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Vapor−Liquid Equilibria in the Systems Ethyl Lactate + Ethanol and Ethyl Lactate + Water

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A simple vapor−liquid equilibrium (VLE) apparatus has been constructed to successfully measure the VLE of binary ethyl lactate systems that have relatively high differences in volatility ($P_2^{sat}/P_1^{sat} \sim 7.0$). Degassing is done in situ, reducing the experimental time considerably. Isothermal VLE of the ethyl lactate + ethanol system was measured at (40.0, 60.1, and 80.2) °C, and the isothermal VLE of the ethyl lactate + water system was measured at (40.0 and 60.0) °C. The ethyl lactate + ethanol system is slightly nonideal, and the ethyl lactate + water system forms a minimum boiling azeotrope. Isothermal data for ethanol + water were measured at 40.0 °C to demonstrate reliability of the apparatus.

Introduction

Interest in lactate esters is increasing due to emphasis on environmentally friendly solvents from bio-derived sources. Lactate esters (primarily ethyl lactate) have excellent solvent properties and low toxicity and are candidates to replace many halogenated solvents including ozone-depleting CFCs, carcinogenic methylene chloride, toxic ethylene glycol ethers, and chloroform.[1] Lactate esters such as ethyl lactate have the ability to dissolve a wide range of chemicals. They can be used to remove greases, silicone oils, and adhesives in cleaning a variety of metal surfaces for fabrication and coating applications. Because ethyl lactate exists in beer, wine, and soy products, it has been approved by the FDA for use in food industries for many years.

Despite their numerous attractive advantages, the production volume of lactate esters used has been small in industry. Traditional batch processing is expensive compared to the potential for continuous processing. New technologies have been developed to yield lactate esters from carbohydrate feedstocks via esterification using reactive distillation or pervaporation membranes.[2,3]

Esterification usually requires distillation to purify the esters. For column designs and process simulation, thermodynamic properties such as reliable vapor−liquid equilibrium (VLE) data of the related components are valuable. Recently, phase equilibrium of the methyl lactate system has been studied, and VLE of some lactate esters with their associated alcohols at 101.33 kPa were made available.[4,5] However, no information for the ethyl lactate + water system has been found in the existing literature. This work presents the equilibrium $P-x-y$ data of the ethyl lactate + ethanol and ethyl lactate + water systems. We have chosen to collect $P-x-y$ data isothermally because the temperature can be kept low where the reactive system ethyl lactate + water is kinetically more stable.

Experimental Details

Chemicals. Ethyl (*S*)-(−)-lactate 98 % and ethyl alcohol (200 proof) were purchased from Sigma Aldrich. Water (HPLC grade) was obtained from J. T. Baker, Inc. Water and ethyl alcohol were used as received. Ethyl lactate was further purified by vacuum distillation. Only 85−90 % of the pre-distilled volume was collected for the VLE experiments. Both the first overhead fraction (5−10 %) and the reboiler residue (5 %) were discarded. No detectable water or ethanol remained in the ethyl lactate after distillation as determined using gas chromatography (GC). The GC procedure will be described in the analytical method section.

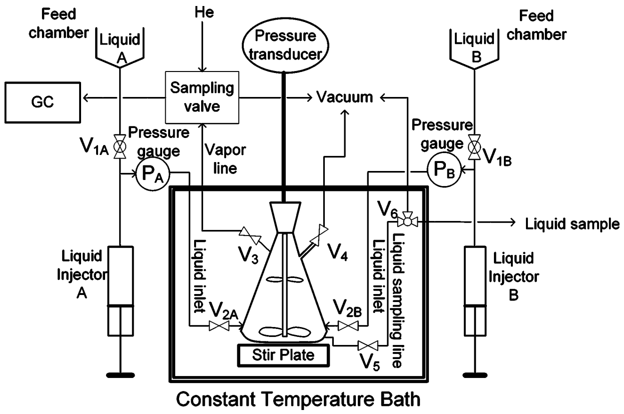

Figure 1. Schematic of the apparatus.

Apparatus. A $P-x-y$ apparatus was constructed for VLE measurements of binary systems from ambient temperature to 353 K (Figure 1). The apparatus is based on the design of similar equipment described in the literature.[6] The apparatus has three main sections: an equilibration section, a feed section, and a sampling section.

