

## Liquid–vapour equilibrium of $\{x\text{BF}_3 + (1 - x)n\text{-butane}\}$ at 195.49 K

Lino M.B. Dias<sup>a,1</sup>, Rui P. Bonifácio<sup>a</sup>, Eduardo J.M. Filipe<sup>a</sup>,  
Jorge C.G. Calado<sup>a,\*</sup>, Clare McCabe<sup>b</sup>, George Jackson<sup>c</sup>

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

<sup>b</sup> Department of Chemical Engineering, Colorado School of Mines, Golden, CO 80401, USA

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

Received 14 June 2002; accepted 4 October 2002

### Abstract

The saturation vapour pressure of  $\{x\text{BF}_3 + (1-x)n\text{-C}_4\text{H}_{10}\}$  has been measured at 195.49 K. The system shows large positive deviations from Raoult's law and liquid–liquid immiscibility over a wide composition range whose limits have been estimated as  $0.39 \pm 0.03 < x < 0.9785$ . The excess molar Gibbs energies ( $G_m^E$ ) have been calculated as a function of composition from the vapour pressure data. For the hypothetical equimolar mixture  $G_m^E(x = 0.5) = (703.9 \pm 29) \text{ J mol}^{-1}$ . The results were interpreted using the statistical associating fluid theory for potentials of variable range (SAFT-VR), as well as compared with those of related systems, such as  $(\text{BF}_3 + n\text{-pentane})$  and  $(\text{BF}_3 + \text{xenon})$ .

© 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Phase equilibria; SAFT; Boron trifluoride; Alkanes; Xenon

### 1. Introduction

Boron trifluoride,  $\text{BF}_3$ , is widely used as a catalyst in a number of industrial processes, including the polymerization of olefins. In such processes the reacting mixture is usually made up of large amounts of  $\text{BF}_3$ , alkanes and alkenes, besides other additives. A detailed knowledge of the phase equilibria of all the corresponding binary mixtures is crucial to the optimization of the whole process. Mixtures of alkanes and alkenes have been extensively investigated, but the same is not true of mixtures of hydrocarbons with boron trifluoride. In this paper we present a vapour–liquid equilibrium study of  $(\text{BF}_3 + n\text{-C}_4\text{H}_{10})$

\* Corresponding author. Tel.: +351-1-8419316; fax: +351-1-8464455.

E-mail address: jcalado@popsrv.ist.utl.pt (J.C.G. Calado).

<sup>1</sup> Present address: Bayer AG Process Development, ZT-TE Fluid Process Technology—Thermophysical Properties and Thermodynamics, Building B310, 51368 Leverkusen, Germany.

mixtures, a non-reactive system whose behaviour is important to the understanding of the polymerization process. As far as we are aware, no other work has been done on ( $\text{BF}_3 + n\text{-C}_4\text{H}_{10}$ ). Some results for the solubility of  $\text{BF}_3$  in  $n\text{-C}_5\text{H}_{12}$ , at three temperatures, have been reported in the literature by Cade et al. [11]; however, the data cover only a limited range of pressures.

In ( $\text{BF}_3 + n\text{-C}_4\text{H}_{10}$ ) both components have relatively simple molecular structures, with few internal degrees of freedom, which makes them good candidates for the testing of statistical theories of liquids.  $\text{BF}_3$  is a quadrupolar (non-polar), planar molecule whereas  $n\text{-C}_4\text{H}_{10}$  is a chain molecule. They are both eminently suitable to quantitative description by theoretically-based equations of state, such as that provided by the statistical associating fluid theory [2] (SAFT). This is an approach in which shape effects and different types of molecular interactions can be separated and quantified, with each contribution dependent on molecular parameters that have a clear physical meaning, such as molecular size or range of the interaction. SAFT also has the ability to account simultaneously for non-sphericity and association effects. For a recent review of SAFT and its applications, the reader is directed to the comprehensive articles of Economou [3] and Muller and Gubbins [4].

Vapour–liquid equilibria measurements of ( $\text{BF}_3 + n\text{-C}_4\text{H}_{10}$ ) mixtures were carried out at 195.49 K, and the corresponding excess Gibbs energy ( $G_m^E$ ) calculated. As expected, the system is highly non-ideal, with a wide liquid–liquid immiscibility range. This behaviour is similar to that found for mixtures of alkanes and perfluoroalkanes.

