DISTILLATION SIMULATION WITH COSMO-RS

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ABSTRACT

COSMO-RS is a novel and efficient method for the *a-priori* prediction of thermodynamic properties of mixtures. It is based on unimolecular quantum chemical calculations that provide the necessary information for the evaluation of molecular interactions in liquids. Thus, the method provides an alternative to group contribution methods such us UNIFAC for the true prediction of activity coefficients and K-values.

The starting point for our work was an existing computer program for performing multicomponent, multistage separation process calculations using Newton's method. The existing code is the one included in the software package *ChemSep*™. The simulation model was combined with the COSMOtherm code that implements the COSMO-RS thermodynamic property prediction methods.

Comparisons of column profiles predicted by COSMO-RS and other models (UNIQUAC and UNIFAC) have shown that sometimes COSMO-RS is in good agreement with these other models and sometimes it is not. On the other hand even conventional activity coefficient models don't always agree with one another!
The conclusion is that COSMO-RS could become an alternative to conventional thermodynamic property models for the preliminary design of distillation processes and for the design of any process for which no data of any kind exists. However, more work is needed in order to show that COSMO-RS is able to predict adequately the VLE behavior of multicomponent mixtures.

It was also found that the combination of computational models is rather more time consuming than, for example, UNIFAC, but the times are not excessive and the approach does not require extreme computational times (as would be the case with other purely predictive methods based on molecular dynamics, for example).

The Equilibrium Stage Model
The starting point for our work was an existing computer program for performing multicomponent, multistage separation process calculations using Newton's method. The existing code is the one included in the software package *ChemSep™* [4,5]. The form of the model used in this program is outlined below.

The equations that model equilibrium stages are termed the MESH equations, MESH being an acronym referring to the different types of equations that form the mathematical model. The *M* equations are the Material balance equations, of which there are two types: **The Total Material Balance**

$$M_j \equiv V_{j+1} + L_{j-1} + F_j - (1 + r_j^V)V_j - (1 + r_j^L)L_j = 0 \qquad (1)$$

and the **Component Material Balances**

$$M_{ij} \equiv V_{j+1}y_{i,j+1} + L_{j-1}x_{i,j-1} + F_j z_{i,j} - (1 + r_j^V)V_j y_{i,j} - (1 + r_j^L)L_j x_{i,j} = 0 \qquad (2)$$

where the r_j are the ratios of sidestream flows to interstage flows.

$$r_j^V = S_j^V / V_j; \quad r_j^L = S_j^L / L_j \qquad (3)$$

The *E* equations are the **Equilibrium relations**

$$E_{i,j} \equiv y_{i,j} - K_{i,j}x_{i,j} = 0 \qquad (4)$$

The S equations are the **Summation equations**

$$S_j^L \equiv \sum_{i=1}^{c} x_{i,j} - 1 = 0; \quad S_j^V \equiv \sum_{i=1}^{c} y_{i,j} - 1 = 0 \qquad (5)$$

and the H equations are the **Heat balance equations**

$$H_j \equiv V_{j+1}H_{j+1}^V + L_{j-1}H_{j-1}^L + F_j H_j^F - (1 + r_j^V)V_j H_j^V - (1 + r_j^L)L_j H_j^L - Q_j = 0 \quad (6)$$

where the superscripted *H*'s are the enthalpies of the appropriate phases or streams.

There are 2*c* + 4 equations per stage. However, only 2*c* + 3 of these equations are independent. In our program both total and component material balances are used and the
two summation equations are combined to give

$$S_j \equiv \sum_{i=1}^{c} y_{i,j} - \sum_{i=1}^{c} x_{i,j} - 1 = 0 \qquad (7)$$

The 2*c* + 3 unknown variables determined by the equations are the *c* vapor mole fractions, $y_{i,j}$, the *c* liquid mole fractions, $x_{i,j}$; the stage temperature, T_j, and the vapor and liquid flowrates: V_j and L_j.

The COSMO-RS Model and its Use for K-Values
COSMO-RS is a novel approach to the *a priori* prediction of thermodynamic data of liquids that combines quantum chemical calculations with dielectric continuum solvation models and with statistical thermodynamics.

In a first step for each of the compounds involved in a chemical process a quantum chemical calculation has to be performed, in which a single compound molecule is treated as a solute in a virtual perfect conductor. Such Conductor-like Screening Model (COSMO) calculations provide the total energy of the compound in the conductor and the polarization charge densities σ on the surface of the molecule, which result from the polarization of the conductor [6]. Density functional theory (DFT) has turned out to be a good level of quantum theory for COSMO-RS. Typical calculation times for industrial compounds are in the range of 1 day on a 1GHz computer. All DFT/COSMO calculations used for this paper have been performed with the program TURBOMOLE [1]. They were taken from the COSMO*base* database, which holds pre-calculated DFT/COSMO files for more than 1000 industrial relevant compounds [12].

In a second step (COSMO for Real Solvents, COSMO-RS) the polarization charge densities from COSMO are used to quantify the interactions of molecular surfaces in dense liquids [7,8,9]. By this novel representation of molecular interactions, the free energies of the surfaces interactions are specified with respect to the different physical forces, i.e. electrostatic interactions, hydrogen bonding, and van der Waals interactions, and characteristic temperature dependencies are taken into account for each of these contributions. Finally a rather accurate and efficient, new approach called COSMOSPACE [10] is used for the evaluation of the statistical thermodynamics of the interacting surfaces of all the compounds in a liquid mixture.

In this way COSMO-RS provides a bridge between theoretical chemistry and chemical engineering thermodynamics, since it allows for the calculation of the thermodynamics of liquids and liquid mixtures, using nothing else than the chemical structure information as input. A detailed description of the COSMO-RS is given in reference c6. All COSMO-RS of this paper have been performed using a linkable version of the COSMO*therm* program [2].

There are two ways to use COSMO-RS:
- The model can be employed to compute the activity coefficients and the K-values follow from
  $$K_i = \gamma_i P_i^S / P$$
  The vapor pressure can be estimated using, for example, the Antoine equation.
- Alternatively, COSMO-RS can compute the vapor pressure as well as the activity coefficient and in essence becomes a model for the entire K-value.

For this work we have employed COSMO-RS only as a method of predicting activity coefficients.

Solving the Model Equations
Newton's method is used to solve the nonlinear process model equations.

