Transferable Potentials for Chloroethenes: Insights into Nonideal Solution Behavior of Environmental Contaminants

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Supporting Information

ABSTRACT: Predicting the nonideal phase behavior of binary and multicomponent systems remains a significant challenge for particle-based simulations. Here, we develop a transferable force field for chloroethenes, common environmental contaminants, that can accurately model the vapor liquid phase equilibria including azeotrope formation. The new all-atom force field reproduces saturated liquid densities, saturated vapor pressures, boiling points, and critical properties within 1, 10, 1, and 1% of the experiment data, respectively. Furthermore, the vapor liquid equilibria of trichloroethylene and 1-propanol binary mixture, which forms a minimum boiling point azeotrope, is predicted with a reasonable accuracy. The microstructure of neat and binary systems is explored using pair correlation functions and spatial distribution functions. As the new force field is consistent with transferable potentials for phase equilibria (TraPPE) force field, it expands the applicability of TraPPE force field to chloroethenes.

1. INTRODUCTION

The lack of clean groundwater presents a significant challenge in meeting the growing demand for water for agricultural, commercial, and industrial needs. Most countries, depending on their stage of economic development and hydrogeological conditions, are facing groundwater contamination problems.1,2 In particular, the contamination of groundwater due to chlorinated aliphatic hydrocarbons is becoming an important environmental concern in regions with significant industrial activity. Chlorinated compounds are extensively used in a large number of industrial processes especially as solvents, degreasing agents, paint removers, adhesives, lubricants, rug-cleaning fluids, pharmaceuticals, and pesticides.3 Because of the extensive use of chloroethenes, these compounds are widely distributed in sediments, soils, and the groundwater.3–5 Chloroethene compounds include chloroethylene or vinyl chloride, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, 1,1-dichloroethylene, trichloroethylene (TCE), and tetrachloroethylene (PCE). Among chloroethenes, TCE and PCE are the major contaminants which are frequently found in the groundwater. In this family of compounds, TCE is considered to be the most hazardous and is a known human carcinogen.6 The presence of dichlorinated ethylene isomers in the water is mainly due to the microbial transformations of TCE and PCE. Often, PCE and TCE readily undergo anaerobic reduction reactions, which lead to substitution of chlorine by hydrogen to yield dichlorinated and chloroethene compounds.7,8

Determination of accurate physicochemical properties of chloroethenes is essential for predicting its environmental impact and designing separation processes. With the increase in computational power and improvements in the force fields, molecular simulations play an important role in computing thermophysical properties.9 Given the importance of chloroethenes, they have been the subject of numerous computational works. In some of the adsorption studies,10–12 the C and H interaction parameters were taken from previous Monte Carlo studies that reported good heat of adsorption of methane in zeolites.13,14 The parameters for chlorine were derived from Lennard-Jones (IJ) parameters of argon as Ar and Cl have similar atomic radii and polarizabilities.10 As such, there are no force field developed specifically for chloroethenes, but some studies15,16 have used optimized potential for liquid simulations (OPLS)17-type force field for chloroalkenes. Delli et al.18 examined the accuracy of OPLS force field for cis and trans-1,2-dichloroethene compounds. The computed thermophysical properties differ significantly from the experimental data. This force field underestimates the saturated liquid density by 1.3–1.6% for cis isomer and 2.3–2.7% for the trans isomer.18 This led authors to develop a new force field by refining the parameters against the available experimental data to investigate the solvation structure and dynamics of both the isomers in supercritical carbon dioxide. Luo and Farrell19 used universal force field19,20,21 for TCE and PCE to study how pH of the

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solution affects adsorption of these compounds on iron surfaces.

