Supplementary Information

Fick Diffusivity, Thermal Diffusivity, Thermal Conductivity, Density, and Mixture Composition of Binary Mixtures of γ-Butyrolactone and 1,4-Butanediol by Light Scattering Techniques and Conventional Methods

Dena Mombeini,[a] Hubert P. Blabus,[a] Michael H. Rausch,[a]
Tobias Klein,[a] Thomas M. Koller,[a,#] Chathura J. Kankanamge,[a]
Michael Geißelbrecht,[b] Peter Wasserscheid,[b,c,d] and Andreas P. Fröba[*,a]*

[a]Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP), Department of Chemical and Biological Engineering (CBI) and Erlangen Graduate School in Advanced Optical Technologies (SAOT), Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Paul-Gordan-Straße 8, 91052 Erlangen, Germany

[b]Forschungszentrum Jülich GmbH, Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), Cauerstraße 1, 91058 Erlangen, Germany

[c]Institute of Chemical Reaction Engineering (CRT), Department of Chemical and Biological Engineering (CBI), Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstraße 3, 91058 Erlangen, Germany

[d]Forschungszentrum Jülich GmbH, Institute for a Sustainable Hydrogen Economy, Am Brainergy Park 4, 52428 Jülich, Germany

[#] The current address of Thomas M. Koller is: Institute of Thermodynamics, Technische Universität Braunschweig, Hans-Sommer-Straße 5, 38106 Braunschweig, Germany

[*] Author to whom correspondence should be addressed. Tel. +49-9131-85-29789, fax +49-9131-85-25878, email andreas.p.froeba@fau.de, ORCID number 0000-0002-9616-3888.

S1. Additional Information on Dynamic Light Scattering

Figures S1 and S2 depict examples of CFs for a thermodynamic state at which a and D_{11} have to be evaluated separately by applying different incident angles Θ_I. In Figure S1, the solid green line represents the fit of the CF by a single exponential for the mixture with $x_{GBL} = 0.75$ at $T = 298.15$ K, $p = 0.103$ MPa, and $\Theta_I = 5.047°$. From the fit, the mean lifetime of the fluctuations in temperature of entropy $\tau_{C,t} = (10.81 \pm 0.27)$ µs can be calculated. Using Eq. (3), the respective thermal diffusivity $a = (8.56 \pm 0.29) \times 10^{-8}$ m^2·s^{-1} can be obtained. In Figure S2, the solid blue line represents the fit of the CF by a single exponential for the same mixture at approximately the same T and p at $\Theta_I = 9.496°$. Here, the mean-life time of the fluctuations in concentration $\tau_{C,c} = (1476 \pm 103)$ µs is used to calculate the Fick diffusivity $D_{11} = (1.78 \pm 0.17) \times 10^{-10}$ m^2·s^{-1} using Eq. (3).