The equilibrium stage model equations can be expressed in the functional form:
$$\mathbf{f}(\mathbf{x}) = \mathbf{0}$$
where **f** is the vector of model equations:
$$\mathbf{f}^T \equiv (\mathbf{f}_1, \mathbf{f}_2, \ldots, \mathbf{f}_{s-1}, \mathbf{f}_s)^T$$

$\mathbf{f}_j$ is a vector of model equations for stage j.

$$\mathbf{f}_j^T \equiv (M_j^T, M_{1,j}, M_{2,j}, ..., M_{c,j}, H_j, E_{1,j}, E_{2,j}, ..., E_{c,j}, S_j^{V-L})^T$$

$\mathbf{x}$ is the vector of variables:

$$\mathbf{x}^T \equiv (\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_{s-1}, \mathbf{x}_s)^T$$

where $\mathbf{x}_j$ is the vector of variables for stage j.

$$\mathbf{x}_j^T \equiv (V_j, y_{1,j}, y_{2,j}, ..., y_{c,j}, L_j, x_{1,j}, x_{2,j}, ..., x_{c,j}, T_j)^T$$

To use Newton's method, we repeatedly solve Equation (7) linearized about a current guess, $\mathbf{x}_k$, of the vector of unknown variables:

$$\mathbf{J}_k \Delta \mathbf{x}_k = -\mathbf{f}(\mathbf{x}_k)$$

where $\mathbf{J}_k$ is the Jacobian matrix at the k-th iteration with elements

$$J_{ij} = \frac{\partial f_i}{\partial x_j}$$

and where

$$\Delta \mathbf{x}_k = \mathbf{x}_{k+1} - \mathbf{x}_k$$

Initial estimates of all variables (including the end stage temperatures and flows) are generated automatically. Vapor and liquid flows are estimated assuming constant molar overflow. The mole fractions of both phases and temperatures on all stages are estimated by performing three iterations of the Wang-Henke method (see Henley and Seader, 1981). Ideal solution K-values are used only for the first of these iterations before switching to a more appropriate thermodynamic model for the remainder of the calculations.

The partial derivatives of thermodynamic properties with respect to temperature and composition were obtained numerically for COSMO-RS and analytically for all other models used for comparison purposes. Composition derivatives are with respect to the unconstrained mole fractions [4].

The method is assumed to have converged when either of the following two criteria are satisfied:

$$\sqrt{\sum_{j=1}^{s} \sum_{i}^{e_j} f_{ij}^2} < \varepsilon \qquad \text{or} \qquad \sqrt{\sum_{j=1}^{s} \sum_{i}^{e_j} |\Delta x_{ij} / x_{ij}|} < \varepsilon$$

where s is the number of stages, e_j is the number of equations for the j-th stage, and ε is a small number. In view of the fact that none of the equations are scaled and enthalpies have units of J/kmol, the latter criterion usually is satisfied first.

Examples
While it is possible to use COSMO-RS to simulate many operations that cannot even be attempted with other models due to a lack of thermodynamic data or even UNIFAC interaction parameters, we do not report such cases here. We believe that it is necessary to compare COSMO-RS to existing methods so as to establish a degree of confidence that the COSMO-RS either is a valid alternative to existing methods or to point out potential weaknesses in the new method, perhaps leading to further improvements.

Several different K-value models are employed in this comparison:

- The K-values estimated from the model used in the DECHEMA collection ($K_i = \gamma_i P_i^S / P$) with COSMO-RS used for the activity coefficient and the vapor pressures estimated using the Antoine equation (this approach is denoted by ● on most figures).
- K-values from the DECHEMA model above but with UNIFAC used for the activity coefficient (▲).
- K-values from the DECHEMA model above but with UNIQUAC used for the activity coefficient with parameters from the DECHEMA handbooks (◄).
- K-values from the DECHEMA model above but with UNIQUAC used for the activity coefficient with parameters estimated from UNIFAC infinite dilution activity coefficients (►).
- The K-values estimated from the method in the book of Prausnitz et al (1980) [11]. This model employs the UNIQUAC equation for activity coefficients (parameters given in the book), the Virial equation of state for the vapor phase fugacity coefficient, and a 5-parameter extended Antoine-like equation for the pure species fugacity coefficient in the liquid (©).

In all cases the enthalpy was calculated from the same model except that the excess enthalpy requires the evaluation of the temperature derivative of the activity coefficient.

Note that not all models are employed for all case studies. It should be noted that the UNIQUAC parameters used for each model were fitted by the authors of the sources of the parameters to data obtained in a consistent way. Thus, for example, the parameters from Prausnitz et al. (1980) [11] were fitted to experimental data while using the virial equation for the vapor phase and the extended Antoine-like equation, whereas those obtained from DECHEMA use just the Antoine equation for the vapor pressure. Thus, all models represent valid ways in which to compute the K-values. The option in which we used UNIFAC at infinite dilution to estimate parameters for UNIFAC is used in practice to obtain parameters that might not be available from fits of actual experimental data.

With the exception of the first, our test cases are taken from papers by Vickery and Taylor (1986a,b) [14,15] and by Venkataraman and Lucia (1988) [13]. Stage numbers include condenser (stage 1) and reboiler (the last stage if present).

Problem 1:

System: Methanol – Water
Stages: 12
Total Condenser (R = 2), Partial reboiler (B = 70 mol/s)
Pressure 1 atm.
Feed: Saturated liquid to stage 9: methanol 30 mol/s, water 70 mol/s

