



Modeling the interfacial properties of Poly(Ethylene oxide-Co-Propylene oxide) polymers at water-toluene interface



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ABSTRACT

Understanding how the structure of demulsifiers affects its interfacial properties is essential to developing new demulsifiers with desired properties. Modeling is an important tool to methodically study the effect of polymer architecture on its microscopic structure and macroscopic properties. Here modified interfacial Statistical Associating Fluid Theory (iSAFT) was used to study the interfacial properties of additives at water-toluene interface. The density profile, surface adsorption and interfacial tension (IFT) was predicted for different architectures of poly (ethylene oxide-co-propylene oxide) (PEO-PPO) at the interface. The predicted IFT was validated against experimental data (for Pluronic, Tetronics and Poloxamer) and the theory was found to be in good agreement with experiments. The effect of molecular weight, branching, PEO:PPO ratio and ordering of the PEO and PPO blocks was studied. It was found that IFT was lowest for high molecular weight and highly branched polymers and the IFT curve went through a minima with varying PEO:PPO ratio. The hydrophilic PEO block on the outside and hydrophobic PPO block as the inside block led to more interfacial adsorption and lowering of IFT compared to the reverse polymer (PPO outside and PEO inside).

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1. Introduction

Petroleum recovered from oil wells is most often present as water-in-oil emulsions. Salts present in the water droplets cause corrosion and scaling issues making it necessary for the water to be removed [1]. The oil-water interface is stabilized by components of the oil such as asphaltenes, resins and solids [2,3]. The rigid interfacial layer formed by these components is not easily disrupted and breaking these emulsions is a significant challenge. There are different methods used for demulsification of water-in-oil emulsions like heating the emulsion to reduce viscosity [1] or applying an electric field to increase collision of droplets and promote coalescence [4] or adding chemical demulsifiers to destabilize the emulsion and induce coalescence [5]. The last method is usually the most cost effective since the demulsifiers can be effective at very low concentrations.

To design novel demulsifiers it is important to understand how they work and how the structure of the demulsifier defines its effectiveness at an interface. The ability of a demulsifier to break an

emulsion depends on the solubility of the demulsifier in the continuous phase (in the water phase for oil in water emulsion and in oil for water-in-oil emulsion), its partitioning to the interface and its rheological properties at the interface [6,7]. While most studies on demulsifiers concentrate on dewatering abilities of demulsifiers [8] (and this is the ultimate test of whether a given demulsifier will work or not), it is important to understand the fundamental properties of the demulsifiers to be able to build new demulsifiers. In this paper, we concentrate on the interfacial activity of the demulsifier and how the polymer architecture affects interfacial structuring and properties.

In a complex system like the water-in-oil emulsion, where multiple factors affect the stabilization of the emulsion, molecular modeling can be a useful tool to methodically study the different factors affecting the system like molecular weight, branching and the chemical moieties present in the molecules. Because of the ease of using molecular models, they can help quickly scan the large parameter space of the complex systems and guide experiments to interesting regions. Also, information like the molecular structuring of the polymer at the interface is extremely difficult to probe in experiments, but can be obtained easily from molecular modeling. Molecular structuring gives insights into how the different chemical moieties affect the partitioning of molecules to the interface

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and its structuring at the interface.

Molecular simulations on the atomistic scale tend to be very slow for the large system sizes required to model interfacial systems. While coarse grained methods like Dissipative Particle Dynamics can speed up the calculations significantly, and have been used to study interfacial systems [9,10], they are still fairly slow. An approach that is fast and particularly suited to study interfacial systems is the classical Density Functional Theory (DFT). Being an equation of state based approach, it is much faster than simulations. Here *modified* interfacial Statistical Associating Fluid Theory (iSAFT) [11], which is based on Wertheim's Thermodynamic Perturbation Theory in a DFT framework, is used. The theory has been successfully applied to a wide variety of interfacial systems [12–14].

Modified iSAFT is applied to study poly(ethylene oxide-co-propylene oxide) (PEO-PPO) at a model water-oil interface. Amphiphilic PEO-PPO block copolymers are commercially available and widely used as demulsifiers [15]. Properties of PEO-PPO copolymers in aqueous environment like its solubility and micelle formation has been widely studied [16,17]. There has also been some work on interfacial tension measurement of PEO-PPO copolymers for water-air [17,18] and water-oil interfaces [19] but most of the work has concentrated on the dewatering ability of PEO-PPO copolymers in crude oil [8,20]. This work is an attempt to systematically study the molecular structuring of the copolymers at interfaces with a goal of gaining fundamental understanding of the interfacial phenomena.

Section 2 describes the potential model and the theory used while Section 3 describes how the parameters were obtained. The results for interfacial properties of polymers with different architectures are discussed in Section 4 and finally Section 5 summarizes the conclusion.

2. Theory

The success of any theory depends on the intermolecular potential used to describe the interaction between molecules. Section 2.1 describes the potential model, Section 2.2 introduces the Density Functional Theory Framework that is used to obtain the equilibrium density profile by minimizing the free energy and finally Section 2.3 forms the link between the potential model described in Section 2.1 and the free energy required in Section 2.2.

