SUPPLEMENTARY MATERIALS

for

Reference Materials for Phase Equilibrium Studies. 1. Liquid-Liquid Equilibria (IUPAC Technical Report) ⁺

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GENERAL NOTE TO ALL SUPPLEMENTS:

Figures S1 through S17 are snapshots from ThermoData Engine software (V. Diky, R. D. Chirico, M. Frenkel, A. Bazyleva, J. W. Magee, E. Paulechka, A. Kazakov, E. W. Lemmon, C. D. Muzny, A. Y. Smolyanitsky, S. Townsend, K. Kroenlein. NIST ThermoData Engine, NIST Standard Reference Database 103b, version 10.4.2, National Institute of Standards and Technology, USA (2020), https://www.nist.gov/mml/acmd/trc/thermodata-engine/srd-nist-tde-103b), and their formatting is preserved as automatically generated.

SUPPLEMENT 1A. Data sources on LLE for aniline (benzenamine) + water

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NOTE:
The following reference mentioned in SDS 96-3 was not included, since it does not contain original LLE data for aniline + water:
Schreinemakers, F. A. H., Z. Phys. Chem., Stoechiom. Verwandschaftsl., 1899, 29, 577.

SUPPLEMENT 1B. Validation of LLE data for aniline (benzenamine) + water

Important note: This model is not recommended for LLE calculations. Its purpose is to prove the consistency with other properties.

Non-Random Two-Liquid excess Gibbs energy model with the Hayden-O'Connell gas phase model (NRTL/HOC model):

$$G^E/(R\cdot T) = x_1\cdot x_2\cdot[c_1\cdot \exp(-k\cdot c_1)/(x_1 + x_2\cdot \exp(-k\cdot c_1)) + c_2\cdot \exp(-k\cdot c_2)/(x_2 + x_1\cdot \exp(-k\cdot c_2))] \qquad \text{(S1)}$$

with temperature dependence

$$c_i = A_i + B_i\,T^{-1} + C_i \ln(T) + D_i\,T + E_i\,T^{-2}, \qquad \text{(S2)}$$

where G^E is the excess Gibbs energy; k is the non-randomness factor; A_i through E_i are the fitted parameters for component i; T is temperature in K; x_i is the mole fraction of component i; and R is the gas constant.

Table S1: Parameters for NRTL/HOC model for aniline (1) + water (2)

Component i	A_i	B_i	C_i	k
Component 1 (aniline)	131.292	-5765.34	-18.9238	0.36444
Component 2 (water)	85.2378	-3111.48	-12.8505	

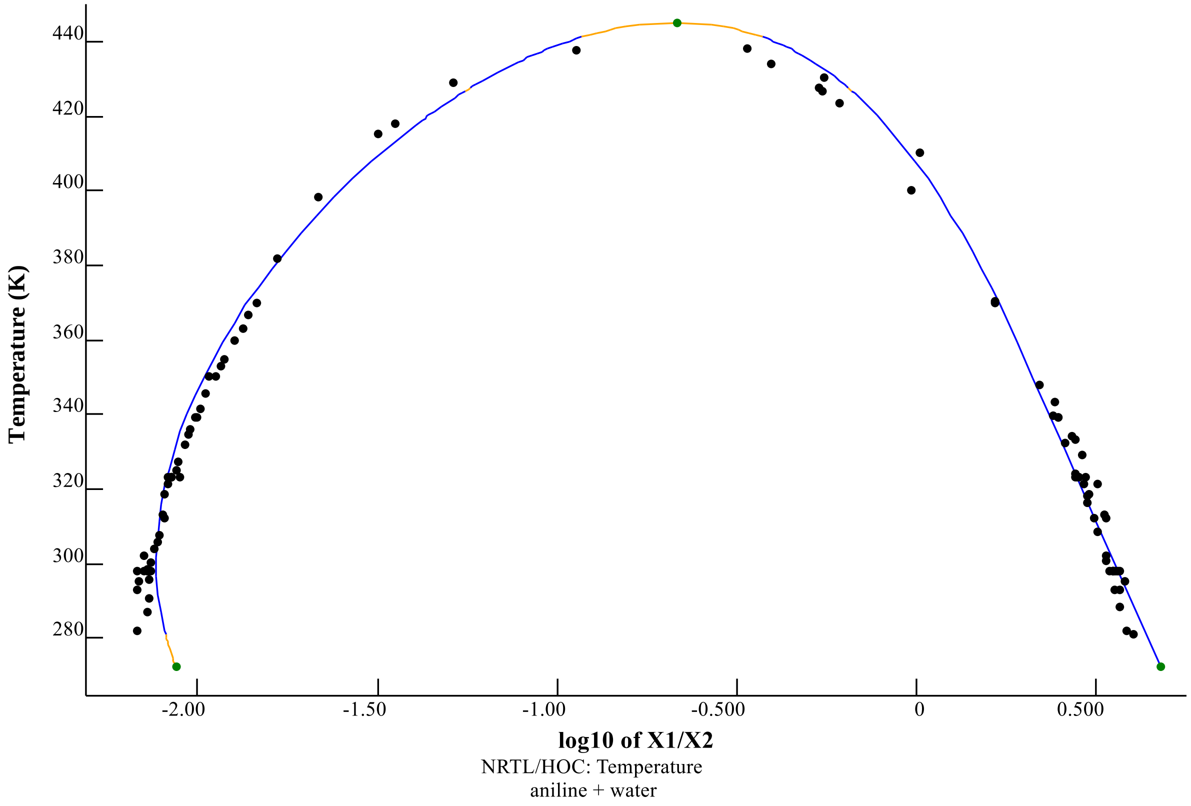
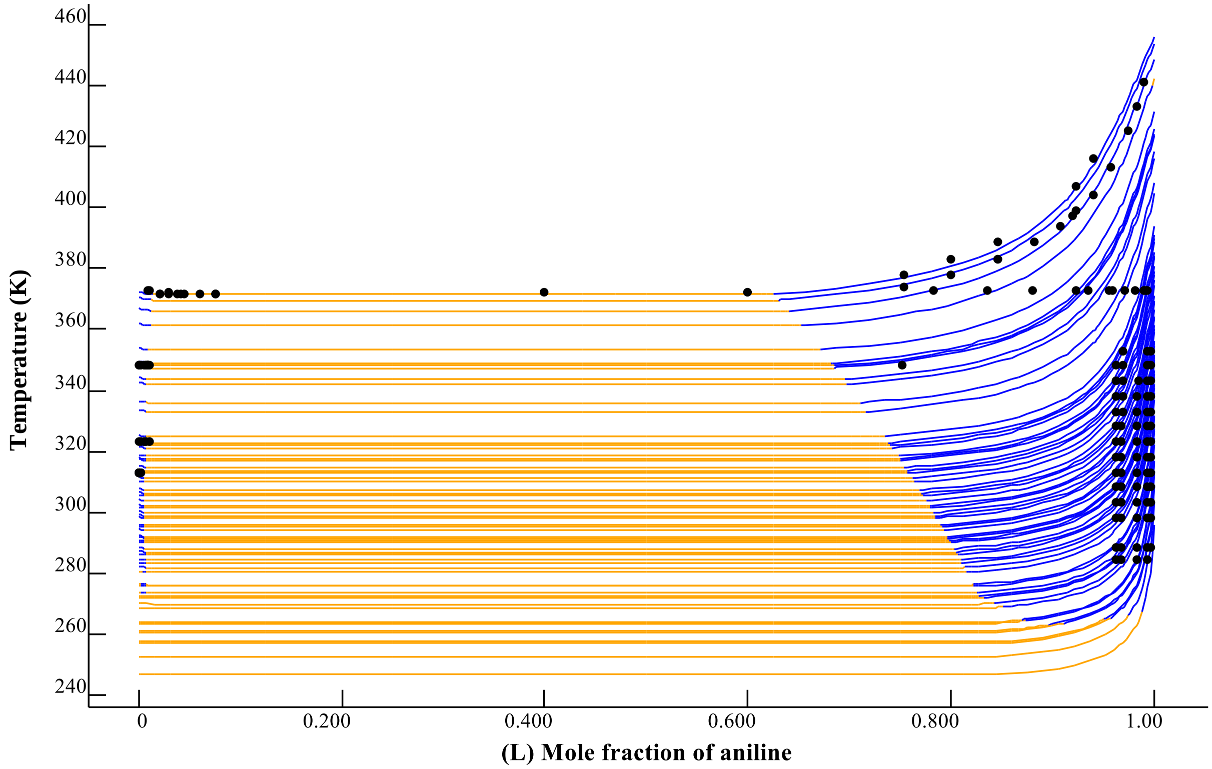
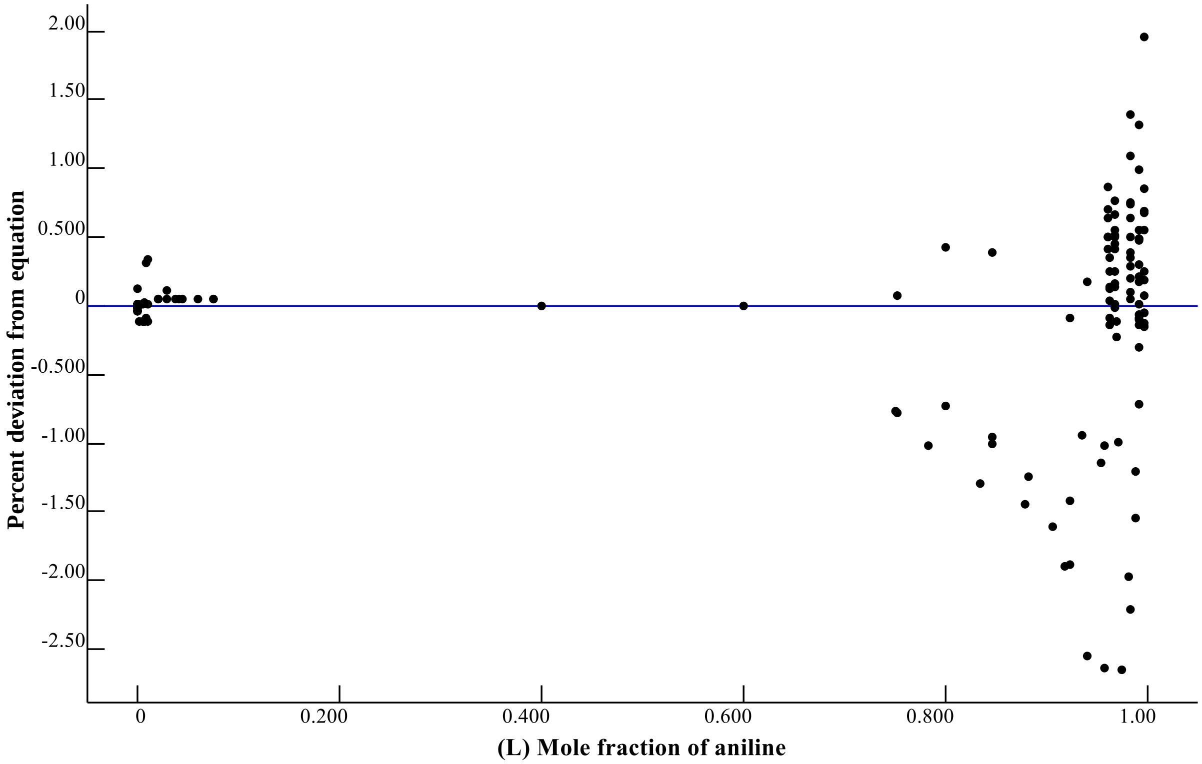


Figure S1: Experimental mole-fraction LLE data (black dots – Supplement 1A) vs the NRTL/HOC model (line) for aniline (1) + water (2). The green dots are predicted upper consolute and monotectic points



Temperature [L, G] - NRTL/HOC
aniline + water

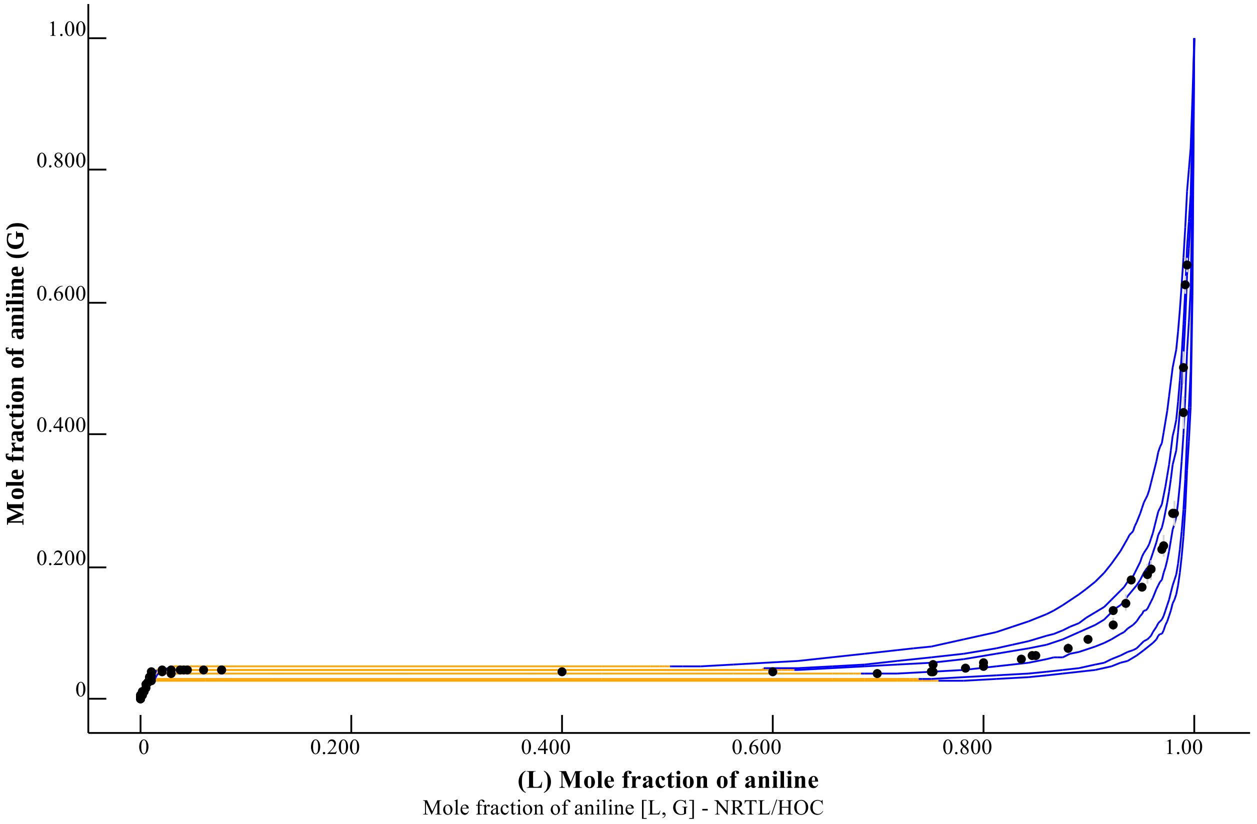
(a)



