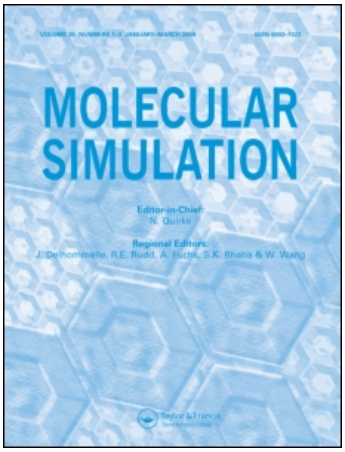

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Molecular dynamics simulation of Henry's constant of argon, nitrogen, methane and oxygen in ethylene oxide

M. Krishnamurthy[a]; S. Murad[a]; J. D. Olson[b]
[a] Chemical Engineering Department, University of Illinois at Chicago, Chicago, IL, USA [b] The Dow Chemical Company, South Charleston, WV, USA

To cite this Article Krishnamurthy, M. , Murad, S. and Olson, J. D.(2006) 'Molecular dynamics simulation of Henry's constant of argon, nitrogen, methane and oxygen in ethylene oxide', Molecular Simulation, 32: 1, 11 — 16
To link to this Article: DOI: 10.1080/08927020500474318
URL: http://dx.doi.org/10.1080/08927020500474318

Molecular Simulation, Vol. 32, No. 1, 15 January 2006, 11–16

Taylor & Francis
Taylor & Francis Group

Molecular dynamics simulation of Henry's constant of argon, nitrogen, methane and oxygen in ethylene oxide

M. KRISHNAMURTHY†, S. MURAD†* and J. D. OLSON‡

†Chemical Engineering Department, University of Illinois at Chicago, Chicago, IL 60607, USA
‡The Dow Chemical Company, South Charleston, WV 25303, USA

(Received January 2006; in final form January 2006)

Molecular dynamics simulations have been carried out to estimate the Henry's constants and solubilities of a range of small nonpolar molecules in ethylene oxide using a scheme that closely mimics experiments. Our results show that the method is reliable for polar–nonpolar sytems, which are generally notoriously difficult to investigate using classical methods. By validating the results for several gases for which experimental results are available, we have been able to estimate the solubility of oxygen, for which experiments have yet to be carried out because of flammability concerns. Our studies have also allowed us to develop a simple correlation for predicting the dependence of Henry's constant on binary interaction parameters. Finally, we also observe that for gas solubilities, small diatomics can effectively be approximated by central Lennard–Jones potential models. This can simplify such simulations considerably.

Keywords: Molecular dynamics; Henry's constant; Polar system; Gas Solubility

1. Introduction

The solubility of gases in liquids is an important problem in phase equilibrium. It is more complicated than conventional vapor–liquid equilibrium, since in many cases the solubility of gases in liquids can be very low (mole fractions of the order of 10^{-5}) at standard pressures, making accurate experimental measurements or theoretical predictions difficult. The importance of gas solubilities is also demonstrated by the numerous data compilations available, e.g. [1]. In particular, oxygen solubility is also needed for the modeling of chemical oxidation processes. Because of flammability concerns, these experiments are particularly difficult to perform, demonstrating the need for reliable theoretical methods.

EPA first registered ethylene oxide as an antimicrobial pesticide in 1948 [2]. Ethylene oxide is used to sterilize hospital items; to treat processed spices and seasonings; and to treat commercial food processing, handling and storage facilities. It has also been approved by EPA for anthrax decontamination [2]. When used directly in the gaseous form or in non-explosive gaseous mixtures with nitrogen or carbon dioxide, ethylene oxide can act as a disinfectant, fumigant, sterilizing agent and insecticide. Ethylene oxide is used as an ingredient or as an intermediate in the production of several other chemicals including ethylene glycol and polyester. Ethylene glycol is used primarily in automotive antifreeze and polyester is used in fibers, film and bottles. It is also used to produce nonionic surfactants in household and industrial detergents. Oxygen dissolved in ethylene oxide can have a significant effect on the behavior of ethylene oxide, but experimental results for oxygen solubility are not available. One objective of our study was to use molecular simulations to estimate the solubility of oxygen in ethylene oxide. The solubility of gases such as argon, nitrogen and methane in ethylene oxide have, however, been measured experimentally [3]. We will, therefore, use the available experimental data to validate and refine our method and potential models and then use them to study oxygen in ethylene oxide.

