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Vapor Liquid Equilibria of the Mixtures Involved in the Esterification of Lactic Acid with Methanol

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Isobaric vapor liquid equilibrium (VLE) data of the reactive quaternary system methanol (1) + water (2) + methyl lactate (3) + lactic acid (4) are presented in this paper. The experimental data were correlated using the UNIQUAC model to describe the chemical and phase equilibrium. The UNIQUAC parameters for some of the binary, nonreactive systems involved in the quaternary mixture were obtained from published VLE data and, in the case of the system water + lactic acid, from experimental VLE data reported in this paper. The rest of the binary UNIQUAC parameters were obtained by an optimization of the correlation of the experimental quaternary VLE data. The results obtained from the correlation were found to be in good agreement with experimental data. The reaction equilibrium constant was also calculated for each experimental data point. A three-dimensional phase diagram was constructed for the quaternary reactive system by using transformed composition variables. No reactive azeotrope was found.

Introduction

Esterification reactions are equilibrium limited reactions; however, if a separation process is superimposed, such as distillation, the new reactive distillation process may overcome the limitations by displacing the equilibrium through products removal.[1] Reactive distillation can be used as an alternative process for recovering and purifying lactic acid from fermentation broths.[2] In such a process, lactic acid reacts with an alcohol, yielding an ester, more volatile than lactic acid, that can be recovered by distillation. The ester can be further hydrolyzed back to lactic acid.

Modeling of reactive distillation for a reliable process engineering synthesis and design is quite complex, as it involves chemical reactions and multicomponent vapor liquid equilibria that influence each other.[3] Thus, for achieving a global understanding of the process, the esterification reaction kinetics of lactic acid with methanol were previously studied in detail.[4]

The objectives of this study are to obtain the VLE experimental data for the quaternary reactive mixture methanol (1) + water (2) + methyl lactate (3) + lactic acid (4) and to correlate such data to obtain the corresponding UNIQUAC binary parameters. As a first step in a thermodynamic study of this system, the VLE of the nonreactive binary mixture methanol + methyl lactate was previously studied.[5] Here, isobaric VLE data for the nonreactive system water + lactic acid are presented together with their correlation with the Wilson, NRTL, and UNIQUAC equations. The quaternary VLE data were correlated by fixing the binary parameters obtained for the nonreactive systems and using the UNIQUAC model to obtain the rest of the binary parameters, so that they can fit the chemical reaction equilibrium in the liquid phase as well as the phase equilibrium.

Experimental Section

Chemicals. Methyl (*S*)-(−)-lactate was purchased from Acros (Belgium) with a reported purity of 97%. It was purified by vacuum distillation, obtaining a final purity of 99.9% by mass, as determined by gas chromatography (GC). Methanol (GC assay, 99.9%) was supplied by Lab-Scan (Ireland) and was stored over activated 3 Å molecular sieves in order to keep it dry. As an additional purity check, some physical properties of the pure components were measured and compared with values reported in the literature. Results were presented in a previous publication.[5]

The water used was distilled twice. Two different aqueous lactic acid solutions were used: (1) A dilute solution was supplied by Acros (Belgium), whose composition corresponded mainly to monomeric lactic acid and water. It was used for VLE measurements of the quaternary reactive system in order to avoid the presence of polymerized lactic acid in the system[6] as far as possible. (2) A concentrated solution was purchased from Fluka. Concentrated solutions are more complex because lactic acid undergoes self-polymerization to form mainly a lactic acid dimer:[6]

$$2CH_3CH(OH)COOH \rightarrow CH_3CH(OH)COOCH(CH_3)COOH + H_2O$$

The amount of monomeric lactic acid was determined by boiling the concentrated solution in a measured excess of sodium hydroxide and back-titration of the final solution. The concentrated solution used had the following composition expressed as mass fraction: monomeric lactic acid, 61.23%; lactyl-lactic acid, 27.69%; and water, 11.08%. This solution was used for experimental determination of the VLE of the system water + lactic acid in order to cover the widest possible concentration range.

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Apparatus and Procedure. The still used in this study was an all-glass still of the Gillespie type with circulation of both the liquid and vapor phases. A detailed description of the apparatus was reported previously.[5,7] 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 (±0.09 kPa) by means of a pressure controller (Normastat 75). Temperature (±0.05 K) was measured with a digital thermometer (Ertco-Hart, model 850).

As reported previously,[4] the lactic acid esterification reaction rate is not negligible, even without the addition of an external catalyst. Therefore, for obtaining VLE data for the reactive quaternary mixture with the Gillespie type still described, chemical equilibrium must be previously reached. To avoid long operation times till chemical and phase equilibria were reached, the still was filled with quaternary mixtures with a composition close to the chemical equilibrium. Another procedure to attain chemical and phase equilibria in a short time is to speed up the reaction by adding a heterogeneous catalyst.[8−11] Once chemical and phase equilibria were reached, samples of liquid and condensed vapor were withdrawn for analysis.

Sample Analysis. The samples were analyzed using a Hewlett-Packard (6890) gas chromatograph (GC) equipped with series connected thermal conductivity and flame ionization detectors so that water and the other components could be detected in the same run. The GC column was a 25 m × 0.25 mm bonded phase fused silica capillary column. Helium, 99.999% pure, was used as carrier gas. The injector and detectors were at 503.15 K and 533.15 K, respectively. The oven was operated at programmed temperature, from 353 K to 493 K at a rate of 40 K min^{-1}. 1,2-Propanediol was used as internal standard for analysis of the quaternary samples. The estimated uncertainty in phase compositions was ±0.0005 mole fraction. Quantitative analysis of monomeric lactic acid in the vapor phase was also carried out by titration with sodium hydroxide, using phenolphthalein as the indicator. This method is only accurate for very weak lactic acid solutions.[12]

Thermodynamics of VLE with Chemical Reaction

The general equation for VLE at constant low pressure, P, and temperature, T, of a given mixture is given by

$$\phi_i y_i P = \gamma_i x_i P_i^{\mathrm{sat}}\, \phi_i^{\mathrm{sat}} \tag{1}$$

where γ_i is the activity coefficient of component i, ϕ_i is its fugacity coefficient, and x_i and y_i are the compositions of the liquid and vapor phases, respectively. P_i^{sat} is its vapor pressure at temperature T, and ϕ_i^{sat} is the fugacity coefficient of pure saturated vapor i at temperature T and the corresponding pressure P_i^{sat}.

