

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

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Abstract: This article is the first of three projected IUPAC Technical Reports resulting from IUPAC Project 2011-037-2-100 (Reference Materials for Phase Equilibrium Studies). The goal of that project was to select reference systems with critically evaluated property values for the validation of instruments and techniques used in phase equilibrium studies for mixtures. This Report proposes seven systems for liquid-liquid equilibrium studies, covering the four most common categories of binary mixtures: aqueous systems of moderate solubility, non-aqueous systems, systems with low solubility, and systems with ionic liquids. For each system, the available literature sources, accepted data, smoothing equations, and estimated uncertainties are given.

Keywords: Reference materials, Phase equilibrium, Liquid-liquid equilibrium, Instrument validation

INTRODUCTION

Reference materials have long been established as necessary for inter-laboratory comparisons and validation of uncertainty claims for applied instrumentation and techniques. While a significant portion of publications in the thermodynamics/thermophysics field nowadays is related to experimental studies of different kinds of phase equilibrium in mixtures, there are no commonly accepted recommendations on reference systems for testing equipment for such experiments. The objective of the IUPAC Project #2011-037-2-100 was to provide lists of recommended reference materials with critically evaluated property values for phase equilibrium studies: vapor-liquid equilibrium (VLE), liquid-liquid equilibrium (LLE), and solid-liquid equilibrium (SLE). The current part (Part 1) of the Technical Report on the Project deals with LLE.

Methods for the measurement of LLE have been described in [1, 2], a classification of LLE types has been given in [3, 4], and the effects of pressure on LLE have been discussed in [5]. An appropriate method should be selected for LLE composition measurement, and identification of the expected LLE type is useful for the selection of that method. For the present purpose, distinctions are made between high and low-solubility LLE, high-pressure, and supercritical LLE phenomena. Low-solubility LLE measurements require special precautions to avoid formation of emulsions, and several methods (such as titration or the polythermal (synthetic) technique) may not be appropriate due to insufficient sensitivity. Special attention should be given to distinguishing LLE from SLE when turbidity measurements are used. LLE can be frequently supercooled to a metastable state [6], and either SLE or metastable LLE can be observed at the same temperature. Sample purity and chemical stability (*e.g.*, possible hydrolysis) should also be carefully considered. All LLE measurement results should be reported in sufficient detail – recommendations on reporting phase-equilibrium data are given in another IUPAC Technical Report [7].

The present recommendations cover high and moderately low-solubility LLE. Suggestions on test systems for validation of LLE measurements have been given in [1]. The mixtures mentioned in [1] are reconsidered here along with a few other systems that were selected after examining the data available in the NIST/TRC SOURCE database [8]. Candidate mixtures were initially selected on the amount of LLE data available. Within each category of LLE (aqueous, non-aqueous, low-solubility, ionic liquids), the mixtures were then ranked by the consistency of the data from independent sources, chemical stability, low toxicity, availability, and low cost, as well as the existence of previous evaluations such as [1] or recommendations in the Solubility Data Series (SDS) [9]. Availability was considered either as existence of commercial samples with purity sufficient for conducting LLE experiments or as the existence of simple purification methods, which can be used for getting the desired purity for the selected compounds. Readers are referred to [10] for typical purification methods applied to many organic liquids.

As a result of the above selection process, seven systems forming LLE have been chosen. All LLE data discussed here are for binary mixtures either at 0.1 MPa or pressures close to vapor saturation, whichever is greater (the current report does not cover high-pressure/supercritical LLE measurements). Literature sources, accepted solubility data, smoothing equations, and uncertainty analysis are given for each mixture listed below. A description of the uncertainty assessment procedure used for the studied systems is detailed for the first mixture, aniline + water. While measured LLE compositions are the basis of the present recommendations and direct comparison with those values is an option, smoothing equations have been included in the present Report to support method validations at any point within the experimental conditions covered for the proposed systems. In addition, an Appendix with reverse calculations of LLE temperatures at specified compositions is also provided, including the temperature uncertainty assessment, to facilitate the use of the smoothing equations in the vicinity of the critical solution temperatures.

The possibility of additional validation of the selected LLE data by checking their consistency with other properties has also been explored. That checking was done by modeling low-pressure LLE with activity-coefficient (AC) models and high-pressure LLE using SAFT (Statistical Associating Fluid Theory) equations of state. Unfortunately, present models can provide only qualitative corroboration of LLE data. An AC model either has a constrained behavior defined by the mathematical model with only 2 or 3 adjustable parameters at a given temperature or is a series that slowly converges to the actual mixture properties. High-pressure behavior is more complex, and accurate modeling is more difficult. The models are shown in different parts of Supplement 1. Other consistency checks (*e.g.*, presented in reference [11]) have not been applied in this work because they would not be superior to the above checks as they could not be implemented in a model-free manner.

CATEGORY 1: AQUEOUS SYSTEMS OF MODERATE SOLUBILITY

The best aqueous systems for the development of reference materials for the quantification of LLE with moderate mutual solubility (showing consolute behavior below the liquid-gas critical temperature) were found to be the following: aniline + water, phenol + water, and nitromethane + water. Consistent LLE data for these systems have been reported in multiple independent sources, and the few outliers can be easily identified and rejected. The LLE data for all three mixtures have been analyzed in the SDS, and smoothing equations have been proposed. We have verified the fit of the SDS equations, analyzed the data published after the SDS assessments, and attempted to validate the LLE data using AC models involving other-property data for these mixtures.

Aniline (benzenamine) + water system

This system belongs to type II [12]. The solubilities for this system have been compiled and critically evaluated in SDS-96-3 [13] (hereafter, abbreviation SDS-X-Y defines “Solubility Data Series, Volume X, Part Y”; if Volume X does not have separate parts, its abbreviation is contracted to SDS-X). The literature sources associated with the LLE data for this system are listed in Supplement 1A. Two additional sources [14, 15] have appeared since that SDS publication, and one publication [16] was not included in the SDS-96-3 evaluation. These additional data are in fair agreement with the earlier work, except for the solubility of aniline in water from [15], which looks erroneous (Figure 1) and, hence, was rejected. An additional validation has been done with an NRTL equation that shows fair agreement with other available data such as VLE pressures and activity coefficients (Supplement 1B).

The equations recommended in the SDS-96-3 evaluation for smoothing LLE data for aniline + water (Equations (1) and (2) in reference [13]) have been adopted in this work. For the solubility of aniline (1) in water (2):

$$\ln x_1 = \ln x_c + a_1(T_c/T - 1) + a_2(1 - T/T_c)^{1/3} + a_3(1 - T/T_c), \quad (1)$$

Where x_1 is mole fraction of aniline; x_c is mole fraction of aniline at the upper consolute point; T is temperature in K; T_c is the upper consolute temperature in K; a_1 , a_2 , and a_3 are empirical parameters; and for the solubility of water (2) in aniline (1):

$$\ln x_2 = \ln(1 - x_c) + b_1(T_c/T - 1) + b_2(1 - T/T_c)^{1/3} + b_3(1 - T/T_c), \quad (2)$$

Where x_2 is mole fraction of water; x_c , T , and T_c have already been defined for Equation (1); b_1 , b_2 , and b_3 are empirical parameters.

The parameters for Equations (1) and (2) taken from SDS-96-3 are listed in Table 1. The smoothed LLE solubility values with the corresponding confidence intervals are given in Table 2.

