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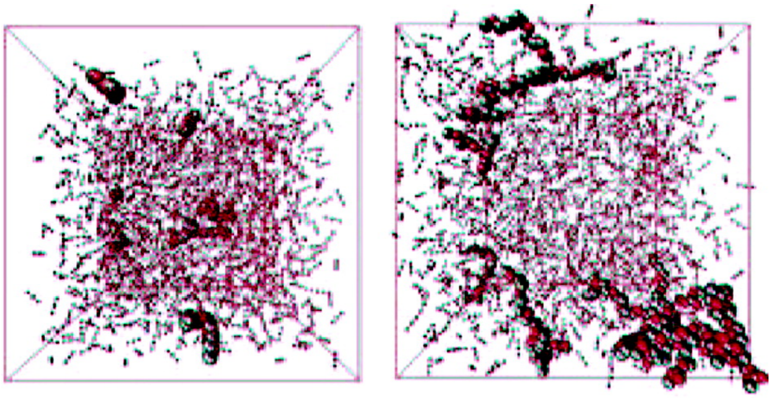

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Microscopic Origins for the Favorable Solvation of Carbonate Ether Copolymers in CO_2

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Abstract: The strong desire for the wide use of carbon dioxide as an environmentally benign process solvent has spurred a large number of attempts to improve its solubility characteristics. Pioneering experimental work by Beckman and co-workers has pointed to carbonate ether copolymers as promising candidates for nonfluorous surfactants. It is demonstrated here that Gibbs ensemble Monte Carlo simulations (using configurational-bias and double-bridging strategies and the transferable potentials for phase equilibria force field) can be employed to accurately predict the phase equilibria of a carbonate ether copolymer with CO_2. The simulations indicate that the greater accessibility of the carbonyl oxygen plays a major role for the CO_2-philicity of this copolymer surfactant.

I. Introduction

Supercritical carbon dioxide has tremendous potential as a versatile, environmentally benign process solvent because of its tunability, accessibility of its critical point, its high abundance, low heat of vaporization, low viscosity, and low cost.[1,2] The use of CO_2 has been limited, though, because of the difficulty in solvating polar and high molecular mass compounds in the neat solvent.[3] This is despite the fact that other nonpolar solvents with similar pure phase properties, specifically short alkanes, often exhibit reasonable solubility for many polar molecules which have difficulty being solvated in CO_2.[3] This underscores the difficulties in developing an understanding of the molecular interactions that govern the solubility and selectivity characteristics of process solvents.

The use of surfactants has been the primary means for increasing the solubility of many cosolvents in CO_2.[4] The most success has been achieved in utilizing block copolymer surfactants composed of a “CO_2-philic” block and another block with favorable interactions with other molecules that would otherwise have low solubility in CO_2, allowing the efficient use of CO_2 for a variety of processes.[5−7] CO_2-philic polymer blocks containing fluorinated alkyl chains or fluoroethers have been found to have relatively high solubility in CO_2, but their practical use has been hindered by their high production cost and low biodegradability.[8] Because of these shortcomings, the development of CO_2-philic hydrocarbon-based surfactants is highly desirable.

A promising class of surfactants was recently introduced by Beckman and co-workers,[8,9] who demonstrated that carbonate polyether copolymers possess high solubility in CO_2 at relatively low pressures. Although other experiments have also pointed to a favorable interaction of CO_2 with carbonyl groups,[10] no molecular-based understanding is currently available that explains the CO_2-philic nature of carbonate-containing copolymers. In fact, ab initio calculations carried out to study the interaction of CO_2 with acetates showed no qualitative difference of the binding energy of CO_2 with a carbonyl oxygen or an ether oxygen[11] (i.e., they cannot explain the higher solubility of carbonate polyether copolymers compared to that of polyether homopolymers). Recently, Tan et al.[12] reported lower solubilities for alternating ether−carbonate copolymers (produced by step growth polymerization) of molecular weight and composition comparable to Beckman’s statistical copolymers. A molecular level understanding of the effects of polymer composition (carbonate fraction) and polymer sequence (alternating, statistical, or block copolymer) is necessary to resolve these discrepancies and to direct the development of improved CO_2-philic polymer surfactant candidates.