When a reaction takes place in the liquid phase, an additional constraint for the chemical potential, μ_i, has to be included,

$$\sum \nu_i \mu_i = 0 \tag{2}$$

where ν_i is the stoichiometric coefficient of component i in the reaction.

The chemical equilibrium constant, K_{eq}, can be estimated from thermodynamic data of the pure components;[3] however, in this work, K_{eq} is obtained from a previous reaction kinetics study.[4] The temperature dependence of K_{eq} can be expressed by the empirical function

Table 1. Antoine Equation[a] Parameters, *A*, *B*, and *C*

compound	Antoine constants *A*	*B*	*C*	temp range/K
methanol[b]	7.21274	1588.63	−32.5988	288.00−512.60
water[c]	7.0436	1636.909	−48.230	373.15−423.15
methyl lactate[d]	7.24147	2016.46	−32.104	207.15−584.00
lactic acid[d]	7.51107	1965.70	−91.021	273.15−500.15

[a] Antoine equation: $\log(p/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) + C]$. [b] Reid et al.[13] [c] Riddick et al.[14] [d] PRO/II Library.[15]

$$\ln K_{\mathrm{eq}} = (-2.60) - \frac{(-1954.2)}{T} \tag{3}$$

This chemical equilibrium constant expressed as a function of the activities ($x\gamma$) of products and reactants is given by

$$K_{\mathrm{eq}} = K_x K_\gamma = \frac{x_3 x_2}{x_4 x_1}\frac{\gamma_3 \gamma_2}{\gamma_4 \gamma_1} \tag{4}$$

where x is the mole fraction of the different components in the liquid phase and γ are the activity coefficients.

Furthermore, the interdependence of the mole fractions in the liquid, x_i, and in the vapor, y_i, phases must be taken into account,

$$\sum_{i=1}^{c} x_i = 1 \tag{5}$$

$$\sum_{i=1}^{c} y_i = 1 \tag{6}$$

To solve the phase equilibrium and the chemical reaction equilibrium simultaneously, an algorithm similar to the one proposed by Barbosa and Doherty[3] has been used in this work; it can solve eqs 1−6 simultaneously.

The vapor pressure of the pure components in eq 1 has been obtained by using Antoine's equation, whose parameters A_i, B_i, and C_i are reported in Table 1. Experimental data can be correlated using several models for liquid phase activity coefficients.[8,9,16,17] The parameters for the quaternary reactive system were obtained using the UNIQUAC equation that was selected to take into account the nonideality of the reacting liquid phase.

Results and Discussion

VLE of the System Water + Lactic Acid. The nonreacting mixture water + lactic acid was studied first to obtain the corresponding UNIQUAC binary parameters. The concentrated aqueous lactic acid solution was used for the VLE experiments, and hence, the presence of lactyllactic acid in the liquid phase must be taken into account. The experimental data obtained for the resulting ternary system at 101.33 kPa, and the activity coefficients are shown in Table 2. For calculation of the activity coefficients, nonideality of the vapor phase was taken into account (eq 1). For a system with a carboxylic acid, dimerization may occur in the vapor phase. To account for this association, the “chemical” theory was used for calculating the fugacity coefficients in this system.[18] The true molar fractions in the vapor phase showed that the concentration of the associated species was negligible compared to that of the nonassociated ones. This may be because of the low concentration of lactic acid in the vapor phase, as its

Table 2. Experimental VLE Data for the System Water (1) + Lactic Acid (2) + Lactyl-Lactic Acid (3) at 103.33 kPa: Liquid Phase Mole Fraction x_i, Vapor Phase Mole Fraction y_i, Temperature T, and Activity Coefficients γ_i

