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Thermodynamic Modeling of High-pressure Equilibrium Data for the Systems L-lactic Acid + (Propane + Ethanol) and L-lactic Acid + (Carbon Dioxide + Ethanol)

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Abstract: This short communication reports the thermodynamic modeling of high-pressure equilibrium data (cloud points) for the systems L-lactic acid + (propane + ethanol) and L-lactic acid + (carbon dioxide + ethanol) from 323.15 K to 353.15 K and at pressures up to 25 MPa.The experimental data were modeled using the Peng-Robinson equation of state with the classical van der Waals quadratic mixing rule (PR-vdW2) and with the Wong-Sandler mixing rule (PR-WS). It is shown that the PR-vdW2 and PR-WS models were both able to satisfactorily represent the phase behavior of the system L-lactic acid + (carbon dioxide + ethanol). However, for the system L-lactic acid + (propane + ethanol), the PR-vdW2 model was not able to appropriately describe its phase behavior.

Keywords: Carbon dioxide; ethanol; L-lactic acid; phase equilibrium; propane; thermodynamic modeling.

The production of high-purity biodegradable polymers is an important issue for their potential applications in medicine and food industry.Biodegradable lactic-acid based polymers have highly promising properties and are easily synthesized from components available from renewable sources [1]. Lactic acid is one of the simplest chiral molecules and is usually found as a mixture of two stereoisomers (L- and D-lactic acid).It is used as a raw material in the synthesis of poly (L-lactic acid) (PLA)[2, 3]. In particular, PLA is important forits biocompatibility and resorbability [4].

Knowledge of the phase equilibriaof the reaction system, which consists of the monomer, the biodegradable polymer and the supercritical/compressed solvent along with the possible presence of a cosolvent, plays a crucial role in the development and optimization of the reaction because the location of the phase boundary of the system is important for establishing appropriate reaction conditions [5, 6].

The phase behavior of L-lactide was studied in supercritical carbon dioxide at high pressures. The L-lactide + carbon dioxide system exhibited the solid – fluid and the liquid – vapor equilibria, which were determined in the temperature range 275 – 355 K and in the pressure range 10 – 80 MPa. This system shows the type of phase behavior where the two branches of the solid L-lactide + liquid + vapor curve end with the first and second critical endpoints [7].

Another study showed the phase behavior of L-lactic acid based polymers of low molecular weight in supercritical carbon dioxide at high pressures. This system also exhibited the solid – fluid and the liquid – vapor equilibria. Supercritical carbon dioxide was a poor solvent for low molecular weight L-lactic acid based polymers. The liquid-vapor equilibrium in this system depended to a great extent on the structure of the end groups, while for the solid – fluid equilibrium, the effect of the molecular weight was more pronounced [1].

A previous study [8]reported the phase equilibrium data (cloud points) of L-lactic acid +(propane + ethanol) and L-lacticacid + (carbon dioxide+ethanol). The phase equilibrium experiments were conducted in a variable-volume view cell employing the static synthetic method from 323.15 K to 353.15 K and at pressures up to 25MPa; the mass ratio of ethanol to carbon dioxide orpropane was maintained at 1:9.The L-lactic acid + (propane + ethanol) exhibited vapor-liquid, liquid-liquid and vapor-liquid-liquid transitions, whereas the L-lactic acid +(carbon dioxide+ ethanol) exhibited only liquid-liquid type transitions [8].

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In addition to experimental data measurements, the development and application of thermodynamics models to represent the phase behavior of multicomponent mixtures plays a crucial role in elucidating the phenomena involved in the fractionation/separation step in the process design and optimization of, for instance, polymerization reactions performed at high pressures. The use of thermodynamics modelsis also relevant to establishing the process flow sheet of a chemical plant. For this purpose, cubic equations of state may be advantageously used to represent experimental phase equilibrium data, allowing process simulation to select appropriate operational conditions [9].

The thermodynamic modeling of the systems L-lactic acid + (propane + ethanol) and L-lactic acid + (carbon dioxide + ethanol) in this work used the previously reported phase equilibrium data [8]. Based on the description of these systems at high pressures, the Peng-Robinson equation of state [10]was employed with the classical van der Waals quadratic mixing rule (PR-vdW2) and with the Wong-Sandler mixing rule (PR-WS) [11, 12] to represent the experimental values found. The calculation procedure for modeling the experimental data of the systems investigated in this work followed the same procedure described previously by Araújo *et al*. [13] and Pinto *et al*. [14].