Gas solubility in liquids is usually expressed in terms of Henry's law, as represented by Refs. [4,5] (in the limit of an ideal gas phase and for low concentrations of gases in

*Corresponding author. Email: murad@uic.edu

Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020500474318

the liquid phase):

$$x_i = \frac{y_i P}{H_{i,j}} \tag{1}$$

$H_{i,j}$ is usually referred to as the Henry's constant and as is self evident, allows for the solubility of the gas (component i) in the liquid (x_i), to be easily estimated, given the pressure P and the mole fraction of the gas in the vapor phase y_i (often 1 for pure gases if the liquid is not volatile). Henry's constant is directly related to the infinite dilution residual chemical potential $\left(\mu_i^{r\infty}\right)$ via the following relationship [6]:

$$H_{i,j} = \rho_{\text{liq}} kT \exp\left(\frac{\mu_i^{r\infty}}{kT}\right) \tag{2}$$

Here ρ_{liq} is the liquid density, T is the temperature and k is the Boltzmann constant. Use of this relationship makes Henry's constant readily amenable to molecular level investigations.

The most widely used molecular simulation approach for calculation of the infinite dilution chemical potential or for studies of phase equilibrium (using molecular simulation) is by using Monte–Carlo (MC) methods such as the Gibbs ensemble MC [7]. A common problem with these techniques is that they become increasingly inefficient at higher densities because of the particle insertions that must be carried out [8–14]. Several methods have also been recently been suggested that circumvent this problem (Widom particle insertion at high densities) [8–14]. However, some of the methods do not work very well at the low concentrations that must be studied when gases dissolve in a liquid [9]. Others have been found to work well, but are not conceptually as simple to understand or implement [14].

We have used a method [6,15] that allows gas solubility to be obtained in a rather straightforward manner in a simulation that is strikingly close to actual experiments [3]. We have also shown [6] that the method works well at densities not easily accessible using the conventional Widom particle insertion techniques [8–14]. In addition, the method is based on molecular dynamics (MD) so that transport properties such as diffusion coefficients can also be obtained easily, if needed.

The method was previously demonstrated and validated for calculation of Henry's constant for Lennard–Jones (12–6) mixtures [6] and more recently for oxygen in benzene [16]. Our previous studies only involved nonpolar fluids, where we found that binary parameters were unnecessary. In this study, we investigate the extension of this method to polar–nonpolar systems and also develop efficient algorithms for estimating binary interactions parameters, which we believe are clearly needed for such mixtures.

2. Method

The MD method used here is based on an extension of the usual NVE algorithm, which has been described in [15]. It will, therefore, only be summarized here. The system consists of a solvent compartment separated from the gas compartment by a semi-permeable membrane. A schematic diagram of the simulation system is shown in figure 1. Periodic boundary conditions then lead to a system infinite in the y- and z-directions (parallel to the membranes). In the x-direction, this leads to alternating gas and solvent sections of width $L_x/2$ (L_x is the system size in the x-direction, i.e. perpendicular to the membranes). The system is made longer in the x direction (in this case $L_x = 4L_y = 4L_z$) to minimize the overall effect of the membranes. In this study, the membrane simply consists of a single layer of molecules arranged in the fcc configuration. The membrane is formed by tethering the molecules that constitute the membrane to their equilibrium positions. A simple harmonic potential has been used, although others could also be used. The membrane is made permeable to the gas molecules but not the solvent molecules. This is accomplished in these studies by adjusting membrane–solvent and –solute binary interaction parameters as well as the size and energy parameters of the membrane molecules, as needed.

The density of the solvent compartment can be fixed corresponding to the state condition of interest. In this study, the density of the solvent was fixed to ensure that

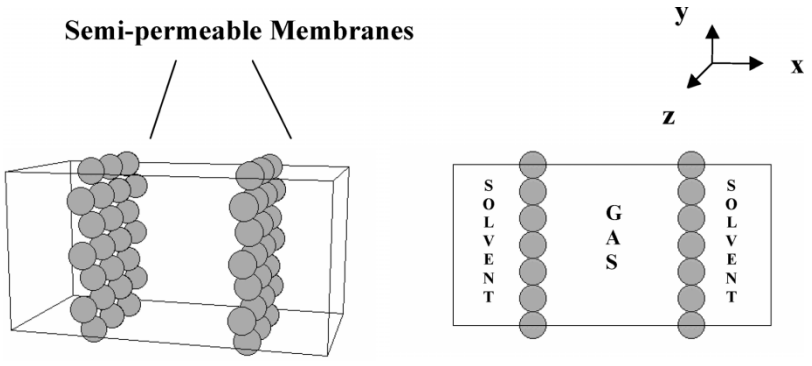

Figure 1. The basic simulation system for investigating Henry's constant for gases dissolved in liquids.