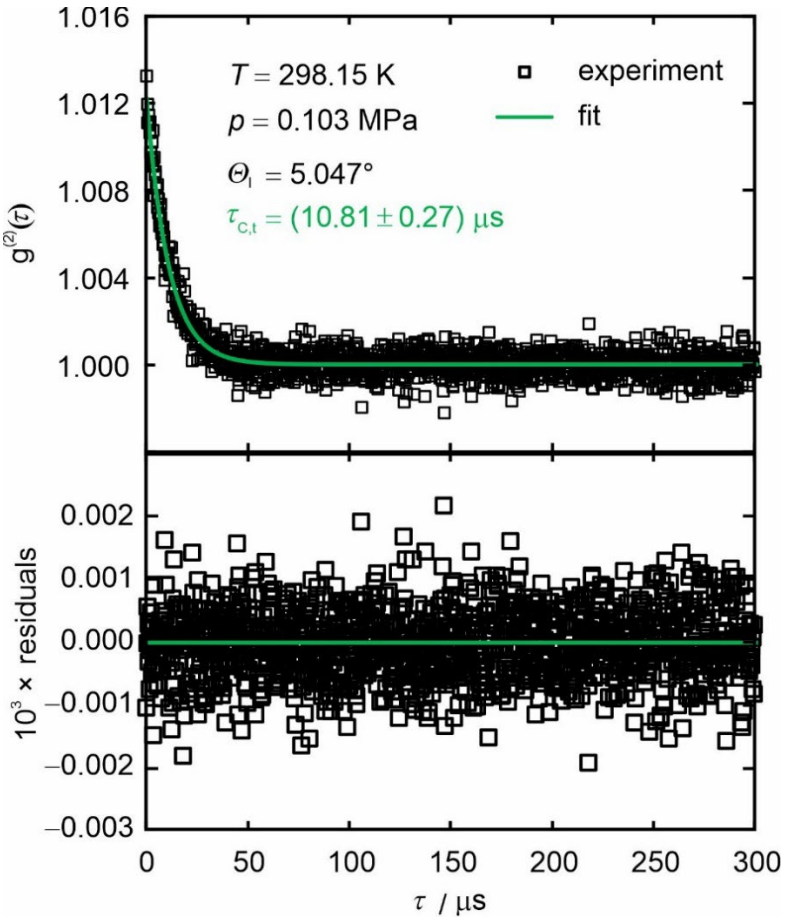

Fig. S1 CF recorded by the LTC for the binary mixture consisting of GBL and BDO with $x_{GBL} = 0.75$ at $T = 298.15$ K, $p = 0.103$ MPa, and $\Theta_I = 5.047°$ (top) and the residuals from the fit (bottom). The solid green line represents the fit according to Eq. (2).

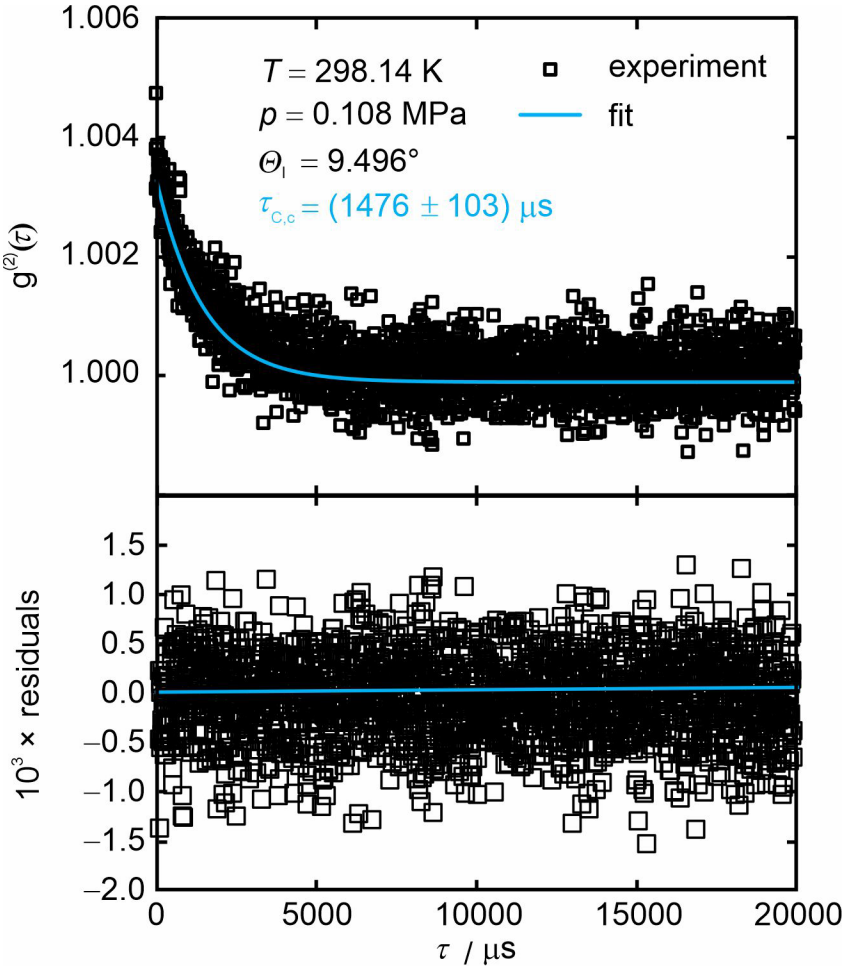

Fig. S2 CF recorded by the LTC for the binary mixture consisting of GBL and BDO with x_{GBL} = 0.75 at T = 298.14 K, p = 0.108 MPa, and Θ_I = 9.496° (top) and the residuals from the fit (bottom). The solid blue line represents the fit according to Eq. (2).