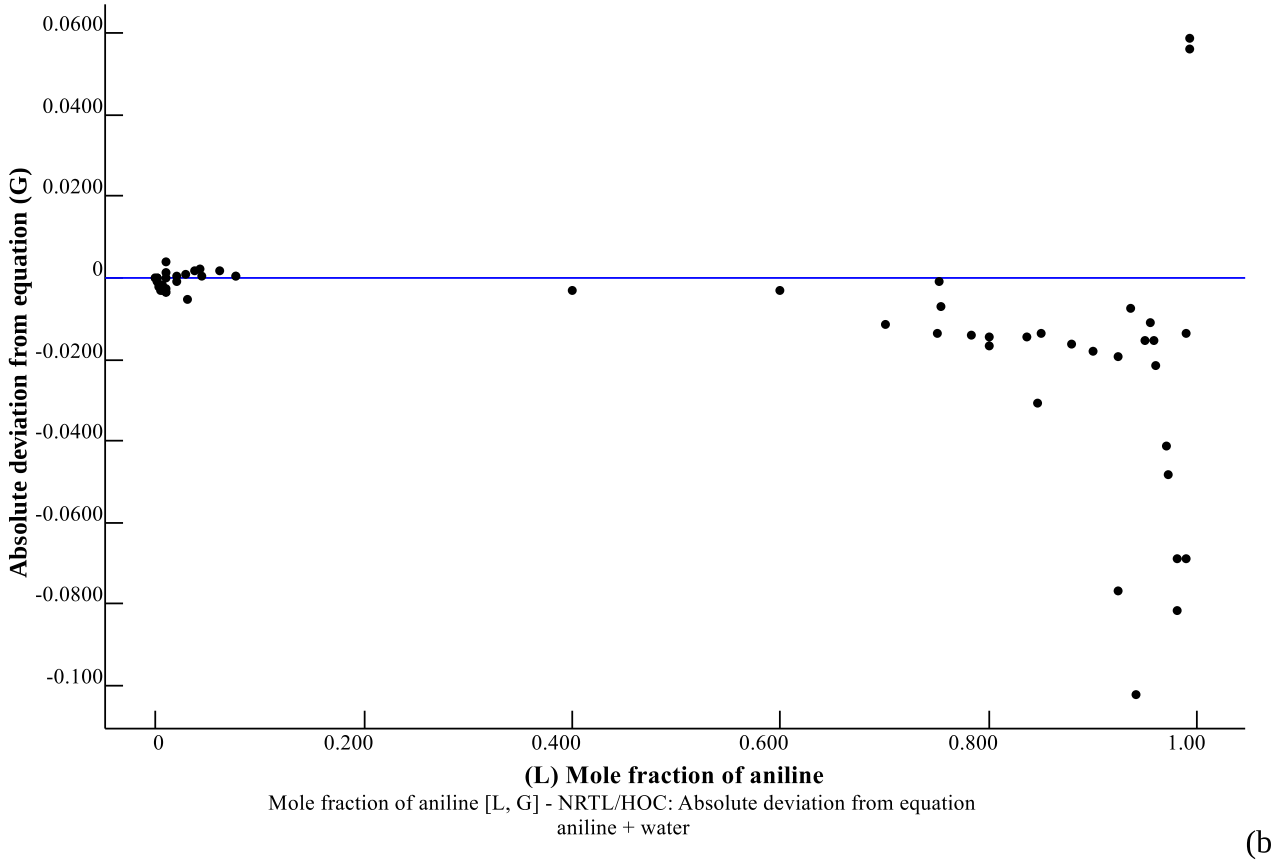
Temperature [L, G] - NRTL/HOC: Percent deviation from equation
aniline + water

(b)

Figure S2: Experimental *PTx* vapor-liquid equilibrium data (dots – Refs. [B1-B7]) vs the NRTL/HOC model (line) for aniline (1) + water (2). Experimental data (a) and their deviations from the model (b)

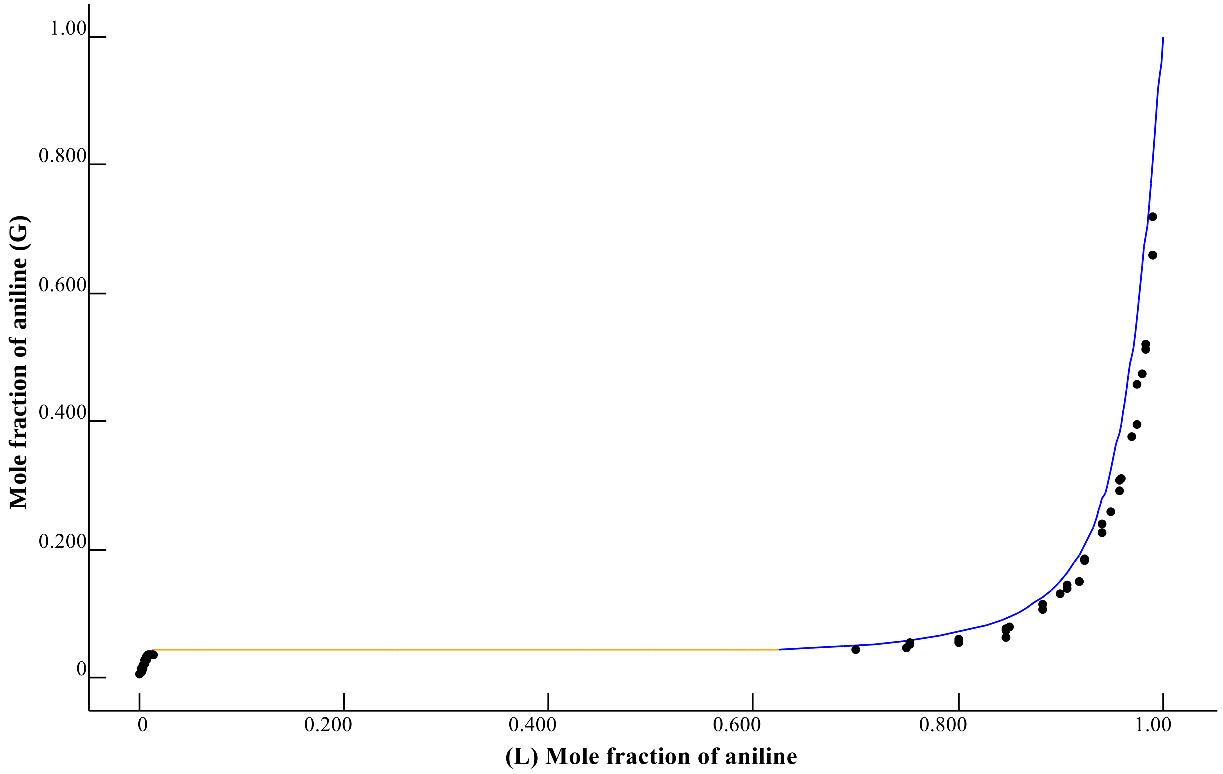


(a)



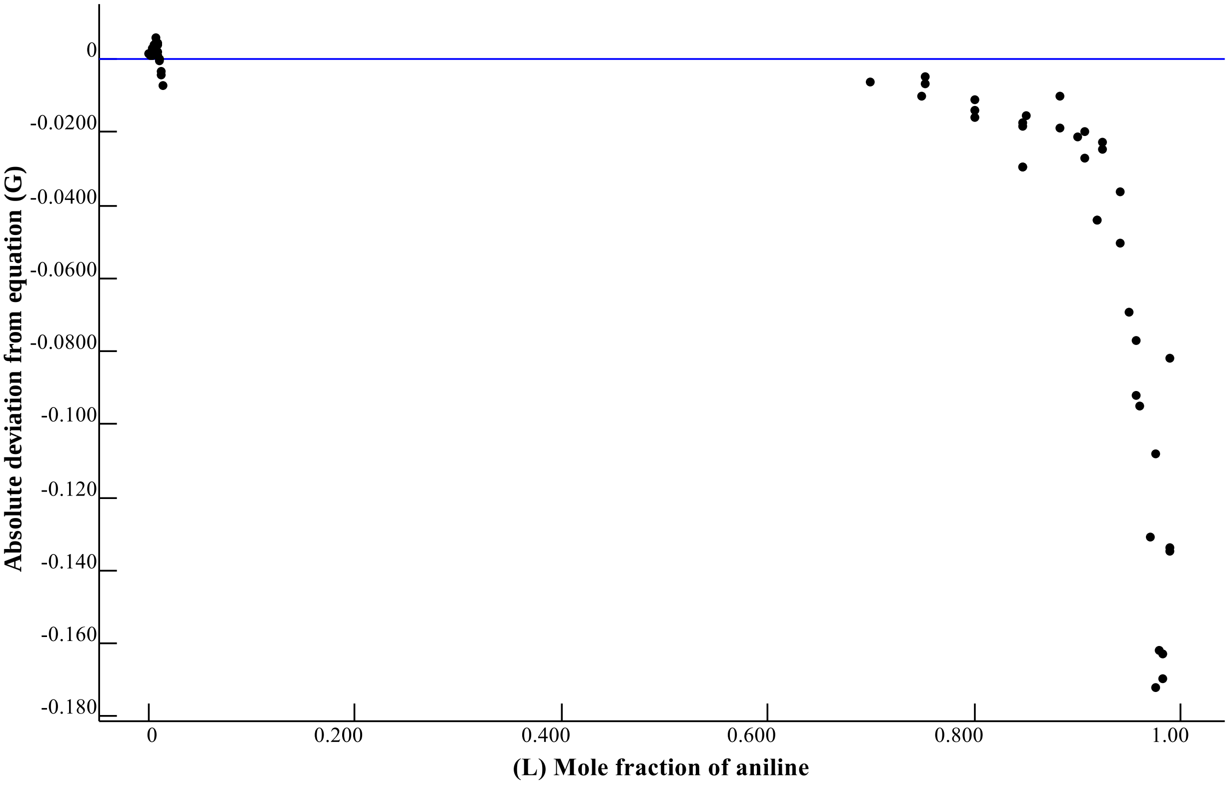
(b)

Figure S3: Experimental *Txy* vapor-liquid equilibrium data (dots – Refs. [B1-B7]) vs the NRTL/HOC model (line) for aniline (1) + water (2). Experimental data (a) and their deviations from the model (b)



Mole fraction of aniline [L, G] - NRTL/HOC
aniline + water

(a)



Mole fraction of aniline [L, G] - NRTL/HOC: Absolute deviation from equation
aniline + water

(b)

Figure S4: Experimental *Pxy* vapor-liquid equilibrium data (dots – Ref. [B2]) vs the NRTL/HOC model (line) for aniline (1) + water (2). Experimental data (a) and their deviations from the model (b)

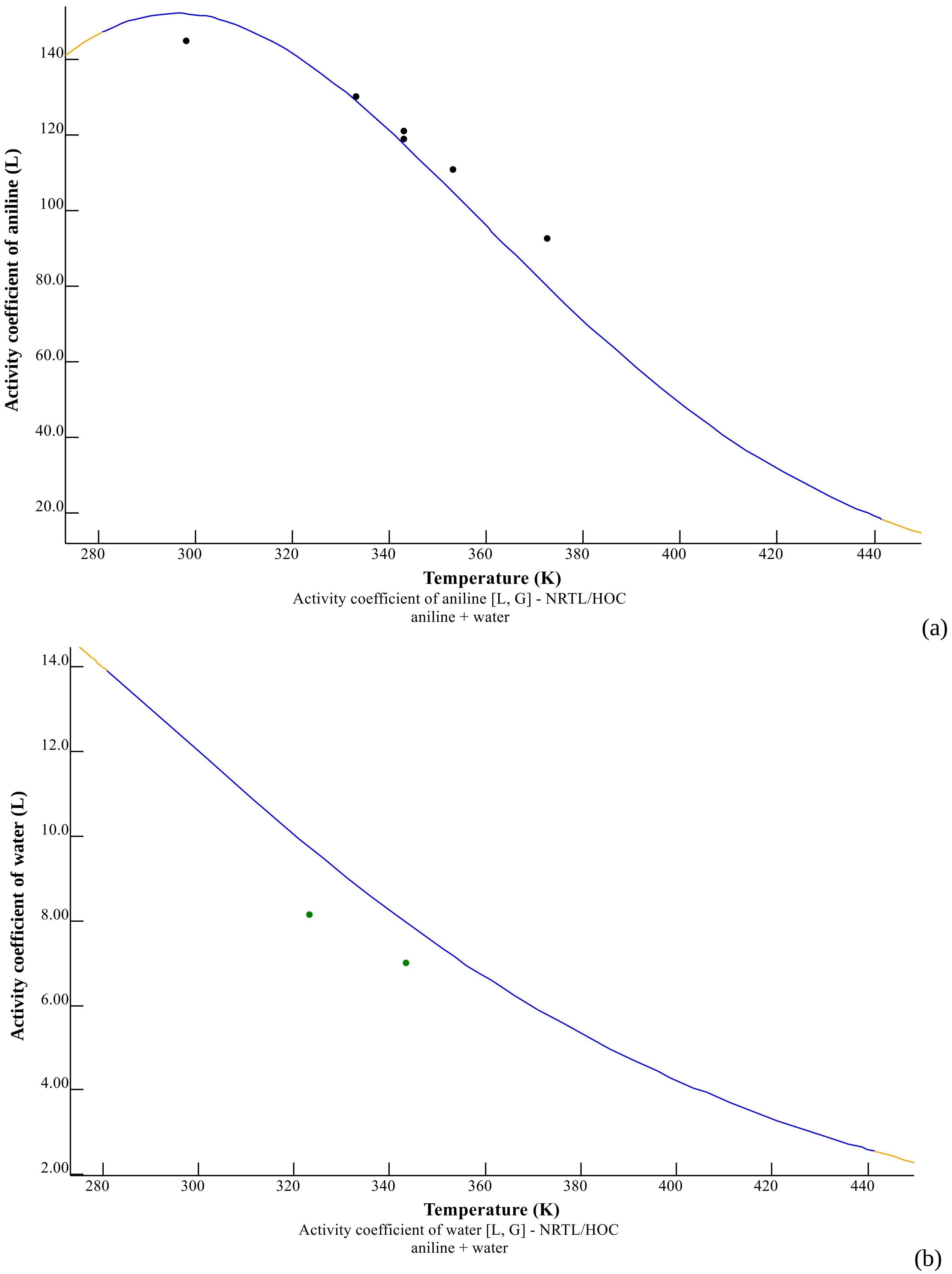


Figure S5: Experimental activity coefficients of aniline and water (dots – Ref. [B8, B9]) vs the NRTL/HOC model (line) for aniline (1) + water (2).