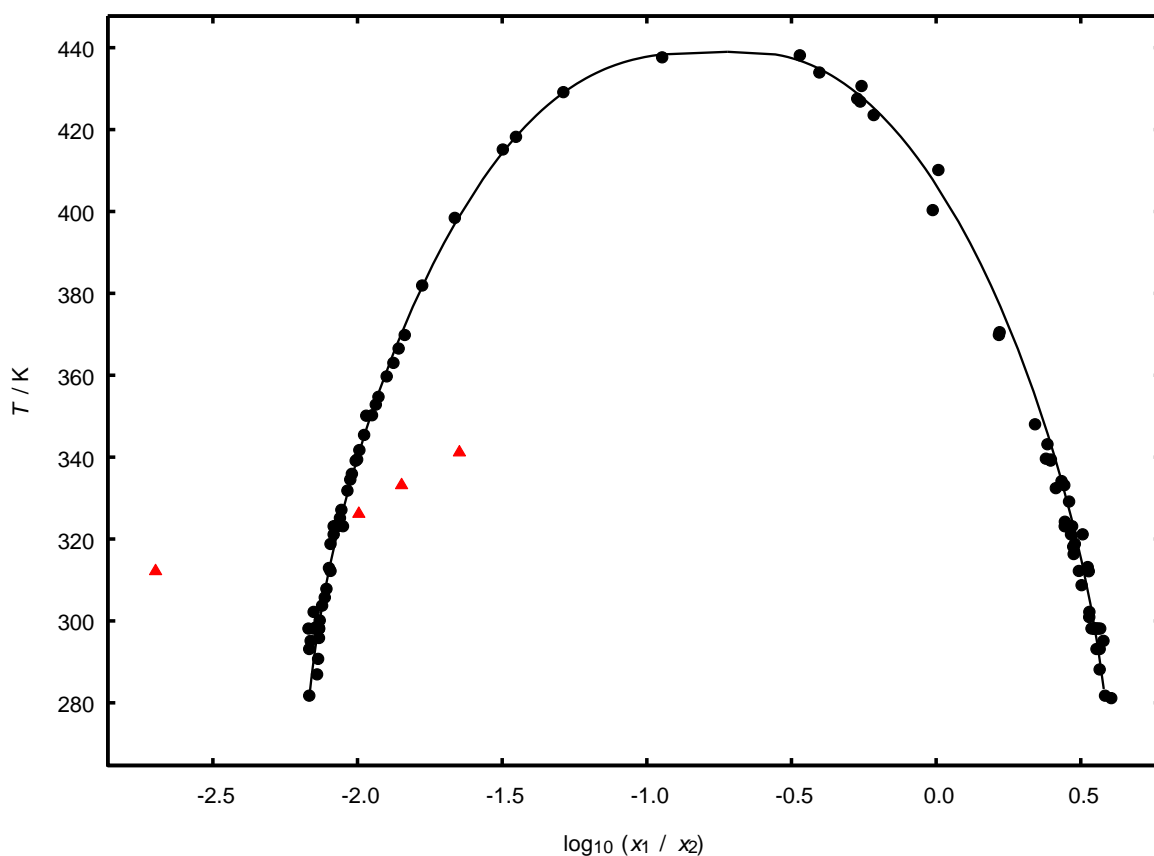


Fig. 1: Experimental mole-fraction LLE data (symbols) for aniline (1) + water (2) in a composition-stretched representation [17] vs. the SDS equation (line) [13]. The rejected solubilities of aniline in water from [15] are shown as red triangles. The points, which are designated as doubtful in the SDS-96-3 evaluation, are not shown in the figure.

Tab. 1: Parameters for Equations (1) and (2) for aniline (1) + water (2) with the lower (T_{\min}) temperature limit of the equations' validity

x_c	T_c/K	a_1	a_2	a_3	b_1	b_2	b_3	T_{\min}/K
0.160	439.0	2.40	-4.003	-4.63	2.08	-0.573	-6.01	280.0

Tab. 2: Smoothed mole fractions of aniline (x_1) in aniline + water mixture for LLE calculated with Equations (1) and (2) using the parameters given in Table 1 ^a

T/K	x_1	x_{1-}	x_{1+}
Liquid phase 1 (water-rich phase)			
280.00	0.00674	0.00639	0.00711
290.00	0.00699	0.00668	0.00732
300.00	0.00734	0.00705	0.00763
310.00	0.00778	0.00751	0.00806
320.00	0.00835	0.00807	0.00863
330.00	0.00905	0.00874	0.00936
340.00	0.00991	0.00954	0.01028
350.00	0.0110	0.0105	0.0114
360.00	0.0123	0.0117	0.0129
370.00	0.0139	0.0132	0.0148
380.00	0.0160	0.0150	0.0171
390.00	0.0188	0.0174	0.0202
400.00	0.0225	0.0207	0.0244
410.00	0.0277	0.0253	0.0303
420.00	0.0358	0.0324	0.0395
430.00	0.0512	0.0460	0.0569
Liquid phase 2 (aniline-rich phase)			
430.00	0.337	0.319	0.355
420.00	0.418	0.400	0.437
410.00	0.481	0.464	0.498
400.00	0.533	0.518	0.548
390.00	0.577	0.563	0.590
380.00	0.614	0.603	0.626
370.00	0.647	0.637	0.656
360.00	0.675	0.666	0.683
350.00	0.699	0.692	0.706
340.00	0.720	0.714	0.726
330.00	0.738	0.732	0.744
320.00	0.754	0.748	0.759
310.00	0.767	0.761	0.772
300.00	0.778	0.772	0.784
290.00	0.787	0.780	0.793
280.00	0.794	0.786	0.801

^a The estimated expanded uncertainties at the 0.95 level of confidence ($k = 2$) for mole fractions have been calculated with the equations given in Table S2 derived as described in Supplement 1C. Since the uncertainties are asymmetric, the upper and lower bounds of the confidence interval (x_{1-} and x_{1+}) are provided in separate columns.

Phenol + water system

This mixture belongs to type II [12] and has been compiled and critically evaluated in SDS-91-1 [18]. The literature sources associated with the LLE data for this system are listed in Supplement 1D, including additional sources that were not cited in the SDS-91-1 evaluation or were published after that evaluation. Those additional data are in fair agreement with the earlier publications and evaluation (Figure 2). Most of the deviant data on phenol solubility in water originate from one source [19], were reported in graphical form only, and have been denoted as doubtful in [18]. An additional validation has been attempted with an NRTL equation that shows a fair agreement with other available property data such as SLE (Supplement 1E), though SLE data are to some extent ambiguous. The source reporting doubtful LLE data

[19] also deviates from the SLE data sources. Formation of an inter-component compound $2\text{C}_6\text{H}_5\text{OH}\cdot\text{H}_2\text{O}$ has been claimed in several reports summarized in [20] and is consistent with SLE data from [21]. Thus, LLE at $T < 289$ K may be supercooled and such data should be used with caution.

The equations recommended in the SDS-91-1 evaluation for smoothing LLE data for phenol + water (Equations (8) and (9) in reference [18]) have been adopted in this work: Equation (1) for the mole-fraction solubility of phenol in water and Equation (2) for the mole-fraction solubility of water in phenol with the parameters listed in Table 3. The smoothed LLE solubilities with the corresponding confidence intervals are given in Table 4.

