Prediction of Thermodynamic Properties of Levulinic Acid via Molecular Simulation Techniques

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ABSTRACT: Second-generation biofuels are a complex mixture of organic compounds that can be further processed to hydrocarbon fuels and other valuable chemicals. One such chemical is levulinic acid (IUPAC name: 4-oxo pentanoic acid), which is a highly versatile ketoacid obtained from cellulose present in agricultural byproducts. For oxygen-containing compounds that decompose at elevated temperatures and pressures, determining the vapor–liquid equilibria data at high temperatures via the experimental route may be challenging. The molecular simulation approach is a cost-effective tool to obtain the necessary data while also allowing us to understand the microscopic origins of macroscopic observable properties. We have employed the transferable potential for phase equilibria-united atom force field to describe the interactions in this system with the parameters for a torsional interaction that are not reported in the literature (levulinic acid is a ketoacid) being determined from density functional theory calculations. We have verified our parameterization via density computations in the isothermal–isobaric ensemble and by comparing our simulation results with the corresponding data from experiments reported in the literature. We have performed grand-canonical transition-matrix Monte Carlo simulations in the temperature range from 580 to 690 K to estimate the vapor–liquid coexistence curves in the temperature–density plane and the Clapeyron plots. From this data, the critical point ($T_C = 755 \text{ K}$, $P_C = 285.4 \text{ kg/m}^3$, and $P_C = 30.57 \text{ bar}$) has been estimated, and this may be used as input to the equations of state employed in process simulation software for design of industrial separation processes including those for “biorefining”. As levulinic acid is a “ketoacid”, hydrogen bonding occurs, and the liquid phase structure has also been studied using radial distribution functions.

1. INTRODUCTION

Levulinic acid is a “ketoacid” obtained by conversion of lignocellulosic biomass and finds use in a variety of chemical applications, for example, as a precursor for the synthesis of liquid transportation fuels. Levulinic acid is also a precursor for the synthesis of value-added chemicals, such as methyltetrahydrofuran, which is an important oxygenated fuel additive and is also employed as a solvent. The commercial value of levulinic acid is further enhanced as it is used in the production of a broad-spectrum herbicide, d-aminolevulinic acid. Also, the nontoxic levulinic acid is being investigated as a reactant in the manufacture of diphenolic acid, which in turn will be used as a replacement for the toxic bisphenol as a plasticizer. A cost-effective production technique for levulinic acid from renewable feedstocks including agricultural by-products has been developed and a 1 ton/day facility is operational in the United States. Ghorpade and Hanna noted that the levulinic acid thus produced can be isolated using filtration followed by vacuum steam distillation or by solvent extraction. The design and optimization of these separation processes (and also other processes) require accurate knowledge of thermodynamic properties, including vapor–liquid coexistence properties, of levulinic acid (besides that of its mixtures). Process simulation software generally employs the equation-of-state approach, which requires the pure component critical properties as input. However, despite the industrial importance of this organic compound, experimental data exists only for low temperatures because of the fact that larger oxygen-containing compounds undergo thermal decomposition at elevated temperatures. The accuracy of the molecular simulation approach depends only on the force field (and its parameterization) employed and can easily circumvent this issue to determine the thermodynamic properties at high temperatures. Other alternatives, for example, group contribution model predictions of thermophysical properties, may not reflect experimental data reliably as the group contribution method is “inherently approximate”. Empirical correlations available also have parameters that are generally obtained via regression in a specific range of temperature and pressure conditions, which may not correspond to the operating conditions of the industrial processes. Hence, molecular simulations are a promising cost-effective alternative tool for predicting thermodynamic properties and additionally enable investigation into the molecular-level behavior of complex organic compounds such as levulinic acid (which contains both the keto group and the carboxylic acid group), the molecule of interest here.

