Microstructures of capped ethylene oxide oligomers in water and \textit{n}-hexane

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This report documents microstructural features of CH$_3$(CH$_2$-O-CH$_2$)$_m$CH$_3$ dissolved in water and \textit{n}-hexane for $m = 11$, $21$, and $31$. Probability densities for end-to-end distance, and the associated potential-of-mean-force (pmf), are more revealing of chain microstructures than are the corresponding results for the radii of gyration. For water, the pmf identifies three distinct regions: loop-closure, globule, and high-extension regions. The globule region affirms a water-swollen chain, and is not evident in the \textit{n}-hexane results. Chain C-atom density profiles from the chain centroid are also different in the water and \textit{n}-hexane cases. For \textit{n}-hexane (but not water), the density profiles are similar for the different chain lengths when the distances are scaled by the observed $\langle R_g^2 \rangle^{1/2}$. For water (but not \textit{n}-hexane) and the smaller chains considered, the carbon material exhibits a distinctive enhanced concentration, or internal condensation, at the centroid core of the structure.
I. INTRODUCTION

Dispersant materials used in response to oil spills\textsuperscript{[1]} undergo a demanding effectiveness approval process, and approved dispersants are stockpiled near drilling activity and possible spill locations. These factors inhibit continuous improvement of dispersants. Rigorous laboratory studies of the molecular-thermodynamic interactions at play in dispersant systems are, therefore, particularly welcome. In addition, effective thermophysical modeling for these systems should improve the fidelity of laboratory-scale simulations of field-scale and ocean-scale oil spill dispersion. A typical prerequisite for development of effective molecularly specific thermophysical models is computational simulation of these solutions on a molecular basis.

Arguably the most important water-soluble synthetic polymers,\textsuperscript{[2,3]} (-CH$_2$-CH$_2$-O-)$_n$ chain molecules are also soluble in common organic solvents and are intrinsic to the dispersant materials in use\textsuperscript{[1]} This report establishes molecular-scale microstructures of PEO oligomers in aqueous solutions, information preparatory to molecular-scale theories of the structure and function of these species in solution.

The molecular versatility of PEO/PEG polymers in solution makes them a challenge for molecularly specific statistical thermodynamic theory. For example, their conformations respond sensitively to the solution environment\textsuperscript{[2,3]} Common-sized PEO molecules are distinctly helical in $n$-propanoic, isobutyric, and isopentanoic acid solutions coexisting with liquid water\textsuperscript{[3]} That helicity emphasizes the contrasting behavior that these chains exhibit generic coil structures in aqueous solutions. Though the helices are not evident in bulk liquid water, and indeed also not in acetic acid nor in isobutanol nor in $n$-butanol, helix formation does seem to require at least a trace of water\textsuperscript{[3]}

The solvent plays an intrinsic role in the solution thermodynamics also. The conformational sensitivity noted above is associated with a polymer size fractionation between those coexisting solutions\textsuperscript{[2,3]} Experimental evaluation of a Flory-Huggins interaction parameter for PEO/PEG in either water or methanol shows compositional dependence that is substantially different in these two cases\textsuperscript{[4,5]}

In many applications\textsuperscript{[6]} and specifically for dispersants used on oil spills\textsuperscript{[1]} the PEO/PEG chains are decorated with junction, head, or capping groups. The work below anticipates those molecular designs, but treats explicitly only the simplest capping group, (methyl) -
Correlations associated with capping groups serve to focus structural analyses and the following work focuses on the radial distributions of capping groups. Alternatively, spatial extensions of chain molecules in solution are often characterized by a mean square-radius of gyration $\langle R_g^2 \rangle$, and that information is addressed below for the cases treated. A conclusion we draw from the recent exhaustive treatment of longer alkanes in water is that distributions of $R_g^2$ are less informative of molecular structure than spatial correlations between chemical groups such as capping groups. The results below should provide further clarification of that issue. We note that single-molecule pulling experiments are becoming a new source of microstructural information, though not yet at the molecular resolution of interest in the present work. Those important experiments do not track the radius of gyration specifically, but instead manipulate lengths between tethered chemical groups.

Numerous traditional statistical thermodynamics theories of aqueous PEO/PEG solutions have been suggested; some representatives were noted in our initial report, and we do not attempt a review here. An alternative non-traditional procedure for theory development accepts that simulations are necessary for evaluation of molecular theories of liquids, that simulations will always be carried-out in any case, and so the simulation work might as well contribute to formulation of physical theories. Of course, analyses for those purposes must express the natural physical concepts underpinning molecular theories, and those analyses must be sufficiently general. We have elsewhere argued that the recent developed molecular quasi-chemical theory does achieve those requirements. That molecular quasi-chemical theory has lead over that past decade to resolution of the most basic puzzles of hydrophobic effects. It is our intention to establish, for the interesting and important aqueous solutions considered here, some of the groundwork required for fully defensible molecular theory.