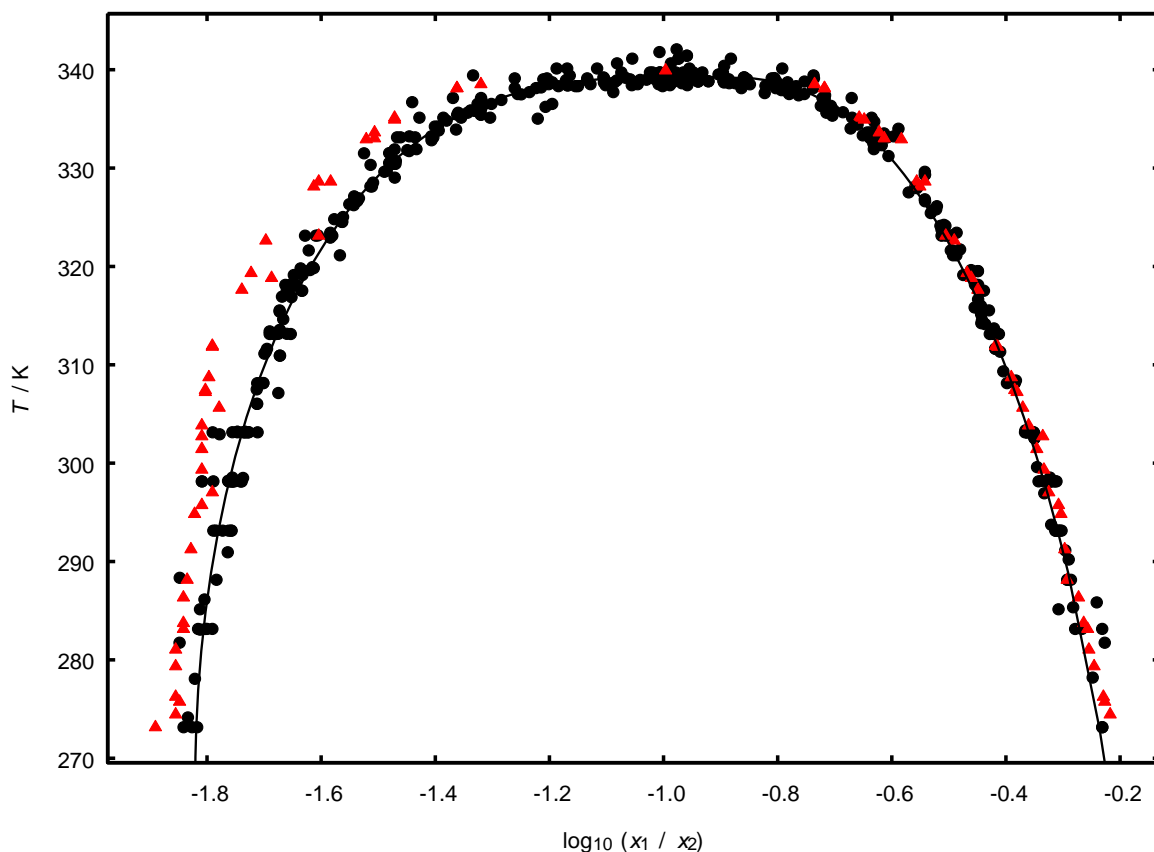


Fig. 2: Experimental mole-fraction LLE data (symbols) for phenol (1) + water (2) in a composition-stretched representation [17] compared with the SDS equation (line) [18]. The data from [19] are shown as red triangles (the data points for $\log_{10}(x_1 / x_2) < -1.3$, *i.e.*, for $x_1 < 0.05$, from that source were not considered reliable in [18]).

Tab. 3: Parameters for Equations (1) and (2) for phenol (1) + water (2) with the lower (T_{\min}) temperature limit of the equations' validity

x_c	T_c/K	a_1	a_2	a_3	b_1	b_2	b_3	T_{\min}/K
0.104	339.3	4.706	-4.048	-3.756	1.283	-0.290	-2.515	273.15

Tab. 4: Smoothed mole fractions of phenol (x_1) in phenol + water for LLE calculated with Equations (1) and (2) using the parameters given in Table 3 ^a

T/K	x_1	x_{1-}	x_{1+}
Liquid phase 1 (water-rich phase)			
273.15	0.0149	0.0140	0.0159
280.00	0.0152	0.0144	0.0160
285.00	0.0155	0.0148	0.0162
290.00	0.0160	0.0154	0.0166
295.00	0.0166	0.0160	0.0171
300.00	0.0173	0.0169	0.0178
305.00	0.0183	0.0179	0.0188
310.00	0.0196	0.0192	0.0200
315.00	0.0213	0.0208	0.0218
320.00	0.0235	0.0229	0.0242
325.00	0.0267	0.0259	0.0276
330.00	0.0316	0.0304	0.0328
335.00	0.0410	0.0392	0.0428
Liquid phase 2 (phenol-rich phase)			
335.00	0.175	0.173	0.178
330.00	0.205	0.203	0.208
325.00	0.229	0.227	0.231
320.00	0.250	0.248	0.251
315.00	0.268	0.266	0.269
310.00	0.284	0.282	0.286
305.00	0.299	0.297	0.301
300.00	0.312	0.310	0.315
295.00	0.325	0.322	0.328
290.00	0.336	0.333	0.339
285.00	0.346	0.342	0.350
280.00	0.356	0.351	0.360
273.15	0.367	0.362	0.373

^a The estimated expanded uncertainties at the 0.95 level of confidence ($k = 2$) for mole fractions have been calculated with the equations given in Table S2 derived as described in Supplement 1C. Since the uncertainties are asymmetric, the upper and lower bounds of the confidence interval (x_{1-} and x_{1+}) are provided in separate columns. Note that the LLE at $T < 289$ K may be metastable.

Nitromethane + water system

This mixture belongs to type II [12] and has been discussed in detail in SDS-71 [22]. The literature sources associated with the LLE data for the system are listed in Supplement 1F, including additional sources that were not cited in the SDS-71 evaluation or were published after that evaluation. Most of the data are consistent, with the prominent exception of [23] (Figure 3).

We fitted Equation (1) for the mole-fraction solubility of nitromethane in water and Equation (2) for the mole-fraction solubility of water in nitromethane with the use of all LLE data (excluding three obviously erroneous data points from [24] and the data from [23], despite a part of those data being consistent with the other sources). The parameters are listed in Table 5. The reliability of the LLE data was corroborated by the fair consistency with other properties, as demonstrated with a UNIQUAC equation in Supplement 1G. The smoothed LLE solubilities with the corresponding confidence intervals are given in Table 6. As the LLE data at $T < 290$ K are from two sources that are not fully consistent for the nitromethane-rich phase, and as we cannot reliably extrapolate the other data to that region, the recommended values for this system are restricted to temperatures above 290 K.

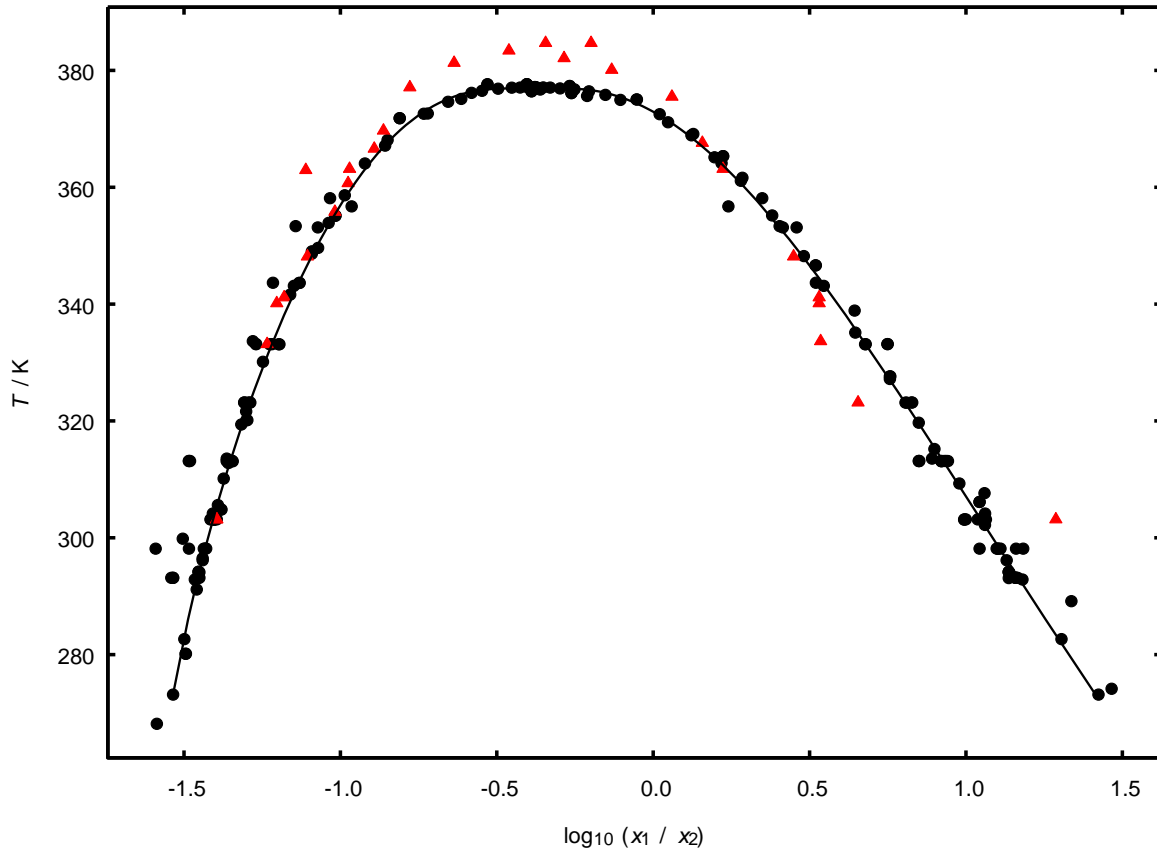


Fig. 3: Experimental mole-fraction LLE data (symbols) for nitromethane (1) + water (2) in a composition-stretched representation [17], compared with the evaluation with parameters from Table 5. The rejected data from [23] and three obviously erroneous data points from [24] are shown as red triangles.

