PREDICTING AND CALCULATING COMPLEX PHASE EQUILIBRIUM IN SUPERCRITICAL FLUID SYSTEMS WITH A NEW TECHNIQUE

Roumiana P. STATEVA*
Department of Chemical Engineering and Chemical Technology,
Imperial College, London SW7 2BY, U.K.

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A general approach to multiphase equilibrium calculations with particular application to vapour–liquid–liquid and liquid–liquid–liquid systems is presented. The capabilities of the new technique to correctly predict and calculate complex phase equilibrium are tested on five highly non-ideal systems, relevant to supercritical fluid extraction. The thermodynamic models applied are the recently proposed MHV2 model and the Redlich–Kwong–Soave cubic equation of state.

Multiphase systems are often encountered in the chemical and petroleum industry. In the petroleum industry, compressed gases or dense fluids at elevated pressures are used in miscible oil displacement in ternary oil recovery schemes. In the chemical industry, for example, distillation processes may contain two liquid phases in either the condenser or on some of the trays. In the cryogenic processing of natural gas systems, the presence of nitrogen in the liquefied natural gas can induce immiscibility and this necessarily affects the process design for these systems. In more recent years, interest has been generated in phase equilibria in supercritical regions of one of the components. This results from the fact that supercritical fluid extraction (SCFE) is becoming the only technological alternative to the usual extraction methods applied in the food and pharmaceutical industries because it usually allows the economic substitution of traditional liquid solvents by cheap non-toxic, environmentally-safe solvents like carbon dioxide or nitrous oxide.

If SCF technology is to be adopted on a wide scale it must have an economic viability which is comparable with present extraction processes. This means that the design of appropriate plant must be carefully optimized. This optimization is crucially dependent upon simulation of the process which is in turn vitally dependent on the

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* Permanent address: Institute of Chemical Engineering, Bulgarian Academy of Sciences, acad. G. Bontchev str., bl. 103, Sofia 1113, Bulgaria.

ability to predict and model the complex phase equlilibria at supercritical conditions, which are characterized by large non-idealities.

Modelling of the multiphase behaviour requires a suitable thermodynamic model and a robust and efficient computational technique.

This paper advocates a new approach and a general strategy to multiphase equilibria predictions and calculations with particular application to vapour–liquid–liquid (VLL) and liquid–liquid–liquid (LLL) systems by using some recently developed concepts of phase-behaviour computations[1,2]. The technique discussed is more general than previous work[3,4] on VLL equilibrium (VLLE) and LLL equilibrium (LLLE).

The main objective of this paper is to evaluate the reliability and effectiveness of the new technique and its computational algorithm to correctly predict the phase configuration and to calculate efficiently the component distribution of highly non-ideal systems, including polar fluids, over wide ranges of temperatures and pressures.

Supercritical fluid mixtures are chosen as test systems since they represent the perfect challenging objective not only for examination of the capabilities (in the above sense) of the proposed techniqe but also for studying the effect of the thermodynamic models used on the accuracy of equilibrium calculations. Five three-component systems, relevant to SCFE, will be discussed later on. Three-component systems seem to be the obvious choice for the test examples since it is for them that one can find reliable experimental data in the available literature.

THEORETICAL

Computational Technique

The new approach to multiphase equilibria predictions and calculations applies a rigorous thermodynamic stability analysis and a simple and elegant yet completely effective method for identifying the phase configuration at equilibrium with the minimum Gibbs energy.