As briefly presented in our previous works [9, 13-16] the mixture parameter for vdW2 can be summarized as

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij} \qquad (1)$$

$$b = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j b_{ij} \qquad (2)$$

with

$$a_{ij} = (a_i a_j)^{1/2}\left(1 - k_{ij}\right) \qquad (3)$$

and

$$b_{ij} = \frac{1}{2}\left(b_i + b_j\right)\left(1 - l_{ij}\right) \qquad (4)$$

where a_i and b_i are the parameters of the pure compounds [10], and l_{ij} and k_{ij} are adjustable parameters.

The mixture parameters a and b for the WS mixing rule are given by [11, 12]

$$\frac{a}{RT} = Q\frac{D}{1-D} \qquad (5)$$

$$b = \frac{Q}{1-D} \qquad (6)$$

where

$$Q = \sum_i \sum_j x_i x_j \left(b_{ij} - \frac{a_{ij}}{RT}\right) \qquad (7)$$

and

$$D = \sum_i x_i \frac{a_i}{b_i RT} + \frac{G^{Ex}\left(T, P, \mathbf{x}\right)}{CRT} \qquad (8)$$

For PR-EoS, the constant C is given by $C = -\frac{1}{\sqrt{2}}\ln\left(1 + \sqrt{2}\right)$.

The combination rule was used considering the reformulated Wong-Sandler mixing rule, by rewriting the cross second virial coefficient in the following form, as presented by Orbey and Sandler [12]:

$$\left(b_{ij} - \frac{a_{ij}}{RT}\right) = \frac{1}{2}\left(b_{ii} - b_{jj}\right) - \frac{\sqrt{a_{ii}a_{jj}}}{RT}\left(1 - K_{ij}\right) \qquad (9)$$

The Non-random two-liquid model (NRTL) [17] was used for the molar excess Gibbs free energy $(G^{Ex}(T, P, x))$ calculation. Thus, the binary interaction parameters fitted for PR-WS model were α_{ij}, Δg_{ij}, Δg_{ji} and K_{ij}.

The binary interaction parameters for both models (PR-vdW2 and PR-WS) were estimated by minimizing the least square objective function (Equation 10) using the stochastic Simulated Annealing method, and the optimization procedure was refined using the Simplex method. The saturation pressure (bubble or dew point) was calculated by implementing an algorithm presented by Ferrari *et al*. [18] and Bender *et al*. [5], which is based on Michelsen's work [19]. The pure component properties of carbon dioxide, propane, ethanol and L-lactic acid are presented in Table **1**, including the purity, supplier, critical properties and acentric factor of all components.

The objective function used in this work was

$$OF = \sum_{i=1}^{n_{obs}} (P_i^{exp} - P_i^{cal})^2 \qquad (10)$$

Where P_i^{exp} and P_i^{cal} are the calculated and experimental saturation pressure values, respectively, and n_{obs} is the number of experimental observations.

The binary interaction parameters were estimated by minimizing the least square objective function of the

Table 1. Characteristic parameters of the pure compounds.

Compound	P_c/MPa	T_c/K	ω	M_w/(g.gmol^{-1})
Propane[a]	4.248	369.83	0.1523	44,094
CO_2[a]	7.383	304.21	0.2236	44.010
Ethanol[a]	6.140	513.90	0.6440	46.0690
L-lactic acid[b]	5.960	675.00	1.022	90.790

P_c, critical pressure; T_c, critical temperature; ω, acentric factor; M_w, molar mass. [a][20] and [b][21].

experimental and calculated pressures using the stochastic particle swarm optimization method [18], and the procedure was refined using the Modified Simplex method [22]. For the binary system {CO_2 (1) + Ethanol (2)}, the interaction parameters were taken from the literature [13].The binary interaction parameters of PR-vdW2 and PR-WS fitted to the experimental values for the systems investigated are shown in Table **2** and Table **3**, respectively. For the system {Propane (1) + Ethanol (2) + L-lactic acid (3)}, when using the PR-WS model, the NRTL model was adopted to compute the molar excess Gibbs energy [14].

