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Isobaric Vapor−Liquid Equilibria for the Binary Systems Benzene + Methyl Ethanoate, Benzene + Butyl Ethanoate, and Benzene + Methyl Heptanoate at 101.31 kPa[†]

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Isobaric vapor−liquid equilibria for the binary systems benzene + methyl ethanoate, benzene + butyl ethanoate, and benzene + methyl heptanoate, at the pressure of (101.31 ± 0.02) kPa, have been determined using an all-glass recirculation still. From experimental data, the activity coefficients were calculated and satisfactorily correlated as a function of the mole fraction using the excess Gibbs energy model equations proposed by Margules, van Laar, Wilson, NRTL, and UNIQUAC. The predictive group-contribution models UNIFAC and ASOG were applied. The thermodynamic consistency of the data was verified with two point-to-point tests. The binary systems showed positive deviations from Raoult's law, and no azeotrope was observed at this pressure.

Introduction

In the chemical industry, vapor−liquid equilibrium (VLE) data are very important in the design and operation of separation processes. These VLE data can be estimated using generalized methods for calculation of the properties of mixtures or can be obtained experimentally. The accuracy of a process simulation depends strongly on the thermodynamic models used to describe the physical behavior of the involved components, and the highest quality experimental data reported in this work contribute to this purpose.

As part of a wide experimental and theoretical study on thermodynamic and physicochemical properties of binary and ternary liquid mixtures containing aromatic hydrocarbons and linear esters, and with the aim of studying in depth the behavior of these kinds of mixtures, we report in this work the isobaric VLE for binary mixtures of benzene + methyl ethanoate, benzene + butyl ethanoate, and benzene + methyl heptanonate. Temperature and mole fractions for the liquid and vapor phases were directly measured at isobaric conditions of $P = (101.31 \pm 0.02)$ kPa. The calculated properties, such as activity coefficients, were correlated by Margules,[1] van Laar,[2] Wilson,[3] NRTL,[4] and UNIQUAC[5] models. Furthermore, experimental VLE compositions were predicted by two group-contribution methods, ASOG[6,7] and the three versions of the UNIFAC (UNIFAC-1,[8] UNIFAC-2,[9] and UNIFAC-3[10,11]).

Experimental Section

The chemicals used were provided by Merck (benzene > 99.7 % and methyl ethanoate > 99.0 %), by Aldrich (butyl ethanoate > 98.0 %), and by Fluka (methyl heptanoate > 99.0 %). These liquids were stored over molecular sieves, Fluka 0.3 nm, to reduce the presence of water. Before use they were degassed in an ultrasonic bath. To test the purity of the liquids, density and refractive index at $T = 298.15$ K were measured and compared with literature values as presented in Table 1.

Table 1. Density ρ and Refractive Index n_D at $T = 298.15$ K and Boiling Temperature T_b at $P = 101.31$ kPa, for the Pure Liquids[a]

	ρ/kg·m^{-3}		n_D		T_b/K	
liquid	exptl	lit.[b]	exptl	lit.[b]	exptl	lit.[b]
benzene	873.67	873.60	1.49765	1.49792	352.97	353.244
methyl ethanoate	927.36	927.90	1.35893	1.35890	330.03	330.018
butyl ethanoate	876.35	876.36	1.39191	1.39180	398.10	399.211
methyl heptanoate	875.88	875.69[c]	1.40945	-	443.63	445.84[d]

[a] Experimental and literature values. [b] Ref 12. [c] Ref 13. [d] Value obtained from PhysProps version 1.6.1, G&P Engineering Software.

Table 2. Intrinsic Properties of the Pure Liquids

	P_c	10^4 V_c	T_c		
liquid	kPa	m^3·mol^{-1}	K	ω	Z_{RA}
benzene	4898[a]	2.59[a]	562.16[a]	0.212[b]	0.2696[c]
methyl ethanoate	4690[a]	2.28[a]	506.8[a]	0.324[b]	0.2550[c]
butyl ethanoate	2950[a]	4.03[a]	579.0[a]	0.417[b]	0.254[d]
methyl heptanoate	2563[e]	5.94[e]	624.48[e]	0.495[f]	0.247[d]

