



Multiscale Molecular Modeling of Amphiphilic Polycarboxybetaine Interactions in Hydrocarbon and Deep Eutectic Solvent Environments for Sustainable Agricultural Biodiesel Purification

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Abstract

Amphiphilic polycarboxybetaines are zwitterionic polymers containing both hydrophilic and hydrophobic regions, with quaternary ammonium and carboxylate groups that enable aggregation and dissolution in diverse solvent environments. In this work, a multiscale molecular modeling approach was employed to investigate amphiphilic polycarboxybetaine interactions in deep eutectic solvent and hydrocarbon environments, providing insights relevant to sustainable agricultural biodiesel purification. Density Functional Theory calculations and classical all-atom Molecular Dynamics simulations were applied to study the solubility and intermolecular interactions of poly (octyl-, tetradecyl-, and octadecyl-grafted aminocrotonate-methacrylic acid) oligomers in octane and tetraethylammonium hydroxide/urea-based deep eutectic solvent. DFT analyses, including optimized geometries, molecular electrostatic potential maps, and non-covalent interaction surfaces, revealed distinct solvent–polymer affinities. MD simulations demonstrated that longer alkyl chains enhance aggregation in octane, while strong interactions between hydroxide ions and carboxylate groups in deep eutectic solvent promote polymer dissolution and stabilization. These multiscale insights highlight the superior solvation ability of deep eutectic solvents compared to hydrocarbons and underscore their potential as green, tunable media for polymer solvation processes associated with biodiesel purification. This study advances molecular-level understanding of how solvent environments modulate amphiphilic polycarboxybetaine behavior, supporting the design of environmentally friendly solvents for energy and materials applications.

Keywords: Amphiphilic polycarboxybetaines; Hydrocarbon; Deep eutectic solvent; Biodiesel purification; Molecular modeling.

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1. Introduction

Zwitterionic polymers, like polybetaine, are gaining attention as solvents and biomaterials for their antifouling, antimicrobial properties, and design flexibility. Polybetaine consists of repeating units with both cationic and anionic functional groups, resulting in a neutral overall structure. Different types of polybetaines offer unique characteristics and applications. Among them, polycarboxybetaines (PCB) are particularly notable for their exceptional hydrating properties.^[1–3] They interact ionically with biomolecules that

contain amino groups, making them ideal for applications requiring hydration and biological compatibility. Poly(sulfobetaines) (PSB) are another notable type, known for their stability and responsiveness to environmental changes. These features make PSBs highly valuable in drug delivery systems, where adaptability is crucial. Poly(phosphobetaines) (PPB) are another class with potential in forming biodegradable nanogels.^[4–6] These nanogels provide key benefits for drug encapsulation and controlled release, combining biocompatibility with enhanced functionality for diverse therapeutic applications.^[7–11]

Amphiphilic PCB, a specific class of zwitterionic polymers, possess both hydrophilic and hydrophobic regions with quaternary ammonium and carboxylate groups, allowing solubility in various environments. Amphiphilic PCBs have

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shown significant promise as paraffin inhibitors in crude oil systems.^[12-15]

Furthermore, PCB's solubility in octane is a critical factor that influences their performance. Traditionally, solvents like N-methyl pyrrolidone, N,N-dimethylformamide, and dimethylacetamide are employed to dissolve PCB.^[16-18] While effective, these solvents pose environmental and safety concerns, necessitating the development of more sustainable alternatives. Deep eutectic solvents (DES) have emerged as promising alternative solvents, providing a sustainable approach to enhance the solubility of poorly soluble compounds.^[19-25] Studies on cellulose dissolution in DES underscore their versatility, as shown by Sirviö and Heiskanen, who demonstrated the 35 wt% of aqueous tetraethylammonium hydroxide (TEAOH) combined with urea dissolved up to 3 wt% cellulose.^[26-27] These insights suggest that DESs could similarly improve the solubility of amphiphilic PCB, offering a sustainable and efficient alternative for industrial applications.

While the solubility of PCB-based polymers in polar aprotic solvents such as N-methyl pyrrolidone, N,N-dimethylformamide, and dimethylacetamide has been extensively studied, and their octanol-water partitioning behavior is well documented, direct experimental data on their solubility in non-polar solvents like octane remains scarce. This gap is critical, as octane serves as a representative non-polar medium relevant to both industrial processing and environmental partitioning scenarios.^[28,29] Without clear solubility data in non-polar systems, understanding the behavior, separation, and environmental fate of PCBs remains incomplete. Moreover, the reliance on traditional polar solvents raises environmental and safety concerns, highlighting the urgent need for alternative, greener solvent systems. DESs have recently emerged as sustainable candidates for improving the solubility of poorly soluble compounds, but their application to amphiphilic PCBs has not been fully explored. Therefore, this study seeks to systematically investigate PCB solubility in octane, filling a critical knowledge gap and supporting the design of more sustainable and efficient solvent systems for industrial applications. In this context, octane is employed as a model hydrocarbon to mimic non-polar oil environments typically encountered in biodiesel production and purification processes. This approach allows us to capture the molecular interactions relevant to real-world biodiesel systems while maintaining computational tractability. By coupling octane-based simulations with deep eutectic solvent environments, the

present work bridges the understanding between non-polar and polar solvent behaviors, offering valuable molecular-level insights for optimizing polymer-assisted biodiesel purification. The findings provide a foundation for developing green solvent systems that enhance separation efficiency, reduce chemical waste, and advance sustainable fuel-processing technologies.

In this work, Density Functional Theory (DFT) calculations, and classical all-atom Molecular Dynamics (MD) simulations were performed to investigate the aggregation and dissolution behavior of amphiphilic PCB in octane and DES environments. The atomistic simulations capture the detailed interactions of amphiphilic PCB, providing insights into the factors that govern their solubility. Specifically, the impact of varying alkyl chain lengths and solvent compositions on aggregation and dissolution behavior was analyzed. The study focuses on oligomers such as poly(octyl-grafted aminocrotonate-methacrylic acid) (P(OACRO-MAA)), poly(tetradecyl-grafted aminocrotonate-methacrylic acid) (P(TDACRO-MAA)), and poly(octadecyl-grafted aminocrotonate-methacrylic acid) (P(ODACRO-MAA)). Additionally, the effects of solvents, including octane and TEAOH/urea-based DES, are explored. In subsequent sections, a description of the theoretical models, DFT calculation methodologies and classical all-atom MD simulation methodologies is presented. The findings aim to provide a comprehensive understanding of amphiphilic PCB behavior, paving the way for the development of advanced, sustainable materials for diverse applications.

2. Methodology

2.1 System of interest

Computational models for DFT calculations and classical all-atom MD simulations were performed on oligomers of P(OACRO-MAA), P(TDACRO-MAA), and P(ODACRO-MAA) (three-monomer units), as amphiphilic PCBs models (Fig. 1a), with octane (Fig. 1b) and TEAOH/urea-based DES (Fig. 1c, and Fig. 1d) as solvents. These models were inspired by experimental studies on similar systems, providing insights into their synthesis and properties.^[11,30,31] Further experimental details supporting these computational designs are available in related literature, ensuring alignment with established methodologies.^[32,33] This approach bridges experimental and computational perspectives, facilitating the investigation of solvent-dependent aggregation and dissolution behaviors of amphiphilic PCBs at the molecular level.

