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Pure Appl. Chem. 2022; 94(11–12): 1225–1247

IUPAC Technical Report

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Reference materials for phase equilibrium studies. 2. Solid–liquid equilibria (IUPAC Technical Report)

Abstract: This article is the second of three projected IUPAC Technical Reports on reference materials for phase equilibrium studies. The goal of this project was to select reference systems with critically evaluated property values for the verification of instruments and techniques used in phase equilibrium studies of mixtures. This report proposes seven systems for solid–liquid equilibrium studies, covering the four most common categories of binary mixtures: aqueous systems with organic solutes, aqueous systems with inorganic solutes, non-aqueous systems, and systems with low solubility. For each system, the available literature sources, accepted data, smoothing equations, and estimated uncertainties are given.

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1 Introduction

Reference materials have long been established as necessary for inter-laboratory comparisons and evaluation 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 equilibria in mixtures, there are no commonly accepted recommendations for reference systems for testing equipment and methodologies for such investigations. 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: liquid–liquid equilibrium (LLE), solid–liquid equilibrium (SLE), and vapor–liquid equilibrium (VLE). The current part (Part 2) of the Technical Report on the Project deals with SLE.

Experimental methods for measuring solubilities of solids in liquids have been described in Refs. [1, 2]. Suggestions for the use of certain mixtures previously discussed in the Solubility Data Series (SDS) [3] for verification of such methods have been given in Ref. [1]. Classification of solid–liquid phase diagrams can be found in Ref. [4]. Simple solubility (phase) diagrams may be complicated by the simultaneous presence of eutectics and solid solutions, as well as formation of intercomponent compounds (solvates, hydrates, *etc.*), metastable equilibria, glass formation, and liquid–liquid separation. Typical complications have been studied in Refs. [5, 6]. Sample purity and chemical stability (*e.g.*, possible hydrolysis) should also be carefully considered. For the purposes of the present project, the following types of systems were considered: aqueous systems with organic solutes, aqueous systems with inorganic solutes, non-aqueous systems, and systems with low solubility. The present recommendations do not cover complex phase diagrams or solubility in supercritical fluids. Ideally, all SLE measurement results should be reported in sufficient detail to allow them to be critically assessed – recommendations on reporting phase-equilibrium data are given in another IUPAC project [7]. It is always useful to estimate the expected phase diagram type for a studied system. This estimate should include possible metastability and formation of solvates, as well

as characterization of the nature of the solid phase. If the solid phase is unknown, the full material balance should be reported, especially for systems with more than two components and/or involving various ionic species (*e.g.*, observed in mixtures with ionic liquids).

To recommend reference systems for the evaluation of SLE measurements, the NIST/TRC SOURCE database available in ThermoData Engine (SRD 103b) [8] was scanned for binary mixtures with the largest amount of SLE data. Within each category of SLE considered, the mixtures were then ranked by the consistency of the data from independent sources, chemical stability, toxicity level, impurities, availability, and cost, as well as the existence of previous evaluations such as those in Ref. [1] or recommendations in the SDS [3]. Availability was considered either as the existence of commercial samples with purity sufficient for conducting SLE 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 [9] for typical purification methods applied to organic components.

As a result of the above selection process, seven systems were chosen. All SLE data discussed here are for binary mixtures either at 0.1 MPa or at pressures close to vapor saturation, whichever is greater (the current report does not cover high-pressure or supercritical SLE measurements). Literature sources, accepted solubility data, smoothing equations, and uncertainty analysis are given for each mixture listed below. Data rejection was done either on the basis of the smart rejection procedure implemented in ThermoData Engine [8] or anomalies or flaws discovered in specific publications. A description of the uncertainty assessment procedure used for the studied systems is detailed in Part 1 of these Technical Reports [10]. Both temperature and composition representations of the SLE data are provided for convenience, except for the low-solubility category, where only compositions as a function of temperature are given, as most experiments are typically done in this mode. Smoothing equations have also been included in the present report to support method verification at any point within the experimental conditions covered for the proposed systems. This report also includes a few reserve systems that are well studied in the literature but have not been evaluated by us; interested researchers may access the associated SDS publications and/or original works provided in the report to make their own comparisons.

2 Category 1: aqueous systems with organic solutes

This category has become one of the most widely studied SLE areas, especially in regard to solubilities of pharmaceuticals in water. Because of the interest in solubilities in biological fluids, special attention must be paid to whether pure water or a buffer solution was used for the SLE experiments. We focused only on solubilities in pure water. Despite the popularity of this area of research, few systems have sufficiently consistent experimental data for reliable assessment. Some obvious systems (*e.g.*, D-glucose + water [5]) exhibit serious complications due to the existence of metastable polymorphs, which preclude unambiguous data interpretation.

2.1 Urea (carbonic diamide) + water system

One of the best-studied systems with consistent experimental SLE data in this category is urea + water. The selected literature sources associated with the SLE data for this system are listed in Supplement 2A. It should be noted that there were also a few series of works on ternary SLE diagrams at fixed temperatures, where urea was one of the solutes and binary SLE data for urea + water were reported [11–14]; however, the binary mixture was not the primary focus of the works, and the solubilities were similar within each series. To avoid any bias of the generated recommendation toward the data from those laboratories, only representative cases were included in the assessment.

Most of the selected sources are consistent, with the prominent exception of all data points from Refs. [14–16] as well as one data point from Ref. [17] and two points from Ref. [12] (Figure 1). The value in
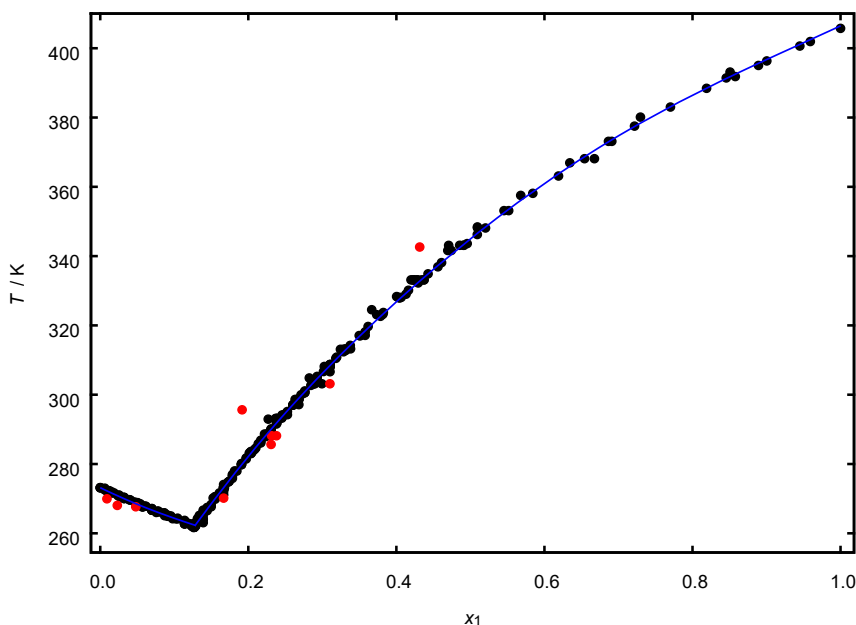
Fig. 1: Experimental mole-fraction SLE data (dots) for urea (1) + water (2) vs the NRTL evaluation with the parameters from Table 1 (blue line). Rejected points from Refs. [12, 14–17] are shown as red dots.

Ref. [16] is accompanied by the sign "+," which probably indicates that the actual solubility is above that reported value. Some researchers (*e.g.*, [12]) have claimed three different states of solid urea. These claims are doubtful given that reliable heat capacity measurements, by adiabatic and triple thermal bridge calorimetries, found no solid-to-solid phase transitions up to the melting point of urea [18–20].

The selected SLE data were smoothed with the NRTL (Non-Random Two-Liquid) excess Gibbs energy model [21] by the ThermoData Engine software [8]. For a binary mixture, this model gives the following expression for the excess molar Gibbs energy G^{E}:

$$G^{\mathrm{E}}/(RT) = x_1 x_2 [c_1 \exp(-\alpha c_1)/(x_1 + x_2 \exp(-\alpha c_1)) + c_2 \exp(-\alpha c_2)/(x_2 + x_1 \exp(-\alpha c_2))] \tag{1}$$

with the temperature-dependent parameters c_i defined as follows:

$$c_i = A_i + B_i (T/\mathrm{K})^{-1} + C_i \ln(T/\mathrm{K}) + D_i (T/\mathrm{K}), \tag{2}$$

where α is an empirical fitting parameter called the "non-randomness parameter"; A_i through D_i are the empirical fitting parameters for component i; T is the temperature in K; x_i is the mole fraction of component i; and R is the molar gas constant.