2.1. Potential model

The potential energy (U) of a system of molecules is approximated as the sum of all pair interactions in the system

$$U = \sum_i \sum_{j < i} u_{ij}(\mathbf{r}_i, \mathbf{r}_j) \quad (1)$$

Here the summation is over all molecules in the system. The effective pair potential, u_{ij} , between a pair of unbonded segments i and j at positions \mathbf{r}_i and \mathbf{r}_j can be broken down into different contributions

$$u_{ij}(\mathbf{r}_i, \mathbf{r}_j) = u_{ij}^{HS}(\mathbf{r}_{ij}) + u_{ij}^{att}(\mathbf{r}_{ij}) + \sum_{A \in \Gamma^{(i)}} \sum_{B \in \Gamma^{(j)}} u_{Ai,Bj}^{assoc}(\mathbf{r}_i, \mathbf{r}_j) \quad (2)$$

where $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the centers of segments i and j . $u_{ij}^{HS}(\mathbf{r}_{ij})$ is the hard sphere potential which accounts for the short-ranged repulsion (excluded volume effects)

$$u_{ij}^{HS}(\mathbf{r}_{ij}) = \begin{cases} \infty & \mathbf{r}_{ij} < \sigma_{ij} \\ 0 & \mathbf{r}_{ij} \geq \sigma_{ij} \end{cases} \quad (3)$$

where σ_{ij} is the average diameter of the two segments. The long range attraction is approximated by a cut-and-shifted Weeks-Chandler-Anderson [21] attraction given by

$$u_{ij}^{att}(\mathbf{r}_{ij}) = \begin{cases} -\epsilon_{ij}^L - u_{ij}^L(r_{ij}^{cut}), & \sigma_{ij} < \mathbf{r}_{ij} < r_{ij}^{min} \\ u_{ij}^L(\mathbf{r}_{ij}) - u_{ij}^L(r_{ij}^{cut}), & r_{ij}^{min} < \mathbf{r}_{ij} < r_{ij}^{cut} \\ 0 & \mathbf{r}_{ij} > r_{ij}^{cut} \end{cases} \quad (4)$$

In this study, the minimum r_{ij}^{min} is located at $2^{(1/6)}\sigma_{ij}$ and the cutoff r_{ij}^{cut} at $3\sigma_{ij}$. ϵ_{ij}^L is the attraction energy between segments i and j and u_{ij}^L is the Lennard-Jones (LJ) potential given as

$$u_{ij}^L(\mathbf{r}_{ij}) = 4\epsilon_{ij}^L \left[\left(\frac{\sigma_{ij}}{\mathbf{r}_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{\mathbf{r}_{ij}} \right)^6 \right] \quad (5)$$

Finally, the hydrogen bond is modeled with a square well potential interaction of conical association sites present near the surface of the hard sphere [22,23]. To imitate the short ranged directional nature of hydrogen bonds, hydrogen bonding occurs when two sites on two different molecules are within a certain distance of each other and are oriented in the right direction. Hydrogen bonding potential for two sites A and B on molecules i and j respectively is given by

$$u_{Ai,Bj}^{assoc}(\mathbf{r}_i, \mathbf{r}_j) = \begin{cases} -\epsilon_{Ai,Bj}^{assoc}, & \mathbf{r}_{ij} < r_c; \theta_{Ai} < \theta_c; \theta_{Bj} < \theta_c \\ 0, & \text{Otherwise} \end{cases} \quad (6)$$

r_c is the cutoff distance and θ_c is the cutoff angle. θ_{Ai} is the angle between the line joining the centers of molecules i and j , and the line from the center of molecule i to the center of site A. θ_{Bj} is defined similarly for site B on molecule j . The double summation in the association term in Equation (2) is over all the association sites on both the segments ($\Gamma^{(i)}$ and $\Gamma^{(j)}$ are the set of all association sites on segments i and j respectively).

Here water is modeled as a single sphere with four hydrogen bonding sites (two hydrogen and two oxygen sites) while the polyethers are modeled as a chain of m tangentially bonded spherical segments. The polymer has three types of association sites – one oxygen and one hydrogen on the end segment representing the terminal OH group of the polymer and one ether oxygen site on all the middle segments. Bonding is allowed only between hydrogen and oxygen sites i.e. $\epsilon_{OO} = \epsilon_{HH} = \epsilon_{Oether-Oether} = \epsilon_{OetherO} = 0$ and $\epsilon_{OH} \neq 0, \epsilon_{OetherH} \neq 0$.

Cross parameters for LJ interaction of two unlike segments i and j are given by

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}(1 - k_{ij}) \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (7)$$

where ϵ_{ii} and ϵ_{jj} are the LJ interaction energies of segments i and j respectively; while σ_i and σ_j are the diameters of segments i and j respectively. k_{ij} is the binary interaction parameter for the two segments. For hydrogen bonding, the cross energy uses a simple arithmetic mean and a geometric mean is used for the hydrogen bond volume (κ). $\kappa = 0.25(1 - \cos\theta_c)^2\sigma^2(r_c - \sigma_{ij})$ is the geometric constraint on the sites to be oriented in the right direction and be at the right distance from each other. θ_c and r_c are the angle and distance constraints on bond formation from Equation (6).

Now that the potential model for the molecules has been defined, a framework is required to go from a microscopic view of intermolecular interactions to the macroscopic properties of the system. Classical Density Functional Theory is a convenient tool to obtain the macroscopic properties of an inhomogeneous system.

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