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ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 8. Properties of Material Streams and Solvent Design

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ABSTRACT: ThermoData Engine (TDE) is the first full-scale software implementation of the dynamic data evaluation concept, as reported in this journal. The present paper describes the first application of this concept to the evaluation of thermophysical properties for material streams involving any number of chemical components with assessment of uncertainties. The method involves construction of Redlich−Kister type equations for individual properties (excess volume, thermal conductivity, viscosity, surface tension, and excess enthalpy) and activity-coefficient models for phase equilibrium properties (vapor−liquid equilibrium). Multicomponent models are based on those for the pure-components and all binary subsystems evaluated on demand through the TDE software algorithms. Models are described in detail, and extensions to the class structure of the program are provided. Novel program features, such as ready identification of key measurements for subsystems that can reduce the combined uncertainty for a particular stream property, are described. In addition, new product-design features are described for selection of solvents for optimized crystal dissolution, separation of binary crystal mixtures, and solute extraction from a single-component solvent. Planned future developments are summarized.
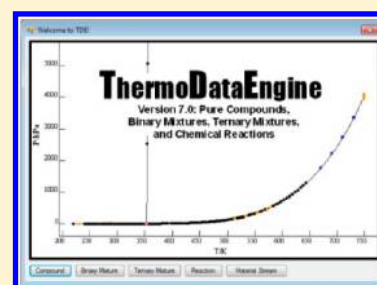
INTRODUCTION

As discussed in the first seven articles of this series,[1−7] the *NIST ThermoData Engine* (TDE) software represents the first full-scale implementation of the concept of dynamic data evaluation for thermophysical properties.[8,9] This concept requires large electronic databases capable of storing essentially all relevant experimental data known to date with metadata and uncertainties. The combination of these databases with expert-system software, designed to automatically generate recommended property values based on available experimental and predicted data, leads to the ability to produce critically evaluated data dynamically or on demand.

TDE has evolved from its first release, limited to thermophysical properties of pure compounds,[10] to on-demand generation of equations of state (EOS),[11] dynamic Web-based updates of local data resources[11] through the TRC-SOURCE data storage system,[12] support for binary mixtures, including phase equilibria,[13] properties of chemical reactions,[14] experiment planning and product design tools,[15] as well as dynamic Web-based dissemination of properties of pure components through the *NIST Web Thermo Tables*,[16] and most recently for evaluation of properties of ternary mixtures, including vapor−liquid equilibrium (VLE) and liquid−liquid equilibrium (LLE) generated through on-demand evaluation of the binary subsystems.[7] TDE is used in a multitude of applications ranging from data quality assurance,[17] to validation of new experimental data,[18] to chemical process and

product design.[19,20] It is also a core component in implementation of the concept of *Global Information Systems in Science* with application to the field of thermodynamics.[21] Other recent additions include a vapor−liquid equilibrium (VLE) data modeling test that complements consistency tests implemented previously for low-pressure/subcritical VLE data,[15,22] as well as addition of the NIST-KT-UNIFAC prediction method[23] for VLE data, which was developed based on data quality factors (i.e., data set weighting factors) described previously[22] and automatic decomposition of molecular structures into KT-UNIFAC groups and subgroups.[24]

The present article describes extension of TDE (version 7, released in 2012)[25] for evaluation of properties of material streams (defined as a mixture with any number of components and specified overall composition). A particular challenge in evaluation of properties for material streams lies in the estimation of uncertainties for calculated values, and this topic is discussed in some detail.

The second major addition to TDE involves tools for recommendation of solvents ("solvent design") for three common separation tasks. Solvent design methods have been reported previously by Gani and co-workers.[26] While that initial implementation was based entirely on predictions, use of models based on

experimental data was recently announced by that group.[27] The major advancements represented in the solvent design tools described here for TDE are assessment of uncertainty, integration with on-demand modeling of experimental data, and efficient analysis tools to allow full exploration of experimental property data, predictions, models, and solvent properties.

■ SCOPE

Compound types within the scope of TDE are unchanged since the initial release of the program.[1] Thermodynamic and transport properties of organic compounds composed of the elements C, H, N, O, F, Cl, Br, I, S, and P, plus industrially important inorganic compounds, such as ammonia and water, are considered. Extension of TDE capabilities to evaluation of properties for material streams has progressed along two paths: one for properties modeled individually (volumetric properties, transport properties, etc.) and one for properties modeled collectively with activity-coefficient (AC) models for phase equilibrium properties. This approach is analogous to that used previously for binary mixtures (version 3)[3] and ternary mixtures (version 6).[7]

The Gibbs Phase Rule specifies the maximum number of phases that may be present and the number of independent state variables required to fully define a property for a system with a given number of components (chemical compounds). These restrictions limit the number of possible system types, but the number of potential phase and variable combinations is very large for multicomponent mixtures involving more than two components. Properties supported in evaluations for material streams are all pure-compound properties for single-component streams, while for multicomponent streams, they are pressure at vapor–liquid equilibrium (VLE), vapor and liquid compositions at VLE, K values (the ratio of the mole fraction in the gas phase to that in the liquid for each component), the mole fraction of material in the vapor phase, and thermodynamic and transport properties of saturated or single fluid phases (liquid or gas for pressure $p < 1$ MPa), such as excess volume, excess enthalpy, viscosity, thermal conductivity, and surface tension. At present, other types of phase equilibria {liquid–liquid equilibria (LLE), solid–liquid equilibria (SLE), etc.} are not addressed. If the existence of LLE, SLE, or supercriticality for a mixture at the requested conditions is suspected based on the program calculations, the user is informed, but no property calculations are performed.

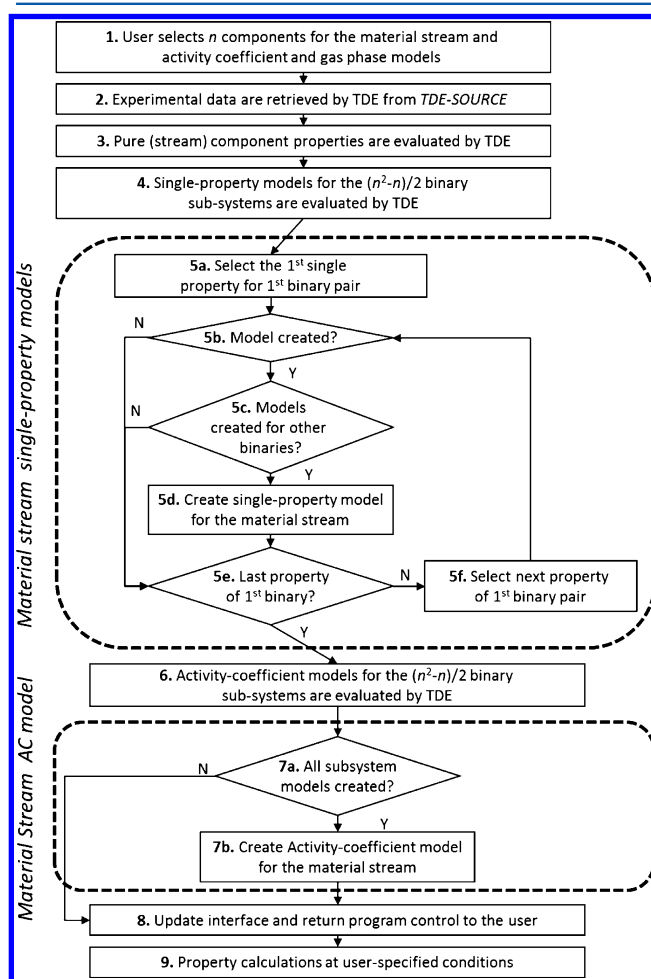## ■ ALGORITHM FOR EVALUATION OF PROPERTIES FOR MATERIAL STREAMS

Evaluation of properties for a single-component material stream (e.g., pure toluene) is identical to that for a pure compound, as described in the first two articles of this series,[1,2] and further description is not needed. As described previously, modeling properties for a binary mixture requires the properties of the two pure components,[3] and modeling properties for a ternary mixture requires that properties of the three binary subsystems be available and modeled.[7] It follows that for a material stream of n components, models for the N binary subsystems must be generated successfully, where

$$N = (n^2 - n)/2 \qquad (1)$$

Evaluation of properties for a multicomponent system involves three major steps: (1) evaluation of the properties for the n pure components, as previously described;[1,2] (2) evaluation of the

properties for the N binary subsystems (described in the third paper of this series,[3] plus criteria and procedures for automatic evaluation described in the seventh article[7]); and (3) calculation of the properties of the multicomponent stream with uncertainty assessment at specified conditions and overall composition.

The general algorithm for property evaluations for multicomponent chemical systems with TDE is shown in Figure 1.

Figure 1. Algorithm for property evaluations for material streams with TDE.

The major steps are numbered in the figure and are described in the paragraphs that follow. An analogous figure was given with the algorithm description for evaluation of properties of ternary systems (Figure 1 of ref 7). Some information is repeated here for clarity and necessary extensions are emphasized.

Step 1: Compound Selection by User. The user initiates the evaluation process by selecting the n components for the mixture, plus the AC model and gas-phase model for representation of the phase equilibrium properties (SLE, LLE, and VLE). The compound selection was described earlier.[1] AC models implemented in TDE are NRTL,[28] Redlich–Kister,[29] UNIQUAC,[30] Van Laar,[31] Wilson,[32] and the UNIFAC[33,34] group-contribution method. Gas-phase models are the ideal-gas, virial,[35] Redlich–Kwong,[36] Peng–Robinson,[37] and Hayden-O'Connell[38] models. Details of model implementation in TDE for AC and gas-phase models for binary systems were described previously.[3] Recently, this research group reported generation of UNIFAC-type group parameters based on data quality factors (i.e., data set

weighting factors)[22] and automatic parsing of molecular structures into KT-UNIFAC groups and subgroups.[23] This parametrization, NIST-KT-UNIFAC,[23] is also implemented in TDE.

Step 2: Experimental Data Are Retrieved from TDE-SOURCE by TDE. Following compound selection by the user, the TDE software retrieves (loads) all experimental data for the components and binary subsystems from the local database, TDE-SOURCE. TDE-SOURCE is an archive of experimental property data from the literature and is a subset of the TRC SOURCE archive, which has been described.[12] Presently (August, 2012), TDE-SOURCE contains 4.8 million experimental property values, including those for 40 000 binary mixtures and 11 000 ternary mixtures. The user can include proprietary or other experimental data. These data are not stored in TDE-SOURCE but are maintained separately to ensure traceability and database integrity. Property values can be modified (corrected) or selected for forced rejection by the user, as described previously.[1,2]

Step 3: Pure-Component Properties Are Evaluated by TDE. Following retrieval and basic processing (normalization) of the available experimental data, the properties of the pure components are evaluated automatically. The dynamic evaluation of pure-component properties was described in the first two articles of this series.[1,2] If evaluated properties for the compounds are available from the NIST REFPROP database,[39] then these are used. The NIST REFPROP database presently includes 105 compounds, including water, many simple hydrocarbons (e.g., methane, ethane, etc.), light alcohols (methanol, ethanol), refrigerants, and other common chemicals. The REFPROP database provides high-quality models; plus, there is little expectation of significant changes in the evaluated properties due to new measurements for these compounds.