The rigorous stability analysis is exercised once and on the initial system only. It is based on the well known tangent-plane criterion[3,4] but uses a different objective function[1,2]. The key point is to locate all zeros ($\boldsymbol{y}^*$) of a functional $\Phi(\boldsymbol{y})$ given as

$$\Phi(\boldsymbol{y}) = \sum_{i=1}^{N_c} [k_{i+1}(\boldsymbol{y}) - k_i(\boldsymbol{y})]^2 \quad , \tag{1}$$

where

$$k_i(\boldsymbol{y}) = \ln \varphi_i(\boldsymbol{y}) + \ln y_i - h_i \qquad i = 1,2,\ldots,N_c \tag{1a}$$

$$h_i = \ln z_i + \ln \varphi_i(\boldsymbol{z}) \qquad i = 1,2,\ldots,N_{\mathrm{c}} \tag{1b}$$

and $k_{N_{\mathrm{c}+1}}(\boldsymbol{y}) = k_1(\boldsymbol{y})$ is assumed. From Eq. (*1*) follows directly, that min $\Phi(\boldsymbol{y}) = 0$, when $k_1(\boldsymbol{y}^*) = k_2(\boldsymbol{y}^*) = \ldots = k_{N_{\mathrm{c}}}(\boldsymbol{y}^*)$.

The zeros of $\Phi(\boldsymbol{y})$ conform to points on *g* hypersurface, where the local tangent hyperplane is parallel to that at $\boldsymbol{z}$. To each zero $\boldsymbol{y}^*$, a number k^* (equal for each y_i^*, $i = 1, 2,\ldots,N_{\mathrm{c}}$, of a zero of the functional) corresponds, such that:

$$k_i^* = \ln y_i^* + \ln \varphi_i(\boldsymbol{y}^*) - h_i \qquad i = 1,2,\ldots,N_{\mathrm{c}}\ . \tag{2}$$

Futhermore, the number k^*, which geometrically is the distance in *g* surface between two such hyperplanes, can be either positive or negative. A positive k^* corresponds to a zero, which represents a more stable state of the system, in comparison to the initial one. A negative k^* – a more unstable one. When all calculated k^* are positive, the initial system is stable. Otherwise, as shown in Fig. 1, it is unstable.

In the language of the geometry of *g* surface multiple zeros $\boldsymbol{y}^*$ of $\Phi(\boldsymbol{y})$ indicate the tendency of the mixture to exhibit different types of phase equilibria – "vapour–liquid", "liquid–liquid", "liquid–liquid–vapour", "liquid–liquid–liquid", etc. of which only one is stable.

Each zero of the functional is characterized through its composition vector $(y_1, y_2,\ldots, y_{N_{\mathrm{c}}})^*$, a corresponding molar volume – $v_{y_{\mathrm{L}}}^*$ or $v_{y_{\mathrm{V}}}^*$, a phase identification ("liquid" or "vapour") in terms of molar Gibbs energy, and either a positive or negative number k^*.

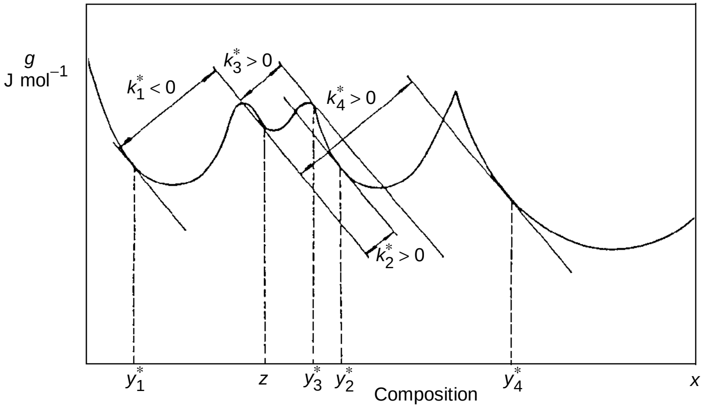

FIG. 1

Molar Gibbs free energy curve and tangent plane distance for a binary mixture: *z* is a mole fraction in the initial phase and y_i^* ($i = 1 - 4$) are zeros of the functional $\Phi(\boldsymbol{y})$

An efficient computational scheme is introduced[1,2], which combines the best features of the Quasi-Newton methods with a superlinear order of convergence, the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm with a line search, and a completely reliable procedure for locating multiple "good" initial estimates. It guarantees that all zeros of the functional will be determined.