During the DFT calculation, the monomer of P(OACRO-MAA) was optimized, followed by octane, deep eutectic solvent (DES), and later P(OACRO-MAA) monomer – octane complex, and P(OACRO-MAA) monomer – DES complex. For the classical all-atom MD simulation, Table 1 summarizes the designed systems used to explore the interactions of amphiphilic PCBs with octane and TEAOH/urea-based DES. Three amphiphilic PCBs (P(OACRO-MAA), P(TDACRO-MAA), and P(ODACRO-MAA)) were examined in two

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distinct setups. In the first setup, ten oligomers of each octane molecules. In the second setup, the PCBs were dissolved in a DES system comprising 500 TEAOH and 1000 urea. The selection of a 10:1000 ratio for PCB to octane (as well as for PCB to DES) was based on its widespread use in the literature as a representative solvation model for PCB in hydrocarbon systems.^[24-26] This ratio ensures a realistic simulation of PCB solvation behavior under typical conditions. Similarly, the choice of a 1:2 TEAOH-to-urea ratio was motivated by its demonstrated effectiveness in enhancing polymer solubility, as reported in previous studies.^[26,27] This specific ratio optimizes the dissolution process, facilitating better interaction between the polymer and the solvent environment. The total number of atoms per simulation system ranged from 25200 to 28600, depending on molecular composition and solvent configuration. These simulations provide a detailed view of the molecular-level interactions between PCBs and their solvent environments. By examining different alkyl chain lengths of PCBs and contrasting solvent polarities, this study investigated the influence of these factors on aggregation and dissolution behaviors. The findings aim to shed light on the solubility and structural organization of PCBs, contributing to a better understanding of their potential applications in diverse fields such as materials science and green solvent systems.

In this study, octane was employed as a simplified model for hydrocarbon-based biofuel oil, which allows computational efficiency but does not fully capture the compositional complexity of real biodiesel mixtures. Similarly, the amphiphilic polycarboxybetaine oligomers (three-monomer units) were used as representative model fragments of the full polymeric membrane systems. While these models successfully reproduce key interaction trends and solvation behaviors, they inherently simplify the chemical and structural diversity present in experimental biodiesel purification media.^[25-30]

The choice of a 1:2 TEAOH-to-urea ratio was based on

amphiphilic PCB were simulated in the presence of 1000 prior experimental and computational studies demonstrating that this composition forms a highly stable eutectic mixture with a strong hydrogen-bonding network. This ratio has been shown to maximize solvation capability and enhance polymer dissolution efficiency in TEAOH/urea-based DESs.^[30-33] Accordingly, this established eutectic ratio was adopted in our simulations to ensure realistic representation of DES–polymer interactions.

2.2 DFT calculations

DFT calculations were performed to explore the intermolecular interactions of P(OACRO-MAA) monomer with octane and DES. Calculations utilized the B3LYP^[34,35] functional, widely recognized for accuracy in systems comparable to ours, along with the 6-311++G(d,p) basis set, as implemented in Gaussian16.^[36] Visualization and detailed analysis of the DFT results were conducted using GaussView 6.0 and the Multiwfn program package.^[37,38]

The first step involved obtaining optimized structures for the P(OACRO-MAA) monomer in the presence of octane, followed by optimization in the presence of DES. The net charge of the P(OACRO-MAA) monomer was modeled as neutral. All optimized structures were confirmed as global energy minima by frequency calculations, which showed no imaginary frequencies. Fig. 2 illustrates the optimized structures.

The optimized structures were used to extract key structural and electronic properties, including bond lengths, MEP maps, RDG, and noncovalent interactions. These results provided comprehensive insights into the nature of interactions in these systems. DFT outcomes were compared with those from classical all-atom MD simulations, strengthening the reliability of conclusions. The DFT calculations not only elucidated molecular-level details but also complemented the dynamic insights obtained from MD simulations.

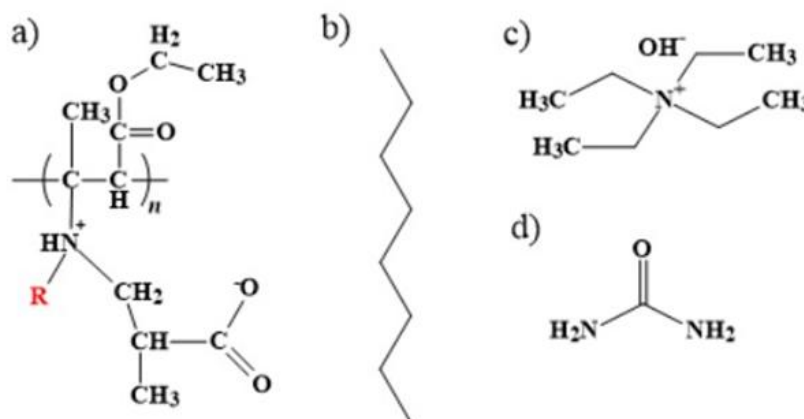


Fig. 1: 2D structures of (a) amphiphilic PCB with varying hydrophobic tail lengths (R = octylamine, tetradecylamine, octadecylamine); (b) octane; (c) tetraethylammonium hydroxide; (d) urea.

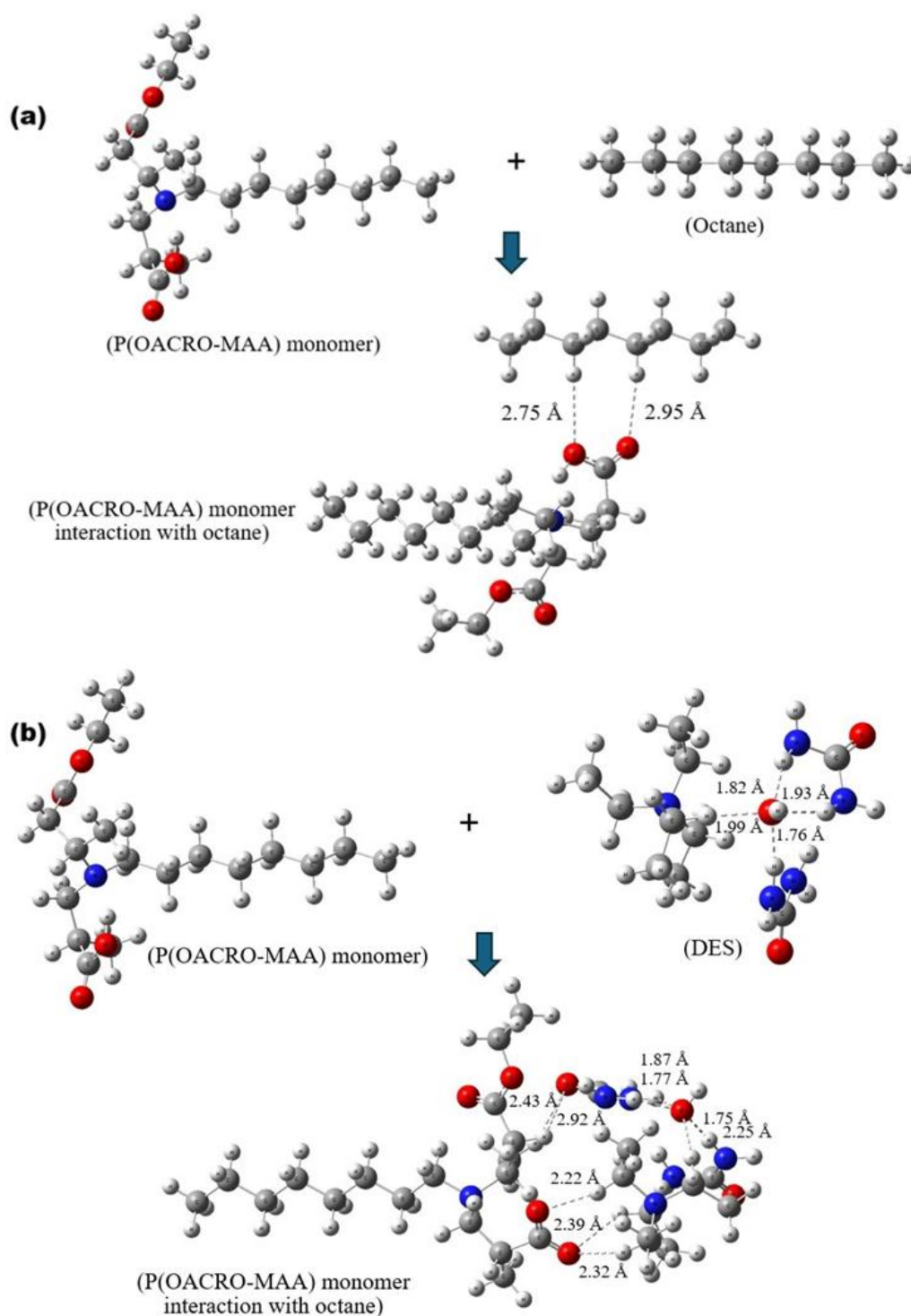


Fig. 2: Optimized structures of (a) P(OACRO-MAA) monomer, octane, and then P(OACRO-MAA) interaction with octane, and (b) optimized structures of P(OACRO-MAA) monomer, DES, and then P(OACRO-MAA) interaction with DES. Color scheme: white (hydrogen); grey (carbon); red (oxygen); blue (nitrogen).

