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In Situ Determination of Phase Equilibria of Methyl Benzoate + Alkane Mixtures Using an Infrared Absorption Method. Comparison with Polar GC-SAFT Predictions[†]

D. NguyenHuynh, J.-P. Passarello, and P. Tobaly*

Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions (LIMHP), CNRS Université Paris 13,
99 avenue J. B. Clément, F-93430, Villetaneuse

Isothermal vapor−liquid equilibrium (VLE) data were measured for mixtures of methyl benzoate with four normal alkanes (from butane to heptane) at temperatures from (353.15 to 453.15) K using an in situ infrared absorption method already validated in previous work. With this method, a mathematical treatment of the absorption spectra allows the determination of the molar density of each species in the liquid phase. Mole fractions and bubble curves are then determined. The newly measured data are compared to calculations made using a purely predictive approach with the polar GC-SAFT equation of state. The agreement with the experimental data is satisfactory (< 10 %) since the data were not used to determine the parameters of the model.

Introduction

The modeling of chemical processes is critically dependent on an accurate knowledge of the thermodynamic behavior of the involved substances. Hence, potentially unreliable results arising from such operations may either generate unnecessary costs or fail to achieve production targets.[1,2] The need for efficient models to reliably estimate phase equilibria of complex systems remains today a major industrial problem. Measurements are costly and time-consuming. Thus, it appears very useful to have methods for realistic evaluation of thermodynamic properties. As the industrial demand is more and more focused toward multifunctional molecules for which only a little is known, such methods should be ideally predictive or at least should require very limited information. However, selected experimental data are still needed to develop or validate such thermodynamic models.

In this context, a predictive model, GC-SAFT (group contribution SAFT equation of state), was recently proposed by Tamouza et al.[3,4] and later extended by NguyenHuynh et al.[5,6] to polar fluids. Polar GC-SAFT has been applied successfully for modeling phase behavior of different types of systems containing polar and/or associative components, such as alcohols, alkyl esters, alkyl ethers, alkyl ketones, alkyl benzenes,[7] etc., and systems containing a small molecule, such as CO_2, N_2, CH_4, CO, etc.[8−10]

Benzoic acid esters are a very interesting class of solvents for a number of valuable applications thanks to their dipolar and hydrophobic nature and their highly selective ability. Alkyl benzoates are used to control thickening, flow, and viscosity properties of cellulose ethers. They are also used as fragrances and antibacterial agents in cosmetic formulations, as plasticizers to produce poly(vinyl chloride) (PVC) polymers, and as textile dye carriers for the treatment of synthetic fibers, among others.

Table 1. Chemical Suppliers and Stated Purities of Used Compounds

component	chemical formula	purity	supplier
methylbenzoate	$C_8H_8O_2$	99 %	ACROS ORGANICS
butane	C_4H_{10}	$[C_nH_m] < 8 \cdot 10^{-4}$ $[iC_4H_{10}] < 3 \cdot 10^{-3}$	AIR LIQUIDE
pentane	C_5H_{12}	> 99 %	ACROS ORGANICS
hexane	C_6H_{14}	> 99.5 %	ACROS ORGANICS
heptane	C_7H_{16}	> 99.5 %	ACROS ORGANICS

The aim of the present work is to complement the phase equilibrium database of mixtures containing multifunctional compounds. Of particular interest is the behavior of mixtures of a multipolar + a nonpolar compound as already noted by Dominik et al.[11] The new data obtained in this work allow us to test and validate the extrapolation and prediction capacity of polar GC-SAFT. In this perspective, vapor−liquid equilibrium measurements of mixtures containing methyl benzoate and normal alkanes were realized.

Experimental Section

Materials. Both the methyl benzoate and the *n*-alkanes were of the highest commercial grade. The purity together with the supplier information about the pure compounds are detailed in Table 1.

Apparatus and System Setup. The apparatus has been described in full detail in previous papers.[12] For the sake of completeness, we recall here the main features and the changes made to adapt it to the present study.

In the high pressure cell already described,[12] the infrared light beam is transmitted through sapphire windows. The optical path length was adjusted by using window spacers 1 mm thick. This path length of 1 mm is convenient as far as the overtones and combination bands of methyl benzoate and *n*-alkanes in the liquid phase are used (in the wavenumber range of (4000 to 8500) cm^{-1}).