Step 4: Single-Property Models for Binary Subsystems Are Evaluated by TDE. Application of the concept of dynamic data evaluation to properties for binary chemical systems was first described in the third article of this series.[3] For properties represented by single equations (excess volume, viscosity, etc.), Redlich−Kister type equations are used to represent the properties. Equations used and the fitting procedures were described,[3] and those procedures were used here, except for viscosities, where a newer formulation was used.[7]

Step 5: Creation of Single-Property Models for Material Streams. The portions of the algorithm specifically related to formulation of models for material streams are shown within the dotted rectangles in Figure 1. The program flow for single-property models is shown in steps 5a through 5f. A model for properties of a material stream is created only if models were successfully created for all binary subsystems. Steps 5a through 5f involve checking for the existence of the requisite binary models. The mathematical details of the composite models for a material stream are provided in Appendix A. Temperature and pressure ranges of validity for the binary models are not considered at this point. In analogy to the procedures for ternary systems,[7] ranges of validity are considered only when properties are calculated at the user's request. At that time, users can determine whether the extrapolated values meet their purposes based on the uncertainty estimates provided in TDE.

Step 6: AC Models for Binary Subsystems Are Evaluated by TDE. In the initial development of the TDE software for fitting AC models for binary systems, substantial user interaction was necessary.[3] Procedures for automatic evaluation have since been improved substantially, and complete details

of the procedures were reported with our description of property evaluations for ternary systems.[7]

Step 7: Creation of AC Models for a Material Stream. Creation of an AC model for a material stream requires successful model creation for all binary subsystems (step 6, Figure 1). Steps 7a and 7b (Figure 1) indicate this requirement. The mathematical formulations for the material stream AC models available in TDE (version 7) are described in Appendix A.

Step 8: Update the User Interface and Return User Control. Here, the user can review all results, including those for the pure components and binary subsystems. Features of the TDE interface for display of experimental data, deviation plots, fitted models, etc., have been described.[1−3] An alternative AC model can be chosen, but this model (and the gas-phase model) must be applied to all binary systems.

Model creation for a material stream can involve creation of many submodels (pures and binaries), and determination of the quality of the combined model poses a particular challenge. Advanced uncertainty assessment tools implemented in TDE for material streams provide quantification of uncertainty contributions from subsystem models for a particular property. These can be used to identify deficiencies in the underlying experimental data that may be corrected through an alternative data weighting. If uncertainties of evaluated properties are too large for an intended application by a user, the uncertainty-contribution analysis can be used as an aid in experiment planning. Details of the uncertainty contribution analysis are provided later in this article.

Step 9: Properties Are Calculated at User-Specified Conditions. Properties of the material stream are calculated with the equations given in Appendix A for single properties and AC models. A key difference between calculations for material streams and other systems in TDE (pures, binaries, ternaries, and chemical reactions) is that only the overall composition is specified by the user and a "flash" calculation is done to determine the phase state (gas, liquid, VLE, LLE, etc.) of the stream at the conditions specified. At present, properties are calculated for single phases (gas or liquid) or for the bubble or dew-point phase boundaries at specified temperatures. Other phase conditions (LLE, SLE, supercritical) are noted in the software output, but no property calculations are performed.

■ UNCERTAINTY EVALUATIONS FOR PROPERTIES OF MATERIAL STREAMS

Reliable uncertainties for thermophysical properties calculated with fitted mathematical models are recognized as key for process design because the absence of such information is a major cause for overdesign, i.e., the design of equipment to withstand temperatures and pressures far in excess of predicted process conditions because the design parameters (properties) are not known with sufficient accuracy.[40,41] This aspect of process design has long been ignored, because the greater problem has been the availability of appropriate data of any kind or quality. The development of the dynamic data evaluation approach, as implemented in TDE, has greatly improved the state of data availability and allows a renewed focus on the uncertainty of the information provided and its impact on process design.

There are two common computational approaches for estimation of model uncertainties: covariance and Monte Carlo. The covariance matrix can be calculated readily for linear and nonlinear models,[42] but certain deficiencies necessitate some empirical adjustments in its application.[1,2] The covariance method is based on the assumption that the model is adequate and that the only

contribution to uncertainty is uncorrelated random error in source data, subject to a normal distribution. Models are assumed to be linear within the variation of the parameters, and covariance is limited to second order. In contrast, the Monte Carlo method is free from the linear approximation and second-order limitation, but other significant problems, such as long computation periods, remain.

Whiting et al.[43−46] published a series of articles concerning the problem of uncertainty estimation in process simulation in which they applied Monte Carlo variation to model parameters to obtain a sample of target property values. The methods used were not described in sufficient detail to reproduce their approach, but, through the article series, their approach evolved from variation of parameters based on parameter variance without consideration of covariance[43] to sampling of raw data with an assumed normal distribution.[46] Hajipour and Satyro[47] used a similar approach in uncertainty analysis applied to thermodynamic models and process design involving pure components. Recently, Theodorou et al.[48] published an attempt to consider all uncertainty contributions to the raw (experimental) values with different distributions and correlation of errors for a single-valued property: enthalpy of combustion of fuels at fixed conditions and composition. The basis for the assumptions used was not described, and application of a similar approach to more complex cases would be very labor-intensive, though targeted application might be useful.

Calculation of uncertainties in TDE is based on the covariance method with some empirical adjustments to partially overcome some limitations of the approach. The general covariance approach has been outlined in previous work.[1,2,7] Uncertainties for properties of material streams represented by single-property equations are calculated analogously to those for ternary systems.[7] Contributions from pure components and binary excess properties are considered

$$u(\psi)^2 = \sum_{i=1}^{n} \left\{ u(\psi_i) \frac{\partial \psi}{\partial \psi_i} \right\}^2 + \{u(\psi_{ex})\}^2 \tag{2}$$

where $u(\psi_i)$ is the uncertainty for the pure-component property, n is the number of components in the material stream, $\partial \Psi / \partial \Psi_i$ is the partial derivative of the mixture property with respect to the pure-component property, and $u(\Psi_{ex})$ is the uncertainty contribution to the mixture property propagated from the binary excess property

$$u(\psi_{ex})^2 = D^T C D \tag{3}$$

where C is the covariance matrix consisting of n blocks of binary-parameter covariance, D is the vector of partial derivatives of the mixture property with respect to the binary parameters, and D^T is transposed D. No covariance is assumed between the binary pairs, and the method does not consider higher-order (ternary and greater) covariance of parameters.

As noted for ternary systems,[7] the covariance method yielded unreasonable uncertainties for properties derived from AC models. An alternative approach was developed and was applied here for material streams. As was done for single properties, no covariance is assumed between the binary pairs, and ternary and greater covariance of parameters is ignored. The total covariance matrix for an empirical AC model is, then, in block-diagonal form, which allows separation of uncertainty contributions from each binary pair

$$u(\psi_{ex})^2 = \sum_{i=1}^{N} D_i^T C_i D_i \tag{4}$$

where the summation is over the N binary subsystems, D_i is the vector of property derivatives with respect to parameters of the i-th binary model, and C_i is the covariance matrix of the i-th binary model.

We believe that in the case of equations of state for mixtures with built-in mixing rules, separation of the uncertainty contributions for the relevant pure compounds and contributions attributed to mixing can be achieved under the assumption that there is no covariance between the pure-compound and mixing parameters. This approach was not implemented here and is outside the scope of this paper.

We also performed some tests of a Monte Carlo-based approach for uncertainty evaluation. Several implementations of the Monte Carlo sampling methods were used to evaluate uncertainties for properties of selected single-component systems. In these limited tests, the Monte Carlo-based methods produced results that were close to those of the covariance method described above, and problems common to both methods (covariance and Monte Carlo) remain the primary concern. Major issues include possible systematic errors in experimental and predicted data, appropriate account of deviations of experimental data from models, model adequacy, extrapolation errors that cannot be well assessed without consideration of the physical nature of each model, and other contributions, such as the choice of gas-phase model in VLE calculations, where no property data or fitted parameters are used. Further research and more extensive testing will be considered in future work.

Uncertainty Estimates for UNIFAC Predictions. Details of the implementation of UNIFAC predictions in TDE were described previously.[3] Covariance for UNIFAC methods is assigned in TDE to provide some estimate of uncertainty for the predicted values. For original UNIFAC, a variance σ^2 equal to

$$\sigma^2 = (25 + 0.25 \cdot \Theta)^2 \ [\text{units are K}^2] \tag{5}$$

is assigned to each interaction parameter with zero covariance, where Θ is the parameter value. For NIST-KT-UNIFAC, variances assigned to the constant term at the midtemperature of model fitting are

$$\sigma^2 = (10 + 0.10 \cdot \Theta_c)^2 \ [\text{units are K}^2] \tag{6}$$

and the values for the temperature-dependent term are

$$\sigma^2 = (0.25 + 0.25 \cdot \Theta_T)^2 \tag{7}$$

with no covariance, where Θ_C and Θ_T are the parameters for the constant term and temperature-dependent term. If the parameters are modified to represent the temperature dependence as A + B/T, the covariance matrix is also modified to block-diagonal. The constants 10 and 0.25 (eqs 6 and 7, respectively) are constant contributions to the variances of the parameters $a_{mk,1}$ and $a_{mk,2}$ in the middle of the temperature range of experimental measurements for each pair of interacting groups m and k (ref 23, eq 11). The constants 0.10 and 0.25 in the second terms of the variance equations (eqs 6 and 7) are proportionality constants for the parameter-dependent terms.

The validity of these methods for uncertainty estimation was checked for pure compounds, binaries, and ternaries by comparison of the assessed uncertainties with experimental uncertainties and curve deviations for the experimental data. These estimates appear adequate for most uncertainties for the

UNIFAC methods, but, in the future, assignment of individual variance values to all UNIFAC parameters is planned.

■ SOFTWARE ARCHITECTURE: MATERIAL STREAMS

Previous articles in this series described pure-compound,[1,2] binary-mixture,[3] chemical reaction,[4] and ternary-mixture objects.[7] In the present work, a fifth object is added: "material stream". The new material stream class (Figure 2) includes objects representing
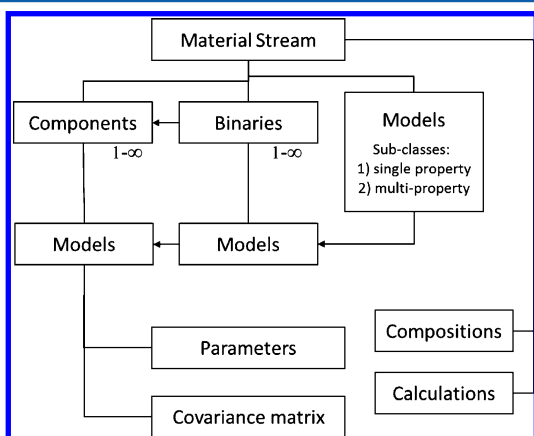
Figure 2. Structure of the *Material Stream* class.

the *n* pure components and $(n^2-n)/2$ binary subsystems. In Figure 2, connecting arrows indicate links to external objects, and lines indicate objects belonging to the parent object. Pure components are represented by compound classes containing all relevant information (identification, molecular structure, property data, and models: equations and covariance matrices).