Table 1: Description of designed classical all-atom MD simulations.

	PCB	Octane	TEA	OH ⁻	Urea	Number of atoms
P(OACRO-MAA)	10	1000	-	-	-	27700
	10	-	500	500	1000	25200
P(TDACRO-MAA)	10	1000	-	-	-	28240
	10	-	500	500	1000	25740
P(ODACRO-MAA)	10	1000	-	-	-	28600
	10	-	500	500	1000	26100

2.3 Classical all-atom MD simulations

Classical all-atom MD simulations were conducted to investigate the aggregation or dissolution behaviors of three amphiphilic PCBs (P(OACRO-MAA), P(TDACRO-MAA), and P(ODACRO-MAA)) in octane and TEOH/urea-based DES, as depicted in Fig. 1. The initial topology and force field parameters for the PCBs, octane, TEOH, and urea were derived from the Automated Topology Builder (ATB) database,^[39] ensuring compatibility with the Gromos54a7 force field.^[40]

A cubic simulation box with dimensions of $5 \times 5 \times 5 \text{ nm}^3$ was constructed, containing oligomers of the PCBs and the solvent molecules, as detailed in Table 1. The initial configurations underwent energy minimization to reduce the maximum force to below 1000 kJ/mol/nm, optimizing the system's stability. Equilibration was conducted in two phases: first in an NVT ensemble at 298 K for 0.1 ns to stabilize temperature, followed by an NPT ensemble for 0.1 ns at 298 K and 1 bar to stabilize pressure. Production runs of 30 ns followed, during which the self-assembly dynamics of the PCBs were observed.

In order to preserve molecular geometry, bond lengths were constrained using the LINCS algorithm. A 1.0 nm cutoff was applied for short-range interactions, while long-range electrostatic interactions were computed using the Particle Mesh Ewald (PME) method with a grid spacing of 0.16 nm.^[41] The Nose-Hoover thermostat maintained the temperature at 298 K,^[42] while the Berendsen barostat^[43] stabilized the pressure at 1 bar. Periodic boundary conditions were applied in all spatial dimensions to simulate an infinite system.

The calculated simulation densities of 0.7 g/cm³ for amphiphilic PCBs in octane system and 1.1 g/cm³ for amphiphilic PCBs in DES system closely matched experimental values reported in the literature, validating the accuracy of the simulation setup.^[28-33] All simulations were performed using GROMACS 2021.4.^[44] Visualization of molecular configurations and analysis of radial distribution functions (RDFs) and interaction energies were conducted using Visual Molecular Dynamics (VMD) software. These simulations provided insights into the self-assembly and solvent interactions of amphiphilic PCBs at the molecular level.

The GROMOS54a7 force field was selected because it is widely validated for simulating organic molecules, zwitterionic species, and hydrogen-bond-rich systems such as TEOH/urea-based DES.^[45-48] Its compatibility with ATB-generated parameters and proven reliability in previous DES and polymer-solvent simulations further support its suitability for the present study.

Although a production run of 30 ns was performed in this study, we acknowledge that this duration may not fully capture long-timescale equilibration processes typically associated with DES systems.^[49-51] Therefore, the results should be interpreted with this limitation in mind.

3. Results and discussion

3.1 DFT calculation results

DFT-based quantum chemical calculations offer crucial insights into the intermolecular interactions of a monomeric representative of P(OACRO-MAA) with octane and TEOH/urea-based DES. This section highlights analyses such as optimized structures, MEP maps, RDG, and NCI snapshots.

3.1.1 Optimized structures

Fig. 2a illustrates the optimized structures of the P(OACRO-MAA) monomer, octane, and their interaction. Initially, the carboxylate group in the P(OACRO-MAA) monomer exhibits distinct bond lengths: the first C–O bond measures 1.20 Å, while the second C–O bond is 1.34 Å. Upon introducing octane, a noticeable interaction occurs near the carboxylate group, leading to slight structural adjustments. The first C–O bond length increased to 1.21 Å, and the second C–O bond extended to 1.35 Å, suggesting a subtle influence of octane on the electronic distribution within the carboxylate group. Additionally, the proximity between the nearest hydrogen atom of octane and the oxygen atom in the carboxylate group shifts, measuring 2.75 Å and 2.95 Å, respectively. These structural variations highlight weak van der Waals interactions between octane and the polar carboxylate group, which may play a role in stabilizing P(OACRO-MAA) in a hydrophobic environment.

Fig. 2b presents the optimized structures of the P(OACRO-MAA) monomer, DES, and their interaction. As noted above, the carboxylate group in P(OACRO-MAA) initially exhibited bond lengths of 1.20 Å and 1.34 Å. Likewise, the ester group has bond lengths of 1.20 Å and 1.35 Å. However, upon introducing DES, significant structural changes occur due to strong interactions with the carboxylate and ester groups. The carboxylate bond lengths increased to 1.24 Å and 1.36 Å, while the ester bond lengths shift slightly to 1.21 Å and 1.34 Å. These changes indicate that DES stabilizes the carboxylate group through hydrogen bonding and electrostatic interactions. Furthermore, the distance between the nearest hydrogen atom of DES and the oxygen atom of the carboxylate group varies from 2.22 Å to 2.92 Å, suggesting strong hydrogen bonding interactions between these molecules. These structural modifications highlight the enhanced stabilization provided by DES compared to non-polar solvents like octane.

3.1.2 Molecular electrostatic potential maps

Fig. 3a presents the MEP maps of the P(OACRO-MAA) monomer, octane, and their interaction. Before introducing octane, the MEP of P(OACRO-MAA) reveals regions of high electronegativity around the carboxylate and ester functional groups, indicating strong electron density localization due to the presence of oxygen atoms. In contrast, pure octane exhibits a lower electronegativity distribution, reflecting its non-polar nature. Upon interaction with octane, a shift in the MEP map occurs, with the higher electronegativity region of the

carboxylate group becoming more localized near octane. This suggests weak but noticeable van der Waals interactions between the polar carboxylate group and the non-polar octane. The redistribution of electron density highlights the limited compatibility of P(OACRO-MAA) with octane, reinforcing the dominance of hydrophobic interactions in non-polar solvents. This analysis underscores the influence of solvent polarity on the electrostatic environment of amphiphilic molecules like P(OACRO-MAA).

In contrast, DES shows higher electronegativity around the oxygen atoms of the ketone group in urea and the chloride ion

(Fig. 3b). Upon interaction with the polymer, negative electrostatic potential of P(OACRO-MAA) becomes more localized around nitrogen and hydrogen atoms of urea and TEA, indicating strong hydrogen bonding and electrostatic interactions. This redistribution of charge suggests that DES provides a more structured and interactive environment compared to octane, facilitating stronger stabilizing interactions. The MEP analysis highlights the enhanced compatibility of P(OACRO-MAA) with DES, reinforcing its suitability for polar solvent applications.