[a] Ref 19. [b] Ref 20. [c] Ref 18. [d] Value calculated with the equation $Z_{RA} = 0.29056 - 0.08775\omega$.[20] [e] Value obtained from PhysProps version 1.6.1, G&P Engineering Software. [f] Calculated from our experimetal data, with Pitzer's equation.[21]

The experimental equipment used for vapor−liquid equilibrium measurements is a dynamic cell with recirculation of both phases. The entire apparatus is built in glass, and it has a low capacity, 60 cm^3 of mixture. A first version of the apparatus was presented by De Alfonso et al.[14] The boiling of the liquid mixture is achieved by warming the solution employing an electric heating wire. This main apparatus is connected to auxiliary equipment to control and measure the thermodynamic variables that characterize the equilibrium conditions, pressure, and temperature. The details of the equipment and support systems have been described previously.[15]

The uncertainties in the measured temperatures and pressures were ± 0.02 K and ± 0.02 kPa, respectively. The composition

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Table 3. Experimental Vapor Pressures, P_i^0, for Methyl Heptanoate

T/K	P_i^0/kPa	T/K	P_i^0/kPa
421.35	53.32	437.59	89.31
421.92	54.65	438.29	90.65
422.77	55.99	438.73	91.98
424.10	58.65	439.35	93.31
425.03	59.99	439.95	94.72
425.50	61.32	440.47	95.87
426.33	62.65	441.35	97.31
427.31	63.99	442.13	98.64
427.75	65.32	442.46	99.98
428.38	66.65	442.96	101.31
428.92	67.98	442.72	98.55
436.39	86.65	443.94	101.31
436.99	87.98		

Table 4. Antoine Constants for the Pure Liquids

liquid	A	B/K	C/K
benzene	6.0305[a]	1211.03[a]	−52.36[a]
methyl ethanoate	6.1299[a]	1130.00[a]	−56.15[a]
butyl ethanoate	6.1534[a]	1368.50[a]	−69.15[a]
methyl heptanoate	6.1627[b]	1416.46[b]	−101.76[b]

[a] Ref 20. [b] Calculated from our experimetal data.

Table 5. Isobaric Vapor−Liquid Equilibrium Data (T, x_1, y_1) and Calculated Values (γ_1, γ_2, G^E/RT) for the Binary Systems at P = 101.31 kPa

T/K	x_1	y_1	γ_1	γ_2	G^E/RT
Benzene (1) + Methyl Ethanoate (2)					
330.22	0.0261	0.0154	1.238	1.009	0.014
330.48	0.0498	0.0305	1.273	1.009	0.021
330.84	0.0785	0.0496	1.297	1.008	0.028
331.44	0.1202	0.0771	1.290	1.005	0.035
331.98	0.1598	0.1017	1.256	1.006	0.042
332.45	0.2059	0.1272	1.219	1.019	0.052
333.07	0.2540	0.1596	1.195	1.024	0.062
333.90	0.3057	0.1961	1.186	1.024	0.069
336.03	0.4357	0.2853	1.127	1.047	0.078
337.38	0.5070	0.3402	1.104	1.060	0.079
339.76	0.6275	0.4362	1.057	1.113	0.075
342.56	0.7310	0.5500	1.045	1.129	0.065
344.46	0.7971	0.6272	1.029	1.171	0.055
345.23	0.8196	0.6560	1.022	1.188	0.049
347.18	0.8702	0.7396	1.021	1.181	0.040
350.35	0.9471	0.8839	1.018	1.179	0.026
351.75	0.9769	0.9495	1.016	1.129	0.019
Benzene (1) + Butyl Ethanoate (2)					
397.19	0.0189	0.0617	1.067	1.008	0.007
395.18	0.0437	0.1361	1.064	1.007	0.009
391.75	0.0884	0.2533	1.057	1.007	0.011
389.71	0.1168	0.3181	1.052	1.007	0.012
384.15	0.1979	0.4765	1.059	1.004	0.015
379.77	0.2712	0.5846	1.054	1.004	0.017
375.27	0.3600	0.6814	1.035	1.012	0.020
372.14	0.4351	0.7410	1.009	1.032	0.022
369.75	0.4894	0.7830	1.009	1.036	0.022
367.22	0.5565	0.8238	0.998	1.055	0.023
365.52	0.6005	0.8495	0.999	1.061	0.023
362.54	0.6821	0.8914	1.001	1.068	0.022
359.71	0.7651	0.9276	1.006	1.067	0.019
358.58	0.7999	0.9410	1.008	1.063	0.018
356.81	0.8599	0.9608	1.007	1.076	0.016
355.47	0.9077	0.9751	1.006	1.090	0.014
354.25	0.9501	0.9875	1.009	1.060	0.012
Benzene (1) + Methyl Heptanoate (2)					
439.48	0.0094	0.0841	1.300	1.002	0.005
436.46	0.0194	0.1650	1.307	1.002	0.007
429.68	0.0434	0.3299	1.306	0.998	0.010
421.19	0.0768	0.5011	1.307	0.992	0.013
411.67	0.1230	0.6516	1.272	0.986	0.018
402.14	0.1870	0.7661	1.197	0.987	0.023
391.25	0.2935	0.8601	1.088	1.008	0.031
386.83	0.3450	0.8894	1.060	1.019	0.033
381.65	0.4065	0.9177	1.051	1.029	0.037
377.14	0.4788	0.9381	1.020	1.061	0.040
372.88	0.5483	0.9542	1.010	1.086	0.043
367.54	0.6478	0.9708	1.001	1.124	0.042
364.95	0.6998	0.9775	1.001	1.143	0.041
362.74	0.7479	0.9826	1.001	1.165	0.039
359.60	0.8222	0.9892	1.001	1.187	0.031
357.16	0.8837	0.9935	1.003	1.230	0.026
355.02	0.9467	0.9969	1.000	1.418	0.018