As noted already, direct high-resolution molecular simulations are necessary for the theory development that is sought. Because these systems are of practical importance, a wide range of simulation calculations have been carried-out. Again, we do not attempt a review here, but merely note a recent contribution that gives access to that substantial available literature.

The results below were obtained by combination of standard molecular simulation procedures appropriate for the sampling requirements of different configurational aspects of $\text{CH}_3(\text{CH}_2-\text{O-CH}_2)_m\text{CH}_3$ chain molecules in water and $n$-hexane solutions. Further specific details are provided in the Appendix. We note here that the combined results support
comparisons over a range of molecule extensions, between different chain molecule lengths, between different-sized simulation systems, and between water and \( n \)-hexane solvents.

A curiosity of this simulation work is that with the typical time-scales and length-scales it is easy to observe (Fig. 1) molecular-scale break-up of a fluid column to produce droplets, and then reformation of a fluid column. We hope in subsequent work to return to these observations with further analysis.

![FIG. 1. Formation and then break-up of a fluid column by reconnection across periodic boundary conditions. For visual convenience, three images are shown laterally in each frame. In this case the droplet/column structure is composed of water with one \( \text{CH}_3(\text{CH}_2-\text{O}-\text{CH}_2)_m\text{CH}_3 \) \((m=11)\) chain molecule (in VDW representation) that here resides near the interface. The majority material in the background is \( n \)-hexane.](image)
II. RESULTS AND DISCUSSION

From small to large end-to-end lengths, the observed probability density (Fig. 2) displays three distinct behaviors, loop-closure, globule, and high-extension (elastic) regions. The loop-closure feature is a realization of a primitive hydrophobic bond, which has been extensively studied by simulation but not yet susceptible to experimental measurement due to solubility limitations. In contrast (Fig. 3), distributions of $R_g^2$ are less distinctive of these microstructural features.

For liquid water the loop-closure feature is largely independent of oligomer size (Fig. 4). This feature in liquid water is different from what is observed in $n$-hexane and for nonsolvated chains (Fig. 5). These points support the identification of the loop-closure feature as an experimentally realizable hydrophobic bond.

The globule region is clear for the hydrated chains, but not for the case of $n$-hexane solvent (Fig. 6). Thus in the more benign organic solvent the chains are collapsed relative to the more swollen hydrated oligomers. This also supports the interpretation of intrachain interactions from the perspective of simple aqueous solution examples.

The profiles of the density of chain C-atoms, measured relative to the chain centroid, are different (Fig. 7) for the two solvents. For $n$-hexane, the density profiles are similar for the different chain lengths when the distances are scaled by the observed $\langle R_g^2 \rangle^{1/2}$. This similarity does not obtain for the case for water. In water and for the smaller chains studied, the carbon material exhibits a distinctive enhanced concentration in the middle of the distribution, a concentration that is not evident for the case of $n$-hexane. This interesting internal condensation is characterized by a length-scale smaller than $\langle R_g^2 \rangle^{1/2}$. Thus the overall density profiles show less similarity on the $\langle R_g^2 \rangle^{1/2}$ scale, and the internal condensation feature is not evident for the largest $m=31$ chain.

III. CONCLUSIONS

The probability density for end-to-end distance (and the associated pmf) for CH$_3$(CH$_2$-O-CH$_2$)$_m$CH$_3$ is more revealing of chain microstructures than are the corresponding results for the radii of gyration. For water, the pmf identifies three distinct regions: loop-closure, globule, and high-extension regions. In water, the loop-closure feature is similar to a prim-
itive hydrophobic bond and is insensitive to chain length. The globule region exposes a water-swollen chain, and is not evident in the \( n \)-hexane results. Chain C-atom density profiles from the chain centroid are different in the water and \( n \)-hexane cases. For \( n \)-hexane (but not water), the density profiles are similar for the different chain lengths when the distances are scaled by the observed \( \langle R_g^2 \rangle^{1/2} \). For water (but not \( n \)-hexane) and the smaller chains considered, the carbon material exhibits a distinctive, enhanced concentration, or internal condensation, at the centroid core of the structure.