Molecular simulation can provide an invaluable tool for the exploration of phase equilibria,[13] allowing the prediction of coexistence properties and the determination of the microscopic

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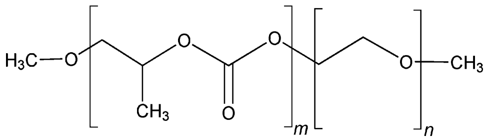
Chart 1. Structure Formula for CARB−PEO Copolymers



factors that govern the macroscopic observables. However, the simulation of phase equilibria for polymeric systems using a realistic description of the system that accurately accounts for the differences in molecular interactions of different chemical groups remains a significant challenge. Another benefit of molecular simulation is that, once the force field has been validated for small molecule systems against available experimental data, it can be used to make predictions for related systems, thereby guiding the development of improved solvents and separation processes.

For this research, we have employed a combination of advanced simulation techniques and a transferable force field to investigate the phase equilibria of a poly(ethylene oxide) (PEO) homopolymer and a polycarbonate poly(ethylene oxide) (CARB−PEO) block copolymer (see Chart 1) with CO$_2$. The goal of this work is to provide a microscopic picture for the origin of the high solubility of CARB−PEO copolymers in CO$_2$.

II. Force Field Development

A quantitatively accurate force field is required to satisfactorily distinguish the characteristics of the phase behavior of closely related polymer systems. The transferable potentials for phase equilibria united atom (TraPPE-UA) force field, which is parametrized to reproduce vapor−liquid coexistence curves of small molecules, provides the parameters for the alkyl and ether groups and CO$_2$.[14−16] This force field utilizes pseudoatoms located at carbon centers for alkyl groups and treats all nonalkyl atoms explicitly. The TraPPE-UA force field has been shown to accurately model the phase behavior for neat CO$_2$ and for binary and ternary mixtures with polar or fluorous compounds.[17−19] Furthermore, the TraPPE-UA ether model has been tested for phase equilibria involving small molecules[16] and for the structural and volumetric properties of high molecular weight poly(ethylene) oxide.[20]

Coupled−decoupled configurational-bias Monte Carlo (CBMC) simulations[21] in the Gibbs ensemble[22] for neat dimethyl carbonate (DMC) were used to extend the TraPPE-UA force field to CARB−PEO polymers. The intramolecular potential parameters and electrostatic charge distributions are based on other carbonate force fields.[23,24] The Lennard-Jones (LJ) parameters for the oxygen atoms of the carbonate group were constrained to the TraPPE-UA values of the ketone and ether force fields,[16] requiring only the parametrization of the LJ parameters for the carbonyl carbon ($\sigma = 3.10$ Å, $\epsilon/k_B = 35$ K and $q = +1.15$ e), and an excellent reproduction of the vapor−liquid coexistence curve for neat DMC was achieved (e.g., saturated liquid densities deviate by less than 1% and the normal boiling point is underestimated by 1° compared to experiment[25]). To test the validity of the TraPPE-UA force field for the modeling of binary mixture of CO$_2$ and (ethers or carbonates), the binary phase diagrams of DMC/CO$_2$ and diethylene glycol diethyl ether (DGDE)/CO$_2$ mixtures were compared with experimental data.[26,27] As is evident from Figure 1, the predicted DMC/CO$_2$ coexistence curve agrees very well with experiment for both the vapor and liquid branches, and the solubility of DGDE in the CO$_2$-rich phase is also well reproduced, but the solubility of CO$_2$ in the DGDE-rich liquid phase is slightly overestimated.

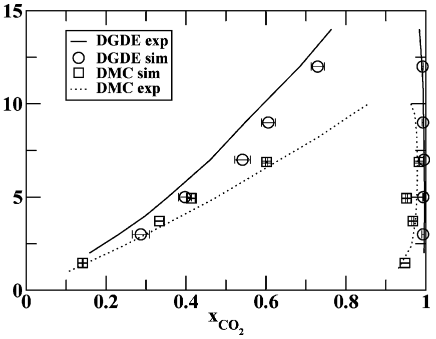


Figure 1. Binary phase diagrams for DGDE and DMC with CO$_2$ at $T = 373$ K and $T = 340$ K, respectively. The error bars correspond to the standard error of the mean.