The thermodynamic stability analysis provides an information which is analyzed and used to gain an insight into the nature of the system's possible phase equilibria. The information is further used in an efficient phase identification procedure[1,2] which implements successive two-phase liquid–vapour and liquid–liquid flash calculations. As a result, the steps of the algorithm mimic the process of phase splitting in a heterogeneous multicomponent mixture until a state with the lowest possible Gibbs energy is obtained. Moreover, physical reasons for accepting or discarding from further consideration a certain mathematical solution, as a non-physical, "pseudo" one, are implemented in the algorithm, which is an additional asset.

An extensive description of the technique and a mathematical proof of its ability to identify the phase configuration corresponding to the state of minimum Gibbs energy is presented elsewhere[2], while the logic behind the phase identification procedure and the performance of its algorithm will be decumented in more detail in Appendices 1 and 2 of the present paper.

Thermodynamic Model

Relibale process simulation of complex systems, especially those used in SCFE, requires more accurate thermodynamic models that can accurately predict the complex interactions between the small, nonpolar solvents and the large, organic, often polar solutes. However, their development presents several challenges: The two aspects of SCF behaviour that render them especially difficult to model are: Firstly, the great asymmetry of most SCF systems of interest – the term "asymmetry" refers to systems with large differences in both size and force constant (or attractive forces) of the molecules involved. Secondly, because SCFE processes operate in the critical region, in the vicinity of physical and mathematical singularities, phase equilibrium calculations are inherently difficult to perform and require more sophisticated solution techniques than in regions of state far removed from the critical point.

Equations of state (EOS) are used widely for phase equilibrium calculations in SCF systems. Of the several EOS which have been applied recently for this purpose, it has been realized that the cubic EOS must be the choice for process design of any highly complex system, because the molecular interactions are too involved to justify the use of more fundamental equations. Moreover, these models cannot be overly complex since phase equilibrium calculations are performed many thousands of times in an optimization or simulation study so that each calculation must be computationally affordable.

To use EOS to model complex phase behaviour of highly non-ideal mixtures, however, mixing rules other than the commonly employed van der Waals one fluid mixing rules are required. Otherwise, no existing cubic EOS with traditional van der Waals mixing rules can yield good solubility data. It is also concluded that the EOS model can predict the partial molar volumes accurately only when proper mixing rules are applied.

The introduction of local-composition theory in the equations of state or more directly into their mixing rules (e.g. the incorporation of g^E models into mixing rule expressions for the attractive term parameter of cubic EOS) has been receiving much attention for more than a decade, as it allows description of vapour–liquid equilibrium in complex systems through a simple EOS (see refs[5–7]). This combination of an EOS, which is applicable to all phases of interest and thereby insures a consistent description of phase equilibria at low as well as at high pressures, even through the critical region, and an excess Gibbs energy model which accurately represents highly non-ideal liquid systems at low pressures seems, from a thermodynamic point of view, to be highly promising. Furthermore, it is important to note that the excess Gibbs function from the g^E model is a function of temperature and composition only, whereas that from the equation of state is a function of pressure as well.

Of special interest is the use of predictive g^E models, such as UNIQUAC equation and the UNIFAC class, which allows EOS to become strictly predictive tools.

The suggestion of incorporating excess Gibbs energy model information into EOS originates from Huron and Vidal[5], who formally matched the excess Gibbs energy of the EOS at infinite pressure with an independently prescribed expression g^E for the excess Gibbs energy. The resulting model was capable of correlating high temperature phase equilibrium but could not directly utilize the parameter tables for existing g^E models, correlated from vapour–liquid equilibrium data at pressures below 0.5 MPa.

Michelsen[6] and later Dahl and Michelsen[8] repeated the matching procedure of Huron and Vidal, using a reference pressure of zero.