Our first example is a very simple textbook type of problem involving a distillation column separating methanol and water. Figure 1 shows the composition profiles for this column obtained using COSMO-RS and, for comparison purposes, UNIFAC. The profiles are very close in this case. In Figures 2 and 3 we show the *T-x-y* and *y-x* diagrams predicted using COSMO-RS and UNIFAC. There are some differences

between the diagrams, but not enough to lead to significant differences between the models when used to design a simple distillation column for this system.
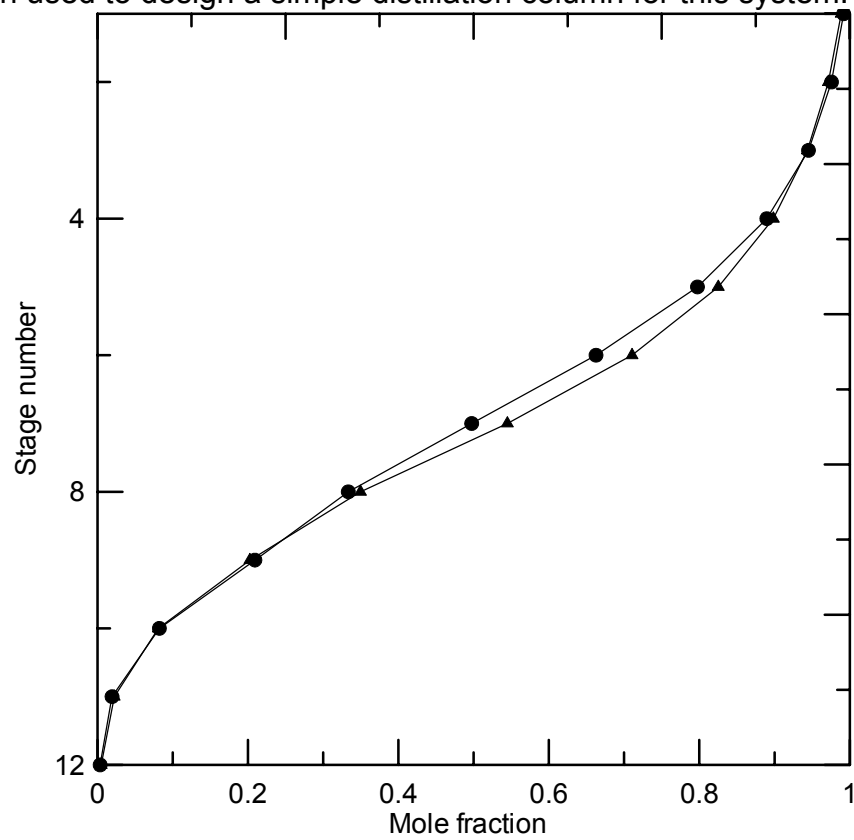

Figure 1: Composition profiles in a simple distillation column for methanol water system predicted by COSMO-RS (●) and UNIFAC (▲).
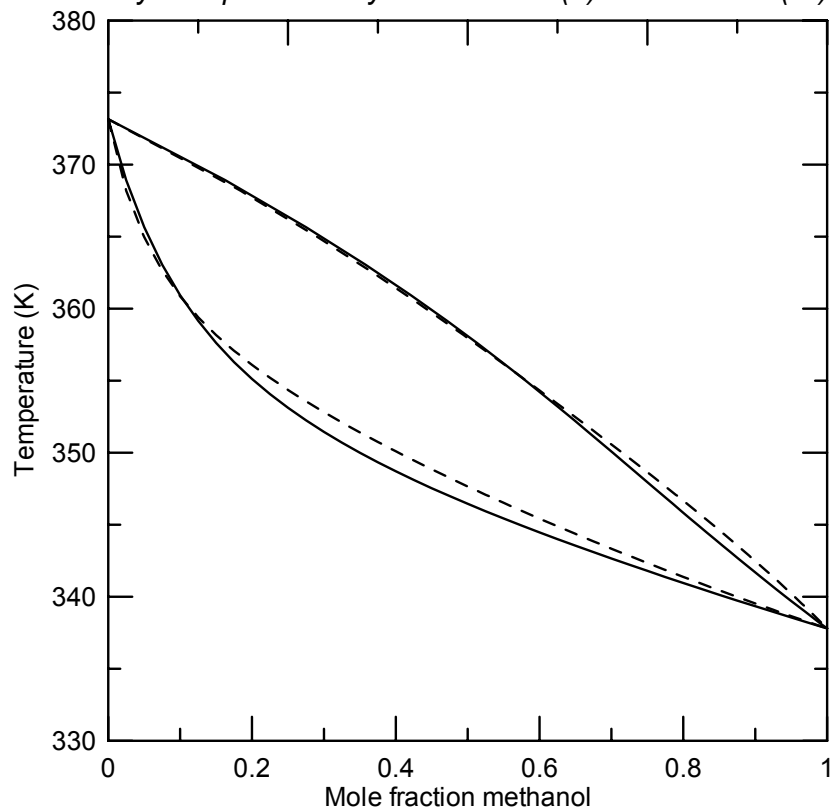

Figure 2: T-x-y diagram for methanol water system predicted by COSMO-RS (broken lines) and UNIFAC (solid lines).
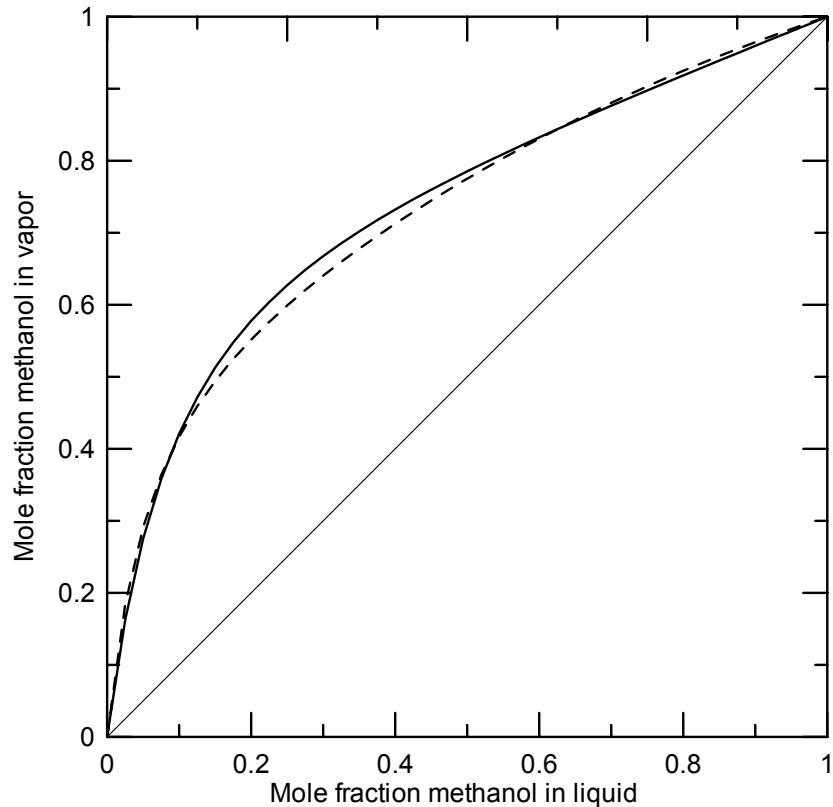
Figure 3: x-y diagram for methanol water system predicted by COSMO-RS (broken line) and UNIFAC (solid line).