the pressure was higher than the saturation pressure in the selected temperature range of 273–323 K (the normal boiling point of ethylene oxide is ~283 K). This fixes the volume of the solvent compartment once the number of solvent molecules is fixed. In these simulations, the solvent compartment consisted of 480 molecules and the two membranes consisted of 64 molecules. In some simulations, some gas molecules were also included in the "solvent" compartment, to facilitate equilibrium. The volume of the gas compartment is set equal to the solvent compartment and up to 80 gas molecules were placed in the compartment, corresponding to the desired initial gas pressure. Thus the entire simulation typically consisted of 624 (480 ethylene oxide, 64 membrane and 80 solute) molecules. The molecules were then given a Gaussian velocity distribution corresponding to the system temperature being investigated.

In the first phase of our studies, we have utilized simple existing intermolecular potential models for ethylene oxide [17,18] and the gases [19,20] included in this study. The potential models are of the form

$$u_{ij} = \sum 4\varepsilon_{ij}\left[\left(\frac{r_{ij}}{\sigma_{ij}}\right)^{-12} - \left(\frac{r_{ij}}{\sigma_{ij}}\right)^{-6}\right] + \frac{q_i q_j}{r_{ij}} \qquad (3)$$

where the summation is over all the active sites of the molecules for which the potential is being calculated. ε and σ are the energy and size parameters, while q is the charge on the site (not all sites have charges) and r the distance between the active sites. For ethylene oxide, a three site united atom (UA) model was used as described in Refs. [17,18]. Argon and methane were modeled using a LJ potential. The diatomic gases (N_2, O_2) were modeled using both a central LJ potential and as well as with a two-center LJ potential. These potential models are known to give a reasonable quantitative picture of a wide range of thermodynamic properties [18–20]. The parameters used in our studies are given in table 1. In addition, the interactions of these molecules with the membrane molecules were fixed by using binary interaction parameters so that only the solute molecules can permeate through the membrane. In our preliminary studies, we used Lorentz–Berthelot mixing rules for estimating ε and σ for the solvent–solute interactions. As will be discussed in the results sections these were then adjusted using available experimental data for argon.

As mentioned earlier, since our simulations conceptually closely mimic an experiment, we can directly use an equation of the form (1) to measure Henry's constant. However, since the solubility of the gases being investigated is rather low at atmospheric pressures, to get reasonable statistics in the simulations being carried out here, we had to study pressure ranges where the ideal gas approximation would not be valid. Therefore, equation (1) must be modified to include gas phase nonideality, as well as the high solvent pressure [4].

$$H_{1,2} = \frac{\phi_1 P_1}{\left(x_2 \exp\left\{\left(P_2 - P_2^{\text{sat}}\right)\bar{V}_2^{\infty}/RT\right\}\right)} \qquad (4)$$

In equation (4), subscript 1 refers to the solute molecules, while 2 to the solvent molecules. The pressure (P_1) of the gas phase is estimated from the density (ρ) of the gas phase (figure 1) and the second virial coefficient, B (note in the gas compartment, only a pure gas is present in our studies) using the virial equation of state.

$$P = (1 + B\rho)\rho RT \qquad (5)$$

The vapor phase fugacity coefficients (ϕ) can similarly be obtained using

$$\ln \phi = 2\rho B - \ln\left(\frac{P}{\rho RT}\right) \qquad (6)$$

Finally, the pressure in the solvent compartment can be calculated from the force on the membranes separating the two compartments, which represents the pressure difference between the two compartments. We used values of B and V_2^{∞} (partial molar volume of the gas dissolved at infinite dilution) reported in Ref. [3] in our studies. If data for V_2^{∞} are unavailable, as is often the case, it is also possible to obtain V_2^{∞} by carrying out a few (at least one) extra simulations and using equation (4) to obtain it. Finally, equation (4) is only valid in the limit of $x_2 \rightarrow 0$. In a previous study, we have demonstrated that for low solubility gases this is indeed true and a typical result is shown in figure 2.

