Vapor−Liquid Equilibrium Data for the Binary Methyl Esters (Butyrate, Pentanoate, and Hexanoate) (1) + Acetonitrile (2) Systems at 93.32 kPa

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We report isobaric vapor−liquid equilibrium measurements of binary systems of methyl butyrate, methyl pentanoate, and methyl hexanoate with acetonitrile at a constant pressure of 93.32 kPa. The measurements were carried out with a small recirculating still. The composition of condensed vapor and liquid phases was calculated indirectly from density measurements made with a vibrating-tube densimeter. These systems exhibit positive deviations from ideality. The thermodynamic consistency of the data was verified with two point-to-point tests. Activity coefficients calculated from experimental data have been correlated by several models and compared with predictions of group-contribution models.

Introduction

This paper is part of our ongoing research project[1] on the behavior of isobaric vapor−liquid equilibria (VLE) in binary mixtures of alkyl esters and nitriles. Properties directly measured, such as temperature and mole fractions for the liquid and vapor phases, were correlated by the Redlich−Kister[2] equation, while calculated properties, such as activity coefficients, were correlated by the Margules,[3] van Laar,[4] Wilson,[5] and NRTL[6] models. Furthermore, experimental VLE compositions were predicted by two group-contribution methods, ASOG[7,8] and the three versions of the UNIFAC (UNIFAC-1,[9] UNIFAC-2,[10] and UNIFAC-3[11,12]).

Experimental Section

Apparatus and Procedure. The experimental equipment used to determine the isobaric VLE consisted of a small device, of around 60 cm^3, that works dynamically with recirculation of both phases. The details of the equipment and support systems have been described previously.[13] The uncertainties in the measured temperatures and pressures were ± 0.02 K and ± 0.2 kPa, respectively. The composition of the liquid and vapor phases was determined by densimetry using standard curves for the mixtures considered, prepared earlier, $\rho = \rho(x)$. The density measurements were made using a Mettler model DA 310 thermostated digital densimeter with a precision of ± 0.01 kg·m^{-3}. The correlations of the density and concentration values for the mixtures were carried out using a polynomial equation of the type:

$$\rho = x_1\rho_1 + x_2\rho_2 + x_1x_2\Sigma A_i(2\,x_1 - 1)^i \qquad (1)$$

and these were 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 units.

Table 1. Densities (ρ) and Refractive Index (n_D) of Pure Compounds Compared with Literature Data at 298.15 K

	ρ/kg·m^{-3}		n_D, 298.15 K	
components	exp	lit.	exp	lit.
methyl butyrate	892.16	892.61[a]	1.3847	1.3847[a]
methyl pentanoate	884.80	884.50[b]	1.3971	1.397[b]
methyl hexanoate	879.47	879.44[b]	1.4048	1.405[b]
acetonitrile	776.62	776.6[a]	1.3418	1.3416[a]

[a] Ref 14. [b] Ref 15.

Materials. The components used were the highest commercial grade (molar fraction, $x \geq 0.995$) available from the manufacturer, Fluka. Before use, components were degassed by ultrasound for several hours and then dried on a molecular sieve (Fluka 0.4 nm) to reduce moisture content prior to use. The physical properties, density (ρ) at 298.15 K and refractive index (n_D) at 298.15 K, determined for all liquids are shown in Table 1 along with literature values for comparison.

Results and Discussion

The experimental values were obtained directly (p, T, x_1, y_1) in the isobaric VLE experiment at a pressure of $p = (93.32 \pm 0.02)$ kPa for the binary systems of methyl esters (butyrate to hexanoate) with acetonitrile. From these values, considering the no ideal behavior of the vapor phase, the activity coefficients of the components of the liquid phase are estimated by

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

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[18] equation. All the necessary parameters are listed in

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Table 2. Intrinsic Properties of the Pure Substances[a]

	T_c	P_c	V_c			μ
components	K	kPa	$m^3 \cdot kgmol^{-1}$	Z_c	ω	D
methyl butyrate	554.54	3475.04	0.3402	0.257	0.3807	1.70
methyl pentanoate	579.48	3231.88	0.4555	0.293	0.4173	1.70
methyl hexanoate	602.26	2758.00	0.4912	0.270	0.4609	1.70
acetonitrile	545.54	4832.63	0.1731	0.184	0.3382	3.53

[a] Ref 18.