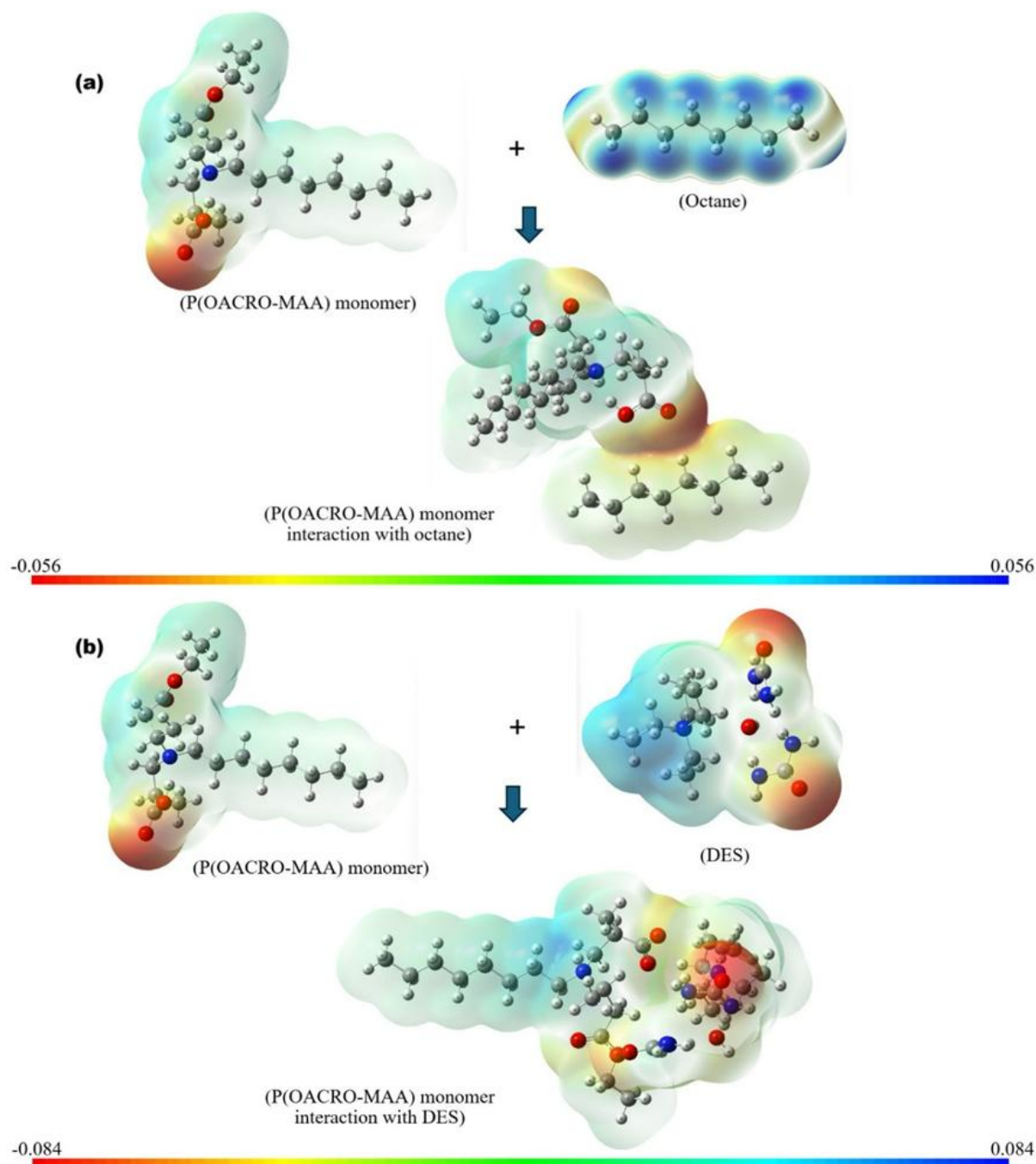


Fig. 3: (a) MEP map of P(OACRO-MAA) monomer, octane, and then P(OACRO-MAA) interaction with octane, and (b) MEP map of P(OACRO-MAA) monomer, DES, and then P(OACRO-MAA) interaction with DES. Color scheme: white (hydrogen); grey (carbon); red (oxygen); blue (nitrogen).

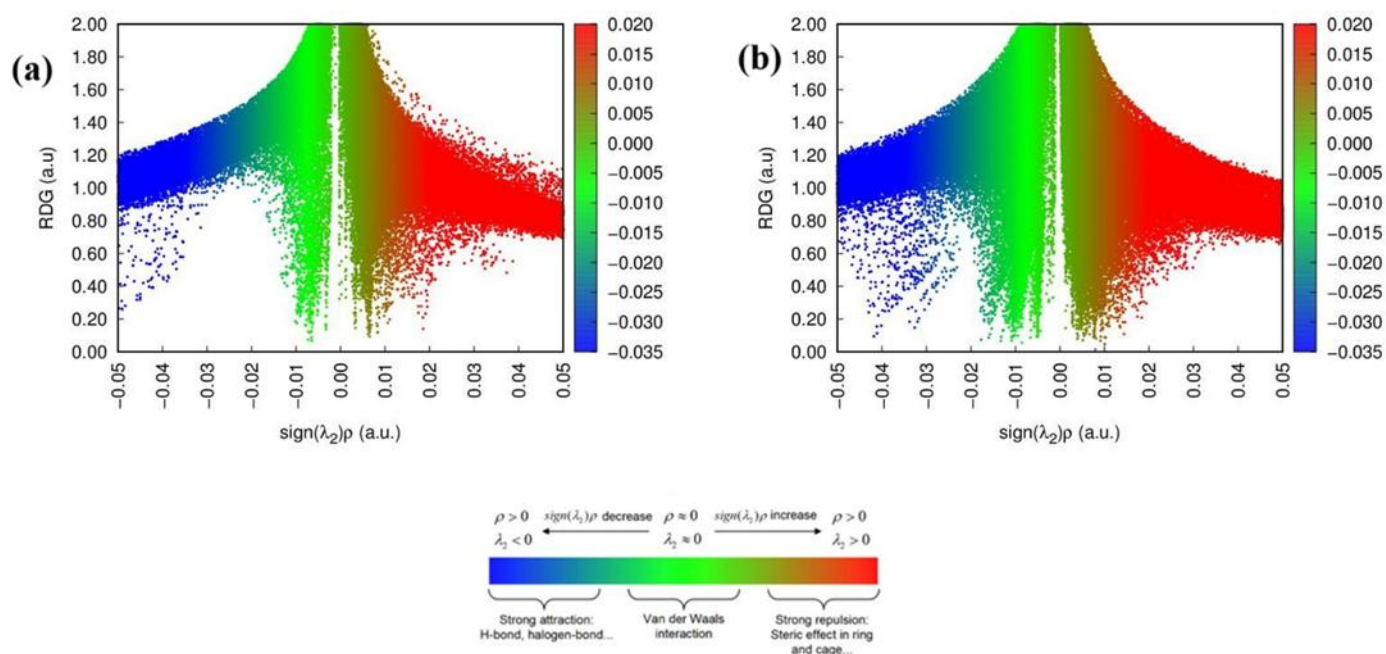


Fig. 4: RDG of P(OACRO-MAA) interaction with (a) octane, and (b) DES.

3.1.3 Reduced density gradient

Fig. 4 presents the RDG analysis of P(OACRO-MAA) interacting with (a) octane and (b) DES, highlighting the nature and strength of noncovalent interactions.

RDG is a valuable tool for identifying regions of high electron density and characterizing interactions such as hydrogen bonding, van der Waals forces, and steric repulsion. In the range of -0.05 to -0.02 a.u., stronger hydrogen bonding interactions are observed in the P(OACRO-MAA) and DES system compared to octane, indicating a more structured and interactive environment in DES. The range of -0.02 to 0.01 a.u. reveals van der Waals interactions in both systems, though these are more pronounced in the octane case due to its non-polar nature (Fig. 4a). In the 0.01 to 0.05 a.u. range, steric repulsion is more noticeable in the P(OACRO-MAA) and octane interaction, whereas it is reduced in DES, suggesting better molecular compatibility in DES (Fig. 4b).

3.1.4 Noncovalent interactions

Fig. 5a illustrates the noncovalent interactions of P(OACRO-MAA) before and after introducing octane. Initially, the monomer exhibits intramolecular hydrogen bonding and van der Waals interactions, particularly between the nitrogen atom and the hydrogen atom of the hydroxyl group, as well as between the nitrogen atom and the hydrogen atoms of the alkyl chains. These interactions contribute to the structural stability of the monomer. Upon introducing octane, these intramolecular interactions remain intact, while new van der Waals interactions emerge between the hydrogen atoms of octane and the carboxylate groups of P(OACRO-MAA). This suggests that the interaction between P(OACRO-MAA) and octane is primarily governed by weak dispersion forces rather than strong electrostatic interactions or hydrogen bonding.