Problem 2:

System: Methanol – Ethanol – Water
Stages: 76
Total Condenser (R = 32), no reboiler
Pressure 1 atm.
Feeds: Liquid at 373 K to stage 12: water 3220 mol/h.
      Liquid at 352 K stage 24: methanol 16 mol/h, ethanol 16 mol/hr, water 68 mol/h.
      Vapor at 373.2 K to stage 76: water 650 mol/h.
Sidestream: Liquid from stage 71 at 224 mol/h.

Example 2 is a more complicated example involving the steam distillation of a methanol – ethanol mixture. The composition profiles obtained with COSMO-RS and with UNIFAC as the activity coefficient models are very similar to each other and are not shown for that reason. In Fig. 4 we show the composition profile by plotting the mole fractions of methanol against the mole fraction of water. Both curves have the same shape and very similar characteristics.
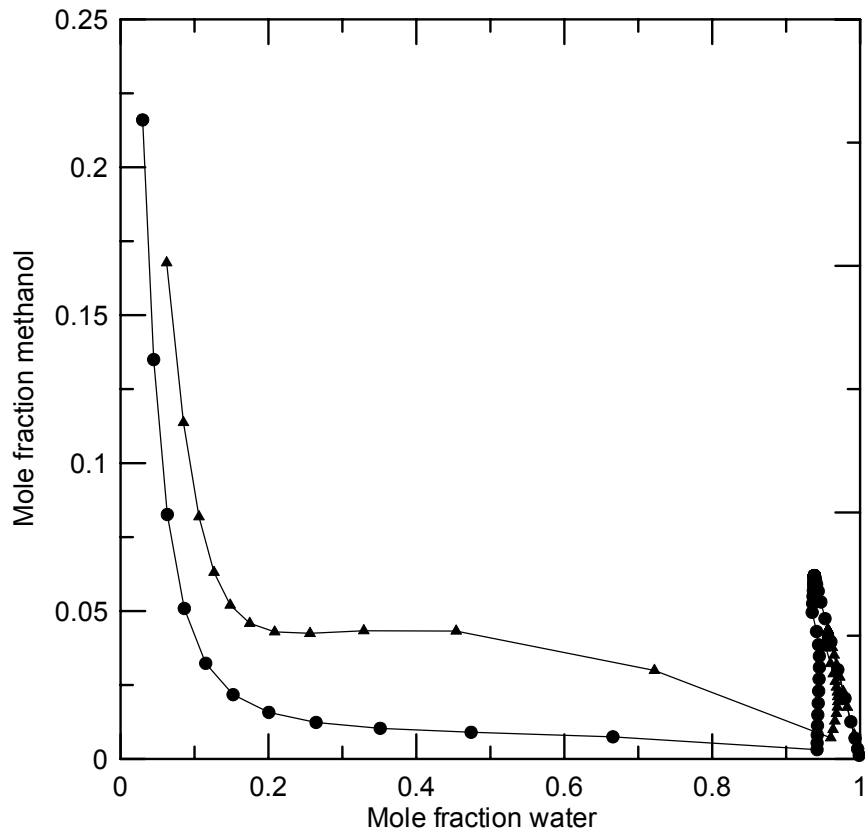
Figure 4: Composition profiles in a steam extractive distillation of a methanol ethanol mixture system predicted by COSMO-RS (●) and UNIFAC (▲).

Problem 3:

System: Acetone – Methanol – Water
Stages: 34
Total Condenser (R = 4), Partial reboiler (B = 202 kmol/h)
Pressure 1 atm.
Feeds: Liquid at 323.2 K to stage 10: water 25 kmol/h.
           Liquid at 329.3 K stage 22: acetone 50 kmol/h, methanol 50 kmol/h.