of the liquid and vapor phases was determined by densimetry, using standard curves, $\rho = \rho(x)$, for the mixtures studied. These experimental data are reported as Supporting Information. The density measurements were made using an Anton Paar DSA-5000 densimeter with an uncertainty of ± 0.01 kg·m^{-3}. The temperature of the cell was controlled with an internal thermostat.

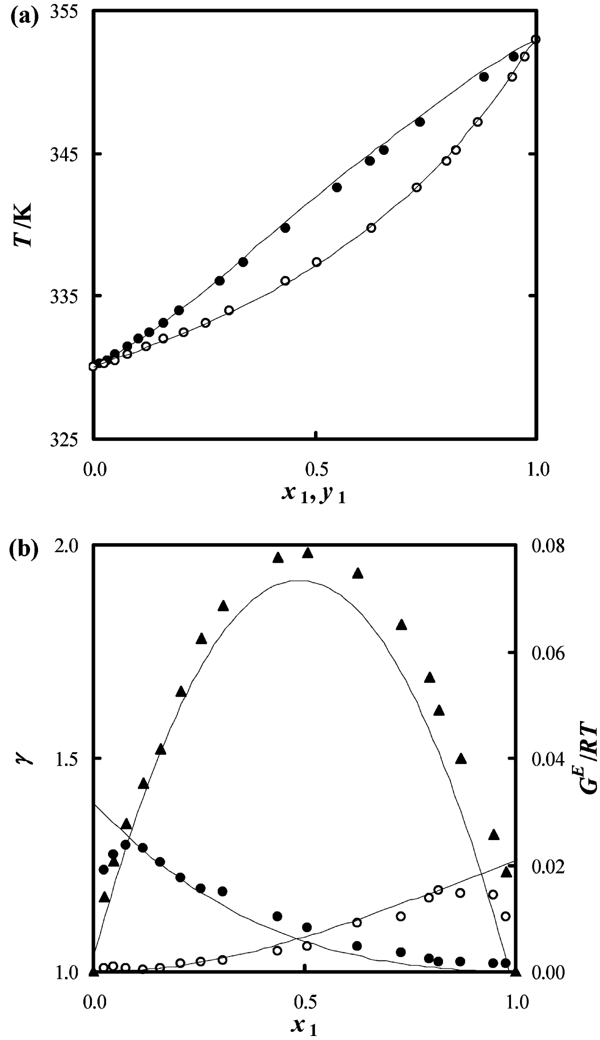

Figure 1. (a) Experimental (T, x, y) for the binary systems at P = 101.31 kPa for benzene (1) + methyl ethanoate (2) and the corresponding fitting curves using UNIFAC-3. (b) Experimental: ●, γ_1; ○, γ_2; ▲, G^E/RT; and —, fitting curves using UNIFAC-3 at P = 101.31 kPa.