From basic thermodynamic relationships, the mole-fraction solubility of component i (x_i) at temperature T can be shown to be:

$$-R \ln(\gamma_i x_i) = \Delta_{\mathrm{fus}} H_{\mathrm{m},i} [1/T - 1/T_{\mathrm{tp},i}] - \Delta_{\mathrm{fus}} C_{p,\mathrm{m},i} [\ln(T/T_{\mathrm{tp},i}) + T_{\mathrm{tp},i}/T - 1], \tag{3}$$

where $T_{\mathrm{tp},i}$ is the triple-point temperature (crystal + liquid + gas) for component i, $\Delta_{\mathrm{fus}} H_{\mathrm{m},i}$ is the enthalpy of fusion of the crystalline form of component i, and $\Delta_{\mathrm{fus}} C_{p,\mathrm{m},i}$ is the heat-capacity difference between the liquid and crystalline form of component i, and γ_i is the activity coefficient of component i, which can be derived from eq. (1) as described in Ref. [21]:

$$\ln(\gamma_1) = x_2^2 [c_1 \{\exp(-\alpha c_1)/(x_1 + x_2 \exp(-\alpha c_1))\}^2 + c_2 \exp(-\alpha c_2)/(x_2 + x_1 \exp(-\alpha c_2))^2] \tag{4}$$

$$\ln(\gamma_2) = x_1^2 [c_2 \{\exp(-\alpha c_2)/(x_2 + x_1 \exp(-\alpha c_2))\}^2 + c_1 \exp(-\alpha c_1)/(x_1 + x_2 \exp(-\alpha c_1))^2] \tag{5}$$

The parameters of the resulting NRTL fit for urea (1) + water (2) are presented in Table 1. This table also contains the melting parameters (for both mixture components) used in the model. For urea, these parameters

Table 1: Parameters for the NRTL model for urea (1) + water (2) for SLE calculations.

Component *i*	Parameters of eq. (2)					Melting parameters for eq. (3)			
	A_i	B_i	C_i	D_i	α	T_{tp}/K	$\Delta_{fus}H_m$/(kJ mol^{-1})	$\Delta_{fus}C_{p,m}$/(J K^{-1} mol^{-1})
Component 1 (urea)	−218.486	128 47.8	31.0788	0	0.217 264	406.46	13.90	21.0
Component 2 (water)	−71.3916	1654.25	11.3364	0		273.16	6.007	38.2

were obtained from the ThermoData Engine [8] as weighted averages of the values reported in the literature (Supplement 2A), while for water they were adopted from the water and ice recommendations from IAPWS (International Association for the Properties of Water and Steam) [22, 23]. Since T_{tp}, $\Delta_{fus}H_m$, and $\Delta_{fus}C_{p,m}$ were assigned fixed values during the NRTL fitting, any inaccuracy in them was absorbed by the fitting parameters α and A_i through D_i, so their uncertainties were not needed for the purposes of the present project and thus were not evaluated.

The performance of the NRTL model relative to the selected experimental data is shown in Figure 1 and as deviation plots in Supplement 2B. Although the NRTL model was based only on the SLE data, available experimental VLE pressures for the mixture (given in Supplement 2B) are also in fair agreement with it, which can serve as additional verification for the selected SLE data and model.

Smoothed solubility data are listed in Table 2. The eutectic point, according to the model, is at $T = (262.30 \pm 0.29)$ K and $x_1 = 0.1283 \pm 0.0061$ with expanded uncertainties U at the 0.95 level of confidence

Table 2: Smoothed mole fractions of urea (x_1) vs SLE temperatures (T_{SLE}) for the urea (1) + water (2) system obtained with the NRTL model using the parameters given in Table 1 (both composition and temperature representations are given for convenience)[a].

Temperature representation (*i.e.*, $T_{SLE} = f(x_1)$)			Composition representation (*i.e.*, $x_1 = f(T_{SLE})$)		
x_1	T_{SLE}/K	$U(T_{SLE})$/K	T_{SLE}/K	x_1	$U(x_1)$
Solid phase = ice			Solid phase = ice		
0.0250	270.67	0.26	272.50	0.0064	0.0024
0.0500	268.37	0.20	270.00	0.0321	0.0039
0.0750	266.27	0.20	267.50	0.0601	0.0077
0.1000	264.34	0.25	265.00	0.091	0.012
0.1250	262.53	0.34	262.50	0.125	0.016
Eutectic point			Eutectic point		
0.1283	262.30	0.29	262.30	0.1283	0.0061
Solid phase = urea			Solid phase = urea		
0.1500	268.53	0.26	265.00	0.1376	0.0060
0.2000	282.18	0.20	270.00	0.1552	0.0058
0.2500	294.69	0.18	275.00	0.1732	0.0055
0.3000	306.18	0.20	280.00	0.1917	0.0053
0.3500	316.83	0.26	285.00	0.2109	0.0051
0.4000	326.81	0.34	290.00	0.2307	0.0048
0.4500	336.18	0.42	295.00	0.2513	0.0046
0.5000	344.99	0.51	300.00	0.2726	0.0044
0.5500	353.25	0.60	305.00	0.2947	0.0042
0.6000	360.96	0.69	310.00	0.3175	0.0040
0.6500	368.11	0.78	315.00	0.3411	0.0038
0.7000	374.72	0.87	320.00	0.3655	0.0036
0.7500	380.81	0.96	325.00	0.3907	0.0035
0.8000	386.4	1.1	330.00	0.4167	0.0033
0.8500	391.7	1.1	335.00	0.4436	0.0032
0.9000	396.7	1.2	340.00	0.4713	0.0031
0.9500	401.6	1.3	345.00	0.5001	0.0030
			350.00	0.5299	0.0029
			355.00	0.5610	0.0029

Table 2: (continued)

	Temperature representation (*i.e.*, $T_{SLE} = f(x_1)$)		Composition representation (*i.e.*, $x_1 = f(T_{SLE})$)		
x_1	T_{SLE}/K	$U(T_{SLE})$/K	T_{SLE}/K	x_1	$U(x_1)$
			360.00	0.5936	0.0028
			365.00	0.6278	0.0028
			370.00	0.6639	0.0029
			375.00	0.7022	0.0029
			380.00	0.7431	0.0030
			385.00	0.7868	0.0031
			390.00	0.8334	0.0032
			395.00	0.8826	0.0034
			400.00	0.9336	0.0035

[a]Expanded uncertainties U at the 0.95 level of confidence (coverage factor 2) were calculated with the equations given in Table S1, derived as described in Supplement 2C.

(coverage factor 2) based on the data scatter. The uncertainty assessment procedure is described in Supplement 1C of the LLE part of this project [10]. Experimental uncertainties of 2 K and 0.03 x_{guest} (where the "guest component" for SLE is the solute) were assumed unless individual uncertainties were assigned to particular data sets. Minimum uncertainties were taken to be 0.25 K and 0.01 x_{guest}. The uncertainties for SLE mole fractions and temperatures are approximated by the equations reported in Supplement 2C.

2.2 Sulfolane ($1\lambda^6$-thiolane-1,1-dione) + water system

The sulfolane + water system was selected as a reserve system due to its interesting behavior with regard to the presence of two consecutive stable crystalline modifications of sulfolane [24, 25] and a possible super-cooling of its high-temperature crystal (form I), giving rise to a metastable SLE [26, 27]. The latter may be used for testing the ability of experimental methods to determine stable equilibrium. Though reported in only two sources [24, 25], the experimental SLE data for the system are very consistent, as seen in Figure 2. A tentative evaluation for this system is described below.
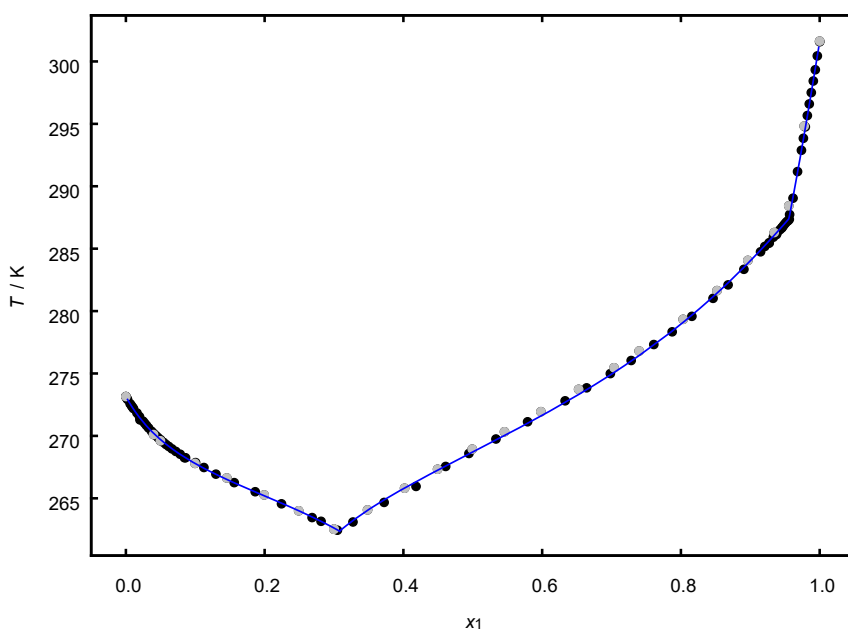

Fig. 2: Experimental mole-fraction SLE data (dots) for sulfolane (1) + water (2) vs the Wilson model with the parameters from Table 3 (blue line). Data from Refs. [24, 25] are shown as black and gray dots, respectively.

