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

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Isobaric vapor−liquid equilibria were measured for the three binary systems of methyl butyrate, methyl pentanoate, and methyl hexanoate with propannenitrile at a constant pressure of 93.32 kPa. The measurements were carried out with in small recirculating still. The composition of condensed vapor and liquid phases was calculated indirectly from density measurements made with a vibrating tube densimeter. 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. These systems exhibit positive deviations from ideality. The methyl butyrate + propannenitrile system formed a minimum boiling azeotrope.

Introduction

In previous work,[1,2] the isobaric vapor−liquid equilibria (VLE) were measured at 93.32 kPa as part of a wider working project on binary systems of alkyl esters and nitriles formed by the first six methyl esters (methanoate to hexanoate) with nitriles. As a follow up to this work, with the aim of studying in depth the behavior of isobaric VLE in binary mixtures, data are presented here for the VLE of three binary mixtures of propanenitrile with three methyl esters (butanoate to hexanoate).

Properties directly measured, such as temperature and mole fractions for the liquid and vapor phases, were correlated by the Redlich−Kister[3] equation, while calculated properties, such as activity coefficients, were correlated by Margules,[4] van Laar,[5] Wilson,[6] and NRTL[7] models. Furthermore, experimental VLE compositions were predicted by two group-contribution methods, ASOG[8,9] and the three versions of UNIFAC (UNIFAC-1,[10] UNIFAC-2,[11] and UNIFAC-3[12,13]).

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.[14] 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, $\rho = \rho(x)$. These relationships were validated by confirming the quality of the results of V^E versus x_1.

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 concentrations values for the mixtures were carried out using a polynomial equation of the type:

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

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 was better than ± 0.001 units.

Materials. The components used were the highest commercial grade (molar fraction, $x \geq 0.995$) available from the manufac-

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

components	ρ/kg·m^{-3} exp	ρ/kg·m^{-3} lit	n_D exp	n_D 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]
propanenitrile	776.85	776.8[a]	1.36368	1.3636[a]

[a] Ref 15. [b] Ref 16.

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

components	T_c K	P_c kPa	V_c m^3·kg·mol^{-1}	Z_c	ω	μ/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
propanenitrile	564.44	4184.22	0.2291	0.205	0.3248	3.50

[a] Ref 19.

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

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
propanenitrile[d]	6.05500	1277.20	55.14	180−564

[a] Ref 20. [b] Ref 21. [c] Ref 19. [d] Ref 22.

