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### Hydrodeoxygenation Model Compounds $\gamma$ -Heptalactone and $\gamma$ -Nonalactone: Density from 293 to 473 K and H<sub>2</sub> Solubility from 479 to 582 K

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



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 H<sub>2</sub> 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.<sup>1</sup> Lignocellulosic biomass, if responsibly harvested,<sup>2,3</sup> 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,<sup>4-7</sup> 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.<sup>6,7</sup> One possible route is the dimerization of LA into a mixture of slightly branched C<sub>10</sub> molecules,<sup>8-11</sup> which themselves require further treatment.

Recently, the hydrodeoxygenation (HDO) of  $\gamma$ -nonalactone (GNL) has been studied as a model compound for the production of hydrocarbons from LA dimers,<sup>12</sup> as the  $\gamma$ -lactone group is typically found in LA dimers.<sup>8</sup> 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  $(H_2)$  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.<sup>12</sup> Because most of the catalyst was fully wetted by the liquid, it was necessary for the H<sub>2</sub> to dissolve in the liquid reaction mixture in order to reach the catalyst and thereby to participate in HDO reactions. Hence, the solubility of H<sub>2</sub> in GNL was an important factor influencing the outcome



Figure 1. Chemical structures of (a)  $\gamma$ -heptalactone (dihydro-5propyl-2(3H)-furanone) and (b)  $\gamma$ -nonalactone (dihydro-5-pentyl-2(3H)-furanone).

of the process. In particular, the temperature and pressure dependence of  $H_2$  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 H<sub>2</sub> in GNL are available in the literature. Most studies involving the

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#### Table 1. Chemicals

chemical	CASRN	supplier	initial mole fraction purity <sup>c</sup>	purification method	final mole fraction purity <sup>d</sup>	analysis method	refractive index after distillation <sup>e</sup>	water content after distillation <sup>f</sup> /wt %
$\gamma$ -heptalactone <sup><i>a</i></sup>	105-21-5	Sigma- Aldrich	0.9938	vacuum distillation	0.9943	GC	1.441477	0.0106
$\gamma$ -nonalactone <sup>b</sup>	104-61-0	Sigma- Aldrich	0.9891	vacuum distillation	0.9999	GC	1.446905	0.0120
hydrogen	1333-74-0	AGA	0.99999	none				

<sup>*a*</sup>Dihydro-5-propyl-2(3*H*)-furanone. <sup>*b*</sup>Dihydro-5-pentyl-2(3*H*)-furanone. <sup>*c*</sup>Reported by manufacturer. <sup>*d*</sup>Accounts for organic impurities and H<sub>2</sub>O. Organic impurities not detected in GNL. <sup>*e*</sup>Dimensionless. Measured at 293.15 K  $\pm$  0.03 K and 0.1 MPa  $\pm$  0.01 MPa. Standard uncertainty: 0.00034. <sup>*f*</sup>Standard uncertainty (standard deviation): 0.0002 wt %.

#### Table 2. Uncertainty Budget of the Density Measurements

source of uncertainty	standard uncertainty for GHL/kg m <sup>-3</sup>	standard uncertainty for GNL/kg m <sup>-3</sup>
standard uncertainty of the calibration of the density meter, $u_{ m s}( ho^{ m calib})^a$	0.036	0.036
standard deviation of distilled water measurements, $u_{ m s}( ho_{ m H2O})$	0.3832	0.3832
root mean square of the differences between the distilled water measurements and the reference values, $u_{\rm s} (\Delta \rho_{\rm H2O})^b$	0.7501	0.7501
uncertainty of water density reference values <sup>b</sup>	$1 \times 10^{-5} \rho$	$1 \times 10^{-5} \rho$
instrument uncertainty reported by manufacturer, $u_{ m s}( ho_{ m ins})$	1	1
sample impurity, $u_{\rm s}(\rho_{\rm s})^c$	$5.73 \times 10^{-4} \rho$	$6.66 \times 10^{-7} \rho$
combined uncertainty, $u_{\rm c}(\rho)$	$\sqrt{1.71 + 3.29 \times 10^{-7} \rho^2}$	$\sqrt{1.71 + 1.00 \times 10^{-10} \rho^2}$