Our third example involves the extractive distillation of acetone and methanol using water as the extractive agent. The column profiles are shown in Figures 5 and 6. For this particular example the UNIQUAC' and UNIFAC models give essentially identical results as is evident in Figure 6. The profiles obtained with COSMO-RS are, however, quite close to those for the other two models.
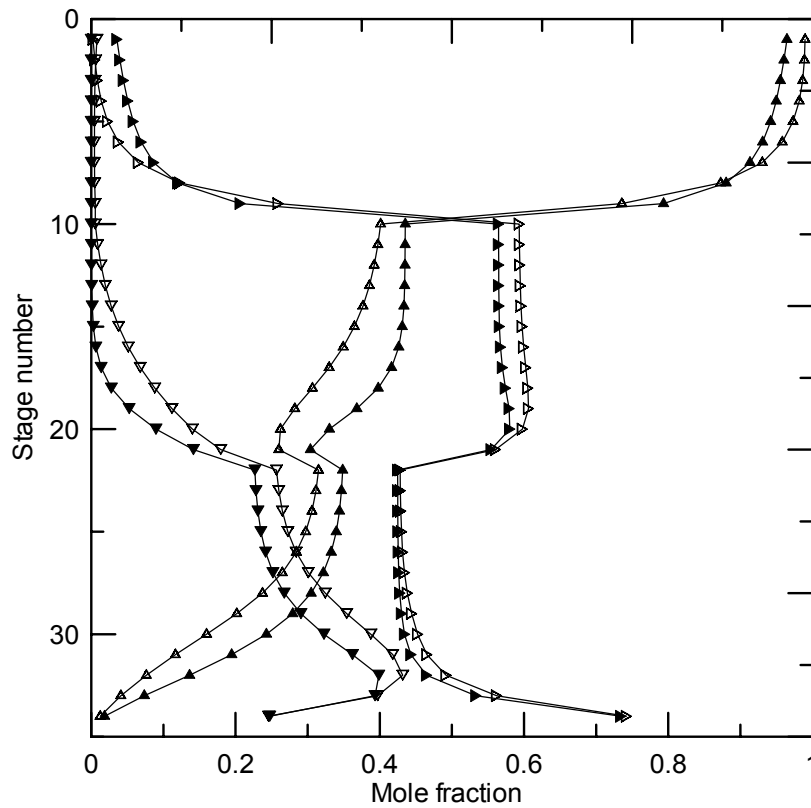
Figure 5: Composition profiles in the extractive distillation of an acetone (▲) - methanol (▼) - water (►) system predicted by COSMO-RS (open symbols) and UNIFAC models (solid symbols).
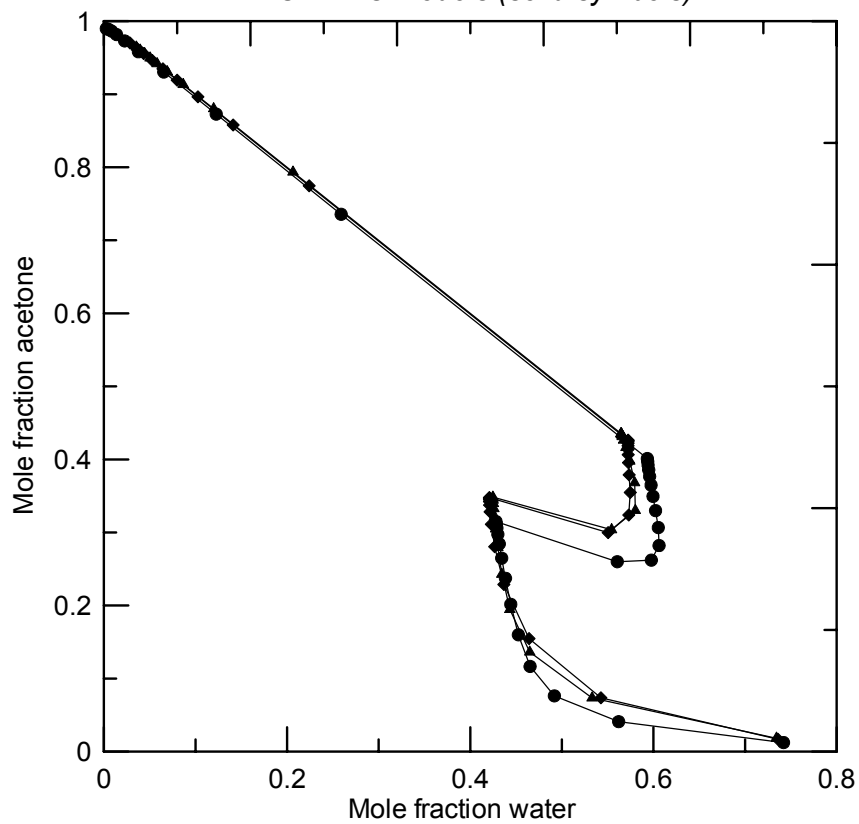

Figure 6: Composition profiles in the extractive distillation of an acetone - methanol - water system predicted by COSMO-RS (●), UNIFAC (▲) and UNIQUAC models (◆).

Problem 4:

System: Acetone – Chloroform – Methanol
Stages: 25
Total Condenser (R = 10), Partial reboiler (B = 75 kmol/h)
Pressure 1 atm.
Feeds: Liquid at 330.7 K to stage 15.
          Acetone 30 kmol/h, methanol 23 kmol/h, chloroform 47 kmol/h.

Example 4 involves the distillation of an acetone – chloroform – methanol mixture. Composition profiles obtained with COSMO-RS and UNIQUAC (this time with parameters estimated from the UNIFAC model at infinite dilution) are shown in Fig. 7.
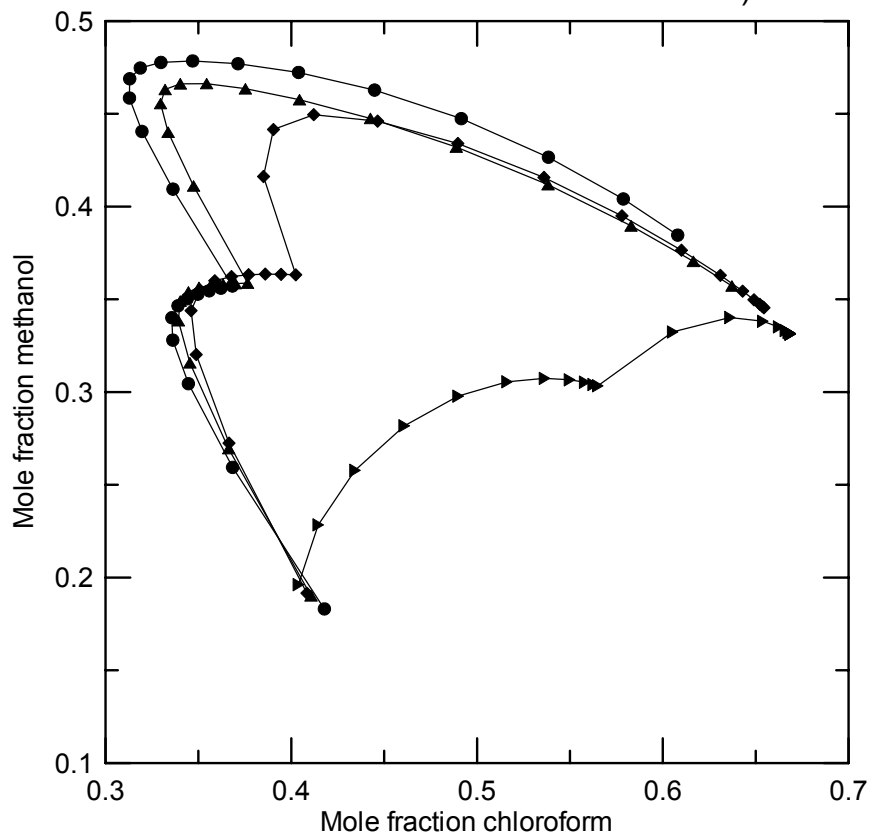

Figure 7: Composition profiles in the distillation of an acetone - chloroform - methanol system predicted by COSMO-RS (●), UNIFAC (▲) and UNIQUAC models (◆ and ►).

In this case there is a significant difference in the profiles predicted by these models, The COSMO-RS model is very close to the UNIFAC model and in reasonable agreement with the UNIQUAC' model as well. However, the UNIQUAC (F) model with parameters estimated from the infinite dilution UNIFAC model is very different. It is important to recognize that this system has three binary azeotropes (two of them minimum boiling) as well as a ternary saddle azeotrope. One might, therefore, expect that the composition profiles for such a system would be particularly sensitive to the (predicted) location of the azeotropes. COSMO-RS has no parameters fitted to the mixture as a whole, thus it is quite an achievement for the COSMO-RS model to be in good agreement with a model fitted to data for this system (UNIQUAC' and UNIFAC).