The expression for the EOS g^E is:

$$(g^E/\boldsymbol{R}T)^{\mathrm{EOS}} = \ln\,(f_0/\boldsymbol{R}T) - \sum_i z_i \ln\,(f_{i0}/\boldsymbol{R}T) \ , \qquad (3)$$

where f_0 is the mixture fugacity at zero pressure and f_{i0} the fugacity of the pure component at zero pressure.

If the equation of state g^E is replaced by a specified g^E correlation, $g^{E^*} = g(T,\boldsymbol{z})$, this results in the implicit mixing rule:

$$q(\alpha) = \sum_{i=1}^{N_c} z_i\, q(\alpha_{ii}) + \frac{g^{E^*}}{\boldsymbol{R}T} + \sum_{i=1}^{N_c} z_i \ln\,(\frac{b}{b_{ii}}) \ , \qquad (4)$$

where α is a dimensionless parameter $\alpha = a/b\boldsymbol{R}T$.
The function $q(\alpha)$ is given by:

$$q(\alpha) = -1 - \ln(u-1) - \alpha \ln \frac{u+1}{u} \quad . \tag{4a}$$

The relation of u to α is through the pressure equation, i.e.:

$$\frac{Pb}{\boldsymbol{R}T} = \frac{1}{u-1} - \frac{\alpha}{u(u+1)} = 0 \quad , \tag{5}$$

or selecting the smaller root of the above equation

$$u = (v/b)_{P=0} = \frac{1}{2}\left(\alpha - 1 - \sqrt{\alpha^2 - 6\alpha + 1}\right) \quad . \tag{5a}$$

Equation (*4*) cannot be used for evaluation of the a (or α) parameter under all conditions, as the function $q(\alpha)$ is defined only for $\alpha > 3 + 2\sqrt{2}$. Dahl and Michelsen[7] suggested the following approximation for $q(\alpha)$:

$$q(\alpha) \approx q_0 + q_1\alpha + q_2\alpha^2 \tag{6}$$

yielding

$$q_1\left(\alpha_{\text{mix}} - \sum_{i=1}^{N_c} z_i \alpha_{ii}\right) + q_2\left(\alpha_{\text{mix}}^2 - \sum_{i=1}^{N_c} z_i \alpha_{ii}^2\right) = \frac{g^{E^*}}{\boldsymbol{R}T} + \sum_{i=1}^{N_c} z_i \ln\left(\frac{b}{b_{ii}}\right) \quad , \tag{7}$$

the modified Huron–Vidal second-order (MHV2) mixing rule. The recommended values of q_1 and q_2 are –0.478 and –0.0047, respectively.
The expression for the fugacity coefficient derived from the MHV2 mixing rule is:

$$\ln \varphi_i = \ln\left[\frac{\boldsymbol{R}T}{P(v-b)}\right] + \left[\frac{1}{v-b} - \frac{\alpha}{v+b}\right] b_{ii} - \ln\left(\frac{v+b}{v}\right)\left[\frac{\partial(n\alpha)}{\partial n_i}\right]_{T,n_j} \quad . \tag{8}$$

Any appropriate model for the excess Gibbs energy can be used in connection with the mixing rule – the modified UNIFAC (see ref.[8]) will be used in the present study. Furthermore, to describe systems containing supercritical components, the gas molecules are considered as new groups in the UNIFAC parameter tables (as suggested in ref.[10]).

RESULTS AND DISCUSSION

One of the most stringent tests for any new technique is its ability to predict complex phase behaviour of multicomponent strongly non-ideal systems from any given model. Also the accuracy of the phase equilibrium calculations from a given thermodynamic model, in our case MHV2 and the Redlich–Kwong–Soave cubic equation of state (RKS cubic EOS), determines whether it is suitable for use in computer-aided modelling and design of SCFE processes.