<sup>*a*</sup>Reported by Baird et al.<sup>20</sup> <sup>*b*</sup>Water IAPWS95 equation of state, NIST.<sup>22</sup> <sup>*c*</sup>Calculated according to the recommendations by Chirico et al.<sup>23</sup> 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 $\ensuremath{\text{m}^{-3}}$	0.188	0.142
combined uncertainty of density measurements, $u_{\rm c}( ho)^a/{\rm kg}~{\rm m}^{-3}$	$\sqrt{1.71 + 3.29 \times 10^{-7} \rho^2}$	$\sqrt{1.71 + 1.00 \times 10^{-10} \rho^2}$
temperature set point in the density meter, $u_{\rm s}(T_a)^b$ /K	0.01	0.01
temperature in solubility setup, from temperature calibrator, $u_{\rm s}(T_b)^{\rm c}$ /K	0.14	0.14
combined temperature uncertainty, $u_c(T)/K$	0.14	0.14
$\left[\frac{\partial\rho}{\partial T}\right]^2 u_c^2(T)_d$	$(K_2 + 2K_3T + K_3p)^2 1.96 \times 10^{-2}$	$(K_2 + 2K_3T + K_5p)^2 1.96 \times 10^{-2}$
pressure set point in the syringe pump coupled to the density meter, $u_{\rm s}(p_a)^e$ /MPa	0.01	0.01
pressure in solubility setup, $u_{s}(p_{b})^{f}$ /MPa	$\sqrt{7.95 \times 10^{-5} + 1.6 \times 10^{-7} p^2}$	$\sqrt{7.95 \times 10^{-5} + 1.6 \times 10^{-7} p^2}$
combined pressure uncertainty, $u_c(p)/MPa$	$\sqrt{1.8 \times 10^{-4} + 1.6 \times 10^{-7} p^2}$	$\sqrt{1.8 \times 10^{-4} + 1.6 \times 10^{-7} p^2}$
$\left[\frac{\partial\rho}{\partial p}\right]^2 u_c^2(p)_d$	$(K_4 + K_5 T)^2 (1.8 \times 10^{-4} + 1.6 \times 10^{-7} p^2)$	$(K_4 + K_5 T)^2 (1.8 \times 10^{-4} + 1.6 \times 10^{-7} p^2)$
Combined uncertainty for GHL, $u_c(\rho^{\rm calc})/{\rm kg}~{\rm m}^{-3}$	$\sqrt{1.745 + 3.29 \times 10^{-7} \rho^2} + \left(\frac{1}{2}\right)$	$\left[\frac{\partial\rho}{\partial T}\right]^2 u_c^2(T) + \left[\frac{\partial\rho}{\partial p}\right]^2 u_c^2(p)$
Combined uncertainty for GNL, $u_c(\rho^{\text{calc}})/\text{kg m}^{-3}$	$\sqrt{1.730 + 1.00 \times 10^{-10} \rho^2} +$	$\left[\frac{\partial\rho}{\partial T}\right]^2 u_c^2(T) + \left[\frac{\partial\rho}{\partial p}\right]^2 u_c^2(p)$

<sup>a</sup>See Table 2. <sup>b</sup>Reported by T. Vielma.<sup>26</sup>  $^{c}T_1$  in Figure 2, corrected with calibrator. See Feeding pump T in Table S3. <sup>d</sup>The coefficients are from eq 1 and reported in Table 7. In the expression, the temperatures and pressures are the calibrated cell temperature ( $T_3$  in Figure 2) and pump pressure (P in Figure 2) in the solubility setup. <sup>e</sup>From manufacturer. <sup>f</sup>P in Figure 2, corrected with calibrator. See Feeding pump p in Table S4.

solubility of a gas in a lactone focus on the  $CO_2 - \gamma$ -valerolactone system.<sup>13-16</sup>

The present study investigates the solubility of  $H_2$  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  $H_2$ , which usually displays a greater affinity to aliphatic structures than to oxygenated ones.<sup>17</sup> In fact, it has been shown that the H<sub>2</sub> solubility behavior of oxygenates tends to converge with the behavior of hydrocarbons, the longer the carbon chain.<sup>17,18</sup> Thus,  $\gamma$ -heptalactone (dihydro-5-propyl-2(3*H*)-furanone, Figure 1a) was studied for comparison, as it was expected to exhibit lower H<sub>2</sub> solubilities than GNL. The densities of GHL and GNL, which are required in the

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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.<sup>19</sup> 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<sub>2</sub> solubility measurements more accurately.

#### EXPERIMENTAL AND COMPUTATIONAL METHODS

**2.1. Materials.**  $\gamma$ -Heptalactone (GHL) and  $\gamma$ -nonalactone (GNL) were purchased from Sigma-Aldrich. Both reagents were provided with a purity of  $\geq$ 98%. 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 chromatorgraphy-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.

**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.<sup>20</sup> 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).<sup>21,22</sup> 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.