(a) Equilibrium Chamber and Isothermal Bath. A modified 125 mL Erlenmeyer flask was used as an equilibrium cell. The cell was placed on a submersible stir plate immersed in the isothermal water bath. Temperature was maintained by a PolyScience series 730 circulator. To minimize water bath evaporation, approximately 1 in. of mineral oil was added to the bath to cover the water's surface when conducting experiments at 80 °C. The bath had fluctuations less than ± 0.01 °C at 40 °C and below, but the variation was ± 0.05 °C at (60 and

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80) °C. Temperature was measured using a thermometer calibrated against a NIST traceable thermometer; the accuracy was better than ± 0.001 °C. Pressure inside the cell was measured using a MKS Baratron model PDR 2000 dual capacitance diaphragm absolute pressure gauge. The pressure gauge provides reliable values between 0.13 and 133 kPa with the resolution of 0.013 kPa and an accuracy of 0.25 % of the reported reading.

The cell was connected to the feed and gas sampling systems using 1/16 in. o.d. 316 stainless steel tubing sealed to the chamber using ACE glass Teflon adapters (Catalog No. 5801-07) and connectors (Catalog Nos. 5854-07 and 5824-24). The Baratron gauge was attached to the top of the cell using a length of glass tubing with a tapered ground glass joint to provide a vacuum tight connection. The Baratron and glass were joined using a Cajon union (SS-4-UT-6).

The liquid and vapor phases were both stirred. Two different vapor-phase stirrer configurations were used in the course of this work. In the first configuration, a vertical length of 1/8 in. stainless steel rod was used to support the vapor-phase agitator. The rod was placed vertically in the center of the equilibrium cell; the bottom end was soldered to a small clip mounted onto a magnetic stir bar. At the middle of the vertical rod, two small arms were created by soldering a wire to the rod. Teflon plumbing tape (1/2 in. × 1 in. × 0.04 in.) was wrapped around the arms to create the agitator. The bar and Teflon tape provided the means of mixing for the liquid and vapor phases simultaneously. However, when the apparatus was modified by adding a liquid-phase sampling section, the equilibrium chamber had to be placed 3/4 in. above the submersible stir plate. Consequently, the magnetic field was considerably reduced, the bottom of the flask was no longer flat, and the vapor stirrer did not work reliably. Thin polypropylene strips (0.06 in. × 3 in. × 0.04 in.) were wrapped around the center of the magnetic stir bar, and small supports were fabricated from Teflon sheet.

(b) Feed Section. Two 125 mL flasks and two liquid injectors were connected using 1/4 in. o.d. polypropylene and 316 stainless steel tubing and Swagelok adapters. Polypropylene tubing provided flexibility for the connection between glass (feed chambers) and stainless steel valves (V_{1A}, V_{1B}) and permitted observation of the liquid level in the feed section. The length of polypropylene tubing was minimized to limit permeability of air from the environment. The flasks were mounted 3 ft above the injectors, providing a hydrostatic head to load the injectors with liquids from the flasks when valves V_{1A} and V_{1B} were opened (Figure 1). The liquid injectors were 30 mL calibrated pumps (High-Pressure Equipment Company 62-6-10) used to meter liquids to the equilibrium cell with the accuracy of ± 0.003 mL of the injected volume. Pressure of the liquids inside the injectors was monitored using inexpensive pressure gauges.

(c) Liquid-Phase Sampling. Degassing of the liquids in the feed section (flasks and injectors) was tedious. However, we found that the liquids could be degassed reliably within the equilibration chamber. Complete degassing was easy to identify by a reliable stable pressure in the chamber after repeatedly pulling the pressure down about 1 kPa. Because of the expected minor shift in composition during degassing after liquids were charged to the equilibrium chamber, a liquid sampling section was added to the apparatus. This modification was done for the ethyl lactate + water system, reducing considerably the experimental time. High vacuum needle valves, purchased from Chemglass (CG-553-02, CG-534-02) were connected by a 4 in. length of 1/4 in. o.d. glass tubing. To take a liquid sample, valve V_6 was first opened to permit evacuation of the sample region. Then valve V_6 was closed before valve V_5 was cracked opened for 10 s to collect approximately 0.2 mL of liquid from the equilibrium cell. No fluctuation in pressure of the equilibration cell was noted when valve V_5 was opened. After sample collection, valve V_5 was closed entirely and valve V_6 was opened fully to permit a narrow Teflon tube connected to a syringe to be inserted for withdrawal of most of the liquid sample. To remove all residual traces of liquid, acetone was added through V_6 and then removed via the syringe apparatus. Any remaining acetone was evaporated under vacuum while the cell was undergoing the next equilibration.

