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Published in:
Journal of Chemical and Engineering Data

DOI:
10.1021/acs.jced.0c00087

Published: 14/05/2020

Document Version
Publisher's PDF, also known as Version of record

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Please cite the original version:
González Escobedo, J. L., Uusi-Kyyyni, P., Puurunen, R. L., & Alopaeus, V. (2020). Hydrodeoxygenation Model Compounds γ-Heptalactone and γ-Nonalactone : Density from 293 to 473 K and H2 Solubility from 479 to 582 K. Journal of Chemical and Engineering Data, 65(5), 2764-2773. https://doi.org/10.1021/acs.jced.0c00087

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Hydrodeoxygenation Model Compounds γ-Heptalactone and γ-Nonalactone: Density from 293 to 473 K and H2 Solubility from 479 to 582 K

José Luís González Escobedo,* Petri Uusi-Kyyny, Riikka L. Puurunen, and Ville Alopaeus

ABSTRACT: Determining the H2 solubility in model compounds that represent lignocellulose derivatives is valuable for the study of upgrading processes such as hydrodeoxygenation. In this work, γ-heptalactone and γ-nonalactone are studied as model compounds at conditions relevant to hydrodeoxygenation. The solubility of H2 in the lactones was determined in the range of 479 to 582 K and 3 to 10 MPa. The solubility measurements were performed in a continuous flow setup based on the visual observation of the bubble point. Furthermore, the densities of the lactones were measured in order to provide the necessary data for the solubility calculations. The density measurements were performed from 293 to 373 K and from 0.16 to 9.9 MPa in a vibrating tube density meter. Using the measurements, a model of the density as a function of temperature and pressure was developed, obtaining average relative deviations on the order of 0.1%. Similarly, the Peng−Robinson equation of state with the Boston−Mathias modification was used to predict the H2 solubility in the lactones. A temperature-dependent model of the symmetric binary parameter of the equation of state was regressed from the data in order to improve the predictions.

INTRODUCTION

The need for sustainable transportation fuels has not been met completely in the current energy mix.1 Lignocellulosic biomass, if responsibly harvested,2,3 can be upgraded to provide renewable transportation fuels. The hydrolysis of lignocellulose into its main polymeric constituents is the foundation for biorefineries based on platform molecules,4−7 one of which is levulinic acid (4-oxopentanoic acid, LA). LA can be obtained from 5-hydroxymethyl furfural, itself derived from hexoses. The upgrading of LA to fuel-compatible compounds has been studied widely.6,7 One possible route is the dimerization of LA into a mixture of slightly branched C10 molecules,8−11 which themselves require further treatment.

Recently, the hydrodeoxygenation (HDO) of γ-nonalactone (GNL) has been studied as a model compound for the production of hydrocarbons from LA dimers,12 as the γ-lactone group is typically found in LA dimers.8 GNL, that is, dihydro-5-pentyl-2(3H)-furanone (Figure 1b), is a cyclic ester with the same carbon chain length as the main chain in LA dimers. In the aforementioned study, GNL reacted with hydrogen (H2) in the presence of a heterogeneous catalyst at conditions in which most of the GNL present in the reactor was liquid; 6 MPa and 473 to 553 K.12 Because most of the catalyst was fully wetted by the liquid, it was necessary for the H2 to dissolve in the liquid reaction mixture in order to reach the catalyst and thereby to participate in HDO reactions. Hence, the solubility of H2 in GNL was an important factor influencing the outcome of the process. In particular, the temperature and pressure dependence of H2 solubility might have affected the kinetics of HDO; it is necessary to know these dependences in order to distinguish the intrinsic reaction kinetics from the mass transfer rates. However, no studies on the solubility of H2 in GNL are available in the literature. Most studies involving the
solubility of a gas in a lactone focus on the CO₂–γ-valerolactone system. 13–16

The present study investigates the solubility of H₂ in GNL at the temperatures of 479, 531, and 582 K, and at pressures ranging from 3 to 10 MPa, which are conditions relevant to HDO. The n-pentyl side chain in GNL is thought to promote the solubility of H₂, which usually displays a greater affinity to aliphatic structures than to oxygenated ones. 17 In fact, it has been shown that the H₂ solubility behavior of oxygenates tends to converge with the behavior of hydrocarbons, the longer the carbon chain. 17,18 Thus, γ-heptalactone (dihydro-5-propyl-2(3H)-furanone, Figure 1a) was studied for comparison, as it has been shown that the H₂ solubility behavior of oxygenates tends to converge with the behavior of hydrocarbons, the longer the carbon chain. 17,18

Table 1. Chemicals

| chemical | CASRN | supplier | initial mole fraction purity | purification method | final mole fraction purity | analysis method | refractive index after distillation | water content after distillation/wt % |
|----------------|--------|----------|-----------------------------|---------------------|--------------------------|----------------|-------------------------------|--------------------------------------|
| γ-heptalactone | 105-21-5 | Sigma-Aldrich | 0.9938 | vacuum distillation | 0.9943 | GC | 1.441477 | 0.0106 |
| γ-nonalactone | 104-61-0 | Sigma-Aldrich | 0.9891 | vacuum distillation | 0.9999 | GC | 1.446905 | 0.0120 |
| hydrogen | 1333-74-0 | AGA | 0.99999 | none | 0.00034 | | | |

“Dihydro-5-propyl-2(3H)-furanone. “Dihydro-5-pentyl-2(3H)-furanone. “Reported by manufacturer. “Accounts for organic impurities and H₂O. Organic impurities not detected in GNL. *Dimensionless. Measured at 293.15 K ± 0.03 K and 0.1 MPa ± 0.01 MPa. Standard uncertainty: 0.00034. *Standard uncertainty (standard deviation): 0.0002 wt %.

