

# On the liquid mixtures of xenon, alkanes and perfluorinated compounds

Clare McCabe,<sup>ab</sup> Lino M. B. Dias,<sup>c</sup> George Jackson<sup>a</sup> and Eduardo J. M. Filipe<sup>\*c</sup>

<sup>a</sup> Department of Chemical Engineering, Imperial College of Science Technology and Medicine, Prince Consort Road, London, UK SW7 2BY

<sup>b</sup> Department of Chemical Engineering, University of Tennessee, Knoxville, Tennessee, TN 37996-2200, USA

<sup>c</sup> Centro de Química Estrutural, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

Received 16th February 2001, Accepted 8th May 2001

First published as an Advance Article on the web 22nd June 2001

The fluid phase behaviour of binary mixtures of xenon and the lighter perfluoro-*n*-alkanes, CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>, and of propane and sulfur hexafluoride (SF<sub>6</sub>) has been examined using the statistical associating fluid theory for potentials of variable attractive range (SAFT-VR). We found that the binary interaction parameters calculated in previous work for (*n*-alkane + perfluoro-*n*-alkane) systems and for (Xe + SF<sub>6</sub>), can be used to predict the existing phase diagrams of (Xe + perfluoro-*n*-alkane) and (propane + SF<sub>6</sub>) mixtures, respectively. These results are consistent with the view that mixtures of (xenon + perfluorinated-compound) can be regarded as a special case of mixtures of (*n*-alkane + perfluorinated-compound) and provide another example of the “alkane-like” behaviour of xenon previously reported.

## 1. Introduction

Liquid mixtures involving alkanes, perfluoroalkanes and noble gases have been extensively studied and used as model systems for the testing of statistical theories of liquids. These chemical families provide a range of molecules whose physical properties gradually change within the homologous series or periodic group, and are therefore especially suited to study the role of size, shape and flexibility on the thermodynamic properties of liquid mixtures. Xenon has received particular attention since it is spherical and structureless in molecular terms, with a high polarisability that enhances dispersion forces. It also affords a liquid range suitable for mixing in the liquid state with a wide variety of other substances.

In previous work<sup>1–3</sup> we have reported low-temperature thermodynamic studies (160–200 K) of mixtures of xenon with the lighter alkanes (methane, ethane, propane, butane and *i*-butane). As expected these mixtures are almost ideal, but surprisingly they exhibit negative excess molar Gibbs energy,  $G_m^E$ , and negative excess molar volume,  $V_m^E$ , (and even negative excess molar enthalpy,  $H_m^E$ , and entropy,  $S_m^E$ , in the case of xenon + ethane), behaviour which closely resembles that seen for mixtures of *n*-alkanes. The experimental results were interpreted using the statistical associating fluid theory (SAFT-VR) of Gil-Villegas *et al.*<sup>4,5</sup> Using the SAFT-VR approach, with simple Lorentz–Berthelot combining rules to determine the cross interaction parameters, we were able to accurately describe the phase behaviour of the (xenon + alkane) systems,<sup>1–3</sup> including excess volumes. These results suggested that the (xenon + *n*-alkane) mixtures can be regarded as a special case of binary mixtures of *n*-alkanes. Further examples of the similarity between xenon and the *n*-alkanes in terms of phase equilibria can be found in mixtures with alcohols,<sup>6</sup> namely methanol. Mixtures of ethane, propane and *n*-butane with methanol show type V phase behaviour in the scheme of Scott and van Konynenburg,<sup>7</sup> while methane displays type III phase behaviour. It has

been found that the (xenon + methanol) system also exhibits type V phase behaviour.

Additionally we have found that the SAFT-VR parameters obtained for xenon lie within the average value of the parameters determined for the *n*-alkanes,<sup>4</sup> with the exception of methane (and to some extent of ethane) which exhibits anomalous behaviour. In other words, xenon can be described by a sphere with approximately the same diameter and intermolecular potential as that used to model the *n*-alkanes. This similarity extends to other microscopic properties. For example, the diameter of the xenon atom—measured, for instance, in terms of van der Waals radii—agrees well with that of the cross-sectional diameter of the *n*-alkanes. Also, the dielectric polarisability of xenon fits well with the linear dependence on *n* exhibited by the *n*-alkanes.

