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LLE DATA CORRELATION USING NRTL MODEL FOR DIFFERENT TYPES OF BINARY SYSTEMS: UCST, LCST AND CLOSED MISCIBILITY LOOPS

María del Mar Olaya^{1,2*}, Paloma Carbonell-Hermida¹, Marina Trives², Juan A. Labarta^{1,2}, Antonio Marcilla^{1,2}

¹ Institute of Chemical Process Engineering, University of Alicante, 03080, Alicante, Spain

² Department of Chemical Engineering, University of Alicante, Apdo. 99, 03080 Alicante, Spain.

Abstract

In this work, LLE data at different temperatures have been correlated for 30 binary systems that presented different miscibility behaviour: 15 upper critical solution temperature (UCST), 5 critical solution temperature (LCST) and 10 closed loop LLE region systems. The NRTL model along with an expression frequently used in literature for the temperature dependence in the binary interaction has allowed an acceptable fitting of all the systems. The parameters obtained have been validated by both the inspection of the Gibbs energy of mixing function regarding the fulfilment of the Gibbs common tangent equilibrium condition, and also the stability of the solution to avoid possible metastable equilibrium solutions. The critical solution temperatures have been calculated by extrapolation using the NRTL parameters obtained for all selected binary systems. Moreover, the NRTL parameter values have been analysed using some proposed representations that also include the boundary curve between miscible (L) and partially miscible (LLE) regions. These graphical representations are useful because they show the parameter value requirements to reproduce UCST, LCST or closed loop behaviours.

Introduction

Modelling of liquid-liquid equilibrium (LLE) data is crucial for designing many chemical processes and separation operations as, for example, solvent extraction. In these cases, the variation of LLE with temperature is especially relevant. The limit of the two-phase region in the temperature vs composition phase diagram is named critical solution (or

* Corresponding author. E-mail address: maria.olaya@ua.es

consolute) temperature. In many cases binary mixtures present upper critical solution temperature (UCST) behaviour, with their mutual miscibility increasing with temperature, while some others show the opposite behaviour with presence of lower critical solution temperature (LCST). There are also some systems where both temperatures UCST and LCST are present. In these cases, the intermediate region may be miscible or immiscible, the latter case presenting a closed loop (or island) type phase diagram.

The existence of UCST behaviour is usually justified by intermolecular forces among molecules. The interpretation of the LCST is more difficult, but it is generally accepted that it occurs when an unfavourable entropy effect is present, that is, when negative entropy of mixing overcomes the negative enthalpies of mixing. The LCST is associated with large differences in thermal expansion of solvent and solute or in free-volume percentage as it occurs between polymer and solvent mixtures [1]. Thus, in general the presence of UCST is the most frequent case for binary mixtures of small (non-polymeric) molecules. The LCST occurs for some specific systems as those involving hydrogen bonding and in many polymer solutions, although UCST and closed miscibility loops can also be present in these mixtures.

Activity coefficient models and equations of state (EOS) have been widely used to model LLE for many systems. At moderate pressures activity coefficient models are preferable, while EOS are used very frequently at high pressures. It has been demonstrated that the original formulation of classic activity coefficient models such as NRTL [2] or UNIQUAC [3] present a very weak dependence on temperature [4]. Consequently, in these cases an adequate function of the binary interaction parameters of these models must be used to capture the dependence of LLE behaviour with temperature. However, it is quite common that different sets of model parameters are published in literature for each of the isothermal LLE data [5-8]. For instance, the LLE Data Collection (Binary Systems) by DECHEMA [9] includes the correlation with NRTL and UNIQUAC of the experimental LLE data sets collected, but no variation of the parameters with temperature is considered, thus providing different sets of parameters for each temperature. This methodology leads to parameter values with limited utility, for example for its direct use in process simulation packages such as Aspen Plus [10] or CHEMCAD [11].