As most of the previous work has involved developing force field for specific chloroethene molecules with limited state point transferability, there is a need for an accurate force field that is consistent across chlorosubstituted ethenes. Here, we develop a transferable force field for chloroethenes, which can accurately predict thermophysical properties such as vapor liquid coexistence curves, critical properties, and azeotrope compositions. In this work, the force field for chloroethenes is derived from the transferable potential for phase equilibria—(TraPPE) force field. We used all-atom representation for chloroethenes in order to provide a more accurate description of charge distribution.23–25

The article is arranged in the following manner. Section 2 describes the force field parameterization for chloroethenes. Section 3 provides the simulation details for computing the force field parameterization for chloroethenes. The intramolecular and intermolecular parameters are listed in Tables 1 and 2. The interactions among unlike atoms are calculated with the Lorentz–Berthelot combining rules.

\[
\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}
\]

\[
\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}
\]

Table 1. Force Field Parameters for Bonded Interactions

| bond          | \( r_0 \) (Å) | bend     | \( \theta_b \) (deg) | \( k_b \) (K/\( \text{rad}^2 \)) | torsion | \( k_T \) (K/\( \text{rad}^2 \)) |
|---------------|---------------|----------|----------------------|---------------------------------|---------|-------------------------------|
| C–H          | 1.08          | \( \angle \text{Cl–C–Cl} \) 114.74 | 99 930.0                | Cl–C–C–Cl                       | 14 668.0 |                              |
| C=C           | 1.320         | \( \angle \text{Cl–C–C} \) 122.74 | 78 630.0                | Cl–C–C–H                        | 15 320.0 |                              |
| C–Cl          | 1.725         | \( \angle \text{Cl–C–H} \) 114.88 | 61 670.0                | H–C–C–H                         | 14 094.0 |                              |
|               |               | \( \angle \text{C–C–H} \) 122.43 | 57 130.0                |                                 |         |                              |
|               |               | \( \angle \text{H–C–H} \) 117.75 | 50 410.0                |                                 |         |                              |

The TraPPE force field includes intramolecular nonbond interaction terms only between atoms separated by four or more bonds. Thus, in the present set of molecules there are no intramolecular nonbond interactions. Bonds were considered rigid with equilibrium bond length obtained from electronic structure calculations (see below). For bend angle and torsional potentials, a harmonic term is used to control the angle:

\[
U_{\text{bend}}(\theta) = \frac{k_b}{2}(\theta - \theta_0)^2
\]

\[
U_{\text{torsion}}(\phi) = \frac{k_T}{2}(\phi - \phi_0)^2
\]

where \( \theta \) and \( \phi \) are the bend and torsional angle, respectively, \( \theta_0 \) and \( \phi_0 \) are the equilibrium bend and torsional angle, respectively, and \( k_b \) and \( k_T \) are the bend and torsional force constants, respectively. The torsional equilibrium angle (\( \phi_0 \)) was kept zero and \( \pi \) for cis and trans configurations of the molecules, respectively. The bending and torsional force constants were calculated by fitting eqs 4 and 5 to the ab initio potential energy curve calculated at the second-order MP2 level of theory36,27 and Dunning’s augmented correlation-consistent polarized valence triple zeta basis set of contracted Gaussian functions (aug-cc-pVTZ).28,29

Additional ab initio geometry optimization calculations were performed using the M06-2X30 density functional with aug-cc-pVTZ basis set to determine equilibrium geometry and partial atomic charges. M06-2X density functional performs better than other density functionals for modeling short- to medium-range correlation.30 For partial atomic charge calculations, 1-octanol is used as the universal continuum solvent in the condensed phase.24,25 Atomic charges for different atoms of various compounds are listed in Table 3. Figure 1 shows the molecular structure of all compounds and atom numbering.

Table 2. Force Field Parameters for Nonbond Interactions

| atom type | \( \epsilon/b_o \) (K) | \( \sigma \) (Å) |
|-----------|------------------------|-----------------|
| C[H_2]    | 27.0                   | 3.72            |
| C[ClH]    | 35.70                  | 3.55            |
| C[Cl_2]   | 30.70                  | 3.54            |
| H          | 25.45                  | 2.36            |
| Cl         | 149.0                  | 3.42            |
corresponding to the atomic charge listed in Table 3. All ab initio calculations were performed using the Gaussian 09 program.31

