Thermodynamics of Liquid Mixtures of Xenon with Alkanes: (Xenon + *n*-Butane) and (Xenon + Isobutane)

Eduardo J. M. Filipe,* Luís F. G. Martins,[†] and Jorge C. G. Calado

Centro de Química Estrutural, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

Clare McCabe[‡] and George Jackson

Imperial College of Science Technology and Medicine, Prince Consort Road, London SW7 2BY, U.K.

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The total vapor pressure of liquid mixtures of (xenon + *n*-butane) has been measured at 182.34 and 195.49 K, and of (xenon + isobutane) at 195.49 K. The liquid molar volumes have also been measured at 182.34 K for both systems. The mixtures follow the behavior already found for other (xenon + alkane) mixtures, i.e., negative deviations from Raoult's law, negative excess molar Gibbs energies (G_m^E) and negative excess molar volumes (V_m^E). The excess molar enthalpy (H_m^E) is approximately zero in the case of (xenon + *n*-butane). The results were interpreted using the statistical association fluid theory for potentials of variable attractive range (SAFT-VR). This study provides further evidence that the (xenon + *n*-alkane) mixtures can be thought of as a particular case of mixtures of *n*-alkanes.

1. Introduction

In a previous paper[1] we reported results on the excess thermodynamic functions of the liquid mixtures (xenon + ethane) and (xenon + propane). The fact that these systems 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, for xenon + ethane), raised the possibility of a relatively strong interaction between xenon and the alkane molecules. Within a site−site framework this could be translated into a strong attraction between the xenon atom and the CH_2/CH_3 groups. The present work deals with the thermodynamics of mixtures of xenon with two isomeric forms of butane, the linear form, *n*-butane, and the branched one, methylpropane (or isobutane), and is a further effort to elucidate the nature of the xenon−alkane interaction.

The methods of investigation are the same as those of previous papers. Saturation vapor pressures and orthobaric densities have been measured isothermally (triple-point cryostat) as a function of composition. The densities were measured, for both systems, at $T = 182.34$ K, the triple point of nitrous oxide, N_2O. The vapor pressures were measured at two temperatures ($T = 182.34$ K and $T = 195.49$ K, the latter being the triple-point temperature of ammonia, NH_3) for the (xenon + *n*-butane) mixture, and at one temperature ($T = 195.49$ K) in the case of (xenon + isobutane). As far as we are aware, no other thermodynamic study has been done on these systems. The mixtures follow the behavior already found for (xenon + ethane); i.e., they exhibit negative deviations from ideality: negative G_m^E and V_m^E. In the case of (xenon + *n*-butane), H_m^E is approximately zero in the temperature range covered in this study.

The general purpose of the project is to correlate molecular shape and interaction. The systems were chosen with the aim

of assessing the relative influence of methyl (CH_3) and methylene (CH_2) groups. *n*-butane and isobutane have the same overall molecular formula, C_4H_{10}, but while linear butane has two methyl groups and two methylene groups, isobutane has three methyl groups and one methine group, CH. The results for the (xenon + isobutane) system can also be compared with those for its structural analogue, (xenon + trimethylboron) ($B(CH_3)_3$) which has been the subject of a previous study[2].

The phase equilibria of both the (xenon + *n*-butane) and (xenon + isobutane) systems was interpreted quantitatively using a recent version of the statistical associating fluid theory, developed to treat potentials of variable attractive range (SAFT-VR).[3] This theory, which had proved successful in the case of the (xenon + ethane) and (xenon + propane) binary mixtures,[1] is again in close agreement with experiment in the case of the butane mixtures. This work provides further evidence that the (xenon + alkane) mixtures can be regarded as a special case of mixtures of alkanes. Xenon behaves as an ennobled alkane.

2. Experimental Section

The apparatus and experimental techniques used to measure the vapor pressures and orthobaric densities have already been described.[4] The compositions were determined from the condensed amounts of each component in a glass pyknometer, after correcting for the amount of substance in the vapor phase. The vapor pressures were measured with a quartz spiral gauge (Texas Instruments model PPG 149) calibrated against a Dead Weight Gauge. The volume of the pyknometer was determined at 182.34 K, using ethane as a calibrating liquid and relying on the molar volume data of Haynes and Hiza.[5] A value of $V_{pyk} = 2.1995 \pm 0.0001$ cm^3 was obtained, the result of three independent measurements.