References for Supplement 1B:

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[B8] Bernauer, M.; Dohnal, V.; Roux, A. H.; Roux-Desgranges, G.; Majer, V., J. Chem. Eng. Data, 2006, 51, 1678.
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SUPPLEMENT 1C. Uncertainty assessment of LLE data

Uncertainty assessments can be done for experimental and recommended data. The uncertainty budget of experimental data includes deviations from the equilibrium state, effects of impurities, uncertainties in measurements of the state variables and property, and processing/reporting mistakes. While typical uncertainty ranges are known for measurement methods, they may be significantly exceeded in an individual case due to deviations from measurement protocols, both in random (detectable as scatter) and systematic (harder to detect) ways. Scatter and inconsistencies of different data sets reveal a part of the combined effect of those contributions. Hence, all contributions represent some lower estimates of the expected uncertainty, and there is no way to strictly determine the upper bound of the range containing the actual error. Increasing the amount of data (including other properties involved in thermodynamic relations) increases the probability that the uncertainty estimation is adequate, provided that the data sets are truly independent (not repeated and not biased due to attempting to match previously published data). For moderate solubilities, the major contributions should be from the measurement uncertainties (we can consider ±0.1 K in temperature and ±(1 to 3) % of the minor component content as good uncertainties), as well as the effects of impurities, which can exceed the measurement errors. For low solubilities, composition error increases, and deviations from the equilibrium state may become dominant (*e.g.*, formation of films or emulsions, sensitivity limit of incipient phase formation detection). While assigning uncertainties, we believe that a measurement at a single temperature (even if an endpoint of a ternary LLE data set) is less reliable than a series of measurements over a temperature range. Practices in particular laboratories may define the levels of expected uncertainties, which exceed the mentioned values. Rounding in a report may also limit the accuracy (for example, mole fraction 0.008 implies at least 0.0005 standard uncertainty).

If the recommended values are calculated by a smoothing equation, the contributions to their uncertainties arise from the uncertainties of the experimental values, scatter, inconsistencies of different data sets (if not included in the first contribution), model bias, and extrapolation errors (if extrapolated). We avoided extrapolation in our smoothing equations because the models we used do not have a sufficient physical basis. There are two major ways of model uncertainty assessment: covariance matrices [C1] and Bayesian or Monte Carlo methods [C2]. Bayesian methods determine relative probabilities of parameter sets on the basis of the deviations, but they require estimates of absolute uncertainties of the experimental data. Covariance methods may use uncertainties of raw data or estimate them from the scatter, but the published implementations do not combine both. Covariance methods consider only up to the second-order cross-contribution from the parameters. From our experience, straightforward covariance methods tend to underestimate the errors in the middle of the state-variables range and overestimate at the edges if the number of parameters exceeds 3. Empirical adjustments allowing handling up to 32 parameters have been developed [C3]. Both Bayesian and covariance methods treat uncertainties as random and tend to converge to zero uncertainties of the expected values as the number of measurements increases. If we take the standard deviation of a single measurement rather than that of the mean, we overestimate the uncertainties. An assumption that some level of systematic error that does not vanish with an increased number of data points seems to be practical. Such an assumption was used in this work as described in [C4]. We estimated the uncertainty of deviations of experimental data from the applied model, which was a function of one variable and had no relation to the number of the model parameters and the extent of their mutual correlation.

The procedure steps are as follows:

1) Relative deviations of the "guest component" mole fraction (x_{guest}) from the smoothing equation were represented by a linear function:

$$\Delta x_{\text{guest}}/x_{\text{guest}} = a \cdot T + b, \tag{S3}$$

where Δx_{guest} is the deviation of the "guest component" mole fraction from the smoothing equation; T is the temperature, and parameters a and b were set to $a = 0$ and $b = 0$. *"Guest component" is the component, whose concentration is smaller than that in the coexisting phase (the other component can be identified as the "host component").*

2) Mole fraction uncertainties of the experimental data were assumed to be $0.03 \cdot x_{\text{guest}}$ unless individual uncertainties were set for particular data sets (never smaller than $0.01 \cdot x_{\text{guest}}$).

3) The covariance matrix for the parameters a and b was calculated using the procedure described in [C4].

4) The covariance-based relative expanded uncertainties $U(x_{\text{guest}})/x_{\text{guest}}$ at the 0.95 level of confidence were calculated and reported in Table S2.

5) Since the uncertainties are asymmetric, the upper and lower bound for each solubility value are calculated as:

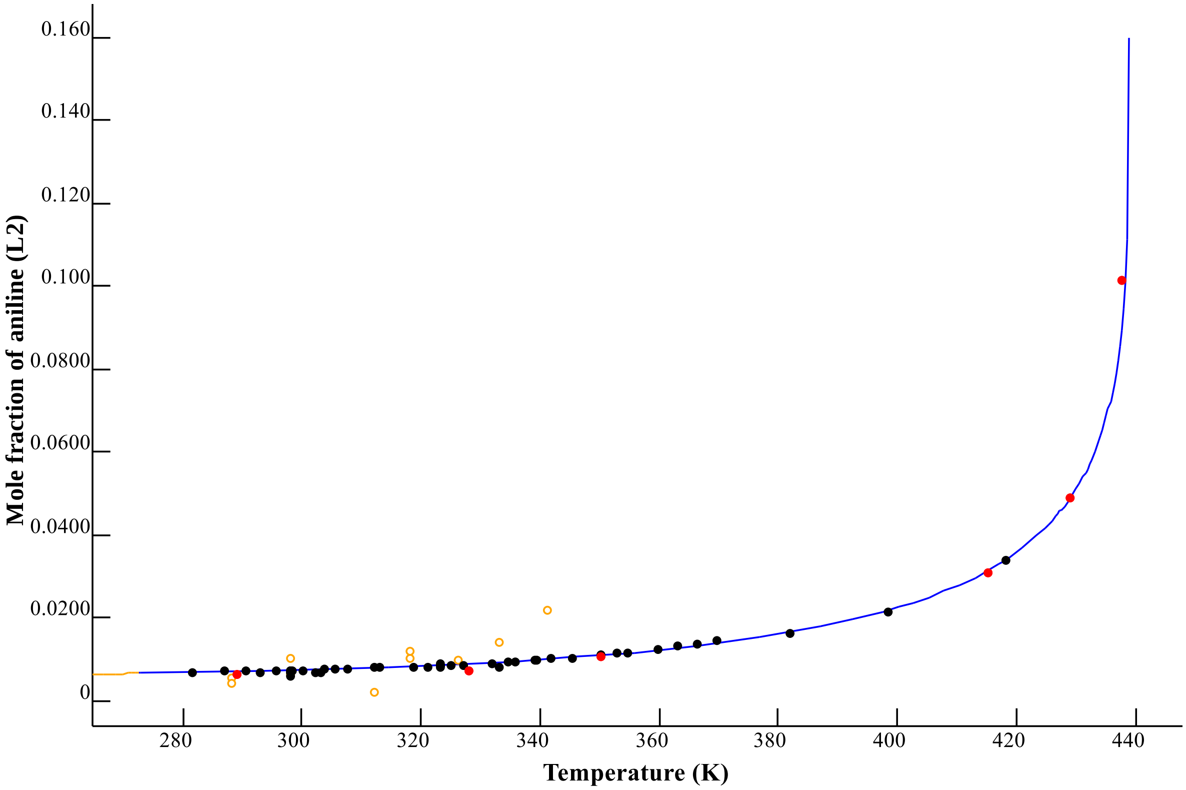
$$x_{\text{guest,range}} = \exp(a \pm U(x_{\text{guest}})/x_{\text{guest}})/[1 + \exp(a \pm U(x_{\text{guest}})/x_{\text{guest}})], \tag{S4}$$

where

$$a = \ln(x_{\text{guest}}/(1 - x_{\text{guest}})), \tag{S5}$$

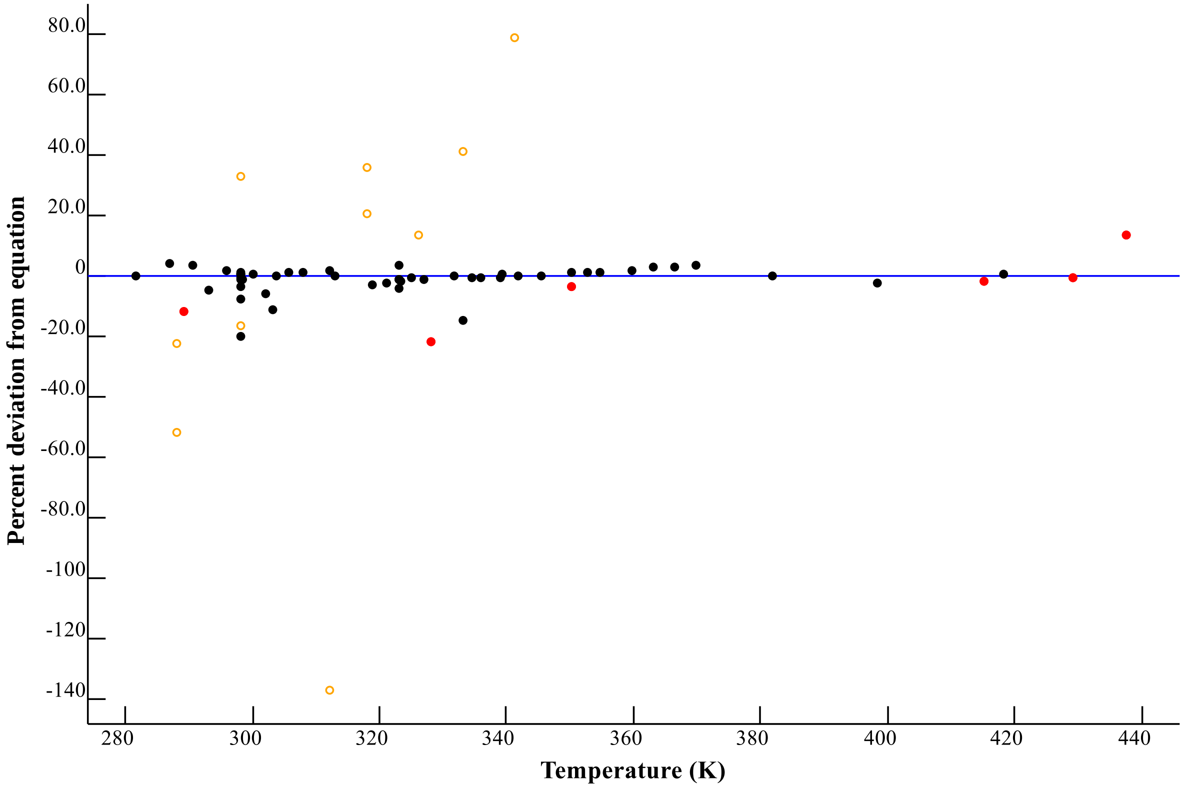
and $x_{\text{guest,range}}$ is the confidence interval of the mole fraction of the "guest component". The corresponding confidence intervals are given in the main-text tables with smoothed solubility values.

Exclusion of apparently erroneous data is a part of the procedure, which can be based on obvious experimental mistakes, high overall level of errors in a particular report or laboratory, unphysical values or behavior, or large scatter or inconsistencies. The latter factor is normally assessed in a statistical analysis. This can be demonstrated using the water-rich phase of the aniline + water system as an example. The data excluded from the uncertainty assessments are shown in Figures S6 in different scales (mole fractions and relative deviation from the "guest component" content). The data sets excluded are [C5] (due to systematic deviation of the trend for an unknown reason) and [C6] (due to huge scatter). Among the remaining data sets, an older work [C7] shows the largest scatter and was involved with a reduced weight in the fitting to verify the SDS equation.



Mole fraction of aniline [L1, L2, G] - SDS 6
aniline + water

(a)



Mole fraction of aniline [L1, L2, G] - SDS 6: Percent deviation from equation
aniline + water

(b)

Figure S6: Experimental mole-fraction LLE data used for uncertainty assessment for the water-rich phase of the aniline (1) + water (2) system, where black dots – the data included into the uncertainty assessment, yellow dot – the data excluded from the uncertainty assessment, red dots – the data from [C7] involved with a reduced weight in the fitting. The corresponding literature sources can be found in Supplement 1A. Experimental data (a), their relative deviations from the model calculated as $100\cdot\ln(x_{\mathrm{exp}}\text{-}x_{\mathrm{calc}})$ (b).

The resulting equations describing the uncertainties for all seven suggested LLE mixtures are summarized in Table S2 (note: all digits in the reported equation parameters are needed to provide values not affected by rounding errors).