In this study, Monte Carlo simulations have been performed to obtain thermodynamic properties, including vapor–liquid coexistence properties, of levulinic acid by employing the transferable potentials for phase equilibria-united atom (TraPPE-UA) force field in conjunction with Monte Carlo

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simulation techniques. Toward achieving this, parameterization of the dihedral interaction of the TraPPE-UA force field not reported in the literature has been performed, whereas the other parameters are assumed to be transferable from the TraPPE-UA force field for other organic molecules.\textsuperscript{18,21,26,28–35} The parameters for the force field used in this study are verified by comparing the liquid densities determined via standard Metropolis Monte Carlo simulations with the corresponding experimental data.\textsuperscript{11} Furthermore, the molecular-level structure of the liquid has been investigated using the results of the same simulations to study the associating-type interactions present in this system. Additionally, we have estimated the vapor–liquid coexistence properties of this compound in the high-temperature range by employing the computationally efficient transition-matrix Monte Carlo (TMMC) simulations in the grand canonical (GC) ensemble. The rest of this article is organized as follows. The force field employed to model the interactions present in the levulinic acid system is described in Section 2, and details of the molecular simulation runs (performed using the open source MCCCS Towhee software package\textsuperscript{37}) are reported in Section 3. Analyses of the results are discussed in Section 4. Section 5 summarizes the conclusions of this study.

2. FORCE FIELD

The first step in any molecular simulation approach is the selection of an appropriate force field to describe the nonbonded and bonded interactions present in the system. In this study, we have adopted the transferable potentials for phase equilibria-united atom (TraPPE-UA) force field to model the interactions present in the system of levulinic acid molecules under consideration. The TraPPE-UA force field has been developed by the Siepmann group at the University of Minnesota. This force field, with highly transferable parameters, is known to predict thermodynamic properties (in particular, vapor–liquid phase coexistence properties) accurately for a wide range of organic molecules at different state conditions.\textsuperscript{36}

The nonbonded interactions are modeled as a sum of the van der Waals interactions modeled using the 12–6 Lennard-Jones (LJ) potential, and electrostatic interactions are modeled with the Coulombic potential (where partial charges are present), as shown in eq 1

\begin{equation}
u_{\text{NB}}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}
\end{equation}

where \(r_{ij}\) is the separation distance between the \(i\)th and \(j\)th united atoms, \(\epsilon_{ij}\) is the LJ well depth, \(\sigma_{ij}\) is the LJ diameter, and \(q_i\) and \(q_j\) are the partial charges on the \(i\)th and \(j\)th united atom. A cutoff distance of 14 Å has been employed with analytical tail corrections being considered beyond the cutoff distance. Coulombic interactions are computed using the Ewald summation method, and the parameters used here are as recommended by the MCCCS Towhee manual.\textsuperscript{37} The parameters employed to model levulinic acid are given in Table 1. The unlike interactions are modeled using the Lorentz–Berthelot combining rules.

\begin{equation}
\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)
\end{equation}

\begin{equation}
\epsilon_{ij} = \sqrt{\epsilon_i^2 + \epsilon_j^2}
\end{equation}

The TraPPE-UA force field is a semiflexible force field as the bond length is held fixed at values reported in Table 2a.

The bond angle bending is described using the harmonic potential shown in eq 3 below.

\begin{equation}
u_{\text{bend}}(\theta) = \frac{k_\theta}{2}(\theta - \theta_0)^2
\end{equation}

In eq 3, \(\theta\) and \(\theta_0\) are the bond angle, equilibrium bond angle, and force constant, respectively, and are listed in Table 2b. The torsional interactions are modeled using eqs 4a or 4b depending on the four united atoms involved, and the parameters for the dihedral interactions are reported in Table 2c.

\begin{equation}
u_{\text{torsion}}(\phi) = c_0 + c_1[1 + \cos(\phi)] + c_2[1 - \cos(2\phi)]
\end{equation}

\begin{equation}
u_{\text{torsion}}(\phi) = c_0 + c_1[1 + \cos(\phi)] + c_2[1 - \cos^2(\phi)]
\end{equation}