(d) Vapor Phase Sampling. The vapor sample system was based on a Valco six-port switching valve (00V-1375V) positioned immediately above the water bath, approximately 8 in. from the equilibrium cell. A high-temperature rotor (SSAC6WE, 225 °C) and preload nut (PLAW30) were chosen as part of the valve assembly. The vapor line was 1/16 in. stainless steel with a 1/16 in. stainless steel valve. The vacuum line was a 6 in. length of 1/16 in. stainless steel connected to a 1/16 in. valve and adapted to vacuum tubing. The He carrier gas entered through 1/16 in. stainless tubing connected to the outlet of the gas chromatography (GC) injector, and 1/16 in. stainless tubing was used to return the sample to the GC oven where it was fed onto the column. The GC was placed as close as practical to the apparatus, using about 24 in. of tubing between the GC and the sample valve. A 1.8 mL sample loop was created by adapting a coiled length of 1/4 in. tubing to the Valco ports. Each vapor sample was equivalent to about 0.3 μL of the related liquid mixture directly injected into the GC. To avoid condensation of the high boiling components, the vapor line was heat-traced and maintained 15−20 °C above the temperature of the equilibrium cell. To collect a vapor-phase sample, the sample loop was evacuated by placing the valve in the "load" position with the vapor line valve V_3 closed and the vacuum valve V_{vc} opened; then the valve V_{vc} was closed, and the vapor line valve was opened. The loading was done within 1 min, and then the valve V_3 was closed and the sampling valve was switched quickly to the "inject" position. No pressure drop in the equilibrium cell was observed during the course of vapor sampling, since the volume of vapor sample was small as compared to the volume of the chamber. Additional details on the vapor and liquid sampling configurations are available from the corresponding author.

Experimental Procedure. A Sargent−Welch two-stage vacuum pump (model 1400) was used to evacuate the apparatus and sample sections and to provide degassing of liquids. Prior to the experiment, the entire system was evacuated and checked for the leaks. A stable base pressure of 0.07−0.09 kPa for 3−4 h indicated that the chamber was leak tight. Liquids were degassed before they were loaded into the injectors. During the degassing process, fluids in the flasks were shaken and tested using the click test for degassing as described by Van Ness and Abbott[7] and Campbell and Bhethanabotla.[8]

When performing experiments where the liquid composition was determined from the quantities of liquids injected, the following tests supplemented the click test to verify complete degassing in the feed lines and injectors and to verify a leak-tight feed section: (1) Pressure of fully loaded injectors with degassed liquids observed from gauges P_A and P_B had to be steady and equal to the vapor pressure of liquids. If the pump A (or B) was operated while V_{1A} (or V_{1B}) was opened and V_{2A} (or V_{2B}) was closed, the displacement of liquid level in the polypropylene feed line had to be proportional to the displacement inside the injector. (2) If the V_{1A} (or V_{1B}) and V_{2A} (or V_{2B}) were closed, the pressure of the injector A (or B) had to increase instantaneously when the pump started to compress the liquid inside that injector.

To inject liquid A (or B) to the equilibrium cell, pressure P_A (or P_B) was raised to approximately 0.3 MPa before valve V_{2A} (or V_{2B}) was opened. After the pressure of the injector dropped, the valve was closed, the injector pressure was restored, and the injected volume was recorded.

To carry out the experiment, 10−20 mL of component 1 of the studied binary system was charged to the equilibrium cell. After the vapor pressure of this pure liquid was measured, a predetermined quantity of the component 2 was added to the cell. After equilibration, vapor and liquid samples were collected. These steps were continued until the liquid mole fraction of component 1 approached 0.1. Afterward, the equilibrium chamber was emptied; the entire system was cleaned and degassed thoroughly. Then, the process was reversed, charging the equilibrium cell first with component 2 and then adding component 1.

