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Vapor−Liquid Equilibria at (33.33, 66.66, and 101.33) kPa and Densities at 298.15 K for the System Methanol + Methyl Lactate

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Isobaric vapor−liquid equilibrium data have been experimentally determined for the binary system methanol + methyl lactate at (33.33, 66.66, and 101.3) kPa. All the experimental data reported were thermodynamically consistent according to the point-to-point method of Fredenslund. The activity coefficients were correlated with the NRTL and UNIQUAC equations for the liquid-phase activity coefficients. The densities and derived excess volumes for the same mixture are also reported at 298.15 K.

Introduction

Catalytic distillation can be an alternative process for recovering purified lactic acid from the aqueous solutions obtained in the fermentation processes where it is generated. In the catalytic distillation process, esterification of lactic acid is carried out to obtain an ester that can be purified by distillation and then hydrolyzed into a purified lactic acid.

For the design of a catalytic distillation process, some basic information is needed such as pure component properties, reaction kinetics, chemical equilibrium, mass transfer characteristics, and vapor−liquid equilibrium of the mixtures involved in the process. In a previous publication,[1] the reaction kinetics of autocatalyzed and heterogeneously catalyzed lactic acid esterification with methanol were measured. The activity coefficients needed to take into account the real behavior of the liquid phase in the correlation of the experimental reaction rates by the different models were predicted by UNIFAC. Accounting for the nonideality of the liquid phase results in a smaller residual error in the fitting process because the models describe more closely the actual reaction kinetics.[2] The use of experimentally determined activity coefficients, instead of predicted values, would further improve the correlation results.

This work is one of a series directed to the experimental determination of the vapor−liquid equilibrium (VLE) of different mixtures that may be formed with the components involved in the esterification of lactic acid with methanol. In this manuscript, a mixture of two nonreacting components is considered, that is, methanol and methyl lactate.

Experimental Section

Chemicals. Methyl (S)-(−)-lactate, purchased from Acros (Belgium) with a reported purity of 97%, was purified by vacuum distillation. The final purity was 99.99 wt %, as determined by gas chromatography (GC). Methanol (Lab-Scan, 99.9%) was stored over activated 3-Å molecular sieves to keep it dry. The water content of methanol and methyl lactate was determined with a Karl-Fisher apparatus (Mitsubishi Kasei CA-20) and was found to be below 0.003 wt % in both cases. As an additional purity check, some physical properties of the pure components were measured and compared with values reported in the literature. The results are presented in Table 1. The experimental boiling point of methyl lactate is not included in this table (see Results and Discussion Section, subsection on Saturation Pressures).

Apparatus and Procedure. Densities, ρ, were measured with an Anton Paar (DMA-5000) densimeter with an accuracy of $\pm 0.005\ \mathrm{kg \cdot m^{-3}}$ and refractive indexes, $n(D)$, with an Abbe-type refractometer with an accuracy of ±0.0002. An all-glass still of the Gillespie type with circulation of both the liquid and vapor phases was used for experimental determination of VLE and vapor pressure data. This apparatus has been previously described and used in our laboratory to obtain experimental vapor pressures and VLE data.[7,8] The still was operated under a nitrogen atmosphere. The total pressure of the system was monitored with a digital manometer and controlled to the desired value (within 0.05 kPa) with a pressure controller (Normastat 75) that allowed dry nitrogen to be injected into or released from the still to achieve an inert atmosphere until thermodynamic equilibrium was reached. Atmospheric pressure was measured with a Lambrecht-type barometer. The boiling point temperature (±0.05 K) in the equilibrium still was measured with a digital thermometer (Ertco-Hart, Model 850).

Sample Analysis. The liquid and vapor phases were analyzed using a Hewlett-Packard GC (Model 6890) equipped with a flame ionization detector (FID). The GC column was a 25 m × 0.5 μm bonded phase fused silica, FFAP, capillary column. The injector and detector were at 453 K and 523 K, respectively. The oven was operated at variable, programmed temperature, from 428 K (where it was kept for 2 min) to 553 K at a rate of $30\ \mathrm{K \cdot min^{-1}}$. Helium ($38\ \mathrm{mL \cdot min^{-1}}$), 99.999% pure, was used as the carrier gas. Concentration measurements were accurate to ±0.0005 mole fraction.