Table S2: Equations describing relative expanded uncertainties for mole-fraction solubilities ($U(x_{\mathrm{guest}})/x_{\mathrm{guest}}$) at the 0.95 level of confidence ($k = 2$) needed to calculate the confidence interval limits using Equations (S4)-(S5) [a]

System	Phase	Equation
Aniline (1) + water (2)	Liquid phase 1 (water-rich)	$U(x_1)/x_1 = (0.102763 – 0.000630802\cdot T + 9.78642\text{e-}07\cdot T^2)^{1/2}$
	Liquid phase 2 (aniline-rich)	$U(x_2)/x_2 = (0.0602507 – 0.000363597\cdot T + 5.56097\text{e-}07\cdot T^2)^{1/2}$
Phenol (1) + water (2)	Liquid phase 1 (water-rich)	$U(x_1)/x_1 = (0.247025 – 0.00158907\cdot T + 2.56081\text{e-}06\cdot T^2)^{1/2}$
	Liquid phase 2 (phenol-rich)	$U(x_2)/x_2 = (0.0324597 – 0.000207881\cdot T + 3.33525\text{e-}07\cdot T^2)^{1/2}$
Nitromethane (1) + water (2)	Liquid phase 1 (water-rich)	$U(x_1)/x_1 = (0.19391 – 0.00119147\cdot T + 1.84367\text{e-}06\cdot T^2)^{1/2}$
	Liquid phase 2 (nitromethane-rich)	$U(x_2)/x_2 = (0.679622 – 0.0041469\cdot T + 6.35657\text{e-}06\cdot T^2)^{1/2}$
Cyclohexane (1) + methanol (2)	Liquid phase 1 (methanol-rich)	$U(x_1)/x_1 = (0.45885 – 0.00301274\cdot T + 4.95067\text{e-}06\cdot T^2)^{1/2}$
	Liquid phase 2 (cyclohexane-rich)	$U(x_2)/x_2 = (1.08277 – 0.0070425\cdot T + 1.1463\text{e-}05\cdot T^2)^{1/2}$
Toluene (1) + water (2)	Liquid phase 1 (water-rich)	$U(x_1)/x_1 = (0.151881 – 0.000888036\cdot T + 1.33839\text{e-}06\cdot T^2)^{1/2}$
	Liquid phase 2 (toluene-rich)	$U(x_2)/x_2 = (0.418817 – 0.00242753\cdot T + 3.60503\text{e-}06\cdot T^2)^{1/2}$
Ethylbenzene (1) + water (2)	Liquid phase 1 (water-rich)	$U(x_1)/x_1 = (1.73309 – 0.0112362\cdot T + 1.82918\text{e-}05\cdot T^2)^{1/2}$
	Liquid phase 2 (ethylbenzene-rich)	$U(x_2)/x_2 = (0.328306 – 0.00214134\cdot T + 3.51247\text{e-}06\cdot T^2)^{1/2}$
Hexan-1-ol (1) + [C$_6$mim][NTf$_2$] (2)	Liquid phase 1 ([C$_6$mim][NTf$_2$]-rich)	$U(x_1)/x_1 = (0.611006 – 0.00408697\cdot T + 6.8374\text{e-}06\cdot T^2)^{1/2}$
	Liquid phase 2 (hexan-1-ol-rich)	$U(x_2)/x_2 = (2.66702 – 0.0178234\cdot T + 2.97876\text{e-}05\cdot T^2)^{1/2}$

[a] [C$_6$mim][NTf$_2$] is 1-hexyl-3-methyl-1*H*-imidazolium bis[(trifluoromethyl)sulfonyl]amide.

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SUPPLEMENT 1D. Data sources on LLE for phenol + water

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SUPPLEMENT 1E. Validation of LLE data for phenol + water

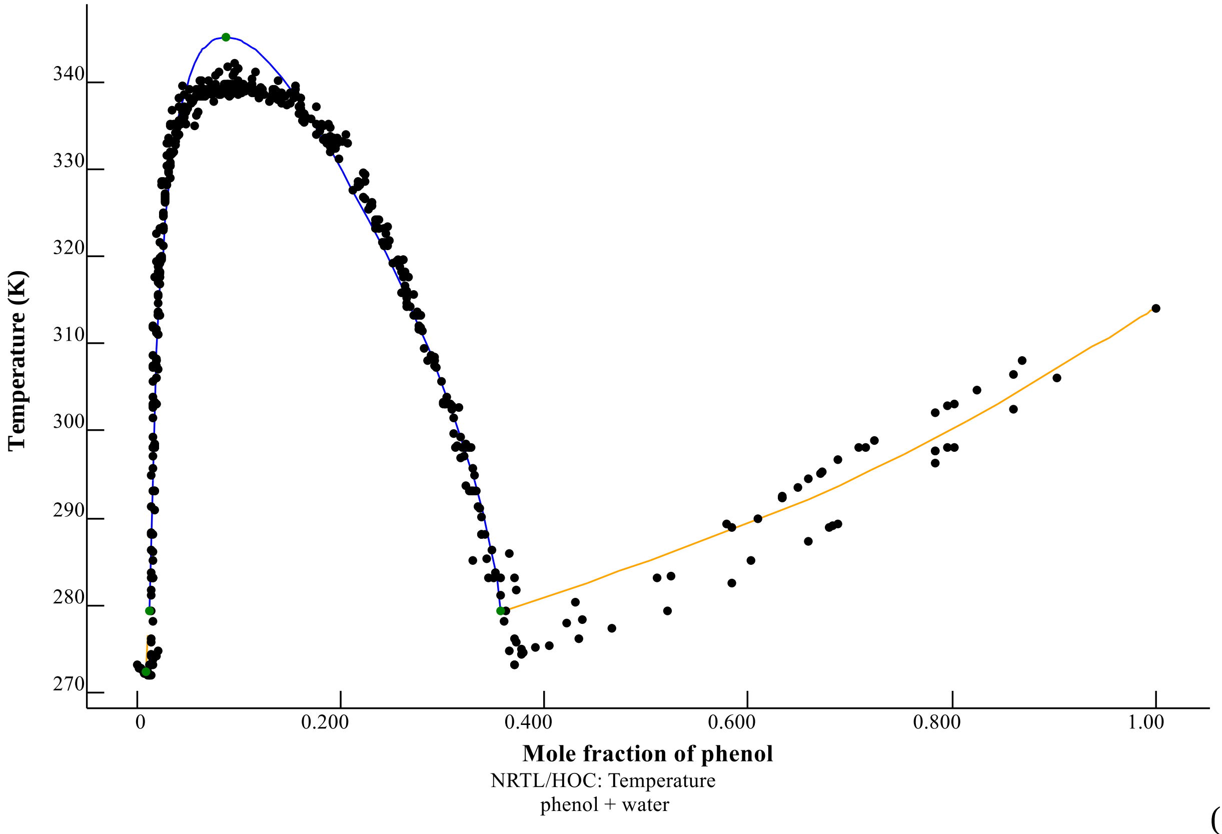
Important note: This model is not recommended for LLE calculations. Its purpose is to prove the consistency with other properties.

Non-Random Two-Liquid excess Gibbs energy model with the Hayden-O'Connell gas phase model (NRTL/HOC model) as given by equations (S1)-(S2).

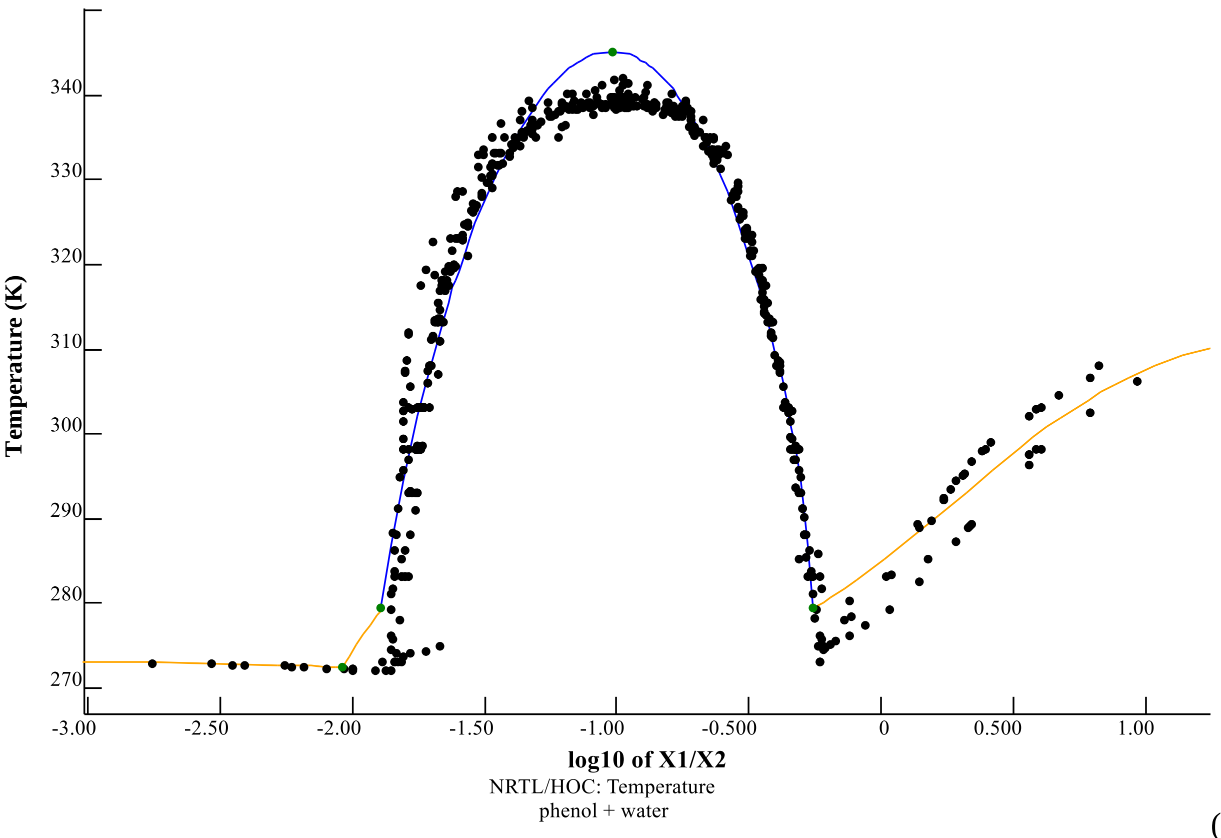
Table S3: Parameters for NRTL/HOC model for phenol (1) + water (2)

Component *i*	A_i	B_i	k
Component 1 (phenol)	1.94932	518.689	0.481657
Component 2 (water)	-6.9486	2225.75	

Solid-liquid equilibrium (SLE) is known with a lower accuracy for this system, and the position of the eutectic point is not reliably determined. A solid-state compound $2C_6H_5OH{\cdot}H_2O$ (not shown here) has been claimed in some reports (*e.g.*, [E1]-[E3]). The NRTL/HOC model is for pure solid phenol, which is apparently metastable below 289 K. The obviously erroneous data from [E4] are not shown in Figure S7 (since the pure phenol melting endpoint from that reference is 10 K lower than the accepted value).



(a)



(b)

Figure S7: Experimental mole-fraction SLE + LLE data (black dots – Supplement 1E for LLE and Refs.[E1-E3, E5-E9] for SLE) vs the NRTL/HOC model (line) for phenol (1) + water (2). The green dots are predicted upper consolute, monotectic, and eutectic points. Regular representation (a) and composition-stretched representation (b).

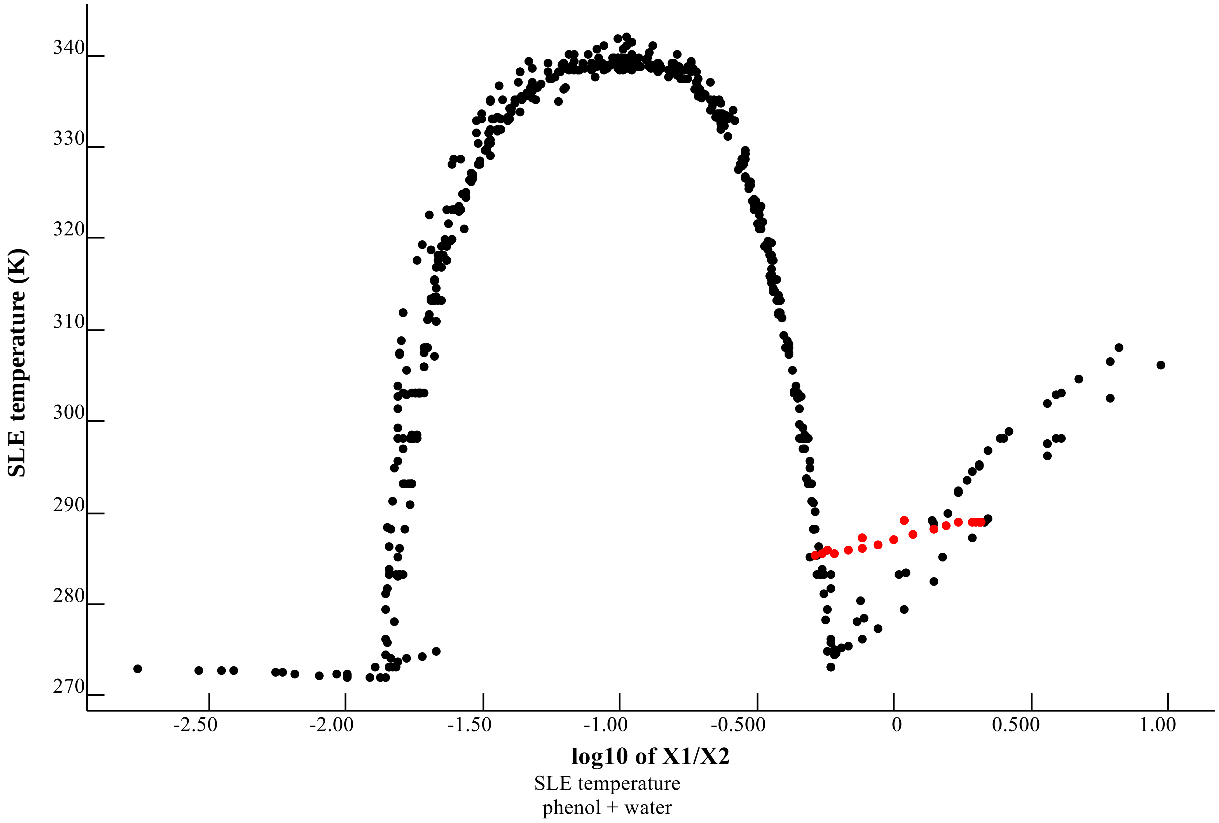


Figure S8: The complete (LLE+SLE) diagram for phenol (1) + water (2). The experimental SLE with an intercomponent compound is highlighted in red.

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The following references mentioned in SDS-71 were not included, since they do not contain original LLE data for nitromethane + water:
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SUPPLEMENT 1G. Validation of LLE data for nitromethane + water

Important note: This model is not recommended for LLE calculations. Its purpose is to prove the consistency with other properties.