Fig. 5b presents the noncovalent interactions of P(OACRO-MAA) with DES. DES itself displays a complex interaction network, including hydrogen bonding, van der Waals interactions, and strong repulsion regions, particularly in the conformations where hydroxide is centered on TEA and two urea molecules. Upon introducing DES, the original intramolecular interactions of P(OACRO-MAA) remain largely preserved. However, new hydrogen bonding and van der Waals interactions form between P(OACRO-MAA) and DES, particularly involving the carboxylate groups of P(OACRO-MAA) and hydrogen atoms of TEA and urea. These new interactions indicate that DES fosters stronger and more diverse noncovalent interactions compared to octane, reinforcing its potential as a stabilizing environment for amphiphilic molecules.

3.2 Classical all-atom MD simulation results

Classical all-atom MD simulations offer crucial insights into the molecular structures and intermolecular interactions of an oligomeric representative of P(OACRO-MAA), P(TDACRO-MAA), and P(ODACRO-MAA) with octane and TEAOH/urea-based DES. Fig. 6 presents molecular snapshots illustrating the behavior of PCBs with varying alkyl chain lengths in octane and TEAOH/urea-based DES. Specifically, the structures of P(OACRO-MAA), P(TDACRO-MAA), and P(ODACRO-MAA) are shown in both environments, providing visual insights into their dissolution and interaction profiles.

In octane (Fig. 6a, 6c, and 6e), the aggregation behavior of PCBs exhibits a decreasing trend with increasing alkyl chain length. Specifically, the shorter alkyl chains of P(OACRO-MAA) (Fig. 6a) lead to significant aggregation of the carboxylate-rich segments, which serve to minimize

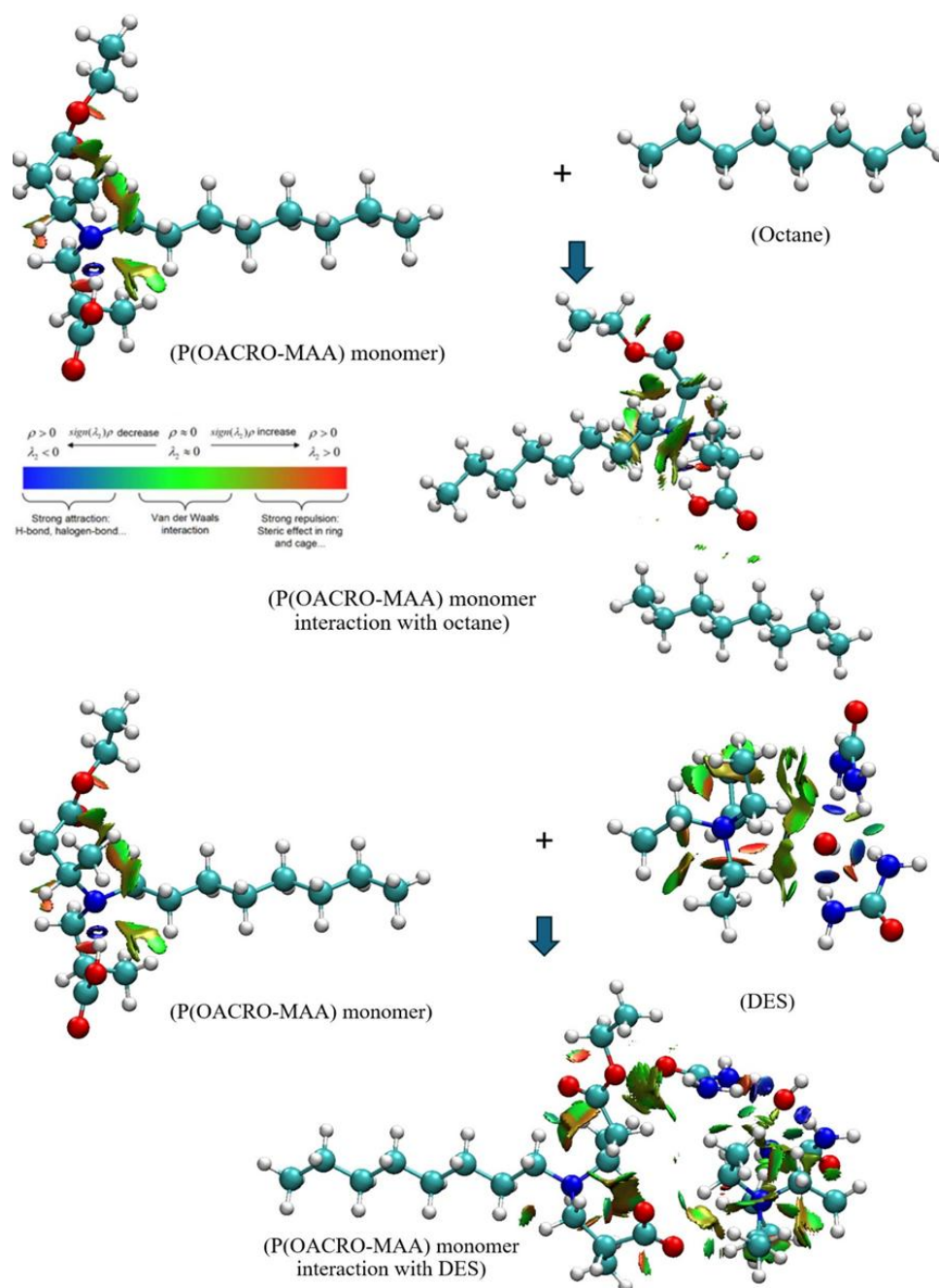


Fig. 5: (a) noncovalent interaction of P(OACRO-MAA) monomer, octane, and then P(OACRO-MAA) interaction with octane, (b) Noncovalent interaction of P(OACRO-MAA) monomer, DES, and then P(OACRO-MAA) interaction with DES. Color scheme: white (hydrogen); grey blue (carbon); red (oxygen); blue (nitrogen).

unfavorable interactions with the non-polar solvent. However, as the alkyl chain length increases, as observed in P(TDACRO-MAA) (Fig. 6c) and P(ODACRO-MAA) (Fig. 6e), the stronger hydrophobic interactions between the longer alkyl chains enhance the polymer's solubility in octane. This P(OACRO-MAA) (Fig. 6b), the carboxylate groups form strong hydrogen bonding interactions with the DES components (as also observed in the DFT and RDG analysis), promoting robust solvation. Similarly, P(TDACRO-MAA) (Fig. 6d) and P(ODACRO-MAA) (Fig. 6f) also demonstrate good solubility in the DES, with the longer alkyl chains further enhancing the interactions between the polymer and the

results in a reduced tendency for aggregation with the PCBs becoming uniformly dispersed. In contrast, in the DESs (Fig. 6b, 6d, and 6f) the PCBs exhibit significantly enhanced dissolution compared to octane, with the polymer chains becoming evenly dispersed throughout the solvent. For solvent matrix.

Visually comparing the two solvents, DES emerges as a better medium for dissolving PCBs across all chain lengths, owing to its ability to balance both hydrophilic and hydrophobic interactions. This enhanced dissolution and stabilization are observed for all polymer variants, highlighting the unique solvation properties of DES.

