

Predicting the solubility of xenon in n-hexane and n-perfluorohexane: a simulation and theoretical study

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The solubility of xenon in n-hexane and n-perfluorohexane has been studied using both molecular simulation and a version of the SAFT approach (SAFT-VR). The calculations were performed close to the saturation line of each solvent, between 200 K and 450 K, which exceeds the smaller temperature range where experimental data are available in the literature. Molecular dynamics simulations, associated with Widom's test particle insertion method, were used to calculate the residual chemical potential of xenon in n-hexane and n-perfluorohexane and the corresponding Henry's law coefficients. The simulation results overestimate the solubility of xenon in both solvents when simple geometric combining rules are used, but are in good agreement if a binary interaction parameter is included. With the SAFT-VR approach we are able to reproduce the experimental solubility for xenon in n-hexane, using simple Lorentz–Berthelot rules to describe the unlike interaction. In the case of n-perfluorohexane as a solvent, a binary interaction parameter was introduced, taken from previous work on (Xe + C₂F₆) mixtures. Overall, good agreement is obtained between the simulation, theoretical and experimental data.

1. Introduction

Systems involving xenon, n-alkanes and n-perfluoroalkanes have proved to be relevant to a number of fields. Xenon is highly soluble in lipids and fats and shows anaesthetic properties at sub-atmospheric pressures. Given its chemical inertia and non-toxicity it could be considered the perfect anaesthetic, and very recently its use has been submitted for regulatory medical approval in Europe [1]. Similarly, fluorinated substances find application in a wide range of industrial and research areas. For example, fluorocarbons are being used as refrigerants and polymer foam blowing agents since the replacement of chlorofluorocarbons, and as high performance lubricants such as DuPont's Krytox. Additionally, because of their inert nature and high solubility for respiratory gases, fluorocarbons have also attracted a lot of interest in medical applications, for example as artificial blood or synthetic oxygen carriers, as fluids in eye surgery and in the treatment of burns [2]. From a more fundamental point of view,

mixtures of hydrocarbons and perfluorocarbons have long been the testing ground for statistical theories of liquids and hydrocarbons, in particular, the focus of intermolecular potential model development in the area of molecular simulation.

Molecular simulations of fluid systems are becoming an increasingly common means to elucidate the structure and predict the properties of pure liquids and their mixtures. In the literature of the past two decades a large number of molecular potential models or force fields have been proposed, describing many classes of compounds, from simple molecules to biological macromolecules. The continuing exponential growth in computing power makes it possible to consider larger systems modelled by increasingly more detailed force fields, where for example recent advances include descriptions of the intra- and intermolecular interactions in which all atoms are explicitly taken into account [3, 4] rather than using a simpler united atom approach. The evolution of computing resources additionally allows more sophisticated quantum mechanical treatments of the intramolecular features in the parametrization of a model. Although spectroscopic and *ab initio* methods

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supply the information required to establish the intramolecular terms, many of the parameters in these models that describe the intermolecular forces have to be reduced from fluid-state properties.

Usually the force fields are parametrized from simulations of pure-fluid properties, considering when possible several species within a homologous family. For example, in the case of the alkanes [4] or the perfluoroalkanes [5], linear, branched, and cyclic molecules of differing molecular weight can all be considered. Interactions between different molecular types are seldom taken into account. In general, it is difficult to foresee how well such molecular models would describe the properties of mixtures. Well chosen experimental data of high accuracy on properties evidencing the role of unlike interactions provide a route to verify and, when necessary, improve this description. The study of phase equilibria offers such a route, and in particular infinite dilution properties present a simpler situation where solute–solute interactions are absent and the focus lies on the solute–solvent interactions.