Moreover, as far as we know, no study has been published discussing the application of the NRTL activity coefficient model, with temperature dependent parameters, to the different UCST, LCST and closed-loop LLE behaviours. Some discussion on this matter regarding other models has been published. For example, Radfarnia et al. [1] established that the most widely used lattice model for polymer solutions, the Flory–Huggins theory [12], cannot describe the lower critical solution temperature (LCST) behaviour. Many other papers have been dedicated to the experimental measurement and correlation of LLE data for polymer solutions. Radfarnia et al. [1] used a free-volume UNIQUAC-NRF model to correlate LLE data for some binary polymer solutions at various temperatures showing LCST behaviour. Jung and Bae [13] proposed an extended Redlick -Kister expansion to model LLE data of various polymer solutions including UCST, LCST, both UCST and LCST, and closed miscibility loops. Von Solms et al. [14] tested the PC-SAFT equation of state to predict and correlate LLE data in systems containing different polymer + solvent mixtures, both associating and non-associating. These systems exhibited upper, lower and both critical solution temperatures. Oh and Bae [15] discussed closed miscibility loop phase behaviour of polymer solutions and proposed a modified double lattice model for this type of system. Yang et al. [16-19] developed a new lattice model for polymer solutions by combining the molecular simulation with statistical mechanics to describe several types of phase diagrams such as UCST, LCST, and closed loop systems.

For non-polymeric mixtures, most papers deal exclusively with correlation of UCST type systems. Domańska et al. [20] studied the UCST LLE behaviour of ionic liquids with alcohols and hydrocarbons and they used the NRTL model, with a linear dependence of the model parameters with temperature, to correlate the experimental data. A similar procedure was used by Królikowska et al. [21] for the correlation of some (ionic liquid + water) binary systems with UCST. Maia et al. [22] also determined LLE data for some aqueous binary systems including ionic liquids and they correlated these data using NRTL and e-NRTL equations with quadratic temperature dependence, but again all these systems belong to UCST type. González et al. [23] provided the coexistence curves of LLE UCST type for mixtures containing aromatic nitriles and used DISQUAC group contribution model to calculate these data. The group contribution equation of state (GC-EoS) has been used to represent the LLE phase behaviour of UCST binary mixtures containing benzene + ionic liquid [24]. Harwood et al. [25] used a Monte Carlo method

to simulate the LLE behaviour for binary dodecane + ethanol mixtures at different total pressures from 0.1 to 100 MPa. The simulations qualitatively reproduced the increase in the UCST with increasing pressure, but the quantitative description presented substantial deviations. They concluded that simulation protocols including force fields must be improved for the description of liquid-liquid equilibria. In some other papers, LCST behaviour is considered. For example, Baudin et al. [26] studied the temperature-dependent phase behavior aqueous mixtures of industrial propylene glycol alkyl ethers (PGAEs) which present a LCST near room temperature. Khoshshima and Dehghani [27] used the PSHC EoS for modelling the VLE and LLE of glycol ether surfactant systems and determined the UCST for hydrocarbons + surfactant mixtures and LCST for water + surfactant mixtures.

Few papers have studied the LLE data correlation of binary systems with closed loop behaviour using different equations of state. For example, Herslund et al. [28] studied the application of the cubic-plus-association (CPA) equation of state to model the LLE behaviour of binary mixtures of water and tetrahydrofuran. Lee [29] used PHSC-AS equation of state for poly(ethylene oxide) aqueous solutions. Avlund et al. [30] applied sPC-SAFT for binary glycol ether-containing mixtures. NguyenHuynh et al. [31] used the PC-SAFT EoS for the prediction of LLE at high pressure based on LLE data at low pressure for 2-alkoxyethanol mixtures. Goldstein and Walker [32] studied and generalized within a high-temperature series expansion the lattice-gas models of phase separating liquid mixtures.

In this paper, the NRTL model with an empirical equation for the temperature dependence of the binary interaction parameters is used for the simultaneous correlation at different temperatures of LLE data sets for a number of binary systems presenting UCST, LCST and closed loop miscibility behaviour. From the correlation results, the critical solution temperatures have been calculated. An analysis of the requirements that should be fulfilled by the model parameters to provide each type of system has also been carried out.

Selected systems

In this paper, experimental LLE data of 30 binary systems were correlated considering temperature dependence of the binary interaction parameters of the NRTL equation.

Table 1 shows the selected binary systems from DECHEMA Chemistry Data Series [9]: 15 UCST, 5 LCST and 10 closed loop type systems. The mixtures are both aqueous and non-aqueous, and have been selected to cover a variety of temperatures and composition intervals for the LLE splitting region. In all cases, the components are non-polymeric molecules.