Results and Discussion

Saturation Pressures. Some vapor pressure data for methanol were obtained with the still described in the Experimental Section. A comparison of the experimental vapor pressures, and those obtained from the Antoine constants taken from the literature,[10] gives an average

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Table 1. Physical Properties of the Pure Compounds

	ρ (kg·m^{-3})		$n(D)$		T_b (101.33 kPa)/K	
compound	experimental	literature	experimental	literature	experimental	literature
methyl lactate	1092.695 (20 °C) 1087.326 (25 °C) 1094.015 (19 °C)	1088 (20 °C)[a] 1.09 × 10^3 (19 °C)[c]	1.4144 (20 °C) 1.4152 (16 °C)	1.4131 (20 °C)[a] 1.4141 (20 °C)[b] 1.4156 (16 °C)[c]		417.95[a] 418.15[b] 417.15−418.14[c]
methanol	786.360 (25 °C)	786.37 (25 °C)[d]	1.3284 (20 °C)	1.3284 (20 °C)[d]	337.65	337.696[d]

[a] Dean.[3] [b] Chahal.[4] [c] Merck.[5] [d] Riddick et al.[6]

Table 2. Antoine Equation[a] Parameters, *A*, *B*, and *C*

	Antoine constants			temperature
compound	*A*	*B*	*C*	range (K)
methyl lactate[b]	7.24147	2016.46	−32.1044	207.15−584.00
methanol[c]	7.21274	1588.63	−32.5988	288.00−512.60

[a] Antoine equation: $\log(P/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) + C]$. [b] (PRO II) Library.[9] [c] Reid et al.[10]

Table 3. Experimental Density Data (ρ) and Derived Excess Molar Volumes (V^E) for the System Methanol (1) + Methyl Lactate (2) at 298.15 K and Different Mole Fractions, x_1

x_1	ρ kg m^{-3}	V^E cm^3 mol^{-1}	x_1	ρ kg m^{-3}	V^E cm^3 mol^{-1}
0.0000	1087.326	0.0000	0.8302	890.696	−0.3704
0.1583	1067.807	−0.2260	0.8830	863.158	−0.2890
0.2681	1051.513	−0.3668	0.9068	849.539	−0.2471
0.3662	1034.168	−0.4559	0.9283	836.434	−0.2043
0.4485	1017.330	−0.5151	0.9474	824.164	−0.1593
0.5214	1000.205	−0.5495	0.9669	810.903	−0.1084
0.5816	984.059	−0.5549	0.9826	799.543	−0.0592
0.6862	950.858	−0.5237	1.0000	786.360	0.0000
0.7646	920.495	−0.4527			

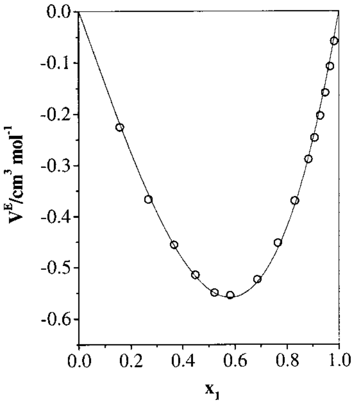

Figure 1. Excess molar volume, V^E, versus mole fraction of methanol, x_1, for the system methanol (1) + methyl lactate (2); the continuous line represents the excess molar volume as calculated by the Redlich−Kister equation.

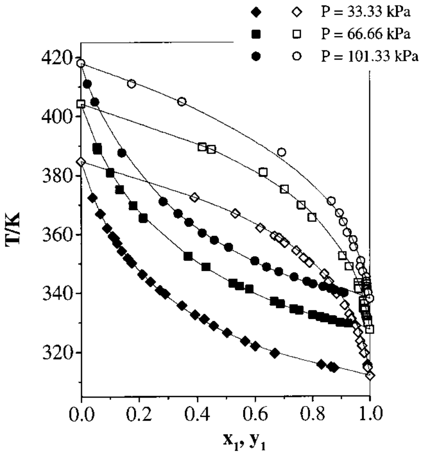

Figure 2. Isobars at 33.33 kPa, 66.66 kPa, and 101.3 kPa for the binary system methanol (1) + methyl lactate (2); the continuous line represents the VLE as calculated by using the NRTL equation with α = 0.4.

absolute deviation of 0.05 kPa, which is in the range of the accuracy of the equipment used in this work for experimental determination of vapor pressures. This indicates that the Antoine constants selected from the literature also fit the experimental *P* vs *T* data obtained in this work for pure components.