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Table 4. Isobaric Vapor−Liquid Equilibrium Data: Temperature T/K; Liquid-Phase and Vapor-Phase (x_1, y_1) Mole Fractions; 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	T/K	x_1	y_1	γ_1	γ_2	G^E/RT
Methyl Butyrate (1) + Propanenitrile (2)																	
367.78	0.0000	0.0000		1.000	0.000	365.90	0.3330	0.3180	1.192	1.080	0.110	368.21	0.6885	0.6039	1.020	1.256	0.085
367.25	0.0381	0.0487	1.531	1.004	0.020	366.01	0.3800	0.3614	1.183	1.084	0.114	368.72	0.7426	0.6594	1.017	1.288	0.077
366.90	0.0719	0.0888	1.495	1.007	0.035	366.23	0.4490	0.4080	1.123	1.124	0.116	369.00	0.7795	0.6845	0.997	1.381	0.069
366.53	0.1189	0.1387	1.428	1.014	0.054	366.33	0.4749	0.4269	1.108	1.138	0.117	369.94	0.8512	0.7685	0.996	1.462	0.053
366.38	0.1471	0.1612	1.348	1.024	0.064	366.64	0.5124	0.4639	1.105	1.136	0.113	371.08	0.9124	0.8461	0.989	1.598	0.031
366.11	0.2009	0.2125	1.312	1.034	0.082	367.02	0.5662	0.5091	1.084	1.157	0.109	372.22	0.9628	0.9276	0.993	1.715	0.013
365.94	0.2250	0.2344	1.299	1.042	0.091	367.34	0.6006	0.5313	1.056	1.188	0.102	372.31	1.0000	1.0000	1.000		0.000
365.86	0.2794	0.2713	1.214	1.069	0.102	367.86	0.6502	0.5751	1.040	1.212	0.092						
Methyl Pentanoate (1) + Propanenitrile (2)																	
367.78	0.0000	0.0000		1.000	0.000	372.36	0.3866	0.2061	1.097	1.136	0.114	384.86	0.8096	0.5728	0.990	1.405	0.056
368.04	0.0461	0.0283	1.454	1.011	0.028	374.17	0.4571	0.2598	1.104	1.138	0.115	386.70	0.8548	0.6328	0.981	1.511	0.043
368.45	0.0878	0.0510	1.358	1.020	0.045	374.96	0.5039	0.2836	1.066	1.179	0.114	389.11	0.9002	0.7159	0.982	1.599	0.031
369.08	0.1349	0.0775	1.315	1.027	0.060	376.27	0.5568	0.3191	1.042	1.210	0.107	391.91	0.9426	0.8195	0.991	1.647	0.021
369.39	0.1689	0.0994	1.334	1.035	0.077	377.83	0.6138	0.3627	1.023	1.245	0.099	393.73	0.9712	0.8917	0.995	1.883	0.013
370.08	0.2359	0.1294	1.215	1.067	0.095	379.04	0.6643	0.3993	1.002	1.307	0.091	396.65	1.0000	1.0000	1.000		0.000
370.74	0.2825	0.1543	1.184	1.083	0.105	380.99	0.7267	0.4589	0.992	1.373	0.081						
371.66	0.3402	0.1836	1.136	1.108	0.111	382.46	0.7620	0.5026	0.991	1.394	0.072						
Methyl Hexanoate (1) + Propanenitrile (2)																	
367.78	0.0000	0.0000		1.000	0.000	376.47	0.3402	0.0989	1.151	1.070	0.092	396.58	0.7680	0.3831	0.998	1.243	0.049
368.83	0.0461	0.0154	1.752	1.001	0.027	379.03	0.4152	0.1274	1.109	1.090	0.093	402.80	0.8450	0.5109	0.994	1.274	0.033
369.14	0.0620	0.0191	1.597	1.006	0.034	380.26	0.4571	0.1416	1.072	1.118	0.092	408.30	0.9002	0.6451	0.997	1.267	0.021
370.31	0.1112	0.0325	1.450	1.012	0.052	382.32	0.5080	0.1658	1.051	1.135	0.087	412.60	0.9426	0.7650	0.995	1.327	0.011
371.80	0.1689	0.0489	1.359	1.020	0.069	383.43	0.5446	0.1797	1.022	1.171	0.084	416.12	0.9712	0.8765	0.999	1.289	0.007
372.10	0.1835	0.0519	1.313	1.027	0.071	387.57	0.6240	0.2350	1.013	1.189	0.073	419.67	1.0000	1.0000	1.000		0.000
373.73	0.2359	0.0700	1.298	1.028	0.083	390.41	0.6764	0.2775	1.003	1.215	0.065						
374.77	0.2871	0.0801	1.175	1.059	0.087	393.95	0.7290	0.3353	1.001	1.223	0.055						

turer, Fluka. All of them were previously degassed with ultrasound for several hours and treated with 0.4 nm molecular sieves (Fluka) to eliminate any trace of moisture.

The physical properties, density ρ and refractive index n_D at 298.15 K, determined for all liquids are shown in Table 1 along with literature value 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 propanenitrile. From these values, considering the nonideal behavior of the vapor phase, the activity coefficients of the components of the liquid phase are calculated by

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

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

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 tests proposed by Fredenslund et al.[23] was applied to all of the mixtures by evaluating the differences between the molar fractions of the vapor phase between the experimental value and that estimated by the method for each equilibrium point.

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 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[24] is $D < 5$ %.

Correlation

The data were correlated using the Margules,[4] Van Laar,[5] Wilson,[6] and NRTL[7] equations for the liquid-phase activity coefficients. Margules[4] and Van Laar[5] constants are calcu-

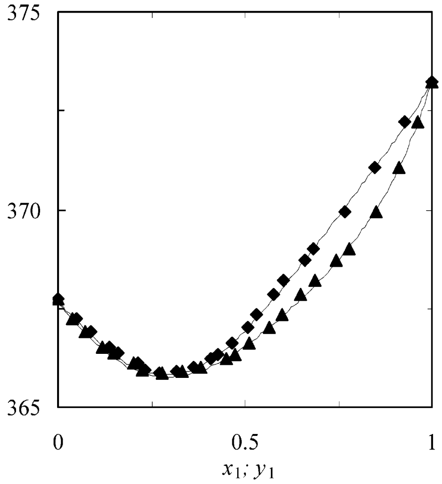

Figure 1. Temperature−composition diagram for the methyl butyrate (1) + propanenitrile (2) system: ▲, experimental liquid-phase mole fractions, x_1; ◆, experimental vapor-phase mole fractions, y_1; −, R−K equation.

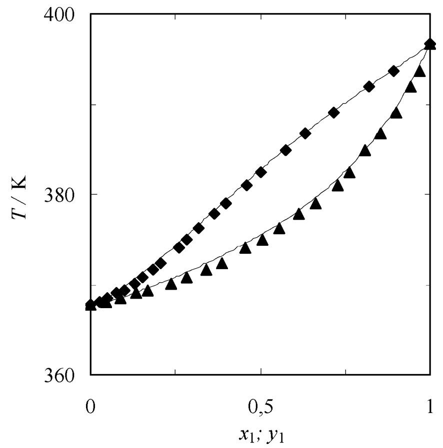

Figure 2. Temperature−composition diagram for the methyl pentanoate (1) + propanenitrile (2) system: ▲, experimental liquid-phase mole fractions, x_1; ◆, experimental vapor-phase mole fractions, y_1; —, R−K equation.