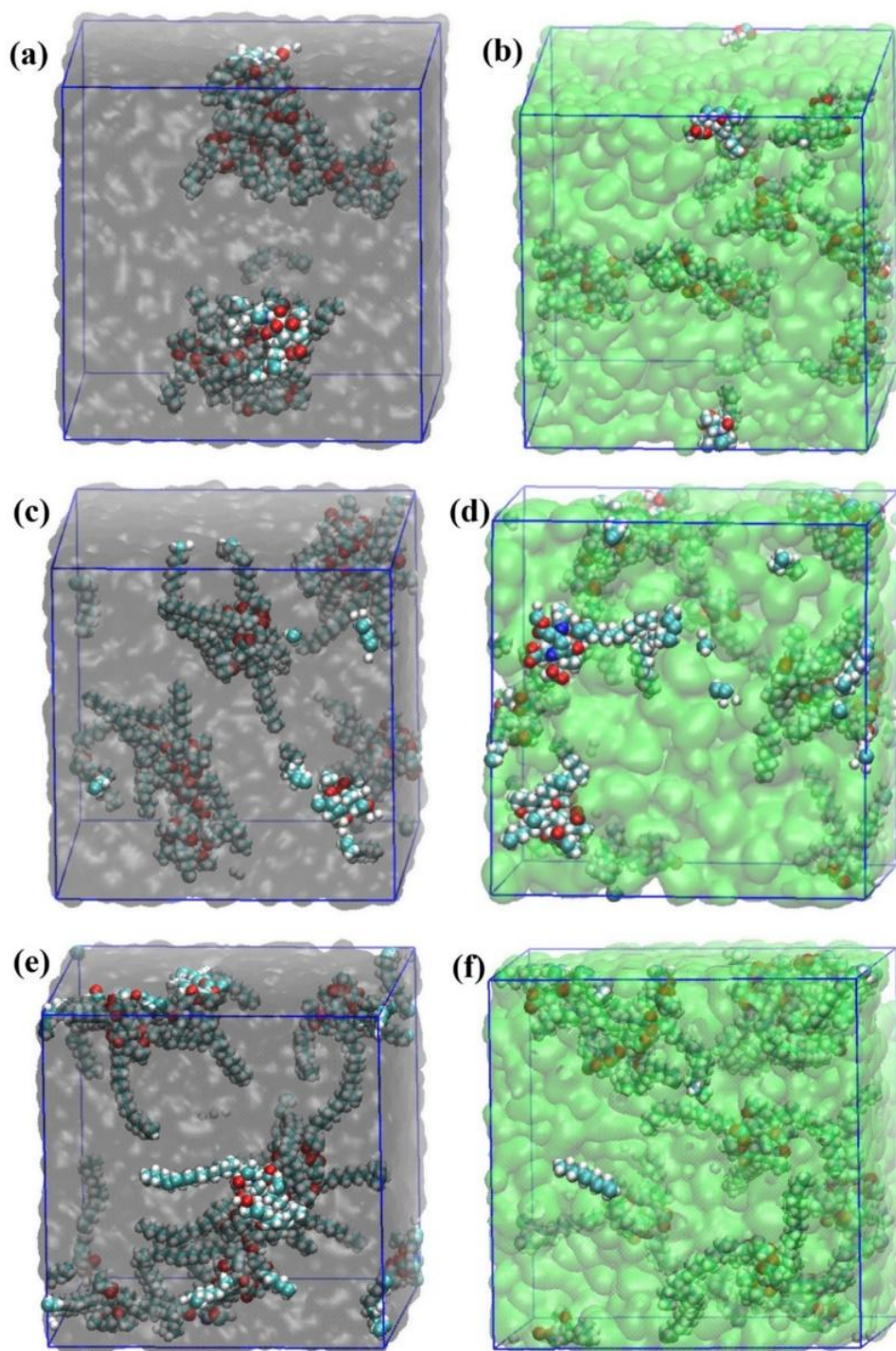


Fig. 6: Snapshot of P(OACRO-MAA) in (a) octane, (b) DES, P(TDACRO-MAA) in (c) octane, (d) DES, and P(ODACRO-MAA) in (e) octane, (f) DES. Color scheme: white (hydrogen); grey blue (carbon); red (oxygen); blue (nitrogen); black transparent iso-surface (octane); green transparent iso-surface (DES).

3.2.1 Radial distribution functions

Fig. 7 depicts the RDF between the oxygen atoms of the carboxylate groups in the three amphiphilic PCBs (P(OACRO-MAA), P(TDACRO-MAA), and P(ODACRO-MAA)) within (a) octane and (b) DES. The RDF values offer critical insights into the spatial organization and interactions of carboxylate groups of PCBs in these different environments.

In octane (Fig. 7a), P(OACRO-MAA) exhibits the highest

RDF peak value of 120.63 at 3.30 Å, indicating a strong and localized interaction between its carboxylate groups. This suggests that shorter alkyl chains enable the carboxylate groups to be in the closer proximity due to weaker hydrophobic interactions with octane. In contrast, P(TDACRO-MAA) and P(ODACRO-MAA) exhibit reduced RDF peak values of 86.39 at 4.65 Å and 42.50 at 5.50 Å, respectively, as the alkyl chain length increases. The longer alkyl chains introduce steric hindrance, causing the

carboxylate groups of PCBs to move farther apart. This observation demonstrates that the polymer's aggregation tendency decreases with longer alkyl chains, which corresponds to improved compatibility with the non-polar octane solvent.

A similar trend is observed in DES (Fig. 7b), but with a shift toward lower RDF peak values, introducing improved solvation of the carboxylate groups due to the hydrogen-bonding network of DES, which we demonstrate later. For P(OACRO-MAA), the RDF peak is 118.29 at 4.50 Å, slightly lower than in octane, yet still indicative of strong solvation interactions. P(TDACRO-MAA) shows a moderate peak value of 50.75 at 4.70 Å, and P(ODACRO-MAA) exhibits the

lowest value of 38.62 at 5.50 Å. These results suggest that the extended hydrogen-bonding and electrostatic interactions within DES effectively disrupt the aggregation of carboxylate groups, promoting enhanced dispersion of polymer in the solvent.

The decreasing RDF peak values with increasing alkyl chain length in both octane and DES highlight the significant effect of chain length on the spatial distribution of carboxylate groups. Shorter chains, as seen with P(OACRO-MAA), favor closer interactions, while longer chains, as in P(TDACRO-MAA), and P(ODACRO-MAA) promote better solvation and reduced aggregation. Optimizing alkyl chain length is key to improving solubility and polymer stability.

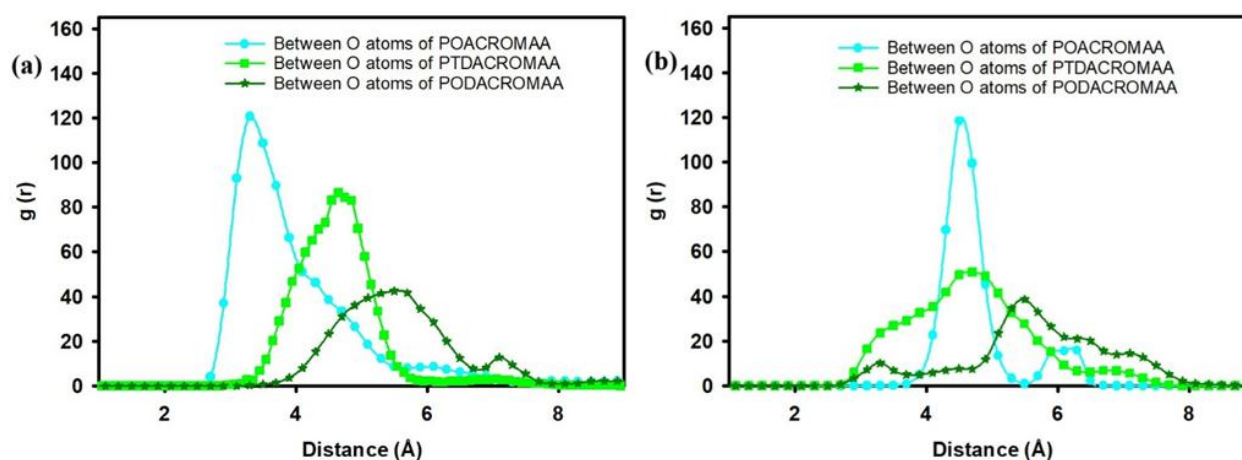


Fig. 7: RDF between oxygen atom of carboxylate group of amphiphilic polycarboxybetaines in (a) octane, and (b) DES.