Table 2. Uncertainty Budget of the Density Measurements

| source of uncertainty | standard uncertainty for GHL/kg m⁻³ | standard uncertainty for GNL/kg m⁻³ |
|-----------------------|------------------------------------|------------------------------------|
| standard uncertainty of the calibration of the density meter, uρcalib | 0.036 | 0.036 |
| standard deviation of distilled water measurements, uρdist | 0.3832 | 0.3832 |
| root mean square of the differences between the distilled water measurements and the reference values, uρDWD | 0.7501 | 0.7501 |
| uncertainty of water density reference values | 1 × 10⁻⁸ ρ | 1 × 10⁻⁸ ρ |
| instrument uncertainty reported by manufacturer, uρins | 1 | 1 |
| sample impurity, uρs | 5.73 × 10⁻⁸ ρ | 6.66 × 10⁻⁸ ρ |
| combined uncertainty, uρ | √(1.71 + 3.29 × 10⁻⁸ ρ²) | √(1.71 + 1.00 × 10⁻¹⁰ ρ²) |

“Reported by Baird et al. 20 “Water IAPWS95 equation of state, NIST. 22 “Calculated according to the recommendations by Chirico et al. 23 See section S2 and Table S2 in the Supporting Information.

Table 3. Uncertainty Budget of Values Calculated in This Work with the Density Model (eq 1)

| source of uncertainty | standard uncertainty for GHL | standard uncertainty for GNL |
|-----------------------|-----------------------------|-----------------------------|
| average absolute deviation of the model, AAD/kg m⁻³ | 0.188 | 0.142 |
| temperature in solubility setup, from temperature calibrator, uρ(T) | 0.14 | 0.14 |
| pressure in solubility setup, from calibrated cell temperature, uρ(p) | 0.01 | 0.02 |
| pressure set point in the syringe pump coupled to the density meter | 0.14 | 0.14 |
| combined pressure uncertainty, uρ(p) | 1.8 × 10⁻⁷ + 1.6 × 10⁻⁷ p² | 1.8 × 10⁻⁷ + 1.6 × 10⁻⁷ p² |

Combined uncertainty for GNL, uρcalc/kg m⁻³

Combined uncertainty for GHL, uρcalc/kg m⁻³

“See Table 2. “Reported by T. Vielman. 26 “T₁ in Figure 2, corrected with calibrator. See Feeding pump T in Table S3. “The coefficients are from eq 1 and reported in Table 7. In the expression, the temperatures and pressures are the calibrated cell temperature (T₁ in Figure 2) and pump pressure (P in Figure 2) in the solubility setup. “From manufacturer. “P in Figure 2, corrected with calibrator. See Feeding pump p in Table S4. 2765
solubility calculations, were measured at different temperatures and pressures, as no references were found in the literature.

To increase the applicability of the measurements to future research, a vapor–liquid equilibrium model is presented in this work. The model consists of the Peng–Robinson equation of state (EoS) using the Boston–Mathias (PR-BM) modification.\textsuperscript{19} The EoS predictions were compared to the measurements, and the binary interaction parameter ($k_{ij}$) of the EoS was regressed in order to provide a model that would represent the $H_2$ solubility measurements more accurately.

\section*{EXPERIMENTAL AND COMPUTATIONAL METHODS}

\subsection*{2.1. Materials.} $\gamma$-Heptalactone (GHL) and $\gamma$-nonalactone (GNL) were purchased from Sigma-Aldrich. Both reagents were provided with a purity of $\geq98\%$. The samples were enantiomeric mixtures (carbon 4 is chiral, Figure 1). In biorefinery processes, enantiomeric lactone mixtures are expected when using heterogeneous catalysts in their production. The reagents were purified by vacuum distillation, and the attained purity was determined from the gas chromatograms of the purified reagent compared to the chromatograms of the raw reagents (Figures S1 and S2). The impurities present in the distilled samples were identified by gas chromatography–mass spectrometry (Table S1). Additionally, the refractive index was monitored with a Dr. Kernchen Abbemat Digital Automatic Refractometer at 293.15 K. Finally, the water content of the distilled reagents was determined with a DL38 Karl Fischer titrator manufactured by Mettler Toledo. The titrations were repeated three times. The reagents and their purity, refractive indexes, and water content are presented in Table 1.

\subsection*{2.2. Density Measurements.} The densities of the lactones were measured at a series of temperatures and pressures ranging from 293 to 473 K and from 0.16 to 9.9 MPa. An Anton Paar DMA HP density meter coupled to a Teledyne ISCO syringe pump was used. The density meter operated by correlating the density of the sample to the characteristic vibration frequency of a u-tube containing the sample. The meter was equipped with a heater to adjust the temperature, and the syringe pump was used to adjust the pressure.

The density meter was calibrated using air and water as described by Baird et al.\textsuperscript{20} Furthermore, the validity of the calibration was checked after the lactone measurements by measuring the density of distilled water at 0.1 MPa and at temperatures between 293 and 348 K. To determine the uncertainties of the density measurements, reference values were obtained from the IAPWS95 equation of state for water (the standard for thermodynamic properties of water).\textsuperscript{21,22} The uncertainty calculation of the density measurements is presented in Table 2. The uncertainties of the temperatures and pressures, at which the densities were measured, are presented in Table 3.