Here, \(\phi\) is the dihedral angle and \(c_i\) represents the \(i\)th coefficient. The parameters (see Table 2c) for the torsion 2–3–5–6 (refer to Figure 1 for the corresponding united atoms) are not reported in the literature and have been calculated using the density functional theory (DFT) approach. This approach has been successfully implemented in the literature for the determination of the missing torsions in other organic compounds such as organic cyclic molecules, acrylates, cyclic alkanes, ethers, etc. To determine the missing torsion parameters, scans of the potential energy surface have been performed at 5\(^\circ\) interval from −180 to 180\(^\circ\) at the B3PW91 level of theory with the 6-31++G(d,p) basis set using Gaussian 03 software.\textsuperscript{58} Figure 2 shows a comparison of the fitted equation (eq 4a) and the DFT results, and these are observed to be in good agreement with the exception of the discrepancies observed near the minima and maxima values, which have been noted in the literature for other compounds also.\textsuperscript{72,39}

There are no improper torsions in the force field describing this molecule.

3. SIMULATION DETAILS

All simulations, in this study, have been performed using the MCCCS Towhee version 7.1.0 software package,\textsuperscript{37} and the

| site | united atom | \(\epsilon/k_B\) (K) | \(\sigma\) (Å) | \(q\) (e) |
|------|-------------|-----------------|---------|-------|
| 1    | CH₃         | 98              | 3.75    | 0.0   |
| 2 (keto) | C       | 40              | 3.82    | 0.424 |
| 3    | CH₂         | 46              | 3.95    | 0.0   |
| 4 (keto) | O       | 79              | 3.05    | −0.424 |
| 5    | CH₂         | 46              | 3.95    | +0.12 |
| 6 (acid) | C(==O)  | 41              | 3.90    | +0.42 |
| 7 (acid) | O(==C)  | 79              | 3.05    | −0.45 |
| 8 (acid) | O       | 93              | 3.02    | −0.46 |
| 9 (acid) | H       | 0               | 0.00    | +0.37 |

Table 1. TraPPE-UA Force-Field Parameters for Nonbonded Interactions\textsuperscript{19,26}
Comparison with experimental data has been provided in at least 250,000 relaxation cycles to attain equilibrium. Production cycles, after performing each of the simulations for 10:30:15:15:30. Averages have been computed over 100,000 center-of-mass translation moves in the frequency ratio con gurational bias regrowth moves, and rotation and translation moves in the cubic simulation box. The trial moves are boundary conditions (PBCs) have been applied in all three directions in the cubic simulation box. The trial moves are volume change moves, aggregation-volume-biased moves, configurational bias regrowth moves, and rotation and center-of-mass translation moves in the frequency ratio 10:30:15:15:30. Averages have been computed over 100,000 production cycles, after performing each of the simulations for at least 250,000 relaxation cycles to attain equilibrium. Comparison with experimental data has been provided in