The results were interpreted using a recent version of the SAFT approach, developed to treat potentials of variable attractive range, (SAFT-VR) [5,6]. Although the theory is able to qualitatively describe the overall pattern of the ( $\text{BF}_3 + n\text{-C}_4\text{H}_{10}$ ) phase diagram, the quantitative agreement is poor. Another system involving  $\text{BF}_3$  recently studied in our group is that of ( $\text{BF}_3 + \text{Xe}$ ) [7]. Since there is considerable evidence, both experimental and theoretical, that xenon behaves much like an  $n$ -alkane when mixed with a variety of other substances, including perfluorinated compounds [8,9], it was deemed useful, for comparative purposes to apply the same theoretical approach to the ( $\text{BF}_3 + \text{Xe}$ ) system.

## 2. Experimental

The vapour pressure measurements were carried out isothermally in an all glass apparatus, using a triple-point cryostat. Ammonia was selected as the cryogenic substance (triple-point temperature,  $T = 195.49$  K). The apparatus and techniques have already been described in detail elsewhere [10]. The mixtures were prepared condensing known amounts of each component into a calibrated pycnometer, with the amount of substance calculated from  $pVT$  measurements. The pressures were measured using a differential capacitance manometer (Datametrics 370, with 3.4 Pa resolution), which had been calibrated against mercury manometers.

The components and cryostat substance, boron trifluoride from Matheson,  $n$ -butane from Linde and ammonia from AirLiquide, had mass fractions 0.995, 0.9995 and 0.999, respectively. They were all further purified by fractionation in a low temperature column. The final purities were checked by measuring the vapour pressure at determined temperatures. At the working temperature of 195.49 K, the vapour pressure of  $\text{BF}_3$  was found to be  $397.80 \pm 0.06$  kPa, in good agreement with the literature value of 398.13 kPa [11]. Likewise, the vapour pressure of  $n$ -butane at the same temperature was  $1.40 \pm 0.01$  kPa, to be compared with 1.36 kPa [12]. Finally, the triple-point pressure of ammonia, was  $6.093 \pm 0.004$  kPa, very similar to the recommended value of  $6.080 \pm 0.003$  kPa [13].

The calculations of the amount of substance and of the excess molar Gibbs energy,  $G_m^E$ , need some ancillary data. The values of the second virial coefficients have already been given both for  $\text{BF}_3$  [7] and  $n$ -butane [12]. The cross second virial coefficients ( $B_{12}$ ) were estimated using a corresponding states method [14]. The resulting values were  $B_{12} = -814.01 \text{ cm}^3 \text{ mol}^{-1}$  at 195.49 K and  $B_{12} = -281.18 \text{ cm}^3 \text{ mol}^{-1}$  at 298.15 K.

### 3. Results

The vapour pressures,  $p$ , of  $\{x \text{ BF}_3 + (1-x)n\text{-C}_4\text{H}_{10}\}$  liquid mixtures at 195.49 K as a function of the liquid mole fraction of  $\text{BF}_3$ ,  $x$ , are recorded in Table 1 and plotted in Fig. 1. The mixture shows large positive deviations from Raoult's law and the vapour pressure remains constant (average value of  $404.03 \pm 0.25 \text{ kPa}$ ) over much of the composition range, a clear sign of phase separation. The presence of two liquid phases could also be confirmed visually. The limits of immiscibility were estimated to be

Table 1

Vapour pressures,  $p$ , and excess molar Gibbs energies,  $G_m^E$ , of  $\{x \text{ BF}_3 + (1-x)n\text{-C}_4\text{H}_{10}\}$ (l) at 195.49 K;  $x$  is the  $\text{BF}_3$  mole fraction in the liquid phase;  $x^o$  the overall mole fraction of  $\text{BF}_3$ ;  $y$  the  $\text{BF}_3$  mole fraction in the vapour phase;  $\delta p$  are the pressure residuals