Such a path length allowed us to record spectra for pressures in the range (1 to 35) bar in the liquid phase. Unfortunately,

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* Corresponding author. E-mail: tobaly@limhp.univ-paris13.fr.

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the vapor phase spectra were not exploitable due to a very weak and noisy signal since vapor densities were very low. However, experimental data obtained on the bubble curve could be easily measured and are sufficient for the purpose of this work.

A pressure gauge with an uncertainty of ± 0.2 % of the full scale, i.e., ± 0.07 bar, was used here. The pressure gauge was calibrated against a dead weight pressure balance, and corrections were also applied to compensate for temperature zero drift. The whole cell is heated by a hot air furnace, and the temperature is stabilized to within ± 0.1 °C using an Eurotherm regulator unit. The temperature was measured by a platinum resistance temperature detector (Pt100). The overall uncertainty on temperature measurements is estimated at ± 0.2 °C.

Experimental Procedure. The reference spectrum through the empty cell was first recorded. Then the cell was filled with the mixture in the following way:

In the case of methyl benzoate + butane, the liquid methyl benzoate was introduced first through the top hole after disconnection of the pressure gauge. The cell was then evacuated to reduce the residual air content to negligible. The butane was then introduced under pressure through the gas inlet. The connecting tubes were also evacuated to ensure no air was introduced in the cell during this operation.

For other mixtures, samples were prepared in advance with various compositions and then introduced into the cell. In that case also, the air in the cell was evacuated by a vacuum pump. The loss of liquid was certainly low when evacuating the cell at room temperature. However, it must be noted that any loss of liquid does not affect the results since in these kinds of experiments it is not necessary to know the exact initial amount introduced into the cell.

For a given mixture, at each temperature, the pressure was set by moving the piston, and then a spectrum was recorded in both phases (liquid and vapor). Recording of the spectra was made as soon as possible, namely, after the system had returned to equilibrium. The equilibrium is reached when the pressure is stable and when subsequent spectra recordings do not show any significant differences. In previous studies, we have noticed that this relaxation time was important near critical points. In the present study since there were no critical points and there were only small pressure steps, the return to the equilibrium was very quick in most cases.

After measurements have been performed for a given mixture, the equipment could be cleaned to remove all remaining components. For this purpose, the cell was completely taken apart, each piece cleaned in a solvent, and then dried in an oven.

Spectral Recordings. Infrared spectra were obtained using a BOMEM MB-155 FTIR spectrometer with a spectral resolution of 4 cm^{-1}.

Mathematical Treatment. Due to overlapping infrared absorption bands of the components (see Figure 1), a mathematical treatment is necessary to separate the contributions of each component. This mathematical procedure has been developed on the basis of a linear relationship between concentration and absorption (Beer−Lambert law). One of its greatest merits is that resulting concentrations are insensitive to baseline variations as demonstrated elsewhere.[13] We briefly recall below the principles of this method.

To limit the effects due to line broadening, the absorbances are integrated over well-chosen frequency domains. These integration zones Z_i are chosen so that the integrals do not depend either on temperature or pressure and so as to maintain the linear relationship with concentrations. Hence, the determination of concentrations C_1 and C_2 requires at least two integration zones yielding a set of two linear equations.

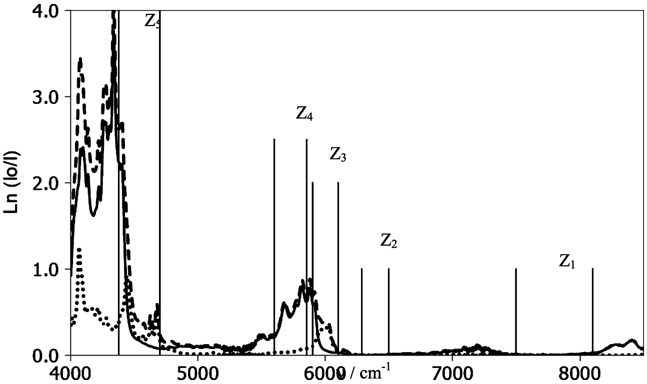

Figure 1. Typical spectrum (baseline corrected) of the methyl benzoate + butane mixture (dashed). Calculated methyl benzoate contribution (dotted). Calculated butane contribution (solid line). Mixture at 353.15 K and 9.12 bar. Five integration zones Z1 to Z5 used for the calculation of C1 and C2.