Results and Discussion

The correlations of density and concentration values for the mixtures were carried out using a polynomial equation of the type[16]

$$\rho = x_1\rho_1 + x_2\rho_2 + x_1x_2\sum_{i=0}^{n} a_i(2x_1 - 1)^i \qquad (1)$$

where ρ is the density of the mixture; ρ_1 and ρ_2 are the densities of components 1 and 2, respectively; x_1 and x_2 are the mole

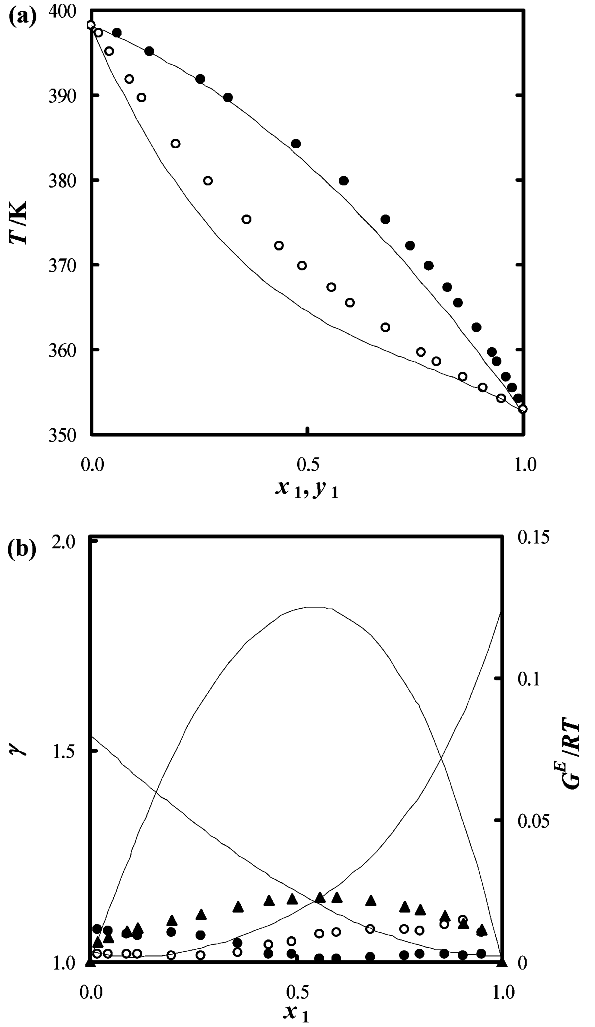

Figure 2. (a) Experimental (T, x, y) for the binary systems at $P = 101.31$ kPa for benzene (1) + butyl ethanoate (2) and the corresponding fitting curves using UNIFAC-1. (b) Experimental: ●, γ_1; ○, γ_2; ▲, G^E/RT; and —, fitting curves using UNIFAC-1 at $P = 101.31$ kPa.

fractions of components 1 and 2, respectively; and a_i are the adjustable parameters.

Equation 1 was then used to calculate the concentration in each of the equilibrium states. The uncertainties of the calculation of the mole fractions for both the liquid phase and the vapor phase were better than ±0.001.

Experimental values of (P, T, x_1, y_1) were obtained directly in the isobaric VLE experiment for the binary systems methyl ethanoate, butyl ethanoate, and methyl heptanoate with benzene at $P = (101.31 \pm 0.02)$ kPa. From these values, considering the nonideal behavior of the vapor phase, the activity coefficients, γ_i, of the components of the liquid phase were calculated from the following equation

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \exp\frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^0)}{RT} \exp\frac{y_j^2 P \delta_{ij}}{RT} \qquad (2)$$

where

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \qquad (3)$$

The second virial coefficients were calculated using the Tsonopoulos[17] empirical equation. The molar liquid volumes, V_i^{L}, of pure compounds were estimated using the modified Rackett equation.[18] All the required parameters are listed in Table 2.