### 3. SIMULATION DETAILS

#### 3.1. Single Component Vapor Liquid Coexistence Curves

A combination of Gibbs ensemble Monte Carlo (GEMC)32−34 method and coupled−decoupled configurational-bias Monte Carlo (CBMC)35−38 was used to determine vapor liquid coexistence curves for all compounds. The canonical version of the GEMC method32 uses two boxes in vapor liquid coexistence curves for all compounds. The total number of molecules in each system is listed in Table 4. A cutoff \((r_{\text{cut}})\) of 14 Å was used for the liquid box with an analytical tail correction to account for the interaction energy beyond the cutoff.39 To compute Coulombic interactions, Ewald summation with the tin foil boundary condition39,40 was used, and the cutoff for the real-space part of Ewald summation was set to \(r_{\text{cut}}\). The Ewald sum convergence parameter \(\kappa\) was set to 3.2/\(r_{\text{cut}}\). The size of the vapor box was adjusted during the equilibrium run, so that 20−40 molecules can be found in the vapor phase. In addition, we increased the cutoff for the real-space part of the Ewald summation for the vapor box in order to lower the number of reciprocal space vectors, which results in reducing the computation time required for the simulation. A minimum of 50 000–100 000 MC cycles was used to equilibrate the system. After equilibration, the production runs were carried out for 100 000 MC cycles. Standard deviation of the ensemble averages were obtained by breaking the production runs into five blocks.

From the vapor liquid coexistence curve data, the critical temperature and critical density were computed by using density scaling law41 and the law of rectilinear diameter42

\[
\rho_{\text{liq}} - \rho_{\text{vap}} = B(T - T_{\text{c}})^\beta
\]

\[
(\rho_{\text{liq}} + \rho_{\text{vap}})/2 = \rho_{\text{c}} + A(T - T_{\text{c}})
\]

where \(A\) and \(B\) are the fitting constants and \(\beta = 0.325\) is the critical exponent. In addition, the normal boiling point for each compound was calculated via Clausius−Clapeyron (CC) equation. The liquid structure was analyzed using radial distribution function (RDF), angular radial distribution function (ARDF), and three-dimensional spatial distribution function (SDF). The details of ARDF and SDF calculations can be found in our previous work.35,43

#### 3.2. Vapor Liquid Equilibria for Binary Mixtures

In order to check the transferability of the force field, we determined the vapor liquid equilibria (VLE) for binary

### Table 3. Partial Atomic Charges for Chloroethenes

| compound     | atom type | \( q \) (e) | compound     | atom type | \( q \) (e) | compound     | atom type | \( q \) (e) |
|--------------|-----------|-------------|--------------|-----------|-------------|--------------|-----------|-------------|
| CE           | C1[CH]   | −0.063      | cis-1,2-DCE  | C1[CH]   | −0.059      | 1,1-DCE     | C1[Cl]   | 0.048       |
|              | C2[H]    | −0.190      | C2[CH]      | C2[H]    | −0.059      | C2[H]       | −0.178    |
| H3           | 0.126     | H3          | 0.137       | H3        | 0.128       |
| H4           | 0.120     | Cl4         | −0.085      | Cl4       | 0.128       |
| H5           | 0.116     | H5          | 0.144       | H5        | 0.126       |
| Cl6          | −0.109    | Cl6         | −0.078      | Cl6       | −0.063      |
| TCE          | C1[CH]   | −0.053      | trans-1,2-DCE| C1[CH]  | −0.056      | ethylene    | C[H]     | −0.206      |
|              | C2[Cl]   | 0.048       | C2[CH]      | C2[Cl]   | −0.056      | H           | 0.103     |
| Cl3          | −0.061    | H3          | 0.141       | Cl5       | −0.084      |
| Cl4          | 0.146     | Cl4         | 0.141       | PCE       | Cl3         | −0.025     |
| Cl5          | −0.041    | H5          | 0.141       | Cl6       | −0.086      |

*CE: chloroethylene, DCE: dichloroethylene, TCE: trichloroethylene, and PCE: tetrachloroethylene.