The baseline is mostly unknown when samples with a high refractive index are introduced in the cell. Consequently, in our mathematical treatment the baseline is considered as an additional unknown quantity defined by the following equation.

$$b = b_1\nu^2 + b_2\nu + b_3$$

where b_1, b_2, and b_3 are constants and ν is the wavenumber.

We end up with a set of five linear equations with five unknowns, C_1, C_2, and b_1, b_2, b_3. The unknowns are calculated by resolving this set of equations. In this process, the correlations existing between the contributions of each molecule on the five integration domains are respected. The true baseline is thus recovered, and the two concentrations C_1 and C_2 are also calculated at the same time.

The choice of the integration frequency domains Z_1 to Z_5, as shown in Figure 1, has been made to keep a linear relationship between integrated intensities and concentrations of molecules. The calibration process involves measurements of spectra of the pure compounds yielding coefficients for C_1 and C_2 in the equations by integration over bands Z_1 to Z_5.

More detailed explanations on the method may be found in Marteau et al.[12−14]

Uncertainties Associated with the Method. The estimated uncertainty on the concentrations of each compound is 0.5 % so that the evaluated uncertainty on mole fractions is 1 %. This method has been tested, validated, and used at moderate and high pressures (up to 200 MPa) with mixtures such as methane + hydrocarbon[12−16] and propane + hydrocarbon.[17]

However, some complementary tests were performed to ensure the validity of the data.

It is known that specific interactions between the components or other effects induced by high densities may affect the spectra and cause the absorption to deviate from Beer−Lambert law for given frequencies. Therefore, as noticed above, the integration bands have to be carefully chosen so that the integrals remain proportional to the concentrations.

As a test of the calibration accuracy, the infrared method has been applied to the spectra of the pure components, i.e., butane, pentane, hexane, and heptane, at various pressures and temper-

Table 2. Comparison of Pure *n*-Alkane Concentrations in the Liquid Phase Determined by the Infrared Method and Reference Data Available on the NIST Webbook Site[23] at Different Temperatures[a]

			C/mol·L^{-1}		
alkanes	T/K	P/bar	this work	NIST data	ref
butane	353.15	10.39	8.611	8.6095	24,25
	373.15	15.86	8.038	8.0369	24,25
	393.15	22.65	7.328	7.3273	24,25
	413.15	31.56	6.276	6.2749	24,25
pentane	373.15	6.00	7.451	7.4488	26
	423.15	16.20	6.388	6.3768	26
hexane	393.15	4.10	6.478	6.4771	26
	413.15	6.33	6.196	6.1948	26
	433.15	9.18	5.883	5.8816	26
	453.15	13.01	5.524	5.5216	26
heptane	433.15	4.77	5.486	5.4842	26
	443.15	5.87	5.364	5.3632	26
	453.15	7.03	5.237	5.2352	26

[a] The ref column points to the original papers and equations used by NIST for each compound. The estimated uncertainty on these reference data is 0.02 mol·L^{-1}.

atures in the liquid state. The obtained concentrations were found to fit the reference ones within differences less than 0.5 % (see Table 2).

Another source of uncertainty may be caused by the noise on the mixture spectrum. However, this uncertainty ($\sim 10^{-3}$) can be neglected with regard to the precision obtained on pure components especially with the FTIR spectrometer which has a much better accuracy than the dispersive spectrometer used in some previous studies.

Another test was performed on the mixture methyl benzoate (1) + heptane (2) at 433.15 K by comparison of the mole fractions of each pure component determined by both the synthetic method and the in situ infrared spectroscopic method. This test was performed to detect any possible error or inconsistency in the calibration or measuring procedure. The cell was filled with known amounts of both compounds, then heated until the temperature of measurement, and then the piston was moved until only one phase was present. Then, the spectrum was recorded and the mole fraction calculated. The estimated uncertainty on mole fraction by the synthetic method is 0.002, while it is 0.01 by the spectroscopic method. The results obtained by the two methods are very close to one another, $x_1 = 0.1024$ by the synthetic method and $x_1 = 0.1050$ by the in situ infrared spectroscopic method. The deviation (0.0026) on mole fraction is lower than the estimated uncertainty of the spectroscopic method.

Results

The VLE data for the mixtures methyl benzoate + butane, pentane, hexane, and heptane are reported in Table 3. For each equilibrium, pressure, temperature, concentrations of both components, and alkane mole fractions in the liquid phase are given.