In previous work, experimental results have been reported on liquid mixtures of xenon with the lighter *n*-alkanes (methane, ethane, propane, *n*-butane and *i*-butane) [6, 7, 8] and *n*-perfluoroalkanes (perfluoromethane and perfluoroethane) [9]. While the former systems are practically ideal (a behaviour that resembles in many ways that of mixtures of *n*-alkanes), the latter show large deviations from ideality and large positive excess functions, much like mixtures of *n*-alkanes and *n*-perfluoroalkanes. Additionally in this previous work, using the statistical associating fluid theory for potentials of variable attractive range (SAFT-VR), it was shown that the behaviour of xenon correlates strongly with that of the *n*-alkanes. In the case of the xenon + alkane systems [7, 8], the experimental phase diagrams and excess volumes could be described accurately using simple Lorentz–Berthelot combining rules to determine the cross interaction parameters. For xenon and the lighter *n*-perfluoroalkanes [9], CF_4 and C_2F_6 , the existing experimental data could be reproduced by introducing a binary interaction parameter obtained from the study of *n*-alkane + *n*-perfluoroalkane binary mixtures. Hence we were able to use the SAFT-VR parameters in a transferable manner.

The present paper extends our previous studies towards heavier components, namely *n*-hexane and *n*-perfluorohexane. The large difference in volatilities in this case, (xenon is already supercritical over much of the liquid range of *n*-hexane and *n*-perfluorohexane) is well suited to a comparison of gas solubility data, rather than phase equilibria. Solubility measurements of gases in liquids often constitute an important source of information about the properties and structure of solutions

[10], and frequently are the only means of obtaining the enthalpy and heat capacity changes associated with the dissolution process. The solubility of xenon in *n*-hexane and *n*-perfluorohexane was calculated from both molecular dynamics simulation (MD) and the SAFT-VR approach. The calculations were performed close to the saturation line of each solvent, between 200 K and 450 K, and compared with experimental data available in the literature.

2. Molecular simulations

The molecules of *n*-hexane and *n*-perfluorohexane were represented by fully flexible potential functions in which all the atoms in the molecules are explicitly represented in the model. An all atom model was chosen to represent the chain molecules of interest, as previous simulation work on the solubility of oxygen in *n*-perfluorohexane [11] had demonstrated that the united atom models proposed by Cui *et al.* [12] for these substances did not perform as well as the OPLS all atom model for the calculation of the chemical potential at infinite dilution. In particular, it was found [11] that the numerical agreement was poorer and the temperature dependence of the solubility was not reproduced correctly. Notwithstanding, the united atom model of Cui *et al.* for perfluorocarbons predicted correctly the phase equilibria with carbon dioxide using simple Lorentz–Berthelot combining rules [13].

In the models used, intermolecular forces are described by pairwise Lennard-Jones terms plus Coulombic interactions, in the form of partial charges placed at the interaction sites. The parameters for the intra- and intermolecular terms were taken from the OPLS-AA force field, both for *n*-hexane [4] and *n*-perfluorohexane [5]. Hence, each molecule contains 20 Lennard-Jones sites, 19 harmonic bonds between pairs of chemically bonded atoms, 36 harmonic valence angles between pairs of bonds sharing one atom, and 45 dihedral angles between pairs of bonds separated by another bond, which are represented by cosine series. Within the same molecule, sites separated by more than three bonds also interact through non-bonded Lennard-Jones and electrostatic terms, similar to the intermolecular ones, but scaled by a factor of one half. Sets of parameters for the intermolecular and non-bonded interactions of C, H, and F atoms, and for all types of bond, valence and dihedral angle, are specified in the force field. The partial charges ascribed to the atoms are +0.06e (H), –0.12e (C in $-\text{CH}_2-$), and –0.18e (C in $-\text{CH}_3$); –0.12e (F), +0.24e (C in $-\text{CF}_2-$), and +0.36e (C in $-\text{CF}_3$). Coulombic interactions were computed using the Ewald summation method over a number of reciprocal vectors ranging from $k_{\text{max}} = 7$ to $k_{\text{max}} = 9$, depending on the temperature and on the molecule. The parameter

controlling the width of the screening charge distribution took a value of $\alpha = 0.225 \text{ \AA}^{-1}$. The intermolecular potential of pure xenon, in the form of a Lennard-Jones function with ($\sigma = 3.9478 \text{ \AA}$ and $\varepsilon = 1.8945 \text{ kJ mol}^{-1}$) was taken from the literature [14]. It was deduced from the vapour pressure and bubble density at $T = 161 \text{ K}$. Another set of parameters [15], deduced from second virial coefficients, was tested and yielded similar results.