The selected SLE data were smoothed with the Wilson-type excess Gibbs energy model [28] by the ThermoData Engine software [8]. For a binary mixture, the model gives the following expressions for the excess molar Gibbs energy, G^E, and activity coefficient of components 1 and 2, γ_1 and γ_2, respectively:

$$G^E/(RT) = -x_1 \ln(x_1 + a_2 x_2) - x_2 \ln(x_2 + a_1 x_1) \tag{6}$$

$$\ln(\gamma_1) = -\ln(x_1 + a_2 x_2) + x_2 [a_2/(x_1 + a_2 x_2) - a_1/(x_2 + a_1 x_1)] \tag{7}$$

$$\ln(\gamma_2) = -\ln(x_2 + a_1 x_1) + x_1 [a_1/(x_2 + a_1 x_1) - a_2/(x_1 + a_2 x_2)] \tag{8}$$

with the temperature-dependent parameter a_i defined as follows:

$$a_i = \exp(A_i + B_i (T/\text{K})^{-1} + C_i \ln(T/\text{K})), \tag{9}$$

where A_i through C_i are the empirical fitting parameters for component i; T is the temperature in K; x_i is the mole fraction of component i; and R is the molar gas constant.

Equation (3) is valid for the solubility curve of component i between its melting and its solid-to-solid phase transition temperatures. Below the solid-to-solid phase transition temperature, eq. (3) is modified to:

$$-R \ln(\gamma_i x_i) = \Delta_{\text{fus}} H_{m,i} [1/T - 1/T_{\text{tp},i}] - \Delta_{\text{fus}} C_{p,m,i} [\ln(T/T_{\text{tp},i}) + T_{\text{tp},i}/T - 1]$$
$$+ \Delta_{\text{trs}} H_{m,i} [1/T - 1/T_{\text{tp(crII--crI)},i}] - \Delta_{\text{trs}} C_{p,m,i} [\ln(T/T_{\text{tp(crII--crI)},i}) + T_{\text{tp(crII--crI)},i}/T - 1], \tag{10}$$

where $T_{\text{tp(crII--crI)},i}$ is the triple-point temperature (crystal II + crystal I + gas) for component i, $\Delta_{\text{trs}} H_{m,i}$ is the enthalpy of the solid-phase transition of component i, and $\Delta_{\text{trs}} C_{p,m,i}$ is the heat-capacity difference between crystal I and crystal II for component i.

The parameters of the resulting Wilson fit for sulfolane (1) + water (2) are presented in Table 3. This table also contains the phase-transition parameters for both mixture components used in the modeling. For water, these parameters were as described above for the urea + water system. For sulfolane, the melting temperature and the enthalpy of the solid-to-solid phase transition were obtained from the ThermoData Engine [8] as weighted averages of the values reported in the literature (Supplement 2D). As described in Ref. [24], the liquidus curve of crystal I (in an orientationally disordered phase) of sulfolane for the sulfolane + water system deviates from the one expected from its enthalpy of fusion, which may indicate the presence of small quantities of water in the solid phase. Hence, the melting enthalpy for sulfolane was modified from the experimental value of pure sulfolane, from 1.4 kJ mol^{-1} [29], to 2.2 kJ mol^{-1} for the model fitting. This increase is consistent with the expectation of the formation of a solid solution. As a result, the solid-to-solid transition temperature used (287.4 K) was also modified from the experimental value of 288.6 K [29] for a better fit. It should be emphasized that the magnitude of the modifications is small, leading to a conclusion that the Wilson model can still be applied, even though a solid solution may be present. At the same time, no presence of water in the ordered phase (crystal II) was detected [24]. There are no heat-capacity data for crystalline sulfolane available to derive $\Delta_{\text{fus/trs}} C_{p,m}$ directly; however, an indirect analysis in Ref. [30] gave $\Delta_{\text{fus}} C_{p,m} = 0$ and $\Delta_{\text{trs}} C_{p,m} = 45.5$ J K^{-1} mol^{-1}.

Table 3: Parameters for the Wilson model for sulfolane (1) + water (2) for SLE calculations.

Component i	Parameters of eq. (9)			Phase-transition parameters for eqs. (3) or (10)[a]			
	A_i	B_i	C_i	type	T_{tp}/K	$\Delta_{\text{fus/trs}} H_m$/(kJ mol^{-1})	$\Delta_{\text{fus/trs}} C_{p,m}$/(J K^{-1} mol^{-1})
Component 1 (sulfolane)	−914.306	371 58.8	138.602	crI–liq	301.6	*2.2*	*0*
				crII–crI	*287.4*	8.04	45.5
Component 2 (water)	−509.031	218 61.9	76.0304	cr–liq	273.16	6.007	38.2

[a]Effective values, as described in the text, are given in *italics*. Abbreviations: liq, cr, crI, and crII are for liquid, crystal, and consecutive crystalline modifications crystal I (high-temperature phase, plastic crystal) and crystal II (low-temperature phase, ordered crystal), respectively.

The performance of the Wilson model with the parameters from Table 3 relative to the selected experimental data is shown in Figure 2 and as deviation plots in Supplement 2E. Since the model was obtained solely to fit the selected SLE data, it cannot be used for deriving other properties (*e.g.*, excess enthalpy or vapor pressures). Additional verification of the selected SLE data was done by simultaneously fitting the Wilson model to the available literature SLE, excess enthalpy, and vapor pressure data between 260 and 323 K. The results of that more generic fit are provided in Supplement 2E, where it is clearly seen that the selected SLE data are in fair agreement with other properties. It must be emphasized that the parameters from Table S2 are not recommended for SLE calculations, since their only purpose is to prove consistency with other properties.

Smoothed solubility data are given in Table 4. The coordinates of the eutectic and phase-transition points derived from the model are $x_1 = 0.3079 \pm 0.0034$ at $T = (262.38 \pm 0.36)$ K and $x_1 = 0.9557 \pm 0.0011$ at T fixed at 287.4 K, respectively, with expanded uncertainties at the 0.95 level of confidence (coverage factor 2) based on the data scatter.

3 Category 2: aqueous systems with inorganic solutes

The most studied mixtures with the easiest handling are aqueous solutions of potassium chloride, sodium chloride, and ammonium chloride. The potassium chloride + water mixture has a basically simple phase

Table 4: Smoothed mole fractions of sulfolane (x_1) vs SLE temperatures (T_{SLE}) for the sulfolane (1) + water (2) system obtained with the Wilson model using the parameters given in Table 3 (both composition and temperature representations are given for convenience) – tentative evaluation.[a]

Temperature representation (*i.e.*, $T_{SLE} = f(x_1)$)			Composition representation (*i.e.*, $x_1 = f(T_{SLE})$)		
x_1	T_{SLE}/K	$U(T_{SLE})$/K	T_{SLE}/K	x_1	$U(x_1)$
Solid phase = ice			Solid phase = ice		
0.0500	269.70	0.14	273.00	0.001 58	0.000 16
0.1000	267.78	0.14	272.50	0.006 85	0.000 22
0.1500	266.40	0.19	270.00	0.043 96	0.000 96
0.2000	265.19	0.26	267.50	0.1093	0.0017
0.2500	263.99	0.34	265.00	0.2082	0.0025
0.3000	262.62	0.43	262.50	0.3041	0.0033
Eutectic point			Eutectic point		
0.3079	262.38	0.36	262.38	0.3079	0.0034
Solid phase = sulfolane (crystal II)			Solid phase = sulfolane (crystal II)		
0.3500	264.11	0.33	262.50	0.3104	0.0033
0.4000	265.79	0.30	265.00	0.3755	0.0031
0.4500	267.28	0.27	267.50	0.4575	0.0029
0.5000	268.72	0.25	270.00	0.5446	0.0027
0.5500	270.16	0.22	272.50	0.6272	0.0024
0.6000	271.65	0.19	275.00	0.7014	0.0022
0.6500	273.24	0.17	277.50	0.7662	0.0020
0.7000	274.95	0.15	280.00	0.8227	0.0018
0.7500	276.84	0.14	282.50	0.8724	0.0015
0.8000	278.95	0.13	285.00	0.9167	0.0013
0.8500	281.33	0.13	Solid phase = sulfolane (crystal I)		
0.9000	284.03	0.14	287.50	0.9560	0.0011
0.9500	287.04	0.16	290.00	0.964 45	0.000 86
Solid phase = sulfolane (crystal I)			292.50	0.972 52	0.000 65
0.9600	288.66	0.16	295.00	0.980 32	0.000 45
0.9700	291.71	0.17	297.50	0.987 91	0.000 29
0.9800	294.89	0.17	300.00	0.995 32	0.000 28
0.9900	298.20	0.17			

