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On the application of force fields for predicting a wide variety of properties: Ethylene oxide as an example

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Abstract

A new molecular model for ethylene oxide (C_2H_4O) is developed and optimized using experimental data on vapor pressure, bubble density, and enthalpy of vaporization. This simple molecular model, consisting of three Lennard–Jones sites plus one static point dipole, is used for predicting a wide variety of thermo-physical properties. These are phase equilibria, thermal, caloric, transport properties, and surface tension. The results from the new molecular model are compared to experimental data and to results obtained with an ethylene oxide model from the literature [Wielopolski and Smith, Mol. Phys. 54 (1985) 467–478]. For all studied properties, the new model gives distinctly improved predictions.

Keywords: Molecular modeling and simulation; Ethylene oxide; Vapor–liquid equilibrium; Critical properties; Caloric properties; Transport properties; Surface tension

1. Introduction

Molecular modeling and simulation has a far better physical background than standard methods regarding thermo-physical properties, e.g. equations of state. Although the molecular approach is computationaly expensive, it is rewarding as it generates reliable predictions. For example, molecular models adjusted to a given set of thermo-physical properties often yield good predictions for properties of different types. This is of particular interest for industrial applications, where a broad variety of properties is needed but often not available. To further study this issue, the Industrial Simulation Collective [1] has organized the Fourth Industrial Fluid Properties Simulation Challenge. The task in 2007 is to calculate for ethylene oxide on the basis of a single given molecular model a total of 17 different properties from three categories. In the frame of the Challenge, two data sets are generated here: one using a newly developed model and one using a model from the literature.

Ethylene oxide (C_2H_4O) is a widely used intermediate in the chemical industry. In 2006, 18 million metric tons were produced mostly by direct oxidation of ethylene, over 75% of which were used for ethylene glycols production [2]. Despite its technical and economical importance, experimental data on thermo-physical properties of ethylene oxide are rare, apart from basic properties at standard conditions [3]. This lack of data is mainly due to the hazardous nature of ethylene oxide. It is highly flammable, reactive, explosive at elevated temperatures, toxic, carcinogenic, and mutagenic. Therefore, it is an excellent example to show that molecular modeling and simulation can serve as a reliable route for obtaining thermo-physical data in cases, where avoiding experiments is highly desirable [4].

In the present work, a new molecular model for ethylene oxide is developed. This model (referred to as "present model" in the following) is based on prior work at our institute [5] and is further optimized to experimental vapor–liquid equilibria (VLE), i.e. saturated liquid density, vapor pressure, and enthalpy of vaporization. Using this model, phase equilibria, thermal, caloric, transport properties, and surface tension are predicted and compared to experimental results, where possible. In those cases where no experimental data are available, present simulation results are compared to the reference values that were provided by IFPSC [1] after the deadline of the Simulation Challenge 2007. As requested by the Simulation Challenge, the same properties are predicted with a molecular model from Wielopolski and Smith [8] (referred to as "Round-Robin model" in the following).

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2. Optimization of the present model

In this section, the development of the present molecular model for ethylene oxide is described. Comparisons with the Round-Robin model and applications to the properties required by the Simulation Challenge are described in the following sections.

The present model consists of three Lennard–Jones (LJ) sites (one for each methylene group and one for the oxygen atom) plus one static point dipole. Thus, the united-atom approach is used. Due to the fact that ethylene oxide is a small molecule, the internal degrees of freedom may be neglected and the model is assumed to be rigid. Experimental data on the molecular structure [9] is used to specify the geometric location of the LJ sites, cf. [5]. The point dipole is located in the center of mass. The interaction energy u_{ij} between two molecules i and j is given by

$$u_{ij} = \sum_{a=1}^{A}\sum_{b=1}^{B} 4\varepsilon_{ab}\left[\left(\frac{\sigma_{ab}}{r_{ijab}}\right)^{12} - \left(\frac{\sigma_{ab}}{r_{ijab}}\right)^{6}\right] + \frac{1}{4\pi\epsilon_0}\frac{\mu^2}{|r_{ijab}|^3} f_{\mathrm{D}}(\boldsymbol{\omega}_i, \boldsymbol{\omega}_j), \quad (1)$$

where $A = B$ is the number of molecular model sites and r_{ijab} the site-site distance. σ and ε are the size and energy parameters of the LJ sites. Unlike ($a \neq b$) parameters are defined by the Lorentz–Berthelot combining rule [10,11]. μ denotes the dipole moment and ϵ_0 the permittivity of vacuum. f_{D} is an expression for the angle dependence of the point dipolar interaction in terms of the orientation vectors $\boldsymbol{\omega}_i$ and $\boldsymbol{\omega}_j$, cf. [12].