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2
438.13	0.1940	0.6202	0.9465	0.0534	0.7530	0.1616
424.34	0.2412	0.6003	0.9680	0.0320	0.8662	0.1604
421.49	0.2698	0.5807	0.9707	0.0293	0.8363	0.1731
416.47	0.2995	0.5546	0.9805	0.0195	0.8679	0.1468
412.97	0.3284	0.5376	0.9811	0.0189	0.8712	0.1715
409.00	0.3521	0.5224	0.9821	0.0179	0.9087	0.2034
407.74	0.3705	0.5075	0.9840	0.0160	0.8964	0.1986
404.20	0.4051	0.4761	0.9855	0.0145	0.9077	0.2170
403.92	0.3999	0.4845	0.9860	0.0140	0.9279	0.2147
403.62	0.4047	0.4818	0.9870	0.0130	0.9261	0.1992
403.20	0.4035	0.4851	0.9873	0.0127	0.9401	0.2058
402.22	0.4104	0.4769	0.9895	0.0105	0.9532	0.1780
401.41	0.4158	0.4725	0.9896	0.0104	0.9633	0.1842
400.85	0.4386	0.4519	0.9906	0.0094	0.9293	0.1790
400.64	0.4401	0.4499	0.9911	0.0089	0.9325	0.1728
398.55	0.4502	0.4451	0.9911	0.0089	0.9695	0.1883
398.29	0.4532	0.4435	0.9916	0.0084	0.9713	0.1840
397.26	0.4692	0.4302	0.9926	0.0074	0.9685	0.1745
396.80	0.4694	0.4299	0.9924	0.0076	0.9815	0.1840
395.20	0.4903	0.4152	0.9931	0.0069	0.9869	0.1846
394.99	0.4928	0.4142	0.9926	0.0074	0.9877	0.2025
393.60	0.5011	0.4075	0.9934	0.0066	1.0142	0.1941
393.01	0.5138	0.3961	0.9939	0.0061	1.0078	0.1917
391.42	0.5341	0.3785	0.9950	0.0050	1.0198	0.1773
389.65	0.5522	0.3645	0.9951	0.0049	1.0427	0.1965
389.62	0.5745	0.3455	0.9955	0.0045	1.0037	0.1930
386.60	0.6030	0.3211	0.9964	0.0036	1.0534	0.1913
386.30	0.6226	0.3043	0.9965	0.0035	1.0302	0.2007
384.14	0.6460	0.2855	0.9967	0.0033	1.0649	0.2235
383.19	0.6615	0.2716	0.9968	0.0032	1.0728	0.2384
382.62	0.6882	0.2496	0.9972	0.0028	1.0513	0.2353
381.59	0.7005	0.2385	0.9976	0.0024	1.0689	0.2220
381.09	0.7035	0.2372	0.9979	0.0021	1.0825	0.2021
380.42	0.7193	0.2245	0.9983	0.0017	1.0829	0.1800
379.78	0.7403	0.2070	0.9984	0.0016	1.0750	0.1890
379.09	0.7573	0.1941	0.9986	0.0014	1.0760	0.1830
378.36	0.7822	0.1722	0.9988	0.0012	1.0676	0.1839
377.54	0.8211	0.1410	0.9989	0.0011	1.0459	0.2149
376.36	0.8628	0.1079	0.9995	0.0005	1.0366	0.1362
374.18	0.9558	0.0342	0.9998	0.0002	1.0091	0.1917

Table 3. Correlation Parameters of the Activity Coefficient Equations for the System Water (1) + Lactic Acid (2) + Lactyl-Lactic Acid (3): A_{ij} and α_{ij}, and Percentage of Average Relative Deviations (%) for the Equilibrium Pressure and Vapor Phase Mole Fraction

equation	equation parameters/K	dev P/%	dev y_2/%
UNIQUAC	$\Delta u_{12} = -84.8$	1.30	10.03
	$\Delta u_{21} = -26.1$		
	$\Delta u_{13} = -2285.8$		
	$\Delta u_{31} = -90.9$		
	$\Delta u_{23} = -2069.1$		
	$\Delta u_{32} = -717.4$		
Wilson	$\Delta\lambda_{12} = 262.2$	1.99	9.42
	$\Delta\lambda_{21} = -341.6$		
	$\Delta\lambda_{13} = 61.5$		
	$\Delta\lambda_{31} = -5606.3$		
	$\Delta\lambda_{23} = -1306.0$		
	$\Delta\lambda_{32} = -9403.9$		
NRTL ($\alpha = 0.3$)	$\Delta g_{12} = 407.7$	1.32	8.70
	$\Delta g_{21} = -454.3$		
	$\Delta g_{13} = 281.0$		
	$\Delta g_{31} = -1417.2$		
	$\Delta g_{23} = -5932.8$		
	$\Delta g_{32} = -2387.6$		
NRTL ($\alpha = 0.47$)	$\Delta g_{12} = 203.1$	1.49	8.54
	$\Delta g_{21} = -299.8$		
	$\Delta g_{13} = 270.2$		
	$\Delta g_{31} = -1032.8$		
	$\Delta g_{23} = -2822.1$		
	$\Delta g_{32} = -1818.0$		
NRTL ($\alpha = 0.8$)	$\Delta g_{12} = 141.3$	1.94	9.35
	$\Delta g_{21} = -216.1$		
	$\Delta g_{13} = 71.3$		
	$\Delta g_{31} = -616.6$		
	$\Delta g_{23} = -1742.6$		
	$\Delta g_{32} = -1446.4$		

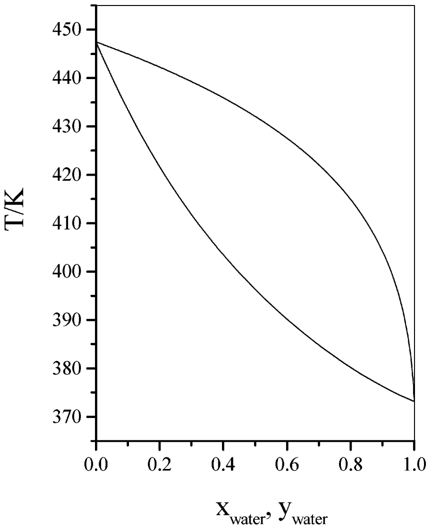

Figure 1. VLE of the binary system water (1) + lactic acid (2) at 101.3 kPa as calculated by using the UNIQUAC equation.

volatility is very low. The fugacity coefficients were also calculated by using the virial equation of state, and the second virial coefficients were obtained from the Hayden and O'Connell[19] correlation. The deviations found in the fugacity coefficients calculated by the two methods were lower than 1%.

The activity coefficients show negative deviations from ideality for monomeric lactic acid, which suggests a strong association between water and lactic acid molecules in the liquid phase.

Experimental VLE data were correlated by the Wilson, UNIQUAC, and NRTL equations. The binary parameters for these equations were determined by minimizing the objective function given in eq 7 through the Simplex−Nelder method

$$\mathrm{FO} = \sum_{j=1}^{n}\sum_{i=1}^{c}(\gamma_{\mathrm{exp},ij} - \gamma_{\mathrm{calc},ij})^2 \tag{7}$$

where n is the number of data points, c is the number of components, and γ_{exp} and γ_{calc} are the experimental and calculated activity coefficients, respectively.