Methyl lactate may undergo self-alcoholysis with the OH group of another methyl lactate molecule when heated.[11] The alcohol groups are exchanged more or less completely through the reaction,

$$n\mathrm{CH_3CHOHCOOCH_3} \rightleftarrows \mathrm{OH[CH(CH_3)COO]}_n\mathrm{CH_3} + (n-1)\mathrm{CH_3OH}$$

Therefore, vapor pressure of methyl lactate could not be experimentally determined with the still described in the previous section because it is necessary to heat the compound up to its boiling point. The Antoine equation parameters, A_i, B_i, and C_i, used for VLE data treatment, were selected from the literature to cover the temperature range of interest in this work and are reported in Table 2.

Densities. The experimental values of the density of the mixtures methanol (1) + methyl lactate (2) at 298.15 K and the values of the excess volume calculated from the density data are reported in Table 3. The excess molar volumes have been correlated by means of the Redlich−Kister equation,[12]

$$V^E = x_1 x_2 \sum_{k=0}^{n} A_k (x_1 - x_2)^k \tag{1}$$

The parameters obtained from the correlation to a first-order polynomial ($k = 1$) were $A_0 = -2.174$ and $A_1 = -0.7592$ with a standard deviation of 0.0101 as calculated by

$$\sigma = \sqrt{\frac{\sum (V^E_{\mathrm{cal}} - V^E_{\mathrm{exp}})_i^2}{N - m}} \tag{2}$$

where *N* is the number of experimental data and *m* the number of adjustable parameters.

Figure 1 shows the experimental values of the excess volume and the fitted curves obtained using eq 1.

Vapor−Liquid Equilibrium. All the variables necessary to totally describe VLE have been experimentally determined. The variables are temperature, pressure, and composition of the liquid and vapor phases. The results of the VLE measurements of the binary system methanol (1)

Table 4. Experimental VLE Data for the Binary System Methanol (1) + Methyl Lactate (2) at 33.33 kPa: Liquid-Phase Mole Fraction, x_1, Vapor-Phase Mole Fraction, y_1, Temperature, T, Activity Coefficients, γ_i, and Fugacity Coefficients, Φ_i.

x_1	y_1	T (K)	γ_1	γ_2	Φ_1	Φ_2
0.0000	0.0000	384.72		0.9999	0.9980	0.9980
0.0403	0.3919	372.47	0.9931	1.0177	0.9954	0.9843
0.0664	0.5320	366.95	0.9701	1.0081	0.9945	0.9783
0.0899	0.6180	362.10	0.9720	1.0349	0.9939	0.9738
0.1096	0.6678	359.36	0.9426	1.0349	0.9935	0.9709
0.1170	0.6834	358.67	0.9245	1.0249	0.9934	0.9701
0.1248	0.7037	356.98	0.9444	1.0420	0.9932	0.9686
0.1407	0.7434	354.38	0.9666	1.0314	0.9929	0.9659
0.1619	0.7694	351.88	0.9479	1.0636	0.9926	0.9637
0.1756	0.7890	350.23	0.9496	1.0668	0.9924	0.9620
0.2115	0.8410	346.37	0.9646	1.0055	0.9919	0.9576
0.2407	0.8576	343.84	0.9479	1.0543	0.9916	0.9553
0.2720	0.8748	341.03	0.9500	1.1071	0.9912	0.9526
0.2907	0.8838	339.65	0.9460	1.1282	0.9910	0.9512
0.3486	0.9122	335.75	0.9459	1.1268	0.9905	0.9468
0.3928	0.9286	332.64	0.9660	1.1516	0.9900	0.9433
0.4242	0.9359	331.16	0.9565	1.1768	0.9898	0.9416
0.4572	0.9514	328.79	0.9933	1.0715	0.9894	0.9385
0.5028	0.9583	326.49	1.0129	1.1526	0.9890	0.9354
0.5611	0.9662	323.62	1.0328	1.2365	0.9885	0.9319
0.6001	0.9730	321.90	1.0513	1.1984	0.9882	0.9293
0.6679	0.9799	319.52	1.0504	1.2203	0.9878	0.9262
0.8301	0.9911	315.73	0.9980	1.2887	0.9871	0.9209
0.8646	0.9933	314.88	0.9978	1.2845	0.9869	0.9195
0.8751	0.9929	314.58	0.9990	1.4948	0.9868	0.9191
1.0000	1.0000	311.80	1.0000		0.9862	0.9146