The time evolution of this initial system setup was then followed using the fifth order predictor–corrector scheme for the translational motion and a fourth order

Table 1. Parameters for intermolecular potential models used.

	Interacting sites	*σ (Å)*	*ε/k (K)*	*q/e*
Ethylene oxide[†]	CH_2	3.68	95.84	0.1608
	O	2.72	71.91	−0.32016
Oxygen	Central LJ	3.36	119.8	0.0
	Diatomic LJ	3.106	43.18	0.0
Nitrogen	Central LJ	3.663	96.92	0.0
	Diatomic LJ	3.321	34.897	0.0
Argon	Central LJ	3.41	119.8	0.0
Methane	Central LJ	3.678	166.78	0.0
Membrane[‡]	Central LJ	0.475–3.8	80.646	0.0

[†] Ref. [9–10]. [‡] Adjusted so that only solute molecules permeate.

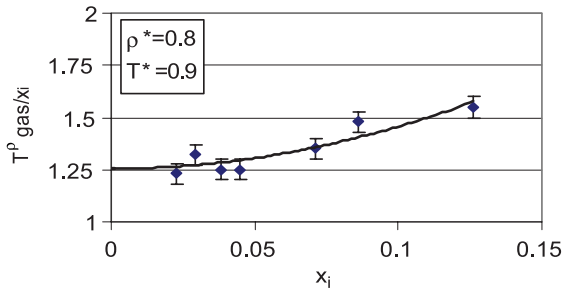

Figure 2. Dependence of Henry's constant on solute concentration in a typical simulation.

predictor–corrector scheme using quaternion for the rotational motion [19]. The system was allowed to equilibrate for 60,000 steps of size 0.00006 based on parameters of CH_2 (table 1). After this, production runs of up to 4,500,000 time steps were carried out. On a 2.4 GHz PC operating on Linux, one such simulation was completed in ~170 h (about 3 h on a typical 64 unit cluster). Once the simulations were completed the properties of the system such as gas pressure, liquid and gas concentrations were estimated from the average properties during the production run.

3. Results

The first gas studied was argon in the temperature range 273–323 K. In our initial investigation, we used the Lorentz–Berthelot mixing rules with the cross parameters set to unity. We ensured the system had reached equilibrium by examining the density profiles and a typical such profile is shown in figure 3. The Henry's constant for this system was then calculated using the method outlined in Section 2 and the results are shown in figure 4. The error bars reported are estimated by changing the permeability of the membrane to the solute gases and the initial configuration of the molecules in the simulation.

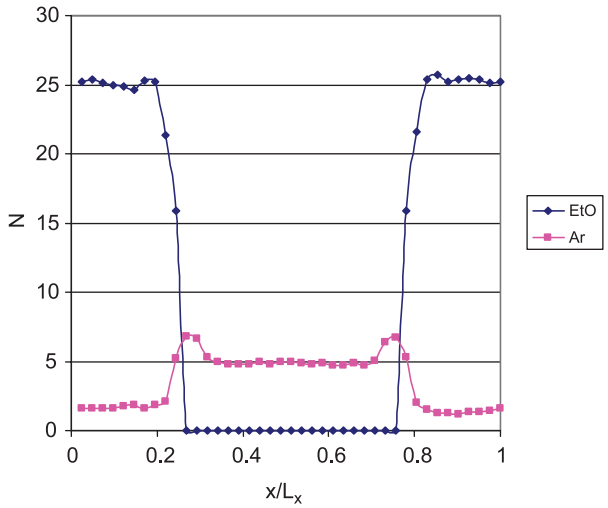

Figure 3. A typical density profile in an equilibrated system. This example is for argon in ethylene oxide.

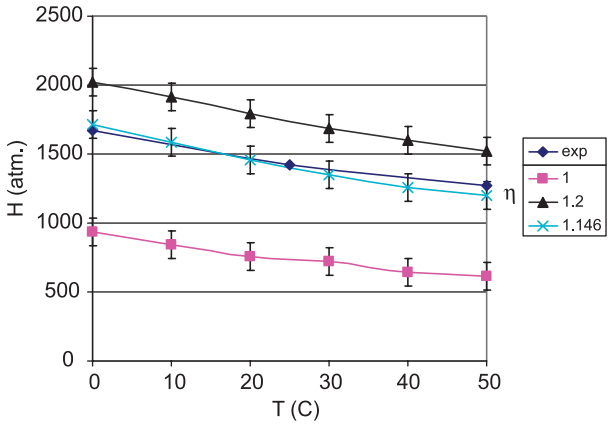

Figure 4. Henry's constant for argon in ethylene oxide compared with experimental data for a range of cross interaction parameters.