The purpose of this work is to examine whether the “alkane-like” behaviour of xenon extends to mixtures involving a perfluorinated compound such as a perfluoro-*n*-alkane or SF<sub>6</sub>. Recently, SAFT-VR has been successfully used to predict the rather complex phase behaviour of *n*-alkane + perfluoro-*n*-alkane binary mixtures.<sup>8</sup> Given the structural similarity of the pure components, these systems surprisingly exhibit substantial deviations from ideality, with large positive excess functions and extensive regions of liquid–liquid immiscibility. As a result of these unusual properties a large amount of experimental work has been devoted to their study (for a concise review see ref. 8). With the SAFT-VR approach the authors were able to correctly describe the transition from type II to type III phase behaviour exhibited by these systems and accurately reproduce both the gas–liquid and liquid–liquid critical lines and heteroazeotropes. The cross or unlike interactions were determined from those of the pure components using modified Lorentz–Berthelot combining rules, in that the unlike dispersion interaction between the alkane and perfluoroalkane segments was calculated using a binary interaction parameter,  $\xi = 0.9206$ , which was obtained from a fit to the high pressure critical line of the (perfluoromethane + *n*-butane) mixture. This parameter was

then successfully transferred to the other systems, (perfluoromethane + methane) through to (perfluoromethane + *n*-hexane) and the phase diagrams examined without any further fitting to experimental mixture data.

In this work we have tried to examine whether the phase behaviour of (*n*-alkane + perfluorinated-compound) mixtures can be used to predict that of (xenon + perfluorinated-compound) mixtures, *i.e.*, use the binary interaction parameters in a transferable fashion. Unfortunately, for (xenon + perfluoro-*n*-alkanes), experimental data for only two such mixtures can be found in the literature, namely (xenon + perfluoromethane)<sup>9</sup> and (xenon + perfluoroethane),<sup>10</sup> and in each case only one temperature has been examined. Both mixtures show positive azeotropes and large positive excess functions, but no liquid–liquid immiscibility. However, the flatness of the vapour pressure curve in the (xenon + perfluoromethane) mixture leaves no doubt about the proximity of an upper critical end point (UCEP), though this can not be proved as the mixture was studied at 159.01 K, already 2.38 K below xenon's triple point temperature (161.39 K). The (xenon + perfluoroethane) mixture was studied at 173.11 K, the triple point temperature of perfluoroethane. Thus, in both systems, the solidification of one of the components is likely to occur before the formation of a second liquid phase. Consequently they can be classified as type I phase behaviour in the scheme of Scott and van Konynenburg.

Additionally, we have recently examined the (Xe + SF<sub>6</sub>) binary mixture.<sup>11</sup> The complete phase diagram, from the triple points up to the mixture critical line was determined experimentally and the results were again interpreted using the SAFT-VR approach. The (Xe + SF<sub>6</sub>) system shows large positive deviations from ideality, but no liquid–liquid phase separation and can thus be classified as type I phase behaviour. In a similar approach to that described above in the study of the (xenon + perfluoro-*n*-alkane) systems, we have examined the (propane + SF<sub>6</sub>) binary mixture with SAFT-VR, using the binary interaction parameter determined for the (xenon + SF<sub>6</sub>) system to calculate the unlike dispersion energy. Hence, from the pure component parameters using the modified Lorentz–Berthelot combining rules, we are able to examine the (propane + SF<sub>6</sub>) phase diagram without fitting to any mixture data. With this approach we accurately predict the phase behaviour, achieving excellent agreement with the experimental data of Rowlinson and co-workers.<sup>12</sup> In all the studied cases, the results show that binary interaction parameters calculated for (alkane + perfluorinated compound) systems can be used to reproduce, within the same level of accuracy, the phase behaviour of (xenon + perfluorinated compound).