$x_{\text{BF}_3}^o$	$x_{\text{BF}_3}$	$y_{\text{BF}_3}$	$p$ (kPa)	$\delta p$ (kPa)	$G_m^E$ (J mol $^{-1}$ )
0.0000	0.0000	0.0000	1.35	–	0
–	0.0825	0.9778	59.00	–4.5	92.81
–	0.1798	0.9916	151.78	9.6	232.54
–	0.2277	0.9934	185.01	–5.2	261.34
–	0.2748	0.9952	245.74	–0.8	332.83
–	0.3314	0.9964	320.29	–3.5	411.89
–	0.3561	0.9968	364.48	3.5	462.73
0.4242	–	–	403.82	–	–
0.9482	–	–	404.10	–	–
0.9668	–	–	403.74	–	–
0.9785	–	–	404.45	–	–
1.0000	1.0000	1.0000	406.76	–	–

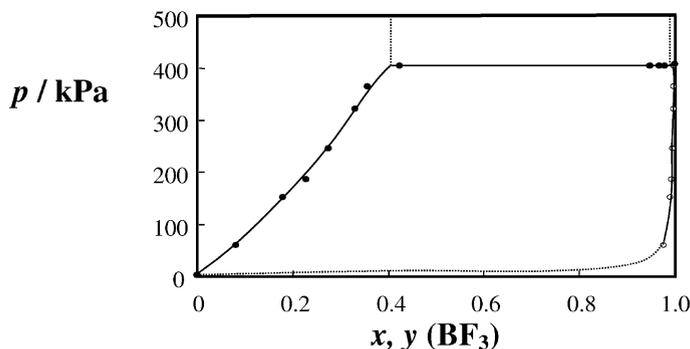


Fig. 1. Vapour pressure of  $\{x \text{ BF}_3 + (1-x)n\text{-C}_4\text{H}_{10}\}$ (l) =  $\{y \text{ BF}_3 + (1-y)n\text{-C}_4\text{H}_{10}\}$ (g) plotted against  $x$  and against  $y$  at 195.49 K. The lines are interpolations of the experimental results.

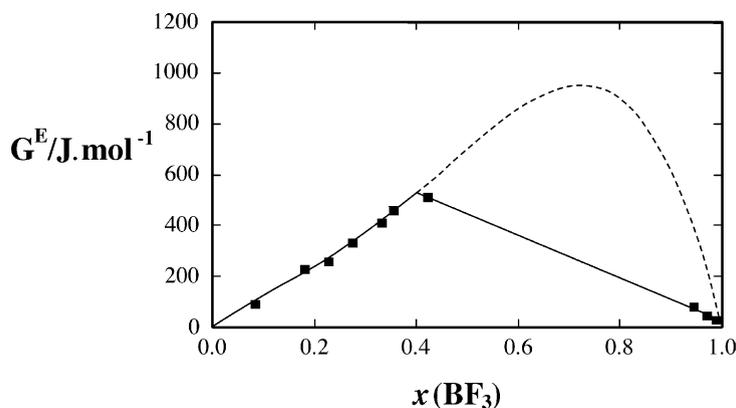


Fig. 2. Excess molar Gibbs energy,  $G_m^E$ , of  $\{x \text{BF}_3 + (1-x)n\text{-C}_4\text{H}_{10}\}$  at 195.49 K. The dashed line is the Redlich–Kister function.

( $0.39 \pm 0.03 < x < 0.9785$ ). Six (out of ten) mixtures lie outside the immiscibility gap. The composition of the vapour phase,  $y$  (the  $n$ -butane mole fraction) and the excess molar Gibbs energy,  $G_m^E$ , were evaluated following Barker's method [15], which minimizes the pressure residuals,  $\delta p = p - p_{\text{cal}}$ . The values of  $\delta p$ , also given in Table 1, are a good indication of the consistency of the experimental data. The excess molar Gibbs energy of each mixture,  $G_m^E$ , was calculated at zero pressure and fitted to a Redlich–Kister-type equation,

$$\frac{G_m^E}{RT} = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2] \quad (1)$$

The fitting parameters  $A$ ,  $B$  and  $C$  and their standard deviations are  $A = (1.732 \pm 0.072)$ ,  $B = (-2.12 \pm 0.20)$  and  $C = (1.25 \pm 0.37)$ . The  $G_m^E$  values are plotted in Fig. 2 against the liquid mole fraction,  $x$ , resulting in a very asymmetric curve. It should be noted, however, that the miscibility zone (six mixtures) covers less than half of the composition range ( $x < 0.4$ ). For the hypothetical equimolar liquid mixture,  $G_m^E(x = 0.5) = (703.9 \pm 29) \text{ J mol}^{-1}$ .