Table 5. Experimental VLE Data for the Binary System Methanol (1) + Methyl Lactate (2) at 66.66 kPa: Liquid-Phase Mole Fraction, x_1, Vapor-Phase Mole Fraction, y_1, Temperature, T, Activity Coefficients, γ_i, and Fugacity Coefficients, Φ_i

x_1	y_1	T (K)	γ_1	γ_2	Φ_1	Φ_2
0.0000	0.0000	404.31		1.0261	0.9983	0.9983
0.0561	0.4189	389.53	0.9336	1.0374	0.9961	0.9866
0.0582	0.4506	388.70	0.9901	1.0118	0.9960	0.9856
0.1014	0.6293	380.85	0.9885	0.9497	0.9951	0.9791
0.1342	0.7032	375.09	0.9879	0.9809	0.9946	0.9754
0.1805	0.7616	369.73	0.9362	1.0264	0.9941	0.9718
0.2157	0.7989	365.50	0.9384	1.0725	0.9937	0.9690
0.3708	0.9047	352.47	0.9533	1.1009	0.9924	0.9588
0.4308	0.9282	348.87	0.9554	1.0767	0.9920	0.9557
0.5241	0.9595	343.38	0.9907	0.9348	0.9914	0.9506
0.5472	0.9594	342.30	0.9876	1.0363	0.9913	0.9498
0.5807	0.9609	341.17	0.9723	1.1371	0.9911	0.9489
0.6666	0.9767	337.14	1.0037	1.0343	0.9906	0.9449
0.6881	0.9816	336.19	1.0138	0.9144	0.9905	0.9439
0.7355	0.9781	334.52	1.0088	1.3940	0.9903	0.9426
0.7534	0.9833	333.92	1.0138	1.1744	0.9902	0.9417
0.8001	0.9860	332.51	1.0123	1.3033	0.9900	0.9403
0.8253	0.9873	331.96	1.0045	1.3907	0.9899	0.9397
0.8426	0.9888	331.31	1.0114	1.4067	0.9898	0.9390
0.8696	0.9924	330.64	1.0105	1.1918	0.9897	0.9382
0.8962	0.9923	329.88	1.0111	1.5770	0.9896	0.9374
0.9247	0.9937	329.52	0.9957	1.8115	0.9895	0.9370
1.0000	1.0000	327.40	1.0108		0.9892	0.9345

Table 6. Experimental VLE Data for the Binary System Methanol (1) + Methyl Lactate (2) at 101.33 kPa: Liquid-Phase Mole Fraction, x_1, Vapor-Phase Mole Fraction, y_1, Temperature, T, Activity Coefficients, γ_i, and Fugacity Coefficients, Φ_i

x_1	y_1	T (K)	γ_1	γ_2	Φ_1	Φ_2
0.0000	0.0000	417.95		1.0130	0.9984	0.9984
0.0225	0.1767	411.05	0.8649	1.0528	0.9976	0.9945
0.0480	0.3492	404.85	0.9301	1.0391	0.9969	0.9903
0.1421	0.6928	387.62	0.9755	0.9753	0.9953	0.9792
0.2843	0.8662	371.10	0.9850	0.9463	0.9940	0.9692
0.3348	0.8944	366.95	0.9825	0.9484	0.9937	0.9666
0.3729	0.9074	364.01	0.9828	0.9948	0.9935	0.9649
0.4187	0.9206	360.35	1.0003	1.0719	0.9931	0.9626
0.4597	0.9421	357.93	1.0103	0.9316	0.9929	0.9606
0.5095	0.9442	355.50	0.9917	1.0984	0.9927	0.9591
0.5996	0.9688	350.85	1.0154	0.9231	0.9922	0.9554
0.6402	0.9672	348.82	1.0201	1.1836	0.9920	0.9541
0.6837	0.9754	347.12	1.0238	1.0909	0.9918	0.9527
0.7358	0.9881	345.32	1.0287	0.6861	0.9916	0.9509
0.7813	0.9890	343.82	1.0245	0.8216	0.9914	0.9497
0.8021	0.9898	342.97	1.0306	0.8761	0.9913	0.9490
0.8373	0.9900	342.04	1.0222	1.0917	0.9912	0.9483
0.8631	0.9906	341.34	1.0186	1.2607	0.9911	0.9478
0.8772	0.9914	340.95	1.0178	1.3099	0.9911	0.9474
0.9010	0.9930	340.24	1.0194	1.3680	0.9910	0.9468
0.9108	0.9938	339.95	1.0204	1.3636	0.9910	0.9465
1.0000	1.0000	337.85	1.0131		0.9907	0.9445