Table 3. Antoine Equation Constants *A*, *B*, and *C*: $\log(P/kPa) = (A - B)/(T/(K - C))$

components	*A*	*B*	*C*	ΔT/K
methyl butyrate[a]	6.30360	1381.06	53.60	200−375
methyl pentanoate[b]	5.9644	1281.06	75.94	281−547
methyl hexanoate[c]	6.03039	1321.69	93.83	277−567
acetonitrile[d]	6.19840	1279.20	49.14	229−545

[a] Ref 19. [b] Ref 20. [c] Ref 18. [d] Ref 21.

Table 2. The vapor pressures (P_i^0) were calculated by the Antoine equation, using the respective constants listed in Table 3. The average deviation between the experimental vapor pressure and the values calculated with Antoine equation was 0.08 kPa. The experimental results (T, x_1, y_1) and the calculated values (γ_1, γ_2, G^E/RT) are compiled in Table 4 and shown in Figures 1 to 6.

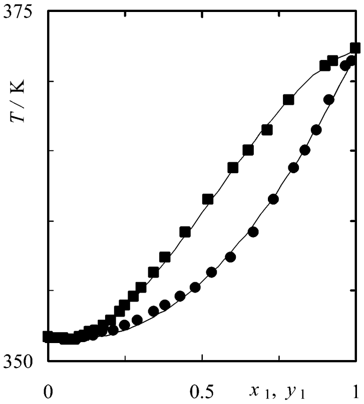

Figure 1. Temperature−composition diagram for the methyl butyrate (1) + acetonitrile (2) system: ▲, experimental liquid-phase mole fractions, x_1; ■, experimental vapor-phase mole fractions, y_1; continued lines from R−K equation.

The thermodynamic consistency of the data was verified using the point-to-point tests proposed by Fredenslund et al.[22] and the one from Wisniak.[23] The results of these consistency tests are shown in Table 5. The studied systems proved to be consistent according to both methods just mentioned. In the last method, the author defines a deviation (D) that should not be exceeded. The limit for this deviation is arbitrary. The criterion

Table 4. Isobaric Vapor−Liquid Equilibrium Data: Temperature (*T*/K), Liquid-Phase and Vapor-Phase Mole Fractions (x_1, y_1), Activity Coefficients (γ_i), and Dimensionless Excess Gibbs Energy (G^E/RT) for the Binary Systems at 93.32 kPa