The mole fractions are easily calculated from the concentrations with the following equation: $x_i = (c_i)/(c_1 + c_2)$.

Usual plots of pressure versus mole fractions are shown in the modeling section below, along with the modeling results (Figures 4 to 7).

Comparison with Polar GC-SAFT Predictions. Since our primary goal was to produce data to compare with polar GC-SAFT predictions on multifonctional compounds and their mixtures, we give here a brief account of these predictions as well as a comparison with the data. More extensive descriptions of the treatment of these kinds of compounds with polar GC-SAFT can be found in Dong Nguyen Huynh's PhD Thesis.[7]

Description of Polar GC-SAFT. GC-SAFT is a group contribution method based on the SAFT equation of state. Within the frame of GC-SAFT, the EOS parameters, i.e., segment parameters (energy ε, diameter σ, VR-SAFT range parameter λ) and chain parameter (m) of the molecule are calculated through group contribution relations inspired by the Lorentz–Berthelot combining rules.[3,4] GC-SAFT is generally applied to compounds belonging to well-defined chemical families (*n*-alkane, 1-alkanol, etc.).

Two versions of the SAFT EOS were used here: VR-SAFT[18] and PC-SAFT.[19] The expressions of the different SAFT EOSs are not recalled here, and the interested reader can refer directly to the original papers for more details. When polar compounds such as methyl benzoate are treated, the equation is extended using an additional multipolar term accounting for dipolar or quadrupolar interactions. As explained in an earlier work,[5,6] expressions for the multipolar part of the free energy $a^{\mathrm{multipolar}}$ are obtained from the theory of Gubbins and Twu[20] for spherical molecules, later extended to chain molecules by Jog and Chapman[21,22] using a "segment approach". In this approach, the multipolar moments are assumed to be localized on certain segments of the chain molecule rather than distributed on the whole molecule. The detailed expressions of $a^{\mathrm{multipolar}}$ may be found in NguyenHuynh et al.[5,6] It is sufficient for the following discussion to notice that this approach introduces two additional parameters for each polar interaction, namely, a dipolar moment μ (or quadrupolar moment Q) and a dipolar fraction x_p^{μ} (or quadrupolar fraction x_p^{Q}).

VLE Property Prediction of Methyl Benzoate and Their Mixtures. Pure Methyl Benzoate. This is both a quadrupolar and a dipolar compound and can be decomposed in five kinds of chemical groups: (CH_2), (CH_3), (COO), $(CH)_{BR}$, and $(C)_{AB}$ as shown in Figure 2.

Most of the group parameters used here were simply those determined earlier with no modification. However, since some parameters were dependent on their environment in the molecule, a few assumptions had to be done to assign them a value.

The following parameters were reused from previous studies without modifications:

(i) All group parameters (energy ε_i, diameter σ_i, VR-SAFT range parameter λ_i, and group chain parameter R_i) related to (CH_2) and (CH_3) chemical groups determined from *n*-alkanes in an earlier work.[3]

(ii) The GC parameters ε_i, σ_i, λ_i, corresponding to the (COO) chemical group determined previously from alkyl esters.[6]

(iii) The GC parameters ε_i, σ_i, λ_i, R_i of $(CH)_{BR}$ and $(C)_{AB}$ chemical groups previously obtained by regressing the database of alkyl benzenes.[5]

However, the chain parameter of group (COO), R_{COO}, had to be estimated. Indeed, in previous studies on linear esters,[6] the latter parameter was found to be dependent on the lengths n and n' (number of carbon atoms) of the alkyl chains connected to each side of the (COO) polar group. The same dependence is used here with the simple assumption that the aromatic ring is equivalent to a chain of length $n = 6$. Hence, in the present case, we use $n = 6$ and $n' = 1$ for the determination of the R_{COO} value.

For the polar parameters, we proceed as follows: The polar fractions x_p^{μ} and x_p^{Q} corresponding to a given chemical function (COO and benzene ring) are reused from the polar fraction of monofunctional compounds (alkyl esters and alkyl benzenes).