## 2. Results and discussion

Before we discuss the results of the SAFT-VR approach for the (xenon + perfluoro-*n*-alkane) systems examined in this paper it is convenient to summarise the main features of the theoretical model; for full details the reader is directed to the original papers.<sup>4,5</sup>

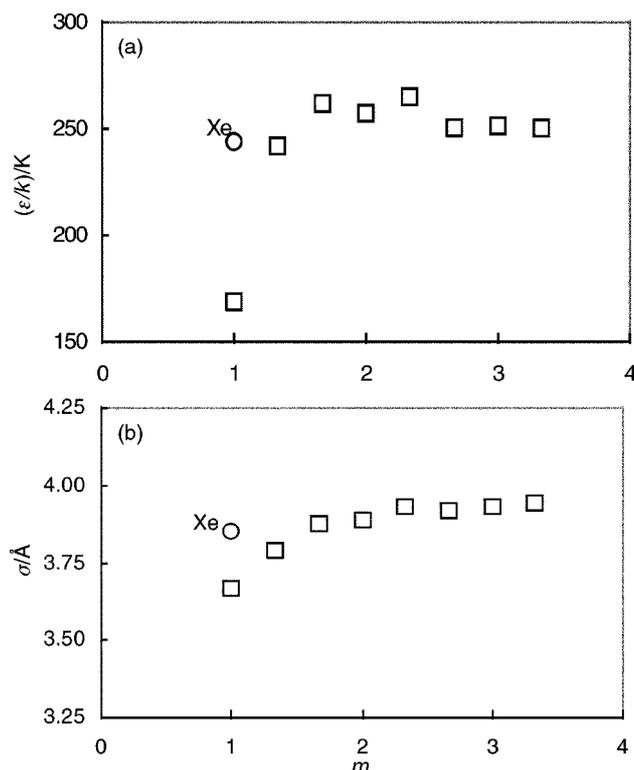
In the SAFT approach molecules are modelled as chains of tangentially bonded spherical segments of hard-core diameter  $\sigma$ . The attractive interactions are described by a square-well potential of variable range  $\lambda_{ij}$  and depth  $\epsilon_{ij}$ . The potential model parameters for the pure components are determined by fitting to experimental vapour pressure and saturated liquid density data over the entire liquid range. The optimised size and energy parameters can then be rescaled to the experimental critical points whenever critical behaviour is to be described. For the *n*-alkanes and perfluoro-*n*-alkanes 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 of carbon atoms  $C$  in the alkyl chain.<sup>13,14</sup> For the *n*-alkanes  $m = 0.3(C - 1) + 1$ , while for the perfluoro-*n*-alkanes  $m = 0.37(C - 1) + 1$ . Values of  $m = 1$  and  $m = 1.37$  are therefore used for perfluoromethane and perfluoroethane respectively. A single sphere is naturally used to model the xenon atom. For SF<sub>6</sub>,  $m$  was determined from the fitting procedure described above. The optimised parameters for xenon, perfluoromethane and perfluoroethane were determined in previous work and are presented in Table 1 with those for SF<sub>6</sub> which are reported here for the first time. Also included are the parameters for the *n*-alkanes from methane up to octane<sup>2</sup> which are plotted for a clearer comparison with those for xenon in Fig. 1. It should be kept in mind that these are effective parameters, which explains the variation in the

**Table 1** Optimised square-well intermolecular potential parameters for some *n*-alkanes, perfluoro-*n*-alkanes, sulfur hexafluoride and xenon<sup>a</sup>