Binary subsystems are represented by binary-mixture objects containing links to the pure components, property data, and models. In analogy to the class structure for ternary systems,[7] models for the calculation of properties of material streams are divided into two groups: those used for representation of single properties (*e.g.*, viscosity, thermal conductivity, excess enthalpy, etc.) and those used to represent multiple properties simultaneously (*i.e.*, AC models for phase equilibrium). This is also analogous to the approach described previously for binary mixtures.[3]

■ INTERFACE FEATURES FOR PROPERTIES OF MATERIAL STREAMS

Material Stream: Property Calculation. Interface features have been described for steps 1 through 8 of Figure 1 in previous articles of this series.[1,3,7] Step 9 of Figure 1 (*Property calculations at user-specified conditions*) requires new interface features described here. An interactive form was designed and implemented that allows ready access to calculation criteria, numerical results, and a detailed uncertainty analysis with links to underlying models and experimental property data for all pure-component and binary subsystems. The single form for material stream property calculations is shown in Figure 3. The form accepts all necessary user input for a given calculation, including selection of (1) calculation type (fixed temperature and pressure, bubble point, and dew point); (2) flash model (*i.e*, the AC model to use for phase-equilibrium calculations); (3) properties to calculate (phase boundary pressure, density, etc.); (4) material composition (*i.e.*, the overall composition of the stream); (5) calculation ranges for variables (temperature and pressure range); and (6) process initiation. The *Flash model* (item 2) and *Material Composition* (item 4) fields are pull-down menus to allow easy access to

Figure 3. The *Material Stream: Property Calculation* and *Material Composition* forms.
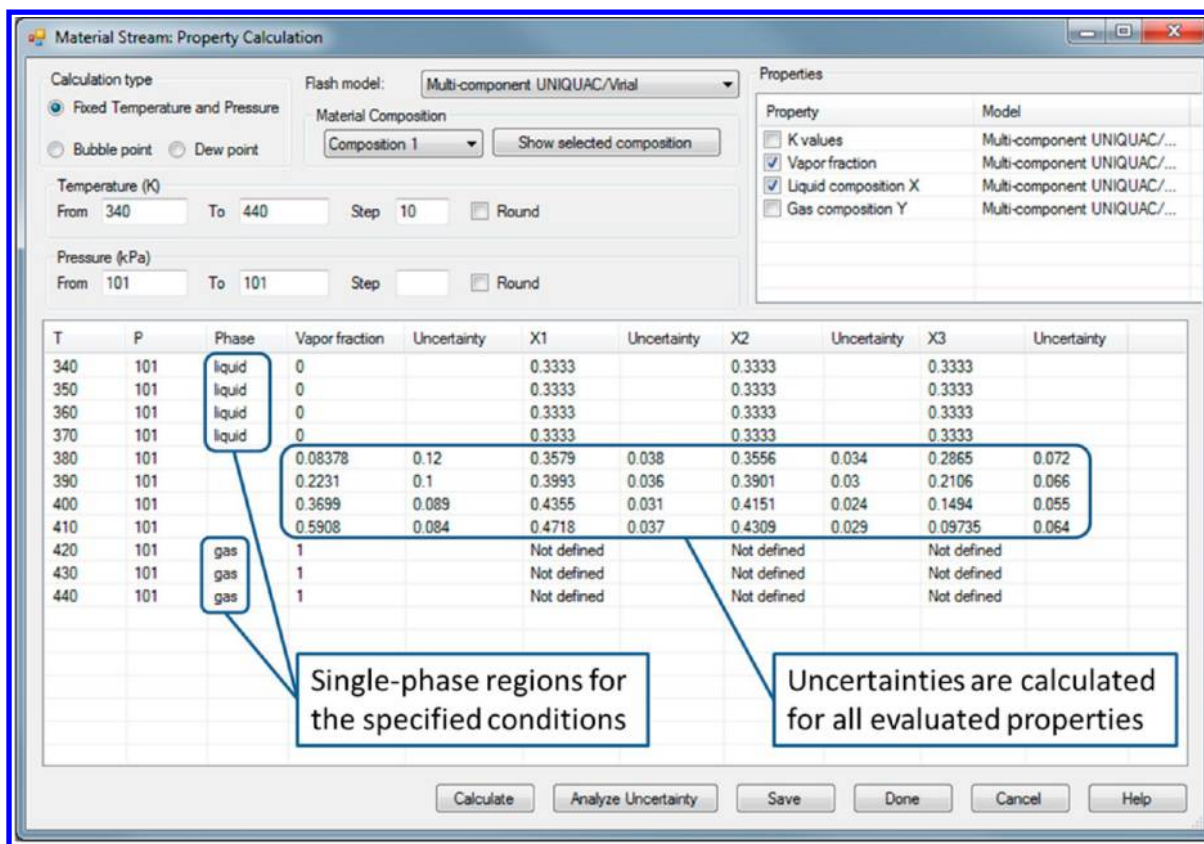
Figure 4. Display of VLE properties in one-phase and two-phase regions on the *Material Stream: Property Calculation* form.

alternative models and stream compositions entered previously by the user. The *Show selected composition* button provides details for the selected overall composition. It is impractical to include this list on the main form because the number of components is unrestricted.

Results of a calculation for the material stream {(cyclohexanol + cyclohexanone + cyclohexane) as specified in Figure 3} are shown in Figure 4. Uncertainties are calculated and displayed for all evaluated numerical results. The identity of the single-phase region is specified in the absence of vapor–liquid equilibrium. "Not defined" appears in the table of results because columns X1 to X3 are compositions for the liquid phase, and no liquid is present at the specified conditions.

The efficacy of the interface design can be shown through a sample calculation for a property stream. This also demonstrates use of the detailed uncertainty analysis to improve the quality (i.e., reduce the uncertainty) for an evaluated property. The example calculation is for the phase boundary pressure (i.e., the "bubble-point" pressure) and liquid density at the bubble point for an equimolar mixture of (cyclohexanol + cyclohexanone + cyclohexane) as illustrated in Figure 3. The results of the calculation in the temperature range 300 to 600 K are shown in Figure 5. In addition to properties and uncertainties, special conditions are identified by the program that are beyond the present scope of TDE evaluation capabilities, such as the calculated presence of liquid–liquid equilibrium, solid phase deposition, or a supercritical state for one of the components (as indicated in Figure 5). The calculation of LLE conditions in TDE was described with property evaluations for ternary systems.[7] The presence of solids is detected through comparison of activities for a component in the liquid with that of the pure solid. Solid solutions are not considered at this time.

Access to detailed uncertainty accounting and underlying models is shown in Figure 6. A calculated value is selected, and the *Analyze Uncertainty* button opens the *Uncertainty Analysis* form (Figure 6). All subsystems are listed on the *Uncertainty Analysis* form together with their percent contribution to the combined uncertainty listed on the *Material Stream: Property Calculation* form (Figure 6). Here, it can be seen that most of the uncertainty for the bubble-point pressure at temperature $T = 460$ K arises from the (cyclohexanol + cyclohexane) system. Direct access to the experimental data and model fitting for this mixture is available through this form, as indicated in the figure.

The topmost form in Figure 7a, is the initial destination when accessing the data for the (cyclohexanol + cyclohexane) system. The properties listed are those used in the fitting of the UNIQUAC model, and the red color and high number for the calculated *Adequacy* indicate that the excess enthalpy is poorly modeled. (Details of this *Model Fitting Control Center* form, including definitions of all quantities, including the *Adequacy*, were described previously.[3]) A plot of the excess enthalpy model and experimental data (Figure 7b) shows that one data set from the literature is in serious disagreement with all others and is probably erroneous. Figure 7c shows that the modeling results are much improved after forced rejection of the anomalous data, and Figure 7d shows the much improved representation of the experimental excess enthalpies by the model. The result of a new property calculation with the improved AC model for (cyclohexanol + cyclohexane) is shown in Figure 8. The uncertainty for the selected property (phase boundary pressure p) has decreased substantially from $0.5 \cdot p$ to $0.3 \cdot p$, relative to the result in Figure 6.