### Table 4. System Size Used for Different Simulations

| compound     | total number of molecules |
|--------------|---------------------------|
| ethylene     | 450                       |
| chloroethylene| 350                      |
| cis-1,2-dichloroethylene| 300          |
| trans-1,2-dichloroethylene| 300          |
| 1,1-dichloroethylene  | 300                       |
| trichloroethylene   | 250                       |
| tetrachloroethylene  | 250                       |
| binary systems        | 440                       |

Figure 1. Molecular structure of compounds and atom numbering.
systems of trichloroethylene/1-propanol and trichloroethylene/dimethyl sulfoxide (DMSO). The VLE was computed at 20 and 100 kPa for trichloroethylene/1-propanol and at 95.3 kPa for trichloroethylene/DMSO system. Force field parameters for 1-propanol were taken from Chen et al. TraPPE UA.47 For modeling DMSO, the ketone oxygen and methyl group LJ parameters were taken from TraPPE force field, whereas the sulfur LJ parameters and partial atomic charges were taken from the OPLS force field.48 The system size for binary systems consists of 440 molecules in total. We used the isothermal–isobaric (NPT)51 version of GEMC to simulate the binary systems. The move probabilities and cutoff were similar to that described in the previous section for the canonical version of GEMC. The systems were equilibrated for 150 000—200 000 MC cycles, and the production runs were performed for at least 200 000 MC cycles.

4. RESULTS AND DISCUSSION

4.1. Single Component Vapor Liquid Coexistence Curves. The vapor liquid coexistence curves (VLCCs), saturated vapor pressure curves (SVPCs), and heat of vaporization curves (HOVCs) for all chloroethene compounds are shown in Figure 2. The plots for ethylene, chloroethylene, trichloroethylene, and tetrachloroethylene are shown in Figure 2A,C,E, respectively, where carbon LJ parameters were adjusted to the pure component fluid properties according to the carbon bonding environment. For all of these compounds, the mean unsigned percentage error for saturated liquid densities and vapor pressure is less than 1 and 10%, respectively. The simulation data ($\rho_{liq}$, $p_{vap}$, and $\Delta H_{vap}$) matches well with the available experimental data.52–56 To assess the transferability of the force field parameters, the predicted VLCCs, SVPCs, and HOVCs for cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, and 1,1-dichloroethylene compound are shown in Figure 2B,D,F. For trans-1,2-dichloroethylene and 1,1-dichloroethylene, the mean unsigned percentage error for saturated liquid densities and vapor pressures is less than 1 and 10%. In the case with cis-1,2-dichloroethylene, the saturated liquid densities are slightly over predicted (approximately 1.5% error) specifically at lower temperatures, and thus saturated vapor pressures are underpredicted. Overall, the mean unsigned percentage error for saturated liquid densities of cis-1,2-dichloroethylene is less than 1.1%. The dipole moment of cis-1,2-dichloroethylene in the gas phase and in the implicit solvent is quite high as compared with 1,1-dichloroethylene. Because of this, the dipole–dipole and dispersion interactions are expected to play a dominant role for this compound, whereas van der Waals dispersion forces are expected to govern thermophysical properties for trans-1,2-dichloroethylene compound. There is a reasonably good agreement for the predicted VLE properties of all of the three dichloroethylene isomers. The numerical data for the saturated liquid and vapor densities and saturated vapor pressures and heat of vaporization obtained from GEMC simulations for all compounds is provided in the Supporting Information. Overall, $\rho_{liq}$, $p_{vap}$, and $\Delta H_{vap}$ obtained from GEMC simulations for all chloroethene compounds are in excellent agreement with the experimental data.52–56

Figure 2. Vapor liquid coexistence curves (first column), CC plots (second column), and enthalpy of vaporization ($\Delta H_{vap}$) curves (third column) for different chloroethenes. (A,C,E) VLCC, CC plot, $\Delta H_{vap}$, respectively, for ethylene, chloroethylene, trichloroethylene, and tetrachloroethylene. (B,D,F) Corresponding data for cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, and 1,1-dichloroethylene. Filled and open symbols represent experimental52 and simulation data, respectively. In the first row, the red squares, violet circles, green triangles, and blue diamonds represent data for ethylene, chloroethylene, trichloroethylene, and tetrachloroethylene, respectively. In the second row, the violet circles, red squares, and blue diamonds represent data for cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, and 1,1-dichloroethylene, respectively. The black down triangle in (A) represents experimental critical point for ethylene,53 and for other compounds,52,54,56 it is shown as black dotted lines due to the nonavailability of critical density.