The volume of the initial charge in the experiments with the ethyl lactate + ethanol system was selected to ensure that error in calculation of liquid compositions from the injected volume would be negligible. For the ethyl lactate + water system, 5 mL of liquid inside the equilibrium chamber was found to be sufficiently large to ensure accurate composition measurements, because the volumes of liquid injections were not critical with the liquid sampling section in place. Both liquid and vapor of the studied binary mixture were well-mixed and were allowed to reach equilibrium before any measurement was performed. Equilibration was identified by the consistency of the equilibrium pressure reading from the Baratron following vapor withdrawals using vacuum and by the reproducibility of the equilibrium vapor-phase composition.

Analytical Methods. Liquid compositions in the ethanol + water and ethyl lactate + ethanol mixtures were calculated from the known volume of each component charged to the cell. For ethyl lactate + water, samples of the liquid phase were taken via the liquid sampling section, and the compositions were determined from GC analysis. Vapor samples of the studied binary mixtures were injected to the gas chromatograph using the vapor sample valve.

The GOW-MAC 350 gas chromatograph was operated under isothermal conditions using a carrier stream of helium at 35 mL/min. The column temperature was 220 °C in experiments involving ethyl lactate, but it was reduced to 150 °C for the ethanol + water system. A thermoconductivity detector was set at 290 °C and 110 mA filament current. The column packing used was Poropak Q 50/80, packed in 6 ft long × 1/8 in. o.d. × 0.085 in. wall stainless steel tubing. To ensure that all vapor samples were analyzed in the column without loss via condensation, 1 ft of 1/16 in. o.d. 316 stainless steel tubing was added to the column and used as a precolumn heater within the GC oven.

Calibrations of known compositions of mixtures were done for each binary system to obtain the correlation between the ratio of GC peak areas and the mixture compositions. From the calibration, the unknown compositions of the injected samples were determined. The amounts of each component in the calibrated mixtures were weighed using an electronic balance with its readability of 0.1 mg. The standard mixtures were prepared gravimetrically in an approximate size of 1.0 ± 0.3 mg; therefore, the deviation in calculation of molar compositions was negligible. To reduce the error due to the possible evaporation of the more volatile component, two duplicate mixtures were prepared for each calibration point. Three GC injections were done for every data point, in both calibration and sample analyses. The difference in the ratio of peak areas of the triplicate GC injections was less than ± 0.05 % of the calculated value.

Table 1. VLE Data for Ethanol (1) + Water (2) at 40.0 °C

$P^{40.0}$/kPa	$x_1^{40.0}$	$y_1^{40.0}$	$P^{40.0}$/kPa	$x_1^{40.0}$	$y_1^{40.0}$
7.41	0	0	14.25	0.158	0.541
7.83	0.005	0.036	14.93	0.201	0.573
8.08	0.007	0.069	15.51	0.256	0.598
8.27	0.010	0.096	15.79	0.319	0.612
8.55	0.014	0.133	16.37	0.418	0.655
8.97	0.020	0.181	16.57	0.448	0.66
9.32	0.026	0.221	16.96	0.518	0.697
9.85	0.035	0.269	17.21	0.583	0.730
10.64	0.050	0.332	17.51	0.682	0.767
11.72	0.075	0.407	17.71	0.748	0.805
12.17	0.085	0.421	17.81	0.828	0.841
13.01	0.108	0.478	17.95	0.892	0.893
13.12	0.111	0.474	18.00	0.943	0.960
13.77	0.136	0.519	18.00	1.000	1.000

Results and Discussion

Ethanol + Water System. Isothermal VLE data for the ethanol + water system at 40.0 °C were collected and compared to literature data for validation of reliability of the constructed VLE apparatus (Table 1). The ethanol + water system was chosen to study because its components are in the system of interest, and 40.0 °C isothermal literature data are available from two independent sources. Both literature and experimental data were regressed using the Britt-Luecke algorithm, maximum-likelihood principle, provided by ASPEN PLUS 12.1. The area test of Redlich−Kister and point-to-point test of Van Ness and Fredenslund were used to check for data reliability.[9−11] The data are considered to pass the area test if the difference between the positive and negative areas is less than 10 %. However, to pass the point-to-point test, the absolute mean deviation between the calculated and experimental vapor compositions should be ≤ 0.01.