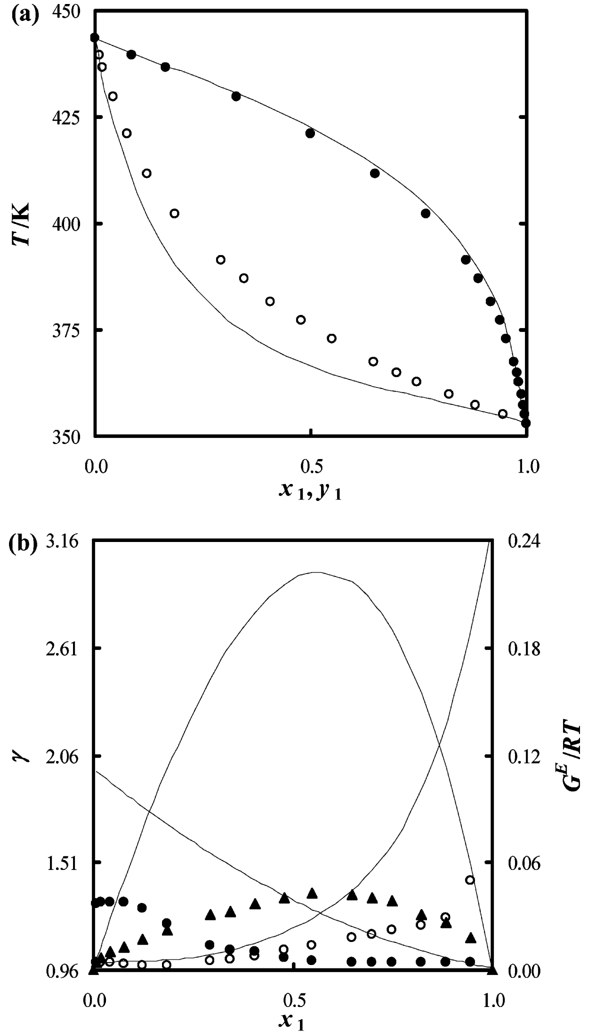

Figure 3. (a) Experimental (T, x, y) for the binary systems at $P = 101.31$ kPa for benzene (1) + methyl heptanoate (2) and the corresponding fitting curves using UNIFAC-1. (b) Experimental: ●, γ_1; ○, γ_2; ▲, G^E/RT; and —, fitting curves using UNIFAC-1 at $P = 101.31$ kPa.

Table 6. Results of Thermodynamic Consistency Tests of VLE Data for the Binary Systems at $P = 101.31$ kPa

	point-to-point tests	
	Fredenslund[22]	Wisniak[23]
binary systems	δy_1[a]	D %[b]
benzene (1) + methyl ethanoate (2)	0.009	1.17
benzene (1) + butyl ethanoate (2)	0.009	4.32
benzene (1) + methyl heptanoate (2)	0.009	4.13

[a] The criterion for passing the test is $\delta y_1 < 0.010$ absolute in mole fraction. [b] The criterion for passing the test is $D < 5$ %.

The vapor pressures, P_i^0, were calculated by the Antoine equation. Experimental vapor pressures of methyl heptanoate, determined experimentally in the temperature range of T = (421.35 to 443.94) K in our laboratory, are presented in Table 3. From the experimental vapor pressure data, we obtained the Antoine constants for methyl heptanoate, which were not available in the literature consulted for the work range. There are data of vapor pressures for methyl heptanoate but in other temperature ranges.[22] These new Antoine constants, together with the Antoine constants for the other pure components, collected from the literature, are given in Table 4.

The experimentally observed values (T, x_1, y_1) and the calculated values (γ_1, γ_2, G^E/RT) are compiled in Table 5 and are also shown in Figures 1, 2, and 3.