#### 4. Discussion

A quantitative interpretation of the results was attempted using the statistical associating fluid theory for potentials of variable attractive range, SAFT-VR [5,6]. The main expressions of the SAFT-VR theory for the square-well potential have been presented elsewhere, and the reader is directed to the original references for full details [5,6].

The SAFT-VR approach describes molecules as chains of  $m$  tangent hard spherical segments with the attractive interactions modeled by a potential of variable attractive range. Each segment is characterized by three parameters, namely the hard-sphere diameter,  $\sigma$ , and the depth,  $\epsilon$ , and width,  $\lambda$ , of the potential well. For the  $n$ -alkanes, a simple empirical relation between the number of carbon atoms,  $n$ , in the alkyl chain and the number of spherical segments,  $m$ , in the model chain has been proposed [16]  $m = 1 + (n - 1)/3$ . A value of  $m = 2.00$  was therefore used for  $n$ -butane. The remaining parameters,  $\sigma$ ,  $\epsilon$  and  $\lambda$ , are determined by fitting the theoretical expressions to the experimental vapor pressure and orthobaric liquid density

Table 2  
Optimized square-well intermolecular potential parameters for boron trifluoride, *n*-butane, *n*-pentane and xenon<sup>a</sup>

Substance	<i>m</i>	$\sigma$ (nm)	$\varepsilon/k$ (K)	$\lambda$
BF <sub>3</sub>	1.60	0.3412	272.6	1.300
<i>n</i> -Butane	2.00	0.3887	256.3	1.501
<i>n</i> -Pentane	2.33	0.3931	265.0	1.505
Xenon	1.00	0.3849	243.9	1.478

<sup>a</sup> *m* is the number of spherical segments,  $\lambda$  the range parameter,  $\sigma$  the diameter of each segment, and  $\varepsilon/k$  the well depth.

data, over the entire liquid range. All these parameters have already been determined for *n*-butane. For BF<sub>3</sub>, *m* was treated as a floating parameter and calculated, alongside  $\sigma$ ,  $\varepsilon$  and  $\lambda$ , from the fitting to the orthobaric properties of the pure substance. All parameters are listed in Table 2.

The usefulness of the BF<sub>3</sub> parameters, here calculated for the first time, can be assessed from a comparison between the calculated values of the vapour pressure and liquid densities and the experimental data from the literature [11,17] (Fig. 3). From the figure we see that with this model for BF<sub>3</sub> we are able to accurately describe the phase behaviour of the pure component.

It is believed that BF<sub>3</sub>, a typical Lewis acid, does not self-associate, but forms a number of adduct compounds when mixed with a variety of substances (Lewis bases, such as ammonia, ethers and alcohols). A possible description of this molecule by the SAFT approach could, therefore, include an association site to account for those strong interactions. However, in the present case association is not possible, because the *n*-butane molecules are devoid of basic character. Moreover, preliminary results obtained by modeling the BF<sub>3</sub> molecule with an additional attractive site, did not lead to any improvement in the description of the phase equilibria of either the pure substance or the (BF<sub>3</sub> + *n*-C<sub>4</sub>H<sub>10</sub>) binary mixture. As a consequence, the possibility of such an attractive site was ignored.

Phase equilibria studies in mixtures require the determination of a number of cross-parameters for the unlike interaction. For both the size and range parameters, the arithmetic mean was used, i.e.