| Table 2. TraPPE-UA Force-Field Parameters for Bonded Interactions$^{19,26}$ |
|-----------------------------|-----------------------------|-----------------------------|
| (a) Rigid Bonds             | (b) Bond Angle Bending      | (c) Dihedral Interactions   |
| stretch                     | type                        | bond length (Å)             |
| 1–2                        | CH$_3$–(C=O)                | 1.52                        |
| 2–3                        | CH$_2$–(C=O)                | 1.52                        |
| 2–4                        | C=O                         | 1.239                       |
| 3–5                        | CH$_2$–CH$_3$               | 1.54                        |
| 5–6                        | CH$_2$–(C=O)                | 1.52                        |
| 6–7                        | C=O                         | 1.214                       |
| 6–8                        | O=–(C=O)                    | 1.364                       |
| 8–9                        | O=–H                        | 0.97                        |
| bend                       | type                        | θ (deg)                     | $k_c$/$k_b$ (K/Å²) |
| 1–2–3                      | CH$_3$–(C=O)–CH$_2$         | 117.2                       | 62,500             |
| 1–2–4                      | CH$_3$–(C=O)                | 121.4                       | 62,500             |
| 2–3–5                      | C=O–(CH$_2$)–CH$_3$         | 114.0                       | 62,500             |
| 3–5–6                      | CH$_2$–(CH$_2$)–C=O         | 114.0                       | 62,500             |
| 3–2–4                      | CH$_3$–(C=O)                | 121.4                       | 62,500             |
| 5–6–7                      | CH$_2$–(C=O)                | 121.4                       | 62,500             |
| 5–6–8                      | CH$_2$–(C=O)                | 111.0                       | 35,300             |
| 6–8–9                      | C=O–(C=O)–O=–H             | 107.0                       | 17,600             |
| 7–6–8                      | O=–(C=O)–O=–H              | 123.0                       | 40,300             |
| torsion                    | type                        | eq #                        | $c_l$/$k_b$ (K)    | $c_l$/$k_b$ (K)    | $c_l$/$k_b$ (K) |
| 1–2–3–5                    | CH$_3$–(C=O)–(CH$_2$)–CH$_3$ | 4a                          | 17.26             | 752.6             | 14.89             | 282.1             |
| 4–2–3–5                    | CH$_2$–(CH$_2$)–(C=O)       | 4a                          | 2035.58           | 736.9             | 57.84             | 293.23            |
| 2–5–3–6                    | C=O–(CH$_2$)–CH$_3$–C=O     | 4a                          | 365.76            | −1444.94          | −934.93           | −771.83           |
| 4–5–6–7                    | CH$_2$–(CH$_2$)–(C=O)       | 4a                          | 2035.58           | 736.9             | 57.84             | 293.23            |
| torsion                    | type                        | eq #                        | $c_l$/$k_b$ (K)    | $c_l$/$k_b$ (K)    | $c_l$ (rad)       |
| 5–6–8–9                    | CH$_2$–(C=O)–O=–H           | 4b                          | 630.0             | 1562.4            | 0                 |
| 7–6–8–9                    | O=–(C=O)–O=–H              | 4b                          | 630.0             | 1562.4            | $\pi$             |

Figure 1. United atom representation of levulinic acid (refer to Table 1).

3.1. Isothermal–Isobaric Ensemble Simulations. Standard Monte Carlo simulations have been performed in the isothermal–isobaric ensemble to first compute the liquid densities at a pressure of 100 kPa and a temperature range of 313.15–338.15 K in intervals of 5 K. These simulations have been performed for purposes of comparison with experimental data reported in the literature. A system size of $N = 300$ levulinic acid molecules has been considered. Periodic boundary conditions (PBCs) have been applied in all three directions in the cubic simulation box. The trial moves are volume change moves, aggregation-volume-biased moves, configurational bias regrowth moves, and rotation and center-of-mass translation moves in the frequency ratio 10:30:15:15:30. Averages have been computed over 100,000 production cycles, after performing each of the simulations for at least 250,000 relaxation cycles to attain equilibrium. Comparison with experimental data has been provided in

Figure 2. Torsional energy as a function of dihedral angle of levulinic acid for C=O–(CH$_2$)–CH$_3$–C=O. Potential energy scans at B3PW91/6-31++ G(d,p) are shown as red circles. The solid line is the fit of eq 4a to the DFT data.

Section 4. Because levulinic acid contains both the keto group and the acid group, we have also investigated the structure of the liquid phases at the conditions specified by calculating the site–site intermolecular radial distribution functions (RDFs). The analyses of the results obtained are reported in Section 4.