Tab. 5: Parameters for Equations (1) and (2) for nitromethane (1) + water (2) with the lower (T_{min}) temperature limit of the equations' validity

x_c	T_c/K	a_1	a_2	a_3	b_1	b_2	b_3	T_{min}/K
0.295	377.15	2.734	-2.691	-5.919	-3.350	-1.206	-3.206	290.0

Tab. 6: Smoothed mole fractions of nitromethane (x_1) in nitromethane + water for LLE calculated with Equations (1) and (2) using the parameters given in Table 5^a

T/K	x_1	x_{1-}	x_{1+}
Liquid phase 1 (water-rich phase)			
290.00	0.0328	0.0310	0.0347
300.00	0.0364	0.0347	0.0381
310.00	0.0409	0.0393	0.0426
320.00	0.0467	0.0450	0.0484
330.00	0.0542	0.0522	0.0562
340.00	0.0641	0.0615	0.0668
350.00	0.0778	0.0741	0.0816
360.00	0.0983	0.0928	0.1039
370.00	0.136	0.127	0.145

T/K	x_1	x_{1-}	x_{1+}
Liquid phase 2 (nitromethane-rich phase)			
370.00	0.549	0.518	0.580
360.00	0.662	0.639	0.685
350.00	0.739	0.722	0.754
340.00	0.796	0.785	0.806
330.00	0.840	0.832	0.848
320.00	0.875	0.868	0.881
310.00	0.902	0.896	0.908
300.00	0.924	0.918	0.930
290.00	0.941	0.935	0.947

^a The estimated expanded uncertainties at the 0.95 level of confidence ($k = 2$) for mole fractions have been calculated with the equations given in Table S2 derived as described in Supplement 1C. Since the uncertainties are asymmetric, the upper and lower bounds of the confidence interval (x_{1-} and x_{1+}) are provided in separate columns.

The system butan-1-ol + water may serve as a reserve test mixture for aqueous LLE measurements, since it was thoroughly analyzed in SDS-82-1 [25] and the corresponding empirical equations were provided there. It has not been selected as primary in this work, since the data scatter is larger for that system in comparison to the selected mixtures. However, butan-1-ol is readily available as a high-purity sample, which may justify using this mixture.

CATEGORY 2: NON-AQUEOUS SYSTEMS

Despite the variety of non-aqueous systems, LLE data for most of them are either rather scattered or have been measured in only one laboratory. A possible cause of the scatter could be the difficulty of drying the components and protecting them from adventitious moisture. As a result, we selected only one system for this category.

Cyclohexane + methanol system

The most-studied non-aqueous system with consistent data is cyclohexane + methanol, which belongs to type II [12] and has been discussed in SDS-56 [26]. The literature sources associated with the LLE data for this system are listed in Supplement 1H, including additional sources that were not cited in the SDS-56 evaluation or were published after that evaluation. We fitted Equation (1) for the mole-fraction solubility of cyclohexane in methanol and Equation (2) for the mole-fraction solubility of methanol in cyclohexane with the use of all LLE data. The parameters are listed in Table 7. Though the reported values of the upper consolute temperature range from 318 to 322 K, a relatively low value of 318.5 K from [27] has been selected because higher values from other sources may be caused by water impurity according to the studies [28, 29]. The selected data and the smoothing equation are shown in Figure 4. The largest deviations (up to mole fraction 0.02, which is 30 % of the “guest component” content, or up to 4 K near the upper consolute temperature) come from three recent sources [30-32], but there are only a few deviating points, and numerous other sources are consistent. The whole data set was rejected only for Ref. [32]. The lower limit of the equation was selected to be the monotectic temperature of 275 K, determined graphically in [26]. The smoothed LLE solubilities with the corresponding confidence intervals are given in Table 8.

Tab. 7: Parameters for Equations (1) and (2) for cyclohexane (1) + methanol (2) with the lower (T_{\min}) temperature limit of the equations' validity

x_c	T_c/K	a_1	a_2	a_3	b_1	b_2	b_3	T_{\min}/K
0.504	318.5	-5.171	-2.423	3.907	16.60	-2.010	-26.60	275.0

Tab. 8: Smoothed mole fractions of cyclohexane (x_1) in cyclohexane + methanol for LLE calculated with Equations (1) and (2) using the parameters given in Table 7 ^a

T/K	x_1	x_{1-}	x_{1+}
Liquid phase 1 (methanol-rich phase)			
275.00	0.109	0.102	0.116
280.00	0.120	0.114	0.126
285.00	0.132	0.126	0.138
290.00	0.146	0.141	0.150
295.00	0.161	0.157	0.165
300.00	0.180	0.176	0.183
305.00	0.203	0.200	0.207
310.00	0.235	0.231	0.240
315.00	0.290	0.283	0.297
Liquid phase 2 (cyclohexane-rich phase)			
315.00	0.715	0.706	0.724
310.00	0.789	0.783	0.795
305.00	0.834	0.829	0.838
300.00	0.865	0.860	0.870
295.00	0.887	0.882	0.893
290.00	0.905	0.899	0.910
285.00	0.918	0.911	0.924
280.00	0.928	0.921	0.934
275.00	0.936	0.928	0.942

^a The estimated expanded uncertainties at the 0.95 level of confidence ($k = 2$) for mole fractions have been calculated with the equations given in Table S2 derived as described in Supplement IC. Since the uncertainties are asymmetric, the upper and lower bounds of the confidence interval (x_{1-} and x_{1+}) are provided in separate columns.