UNIversal QUAsiChemical model with the Hayden-O’Connell gas phase model (UNIQUAC/HOC model):

$$G^E/(RT) = -q_1 \cdot x_1 \cdot \ln(t_1 + t_2 \cdot t_{21}) - q_2 \cdot x_2 \cdot \ln(t_2 + t_1 \cdot t_{12}) + x_1 \cdot \ln(f_1/x_1) + x_2 \cdot \ln(f_2/x_2) + 5\{q_1 \cdot x_1 \cdot \ln(t_1/f_1) + q_2 \cdot x_2 \cdot \ln(t_2/f_2)\}, \tag{S6}$$

$$t_{12} = \exp\{-u_{12}/(R \cdot T)\}, \tag{S7}$$

$$t_{21} = \exp\{-u_{21}/(R \cdot T)\}, \tag{S8}$$

$$t_1 = (x_1 \cdot q_1)/\{x_1 \cdot q_1 + (1 - x_1) \cdot q_2\}, \tag{S9}$$

$$t_2 = \{(1 - x_1) \cdot q_2\}/\{x_1 \cdot q_1 + (1 - x_1) \cdot q_2\}, \tag{S10}$$

$$f_1 = (x_1 \cdot r_1)/\{x_1 \cdot r_1 + (1 - x_1) \cdot r_2\}, \tag{S11}$$

$$f_2 = \{(1 - x_1) \cdot r_2\}/\{x_1 \cdot r_1 + (1 - x_1) \cdot r_2\} \tag{S12}$$

with temperature dependence

$$u_{ij} = A_{ij} + B_{ij}\,T^{-1} + C_{ij} \ln(T) + D_{ij}\,T + E_{ij}\,T^{-2}, \tag{S13}$$

where G^E is excess Gibbs energy, u_{ij} are the interaction parameters, r_i and q_i are the combinatorial parameters for component i; A_{ij} through E_{ij} are the fitted parameters for the interaction parameters, T is temperature in K, x_i are mole fractions of the components, and R is the gas constant.

Table S4: Parameters for UNIQUAC/HOC model for nitromethane (1) + water (2)

Component parameters		
Component *i*	r_i	q_i
Component 1 (nitromethane)	2.0086	1.868
Component 2 (water)	0.92	1.4

Interaction parameters					
Term	A_{ij}	B_{ij}	C_{ij}	D_{ij}	E_{ij}
u_{12}	3.56535	-2566.97	-0.0397715	0.00486356	220515
u_{21}	-2.12103	461.839	0.138815	-0.000837181	-60277.6

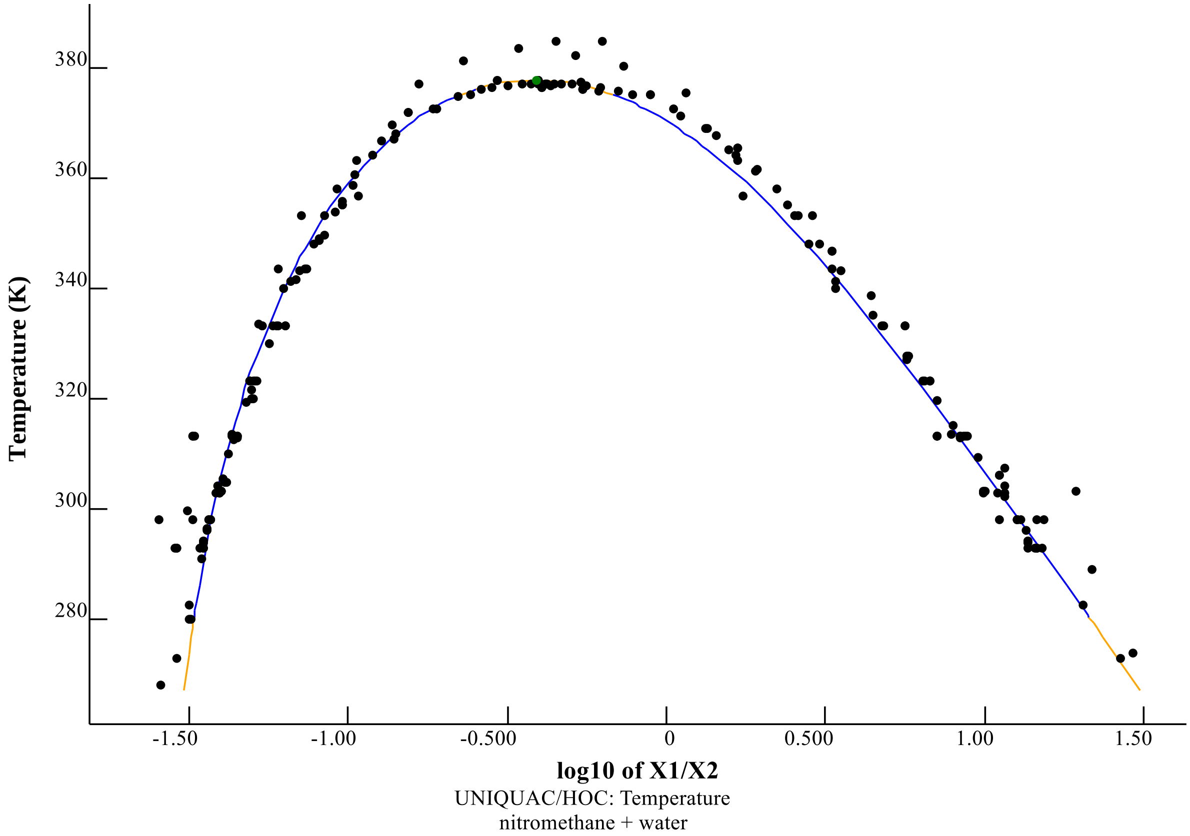
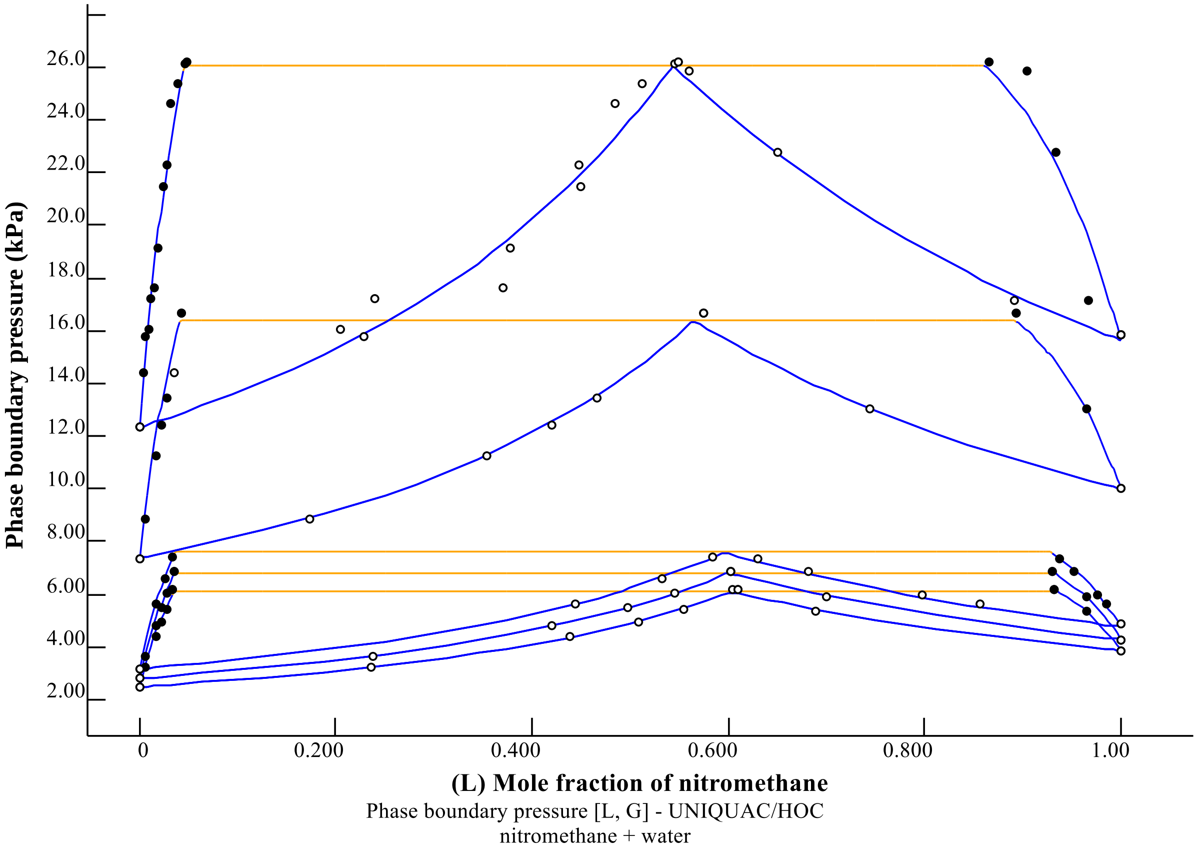
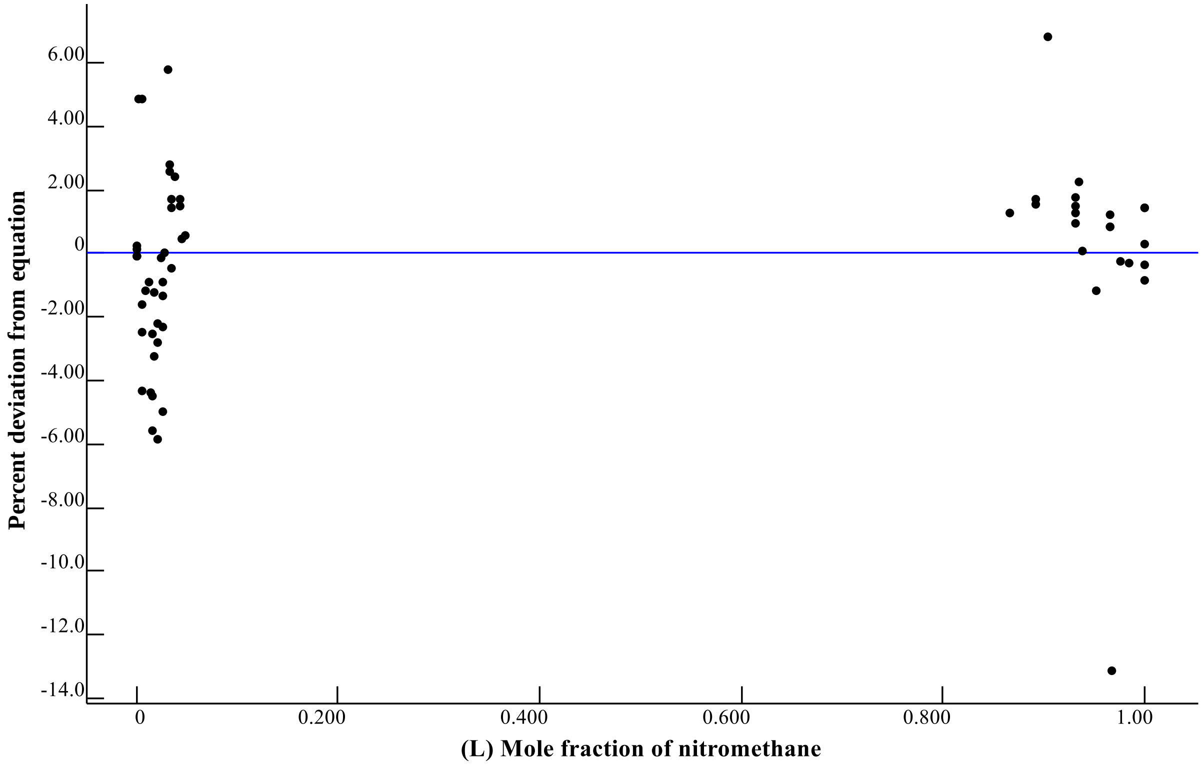


Figure S9: Experimental mole-fraction LLE data (black dots – Supplement 1F) vs the UNIQUAC/HOC model (line) for nitromethane (1) + water (2). The green dot is predicted upper consolute point

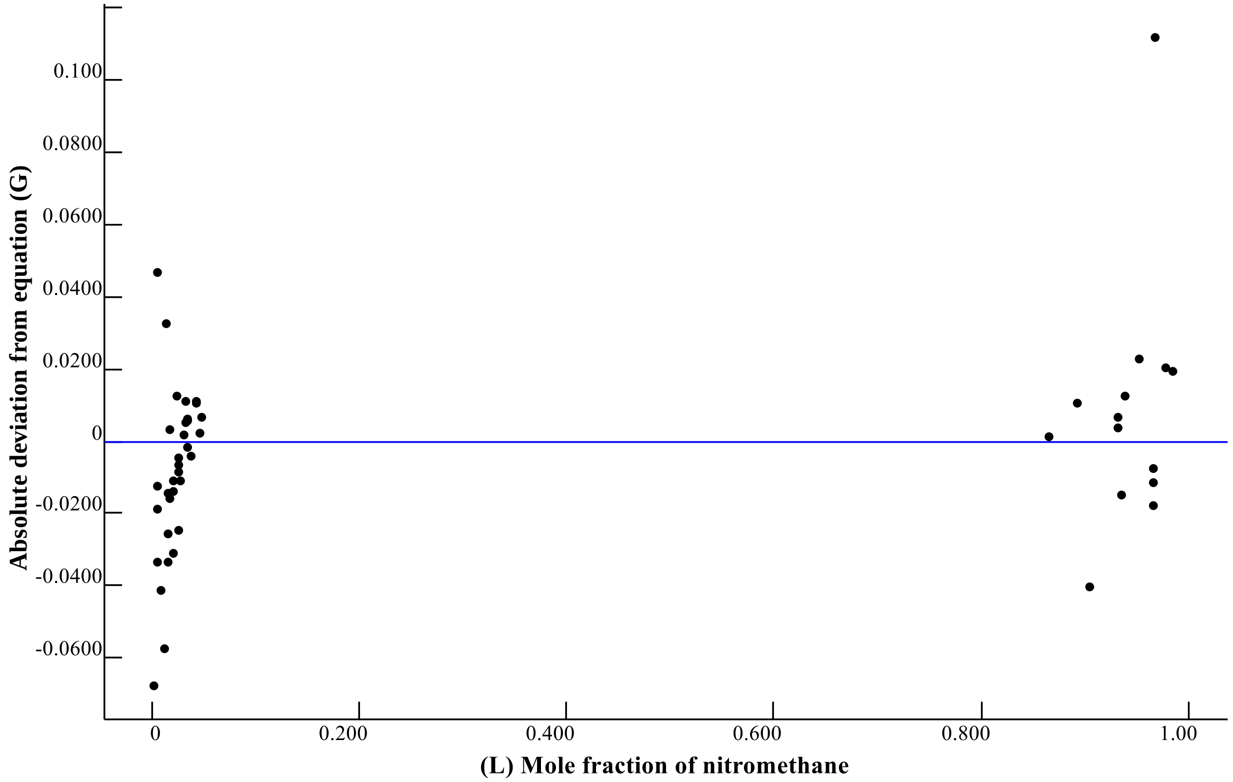


(a)