3.2. Grand Canonical Ensemble Simulations. We have performed transition-matrix Monte Carlo (TMMC) simulations in the grand canonical (GC) ensemble to derive the vapor–liquid coexistence data, viz., the phase diagram in the
temperature--density plane and Clapeyron plot. The single-box GC-TMMC simulation technique has been employed to perform the simulation here as it is known to be computationally more efficient than the traditionally employed two-box simulation techniques, such as the Gibbs ensemble Monte Carlo method. This is because information from the rejected Monte Carlo moves is also used to compute the particle number probability distribution (PNPD) at any arbitrary value of the chemical potential and the PNPD at a coexistence value of the chemical potential can be determined via histogram reweighting. In this study, GC-TMMC simulations have been performed at arbitrary chemical potentials in a cubic box of length 50 Å and in a temperature range from 580 to 690 K. Experimental data for phase coexistence behavior is not available in the literature at these high temperatures. The particle numbers range from a minimum value of 0 to a maximum of 950. The frequencies of attempted trials in these simulations are 40% particle insertions/deletions, 15% aggregation-volume-biased moves, 10% configuration-biased regrowths, 15% center-of-mass translation moves, and 20% rotation moves. Again, PBCs have been applied in the x-, y-, and z-directions in the cubic simulation box. The vapor and liquid coexistence densities and the saturation pressure at a given temperature have been determined from the particle number probability distributions obtained at the end of each simulation run. These coexistence properties are then fitted to the scaling law and the law of rectilinear diameters to calculate the critical properties. The discussion on the results, thus derived, is given in Section 4.

4. RESULTS AND DISCUSSION

4.1. Isothermal--Isobaric Ensemble Simulations. 4.1.1. Density of Liquid Levulinic Acid. The liquid densities obtained from the single-box Metropolis MC simulations have been compared with the experimental data at 100 kPa and in the temperature range 313.15 to 338.15 K (in Table 3).

Table 3. Comparison of Simulation Results with Experimental Data for Liquid Densities at 100 kPa

| T (K)  | simulation results (g/cm³) | experimental data (g/cm³) | % relative deviation |
|-------|--------------------------|--------------------------|---------------------|
| 313.15 | 1.080(3)                  | 1.123                    | 3.86                |
| 318.15 | 1.075(3)                  | 1.119                    | 3.90                |
| 323.15 | 1.073(3)                  | 1.115                    | 3.92                |
| 328.15 | 1.066(3)                  | 1.110                    | 3.98                |
| 333.15 | 1.060(4)                  | 1.106                    | 4.18                |
| 338.15 | 1.059(3)                  | 1.102                    | 3.87                |

The number in the parenthesis indicates the uncertainty in the simulation results.

4.1.2. Structure of Liquid Levulinic Acid. As levulinic acid is a ketoacid, the molecular-level structure of this liquid is important, and we have examined this by computing the site--site intermolecular RDFs. Figure 3 shows the RDFs present between the partially charged pseudoatoms at 313.15 K. The variation of the structure with temperature has also been investigated, and it was found that the RDFs at 313.15 K are representative of the structure at the higher temperatures (318.15–338.15 K) also.

In Figure 3a, we analyze the presence of hydrogen bonding on the basis of the procedure followed by Stubbs et al.19 for pure systems containing diols or glycols, who stated the criterion for hydrogen bonding to occur as the distance between the closest oxygen and the given hydroxyl hydrogen in the –OH group to be less than 3.3 Å. We have also considered only the separation distance between the oxygen and the hydrogen with partial charges present in the system instead of the more rigorous geometric and/or energetic criteria. As seen in Figure 3a, the first peak in the RDF of H9−O4 (see Figure 1) occurs at r = 1.89 Å, and this intermolecular distance (r) indicates the existence of hydrogen bond. The height of this peak reduces from g(r) = 2.1 at 313.15 K to g(r) = 1.722 at 338.15 K, which is the expected behavior (i.e., the number of hydrogen bonds will decrease as temperature will increase). Additionally, the RDF for H9−O7 at 313.15 K in Figure 3a shows a first peak height of g(r) = 3.94 at the same separation distance of r = 1.89 Å. This indicates that the H9−O7 hydrogen bonds are stronger than those of H9−O4, which can be explained by the fact that the partial charge on O7 (in the carboxylic acid group) is −0.45e as compared to −0.42e on O4 (in the keto group). However, although the partial charge on O8 is −0.46e (which is slightly higher than that on O7), the RDF of H9−O8 shows a plateau beginning at r ~ 2.03 Å (at higher temperatures, r ~ 2.17 Å) and the highest RDF peak (with a much shorter peak height g(r) = 1.32) at a separation distance of r = 3.99 Å. This is possibly because of the positions occupied by the O7 and O8 atoms relative to the position of H9 in the acid group, which results in more probability of hydrogen bonds being formed with O7 than with O8 as there is an intramolecular covalent bond existing between O8 and H9.