Table 2: Interaction energy for amphiphilic polycarboxybetaines in octane, and DES.

Between	Interaction energies (kJ/mol)					
	P(OACRO-MAA)		P(TDACRO-MAA)		P(ODACRO-MAA)	
	Electrostatic	Van der Waals	Electrostatic	Van der Waals	Electrostatic	Van der Waals
PCBs (in octane)	-1524.45	-132.96	-444.38	-111.52	-420.38	-137.72
PCBs and octane	-1.05	-313.74	1.81	-473.52	3.04	-543.23
PCBs (DES)	-1455.84	-99.38	-369.18	-92.426	-351.53	-128.04
PCB and TEA	-35.58	-182.40	-28.59	-210.13	-12.72	-237.95
PBC and OH ⁻	-72.34	-2.84	-59.48	-4.64	-70.95	-6.35
PBC and urea	-185.35	-191.74	-227.64	-215.87	-213.65	-237.87

Fig. 8 provides further intermolecular interactions of amphiphilic polycarboxybetaines (PCBs) (P(OACRO-MAA), P(TDACRO-MAA), and P(ODACRO-MAA)) with octane and DES. In octane, the RDF between the oxygen atoms of the carboxylate group in PCBs and the hydrogen atoms of octane (Fig. 8a) highlights the role of alkyl chain length in modulating hydrophobic interactions. Specifically, longer alkyl chains in PCBs result in higher RDF peaks, signifying enhanced compatibility and solubility in the non-polar octane medium. For instance, the RDF peak value between the carboxylate oxygen of P(OACRO-MAA) and octane hydrogen is 0.41 at 2.7 Å, increasing to 0.54 for P(TDACRO-MAA) and 0.62 for P(ODACRO-MAA) at the same distance. This trend reflects stronger hydrophobic interactions with longer chains, which improve the aggregation behavior of PCBs in octane.

Moderate interactions are observed between the carboxylate oxygen and tetraethylammonium hydrogen in DES (Fig. 8b), with RDF peak values ranging from 0.58 at 2.5 Å for P(OACRO-MAA) to 0.80 at 4.39 Å for P(ODACRO-MAA). These interactions indicate significant electrostatic interactions and hydrogen bonding contributions from tetraethylammonium ions.

The RDF analysis reveals a more interactive and structured environment in DES compared to octane.

However, the strongest interactions in DES are observed between the carboxylate oxygen of PCBs and hydroxide hydrogen, driven by hydrogen bonding. The peak RDF value for this interaction increases with alkyl chain length, from 1.70 at 2.1 Å for P(OACRO-MAA) to 3.15 at 2.1 Å for P(ODACRO-MAA). This finding highlights the dominant role

of hydroxide ions in stabilizing PCBs in DES (Fig. 8c).

The relatively weaker yet notable interactions between the carboxylate oxygen and urea hydrogen show RDF peak values from 0.29 at 4.64 Å for P(OACRO-MAA) to 0.53 at 3.7 Å for P(ODACRO-MAA), indicating the role of urea in the solvation dynamics of PCBs in DES (Fig. 8d).

The RDF values for interactions in DES surpass those in octane, demonstrating the higher affinity of PCBs for the

interactive DES environment. This distinction emphasizes the suitability of DES for stabilizing and dissolving amphiphilic PCBs, with hydroxide ions playing a crucial role in forming strong hydrogen bonds. The findings highlight the interplay between alkyl chain length and solvent polarity in governing PCB aggregation and dissolution, offering insights for designing tailored solvent systems for specific applications.

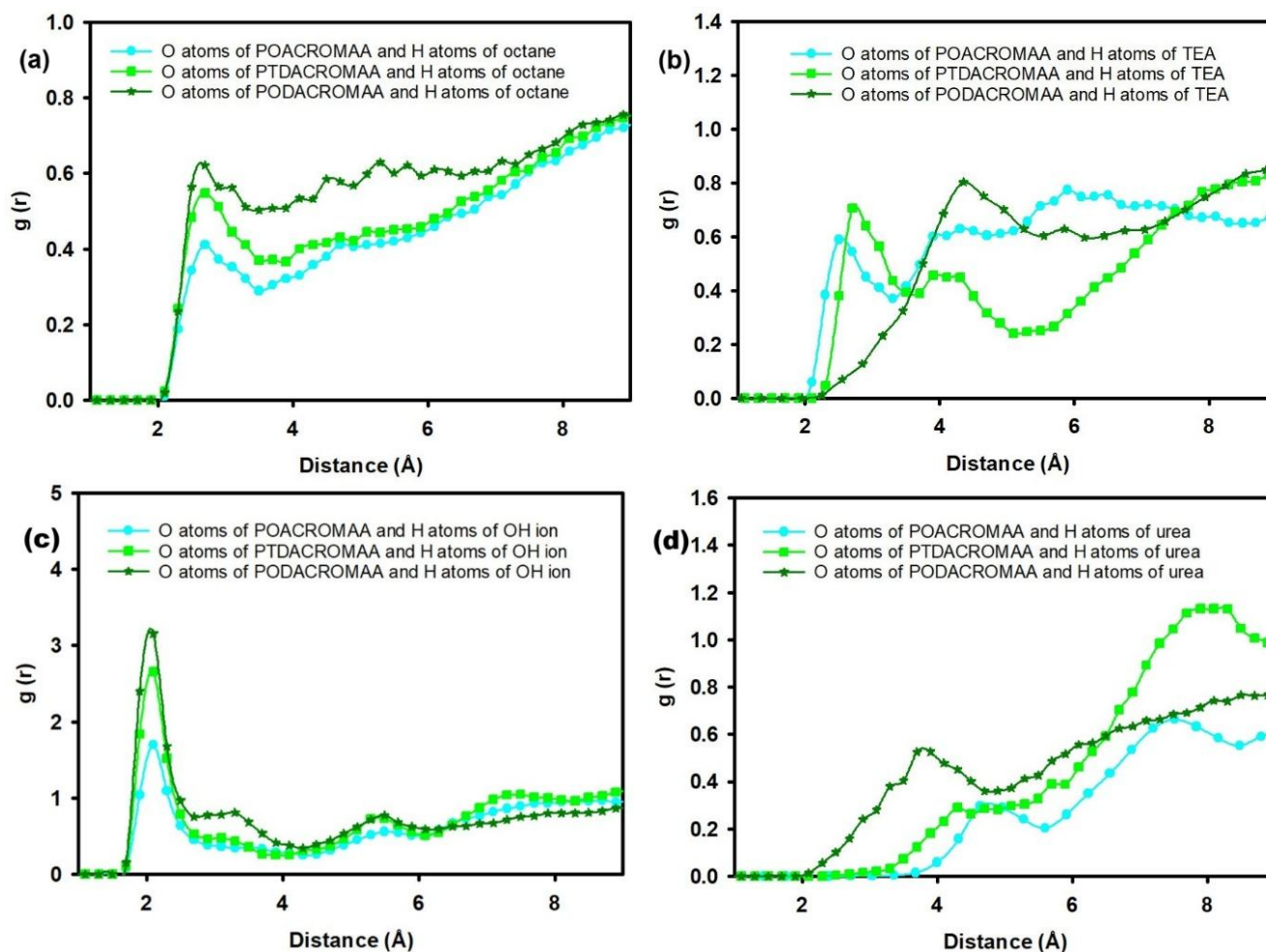


Fig. 8: Radial distribution function (a) between oxygen atom of carboxylate of amphiphilic polycarboxybetaine and hydrogen atom of octane, (b) between oxygen atom of carboxylate of amphiphilic polycarboxybetaine and hydrogen atom of tetraethylammonium, (c) between oxygen atom of carboxylate of amphiphilic polycarboxybetaine and hydrogen atom of hydroxide, and (d) between oxygen atom of carboxylate of amphiphilic polycarboxybetaine and hydrogen atom of urea.