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

$$\rho(T, p) = K_1 + K_2 T + K_3 T^2 + K_4 p + K_5 T p \tag{1}$$

The values of the coefficients are reported in Table 7. For the regression, the "fitnlm" function in MATLAB<sup>25</sup> 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

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

$$ARD = \frac{100}{N} \sum_{i=1}^{N} \frac{|\rho_i^{\text{meas}} - \rho_i^{\text{calc}}|}{\rho_i^{\text{meas}}}$$
(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.

**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.<sup>27,28</sup> (Figure 2). Before the measurements,



Figure 2. Scheme of the continuous flow apparatus used for the  $H_2$  solubility 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<sup>-1</sup>. For the determination of the saturation point

 $1.9 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ 

 $5.0 \times 10^{-4} O_{\rm T} \ {\rm cm}^3 \ {\rm s}^{-1}$ 

see Table 3

 $x_{\rm H2,L} - x_{\rm H2.GL}$ 

 $\frac{Q_{\rm L}\rho_{\rm L}}{\tilde{V}_{\rm H2}M_{\rm L}\left(\frac{Q_{\rm H2}}{\tilde{V}_{\rm H2}}+\frac{Q_{\rm L}\rho_{\rm L}}{M_{\rm t}}\right)^2} \bigg|^2 1.2 \times 10^{-3}$ 

 $-\frac{Q_{\rm H2}\rho_{\rm L}}{\tilde{V}_{\rm H2}M_{\rm L}\left(\frac{Q_{\rm H2}}{\tilde{V}_{\rm L2}}+\frac{Q_{\rm L}\rho_{\rm L}}{M}\right)^2}\right|^2 2.5 \times 10^{-7} Q_{\rm L}^2$ 

 $\left| -\frac{Q_{H2}Q_{L}}{\tilde{V}_{H2}M_{L}\left(\frac{Q_{H2}}{\tilde{u}_{c}}+\frac{Q_{L}\rho_{L}}{\tilde{u}_{c}}\right)^{2}}\right|^{2} \left| u_{c}^{2}(\rho^{calc})\right|^{2}$ 

 $\sqrt{\left(\frac{1}{2}\right)^2 u_c^2(x_{H2,L}) + \left(\frac{1}{2}\right)^2 u_c^2(x_{H2,LG})}$ 

 $\left\| \frac{\partial x_{\text{H2}}}{\partial Q_{\text{H2}}} \right\|^2 u_c^2 (Q_{\text{H2}}) + \left| \frac{\partial x_{\text{H2}}}{\partial Q_r} \right|^2 u_c^2 (Q_{\text{L}}) + \left| \frac{\partial x_{\text{H2}}}{\partial \rho^{\text{calc}}} \right|^2 u_c^2 (\rho^{\text{calc}})$ 

0.01 cm<sup>3</sup>

0.80 MPa  $3.5 \times 10^{-2} \text{ cm}^3 \text{ s}^{-1}$ 

0.14 K

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standard uncertainty

#### Table 4. Uncertainty Budget of the H<sub>2</sub> Mole Fractions $(x_{H2})$ in the Solubility Measurements

source of uncertainty maximum absolute deviation of H<sub>2</sub> flow calibration factor,  $u_s(Q_{H2})^a$ pump volume in H<sub>2</sub> flow calibration,  $u_s(\Delta v)^b$ temperature of feeding pump used to calibrate H<sub>2</sub> mass flow,  $u_c(T)^c$ pressure of feeding pump used to calibrate H<sub>2</sub> mass flow,  $u_c(p)^d$ combined uncertainty of the H<sub>2</sub> volumetric flow calibration,  $u_c(Q_{H2})^e$ 

$$\left[\frac{\partial x_{\rm H2}}{\partial Q_{\rm H2}}\right]^2 u_{\rm c}^2(Q_{\rm H2})_{f}$$

lactone flow uncertainty,  $u_s(Q_L)^b$ 

$$\left[\frac{\partial x_{\rm H2}}{\partial Q_{\rm L}}\right]^2 u_s^2(Q_{\rm L})_f$$

combined uncertainty of calculated density,  $u_c(\rho^{calc})$ 

$$\left[\frac{\partial x_{H2}}{\partial \rho^{\text{calc}}}\right]^2 u_c^2 (\rho^{\text{calc}})_f$$

combined H<sub>2</sub> mole fraction uncertainty,  $u_c(x_{H2,L})$ ,  $u_c(x_{H2,LG})$ 

composition distance between the last composition observed in the liquid region and in the gas—liquid region

combined uncertainty of H<sub>2</sub> bubble point,  $u_c(x_{H2,L-LG})$ 

<sup>*a*</sup>Deviation of H<sub>2</sub> mass flow controller signal calibrated with calibration factor (section S4, eq S2) with respect to H<sub>2</sub> mass flow determined with the feeding pump (section 2.4). <sup>*b*</sup>According to the manufacturer. <sup>*c*</sup>Table S3. <sup>*d*</sup>Equation in Table S4 with p = 2.002 MPa. <sup>*e*</sup>Calculation:

$$u_{\rm c}(Q_{\rm H2}) = \left(u_{\rm s}^2(Q_{\rm H2}) + \left[\frac{\partial Q_{\rm pump}}{\partial(\Delta v_{\rm pump})}\right]^2 u_{\rm s}^2(\Delta v) + \left[\frac{\partial Q_{\rm pump}}{\partial T_{\rm pump}}\right]^2 u_{\rm c}^2(T) + \left[\frac{\partial Q_{\rm pump}}{\partial p_{\rm pump}}\right]^2 u_{\rm c}^2(p)\right)^{1/2}$$

Further details in Section S4. <sup>f</sup>Symbols:  $Q_{H2}$ , volumetric flow of  $H_{2}$ ;  $Q_{L}$ , volumetric flow of lactone;  $\rho_{L}$ , density of lactone;  $\tilde{V}_{H2}$  molar volume of  $H_{2}$  at normal conditions (22 414 cm<sup>3</sup> mol<sup>-1</sup>);  $M_{L}$  molecular mass of lactone.

at any given conditions, the lactone flow rate was varied between 0.3 and 1.6 mL min<sup>-1</sup> while the flow inside the equilibrium cell was monitored with the camera. The appearance of bubbles in the flow (gas-liquid region) was assumed to indicate that the saturation point had been attained. The composition at the saturation point was estimated by averaging the lowest value of the lactone flow rate observed in the liquid region and the highest value observed in the gas-liquid region (eq 5). To ensure that the measurements were performed at equilibrium, some GNL measurements were repeated at different residence times (volume of heated zone  $\sim 2.1$  mL) by increasing the H<sub>2</sub> flow rate to 6.4 mL min<sup>-1</sup>. The assumption was that different apparent bubble points would be observed with different residence times if the steady state were governed by mass transfer, whereas the same bubble point would be observed if the steady state were governed by phase equilibrium. Finally, at the end of each run, the H<sub>2</sub> collected in the stabilizing pump was diluted with a large amount of N2 and flushed into the ventilation system in order to avoid ignition.

The instruments that were used to measure the key parameters in the solubility determinations were calibrated.

First, the temperature measurements in the equilibrium cell and in the feeding pump (Figure 2) were calibrated with an ASL digital thermometer, model CTR-2000-024, which was certified by the Finnish National Standards Laboratory (MIKES). Second, the pressure measurements in the equilibrium cell and in the feeding pump (Figure 2) were calibrated with a Beamex MC2-PE calibrator equipped with an EXT60 pressure module. The manufacturer certified the calibrator. Finally, the H<sub>2</sub> mass flow controller was calibrated by allowing  $H_2$  to flow into the feeding pump while the time and the increase in volume at constant temperature and pressure were recorded; the volume was recorded with the sensor of the feeding pump, and the time was recorded with the control software of the solubility apparatus. Details on the calibration of H<sub>2</sub> flow are presented in section S4. The temperature and pressure calibration data were used to build calibration curves, with which the measurements were corrected. For the H<sub>2</sub> flow, a calibration factor was used. The uncertainty budgets of the H<sub>2</sub> mole fractions, the temperatures, and the pressures at saturation point are reported in Table 4, and Tables S3, and S4, respectively.

**2.5. Calculations.** From the flow measurements, the H<sub>2</sub> molar fractions  $(x_{H2})$  in the H<sub>2</sub>-lactone mixture were calculated as

$$x_{\rm H2} = \frac{\frac{Q_{\rm H2}}{\bar{V}_{\rm H2}}}{\frac{Q_{\rm H2}}{\bar{V}_{\rm H2}} + \frac{Q_{\rm I}\rho^{\rm calc}}{M_{\rm L}}}$$
(4)

where  $Q_{\rm H2}$  (cm<sup>3</sup> min<sup>-1</sup>) is the calibrated H<sub>2</sub> volumetric flow at normal conditions and  $\tilde{V}_{\rm H2}$  is the molar volume of H<sub>2</sub> at normal conditions (22 414 cm<sup>3</sup> mol<sup>-1</sup>). For the lactone,  $Q_{\rm L}$ (cm<sup>3</sup> min<sup>-1</sup>) is the volumetric flow,  $\rho^{\rm calc}$  (g cm<sup>-3</sup>) is the density determined with eq 1 from the temperature and pressure of the measurement, and  $M_{\rm L}$  (g mol<sup>-1</sup>) is the molecular mass. Once the flows were converted to molar fractions, the composition of the mixture at saturation point ( $x_{\rm H2}^{\rm sat}$ ) could be calculated from the observations:

$$x_{\rm H2}^{\rm sat} = \frac{x_{\rm H2,L} + x_{\rm H2,GL}}{2} \tag{5}$$

where  $x_{H2,L}$  is the H<sub>2</sub> molar fraction at the lowest lactone flow rate observed in the liquid region, and  $x_{H2,GL}$  is the H<sub>2</sub> 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  $x_{H2} = 0$ . The vapor pressures at the tested temperatures were calculated with the model by Emel'yanenko et al.,<sup>29</sup> 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 Plus<sup>30</sup> with the temperatures used in the solubility measurements and an  $x_{H2}$  range of 0 to 0.2. The EoS model required the input of the physical properties of the lactones. Although Emel'yanenko et al.<sup>29</sup> 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.<sup>31</sup> 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.<sup>32</sup> This method was found by Nannoolal et al.<sup>32</sup> 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 ( $\Delta H_f^\circ$ and  $\Delta G_f^\circ$ ), and the ideal gas heat capacity ( $C_p$ ) polynomial coefficients. They were calculated using Joback's method.<sup>33</sup> Furthermore, the vapor pressure data and extended Antoine equation coefficients were taken from Emel'yanenko et al.<sup>29</sup>

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For the calculations, the PR-BM method was used. The Peng–Robinson EoS is  $^{34}$ 

$$p = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2}$$
(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<sup>34</sup>

$$a = 0.45724 \frac{R^2 T_c^2}{P_c}$$
(8)

$$b = 0.07780 \frac{RT_c}{P_c} \tag{9}$$

The Boston–Mathias modification for mixtures provides mixing rules, according to which  $^{19}\,$ 

$$b = \sum_{i} b_{i} x_{i} \tag{10}$$

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:<sup>19</sup>

$$a = a^{(0)} + a^{(1)} \tag{11}$$

The symmetric mixing rule is<sup>19</sup>

$$a^{(0)} = \sum_{i} x_{i} \sum_{j} x_{j} (a_{i}a_{j})^{1/2} (1 - k_{ij})$$
(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:<sup>19</sup>

$$a_{i} = a_{ci} [1 + \beta_{i}^{(1)} (1 - \sqrt{T_{ri}}) + \beta_{i}^{(2)} (1 - \sqrt{T_{ri}})^{2} + \beta_{i}^{(3)} (1 - \sqrt{T_{ri}})^{3}]^{2}$$
(13)

where  $a_{ci}$  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  $T_{ri}$  is the reduced temperature. The asymmetric mixing rule is<sup>19</sup>

$$a^{(1)} = \sum_{i} x_{i} \sum_{j} x_{j}^{2} (a_{i}a_{j})^{1/2} l_{ij}$$
(14)

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

$$k_{ij} = A + BT + \frac{C}{T} \tag{15}$$

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-

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Table 5. Measured Densities ( $\rho$ ) of GHL as a Function of Temperature (T) and Pressure (p) and Standard Uncertainty of Density Measurements ( $u_s(\rho)$ )

$T^a/K$	р <sup><i>b</i></sup> /МРа	$ ho/{ m kg}~{ m m}^{-3}$	$u_{\rm s}(\rho)^c/ \text{ kg m}^{-3}$	$T^{a}/K$	р <sup>b</sup> /МРа	$ ho/{\rm kg}~{\rm m}^{-3}$	$u_{\rm s}( ho)^c$ / kg m <sup>-3</sup>
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	7.958	919.4	1.41
298.15	0.189	992.7	1.43	393.15	9.908	921.3	1.41
298.15	2.023	993.8	1.43	423.15	0.189	885.8	1.40
298.15	3.998	995.0	1.43	423.15	2.023	887.9	1.40
298.15	5.966	996.2	1.43	423.15	3.998	890.1	1.40
298.15	7.958	997.4	1.43	423.15	5.966	892.4	1.40
298.15	9.908	998.6	1.43	423.15	7.958	894.5	1.40
318.15	0.189	976.0	1.42	423.15	9.908	896.5	1.41
318.15	2.023	977.3	1.42	443.15	0.189	867.9	1.40
318.15	3.998	978.6	1.42	443.15	2.023	870.3	1.40
318.15	5.966	979.9	1.42	443.15	3.998	872.8	1.40
318.15	7.958	981.2	1.42	443.15	5.966	875.1	1.40
318.15	9.908	982.4	1.42	443.15	7.958	877.5	1.40
348.15	0.189	950.5	1.42	443.15	9.908	879.8	1.40
348.15	2.023	951.9	1.42	458.15	0.189	854.1	1.40
348.15	3.998	953.5	1.42	458.15	2.023	856.7	1.40
348.15	5.966	955.0	1.42	458.15	3.998	859.5	1.40
348.15	7.958	956.4	1.42	458.15	5.966	862.1	1.40
348.15	9.908	957.9	1.42	458.15	7.958	864.7	1.40
373.15	0.189	929.2	1.41	458.15	9.908	867.1	1.40
373.15	2.023	930.9	1.41	473.15	0.189	839.9	1.39
373.15	3.998	932.6	1.41	473.15	2.023	843.0	1.39
373.15	5.966	934.3	1.41	473.15	3.998	846.0	1.39
373.15	7.958	936.0	1.41	473.15	5.966	848.9	1.40
373.15	9.908	937.6	1.41	473.15	7.958	851.6	1.40
				473.15	9.908	854.3	1.40

