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Phase Behavior of Ethyl Linolenate Isomers in Supercritical Carbon Dioxide

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Abstract

Fundamental thermodynamic data for the α-linolenic acid ethyl ester–carbon dioxide system and the γ-linolenic acid ethyl ester–carbon dioxide system have been obtained under supercritical conditions. Critical loci, phase behavior, and partial molar volume measurements have been undertaken for a limited range of concentrations of both ethyl linolenate isomers. The Peng-Robinson equation of state, while providing acceptable qualitative predictions of system behavior, did not provide reliable quantitative correlations of the experimental data.

INTRODUCTION

Theoretical Background

The partial molar volume of a component represents the change in volume of a system as the number of moles of that component changes. This is represented by

$$\overline{V}_i = \left(\frac{\partial nV}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{1}$$

The molar volume of a mixture is related to the partial molar volumes of the individual components by

$$nV = \sum_{i}^{n} n_i\overline{V}_i \tag{2}$$

It can be seen from this equation that it is possible to decrease the volume occupied by a mixture by adding a component with a negative partial molar volume. The concept of partial molar volume is of significance when predicting phase behavior because it is actually the pressure derivative of the chemical potential, as shown in the following:

$$\mu_i = \left(\frac{\partial nG}{\partial n_i}\right)_{T,P,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} = \frac{\partial}{\partial P}\left(\left(\frac{\partial nG}{\partial n_i}\right)_{T,P,n_j}\right)_{T,n}$$

$$= \frac{\partial}{\partial n_i}\left(\left(\frac{\partial nG}{\partial P}\right)_{T,n}\right)_{T,P,n_j} \tag{3}$$

Now

$$d(nG) = (nV)dP - (nS)dT + \sum (\mu_i dn_i)$$

At constant temperature and composition,

$$\left(\frac{\partial nG}{\partial P}\right)_{T,n} = nV \tag{4}$$

Substituting Eq. (4) into Eq. (3),

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} = \left(\frac{\partial nV}{\partial n_i}\right)_{T,P,n_j} \tag{5}$$

and

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} = \overline{V}_i \tag{6}$$

The ability of an equation of state to accurately represent partial molar volume data is a stringent test as it requires the differentiated form of the equation to be correct (*1*). Should this criterion, in addition to the requirement that solubility data be predicted accurately, be applied in the assessment of an equation of state, then both the first-order and differentiated forms of the equation of state will be tested.

Also, the comparison of simulated chemical potential and partial molar volume at infinite dilution μ_1^∞ and $\overline{V}_1^\infty$, respectively, with experimental measurements can lead to the development of better intermolecular potential models for solvent–solute interactions (*2*).

In order to obtain partial molar volume data experimentally, the relationship between pressure and volume at constant temperature and composition is required. This is illustrated mathematically as follows:

For any partial molar property, M, at constant temperature and pressure, the Gibbs-Duhem equation may be written as

$$\sum x_i d\overline{M}_i = 0 \tag{7}$$

However,

$$M = \sum x_i \overline{M}_i \tag{8}$$

For a binary system, the differentiated form of Eq. (8) gives

$$dM = \overline{M}_1 dx_1 + \overline{M}_2 dx_2 + x_1\, d\overline{M}_1 + x_2 d\overline{M}_2 \tag{9}$$

Substituting Eq. (7) into Eq. (9),

$$dM = \overline{M}_1 dx_1 + \overline{M}_2 dx_2 \tag{10}$$

Multiplying both sides of Eq. (10) by (x_1/dx_2) at constant T and P, and knowing that $dx_1 = -dx_2$:

$$x_1 \left(\frac{\partial M}{\partial x_2}\right)_{T,P} = -x_1\overline{M}_1 + x_1\overline{M}_2$$

From Eq. (8),

$$(1 - x_2) \left(\frac{\partial M}{\partial x_2}\right)_{T,P} = x_2\overline{M}_2 - M + (1 - x_2)\overline{M}_2$$

$$\overline{M}_2 = M + (1 - x_2) \left(\frac{\partial M}{\partial x_2}\right)_{T,P} \tag{11}$$

or

$$\overline{V}_2 = V + (1 - x_2)\left(\frac{\partial V}{\partial x_2}\right)_{T,P} \tag{12}$$