[a]Expanded uncertainties U at the 0.95 level of confidence (coverage factor 2) were calculated with the equations given in Table S1, derived as described in Supplement 2C.
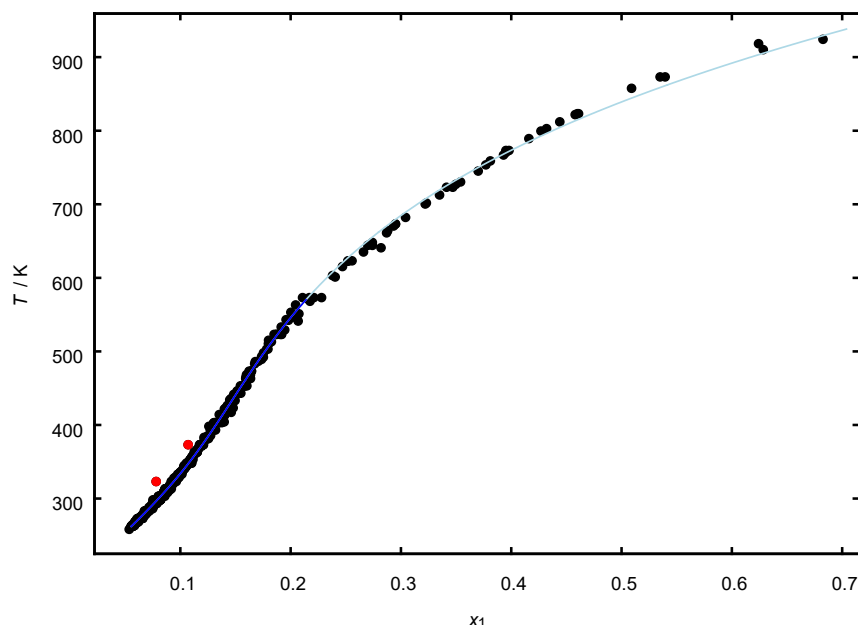
Fig. 3: Experimental mole-fraction solubility data for potassium chloride (1) in water (2) cited in Refs. [31, 32] (excluding rejected points) as well as all additional data from Supplement 2F (dots) vs the SDS eq. (11) with the parameters from Table 5 (line: dark blue — within the temperature range accepted for the purpose of this report as indicated in Table 5, light blue — outside of that temperature range). Two deviating points from additional sources [33, 34] are highlighted in red.

diagram, although hydrate formation is reported in the vicinity of the eutectic point [31, 32]. Sodium chloride forms a hydrate below 273.15 K, and the anhydrous salt solubility is nearly independent of temperature near room temperature. For this category, only anhydrous salt solubilities were considered. In addition, since molality units are commonly used for electrolytes, the tables with recommended solubilities also contain this composition expression for convenience.

3.1 Potassium chloride + water system

The solubility of potassium chloride in water was discussed in SDS-47 [31] (hereafter, the abbreviation SDS-X-Y is used for "*Solubility Data Series*, Volume X, Part Y"; if Volume X does not have separate parts, its abbreviation is contracted to SDS-X) and in Krumgalz's review [32]. Additional data sources available from the NIST/TRC Source database [8] (Supplement 2F) do not affect their evaluations, since they are consistent with the previous data except for two points from Refs. [33, 34]. The experimental data cited in Refs. [31, 32] (excluding the points consistently rejected in both reviews) as well as all additional data from Supplement 2F are shown in Figure 3.

The two solubility evaluations [31, 32] are comparable, but the SDS one was selected here due to its better performance at lower temperatures, which is of interest for the current project. Interested readers are referred to the supporting information spreadsheet file from Ref. [32] for the plot showing deviations of available literature data from Krumgalz's evaluation. The mole-fraction solubility of potassium chloride in water between 262 and 1044 K was smoothed in Ref. [31] by the following equation:

$$2\ln\left[2x_1/(1+x_1)\right] = 2\ln\left[2m_1/\left(M_2^{-1}+2m_1\right)\right] = A\left(T/\mathrm{K}\right)^{-1} + B\ln\left(T/\mathrm{K}\right) + C\left(T/\mathrm{K}\right) + D + J\left(T/\mathrm{K}\right)^2, \qquad (11)$$

where A through J are the empirical fitting parameters; T is the temperature in K; x_1 is the mole fraction of the salt; m_1 is the molality of the salt in mol kg^{-1}; and M_2 is the molar mass of water in kg mol^{-1}. The equation parameters for the system are listed in Table 5.

Table 5: Parameters for eq. (11) for potassium chloride (1) + water (2) and sodium chloride (1) + water (2) for SLE calculations within the temperature range from T_{min} to T_{max} accepted for the purpose of this report.

System	A	B	C	D	J	T_{min}/K	T_{max}/K
Potassium chloride (1) + water (2) [31]	−7262.7	−36.0456	0.06294	208.489	$-1.532\,01 \times 10^{-5}$	262.505	570
Sodium chloride (1) + water (2)	4473.5	33.9515	−0.08580	−189.763	$3.920\,63 \times 10^{-5}$	273.15	635

It is clear from Figure 3 and Figure S5 in Supplement 2G that the SDS evaluation has a bias above 570 K. Accordingly, we restrict our recommendation in Table 5 to T/K ≤ 570. It is also suggested in Ref. [32] that an unstable form of KCl·xH$_2$O may be formed below 268 K. Though this claim is made in very few works, some care should be taken below 268 K to confirm the solid phase identity.

Smoothed solubility data calculated from the equation from Ref. [31] are given in Table 6. The eutectic point is at $T = 262.505$ K with calculated $x_1 = 0.0558$ as reported in Ref. [31]. The SDS-47 [31] relative uncertainty estimate for the whole temperature range was 2.5 %. Based on the scatter analysis (Figure S5), we estimated the uncertainties in Table 6 for both temperature and composition representations.

Table 6: Mole-fraction and molality solubility (x_1 and m_1, respectively) of potassium chloride (1) in water (2) evaluated by eq. (11) with the parameters from Table 5, with our estimation of uncertainties U (solid phase = crystalline potassium chloride in all cases; both composition and temperature representations are given for convenience).[a]

Temperature representation (*i.e.*, $T_{SLE} = f(x_1)$)				Composition representation (*i.e.*, $x_1 = f(T_{SLE})$)			
m_1/(mol kg^{-1})	x_1	T_{SLE}/K	$U(T_{SLE})$/K	T_{SLE}/K	m_1/(mol kg^{-1})	x_1	$U(x_1)$
3.293	0.0560	262.84	0.86	265.00	3.384	0.0575	0.0011
3.543	0.0600	268.78	0.80	270.00	3.595	0.0608	0.0010
3.796	0.0640	274.76	0.75	275.00	3.806	0.064 16	0.000 95
4.050	0.0680	280.81	0.70	280.00	4.016	0.067 47	0.000 89
4.307	0.0720	286.95	0.65	285.00	4.225	0.070 74	0.000 84
4.566	0.0760	293.20	0.61	290.00	4.433	0.073 96	0.000 81
4.827	0.0800	299.58	0.58	295.00	4.640	0.077 14	0.000 79
5.090	0.0840	306.10	0.55	300.00	4.844	0.080 26	0.000 78
5.356	0.0880	312.78	0.54	305.00	5.046	0.083 33	0.000 79
5.624	0.0920	319.64	0.54	310.00	5.246	0.086 35	0.000 82
5.895	0.0960	326.68	0.55	315.00	5.443	0.089 31	0.000 86
6.168	0.1000	333.93	0.57	320.00	5.638	0.092 21	0.000 91
6.443	0.1040	341.38	0.60	325.00	5.831	0.095 06	0.000 97
6.721	0.1080	349.06	0.64	330.00	6.020	0.0978	0.0010
7.001	0.1120	356.95	0.69	335.00	6.208	0.1006	0.0011
7.284	0.1160	365.07	0.74	340.00	6.392	0.1033	0.0012
7.569	0.1200	373.40	0.79	345.00	6.575	0.1059	0.0013
7.857	0.1240	381.94	0.85	350.00	6.755	0.1085	0.0014
8.148	0.1280	390.66	0.92	355.00	6.932	0.1110	0.0015
8.442	0.1320	399.55	0.98	360.00	7.108	0.1135	0.0016
8.738	0.1360	408.6	1.0	365.00	7.282	0.1160	0.0017
9.036	0.1400	417.7	1.1	370.00	7.453	0.1184	0.0018
9.338	0.1440	426.9	1.2	375.00	7.624	0.1208	0.0019
9.642	0.1480	436.1	1.3	380.00	7.792	0.1231	0.0020
9.950	0.1520	445.3	1.3	385.00	7.960	0.1254	0.0021
10.26	0.1560	454.4	1.4	390.00	8.126	0.1277	0.0022
10.57	0.1600	463.5	1.5	395.00	8.292	0.1300	0.0023
10.89	0.1640	472.5	1.5	400.00	8.456	0.1322	0.0024
11.21	0.1680	481.3	1.6	405.00	8.621	0.1344	0.0025
11.53	0.1720	490.0	1.7	410.00	8.784	0.1366	0.0026
11.86	0.1760	498.5	1.8	415.00	8.948	0.1388	0.0027

Table 6: (continued)