Correlation

LLE data correlation of the selected binary systems was carried out using the NRTL model. The equilibrium criterion based on isoactivity was used in the correlation, so the calculated concentrations must satisfy the following equation:

$$F(a) = \sum_{n=1}^{nd} \sum_{i=1}^2 \left((a_{i,n})_I - (a_{i,n})_{II} \right)^2 = 0 \quad (1)$$

where $a_{i,n}$ is the activity of the i -component in tie-line n ; I and II represent the two liquid phases in equilibrium and nd is the total number of tie-lines.

In order to correlate the equilibrium data for all temperatures in each system, temperature dependence was considered in the NRTL binary interaction parameters. A mathematical formulation similar to the one included in Aspen Plus [10] or CHEMCAD [11] was employed.

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T + d_{ij} T \quad (2)$$

where a_{ij} , b_{ij} , c_{ij} and d_{ij} are the fitting parameters and T is the temperature in K. When temperature dependence is used in the NRTL model, it can also include the non-randomness parameter α_{ij} (Eq.(3)).

$$\alpha_{ij} = e_{ij} + f_{ij}(T - 273.15) \quad (3)$$

However, the value of 0.2 [9] suggested for the LLE was used in all the correlations, so $e_{ij} = 0.2$ and $f_{ij} = 0$.

The model parameters were optimised using the GRG (Generalized Reduced Gradient) Nonlinear method to minimize the composition objective function defined in Eq. (4).

$$O.F.(x) = \min \sum_{n=1}^{nd} \sum_{i=1}^2 \left[\left((x_{i,n})_{\text{exp}} - (x_{i,n})_{\text{cal}} \right)_I^2 + \left((x_{i,n})_{\text{exp}} - (x_{i,n})_{\text{cal}} \right)_{II}^2 \right]$$

subject to $F(a) < \varepsilon$ (4)

where x_i is the mole fraction of the i -component; *exp* and *cal* are the experimental and calculated equilibrium data and ε is an extremely low tolerance value ($\varepsilon < 10^{-9}$) guaranteeing the fulfilment of the isoactivity equilibrium condition given by Eq.(1). Additionally, mass balances must be accomplished in each phase.

The mean deviation (%) between experimental (*exp*) and calculated (*cal*) LLE data have been obtained using Eq. (5):

$$\sigma = 100 \times \sqrt{\frac{\sum_{n=1}^{nd} \sum_{i=1}^2 \left[\left((x_{i,n})_{\text{exp}} - (x_{i,n})_{\text{cal}} \right)_I^2 + \left((x_{i,n})_{\text{exp}} - (x_{i,n})_{\text{cal}} \right)_{II}^2 \right]}{4 \cdot nd}} \quad (5)$$

Consistency of correlation

The correlation results for the 30 binary systems were checked using the Gibbs common tangent criterion along with the Gibbs stability test in order to guarantee the consistency of the parameter sets obtained and discard any possible metastable solution. To that aim, the dimensionless Gibbs energy of mixing ($g^M = G^M/RT$) and the second derivative (d^2g^M/dx_1^2) were calculated and represented versus composition (mole fraction) and temperature in 3D-figures. The topological analysis of these 3D-figures consisted in: i) checking of the existence of tangent lines in the calculated LL compositions, which should not intersect the g^M function in any other composition at the same temperature, and ii) checking of the sign change (+/-) for the second derivative (d^2g^M/dx_1^2) that should be what is expected for each type of system. The visual inspection by rotation of these 3D-representations allowed the validation of the correlation results ensuring the consistency of the parameters obtained.

Critical solution temperature calculation

As shown in Figure 1, the second derivative of the dimensionless Gibbs energy of mixing (d^2g^M/dx_1^2) at different temperatures can be used in order to determine the UCST and LCST, or both, depending on the type of system. For a given temperature, d^2g^M/dx_1^2 is

positive over the whole composition range for homogenous systems. However, if the binary system presents two liquid phases in equilibrium at the selected temperature, this curve presents a negative region cutting the x axis (i.e. $d^2g^M/dx_1^2 = 0$) at two points. Thus, the transition temperature between the homogeneous and heterogeneous behavior is that causing the x-axis tangency of the d^2g^M/dx_1^2 vs x_1 curve, i.e. a single solution to the equation $d^2g^M/dx_1^2 = 0$. If according to Figure 1 is $T_3 < T_2 < T_1$, then T_2 is the most common case of UCST, while T_2 is a LCST for $T_1 < T_2 < T_3$. The calculations of the corresponding critical solution temperatures were implemented in Matlab [33] and complex derivative approximations [34] were employed to obtain d^2g^M/dx_1^2 .