3.2.2 Interaction energies

Table 2 provides a detailed overview of the interaction energies for amphiphilic polycarboxybetaines (PCBs) (P(OACRO-MAA), P(TDACRO-MAA), and P(ODACRO-MAA)) in octane and deep eutectic solvents (DES), emphasizing the distinct contributions of electrostatic and van der Waals forces in these environments. The observed trends align with RDF results, reinforcing the importance of solvent type and PCB structure in determining intermolecular interactions.

In octane, van der Waals interactions play a more dominant role compared to electrostatic interactions, which aligns with

the non-polar nature of the solvent. The van der Waals interaction energies between PCBs and octane range from -313.74 kJ/mol for P(OACRO-MAA) to -543.23 kJ/mol for P(ODACRO-MAA). This increasing trend suggests that longer alkyl chains enhance dispersion interactions, consistent with the RDF results showing increased hydrophobic interactions for longer chains.

Electrostatic interactions in octane are weaker and exhibit distinct behavior depending on the PCB type. All PCBs maintain electrostatic interactions within the range of -1524.45 kJ/mol to -420.38 kJ/mol within the octane phase. This suggests that, despite their amphiphilic nature, these

PCBs retain significant electrostatic interactions, likely due to residual charge effects. The van der Waals interactions within the PCBs themselves also vary, with P(OACRO-MAA) showing the strongest internal interactions (-132.96 kJ/mol), while P(TDACRO-MAA) and P(ODACRO-MAA) exhibit weaker van der Waals interactions, at -111.52 kJ/mol and -137.72 kJ/mol, respectively.

In DES, electrostatic interactions dominate, highlighting the highly structured and interactive nature of this solvent. The electrostatic interactions among PCBs in DES range from -1455.84 kJ/mol for P(OACRO-MAA) to -351.53 kJ/mol for P(ODACRO-MAA), confirming that DES promotes strong ion-dipole interactions that stabilize the system. The van der Waals interactions within PCBs in DES are generally weaker compared to those in octane, suggesting that DES stabilizes PCBs primarily through electrostatic interactions rather than dispersion forces.

Key interactions occur between PCBs and hydroxide ions, with electrostatic energy ranging from -72.34 kJ/mol for P(OACRO-MAA) to -70.95 kJ/mol for P(ODACRO-MAA). These values are notably lower than the previous dataset but still indicate strong stabilizing interactions driven by hydrogen bonding. The van der Waals interactions with hydroxide ions are minimal, reinforcing the dominance of electrostatic effects. Moderate electrostatic interactions are observed between PCBs and tetraethylammonium (TEA) ions, decreasing from -35.58 kJ/mol for P(OACRO-MAA) to -12.72 kJ/mol for P(ODACRO-MAA). This decrease suggests that TEA plays a secondary stabilizing role in DES, with its impact diminishing for longer alkyl chains. The van der Waals interactions with TEA, however, increase slightly, indicating enhanced dispersion forces for longer chains.

Stronger interactions are noted between PCBs and urea, with electrostatic energies varying from -185.35 kJ/mol for P(OACRO-MAA) to -213.65 kJ/mol for P(ODACRO-MAA). The van der Waals interactions with urea also show a steady increase, reaching -237.87 kJ/mol for P(ODACRO-MAA), further reinforcing urea's role in stabilizing the PCBs within DES. The interaction energy analysis corroborates the RDF findings, underscoring the structured interactions in DES compared to the more dispersed interactions in octane. DES fosters stronger electrostatic interactions, particularly with hydroxide ions, while octane primarily relies on hydrophobic van der Waals forces. These insights highlight DES as a superior medium for stabilizing amphiphilic molecules, making it a promising solvent system for applications requiring strong ion-dipole interactions. The results also provide a basis for optimizing solvent selection in PCB-based formulations, enhancing their performance in targeted applications.

Experimental studies have further validated the strong interaction potential of zwitterionic polymers, such as PCBs, in DES environments, supporting the trends observed in our computational analysis. Rumyantsev *et al.* demonstrated that carboxybetaine-based DESs establish strong hydrogen-

bonding networks with water, significantly altering solute organization and enhancing solubility, a behavior consistent with the hydrogen-bond-dominated interactions identified in our DES-PCB systems.^[52] Similarly, Russo *et al.* showed that zwitterionic carboxybetaine- and sulfobetaine-based DESs effectively dissolved polymers, enabling the fabrication of porous PVDF and PAN membranes through the Non-Solvent Induced Phase Separation method.^[53] This underscores the capability of DESs to solubilize complex polymeric systems, aligning with our findings on enhanced PCB stability in DES. Furthermore, Lomba *et al.* highlighted the cryoprotective properties of zwitterionic polymers like PCBs when combined with DESs, due to their biocompatibility and ability to stabilize molecular structures via strong hydrogen bonding.^[54] Together, these experimental results reinforce the conclusion that DESs offer a robust and sustainable medium for stabilizing and dissolving amphiphilic PCBs, validating the relevance and reliability of our DFT and MD simulation outcomes.

In addition, the strong hydrogen-bond networks formed between PCBs and DES components, particularly TEAOH and urea, suggest enhanced polymer solubility due to improved solvent-polymer compatibility and reduced interfacial tension. Likewise, the pronounced structuring and stable solvent cages identified in our MD simulations are indicative of higher viscosity in DES-rich environments, a characteristic frequently reported for hydrogen-bonded eutectic systems.^[49-51,54] These molecular-level insights therefore provide a mechanistic rationale for the experimentally observed solubility enhancement and viscosity trends in PCB-DES systems.

4. Conclusion

In this study, we explored the intermolecular interactions and molecular structures of amphiphilic polycarboxybetaines (PCBs), including P(OACRO-MAA), P(TDACRO-MAA), and P(ODACRO-MAA), with varying alkyl chain lengths in both octane and deep eutectic solvent (DES) environments using Density Functional Theory (DFT) and classical all-atom Molecular Dynamics (MD) simulations. Our objective was to assess how alkyl chain length and solvent polarity influence PCB behavior at the molecular level. DFT-optimized geometries revealed that P(OACRO-MAA) exhibited stronger interactions with DES than with octane, attributed to extensive hydrogen bonding and electrostatic stabilization between carboxyl and ester groups and DES components. Molecular electrostatic potential (MEP) and non-covalent interaction (NCI) analyses further confirmed that hydrogen bonding and van der Waals forces predominantly stabilize DES-polybetaine complexes, while octane interactions are governed by hydrophobic dispersion forces.

MD simulations corroborated these findings, showing that PCBs experience enhanced aggregation in octane as alkyl chain length increases, whereas DES provides a highly interactive hydrogen-bonding network that stabilizes

individual polymer chains. Radial distribution function and interaction energy analyses identified hydroxide ions as the key contributors to carboxylate stabilization, assisted by tetraethylammonium and urea molecules.

Importantly, octane was employed as a model hydrocarbon to mimic non-polar oil phases commonly found in biodiesel systems, enabling a realistic assessment of polymer–solvent interactions relevant to agricultural crude biodiesel purification. The comparative insights between octane and DES reveal how solvent polarity and hydrogen-bonding capacity dictate the solubility and dispersion of amphiphilic PCBs. These results underscore the potential of DES as a green, tunable, and efficient solvent system for sustainable agricultural biodiesel purification and related separation processes.

Future studies should integrate experimental validation and explore a wider range of DES compositions to optimize polymer-assisted purification technologies and expand their applicability across energy and materials science domains.

Nomenclature

DES – Deep eutectic solvent

DFT – Density functional theory

MD – Molecular dynamics

MEP – Molecular electrostatic map

NCI – Noncovalent interactions

PCB – Polycarboxybetaines

PSB – Polysulfobetaines

PPB – Polyphosphobetaines

P(OACRO-MAA) – Poly(octyl-grafted aminocrotonate-methacrylic acid)

P(TDACRO-MAA) – Poly(tetradecyl-grafted aminocrotonate-methacrylic acid)

P(ODACRO-MAA) – Poly(octadecyl-grafted aminocrotonate-methacrylic acid)

RDF – Radial distribution function

RDG – Reduced density gradient

TEAOH – Tetraethylammonium hydroxide

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability

Data will be made available on request.

Supporting Information

Not applicable.

CRedit Statement

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