The uncertainly analysis form also provides calculated measures of property variation with changes in process parameters.
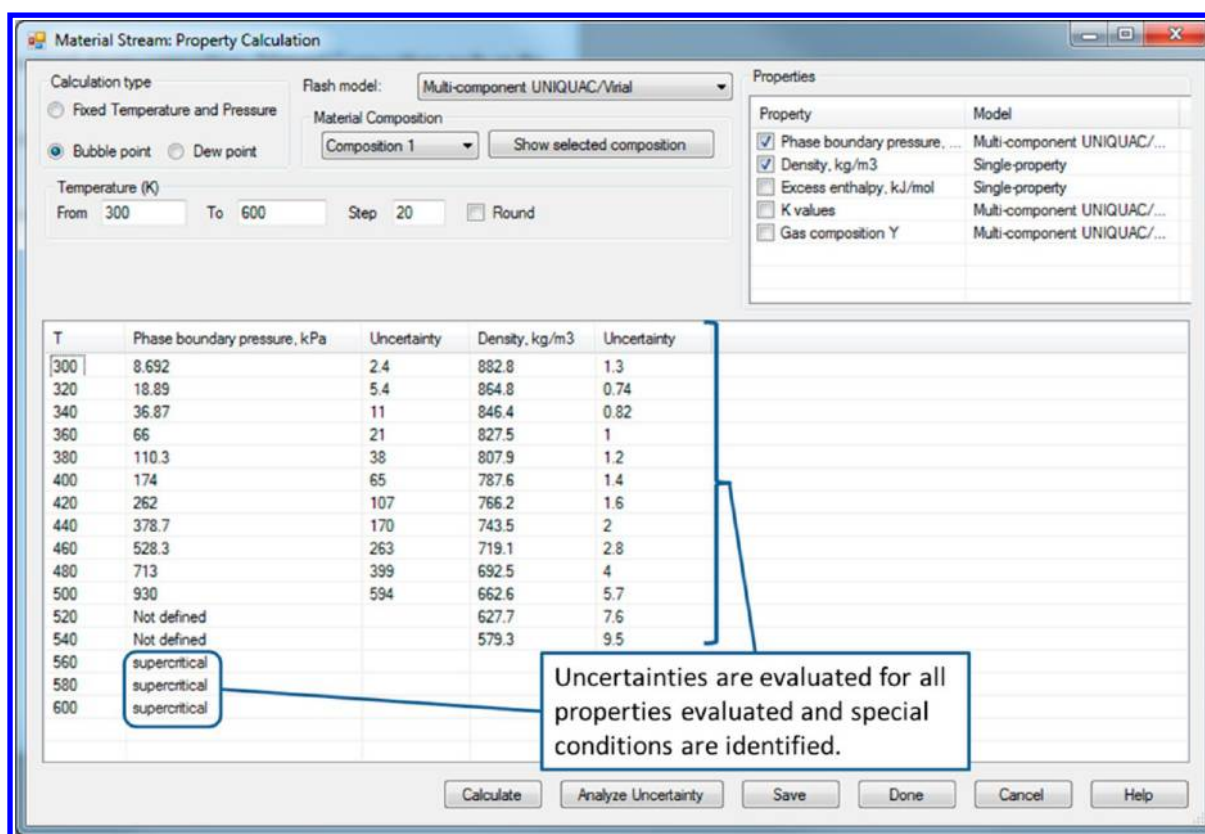
Figure 5. Display of uncertainties and special conditions in the *Material Stream: Property Calculation* form.
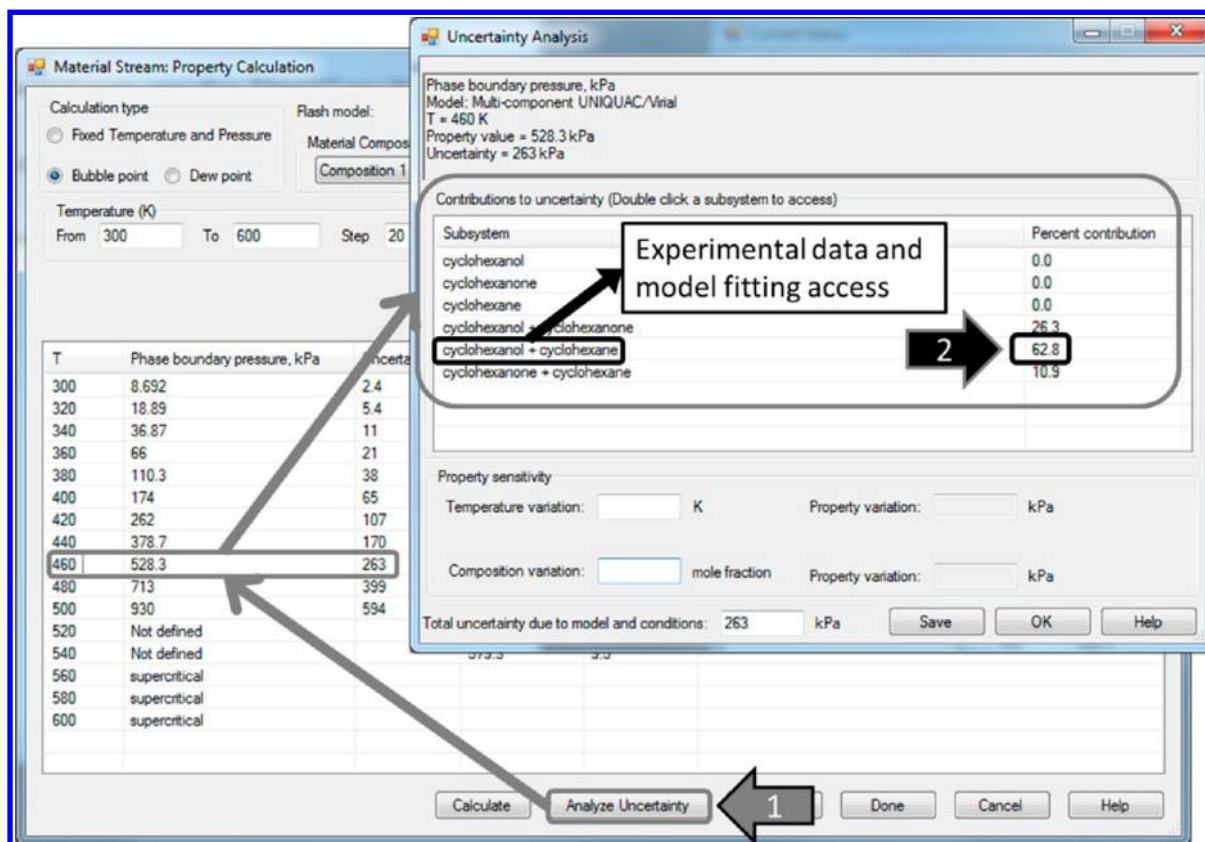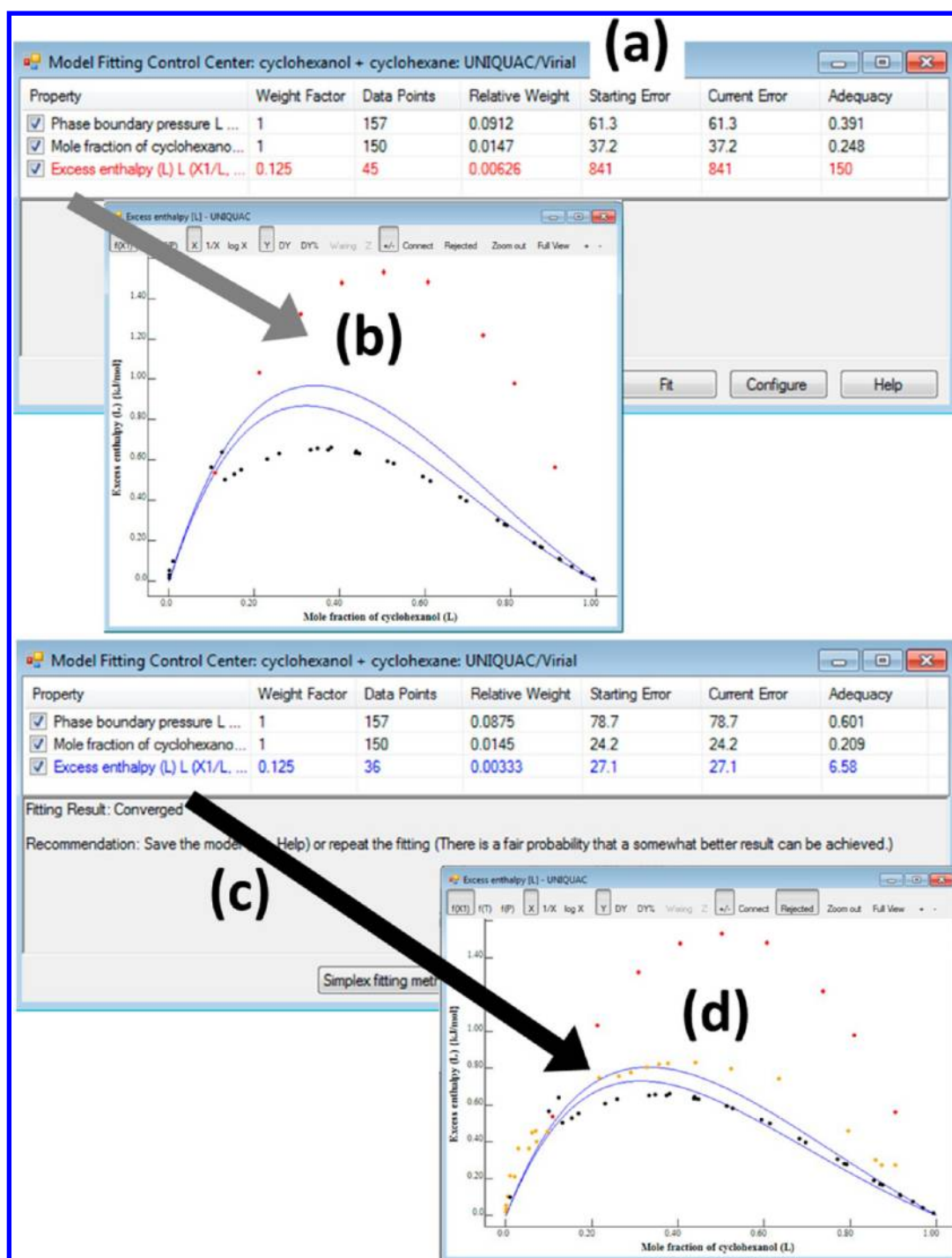

Figure 6. Mechanism for access to detailed uncertainty analysis, experimental data, and models through the *Material Stream: Property Calculation* form.

Figure 7. (a) The *Model Fitting Control Center* interface in TDE with poor model representation indicated for excess enthalpies for the (cyclohexanol + cyclohexane) system; (b) plot of excess enthalpy against mole fraction with anomalous data indicated; (c) the *Model Fitting Control Center* after rejection of anomalous data and refit; (d) plot of excess enthalpy against mole fraction after rejection of anomalous data and refit.

In Figure 9, a temperature variation of 2 K yields a pressure variation of 22 kPa, and a composition variation of 0.05 mol fraction results in a property variation of 89 kPa, which shows that the results for this example are more sensitive to the specified uncertainty in the feed composition.

ALGORITHM FOR SOLVENT DESIGN

In TDE version 5.0,[5] tools for product design of pure components were implemented, and the algorithm and interface features were described. In the present work, the first product-design tools for mixtures, *solvent design*, are described. Solvent design is implemented to aid three common industrial and laboratory tasks. All evaluations are for a user-specified temperature and pressure near 0.1 MPa. These are as follows: (1) *Solvent for Solid*; selection of the best single-component solvent for a crystalline solute (i.e., the solvent with highest solubility of solute); (2) *Selective Solvent for Solid*; selection of a single-component solvent for preferential dissolution of one component from a solid binary mixture; and (3) *Solvent for Extraction*; selection of a single-component
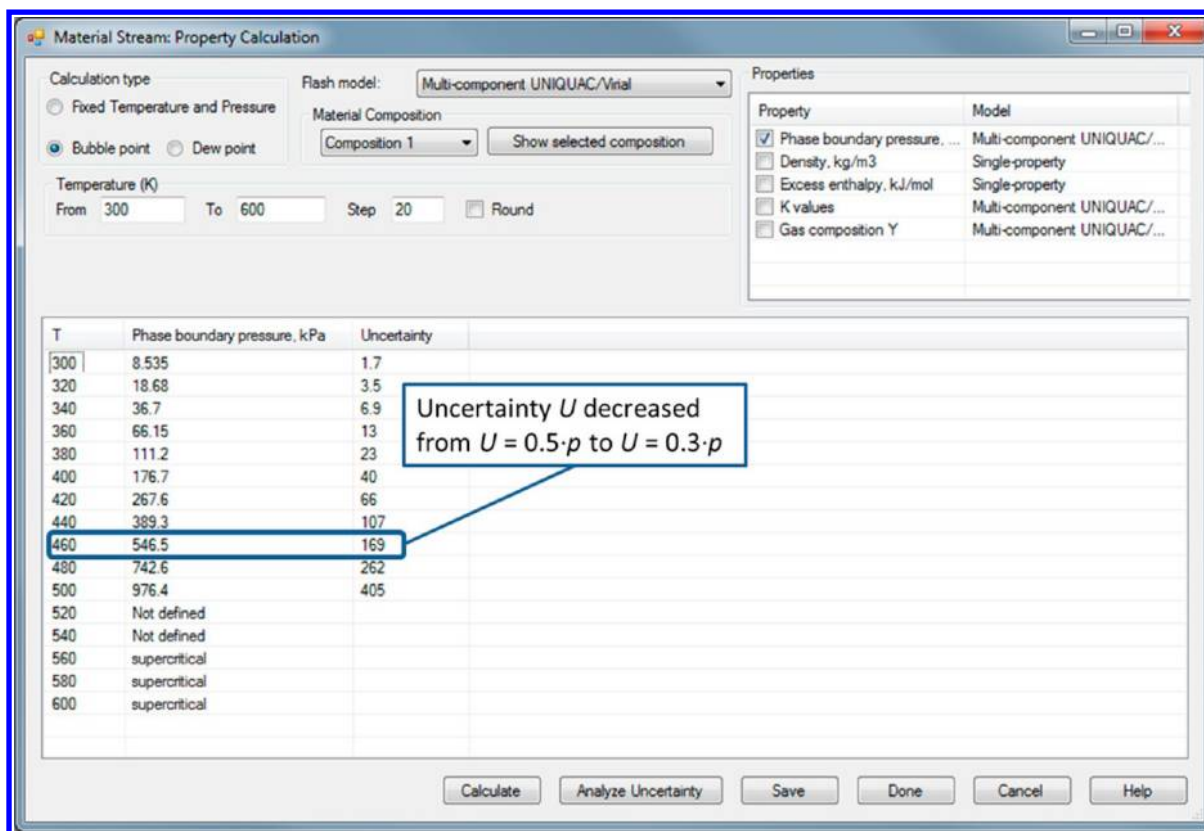
Figure 8. Display of improved uncertainty for the evaluated phase boundary pressures after rejection of anomalous data and model refitting.

solvent for extraction of one component from a liquid binary mixture.

In all cases, solvents are selected from two existing substance pools. For some analyses in TDE, structure-drawing tools allow the user to specify molecules not included in the collection supplied; however, this feature is not implemented for solvent design. Two solvent pools are provided for which properties necessary for solvent design have been pre-evaluated with the TDE algorithms;[1] the TDE-SOURCE database (presently, with more than 27 000 compounds) and a Solvent Database, which is a subset of TDE-SOURCE that contains approximately 600 common solvents. The program returns ordered lists of prospective solvents based on criteria specified by the user. Ordering is based on a "preference criterion" that is different for each task. Below, terms (conceptual and mathematical) are described that underlie considerations and models for each solvent-design task, together with the general algorithm.