A convenient reference point to use is that of infinite dilution (i.e., as $x_2 \to 0$), and the above equation simplifies to

$$\overline{V}_2^{\infty} = V_1 + \left(\frac{\partial V}{\partial x_2}\right)_{T,P}^{\infty} \tag{13}$$

In the modeling process it is generally difficult to calculate the partial differential in Eq. (12) because accurate volumetric data as a function of composition is difficult to generate. Hence the general approach is to express the partial differential in the pressure explicit form as shown in Eq. (14). The partial molar volume of the solute can then be predicted by using a pressure-explicit equation of state.

$$\left(\frac{\partial V}{\partial x_2}\right)_{T,P} = \frac{-\left(\frac{\partial P}{\partial x_2}\right)_{T,V,n_1}}{\left(\frac{\partial P}{\partial V}\right)_{T,n_1}} \tag{14}$$

EXPERIMENTAL

Apparatus and Procedures for Critical Locus Determination

The objective of initial experiments was to determine the critical loci for the α-ethyl linolenate (AEL) and γ-ethyl linolenate (GEL)–carbon dioxide systems.

The critical locus experiments were performed in a specially designed high pressure test apparatus which incorporated a sight gauge. The apparatus is shown schematically in Fig. 1. This technique for determining the critical point of the binary mixtures involved visual observation of the transition from a two-phase state to a single-phase state, and vice versa. In the studies reported in this paper, the disappearance of the meniscus was rapid, and was usually accompanied by cloudiness or opalescence. In order to determine the critical locus of the two ester–carbon dioxide binary systems, the critical points of the mixtures were determined over a range

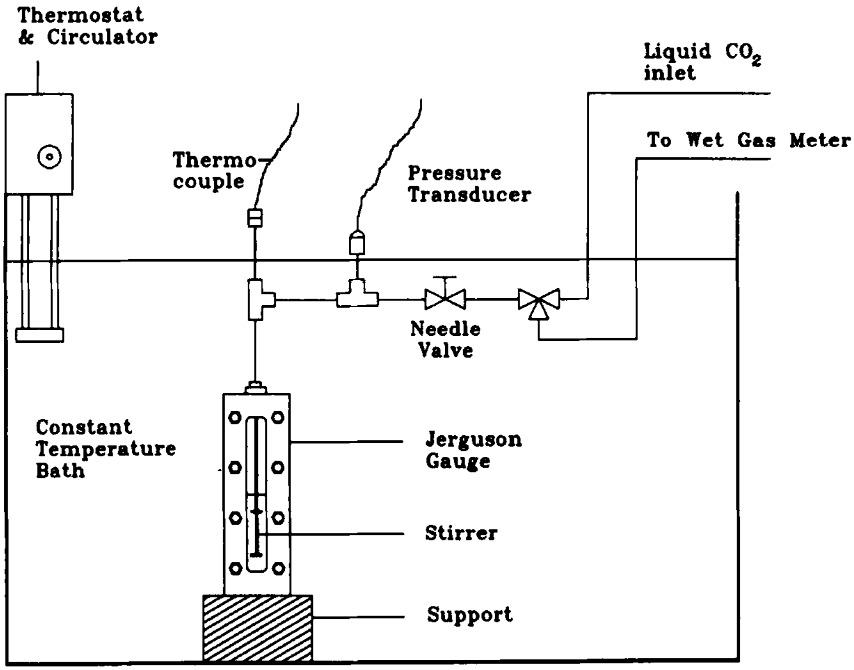

FIG. 1. Equipment setup for critical locus determination.

of compositions. This range was limited by the maximum temperature to which the apparatus could safely be subjected.

The major item of the apparatus was a Jerguson sight gauge rated to 240 bar and 40°C, with a borosilicate glass window on one face. The sight gauge was fitted with a thermocouple and pressure transducer (Druck Model)—the accuracy of the latter was 0.1% full scale. A needle valve was used to seal off the volume inside the sight gauge, thus enabling the volume to be held constant throughout the experiment. A three-way valve mounted external to the apparatus provided access to a wet gas meter or carbon dioxide reservoir. A manually operated magnetic agitator was used to ensure that the contents of the sight gauge were well mixed.

After considerable experimentation, it was found that greater accuracy and reproducibility of critical measurements for this system were obtained by taking each binary mixture into the supercritical region first and determining the conditions at which a meniscus formed upon cooling. Each data point required between 4 to 6 h for an accurate determination.