Both solvents were simulated in cubic boxes containing 200 molecules by the molecular dynamics method using the package DL_POLY [16], modified to treat the OPLS-AA dihedral potential for perfluoroalkanes. The simulations were performed using timesteps of 0.5 fs for n-hexane and 1 fs for perfluorohexane. These values for the timestep were found after tests of energy conservation in the NVE ensemble. With these settings, the total energy does not drift and show relative rms fluctuations of 5×10^{-5} . Initially, a regular starting configuration at low density and low temperature was equilibrated in the NVE ensemble, in order to allow for relaxation of the intramolecular modes. The resulting configuration was then equilibrated at a single constant temperature and pressure (Nose–Hoover thermostat and barostat) during a 100 ps run, following which further equilibrations of 100 ps were performed, now at the desired temperatures and at pressures slightly above the saturated vapour pressure. Spherical cutoff radii of 12 \AA were adopted for the non-bonded interactions. After equilibration, at each temperature, samples of 1000 solvent configurations were saved from runs of 100 ps.

Xenon was then inserted at 6×10^4 random positions in each one of the 10^3 solvent configurations, leading to stable average values for the residual chemical potential of this solute at infinite dilution, μ_2^r [17]:

$$\mu_2^r = -kT \frac{\langle V \exp(u_{TP}/kT) \rangle_{NpT}}{\langle V \rangle_{NpT}}, \quad (1)$$

where u_{TP} is the interaction energy of the test particle with a configuration of solvent molecules, V is the volume of the solvent in a given configuration and $\langle \dots \rangle_{NpT}$ denotes an isothermal–isobaric ensemble average. The Henry's law coefficients, $H_{2,1}(p, T)$, can be calculated directly from the temperature T , pure solvent density ρ_1 and residual chemical potential of the solute at infinite dilution μ_2^r , following [18]:

$$H_{2,1}(p, T) = \lim_{x_2 \rightarrow 0} [RT \rho_1 \exp(\mu_2^r/RT)]. \quad (2)$$

x_2 is the solute mole fraction.

3. SAFT-VR model

In the SAFT-VR approach molecules are modelled as chains of tangentially bonded spherical segments of hard

core diameter σ , with the attractive interactions being described in this work by a square-well potential of variable range λ_{ij} and depth ε_{ij} .

Within the SAFT formalism the free energy of a mixture of associating chain molecules can be written as the sum of four separate contributions:

$$\frac{A}{NkT} = \frac{A^{\text{IDEAL}}}{NkT} + \frac{A^{\text{MONO.}}}{NkT} + \frac{A^{\text{CHAIN}}}{NkT} + \frac{A^{\text{ASSOC.}}}{NkT}, \quad (3)$$

where N is the number of molecules, k Boltzmann's constant, and T the temperature. A^{IDEAL} is the ideal free energy, $A^{\text{MONO.}}$ is the contribution to the free energy due to the monomeric segments, A^{CHAIN} the contribution due to the formation of a chain of m monomers, and $A^{\text{ASSOC.}}$ is the contribution due to association. We shall not consider the association term since we are dealing with non-associating systems.

The monomer free energy is written as a second-order high temperature perturbation expansion [19]:

$$\frac{A^{\text{MONO.}}}{NkT} = \frac{A^{\text{HS}}}{NkT} + \frac{1}{kT} \frac{A_1}{NkT} + \frac{1}{(kT)^2} \frac{A_2}{NkT}, \quad (4)$$

where A^{HS} is the free energy of the reference hard sphere fluid given by Boublik [20] and Mansoori *et al.* [21], A_1 is the mean attractive attractive energy, and A_2 describes the energy fluctuations.