Task 1: Solvent for Solid. The property under consideration is the mole fraction solubility of the user-selected solute in a solvent at a specified temperature T. The solubility x (mole fraction of solute) is calculated based on the following thermodynamic relationship

$$x = \gamma^{-1} \cdot \exp[\{T \cdot \Delta_{cr}^1 S(T) - \Delta_{cr}^1 H(T)\}/R \cdot T] \qquad (8)$$

where γ is the activity coefficient of the solute, $\Delta_{cr}^1 H(T)$ and $\Delta_{cr}^1 S(T)$ are the enthalpy and entropy of fusion adjusted to temperature T, and R is the gas constant. The preference criterion for this task is the solubility x, meaning the solvent that yields the highest value of x is ranked first in a list returned to the user.

Temperature adjustment of the enthalpy of fusion is based on the following equation

$$\Delta_{cr}^1 H(T) = \Delta_{cr}^1 H + \sum \Delta H_{tr}$$
$$+ \int_T^{T_{fus}} \{C_p(T = T_{fus}, \text{l})$$
$$- C_p(T = T_{fus}, \text{cr})\} dT \qquad (9)$$

where $\Delta_{cr}^1 H$ is the enthalpy of fusion at the fusion temperature T_{fus}, ΔH_{tr} are the enthalpies of solid–solid phase transitions that may occur between the temperatures T and T_{fus}, and the integrated term is the difference between the crystal and liquid heat capacities. This heat capacity difference is assumed constant and taken at T_{fus}. An analogous integrated term may also be added for changes in heat capacity at solid–solid phase transitions; however, these are generally small. Adjustment of the entropy of fusion is analogous.

Task 2: Selective Solvent for a Binary Solid Mixture. The property considered is, again, mole fraction solubility, but here, the user specifies the process temperature and two solutes; a primary *solute* and a *contaminant*. Results of this task could be applied in analysis of an industrial leaching operation. The solubilities of the solute and contaminant are calculated exactly as in Task 1. It is assumed that interactions between the dissolved solute and contaminant can be ignored. The preference criterion for this task is the selectivity s, which is calculated as

$$s = x_s/x_c \qquad (10)$$

where x_s and x_c are the calculated solubilities for the solute and contaminant, respectively. The user can reverse the roles of the solute and contaminant to possibly obtain a higher selectivity value.

Task 3: Solvent for Extraction of a Solute from a Binary Liquid Mixture. The system under consideration involves three

Figure 9. Calculation form for evaluation of property sensitivity to variations in process conditions within the *Uncertainty Analysis* form.

components, two of which are specified by the user. The user specifies a *solute* and a *carrier*, which is a solvent in which the *solute* is dissolved. The program returns a list of possible *solvents* that can serve as extractants for the solute. This task is inherently more complex than Tasks 1 or 2 because the mutual solubility of the carrier and proposed solvent must be considered. Liquid—liquid extraction only is considered.

The key property for this task is the distribution coefficient D, defined as the ratio of the mole fraction of solute in the solvent to that in the carrier. D is approximated as

$$D = \gamma_2^\infty / \gamma_1^\infty \tag{11}$$

where γ_2^∞ is the infinite-dilution activity coefficient of the solute in the carrier, and γ_1^∞ is the infinite-dilution activity coefficient of the solute in the proposed solvent.

Several additional properties are defined within this task that can be used to further refine the search results; *selectivity, solvent loss, carrier loss*, and *solvent power*. The *selectivity s* is defined as the ratio of the abilities of the solvent to dissolve the solute and carrier and is approximated as

$$s = \gamma_3^\infty / \gamma_1^\infty \tag{12}$$

where γ_3^∞ is the infinite-dilution activity coefficient of the solute in the solvent, and γ_3^∞ is the infinite-dilution activity coefficient of the carrier in the solvent.

Solvent loss S_L is a measure of the degree of solvent dissolved in the carrier and is approximated as

$$S_L = 1/\gamma_4^\infty \tag{13}$$

where γ_4^∞ is the infinite-dilution activity coefficient of the solvent in the carrier. If the solubility is low, S_L is nearly equal to the mole fraction solubility of the solvent in the carrier. Large values of S_L may indicate complete miscibility between the carrier and solvent, making extraction impossible.

Carrier loss C_L is analogous to *Solvent loss* and is a measure of carrier loss in the proposed solvent. It is approximated as

$$C_L = 1/\gamma_3^\infty \tag{14}$$

where γ_3^∞ is the infinite-dilution activity coefficient of the carrier in the solvent. In analogy to S_L, it is near the mole fraction solubility of the carrier in the proposed solvent, if the solubility is low, and large values of C_L may indicate complete miscibility.

The final additional property is *solvent power P*, which represents the ability of the proposed solvent to dissolve the solute. It is approximated as

$$P = 1/\gamma_1^\infty \tag{15}$$

where γ_1^∞ is the infinite-dilution activity coefficient of the solute in the proposed solvent and is near the mole fraction solubility, if the solubility is low. The *solvent power* is a measure of the mutual affinity between the solvent and solute.

The TDE interface for solvent selection is shown in Figure 10, and the general algorithm is shown in Figure 11. The TDE software includes a database of approximately 10 000 pre-fitted AC models for binary mixtures generated based on the
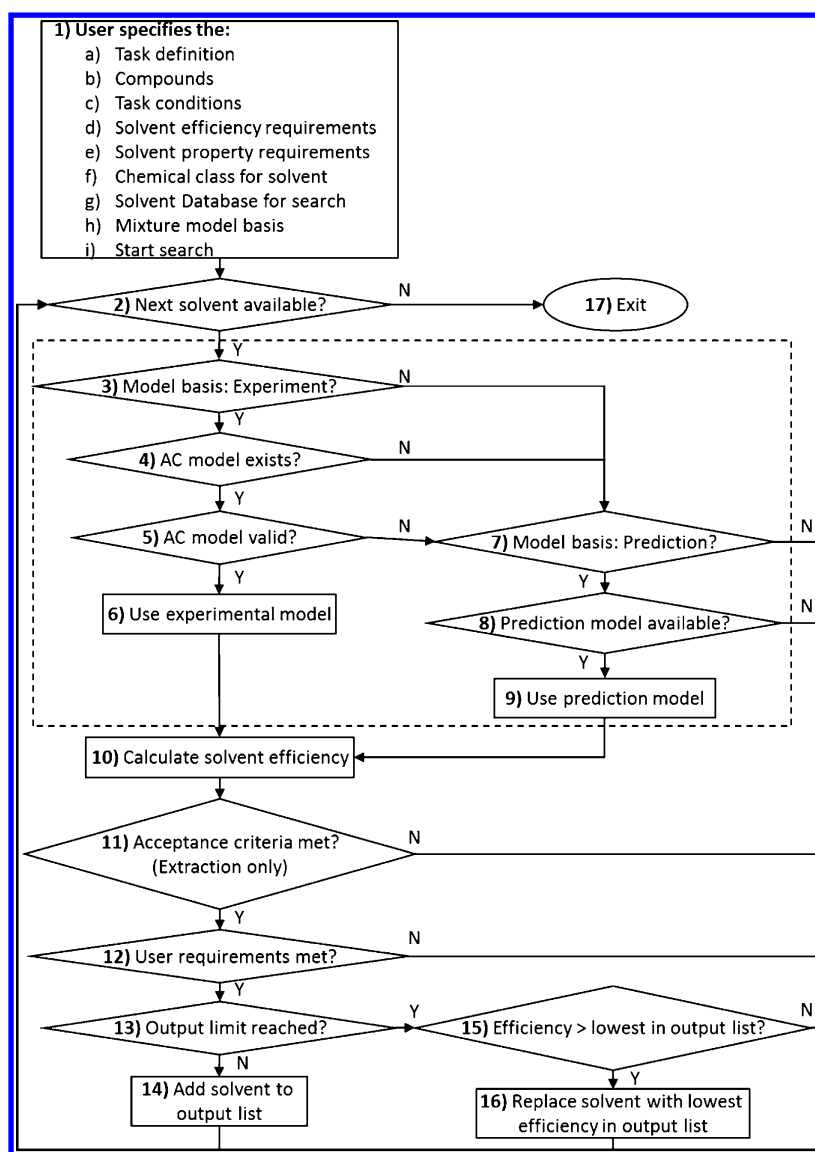
Figure 10. The *Product Design* form for specification of all user-controlled parameters in solvent design for three tasks; solvent for solid, selective solvent for a binary solid mixture, and solvent for extraction of a solute from a binary liquid mixture. The output (list of suggested solvents) display is indicated along with links for comprehensive data and model exploration.

experimental data in TDE-SOURCE. The algorithm for automatic generation of these fitted models was described recently.[7] The NRTL and UNIQUAC models are evaluated, and model parameters for the better representation of the experimental data are stored. Similarly, a database of pre-evaluated pure-component properties and models is included. Evaluation methods for pure components were described in the first paper of this series.[1] The pure component database was described previously with initial implementation of product design in TDE.[5]

Once one of the three solvent-selection tasks is chosen, the user is provided with a series of options to control the extent and basis of the solvent search and to constrain the returned results (*i.e.*, the list of suggested solvents) based on solvent efficiency, pure-component properties, and chemical class. The user interface for selection/entry of the necessary information is a single form (Figure 10) with a minimum of subforms. Steps 1 through 7 in Figure 10 represent all user control parameters; details and design considerations for each follow.

Step 1: Compound Specifications (Figure 10). Only the top two lines of the *Product Design* form for solvent selection are task-dependent. These are shown at the top of Figure 10 separated by dashed lines. For *Solvent for Solid*, only the

crystalline solute is specified by the user. The program checks to ensure that the solute is a solid at the specified conditions on initiation of the search. For *Selective Solvent for a Binary Solid Mixture*, the user selects a solid solute and contaminant, and for *Solvent for Extraction of a Solute from a Binary Liquid Mixture*, the user selects a solute and carrier solvent. The user can reverse the roles of the solute and contaminant in Task 2 or the solute and carrier in Task 3 with the *Switch Roles* button, as indicated at step 2 of Figure 10.

Step 2: Condition Specification (Figure 10). The only condition that must be specified by the user is temperature. The pressure is also a state variable for all three solvent-selection tasks, but because SLE and LLE are relatively insensitive to pressure, all evaluations are done for pressure $p \approx 0.1$ MPa. The solubility of gases is not considered at this time.

Step 3: Solvent Efficiency and Property Requirements (Figure 10). Solvent efficiency requirement choices are task dependent and involve specification of an upper limit, a lower limit, or both. For *Solvent for Solid*, the only quantity calculated is the solubility of the solute, and the user can specify limits for this value in mole or mass fraction. For *Selective Solvent for a Binary Solid Mixture*, choices are extended to include the solubility for

Figure 11. Algorithm for solvent design with TDE.

the solute and the selectivity (*i.e.*, the relative solubility defined earlier). *Solvent for Extraction* is a substantially more complex task, and a greater degree of control is offered to the user. Distribution coefficient, selectivity, solvent power, solvent loss, and carrier loss limits can all be specified. Mathematical definitions were provided earlier. The user can also specify limits for pure solvent thermodynamic and transport properties for all three tasks (heat capacity, density, vapor pressure, normal melting temperature, normal boiling temperature, critical temperature, enthalpy of vaporization, surface tension, viscosity, and thermal conductivity).

Step 4: Chemical Class Specification (Figure 10). Here, the user may choose to include or exclude specific compound classes, such as halogenated compounds, alcohols, acids, etc. These classes were first implemented in TDE for pure-component product design[5] and are the same for all tasks.

Step 5: Solubility Model Basis (Figure 10). The default selection here is to apply prediction for all activity coefficients based on the users selection of either original UNIFAC[33,34] or NIST KT-UNIFAC parameters.[23] The original UNIFAC parameters are those listed by Poling et al.,[49] augmented with

those published by Wittig et al.[50] The user can choose to limit searches to only those systems for which prefitted binary AC models are stored in a local database. This is done by selecting *Experiment* on the form. If results based on experiment or prediction are allowed by the user, then results based on experiment are preferred, if available.