Table 3. Experimental VLE Data for the Investigated Binary Systems and Comparison with SAFT Predictions[a]

				measured	(VR-SAFT)		(PC-SAFT)	
T/K	C_1/mol·L^{-1}	C_2/mol·L^{-1}	x_2	*P*/bar	*P*/bar	AAD *P* (%)	*P*/bar	AAD *P* (%)
Methylbenzoate (1) + Butane (2) Mixture								
353.15	0.0	8.611	1.0000	10.39	10.107	−2.68	10.084	−2.91
	1.695	7.373	0.8130	9.12	8.639	−5.25	8.597	−5.71
	2.087	7.072	0.7721	8.78	8.452	−3.75	8.407	−4.26
	2.802	6.367	0.6944	8.41	8.147	−3.08	8.088	−3.77
	3.746	5.386	0.5898	7.89	7.751	−1.77	7.654	−3.00
	4.731	3.669	0.4386	6.98	6.964	−0.22	6.780	−2.86
	5.375	2.876	0.3485	5.98	6.235	4.27	5.999	0.32
	5.991	1.884	0.2393	4.55	4.950	8.70	4.682	2.81
	6.406	1.299	0.1686	3.24	3.825	18.16	3.574	10.41
	6.622	1.008	0.1321	2.45	3.141	28.46	2.916	19.27
373.15	0.0	8.038	1.0000	15.86	15.313	−3.45	15.213	−4.08
	1.574	7.037	0.8172	13.35	12.922	−3.17	12.795	−4.13
	2.044	6.783	0.7684	12.93	12.535	−3.05	12.410	−4.02
	2.777	6.111	0.6876	12.15	11.974	−1.43	11.838	−2.55
	3.676	4.767	0.5646	11.24	11.112	−1.11	10.920	−2.82
	4.861	3.520	0.4223	9.67	9.758	0.89	9.461	−2.19
	5.496	2.674	0.3273	7.93	8.449	6.55	8.090	2.02
	6.063	1.805	0.2294	5.61	6.631	18.13	6.254	11.42
	6.450	1.307	0.1685	4.15	5.218	25.79	4.872	17.46
	6.639	1.020	0.1332	3.35	4.291	28.24	3.983	19.03
393.15	0.0	7.328	1.0000	22.65	22.246	−1.79	22.051	−2.65
	1.535	6.725	0.8141	18.76	18.406	−1.89	18.149	−3.26
	1.982	6.416	0.7640	18.04	17.770	−1.49	17.526	−2.84
	2.777	5.842	0.6778	16.73	16.789	0.34	16.543	−1.13
	3.758	4.517	0.5458	15.09	15.227	0.92	14.908	−1.19
	4.919	3.257	0.3983	12.36	12.882	4.18	12.429	0.51
	5.591	2.473	0.3067	9.82	10.885	10.84	10.374	5.63
	6.127	1.727	0.2198	7.23	8.505	17.69	8.000	10.70
	6.464	1.272	0.1644	5.17	6.716	29.97	6.262	21.18
	6.644	1.306	0.1350	4.14	5.676	37.19	5.268	27.31
413.15	0.0	6.276	1.0000	31.56	31.212	−1.11	30.956	−1.92
	1.317	6.297	0.8270	25.82	25.558	−1.01	25.114	−2.73
	1.732	5.985	0.7756	24.63	24.529	−0.42	24.123	−2.06
	2.511	5.474	0.6855	22.26	22.925	3.01	22.543	1.29
	3.566	4.456	0.5555	19.74	20.571	4.21	20.116	1.90
	4.527	2.940	0.3937	15.17	16.785	10.67	16.157	6.53
	5.095	2.184	0.3000	11.76	13.882	18.03	13.196	12.20
	5.549	1.555	0.2189	8.45	10.859	28.45	10.200	20.66
	5.820	1.146	0.1645	6.28	8.551	36.25	7.966	26.93
	5.976	0.947	0.1368	5.00	7.287	45.77	6.760	35.23
OAAD						10.58		7.82
Methylbenzoate (1) + Pentane (2) Mixture								
373.15	0.0	7.451	1.0000	6.00	5.893	−1.76	5.923	−1.26
	1.207	6.539	0.8442	5.22	5.108	−2.09	5.112	−2.01
	1.238	6.500	0.8400	5.12	5.092	−0.51	5.096	−0.44
	1.641	6.249	0.7920	4.95	4.922	−0.56	4.919	−0.61
	1.698	6.203	0.7851	4.81	4.814	0.06	4.807	−0.09
	3.280	4.862	0.5972	4.28	4.373	2.26	4.335	1.36
	4.153	3.799	0.4777	3.94	4.029	2.26	3.957	0.42
	5.483	2.235	0.2896	2.83	3.186	12.55	3.060	8.08
	6.234	1.277	0.1700	2.21	2.259	2.33	2.128	−3.60
393.15	1.249	6.314	0.8349	7.72	7.720	−0.03	7.688	−0.44
	3.264	4.810	0.5957	6.37	6.524	2.50	6.443	1.22
	4.079	3.777	0.4808	5.78	5.945	2.84	5.823	0.73
	5.413	2.321	0.3001	4.41	4.668	5.74	4.483	1.55
	6.200	1.364	0.1803	3.32	3.326	0.31	3.138	−5.37
423.15	0.0	6.388	1.0000	16.20	15.925	−1.70	15.928	−1.69
	1.043	5.778	0.8471	13.64	13.506	−0.96	13.387	−1.83
	1.073	5.750	0.8427	13.49	13.451	−0.27	13.331	−1.17
	2.863	4.500	0.6111	10.59	11.101	4.85	10.921	3.15
	3.586	3.550	0.4974	9.49	9.999	5.38	9.771	2.97
	4.782	2.238	0.3189	6.91	7.767	12.33	7.459	7.88
	5.518	1.356	0.1972	5.07	5.577	9.95	5.270	3.89
453.15	0.961	5.236	0.8450	21.33	21.554	1.03	21.304	−0.14
	0.956	5.183	0.8443	21.14	21.539	1.91	21.289	0.72
	2.744	4.278	0.6093	16.30	17.273	5.94	16.938	3.89
	3.451	3.415	0.4974	14.25	15.353	7.78	14.960	5.02
	4.726	2.142	0.3119	9.79	11.445	16.90	10.961	11.96
	5.405	1.400	0.2057	7.38	8.485	14.91	8.020	8.61
OAAD						4.43		2.97