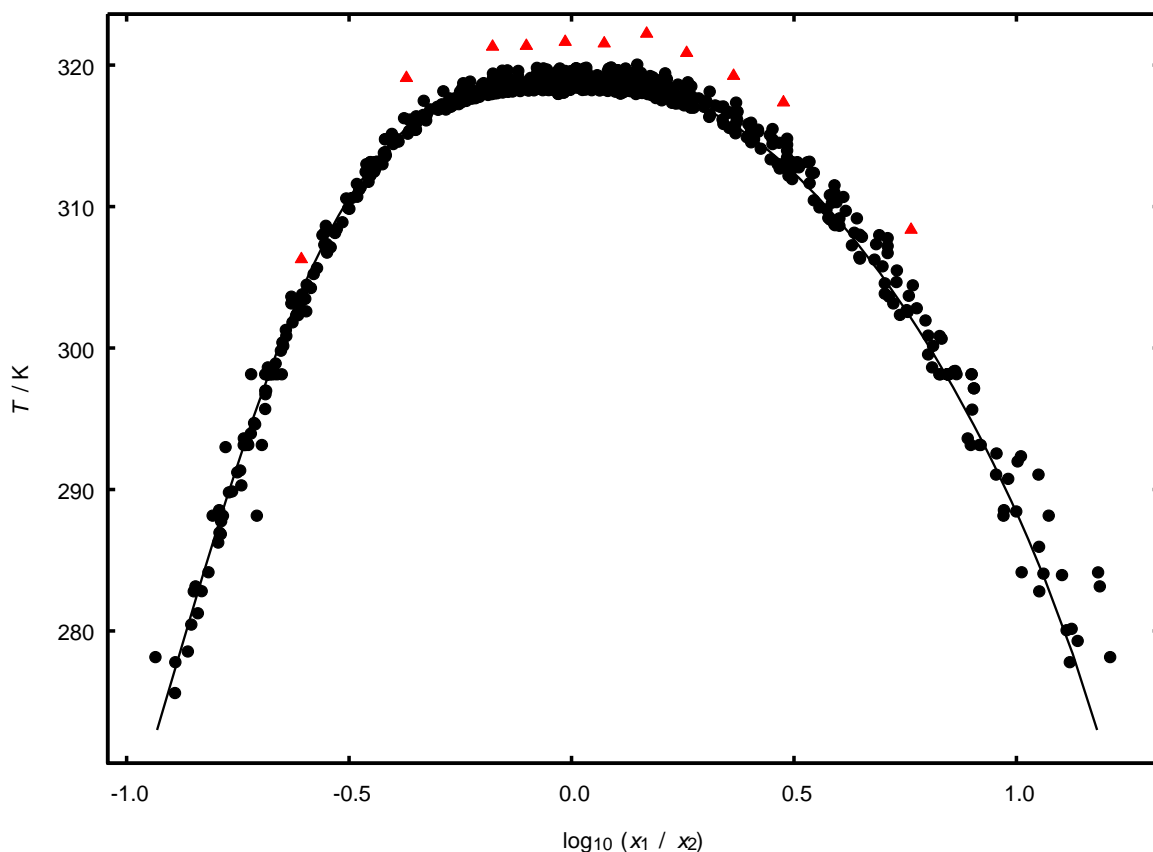


Fig. 4: Experimental mole-fraction LLE data (symbols) for cyclohexane (1) + methanol (2) in a composition-stretched representation [17] compared with the evaluation with parameters from Table 7 (line). The rejected data from [32] are shown as red triangles.

A promising system with less-hygroscopic components is acetonitrile + octane, which has been discussed in SDS-78 [33]. Unfortunately, the reported solubility of acetonitrile in octane relative to that in hexane and decane (involving data from the same sources) changes inconsistently and so needs additional investigation before it can be considered as a suitable reference system.

CATEGORY 3: SYSTEMS WITH LOW SOLUBILITY

Methylbenzene (toluene) + water and ethylbenzene + water systems

Arguably the most studied binary mixture with low solubility is benzene + water, reviewed in SDS-81-2 [34]. However, this system has been excluded from consideration in the current project due to the toxicity of benzene and restrictions on its use. Hence, we selected two other similar well-studied mixtures, toluene + water and ethylbenzene + water, for this low-solubility category. The LLE data were discussed in SDS-81-5 [35] (for toluene + water) and SDS-81-6 [36] (for ethylbenzene + water). The literature sources associated with the LLE data for these two systems are listed in Supplements 1I and 1J, respectively, including additional sources that were not cited in the SDS-81-5 and SDS-81-6 evaluations or were published after those evaluations (Figures 5-6).

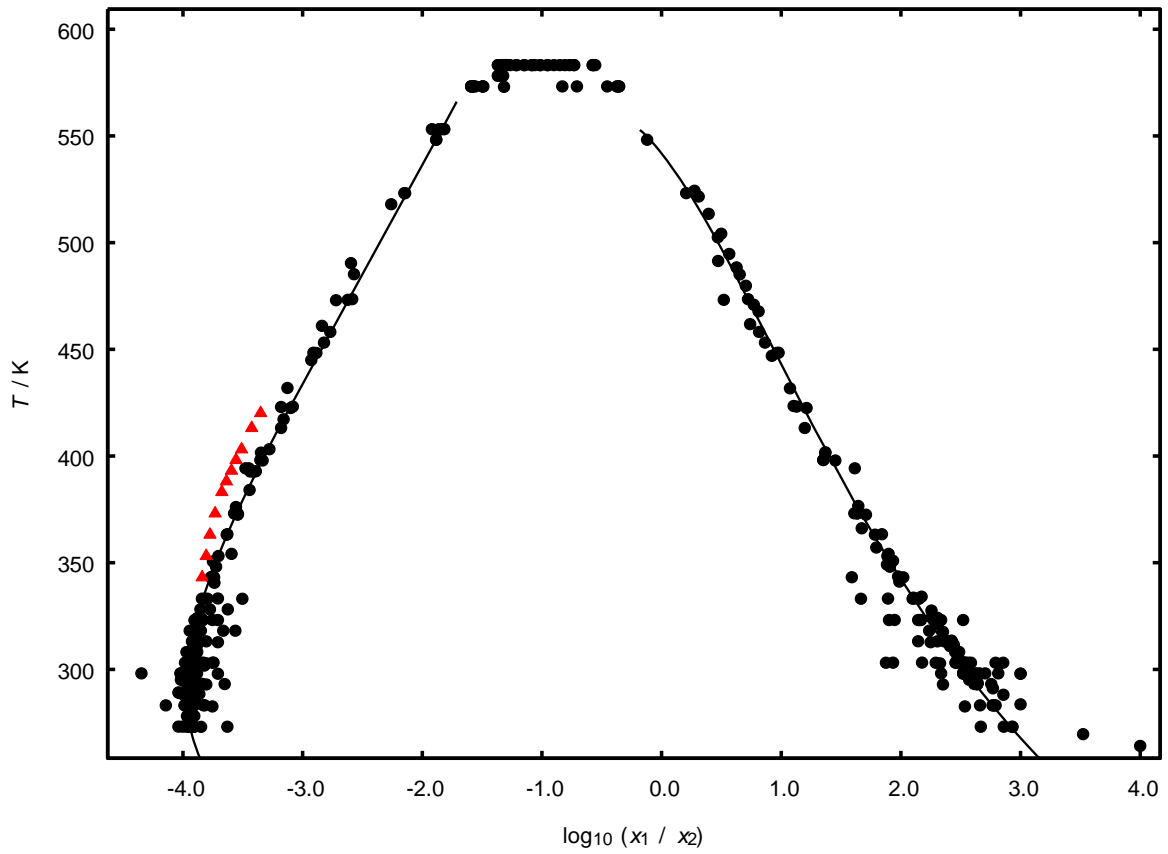


Fig. 5: Experimental mole-fraction LLE data (symbols) for toluene (1) + water (2) in a composition-stretched representation [17] compared with the SDS equations (lines) [35]. A deviating data set from [37] is shown as red triangles. Other rejected data believed erroneous are shown in Figure S12 in Supplement 11.