Results

Tables 2, 3 and 4 show the results obtained using the NRTL model for the correlation of the selected UCST, LCST and closed loop type systems, respectively. These tables include the temperature dependent parameters obtained according to Eq. (2), the critical solution temperatures UCST, LCST or both, and the composition (mole fraction of component 1)) of these critical points, and the mean deviations (%) calculated by using Eq. (5). Figure 2 shows, as an example, the experimental and calculated compositions (mole fractions) for one binary system of each type (UCST, LCST and closed loop). Similar representations for all the systems listed in Table 1 are represented in Figures S1 to S30 in Supporting Information (SI). These figures also include the critical solution temperatures calculated by extrapolation from the correlation results.

From these results it follows that the NRTL model, with temperature dependent parameters formulated by Eq. (2), has been able to reproduce the different LLE behaviours (UCST, LCST and closed loop) with an acceptable precision for all the 30 selected systems. The mean deviations obtained for some UCST systems have been higher than those for LCST systems. This is due to the marked asymmetry in the binodal curve that present some of the selected UCST systems (e.g. S5), which leads to a noticeable deviation in the tie-line closer to the UCST point, providing a value of 2% for the mean deviation. The highest deviation 3.26% has been obtained for S23 closed loop type system. This result is justified by the difficulty for the model to represent simultaneously both the upper and lower critical solution temperatures (UCST and LCST). This fact is illustrated later, when g^M surfaces for closed loop systems are shown

and discussed. Moreover, for some of the selected systems we checked that removing some of the parameters in Eq. (2), a different set of values could be obtained for all the other parameters providing similar deviations between experimental and calculated LLE compositions. We tried to find out which were the minimum number of parameters required to model each type of system (UCST, LCST and closed loop) but we didn't find a systematic general behaviour. In most cases, parameter addition leads to a significant decrease in standard deviation. For example, Table 5 shows the results obtained using six different combinations of parameters for the S1 system. In all cases, the parameter b_{ij} that corresponds with the original formulation of the NRTL model has been included and sequentially combined with the other parameters. The lowest mean deviation (0.28%) was obtained when we used all the parameters in Eq. (2), whereas the best result obtained when removing parameters one by one was almost doubling the standard deviation (i.e. using the combination of b_{ij} , c_{ij} and d_{ij} , the mean deviation was of 0.53%). Consequently, we decided to use all the parameters in Eq. (2) for all the correlations to ensure the best correlation results provided by the model used.

Regarding the critical solution temperatures, determined for all the systems by extrapolation from the correlation parameters obtained, its reliability depends basically on two factors: a) the deviation between experimental and calculated LLE data, and b) the temperature difference that exists between the LLE data closer to the critical solution point and the calculated critical solution temperature (ΔT_c). Obviously, in both cases small values are preferable. These conditions are satisfied for most of the systems except for the S18 and S19 systems, where the LCST calculation involves 35.8 and 31.9°C for ΔT_c , respectively, and for S24 and S25 closed loop systems with differences of 44.9°C and 20.6 °C for ΔT_c , respectively, also in the LCST calculation. For this reason, the critical solution temperatures in Tables 3 and 4 for these systems have been marked with an asterisk (*). In these cases, it would be advisable to measure experimentally additional tie-lines closer to the critical solution point to perform more reliable LCST calculations.

To validate the correlation results, the Gibbs energy of mixing (g^M) and the second derivative (d^2g^M/dx_1^2) surfaces were calculated using the model parameters obtained, and graphically represented versus x_1 (mole fraction) and temperature. As examples, in Figures 3, 4 and 5, these representations are shown for the S5 (with UCST), S19 (with LCST) and S23 (closed loop type) binary systems. In Figures 3a, 4a and 5a it is possible to observe that LLE tie-lines are tangent to the g^M surface (at the corresponding

temperatures) for the liquid mixtures calculated using the NRTL parameters obtained in the correlations carried out. In Figures 3b, 4b and 5b, the second derivative (d^2g^M/dx_1^2) function is represented along with the plane $d^2g^M/dx_1^2=0$ to observe the region where it takes negative values corresponding with the existence of LLE splitting. In these figures the magenta points identify the calculated critical solution temperatures (UCST or LCST).