Fig. (**1**) presents the pressure-temperature diagram obtained for the {Propane (1) + Ethanol (2) + L-lactic acid (3)} system, where it can be observed that the PR-vdW2 model (continuous line) only fitted the vapor-liquid bubble point (VLE-BP) transition data.

Fig. (**2**) presents the pressure-temperature diagram obtained for the {CO_2 (1) + Ethanol (2) + L-lactic acid (3)} system. This diagram shows the good performance of the PR-vdW2 model (continuous line) and the adequate strategy adopted for phase equilibrium data modeling, as corroborated in Table **2** by the low values of the absolute

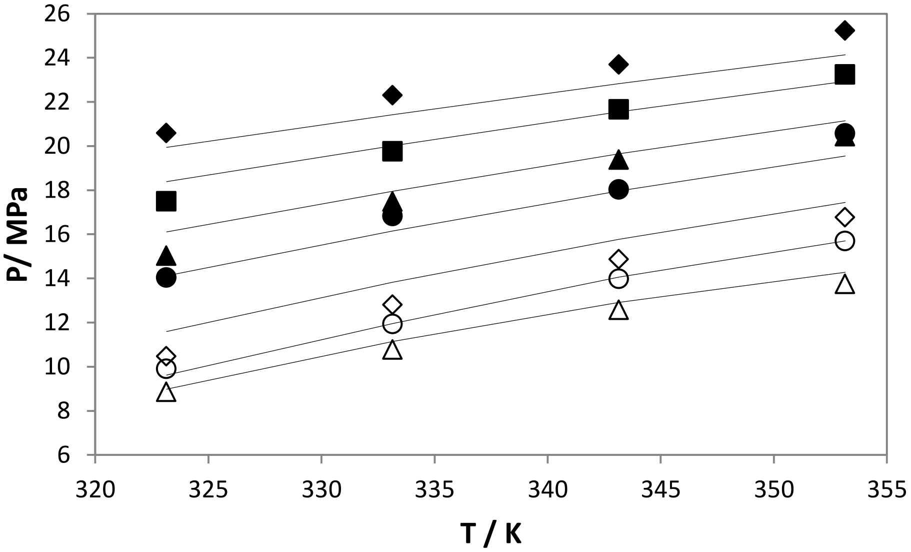

Fig. (2). Pressure-temperature diagram of the system {CO_2 (1) + Ethanol (2) + L-lactic acid (3)} (LLE) (♦: $w_3 = 0.0663$; ■: $w_3 = 0.0589$; ▲: $w_3 = 0.0485$; ●: $w_3 = 0.0396$; ◊: $w_3 = 0.0286$; ○: $w_3 = 0.0199$; Δ: $w_3 = 0.0105$). The continuous line denotes the calculated values from PR-vdW2, using the fitted interaction parameters.

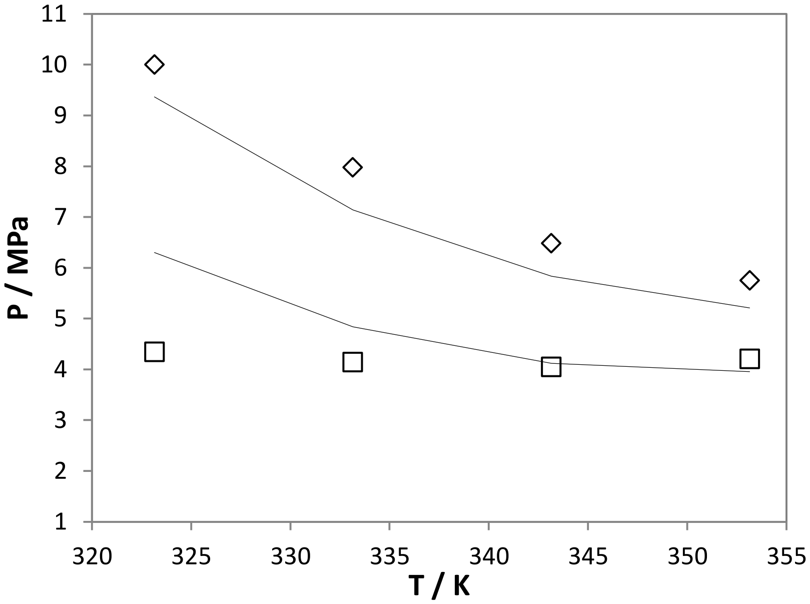

Fig. (3). Pressure-temperature diagram of the system {Propane (1) + Ethanol (2) + L-lactic acid (3)} (LLE) (◊: w3 = 0.0501; □: w3 =0.0447). The continuous line denotes the calculated values from PR-WS, using the fitted interaction parameters.

error (abs error) and the Root Mean Square Deviation (RMSD), hence showing the good agreement between the experimental and calculated pressure transition values [23].