The usual procedure in such cases is to compare the predictions of a particular model and parameter set to experimentally measured equilibrium data and arrive at a mean deviation (e.g. average absolute relative deviations of the mole fractions). This, however, can be misleading, especially for highly non-ideal systems, because it is possible that the overall mean error may appear acceptable and yet some specific regions of the concentration and pressure–temperature space may be relatively poorly predicted. Thus, the results would be meaningless if the thermodynamic model does not accurately predict the extent of a multiphase region. That is why the capabilities of the models applied in the present study are further discussed in the above aspect.

Test Systems

The extraction of organic compounds from aqueous solutions using supercritical fluids has attracted considerable attention in the recent years. Experimental studies of the phase equilibrium behaviour in ternary systems that include water, a polar organic compound and a supercritical fluid have demonstrated that an important characteristic of such systems is the presence of multiphase co-existence regions.

One particular potential application of the SCFE in the above field is the separation of the alcohols from dilute aqueous solutions. Aliphatic alcohols are known to form highly non-ideal mixtures with water and organic solvents. Non-ideality of such multicomponent mixtures is utilized in alcohol extraction due to the ease of forming two liquid phases. A typical example is the separation of ethanol from the solutions produced in biochemical processes.

Carbon Dioxide–Ethanol–Water System

For the dehydration of ethanol, supercritical CO_2 has been extensively considered, since it is non-flammable and non-toxic, and allows ambient-temperature operations to be performed. Though a knowledge of the phase equilibria of the system is essential for applications there has been little work done on measurements of these phase equilibria[11].

We studied the system at two temperatures T_1 = 304.2 K and T_2 = 308.2 K. The thermodynamic model applied is the MHV2 model.

At T_1 = 304.2 K the system exhibits VLLE and the changes in the three phase equilibrium compositions with pressure have been studied at P_1 = 6.78 MPa, P_2 = 6.87 MPa and P_3 = 6.99 MPa.

The comparison between the calculated and measured compositions[11] in the three equilibrium phases is given in Table I.

The thermodynamic model in general predicts qualitatively well the trends in the behaviour of the equilibrium phases, e.g. the experimentally observed fact that the composition of the water-rich liquid phase L_1 changes considerably with a small change of pressure. However, the agreement between the theoretically predicted and experimental data is not fully quantitative. There may be a number of reasons for this. One may be that the MHV2 model probably is still inadequate for the system studied which contains highly associated components – water and ethanol molecules are associated with each other and make cross-associated molecules. Addition of CO_2 in aqueous ethanol solution may have some influence on the association equilibria of the system. The interaction between CO_2 and self-associated H_2O and C_2H_5OH molecules could eventually be taken into account in the mixing rule. However, the interaction between CO_2 and cross-associated H_2O and C_2H_5OH molecules cannot be included. For more accurate estimation it may be necessary to develop mixing rules which take the latter into account.

TABLE I
VLLE predictions for the system CO_2–C_2H_5OH–H_2O. Comparison between the calculated and measured compositions[11] (all composition data are mole fractions)

Component	Experimental			Calculated		
	$liquid_1$	$liquid_2$	vapor	$liquid_1$	$liquid_2$	vapor
			T = 304.2 K; P = 6.78 MPa			
CO_2	0.534	0.862	0.994	0.2445	0.9547	0.9936
C_2H_5OH	0.339	0.114	0.005	0.4209	0.0421	0.0054
H_2O	0.127	0.024	0.001	0.3346	0.0032	0.0009
			T = 304.2 K; P = 6.87 MPa			
CO_2	0.277	0.929	0.992	0.1720	0.9656	0.9941
C_2H_5OH	0.390	0.056	0.006	0.3294	0.0314	0.0049
H_2O	0.333	0.015	0.002	0.4986	0.0030	0.0010
			T = 304.2 K; P = 6.99 MPa			
CO_2	0.050	0.959	0.988	0.1010	0.9771	0.9947
C_2H_5OH	0.150	0.024	0.007	0.1978	0.0202	0.0042
H_2O	0.800	0.017	0.005	0.7012	0.0027	0.0011

Finally, the system has been studied at T = 308.2 K, which is slightly above the critical temperature of CO_2 ($T_{CO_2}^{crit}$ = 304.15 K), and P = 10.1 MPa. Under these conditions, liquid–(supercritical) fluid behaviour is predicted only as demonstrated by the experiment[11]. Due to a lack of space the results of the calculations are not presented in this paper.