Problem 5:

System: Acetone – Methanol – Water – Ethanol
Stages: 50
Total Condenser (R = 3), Partial reboiler (B = 124 kmol/h)
Pressure 1 atm.
Feeds: Liquid at 321.9 K to stage 6: water 50 kmol/h.
               Liquid at 310.8 K stage 21:
               Acetone 25 kmol/h, methanol 65 kmol/h,
               ethanol 5 mol/h, water 5 mol/h.

Our next example is a four component system involving acetone, ethanol, methanol, and water in a column similar to, but not absolutely identical to an example from Venkataraman and Lucia (1988) [13]. The column has 50 stages (42 in the original) and feeds to stages 6 and 21. Composition profiles for this process are shown in Figs. 8 and 9. In this example the composition profiles are in very good agreement. There is a modest discrepancy in the profiles of acetone and methanol at the top of the column.
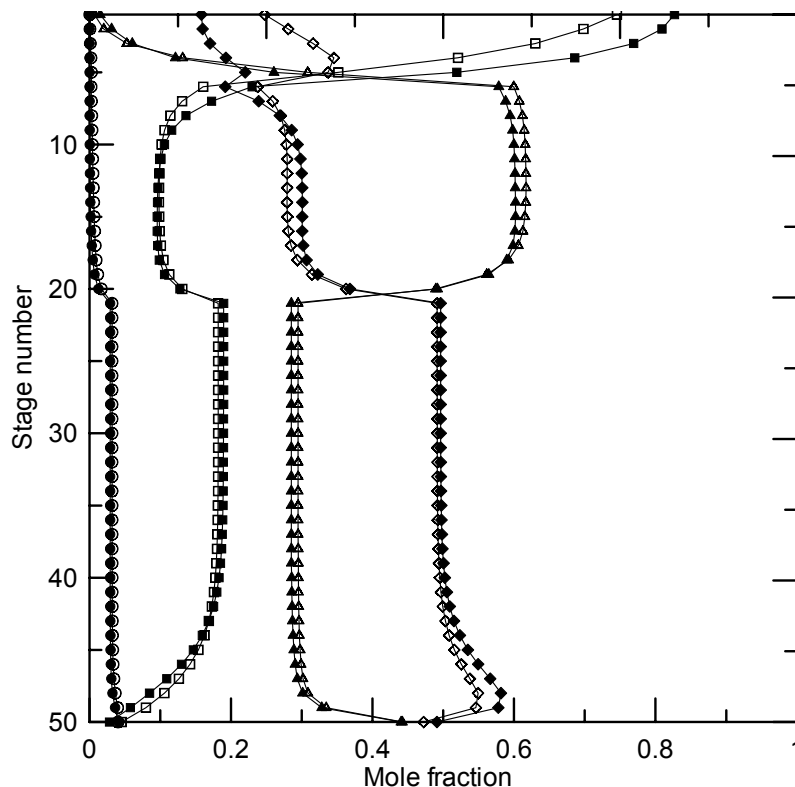

Figure 8: Composition profiles in the extractive distillation of an acetone (■) – methanol (♦) – ethanol (●) – water (▲) system predicted by COSMO-RS (open symbols) and UNIQUAC model with parameters estimated from UNIFAC (solid symbols).
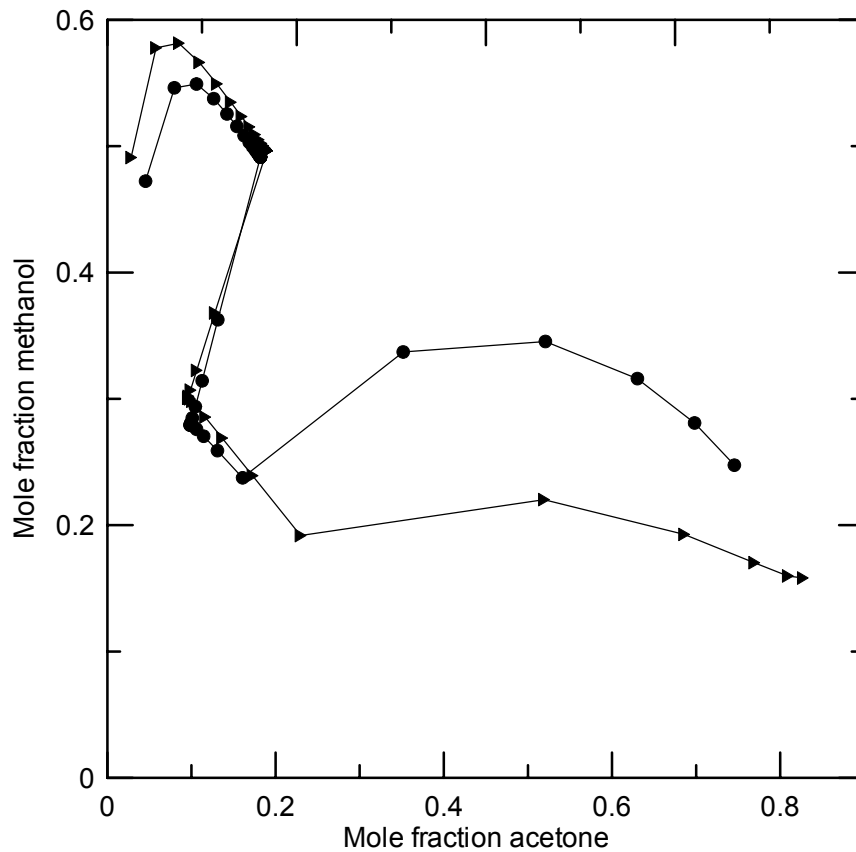
Figure 9: Composition profiles in the distillation of an acetone - methanol - ethanol - water system predicted by COSMO-RS (●) and UNIQUAC models (►).

Problem 6:

System: Ethanol – t-Butanol – Water
Stages: 45
Total Condenser (R = 12.5), partial reboiler (B = 45 kmol/h)
Pressure 1 atm.
Feeds: Liquid at 352.2 K to stage 25:
           Ethanol 55 kmol/h, t-butanol 20 kmol/hr, water 25 kmol/h.