Substance	$m$	$\lambda$	$(\epsilon/k)/K$	$\sigma/\text{\AA}$
Perfluoromethane	1.00	1.287	278.6	4.346
Perfluoroethane	1.37	1.339	289.0	4.436
Sulfur hexafluoride <sup>b</sup>	1.46	1.381	204.1	4.151
Xenon	1.00	1.478	243.3	3.849
Methane	1.00	1.444	168.8	3.670
Ethane	1.33	1.449	241.8	3.788
Propane	1.67	1.452	261.9	3.873
Butane	2.00	1.501	256.3	3.887
Pentane	2.33	1.505	265.0	3.931
Hexane	2.67	1.552	250.4	3.920
Heptane	3.00	1.563	251.3	3.933
Octane	3.33	1.574	250.3	3.945

<sup>a</sup>  $m$  is the number of spherical segments in the model,  $\lambda$  the range parameter,  $\sigma$  the diameter of each segment, and  $\epsilon/k$  the well depth.  
<sup>b</sup> Parameters that have been re-scaled to the critical point of the pure component.



**Fig. 1** (a) Intermolecular potential depth parameter,  $\epsilon$ , and (b) segment diameter,  $\sigma$ , as obtained from the SAFT-VR theory for xenon (○) and the *n*-alkanes (□) as a function of the number of spherical segments,  $m$ , used to model the chain molecule.

parameters even for the higher  $n$ -alkanes. As can be seen, the  $n$ -alkanes, except for methane and ethane, are described by parameters within an average value of  $\sigma = 0.3915 \pm 0.0029$  nm and  $\varepsilon/k = 256.0 \pm 6.4$  K. It is surprising to see that the parameters for xenon are very close to these average values. As previously stated, according to this model, xenon can be represented as a sphere with almost the same diameter and potential as those suited to describe the  $n$ -alkanes.

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

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2, \quad (1)$$

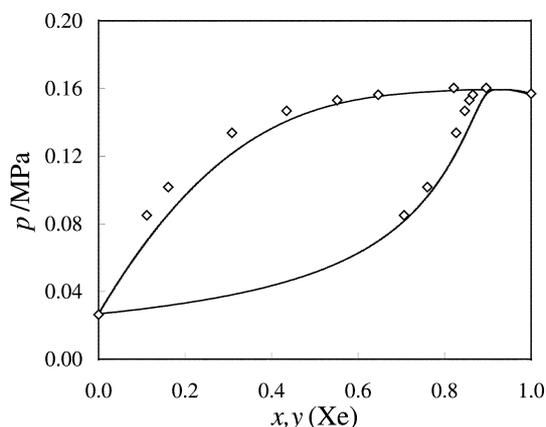
while for the unlike energy parameter, deviations from the Berthelot combining rule were allowed through the binary interaction parameter  $\xi$ ,

$$\varepsilon_{12} = \xi \sqrt{\varepsilon_{11}\varepsilon_{22}} \quad (2)$$

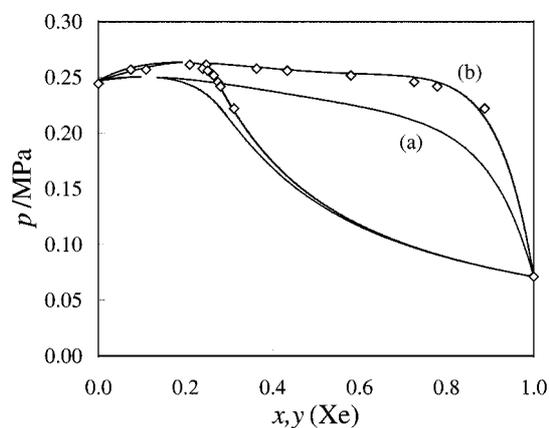
the value of which was taken from earlier work on the ( $n$ -alkane + perfluoro- $n$ -alkane)<sup>8</sup> and (xenon + SF<sub>6</sub>)<sup>11</sup> mixtures. The unlike range parameter was determined from the arithmetic mean,

$$\lambda_{12} = \frac{\sigma_{11}\lambda_{11} + \sigma_{22}\lambda_{22}}{\sigma_{11} + \sigma_{22}}. \quad (3)$$