In addition, we also carried out simulations at several pressures. These should not effect the Henry's constant calculated using our methodology and are a measure of any errors inherent in our scheme. The results shown in figure 3 are qualitatively correct, in the sense that they show the correct temperature dependence. However, with the cross parameters set to 1.0, the simulations do under predict the Henry's constant by almost a factor of 2. This is not surprising since the cross parameters for polar–nonpolar fluids are never expected to be negligible. We then tried using only one cross parameter for size, η defined as

$$\sigma_{ij} = \frac{\eta(\sigma_i + \sigma_j)}{2} \tag{7}$$

The first value of η we then tested was 1.2. As can be seen from the result in figure 3, this over predicted the Henry's constant by about 20%. Instead of testing additional values, we attempted to correlate the effect of η on the Henry's constant. The relationship we tested was of the form

$$\frac{H_1}{H_2} = \left(\frac{\eta_1}{\eta_2}\right)^N \tag{8}$$

We fitted the data for $\eta = 1.0$ and 1.2 for the entire temperature range to obtain the value of N that best fit the data. Our analysis resulted in a value of $N = 4.778$ for such a fit. We then estimated the value of η that best fit the experimental data for argon and the value of $\eta = 1.146$ appeared to be the optimal value. The results for $\eta = 1.146$ are shown in figure 4 and confirm the validity of this simple correlation. The next important step was to determine if the values of η obtained for ethylene oxide–argon cross parameters were transferable to other non-polar gases as well. We, therefore, tried using $\eta = 1.146$ for ethylene oxide–nitrogen as well. The results obtained are given in figure 5. For Henry's constant we believe these results are remarkably accurate (within the experimental error for these systems). Although, we could have improved the fit with a slightly higher values of $\eta = 1.146$, for consistency we have used this value here. For completing the picture of

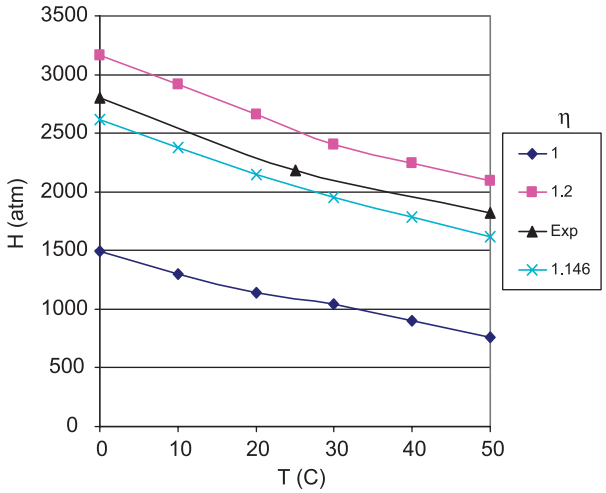

Figure 5. Henry's constant for nitrogen in ethylene oxide compared with experimental data for a range of cross interaction parameters.

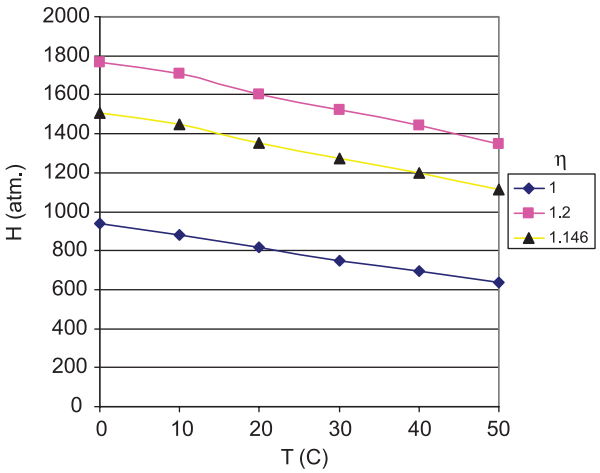

Figure 7. Henry's constant for oxygen in ethylene oxide for a range of cross interaction parameters.

the η dependence of the Henry's constant, we also have shown the results for $\eta = 1$ and 1.2 in figure 5. They follow the patterns observed for argon.

