Liquid-in-Oil Microemulsions. *J. Am. Chem. Soc.* **2005**, *127*, 7302–7303.
- (9) Danielsson, I.; Lindman, B. The Definition of Microemulsion. *Colloids Surf.* **1981**, *3*, 391–392.
- (10) Khan, M. F.; Singh, M. K.; Sen, S. Measuring Size, Size Distribution, and Polydispersity of Water-in-Oil Microemulsion Droplets Using Fluorescence Correlation Spectroscopy: Comparison to Dynamic Light Scattering. *J. Phys. Chem. B* **2016**, *120*, 1008–1020.
- (11) Jadhav, C. M.; Shinde, S. M.; Kate, V. K.; Payghan, S. A. Investigating Application of Non Aqueous Microemulsion for Drug Delivery. *Asian J. Biomed. Pharm. Sci.* **2014**, *4*, 1–9.
- (12) Correa, N. M.; Silber, J. J.; Riter, R. E.; Levinger, N. E. Nonaqueous Polar Solvents in Reverse Micelle Systems. *Chem. Rev.* **2012**, *112*, 4569–4602.
- (13) Cheng, S.; Zhang, J.; Zhang, Z.; Han, B. Novel Microemulsions: Ionic Liquid-in-Ionic Liquid. *Chem. Commun.* **2007**, *24*, 2497–2499.
- (14) Gradzielski, M.; Duvail, M.; de Molina, P. M.; Simon, M.; Talmon, Y.; Zemb, T. Using Microemulsions: Formulation Based on Knowledge of Their Mesostucture. *Chem. Rev.* **2021**, *121*, 5671–5740.
- (15) Pal, M.; Rai, R.; Yadav, A.; Khanna, R.; Baker, G. A.; Pandey, S. Self-Aggregation of Sodium Dodecyl Sulfate within (Choline Chloride + Urea) Deep Eutectic Solvent. *Langmuir* **2014**, *30*, 13191–13198.
- (16) Wu, J.; Yin, T. Amphiphilic Deep Eutectic Solvent Based on Lidocaine and Lauric Acid: Formation of Microemulsion and Gel. *Langmuir* **2022**, *38*, 1170–1177.
- (17) Sakuragi, M.; Tsutsumi, S.; Kusakabe, K. Deep Eutectic Solvent-Induced Structural Transition of Microemulsions Explored with Small-Angle X-Ray Scattering. *Langmuir* **2018**, *34*, 12635–12641.
- (18) Berkman, M.; Güleç, K. Pseudo Ternary Phase Diagrams: A Practical Approach for the Area and Centroid Calculation of Stable Microemulsion Regions. *Istanbul J. Pharm.* **2021**, *51*, 42–49.
- (19) Kaur, G.; Chiappisi, L.; Prévost, S.; Schweins, R.; Gradzielski, M.; Mehta, S. K. Probing the Microstructure of Nonionic Microemulsions with Ethyl Oleate by Viscosity, ROESY, DLS, SANS, and Cyclic Voltammetry. *Langmuir* **2012**, *28*, 10640–10652.
- (20) Agjeienko, V.; Buchner, R. Densities, Viscosities, and Electrical Conductivities of Pure Anhydrous Reline and Its Mixtures with Water in the Temperature Range (293.15 to 338.15) K. *J. Chem. Eng. Data* **2019**, *64*, 4763–4774.
- (21) Kadyan, A.; Pandey, S. Microviscosity Offered by Ionic Liquids and Ionic Liquid-Glycol Mixtures Is Probe Dependent. *J. Phys. Chem. B* **2017**, *121*, 1081–1091.
- (22) Baker, G. A.; Baker, S. N.; McCleskey, T. M. Noncontact Two-Color Luminescence Thermometry Based on Intramolecular Luminophore Cyclization within an Ionic Liquid. *Chem. Commun.* **2003**, *23*, 2932–2933.