\subsection*{2.3. Density Model.} The measured densities were used to regress a density model ($\rho(T, p)$, kg m$^{-3}$) as a function of temperature ($T$, K) and pressure ($p$, MPa), which Zaitseva et al.\textsuperscript{24} found to provide the best correlation for the density of $\gamma$-valerolactone:

$$\rho(T, p) = K_1 + K_2T + K_3T^2 + K_4p + K_5Tp$$ \hspace{1cm} (1)

The values of the coefficients are reported in Table 7. For the regression, the “fitnlm” function in MATLAB\textsuperscript{25} software was used. Furthermore, the fit of the regression to the data was evaluated by calculating the average absolute deviation (AAD) and the average relative deviation (ARD), which are defined as

$$\text{AAD} = \frac{1}{N} \sum_{i=1}^{N} |\rho_{i}^{\text{meas}} - \rho_{i}^{\text{calc}}|$$ \hspace{1cm} (2)

$$\text{ARD} = \frac{100}{N} \sum_{i=1}^{N} \frac{|\rho_{i}^{\text{meas}} - \rho_{i}^{\text{calc}}|}{\rho_{i}^{\text{meas}}}$$ \hspace{1cm} (3)

where $N$ is the number of measurements, $\rho_{i}^{\text{meas}}$ is the measured density, and $\rho_{i}^{\text{calc}}$ is the corresponding density calculated with eq 1.

The use of eq 1 in $H_2$ solubility calculations introduced additional uncertainties aside of the uncertainty of the density measurements. These additional uncertainties were compounded into a combined uncertainty due to density calculations, as reported in Table 3.

\subsection*{2.4. Solubility Measurements.} The solubility of $H_2$ in the purified lactones was measured in a high-pressure, continuous-flow apparatus equipped with a camera, which was described by Saajanlehto et al.\textsuperscript{27,28} (Figure 2). Before the measurements,

the lactone sample was degassed in an ultrasonic bath with the aid of a vacuum pump. For safety, a pressure test was conducted in the apparatus before the measurements, and a $N_2$ atmosphere was generated inside the oven. Afterward, the oven was heated to the desired temperature, the feeding pump was evacuated, the lactone sample was injected to the feeding pump, the stabilizing pump was set to the desired pressure, and $H_2$ was allowed to flow (normal temperature and pressure) at 5.3 nmL min$^{-1}$. For the determination of the saturation point

![Figure 2. Scheme of the continuous flow apparatus used for the $H_2$ solubility measurements.](https://dx.doi.org/10.1021/acs.jced.0c00087)
Table 4. Uncertainty Budget of the H₂ Mole Fractions (x_{H₂}) in the Solubility Measurements

| source of uncertainty | standard uncertainty |
|-----------------------|----------------------|
| maximum absolute deviation of H₂ flow calibration factor, \( u(Q_{H₂}) \) | \( 1.9 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \) |
| pump volume in H₂ flow calibration, \( u(V) \) | \( 0.01 \text{ cm}^3 \) |
| temperature of feeding pump used to calibrate H₂ mass flow, \( u(T) \) | \( 0.14 \text{ K} \) |
| pressure of feeding pump used to calibrate H₂ mass flow, \( u(p) \) | \( 0.80 \text{ MPa} \) |

\[
\left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} = \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} + \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}}
\]

where \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} \) is the calculated volumetric flow rate, \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} \) is the measured volumetric flow rate, and \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}} \) is the uncertainty in the volumetric flow rate.

\[
\left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} = \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} + \left[ \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} \right]_{\text{uncertainty}}
\]

where \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} \) is the measured volumetric flow rate, \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} \) is the calculated volumetric flow rate, and \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}} \) is the uncertainty in the volumetric flow rate.

\[
\left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} = \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} + \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}}
\]

where \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} \) is the calculated volumetric flow rate, \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} \) is the measured volumetric flow rate, and \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}} \) is the uncertainty in the volumetric flow rate.

\[
\left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} = \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} + \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}}
\]

where \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} \) is the calculated volumetric flow rate, \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} \) is the measured volumetric flow rate, and \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}} \) is the uncertainty in the volumetric flow rate.

\[
\left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} = \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} + \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}}
\]

where \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} \) is the calculated volumetric flow rate, \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} \) is the measured volumetric flow rate, and \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}} \) is the uncertainty in the volumetric flow rate.

\[
\left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} = \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} + \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}}
\]

where \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} \) is the calculated volumetric flow rate, \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} \) is the measured volumetric flow rate, and \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}} \) is the uncertainty in the volumetric flow rate.

\[
\left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} = \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} + \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}}
\]

where \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{cal}} \) is the calculated volumetric flow rate, \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{meas}} \) is the measured volumetric flow rate, and \( \left( \frac{\partial Q_{H₂}}{\partial V} \right)_{\text{uncertainty}} \) is the uncertainty in the volumetric flow rate.
2.5. Calculations. From the flow measurements, the H₂ molar fractions \( x_{H_2} \) in the H₂-lactone mixture were calculated as

\[
x_{H_2} = \frac{Q_{H_2}}{V_{H_2}} + \frac{Q_{o_{H_2}}}{M_L}
\]

(4)

where \( Q_{H_2} \) (cm³ min⁻¹) is the calibrated H₂ volumetric flow at normal conditions and \( V_{H_2} \) is the molar volume of H₂ at normal conditions (22.414 cm³ mol⁻¹). For the lactone, \( Q_{o_{H_2}} \) (cm³ min⁻¹) is the volumetric flow, \( p_{calc} \) (g cm⁻³) is the density determined with eq 1 from the temperature and pressure of the measurement, and \( M_L \) (g mol⁻¹) is the molecular mass. Once the flows were converted to molar fractions, the composition of the mixture at saturation point \( x_{H_2}^{sat} \) could be calculated from the observations:

\[
x_{H_2}^{sat} = \frac{x_{H_2,L} + x_{H_2,GL}}{2}
\]

(5)

where \( x_{H_2,L} \) is the H₂ molar fraction at the lowest lactone flow rate observed in the liquid region, and \( x_{H_2,GL} \) is the H₂ molar fraction at the highest lactone flow rate in the gas–liquid region. The determination of the uncertainties in the saturation compositions is reported in Table 4.

