IUPAC Technical Report

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Reference materials for phase equilibrium studies. 1. Liquid–liquid equilibria (IUPAC Technical Report)

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 this project is to select reference systems with critically evaluated property values for the validation of instruments and techniques used in phase equilibrium studies of 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: Instrument validation; liquid–liquid equilibrium; phase equilibrium; reference materials.

CONTENTS

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1 Introduction

Reference materials have long been established as necessary for inter-laboratory comparisons and validation of uncertainty claims for applied instrumentation and techniques. Although 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 for 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 Refs. [1, 2], a classification of LLE types has been given in Refs. [3, 4], and the effects of pressure on LLE have been discussed in Ref. [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 the 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 the validation of LLE measurements have been given in Ref. [1]. The mixtures mentioned in Ref. [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 based on the amount of LLE data available. Within each category of LLE (aqueous, non-aqueous, low-solubility, and ionic liquids), the mixtures were then ranked by the consistency of the data from independent sources, chemical stability, toxicity level, availability, and 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 the existence of commercial samples with purity sufficient for conducting LLE experiments or as the existence of simple purification methods, which can be used for obtaining the desired purity for the selected compounds. Readers are referred to Ref. [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. Although the 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. This 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, the 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 two or three 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.

2 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.

2.1 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, the 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 this 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 Ref. [15], which looks erroneous (Fig. 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).
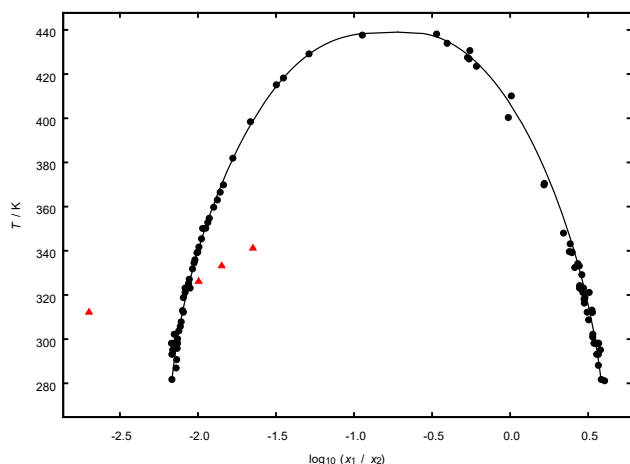

Fig. 1: Experimental mole-fraction LLE data (symbols) for aniline (1) + water (2) in a composition-stretched representation [17] *vs.* the SDS equation (line) [13]. The rejected solubilities of aniline in water from Ref. [15] are shown as red triangles. The points, which are designated as doubtful in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

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

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

where x_1 is the mole fraction of aniline; x_c is the mole fraction of aniline at the upper consolute point; T is the temperature in K; T_c is the upper consolute temperature in K; and a_1, a_2, and a_3 are empirical parameters;

For the solubility of water (2) in aniline (1):

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

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

The parameters for Eqs. (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.

Table 1: Parameters for Eqs. (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

Table 2: Smoothed mole fractions of aniline (x_1) in the aniline + water mixture for LLE calculated with Eqs. (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	0.006 74	0.006 39	0.007 11
290.00	0.006 99	0.006 68	0.007 32
300.00	0.007 34	0.007 05	0.007 63
310.00	0.007 78	0.007 51	0.008 06
320.00	0.008 35	0.008 07	0.008 63
330.00	0.009 05	0.008 74	0.009 36
340.00	0.009 91	0.009 54	0.010 28
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

Table 2: (continued)

T/K	x_1	x_{1-}	x_{1+}
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. Because the uncertainties are asymmetric, the upper and lower bounds of the confidence interval (x_{1-} and x_{1+}) are provided in separate columns.

2.2 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 this evaluation. These additional data are in fair agreement with the earlier publications and evaluation (Fig. 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 Ref. [18]. An additional validation has been attempted with an NRTL equation that shows fair agreement with other available property data such as SLE (Supplement 1E), although SLE data are to some extent ambiguous. The source reporting doubtful LLE data [19] also deviates from the SLE data sources. The formation of an inter-component compound $2C_6H_5OH \cdot H_2O$ has been claimed in several reports summarized in Ref. [20] and is consistent with SLE data from Ref. [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 (Eqs. (8) and (9) in reference [18]) have been adopted in this work: Eq. (1) for the mole-fraction solubility of phenol in water and Eq. (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 Ref. [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 Ref. [18]).