The fitted parameters together with the average relative deviations of the equilibrium pressure (dev P/%) and lactic acid mole fraction in the vapor phase (dev y_2/%) are presented in Table 3. The individual absolute deviations were found to be randomly distributed in both cases. In the NRTL model, several values for the nonrandomness parameter, α, have been set, since the largest variation of that parameter appears in aqueous organic systems.[20] From the binary parameters obtained from the activity coefficient equations it is possible to calculate the binary system water (1) + lactic acid (2). Figure 1 shows the T versus x, y diagram as calculated using the corresponding UNIQUAC binary parameters.

VLE of the Quaternary System Methanol (1) + Water (2) + Methyl Lactate (3) + Lactic Acid (4). The VLE experimental data at 101.33 kPa for the quaternary reactive mixture, vapor and liquid compositions and equilibrium temperature, are listed in Table 4. In this work,

Table 4. Experimental VLE Data for the Quaternary System Methanol (1) + Water (2) + Methyl Lactate (3) + Lactic Acid (4) at 103.33 kPa: Liquid Phase Mole Fraction x_i, Vapor Phase Mole Fraction y_i, Temperature T, Activity Coefficients γ_i, Fugacity Coefficients ϕ_i, and Equilibrium Reaction Constants K_{eq}

T/K	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3	γ_4	ϕ_1	ϕ_2	ϕ_3	ϕ_4	K_{eq}
347.62	0.5413	0.4126	0.0370	0.8160	0.1804	0.0035	1.0503	1.1644	1.2975	0.8513	0.9656	0.9812	0.9555	0.8799	5.24
348.76	0.4872	0.4407	0.0596	0.8044	0.1890	0.0065	1.1052	1.0894	1.4282	0.5785	0.9664	0.9815	0.9562	0.8843	10.49
350.08	0.4132	0.5333	0.0390	0.8320	0.1644	0.0035	1.2871	0.7421	1.1007	0.4637	0.9671	0.9823	0.9570	0.8887	4.75
350.45	0.4649	0.4214	0.0957	0.7607	0.2279	0.0114	1.0328	1.2811	1.4358	0.3618	0.9676	0.9816	0.9574	0.8909	23.69
350.96	0.4394	0.4451	0.0911	0.7826	0.2069	0.0104	1.1044	1.0790	1.3466	0.3838	0.9678	0.9820	0.9576	0.8912	12.93
351.26	0.4248	0.4593	0.0909	0.7700	0.2191	0.0108	1.1125	1.0937	1.3817	0.3724	0.9680	0.9820	0.9579	0.8923	14.36
351.43	0.4209	0.4616	0.0893	0.7701	0.2189	0.0109	1.1163	1.0800	1.4033	0.4336	0.9681	0.9820	0.9580	0.8919	10.87
351.58	0.4073	0.4713	0.0891	0.7575	0.2316	0.0018	1.1291	1.1121	1.3860	0.3750	0.9683	0.9819	0.9581	0.8925	11.62
351.74	0.3598	0.5779	0.0393	0.7313	0.2638	0.0048	1.2271	1.0258	1.3931	0.5211	0.9685	0.9816	0.9586	0.8934	6.12
351.81	0.4039	0.4778	0.0872	0.7622	0.2274	0.0103	1.1365	1.0670	1.3465	0.3838	0.9684	0.9820	0.9583	0.8932	10.91
352.65	0.3656	0.5178	0.0829	0.7323	0.2567	0.0109	1.1723	1.0741	1.4320	0.3376	0.9690	0.9820	0.9590	0.8964	13.57
352.80	0.3873	0.4916	0.0855	0.7443	0.2445	0.0111	1.1188	1.0714	1.4130	0.3805	0.9690	0.9822	0.9590	0.8959	10.83
352.80	0.4595	0.2208	0.2892	0.8430	0.1364	0.0205	1.0678	1.3326	0.7694	0.2552	0.9687	0.9835	0.9582	0.8968	17.12
353.03	0.3483	0.5378	0.0806	0.7280	0.2616	0.0103	1.2075	1.0381	1.3681	0.3645	0.9692	0.9820	0.9592	0.8973	12.05
353.44	0.3884	0.4230	0.1593	0.7419	0.2398	0.0182	1.0879	1.1904	1.2061	0.2711	0.9694	0.9824	0.9592	0.8998	28.88
353.57	0.3346	0.5532	0.077	0.7162	0.2730	0.0107	1.2141	1.0305	1.4445	0.3438	0.9696	0.9821	0.9596	0.8991	13.24
354.08	0.3603	0.5787	0.0393	0.7528	0.2420	0.0051	1.1645	0.8560	1.3318	0.4390	0.9698	0.9826	0.9599	0.9011	6.51
354.67	0.3898	0.2077	0.3590	0.8167	0.1454	0.0378	1.1445	1.4013	1.0519	0.2565	0.9698	0.9840	0.9589	0.9012	22.10
354.72	0.3035	0.5830	0.0710	0.6562	0.3330	0.0107	1.1799	1.1387	1.5057	0.3593	0.9705	0.9818	0.9607	0.9019	12.95