Figs. (**3** and **4**) present the pressure-temperature diagram obtained for the {Propane (1) + Ethanol (2) + L-lactic acid (3)} system for all overall mass fractions. These figures show that the PR-WS model (continuous line)was able to fit both the liquid-liquid (LLE) (Fig. **3**) and the vapor-liquid bubble point (VLE-BP) (Fig. **4**)transition data.These diagrams show the good performance of the PR-WS model (continuous line) and the adequate strategy adopted for all phase equilibrium data modeling.

Fig. (**5**) presents the pressure-temperature diagram obtained for the system {CO_2 (1) + Ethanol (2) + L-lactic acid (3)}. Like the PR-vdW2 model, the PR-WS model (continuous line) showed good performance and demonstrated that the strategy adopted was adequate for the phase equilibrium data modeling. This determination can be verified by inspectingthe absolute error (abs error) and Root

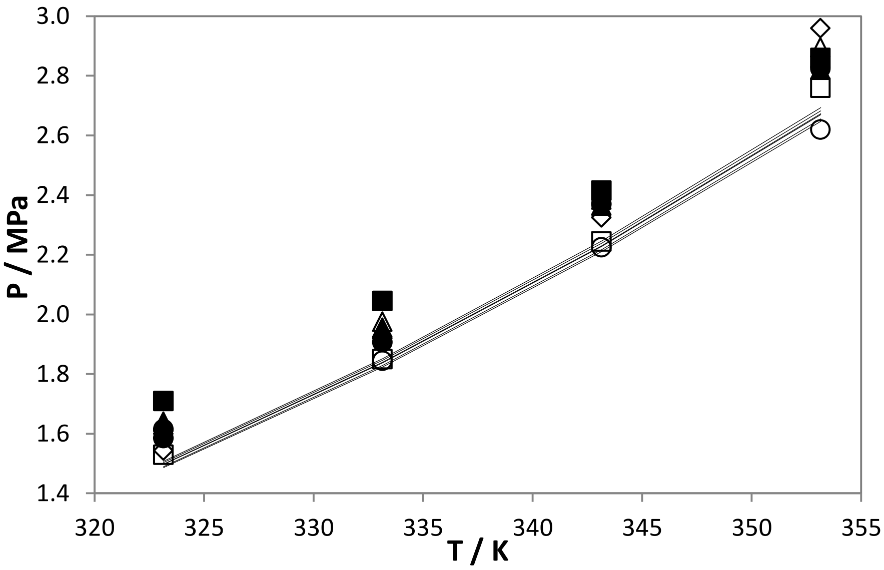

Fig. (4). Pressure-temperature diagram of the system {Propane (1) + Ethanol (2) + L-lactic acid (3)} (VLE-BP) (▲: w3 = 0.0396; ●: w3 = 0.0347; ■: w3 = 0.0271; ○: w3 = 0.0253; Δ: w3 = 0.0199; ◊: w3 = 0.0150; □: w3 =0.0100). The continuous line denotes the calculated values from PR-SW, using the fitted interaction parameters.