Table 3: Parameters for Eqs. (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

Table 4: Smoothed mole fractions of phenol (x_1) in phenol + water for LLE calculated with Eqs. (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. Because 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.

2.3 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 this evaluation. Most of the data are consistent, with the prominent exception of Ref. [23] (Fig. 3).
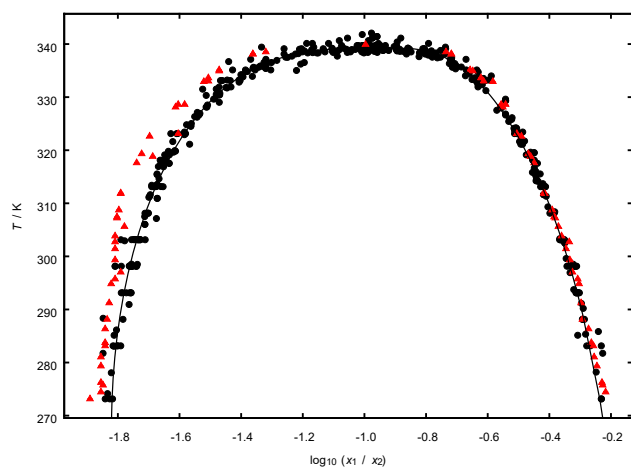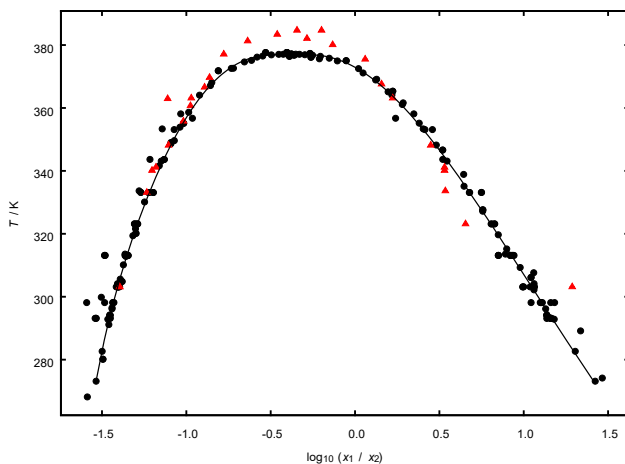

Fig. 3: Experimental mole-fraction LLE data (symbols) for nitromethane (1) + water (2) in a composition-stretched representation [17], compared with the evaluation with parameters from Table 5 (line). The rejected data from Ref. [23] and three obviously erroneous data points from Ref. [24] are shown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

Table 5: Parameters for Eqs. (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

We fitted Eq. (1) for the mole-fraction solubility of nitromethane in water and Eq. (2) for the mole-fraction solubility of water in nitromethane with the use of all LLE data (excluding three obviously erroneous data points from Ref. [24] and the data from Ref. [23], despite a part of these 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 this region, the recommended values for this system are restricted to temperatures above 290 K.

The system butan-1-ol + water may serve as a reserve test mixture for aqueous LLE measurements because 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 because the data scatter is larger for this system in comparison to the selected mixtures. However, butan-1-ol is readily available as a high-purity sample, which may justify using the reserve butan-1-ol + water system.

Table 6: Smoothed mole fractions of nitromethane (x_1) in nitromethane + water for LLE calculated with Eqs. (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
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. Because the uncertainties are asymmetric, the upper and lower bounds of the confidence interval (x_{1-} and x_{1+}) are provided in separate columns.

3 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.