UNIQUAC with the Hayden and O'Connell (HOC) virial coefficient correlation were used to evaluate thermodynamic consistency. The point-to-point test value was 0.011, significantly smaller than that of 0.063 from Udovenko and Fatkulina[12] and 0.248 from Mertl.[13] In the available literature, these are the only isothermal VLE data that can be found for the ethanol + water system at 40.0 °C. Neither data from Udovenko and Fatkulina nor this work passed the area test, but the value of 10.40 %, which is obtained from this work, is smaller than Udovenko and Fatkulina's value and close to the accepted value. The smoothness of the $P-x-y$ curve in Figure 2 and results from the thermodynamic consistency tests show that the VLE data of ethanol + water from this work are very reliable and more consistent than existing literature data at 40 °C.

Ethyl Lactate + Ethanol System. VLE were measured at (40.0, 60.1, and 80.2) °C for this system (Table 2). To minimize the effects of any systematic errors in particular run, the VLE experiments were performed at least five times using different increments and decrements of each component molar fraction at the reported temperature. All the activity coefficient models listed in Table 3 provide similar correlation of experimental data. The value of α used in the NRTL-HOC equation is 0.3. Figure 3 shows the representation of the UNIQUAC with the HOC correlation. The same nonlinear regression method and

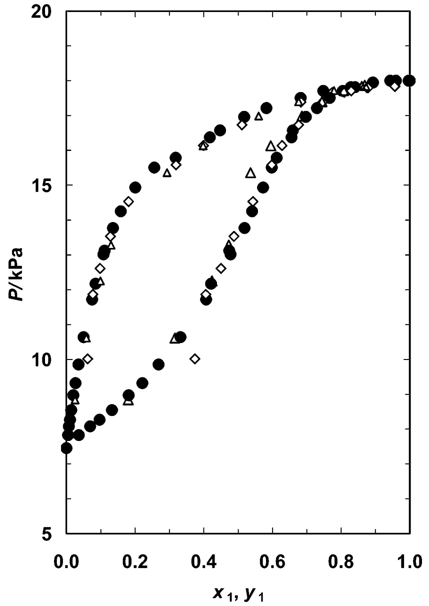

Figure 2. *P*−*x*−*y* of ethanol (1) + water (2) at 40.0 °C: ●, this work; △, Udovenko and Fatkulina,[12] and ◇, Mertl.[13]

consistency tests were used as described. For the HOC method, the η values were assumed to be 1.3 for ethyl lactate + ethanol and 0.53 for ethyl lactate with itself. These values were based on the assumption that solvation of ethyl lactate would be similar to that of ethyl acetate in ethyl acetate + ethanol mixture and that ethyl lactate pure self-interactions would be similar to ethyl acetate pure self-interactions. It should be noted that the calculated vapor fugacity coefficient of ethyl lactate is in the range of 0.990 to 0.998 and that for ethanol is from 0.993 to 0.999 at the system pressure.

Data are combined from at least five different runs for each reported temperature as described. All *P*−*x*−*y* diagrams are smooth and do not exhibit any trends of systematic error within specific runs. All experimental data satisfied the point-to-point test, but only data at 40.0 °C passed the area test. The area test results were 31 % and 19 % for data at (60.1 and 80.2) °C, respectively. The inconsistency could be due to the error in measuring the vapor phase at low concentration of ethyl lactate where the GC detection was limited. Another potential source of error could be minor decomposition of the ethyl lactate in the GC detector during vapor-phase analysis. It was noted during runs that the outlet lines of the thermal conductivity detector gradually became restricted due to deposits over a period of

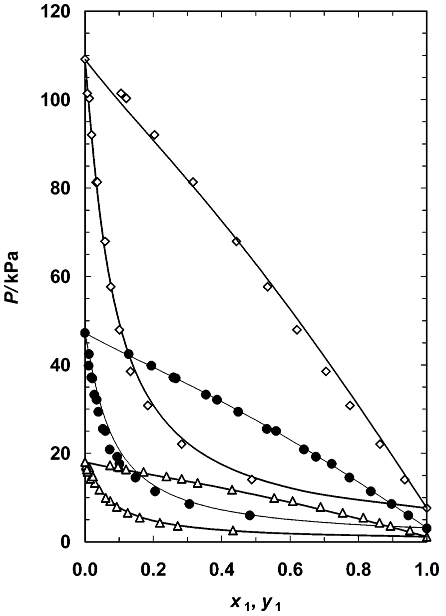

Figure 3. *P*−*x*−*y* of ethyl lactate (1) + ethanol (2) system: △, 40.0 °C; ●, 60.1 °C; ◇, 80.2 °C. Solid lines are the representation of UNIQUAC with HOC correlation.