355.26	0.2781	0.6091	0.0696	0.6457	0.3425	0.0117	1.2443	1.0973	1.6395	0.3962	0.9708	0.9819	0.9611	0.9028	12.88
355.71	0.2654	0.6229	0.0668	0.6372	0.3511	0.0115	1.2673	1.0805	1.6462	0.4207	0.9711	0.9820	0.9614	0.9035	11.67
355.94	0.3584	0.4026	0.1932	0.7223	0.2536	0.0240	1.0051	1.1980	1.1755	0.2982	0.9708	0.9831	0.9606	0.9049	21.17
355.98	0.3219	0.5615	0.0762	0.6939	0.2946	0.0144	1.1272	0.9957	1.4092	0.3539	0.9710	0.9826	0.9612	0.9052	11.57
356.29	0.2555	0.6346	0.0649	0.6445	0.3440	0.0113	1.3057	1.0159	1.6250	0.3718	0.9714	0.9822	0.9617	0.9057	12.16
356.33	0.2225	0.6969	0.0418	0.5983	0.3930	0.0085	1.3907	1.0546	1.8989	0.3767	0.9716	0.9818	0.9621	0.9072	12.92
356.69	0.2410	0.6515	0.0628	0.6029	0.3851	0.0118	1.2783	1.0901	1.7216	0.3984	0.9718	0.9820	0.9622	0.9069	14.01
357.21	0.2286	0.6679	0.0610	0.5925	0.3952	0.0121	1.3018	1.0692	1.7789	0.4063	0.9721	0.9821	0.9626	0.9085	15.08
357.63	0.2216	0.6724	0.0591	0.5905	0.3971	0.0122	1.3199	1.0500	1.8174	0.3587	0.9723	0.9822	0.9628	0.9097	15.39
357.65	0.1999	0.7180	0.0412	0.5846	0.4055	0.0097	1.4474	1.0032	2.0690	0.4119	0.9724	0.9822	0.9629	0.9099	12.62
358.08	0.2062	0.6829	0.0577	0.5663	0.4204	0.0131	1.3402	1.0754	1.9607	0.3084	0.9727	0.9822	0.9632	0.9113	18.31
358.11	0.3572	0.2175	0.3658	0.7992	0.1614	0.0392	1.0896	1.2979	0.9222	0.2746	0.9717	0.9847	0.9609	0.9087	14.98
358.48	0.1931	0.7226	0.0398	0.5495	0.4407	0.0096	1.3707	1.0487	2.0491	0.3606	0.9730	0.9821	0.9637	0.9126	14.55
358.90	0.1958	0.7215	0.0381	0.5234	0.4662	0.0102	1.2702	1.0932	2.2311	0.3509	0.9733	0.9821	0.9641	0.9141	17.24
359.20	0.1795	0.7078	0.0549	0.5596	0.4270	0.0131	1.4666	1.0092	1.9640	0.3977	0.9732	0.9825	0.9639	0.9116	12.73
359.64	0.1721	0.7169	0.0518	0.5266	0.4600	0.0131	1.4186	1.0551	2.0382	0.3791	0.9736	0.9824	0.9644	0.9132	14.58
359.74	0.1626	0.7563	0.0389	0.5237	0.4653	0.0108	1.4887	1.0078	2.2322	0.3528	0.9737	0.9824	0.9645	0.9163	18.32
359.96	0.1520	0.7616	0.0377	0.5102	0.4786	0.0109	1.5400	1.0207	2.3059	0.4527	0.9739	0.9824	0.9648	0.9143	13.11
360.01	0.1693	0.7185	0.0505	0.5284	0.4581	0.0132	1.4295	1.0337	2.0783	0.3562	0.9738	0.9825	0.9645	0.9142	14.68
360.36	0.1429	0.7666	0.0367	0.5025	0.4864	0.0108	1.5932	1.0149	2.3077	0.3998	0.9741	0.9821	0.9650	0.9155	13.44
360.94	0.2459	0.4684	0.2056	0.6085	0.3541	0.0370	1.0992	1.1839	1.3746	0.3452	0.9737	0.9836	0.9637	0.9130	20.98
361.06	0.1502	0.7404	0.0482	0.4986	0.4873	0.0137	1.4704	1.0250	2.1658	0.4486	0.9745	0.9826	0.9653	0.9148	13.04
361.07	0.1559	0.7549	0.0362	0.4642	0.5240	0.0115	1.3183	1.0805	2.4186	0.3897	0.9747	0.9824	0.9657	0.9178	16.81
361.09	0.1349	0.7814	0.0341	0.4656	0.5226	0.0115	1.5269	1.0402	2.5595	0.4161	0.9747	0.9824	0.9657	0.9179	16.65
361.59	0.1234	0.7868	0.0333	0.4557	0.5329	0.0111	1.6075	1.0336	2.4809	0.3555	0.9750	0.9825	0.9661	0.9193	16.89
361.66	0.1393	0.7517	0.0448	0.5048	0.4816	0.0132	1.5738	0.9755	2.1817	0.4134	0.9747	0.9829	0.9656	0.9164	12.31
361.68	0.1497	0.7611	0.0353	0.4774	0.5108	0.0115	1.3847	1.0209	2.4201	0.3697	0.9749	0.9827	0.9659	0.9192	16.03
362.01	0.1268	0.7791	0.0357	0.4391	0.5484	0.0121	1.4875	1.0572	2.4798	0.4464	0.9753	0.9826	0.9664	0.9181	14.84
362.03	0.1908	0.6285	0.0881	0.4985	0.4801	0.0208	1.1214	1.1470	1.7241	0.4189	0.9478	0.9830	0.9656	0.9125	13.20
362.24	0.1207	0.7944	0.0320	0.4692	0.5193	0.0112	1.6576	0.9736	2.5484	0.3648	0.9752	0.9828	0.9662	0.9207	16.30
362.28	0.1256	0.7632	0.0431	0.4423	0.5436	0.0137	1.5001	1.0589	2.3025	0.3768	0.9753	0.9827	0.9664	0.9187	16.61
362.36	0.1207	0.7875	0.0337	0.4301	0.5575	0.0120	1.5137	1.0492	2.5685	0.4397	0.9755	0.9826	0.9666	0.9191	15.33