While the method outlined above was used to determine the actual critical loci for the systems, the phase behavior of both systems was also observed. Each mixture was examined for evidence of immiscibility or other unusual behavior.

APPARATUS AND PROCEDURE FOR PARTIAL MOLAR VOLUME MEASUREMENTS

The relationship between partial molar volume and composition was determined indirectly by using a constant volume apparatus. This apparatus was similar to that used in the critical locus experiments as shown in Fig. 1, the only difference being that the Jerguson sight gauge was replaced with a length of 3/4" o.d. stainless steel tubing. The tube served as the main experimental vessel and occupied over 90% of the internal volume of the rig.

The constant volume apparatus was charged with a solute–solvent mixture of known composition. The system was then raised to the supercritical state. The supercritical mixture contained within the vessel was bled out in small amounts, and the change in pressure as well as the volume of carbon dioxide removed was recorded. As the vessel contents were in the one-phase region, the whole evacuation process was assumed to occur at constant composition.

The amount of ester released at each stage of depressurizing was obtained and the molar density of the system reevaluated. This procedure was carried out at various compositions. The molar volume at each stage was then calculated from the inverse of the calculated molar density. From these results, plots of molar volume against molar composition at the various pressures were obtained. The partial molar volume at each pressure was then obtained by using the relationship defined by Eq. (13).

RESULTS AND DISCUSSION

Critical Locus Experiments

The critical locus of the AEL–CO_2 system was determined for ester concentrations in the range from 0 to 0.73 wt%. Liquid–liquid immiscibility was observed with ester concentrations higher than 0.737 wt%.

For the GEL–CO_2 system, the composition range studied was from 0 to 0.8 wt% ester. At ester concentrations higher than 0.803 wt%, immiscibility was also observed.

Influence of composition on the critical temperature and pressure for the two ethyl linolenate isomers are shown in Figs. 2 and 3, respectively. The projected critical loci for both isomers are illustrated in Fig. 4. The data in Figs. 2 through 4 were correlated with a second degree polynomial.

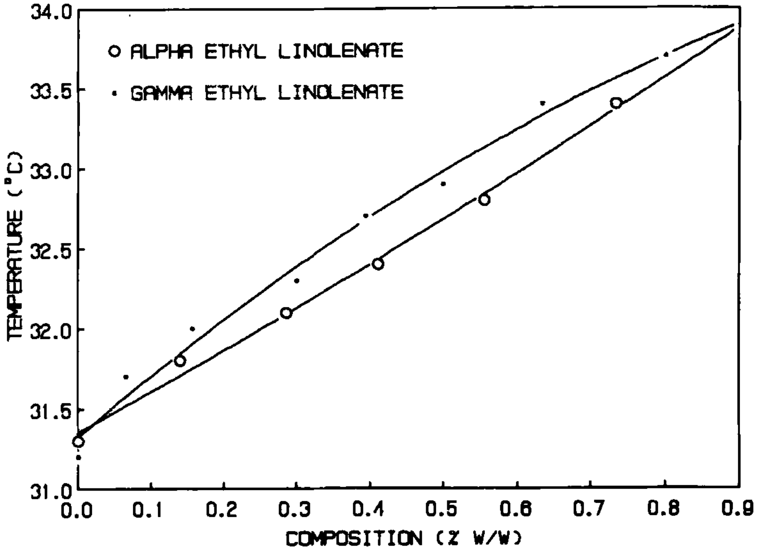

FIG. 2. Temperature–composition curves for the critical locus of the AEL–CO_2 system.

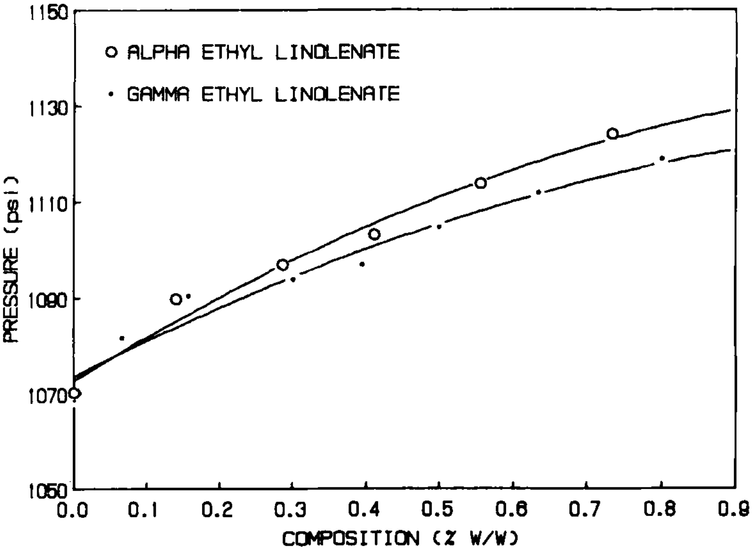

FIG. 3. Pressure–composition curves for the critical locus of the GEL–CO_2 system.