T/K	x_1	y_1	γ_1	γ_2	G^E/RT	T/K	x_1	y_1	γ_1	γ_2	G^E/RT
Methyl Butyrate (1) + Acetonitrile (2)											
351.67	0.0000	0.0000		1.000	0.000	353.94	0.3817	0.2511	1.209	1.131	0.149
351.62	0.0162	0.0181	2.220	1.000	0.013	354.59	0.4286	0.2784	1.168	1.157	0.150
351.61	0.0300	0.0314	2.081	1.000	0.022	355.22	0.4777	0.3049	1.124	1.196	0.149
351.58	0.0497	0.0498	1.995	1.003	0.037	356.29	0.5347	0.3428	1.090	1.230	0.142
351.57	0.0622	0.0594	1.902	1.006	0.046	357.36	0.5946	0.3826	1.056	1.285	0.134
351.56	0.0953	0.0847	1.771	1.015	0.068	359.19	0.6696	0.4481	1.034	1.336	0.118
351.69	0.1203	0.1022	1.685	1.020	0.080	361.49	0.7353	0.5203	1.015	1.357	0.092
351.83	0.1459	0.1201	1.625	1.025	0.092	363.72	0.7999	0.6012	1.005	1.401	0.071
352.03	0.1756	0.1352	1.510	1.038	0.103	365.01	0.8374	0.6505	0.997	1.458	0.059
352.16	0.2116	0.1541	1.422	1.057	0.118	366.47	0.8748	0.7126	0.999	1.495	0.050
352.49	0.2487	0.1807	1.403	1.064	0.131	368.58	0.9149	0.7809	0.983	1.586	0.024
352.90	0.2909	0.2037	1.333	1.082	0.140	371.06	0.9683	0.9025	0.994	1.768	0.012
353.53	0.3442	0.2339	1.267	1.104	0.146	372.31	1.0000	1.0000	1.054		0.000
Methyl Pentanoate (1) + Acetonitrile (2)											
351.67	0.0000	0.0000		1.000	0.000	359.11	0.3971	0.1401	1.132	1.144	0.130
351.96	0.0166	0.0106	2.653	0.997	0.014	361.05	0.4810	0.1696	1.057	1.214	0.127
352.12	0.0238	0.0138	2.395	0.997	0.018	363.60	0.5526	0.2106	1.046	1.246	0.123
352.42	0.0381	0.0203	2.176	0.996	0.026	365.98	0.6177	0.2498	1.024	1.297	0.114
352.60	0.0545	0.0274	2.040	1.000	0.039	369.31	0.6908	0.3099	1.017	1.347	0.104
352.94	0.0741	0.0353	1.909	1.003	0.050	375.33	0.7933	0.4279	1.008	1.424	0.079
353.41	0.0939	0.0431	1.808	1.002	0.058	378.50	0.8270	0.4926	1.008	1.391	0.064
353.81	0.1184	0.0511	1.675	1.009	0.069	380.14	0.8454	0.5292	1.008	1.386	0.057
354.46	0.1537	0.0624	1.539	1.019	0.082	384.38	0.8950	0.6318	1.000	1.437	0.038
354.80	0.1783	0.0701	1.472	1.030	0.093	388.31	0.9292	0.7339	0.998	1.401	0.022
356.22	0.2537	0.0925	1.297	1.061	0.110	390.25	0.9478	0.7898	0.996	1.433	0.015
357.18	0.2935	0.1086	1.271	1.071	0.119	392.80	0.9725	0.8703	0.995	1.582	0.008
357.86	0.3364	0.1195	1.191	1.104	0.124	396.65	1.0000	1.0000	1.000		0.000
Methyl Hexanoate (1) + Acetonitrile (2)											
351.67	0.0000	0.0000		1.000	0.000	362.96	0.4271	0.0721	1.111	1.163	0.132
352.56	0.0263	0.0068	2.577	0.993	0.018	365.08	0.4755	0.0853	1.087	1.181	0.127
352.88	0.0381	0.0093	2.401	0.993	0.027	366.88	0.5178	0.0967	1.058	1.206	0.120
353.16	0.0486	0.0109	2.181	0.994	0.032	368.39	0.5627	0.1061	1.011	1.261	0.108
353.47	0.0684	0.0143	2.007	1.002	0.050	373.29	0.6435	0.1431	0.994	1.300	0.089
353.98	0.0843	0.0179	1.997	1.000	0.059	377.64	0.7099	0.1812	0.974	1.363	0.071
354.31	0.1016	0.0194	1.773	1.008	0.065	383.72	0.7696	0.2449	0.981	1.356	0.055
355.17	0.1332	0.0248	1.668	1.013	0.079	387.97	0.8137	0.2979	0.976	1.405	0.044
355.99	0.1679	0.0299	1.544	1.024	0.093	397.32	0.8765	0.4429	0.989	1.356	0.028
356.61	0.2015	0.0335	1.406	1.044	0.103	403.64	0.9153	0.565	0.990	1.347	0.016
357.78	0.2449	0.0409	1.349	1.059	0.116	407.77	0.9388	0.6587	0.993	1.340	0.011
358.92	0.2893	0.0481	1.284	1.080	0.127	409.10	0.9522	0.7189	0.963	2.209	0.002
360.93	0.3552	0.0601	1.206	1.109	0.133	419.67	1.0000	1.0000	1.000		0.000