For all compounds, the predicted critical temperature ($T_{C}$) and normal boiling point ($T_{B}$) are listed in Table 5. Table 5 is divided into two sections based on the molecules included in the parameterization process and molecules included in the validation set to test the molecule transferability. The critical properties and normal boiling point for all compounds are in excellent agreement with the experimental data.52–56 For all compounds considered in the present work, there average error in $T_{C}$ and $T_{B}$ is approximately 1%.

4.2. VLE Phase Diagram for Binary Mixtures. The binary mixture of trichloroethylene and 1-propanol forms a nonideal mixtures leading to the formation of a minimum
boiling point azeotrope. The temperature–composition diagram of the binary mixtures of trichloroethylene/1-propanol at different pressures (20 and 100 kPa) are depicted in Figure 3A,B. The new force field reproduces the shape of the experimental $T_{xy}$ diagram reasonably well.\(^\text{57}\) However, the TCE mole fraction is somewhat underpredicted. Moreover, the boiling points for trichloroethylene and 1-propanol are also underpredicted by 1–2 K at both pressures. Generally, the location of azeotrope is of particular interest, and it is often difficult to accurately predict the location with simulations. Specifically for 100 kPa, the compositions obtained from the simulations around azeotrope provide a good match when compared with the experimental data. Overall, both binary phase diagrams at different pressures demonstrate that the force field parameters for chloroethenes with alcohol compounds provide a satisfactory treatment of the interaction potential. In order to further test the accuracy of the proposed force field, the $T_{xy}$ phase diagram is predicted for the binary mixture of trichloroethylene and DMSO at 95.3 kPa, which is shown in Figure 3C. Particularly, the compositions obtained from Monte Carlo simulations in the vapor phase are in good agreement with the experimental data. However, the liquid phase TCE mole fraction is somewhat underpredicted especially at higher temperatures.

### 4.3. Microscopic Structure of TCE/1-Propanol Mixtures

Isothermal–isobaric simulations were used to investigate the cluster size distributions for 1-propanol in trichloroethylene/1-propanol mixtures at different state points of the binary VLE. The state points located at the left and right of the azeotrope were chosen to investigate the cluster size distributions due to hydrogen bonding. Figure 4 shows the population of propanol aggregate distributions at 20 and 100 kPa. Hydrogen bonds were identified using the following criteria: $r_{\text{OO}} \leq 3.3 \, \text{Å}$, $r_{\text{OH}} \leq 2.5 \, \text{Å}$, and $\cos \theta_{\text{OH-OL}} \leq -0.1$, where $r_{\text{OO}}$, $r_{\text{OH}}$, and $\cos \theta_{\text{OH-OL}}$ are the oxygen–oxygen distance, oxygen–hydrogen distance, the angle between the OH bond vector on the donating molecule and the oxygen lone pair vector on the accepting molecule, respectively.\(^\text{58,59}\) At the left of the azeotrope, the figure shows the larger number of clusters having 2–6 molecules at both pressures. Moreover, it also shows a smaller fraction of a cluster having larger aggregates containing 7–12 molecules. However, when considering the composition to the right of the azeotrope, we observe smaller clusters (1–5 molecules) at both pressures. In other words, the transition from larger aggregates (more than 7–12 molecules) to the smaller aggregates was observed when moving from left of the azeotrope to the right.

![Figure 3](image1.png) **Figure 3.** Temperature composition ($T_{xy}$) phase diagram of trichloroethylene and 1-propanol at 20 (A) and 100 kPa (B). Temperature composition ($T_{xy}$) phase diagram of trichloroethylene and DMSO at 95.3 kPa (C). The dotted line and square symbols represents experimental\(^\text{57,58}\) and simulation data.