All substances (*n*-butane, isobutane, and xenon purchased from Linde with stated purities of 99.95%, 99.95%, and 99.99%, respectively; nitrous oxide and ammonia from Air Liquide with stated purities of 99% and 99.9%, respectively) were further

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[†] Present address: Departamento de Química, Universidade da Madeira, Caminho da Penteada, 9000 Funchal, Portugal.
[‡] Present address: Department of Chemical Engineering, University of Tennessee, Knoxville, TN 37996.

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TABLE 1: Total Vapor Pressure and Excess Molar Gibbs Energy of (Xenon + n-Butane) at 182.34 and 195.49 K and (Xenon + Isobutane) at 195.49 K[a]

T/K	x	y	p/kPa	R_p/kPa	$G_m^E/J\ mol^{-1}$
			Xe + n-C$_4$H$_{10}$		
182.34	0	0	0.423		0
	0.21893	0.99280	48.27	0.11	−20.84
	0.36781	0.99649	82.15	−0.20	−40.01
	0.54963	0.99837	128.12	0.015	−48.78
	0.65478	0.99897	156.47	0.36	−44.04
	0.81350	0.99956	198.33	−0.45	−33.88
	1	1	248.22		0
195.49	0	0	1.40		0
	0.21106	0.98595	80.29	0.14	−29.24
	0.37867	0.99375	147.84	−0.34	−48.24
	0.52745	0.99661	213.70	0.26	−51.53
	0.66399	0.99810	276.68	0.15	−47.82
	0.80279	0.99908	342.09	−0.35	−35.95
	1	1	436.88		0
			Xe+ i-C$_4$H$_{10}$		
	0	0	2.720		0
	0.13142	0.95262	51.07	−0.31	−22.78
	0.22651	0.97538	89.51	0.47	−28.96
	0.38055	0.98795	151.85	−0.32	−41.54
	0.65170	0.99595	270.08	0.24	−43.11
	0.78399	0.99792	331.55	−0.17	−38.15
	0.89752	0.99916	386.60	−0.35	−24.59
	0.92547	0.99942	401.26	0.55	−15.99
	1	1	436.88		0

[a] R_p are the pressure residuals defined as $R_p = p_{exp} − p_{calc}$.

purified by fractional distillation. In the case of the cryostat fluids (nitrous oxide and ammonia) a double distillation was carried out. The final purity of the samples was checked through the constancy of the triple point pressure during melting or through their vapor pressures at the working temperatures. The triple point pressures of nitrous oxide and ammonia were found to be 87.869 ± 0.008 kPa (cf. 87.865 kPa[6]) and 6.093 ± 0.004 kPa (cf. 6.080 ± 0.003 kPa[6]), respectively. For the remaining substances the following vapor pressures were obtained: 248.19 ± 0.08 kPa at 182.34 K (cf. 248.24 kPa[7]) and 436.88 kPa at 195.49 K (cf. 436.82 kPa[8]), for xenon; 0.423 ± 0.004 kPa at 182.34 K (cf. 0.423 kPa[9]) and 1.40 ± 0.01 kPa at 195.49 K (cf. 1.36 kPa[9]), for n-butane; 2.720 ± 0.008 at 195.49 K (cf. 2.64 kPa[10]), for isobutane.

For xenon, the sources of the second virial coefficients needed to perform the calculations have already been given.[1] For n-butane and isobutane, at low temperature, they were estimated using the correlation of Leland,[11] and at room temperature they were taken from the compilation of Dymond.[12] The cross second virial coefficients (B_{12}) were estimated using a corresponding states method.[13] The resulting values were $B_{12} = −828\ cm^3\ mol^{-1}$ at 182.34 K, $B_{12} = −711\ cm^3\ mol^{-1}$ at 195.49 K, and $B_{12} = −293\ cm^3\ mol^{-1}$ at 298.15 K, for the (xenon + n-butane) system, and $B_{12} = −784\ cm^3\ mol^{-1}$ at 182.34 K, $B_{12} = −675\ cm^3\ mol^{-1}$ at 195.49 K, and $B_{12} = −279\ cm^3\ mol^{-1}$ at 298.15 K, for the (xenon + isobutane) system.