S2. Additional Information on Sample Stability

Figure S3 shows the thermal diffusivity a of pure GBL as a function of T measured by DLS in the T range from (298 to 473) K. To investigate possible changes of the sample at high T, check measurements were performed at T = 373 K after measuring at T = (423, 473, and 498) K. The values for a from these check measurements are by (4.9, 8.1, and 18) %, respectively, lower than that from the initial measurement at T = 373 K. Figure S4 shows the change in the laser beam passing through the sample from green during DLS measurements at T = 298 K to yellow after measurements at T = 498 K. At T = 448 K, a continuous increase in pressure with an approximate rate of 20 kPa·h^{-1} was observed. At T = 498 K, measurements were not possible due to the presence of strong long-term contributions in the CFs. All these observations could indicate a possible change of the sample at elevated T. On this basis, measurements at $T \leq 398$ K are considered to provide reliable a data for pure GBL, where there is no indication of any changes in the sample composition. Data obtained at in $T > 398$ K may be compromised by changes of the sample.

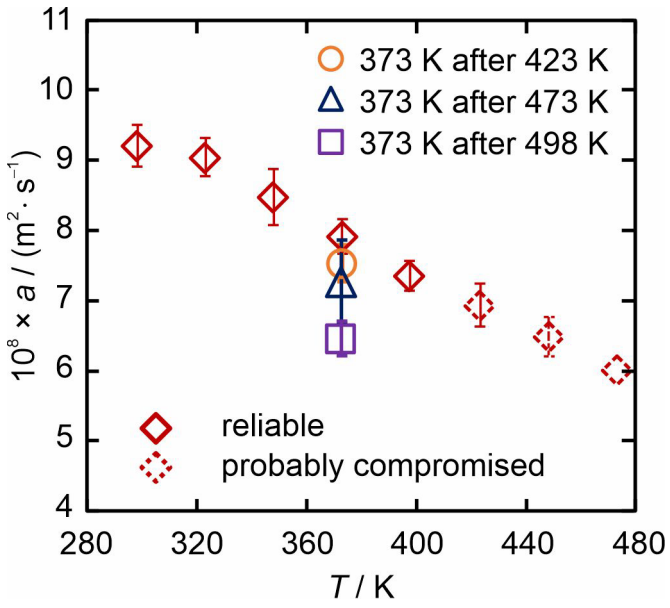

Fig. S3 Experimental data for a of pure GBL a function of T at about 0.2 MPa. Markers with contours of solid and broken lines indicate reliable and probably compromised measurement data.

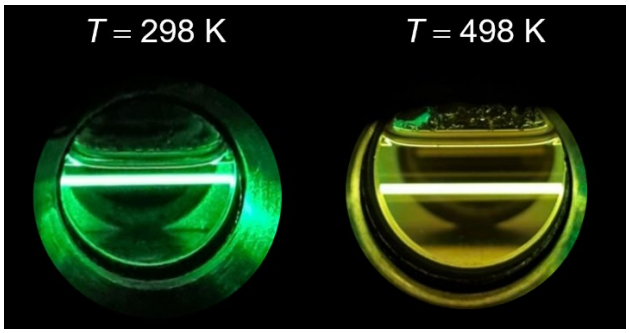

Fig. S4 Images of laser beam passing through pure GBL during DLS measurements at $T = 298$ K and after measurements at $T = 498$ K.