Table 7. Constants and Standard Deviations, σ (γ_i), for Van Laar, Margules, Wilson, NRTL (α = 0.5), and UNIQUAC Models

Margules[1]		Van Laar[2]		Wilson[3]		NRTL[4]		UNIQUAC[5]	
				Benzene (1) + Methyl Ethanoate (2)					
A_{12}	0.1489	A_{12}	0.0762	Λ_{12}	0.9419	τ_{12}	−0.1451	τ_{12}	1.3792
A_{21}	0.1924	A_{21}	0.3432	Λ_{21}	0.7538	τ_{21}	0.4505	τ_{21}	0.4260
σ (γ_1)	0.06	σ (γ_1)	0.16	σ (γ_1)	0.03	σ (γ_1)	0.05	σ (γ_1)	0.04
σ (γ_2)	0.15	σ (γ_2)	0.24	σ (γ_2)	0.09	σ (γ_2)	0.03	σ (γ_2)	0.02
				Benzene (1) + Butyl Ethanoate (2)					
A_{12}	0.0802	A_{12}	0.0277	Λ_{12}	1.2635	τ_{12}	0.0454	τ_{12}	1.2908
A_{21}	0.0441	A_{21}	0.1017	Λ_{21}	0.6817	τ_{21}	0.0392	τ_{21}	0.5609
σ (γ_1)	0.06	σ (γ_1)	0.02	σ (γ_1)	0.02	σ (γ_1)	0.01	σ (γ_1)	0.01
σ (γ_2)	0.02	σ (γ_2)	0.04	σ (γ_2)	0.02	σ (γ_2)	0.02	σ (γ_2)	0.01
				Benzene (1) + Methyl Heptanoate (2)					
A_{12}	0.1020	A_{12}	0.0538	Λ_{12}	1.3050	τ_{12}	0.1108	τ_{12}	1.3584
A_{21}	0.0899	A_{21}	0.1620	Λ_{21}	0.5980	τ_{21}	0.1771	τ_{21}	1.4220
σ (γ_1)	0.05	σ (γ_1)	0.11	σ (γ_1)	0.10	σ (γ_1)	0.05	σ (γ_1)	0.04
σ (γ_2)	0.06	σ (γ_2)	0.05	σ (γ_2)	0.07	σ (γ_2)	0.03	σ (γ_2)	0.04

The thermodynamic consistency of the data was verified using the point-to-point tests proposed by Fredenslund et al.[23] and the one from Wisniak.[24] The results of these consistency tests are shown in Table 6. These systems proved to be consistent according to both methods. The criterion for passing the tests of consistency are: for Fredenslund,[23] $\delta y_1 < 0.010$ absolute in mole fraction, and for Wisniak,[24] $D < 5$ %.

The data were correlated using the Margules,[1] van Laar,[2] Wilson,[3] NRTL,[4] and UNIQUAC[5] equations for the liquid-phase activity coefficients. Margules[1] and van Laar[2] constants are calculated by linear regression of activity coefficient data using eqs 4 and 5, respectively.

$$\frac{x_1 \log \gamma_1 + x_2 \log \gamma_2}{x_1 x_2} = A_{12} + x_1(A_{21} - A_{12}) \qquad (4)$$

$$\frac{x_1}{x_1 \log \gamma_1 + x_2 \log \gamma_2} = \frac{1}{A_{12}} + \frac{1}{A_{21}} \frac{x_1}{x_2} \qquad (5)$$

where x_1 and x_2 are the mole fractions of components 1 and 2, respectively; $\gamma_1$and γ_2 are the activity coefficients of components 1 and 2, respectively; and A_{12} and A_{21} are the constants of the models.

Wilson[3] constants are calculated by nonlinear regression based on the method proposed by Apelblat and Wisniak.[25]

The constants of the NRTL[4] and UNIQUAC[5] models are found by least-squares minimizing the objective function

$$\mathrm{OF} = \min \sum_{i=1}^{n} [(\ln \gamma_{1,i}^{\mathrm{calcd}} - \ln \gamma_{1,i}^{\mathrm{exptl}})^2 + (\ln \gamma_{2,i}^{\mathrm{calcd}} - \ln \gamma_{2,i}^{\mathrm{exptl}})^2] \qquad (6)$$

where n is the number of data points. The nonrandom parameter, α, in the NRTL model was fixed in 0.5, and the structural parameters r and q for UNIQUAC are obtained from atomic and molecular structure data: the van der Waals group volumes, V_k, and surface areas, A_k.[26]

The model constants and the standard deviations between the experimental and the calculated values of activity coefficients are reported in Table 7, showing that, in general, the deviations obtained are reasonably small.