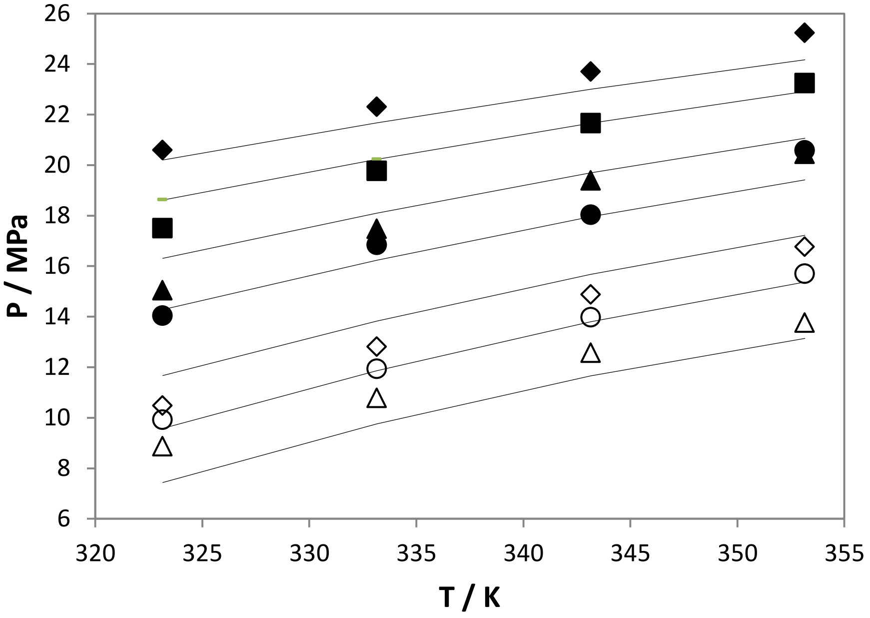

Fig. (5). Pressure-temperature diagram of thesystem{CO_2 (1) + Ethanol (2) + L-lactic acid (3)} (LLE) (♦: w_3 = 0.0663; ■: w_3 = 0.0589; ▲: w_3 = 0.0485; ●: w_3 = 0.0396; ◊: w_3 = 0.0286; ○: w_3 = 0.0199; Δ: w_3 = 0.0105). The continuous line denotes the calculated values from PR-SW, using the fitted interaction parameters.

Mean Square Deviation (RMSD) in Table **3**, which are low for both systems, attesting the good agreement between the experimental and calculated (PR-WS model) pressure transition values [23].

This work reported the thermodynamic modeling of high-pressure phase equilibrium data for the systems L-lactic acid + (propane + ethanol) and L-lactic acid + (carbon dioxide + ethanol) in the temperature range of 323.15 K to 353.15 K and at pressures up to 25 MPa. In general, both systems investigated were modeled using the Peng-Robinson equation ofstate coupled with the Wong-Sandler mixing rule. However, the Peng-Robinson equation of state with the classical van der Waals quadratic mixing rule was unable to represent the system L-lactic acid + (propane + ethanol), possiblydue to the high asymmetry exhibited by this systemin terms of the molecular size and intermolecular forces.The thermodynamic modeling performed in this work may be of great value for conducting polymerization reactions of such lactones in compressed carbon dioxide and propane.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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LIST OF SYMBOLS

Abs error = absolute error
a_i and b_i = parameters of pure components
C = constant for PR-EoS
$\underline{G}^{Ex}$ = molar excess Gibbs free energy
l_{ij} and k_{ij} = adjustable binary interaction parameters for PR-vdW2
LLE = liquid-liquid equilibria
M_w = molar mass
OF = objective function
P_c = critical pressure
P_i^{cal} = calculated saturation pressure
P_i^{exp} = experimental saturation pressure
PR-EoS = Peng-Robinson equation of state
PR-vdW2 = Peng-Robinson equation of state with the classical van der Waals quadratic mixing rule
PR-WS = Peng-Robinson equation of state with the Wong-Sandler mixing rule
RMSD = root mean square deviation
T_c = critical temperature
VLE-BP = vapor-liquid (bubble point) equilibria
w3 = mass fraction of L-lactic acid
x = molar fraction
α_{ij}, g_{ij}, g_{ji} and K_{ij} = adjustable binary interaction parameters for PR-WS
ω = acentric factor

REFERENCES

[1] J. Gregorowicz and P. Bernatowicz, "Phase behaviour of l-lactic acid based polymers of low molecular weight in supercritical carbon dioxide at high pressures," *The Journal of supercritical fluids*, vol. 51, pp. 270-277, 2009.

[2] S. Dutkiewicz, "Synthesis of poly (L (+) lactic acid) by polycondensation method in solution," *Fibres & Textiles in Eastern Europe*, vol. 11, pp. 66-70, 2003.

[3] J. Lunt, "Large-scale production, properties and commercial applications of polylactic acid polymers," *Polymer Degradation and Stability*, vol. 59, pp. 145-152, 1998.