Our sixth example involves the distillation of an ethanol – t-butanol – water mixture. Composition profiles for this example are shown in Figure 10.
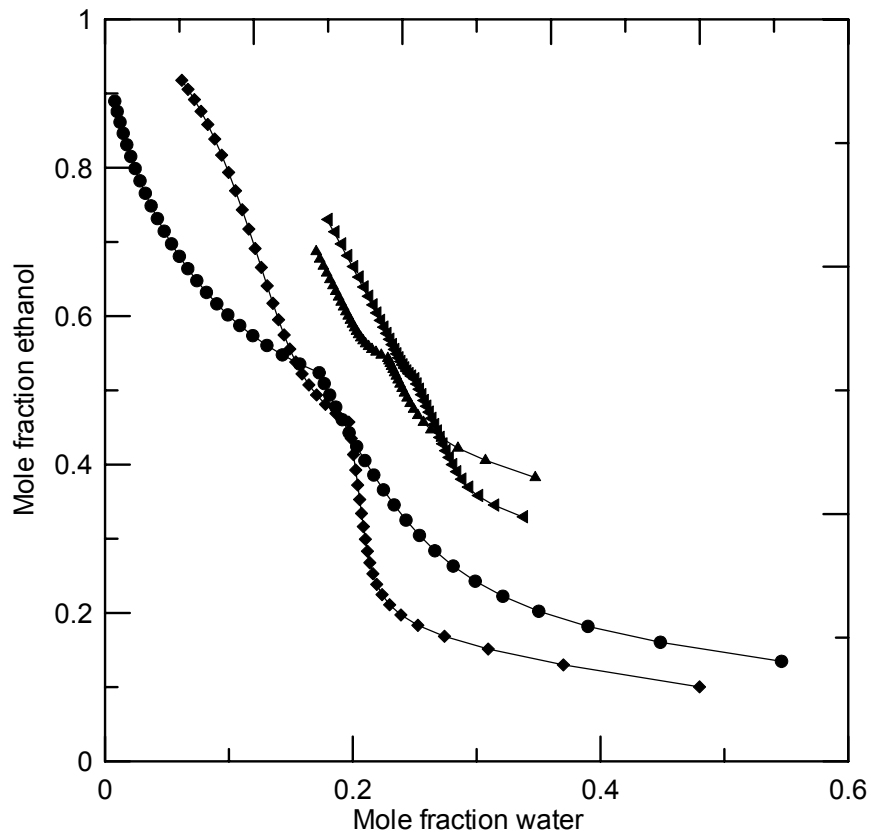
Figure 10: Composition profiles in the distillation of an ethanol – t-butanol – water system predicted by COSMO-RS (●), UNIFAC (▲) and UNIQUAC models (◆ and ◄).

What is immediately obvious here is the very great difference between the composition profiles for the various UNIQAC/UNIFAC models considered. It is also interesting to note that, in this case, COSMO-RS is not all that different from the UNIQUAC' model from the book of Prausnitz et al. (1980) [11].

Problem 7:

System: Methanol – Ethanol – n-Propanol – Water
Stages: 21
Total Condenser (R = 2.5), partial reboiler (B = 55 mol/h)
Pressure 1 atm.
Feeds: Liquid at 331.5 K stage 11:
            Methanol 25 mol/h, ethanol 25 mol/hr, n-propanol 25 mol/h,
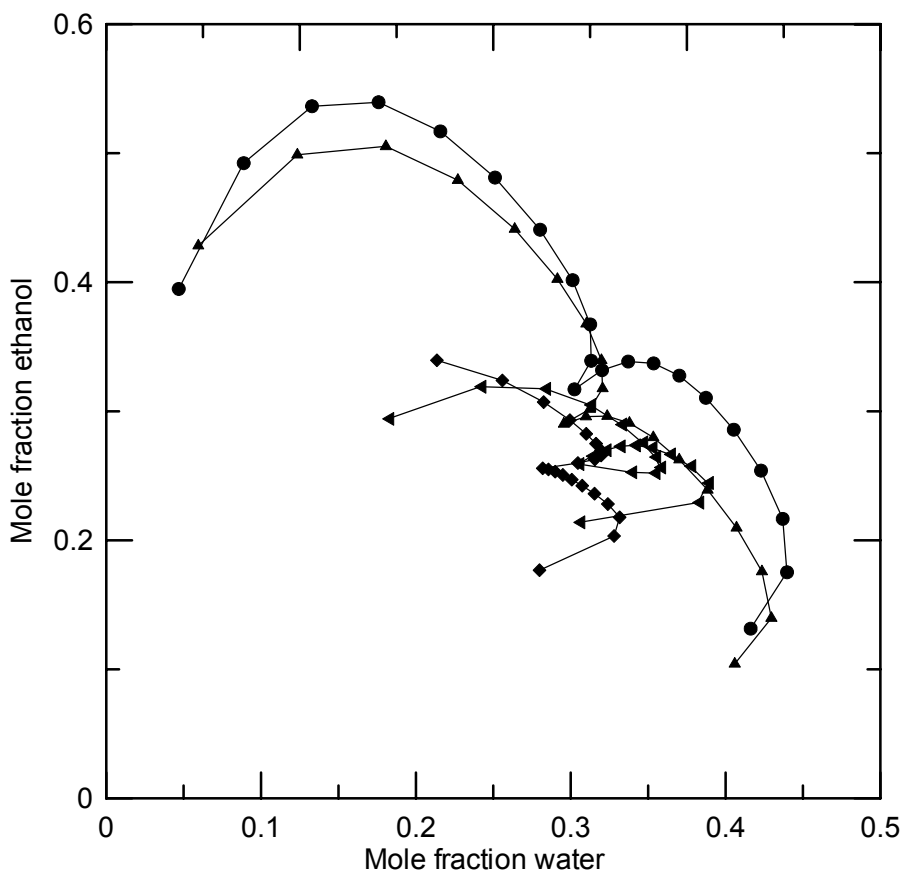   water 25 mol/h.

Figure 11: Composition profiles in the distillation of methanol – ethanol – n-propanol – water system predicted by COSMO-RS (●), UNIFAC (▲) and UNIQUAC models (◆ and ◄).

Composition profiles for our final example are shown in Figures 11. Again, we see a significant difference between the various models, but now COSMO-RS is close to the profiles obtained with UNIFAC whereas the two UNIQUAC models (UNIQUAC' from Prausnitz et al., and the standard UNIQUAC with parameters from the DECHEMA collection) are very different.