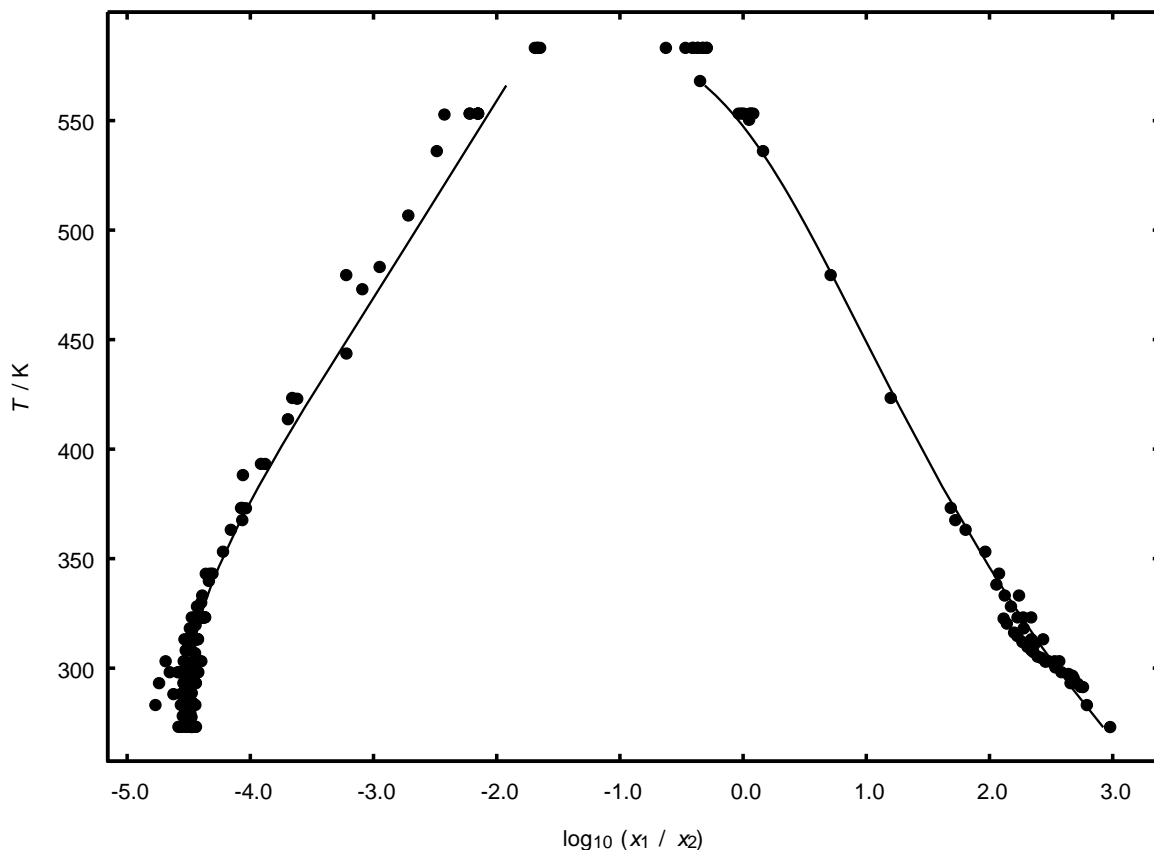


Fig. 6: Experimental mole-fraction LLE data (symbols) for ethylbenzene (1) + water (2) in a composition-stretched representation [17] compared with the SDS equations (lines) [36]. Rejected data believed erroneous are shown in Figure S13 in Supplement 1J.

The equations recommended in the SDS-81-5 [35] and SDS-81-6 [36] evaluations for smoothing LLE data for hydrocarbon + water have been adopted in this work. For the mole-fraction solubility of hydrocarbons in water (x_1):

$$\ln(x_1) = \ln(x_{\min,1}) + D[(T_{\text{ms}}/T) \ln(T_{\text{ms}}/T) + 1 - (T_{\text{ms}}/T)], \quad (3)$$

and for the mole-fraction solubility of water in hydrocarbons ($x_2 = 1 - x_1$):

$$\ln(x_2) = d_1 + d_2(1/T_r - 1) + d_3(1 - T_r)^{1/3} + d_4(1 - T_r), \quad (4)$$

where T_{ms} is the temperature of the minimum mole-fraction solubility of the hydrocarbon ($x_{\min,1}$); T is temperature in K; d_1 , d_2 , d_3 , and d_4 are empirical parameters; $T_r = T/T_c$, where T_c is an adjustable parameter, which is close to the three-phase liquid-liquid-gas critical temperature (also known as upper critical end point or UCEP, which is the maximum temperature of L1 + L2 + G coexistence).

The parameters for Equations (3) and (4) for toluene + water and ethylbenzene + water taken from SDS-81-5 and SDS-81-6 are summarized in Table 9 and the evaluations are shown in Figures 5 and 6. The toluene + water system belongs to type III [12] with an UCEP of 556.1 K (or 558 K [38]) that defines the upper temperature limit of validity of Equations (3) and (4). The ethylbenzene + water system shows a similar behavior, with UCEP reported values of 574 K [38] and 568 K [39]. However, the upper limit of the temperature range for that system is restricted to 450 K (below UCEP) due to a limited number of experimental points above 450 K, the fitting procedure in SDS-81-6 was based on.

The change in the LLE behavior from benzene to toluene looks reasonable, as does the subsequent change to ethylbenzene (Figure 7). A qualitative consistency test using other properties is given in Supplement 1K. The smoothed LLE solubilities are given in Tables 10 and 11.

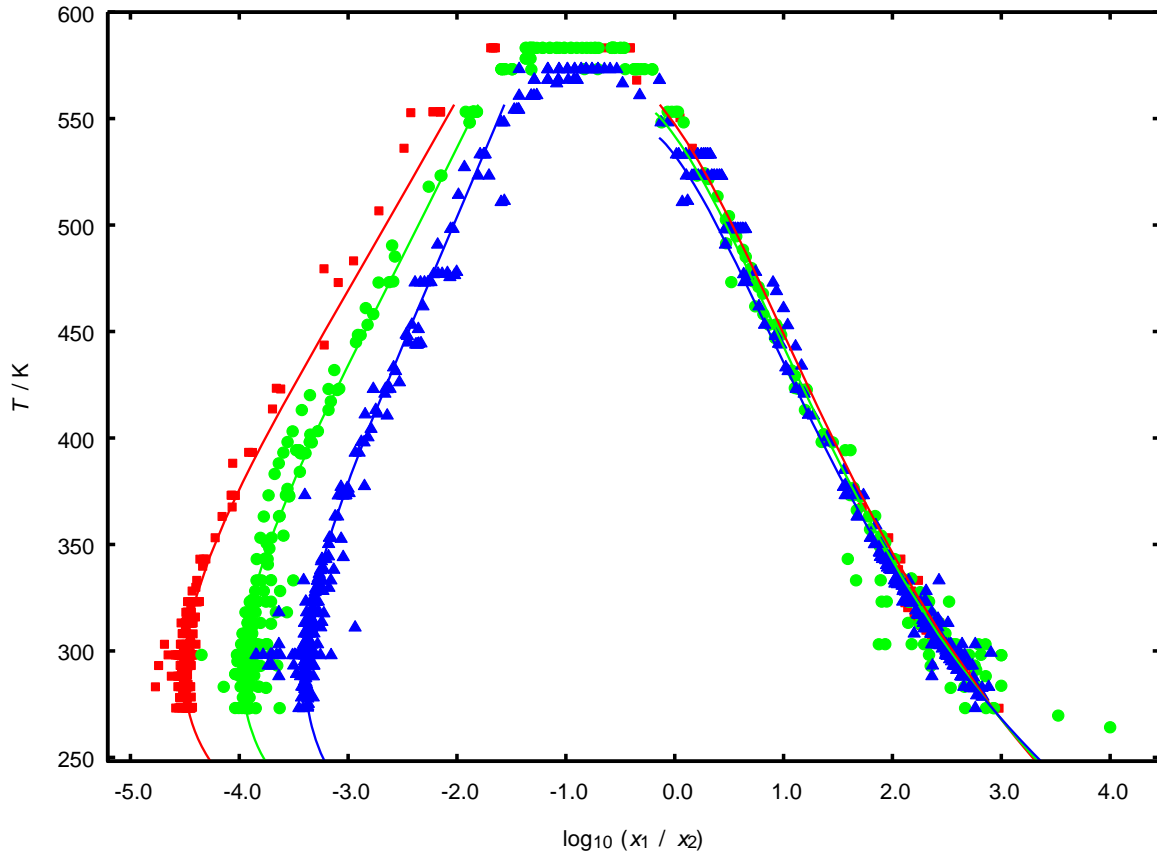


Fig. 7: Variation in the LLE behavior for the systems water (2) + benzene (1), toluene (1), and ethylbenzene (1). The data points and lines are red for water + ethylbenzene (squares), green for water + toluene (circles), and blue for water + benzene (triangles). Symbols are experimental values; lines are the SDS equations [34-36]. The experimental data for benzene + water were taken from Ref. [34].