Appendix: Simulation Specifics

Two different simulation techniques were used for the molecular dynamics calculations. The first class of calculations used parallel tempering\(^{21}\) to achieve enhanced sampling of the mixing characteristics with water or \( n \)-hexane solvent, and of \( \text{CH}_3(\text{CH}_2-\text{O-CH}_2)_m\text{CH}_3 \) chain conformations. The chain molecules were represented by a generalized amber force field (GAFF),\(^{22}\) the SPC/E model for water,\(^{23}\) and optimized potentials for liquid simulations (OPLS-AA) were used to describe \( n \)-hexane in those simulations.\(^{24}\) GROMACS 4.5.3 molecular dynamic simulation package\(^{25}\) was used for all parallel tempering simulations spanning the 256-550K temperature range with 32 replicas (for \( m = 11, \) and 21, cases) and 40 replicas (for \( m = 31 \)). Long-range electrostatic interactions were treated in standard periodic boundary conditions using the particle mesh Ewald method with a cutoff of 0.9nm. The Nosé-Hoover thermostat maintained the constant temperature and chemical bonds involving hydrogen atoms were constrained by the LINCS algorithm. Energy minimization and constant pressure density equilibration was performed at 300K to set the constant volume conditions, and then production calculations for each replica set were extended to 10 ns. Parallel tempering swaps were attempted at a rate of 100/ns, and the temperature grid chosen resulted in a success rates of 15-25%.

The second class of simulations obtained higher spatial resolution in the loop closure region using the windowing stratification method.\(^{26,27}\) In these simulations a harmonic interaction between the capping atoms of the \( \text{CH}_3(\text{CH}_2-\text{O-CH}_2)_m\text{CH}_3 \) chain was exploited to concentrate the sampling of the end-to-end distance to each particular window. For a \( \text{CH}_3(\text{CH}_2-\text{O-CH}_2)_m\text{CH}_3 \) chain in water or \( n \)-hexane, we performed simulations with radial displacement coordinate covering the range from 3.0-10.0Å uniformly with 15 windows. Tra-
jectories were recorded for 10ns/window at the temperature of 297.1K. $P(r)$ was then reconstructed over the whole range using the weighted histogram analysis method (WHAM).
FIG. 2. (upper) Probability density $P(r)$ for end-to-end (methyl-methyl) length for [CH$_3$(CH$_2$-O-CH$_2$)$_m$CH$_3$](aq) with $m = 21$. The normalization of this graph is chosen to suggest the analogy with conventional atom-atom radial distribution function in liquids. (lower) Potential of the average end-to-end forces showing distinct loop-closure, globule, and high-extension regions. The choice of normalization for the upper panel sets the origin of the y-axis of the lower panel, and the same convention is followed in both cases. Results here for $r < 1.0$ nm were are obtained utilizing the WHAM procedure. Those high resolution results were matched to overall observation of $P(r)$ from molecular simulations with parallel tempering.
FIG. 3. For [CH$_3$(CH$_2$-O-CH$_2$)$_m$CH$_3$](aq), distributions of square-radius of gyration displaced vertically for visual convenience, extracted utilizing GROMACS analysis tools. Scaling of the abscissa brings the results for different lengths into a similar range: $\langle R_g^2 \rangle^{1/2} = 0.61, 0.84,$ and 1.22 nm for $m = 11, 21,$ and 31, respectively. These values are larger than the ideal $(1/\sqrt{6})$ proportion of the observed $\langle r^2 \rangle^{1/2}$

FIG. 4. High resolution results for $r < 1$ nm for several chain lengths from windowing/WHAM calculations.
FIG. 5. In the loop-closure region, the $[\text{CH}_3(\text{CH}_2-\text{O-CH}_2)_m\text{CH}_3]$ ($m = 21$) oligomer behaves differently in $n$-hexane and water, and the results for $n$-hexane are similar to those obtained with no solvent (ideal gas case). The temperature variation here is small, $T = 297$ K (water), 302 K (ideal), and 297 K ($n$-hexane).
FIG. 6. (upper) For CH$_3$(CH$_2$-O-CH$_2$)$_m$CH$_3$ (aq) chains, at constant density corresponding to 300K and $p = 1$ atm: parallel tempering results for different chain lengths and system sizes overlap each other on normalized end-to-end distance. Globule and high-extension regions are separated at $r \approx \langle r^2 \rangle^{1/2}$ for these chain lengths and system sizes. (lower) Corresponding results for $n$-hexane at constant density ($T = 300$K and $p = 1$ atm): Separation of a globule region and a high extension region is indistinct here. A Gaussian (parabola) model satisfactorily fits the data in this high extension regime.
FIG. 7. CH$_3$(CH$_2$-O-CH$_2$)$_m$CH$_3$ chain C-atom density profiles from the chain centroid shows higher concentration of polymer C-atoms in water the middle of distribution which is absent for $n$-hexane solvated polymer.
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