Theoretical Predictions. Group contribution methods ASOG[6,7] and the three versions of the UNIFAC (UNIFAC-1,[8] UNIFAC-2,[9] and UNIFAC-3[10,11]) were used to estimate the VLE values for the mixtures presented in this work. In Table 8, the average deviations in vapor-phase compositions and bubble point temperatures between the experimental and predicted values are reported. From the examination of the standard deviations, in employing the different models for the systems investigated, presented in Table 8, it can be remarked that:

(a) models UNIFAC-3 and ASOG provide better results to predict the vapor−liquid equilibrium of the mixture benzene + methyl ethanoate, whereas

(b) for the mixtures benzene + butyl ethanoate and benzene + methyl heptanoate, only UNIFAC-1 predicts γ_i greater than unity, in agreement with experimental results, while UNIFAC-2, UNIFAC-3, and ASOG predict γ_i less than 1.

Table 8. Average Deviations between the Calculated and Experimental Vapor Phase Mole Fractions Δy_1 and Temperature ΔT/K Using Predictive Models and the Corresponding Standard Deviation in Activity Coefficients σ (γ_i)

predictive model	ΔT/K	Δy	σ (γ_1)	σ (γ_2)
		Benzene (1) + Methyl Ethanoate (2)		
UNIFAC-1[8]	0.71	0.0069	0.096	0.036
UNIFAC-2[9]	0.77	0.0097	0.092	0.048
UNIFAC-3[10,11]	0.15	0.0098	0.048	0.033
ASOG[6,7]	0.24	0.0097	0.028	0.027
		Benzene (1) + Butyl Ethanoate (2)		
UNIFAC-1[8]	2.66	0.0326	0.226	0.234
UNIFAC-2[9]	1.64	0.0155	0.126	0.120
UNIFAC-3[10,11]	1.65	0.0168	0.136	0.117
ASOG[6,7]	1.29	0.0137	0.116	0.073
		Benzene (1) + Methyl Heptanoate (2)		
UNIFAC-1[8]	5.93	0.0533	0.391	0.429
UNIFAC-2[9]	4.60	0.0358	0.327	0.242
UNIFAC-3[10,11]	4.06	0.0347	0.315	0.222
ASOG[6,7]	4.03	0.0352	0.330	0.187

Figures 1, 2, and 3 present comparisons of the experimental and predicted VLE data for the binary systems investigated. Also see the Supporting Information.

Conclusions

Vapor−liquid equilibrium data at P = 101.31 kPa for the binary systems benzene + methyl ethanoate, benzene + butyl ethanoate, and benzene + methyl heptanoate were determined. The experimental data for the three systems evidence that these systems do not form an azeotrope at this pressure. The activity coefficient data show that the systems investigated do not deviate significantly from ideality.

The experimental results were correlated using well-known equations for the reduction of the data of VLE, such as the Margules, van Laar, Wilson, NRTL, and UNIQUAC. The equations appeared to be suitable for correlating the data for the mixtures considered here, except the Van Laar equation for the systems benzene + methyl ethanoate and benzene + methyl hepatanoate and the Wilson equation for the benzene + methyl heptanoate system, where the deviations obtained were slightly high.

The UNIFAC and ASOG group contribution methods have been employed to estimate the isobaric VLE of the binary systems. UNIFAC-3 and ASOG provide good results to predict the vapor−liquid equilibrium of the mixture benzene + methyl ethanoate. For the mixtures benzene + butyl ethanoate and benzene + methyl heptanoate, only UNIFAC-1 gives result in concordance with experimental values of γ_i, in the sense that they are greater than one, but this model is the one that gives the highest deviation in all the properties compared for these two systems. The predictions with any of the models are unacceptable for these two systems. The poor results to predict the vapor−liquid equilibrium of the mixtures benzene + butyl ethanoate and benzene + methyl heptanoate can be due to that there are not enough data for these types of mixtures to estimate the group contribution parameters.

Supporting Information Available:

Experimental densities for the binary mixtures benzene + methyl ethanoate, benzene + butyl ethanoate, and benzene + methyl heptanoate, used to calculate VLE compositions. Figures with experimental and predicted γ_i values for the binary systems investigated. This material is available free of charge via the Internet at http://pubs.acs.org.

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