Table 3 Continued

				measured	(VR-SAFT)		(PC-SAFT)	
T/K	$C_1/\mathrm{mol \cdot L^{-1}}$	$C_2/\mathrm{mol \cdot L^{-1}}$	x_2	P/bar	P/bar	AAD P (%)	P/bar	AAD P (%)
Methylbenzoate (1) + Hexane (2) Mixture								
393.15	0.0	6.478	1.0000	4.10	3.979	−2.90	3.995	−2.51
	0.951	5.893	0.8611	3.65	3.502	−4.11	3.500	−4.17
	2.463	4.884	0.6648	3.20	3.030	−5.22	3.005	−6.01
	3.998	3.589	0.4736	2.60	2.635	1.24	2.580	−0.88
	5.380	2.405	0.3089	2.04	2.178	6.82	2.095	2.74
	6.506	1.259	0.1621	1.36	1.487	9.69	1.399	3.19
	7.007	0.680	0.0884	0.92	0.959	4.21	0.890	−3.23
413.15	0.0	6.196	1.000	6.33	6.160	−2.62	6.167	−2.50
	0.883	5.749	0.8669	5.69	5.426	−4.67	5.403	−5.08
	2.167	4.695	0.6842	4.84	4.687	−3.16	4.634	−4.25
	3.601	3.572	0.4980	3.92	4.041	3.10	3.953	0.85
	4.830	2.351	0.3274	3.24	3.307	2.19	3.184	−1.63
	5.820	1.209	0.1720	2.03	2.247	10.76	2.118	4.39
	6.292	0.670	0.0962	1.39	1.485	6.49	1.383	−0.85
433.15	0.0	5.883	1.0000	9.18	9.126	−0.55	9.129	−0.52
	0.849	5.493	0.8661	8.30	7.997	−3.59	7.943	−4.24
	2.162	4.593	0.6800	6.85	6.825	−0.36	6.728	−1.78
	3.556	3.518	0.4973	5.51	5.820	5.56	5.679	3.00
	4.774	2.358	0.3306	4.27	4.718	10.60	4.537	6.35
	5.774	1.243	0.1771	2.93	3.214	9.73	3.032	3.51
	6.247	0.742	0.1061	2.09	2.247	7.62	2.098	0.48
453.15	0.0	5.524	1.0000	13.01	13.031	0.18	13.052	0.34
	2.390	5.183	0.8651	11.49	11.349	−1.25	11.262	−2.01
	6.206	4.414	0.6781	9.71	9.590	−1.24	9.435	−2.84
	10.328	3.431	0.4967	7.61	8.087	6.24	7.878	3.50
	13.926	2.310	0.3314	5.94	6.486	9.21	6.231	4.93
	16.901	1.260	0.1841	4.06	4.495	10.77	4.245	4.61
	6.209	0.807	0.1150	3.14	3.214	2.45	3.007	−4.15
OAAD						4.88		3.02
Methylbenzoate (1) + Heptane (2) Mixture								
433.15	0.0	5.486	1.0000	4.77	4.636	−2.83	4.618	−3.20
	0.580	4.900	0.8942	4.40	4.234	−3.88	4.197	−4.70
	1.995	4.220	0.6790	3.69	3.570	−3.29	3.506	−5.02
	3.269	3.284	0.5012	3.07	3.091	0.77	3.006	−2.03
	4.419	2.054	0.3173	2.55	2.511	−1.63	2.404	−5.85
443.15	0.0	5.364	1.0000	5.87	5.679	−3.32	5.656	−3.72
	0.576	4.817	0.8932	5.27	5.180	−1.71	5.132	−2.63
	1.960	4.134	0.6783	4.40	4.357	−0.96	4.275	−2.83
	3.237	3.243	0.5004	3.67	3.756	2.44	3.648	−0.50
	4.414	2.080	0.3202	2.98	3.050	2.24	2.919	−2.15
453.15	0.0	5.237	1.0000	7.03	6.889	−1.98	6.861	−2.37
	0.571	4.811	0.8940	6.45	6.285	−2.61	6.225	−3.55
	1.937	4.069	0.6774	5.32	5.265	−1.12	5.162	−3.07
	3.199	3.186	0.4990	4.43	4.518	1.89	4.385	−1.09
	4.379	2.061	0.3300	3.57	3.711	3.88	3.555	−0.50
OAAD						2.30		2.88