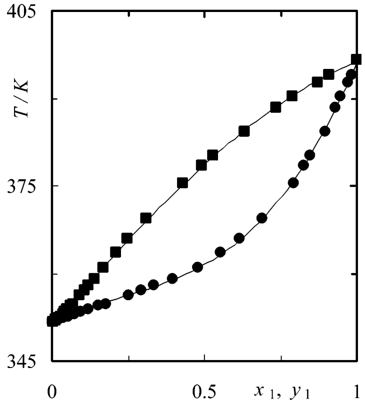

Figure 2. Temperature−composition diagram for the methyl pentanoate (1) + acetonitrile (2) system: ▲, experimental liquid-phase mole fractions, x_1; ■, experimental vapor-phase mole fractions, y_1; continued lines from R−K equation.

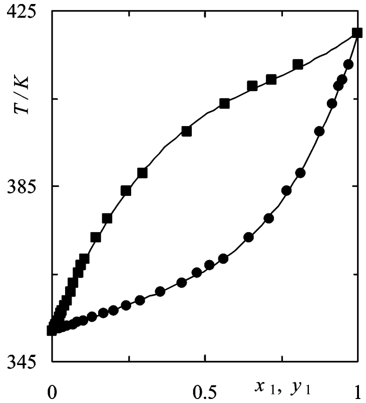

Figure 3. Temperature−composition diagram for the methyl hexanoate (1) + acetonitrile (2) system: ▲, experimental liquid-phase mole fractions, x_1; ■, experimental vapor-phase mole fractions, y_1; continued lines from R−K equation.

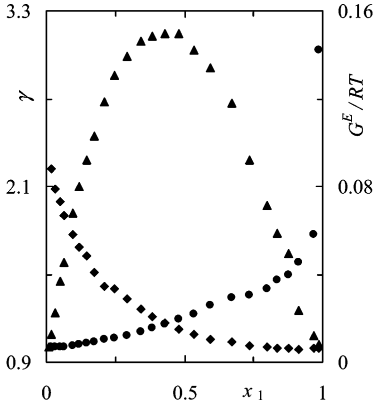

Figure 4. Experimental activity coefficients and dimensionless G^E/RT against liquid composition, x_1, for the methyl butyrate (1) + acetonitrile (2) system. ▲, G^E/RT; ◆, γ_1; ●, γ_2.

for passing the test of consistency proposed by Fredenslund is $\delta y_1 < 0.010$ absolute in mole fraction, and the criterion for passing the one proposed by Wisniak[23] is $D < 5$ %.

Correlation

The data were correlated using the Margules,[3] Van Laar,[4] Wilson,[5] and NRTL[6] equations for the liquid-phase activity coefficients. The VLE values calculated with the previous correlating equations together with experimental data for the three systems presented in this paper are available as Supporting Information in tables (SI Tables 1 to 12).

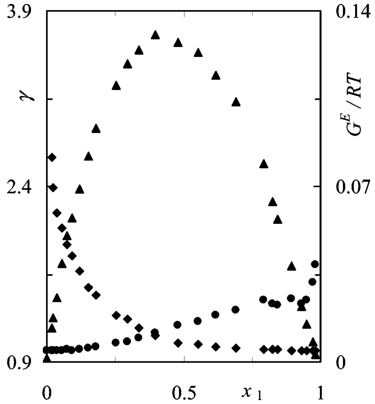

Figure 5. Experimental activity coefficients and dimensionless G^E/RT against liquid composition, x_1, for the methyl pentanoate (1) + acetonitrile (2) system. ▲, G^E/RT; ◆, γ_1; ●, γ_2.