Temperature representation (*i.e.*, $T_{SLE} = f(x_1)$)				Composition representation (*i.e.*, $x_1 = f(T_{SLE})$)			
$m_1/(\text{mol kg}^{-1})$	x_1	T_{SLE}/K	$U(T_{SLE})/K$	T_{SLE}/K	$m_1/(\text{mol kg}^{-1})$	x_1	$U(x_1)$
12.18	0.1800	506.9	1.8	420.00	9.112	0.1410	0.0028
12.52	0.1840	515.0	1.9	425.00	9.276	0.1432	0.0029
12.85	0.1880	523.0	2.0	430.00	9.441	0.1454	0.0030
13.19	0.1920	530.8	2.1	435.00	9.606	0.1475	0.0032
13.53	0.1960	538.4	2.1	440.00	9.773	0.1497	0.0033
13.88	0.2000	545.8	2.2	445.00	9.940	0.1519	0.0034
14.23	0.2040	553.0	2.3	450.00	10.11	0.1541	0.0035
14.58	0.2080	560.1	2.4	455.00	10.28	0.1562	0.0036
14.93	0.2120	566.9	2.5	460.00	10.45	0.1584	0.0037
				465.00	10.63	0.1607	0.0038
				470.00	10.80	0.1629	0.0039
				475.00	10.98	0.1651	0.0040
				480.00	11.16	0.1674	0.0041
				485.00	11.34	0.1697	0.0043
				490.00	11.53	0.1720	0.0044
				495.00	11.72	0.1743	0.0045
				500.00	11.91	0.1767	0.0046
				505.00	12.11	0.1791	0.0047
				510.00	12.31	0.1815	0.0048
				515.00	12.52	0.1840	0.0049
				520.00	12.72	0.1865	0.0050
				525.00	12.94	0.1890	0.0051
				530.00	13.16	0.1916	0.0052
				535.00	13.38	0.1942	0.0054
				540.00	13.61	0.1969	0.0055
				545.00	13.84	0.1996	0.0056
				550.00	14.08	0.2023	0.0057
				555.00	14.32	0.2051	0.0058
				560.00	14.57	0.2080	0.0059
				565.00	14.83	0.2109	0.0060
				570.00	15.10	0.2138	0.0061

[a]Expanded uncertainties U at the 0.95 level of confidence (coverage factor 2) were calculated with the equations given in Table S1, derived as described in Supplement 2C.

Thermodynamic evaluation of potassium chloride + water that corroborated the solubility data by models consistent with other property data have been done by Pabalan and Pitzer [35] and Archer [36]. The most recent publication Ref. [37] cites those and re-applies the Pitzer model. We additionally verified the consistency of the solubility data with other measured thermodynamic properties with the Pitzer model using the parameters and procedures implemented in the PHREEQC program [38, 39] designed for aqueous geochemical calculations, as shown in Figure S6 in Supplement 2G. It should be noted that the comparison is limited to $T/K \leq 523$.

3.2 Sodium chloride + water system

The solubility of sodium chloride (1) in water (2) has been evaluated in NIST Technical Note 1387 [40], in SDS-47 [31], by Krumgalz [32], and discussed briefly by one of us [41]. The last included some key experimental details, such as the correct drying of solid sodium chloride, that are often overlooked. It should be noted that a hydrate NaCl·2H$_2$O is formed at $T < 273.15$ K: the peritectic point is $T = 273.15$ K and $x_1 = 0.0990$ according to SDS-47 [31]. However, it appears that there were not enough consistent experimental data to develop a
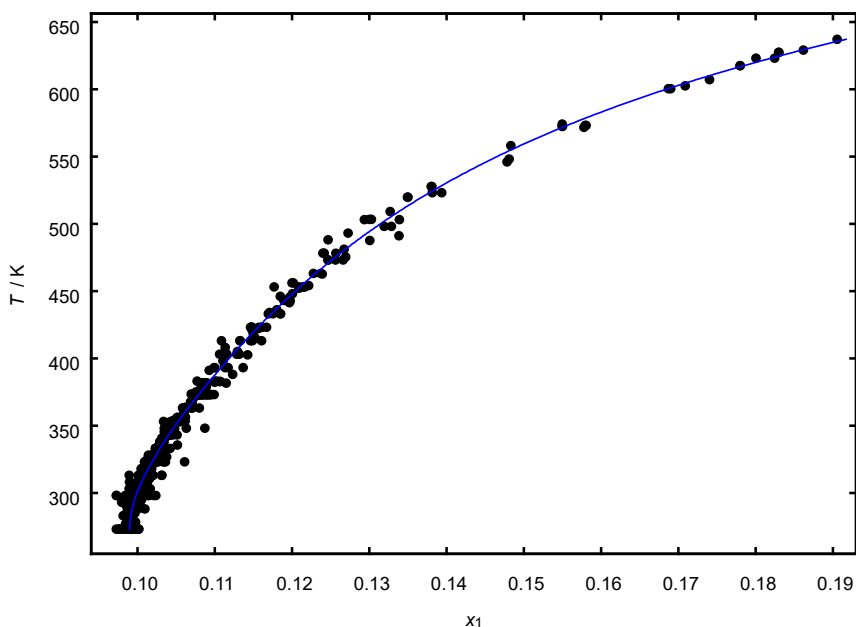
Fig. 4: Experimental mole-fraction solubility data for sodium chloride (1) in water (2) cited in Refs. [31, 32] (excluding rejected points) as well as all additional data from Supplement 2H (dots) vs the SDS-type eq. (11) with the parameters from Table 5 (blue line).

reliable solubility equation for the hydrate region, especially due to difficulties in handling NaCl·2H$_2$O. Consequently, we considered only the solubility profile for anhydrous sodium chloride (*i.e.*, above 273.15 K). Additional data sources available from the NIST/TRC Source database [8] for that phase diagram portion (Supplement 2H) are generally consistent with the previous data. The experimental data cited in Refs. [31, 32] (excluding the points consistently rejected in both reviews) as well as all additional data from Supplement 2H are shown in Figure S7 in Supplement 2H.

In contrast to the potassium chloride + water system, the two solubility evaluations [31, 32] are not fully consistent, especially at the low-temperature and high-temperature ends. Moreover, they both have some fitting issues leading to offsets relative to the available experimental data in some temperature regions. Interested readers are referred to the supporting information spreadsheet file from Ref. [32] for the plot showing deviations of available literature data from Krumgalz's evaluation. Since no similar deviation can be found for the SDS-47 evaluation in Ref. [31], the corresponding deviation plot is shown in Figure S8a in Supplement 2I. Consequently, we decided to refit equation (11) to the mole-fraction solubilities of anhydrous sodium chloride in water shown in Figure S7 but to limit the data to temperatures below the critical temperature of water (Figure 4) as the current report does not cover supercritical SLE measurements. Accordingly, we restrict our recommendations to $273 \le T/K \le 635$. The fitting was done by the least-squares method with enforcement of the peritectic-point coordinate from Ref. [31] within the uncertainty of the fit. The resulting parameters are listed in Table 5. The performance of the evaluation relative to the available experimental data is shown in Figure 4 and Figure S8 in Supplement 2I.

The thus-calculated smoothed solubility data are given in Table 7. Because of a steep temperature rise with increasing concentration of sodium chloride, the representation of the SLE temperature as a function of the mole-fraction solubility would not be practical and so is not provided. Based on the scatter analysis (Figure S8), we estimated the uncertainties in Table 7 for the composition representation.

Thermodynamic evaluations of sodium chloride + water that corroborated the solubility data by models consistent with other property data have been done by Pitzer et al. [42], Archer [43], and Krumgalz [32]. We additionally verified the consistency of the solubility data with other measured thermodynamic properties with the Pitzer model using the parameters and procedures implemented in the PHREEQC program [38, 39], as shown in Figure S9 in Supplement 2I. It should be noted that the comparison is limited to $T/K \le 523$. In contrast to the present model, the Krumgalz polynomial equation [32] and the Pitzer model from PHREEQC [38, 39] show a minimum-solubility temperature around 285 K, which may be a fitting artifact that cannot be reliably proven because of the experimental data scatter in that temperature region.

Table 7: Mole-fraction and molality solubility (x_1 and m_1, respectively) of sodium chloride (1) in water (2) evaluated by eq. (11) with the parameters from Table 5 (solid phase = crystalline sodium chloride in all cases).[a]

T_{SLE}/K	m_1/(mol kg^{-1})	x_1	$U(x_1)$
275.00	6.099	0.098 99	0.000 94
280.00	6.103	0.099 05	0.000 89
285.00	6.111	0.099 18	0.000 84
290.00	6.125	0.099 37	0.000 80
295.00	6.142	0.099 63	0.000 76
300.00	6.163	0.099 93	0.000 72
305.00	6.187	0.100 28	0.000 70
310.00	6.214	0.100 67	0.000 68
315.00	6.243	0.101 10	0.000 67
320.00	6.275	0.101 56	0.000 66
325.00	6.308	0.102 05	0.000 67
330.00	6.344	0.102 57	0.000 68
335.00	6.382	0.103 11	0.000 70
340.00	6.421	0.103 68	0.000 73
345.00	6.461	0.104 26	0.000 77
350.00	6.503	0.104 87	0.000 81
355.00	6.547	0.105 50	0.000 85
360.00	6.592	0.106 14	0.000 90
365.00	6.637	0.106 80	0.000 95
370.00	6.684	0.1075	0.0010
375.00	6.733	0.1082	0.0011
380.00	6.782	0.1089	0.0011
385.00	6.832	0.1096	0.0012
390.00	6.884	0.1103	0.0012
395.00	6.936	0.1111	0.0013
400.00	6.990	0.1118	0.0014
405.00	7.045	0.1126	0.0014
410.00	7.101	0.1134	0.0015
415.00	7.159	0.1142	0.0016
420.00	7.217	0.1151	0.0016
425.00	7.277	0.1159	0.0017
430.00	7.339	0.1168	0.0018
435.00	7.402	0.1177	0.0019
440.00	7.466	0.1186	0.0019
445.00	7.532	0.1195	0.0020
450.00	7.600	0.1204	0.0021
455.00	7.670	0.1214	0.0021
460.00	7.742	0.1224	0.0022
465.00	7.815	0.1234	0.0023
470.00	7.891	0.1245	0.0024
475.00	7.970	0.1255	0.0024
480.00	8.050	0.1267	0.0025
485.00	8.133	0.1278	0.0026
490.00	8.219	0.1290	0.0026
495.00	8.308	0.1302	0.0027
500.00	8.400	0.1314	0.0028
505.00	8.495	0.1327	0.0029
510.00	8.593	0.1341	0.0029
515.00	8.696	0.1354	0.0030
520.00	8.801	0.1369	0.0031
525.00	8.911	0.1383	0.0032
530.00	9.026	0.1399	0.0032
535.00	9.144	0.1414	0.0033
540.00	9.268	0.1431	0.0034