$$\sigma_{12} = \frac{(\sigma_{11} + \sigma_{22})}{2} \quad (2)$$

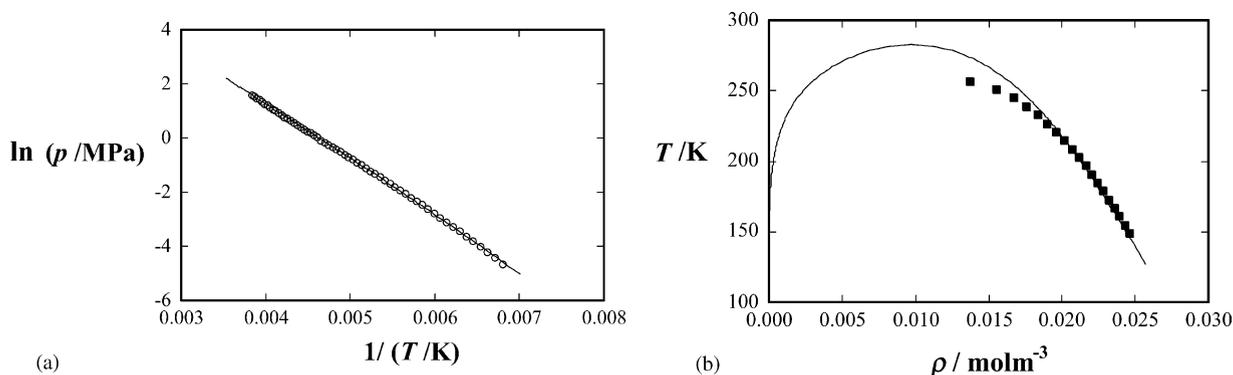


Fig. 3. (a) Vapour pressure curve for BF<sub>3</sub>. (b) Vapour–liquid coexistence densities for BF<sub>3</sub>. The continuous curves are the SAFT-VR results obtained using parameters fitted simultaneously to vapour pressure and saturated liquid densities.

which is known as the Lorentz combination rule, and

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

For the energy parameters, allowance was made for deviations from the geometric mean (the well-known Berthelot combining rule)

$$\varepsilon_{ij} = \xi(\varepsilon_{ii}\varepsilon_{jj})^{1/2} \quad (4)$$

The SAFT-VR description of the vapour-liquid-liquid equilibrium for the ( $\text{BF}_3 + n\text{-C}_4\text{H}_{10}$ ) system, at 195.49 K, is represented in Fig. 4a. The best fit to the experimental data is obtained with a value of  $\xi = 0.866$ . The theory is able to qualitatively predict the highly asymmetric phase diagram of this system.

In the literature there is a limited amount of experimental data for the ( $\text{BF}_3 + n\text{-pentane}$ ) system [1]. SAFT-VR should be able to model this system with the same value of  $\xi = 0.866$  for the unlike interaction as was used for ( $\text{BF}_3 + n\text{-butane}$ ) (Fig. 4b). It is surprising that in the case of *n*-pentane, the theory appears to predict the experimental results much better than it does with *n*-butane. However, it should be observed that the experimental data cover only a very limited range of the phase diagram and show considerable scatter.

A useful comparison can be drawn between these results and those for other binary mixtures involving perfluorocompounds and *n*-alkanes. The first perfluoroalkane is  $\text{CF}_4$ , a tetrahedral molecule whose first non-zero multipole moment is the octopole. The ( $\text{CF}_4 + n\text{-C}_4\text{H}_{10}$ ) system has been extensively investigated over the whole fluid range. It exhibits a rather complex phase behaviour in the transition from types II and III, in the classification of van Konynenburg and Scott [18]. The phase diagram of this system, as well as those for other systems involving perfluorinated substances such as  $\text{C}_2\text{F}_6$  [9], and  $\text{SF}_6$  [19], can be well described by the SAFT-VR equation of state [20]. This leads us to believe that the poor performance of SAFT-VR in what concerns the ( $\text{BF}_3 + n\text{-C}_4\text{H}_{10}$ ) mixtures is due to an inadequate description of the  $\text{BF}_3$  molecule. Unlike the perfluoroalkanes previously studied,  $\text{BF}_3$  has a quadrupole moment, a planar geometry and a double bond delocalized over the whole molecule. The combined presence of all these factors, none of which can be explicitly taken into account by the theory, could be the reason for the poor quantitative agreement between theory and experiment in the case of the ( $\text{BF}_3 + n\text{-C}_4\text{H}_{10}$ ) system. The