362.49	0.2299	0.4339	0.2276	0.5887	0.3694	0.0413	1.0820	1.2573	1.2986	0.3478	0.9745	0.9840	0.9645	0.9126	17.17
362.59	0.2614	0.3775	0.2673	0.6570	0.2992	0.0433	1.0584	1.1669	1.1543	0.3340	0.9742	0.9846	0.9640	0.9146	15.68
362.64	0.1141	0.8018	0.0310	0.4276	0.5602	0.0118	1.5780	1.0247	2.7146	0.4733	0.9756	0.9827	0.9668	0.9199	15.27
362.68	0.2524	0.4110	0.2444	0.6320	0.3253	0.0422	1.0516	1.1611	1.2248	0.3383	0.9744	0.9844	0.9642	0.9151	17.26
362.78	0.1092	0.8033	0.0301	0.4234	0.5647	0.0115	1.6254	1.0256	2.7080	0.4344	0.9757	0.9827	0.9669	0.9203	15.17
362.92	0.1135	0.7933	0.0322	0.4244	0.5633	0.0119	1.5597	1.0305	2.6023	0.4063	0.9757	0.9828	0.9670	0.9206	15.64
363.05	0.2405	0.4356	0.2262	0.6059	0.3514	0.0422	1.0454	1.1667	1.3041	0.3130	0.9746	0.9843	0.9646	0.9163	19.52
363.14	0.1153	0.7740	0.0410	0.4151	0.5700	0.0144	1.4914	1.0600	2.4609	0.4374	0.9759	0.9828	0.9671	0.9190	15.79
363.39	0.2514	0.3746	0.2818	0.6438	0.3081	0.0476	1.0511	1.1751	1.1638	0.3247	0.9746	0.9847	0.9644	0.9168	18.23
363.55	0.1098	0.7815	0.0391	0.4385	0.5473	0.0137	1.6325	0.9927	2.4090	0.4281	0.9759	0.9831	0.9671	0.9198	13.69
363.56	0.1033	0.8028	0.0315	0.4022	0.5850	0.0124	1.5920	1.0324	2.6919	0.3828	0.9761	0.9829	0.9675	0.9225	17.93
363.72	0.2592	0.3273	0.3134	0.6682	0.2795	0.0518	1.0469	1.2054	1.1217	0.2937	0.9747	0.9851	0.9642	0.9174	17.39
363.75	0.1038	0.7890	0.0373	0.4044	0.5815	0.0136	1.5836	1.0368	2.4847	0.4211	0.9762	0.9829	0.9675	0.9207	15.65
363.87	0.0981	0.8159	0.0283	0.3949	0.5928	0.0119	1.6305	1.0175	2.8589	0.4064	0.9763	0.9829	0.9677	0.9233	17.91
364.06	0.2602	0.3027	0.3450	0.6837	0.2624	0.0534	1.0556	1.2083	1.0367	0.3131	0.9748	0.9853	0.9643	0.9182	16.52
364.22	0.0954	0.8132	0.0301	0.3842	0.6031	0.0123	1.6132	1.0251	2.7279	0.3749	0.9765	0.9830	0.9680	0.9243	19.35
364.28	0.0959	0.8065	0.0300	0.3578	0.6290	0.0127	1.4910	1.0755	2.8175	0.4234	0.9767	0.9829	0.9682	0.9226	17.95
364.40	0.0949	0.8146	0.0294	0.3726	0.6145	0.0125	1.5633	1.0357	2.8138	0.3725	0.9767	0.9830	0.9681	0.9248	20.64
364.58	0.0935	0.7967	0.0354	0.3934	0.5923	0.0138	1.6644	1.0140	2.5664	0.3780	0.9766	0.9831	0.9680	0.9229	16.76
364.98	0.0892	0.8168	0.0279	0.3738	0.6136	0.0121	1.6381	1.0095	2.8068	0.4158	0.9769	0.9832	0.9684	0.9241	16.08
365.07	0.2529	0.3186	0.3338	0.6613	0.2813	0.0569	1.0175	1.1851	1.0960	0.2877	0.9753	0.9854	0.9648	0.9209	19.70
365.14	0.0876	0.8157	0.0287	0.3591	0.6282	0.0122	1.5948	1.0287	2.7340	0.4005	0.9771	0.9831	0.9686	0.9247	17.28
365.15	0.0917	0.8026	0.0341	0.3933	0.5922	0.0139	1.6674	0.9854	2.6223	0.4549	0.9768	0.9833	0.9682	0.9222	14.18
365.23	0.0856	0.8230	0.0289	0.3596	0.6267	0.0132	1.6299	1.0138	2.9360	0.4335	0.9771	0.9832	0.9686	0.9249	18.72
365.45	0.0870	0.8115	0.0325	0.3829	0.6029	0.0136	1.6950	0.9812	2.6665	0.4643	0.9770	0.9833	0.9685	0.9231	14.59
365.56	0.0806	0.8127	0.0312	0.3666	0.6199	0.0129	1.7455	1.0032	2.6118	0.4224	0.9772	0.9833	0.9687	0.9236	14.82
365.58	0.0819	0.8244	0.0275	0.3211	0.6656	0.0127	1.5042	1.0609	2.9225	0.4807	0.9775	0.9831	0.9692	0.9242	17.88
365.76	0.0827	0.8123	0.0312	0.3638	0.6220	0.0136	1.6776	0.9997	2.7451	0.4268	0.9773	0.9833	0.9688	0.9241	15.89
365.77	0.0800	0.8163	0.0303	0.3895	0.5969	0.0130	1.8553	0.9544	2.6817	0.4293	0.9771	0.9835	0.9686	0.9238	13.55
365.80	0.2283	0.3275	0.3380	0.6528	0.2909	0.0557	1.0873	1.1606	1.0281	0.2948	0.9756	0.9855	0.9652	0.9208	16.98
366.01	0.0783	0.8216	0.0290	0.3667	0.6199	0.0128	1.7721	0.9760	2.7340	0.4372	0.9774	0.9834	0.9689	0.9247	14.77