3. Results

Xenon + n-Butane System. The vapor pressures, p, of (xenon + n-butane) mixtures at 182.34 and 195.49 K as a function of the liquid mole fraction of xenon, x, are recorded in Table 1 and plotted in Figure 1a. The mole fraction of xenon in the vapor phase, y, was evaluated according to Barker's method,[14] which minimizes the pressure residuals, $R_p = p − p_{cal}$. The values of R_p, also given in Table 1, are a good indication of the self-consistency of the experimental data. The excess molar Gibbs energy of each mixture, G_m^E, was calcu-
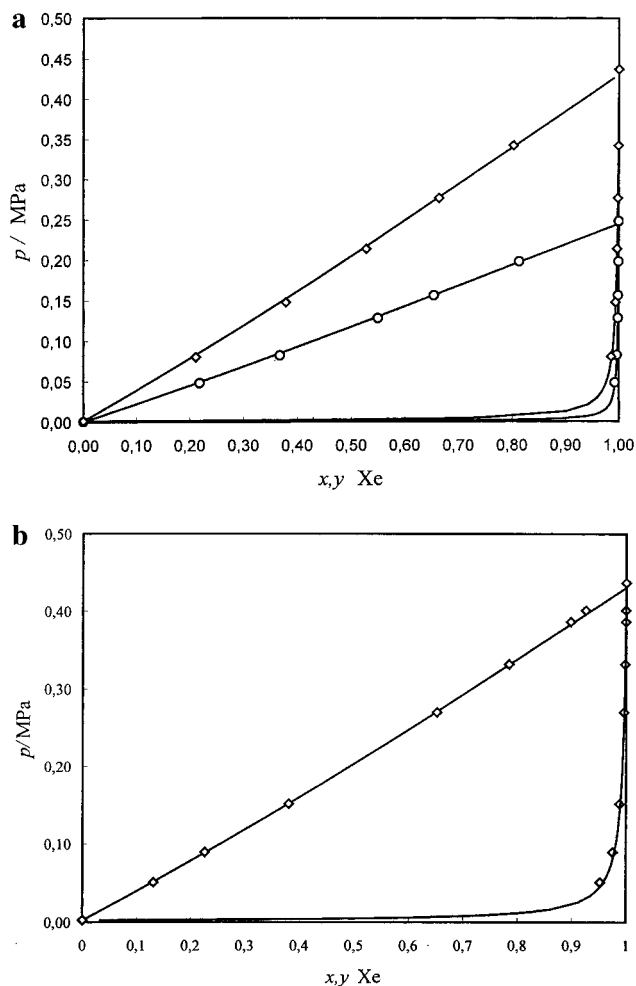
Figure 1. Vapor−liquid equilibrium data for the (a) (xenon + n-butane) and (b) (xenon + isobutane) binary mixtures and their comparison with the SAFT-VR predictions. Experimental results at 182.34 K (circles) and 195.49 K (diamonds); theoretical predictions (continuous curves).

TABLE 2: Excess Molar Gibbs Energy of (Xenon + n-Butane) and (Xenon + Isobutane) Mixtures, Values for the Equimolar Mixture, $G_{1/2}^E$, and Coefficients of Eq 1

T/K	A	B	C	$G_{1/2}^E/J\ mol^{-1}$
		xenon + n-butane		
182.34	−0.126 ± 0.015	0.047 ± 0.021	0.050 ± 0.027	−47.6 ± 5.7
195.49	−0.129 ± 0.0079	0.021 ± 0.011	0.019 ± 0.014	−52.3 ± 3.2
		xenon + isobutane		
195.49	−0.108 ± 0.0062	0.024 ± 0.010	−0.046 ± 0.013	−43.9 ± 2.5

lated at zero pressure and fitted to a Redlich−Kister type equation,

$$G_m^E/RT = x(1 − x)[A + B(1 − 2x) + C(1 − 2x)^2] \quad (1)$$

The fitting parameters A, B, and C and their standard deviations are recorded in Table 2, along with the value of G_m^E for the equimolar mixture. The G_m^E results at 182.34 and 195.49 K are plotted in Figure 2a. The excess molar enthalpy, H_m^E, can be estimated within the limits of uncertainty of $G_m^E(x = 0.5)$ at both temperatures; for the equimolar composition, a value of $H_m^E(x = 0.5) = 17\ J\ mol^{-1}$ was found.