The next important challenge was to examine the solubility of methane in ethylene oxide. This was a challenge because the temperature dependence observed experimentally is significantly different than that of argon or nitrogen (the solubility and Henry's constant are essentially independent of temperature). The results obtained for methane–ethylene oxide with a value of $\eta = 1.146$ are shown in figure 6. The results show a remarkable agreement with the observed experimental trend of temperature independence of the Henry's constant. Once again for completeness to check the validity of our proposed correlation (equation (8)), we show the results for $\eta = 1.0$ and 1.2 as well. Finally, no experimental results are available for oxygen. As mentioned earlier, this is one system that is not often studied experimentally because of concerns related to flammability of the mixtures. We have, therefore, predicted results from our simulation methodology for oxygen as shown in figure 7. We have provided results for $\eta = 1.146$, as well as 1.0 and 1.2. Although, no experimental data is available, we feel fairly confident based on our experience with other similar systems, that these results should be fairly reliable estimates of the Henry's constants of oxygen in ethylene oxide.

Another issue that we investigated in our simulations concerned the appropriate potential for small diatomics for gas solubility. For both nitrogen and oxygen, we investigated central LJ potentials (results shown in figures 5 and 7) as well as site–site LJ potentials with two active sites. The results were qualitatively similar, with the diatomic model as expected giving slightly better agreement with experimental results. Results for the diatomic model for nitrogen are given in figure 8, in the same format as those for the other systems studied.

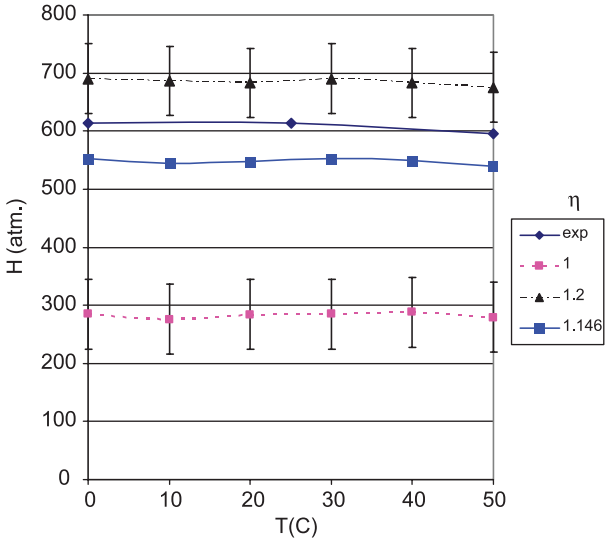

Figure 6. Henry's constant for methane in ethylene oxide compared with experimental data for a range of cross interaction parameters.

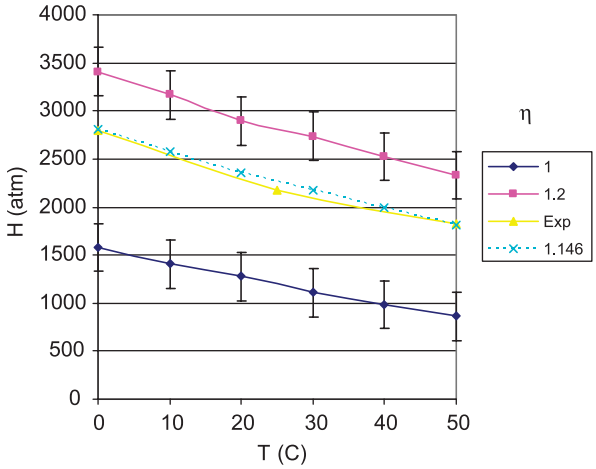

Figure 8. Henry's constant for nitrogen in ethylene oxide compared with experimental data for a site–site diatomic model for nitrogen.

4. Conclusions

We have shown that a recently developed MD method for estimating the solubility of gases in liquids, works reliably for polar–nonpolar systems as well. In the past, it was tested for LJ and polyatomic systems. We have found that the usual Lorentz–Berthelot mixing rules do not work well for such systems. However, with binary interaction parameters for σ, the results are satisfactory. Another important determination from our work is that the Henry's constant correlate quite well with the binary interaction parameter by a relationship of the type used in equation (8). In addition, our results have also shown that the cross interaction parameters appear to be transferable for similar polar–nonpolar components. In our case, we were able to use the same cross parameters for argon, methane, nitrogen and have estimated them to be the same for oxygen. Finally, for gas solubilities, central LJ potentials work quite well for small diatomics of the type studied here. While the results are slightly better with two site LJ interactions, it is unclear whether they justify the additional cost associated with the inclusion of two sites.