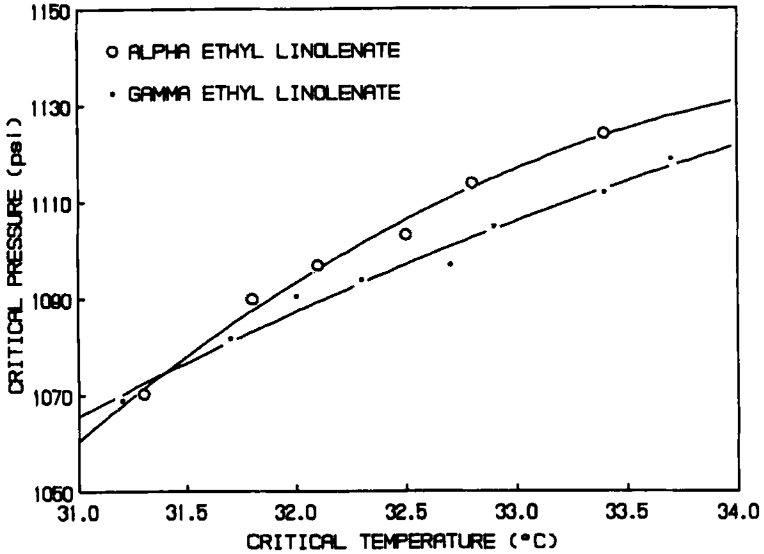

FIG. 4. Projected critical loci for both AEL and GEL.

The accuracy of the method used to determine the critical locus is illustrated by the prediction of critical properties of pure carbon dioxide. The critical pressure and temperature for carbon dioxide were found to be 73.1 atm and 31.0°C, respectively. These values compare favorably with literature values of 72.8 atm and 31.1°C (*3*).

The phase behavior observed was similar for both ester–carbon dioxide systems and corresponded to either Type III or V systems (*4*, *5*), mainly because both phase types exhibit partial immiscibility that extends into the critical region.

Partial Molar Volume

The partial molar volume study was undertaken at 40.6°C. The experimental results were compared with calculated values obtained from the Peng-Robinson Equation of State (P-R EOS) (*6*). In the modeling process, the acentric factor for both esters was estimated to be 0.752. The value of 0.752 is reasonable because the species concerned are long, straight hydrocarbon chains and are expected to be highly nonspherical. The same value was used for both esters because the estimation methods used (*7*) do not take into account the location of the double bonds. The critical temperatures and pressures were estimated from a recently reviewed critical constants estimation procedure (*8*). The normal boiling points for both esters were estimated to be 590.3 K by using the Clausius-Clapeyron relationship as data for the boiling points at various reduced pressures were available.

The partial molar volume experiments were undertaken at very low concentrations of the ethyl esters. The dependence of solution molar volume on composition for both AEL and GEL at various pressures and at a constant temperature of 40.6°C is illustrated in Figs. 5 and 6. For the composition range studied, the solution molar volume varied linearly with composition. Thus, the relationships given by Eq. (13) can be used to obtain the partial molar volume at infinite dilution from the experimental data.