Step 6: Search Database Specification (Figure 10). The user can choose to search for solvents within either of two databases: the Solvent Database of 600 common solvents and the entire TDE-SOURCE database with more than 27 000 compounds. The Solvent Database is included to allow faster searches and to limit results to known industrial solvents. Search time periods for the entire TDE-SOURCE rarely exceed a few minutes on a modern computer.

Step 7: Output Limit for Number of Solvents (Figure 10). The user can choose to limit the maximum number of solvents that can be returned by the program to 25, 50, or 100. This is a convenience to make the output list more manageable.

Step 8: Start Solvent Search (Figure 10). At this step, the user chooses to begin the search, and control is passed to the software.

Figure 12. Example of a completed Product Design form to search for a selective solvent for a binary solid mixture and (bottom) the search results. Access links to data exploration tools are circled in the lower right.

Algorithm for Solvent Selection. The algorithm for solvent selection based on the user selections is shown in Figure 11. In the following paragraphs, each step in this algorithm is described, along with any special considerations for particular solvent-selection tasks.

Step 1: User Specifications (Figure 11). The first step in Figure 11 shows a summary of the control selections made by the user. These selections control many steps within the algorithm.

Before starting the search, the program checks for possible problems with temperature/role/phase combinations, such as a solute specified as a solid at a condition (temperature) above its normal melting temperature, or a carrier (in Solvent for Extraction) that is similarly at a temperature that is too low. A warning is provided to the user in the case of *Solvent for Extraction*, when the temperature is out of range. For the tasks involving solid solubilities alone, the program does not proceed
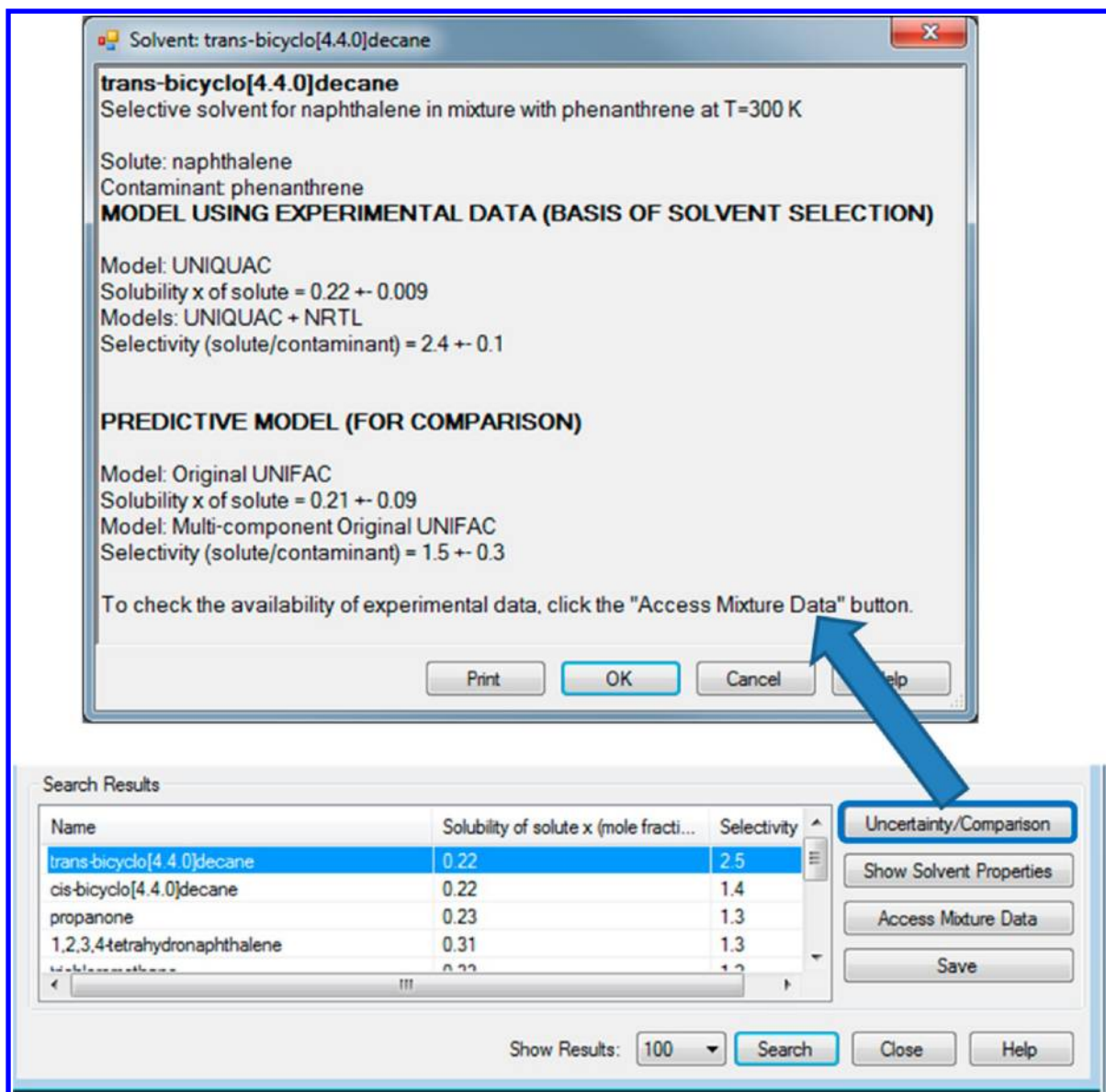
Figure 13. Access to uncertainties and model details from the Product Design form.

and requires the user to correct the conditions to adequately specify the problem.

Step 2: Next Solvent? (Figure 11). Once the search begins, the program cycles through all prospective solvent choices (600 in the Solvent Database or 27 000 in TDE-SOURCE) until the list is exhausted.

Step 3: Model Basis: Experiment? (Figure 11). If the user allows that all AC models for evaluation of activity coefficients be based on some experimental data, the database of pre-evaluated models is used. This greatly reduces the number of prospective solvents, because the 10 000 pre-evaluated AC models are a very small portion of the total number of possible compound combinations. This is why AC models based on predictions are the default choice. Once the search is completed, the user can explore any available mixture data and compare predicted and experimental values, if both are available.

Steps 4 and 5: Model Existence and Validity (Figure 11). At step 4, the program checks if a model exists. An important validity check is done at step 5, where the program checks the uncertainty calculated for the required activity coefficient(s) γ

from the experiment-based AC model. If the uncertainties are too large (here, larger than the value of γ), then the model is not used. All pre-evaluated models have limited ranges of application, so model validity can be tested only after specification of the temperature for the task.

Step 6: Use Experimental Model (Figure 11). Here, the model has passed the validity test and can be used to calculate the solvent efficiency (step 10).

Step 7: Model Basis: Prediction? (Figure 11). If the user has chosen to disallow prediction of activity coefficients, the solvent is rejected, and the program cycle returns to step 2 (next solvent).

Step 8: Prediction Model Available? (Figure 11). The prediction models implemented in TDE (original UNIFAC and NIST-KT-UNIFAC) are group-contribution methods with incomplete coverage for all possible required groups. Recently, this research group reported a new efficient method for evaluation of UNIFAC parameters based on newly published experimental data.[23] Although this will help keep the parameters current with the existing literature, comprehensive coverage is likely to
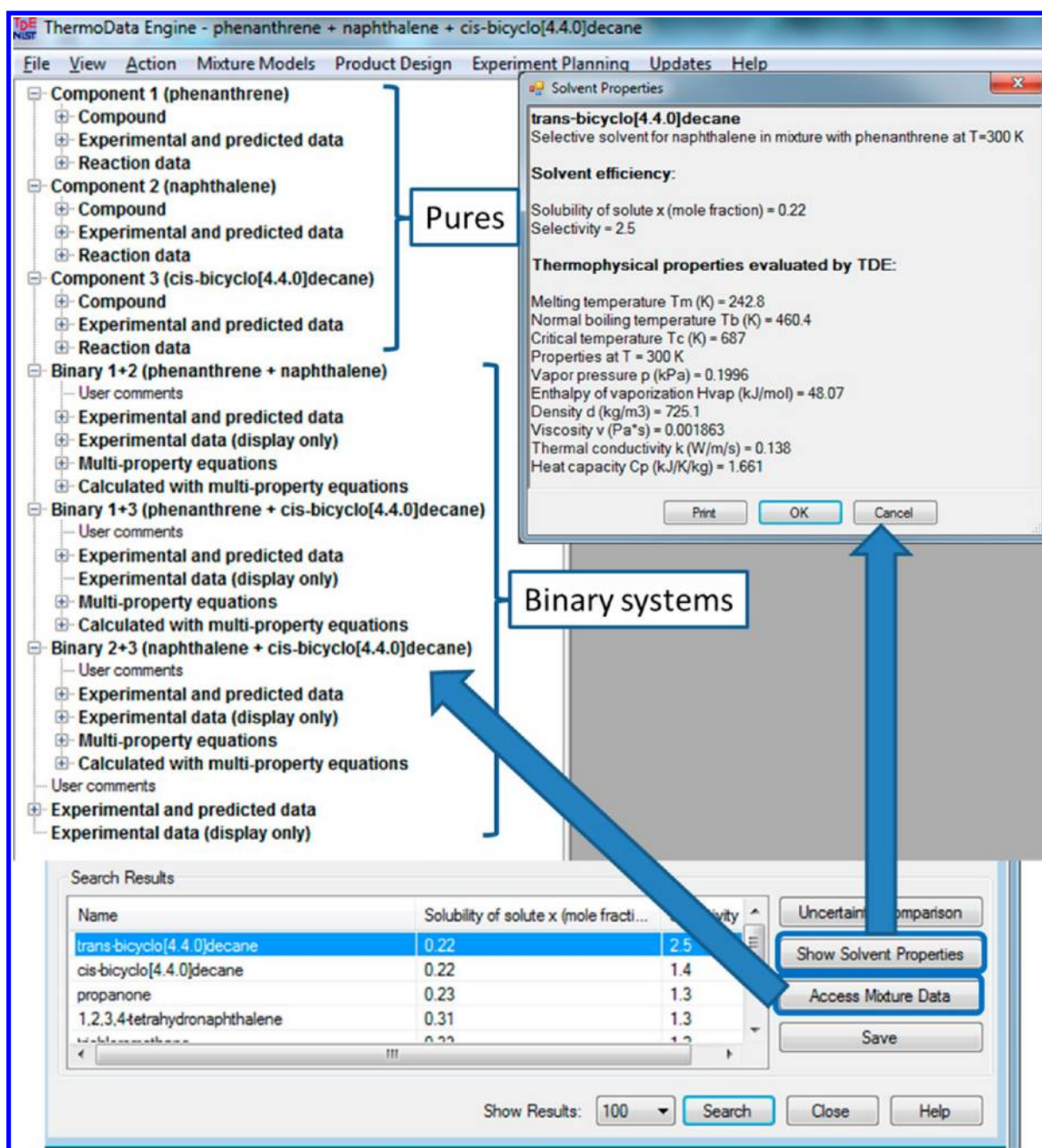
Figure 14. Access to evaluated solvent properties at the process conditions and access to experimental and predicted data and models for all pure and binary chemical systems involved in the solvent assessment.

remain an elusive goal. If a prediction cannot be applied, the solvent is skipped, and the program moves to the next candidate.

Step 9: Use Prediction Model (Figure 11). Here, all prediction model parameters are available, and the model can be used to calculate the solvent efficiency (step 10). The portion of Figure 11 enclosed by the dashed line is completed once for Task 1 {for the (solvent + solute)}, twice for Task 2 {for the (solvent + solute) and (solvent + contaminant)}, and three times for Task 3 {for the (solvent + solute), (solvent + carrier), and (solute + carrier)}.