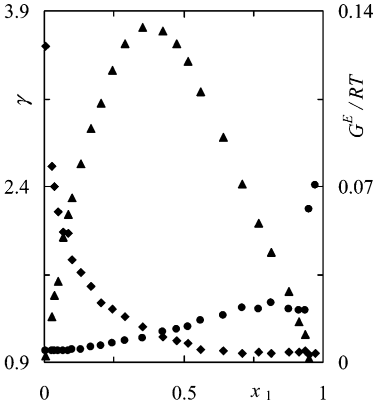

Figure 6. Experimental activity coefficients and dimensionless G^E/RT against liquid composition, x_1, for the methyl hexanoate (1) + acetonitrile (2) system. ▲, G^E/RT; ◆, γ_1; ●, γ_2.

Table 5. Results of Thermodynamic Consistency Tests of VLE Data for Three Binary Systems at 93.32 kPa

	point-to-point tests	
binary systems	Fredenslund[22] δy_1[a]	Wisniak[23] D/%[b]
methyl butyrate (1) + acetonitrile (2)	0.0058	2.2
methyl pentanoate (1) + acetonitrile (2)	0.0064	2.1
methyl hexanoate (1) + acetonitrile (2)	0.0052	1.6

[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 $D < 5$ %.

Margules[3] and Van Laar[4] constants are calculated by linear regression of activity coefficient data using eq 4 and eq 5:

$$\frac{x_1 \log \gamma_1 + x_2 \log \gamma_2}{x_1 x_2} = A + x_1(B - A) \quad (4)$$

$$\frac{x_1}{x_1 \log \gamma_1 + x_2 \log \gamma_2} = \frac{1}{A} + \frac{1}{B}\frac{x_1}{x_2} \quad (5)$$

Wilson[5] constants are calculated by no linear regression based in the method proposed by Apelblat and Wisniak.[24] The constants of the NRTL[6] model are found by least-squares minimizing the objective function:

$$\sum([(\ln \gamma_1)^2 + (\ln \gamma_2)^2]^{\text{calc}} - [(\ln \gamma_1)^2 + (\ln \gamma_2)^2]^{\text{exp}})^2 \quad (6)$$

These constants are reported in Table 6 with average deviations in activity coefficients between the experimental and the calculated values.

Table 6. Constants and Average Deviations, for Van Laar,[4] Margules,[3] Wilson,[5] and NRTL[6] Models

		average deviation/% $100\Sigma|\gamma_{\mathrm{exp}} - \gamma_{\mathrm{calc}}|/(\gamma_{\mathrm{exp}}\cdot n)$	
models	constants	γ_1	γ_2
	Methyl Butyrate (1) + Acetonitrile (2)		
Van Laar	$A = 0.8996$, $B = 0.3882$	2.3	2.4
Margules	$A = 0.8070$, $B = 0.3575$	1.4	2.0
Wilson (order 3)	$\Lambda_{12} = 0.3203$, $\Lambda_{21} = 1.2563$	1.8	1.3
NRTL ($\alpha = 0.3$)	$\tau_{12} = -0.3209$, $\tau_{21} = -0.9644$	6.3	6.1
	Methyl Pentanoate (1) + Acetonitrile (2)		
Van Laar	$A = 0.8025$, $B = 0.3520$	3.8	2.4
Margules	$A = 0.7337$, $B = 0.3278$	4.2	1.6
Wilson (order 3)	$\Lambda_{12} = 0.4229$, $\Lambda_{21} = 1.1546$	1.8	4.3
NRTL ($\alpha = 0.3$)	$\tau_{12} = -0.3347$, $\tau_{21} = 0.9425$	3.4	4.0
	Methyl Hexanoate (1) + Acetonitrile (2)		
Van Laar	$A = 0.0914$, $B = 0.2809$	18.4	8.0
Margules	$A = 0.7790$, $B = 0.1521$	5.1	4.4
Wilson (order 3)	$\Lambda_{12} = 0.2011$, $\Lambda_{21} = 1.5945$	4.2	5.4
NRTL ($\alpha = 0.3$)	$\tau_{12} = -1.0424$, $\tau_{21} = 2.6380$	4.8	5.1