This corresponds to the MX3b mixing rule of ref. 5. The SAFT-VR predictions for the (xenon + perfluoroethane) and (xenon + perfluoromethane) binary mixtures are compared with the experimental data in Fig. 2 and 3. In both cases a value of  $\xi = 0.9206$  was used, taken from ref. 8 where it was determined from the (perfluoromethane +  $n$ -butane) binary mixture and successfully used to reproduce the phase equilibria of (perfluoromethane +  $n$ -alkanes) from methane to  $n$ -hexane. As can be seen from Fig. 2, in the case of (xenon + perfluoroethane) the theory describes the gas-liquid coexistence envelope and azeotrope in very good agreement with the experimental data. In Fig. 3 we present the SAFT-VR prediction for the (xenon + perfluoromethane) binary mixture. The shift in the azeotrope from the alkane rich to the xenon rich phase is correctly predicted and the overall description of the phase diagram can be considered quite good. However, in this case when we use the  $\xi$  parameter from previous work (Fig. 3(a)) the agreement is less accurate, but within the same accuracy as the original (alkane + perfluoroalkane) work. We also have noted that a  $\xi$  of 0.90, as shown by line (b) in Fig. 3, very accurately describes the phase diagram for this system and is very close to the original  $\xi$  of 0.9206.

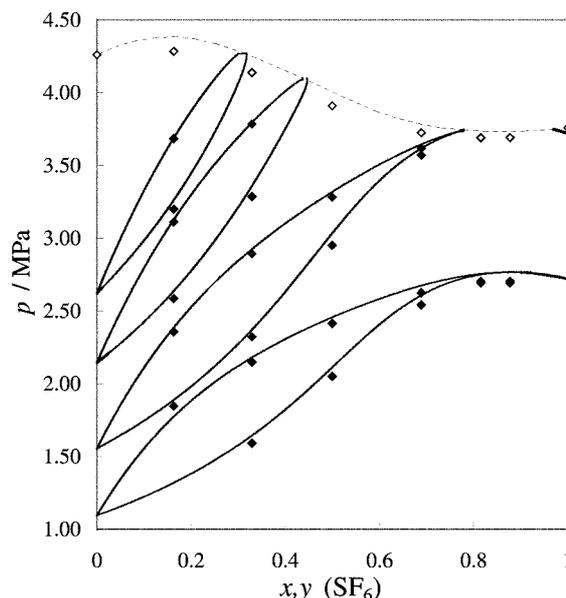


**Fig. 2** Vapour-liquid equilibrium for the (xenon + perfluoroethane) binary mixtures compared with the SAFT-VR predictions. The symbols represent the experimental results<sup>7</sup> at 173.11 K and the theoretical predictions are shown by the continuous curve.



**Fig. 3** Vapour-liquid equilibrium for the (xenon + perfluoromethane) binary mixture compared with the SAFT-VR predictions. The symbols represent the experimental results<sup>6</sup> at 159.01 K and the theoretical predictions are shown by the continuous curves: (a)  $\xi = 0.9206$ ; (b)  $\xi = 0.90$ .

Finally, the theoretical predictions for the (propane + SF<sub>6</sub>) binary mixture are compared with the experimental data in Fig. 4. For this system we determined the  $p,T$  projection of the phase diagram, as well as a number of constant temperature slices. A value of  $\xi = 0.9139$ , obtained from the (xenon + SF<sub>6</sub>) binary mixture,<sup>11</sup> was used in the calculations to determine the unlike dispersion interaction. The (xenon + SF<sub>6</sub>) system has no azeotrope and the critical line shows a minimum in temperature at a xenon mol fraction of around 0.85. The phase diagram of (propane + SF<sub>6</sub>), on the other hand, is much more complex. As can be seen from Fig. 4, this system shows an azeotropic line that meets the mixture critical line at a mol fraction of propane around 0.15. Furthermore, the mixture critical line shows a minimum in pressure and temperature at this composition and a maximum in pressure at 0.82 mol fraction of propane. As can be seen from the figure, all these features are mirrored by the theoretical predictions. Moreover, the quantitative agreement between the SAFT-VR prediction and the experimental data is very good, especially since we did not fit to any binary mixture data for the (propane + SF<sub>6</sub>) system.