Table 4 (Continued)

T/K	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3	γ_4	ϕ_1	ϕ_2	ϕ_3	ϕ_4	K_{eq}
366.15	0.2269	0.2893	0.3754	0.6374	0.2963	0.0657	1.0578	1.3230	1.0773	0.2841	0.9758	0.9856	0.9652	0.9216	20.94
366.12	0.1990	0.4111	0.2711	0.5598	0.3874	0.0520	1.0594	1.2159	1.1819	0.3444	0.9761	0.9849	0.9661	0.9186	18.57
366.13	0.2292	0.2594	0.4071	0.6650	0.2691	0.0651	1.0919	1.3395	0.9834	0.3914	0.9757	0.9858	0.9651	0.9176	13.61
366.14	0.1136	0.6844	0.0824	0.3630	0.6109	0.0250	1.2045	1.1492	1.8718	0.4680	0.9773	0.9835	0.9686	0.9152	15.84
366.57	0.0712	0.8236	0.0280	0.3483	0.6380	0.0130	1.8189	0.9817	2.8117	0.4548	0.9777	0.9835	0.9693	0.9243	14.03
367.21	0.0667	0.8312	0.0260	0.3255	0.6609	0.0129	1.7795	0.9842	2.9307	0.4452	0.9781	0.9836	0.9698	0.9261	15.52
367.26	0.0661	0.8285	0.0251	0.3149	0.6716	0.0127	1.7340	1.0015	2.9849	0.4800	0.9782	0.9836	0.9700	0.9245	14.07
367.40	0.0625	0.8336	0.0248	0.2856	0.7006	0.0130	1.6556	1.0330	3.0788	0.4836	0.9784	0.9835	0.9703	0.9252	16.58
367.69	0.0576	0.8385	0.0240	0.2806	0.7059	0.0127	1.7493	1.0238	3.0725	0.4716	0.9786	0.9836	0.9705	0.9260	16.66
367.97	0.0559	0.8433	0.0228	0.2914	0.6955	0.0123	1.8554	0.9929	3.0878	0.4756	0.9786	0.9837	0.9705	0.9266	15.35
369.59	0.0824	0.7035	0.0744	0.3012	0.6724	0.0251	1.2371	1.0854	1.8107	0.4206	0.9790	0.9843	0.9707	0.9203	17.17
370.28	0.0790	0.6588	0.0952	0.3160	0.6505	0.0316	1.3267	1.0938	1.7335	0.4560	0.9791	0.9846	0.9706	0.9141	14.90
370.42	0.1571	0.3588	0.3332	0.5125	0.4270	0.0590	1.0755	1.3135	0.9167	0.3973	0.9779	0.9857	0.9682	0.9185	14.21
370.73	0.0763	0.6933	0.0795	0.2915	0.6776	0.0291	1.2499	1.0654	1.8767	0.4679	0.9794	0.9846	0.9711	0.9173	16.38
371.51	0.0865	0.6298	0.1152	0.3121	0.6504	0.0354	1.1519	1.0951	1.5268	0.4666	0.9795	0.9849	0.9710	0.9148	15.49
372.91	0.0966	0.5618	0.1496	0.3243	0.6273	0.0458	1.0275	1.1270	1.4395	0.4672	0.9798	0.9854	0.9711	0.9119	15.31
374.55	0.1001	0.4820	0.2135	0.3865	0.5518	0.0590	1.1244	1.0913	1.2171	0.4328	0.9799	0.9861	0.9708	0.9138	13.73
376.58	0.1055	0.3836	0.3041	0.4109	0.5042	0.0819	1.0678	1.1682	1.0956	0.4119	0.9804	0.9868	0.9708	0.9171	15.56
377.27	0.1185	0.2942	0.3960	0.4706	0.4216	0.1048	1.0666	1.2445	1.0473	0.4296	0.9803	0.9875	0.9700	0.9185	14.62
381.90	0.0954	0.2425	0.4510	0.4227	0.4401	0.1335	1.0412	1.3476	0.9830	0.3780	0.9818	0.9884	0.9713	0.9245	18.28

Table 5. UNIQUAC Binary Parameters for the Quaternary System Methanol (1) + Water (2) + Methyl Lactate (3) + Lactic Acid (4) at 103.33 kPa

subsystem (i, j)	A_{ij}/K	A_{ji}/K	ref
methanol (1)−water (2)	−192.6	325	Kojima et al.[21]
methanol (1)−methyl lactate (3)	866.6	−164.4	Sanz et al.[5]
methanol (1)−lactic acid (4)	322.59	17.14	correlation of the quaternary VLE data
water (2)−methyl lactate (3)	−20.05	325.31	correlation of the quaternary VLE data
water (2)−lactic acid (4)	−84.8	−26.1	this work
methyl lactate (3)−lactic acid (4)	367.14	−302.09	correlation of the quaternary VLE data

Table 6. Azeotrope Composition of the System Water + Methyl Lactate

P/kPa	T/K	x_{water}	$x_{\text{methyl lactate}}$	reference
101.33	371.10	0.880	0.120	this work (predicted values)
101.33	370.93−373.15	0.91−0.93	0.09−0.07	Weisberg and Stimpson[22]
101.33	371.48−372.04	0.96	0.04	Schopmeyer and Arnold[23]
100.23	372.25	0.941	0.059	Troupe and Kore[24]
101.33	372.15−372.65	0.95	0.05	Chahal[12]

102 experiments were carried out. VLE data at high concentration of monomeric lactic acid were not determined in order to avoid its dimerization.