As it would be expected for systems with UCST, the g^M surface becomes more negative when temperature increases promoting miscibility (Figure 3a). Contrarily, for LCST type systems, the g^M surface becomes more positive when temperature increases promoting immiscibility (Figure 4a). By extension, g^M function for closed loop type systems should present both behaviours. That is, when temperature increases at lower T values, the g^M surface becomes more positive but at higher T values the opposite happens, as Figure 5a shows. As consequence, the model used for the LLE correlation for closed loop type systems must necessarily provide a g^M function with the topology described and so with changes of curvature in two directions: i) in the x_1 direction at constant T (to satisfy the required common tangent equilibrium condition), and ii) in the T direction at constant x_1 (for the necessary evolution of the miscibility with temperature just discussed). Otherwise, the model should not be used for the correlation of this type of systems. The NRTL model with the temperature dependence used in the present paper has demonstrated that it satisfies these topological requirements, being adequate for correlation of closed loop type systems.

Moreover, we have studied the NRTL parameter values required to reproduce each type of system (UCST, LCST and closed loop). With this aim, in Figure 6 we represent $\tau_{ji} = f(\tau_{ij})$ obtained for each system along with the boundary definition between miscible (L) and partially miscible (LLE) regions that we have previously published [35]. This boundary definition $\tau_{ji}^B = f(\tau_{ij})$, adapted to a unique equation that is valid for the τ_{ji} interval used in this study, is given by the following equation:

$$-5 < \tau_{ij} < 7 \quad \tau_{ji}^B = -2.123 \cdot 10^{-3} \cdot \tau_{ij}^3 + 7.601 \cdot 10^{-2} \cdot \tau_{ij}^2 - 1.202 \cdot \tau_{ij} + 2.534 \quad (6)$$

The i - j pair is totally miscible for $\tau_{ji} < \tau_{ji}^B$ and splits in LLE for $\tau_{ji} > \tau_{ji}^B$. These restrictions, which depend on the non-randomness parameter (α_{ij}), have been obtained for $\alpha_{ij}=0.2$ that also is the value used in the present work. Figure 6 shows that all the NRTL parameter values obtained as a result of the correlations are within the LL region, being located on

the boundary those corresponding with the critical solution points. This implies that UCST and LCST type systems only have one point on this boundary, while closed loop systems have two points on it. However, these Figures 6a-c do not show the evolution of the parameter values with temperature, which would allow differentiating between UCST and LCST behaviours. For this purpose, we have defined the variable $\Delta\tau = \tau_{21} - \tau_{21}^B$ that represents the difference between τ_{21} obtained in the correlation for each τ_{12} and its value on the boundary (τ_{21}^B). In Figure 7, this variable has been represented versus temperature (K) for UCST, LCST and closed loop systems. The expected behaviour for these curves is the following:

- For systems with UCST: decreasing curves that intersect the x axis ($\Delta\tau = 0$) at the UCST point.
- For systems with LCST: increasing curves that intersect the x axis ($\Delta\tau = 0$) at the LCST point.
- For closed loop systems: curves with a maximum and two intersection points in the x axis ($\Delta\tau = 0$) corresponding with the LCST and UCST points.

For most systems in Figure 7 the behaviour is the expected one, except curves for S6, S9, S10 and S15 (Figure 7a) and S16 (Figure 7b) that present a maximum and therefore they would correspond with a closed loop correlation result if a wider range of temperatures is considered. All curves in Figure 7c present the expected closed loop behaviour. This means that systems that had been initially classified as UCST or LCST (in view of the experimental LLE data as a function of temperature) can lead to correlation results corresponding with closed loop systems, beyond the fitted LLE experimental data. It is important to know this possibility, especially when the model parameters are going to be used to extrapolate additional LLE data at other temperatures. This situation is likely to occur for UCST or LCST systems with very small changes in the composition of one liquid phase with temperature, in other words, when one of the branches of the binodal curve is almost vertical. In some of these cases, the experimental LLE data itself already shows a very slight change in the curvature, as it can be observed in Figures S6, S9 and S19 in SI, which favour this situation. It is important to know this possibility when the model parameters are going to be used to extrapolate additional LLE data. Because in the $\Delta\tau$ versus T representation monotone decreasing and increasing curves are required for

types UCST and LCST systems, respectively, the following conditions for the first derivative $d\tau/dT$ should be fulfilled:

- Systems with UCST: $d\tau/dT < 0$
- Systems with LCST: $d\tau/dT > 0$
- Systems with closed miscibility loop: a change of sign in the $d\tau/dT$ function must be present, with $d\tau/dT = 0$ corresponding to temperature of the largest LLE tie-line.