Phase boundary pressure [L, G] - UNIQUAC/HOC: Percent deviation from equation
nitromethane + water

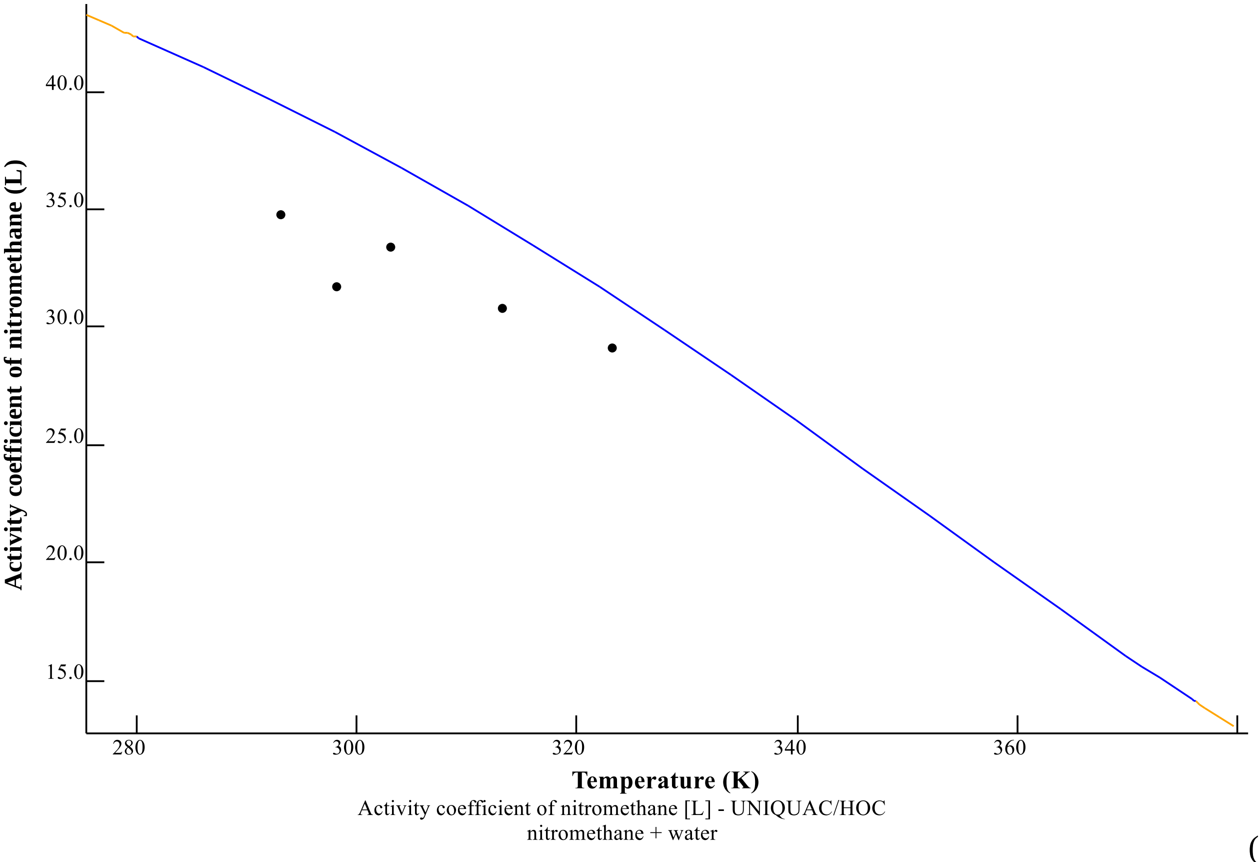
(b)



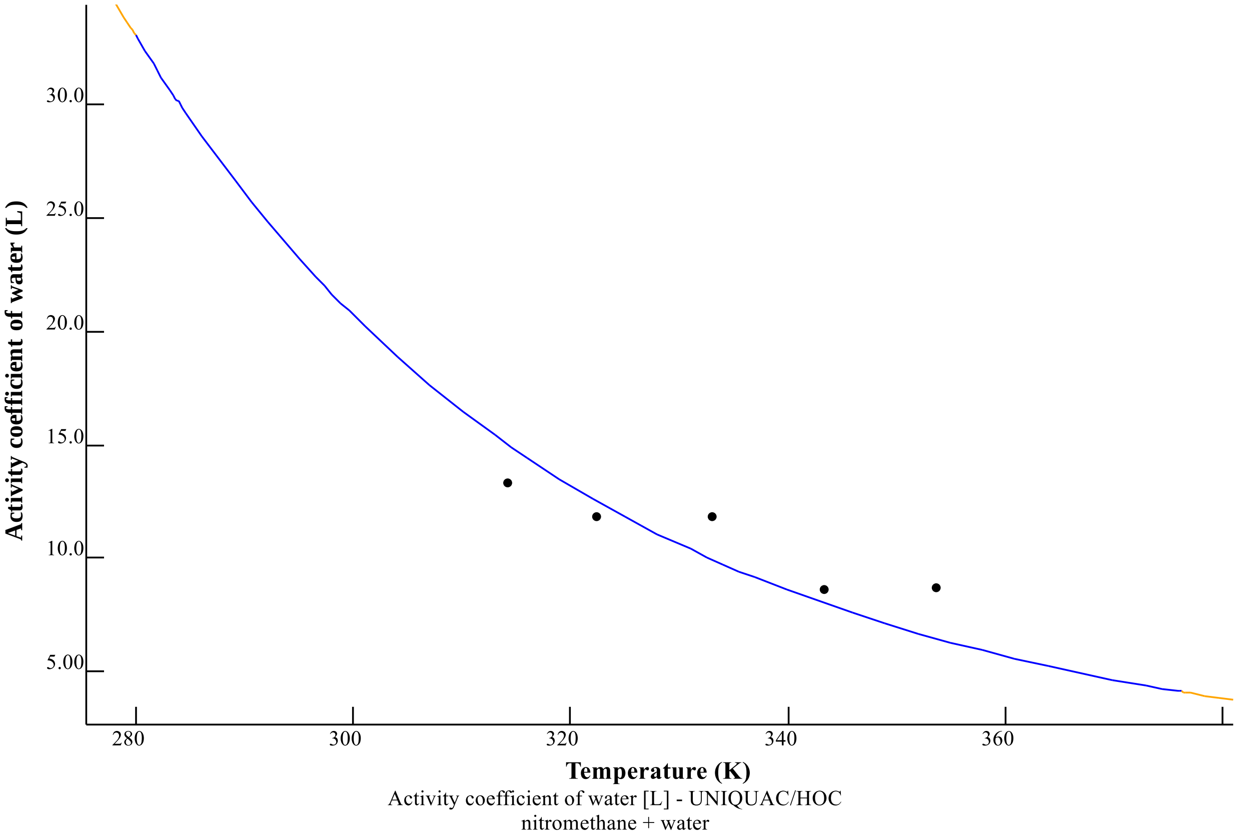
Mole fraction of nitromethane [L, G] - UNIQUAC/HOC: Absolute deviation from equation
nitromethane + water

(c)

Figure S10: Experimental vapor-liquid equilibrium data (dots – Refs. [G1-G5]) vs the UNIQUAC/HOC model (line) for nitromethane (1) + water (2). Experimental *PTxy* data (a), deviations for *PTx* data from the model (b), deviations for *Txy* data from the model (c)



(a)



(b)

Figure S11: Experimental activity coefficients of nitromethane and water (dots – Ref. [G6, G7]) vs the UNIQUAC/HOC model (line) for nitromethane (1) + water (2).

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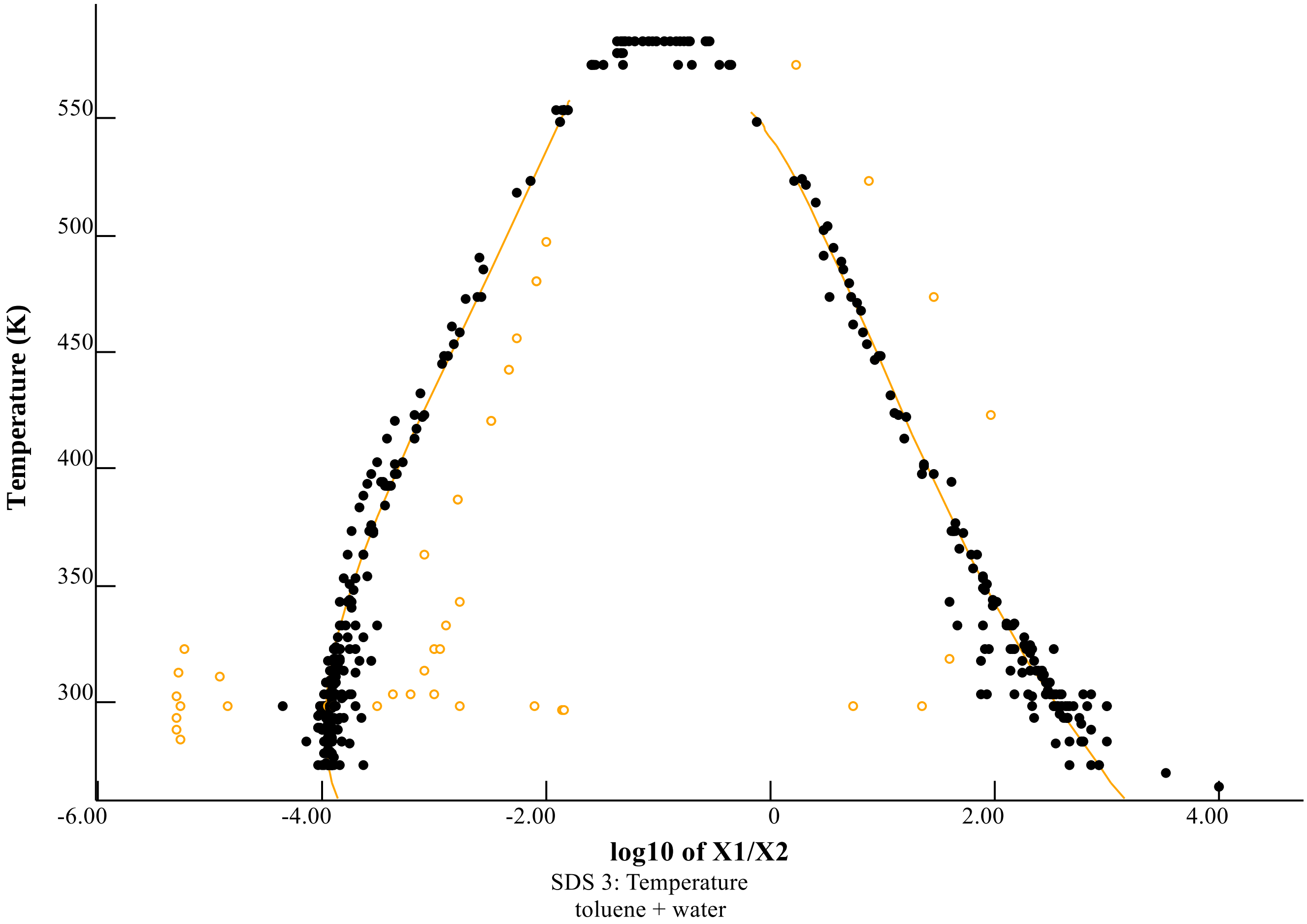

Figure S12: A complete collection of experimental mole-fraction LLE data for toluene (1) + water (2) in a composition-stretched representation involving the data believed to be erroneous (hollow amber circles). Line is the selected model representation as described in the main text.

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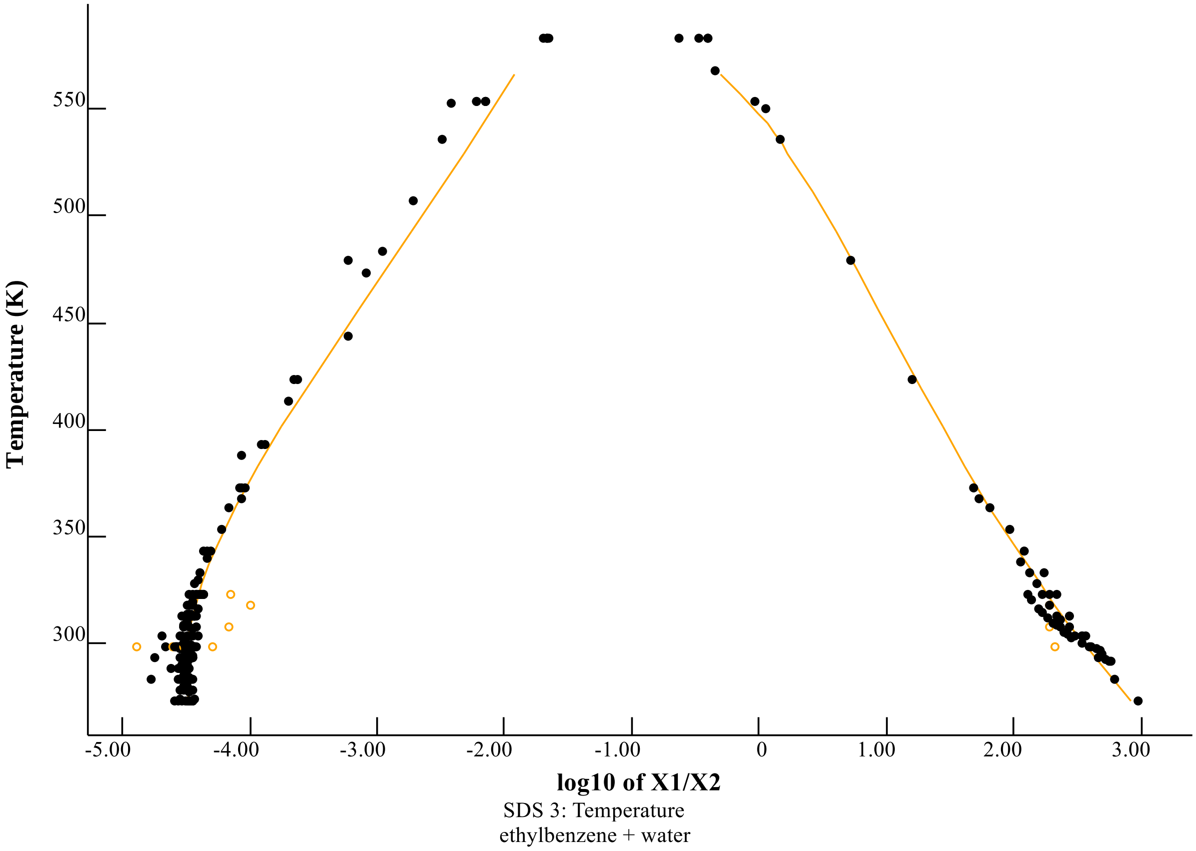


Figure S13: A complete collection of experimental mole-fraction LLE data for ethylbenzene (1) + water (2) in a composition-stretched representation involving the data believed to be erroneous (hollow amber circles). Line is the selected model representation as described in the main text.