The vapor phase fugacity coefficients (Table 4) have been calculated using the virial equation of state truncated after the second term and the second virial coefficients from the Hayden and O'Connell[19] correlation. Because of the low vapor pressure of lactic acid, it was not necessary to use the "chemical" theory as was proved for the system water + lactic acid.

The activity coefficients (Table 4) were calculated taking into account the nonideality of the vapor phase (eq 1). Methanol, water, and methyl lactate show positive deviations from Raoult's law, while lactic acid always shows strong negative deviations.

The esterification reaction equilibrium constant, K_{eq} (Table 4), was calculated for each run by eq 4.

Experimental VLE data for this reactive quaternary system were correlated using the UNIQUAC equation. Following the method described by other authors,[8] the UNIQUAC parameters used for the quaternary system were as follows: for the systems methanol + water[21] and methanol + methyl lactate,[5] they were obtained from the literature; and for the system water + lactic acid, they were obtained in this work. The remaining binary parameters were obtained directly from the quaternary VLE data correlation. All the binary UNIQUAC parameters are listed in Table 5. Data correlation was performed by minimizing the objective function given in eq 7 through the Simplex−Nelder method.

To evaluate the quality of the correlation, the experimental variables have been recalculated by taking into account phase and chemical equilibrium simultaneously.

The average absolute deviations between experimental and calculated variables were the following: $\Delta x_3 = 0.0039$, $\Delta x_4 = 0.0038$, $\Delta y_1 = 0.0205$, $\Delta y_2 = 0.0203$, $\Delta y_3 = 0.0012$, $\Delta y_4 = 0.0001$, and $\Delta T = 1.05$ K. These average values show a fairly good agreement between calculated and experimental data. The individual absolute deviations were found to be randomly distributed in all cases.

The binary UNIQUAC parameters calculated from the quaternary VLE data correlation allow us to calculate the binary reactive systems that could not be experimentally determined in the circulation still. For instance, those calculations predict a minimum azeotrope for the binary reactive system water + methyl lactate, which has been previously reported in the literature and is described in Table 6.

Reactive Phase Diagrams. Once the composition, pressure, and temperature at equilibrium were determined, the so-called reactive phase diagram can be plotted.

For a graphical representation of a quaternary system, Barbosa and Doherty[25] introduced a set of transformed composition variables:

$$X_i = \frac{(x_i/\nu_i - x_k/\nu_k)}{(\nu_k - \nu_T x_k)} \qquad i = 1, ..., c; \quad i \neq k \qquad (8)$$

$$Y_i = \frac{(y_i/\nu_i - y_k/\nu_k)}{(\nu_k - \nu_T y_k)} \qquad i = 1, ..., c; \quad i \neq k \qquad (9)$$

where ν_i is the stoichiometric coefficient of component i in the reaction, the subscript k is the reference component,

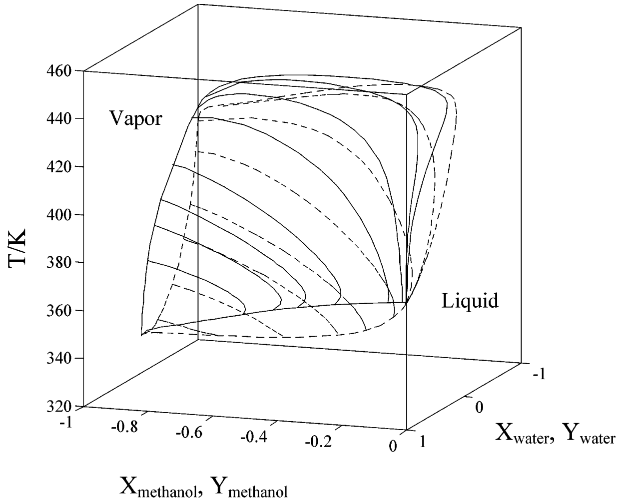

Figure 2. Calculated surfaces for the transformed compositions of the liquid (- - -) and vapor (—) phases of water and methanol.

and ν_T is defined as

$$\nu_T = \sum_{i=1}^{c} \nu_i \tag{10}$$

The calculation of the transformed composition variables was carried out by taking methyl lactate as the reference component. Two constraints for these new composition variables should be satisfied,

$$-X_1 + X_2 - X_4 = 1 \tag{11}$$

$$-Y_1 + Y_2 - Y_4 = 1 \tag{12}$$

By using the transformed composition variables the condition for a reactive azeotrope can be expressed as[25]

$$X_i = Y_i \tag{13}$$

Figure 2 shows a plot of the reactive surfaces calculated by using the transformed molar fractions. It is clear from this figure that the two surfaces do not have a common tangent plane, which means that reactive azeotropy does not occur for this particular system. This result meets the conditions, regarding relative volatility, established by Barbosa and Doherty[3] for reactive azeotropy. In this case the volatility of both products (water and methyl lactate) lies between the volatility of the reactants.

Conclusions

The VLE quaternary reactive system methanol + water + methyl lactate + lactic acid has been experimentally determined. This is a complex system, not only because it is formed by four components but also because it is a reactive system. UNIQUAC proved to be a good model for description of this system where phase and chemical equilibrium had to be taken into account simultaneously. Six of the twelve parameters needed in the UNIQUAC equation were obtained independently from binary nonreactive mixtures; this way, only the remaining six parameters needed to be obtained directly from the correlation of the quaternary system. The parameters of the quaternary system allowed us to calculate the VLE of the binary reactive mixtures that were difficult to measure experimentally because of the tendency of the reaction to take place to some extent. This calculation showed a minimum-boiling azeotrope for the system water + methyl lactate at high water composition. No azeotrope was observed for the quaternary reactive system.

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