3.1 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 this evaluation. We fitted Eq. (1) for the mole-fraction solubility of cyclohexane in methanol and Eq. (2) for the mole-fraction solubility of methanol in cyclohexane with the use of all LLE data. The parameters are listed in Table 7. Although the reported values of the upper consolute temperature range from 318 to 322 K, a relatively low value of 318.5 K from Ref. [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 Fig. 4. The largest deviations (up to a mole fraction of 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 Ref. [26]. The smoothed LLE solubilities with the corresponding confidence intervals are given in Table 8.
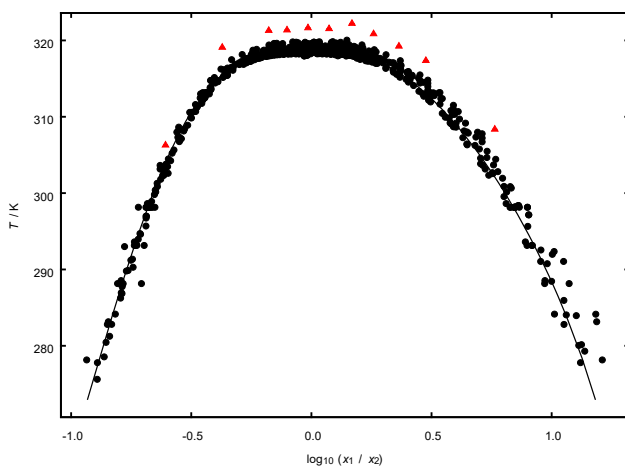

Fig. 4: Experimental mole-fraction LLE data (symbols) for cyclohexane (1) + methanol (2) in a composition-stretched representation [17] compared with the evaluation with parameters from Table 7 (line). The rejected data from Ref. [32] are shown as red triangles.

Table 7: Parameters for Eqs. (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

Table 8: Smoothed mole fractions of cyclohexane (x_1) in cyclohexane + methanol for LLE calculated with Eqs. (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 1C. Because the uncertainties are asymmetric, the upper and lower bounds of the confidence interval (x_{1-} and x_{1+}) are provided in separate columns.

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.

4 Category 3: Systems with low solubility

4.1 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 (Figs. 5 and 6).

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):

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

and for the mole-fraction solubility of water in hydrocarbons ($x_2 = 1 - x_1$):
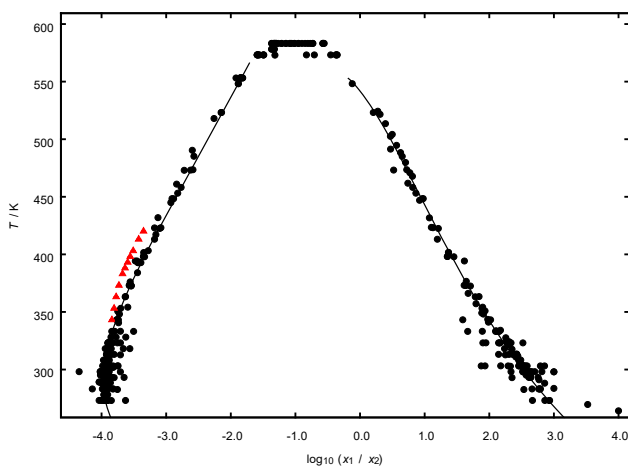
Fig. 5: Experimental mole-fraction LLE data (symbols) for toluene (1) + water (2) in a composition-stretched representation [17] compared with the SDS equations (lines) [35]. A deviating data set from Ref. [37] is shown as red triangles. Other rejected data believed erroneous are shown in Fig. S12 in Supplement 1I.
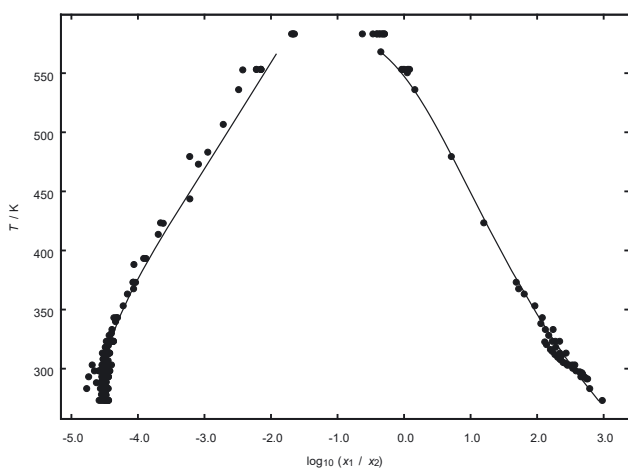

Fig. 6: Experimental mole-fraction LLE data (symbols) for ethylbenzene (1) + water (2) in a composition-stretched representation [17] compared with the SDS equations (lines) [36]. Rejected data believed erroneous are shown in Fig. S13 in Supplement 1J.