Table 2. VLE Data for Ethyl Lactate (1) + Ethanol (2) Systems at (40.0, 60.1, and 80.2) °C

$P^{40.0}$/kPa	$x_1^{40.0}$	$y_1^{40.0}$	$P^{60.1}$/kPa	$x_1^{60.1}$	$y_1^{60.1}$	$P^{80.2}$/kPa	$x_1^{80.2}$	$y_1^{80.2}$
1.12	1.000	1.000						
2.57	0.951	0.433	3.03	1.000	1.000			
3.59	0.893	0.271	5.97	0.946	0.482			
4.28	0.862	0.219	8.55	0.897	0.306			
5.45	0.814	0.160	11.41	0.836	0.205			
6.55	0.754	0.125	14.51	0.774	0.148	7.63	1.000	1.000
7.91	0.689	0.093	17.64	0.722	0.101	14.08	0.935	0.488
9.21	0.608	0.074	19.24	0.675	0.095	22.08	0.863	0.283
9.92	0.554	0.061	20.86	0.641	0.073	30.82	0.775	0.184
11.76	0.430	0.042	25.05	0.559	0.060	38.54	0.705	0.133
13.31	0.329	0.029	25.52	0.532	0.052	47.94	0.620	0.101
14.23	0.283	0.015	29.38	0.448	0.039	57.66	0.534	0.075
14.76	0.239	0.024	32.10	0.386	0.034	67.94	0.443	0.059
15.81	0.172	0.008	33.26	0.354	0.027	81.30	0.316	0.032
16.81	0.102	0.012	36.97	0.266	0.022	81.37	0.316	0.036
16.99	0.097	0.004	37.17	0.259	0.019	92.05	0.203	0.020
17.31	0.073	0.003	39.81	0.195	0.011	100.31	0.121	0.013
16.37	0.120	0.006	42.46	0.128	0.012	101.42	0.106	0.007
18.01	0.000	0.000	47.21	0.000	0.000	109.12	0.000	0.000

Table 3. Binary Parameters of Ethyl Lactate (1) + Ethanol (2) System and Average Absolute Percent Deviation (%) for Equilibrium Pressure (*P*) and Vapor-Phase Mole Fractions (y_1, y_2)[a]

		binary parameters		average absolute percent deviation		
equation		b_{12}/K	b_{21}/K	*P*/%	y_1/%	y_2/%
UNIQUAC-IG	$\tau_{ij} = \exp(b_{ij}/T)$	−43.00	−23.10	3.3	23.2	1.5
UNIQUAC-HOC	$\tau_{ij} = \exp(b_{ij}/T)$	−40.03	−29.40	3.1	24.7	1.4
NRTL-HOC	$G_{ij} = \exp(-\ 0.3b_{ij}/T)$	−298.69	585.62	3.8	24.8	1.5
Van Laar-HOC	$A_{ij} = b_{ij}/T$	169.19	65.21	3.3	24.7	1.5
WILSON-HOC	$\Lambda_{ij} = \exp(b_{ij}/T),\ V_i/V_j = 1$	−198.48	71.55	3.7	24.8	1.5

[a] The vapor-phase Hayden−O'Connell parameters are given in the text.