[4] C. C Chen, J.-Y Chueh, H. Tseng, H.-M. Huang, S.-Y. Lee, "Preparation and characterization of biodegradable PLA polymeric blends," *Biomaterials*, vol. 24, pp. 1167-1173, 2003.

[5] J.P. Bender, M. Feitein, E. Franceschi, M.L. Corazza, J.V. Oliveira, "Phase behaviour of binary systems of lactones in carbon dioxide," *The Journal of Chemical Thermodynamics,* vol. 42, pp. 48-53, 2010.

[6] J. P. Bender, "Phase behaviour of the ternary system {poly(ε-caprolactone) + carbon dioxide + dichloromethane}," *The Journal of Chemical Thermodynamics*, vol. 42, pp. 229-233, 2010.

[7] J. Gregorowicz, "Phase behaviour of l-lactide in supercritical carbon dioxide at high pressures," *The Journal of supercritical fluids,* vol. 46, pp. 105-111, 2008.

[8] I. C. N. Debien, "High-pressure phase equilibrium data for the L-lactic acid + (propane + ethanol) and the L-lactic acid + (carbon dioxide + ethanol) systems," *Journal of Supercritical Fluids,* vol. 79, pp. 27-31, Jul 2013.

[9] R. M. Charin, "Phase equilibrium data and thermodynamic modeling of the system propane plus NMP plus methanol at high pressures," *Journal of Supercritical Fluids,* vol. 55, pp. 662-670, Dec 2010.

[10] D.-Y. Peng and D. B. Robinson, "A New Two-Constant Equation of State," *Industrial & Engineering Chemistry Fundamentals,* vol. 15, pp. 59-64, 1976.

[11] D. S. H. Wong and S. I. Sandler, "A theoretically correct mixing rule for cubic equations of state," *AIChE Journal,* vol. 38, pp. 671-680, 1992.

[12] H. Orbey and S. I. Sandler, Modeling vapor-liquid equilibria: cubic equations of state and their mixing rules vol. 1: Cambridge University Press, 1998.

[13] O. A. S. Araújo, "Phase behaviour measurements for the system (carbon dioxide + biodiesel + ethanol) at high pressures," The *Journal of Chemical Thermodynamics,* vol. 47, pp. 412-419, 2012.

[14] L.F. Pinto, D. I. S. da Silva, F. R. da Silva, *et al*., "Phase equilibrium data and thermodynamic modeling of the system (CO2 + biodiesel + methanol) at high pressures," *The Journal of Chemical Thermodynamics,* vol. 44, pp. 57-65, 2012.

[15] P. S. Gaschi, M. R. Mafra, P.M. Ndiaye, M.L. Corazza, "Phase equilibrium measurements and thermodynamic modelling for the system (CO_2+ethyl palmitate+ethanol) at high pressures," *The Journal of Chemical Thermodynamics,* vol. 57, pp. 14-21, 2013.

[16] R. M. Charin, *et al*., "Phase equilibrium data and thermodynamic modelling of the system (propane+ DMF+ methanol) at high pressures," The Journal of Chemical Thermodynamics, vol. 43, pp. 413-419, 2011.

[17] H. Renon and J. M. Prausnitz, "Local compositions in thermodynamic excess functions for liquid mixtures," AIChE Journal, vol. 14, pp. 135-144, 1968.

[18] J. C. Ferrari, *et al*., "Application of stochastic algorithms for parameter estimation in the liquid–liquid phase equilibrium modeling," Fluid Phase Equilibria, vol. 280, pp. 110-119, 2009.

[19] M. L. Michelsen, "Saturation point calculations," Fluid Phase Equilibria, vol. 23, pp. 181-192, 1985.

[20] B. E. Poling, *et al*., The properties of gases and liquids, Fifth ed. New York: McGraw-Hill, 2001.

[21] R. Rowley, *et al*., DIPPR Data Compilation of Pure Chemical Properties, 2006.

[22] J. A. Nelder and R. Mead, "A simplex method for function minimization," The computer journal, vol. 7, pp. 308-313, 1965.

[23] I. Dalmolin, *et al*., "Phase behaviour and thermodynamic modelling for the system (grape seed oil + carbon dioxide + ethanol) at high pressures," The Journal of Chemical Thermodynamics, vol. 68, pp. 71-74, 2014.

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