The solubility measurements were complemented with the vapor pressures of GHL and GNL. The vapor pressures correspond to the intercept of the saturation \( P-x \) isotherms, that is, the pressure at \( x_{H_2} = 0 \). The vapor pressures at the tested temperatures were calculated with the model by Emel’yanenko et al.²⁹ who validated the model in a temperature range of 296 to 363 K. Hence, the model was extrapolated for the present case, as no other models were available.

2.6. Vapor–Liquid Equilibrium Model. For each of the lactones, a vapor–liquid phase binary analysis was set up in Aspen Plus²⁸ with the temperatures used in the solubility measurements and an \( x_{H_2} \) range of 0 to 0.2. The EoS model required the input of the physical properties of the lactones. Although Emel’yanenko et al.²⁹ have measured the vapor pressures of GHL and GNL, the critical data were not found in the literature. The most closely related information was the measurement by Wilson et al.³¹ of the critical temperature and pressure of \( \gamma \)-butyrolactone. Therefore, it was necessary to estimate the critical temperature \( T_c \) and pressure \( p_c \) of GHL and GNL, which was performed using Nannoolal’s method.³² This method was found by Nannoolal et al.³² to produce the least average absolute errors in the prediction of the critical properties of \( \gamma \)-butyrolactone, 0.0 K \( T_c \) and 0 kPa \( p_c \) compared to 10 other methods. The acentric factor \( (\omega) \) was calculated as

\[
\omega = -1 - \log_{10} \left( \frac{p_{0.7T_c}}{p_c} \right)
\]

(6)

where \( p_{0.7T_c} \) is the vapor pressure at a temperature of 0.7 \( T_c \). The software required other properties, which are not included in the equation of state, such as the critical volume \( (V_c) \), the ideal gas standard enthalpy and free energy of formation \( (\Delta H^o_c \text{ and } \Delta G^o_c) \), and the ideal gas heat capacity \( (C_p) \) polynomial coefficients. They were calculated using Joback’s method.³³

Furthermore, the vapor pressure data and extended Antoine equation coefficients were taken from Emel’yanenko et al.²⁹

For the calculations, the PR-BM method was used. The Peng–Robinson EoS is

\[
p = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2}
\]

(7)

where \( R \) is the gas constant, \( T \) is the temperature, \( v \) is the volume, and \( a \) and \( b \) are parameters determined by the critical properties of the components and by suitable mixing rules. For pure components parameters \( a \) and \( b \) are

\[
a = 0.45724 \frac{R^2T^2_c}{p_c}
\]

(8)

\[
b = 0.07780 \frac{RT_c}{p_c}
\]

(9)

The Boston–Mathias modification for mixtures provides mixing rules, according to which ³⁹

\[
b = \sum_i b_x_i
\]

(10)

where \( b_i \) are the pure component \( b \) parameters (eq 9) of the mixture components and \( x_i \) are the mole fractions of the components. Parameter \( a \) includes a symmetric \( (a^{(0)}) \) and an asymmetric \( (a^{(1)}) \) mixing rule:

\[
a = a^{(0)} + a^{(1)}
\]

(11)

The symmetric mixing rule is ³⁹

\[
a^{(0)} = \sum_i x_i (a_i a_j)^{1/2} (1 - k_{ij})
\]

(12)

where \( x_i \) and \( x_j \) are the mole fractions of the mixture components, \( a_i \) and \( a_j \) are the pure component \( a \) parameters of the mixture components, and \( k_{ij} \) is the binary interaction parameter. Temperature-dependent \( a_i \) and \( a_j \) are used:³⁹

\[
a_i = a_i[1 + \beta_i^{(1)}(1 - \sqrt{T_i}) + \beta_i^{(2)}(1 - \sqrt{T_i})^2 + \beta_i^{(3)}(1 - \sqrt{T_i})^3]^2
\]

(13)

where \( a_i \) is the \( a \) parameter of the pure component at critical temperature \( (eq 8) \), \( \beta_i^{(1)} \), \( \beta_i^{(2)} \), and \( \beta_i^{(3)} \) are empirical coefficients, and \( T_{ij} \) is the reduced temperature. The asymmetric mixing rule is ³⁹

\[
a^{(1)} = \sum_i x_i \sum_j x_j^2 (a_i a_j)^{1/2} l_{ij}
\]

(14)

where \( l_{ij} = -l_{ji} \) is the asymmetric binary interaction parameter. In this work, the symmetric binary interaction parameter \( (k_{ij} = k_{ji}) \) was correlated to temperature as ³⁰

\[
k_{ij} = A + BT + \frac{C}{T}
\]

(15)

where \( A, B, \) and \( C \) are empirical parameters.

To determine the value of \( k_{ij} \) at each temperature, a regression of the solubility measurements was performed for each temperature using the least-squares method with the maximum likelihood objective function in Aspen. With the regressed \( k_{ij} \) values and the corresponding temperatures, the parameters in eq 15 were determined with nonlinear regression using the “fitnlm” function in MATLAB. Afterward, the PR-
Table 5. Measured Densities ($\rho$) of GHL as a Function of Temperature ($T$) and Pressure ($p$) and Standard Uncertainty of Density Measurements ($u(\rho)$)