[a] OAAD is the overall average absolute deviation for a given mixture.

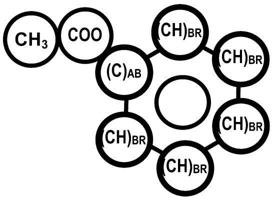

Figure 2. Group decomposition of methylbenzoate.

In previous studies, a dependence of the dipolar moment of ester compounds on n and n' as above was introduced (eq 8 in a recent article[6]). This equation is used here for methyl benzoate with the same assumption as above, namely, $n = 6$ and $n' = 1$.

Previous studies on alkyl benzenes have also been used to assign a value to the quadrupolar moment of methyl benzoate. It has been assumed here that in this respect methyl benzoate should be equivalent to ethyl benzene (namely, alkyl chain length = 2). Hence, the quadrupolar moment of ethyl benzene has been reused for methyl benzoate.

Predictions on Pure Methyl Benzoate. Before comparing with mixture data measured in this work, we test the predictions on pure methyl benzoate. To our best knowledge, no liquid volume data are reported in the literature, and only vapor pressure experimental data are available. The prediction results obtained by polar GC-SAFT are represented in Figure 3, and the deviations are reported in Table 4. Notice that the relative deviations for GC-PC-SAFT are higher than for VR-SAFT. This is generally a satisfactory agreement since the data were not used at all for the determination of the parameters.

Predictions on Mixtures. To test the extrapolation and prediction capacity of polar GC-SAFT, we present in the next paragraph the prediction results obtained on phase equilibrium (VLE) of methyl benzoate + n-alkane mixtures without any binary interaction parameter ($k_{ij} = l_{ij} = 0$).

Generally, a good agreement between experimental data (measured in this work) and prediction results is obtained by polar GC-SAFT, as shown in Figures 4 to 7 and Table 3.

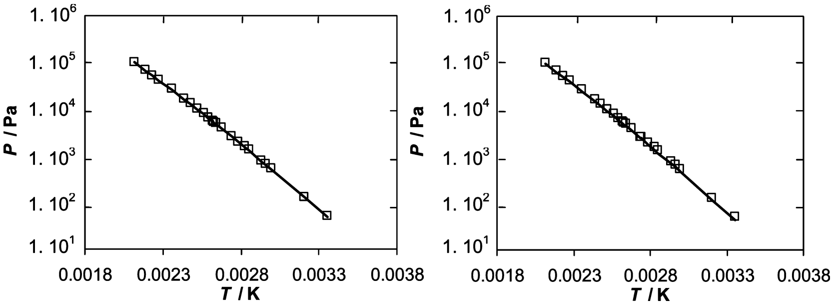

Figure 3. Prediction results obtained on vapor pressure with polar GC-VR-SAFT (—) (left) and polar GC-PC-SAFT (—) (right). □, experimental data taken from DIPPR.[27]