Carbon Dioxide–2-Propanol–Water System

This system has been extensively studied experimentally by DiAndreth and Paulaitis[12]. The phase behaviour exhibited by this three-component system is complex, particularly at conditions approaching the critical point of carbon dioxide. According to DiAndreth and Paulaitis an LLG region exists at T = 333.15 K which is bounded from above in pressure by a gas–liquid critical end point and bounded from below in pressure by LL critical end point. At T = 323.15 K, the same three-phase region is bounded above in pressure by a formation of a fourth fluid phase. This four-phase, LLLG region is most likely the one observed at T = 313.15 K and P = 7.8 MPa. Furthermore, a second three-phase region, corresponding to LLL equilibria also exists at 313.15 K (at higher pressures, when one of the four phases will disappear to give three equilibrium phases), with two of the liquid phases apparently near a density inversion.

We studied the system at T = 323.15 K and two different pressures P_1 = 9.4 MPa and P_2 = 9.9 MPa. The MHV2 model fails completely to predict the complex phase behaviour of the system at these conditions. This might be a result of inappropriate numerical values for the correspoding group interaction parameters in the parameter tables[8], especially for the 2-propanol–water interaction.

An accurate global description of the phase behavior for the carbon dioxide–2-propanol–water system is appropriately obtained using the new technique with the RKS cubic EOS as the thermodynamic model fitted to the existing three-phase experimental data of DiAndreth and Paulaitis[12].

The sum of absolute relative deviations between the calculated vapour and liquid component fugacities is used as the objective function in the minimization procedure for the determination of the binary interaction coefficients, as suggested in ref.[13]. The values of k_{ij} parameters are the following: k_{12} = 0.1896, k_{13} = –0.1269, k_{23} = –0.3080, where the subscripts 1, 2 and 3 correspond to carbon dioxide, 2-propanol and water, respectively.

As a result not only the extent of the regions of multiphase behaviour (observed in the experiment) of the system are correctly predicted by the model but there is a good quantitative agreement between the calculated and measured phase compositions.

Details of the calculations, following the steps of the phase identification procedure, and the set of initial estimates for the subsequent three-phase VLL flash computations are given in Appendix 1. A comparison between the calculated and measured compositions[12] of the system in the three equilibrium phases are given in Table II.

Butane–2-Butanol–Water System

It is a well established fact that ternary-phase behaviour of a system is determined to a large extent by the phase behaviour of its appropriate binaries. Water–butane binary has the highest degree of molecular asymmetry, its behaviour is most non-ideal, and hence it is expected that the butane–2-butanol–water behaviour will be most sensitively dependent on the properties of the water–butane system. As other hydrocarbons in mixtures with water, butane forms a similar discontinuous critical locus and a three-phase VLL curve which ends at an upper critical end point (UCEP) – hence for the water–butane system at temperatures below UCEP there are two LL phases above the VLL curve, and a VL region below the VLL curve, the former extending down to the vapour pressure curve for water.

Unlike 2-propanol–water, the 2-butanol–water system is known to have limited miscibility (LL) at low temperatures. The mutual solubilities depend on temperature and to a lesser extent, on pressure. The third binary, 2-butanol–butane, should behave similarly to other alcohol–hydrocarbon systems, that is with no LL miscibility gap. However, there are no experimental VLE data available to quantify phase compositions and boundaries for this binary.