As in other versions of the SAFT approach, the free energy contribution due to chain formation is given by the number of contacts $(m - 1)$ in the chain, and the contact pair distribution function $g^{\text{MONO.}}(\sigma)$ of the reference monomer fluid which, for a pure fluid, is given by

$$\frac{A^{\text{CHAIN}}}{NkT} = -(m - 1) \ln g^{\text{MONO.}}(\sigma). \quad (5)$$

In the SAFT-VR approach, $g^{\text{MONO.}}(\sigma)$ is written as a first-order perturbation expansion:

$$g^{\text{MONO.}}(\sigma) = g^{\text{HS}}(\sigma) + \frac{1}{kT} g_1(\sigma), \quad (6)$$

where $g^{\text{HS}}(\sigma)$ is the hard sphere radial distribution function. A closed form for $g_1(\sigma)$ can be obtained from the pressure expression (the Clausius virial theorem) and the first derivative of the free energy with respect to the density. For full details of the SAFT-VR approach the reader is directed to the original papers [22, 23].

The potential model parameters $\sigma, \varepsilon, \lambda$ for each pure component are determined by fitting to experimental vapour pressure and saturated liquid density data over the entire liquid range. For the n-alkanes and n-perfluoroalkanes simple empirical relationships proposed in earlier work are used to determine the number of spherical segments m in the model chain in relation to the number C of carbon atoms in the alkyl chain [24,

Table 1. Optimized square-well intermolecular potential parameters for n-hexane, n-perfluorohexane and xenon.^a

Substance	m	λ	$(\varepsilon/k)/\text{K}$	σ/nm
xenon	1.00	1.478	243.3	0.3849
n-hexane	2.67	1.552	250.4	0.3920
n-perfluorohexane	2.85	1.432	283.1	0.4456

^a m is the number of spherical segments in the model, λ the range parameter, σ the diameter of each segment, and ε/k the well depth.

25]. For the n-alkanes $m = 0.3(C - 1) + 1$, while for the n-perfluoroalkanes $m = 0.37(C - 1) + 1$. Values of $m = 2.67$ and $m = 2.85$ are therefore used for n-hexane and n-perfluorohexane respectively. A single sphere is naturally used to model the xenon atom [7]. The optimized parameters for xenon and n-hexane were determined in previous work and are presented in table 1 with those for n-perfluorohexane that are reported here for the first time. Figure 1 presents the vapour pressure curve and the vapour–liquid coexistence envelope of n-perfluorohexane predicted by the SAFT-VR approach compared with experimental data. Very limited experimental data are available in the literature for the complete vapour pressure curve or saturated liquid density of n-perfluorohexane and there are obvious inconsisten-

cies between the available sources [26]. An improvement in the accuracy of the SAFT-VR prediction compared with experimental data is anticipated if reliable consistent data become available over the entire fluid region.

The study of phase equilibria in mixtures additionally requires the determination of a number of unlike parameters. The unlike size parameter was calculated using the Lorentz combining rule

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2, \quad (7)$$

and the unlike energy parameter from the Berthelot combining rule

$$\varepsilon_{ij} = \xi(\varepsilon_{ii}\varepsilon_{jj})^{1/2} \quad (8)$$

where deviations from the geometric mean can be allowed for through the binary interaction parameter ξ . For the (xenon + n-hexane) system we used $\xi = 1$, since with this approximation we have been able to quantitatively describe a number of (xenon + n-alkane) systems [7, 8]. For (xenon + n-perfluorohexane) we used $\xi = 0.9206$, which is taken from earlier work on the binary mixtures of (n-perfluoromethane + n-alkanes) [27]. With this value of ξ we could also reproduce data for (xenon + perfluoromethane) and (xenon + perfluoroethane) [9]. The unlike range parameter was determined from the arithmetic mean,

$$\lambda_{12} = \frac{\sigma_{11}\lambda_{11} + \sigma_{22}\lambda_{22}}{\sigma_{11} + \sigma_{22}}. \quad (9)$$