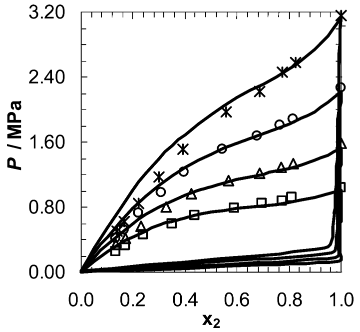

Figure 4. Measured *PTx* data for the methylbenzoate (1) + butane (2) system at □, 353.15 K; △, 373.15 K; ○, 393.15 K; and *, 413.15 K. Comparison with polar GC-VR-SAFT prediction (—).

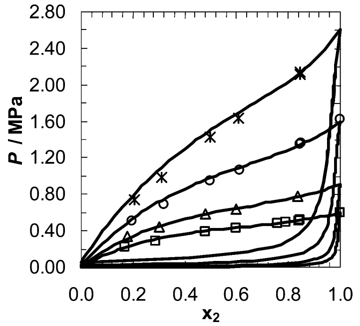

Figure 5. Measured *PTx* data for the methylbenzoate (1) + pentane (2) system at □, 373.15 K; △, 393.15 K; ○, 423.15 K; and *, 453.15 K. Comparison with polar GC-PC-SAFT prediction (—).

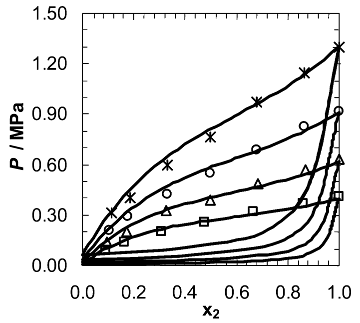

Figure 6. Measured *PTx* data for the methylbenzoate (1) + hexane (2) system at □, 393.15 K; △, 413.15 K; ○, 433.15 K; and *, 453.15 K. Comparison with polar GC-VR-SAFT prediction (—).

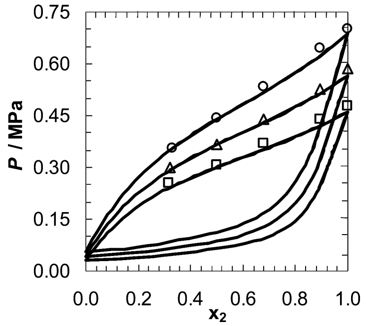

Figure 7. Measured *PTx* data for the methylbenzoate (1) + heptane (2) system at □, 433.15 K; △, 443.15 K; and ○, 453.15 K. Comparison with polar GC-PC-SAFT prediction (—).

Table 4. Average Absolute Deviations on Predicted Vapor Pressure and Saturated Liquid Volume for Pure Methyl Benzoate, with the Two Polar GC-SAFT EOS Versions[a]

vapor pressures				saturated liquid volumes			
		AAD Psat (%)				AAD vliq (%)	
T range (K)	Npt[b]	VR-SAFT	PC-SAFT	*T* range (K)	Npt[b]	VR-SAFT	PC-SAFT
298 to 473	33	3.67	9.88	273 to 308	8	1.00	2.49

[a] Data taken from DIPPR.[27] [b] Npt is the number of data points.

Predicted bubble pressures with both versions of the equation and related deviations are also reported in Table 3. Notice that the agreement is of the same order for both versions of GC-SAFT. It seems that the higher deviations on vapor pressures for GC-PC-SAFT do not affect very much the results for mixtures, perhaps because the vapor pressures of the considered alkanes were much higher as seen in Figures 4 to 7. It must be stressed again that these results are very satisfactory since here the approach is fully predictive. More precisely, the mixture data were not used to fit the model, and no binary interaction parameters were used. Moreover, the pure alkane parameters were determined by group contribution, and the methyl benzoate parameters were also determined without using pure compound data as explained above.

Conclusions

Isothermal VLE properties were measured for four binary systems methyl benzoate + *n*-alkane at temperatures ranging from (353.15 to 453.15) K using an in situ infrared spectroscopic method. A satisfactory agreement (< 10 % on bubble pressure) has been observed between the new data and prediction results obtained using polar GC-SAFT without binary interaction parameters ($k_{ij} = l_{ij} = 0$).

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