<sup>a</sup>Standard uncertainty u(T) = 0.01 K. <sup>b</sup>Standard uncertainty u(p) = 0.01 MPa. <sup>c</sup>See Table 2.

BM simulations were run in Aspen using the temperaturedependent  $k_{ij}$  model. For comparison, the simulations were run also with  $k_{ij} = 0$ . 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)<sup>35–37</sup> and  $\gamma$ -valerolactone (GVL).<sup>24</sup> 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.<sup>17</sup> Table 6. Measured Densities  $(\rho)$  of GNL as a Function of Temperature (T) and Pressure (p)

$T^{a}/K$	р <sup>ь</sup> /МРа	$\rho^c/{\rm kg}~{\rm m}^{-3}$	$T^{a}/K$	р <sup>b</sup> /МРа	$\rho^c/{\rm kg}~{\rm m}^{-3}$
293.15	0.164	964.5	398.15	0.164	881.2
293.15	2.003	965.6	398.15	2.003	883.0
293.15	3.983	966.7	398.15	3.983	884.9
293.15	5.950	967.9	398.15	5.950	886.7
293.15	7.925	969.0	398.15	7.925	888.6
293.15	9.894	970.1	398.15	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	944.7	443.15	0.164	844.2
318.15	2.003	946.0	443.15	2.003	846.5
318.15	3.983	947.3	443.15	3.983	848.9
318.15	5.950	948.5	443.15	5.950	851.2
318.15	7.925	949.8	443.15	7.925	853.5
318.15	9.894	951.0	443.15	9.894	855.7
348.15	0.164	921.1	458.15	0.164	831.6
348.15	2.003	922.5	458.15	2.003	834.1
348.15	3.983	924.0	458.15	3.983	836.7
348.15	5.950	925.5	458.15	5.950	839.2
348.15	7.925	926.9	458.15	7.925	841.7
348.15	9.894	928.3	458.15	9.894	844.1
373.15	0.164	901.2	473.15	0.164	818.8
373.15	2.003	902.8	473.15	2.003	821.6
373.15	3.983	904.4	473.15	3.983	824.4
373.15	5.950	906.1	473.15	5.950	827.1
373.15	7.925	907.8	473.15	7.925	829.8
373.15	9.894	909.4	473.15	9.894	832.3
<sup>a</sup> Standard	uncertainty	u(T) = 0.01	K. <sup>b</sup> Stand	lard uncerta	unty $u(p) =$
0.01 MPa.	<sup>c</sup> Standard	uncertainty u	$(\rho) = 1.3$	51 kg m <sup>-3</sup> . S	See Table 2.

The solubility of H<sub>2</sub> in both lactones increased as a function of temperature. The increase of H<sub>2</sub> solubility with increasing temperature has been widely documented for hydrocarbons and oxygenated organic compounds,<sup>17,38</sup> including cyclic esters such as 1,2-butylene carbonate.<sup>39</sup> One further observation on the temperature dependence of the solubility is that, in GNL, the solubility increased more markedly from 479 to 531 K than from 531 to 582 K. This observation is evident from the slopes of the linear regressions of the  $x_{H2}$  vs p isotherms (eq S8 and

Table S5). For GNL, the difference between the slopes of the 479 K isotherm and the 531 K isotherm is ~24 MPa, whereas the difference between the slopes of the 531 K isotherm and the 582 K isotherm is only ~13 MPa. In comparison, for GHL, the differences between the slopes are roughly the same. The nonlinear dependence of H<sub>2</sub> solubility in GNL on 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  $\gamma$ -butyrolactone,<sup>32</sup> 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  $H_2$  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 negatively using  $k_{ij} = 0$  and positively when using the temperature-dependent  $k_{ij}$  model (Figure 6). Furthermore, the EoS provided isotherms displaying an upward concavity, whereas the measurements aligned almost linearly (Table S5) and with a slight downward concavity. The use of the  $k_{ij}$  model allowed reducing the deviations slightly (Table 12).