SUPPLEMENT 1K. Consistency of LLE data for methylbenzene (toluene) + water and ethylbenzene + water with other properties tested by SAFT equations

Building models that could verify the consistency of low liquid solubility with other properties is a challenge because other properties belong to high temperatures and pressures and involve critical and supercritical regions. Despite the currently available models provide basically qualitative overall agreement, we believe such modeling is still useful in order to corroborate our understanding of the phenomena, types and regions of phase equilibria, and the absence of unacceptable inconsistencies.

The molecular-based models belonging to the family of Statistical Associating Fluid Theory (SAFT) are more sophisticated than NRTL and other G^E-based models. Therefore, they can be considered as inferior for the precise local fitting of some particular data. At the same time, SAFT models can be implemented in an entirely predictive manner without any previous consideration of mixture data, yielding qualitatively reasonable results in the whole thermodynamic phase space. Such results can be used for raw estimations of auxiliary thermodynamic properties of mixtures in very wide P-T ranges and the general picture of phase behavior, such as its topology, approximate borders of phase split regions, etc. This information can be particularly important in engineering practice if no data are available.

The Critical Point-based Perturbed Chain version of SAFT (CP-PC-SAFT) is the only SAFT approach obeying the pure compounds' critical temperatures and pressures. A typical drawback of this feature is underestimating the extent of LLE phase splits in the x-T projection. In the case of the aqueous systems of toluene and ethylbenezene, this drawback results in poor results for the water-rich phases along liquid-liquid-vapor equilibrium (LLVE) as shown in Figures S14. In particular, the model substantially overpredicts the hydrocarbon solubility in these phases. At the same time, it predicts in a reasonable manner the compositions of the hydrocarbon-rich phases, upper critical end points (UCEP) and the LLVE pressures (Figure S15). The UCEP temperatures predicted with CP-PC-SAFT are 560.2 K for toluene + water and 578.9 K for ethylbenzene + water, which are in fair agreement with the experimental values presented in the main text. The details and consistency with other properties have been published previously in [K1].

The Variable Range version of SAFT with Mie-potential implemented for both dispersion and associative inter-molecular interactions (SAFT-VR-Mie-Mie) is one of the most recent and sophisticated models of the family. It does not obey the pure compound critical points but yields more accurate predictions of LLVE. The compositions for both sides of the LLE split as well as UCEP and the LLVE pressures are reasonably predicted (Figures S16 and S17). The UCEP temperatures predicted with SAFT-VR-Mie-Mie are 559.1 K for toluene + water and 585.5 K for ethylbenzene + water, which are in fair agreement with the experimental values presented in the main text. The details and additional discussion of the results have been given in [K2].

An advantage of obeying the pure compound critical points by CP-PC-SAFT becomes evident while considering the over-all picture of phase behavior shown in Figure S18.

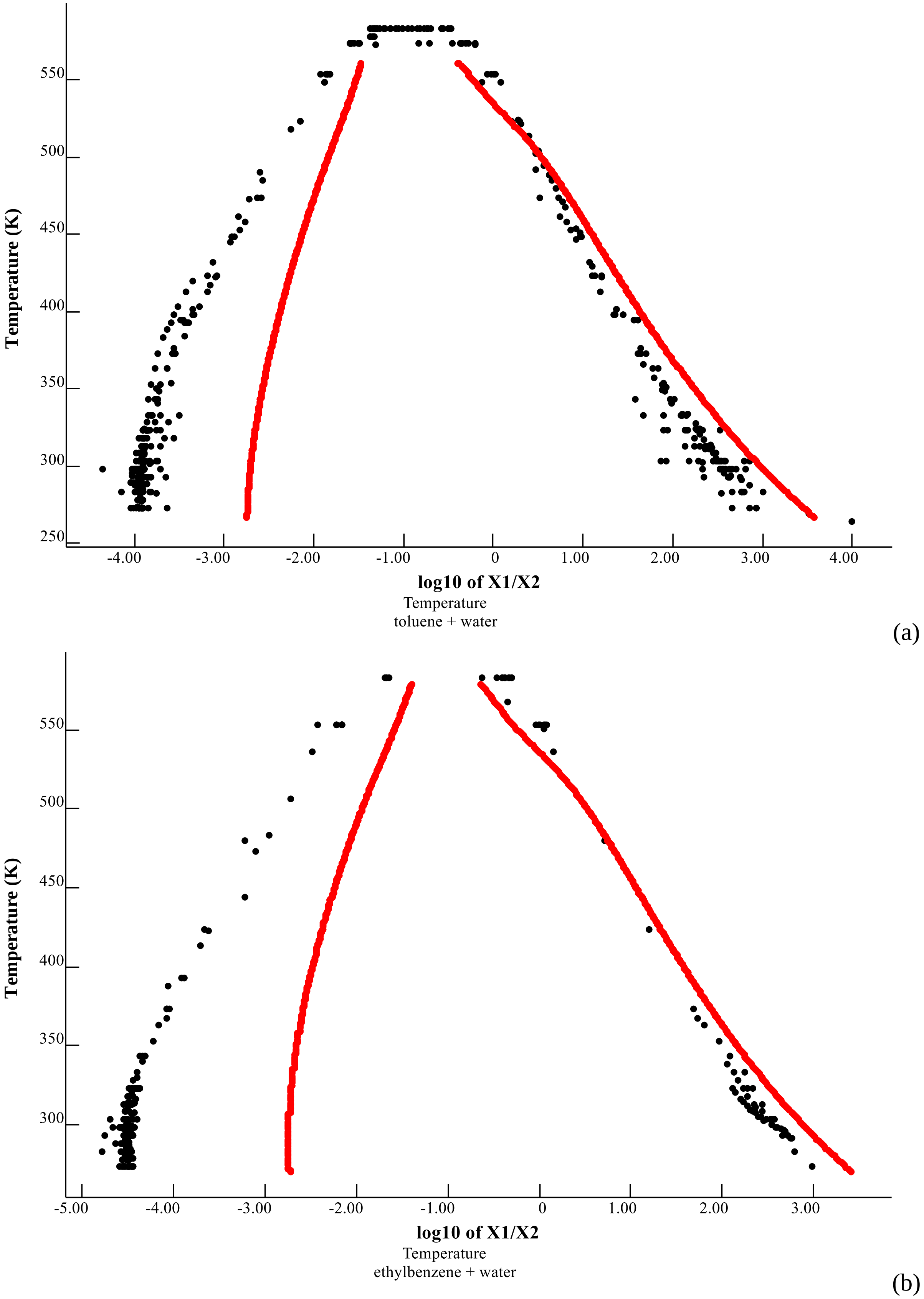
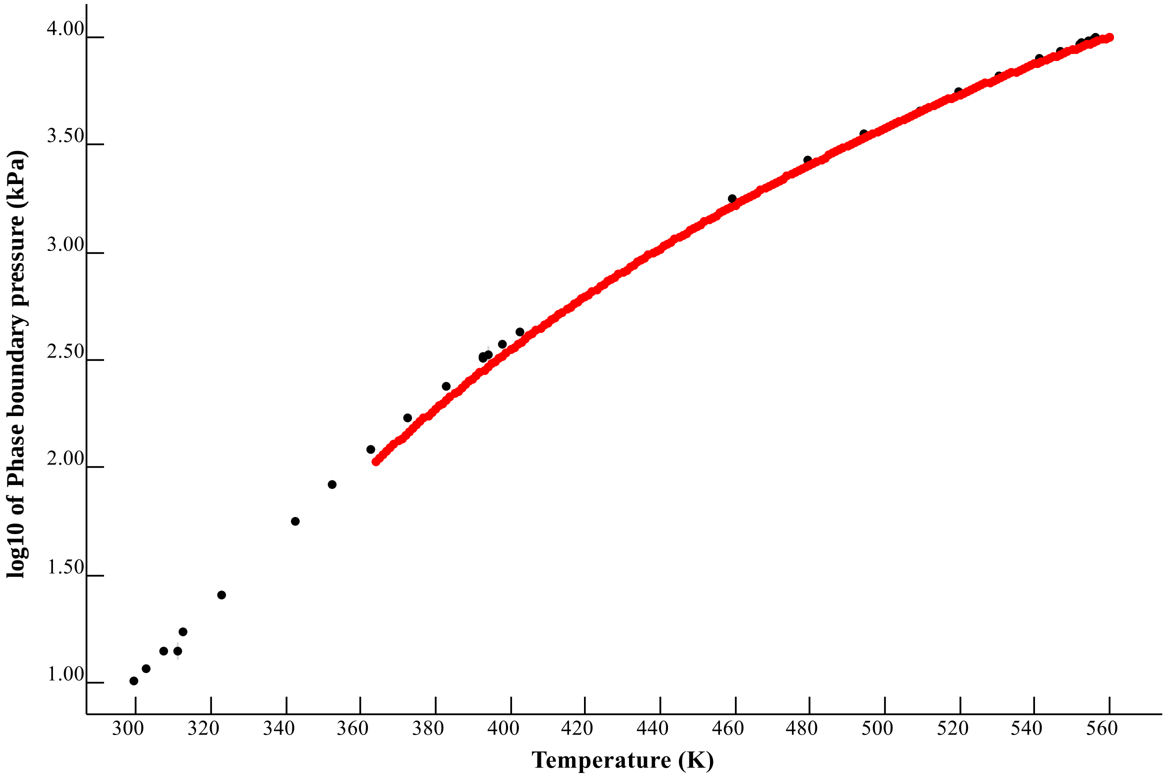
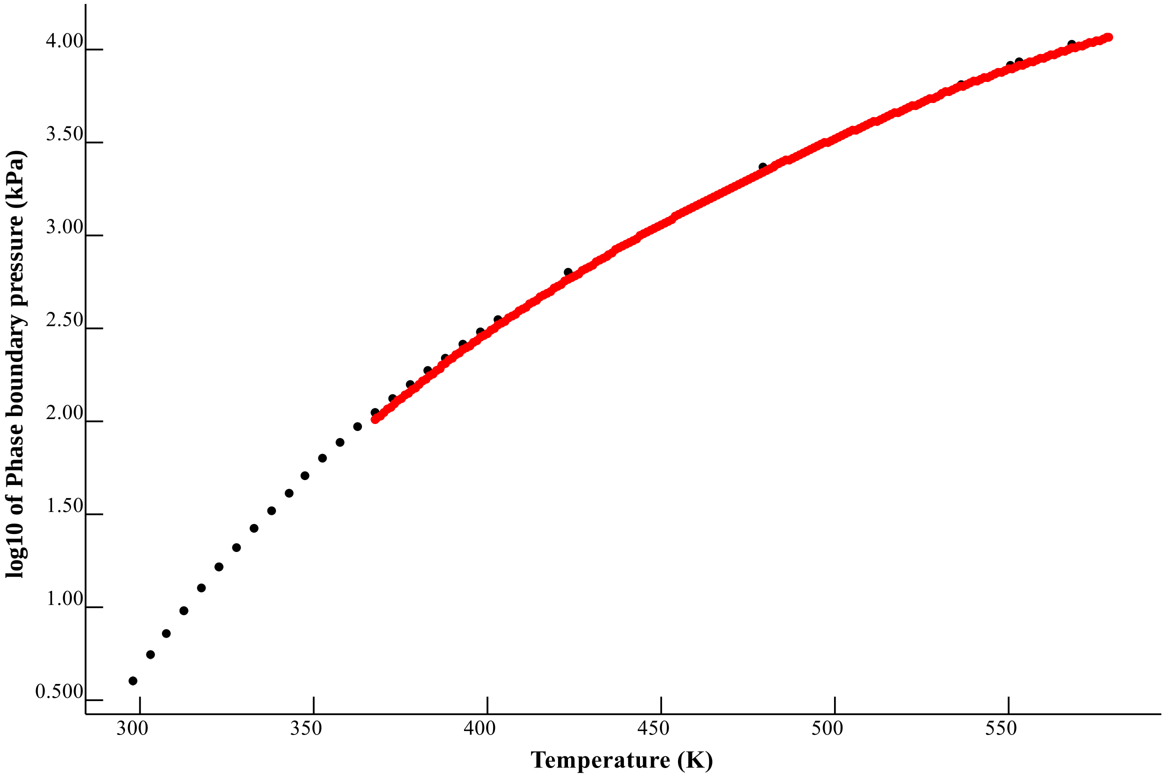


Figure S14: Experimental mole-fraction LLE data for (a) toluene (1) + water (2) and (b) ethylbenzene (1) + water (2) vs the CP-PC-SAFT model (red dots). Black dots are experimental data from Supplements 1I and IJ.



log10 of Phase boundary pressure [L1, L2, G]
toluene + water

(a)



log10 of Phase boundary pressure [L1, L2, G]
ethylbenzene + water

(b)

Figure S15: Experimental LLVE pressures for (a) toluene (1) + water (2) and (b) ethylbenzene (1) + water (2) vs the CP-PC-SAFT model (red dots). Black dots are experimental data from [K3-K8].