| $T^\circ$/K | $p^b$/MPa | $\rho$/kg m$^{-3}$ | $u(\rho)$ | $T^\circ$/K | $p^b$/MPa | $\rho$/kg m$^{-3}$ | $u(\rho)$ |
|------------|-----------|-------------------|----------|------------|-----------|-------------------|----------|
| 293.15     | 0.189     | 996.9             | 1.43     | 393.15     | 0.189     | 912.0             | 1.41     |
| 293.15     | 2.023     | 998.1             | 1.43     | 393.15     | 2.023     | 913.9             | 1.41     |
| 293.15     | 3.998     | 999.3             | 1.43     | 393.15     | 3.998     | 915.8             | 1.41     |
| 293.15     | 5.966     | 1000.5            | 1.43     | 393.15     | 5.966     | 917.7             | 1.41     |
| 293.15     | 9.908     | 1002.8            | 1.43     | 393.15     | 9.908     | 919.4             | 1.41     |
| 298.15     | 0.189     | 992.7             | 1.43     | 423.15     | 0.189     | 885.8             | 1.40     |
| 298.15     | 2.023     | 993.8             | 1.43     | 423.15     | 2.023     | 887.9             | 1.40     |
| 298.15     | 3.998     | 995.0             | 1.43     | 423.15     | 3.998     | 890.1             | 1.40     |
| 298.15     | 5.966     | 996.2             | 1.43     | 423.15     | 5.966     | 892.4             | 1.40     |
| 298.15     | 7.958     | 997.4             | 1.43     | 423.15     | 7.958     | 894.5             | 1.40     |
| 298.15     | 9.908     | 998.6             | 1.43     | 443.15     | 9.908     | 896.5             | 1.41     |
| 318.15     | 0.189     | 976.0             | 1.42     | 443.15     | 0.189     | 867.9             | 1.40     |
| 318.15     | 2.023     | 977.3             | 1.42     | 443.15     | 2.023     | 870.3             | 1.40     |
| 318.15     | 3.998     | 978.6             | 1.42     | 443.15     | 3.998     | 872.8             | 1.40     |
| 318.15     | 5.966     | 979.9             | 1.42     | 443.15     | 5.966     | 875.1             | 1.40     |
| 318.15     | 7.958     | 981.2             | 1.42     | 443.15     | 7.958     | 877.5             | 1.40     |
| 348.15     | 0.189     | 950.5             | 1.42     | 458.15     | 0.189     | 854.1             | 1.40     |
| 348.15     | 2.023     | 951.9             | 1.42     | 458.15     | 2.023     | 856.7             | 1.40     |
| 348.15     | 3.998     | 953.5             | 1.42     | 458.15     | 3.998     | 859.5             | 1.40     |
| 348.15     | 5.966     | 955.0             | 1.42     | 458.15     | 5.966     | 862.1             | 1.40     |
| 348.15     | 7.958     | 956.4             | 1.42     | 458.15     | 7.958     | 864.7             | 1.40     |
| 373.15     | 0.189     | 939.2             | 1.41     | 473.15     | 0.189     | 839.9             | 1.39     |
| 373.15     | 2.023     | 930.9             | 1.41     | 473.15     | 2.023     | 843.0             | 1.39     |
| 373.15     | 3.998     | 932.6             | 1.41     | 473.15     | 3.998     | 846.0             | 1.39     |
| 373.15     | 5.966     | 934.3             | 1.41     | 473.15     | 5.966     | 848.9             | 1.40     |
| 373.15     | 7.958     | 936.0             | 1.41     | 473.15     | 7.958     | 851.6             | 1.40     |
| 373.15     | 9.908     | 937.6             | 1.41     | 473.15     | 9.908     | 854.3             | 1.40     |

"Standard uncertainty $u(T) = 0.01$ K. b Standard uncertainty $u(p) = 0.01$ MPa. See Table 2.

BM simulations were run in Aspen using the temperature-dependent $k_i$ model. For comparison, the simulations were run also with $k_i = 0$. Finally, the AAD and the ARD were calculated analogously to eqs 2 and 3 for the saturation pressures obtained from the model compared to the saturation pressures from the measurements.

# RESULTS AND DISCUSSION

## 3.1. Density Measurements

The measured densities of GHL and GNL are presented in Tables 5 and 6, respectively, for temperatures of 293 to 473 K and pressures of 0.16 to 9.9 MPa. A selection of the data is plotted for both lactones in Figure 3 as isotherms of density with respect to pressure. Additionally, the parameters of the density model (eq 1) are reported in Table 7 along with the corresponding AAD and ARD. The values obtained for AAD are 3 orders of magnitude smaller than the measured densities. Furthermore, the isotherms described by the model overlap with the data in Figure 3. Hence, the model provides an excellent prediction of the densities.

The densities of both lactones decreased markedly with respect to temperature and increased slightly with respect to pressure. Similar trends have been reported in the literature for $\gamma$-butyrolactone (GBL)$^{35-37}$ and $\gamma$-valerolactone (GVL).$^{24}$ Furthermore, for any given temperature and pressure, GHL was denser than GNL. By comparing the data from this work to data on GBL and GVL from the literature, it becomes apparent that the density of the $\gamma$-lactones is greater when the molecular mass is lower. This trend is illustrated in Figure 4.

## 3.2. Solubility Measurements

The saturation points of H$_2$ in GHL and GNL are presented in Tables 8 and 9, respectively. The temperature range of the measurements is 479 to 582 K and the pressure range is 3 to 10 MPa. The GHL data are plotted in Figure 5 and the GNL data are plotted in Figure 6. No changes in the results were observed by varying the residence time in the measurements with GNL (compare footnotes d vs e and f vs g in Table 9). Thus, the measurements were repeatable, and they likely proceeded at equilibrium.

From the results, the H$_2$ solubility expressed in mole fraction was 10% to 44% greater in GNL than in GHL. However, if the results are expressed in molality, the difference is considerably less; the saturation molal concentrations of H$_2$ were only 6% to 22% greater in GNL than in GHL at 479 and 531 K. Furthermore, at 582 K and below 10 MPa, H$_2$ molality in GNL was 8% to 10% less than in GHL. Therefore, it seems that the greater H$_2$ solubility in GNL than in GHL can be accounted partly by the greater molecular mass of the former. Thus, the aliphatic nature of the side chain, in opposition to the ester ring, might not have been the only factor that promoted H$_2$ solubility, as was initially thought. Indeed, it has been reported that H$_2$ solubilities in numerous organic solvents not only depend on their chemical nature, but that it also increases as a function of their molecular mass.$^{17}$
The solubility of H₂ in both lactones increased as a function of temperature. The increase of H₂ solubility with increasing temperature has been widely documented for hydrocarbons, including cyclic esters. The increase of H₂ solubility with increasing temperature is likely to influence the kinetics of the HDO of GNL.