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<sup>-3</sup> for GHL and 72.9 kg m<sup>-3</sup> for GNL. The ARD was 51.5% for GHL and 8.0% for GNL. Compared to the deviation values obtained with our density model (Table 7), the deviation of the EoS is considerably large. Thus, the use of the density model instead of the EoS is justified for density calculations.



**Figure 3.** Densities of (a) GHL and (b) GNL measured at constant temperatures of 298 K ( $\bigcirc$ ), 348 K ( $\bigtriangledown$ ), 393 K for GHL (yellow  $\triangle$ ), 398 K for GNL (blue  $\triangle$ ), 443 K ( $\diamondsuit$ ), and 473 K ( $\square$ ). The dashed lines are the isotherms calculated with the fitted density model (eq 1). Note the different scales.

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Table 7. Parameters of the Density Model  $(K_1-K_5, eq 1)$ , Average Absolute Deviation (AAD, eq 2), and Average Relative Deviation (ARD, eq 3)

compound	$K_1/\mathrm{kg}~\mathrm{m}^{-3}$	$K_2/{\rm kg}~{\rm m}^{-3}~{\rm K}^{-1}$	$K_3/{\rm kg}~{\rm m}^{-3}~{\rm K}^{-2}$	$K_4/\mathrm{kg}~\mathrm{m}^{-3}~\mathrm{MPa}^{-1}$	$K_5/{\rm kg}~{\rm m}^{-3}~{\rm K}^{-1}~{\rm MPa}^{-1}$	AAD	ARD
GHL	1226.2	-0.728	$-1.84 \times 10^{-4}$	-0.825	$4.67 \times 10^{-3}$	0.188	0.02%
GNL	1183.6	-0.71	$-1.26 \times 10^{-4}$	-0.744	$4.37 \times 10^{-3}$	0.142	0.02%



**Figure 4.** Density dependence on temperature at 5 MPa in four  $\gamma$ -lactones:  $\gamma$ -butyrolactone (data from Ihmels et al.,<sup>35</sup> red  $\Box$ ),  $\gamma$ -valerolactone (data from Zaitseva et al.,<sup>24</sup> green  $\triangle$ ), GHL (calculated with eq 1, ----), and GNL (calculated with eq 1, ---).

Table 8. Measured Mole Fractions of H<sub>2</sub> in GHL  $(x_{H2})$  at Saturation Point for Temperature *T* and Pressure *p* with Their Respective Standard Uncertainties  $(u_s)$ 

$T^a/K$	p/MPa	u <sub>s</sub> (p) <sup>b</sup> /kPa	$x_{\rm H2}$	$u_{\rm s}(x_{\rm H2})^c$				
479.1	3.01	3.1	0.0161	$1.5 \times 10^{-02}$				
479.1	6.01	3.4	0.0335	$7.5 \times 10^{-03}$				
479.1	8.01	3.8	0.0466	$5.4 \times 10^{-03}$				
479.1	10.0	4.1	0.0592	$4.2 \times 10^{-03}$				
530.6	3.03	3.1	0.0186	$1.3 \times 10^{-02}$				
530.6	6.52	3.5	0.0459	$5.5 \times 10^{-03}$				
530.6	10.0	4.1	0.0691	$3.6 \times 10^{-03}$				
582.1	4.01	3.2	0.0354	$7.1 \times 10^{-03}$				
582.1	6.02	3.4	0.0516	$4.9 \times 10^{-03}$				
582.1	8.02	3.8	0.0693	$3.6 \times 10^{-03}$				
582.1	9.08	4.0	0.0781	$3.2 \times 10^{-03}$				
$u_s(T) = 0.18$ K, see equilibrium cell T Table S3. <sup>b</sup> See equilibrium								
ell p Table	e <mark>S4</mark> . <sup>°</sup> See <i>u</i> <sub>c</sub>	ell p Table S4. <sup>c</sup> See $u_c(x_{H2, L-LG})$ in Table 4.						