4. Results and discussion

As a test of the suitability of the potential models chosen for the solvents in the MD simulations, the liquid densities obtained from the NPT simulations are compared in figure 2 for n-hexane and in figure 4 for n-perfluorohexane, with the experimental data from the literature. Full details of the simulation results can be found in table 2. In both cases agreement is reasonable near room temperature but deviations are evident above 400 K. The force field used to describe n-perfluorohexane reproduces the experimental density more accurately than that used for n-hexane. The simulated density of the n-hexane shows errors within 2% up to 400 K, whereas simulation results for n-perfluorohexane reproduce the experimental data within 1% at the temperatures where the latter are available for comparison.

In the MD simulations, the Henry's law coefficients were calculated initially assuming geometric mean combining rules for the Lennard-Jones parameters σ and ε describing the xenon–solvent interactions. The experimental values for the Henry's law coefficients determined at the saturation pressure of the pure solvent are compared directly with the simulated results at pressures slightly above the vapour pressure. This

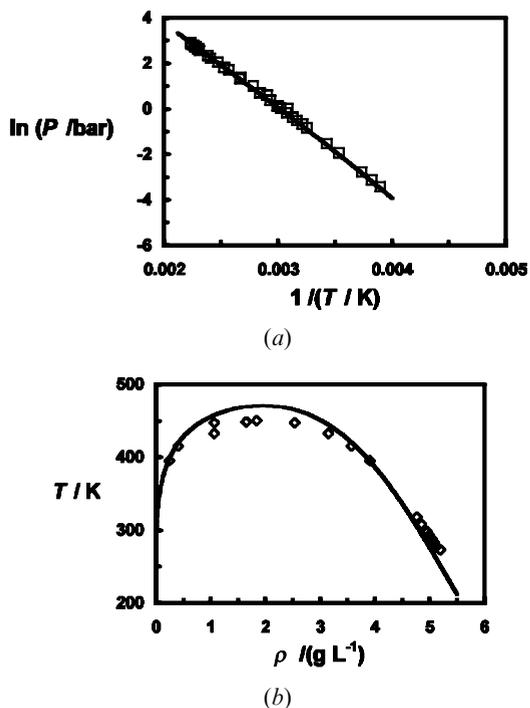


Figure 1. (a) Vapour pressures as a Clausius–Clapeyron representation and (b) vapour–liquid coexistence densities for n-perfluorohexane compared with the SAFT-VR predictions. The symbols represent the experimental data and the continuous curves the SAFT-VR predictions.

Table 2. Simulation results for the Henry's law coefficient of xenon in n-hexane and in n-per-fluorohexane.

$\frac{T}{K}$	$\frac{p}{\text{bar}}$	$\frac{\rho}{\text{mol L}^{-1}}$	$\frac{\mu^r}{\text{kJ mol}^{-1}}$	$\ln\left(\frac{H_{2,1}}{\text{bar}}\right)$	$\frac{\mu^r}{\text{kJ mol}^{-1}}$	$\ln\left(\frac{H_{2,1}}{\text{bar}}\right)$
Xe + C ₆ H ₁₄			$\xi = 1$		$\xi = 0.895$	
200	0.1	8.73	-8.92	-0.39	-5.81	1.48
250	0.1	8.16	-7.02	1.76	-4.29	3.07
280	0.5	7.75	-6.72	2.31	-4.17	3.40
300	0.5	7.53	-6.13	2.78	-3.68	3.76
330	1.0	7.13	-5.63	3.22	-3.35	4.05
350	2.0	6.89	-5.23	3.50	-3.05	4.25
400	6.0	6.11	-4.49	3.96	-2.63	4.52
450	15.0	5.09	-3.72	4.25	-2.22	4.66
Xe + C ₆ F ₁₄			$\xi = 1$		$\xi = 0.820$	
200	1	5.77	-8.10	-0.31	-3.72	2.33
250	1	5.37	-6.13	1.77	-2.23	3.64
280	1	5.11	-5.62	2.37	-2.01	3.92
300	1	4.91	-5.37	2.65	-1.96	4.02
330	3	4.67	-4.53	3.20	-1.37	4.35
350	3	4.50	-4.21	3.43	-1.18	4.47
400	9	3.91	-3.50	3.82	-0.98	4.57