The orthobaric molar volumes, V_m, of (xenon + n-butane) mixtures at 182.34 K are recorded in Table 3. The excess molar volumes, V_m^E, do not refer to zero pressure since, owing to the low pressures involved, the corrections would be within

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a

b
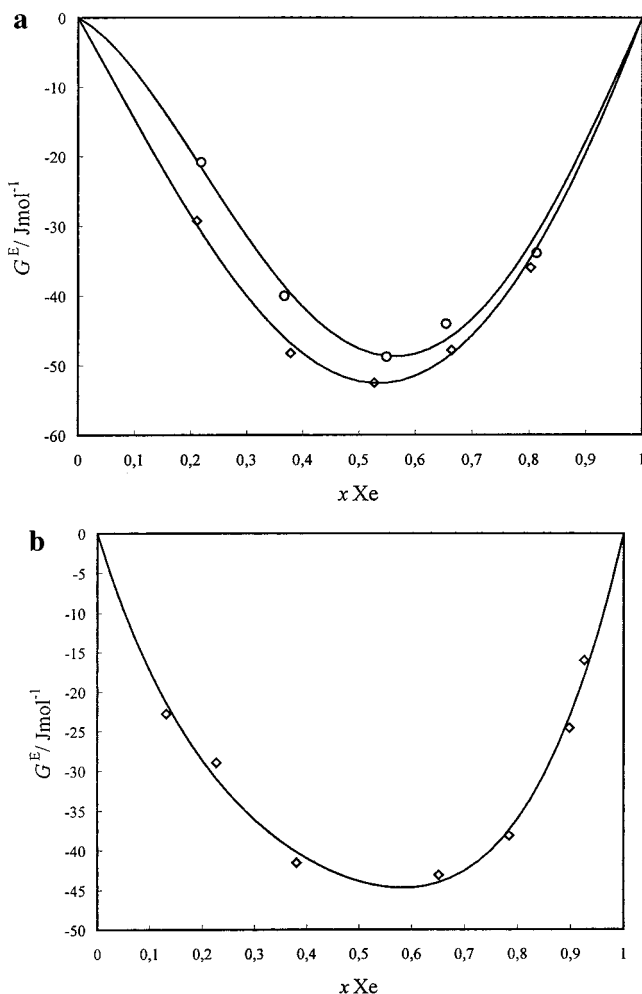
Figure 2. Excess molar Gibbs energy for the (a) (xenon + *n*-butane) and (b) (xenon + isobutane) binary mixtures at 182.34 K (circles) and 195.49 K (diamonds).

TABLE 3: Molar Volumes and Excess Molar Volumes of (Xenon + *n*-Butane) and (Xenon + Isobutane) Mixtures at 182.34 K and under Saturation Vapor Pressure[a]

x_{Xe}	$V_m/cm^3\,mol^{-1}$	$V_m^E/cm^3\,mol^{-1}$	$R_V/cm^3\,mol^{-1}$
	Xe + *n*-C$_4$H$_{10}$		
0	84.145	0	
0.11261	79.662	−0.242	0.049
0.13636	78.596	−0.413	−0.070
0.30622	71.982	−0.629	0.012
0.37159	69.426	−0.723	−0.0049
0.47461	65.543	−0.726	0.070
0.63140	59.510	−0.854	−0.057
0.64897	58.900	−0.802	−0.015
0.79668	53.550	−0.588	0.017
1	46.480	0	
	Xe + *i*-C$_4$H$_{10}$		
0	85.665	0	
0.26585	75.075	−0.173	0.0084
0.46610	67.055	−0.346	−0.031
0.61508	61.187	−0.376	0.012
0.65527	59.612	−0.392	0.0043
0.77347	54.993	−0.363	0.012
0.88762	50.620	−0.263	−0.0057
1	46.480	0	

a R_V are the volume residuals defined as $R_V = V_m^E - V_m^E$ (eq 3).