Table 4. VLE Data for Ethyl Lactate (1) + Water (2) System at (40.0 and 60.0) °C

$P^{40.0}$/kPa	$x_1^{40.0}$	$y_1^{40.0}$	$P^{60.0}$/kPa	$x_1^{60.0}$	$y_1^{60.0}$
			3.03	1.000	1.000
			4.91	0.973	0.594
			6.01	0.949	0.457
1.12	1.000	1.000	7.04	0.938	0.405
1.23	0.994	0.941	7.83	0.912	0.351
1.44	0.985	0.811	9.04	0.892	0.319
1.63	0.975	0.722	8.53	0.891	0.315
1.76	0.970	0.661	10.44	0.856	0.280
1.87	0.964	0.626	11.56	0.808	0.222
2.00	0.958	0.584	13.21	0.763	0.198
2.12	0.952	0.560	14.72	0.694	0.152
2.28	0.945	0.500	16.03	0.638	0.135
2.44	0.935	0.474	16.97	0.568	0.115
3.05	0.903	0.388	18.01	0.518	0.089
3.25	0.874	0.361	18.40	0.488	0.094
3.93	0.834	0.272	19.04	0.446	0.092
4.56	0.770	0.240	19.55	0.399	0.078
5.20	0.699	0.197	20.01	0.328	0.078
6.07	0.620	0.153	20.40	0.248	0.071
7.01	0.502	0.111	20.57	0.248	0.066
7.27	0.433	0.103	20.61	0.197	0.059
7.47	0.374	0.073	20.70	0.187	0.059
7.48	0.367	0.094	20.70	0.146	0.055
7.56	0.300	0.068	20.72	0.106	0.052
7.48	0.252	0.087	20.69	0.070	0.049
7.64	0.225	0.061	20.68	0.042	0.044
7.67	0.171	0.050	20.41	0.027	0.033
7.61	0.137	0.085	20.48	0.023	0.032
7.65	0.124	0.046	20.56	0.022	0.027
7.61	0.073	0.039	20.33	0.012	0.012
7.49	0.025	0.015	20.15	0.005	0.005
7.47	0.000	0.000	20.01	0.000	0.000

several hours. The lines were kept clear using a syringe cleaning wire, but this method did not allow determination of the extent of decomposition. Plugging of lines was not noted on the GC used to analyze the liquid samples. Additional experimental runs were consistent with each other, as compiled in the tables and figures, and did not improve the results of the consistency tests.

The prediction of isobaric VLE data of ethyl lactate + ethanol at 101.33 kPa using the binary parameters obtained from the reported data are in good agreement with Peña-Tejedor et al.[14] For the ethyl lactate + water system at 40.0 °C, with Peña-Tejedor's binary parameters, the activity coefficients at infinite dilution of ethanol and ethyl lactate are predicted to be 1.38 and 1.35, respectively, using the UNIQUAC-HOC model. From this work, these values are 1.25 and 1.67, respectively. Similar results were obtained for the data at (60.1 and 80.2) °C.

The $P-x$ bubble line is nearly linear, and the infinite dilution activity coefficients are not large. The ethyl lactate + ethanol system thus can be considered slightly nonideal. This is due to the presence of the hydroxyl group in ethyl lactate, such that the interaction between ethyl lactate molecules is similar to their interaction with the ethanol molecule.

Ethyl Lactate + Water System. VLE at (40.0 and 60.0) °C were measured for the ethyl lactate + water binary system (Table 4). Ethyl lactate was hydrolyzed significantly at 80 °C, as verified by the presence of ethanol in GC analyses. Hydrolysis was not detected in the experiments performed at (40.0 and 60.0) °C. The VLE experiments at each listed temperature were performed five times; the same methods as described for the ethyl lactate + ethanol system were used. Figure 4 shows that the system has a minimum boiling azeotrope, occurring at 5−7 mol % ethyl lactate. Due to the narrow phase envelope at high water concentrations, it was not possible to determine the exact azeotrope composition using gas chromatography, even though the analysis was very reproducible.

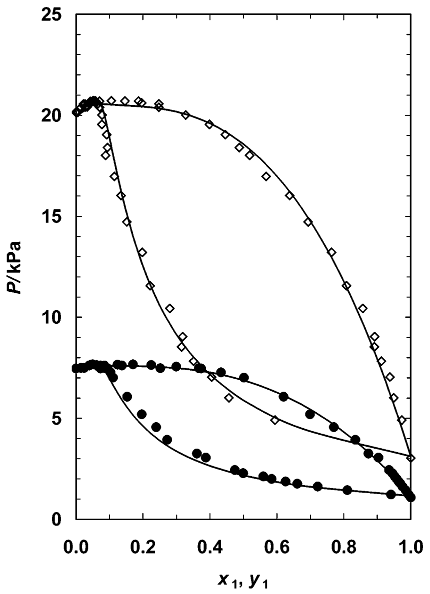

Figure 4. $P-x-y$ of ethyl lactate (1) + water (2) system: ●, 40.0 °C; ◊, 60.0 °C. Solid lines are the representation of UNIQUAC with HOC correlation.