Numerical Issues

Many of the test cases have served as test cases for distillation algorithms and, in times past, would have been considered to be difficult to converge. None of these examples posed any convergence difficulties in this study. Moreover, convergence of the program was largely unaffected by the choice of activity coefficient model. That is, the program would take the same number of iterations regardless of what activity coefficient model was used. There is, however, a significant difference in the times required by the different methods. The test cases that were solved using UNIQUAC or UNIFAC were done in times too short to record (on a 1.8 GHz personal computer). COSMO-RS required significantly more time, of the order of minutes for the larger problems (Problem 7, for example, required 8 iterations and 5 minutes 57 seconds). However, it is essential to note that the derivatives of the activity coefficients with respect to temperature and mole fraction were obtained by numerical means. Thus, these properties were being evaluated many more times than was the case for the other models. The time required by COSMO-RS will always be greater than that needed for UNIQUAC or UNIFAC, for example, but when the derivatives are

available analytically, as will shortly be the case, we expect that the time required will be reduced significantly (by a factor of 4 or more for Problem 7).

For the mixtures considered here the molecules are small and the setup time for the initial DFT/COSMO calculations is of the order of a couple of hours on a current PC. That was not necessary for the present study since the necessary calculations had already been done for all the species involved in this study and the results available in the extensive COSMO-RS database. For more complicated (larger) compounds the setup time will be longer. However, it need be done only once per component and the existing COSMO-RS database is quite extensive.

Concluding Remarks

We have combined an existing equilibrium stage distillation simulation program (ChemSep^{TM}) with a new method for predicting thermodynamic properties of liquid mixtures (COSMO-RS).

We have *not* focused on demonstrating those instances where COSMO-RS offers perhaps its most significant advantage: handling of systems for which no VLE data of any kind is available, distinguishing between isomers, modeling chemicals important in environmental applications, solvent screening for liquid extraction [3], to name but a few. Instead, we have modeled systems whose thermodynamics is relatively well known in problems frequently used as test cases for distillation simulation methods. To the best of our knowledge, this is the first time that COSMO-RS has been used to model distillation operations.

Comparisons of column profiles predicted by COSMO-RS and several more conventional models (variations on the theme of UNIQUAC and UNIFAC) has shown that sometimes COSMO-RS is in very good agreement with these other models and sometimes the agreement is less good. On the other hand, we have also shown that even conventional activity coefficient models don't always agree with one another! The present study has focused on systems for which UNIQUAC and UNIFAC parameters are available and these models would, therefore, be expected to out perform COSMO-RS. In a later work we will investigate more complicated systems involving larger molecules and systems for which UNIFAC parameters are not available.

The conclusion that leaps most readily to mind will not come as a surprise to any engineer with expertise in equilibrium stage modeling. That is: know your thermo! We believe that COSMO-RS has a great deal of promise for the future. At present, however, one must use a tool like COSMO-RS in much the same way that one uses *any* thermodynamic model: with care.

NOTATION

c	Number of components	-
c_t	Total concentration	$mol \cdot m^{-3}$
F_j	Molar feed stream to stage j	$mol \cdot s^{-1}$
$f_{i,j}$	Molar feed flow of component i to stage j	$mol \cdot s^{-1}$
H	Enthalpy, homotopy function	$J \cdot mol^{-1}$

$K_{i,j}$	Equilibrium constant of component i on stage j	-
L_j	Molar liquid flow rate 1 from stage j	$mol{\cdot}s^{-1}$
P_j	Pressure on stage j	Pa
Q_j	Heat duty on stage j	$J{\cdot}s^{-1}$
R	Gas constant	$J{\cdot}mol^{-1}{\cdot}K^{-1}$
T	Temperature	K
V_j	Molar vapor flow rate from stage j	$mol{\cdot}s^{-1}$
$x_{i,j}$	Mole fraction of component i on stage j	-
$y_{i,j}$	Mole fraction of component i on stage j, vapor phase	-

Greek symbols

γ_i	Activity coefficient of component i	-
$\delta_{i,k}$	Kronecker delta	-
ε	Convergence tolerance	-
μ	Chemical potential	$J{\cdot}mol^{-1}$
ρ	Density	$kg{\cdot}m^{-3}$

Superscripts

F	Feed quantity or property	-
L	Liquid phase quantity or property	-
V	Vapor phase quantity or property	-

Subscripts

i	component number	-
j	stage number	-
k	Alternative component number	-

REFERENCES

1. Ahlrichs, R., M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Letters*, **162**, 165 (1989)

2. COSMOtherm program, Release CT1.2, COSMOlogic GmbH&CoKG, Leverkusen, Germany (2002)

3. Eckert, F., and A. Klamt, *AIChE J*, **48**, 369-385 (2002)

4. Kooijman, H.A. and R. Taylor, *CACHE News*, Fall 1992, pp 1-9

5. Kooijman, H.A. and R. Taylor, *The ChemSep Book,* Books on Demand, Norderstedt, Germany (2000).

6. Klamt, A. and G. Schüürmann, *J. Chem. Soc. Perkin Trans.*, **2**, 799 (1993)

7. Klamt, A., *J. Phys. Chem.*, **99**, 2224 (1995)

8. Klamt, A., V. Jonas, T. Buerger, J.C.W. Lohrenz, *J. Phys. Chem.*, **102**, 5074 (1998)

9. Klamt, A., Eckert, F., *Fluid Phase Equilibria*, **172**, 43 (2000)

10. Klamt, A. G. Krooshof, and R. Taylor, *AIChE J* accepted (2002)

11. Prausnitz, J., T. Anderson, E. Grens, C. Eckert, R. Hsieh, and J. O'Connell, Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria, Prentice Hall, Englewood Cliffs, N.J. (1980).

12. Schäfer, A., Klamt, A., Sattel, D., Lohrenz, J.C.W., and Eckert, F., *Phys. Chem. Chem. Phys. 2*, 2187 (2000)

13. Venkataraman, S. and A. Lucia, *Comput. Chem. Eng.*, **12**, 55-69 (1988)

14. Vickery, D.J. and R. Taylor, *AIChE J*, **32**, 547 (1986)

15. Vickery, D.J. and R. Taylor, AIChE National Meeting, New Orleans, April 1986.