Tab. 9: Parameters for Equations (3) and (4) for toluene + water and ethylbenzene + water with the lower (T_{\min}) and upper (T_{\max}) temperature limits of the equations' validity

System	$\ln(x_{\min,1})$	D	T_{ms}/K	d_1	d_2	d_3	d_4	T_c/K	T_{\min}/K	T_{\max}/K
Toluene + water	-9.14	35.7	290	-0.495	-3.700	-0.102	-4.641	553.0	273.15	556.1
Ethylbenzene + water	-10.37	40.9	290	-0.383	-3.167	-0.009	-5.655	566.9	273.15	450.0

Tab. 10: Smoothed mole fractions of toluene (x_1) in toluene + water for LLE calculated with Equations (3) and (4) using the parameters given in Table 9^a

T/K	x_1	x_{1-}	x_{1+}
Liquid phase 1 (water-rich phase)			
273.15	0.000115	0.000104	0.000126
280.00	0.000110	0.000100	0.000120
290.00	0.000107	0.000099	0.000117
300.00	0.000109	0.000101	0.000118
310.00	0.000116	0.000108	0.000124
320.00	0.000126	0.000118	0.000135

<i>T/K</i>	x_1	x_{1-}	x_{1+}
330.00	0.000141	0.000132	0.000151
340.00	0.000161	0.000150	0.000172
350.00	0.000187	0.000175	0.000201
360.00	0.000221	0.000205	0.000238
370.00	0.000264	0.000244	0.000287
380.00	0.000320	0.000293	0.000349
390.00	0.000389	0.000354	0.000428
400.00	0.000478	0.000431	0.000530
410.00	0.000590	0.000527	0.000661
420.00	0.000732	0.000648	0.000827
430.00	0.00091	0.00080	0.00104
440.00	0.00114	0.00099	0.00131
450.00	0.00142	0.00122	0.00166
460.00	0.00178	0.00151	0.00210
470.00	0.00223	0.00188	0.00266
480.00	0.00280	0.00233	0.00337
490.00	0.00351	0.00289	0.00427
500.00	0.00440	0.00359	0.00541
510.00	0.0055	0.0044	0.0068
520.00	0.0069	0.0055	0.0087
530.00	0.0086	0.0068	0.0109
540.00	0.0108	0.0084	0.0138
550.00	0.0134	0.0104	0.0174
Liquid phase 2 (toluene-rich phase)			
550.00	0.43	0.33	0.53
540.00	0.51	0.42	0.61
530.00	0.59	0.49	0.68
520.00	0.649	0.563	0.726
510.00	0.702	0.626	0.769
500.00	0.748	0.682	0.804
490.00	0.788	0.731	0.835
480.00	0.821	0.775	0.860
470.00	0.850	0.812	0.882
460.00	0.875	0.844	0.900
450.00	0.896	0.872	0.916
440.00	0.914	0.895	0.930
430.00	0.929	0.915	0.941
420.00	0.942	0.931	0.951
410.00	0.9527	0.9443	0.9598
400.00	0.9616	0.9554	0.9670
390.00	0.9691	0.9645	0.9731
380.00	0.9753	0.9720	0.9782
370.00	0.9804	0.9780	0.9825
360.00	0.9846	0.9828	0.9861
350.00	0.9879	0.9866	0.9891
340.00	0.99067	0.98969	0.99156
330.00	0.99286	0.99210	0.99355
320.00	0.99460	0.99400	0.99514
310.00	0.99596	0.99548	0.99639
300.00	0.99702	0.99664	0.99737

<i>T/K</i>	x_1	x_{1-}	x_{1+}
290.00	0.99784	0.99753	0.99811
280.00	0.99846	0.99821	0.99867
273.15	0.99879	0.99858	0.99896

^a The estimated expanded uncertainties at the 0.95 level of confidence ($k=2$) for mole fractions have been calculated with the equations given in Table S2 derived as described in Supplement 1C. Taking into account the difficulties in measuring small concentrations and conducting high-temperature measurements, we assumed the default single-measurement uncertainty at $0.10 \cdot x_{\text{guest}}$ instead of $0.03 \cdot x_{\text{guest}}$ described in Supplement 1C. Since the uncertainties are asymmetric, the upper and lower bounds of the confidence interval (x_{1-} and x_{1+}) are provided in separate columns.

Tab. 11: Smoothed mole fractions of ethylbenzene (x_1) in ethylbenzene + water for LLE calculated with Equations (3) and (4) using the parameters given in Table 9 ^a

<i>T/K</i>	x_1	x_{1-}	x_{1+}
Liquid phase 1 (water-rich phase)			
273.15	0.0000338	0.0000286	0.0000401
280.00	0.0000322	0.0000278	0.0000372
290.00	0.0000314	0.0000280	0.0000351
300.00	0.0000321	0.0000293	0.0000352
310.00	0.0000342	0.0000313	0.0000373
320.00	0.0000378	0.0000341	0.0000418
330.00	0.0000429	0.0000376	0.0000489
340.00	0.0000500	0.0000423	0.0000589
350.00	0.000059	0.000048	0.000073
360.00	0.000072	0.000056	0.000092
370.00	0.000088	0.000066	0.000117
380.00	0.000109	0.000079	0.000151
390.00	0.000137	0.000095	0.000198
400.00	0.000174	0.000116	0.000261
410.00	0.000221	0.000141	0.000346
420.00	0.00028	0.00017	0.00046
430.00	0.00036	0.00021	0.00062
440.00	0.00047	0.00026	0.00083
450.00	0.00061	0.00033	0.00112
Liquid phase 2 (ethylbenzene-rich phase)			
450.00	0.907	0.881	0.928
440.00	0.923	0.903	0.940
430.00	0.937	0.921	0.950
420.00	0.948	0.936	0.958
410.00	0.9578	0.9489	0.9653
400.00	0.9658	0.9592	0.9714
390.00	0.9724	0.9676	0.9765
380.00	0.9779	0.9745	0.9809
370.00	0.9824	0.9800	0.9845
360.00	0.9861	0.9844	0.9875
350.00	0.98907	0.98798	0.99005
340.00	0.99149	0.99079	0.99213
330.00	0.99344	0.99300	0.99385
320.00	0.99499	0.99472	0.99524
310.00	0.99622	0.99604	0.99638

<i>T/K</i>	x_1	x_{1-}	x_{1+}
300.00	0.99718	0.99705	0.99730
290.00	0.99792	0.99781	0.99803
280.00	0.99849	0.99839	0.99859
273.15	0.99880	0.99871	0.99889

^a The estimated expanded uncertainties at the 0.95 level of confidence ($k = 2$) for mole fractions have been calculated with the equations given in Table S2 derived as described in Supplement 1C. Taking into account the difficulties in measuring small concentrations and conducting high-temperature measurements, we assumed the default single-measurement uncertainty at $0.10 \cdot x_{\text{guest}}$ instead of $0.03 \cdot x_{\text{guest}}$ described in Supplement 1C. Since the uncertainties are asymmetric, the upper and lower bounds of the confidence interval (x_{1-} and x_{1+}) are provided in separate columns.

CATEGORY 4: SYSTEMS WITH IONIC LIQUIDS

Hexan-1-ol + 1-hexyl-3-methyl-1*H*-imidazolium bis[(trifluoromethyl)sulfonyl]amide system

Though LLE measurements for ionic liquids are generally less accurate and more affected by hydrolysis, impurities, and moisture, they are a popular object of research nowadays. Consequently, we have selected one of the most studied and stable mixtures, hexan-1-ol + 1-hexyl-3-methyl-1*H*-imidazolium bis[(trifluoromethyl)sulfonyl]amide (abbreviation [C₆mim][NTf₂] used hereafter), which belongs to type II [12] and was employed in an earlier IUPAC project [40]. The data sources are listed in Supplement 1L. A smoothing equation was proposed in [40] for LLE for this mixture. We have updated that LLE representation by including new data [41-44] and using fitting Equations (1) and (2). The parameters are listed in Table 12. Unfortunately, one report [44] deviates from all other investigations, which challenges the accuracy of the LLE data (Figure 8). We considered the presence of water and hydrolysis products as possible reasons for such disagreement. While water would probably make the upper consolute temperature higher, as for cyclohexane + methanol above, it is not likely that all experiments except one had the same amount of water impurity. Other impurities such as hydrolysis products could lower the consolute temperature, so we propose this recommendation as provisional and suggest exploration of the effects of third components, especially water, on the LLE for this system, as was done for some non-aqueous mixtures forming LLE [45]. The smoothed LLE solubilities with the corresponding confidence intervals are given in Table 13. Since accurate extrapolation below 288 K cannot be done on the basis of the available data, the recommended values for this system are restricted to temperatures above 288 K.