The data are fitted with several thermodynamic models, and the binary parameters determined are listed in Table 5. All of the selected activity models fit the data equally well; the deviations are given in Table 5. The HOC η value of 1.3 was used for ethyl lactate with water (based on the literature value for ethyl acetate + water), and the same method as described above was applied for data regression. The azeotrope composition is predicted to be at 6.5−6.7 mol % ethyl lactate, based on the UNIQUAC-HOC fit.

The data satisfy the area test but are less satisfactory when analyzed via the point-to-point test. The values of 8.6 % and 0.04 for area and point-to-point tests, respectively, were obtained for the VLE data at 40.0 °C. Likewise, the values for data at 60.0 °C were 4.6 % and 0.037. Because the point-to-point test is more significant for isothermal VLE than the area test, the data were carefully reevaluated, including the regression used to generate the GC calibration curve. It was found that the difference in calculation of phase compositions using different

Table 5. Binary Parameters of Ethyl Lactate (1) + Water (2) System and Average Absolute Percent Deviation (%) for Equilibrium Pressure (*P*) and Vapor-Phase Mole Fractions (y_1, y_2)[a]

equation		binary parameters		average absolute percent deviation		
		b_{12}/K	b_{21}/K	P/%	y_1/%	y_2/%
UNIQUAC-IG	$\tau_{ij} = \exp(b_{ij}/T)$	250.51	−133.02	2.4	22.0	4.1
UNIQUAC-HOC	$\tau_{ij} = \exp(b_{ij}/T)$	248.19	−131.44	2.4	22.2	4.1
NRTL-HOC	$G_{ij} = \exp(-0.3b_{ij}/T)$	−87.07	967.20	3.4	21.6	3.8
Van Laar-HOC	$A_{ij} = b_{ij}/T$	895.05	307.06	3.4	21.4	4.2
Wilson-HOC	$\Lambda_{ij} = \exp(b_{ij}/T)$, $V_i/V_j = 1$	−978.35	−51.56	2.1	22.9	5.0

[a] The vapor-phase Hayden−O'Connell parameters are given in the text.

representations of the GC calibration curve is negligible. However, the consistency tests are very sensitive to a small change in vapor phase composition. For example, if data point at $P = 1.2$ kPa in Table 4 is omitted, the value of the point-to-point test changes from 0.04 to 0.026. We have also evaluated point-to-point consistency using Legendre polynomials[11] and the Modified Margules[15] method to represent the excess Gibbs energy, but the differences between the calculated and measured values in vapor composition are also larger than the target of 0.01. Consistency failure due to inadequacy of the HOC method is unlikely because the vapor fugacity coefficients are near 0.989 and 0.993 across the composition range for ethyl lactate and water, respectively. Additional experimental runs were consistent with each other as shown in the tables and figures and did not improve the consistency test results.

Fitting of the ethyl lactate + water system is challenging because the infinite dilution activity coefficients are large. These coefficients are 17.7 for ethyl lactate and 2.8 for water from UNIQUAC-HOC in ASPEN 12.1. The UNIQUAC-HOC fails to represent the vapor phase accurately at 40.0 °C and fails to represent the pressure maximum accurately at 60.0 °C, as shown in Figure 4.

The vapor-phase analysis in this system may be subject to the same potential decomposition of ethyl lactate as mentioned earlier. Degradation was more noticeable in this system than in the ethyl lactate + ethanol system.

Summary and Conclusions

This work presents a simple design of an isothermal VLE apparatus that is capable of measuring the vapor pressure of single components down to about 0.7 kPa and the VLE of nonideal binary systems. The $P-x-y$ apparatus is valuable for collecting data at low temperature, where reactive chemicals are kinetically more stable. With the liquid sampling section and the ability to perform the degassing in situ, the apparatus can be extended to multicomponent systems. Data have been evaluated with standard consistency tests, and all data sets passed or nearly passed at least one of the standard tests.

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