Acknowledgements

This research was supported by grants from the National Science Foundations (CTS-0314023) and the Petroleum Research Fund administered by the American Chemical Society. The authors would like to thank Drs J. T. Miller (British Petroleum) and Y. Chernyak (Huntsman Corp.) for helpful discussions.

References

[1] R. Battino. *Solubility Data Series*, Pergamon Press, Oxford (1981).
[2] US-EPA, Pesticides: Topical & chemical fact sheets, ethylene oxide, Available online at: http://www.epa.gov/pesticides/factsheets/chemicals/etofactsheet.htm.
[3] J.D. Olson. Solubility of nitrogen, argon, methane and ethane in ethylene oxide. *J. Chem. Eng. Data*, **22**(3), 326 (1977).
[4] J.M. Prausnitz, R.N. Lichtenhaler, E. Gomes de Azevedo. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3 ed., Prentice Hall, New Jersey, NJ (1986).
[5] H.S. Taylor. *A Treatise on Physical Chemistry*, vol. 1, p. 237, van Nostrand, New York, NY (1925).
[6] S. Murad, S. Gupta. A simple molecular dynamics simulation for calculating Henry's constant and solubility of gases in liquids. *Chem. Phys. Lett.*, **319**(1,2), 60 (2000).
[7] A.Z. Panagiotopoulos. Direct determination of phase coexistence properties of fluids by Monte Carlo simulation in a new ensemble. *Mol. Phys.*, **61**(4), 813 (1987).
[8] P.J.G. Powles, B. Holtz, W.A.B. Evans. New method for determining the chemical potential for condensed matter at high density. *J. Chem. Phys.*, **101**(9), 7804 (1994).
[9] R.L. Rowley, M.W. Schuck, J.C. Perry. A direct method for determination of chemical potential with molecular dynamics simulations. Part 2. Mixtures. *Mol. Phys.*, **86**(1), 125 (1995).
[10] P. Bryk, A. Patrykiejew, O. Pizio, S. Sokolowski. The chemical potential of Lennard–Jones associating fluids from osmotic Monte Carlo simulations. *Mol. Phys.*, **92**(6), 949 (1997).
[11] J.T. Slusher. Estimation of infinite dilution activity coefficients in aqueous mixtures via molecular simulation. *Fluid Phase Equil.*, **153**(1), 45 (1998).
[12] G.C. Boulougouris, J.R. Errington, I.G. Economou, A.Z. Panagiotopoulos, D.N. Theodorou. Molecular simulation of phase equilibria for water–*n*-butane and water–*n*-hexane mixtures. *J. Phys. Chem. B*, **104**, 4958 (2000).
[13] N.G. Parsonage. Computation of the chemical potential in high density fluids by a Monte Carlo method. *Mol. Phys.*, **89**(4), 1133 (1996).
[14] D.A. Kofke, P.T. Cummings. Quantitative comparison and optimization of methods for evaluating the chemical potential by molecular simulation. *Mol. Phys.*, **92**(6), 973 (1997).
[15] S. Murad, J.G. Powles. A computer simulation of the classic experiment on osmosis and osmotic pressure. *J. Chem. Phys.*, **99**(9), 7271 (1993).
[16] S. Murad, S. Gupta. Molecular dynamics simulation for Henry's constant of oxygen in benzene. *Fluid Phase Equil.*, **187**, 29 (2001).
[17] P.A. Wielopolski, E.R. Smith. Molecular dynamics studies of dielectric behavior and orientational correlations of liquid ethylene oxide (oxirane). *Mol. Phys.*, **54**(2), 467 (1985).
[18] J.D. Moore. Personal Comunication (2003); J.D. Moore, T.D. Francis, S. Enders, D.J. Frurip, J.D. Olson. Predicting the Henry's law constants of oxygen and other gases in ethylene oxide by molecular simulation. AIChE Annual Meeting, San Francisco, CA, November (2003).
[19] M.P. Allen, D.J. Tildesley. *Computer Simulation of Liquids*, Clarendon Press, Oxford (1987).
[20] J. Vrabec, J. Stoll, H. Hasse. A set of molecular models for symmetric quadrupolar fluids. *J. Chem. Phys. B*, **105**(48), 12126 (2001).