### 3.3. Lactone Property Estimations

As Nannoolal’s method has been determined to provide the best approximation to the critical properties of γ-butyrolactone, the critical temperatures (T_c) and pressures (p_c) of GHL and GNL were calculated with this method for use in the PR-BM model. These properties are reported in Table 10. The other properties that were required for input in Aspen are listed in Table S6.

### 3.4. EoS Models

The H₂ bubble points that were calculated with the PR-BM method, both with the temperature-dependent k_ij model and with the model using k_ij = 0, are plotted in Figure 5 for GHL and in Figure 6 for GNL. Furthermore, the coefficients regressed for the k_ij model (eq 15) are reported in Table 11. The deviations reported in Table 11 are of the k_ij calculated with the temperature-dependent model, taking as a reference the k_ij values obtained from the regression with the solubility data. On the other hand, the deviations, AAD and ARD, of the EoS results with respect to the solubility measurements are presented in Table 12.

The deviations of the PR-BM EoS were greater for GNL than for GHL. For GHL, the model predictions are very close to the data (Figure 5). However, for GNL, the EoS deviated considerably large. Thus, the use of the density model instead of the EoS is justifiable.

The pure-component PR-BM EoS was also tested to predict the densities of the pure lactones for comparison with the density model developed in this work (eq 1 and Table 7). The AAD of the predictions of the EoS was 499.3 kg m⁻³ for GNL. Compared to the deviation values obtained with our density model (Table S5), the deviation of the EoS is considerably large. Thus, the use of the density model instead of the EoS is justified for density calculations.

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### Table 6. Measured Densities (ρ) of GNL as a Function of Temperature (T) and Pressure (p)

| T°/K | p / MPa | ρ / kg m⁻³ | T°/K | p / MPa | ρ / kg m⁻³ |
|------|--------|------------|------|--------|------------|
| 293.15 | 0.164  | 964.5      | 393.15 | 0.164  | 881.2      |
| 293.15 | 2.003  | 965.6      | 393.15 | 2.003  | 883.0      |
| 293.15 | 3.983  | 967.7      | 393.15 | 3.983  | 885.1      |
| 293.15 | 5.950  | 969.7      | 393.15 | 5.950  | 887.7      |
| 293.15 | 7.925  | 970.0      | 393.15 | 7.925  | 888.6      |
| 293.15 | 9.894  | 971.1      | 393.15 | 9.894  | 890.3      |
| 298.15 | 0.164  | 960.5      | 423.15 | 0.164  | 860.8      |
| 298.15 | 2.003  | 961.6      | 423.15 | 2.003  | 862.8      |
| 298.15 | 3.983  | 962.8      | 423.15 | 3.983  | 865.0      |
| 298.15 | 5.950  | 964.0      | 423.15 | 5.950  | 867.1      |
| 298.15 | 7.925  | 965.2      | 423.15 | 7.925  | 869.2      |
| 298.15 | 9.894  | 966.3      | 423.15 | 9.894  | 871.2      |
| 318.15 | 0.164  | 954.7      | 443.15 | 0.164  | 844.2      |
| 318.15 | 2.003  | 956.0      | 443.15 | 2.003  | 846.5      |
| 318.15 | 3.983  | 957.3      | 443.15 | 3.983  | 848.9      |
| 318.15 | 5.950  | 958.3      | 443.15 | 5.950  | 851.2      |
| 318.15 | 7.925  | 959.8      | 443.15 | 7.925  | 853.5      |
| 318.15 | 9.894  | 961.0      | 443.15 | 9.894  | 855.7      |
| 348.15 | 0.164  | 944.8      | 458.15 | 0.164  | 831.6      |
| 348.15 | 2.003  | 946.0      | 458.15 | 2.003  | 834.1      |
| 348.15 | 3.983  | 947.1      | 458.15 | 3.983  | 836.7      |
| 348.15 | 5.950  | 948.5      | 458.15 | 5.950  | 839.2      |
| 348.15 | 7.925  | 949.8      | 458.15 | 7.925  | 841.7      |
| 348.15 | 9.894  | 951.0      | 458.15 | 9.894  | 844.1      |
| 373.15 | 0.164  | 934.1      | 473.15 | 0.164  | 818.8      |
| 373.15 | 2.003  | 935.9      | 473.15 | 2.003  | 821.6      |
| 373.15 | 3.983  | 937.3      | 473.15 | 3.983  | 824.4      |
| 373.15 | 5.950  | 938.7      | 473.15 | 5.950  | 827.1      |
| 373.15 | 7.925  | 940.1      | 473.15 | 7.925  | 829.8      |
| 373.15 | 9.894  | 941.4      | 473.15 | 9.894  | 832.3      |

“Standard uncertainty u(T) = 0.01 K. Standard uncertainty u(p) = 0.01 MPa. Standard uncertainty u(ρ) = 1.31 kg m⁻³. See Table 2.”

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Figure 3. Densities of (a) GHL and (b) GNL measured at constant temperatures of 298 K (○), 348 K (△), 393 K for GHL (yellow △), 398 K for GNL (blue △), 443 K (◇), and 473 K (□). The dashed lines are the isotherms calculated with the fitted density model (eq 3). Note the different scales.

