588 *J. Chem. Eng. Data* **2008,** *53,* 588–590

Biodegradable Polymer-Phase Behavior: Liquid–Liquid Equilibrium of Ethyl Lactate and Poly(Lactic Acid)

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Liquid–liquid equilibrium data of ethyl lactate and poly(lactic acid) binary mixtures were measured at 0.1 MPa nominal pressure in the temperature range from (260 to 265) K. Cloud-point temperatures were measured using a dynamic method with visual detection of phase transitions (naked-eye determination of turbidity). This system exhibits an upper critical solution temperature (UCST) at $T_c = 265.1$ K and $w_{PLA,c} = 0.03776$. The experimental data were modeled with the PC-SAFT equation of state, and new parameters for both compounds within the PC-SAFT frame are provided. The model correlates well with the observed experimental data.

Introduction

The use of long-lasting materials for short time applications is inexcusable. For instance, food packaging and transportation in conventional plastic boxes and bags constitutes a critical example of such a baseless societal attitude, one that impacts our daily lives. Thus, the design and development of biodegradable materials from renewable sources, which display the required properties for a specific application, although technically challenging ought to be a priority. Poly(lactic acid), PLA, a biodegradable, aliphatic polyester synthesized from lactic acid which has been used for almost four decades in the medical and pharmaceutical areas is now available at competitive prices for new applications such as, for example, food packaging. Its mechanical and tensile properties are similar to those of conventional polymers, and data on barrier properties of gases and aromas have been published recently in the last couple of years.[1–5]

Although mapping liquid–liquid equilibria (LLE) between these polymers and several solvents is paramount for polymer processing, only a few reports are available in the literature, almost all of them involving ternary liquid mixtures[6] and/or supercritical fluids.[7–10] Lee et al.[11] studied the phase behavior of PLAs of a range of molecular weights and dialkyl (butyl, pentyl, hexyl) phthalates in which they found upper critical solution temperature (UCST)-type phase separation at temperatures from ca. (310 to 430) K. Ethyl lactate, also a biodegradable substance, and an FDA approved aroma, is one of the few liquid solvents that presents partial miscibility with PLA (not too far from ambient conditions). Therefore, it is a good candidate to be used as an environmentally acceptable liquid-phase switch for PLA dissolution/precipitation.

In this work, the liquid–liquid equilibrium data of binary mixtures of ethyl lactate and poly(lactic acid) were measured at 0.1 MPa. The chemical structures of both compounds are illustrated in Figure 1.

Experimental Section

Materials. PLA (CAS 26100-51-6) was supplied by Cargill Dow−Nature Works with a polydispersity of 1.46 and a labeled molecular weight, MW, of 98 980. This PLA presents an L-lactic/D-lactic unit ratio of 82:18. Ethyl lactate (CAS 97-64-3) was supplied by Sigma-Aldrich with a stated purity greater than 98 %. Both chemicals were used without further purification.

Apparatus and Procedures. The cloud-points were measured by a turbidimetry method with naked-eye, visual detection. The experimental apparatus and standard procedures were described elsewhere.[12] PLA solutions with different compositions were prepared by gravimetry using an analytical high-precision balance (± 0.01 mg) (model Precisa 40 SM-200A). The uncertainty in the mass fraction was $\pm 2 \cdot 10^{-5}$. Temperatures were measured with a Pt100-4 wires resistance thermometer connected to a multimeter, Keythley 199 system DMM/Scanner (± 0.001 Ω), providing us with an uncertainty of ± 0.05 K. The overall average uncertainty of the cloud-point temperatures is obviously greater, amounting to about ± 0.15 K. The reported data are the average of two independent measurements for each composition.

Results and Modeling

The liquid–liquid equilibrium experimental data are reported in Table 1 and illustrated in Figure 2. The system exhibits an UCST at $T_c = 265.1$ K and $w_{PLA,c} = 0.03776$. These coordinates of the critical point were calculated using the law of rectilinear diameters (see, for instance, ref 14). First, the experimental data were fitted to a convenient equation (see Table 2). The choice of this empirical equation rests on the very low value of the standard deviation, STD, of the experimental values. Then, the interpolated calculated results from the fitting equation were used to determine the segmental tie-lines and respective medium value (law of rectilinear diameters). The fitting equation parameters are also listed in Table 2.

The perturbed chain-statistical associating fluid theory (PC-SAFT)[13] equation of state was fitted to experimental data. SAFT-based models have long successfully been used for modeling liquid–liquid and vapor–liquid equilibria.[13,15] The PC-SAFT equation is formulated in terms of the residual Helmholtz

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10.1021/je700576k CCC: $40.75

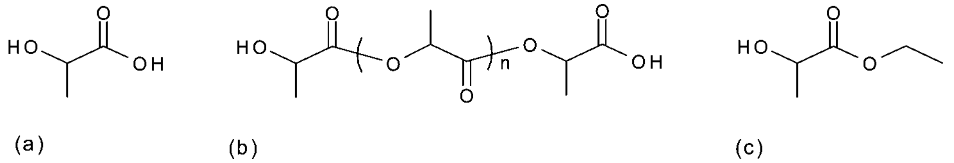

Figure 1. (a) Lactic acid, (b) poly(lactic acid), and (c) ethyl lactate molecular structures.