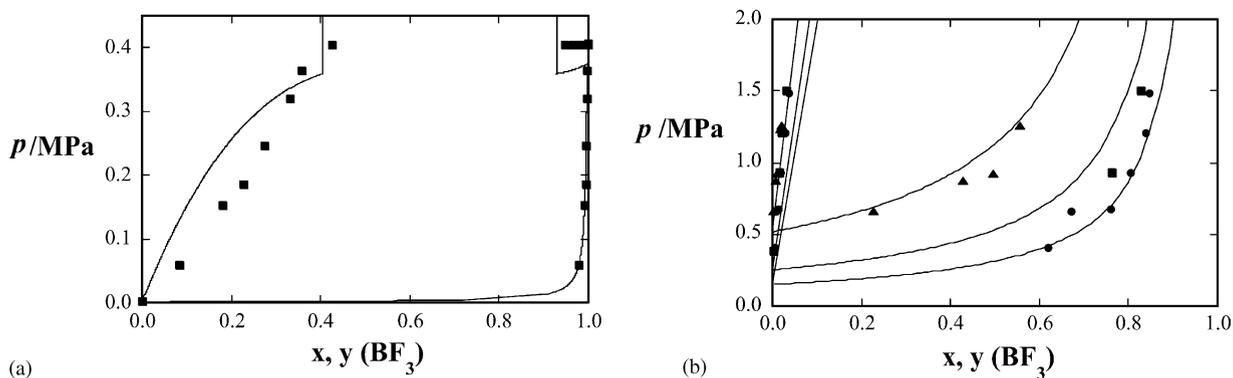


Fig. 4. Vapour-liquid equilibrium for: (a)  $\{x \text{BF}_3 + (1-x)n\text{-C}_4\text{H}_{10}\}$  at 195.49 K; (b) ( $\text{BF}_3 + n\text{-C}_5\text{H}_{12}$ ) at 322 K (●), 339 K (■) and 366 K (▲). The symbols represent the experimental results and the SAFT-VR predictions are shown by the continuous curve.

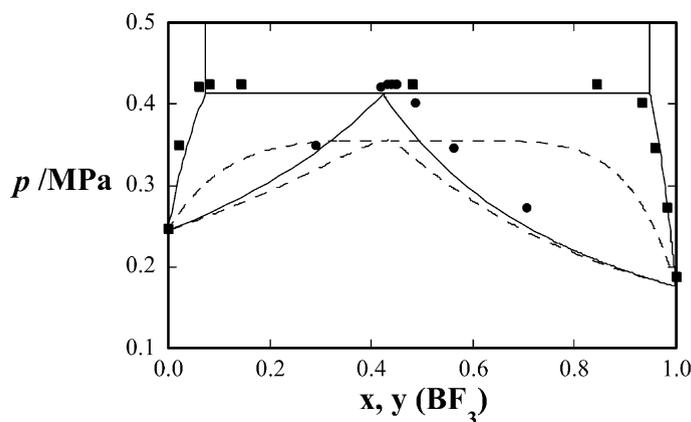


Fig. 5. Vapour–liquid equilibrium for (BF<sub>3</sub> + xenon) at 182.34 K. The symbols represent the experimental results and the SAFT-VR predictions are shown by the curves. Dashed line obtained with a  $\xi = 0.832$  and solid line  $\xi = 0.8$ .

fact that BF<sub>3</sub>, although being lighter than CF<sub>4</sub> (one fluorine atom less), is less volatile than CF<sub>4</sub>, implies that the BF<sub>3</sub>–BF<sub>3</sub> interactions are stronger than the CF<sub>4</sub>–CF<sub>4</sub> interactions and provides further evidence of the different nature of the intermolecular forces in BF<sub>3</sub> when compared with a typical perfluorinated molecule.

Another class of interesting mixtures, related to the one under discussion, is that generated by the substitution of the hydrocarbon by xenon. This follows from a recent finding that liquid xenon displays a behaviour that resembles that of the *n*-alkanes when mixed with a number of substances, including perfluorinated compounds. These findings have been corroborated by the theory in a number of recent papers on the phase behaviour of binary systems involving xenon [8,9,12,21]. The calculated SAFT parameters for xenon lie within the average value of those used to describe the *n*-alkanes; moreover, interaction parameters obtained for binary mixtures containing alkanes can be transferred to the corresponding mixtures involving xenon. If the analogy holds, the value of  $\xi = 0.866$  taken from the (BF<sub>3</sub> + *n*-butane) system should apply to the corresponding (BF<sub>3</sub> + xenon) system. However, this assumption is not confirmed by the theory (Fig. 5), and a much better fitting is obtained with a value of  $\xi = 0.80$  for the deviation of the cross-energy parameter from the geometric mean. Hence it seems that the transferability of molecular parameters observed for other xenon and alkane binary mixtures appears to break down for systems involving BF<sub>3</sub>. Again, we believe that this is due to the inadequacy of the underlying model for BF<sub>3</sub>. A more realistic description of the BF<sub>3</sub> molecule than that provided by this version of SAFT-VR is needed if we are to obtain a quantitative account of the phase diagram.