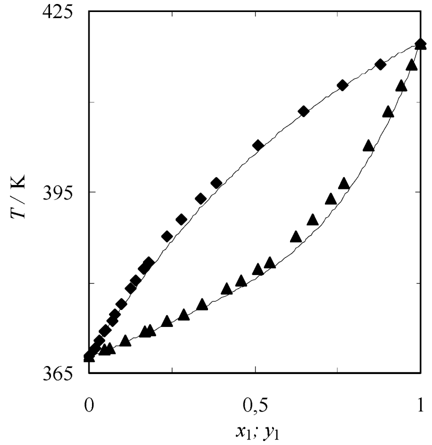

Figure 3. Temperature−composition diagram for the methyl hexanoate (1) + propanenitrile (2) system: ▲, experimental liquid-phase mole fractions, x_1; ◆, experimental vapor-phase mole fractions, y_1; —, R−K equation.

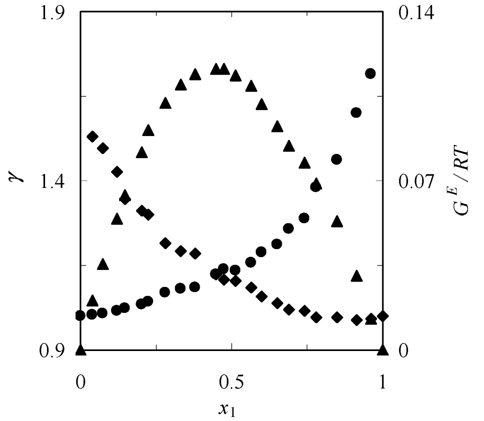

Figure 4. Experimental activity coefficients and dimensionless G^E/RT against liquid composition x_1 for the methyl butyrate (1) + propanenitrile (2) system: ▲, G^E/RT; ◆, γ_1; ●, γ_2.

lated by linear regression of activity coefficient data using eqs 4 and 5:

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

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

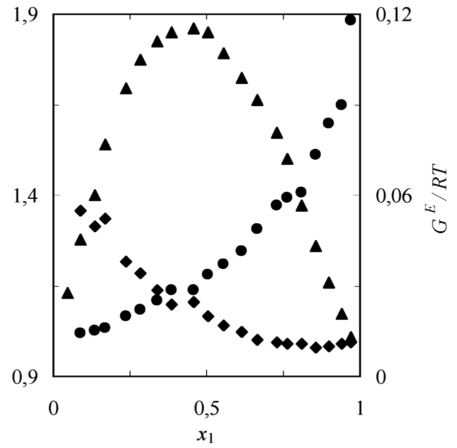

Figure 5. Experimental activity coefficients and dimensionless G^E/RT against liquid composition x_1 for the methyl pentanoate (1) + propanenitrile (2) system: ▲, G^E/RT; ◆, γ_1; ●, γ_2.

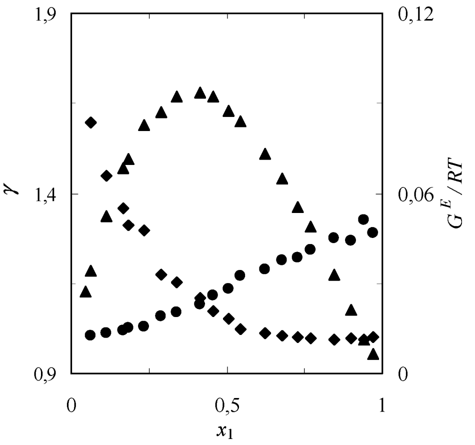

Figure 6. Experimental activity coefficients and dimensionless G^E/RT against liquid composition x_1 for the methyl hexanoate (1) + propanenitrile (2) system: ▲, G^E/RT; ◆, γ_1; ●, γ_2.

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

binary systems	point-to-point tests	
	ref 23	ref 24
	δy_1[a]	D/%[b]
methyl butyrate (1) + propanenitrile (2)	0.0092	2.4
methyl pentanoate (1) + propanenitrile (2)	0.0074	2.1
methyl hexanoate (1) + propanenitrile (2)	0.0066	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 $D < 5$ %.

The Wilson[6] constants are calculated by nonlinear regression based in the method proposed by Apelblat and Wisniak.[25] 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.