Figure S5 shows the thermal diffusivity measured for pure BDO as a function of T in the range from (298 to 473) K. The generally rather large measurement uncertainties observed for BDO are also often seen for other fluids with relatively high viscosity. The result of a check measurement at $T = 373$ K after the measurement at $T = 398$ K is by 9 % lower than that of the initial measurement at 373 K and associated with a increased relative expanded uncertainty of 19 %. While long-term contributions in the experimental CFs became already more pronounced at $T = 448$ K, the CFs recorded at 473 K could only be fitted adequately by using a function with two exponentials. The underlying additional signal contributions may be related to changes in the composition of the initially pure BDO sample. Furthermore, a continuous increase in p with an approximate rate of 20 kPa·h^{-1} along with measurable fluctuations in p was observed at $T = 498$ K. Based on these observations, only measurements at $T \leq 423$ K are considered to be reliable for pure BDO.

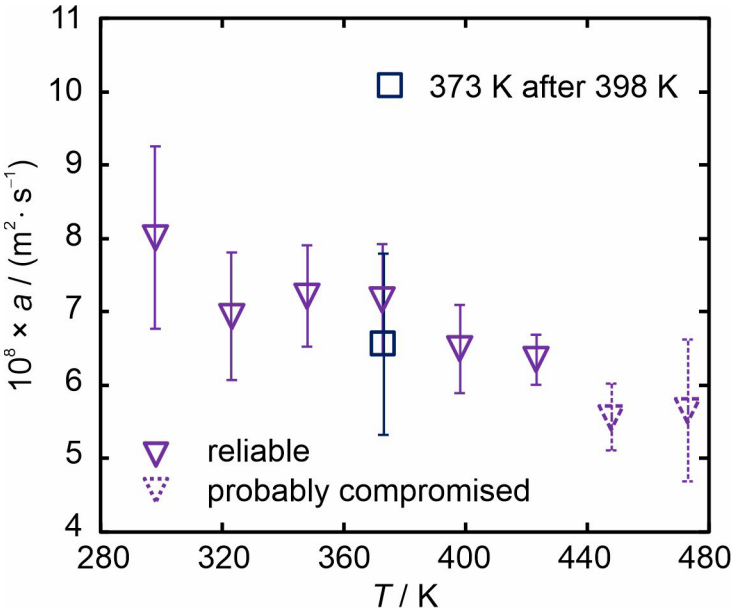

Fig. S5 Experimental data for thermal diffusivity a of pure BDO as function of T at about 0.2 MPa. Markers with contours of solid and broken lines indicate reliable and probably compromised measurement data.

In Figure S6, D_{11} is presented as a function of T in a range between (298 and 473) K for the mixture with x_{GBL} = 0.25, where the data stem from measurements with two different fillings of the sample cell. In the results from the first filling, a distinct increase of the relative expanded uncertainty to 57 % can be observed at T = 423 K. The result from check measurements at T = 373 K after measuring at 398 K is by about 20 % smaller than the previously obtained value. The result from an additional check measurement at T = 348 K after measuring at 423 K is by 40 % larger than the initially measured D_{11}, where the previous exposure time at T = 423 K was about 10 h. Measurements with the second filling aimed to reduce the exposure time of the sample to elevated T while performing additional check measurements to be sure about the state of the sample studied. Here, the measurements at a given T lasted about 4 h. The result from the check measurement at T = 348 K after measuring at 373 K showed an increase of 11 % in D_{11}, which is, however, clearly within the measurement uncertainty. The expanded uncertainty of the measurement at T = 423 K is 17 %, which is significantly lower compared to that at the same T for the first filling and might be related to the shorter corresponding exposure time. A further check measurement performed at T = 348 K after measuring at 423 K showed an increase of 32 % in D_{11}, which is somewhat lower compared to the corresponding increase observed in the measurement for the first filling with longer exposure time. At T = (448 and 473) K, with exposure times of about 4 h for each T, relative expanded uncertainties of (35 and 32) % were observed. At T = 473 K, a continuous increase in pressure with an approximate rate of 10 kPa·h^{-1} was observed and strong long-term contributions appeared in the CFs. Considering all these observations, it can be concluded that longer exposure time at higher T could potentially accelerate changes in the sample composition. Based on the observations from both fillings for the mixture with x_{GBL} = 0.25, D_{11} values for $T \leq$ 423 K are referred to as reliable data. Figure S7 shows the corresponding results for a, from which no further conclusions can be drawn. The measurements for the further mixtures were performed with one filling of the sample cell for each of the mixtures. Exposure times at elevated T were kept at the possible minimum while integrating check measurements to ensure reliability of the finally reported data. Since the observations were virtually the same like for the mixture with x_{GBL} = 0.25 and a rather constant change in p with an approximate rate of 10 kPa·h^{-1} at (473 and 498) K was found for the mixtures with x_{GBL} = (0.50 and 0.75), the data measured at $T \leq$ 423 K are considered to be reliable for all three mixtures.