Table 7: (continued)

T_{SLE}/K	$m_1/(mol\ kg^{-1})$	x_1	$U(x_1)$
545.00	9.396	0.1448	0.0035
550.00	9.530	0.1465	0.0035
555.00	9.670	0.1484	0.0036
560.00	9.815	0.1503	0.0037
565.00	9.967	0.1522	0.0037
570.00	10.13	0.1543	0.0038
575.00	10.29	0.1564	0.0039
580.00	10.46	0.1586	0.0040
585.00	10.65	0.1609	0.0040
590.00	10.84	0.1633	0.0041
595.00	11.03	0.1658	0.0042
600.00	11.24	0.1684	0.0043
605.00	11.46	0.1711	0.0043
610.00	11.69	0.1740	0.0044
615.00	11.93	0.1769	0.0045
620.00	12.19	0.1800	0.0046
625.00	12.45	0.1832	0.0046
630.00	12.74	0.1866	0.0047
635.00	13.03	0.1901	0.0048

[a]Expanded uncertainties U at the 0.95 level of confidence (coverage factor 2) were calculated with the equations given in Table S1, derived as described in Supplement 2C.

It should be also noted that the solubility equations provided in Refs. [31, 32] for the hydrate region of the NaCl + water phase diagram are fairly consistent (the maximum difference in mole-fraction compositions reaches 0.7 %), so researchers interested in working with salt hydrates at sub-zero temperatures can use any of them, but we believe that we do not have sufficient information at the present time to recommend that region for method testing.

3.3 Additional note: reserve system

The solubility of ammonium chloride in water was discussed in SDS-47 [31] and assessed in Ref. [44]. The system ammonium chloride + water may be used as a reserve test mixture for SLE measurements. Additional data sources for it are listed in Supplement 2J.

4 Category 3: non-aqueous systems

The most studied SLE data sets for non-aqueous systems belong to aromatic hydrocarbons.

4.1 Naphthalene (bicyclo[4.4.0]deca-1,3,5,7,9-pentaene) + toluene (methylbenzene) system

One of the best studied organic systems with consistent data is naphthalene + benzene [45], which unfortunately was excluded from consideration in the current project due to the toxicity of benzene and restrictions on its use. A similar but less toxic system is naphthalene + toluene discussed in SDS-59 [45] and SDS-98-3 [46]. Two additional sources [47, 48] were not mentioned in those reviews. The selected literature sources associated with the SLE data for this system are listed in Supplement 2K. The experimental SLE data are generally consistent; only two points from Ref. [17] deviate noticeably from the other data (Figure 5).
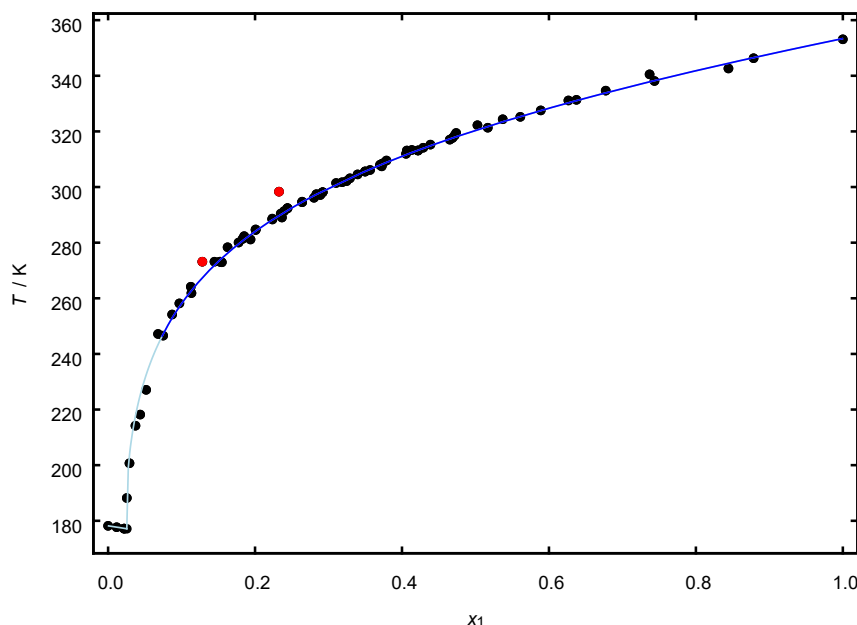
Fig. 5: Experimental mole-fraction SLE data (dots) for naphthalene (1) + toluene (2) vs the NRTL evaluation with the parameters from Table 8 (line: dark blue — within the temperature range accepted for the purpose of this report as indicated in the text, light blue — outside of that temperature range). Two rejected points from Ref. [17] are shown as red dots.

The selected SLE data were smoothed with the NRTL model given by eqs. (1)–(5) with the use of the ThermoData Engine software [8]. Since there is only one experimental work at $T < 247$ K, naphthalene solubilities below that temperature were not included in the fit. The parameters of the resulting NRTL fit for naphthalene (1) + toluene (2) are presented in Table 8. This table also contains the melting parameters for both mixture components used in the modeling. For naphthalene, the melting parameters were adopted from Ref. [49] (note: the selected melting temperature and the enthalpy of fusion are in excellent agreement with the recommendations of Ref. [50]); for toluene, they were taken from Ref. [51]. Since T_{tp}, $\Delta_{fus}H_m$, and $\Delta_{fus}C_{p,m}$ were assigned fixed values during the NRTL fitting, any inaccuracy in them was absorbed by the fitting parameters α, A_i, and B_i, so their uncertainties were not needed for the purposes of the present project and thus were not evaluated.

The performance of the NRTL model relative to the selected experimental data is shown in Figure 5 and as deviation plots in Supplement 2L. Although the present model was developed using only the SLE data, available experimental VLE pressures for this system (shown in Supplement 2L) are in good agreement with it, which can serve as additional verification for the selected SLE data and model. Since naphthalene + aromatic hydrocarbon systems are in general nearly ideal, an additional verification became possible, namely a comparison of the naphthalene solubility profiles in the homologous solvent series: benzene, toluene, and ethylbenzene. The comparison over the range of validity of the developed NRTL model is shown in Figure S12 in Supplement 2L, where all the experimental data for the three mixtures are in excellent agreement.

Smoothed solubility data are given in Table 9. The coordinates of the eutectic point cannot be reliably found from the developed NRTL model, since the fit was limited to temperatures above 247 K, as discussed above.

Table 8: Parameters for the NRTL model for naphthalene (1) + toluene (2) for SLE calculations.

Component *i*	Parameters of eq. (2)					Melting parameters for eq. (3)		
	A_i	B_i	C_i	D_i	α	T_{tp}/K	$\Delta_{fus}H_m$/(kJ mol^{-1})	$\Delta_{fus}C_{p,m}$/(J K^{-1} mol^{-1})
Component 1 (naphthalene)	−3.115 53	1309.5	0	0	0.285 777	353.37	18.993	13.1
Component 2 (toluene)	2.282 92	−919.353	0	0		178.19	6.636	45.9

Table 9: Smoothed mole fractions of naphthalene (x_1) vs SLE temperatures (T_{SLE}) for the naphthalene (1) + toluene (2) system obtained with the NRTL model using the parameters given in Table 8 (both composition and temperature representations are given for convenience, solid phase = naphthalene in all cases).[a]

Temperature representation (*i.e.*, $T_{SLE} = f(x_1)$)			Composition representation (*i.e.*, $x_1 = f(T_{SLE})$)		
x_1	T_{SLE}/K	$U(T_{SLE})/K$	T_{SLE}/K	x_1	$U(x_1)$
0.0750	247.18	0.61	250.00	0.0807	0.0068
0.1000	258.09	0.59	255.00	0.0921	0.0065
0.1250	266.43	0.57	260.00	0.1052	0.0061
0.1500	273.23	0.56	265.00	0.1203	0.0058
0.1750	278.99	0.54	270.00	0.1376	0.0055
0.2000	284.01	0.52	275.00	0.1573	0.0051
0.2250	288.47	0.51	280.00	0.1798	0.0048
0.2500	292.50	0.49	285.00	0.2053	0.0045
0.2750	296.17	0.48	290.00	0.2342	0.0042
0.3000	299.56	0.46	295.00	0.2668	0.0039
0.3250	302.71	0.44	300.00	0.3034	0.0036
0.3500	305.65	0.43	305.00	0.3443	0.0033
0.3750	308.43	0.41	310.00	0.3898	0.0030
0.4000	311.05	0.39	315.00	0.4403	0.0028
0.4250	313.54	0.38	320.00	0.4958	0.0025
0.4500	315.91	0.36	325.00	0.5566	0.0023
0.4750	318.18	0.35	330.00	0.6227	0.0022
0.5000	320.36	0.33	335.00	0.6942	0.0020
0.5500	324.48	0.30	340.00	0.7710	0.0020
0.6000	328.33	0.27	345.00	0.8528	0.0020
0.6500	331.95	0.24	350.00	0.9393	0.0020
0.7000	335.39	0.21			
0.7500	338.67	0.19			
0.8000	341.81	0.17			
0.8500	344.83	0.15			
0.9000	347.76	0.14			
0.9500	350.60	0.14			