III. Polymer/CO$_2$ Simulation Details

Two separate polymer/CO$_2$ systems were investigated containing either PEO homopolymer ($m = 0$ and $n = 11$ in Chart 1, $M_w = 530$ g/mol) or CARB−PEO copolymer ($m = 2$, $n = 7$, and $M_w = 558$ g/mol, i.e., with a CARB weight fraction of 37%) at a temperature of 335 K and a pressure of 16 MPa. Although many experimental observations for the phase behavior of CARB−PEO were carried out at 293 K, temperatures above the critical point are more relevant for applications and greatly facilitate simulations. The Gibbs ensemble simulations utilize two separate simulation boxes for the CO$_2$-rich and polymer-rich phases. Two thousand CO$_2$ molecules together with 40 PEO or CARB−PEO polymer chains were used for each system. In addition to the full-sized polymer chains, each with n_r total repeat units, a single chain was added for each length ranging from 1 to $n_r - 1$ repeat units, along with dimethyl ether for the PEO system and DMC for the CARB−PEO system. The purpose for including these shorter chains is to allow for CBMC swatch moves.[28] These moves can be used to exchange a full-sized polymer with another chain having $n_r - 1$ repeat units, which in a subsequent swatch move can be exchanged with a chain with $n_r - 2$, etc., until it is exchanged with either dimethyl ether or DMC, which are readily swapped between the two phases. To enhance the sampling of the conformational degrees of freedom for the polymers, the following special Monte Carlo moves were used. The self-adapting fixed-endpoint CBMC algorithm[29] was used for both

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systems, the CBMC reptation move[20] was used for the PEO homopolymers, and the length-conserving double-bridging move[30] was used for the CARB−PEO copolymer. A spherical potential truncation at 12 Å together with analytic tail corrections for the LJ interactions and Ewald summation for the electrostatic interactions were used for this work. More than 10 000 MC cycles were performed to equilibrate each system, and 50 000 and 150 000 MC cycles of production were carried out for the PEO and CARB−PEO systems, respectively. The higher number of cycles and the length-conserving double-bridging move were only used for the CARB−PEO system because of the increased difficulty in sampling its conformational degrees of freedom in comparison with PEO.

IV. Results and Discussion

The Gibbs ensemble Monte Carlo simulations yielded CO_2-rich phases with 3.1 ± 0.2% and 5.1 ± 0.2% (w/w) for the PEO and CARB−PEO systems, respectively. This agrees qualitatively with the experimental observation that introducing carbonyl oxygens into polymer chains results in a higher solubility in CO_2.[8,12] Unfortunately, a direct comparison to experiment is hampered by the complexity of the parameter space for this systems, that is, the solubilities of the PEO and CARB−PEO polymers depend on temperature, molecular weight, carbonyl content, microstructure (statistical, alternating, or block copolymers), and nature of the terminal group (e.g., −OH, −O-alkyl, or $-O-CO-CH_3$).[8,9,12] Sarbu et al.[9] reported a similar cloud point pressure (at ambient temperature) for a CARB−PEO copolymer with a total of about 103 repeat units and a carbonate fraction of 34% and a PEO homopolymer with 16 repeat units (i.e., a strong enhancement of the solubility). Tan et al.[12] observed a dramatic decrease in the cloud point pressure for alternating copolymers of similar molecular weight (about 8200 g/mol) when the carbonate content is increased from 8.8 to 12.4%. In particular, a cloud point pressure of about 29 MPa at 333 K was determined for a polymer with an average molecular weight of 3780 g/mol and a carbonate content of 12.4%. It should be noted that all of these experiments were performed using polydisperse carbonate copolymers with average molecular weights about 1 order of magnitude larger than those simulated here. Unfortunately, at present it would be impossible to extend the simulations to the same molecular weight regime as used in the experimental studies. However, the simulation data are consistent with the experimental observations by Sarbu et al.[9] and Tan et al.[12] that addition of a moderate fraction of carbonate segments increases the solubility. A more direct comparison is possible for the PEO homopolymer: for a system of CO_2 and 2.2 wt % PEO (with $n \simeq 8$), the experimental cloud point was determined to be 20.3 MPa at 333 K[31] (i.e., pointing to a slight overestimation of the PEO solubility for the simulations).

The qualitative agreement between simulations and experiment for the macroscopic composition observables for the polymer/CO_2 systems and the quantitative agreement for small molecules with CO_2 (see Figure 1) provides confidence for the molecular-level analysis presented in the following. In Figure 2, snapshots of the CO_2-rich phases for the CARB−PEO and PEO systems are shown. Polymer aggregation is only present for the CARB−PEO copolymer; a result that is also supported from analysis of polymer segment−polymer segment radial distribution functions (RDFs) and number integrals (not shown).