![Figure 4](image2.png) **Figure 4.** Population of 1-propanol aggregates at 20 and 100 kPa. Red circles and black diamonds represent data left ($T = 313.95 \, \text{K}$, $x_{1\text{-propanol}} = 0.68$) and right ($T = 310.35 \, \text{K}$, $x_{1\text{-propanol}} = 0.04$) of the azeotrope compositions, respectively, at 20 kPa. Similarly, green circles and indigo diamonds represent data at the left ($T = 354.15 \, \text{K}$, $x_{1\text{-propanol}} = 0.62$) and right ($T = 354.15 \, \text{K}$, $x_{1\text{-propanol}} = 0.06$) of the azeotrope, respectively, at 100 kPa.
and 100 kPa, respectively. For both pressures, the most noticeable is the large enhancements for the heights of first peaks for the OO and OH RDFs. The heights of the first peak for the OO and OH RDFs appears near 2.71 and 1.78 Å for both pressures considered, and the second peak is located near 3.15 Å for OH RDF. Considering 20 kPa RDF plot, there is a large increase in the height of the peaks for OO and OH RDFs as compared to 100 kPa RDF analysis. These large peaks clearly indicate the presence of hydrogen bonding for all compositions and temperatures. The peak heights are significantly large on the right side of the azeotrope location primarily because of the lower mole fraction of propanol in the liquid phase. The first peak in the OO RDF yields coordination numbers of 2.42 \((x_{\text{propanol}} = 0.68)\) and 1.79 \((x_{\text{propanol}} = 0.04)\), and the coordination number from OH RDF are 0.99 \((x_{\text{propanol}} = 0.68)\) and 0.73 \((x_{\text{propanol}} = 0.04)\) for 20 kPa. The first peak in the OO RDF yields coordination numbers of 2.25 \((x_{\text{propanol}} = 0.62)\) and 1.32 \((x_{\text{propanol}} = 0.06)\), and the coordination number from OH RDF are 0.91 \((x_{\text{propanol}} = 0.62)\) and 0.56 \((x_{\text{propanol}} = 0.06)\) for 100 kPa.

4.4. Microscopic Structure of Neat Liquids. Figure 6A–D shows RDFs for carbon–carbon (C–C), carbon–chlorine (C–Cl), chlorine (Cl)–chlorine (Cl), and center of mass separations for tetrachloroethylene molecule at 293 K. All of the RDF plots were compared with the results obtained from molecular dynamics simulations carried out in Gereben and Pusztai work.\(^{15}\) In Gereben and Pusztai work,\(^{15}\) LJ parameters are taken from OPLS-AA\(^{17}\) and used in combination with two different sets of partial atomic charges (ED_MID and ED_CI). In the C–C and C–Cl plots, the location of the first coordination shell peak is at 6 and 4.95 Å, respectively, which is in good agreement with ED_MID and ED_CI simulation data. All RDF analyses from our force field simulations are in good agreement with Gereben and Pusztai work.\(^{15}\) However, the Gereben and Pusztai\(^{15}\) included intramolecular Cl–Cl terms in their plot along with intermolecular terms (Figure 6C). This leads to two sharp peaks at short distances and distorts the intermolecular RDF. The long-range behavior is in good agreement with our force field. Figure 6D results are in excellent agreement with the ED_MID center of mass RDF plot. As depicted by Gereben and Pusztai work,\(^{15}\) a shoulder is observed between 3.9 and 4.1 Å for the ED_MID charge sets and our simulation results also confirm this noteworthy feature at 3.95 Å, as shown in Figure 6D. In addition, the location of the first coordination shell peak is at 6.35 Å approximately as compared to 6.3 Å in their work.