[a]Expanded uncertainties U at the 0.95 level of confidence (coverage factor 2) were calculated with the equations given in Table S1, derived as described in Supplement 2C.
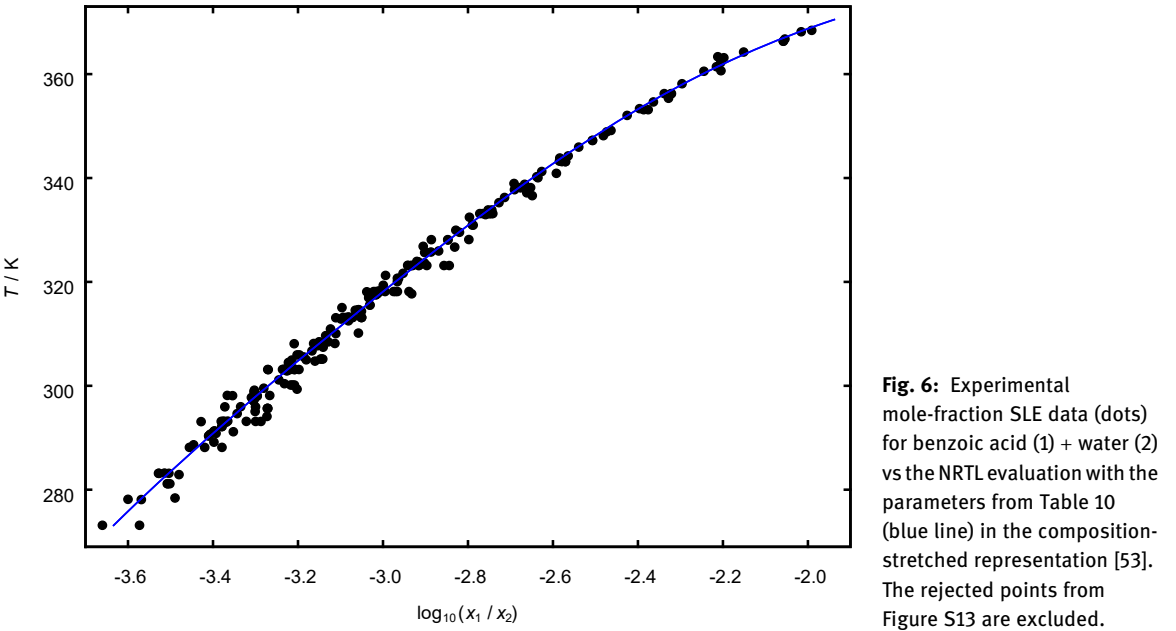
4.2 Additional note: reserve systems

Reserve non-aqueous systems can be naphthalene + tetrachloromethane, discussed in SDS-59 [45] and SDS-98-3 [46], and benzoic acid + cyclohexane, discussed in SDS-99 [52] with additional data sources listed in Supplement 2M.

5 Category 4: systems with low solubility

5.1 Benzoic acid (benzenecarboxylic acid) + water system

A convenient and well-studied system is benzoic acid + water. The available experimental SLE and LLE data are listed in Supplement 2N. Both SLE and LLE data (the latter can apparently be supercooled) are shown in Figure S13 in Supplement 2N, where all rejected points are identified. Only the side corresponding to the low solubility of benzoic acid in water was considered for this category (Figure 6, given in the composition-stretched representation [53] for convenience) – from the eutectic temperature to the monotectic point.

Fig. 6: Experimental mole-fraction SLE data (dots) for benzoic acid (1) + water (2) vs the NRTL evaluation with the parameters from Table 10 (blue line) in the composition-stretched representation [53]. The rejected points from Figure S13 are excluded.

The selected SLE data have been smoothed with the NRTL model given by eqs. (1)–(5) with the use of the ThermoData Engine software [8]. The parameters of the resulting NRTL fit for benzoic acid (1) + water (2) are presented in Table 10. The table also contains the melting parameters for both mixture components used in the modeling. For water, these parameters were as described in the urea + water section. For benzoic acid, the melting temperature and enthalpy of fusion were taken from the recommendations in [50], which are based on a precise experimental work [54]; the $\Delta_{fus}C_{p,m}$ value was taken as the average of two values obtained by adiabatic calorimetry in the vicinity of the melting point [55, 56]. Since T_{tp}, $\Delta_{fus}H_m$, and $\Delta_{fus}C_{p,m}$ were assigned fixed values during the NRTL fitting, any inaccuracy in them was absorbed by the fitting parameters α and A_i through D_i, so their uncertainties were not needed for the purposes of the present project and thus were not evaluated.

Smoothed solubility data are given in Table 11. Because of a steep temperature rise with increasing concentrations of benzoic acid, the representation of the SLE temperature as a function of the mole-fraction solubility would not be practical and, hence, is not provided. The eutectic and monotectic points evaluated from the model are as follows: $T = (273.137 \pm 0.005)$ K and $x_1 = 0.000\,232 \pm 0.000\,010$; $T = (370.5 \pm 2.0)$ K and $x_1(\text{side 1}) = 0.011 \pm 0.002$ and $x_1(\text{side 2}) = 0.37 \pm 0.06$, respectively (with expanded uncertainties at the 0.95 level of confidence, coverage factor 2). Note that extra care should be taken regarding the solubilities at high temperatures, since LLE in benzoic acid + water can be supercooled below the monotectic temperature, according to several sources listed in Supplement 2N.

The performance of the NRTL model relative to the selected experimental data is shown in Figure 6 and as a deviation plot (Figure S14) in Supplement 2O. Although the NRTL model was developed using only the SLE data, it predicts the existence and position of the LLE reasonably well, as shown in Figure S15 in Supplement 2O, which can serve as additional verification for the selected SLE data and model.

Table 10: Parameters for the NRTL model for benzoic acid (1) + water (2) for SLE calculations.

Component i	Parameters of eq. (2)					Melting parameters for eq. (3)		
	A_i	B_i	C_i	D_i	α	T_{tp}/K	$\Delta_{fus}H_m$/ (kJ mol^{-1})	$\Delta_{fus}C_{p,m}$/ (J K^{-1} mol^{-1})
Component 1 (benzoic acid)	37.1725	−3714.19	0	−0.062 770 7	0.477 312	395.50	18.063	58.3
Component 2 (water)	−2.630 81	5623.50	0	−0.029 378 7		273.16	6.007	38.2

Table 11: Smoothed mole fractions of benzoic acid (x_1) vs SLE temperatures (T_{SLE}) for the benzoic acid (1) + water (2) system obtained with the NRTL model using the parameters given in Table 10 (solid phase = benzoic acid).[a]

T_{SLE}/K	x_1	$U(x_1)$	$U(x_1)/x_1$
273.15	0.000 232	0.000 009	0.04
275.00	0.000 245	0.000 010	0.04
280.00	0.000 284	0.000 010	0.04
285.00	0.000 331	0.000 011	0.03
290.00	0.000 387	0.000 011	0.03
295.00	0.000 455	0.000 012	0.03
300.00	0.000 537	0.000 012	0.02
305.00	0.000 635	0.000 013	0.02
310.00	0.000 753	0.000 014	0.02
315.00	0.000 895	0.000 017	0.02
320.00	0.001 067	0.000 020	0.02
325.00	0.001 276	0.000 025	0.02
330.00	0.001 531	0.000 033	0.02
335.00	0.001 847	0.000 045	0.02
340.00	0.002 242	0.000 061	0.03
345.00	0.002 748	0.000 083	0.03
350.00	0.003 41	0.000 11	0.03
355.00	0.004 32	0.000 16	0.04
360.00	0.005 61	0.000 23	0.04
365.00	0.007 59	0.000 34	0.04
370.00	0.010 94	0.000 53	0.05

[a]Expanded uncertainties U at the 0.95 level of confidence (coverage factor 2) were calculated with the equations given in Table S1, derived as described in Supplement 2C.