**Fig. 4** Vapour-liquid equilibrium for the (propane + sulfur hexafluoride) binary mixture compared with the SAFT-VR predictions. The symbols represent the experimental results<sup>12</sup> and the theoretical predictions are shown by the continuous curves.

### 3. Conclusion

The statistical associating fluid theory for potentials of variable attractive range (SAFT-VR) was used to describe the phase behaviour of mixtures of xenon and the lighter perfluoro-*n*-alkanes, CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>, and that of the (propane + SF<sub>6</sub>) mixture. The experimental data could be reproduced using binary interaction parameters calculated in previous work for (*n*-alkane + perfluoro-*n*-alkane) and (xenon + SF<sub>6</sub>) systems. This enables the theory to be used in a truly predictive sense for each system studied, since no additional fitting to experimental mixture data needs to be performed. The present results, for mixtures involving a perfluorinated compound, suggest that, in general, the phase behaviour of mixtures of an *n*-alkane with a second component is mirrored by that of xenon with that same component, after taking into account the difference in chain length. Additional experimental data involving related systems would be desirable to support this generalisation. Ultimately, this work provides another example of the “alkane-like” behaviour of xenon previously reported.

### Acknowledgements

LMBD wishes to thank Fundação para a Ciência e Tecnologia for financial support and P. T. Cummings for his hospitality during a visit to the University of Tennessee where some of the calculations reported were performed.

### References

- 1 L. M. B. Dias, C. McCabe, E. J. M. Filipe and J. C. G. Calado, *J. Phys. Chem. B*, submitted.
- 2 E. J. M. Filipe, E. J. S. Gomes de Azevedo, L. F. G. Martins, V. A. M. Soares, J. C. G. Calado, C. McCabe and G. Jackson, *J. Phys. Chem. B*, 2000, **104**, 1315.
- 3 E. J. M. Filipe, L. F. G. Martins, J. C. G. Calado, C. McCabe and G. Jackson, *J. Phys. Chem. B*, 2000, **104**, 1322.
- 4 A. Gil-Villegas, A. Galindo, P. J. Whitehead, S. J. Mills, G. Jackson and A. N. Burgess, *J. Chem. Phys.*, 1997, **106**, 4168.
- 5 A. Galindo, L. A. Davies, A. Gil-Villegas and G. Jackson, *Mol. Phys.*, 1998, **93**, 241.
- 6 T. A. Gricus, K. D. Luks and C. L. Patton, *Fluid Phase Equilib.*, 1995, **108**, 219.
- 7 P. H. van Konynenburg and R. L. Scott, *Philos. Trans. R. Soc. London Ser. A*, 1980, **298**, 495.
- 8 C. McCabe, A. Galindo, A. Gil-Villegas and G. Jackson, *J. Phys. Chem. B*, 1998, **102**, 8060.
- 9 L. Q. Lobo, D. W. McClure, L. A. K. Staveley, P. Clancy, K. E. Gubbins and C. G. Gray, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 425.
- 10 S. C. Aldersley, L. Q. Lobo and L. A. K. Staveley, *J. Chem. Thermodyn.*, 1979, **11**, 597.
- 11 L. M. B. Dias, C. McCabe, E. J. M. Filipe and J. C. G. Calado, *J. Phys. Chem. B*, submitted.
- 12 H. P. Clegg and J. S. Rowlinson, *Trans. Faraday Soc.*, 1955, **51**, 1333.
- 13 G. Jackson and K. E. Gubbins, *Pure Appl. Chem.*, 1989, **61**, 1021.
- 14 A. L. Archer, M. D. Amos, G. Jackson and I. A. McLure, *Int. J. Thermophys.*, 1996, **17**, 201.