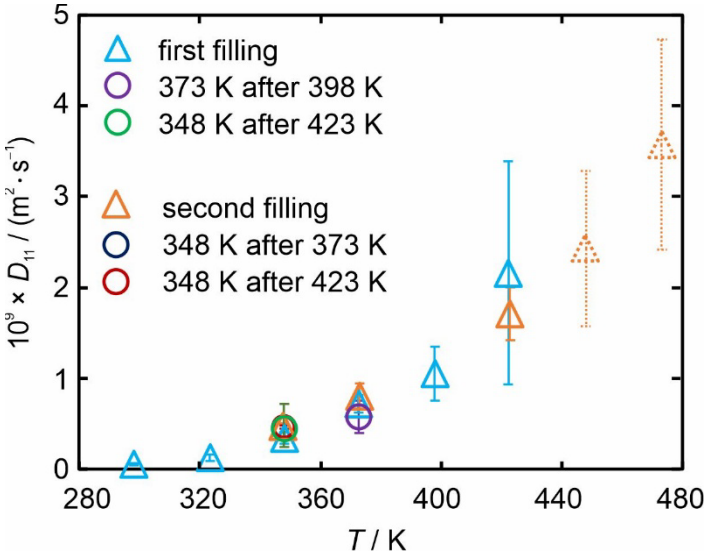

Fig. S6 Experimental data for the Fick diffusivity D_{11} of the mixture with $x_{GBL} = 0.25$ as a function of T at about 0.2 MPa measured with two different fillings of the sample cell. Markers with contours of solid and broken lines indicate reliable and probably compromised measurement data.

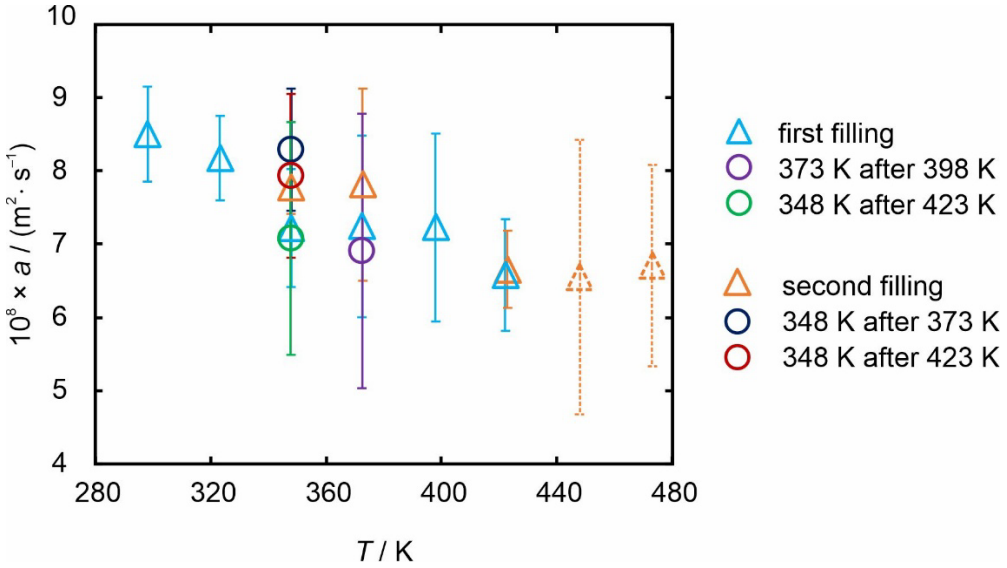

Fig. S7 Experimental data for the thermal diffusivity a of the mixture with $x_{GBL} = 0.25$ as a function of T at about 0.2 MP measured with two different fillings of the sample cell. Markers with contours of solid and broken lines indicate reliable and probably compromised measurement data.