Table 7. Correlation Parameters of the Activity Coefficient Equations for the Binary System Methanol (1) + Methyl Lactate (2): A_{12}, A_{21}, and α_{12}, and Root Mean Squared Deviations for Equilibrium Pressure, Temperature and Vapor and Liquid Compositions

	equation parameters[a]			root mean square deviations			
equation	A_{12}[a]	A_{21}	α_{12}	P (kPa)	T (K)	x_1	y_1
UNIQUAC	7205.23	−1367.20		0.19	0.23	0.0099	0.0074
NRTL	24874.43	−725.48	0.4	0.20	0.21	0.0090	0.0070
NRTL	19178.79	−789.62	0.47	0.24	0.28	0.0088	0.0070

[a] A_{12} and A_{21} are in $J\cdot mol^{-1}$.

+ methyl lactate (2) at three different pressures (33.33, 66.66, and 101.33) kPa are presented in Tables 4 −6 and Figure 2.

The activity coefficients show slight deviations from Raoult's law, which indicates different molecular interactions between equal and different molecules. Both molecules, methanol and methyl lactate, have an OH group that can form hydrogen bonds either with similar or different molecules. The observed deviations from ideality may be due to the tendency of methanol to self-associate at high concentrations while at low concentrations the tendency to hydrogen bond with methyl lactate would be predominant. This phenomena, occurring because of the different size or a significant difference between the boiling points of both molecules, would explain the inversion observed in Raoult's law deviations.[8]

Vapor-phase fugacity coefficients of each component in the mixture, Φ_i and Φ_i^o, were estimated by the virial equation of state[13] and second virial coefficients were calculated with the Hayden and O'Connell[14] correlation.

The Fredenslund et al.[15] point-to-point test was applied to the experimental data for thermodynamic consistency. The average values of the residuals, $\Delta y = |y_{exp} - y_{calc}|$ (y = mole fraction), were $\Delta y = 0.0098$, $\Delta y = 0.0080$, and $\Delta y = 0.0060$ for the systems determined at 33.33 kPa, 66.66 kPa, and 101.33 kPa, respectively, indicating that the VLE results for the three systems are thermodynamically consistent. Pressure deviations were also evaluated because the boiling points of the two components are fairly different.[15] The average values for $\Delta P = |P_{exp} - P_{calc}|$ were $\Delta P = 0.14$ kPa, $\Delta P = 0.08$ kPa, and $\Delta P = 0.06$ kPa for the systems determined at 33.33 kPa, 66.66 kPa, and 101.33 kPa, respectively. These values were close to the accuracy achieved by the pressure controller (0.05 kPa). Residuals for P and y were randomly distributed along the entire composition range.

Experimental (P, T, x, y) data were correlated with a nonlinear regression method based on the maximum likelihood principle.[16] The NRTL and UNIQUAC liquid-phase activity coefficient models were used for data correlation. Two different preset values of the parameter α_{12} were used in the NRTL equation. All the experimental data obtained at different pressures were correlated together to obtain more representative parameters.[17] Table 7 reports the results obtained, that is, adjustable parameters, A_{12} and A_{21}, for the activity coefficient equations, and root-mean-squared deviations for pressure, temperature, and vapor- and liquid-phase compositions.

Because the relative volatility for the system methanol (1) + methyl lactate (2) is fairly high, only a few distillation stages would be needed to separate the mixture into its components. The relative volatility increases slightly as the pressure decreases, thus favoring separation.

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