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https://dx.doi.org/10.1021/acs.jced.0c00087

J. Chem. Eng. Data 2020, 65, 2764–2773
In this work, the densities and H₂ solubilities of GHL and GNL were measured at the temperature and pressure ranges of 479 to 582 K and 3 to 10 MPa. Furthermore, a semiempirical density model and an EoS description of the H₂ saturation isotherms were presented for each lactone.

The densities of GHL and GNL decreased strongly as a function of temperature and increased slightly with respect to pressure. Furthermore, GHL was denser than GNL. As for the density model, it fit remarkably well to the measurements in the tested ranges (293 to 473 K and 0.16 to 9.9 MPa).

Concerning the solubility of H₂, the curves of saturation (H₂ pressure against H₂ mole fraction) were almost linear with both lactones. Likewise, the solubility increased with respect to temperature, although, in GNL, the increase was greater from 479 to 531 K than from 531 to 582 K. It was also observed that H₂ solubility was greater in GNL than in GHL. Some of the factors that favored H₂ solubility in GNL could have been the molecular mass of the lactone and the aliphatic nature of its side chain.

The PR-BM EoS was used to reproduce the H₂ solubility in GHL. The symbols are data points at 479 K (···), 531 K (- - -), and 582 K (--; Table 9). The dashed lines correspond to the PR-BM model with k₁ = 0 at 479 K (--), 531 K (- - -), and 582 K (--···). The solid lines correspond to the PR-BM model with the regressed k₁ at 479 K (yellow line), 531 K (light red line), and 582 K (dark red line). The points at xH₂ = 0 were taken from the GHL vapor pressure model by Emel'yanenko et al.²⁹

### Table 7. Parameters of the Density Model (K₁ – K₅, eq 1), Average Absolute Deviation (AAD, eq 2), and Average Relative Deviation (ARD, eq 3)

| compound | K₁/ kg m⁻³ | K₂/ kg m⁻³ K⁻¹ | K₃/ kg m⁻³ K⁻² | K₄/ kg m⁻³ M⁻¹ | K₅/ kg m⁻³ M⁻¹ | AAD | ARD |
|----------|-------------|----------------|----------------|----------------|----------------|------|-----|
| GHL      | 1226.2      | -0.728         | -1.84 × 10⁻⁴   | -0.825         | 4.67 × 10⁻³    | 0.188 | 0.02% |
| GNL      | 1183.6      | -0.71          | -1.26 × 10⁻⁴   | -0.744         | 3.47 × 10⁻³    | 0.142 | 0.02% |

**Figure 4.** Density dependence on temperature at 5 MPa in four γ-lactones: γ-butyrolactone (data from Ihmels et al.,³⁵ red □), γ-valerolactone (data from Zaitseva et al.,³⁶ green △), GHL (calculated with eq 1, -····), and GNL (calculated with eq 1, - - -).

**Table 8.** Measured Mole Fractions of H₂ in GNL (xH₂) at Saturation Point for Temperature T and Pressure p with Their Respective Standard Uncertainties (uᵢ)

| T/K     | p/MPa | u(p)³/kPa | xH₂     | u(xH₂)³ |
|---------|-------|-----------|---------|---------|
| 479.1   | 3.01  | 3.1       | 0.0161  | 1.5 × 10⁻⁵ |
| 479.1   | 6.01  | 3.4       | 0.0335  | 7.5 × 10⁻⁵ |
| 479.1   | 8.01  | 3.8       | 0.0466  | 5.4 × 10⁻⁵ |
| 479.1   | 10.0  | 4.1       | 0.0592  | 4.2 × 10⁻⁵ |
| 530.6   | 3.03  | 3.1       | 0.0186  | 1.3 × 10⁻⁵ |
| 530.6   | 6.52  | 3.5       | 0.0459  | 5.5 × 10⁻⁵ |
| 530.6   | 10.0  | 4.1       | 0.0691  | 3.6 × 10⁻⁵ |
| 582.1   | 4.01  | 3.2       | 0.0354  | 7.1 × 10⁻⁵ |
| 582.1   | 6.02  | 3.4       | 0.0516  | 4.9 × 10⁻⁵ |
| 582.1   | 8.02  | 3.8       | 0.0693  | 3.6 × 10⁻⁵ |
| 582.1   | 9.08  | 4.0       | 0.0781  | 3.2 × 10⁻⁵ |

**Figure 5.** Experimental data and PR-BM models of H₂ solubility in GHL. The symbols are data points at 479 K (□), 531 K (○), and 582 K (△). The dashed lines correspond to the PR-BM model with k₁ = 0 at 479 K (--), 531 K (- - -), and 582 K (--; Table 9). The solid lines correspond to the PR-BM model with the regressed k₁ at 479 K (yellow line), 531 K (light red line), and 582 K (dark red line). The points at xH₂ = 0 were taken from the GHL vapor pressure model by Emel'yanenko et al.²⁹

**Table 9.** Measured Mole Fractions of H₂ in GNL (xH₂) at the Saturation Point for Temperature T and Pressure p with Their Respective Standard Uncertainties (uᵢ)