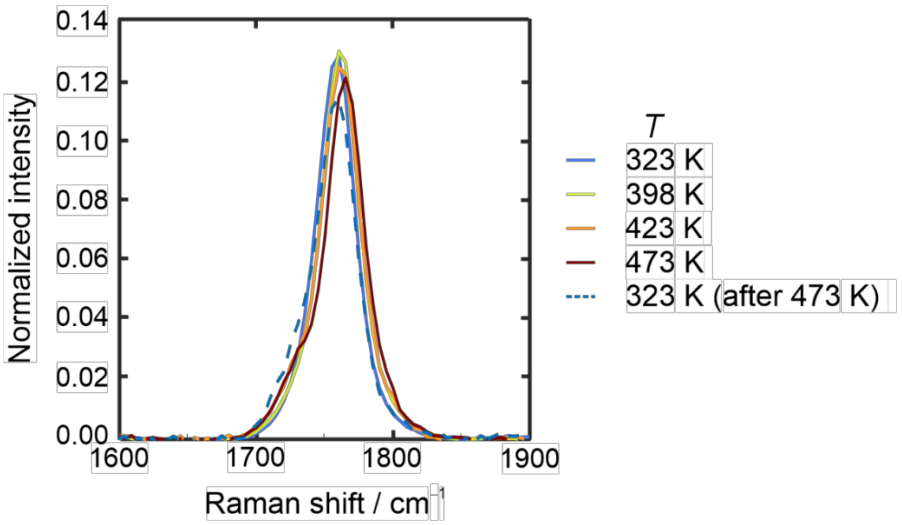

Fig. S8 Baseline-corrected normalized isotropic Raman spectra related to the C=O stretching domain at $\nu \approx 1770$ cm^{-1} for the binary mixture of GBL and BDO with $x_{GBL} = 0.75$ and $T = (323, 398, 423, 473)$ K. Different colors represent different temperatures. The solid lines correspond to the measurement series recorded from low to high temperatures, while the dashed line denotes the check measurement performed at $T = 323$ K following the experiments at elevated temperatures.

S3. Additional Information on the Calibration of PDRS

Table S1. The intensity ratio I_r obtained from the isotropic Raman spectra of the binary mixtures of GBL and BDO as a function of x_{GBL} at T = (298, 323, and 373) K.[a]

	T = 298 K		T = 323 K		T = 373 K	
x_{GBL}	$I_r = I_{GBL} / I_{BDO}$	100 × $U_r(I_r)$	$I_r = I_{GBL} / I_{BDO}$	100 × $U_r(I_r)$	$I_r = I_{GBL} / I_{BDO}$	100 × $U_r(I_r)$
0.9001	31.3	18	33.2	18	36.4	19
0.7983	12.6	15	12.8	16	13.8	16
0.6998	7.5	14	7.9	14	7.7	14
0.6000	4.92	12	5.02	12	9.8	13
0.4991	3.17	11	3.27	11	3.19	12
0.4000	2.19	9.4	2.22	9.5	2.22	9.5
0.3011	1.44	8.2	1.44	8.8	1.43	10
0.1995	0.843	8.1	0.852	8.5	0.844	10
0.0982	0.379	8.6	0.382	9.0	0.369	10

[a]The estimated absolute expanded uncertainty of x_{GBL} determined according to the gravimetric sample preparation is 0.0001. The uncertainties for I_i were calculated by relating the residuals from the fitting process to the integrated area, i.e. $U(I_i) = I_{residual,i} / I_{fit,i}$. All uncertainties are given on a confidence level of 0.95 (coverage factor k = 2).