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

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

The parameters for Eqs. (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 Figs. 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 Eqs. (3) and (4). The ethylbenzene + water system shows a similar behavior, with reported UCEP values of 574 K [38] and 568 K [39]. However, the upper limit of the temperature range for this system is restricted to 450 K (below UCEP) due to a limited number of experimental points above 450 K, which 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 (Fig. 7). A qualitative consistency test using other properties is given in Supplement 1K. The smoothed LLE solubilities are given in Tables 10 and 11.

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

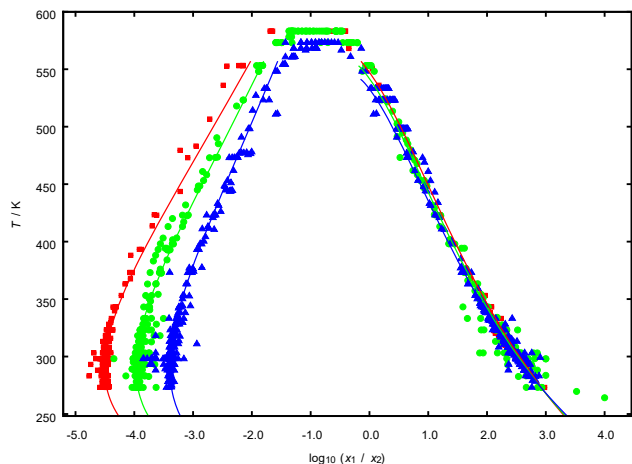| System	$\ln(x_{min,1})$	D	T_{ms}/K	d_1	d_2	d_3	d_4	T_c/K	T_{min}/K	T_{max}/K
Toluene (1) + water (2)	−9.14	35.7	290	−0.495	−3.700	−0.102	−4.641	553.0	273.15	556.1
Ethylbenzene (1) + water (2)	−10.37	40.9	290	−0.383	−3.167	−0.009	−5.655	566.9	273.15	450.0

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].

Table 10: Smoothed mole fractions of toluene (x_1) in toluene + water for LLE calculated with Eqs. (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	0.000 115	0.000 104	0.000 126
280.00	0.000 110	0.000 100	0.000 120
290.00	0.000 107	0.000 099	0.000 117
300.00	0.000 109	0.000 101	0.000 118
310.00	0.000 116	0.000 108	0.000 124
320.00	0.000 126	0.000 118	0.000 135
330.00	0.000 141	0.000 132	0.000 151
340.00	0.000 161	0.000 150	0.000 172
350.00	0.000 187	0.000 175	0.000 201
360.00	0.000 221	0.000 205	0.000 238
370.00	0.000 264	0.000 244	0.000 287
380.00	0.000 320	0.000 293	0.000 349
390.00	0.000 389	0.000 354	0.000 428
400.00	0.000 478	0.000 431	0.000 530
410.00	0.000 590	0.000 527	0.000 661
420.00	0.000 732	0.000 648	0.000 827
430.00	0.000 91	0.000 80	0.001 04
440.00	0.001 14	0.000 99	0.001 31
450.00	0.001 42	0.001 22	0.001 66
460.00	0.001 78	0.001 51	0.002 10
470.00	0.002 23	0.001 88	0.002 66
480.00	0.002 80	0.002 33	0.003 37
490.00	0.003 51	0.002 89	0.004 27
500.00	0.004 40	0.003 59	0.005 41
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

Table 10: (continued)

T/K	x_1	x_{1-}	x_{1+}
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	0.990 67	0.989 69	0.991 56
330.00	0.992 86	0.992 10	0.993 55
320.00	0.994 60	0.994 00	0.995 14
310.00	0.995 96	0.995 48	0.996 39
300.00	0.997 02	0.996 64	0.997 37
290.00	0.997 84	0.997 53	0.998 11
280.00	0.998 46	0.998 21	0.998 67
273.15	0.998 79	0.998 58	0.998 96

[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 $0.10 \cdot x_{guest}$ instead of $0.03 \cdot x_{guest}$ described in Supplement 1C. Because the uncertainties are asymmetric, the upper and lower bounds of the confidence interval (x_{1-} and x_{1+}) are provided in separate columns.