Step 10: Calculate Solvent Efficiency (Figure 11). The solvent efficiency is calculated with the selected experiment-based or a prediction-based model. As noted earlier (Figure 10, step 5), the experiment-based results are preferred, if the user allows both types of evaluations.

Step 11: Acceptance Criteria Met? (*Solvent for Extraction* only) (Figure 11). Special acceptance criteria must be met in the case of *Solvent for Extraction* (Task 3), because LLE is involved. (Tasks 1 and 2 involve SLE only.) Acceptance criteria are as follows: (1) selectivity greater than one (*i.e.*, the solvent must have a stronger tendency to dissolve the solute than the carrier, and (2) some evidence for an LLE split between the solvent and carrier must exist. If the AC model is original UNIFAC or NIST-KT-UNIFAC, the sum of solvent and carrier losses must be less than one. If the AC model is based on experimental data, then the stored model must show an LLE split between solvent and carrier at the extraction temperature entered by the user. The temperature range of LLE is stored with the model parameters for all stored binary AC models to lessen the overall computation time. At the end of the process, the user can explore available

experimental data and models for any mixture through the solvent selection interface, as will be described later.

Step 12: User Requirements Met? (Figure 11). As described earlier (Figure 11, step 1), the user has the option to require specific property ranges for thermodynamic and transport properties for the solvent, as well as ranges for measures of solvent efficiency. All requirements established by the user must be passed at this step or the solvent is rejected.

Steps 13 through 17: Output Control (Figure 11). The output for this process is a list of compounds with up to 25, 50, or 100 compounds, as specified by the user. If the solvent has passed all previous steps and the limit of compounds has not been reached, the solvent is added to the output list (step 14). If the limit has been reached, the task-specific solvent efficiency is used to rank the solvent (step 15), and the output solvent list is updated, as needed (step 16). Solvent ranking is based on solubility for Task 1 (eq 8), selectivity for Task 2 (eq 10), and distribution coefficient for Task 3 (eq 11). When the list of prospective solvents has been exhausted, control is returned to the user for exploration and saving of results (step 17).

■ INTERFACE FEATURES FOR SOLVENT DESIGN

Interface features for solvent design are demonstrated here through an example of Task 2 (Selective Solvent for a Binary Solid Mixture). The example involves search for a solvent to separate a solid mixture of phenanthrene and naphthalene. The completed user interface is shown in the upper portion of Figure 12, where it is seen that the user has added an efficiency requirement (solubility of naphthalene must exceed 0.15 mol fraction) and two property requirements (a minimum normal boiling temperature and maximum melting temperature). Also, the solubility models must be based on fits to experimental data, as indicated by the *Experiment* check box, and the entire TDE-SOURCE database is considered.

The search is initiated by the user through the *Search* button at the bottom of the form, and the resulting list of suggested solvents is returned, as shown in the insert at the bottom of Figure 12. Once results are returned, the three buttons to the right of the solvent list are activated to provide access to details of the results and to allow exploration of underlying properties and models.

The *Uncertainty/Comparison* link (Figure 13) provides access to details concerning results for the particular solvent chosen (here, trans-bicyclo[4.4.0]decane, also known as trans-decalin). Information provided includes the AC models used {here, UNIQUAC for (naphthalene + solvent) and NRTL for (phenanthrene + solvent)}, the solubility of the solute in the solvent with the evaluated uncertainty, the calculated selectivity and its uncertainty, plus the analogous values based on prediction (UNIFAC) for comparison.

The *Show Solvent Properties* link (Figure 14) provides access to a list of solvent properties at the selected problem conditions (here, temperature T = 300 K and the default pressure p = 0.1 MPa). The *Access Mixture Data* link loads all of the underlying experimental data and models into the primary TDE interface (i.e., the Navigation Tree), details of which have been described previously.[1,3] The Navigation Tree provides access to tables of experimental data, model parameters, deviation plots, etc., for comprehensive data exploration. For example, Figure 15 shows the SLE phase diagram for the system (naphthalene + solvent), including the available experimental data (black dots) and the curve calculated with the fitted UNIQUAC model.
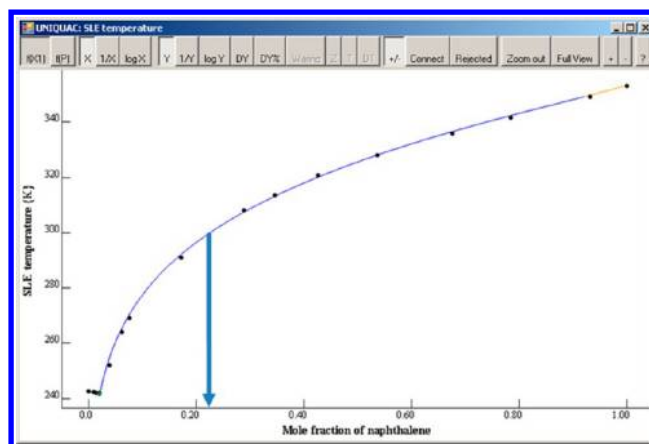
Figure 15. Plot of solid−liquid equilibrium temperature for the system (naphthalene + trans-bicyclo[4.4.0]decane) accessed through the TDE navigation tree shown in Figure 14. The arrow (added here) indicates the solubility of naphthalene at the process conditions specified in Figure 12. The black dots are literature values, and the line represents the fitted UNIQUAC model.

■ CONCLUSIONS AND FUTURE DEVELOPMENT

The algorithm for extension of dynamic data evaluation for material streams has been developed and implemented in TDE. The second important enhancement reported here is solvent design within the product-design features of the software. These are described for selection of solvents for optimized crystal dissolution, separation of binary crystal mixtures, and solute extraction from a single-component solvent. These new features have been implemented in NIST ThermoData Engine software (version 7).[25]

Future plans for improvement of TDE include implementation of advanced group-contribution methods for prediction of enthalpies of formation of pure compounds in the liquid and gas phases, incorporation of a new NIST-Modified-UNIFAC model, currently under development for prediction of phase equilibria, and incorporation of equations of state for binary mixtures.

■ APPENDIX A: MATHEMATICAL FORMULATION OF MODELS FOR MATERIAL STREAMS

Data evaluation for a material stream includes evaluation for n pure components and $(n^2-n)/2$ binary mixtures. Two types of binary models are used to calculate properties of material streams. The Redlich−Kister equation is used to fit excess volume, excess enthalpy, viscosity, thermal conductivity, surface tension, and index of refraction for single phase (liquid or gas) systems. The form Ψ^{ex} used for excess volume and excess enthalpy is

$$\Psi^{ex} = \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=0}^{nTerms} a_{ijk} \cdot x_i \cdot x_j \cdot (x_i - x_j)^k \tag{A1}$$

where a_{ijk} are binary parameters for components i and j. Bulk properties Z (except viscosity and density) are calculated as

$$Z = \sum_{i=1}^{n} x_i \cdot Z_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=0}^{nTerms} a_{ijk} \cdot x_i \cdot x_j \cdot (x_i - x_j)^k \tag{A2}$$

Density ρ is calculated as

$$\rho = \sum_{i=1}^{n} x_i \cdot M_i / V_m;$$

$$V_m = \sum_{i=1}^{n} x_i \cdot M_i / \rho_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=0}^{nTerms} a_{ijk} \cdot x_i \cdot x_j \cdot (x_i - x_j)^k \tag{A3}$$

where M_i is the molar mass of component i. Viscosity η is calculated as

$$\ln(\eta/\eta^\circ) = \sum_{i=1}^{n} x_i \cdot \ln(\eta_i/\eta^\circ)$$
$$+ \left\{ \frac{1}{2} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{k=0}^{nTerms} a_{ijk} \cdot x_i \cdot x_j \cdot (x_i - x_j)^k \right\} \quad (A4)$$

where η° is 1 Pa·s.

Activity-coefficient (AC) models for ternary mixtures were implemented in accordance with the methods described by Novak.[51]

AC Models for Material Streams (Multicomponent Mixtures)

All AC models for material streams can be obtained readily by conversion of models given previously for three components[7] to models for n components. Conversion of the NRTL model is given here as an example. All other model conversions are analogous.

NRTL Model for Ternary Systems

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{3} x_j \cdot \tau_{ji} \cdot G_{ji}}{\sum_{k=1}^{3} x_k \cdot G_{ki}}$$
$$+ \sum_{j=1}^{3} \frac{x_j \cdot G_{ij}}{\sum_{k=1}^{3} x_k \cdot G_{kj}} \cdot \left(\tau_{ji} - \frac{\sum_{m=1}^{3} x_m \cdot \tau_{mj} \cdot G_{mj}}{\sum_{k=1}^{3} x_k \cdot G_{kj}} \right) \quad (A5)$$

where $G_{ji} = \exp(-\alpha_{ij} \cdot \tau_{ij})$, and α_{ij} and τ_{ij} are binary NRTL parameters at a given temperature. Parameter τ_{12} is binary parameter c_1, τ_{21} is binary parameter c_2, α_{12} and α_{21} are binary parameter k for a mixture of components 1 and 2; $\tau_{ii} = 0$, and $\alpha_{ii} = 0$. The binary parameters c_1, c_2, and k were defined previously.[3]

NRTL Model for Multicomponent Systems

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{n} x_j \cdot \tau_{ji} \cdot G_{ji}}{\sum_{k=1}^{n} x_k \cdot G_{ki}}$$
$$+ \sum_{j=1}^{n} \frac{x_j \cdot G_{ij}}{\sum_{k=1}^{n} x_k \cdot G_{kj}} \cdot \left(\tau_{ji} - \frac{\sum_{m=1}^{n} x_m \cdot \tau_{mj} \cdot G_{mj}}{\sum_{k=1}^{n} x_k \cdot G_{kj}} \right) \quad (A6)$$

where $G_{ji} = \exp(-\alpha_{ij} \cdot \tau_{ij})$, and α_{ij} and τ_{ij} are binary NRTL parameters at a given temperature. Parameter τ_{12} is binary parameter c_1, τ_{21} is binary parameter c_2, α_{12} and α_{21} are binary parameter k for a mixture of components 1 and 2; $\tau_{ii} = 0$, and $\alpha_{ii} = 0$. The binary parameters c_1, c_2, and k were defined previously.[3]

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Notes

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■ **REFERENCES**

(1) Frenkel, M.; Chirico, R. D.; Diky, V.; Yan, X.; Dong, Q.; Muzny, C. D. ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. *J. Chem. Inf. Model.* **2005**, *45*, 816−838.

(2) Diky, V.; Muzny, C. D.; Lemmon, E. W.; Chirico, R. D.; Frenkel, M. ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 2: Equations of State on Demand and Dynamic Updates over the Web. *J. Chem. Inf. Model.* **2007**, *47*, 1713−1725.

(3) Diky, V.; Chirico, R. D.; Kazakov, A. F.; Muzny, C. D.; Frenkel, M. ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 3: Binary Mixtures. *J. Chem. Inf. Model.* **2009**, *49*, 503−517.

(4) Diky, V.; Chirico, R. D.; Kazakov, A. F.; Muzny, C. D.; Frenkel, M. ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 4: Chemical Reactions. *J. Chem. Inf. Model.* **2009**, *49*, 2883−2896.

(5) Diky, V.; Chirico, R. D.; Kazakov, A. F.; Muzny, C. D.; Magee, J. W.; Abdulagatov, I.; Kang, J. W.; Kroenlein, K.; Frenkel, M. ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 5. Experiment Planning and Product Design. *J. Chem. Inf. Model.* **2011**, *51*, 181−194.