Table 1. Cloud-Point Temperatures, *T*, of Ethyl Lactate + PLA Mixtures of Different PLA Mass Fractions, w_{PLA}, and Their Uncertainty, δ

w_{PLA}	T/K	δ/K
0.0118	262.3	0.4
0.0185	264.1	0.1
0.0368	264.83	0.05
0.0554	264.6	0.2
0.0679	263.82	0.04
0.0931	260.31	0.04

Table 2. Fitting Equation and Its Parameters and Rectilinear-Diameter Method Results (Calculated Critical Coordinates)[a]

$$T/\text{K} = a + bw_{PLA}^{2,5} + cw_{PLA}^{3} + d(\ln w_{PLA})/w_{PLA}^{2}$$

parameters	a	265.02
	b	3922.17
	c	−18728.59
	d	$8.60 \cdot 10^{-5}$
STD		0.0633
critical constants	$w_{PLA,c}$	0.03776
	T_c/K	265.1

[a] STD is the standard deviation.

Table 3. Pure Component Parameters for Application in the PC-SAFT Equation of State[a]

parameter	PLA	ethyl actate
m	2500	2.937
m/MW	0.0253	0.0249
σ/Å	4.100	3.780
(ϵ/k_B)/K	195.0	322.2
$1 - k_{ij}$	1.0434	

[a] m is the number of segments of the chain; σ is the size of each segment (LJ diameter); ϵ is the energy of the segments; and $(1 - k_{ij})$ is the binary interaction parameter.

energy of the fluid (A^{res}) relative to that of an ideal gas at the same temperature and density. It can be obtained as the sum of independent microscopic contributions

$$A^{res} = A^{hs} + A^{disp} + A^{chain} + A^{assoc} \tag{1}$$

where A^{hs} is the hard-sphere contribution; A^{disp} accounts for the pairwise attractive intermolecular interactions of the reference system; A^{chain} evaluates the free energy due to the formation of a chain from units of the reference system; and A^{assoc} takes into account the contribution due to site–site association. Assuming that ethyl lactate is a nonassociative liquid

$$A^{res} = A^{hs} + A^{disp} + A^{chain} \tag{2}$$

Due to a lack of data, in the present case, both the solvent and the polymer were modeled as nonassociating compounds. Each nonassociating fluid is fully described by three parameters: number of segments, m, segment diameter (size of each segment, LJ diameter), σ, and segment interaction energy, ϵ. A binary interaction parameter $(1 - k_{ij})$ was used to correct for the mixing rule. Table 3 lists the pure component parameters for both PLA and ethyl lactate. The solvent parameters were adjusted to the available density and vapor pressure data of the pure component (five data points), and an absolute average deviation, AAD, of 5.0 % and 0.81 % for the vapor pressure and liquid density, respectively, was obtained. The polymer parameters were fitted, together with $(1- k_{ij})$, to the six liquid–liquid equilibria data points determined in this work. The value of the binary interaction parameter has to be regarded as an *effective* value because the level of model simplicity is high (no association). Nonetheless, despite the fact that association is not explicitly taken into account, the correlation performance of PC-SAFT as depicted in Figure 2 is good, particularly due to the prediction of an UCST-type of phase separation.

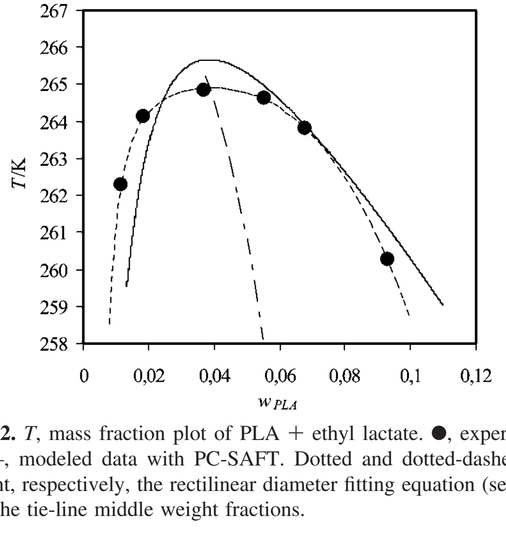

Figure 2. *T*, mass fraction plot of PLA + ethyl lactate. ●, experimental data; —, modeled data with PC-SAFT. Dotted and dotted-dashed lines represent, respectively, the rectilinear diameter fitting equation (see Table 2) and the tie-line middle weight fractions.

In conclusion, ethyl lactate is a good candidate to be used in clean processes involving the extraction and purification of PLA. The currently used (nonassociation) PC-SAFT model is a first step toward a more complete, future description of this complex system.

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Received for review October 5, 2007. Accepted November 27, 2007.

JE700576K