These conditions could be imposed during the correlation data in case the miscibility behaviour of the system was known over the entire range of temperatures. However, in some cases as the S6, S9 and S19 systems, the miscibility behaviour beyond the experimental LLE data is unknown. In other words, we don't really know if these systems are UCST (S6 and S9) and LCST (S19), as they were initially classified, or closed loop systems and thus no restriction during the correlation has been imposed. In these cases, the correlation results provided by the model are those that better reproduce the experimental LLE data and must only be used with guarantees at temperatures within the experimental ones.

Conclusions

The NRTL model along with the equation of the temperature dependence used in this work has allowed the correlation of the experimental LLE data for the different type of binary systems selected: UCST, LCST and closed loop types. Due to the temperature dependence in the NRTL model itself is so weak, it is really the function used in the parameters for the temperature dependence which gives the model the ability to reproduce all the different behaviours. Deviations between experimental and calculated LLE data are slightly higher for closed loop systems because of the higher difficulty for the model to reproduce both UCST and LCST opposite behaviours for the same system and set of parameters. The correlation results have been validated using the Gibbs common tangent criterion and the Gibbs stability test in order to guarantee the consistency of all the parameter sets obtained and discard any possible metastable solution. Moreover, the parameters obtained in the correlations have been used to calculate the temperatures for which $(d^2g^M/dx_1^2) = 0$ and thus obtain the critical solution temperatures (UCST and/or

LCST) for all selected systems. Finally, some representations for the parameter values obtained as a result of the correlations are used to inspect the correlation results obtained.

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Supporting Information

Representation of the experimental and calculated mole fractions for all the thirty systems selected (Table 1), including the critical solution temperatures calculated by extrapolation.

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Table 1. Binary systems correlated using the NRTL model with parameters dependent on temperature.

Critical temperature	No. System	Component (1) + (2)
UCST	S1	Formic acid + benzene
	S2	Nitromethane + glycerol
	S3	Nitromethane + 1-butanol
	S4	Nitromethane + 1-pentadecanol
	S5	Furfural + water
	S6	Cyclohexanol + water
	S7	Phenol + octane
	S8	Phenol + water
	S9	1-Butanol + water
	S10	2-Methyl-1-propanol + water
	S11	3-Nitrophenol + water
	S12	2-Nitroaniline + water
	S13	Aniline + water
	S14	Benzoic acid + water
	S15	4-Methylphenol + water
LCST	S16	3-Ethyl-4-methylpyridine + water
	S17	1-Ethyl-3-isopropyl glycerol ether + water
	S18	2,2-Dimethyl-1,3-oxopropane + water
	S19	2-Methyltetrahydrofuran + water
	S20	Propanal + water
Closed loop	S21	Tetrahydrofuran + water
	S22	3-Buten-2-one + water
	S23	Glycerol + 3-aminotoluene
	S24	Glycerol + benzyl ethyl amine
	S25	2,6-Dimethylpyridine + water
	S26	1-Azacycloheptane + water
	S27	Nicotine + water
	S28	2-Butoxyethanol + water
	S29	Glycerol + 2-methoxyphenol
	S30	1-Propoxy-2-propanol + water

Table 2. NRTL correlation results of binary LLE data for selected UCST systems: model parameters, critical solution temperature and composition (mole fraction), and mean deviation (%).