The molar volume for carbon dioxide at various pressures was obtained by using the equation proposed by Huang et al. (9). In the region considered in this paper, this equation yields a better estimate than the Bender equation for the density and hence the molar volume of pure carbon dioxide. The binary interaction parameter for the P-R EOS was obtained by using a direct search method to optimize the following objective function:

$$\mathrm{OF} = \sum_{i}^{n} \left(\frac{\bar{V}_i^{\mathrm{Expt}} - \bar{V}_i^{\mathrm{Calc}}}{\bar{V}_i^{\mathrm{Expt}}} \right)^2$$

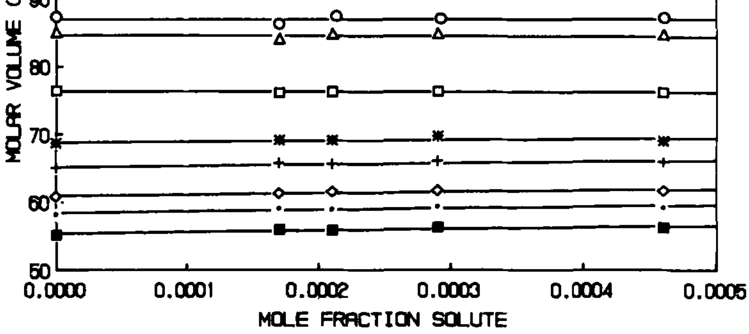

FIG. 5. Molar volume of the AEL–CO_2 system at low solute concentrations.

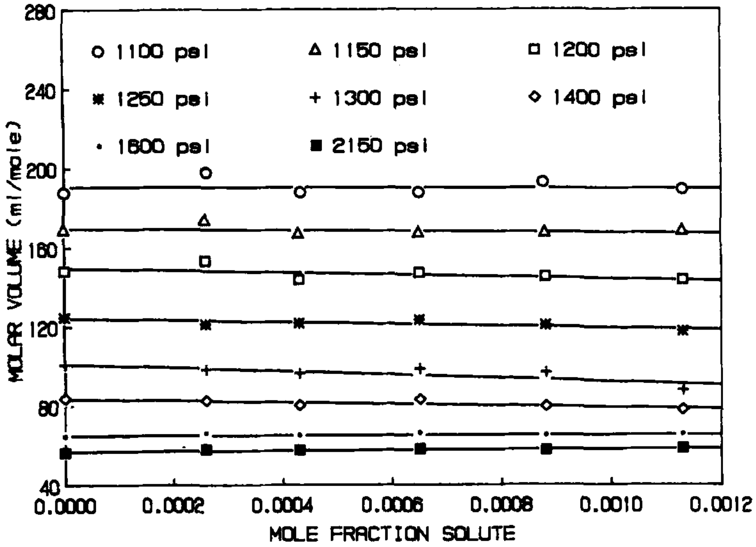

FIG. 6. Molar volume of the GEL–CO_2 system at low solute concentrations.

In P-R EOS, the original van der Waals mixing rule was used. The experimental and calculated partial molar volumes for AEL and GEL are shown in Figs. 7 and 8, respectively. It is clear that the partial molar volumes of the two isomers are quite different. Although the P-R EOS was able to describe this relativity, the overall fit of the experimental data was poor.

The partial molar volumes of the AEL-CO_2 and GEL–CO_2 systems are large and negative in the vicinity of the critical region, where compressibility is the greatest. This commonly observed phenomenon provides an indication of the amount of solvent molecules collapsing around the solute molecule (*10*). It is clear from Figs. 7 and 8 that the GEL–CO_2 system exhibits a larger negative partial molar volume than the AEL–CO_2 system. This suggests that more solvent molecules are collapsing around the GEL molecules, thereby creating a larger negative partial molar volume, thus indicating a more pronounced influence of the GEL structure on the solute–solvent interaction.

The structures of AEL and GEL are shown in Fig. 9. Eight carbons separate the first double bond from the ester group in AEL as opposed to five carbons in GEL. It is postulated that the close location of the double bond to the ester group resulted in stronger solute–solvent interaction. This might be caused by the electron cloud from the double bond being drawn toward the electronegative ester group, thus creating a partial pos-