#### List of symbols

$B_{12}$	cross second virial coefficient
$g$	gas
$G_m^E$	excess molar Gibbs energy
$l$	liquid
$m$	number of spherical segments
$p$	pressure

$\delta p$	pressure residuals
$T$	temperature
$x^0$	overall mole fraction of $\text{BF}_3$
$x$	liquid phase mole fraction of $\text{BF}_3$
$y$	gas phase mole fraction of $\text{BF}_3$

#### Greek letters

$\varepsilon$	square well depth
$\lambda$	square well width
$\xi$	binary interaction parameter
$\rho$	density
$\sigma$	hard core diameter

### Acknowledgements

LMBD wishes to thank Fundação para a Ciência e a Tecnologia for financial support. We are also grateful to BP Chemicals for their support. We should also like to thank Amparo Galindo for useful discussions.

### References

- [1] G.N. Cade, R.E. Dunn, H.J. Hepp, *J. Am. Chem. Soc.* 68 (1946) 2454–2455.
- [2] W.G. Chapman, G. Jackson, K.E. Gubbins, *Mol. Phys.* 65 (1988) 1057–1079.
- [3] I.G. Economou, *Ind. Eng. Chem. Res.* 41 (2001) 953–962.
- [4] E.A. Muller, K.E. Gubbins, *Ind. Eng. Chem. Res.* 40 (2001) 2193–2211.
- [5] A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burgess, *J. Chem. Phys.* 106 (1997) 4168–4186.
- [6] A. Galindo, L.A. Davies, A. Gil-Villegas, G. Jackson, *Mol. Phys.* 93 (1998) 241–252.
- [7] J.C.G. Calado, E.J.M. Filipe, *J. Chem. Soc., Faraday Trans.* 92 (1996) 215–218.
- [8] E.J.M. Filipe, E.J.S. Gomes de Azevedo, L.F.G. Martins, V.A.M. Soares, J.C.G. Calado, C. McCabe, G. Jackson, *J. Phys. Chem. B.* 104 (2000) 1315–1321.
- [9] C. McCabe, L.M.B. Dias, G. Jackson, E.J.M. Filipe, *Phys. Chem. Chem. Phys.* 3 (2001) 2852–2855.
- [10] J.C.G. Calado, E.J.S. Gomes de Azevedo, V.A.M. Soares, *Chem. Eng. Commun.* 5 (1980) 149–163.
- [11] H.S. Both, Carter, *J. Phys. Chem.* 36 (1932) 1359–1363.
- [12] E.J.M. Filipe, L.F.G. Martins, J.C.G. Calado, C. McCabe, G. Jackson, *J. Phys. Chem. B.* 104 (2000) 1322–1325.
- [13] L.A. K. Staveley, L.Q. Lobo, J.C.G. Calado, *Cryogenics* 21 (1981) 131–144.
- [14] R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, Singapore, 1988.
- [15] J.A. Barker, *Aust. J. Chem.* 6 (1953) 207–210.
- [16] A.L. Archer, M.D. Amos, G. Jackson, I.A. McLure, *Int. J. Thermophys.* 17 (1996) 201–211.
- [17] R.L. Rowley, W.V. Wilding, J.L. Oscarson, N.A. Zundel, T.L. Marshall, T.E. Daubert, R.P. Danner, DIPPR® Data Compilation of Pure Compound Properties, Design Institute for Physical Properties, AIChE, New York, 2001.
- [18] P.H. van Konynenburg, R.L. Scott, *Philos. Trans. R. Soc. London A* 298 (1980) 495.
- [19] L.M.B. Dias, T. Cordeiro, C. McCabe, E.J.M. Filipe, J.C.G. Calado, *J. Phys. Chem.*, submitted for publication.
- [20] C. McCabe, A. Galindo, A. Gil-Villegas, G. Jackson, *J. Phys. Chem. B* 102 (1998) 8060–8069.
- [21] E.J.M. Filipe, L.M.B. Dias, J.C.G. Calado, C. McCabe, G. Jackson, *Phys. Chem. Chem. Phys.* 4 (2002) 1618–1621.