Furthermore, another essential structural detail concerning positioning of the molecules can be gleaned from ARDF. Because ARDF resolves the angle in addition to the radial distance (as in RDFs), they can provide information about relative orientation of the molecules in the liquid phase. Figure 7 shows ARDF for chloroethylene, trichloroethylene, and tetrachloroethylene at 255, 288, and 293 K, respectively. For ARDF, the distance is based on the center of mass of the molecule. In the case of chloroethylene, and trichloroethylene, the angles were defined based on the vectors that closely align with the dipole moment vector of molecules. For chloroethylene, the angle is calculated between vectors from chlorine (Cl6) to carbon atom (C1) (see Figure 1). Similarly, for trichloroethylene, the angle is calculated between vectors from chlorine (Cl6) to carbon atom (C1) (see Figure 1). With no dipole moment for tetrachloroethylene, the long axis was defined by the vectors pointing from first carbon atom to the second carbon atom.

Figure 7A for chloroethylene molecule shows a strong inclination for antiparallel orientation in the first solvation shell. The ARDF plot for chloroethylene shows a considerably higher peak near \(r \approx 4.1–4.3\) Å and 180°, which shows the preference for antiparallel orientation. For the trichloroethylene liquid phase, there are a few dominating peaks near parallel and antiparallel orientations, which basically covers a wide range of angle domain between 5.7 < \(r < 6.1\) Å. The chloroethylene and trichloroethylene molecule prefers to align with an angle that maximizes the interaction between chlorine and hydrogen atoms and that seems to get enhanced in the antiparallel orientation. Because of the symmetry of the tetrachloroethylene
molecule, it prefers to be in parallel or antiparallel orientation, as shown in Figure 7C. The peaks are mostly located between 4.9 < r < 5.3 Å.

Figure 8 shows SDF for the liquid phase of chloroethylene, trichloroethylene and tetrachloroethylene at 255, 288, and 293 K, respectively. The surfaces shown in the figure corresponds to the 25% most likely positions of molecules in the first solvation shell. The center for each molecule was defined between the midpoints of the carbon–carbon bond. Figure 8A,B,C shows higher density distribution around a particular molecule within the first solvation shell. Because of the symmetry of tetrachloroethylene molecule, the density distribution analysis reflects the same symmetry where molecules in the first solvation shell occupy the region in between chlorine atoms. In the case with chloroethylene and trichloroethylene, the density distribution is focused largely on the single chlorine and hydrogen atom in the particular molecule. This is predominantly due to the stronger interaction between chlorine and hydrogen atoms.

5. CONCLUSIONS

In this work, we have presented a transferable force field for chloroethenes, which can accurately predict the VLCCs, saturated vapor pressure, critical properties, boiling temperatures, and structural properties (RDFs, ARDF, SDF). The nonbonded interaction parameters for molecules depend mainly on the bonding environment. Considering the bonding environment of the carbon atom, different epsilon and sigma parameters were parameterized for (C)H_xCl_y. The force field shows satisfactory agreement with the experimental data for neat component properties and yields a suitable agreement for critical properties and boiling points for all compounds considered. Moreover, the force field predicts binary phase diagram of trichloroethylene/1-propanol and trichloroethylene/DMSO at different pressures fairly well. Near azo trope or far from azo trope, the force field is able to nicely predict the shape of the experimental curve. The structural analysis of 1-propanol in the binary mixture of trichloroethylene/1-propanol was also performed, where there is a significant increase in smaller clusters formation while going from left to the right of the azo trope composition. The RDFs for binary mixtures demonstrate extensive hydrogen bonding between 1-propanol molecules at 20 and 100 kPa pressures. In addition, the RDFs for pure chloroethylene compounds were obtained and compared with the available literature data. The ARDF and SDP analyses provide the detailed microscopic view of the first coordination shell where parallel and antiparallel configurations are preferred. Furthermore, the present work extends the applicability of popular TraPPE force field to chloroethenes that are major environmental contaminants.

ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00044.

VLE numerical data obtained from the Monte Carlo simulations for pure components and binary mixtures, gas and solvent phase dipole moments, and the RDF plots for chloroethene compounds (PDF)

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The authors declare no competing financial interest.

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