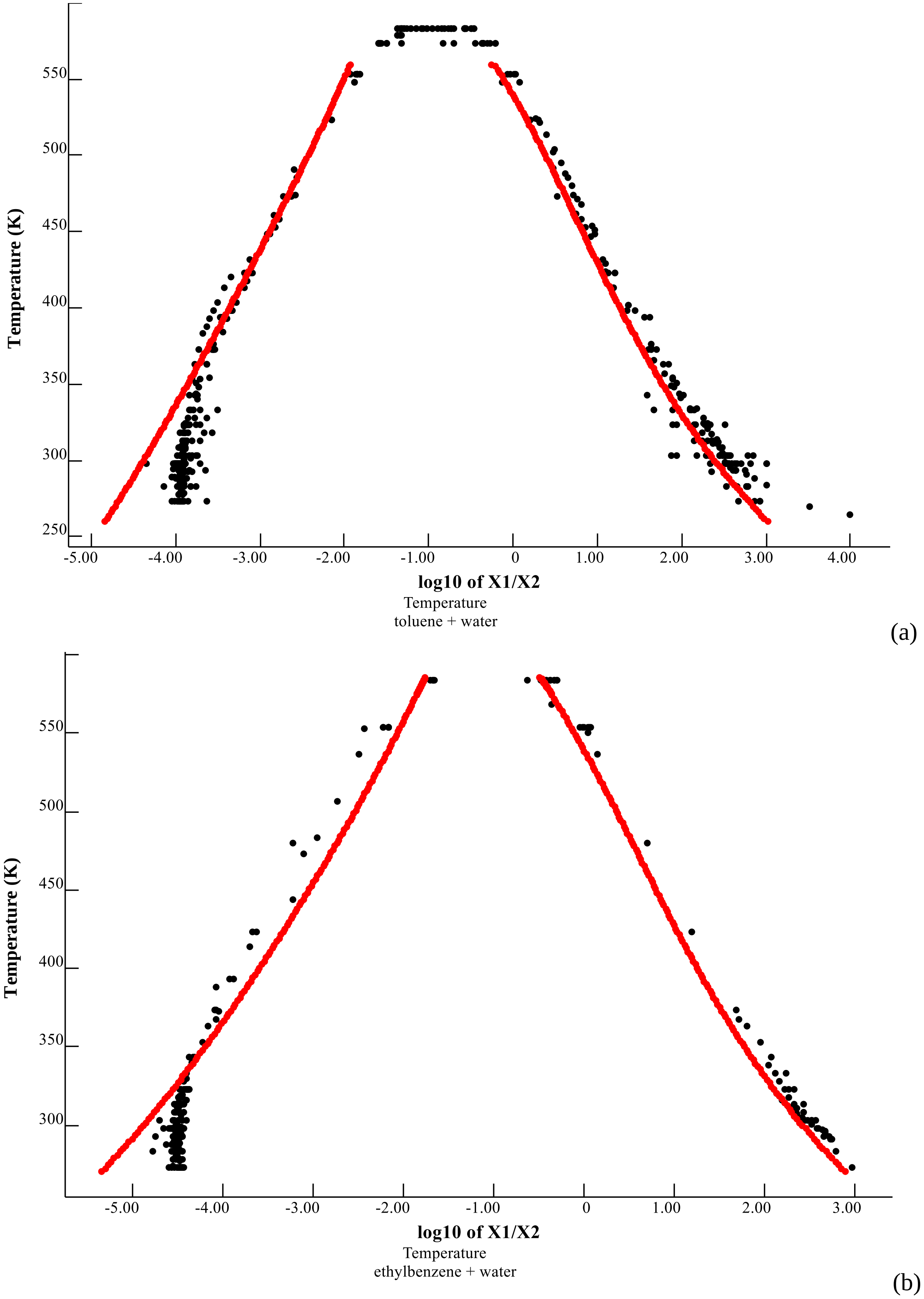
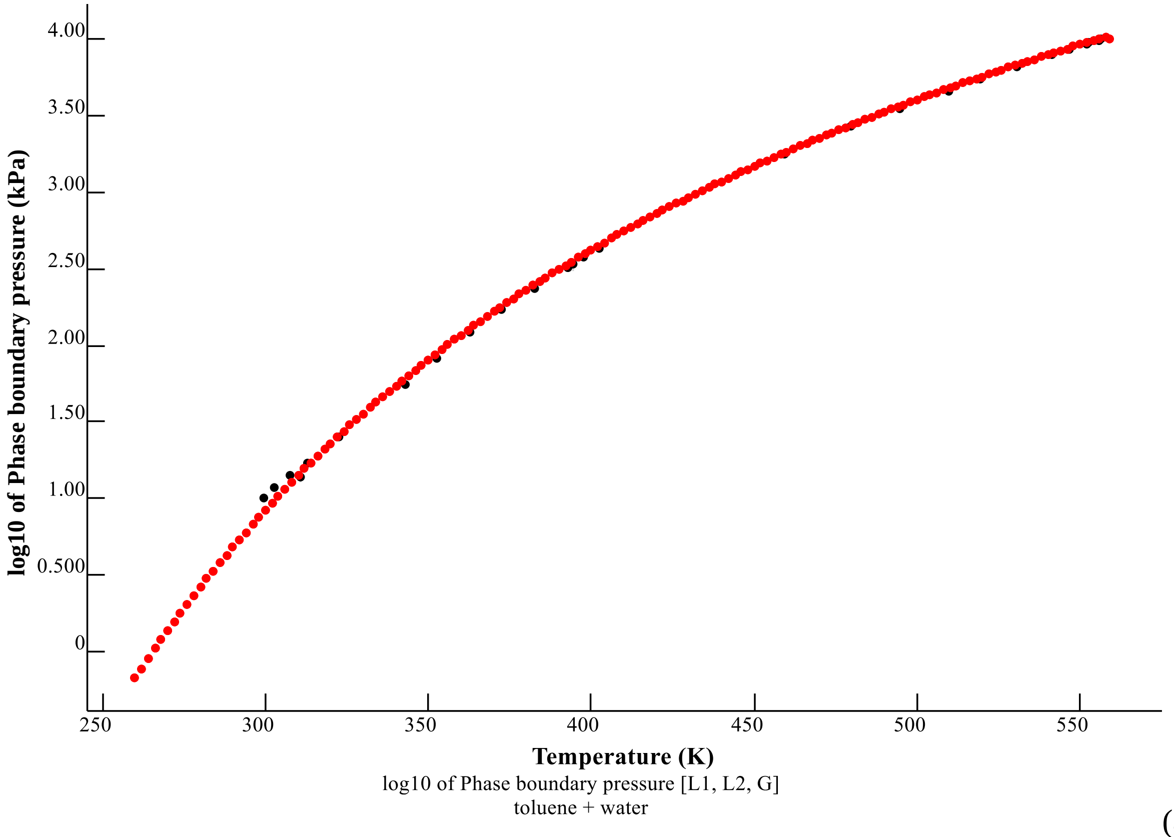
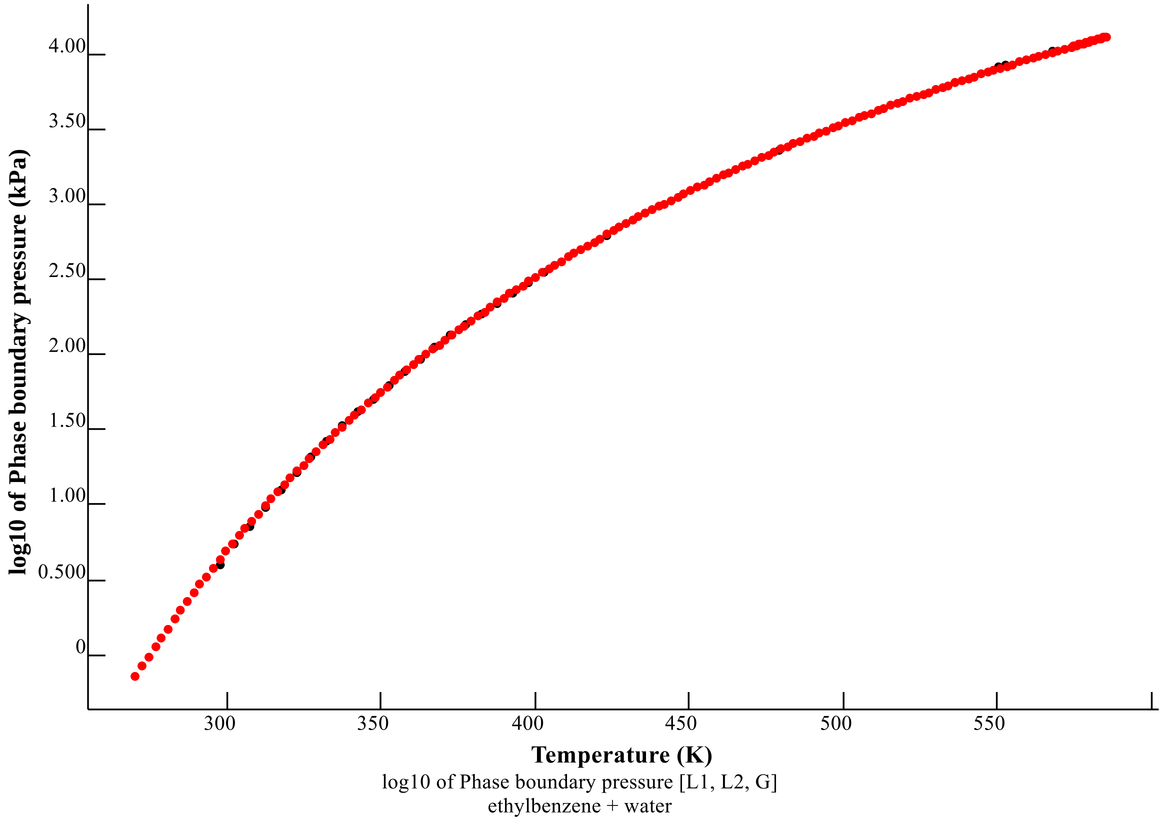


Figure S16: Experimental mole-fraction LLE data for (a) toluene (1) + water (2) and (b) ethylbenzene (1) + water (2) vs the SAFT-VR-Mie-Mie model (red dots). Black dots are experimental data from Supplements 1I and IJ.



(a)



(b)

Figure S17: Experimental liquid-liquid-vapor equilibrium pressures for (a) toluene (1) + water (2) and (b) ethylbenzene (1) + water (2) vs the SAFT-VR-Mie-Mie model (red dots). Black dots are experimental data from [K3-K8].

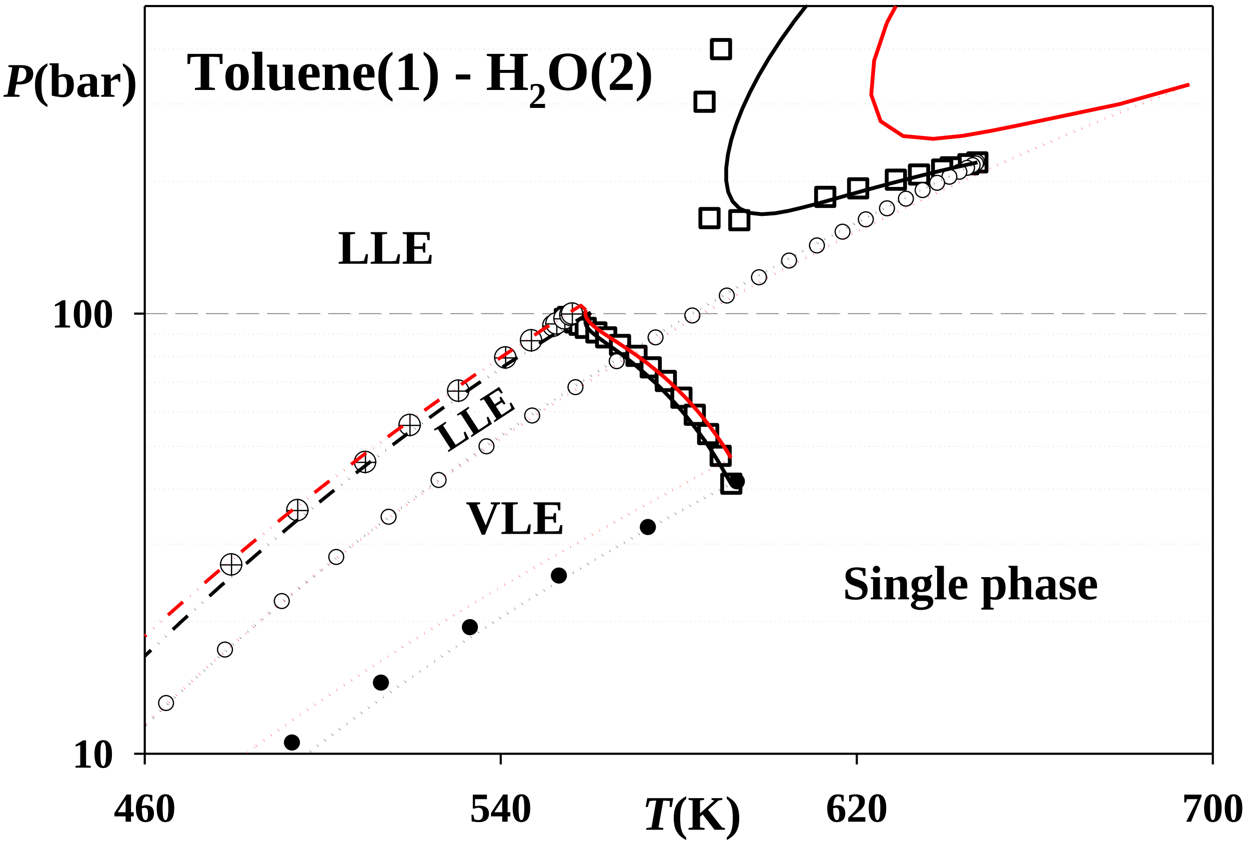


Figure S18: Phase diagram for toluene (1) + water (2). Experimental data: ⊕ – LLVE [K4], ○ – vapor pressure of water [K9], ● – vapor pressures of toluene [K10], □ – critical points [K4, K11]. Dotted-dotted-dashed lines – predicted LLVE, dashed lines – predicted vapor pressures, solid lines – predicted critical loci. Black lines – CP-PC-SAFT, red lines – SAFT-VR-Mie-Mie.

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