The presence of partial charges on the C2, C5, and C6 united atoms results in associating-type interactions with O4, O7, and O8 pseudoatoms. These weaker attractive interactions are noted in the intermolecular RDFs illustrated in Figure 3b for C6−O7 (primary peak height g(r) = 1.538 at r = 3.57 Å) and C6−O8 (primary peak height g(r) = 1.76 at r = 3.85 Å), where C6, O7, and O8 are all united atoms in the carboxylic acid group, whereas the RDF for C6−O4 indicates that these atoms scarcely influence each other. The primary peak in the RDF of C2−O8 shown in Figure 3c occurs at r = 3.99 Å with a peak height of g(r) = 1.336, whereas the C2−O7 and C2−O4 RDFs have lower peak heights, indicating very weak correlations between the positions of these atoms. In Figure 3d, the RDFs of the CH3 united atom (site # 5 in Figure 1 and represented as C5 in legend of Figure 3d) with the keto group oxygen atom, O4, and with the O7 atom in the carboxylic acid group show the appearance of a plateau at r ~ 4 Å and the highest peaks at r ~ 5 Å, whereas the CH3−O4 RDF shows the first peak at a separation distance of r = 4.97 Å. However, the highest peak height of g(r) = 1.438 is observed in the CH3−O7 RDF with the other first peak heights being lower than this, indicating a stronger attractive interaction between CH3 and O7 as compared to that in CH3−O8 and CH3−O7.

4.2. Grand Canonical Ensemble Simulations. 4.2.1. Vapor–Liquid Coexistence Properties. We have also attempted to predict the high-temperature fluid phase behavior of levulinic acid as the experimental data is limited to low
vapor pressure data in the temperature range of 375–519 K.\textsuperscript{18} The normal boiling point of levulinic acid is 518.7 K.\textsuperscript{18} We note here again the transferability of the TraPPE-UA parameters reported in the literature to the force field used to describe the interactions in levulinic acid (with the exception of one missing dihedral interaction that has been determined in this study). The vapor–liquid coexistence data for levulinic acid as obtained from our GC-TMMC simulations are reported in Table 4.

The pure component coexistence densities for the vapor and liquid phases in equilibrium are also shown in Figure 4 as a function of temperature. Due to the unavailability of experimental data in the high-temperature range, a comparison has not been provided. We, therefore, report the comparison of the experimental data with simulation results (available in the literature) of 2-pentanone\textsuperscript{19} and pentanoic acid\textsuperscript{26} as levulinic acid (C\textsubscript{3}H\textsubscript{8}O\textsubscript{3}) is a ketoacid and has been stated previously the parameters of the force field (describing the interactions in levulinic acid) have been transferred from these two compounds. The agreement between TraPPE-UA-based simulation results and experimental data, reported in the literature for 2-pentanone, is reasonable. For ketones, the TraPPE-UA force field predicts the coexistence liquid densities and critical temperatures within 1\% relative deviation when compared with experiments. The parameters of the force field (which include the >C==O group) were determined from...
simulations of acetone, and these parameters have been used without modification to estimate the vapor–liquid phase coexistence of 2-pentanone. For pentanoic acid, there is excellent agreement of simulation predictions with experimental liquid phase coexistence densities (though we note here that experimentally determined saturated vapor phase density values are not reported in the literature), demonstrating the transferability of the force-field parameters regressed from acetic acid properties.