<i>No. System</i>	<i>i</i>	<i>j</i>	<i>a_{ij}</i>	<i>b_{ij}</i> (K)	<i>c_{ij}</i>	<i>d_{ij}</i> (K ⁻¹)	<i>UCST</i> (°C)	<i>x_{1,UCST}</i>	<i>σ</i> (%)
S1	1	2	-13,320	981,09	2,1480	-0,0004	75,6	0,616	0,28
	2	1	7,8180	-2024,6	1,9850	-0,0379			
S2	1	2	-5,0300	123,37	1,0360	-0,0002	133,2	0,540	1,01
	2	1	6,3110	1571,3	-0,34300	-0,0178			
S3	1	2	51,370	1309,4	-9,5270	-0,0004	18,0	0,581	0,87
	2	1	19,420	-2273,0	-0,00200	-0,0377			
S4	1	2	-113,63	6985,0	17,370	-0,0098	80,0	0,870	0,57
	2	1	-5,1760	3786,0	-1,0560	-0,0022			
S5	1	2	-87,290	3406,2	14,660	-0,0254	124,8	0,192	2,00
	2	1	75,530	-6010,4	-7,3000	-0,0322			
S6	1	2	7,0260	-1696,7	0,75100	-0,0218	189,8	0,111	0,45
	2	1	3,3800	-2022,8	2,5700	-0,0199			
S7	1	2	-0,92800	6176,0	-8,0200	0,0925	49,8	0,586	0,10
	2	1	14,640	-8233,7	10,030	-0,1440			
S8	1	2	-20,230	-2319,6	7,9260	-0,0637	69,6	0,091	0,54
	2	1	15,950	-769,65	-1,3270	0,0011			
S9	1	2	62,670	-2153,3	-10,110	0,0034	127,3	0,121	0,54
	2	1	27,210	-5621,7	2,4220	-0,0559			
S10	1	2	-4,5290	775,49	0,31600	-0,0025	133,9	0,131	0,73
	2	1	43,730	-6847,0	0,29400	-0,0582			
S11	1	2	-96,890	5099,7	13,890	-0,0055	99,0	0,080	0,35
	2	1	190,00	-14766	-18,310	-0,0935			
S12	1	2	-23,990	-2068,6	7,6920	-0,0438	210,8	0,120	0,35
	2	1	32,510	-502,58	-4,3190	0,0010			
S13	1	2	-39,510	-346,40	9,0840	-0,0371	170,2	0,162	0,57
	2	1	41,690	-1417,7	-5,6310	0,0005			
S14	1	2	-48,140	-3714,5	15,430	-0,0957	116,3	0,071	0,70
	2	1	123,99	-15972	-6,1840	-0,1006			
S15	1	2	-97,800	2811,8	17,160	-0,0359	145,9	0,091	0,39
	2	1	67,370	-9243,3	-1,3630	-0,0734			

Table 3. NRTL correlation results of binary LLE data for selected LCST systems: model parameters, critical solution temperature and composition (mole fraction), and mean deviation (%).

<i>No. System</i>	<i>i</i>	<i>j</i>	<i>a_{ij}</i>	<i>b_{ij}</i> (K)	<i>c_{ij}</i>	<i>d_{ij}</i> (K ⁻¹)	<i>LCST</i> (°C)	<i>x_{i,LCST}</i>	<i>σ</i> (%)
S16	1	2	30,560	-9352,8	3,0350	-0,0662	8,7	0,041	0,62
	2	1	0,14100	2516,0	-0,00100	0,0004			
S17	1	2	370,90	-19224	-53,950	-0,0054	32,2	0,091	0,19
	2	1	-242,00	12155	35,490	0,0168			
S18	1	2	-244,80	5664,3	43,670	-0,0781	-35,8*	0,243	0,07
	2	1	-184,70	4384,9	33,320	-0,0538			
S19	1	2	0,02200	-1873	2,2600	-0,0215	-31,9*	0,253	0,11
	2	1	-0,01800	1138,0	-1,4590	0,0268			
S20	1	2	-95,630	-6,3028	20,490	-0,0685	12,7	0,424	0,43
	2	1	-102,70	-6,5408	21,040	-0,0511			

*High uncertainty

Table 4. NRTL correlation results of binary LLE data for selected closed loop type systems: model parameters, critical solution temperatures and compositions (mole fraction), and mean deviation (%).