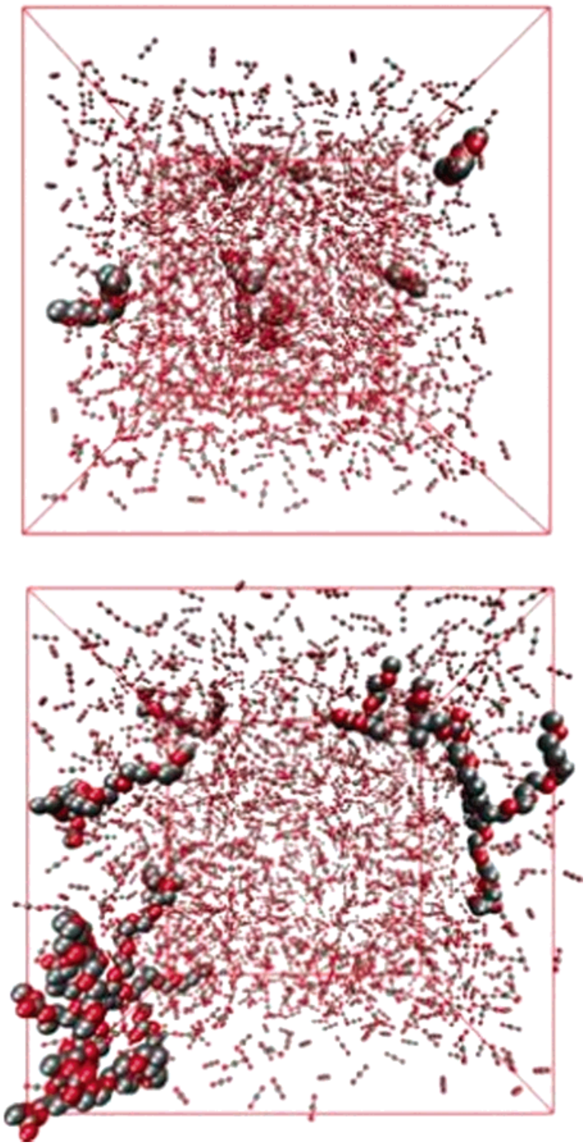

Figure 2. Snapshots of the CO_2-rich phases for the PEO system (top) and the CARB−PEO system (bottom).

To determine the effect of individual repeat units on the CO_2 solubilities of the polymers used here, the Gibbs free energies of transfer per repeat unit were calculated. Gibbs ensemble simulations allow for the direct computation of the Gibbs free energies of transfer for multiple solvents[33−35] from the ratio of the number densities of a particular species in the two phases

$$\Delta G_{a\rightarrow b} = -RT \ln\left(\frac{\rho_b}{\rho_a}\right) \qquad (1)$$

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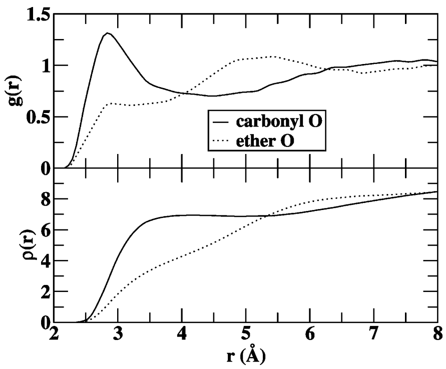

Figure 3. RDFs (top) and radial number densities (bottom) for CO_2 around carbonyl and ether oxygens.

where ρ_a and ρ_b are the solute number densities in phases a and b, respectively, R is the molar gas constant, and T is the absolute temperature.

Since the present simulations contained a variety of shorter polymers (to enhance the sampling of phase transfers), it is possible to extract the incremental free energies for each type of repeat unit. For the PEO homopolymer, the incremental Gibbs free energy of transfer for an EO repeat unit is extracted from the average of the differences in transfer free energies between dimethyl ether and PEO with one repeat unit ($n = 1$ and $m = 0$ in Chart 1), between PEOs with $n = 1$ and $n = 2$, and so forth, up to the full length of the PEO homopolymer ($n = 11$). For the CARB−PEO copolymer, the incremental Gibbs free energies for the EO repeat units are extracted from the average of the differences between CARB−PEO with $m = 1$ and $n = 1$ in Chart 1, and $m = 1$ and $n = 2$, and so forth, until $m = 1$ and $n = 7$. To determine the incremental Gibbs free energy of the carbonate repeat unit, the transfer free energy difference between CARB−PEO copolymer with $m = 1$ and $n = 7$ and the full sized polymer ($m = 2$ and $n = 7$) was calculated. The values obtained for these incremental Gibbs free energies of transfer are $+0.9 \pm 0.1$ kJ/mol for the PEO homopolymer, $+0.9 \pm 0.1$ kJ/mol for the same EO repeat unit in the CARB−PEO copolymer, and -1.1 ± 0.2 kJ/mol for the carbonate repeat unit in the CARB−PEO copolymer. These results show the importance of chemical composition in designing a CO_2-philic polymer surfactant. It is interesting to note that the incremental Gibbs free energy of the EO repeat unit does not differ between the PEO homopolymer and the CARB−PEO copolymer even though some aggregation is observed for the CARB−PEO system. The negative Gibbs free energy of transfer for the carbonate repeat unit signals its favorable solvation in supercritical CO_2, thereby leading to a solubility enhancement for the molecular weights and compositions studied here. However, it should be noted that our simulation looks at a block copolymer architecture, and additional simulations that probe the link between molecular sequence and solubility would be very useful (i.e., computing the incremental Gibbs free energy for a carbonate unit that is sandwiched between two EO units as found in alternating copolymers[12]) but are outside the scope of this study.