A point dipole can, e.g. when a simulation program does not support this interaction site, be approximated by two point charges $\pm q$ separated by a distance l. Limited to small l, one is free to choose this distance as long as $\mu = ql$ holds. However, the computational effort increases through this separation for the interaction between two dipoles roughly by a factor of 4.

A set of five adjustable parameters, i.e. the four LJ parameters $\sigma_{\mathrm{CH_2}}$, $\varepsilon_{\mathrm{CH_2}}$, σ_{O}, ε_{O}, and the dipole moment μ, is optimized. This is done by a Newton scheme using correlations to experimental bubble density, vapor pressure, and enthalpy of vaporization data over the full range of the VLE between triple point and critical point.

The correlations to experimental data are taken from the DIPPR database [3]. For ethylene oxide the correlations to saturated liquid density and vapor pressure are based on real experimental data points from 222 to 461 K and 213 to 469 K, respectively. Note that the correlation to enthalpy of vaporization is based on three experimental data points in the range from 284 to 298 K only. Additionally used data points for enthalpy of vaporization come from predictions from various authors, mostly based on the Clausius–Clapeyron equation. The DIPPR correlations are used as they are assumed as best practice. The saturated vapor density of ethylene oxide is calculated from the correlations for saturated liquid density, vapor pressure, and enthalpy of vaporization using the Clausius–Clapeyron equation. This data is only used in some figures for graphical reasons, but is not included in the model optimization process.

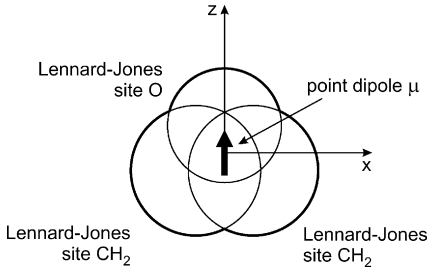

Fig. 1. Geometry of the present model for ethylene oxide. Note that all sites of the present model are within the x–z-plane.

Following the optimization procedure of Stoll [5], i.e. a Newton scheme, an optimized parameter set is obtained after three iteration cycles. The geometry of the optimized model is shown in Fig. 1, while the model parameters are listed in Table 1. The resulting dipole moment from the optimization (2.459 D) is about 30% higher than the experimental gas phase dipole moment of ethylene oxide (1.89 D) reported by McClellan [6]. This increase reflects the stronger electrostatic interactions in the liquid state and is in typical range.

Simulation results for the VLE from the present model and the Round-Robin model are given in Table 2. In Figs. 2–4 , saturated densities, vapor pressure, and enthalpy of vaporization are shown for both models. VLE simulation details for both models are given in Appendix A. The present model describes the vapor pressure p_σ, the saturated liquid density ρ', and the enthalpy of vaporization Δh_{v} with mean relative deviations of $\delta p_\sigma = 1.5\%$, $\delta\rho' = 0.4\%$, and $\delta\Delta h_{\mathrm{v}} = 1.8\%$, respectively, cf. Fig. 5.

The model, as specified in Table 1 (present model), is used for calculating other properties discussed in the subsequent sections. No further parameter adjustments are made and thus all results for properties except p_σ, ρ', and Δh_{v} are fully predictive.

Table 1
Coordinates and parameters of the present molecular model for ethylene oxide

Interaction site	x (Å)	y (Å)	z (Å)	σ (Å)	$\varepsilon/k_{\mathrm{B}}$ (K)	θ (°)	φ (°)	μ (D)
CH_2(1)	0.78000	0	−0.48431	3.5266	84.739	–	–	–
CH_2(2)	−0.78000	0	−0.48431	3.5266	84.739	–	–	–
O(3)	0	0	0.73569	3.0929	62.126	–	–	–
Dipole	0	0	0	–	–	0	0	2.459

The three Lennard–Jones sites are denoted by the molecular group which they represent, while the single dipolar site is denoted "Dipole". All coordinates are in principal axes with respect to the center of mass. The orientation of the electrostatic site is definded in standard Euler angles, where φ is the azimuthal angle with respect to the x–z-plane and θ is the inclination angle with respect to the z-axis.