5.2 Naphthalene (bicyclo[4.4.0]deca-1,3,5,7,9-pentaene) + water system

Another well-studied system featuring low solubilities is naphthalene + water. The solubilities for this system have been compiled and critically evaluated in SDS-81-9 [57]. The available literature sources associated with the SLE data for this system are listed in Supplement 2P. Fourteen sources in addition to those cited in SDS-81-9 have been included in the list. Because of these additions, it was decided to update the solubility equation. Most of the experimental SLE data are in fair agreement with each other, except for seven values from Refs. [58–63], which look obviously erroneous (Figure 7) and thus were rejected.
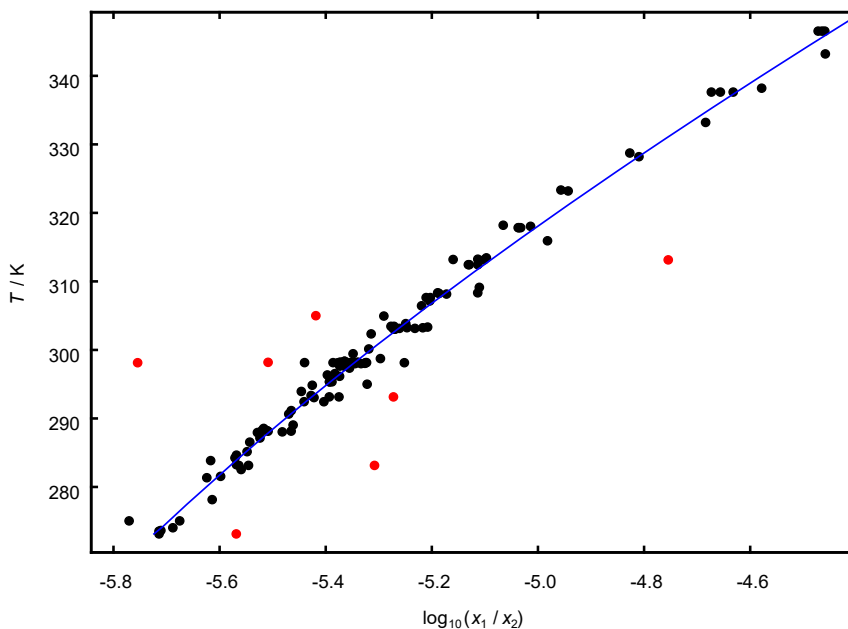

Fig. 7: Experimental mole-fraction SLE data (dots) for naphthalene (1) + water (2) vs the smoothing eq. (12) (blue line) in the composition-stretched representation [53]. Rejected data from [58–63] are highlighted in red.

Table 12: Smoothed mole fractions of naphthalene (x_1) vs SLE temperatures (T_{SLE}) for the naphthalene (1) + water (2) system obtained with eq. (12) (solid phase = naphthalene).[a]

T_{SLE}/K	$10^6 \, x_1$	$10^6 \, U(x_1)$	$U(x_1)/x_1$
273.15	1.889	0.089	0.05
275.00	2.003	0.089	0.04
280.00	2.356	0.090	0.04
285.00	2.789	0.091	0.03
290.00	3.324	0.092	0.03
295.00	3.987	0.097	0.02
300.00	4.81	0.11	0.02
305.00	5.84	0.14	0.02
310.00	7.12	0.20	0.03
315.00	8.74	0.29	0.03
320.00	10.77	0.41	0.04
325.00	13.36	0.60	0.04
330.00	16.64	0.86	0.05
335.00	20.8	1.2	0.06
340.00	26.2	1.7	0.07
345.00	33.1	2.4	0.07
350.00	42.0	3.4	0.08

[a]Expanded uncertainties U at the 0.95 level of confidence (coverage factor 2) were calculated with the equations given in Table S1, derived as described in Supplement 2C.

The mole-fraction solubility data of naphthalene (x_1) in water were smoothed by the least-squares method with the following empirical equation:

$$\ln(x_1) = -44.39 + 0.107\,58\,(T/K) - 20.84 \ln(T/298.15\,K), \tag{12}$$

where T is the temperature in K; x_1 is the mole fraction of the solute. This equation is valid from 273.15 to 350 K.

The performance of the evaluation relative to the available experimental data is shown in Figure 7 and Figure S16 in Supplement 2P. It should be noted that the current evaluation by eq. (12) is generally consistent with that of SDS-81-9 [57] – the relative difference is not more than 6 %, which is within the claimed uncertainties.

Smoothed solubility data are given in Table 12. Due to the extremely small solubility, the representation of the SLE temperature as a function of the mole-fraction solubility would not be practical and, hence, is not provided. Since the solubility of naphthalene in water is very small, the eutectic temperature cannot significantly depart from the melting temperature of pure water and was estimated to be $T = (273.15 \pm 0.01)$ K. The eutectic composition thus derived from eq. (12) is $x_1 = (1.89 \pm 0.09) \times 10^{-6}$. The uncertainties are expanded uncertainties at the 0.95 level of confidence (coverage factor 2).

5.3 Additional notes: excluded system and reserve systems

We considered including the anthracene + water system as a reserve system due to its extremely low solubility and the large number of fairly consistent measurements available. The solubilities for this system have been compiled and critically evaluated in SDS-81-11 [64]. The available literature sources associated with the SLE data for this system are collected in Supplement 2Q and are shown in Figure S17. Unfortunately, two distinct clusters of the SLE data are apparent. A possible explanation is the presence of phenanthrene as an impurity in commercial anthracene [65]. Phenanthrene is about 20 times more soluble in water than in anthracene [64], and it forms a solid solution with anthracene [66], which potentially explains the higher solubilities reported in some works. However, the absence of detailed information about the sample purities precludes a definite conclusion.

Other reserve test systems for this category of solubility data could be water + 2-hydroxybenzoic acid (SDS-90-1 [67]) and water + 4-hydroxybenzoic acid (SDS-90-1 [67]). However, special care should be taken with the solubilities of such systems, since hydroxybenzoic acids may form metastable LLE with water [68–70].

6 Summary

Reference binary mixtures from the four most common categories of binary mixtures—aqueous systems with organic solutes, aqueous systems with inorganic solutes, non-aqueous systems, and systems with low solubility—have been proposed for testing and verification of experimental methods and equipment for measurements of solid–liquid equilibria (SLE). The available literature sources, accepted solubility data, covered experimental condition ranges, smoothing equations, estimated uncertainties, and identified precautions are provided for each mixture in the report. Supplementary materials provide lists of citations and additional verification of the selected data and smoothing equations. All of the proposed data cover ambient conditions (of temperature and pressure) and have system-specific extensions (down to 260 K and up to 635 K in temperature and up to the vapor-saturation pressure). The systems are as follows:

- urea + water (Tables 1 and 2),
- potassium chloride + water (Tables 5 and 6),
- sodium chloride + water (Tables 5 and 7),
- naphthalene + toluene (Tables 8 and 9),
- benzoic acid + water (Tables 10 and 11),
- naphthalene + water (eq. (12) and Table 12).

One reserve system, sulfolane + water, was analyzed by us (Tables 3 and 4) and included into the report due to its phase behavior, which is valuable for instrument verification (presence of two consecutive stable crystalline modifications of sulfolane and ability to supercool), but this evaluation should be treated as tentative. This report also identifies a few other reserve systems that have been well studied in the literature but not evaluated by us; interested researchers may access the existing evaluations and/or original works cited in the report to make their own comparisons.

To facilitate the use of the smoothing equations from this report, a free online calculator has been developed and made available for each selected system at https://trc.nist.gov/reference-systems.

Systems for testing and verification of an experimental method should be chosen from the above list on the basis of the specifics of the technique and planned applications. The proposed systems are explicitly selected to be systems with simple phase behavior possessing minimal experimental complications to facilitate the testing procedure, and they do not cover all possible scenarios in SLE measurements. Researchers interested in more complex cases and needing more information about potential complications in SLE measurements in general are referred to publications mentioned in the Introduction.

7 Supporting materials

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

List of symbols

α	non-randomness parameter in the NRTL model
γ_i	activity coefficient of component i
$\Delta_{\mathrm{fus}}C_{p,\mathrm{m},i}$	isobaric molar heat-capacity difference (liquid – crystal) for component i
$\Delta_{\mathrm{fus}}H_{\mathrm{m},i}$	molar enthalpy of fusion of component i

$\Delta_{trs}C_{p,m,i}$	isobaric molar heat-capacity difference (crystal I − crystal II) for component i
$\Delta_{trs}H_{m,i}$	molar enthalpy of the solid-phase transition from crystal II to crystal I of component i
G^E	excess molar Gibbs energy
m_i	molality of component i
M_i	molar mass of component i
R	molar gas constant
T	thermodynamic temperature
T_{SLE}	SLE temperature (*i.e.*, temperature corresponding to the liquidus phase boundary)
$T_{tp,i}$	triple-point temperature (crystal + liquid + gas) for component i
$T_{tp(crII-crI),i}$	triple-point temperature (crystal II + crystal I + gas) for component i
U	expanded uncertainty at the specified level of confidence and corresponding coverage factor
x_i	mole fraction of component i

List of abbreviations and acronyms

cr	crystal
crI	crystal I (high-temperature crystalline phase)
crII	crystal II (low-temperature crystalline phase)
IAPWS	International Association for the Properties of Water and Steam
IUPAC	International Union of Pure and Applied Chemistry
liq	liquid
LLE	Liquid–liquid equilibrium
NIST	National Institute of Standards and Technology
NRTL model	Non-random two-liquid model
SDS	Solubility Data Series
SLE	Solid–liquid equilibrium
SRD	Standard Reference Database
TRC	Thermodynamics Research Center
VLE	Vapor–liquid equilibrium

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