S4. Additional Information on the Excess Molar Volume of the Mixtures Studied

For three binary mixtures prepared from GBL and BDO, the excess molar volume V_m^E was calculated by using the experimental ρ data measured with the DMA 5000 M according to

$$V_m^E = \frac{\sum_i x_i M_i}{\rho_{mix}} - \sum_i \frac{x_i M_i}{\rho_i}. \quad \text{(S1)}$$

Here, ρ_{mix} is the density measured for the mixture, i represents the pure mixture components GBL and BDO, M_i and ρ_i are their molar masses and measured densities, and x_i is their amount fraction in the corresponding mixtures.

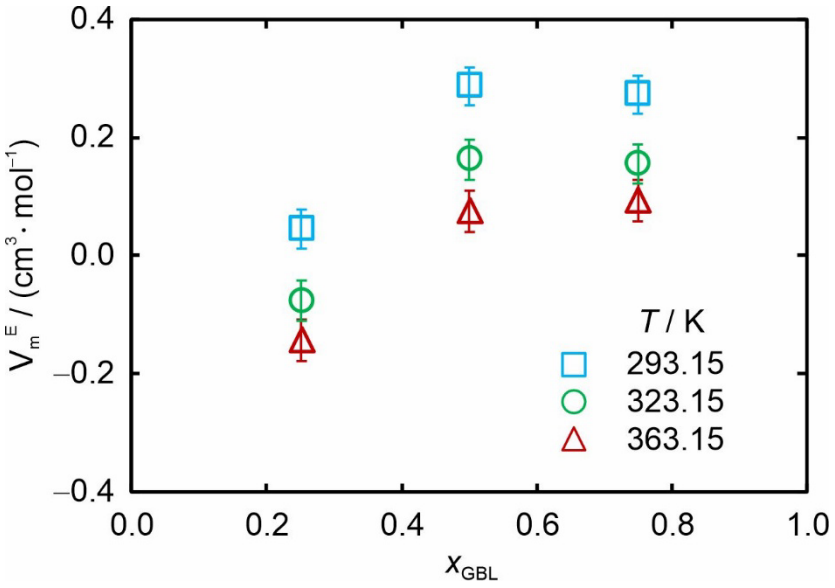

Fig. S9 Excess molar volume V_m^E of the studied systems with x_{GBL} = (0.25, 0.50, 0.75) with varying T as a function of x_{GBL} at 0.1 MPa.

S5. Additional Information Required for the Evaluation of Measurements with the GPPI

Table S2. Measured refractive index n_D of the studied systems with varying x_{GBL} as a function of temperature T at 0.1 MPa.[a,b]

x_{GBL} = 0.00		x_{GBL} = 0.25		x_{GBL} = 0.50	
T / K	n_D	T / K	n_D	T / K	n_D
292.8	1.4454	293.0	1.4435	292.8	1.4423
303.3	1.4425	302.6	1.4411	303.6	1.4385
313.2	1.4398	312.6	1.4379	313.0	1.4352
322.7	1.4371	322.6	1.4347	323.2	1.4314
333.4	1.4338	332.4	1.4312	332.6	1.4280
342.9	1.4310	342.8	1.4278	342.7	1.4242
352.6	1.4279	352.9	1.4235	352.7	1.4203
362.2	1.4247	361.1	1.4211	361.8	1.4174
x_{GBL} = 0.75		x_{GBL} = 1.00			
T / K	n_D	T / K	n_D		
292.8	1.4384	293.1	1.4359		
303.0	1.4346	303.2	1.4317		
313.3	1.4304	313.0	1.4279		
322.7	1.4262	322.7	1.4234		
333.0	1.4220	332.7	1.4194		
342.9	1.4181	342.9	1.4150		
352.5	1.4136	353.3	1.4099		
361.1	1.4108	362.1	1.4059		

[a] T was measured with an expanded uncertainty of $U(T)$ = 0.5 K. The relative uncertainty $U_r(n_D)$ of n_D measured by Abbe refractometer (NAR-2T from ATAGO) is 0.0002. All uncertainties are given on a confidence level of 0.95 (coverage factor k = 2).