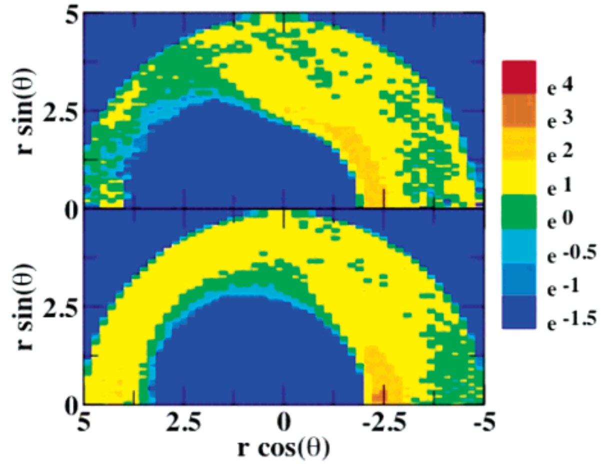

Figure 4. RADF for carbonyl oxygens (top) and ether oxygens (bottom) with with CO_2 carbons. θ is defined by the functional group oxygen to CO_2 carbon vector with either the C═O bond vector, for the carbonyl group, or the dipole vector of the CH_2−O−CH_2 segment, for the ether group. A value of unity for the RADF corresponds to the probability being equal to a uniform distribution of CO_2 molecules (with the same average density).

Figure 3 depicts the RDFs and corresponding number densities for the carbonyl or ether oxygen with the carbon of CO_2. Although the LJ diameter of the carbonyl oxygen (3.04 Å) is larger than that of the ether oxygen (2.85 Å), the first peak for the carbonyl oxygen is at the same separation, but is significantly stronger than that for the ether oxygen. The local density of CO_2 molecules in the first solvation shell around the carbonyl oxygen is significantly enhanced compared to that of the ether oxygen, thereby providing a microscopic reason for the unique solubility enhancement of the carbonate group.

Three-dimensional radial-angular distribution functions (RADF) in polar coordinates are compared for the carbonyl and ether groups in Figure 4. The main peaks for both groups are located at small values of $r \sin\theta$ and near $r \cos\theta = -2.5$ Å. Although the peak height for the ether oxygen is slightly enhanced compared to that of the carbonyl oxygen, the carbonyl peak is much broader with respect to θ, in particular at lower values of r. This larger accessible area around the carbonyl group allows for additional CO_2 molecules in the first solvation shell, thereby explaining why the carbonyl group enhances solubility even though the binding enthalpy does not discriminate between acetate carbonyl and ether oxygens.[11]

V. Conclusions

In conclusion, this study demonstrates that the accessible surface area of the more exposed carbonyl oxygen leads to an enhanced local CO_2 density around this functional group and correspondingly to an enhanced solubility for CARB−PEO copolymer compared to that of the PEO homopolymers with its sterically hindered ether oxygen. A similar argument might explain the enhanced solubility of fluorocarbons where the fluorine atoms expose a large surface area for attractive interactions with CO_2. Of course, other factors also contribute to enhanced polymer solubility, among those are the strength of the polymer−polymer interactions, its conformational flexibility that can usually be linked to the glass transition temperature of the neat polymer,[9,31] and the molecular topology, which has been shown to have very strong effects on the surfactant solubility.[12,32] In future work, we plan to investigate the effects of copolymer sequence and end group substitution by computing the solubilities of an alternating CARB−PEO polymers with the same number of repeat units (e.g., $(EO)_2$−CARB−$(EO)_3$−CARB−$(EO)_2$) and of hydroxyl and acetate group terminated CARB−PEO copolymers. The findings of this work suggest that the accessible surface area of polar groups (oxygen or fluorine) should be taken into account as a design element for the development of CO_2-philic surfactants.

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