5 Category 4: Systems with ionic liquids

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

Although 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 [C$_6$mim][NTf$_2$] 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 Ref. [40] for the LLE for this mixture. We have updated this LLE representation by including new data [41–44] and using fitting Eqs. (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 (Fig. 8). We considered the presence of water and hydrolysis products as possible reasons for such a disagreement. Although 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 the third components, especially water, on the LLE for this

Table 11: Smoothed mole fractions of ethylbenzene (x_1) in ethylbenzene + water for LLE calculated with Eqs. (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	0.000 033 8	0.000 028 6	0.000 040 1
280.00	0.000 032 2	0.000 027 8	0.000 037 2
290.00	0.000 031 4	0.000 028 0	0.000 035 1
300.00	0.000 032 1	0.000 029 3	0.000 035 2
310.00	0.000 034 2	0.000 031 3	0.000 037 3
320.00	0.000 037 8	0.000 034 1	0.000 041 8
330.00	0.000 042 9	0.000 037 6	0.000 048 9
340.00	0.000 050 0	0.000 042 3	0.000 058 9
350.00	0.000 059	0.000 048	0.000 073
360.00	0.000 072	0.000 056	0.000 092
370.00	0.000 088	0.000 066	0.000 117
380.00	0.000 109	0.000 079	0.000 151
390.00	0.000 137	0.000 095	0.000 198
400.00	0.000 174	0.000 116	0.000 261
410.00	0.000 221	0.000 141	0.000 346
420.00	0.000 28	0.000 17	0.000 46
430.00	0.000 36	0.000 21	0.000 62
440.00	0.000 47	0.000 26	0.000 83
450.00	0.000 61	0.000 33	0.001 12
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	0.989 07	0.987 98	0.990 05
340.00	0.991 49	0.990 79	0.992 13
330.00	0.993 44	0.993 00	0.993 85
320.00	0.994 99	0.994 72	0.995 24
310.00	0.996 22	0.996 04	0.996 38
300.00	0.997 18	0.997 05	0.997 30
290.00	0.997 92	0.997 81	0.998 03
280.00	0.998 49	0.998 39	0.998 59
273.15	0.998 80	0.998 71	0.998 89

[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 $0.10 \cdot x_{guest}$ instead of $0.03 \cdot x_{guest}$ described in Supplement 1C. Because the uncertainties are asymmetric, the upper and lower bounds of the confidence interval (x_{1-} and x_{1+}) are provided in separate columns.

Table 12: Parameters for Eqs. (1) and (2) for hexan-1-ol (1) + [C$_6$mim][NTf$_2$] (2) with the lower (T_{min}) temperature limit of the equations' validity.

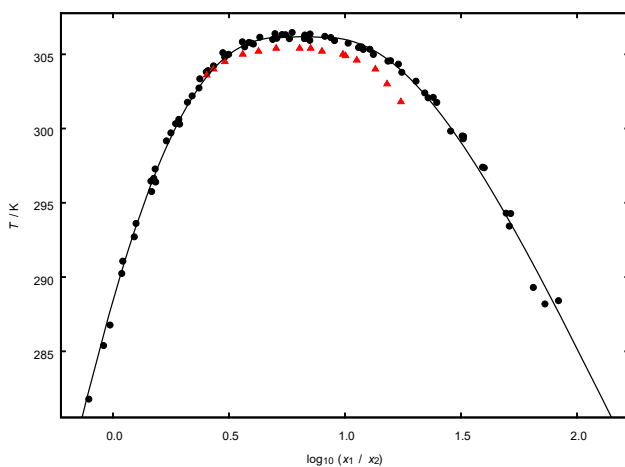| x_c	T_c/K	a_1	a_2	a_3	b_1	b_2	b_3	T_{min}/K
0.870	306.2	−4.286	−0.7482	0	−12.76	−3.994	0	288.0

Fig. 8: Experimental mole-fraction LLE data (symbols) for hexan-1-ol (1) + [C$_6$mim][NTf$_2$] (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.

Table 13: Smoothed mole fractions of hexan-1-ol (x_1) in hexan-1-ol (1) + [C$_6$mim][NTf$_2$] (2) for LLE calculated with Eqs. (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
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 1C. Because 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.

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. Because 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.

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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Appendix

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

Table A: Smoothed LLE temperatures back-calculated for selected compositions with Eqs. (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

Table A: (continued)

w_1	x_1	T_{LLE}/K
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
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; and $U(T_{LLE})$, expanded uncertainty at the 0.95 level of confidence (k = 2) for T_{LLE}.

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