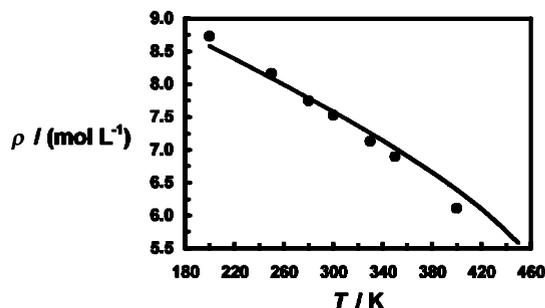
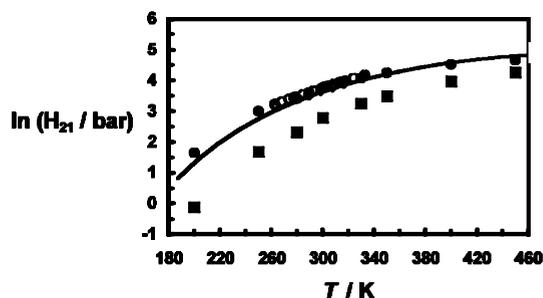


Figure 2. Density of liquid n-hexane: a comparison of the present simulations (●) with the correlation established by Cibulka [30] (—).

direct comparison is legitimate because the corrections to $H_{2,1}$ due to compression of the solvent are negligible [28]. As can be seen in figure 3, the Henry's law coefficients for xenon in n-hexane calculated in this manner underestimate by a factor of about 0.5 the experimental values, but essentially describe the correct temperature dependence over the limited range of experimental data. The discrepancies between the simulation results and the experimental data can be removed almost entirely by introducing a binary interaction parameter ξ , as in equation (8). The optimal value was found to be $\xi = 0.895$. The geometric mean was maintained for the unlike parameters σ_{ij} .

The results of the SAFT-VR calculations for the xenon + n-hexane system are also presented in figure 3. The Henry's constants were calculated from the chemical potential of xenon in the solvent at infinite dilution [29]. In previous work on binary mixtures of

Figure 3. Henry's law coefficient for xenon in liquid n-hexane. The present simulation results were obtained using: the geometric mean as a combining rule for Xe-C and Xe-H interactions (■); or by introducing a binary interaction parameter, $\xi = 0.933$ (●). Also shown are the experimental data of Pollack and Himm [31] (Δ), of Clever [32] (\diamond), and of Bonifácio *et al.* [33] (\circ). Values calculated using the SAFT-VR equation with Lorentz-Berthelot combining rules are also shown (—).

n-alkanes and xenon + n-alkanes, it was found that simple Lorentz-Berthelot combining rules accurately predict the phase behaviour of these simple systems. Therefore, it is not surprising that in the case of xenon in n-hexane the SAFT-VR results reproduce almost quantitatively the experimental data without deviation from the Lorentz-Berthelot combining rules. The SAFT-VR results are therefore true predictions, since no parameters were fitted to experimental data on the mixtures.