Prediction of VLE. The ASOG[8,9] group-contribution method and the three versions of UNIFAC (UNIFAC-1,[10] UNIFAC-2,[11] and UNIFAC-3[12,13]) 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-

Table 6. Constants and Average Deviations for Van Laar,[5] Margules,[4] Wilson,[6] and NRTL[7] Models

models	constants	average deviation/% $100\sum\lvert\gamma_{\mathrm{exp}} - \gamma_{\mathrm{calc}}\rvert/(\gamma_{\mathrm{exp}}n)^a$	
		γ_1	γ_2
Methyl Butyrate (1) + Propanenitrile (2)			
Van Laar	$A = 0.2720$, $B = 0.1563$	3.7	2.8
Margules	$A = 0.2394$, $B = 0.1566$	2.1	2.7
Wilson (order 2)	$\Lambda_{12} = 0.6839$, $\Lambda_{21} = 0.8849$	0.0	2.3
NRTL ($\alpha = 0.3$)	$\tau_{12} = 0.8180$, $\tau_{21} = -0.2156$	3.5	1.7
Methyl Pentanoate (1) + Propanenitrile (2)			
Van Laar	$A = 0.1464$, $B = 0.1959$	3.5	7.7
Margules	$A = 0.2514$, $B = 0.1541$	4.9	5.4
Wilson (order 2)	$\Lambda_{12} = 0.6851$, $\Lambda_{21} = 0.8822$	4.9	5.3
NRTL ($\alpha = 0.3$)	$\tau_{12} = 1.2474$, $\tau_{21} = -0.4995$	5.9	4.7
Methyl Hexanoate (1) + Propanenitrile (2)			
Van Laar	$A = 0.2271$, $B = 0.1128$	2.4	1.1
Margules	$A = 0.2487$, $B = 0.0919$	1.1	1.3
Wilson (order 3)	$\Lambda_{12} = 0.3240$, $\Lambda_{21} = 1.5013$	1.3	0.9
NRTL ($\alpha = 0.3$)	$\tau_{12} = -0.7144$, $\tau_{21} = 1.5392$	1.1	1.1

[a] n, number of experimental data points.

Table 7. Average Deviations between Calculated and Experimental Vapor-Phase Mole Fractions Δy_1 and Temperature ΔT/K for the Three Binary Systems Using UNIFAC[10−13] and ASOG[8,9] Models

models	average deviations	
	Δy_1	ΔT/K
Methyl Butyrate (1) + Propanenitrile (2)		
ASOG	0.283	0.022
UNIFAC-1	0.045	0.004
UNIFAC-2	0.030	0.001
UNIFAC-3	0.027	0.001
Methyl Pentanoate (1) + Propanenitrile (2)		
ASOG	0.476	0.005
UNIFAC-1	0.346	0.011
UNIFAC-2	0.376	0.008
UNIFAC-3	0.374	0.009
Methyl Hexanoate (1) + Propanenitrile (2)		
ASOG	0.553	0.034
UNIFAC-1	0.239	0.012
UNIFAC-2	0.038	0.002
UNIFAC-3	0.036	0.001

[a] $$\Delta y_i = \frac{\sum\left|\frac{y_{i\ \mathrm{exp}} - y_{i\ \mathrm{cal}}}{y_{i\ \mathrm{exp}}}\right|}{n} \text{ and } \Delta T_i = \frac{\sum\left|\frac{T_{i\ \mathrm{exp}} - T_{i\ \mathrm{cal}}}{T_{i\ \mathrm{exp}}}\right|}{n}$$
where n is the number of experimental data points.

point temperatures between the experimental and the calculated values.

The predictions deviate from experimental data for more than 50 % for the ASOG[8,9] method and around 5 % for the UNIFAC-3[12,13] method for vapor-phase compositions and 5 % for the ASOG[8,9] method and around 0.1 % for the UNIFAC-3[12,13] method for bubble-point temperatures. For the other two models of UNIFAC,[10,11] the values of the deviation of the vapor phase and the temperature of bubble point are between those of the methods of ASOG[8,9] and UNIFAC-3.[12,13]

Conclusions

VLE data at 93.32 kPa for the binary systems methyl butyrate (1) + propanenitrile (2), methyl pentanoate (1) + propanenitrile (2), and methyl hexanoate (1) + propanenitrile were determined. The experimental data for the system methyl butyrate (1) + propanenitrile evidence that this system 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 classics equations for the reduction the data of VLE, such as the van Laar,[5] Margules,[4] Wilson,[6] and NRTL[7] equations. According to standard deviations shown in Table 6, all equations appeared to be suitable for correlating the data for the mixtures considered here. The UNIFAC-3[12,13] method produced good predictions of isobaric data, probably due to the kindness of its parameters, whereas the ASOG[8,9] method poorly reproduces the results of the isobaric VLE. The results of other two methods, UNIFAC-1 and 2,[10,11] are between the values of the UNIFAC-3[12,13] and ASOG[8,9] methods.

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