(6) Kroenlein, K.; Muzny, C. D.; Diky, V.; Kazakov, A. F.; Chirico, R. D.; Magee, J. W.; Abdulagatov, I.; Frenkel, M. ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 6. Dynamic Web-Based Data Dissemination through the *NIST Web Thermo Tables*. *J. Chem. Inf. Model.* **2011**, *51*, 1506−1512.

(7) Diky, V.; Chirico, R. D.; Muzny, C. D.; Kazakov, A. F.; Kroenlein, K.; Magee, J. W.; Abdulagatov, I.; Kang, J. W.; Frenkel, M. ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 7. Ternary Mixtures. *J. Chem. Inf. Model.* **2012**, *52*, 260−276.

(8) (a) Wilhoit, R. C.; Marsh, K. N. Future Directions for Data Compilation. *Int. J. Thermophys.* **1999**, *20*, 247−255. (b) Frenkel, M. Dynamic Compilation: A Key Concept for Future Thermophysical Data Evaluation. In *Forum 2000: Fluid Properties for New Technologies − Connecting Virtual Design with Physical Reality*; Rainwater, J. C., Friend, D. G., Hanley, H. J. M., Harvey, A. H., Holcomb, C. D., Laesecke, A., Magee, J. W., Muzny, C. D., Eds.; NIST Special Publication 975; National Institute of Standards and Technology: Gaithersburg, MD, 2001; pp 83−84.

(9) Frenkel, M. Global Communications and Expert Systems in Thermodynamics: Connecting Property Measurement and Chemical Process Design. *Pure Appl. Chem.* **2005**, *77*, 1349−1367.

(10) Frenkel, M.; Chirico, R. D.; Diky, V.; Yan, X.; Dong, Q.; Muzny, C. D. *NIST ThermoData Engine, NIST Standard Reference Database 103*, version 1.0; Standard Reference Data Program, National Institute of Standards and Technology: Gaithersburg, MD, 2004.

(11) Frenkel, M.; Chirico, R. D.; Diky, V.; Muzny, C. D.; Lemmon, E. W.; Yan, X.; Dong, Q. *NIST ThermoData Engine, NIST Standard Reference Database 103*, version 2.0; Standard Reference Data Program, National Institute of Standards and Technology: Gaithersburg, MD, 2006.

(12) Frenkel, M.; Dong, Q.; Wilhoit, R. C.; Hall, K. R. TRC SOURCE Database: A Unique Tool for Automatic Production of Data Compilations. *Int. J. Thermophys.* **2001**, *22*, 215−226.

(13) Frenkel, M.; Chirico, R. D.; Diky, V.; Muzny, C. D.; Kazakov, A. F.; Lemmon, E. W. *NIST ThermoData Engine, NIST Standard Reference Database 103b-Pure Compounds and Binary Mixtures*, version 3.0; Standard Reference Data Program, National Institute of Standards and Technology: Gaithersburg, MD, 2008.

(14) Frenkel, M.; Chirico, R. D.; Diky, V.; Muzny, C. D.; Kazakov, A. F. *NIST ThermoData Engine, NIST Standard Reference Database 103b-Pure Compounds, Binary Mixtures, and Chemical Reactions*, version 4.0;

Standard Reference Data Program, National Institute of Standards and Technology: Gaithersburg, MD, 2009.

(15) Diky, V.; Chirico, R. D.; Kazakov, A. F.; Muzny, C. D.; Magee, J. W.; Abdulagatov, I.; Kang, J. W.; Kroenlein, K.; Frenkel, M. *NIST ThermoData Engine, NIST Standard Reference Database 103b-Pure Compounds, Binary Mixtures, and Chemical Reactions*, version 5.0; Standard Reference Data Program, National Institute of Standards and Technology: Gaithersburg, MD, 2010.

(16) Kroenlein, K.; Muzny, C. D.; Kazakov, A. F.; Diky, V.; Chirico, R. D.; Magee, J. W.; Abdulagatov, I.; Frenkel, M. *NIST Web Thermo Tables (WTT). Lite Edition, NIST Standard Reference Subscription Database 202*, http://www.nist.gov/srd/nistwebsub2.cfm; *Professional Edition, NIST Standard Reference Subscription Database 203*, http://www.nist.gov/srd/nistwebsub3.cfm (accessed Nov 26, 2012).

(17) Frenkel, M.; Chirico, R. D.; Diky, V.; Muzny, C. D.; Dong, Q.; Marsh, K. N.; Dymond, J. H.; Wakeham, W. A.; Stein, S. E.; Königsberger, E.; Goodwin, A. R. H.; Magee, J. W.; Thijssen, M.; Haynes, W. M.; Watanasiri, S.; Satyro, M.; Schmidt, M.; Johns, A. I.; Hardin, G. R. New Global Communication Process in Thermodynamics: Impact on Quality of Published Experimental Data. *J. Chem. Inf. Model.* **2006**, *46*, 2487−2493.

(18) Cummings, P. T.; de Loos, T.; O'Connell, J. P.; Haynes, W. M.; Friend, D. G.; Mandelis, A.; Marsh, K. N.; Brown, P. L.; Chirico, R. D.; Goodwin, A. R. H.; Wu, J.; Weir, R. D.; Trusler, J. P. M.; Pádua, A.; Rives, V.; Schick, C.; Vyazovkin, S.; Hansen, L. D. Joint Statement of Editors of Journals Publishing Thermophysical Property Data: Process for Article Submission for The Journal of Chemical Thermodynamics, Fluid Phase Equilibria, International Journal of Thermophysics, Thermochimica Acta, and Journal of Chemical Engineering Data. *Fluid Phase Equilib.* **2009**, *276*, 165−166; *Int. J. Thermophys.* **2009**, *30*, 371−373; *J. Chem. Eng. Data* **2009**, *54*, 2−3; *J. Chem. Thermodyn.* **2009**, *41*, 575−576; *Thermochim. Acta* **2008**, *484*, vii−viii.

(19) Frenkel, M. Thermophysical and Thermochemical Properties on-Demand for Chemical Process and Product Design. *Comput. Chem. Eng.* **2011**, *35*, 393−402.

(20) Watanasiri, S. Development of on-Demand Critically Evaluated Thermophysical Properties Data in Process Simulation. *Pure Appl. Chem.* **2011**, *83*, 1255−1281.

(21) Frenkel, M. Global Information Systems in Science: Application to the Field of Thermodynamics. *J. Chem. Eng. Data* **2009**, *54*, 2411−2428.

(22) Kang, J. W.; Diky, V.; Chirico, R. D.; Magee, J. W.; Muzny, C. D.; Abdulagatov, I.; Kazakov, A. F.; Frenkel, M. A Quality Assessment Algorithm for Vapor-Liquid Equilibrium Data. *J. Chem. Eng. Data* **2010**, *55*, 3631−3640.

(23) Kang, J. W.; Diky, V.; Chirico, R. D.; Magee, J. W.; Muzny, C. D.; Abdulagatov, I.; Kazakov, A. F.; Frenkel, M. A New Method for Evaluation of UNIFAC Interaction Parameters. *Fluid Phase Equilib.* **2011**, *309*, 68−75.

(24) Kang, J. W.; Abildskov, J.; Gani, R.; Cobas, J. Estimation of Mixture Properties from First- and Second-Order Group Contributions with UNIFAC Model. *Ind. Eng. Chem. Res.* **2002**, *41*, 3260−3273.

(25) Frenkel, M.; Chirico, R. D.; Diky, V.; Muzny, C. D.; Kazakov, A. F.; Magee, J. W.; Abdulagatov, I. M.; Kroenlein, K.; Diaz-Tovar, C.; Kang, J. W.; Gani, R. *NIST ThermoData Engine, NIST Standard Reference Database 103b-Pure Compounds, Binary Mixtures, and Chemical Reactions*, version 7.0; Standard Reference Data Program, National Institute of Standards and Technology: Gaithersburg, MD, 2012.

(26) Modarresi, H.; Conte, E.; Abildskov, J.; Gani, R.; Crafts, P. Model-Based Calculation of Solid Solubility for Solvent Selections - A Review. *Ind. Eng. Chem. Res.* **2008**, *47*, 5234−5242.

(27) Gani, R.; Sansonetti, S. Property Modelling and Databases in Product-Process Design. 18th Symposium on Thermophysical Properties, Boulder CO, June 24−29, 2012.

(28) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14* (1), 135−144.

(29) Redlich, O.; Kister, A. T. Thermodynamics of Nonelectrolyte Solutions - x-y-t relations in a Binary System. *Ind. Eng. Chem.* **1948**, *40*, 341−345.

(30) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21* (1), 116−128.

(31) Van Laar, J. J. The Vapor Pressure of Binary Mixtures. *Z. Phys. Chem.* **1910**, *72*, 723−751.

(32) Wilson, G. M. Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

(33) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. *AIChE J.* **1975**, *21*, 1086−1099.

(34) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor Liquid Equilibrium Using UNIFAC*; Elsevier: Amsterdam, 1977.

(35) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw Hill: New York, 2001; p 6.28.

(36) Redlich, O.; Kwong, J. N. S. On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions. *Chem. Rev.* **1949**, *44*, 233−244.

(37) Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

(38) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hseih, R. *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*; Prentice Hall: New York, 1980.

(39) Lemmon, E. W.; Huber, M. L.; McLinden, M. O. *NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP*, version 9.0; Standard Reference Data Program, National Institute of Standards and Technology: Gaithersburg, 2010.

(40) Larsen, A. H. Data Quality for Process Design. *Fluid Phase Equilib.* **1986**, *29*, 47−58.

(41) Machietto, S.; Maduabeuke, G.; Szczepanski, R. Exact Determination of Process Sensitivity to Physical Properties. *Fluid Phase Equilib.* **1986**, *29*, 59−67.

(42) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes: The Art of Scientific Computing*, 3rd ed.; Cambridge University Press: 2007.

(43) Reed, M. E.; Whiting, W. B. Sensitivity and Uncertainty of Process Designs to Thermodynamic Model Parameters: A Monte Carlo Approach. *Chem. Eng. Commun.* **1993**, *124*, 39−48.

(44) Whiting, W. B.; Tong, T.-M.; Reed, M. E. Effect of Uncertainties in Thermodynamic Data and Model Parameters on Calculated Process Performance. *Ind. Eng. Chem. Res.* **1993**, *32*, 1367−1371.

(45) Whiting, W. B. Effects of Uncertainties in Thermodynamic Data and Models on Process Calculations. *J. Chem. Eng. Data* **1996**, *41*, 935−941.

(46) Vasquez, V. R.; Whiting, W. B. Effect of Systematic and Random Errors in Thermodynamic Models on Chemical Process Design and Simulation: A Monte Carlo Approach. *Ind. Eng. Chem. Res.* **1999**, *38*, 3036−3045.

(47) Hajipour, S.; Satyro, M. A. Uncertainty Analysis Applied to Thermodynamic Models and Process Design − 1. Pure Components. *Fluid Phase Equilib.* **2011**, *307*, 78−94.

(48) Theodorou, D.; Zannikou, Y.; Anastopoulos, G.; Zannikos, F. Coverage Interval Estimation of the Measurement of Gross Heat of Combustion of Fuel by Bomb Calorimetry: Comparison of ISO GUM and Adaptive Monte Carlo Method. *Thermochim. Acta* **2011**, *526*, 122−129.

(49) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw Hill: New York, 2001; pp 8.78−8.94.

(50) Wittig, R.; Lohmann, J.; Gmehling, J. *Ind. Eng. Chem. Res.* **2003**, *42*, 183−188.

(51) Novak, J. P.; Matous, J.; Pick, J. *Liquid-liquid Equilibria*; Elsevier: Amsterdam, 1987; pp 283−288.