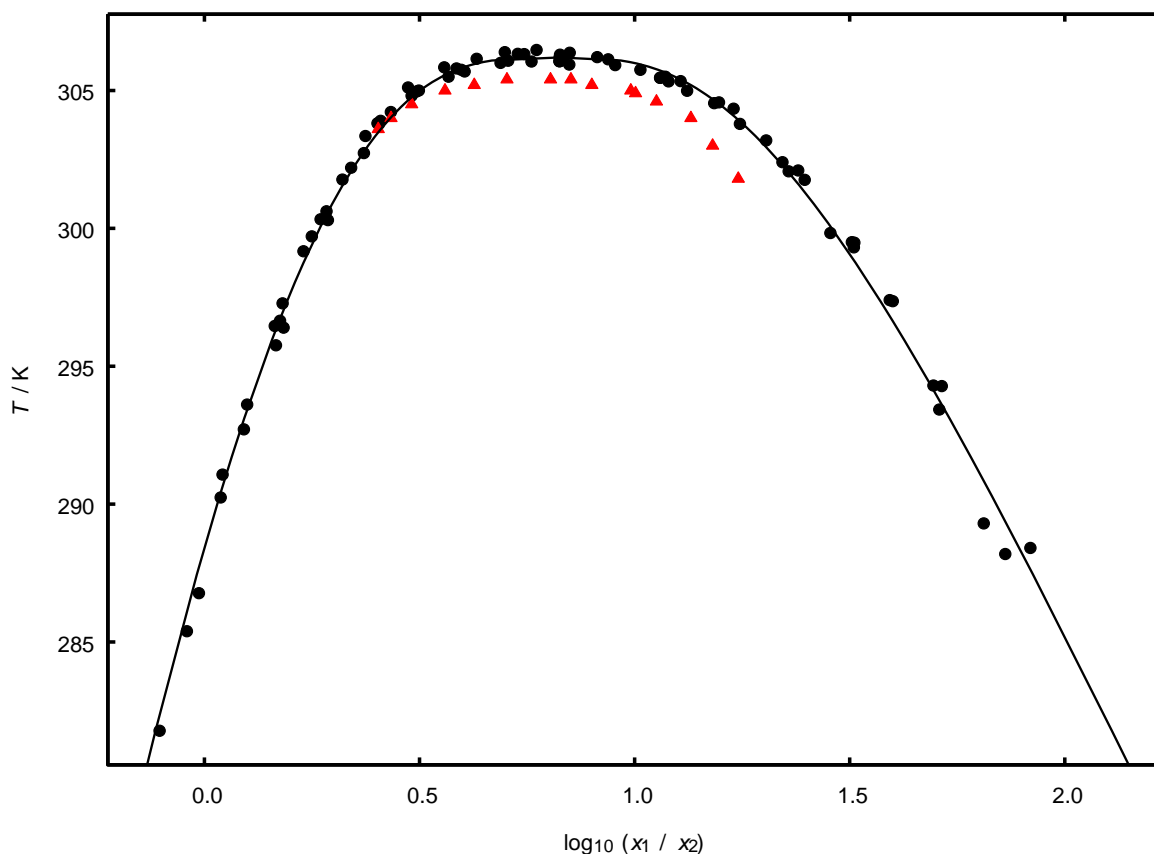


Fig. 8: Experimental mole-fraction LLE data (symbols) for hexan-1-ol (1) + [C₆mim][NTf₂] (2) in a composition-stretched representation [17] compared with the evaluation with parameters from Table 12 (line). The data from [44] are shown as red triangles.

Tab. 12: Parameters for Equations (1) and (2) for hexan-1-ol (1) + [C₆mim][NTf₂] (2) with the lower (T_{\min}) temperature limit of the equations' validity

x_c	T_c/K	a_1	a_2	a_3	b_1	b_2	b_3	T_{\min}/K
0.870	306.2	-4.286	-0.7482	0	-12.76	-3.994	0	288.0

Tab. 13: Smoothed mole fractions of hexan-1-ol (x_1) in hexan-1-ol (1) + [C₆mim][NTf₂] (2) for LLE calculated with Equations (1) and (2) using the parameters given in Table 12^a

T/K	x_1	x_{1-}	x_{1+}
Liquid phase 1 ([C ₆ mim][NTf ₂]-rich phase)			
288.0	0.496	0.487	0.504
290.0	0.517	0.510	0.524
292.0	0.540	0.534	0.546
294.0	0.564	0.559	0.569
296.0	0.590	0.586	0.594
298.0	0.618	0.614	0.622
300.0	0.649	0.646	0.653
302.0	0.685	0.681	0.689
304.0	0.730	0.726	0.734

T/K	x_1	x_{1-}	x_{1+}
306.0	0.813	0.809	0.817
Liquid phase 2 (hexan-1-ol-rich phase)			
306.0	0.9088	0.9048	0.9127
304.0	0.9452	0.9431	0.9472
302.0	0.9582	0.9568	0.9595
300.0	0.9664	0.9654	0.9673
298.0	0.9723	0.9715	0.9731
296.0	0.9768	0.9760	0.9776
294.0	0.9804	0.9796	0.9812
292.0	0.9834	0.9825	0.9841
290.0	0.9858	0.9849	0.9866
288.0	0.9878	0.9869	0.9886

^a The estimated expanded uncertainties at the 0.95 level of confidence ($k = 2$) for mole fractions have been calculated with the equations given in Table S2 derived as described in Supplement IC. Since the uncertainties are asymmetric, the upper and lower bounds of the confidence interval (x_{1-} and x_{1+}) are provided in separate columns. The recommendation is provisional, based on an assumption that the data from [44] are inaccurate.

APPENDIX

To avoid the need for reverse calculations using Equations (1) and (2) by the readers, LLE temperatures in the vicinity of the corresponding upper consolute temperatures for five suggested mixtures were calculated and listed in Table A. The corresponding uncertainties for the LLE temperatures were also evaluated and reported.

Tab. A: Smoothed LLE temperatures back-calculated for selected compositions with Equations (1) and (2) using the corresponding parameters provided in the text for the corresponding suggested mixtures ^a

w_1	x_1	T_{LLE}/K
Aniline (1) + water (2): $U(T_{LLE}) = 2.0$ K		
0.2000	0.0461	427.5
0.3000	0.0766	436.4
0.4000	0.1142	438.7
0.5000	0.1621	439.0
0.6000	0.2249	438.1
0.7000	0.3110	432.5
0.8000	0.4362	417.3
Phenol (1) + water (2): $U(T_{LLE}) = 1.0$ K		
0.1500	0.0327	330.8
0.2500	0.0600	338.4
0.3500	0.0934	339.3
0.4500	0.1354	338.8
0.5500	0.1896	332.8
Nitromethane (1) + water (2): $U(T_{LLE}) = 1.0$ K		
0.3000	0.1123	364.7
0.4000	0.1644	373.8
0.5000	0.2279	376.8
0.6000	0.3069	377.1
0.7000	0.4078	376.3

w_1	x_1	T_{LLE}/K
0.8000	0.5414	370.5
Cyclohexane (1) + methanol (2): $U(T_{LLE}) = 0.8$ K		
0.5000	0.2757	314.0
0.6000	0.3635	317.7
0.7000	0.4704	318.5
0.8000	0.6036	318.1
0.9000	0.7741	311.3
Hexan-1-ol (1) + [C ₆ mim][NTf ₂] (2): $U(T_{LLE}) = 0.5$ K		
0.4000	0.7448	304.5
0.5000	0.8141	306.0
0.6000	0.8679	306.2
0.7000	0.9109	306.0
0.8000	0.9460	303.9

^a Symbols used: w_1 – mass fraction of component 1, x_1 – mole fraction of component 1, T_{LLE} – liquid-liquid equilibrium temperature for the stated composition, $U(T_{LLE})$ – expanded uncertainty at the 0.95 level of confidence ($k = 2$) for T_{LLE} .

SUPPORTING MATERIALS

All supplements mentioned in the text can be found online as Supporting Information Materials to this paper. In addition, a website (<https://trc.nist.gov/reference-systems>) has been developed to provide additional calculation support for all suggested mixtures.

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