No. System	i	j	a_{ij}	b_{ij} (K)	c_{ij}	d_{ij} (K ⁻¹)	UCST (°C)	$x_{i,UCST}$	LCST (°C)	$x_{i,LCST}$	σ (%)
S21	1	2	-122,10	-6,3316	25,040	-0,0722	138,3	0,192	70,8	0,232	0,75
	2	1	-147,30	-6,5670	30,010	-0,0712					
S22	1	2	-35,910	-6939,6	16,780	-0,1242	86,3	0,202	26,4	0,273	0,61
	2	1	-175,30	9693,4	24,110	0,0289					
S23	1	2	-68,670	70,219	14,950	-0,0499	120,6	0,505	3,1	0,596	3,26
	2	1	-136,60	-11,676	28,360	-0,0807					
S24	1	2	-0,77900	-136,08	1,1440	-0,0080	311,3	0,566	15,1*	0,717	2,00
	2	1	-60,820	4,3864	11,950	-0,0250					
S25	1	2	-170,80	-7,0859	33,820	-0,0848	164,4	0,101	39,4*	0,071	0,54
	2	1	22,200	-2,4209	-2,4050	-0,0038					
S26	1	2	-113,60	-141,31	21,740	-0,0466	224,0	0,111	66,3	0,061	0,67
	2	1	-148,50	25,449	31,870	-0,0884					
S27	1	2	-334,70	-6,3761	65,810	-0,1540	233,6	0,071	56,4	0,041	1,43
	2	1	207,30	-6,5299	-39,080	0,0849					
S28	1	2	-129,40	-6,4518	25,790	-0,0706	128,7	0,061	47,4	0,061	0,65
	2	1	-318,70	-6,6442	67,000	-0,1884					
S29	1	2	-79,450	-13,548	16,890	-0,0513	84,5	0,545	38,4	0,545	0,75
	2	1	-330,60	-15,043	68,920	-0,2060					
S30	1	2	-139,20	-4,6567	28,110	-0,0778	176,0	0,091	31,7	0,101	0,87
	2	1	5,7140	-2,4595	-0,22200	0,0042					

*High uncertainty

Table 5. NRTL correlation results of binary LLE data for the S1 system using different combination of model parameters and mean deviation (%) obtained.

Combination of parameters	<i>i</i>	<i>j</i>	<i>a_{ij}</i>	<i>b_{ij}</i> (K)	<i>c_{ij}</i>	<i>d_{ij}</i> (K ⁻¹)	σ (%)
1	1	2	-	560.48	-	-	5.58
	2	1	-	267.47	-	-	
2	1	2	-3.8061	1838.2	-	-	2.14
	2	1	0.82503	-0.15599	-	-	
3	1	2	-	1009.9	-0.18882	-	1.03
	2	1	-	668.32	-0.23194	-	
4	1	2	-	553.81	-	0.00091	0.69
	2	1	-	717.10	-	-0.00457	
5	1	2	-	290.48	0.31224	-0.00214	0.53
	2	1	-	181.22	0.71368	-0.01219	
6	1	2	-13.316	981.09	2.1482	-0.00038	0.28
	2	1	7.8178	-2024.6	1.9850	-0.03793	

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Figure 1. UCST or LCST determination employing d^2g^M/dx_1^2 for a binary system.

Figure 2. Experimental and calculated (NRTL) LLE data (mole fractions) for some selected binary systems: a) S1 (UCST), b) S16 (LCST), and c) S21 (closed loop).

a)

b)

Figure 3. Checking of correlation results (NRTL) for S5 (with UCST): a) calculated g^M surface and b) second derivative (d^2g^M/dx_1^2) surface versus composition (mole fraction) and temperature.

a)

b)

Figure 4. Checking of correlation results (NRTL) for S19 (with LCST): a) calculated g^M surface and b) second derivative (d^2g^M/dx_1^2) surface versus composition (mole fraction) and temperature.

a)

b)

Figure 5. Checking of correlation results (NRTL) for S23 (closed loop type): a) calculated g^M surface and b) second derivative (d^2g^M/dx_1^2) surface versus composition (mole fraction) and temperature.

Figure 6. NRTL parameters τ_{21} vs τ_{12} obtained in the LLE correlation of the selected systems: a) UCST, b) LCST and c) closed loop types. Boundary curve between miscible (L) and partially miscible (LLE) regions has also been represented.

Figure 7. Representation of $\Delta\tau$ vs temperature (K) obtained in the LLE correlation of the selected systems: a) UCST, b) LCST and c) closed loop types.