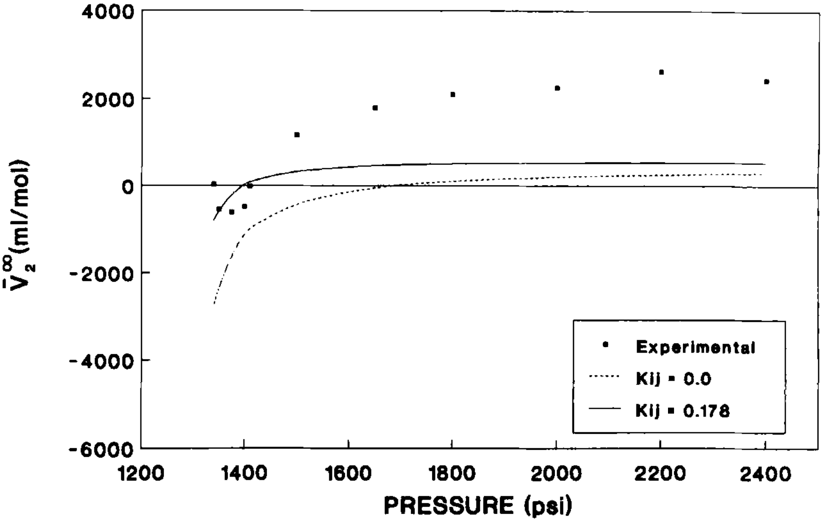

FIG. 7. Partial molar volume of AEL as a function of pressure at infinite dilution.

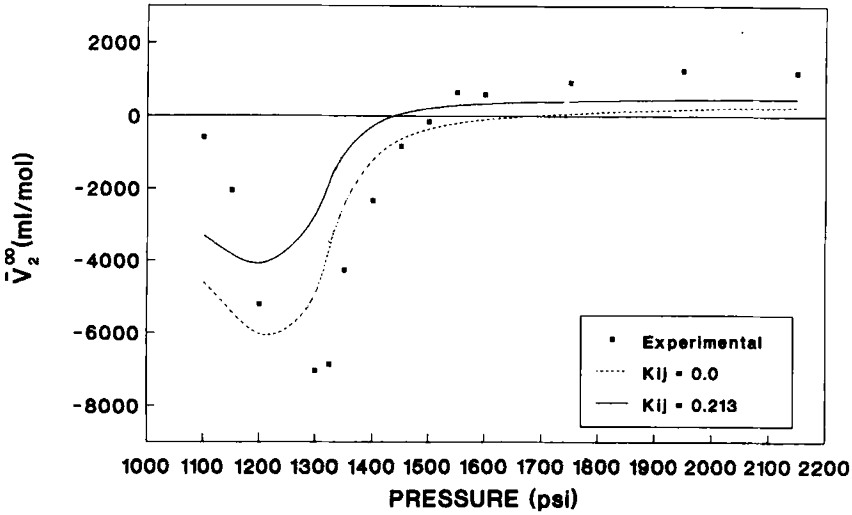

FIG. 8. Partial molar volume of GEL as a function of pressure at infinite dilution.

(i) gamma ethyl linolenate

(ii) alpha ethyl linolenate

FIG. 9. Structures of alpha and gamma ethyl linolenate.

itive charge on the double bond site and a partial negative charge on the ester group. Since the first double bond of GEL is closer to the ester group, the magnitude of the dipole will be greater, with a consequent increase in magnitude of the solvent–solute interaction.

The errors associated with the determinations of critical loci and partial molar volumes were similar. The overall error for temperature measurement was ±0.5°C, and the error associated with pressure measurement was ±7 psi. The wet gas meter used to measure the amount of CO_2 was calibrated against a known mass of CO_2 and was found to be accurate to ±1.5%.

CONCLUSION

The critical loci obtained for the two ethyl esters of linolenic acid were similar. The limit of miscibility of the α-ethyl linolenate in supercritical carbon dioxide was 0.737 wt%. At this composition the mixture critical point was 33.4°C and 1124 psi (7.62 MPa), an increase of approximately 2.3°C and 54 psi over the critical temperature and pressure, respectively, of pure carbon dioxide.

The limit of miscibility of the γ-ethyl linolenate–carbon dioxide system was 0.803 wt%. The critical mixture temperature and pressure at this composition were 33.7°C and 1119 psi (7.61 MPa), respectively.

The partial molar volume obtained for both α- and γ-ethyl linolenate indicated a significant structural influence on the solute–solvent interaction. The P-R EOS provided a satisfactory means of describing the qualitative nature of the experimental data.

NOMENCLATURE

AEL	alpha ethyl linolenate
G	Gibbs free energy
GEL	gamma ethyl linolenate
M	any molar property

$\overline{M}$	any partial molar property
OF	objective function
P	pressure
S	entropy
T	temperature
V	molar volume
$\overline{V}_i$	partial molar volume of component i
μ	chemical potential
x	mole fraction

Subscript

1	solvent
2	solute
i	component i

Superscript

Calc	calculated value
Expt	experimental value
∞	at infinite dilution

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