The results for xenon in n-perfluorohexane are depicted in figure 5. In this case, the simulated Henry's law coefficients are significantly lower than the experi-

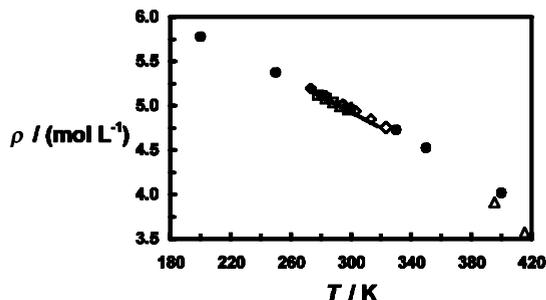


Figure 4. Density of liquid n-perfluorohexane. The plot shows a comparison of the present simulations (●) with the experimental data of Kennan and Pollack [34] (□), Taylor and Reed [35] (△), Narayana and Swamy [36] (×), Styles and Cady [37] (◇), and the correlation given in Beilstein [38] (—).

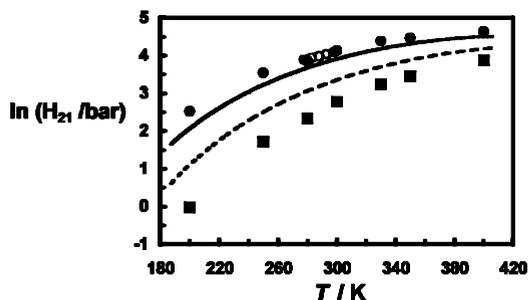


Figure 5. Henry's law coefficient for xenon in liquid n-perfluorohexane. The present simulation results were obtained using: the geometric mean as a combining rule for Xe-C and Xe-F interactions (■); or by introducing a binary interaction parameter, $\xi = 0.825$ (●). Also shown are the experimental data of Kennan and Pollack [34] (○). Values calculated using SAFT equation with Lorentz-Berthelot combining rules (---) and also assuming a binary interaction parameter of $k_{ij} = 0.92$ (—) are shown.

mental, by a factor of about 0.3, but again the correct temperature dependence is essentially reproduced. The same approach was followed to find a best fit value for the binary interaction parameter, which for xenon in n-perfluorohexane is $\xi = 0.820$. In the SAFT-VR calculations for n-perfluorohexane as a solvent, a binary interaction parameter had to be introduced in order to reproduce the experimental results. However, bearing in mind the previous application of SAFT-VR to alkanes + perfluoroalkanes and to xenon + light perfluoroalkanes, this was to be expected. The same value for ξ used in an earlier study of alkane + perfluoroalkane binary mixtures [9], $\xi = 0.92$ was used to determine the cross interaction in this case, hence avoiding the need to fit ξ to the experimental mixture data. Using ξ in this transferable fashion is shown to yield good results for the xenon + perfluorohexane system. A slight improvement would be possible if the parameter

ξ were fitted to this specific system, but we believe the value gained in being able to use SAFT-VR in this predictive sense outweighs the small improvement in accuracy that would result.

5. Conclusion

Molecular dynamics simulations using the OPLS-AA force field have been performed alongside calculations with the SAFT-VR equation of state. The OPLS-AA model gives quantitative results for the density of liquid n-hexane and n-perfluorohexane up to 400 K, corresponding to reduced temperatures of about $T_r = T/T_c = 0.8$. However, the prediction of the solubility of xenon in both solvents using simple geometric mean combining rules to determine the unlike interactions from those of the pure components yields only qualitative agreement with experimental data. By adjusting the binary interaction parameter for the unlike dispersion interaction, good agreement is obtained between the simulation results and experiment.

The SAFT-VR results reproduce closely the experimental solubility of xenon in n-hexane over the range of temperatures studied using simple Lorentz-Berthelot combining rules for the unlike interactions. For n-perfluorohexane as a solvent a binary interaction parameter had to be introduced. This was taken from previous work on n-alkane + n-perfluoroalkane binary mixtures; hence by using the parameter ξ in a transferable fashion we eliminate the need to fit to the mixture data of the system of interest.

The solubility of xenon in n-perfluorohexane is about one half of that in n-hexane. Without the introduction of a binary interaction parameter this relation is not obtained, since both the simulation and the SAFT-VR results alone would tell us that xenon is more soluble in n-perfluorohexane than in n-hexane.

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