experimental error. The molar volume of pure *n*-butane could not be measured experimentally with our technique because this substance condenses easily in the pyknometer stem. This quantity was taken from Haynes and Hiza.[5] The V_m^E values were fitted to a Redlich−Kister type equation,

$$V_m^E/(cm^3\,mol^{-1}) = x(1 - x)[D + E(1 - 2x) + F(1 - 2x)^2]$$
(2)

with $D = -3.23 \pm 0.21$ cm^3 mol^{-1}, $E = 0.66 \pm 0.35$ cm^3 mol^{-1}, $F = -0.33 \pm 0.75$ cm^3 mol^{-1} and $V_m^E(x = 0.5) = -0.806 \pm 0.052$ cm^3 mol^{-1}. The V_m^E values and their fitting equation are plotted in Figure 3.

Xenon + Isobutane System. The vapor pressures of (xenon + isobutane) at 195.49 K are given in Table 1 and plotted in Figure 1b. Barker's method was again used to evaluate the composition of the vapor phase. Parameters *A, B,* and *C*, with their standard deviations, are recorded in Table 2 and the G_m^E curve is shown in Figure 2b.

The orthobaric molar volumes and the corresponding excess molar volumes at 182.34 K for this system can be found in Table 3. As before, the V_m^E values were not corrected to zero pressure. As explained for *n*-butane, the molar volume of pure isobutane could not be experimentally determined and was taken from ref 4. The V_m^E values were fitted to eq 2 leading to $D = -1.34 \pm 0.058$ cm^3 mol^{-1}, $E = 1.16 \pm 0.12$ cm^3 mol^{-1}, $F = -0.57 \pm 0.25$ cm^3 mol^{-1}, and $V_m^E(x = 0.5) = -0.336 \pm 0.015$ cm^3 mol^{-1}. The V_m^E values and curve are plotted in Figure 3.

4. Discussion

The values of the three major excess functions for the equimolar mixtures of xenon and the light alkanes (C$_2$−C$_4$) are summarized in Table 4. Some general remarks can be made about these results. Both $G_m^E(x = 0.5)$ and $V_m^E(x = 0.5)$ decrease as the number of carbon atoms in the *n*-alkane molecule increases. This trend probably arises from the increasing number of interaction sites on the alkane molecule. More difficult to
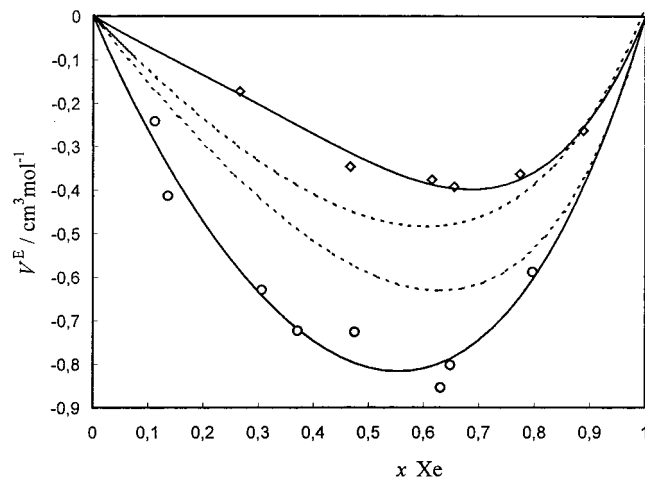
Figure 3. Excess molar volumes for the (xenon + *n*-butane) (circles) and (xenon + isobutane) (diamonds) binary mixtures at 182.34 K, compared with the SAFT-VR predictions (dashed curves).

TABLE 4: Excess Molar Functions for the Equimolar Mixtures of Xenon and Light Alkanes

system	T/K	$G_{1/2}^E/J\,mol^{-1}$	$V_{1/2}^E/cm^3\,mol^{-1}$	$H_{1/2}^E/J\,mol^{-1}$
xenon + ethane[a]	161.40	−28.5	−0.115	−51.7
	182.34	−28.0		
xenon + propane[a]	161.40	−14.8	−0.308	
	182.34	−32.8		142
	195.49	−45.3		
xenon + *n*-butane	182.34	−47.6	−0.806	17
	195.49	−52.3		
xenon + isobutane	182.34		−0.336	
	195.49	−43.9		

a Reference 1.