Table 7. Average Deviations between the Calculated and Experimental Vapor-Phase Mole Fractions (Δy_1) and Temperature (ΔT/K) for the Three Binary Systems Using UNIFAC[9−12] and ASOG[7,8] Models[a]

	average deviations	
models	Δy_1	ΔT/K
Methyl Butyrate (1) + Acetonitrile (2)		
ASOG	0.554	0.340
UNIFAC-1	0.299	0.013
UNIFAC-2	0.042	0.003
UNIFAC-3	0.028	0.001
Methyl Pentanoate (1) + Acetonitrile (2)		
ASOG	0.711	0.037
UNIFAC-1	0.319	0.013
UNIFAC-2	0.120	0.005
UNIFAC-3	0.046	0.001
Methyl Hexanoate (1) + Acetonitrile (2)		
ASOG	1.082	0.051
UNIFAC-1	0.968	0.030
UNIFAC-2	0.139	0.007
UNIFAC-3	0.068	0.002

[a] $\Delta y_i = [\Sigma|(y_{i\mathrm{exp}} - y_{i\mathrm{cal}})/y_{i\mathrm{exp}}|]/n_{\mathrm{D}}$; $\Delta T_i = [\Sigma|(T_{i\mathrm{exp}} - T_{i\mathrm{cal}})/T_{i\ \mathrm{exp}}|]/n_{\mathrm{D}}$. n_{D} = data number.

Prediction of VLE. The ASOG[7,8] group-contribution method and the three versions of the UNIFAC (UNIFAC-1,[9] UNIFAC-2,[10] and UNIFAC-3[11,12]) were used to estimate the VLE values for mixtures presented in this work. In Table 7 are reported the average deviations in vapor-phase compositions and bubble point temperatures between the experimental and the calculated values.

The predictions deviate from experimental data for more than 50 % for the ASOG[7,8] method, around 5 % for the UNIFAC-3[11,12] method for vapor-phase compositions, 5 % for the ASOG[7,8] method, and around 0.1 % for the UNIFAC-3[11,12] method for bubble point temperatures. For the other two models of UNIFAC,[9,10] the values of the deviation of the vapor phase and the temperature of bubble point are between those of the methods of ASOG3[7,8] and UNIFAC-3.[11,12]

Conclusions

VLE data at 93.32 kPa for the binary systems methyl butyrate (1) + acetonitrile (2), methyl pentanoate (1) + acetonitrile (2), and methyl hexanoate (1) + acetonitrile were determined. The experimental data for the system methyl butyrate (1) + acetonitrile show that this system could present an azeotrope at other conditions of pressure. The activity coefficient data show that the studied systems deviate significantly from ideality. The experimental data were tested for thermodynamic consistency and found to be consistent. The experimental results were correlated using well-known various, now classic, equations for the reduction the data of VLE, such as the van Laar,[4] Margules,[3] Wilson,[5]and NRTL[6] equations. According to the standard deviations shown in Table 6, all equations appeared to be suitable for correlating the data for the mixtures considered here. The UNIFAC-3[11,12] method produced good predictions of isobaric data, probably due to the kindness of its parameters, whereas the ASOG[7,8] method poorly reproduces the results of the isobaric VLE. The results of other two methods, UNIFAC-1 and -2,[9,10] are between the values of the UNIFAC-3[11,12] and the ASOG[7,8] methods.

Supporting Information Available:

Tables 1 to 12 showing calculated VLE values with Margules,[3] van Laar,[4] Wilson,[5]and NRTL[6] models (T, y_1, γ_1, γ_2) at experimental x_1 and $P = 93.32$ kPa; parameters presented in Table 6 of this work; experimental data (T, x_1, y_1) drawn as points and the correlation model as continuous lines.

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