| T/K     | p/MPa | u(p)³/kPa | xH₂     | u(xH₂)³ |
|---------|-------|-----------|---------|---------|
| 479.1   | 3.02  | 3.1       | 0.0232  | 1.1 × 10⁻² |
| 479.1²   | 6.01  | 3.4       | 0.0431  | 5.8 × 10⁻³ |
| 479.1³   | 6.01  | 3.4       | 0.0427  | 4.9 × 10⁻³ |
| 479.2   | 8.01  | 3.8       | 0.0545  | 4.6 × 10⁻³ |
| 479.2   | 10.0  | 4.1       | 0.0753  | 3.3 × 10⁻⁵ |
| 530.6   | 3.02  | 3.1       | 0.0274  | 9.1 × 10⁻⁵ |
| 530.6⁴   | 6.02  | 3.4       | 0.0518  | 4.9 × 10⁻⁵ |
| 530.6⁵   | 6.02  | 3.4       | 0.0518  | 4.1 × 10⁻⁵ |
| 530.6⁶   | 8.01  | 3.8       | 0.0671  | 3.7 × 10⁻⁵ |
| 530.6⁷   | 10.0  | 4.1       | 0.0907  | 2.7 × 10⁻⁵ |
| 582.1⁸   | 3.10  | 3.1       | 0.0274  | 9.1 × 10⁻⁵ |
| 581.5⁹   | 3.00  | 3.1       | 0.0272  | 9.2 × 10⁻⁵ |
| 582.0   | 6.01  | 3.4       | 0.0566  | 4.4 × 10⁻⁵ |
| 582.0   | 8.01  | 3.8       | 0.0771  | 3.2 × 10⁻⁵ |
| 581.9   | 10.0  | 4.1       | 0.0989  | 2.5 × 10⁻⁵ |

αᵢ(T) = 0.18 K, see equilibrium cell T in Table S3.²⁶ See equilibrium cell p Table S4.²⁶ See uᵢ(xH₂, L, I, C) in Table 4.²⁶ Measurement with liquid residence time of 2.9 min.²⁶ Repeated measurement with liquid residence time of 2.4 min.²⁶ Measurement with liquid residence time of 3.6 min.²⁶ Repeated measurement with liquid residence time of 3.0 min.²⁶ Measurements repeated at equal liquid residence time of 2.0 min.²⁶
Figure 6. Experimental data and PR-BM models of H₂ solubility in GNL. The symbols are data points at 479 K (⊐), 531 K (⊙), and 582 K (△). The dashed lines correspond to the PR-BM model with \( k_{ij} = 0 \) at 479 K (···, overlaps with green line), 531 K (---), and 582 K (----). The solid lines correspond to the PR-BM model with the regressed \( k_{ij} \) at 479 K (light blue line), 531 K (dark blue line), and 582 K (green line). The points at \( x_{H_2} = 0 \) were taken from the GNL vapor pressure model by Emel'yanenko et al.²⁹

Table 10. Properties Estimated with Nannoolal’s Method⁽²⁾ for the PR-BM Model

| compound | critical temperature, \( T_c / K \) | critical pressure, \( p_c / \text{MPa} \) | acentric factor, \( \omega \) |
|----------|-------------------------------|-------------------------------|-------------------------------|
| GHL      | 748.2                         | 3.315                         | 0.8283                        |
| GNL      | 786.2                         | 2.738                         | 0.5092                        |

Table 11. Parameters Regressed for the PR-BM Binary Parameter (\( k_{ij} \)) Temperature Correlation (eq 15) with Solubility Data of GHL and GNL

\[
\begin{array}{cccc}
A & B/K^{-1} & C/K & \text{AAD}^{a} & \text{ARD}^{b} \\
\hline
\text{GHL} & 14.697 & -1.3417 \times 10^{-2} & -3947.9 & 1.94 \times 10^{-4} & 0.33\% \\
\text{GNL} & -28.244 & 2.8635 \times 10^{-2} & 7158.7 & 1.59 \times 10^{-4} & 0.03\% \\
\end{array}
\]

\(^{a}\)Average absolute deviation of eq 15 with respect to regressed \( k_{ij} \) values.

\(^{b}\)Average relative deviation of eq 15 with respect to regressed \( k_{ij} \) values.

Table 12. Average Absolute Deviation (AAD) and Average Relative Deviation (ARD) of the PR-BM Models for H₂ Solubility in GHL and GNL with Respect to the Solubility Data

| compound, \( k_{ij} (T) \) | AAD  | ARD |
|---------------------------|------|-----|
| GHL, \( k_{ij} (T)^{a} \) | 0.247 | 4.0\% |
| GHL, \( k_{ij} = 0^{b} \)  | 0.645 | 9.0\% |
| GNL, \( k_{ij} (T)^{a} \)  | 0.968 | 13\% |
| GNL, \( k_{ij} = 0^{b} \)  | 1.04  | 16\% |

\(^{a}\)The model included the temperature correlation of the symmetric binary parameter. \(^{b}\)The model did not include the symmetric binary parameter.

The data were mitigated slightly by applying a temperature-dependent model of the symmetric binary interaction parameter (\( k_{ij} \)).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.0c00087.

Sample purity analysis; uncertainty of density measurements due to impurities; uncertainty budgets of temperature and pressure measurements; details on the calibration and uncertainty calculation of H₂ flow; linear regressions of solubility data; parameters used in Aspen simulations (PDF)

AUTHOR INFORMATION

Corresponding Author

José Luis González Escobedo — Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Aalto 00076, Finland; orcid.org/0000-0001-8357-201X; Email: jose.gonzalezescobedo@aalto.fi

Authors

Petri Uusi-Kyyny — Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Aalto 00076, Finland; orcid.org/0000-0002-8339-4601

Riikka L. Puurunen — Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Aalto 00076, Finland; orcid.org/0000-0001-8722-4864

Ville Alopaeus — Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Aalto 00076, Finland; Department of Chemical Engineering, Mid Sweden University, Sundsvall 85170, Sweden

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jced.0c00087

Author Contributions

The conceptualization of the study was made by all the authors. The experimental methodology was developed by P.U.K. and V.A. The measurements were performed by J.L.G.E. and P.U.K. The computer simulations were performed by J.L.G.E. and P.U.K. The original draft of the manuscript was produced by J.L.G.E.

Funding

José Luis González Escobedo acknowledges personal grants from Fortum Foundation (no. 201800142) and from the Finnish Foundation for Technology Promotion (no. 6712).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The Finnish National Bioeconomy Research Infrastructure is acknowledged for providing some equipment.

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