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understand is the evolution of H_m^E throughout the series: negative in the case of (xenon + ethane), positive for (xenon + propane), and approximately zero for (xenon + n-butane). The interpretation of these results requires a more detailed discussion, involving the temperature dependence of H_m^E, and will be the object of a future publication.

The butane mixtures follow the behavior of (xenon + propane). The two systems, (xenon + n-butane) and (xenon + isobutane), show approximately the same value of G_m^E for the equimolar mixture, but widely different values of V_m^E. These are both negative, but whereas for (xenon + n-butane) $V_m^E(x = 0.5) = -1.063$ cm³ mol⁻¹, for (xenon + i-butane) it is only $V_m^E(x = 0.5) = -0.334$ cm³ mol⁻¹. This is probably the result of the packing of molecules with different shapes (isobutane is a quasi-spherical molecule, whereas n-butane is an elongated body). G_m^E, on the contrary, is rather insensitive to packing arrangements. In a recent publication,[2] the (xenon + isobutane) mixture has been investigated by Monte Carlo computer simulation. The molecules were modeled as fused hard sphere particles; i.e., each atom was taken to be a hard sphere. It was found that the experimental results compared well with those of the simulations. Given the simplified nature of the fused hard spheres model, which accounts only for molecular shape, this agreement shows that shape and packing are, indeed, the key factors in determining the value of V_m^E in the case of (xenon + isobutane).

A quantitative interpretation of the results was attempted using the statistical associating fluid theory for potentials of variable attractive range, SAFT-VR.[3,15] The main expressions of the SAFT-VR theory for the square-well potential have been presented before;[1] the reader is directed to the original references[3,15] for full details. The SAFT-VR approach describes molecules as chains of m tangent hard segments with the attractive interactions modeled by a square-well potential of variable attractive range. Each segment is characterized by three parameters, namely, the hard-sphere diameter, σ, and the depth ϵ and width λ of the potential well. For the n-alkanes a simple empirical relationship 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.[16,17]

$$m = 1 + (n - 1)/3 \tag{3}$$

A value of $m = 2.00$ was, therefore, used for n-butane and a single sphere modeled the xenon atom. The remaining pure substance parameters, σ, ϵ, and λ, are determined by fitting the theoretical expressions to the experimental vapor pressure and saturated liquid density data, from the triple point up to near the critical point. In the previous paper in this series it was shown that the parameters calculated for xenon using this model lie within the average values of the parameters obtained for the n-alkanes. This implies that xenon can be treated as the first member of the n-alkane family and, ultimately, that the (xenon + n-alkane) mixtures can be considered as a particular case of mixtures of n-alkanes.

A shortcoming of the SAFT-VR theory in this form is its inability to account explicitly for branching in the alkane chain. Hence, for a given number of carbon atoms eq 3 will give a similar number of spheres regardless of any peculiarities in molecular structure. Therefore, the number of spheres, m, of the isobutane molecule was calculated, alongside the size and energy parameters. All the parameters are listed in Table 5.

TABLE 5: Optimized Square-Well Intermolecular Potential Parameters for Some Alkanes and Xenon[a]

substance	m	σ/nm	ϵ/k (cm⁻¹)	λ
n-butane	2	0.3887	257.2	1.501
isobutane	1.9	0.4106	289.9	1.458
xenon	1	0.3849	243.9	1.478

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

The Lorentz−Berthelot combining rules were used to determine the unlike parameters for the cross-interaction, enabling the SAFT-VR approach to be completely predictive in the sense that no experimental results for the mixtures are needed to perform the calculations and no interaction or fitting parameters are used.

Constant temperature $p−x$ slices of the (xenon + n-butane) and (xenon + isobutane) phase diagrams are presented in Figure 1a,b. As can be seen, the results are in excellent agreement with the experimental data. The phase compositions are well described for both systems, as is the temperature dependence in the case of (xenon + n-butane). Finally, in Figure 3 the experimental excess molar volumes for both systems are compared with the SAFT-VR predictions. Again, the theory is able to predict both the sign and order of magnitude of the experimental values. It should be stressed that the results are pure predictions, since no experimental data for the mixtures were used in the calculations.

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