From the particle number probability distribution obtained from the GC-TMMC simulations, we can directly calculate the vapor pressure, unlike that in the traditionally employed Gibbs ensemble MC simulations. Figure 5 shows the Clapeyron plot illustrating the behavior of the vapor pressure (In \(P^\text{sat}\)) with the inverse temperature (1/\(T\)). Again, comparison with experiment is not provided for levulinic acid in the temperature range 580–690 K because of the lack of corresponding experimentally measured values for the saturation pressures. The experimental results shown are reported in the temperature range 375–519 K, and we note that the deviations of the slope of the simulation predictions from that of the extrapolated experimental data increase as the temperature increases. However, for 2-pentanone, the vapor pressures are overpredicted by the TraPPE-UA force field because, as stated by Stubbs et al., the original parameters employed for the \(\text{CH}_1\) and \(\text{CH}_2\) united atoms in the \(n\)-alkanes result in 10% overprediction of the saturation pressures as one of the limitations of the united atom approach is the tradeoff between transferability of the parameters and the accuracy of the predictions. Improvement in agreement may be achieved by following the recommendations of Stubbs et al., which involve either using explicit hydrogen representation of the TraPPE family of force fields or fitting the parameters specifically to experimental results for 2-pentanone. However, this is beyond the scope of this study and we have assumed transferability of the relevant parameters. Additionally, we note that it is also well known that the TraPPE-UA force field overestimates the vapor pressures of carboxylic acids (including pentanoic acid) as compared with experimental results and that at a temperature of 400 K the saturation pressure was overpredicted by a factor of 2.6 with the reported relative errors increasing with decreasing temperatures. This is because, as noted by Kamath et al., the parameterization of the TraPPE-UA force field has been developed such that accurate estimates of the coexistence liquid densities and critical temperature are obtained, and this in effect fixes the simulated vapor pressures.

Thus, for levulinic acid, we anticipate that the predictions for the coexistence densities in the temperature range of 580–690 K will be reasonably good though the vapor pressures are expected to be overestimated because of the limitations of the TraPPE-UA force field. From the simulation data generated in this study, we have determined the critical temperature, density, and pressure to be 755 K, 285.4 kg/m\(^3\), and 30.57 bar, respectively. Because experimental results for the critical point of levulinic acid are not available, we have compared our values with the corresponding group contribution values. From group contribution methods, the critical point values are estimated to be 716.8 K, 350.06 kg/m\(^3\), and 39.4 bar.

5. CONCLUSIONS

Levulinic acid is a commercially important organic compound, which may be derived sustainably from lignocellulosic biomass. The experimental vapor–liquid equilibrium data for this compound is limited to a temperature range of 375–519 K (normal boiling point), where the vapor pressures are relatively low. Because experiments in the high-temperature range to determine the coexistence behavior are challenging for this large oxygen-containing compound, we have adopted the molecular simulation approach in conjunction with the TraPPE-UA force field to generate the necessary data at elevated temperatures and also to investigate the microscopic properties of this molecule. In this force field, the parameters are assumed to be transferable from other organic compounds, except for the dihedral interaction not reported in the literature, and the parameters for the missing torsion have been determined using the DFT approach in this study. The parameterization of the force field has been verified by comparing the liquid densities computed using isothermal–isobaric ensemble Monte Carlo simulations with the experimental results available in the literature (where we observed the maximum relative deviation to be within 5% of literature data). As levulinic acid is a ketoacid, we have also examined the associating-type interactions present among the united atoms with partial charges in the liquid phase and have also analyzed the hydrogen bonding that occurs between the hydroxyl hydrogen and the three oxygen atoms present in the molecule. We have then performed GC-TMMC simulations to obtain the PNPD at high temperature (ranging from 580 to 690 K) from which we have estimated the coexistence densities of the vapor and liquid phases as well as the vapor pressures. As there is no experimental data for comparison in the temperature range studied here, we have reviewed the literature for the accuracy of the TraPPE-UA force field predictions for 2-pentanone and pentanoic acid. From these, we anticipate that our computation of the coexistence densities should be reasonably accurate though the vapor pressures are expected to be overestimated. The critical point of levulinic acid (which is not reported in the literature) has also been estimated from the simulation-generated data as the critical point is an input to the equation-of-state approach employed in process simulation software used to design and optimize separation processes.
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The authors declare no competing financial interest.

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