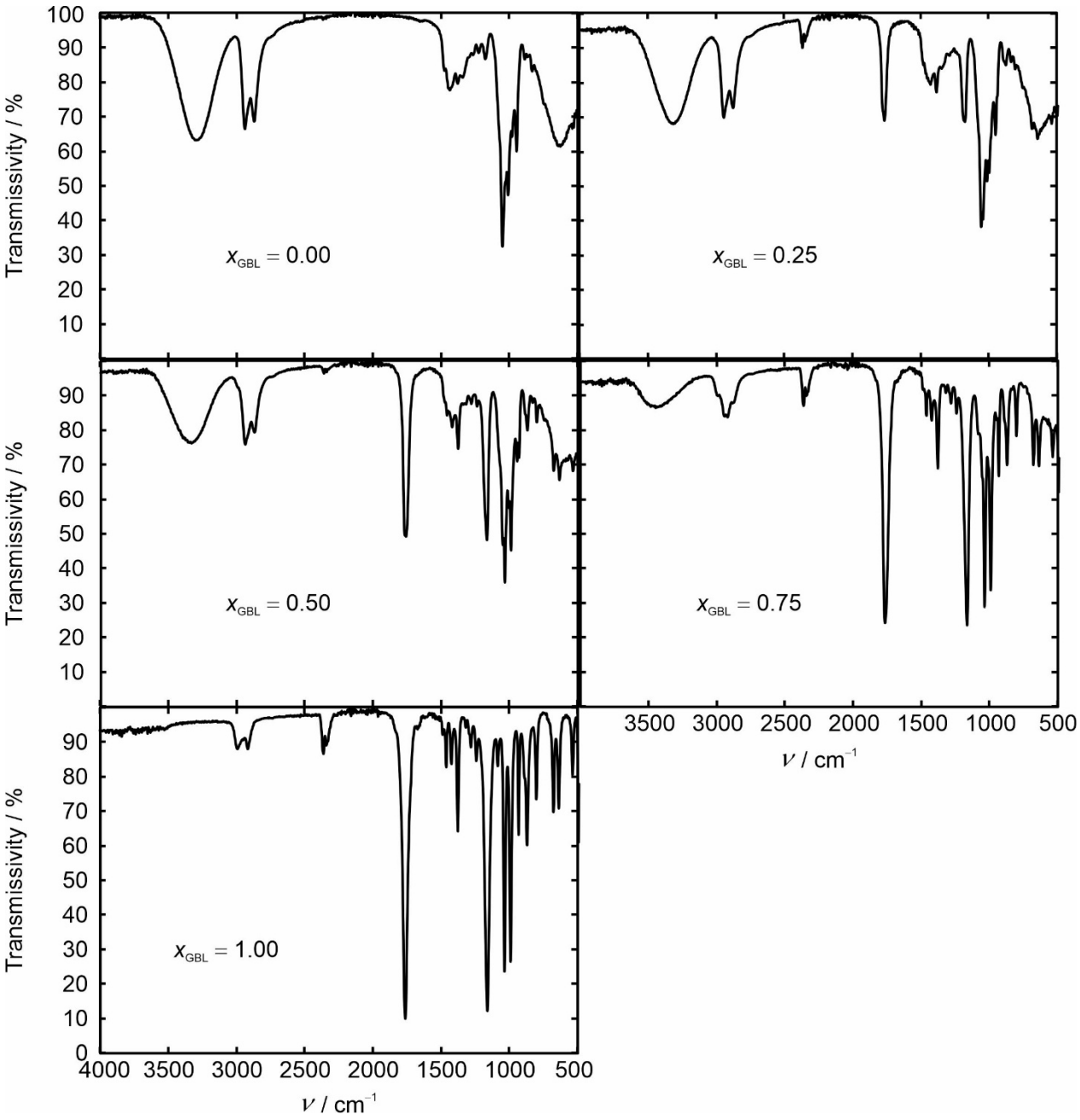

Fig. S10 Transmission spectra for the studied systems with different x_{GBL} measured at ambient temperature of about 293 K at 0.1 MPa. The corresponding data are available as a separate data file.