#### CONCLUSIONS

In this work, the densities and  $H_2$  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  $H_2$  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  $H_2$ , the curves of saturation ( $H_2$  pressure against  $H_2$  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  $H_2$  solubility was greater in GNL than in GHL. Some of the factors that favored  $H_2$  solubility in GNL could have been the

Table 9. Measured Mole Fractions of $H_2$ in GNL $(x_{H2})$ at
the Saturation Point for Temperature T and Pressure p with
Their Respective Standard Uncertainties $(u_s)$

$T^{a}/K$	p/MPa	$u_{\rm s}(p)^{b}/{\rm kPa}$	$x_{\rm H2}$	$u_{\rm s}(x_{\rm H2})^c$
479.1	3.02	3.1	0.0232	$1.1 \times 10^{-02}$
479.2 <sup>d</sup>	6.01	3.4	0.0431	$5.8 \times 10^{-03}$
479.1 <sup>e</sup>	6.02	3.4	0.0427	$4.9 \times 10^{-03}$
479.2	8.01	3.8	0.0545	$4.6 \times 10^{-03}$
479.2	10.0	4.1	0.0753	$3.3 \times 10^{-03}$
530.6	3.02	3.1	0.0274	$9.1 \times 10^{-03}$
530.6 <sup>f</sup>	6.02	3.4	0.0518	$4.9 \times 10^{-03}$
530.7 <sup>g</sup>	6.02	3.4	0.0518	$4.1 \times 10^{-03}$
530.6	8.01	3.8	0.0671	$3.7 \times 10^{-03}$
530.6	10.0	4.1	0.0907	$2.7 \times 10^{-03}$
582.0 <sup>h</sup>	3.10	3.1	0.0274	$9.1 \times 10^{-03}$
581.5 <sup>h</sup>	3.00	3.1	0.0272	$9.2 \times 10^{-03}$
582.0	6.01	3.4	0.0566	$4.4 \times 10^{-03}$
582.0	8.01	3.8	0.0771	$3.2 \times 10^{-03}$
581.9	10.0	4.1	0.0989	$2.5 \times 10^{-03}$

 ${}^{a}u_{s}(T) = 0.18$  K, see equilibrium cell *T* in Table S3. <sup>b</sup>See equilibrium cell *p* Table S4. <sup>c</sup>See  $u_{c}(x_{H2, L-LG})$  in Table 4. <sup>d</sup>Measurement with liquid residence time of 2.9 min. <sup>e</sup>Repeated measurement with liquid residence time of 3.6 min. <sup>g</sup>Repeated measurement with liquid residence time of 3.0 min. <sup>h</sup>Measurements repeated at equal liquid residence time of 2.0 min.



**Figure 5.** Experimental data and PR-BM models of H<sub>2</sub> solubility in GHL. The symbols are data points at 479 K ( $\Box$ ), 531 K ( $\bigcirc$ ), and 582 K ( $\triangle$ ). The dashed lines correspond to the PR-BM model with  $k_{ij} = 0$  at 479 K ( $\cdots$ ), 531 K (- - -), and 582 K (----). The solid lines correspond to the PR-BM model with the regressed  $k_{ij}$  at 479 K (yellow line), 531 K (light red line), and 582 K (dark red line). The points at  $x_{H2} = 0$  were taken from the GHL vapor pressure model by Emel'yanenko et al.<sup>29</sup>

molecular mass of the lactone and the aliphatic nature of its side chain.

The PR-BM EoS was used to reproduce the  $H_2$  solubility measurements using Aspen Plus. The software required the input of thermodynamic and critical properties, which were estimated with Nannoolal's method, as they were not available in the literature. The EoS model was more accurate for GHL than for GNL. The deviations of the EoS model with respect to



**Figure 6.** Experimental data and PR-BM models of H<sub>2</sub> solubility in GNL. The symbols are data points at 479 K ( $\Box$ ), 531 K ( $\bigcirc$ ), and 582 K ( $\triangle$ ). 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  $x_{H2} = 0$  were taken from the GNL vapor pressure model by Emel'yanenko et al.<sup>29</sup>

## Table 10. Properties Estimated with Nannoolal's Method<sup>32</sup> for the PR-BM Model

compound	critical temperature, $T_{\rm c}/{ m K}$	critical pressure, p <sub>c</sub> /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

	Α	$B/K^{-1}$	C/K	AAD <sup>a</sup>	ARD <sup>b</sup>
GHL	14.697	$-1.3417 \times 10^{-2}$	-3947.9	$1.94 \times 10^{-4}$	0.33%
GNL	-28.244	$2.8635 \times 10^{-2}$	7158.7	$1.59 \times 10^{-4}$	0.03%
<sup><i>a</i></sup> Average	absolute	deviation of eq	15 with	respect to regre	ssed $k_{ii}$

values. <sup>*b*</sup>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  $H_2$  Solubility in GHL and GNL with Respect to the Solubility Data

	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%

<sup>*a*</sup>The model included the temperature correlation of the symmetric binary parameter. <sup>*b*</sup>The model did not include the symmetric binary parameter.

the data were mitigated slightly by applying a temperaturedependent 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  $H_2$  flow; linear regressions of solubility data; parameters used in Aspen simulations (PDF)

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#### **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.

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#### Notes

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