The system has been extensively studied experimentally by Radosz[14]. Since water and butane form three phases below the UCEP, it is not unexpected to find three phases upon adding 2-butanol at similar conditions. However, instead of a single VLL curve, a

TABLE II
Results of the calculations for the system CO_2–2-propanol–H_2O. Comparison between the calculated and measured compositions[12] (all composition data are mole fractions)

Component	Experimental			Calculated		
	liquid$_1$	liquid$_2$	vapor	liquid$_1$	liquid$_2$	vapor
			T = 323.15 K; P = 9.4 MPa			
CO_2	0.127	0.274	0.849	0.0317	0.2945	0.9005
2-Propanol	0.142	0.258	0.078	0.0200	0.2716	0.0733
H_2O	0.731	0.468	0.073	0.9483	0.4339	0.0262
Volume	28.74	40.94	91.25	26.05	49.75	85.90
			T = 323.15 K; P = 9.9 MPa			
CO_2	0.111	0.275	0.778	0.0320	0.3023	0.8833
2-Propanol	0.134	0.261	0.127	0.0199	0.2671	0.0821
H_2O	0.754	0.465	0.095	0.9481	0.4286	0.0346
Volume	29.16	41.18	65.61	26.04	49.87	8.16

broad VLL band which extends to temperatures far above the 2-butanol–water upper critical solution temperature (UCST) has been found[14]. For example at T = 393 K, which is above the 2-butanol–water UCST but below the butane critical temperature (425 K), the three-phase pressure range is measured to be between 0.5 – 2 MPa.

We studied the phase behaviour of the system at two temperatures – T_1 = 393 K (butane is subcritical) and T_2 = 449 K (supercritical butane). The thermodynamic model applied is the MHV2 model.

At T = 393 K two cases are tested at P_1 = 1.72 MPa and P_2 = 2.03 MPa. The comparison between the measured and calculated phase compositions at T = 393.4 K and P = 2.03 MPa is given in Table III.

The three-phase VLL regions at the above pressures, as predicted and calculated by the new technique, are shown in Fig. 2. The type of the equilibrium phases of the system at the above conditions is correctly predicted by the phase identification procedure, however, the extent of the three-phase region at P = 2.03 MPa is underpredicted

TABLE III

VLL predictions for the system C_4H_{10}–2-butanol–H_2O. Comparison between the calculated and measured compositions[14] (all composition data are mole fractions)

Component	Experimental			Calculated		
	liquid$_1$	liquid$_2$	vapor	liquid$_1$	liquid$_2$	vapor
			T = 393.4 K; P = 2.03 MPa			
C_4H_{10}	0.0002	0.4730	0.8530	0.0002	0.7827	0.8610
2-Butanol	0.0080	0.3520	0.0520	0.0065	0.1917	0.0498
H_2O	0.9918	0.1750	0.0950	0.9933	0.0256	0.0891

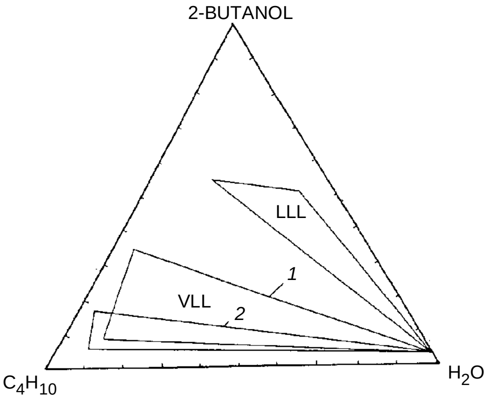

FIG. 2

Phase diagram of C_4H_{10}–2-butanol–H_2O system at T = 393 K (subcritical C_4H_{10}). The VLL phase regions at P_1 = 1.72 MPa (*1*) and P_2 = 2.03 MPa (*2*) are shown. A three-phase LLL region at P_1 = 1.72 MPa, predicted by the model is shown as well considerably in comparison to the one measured experimentally (not shown on the Fig. 2) mainly due to the very poor predictions of the composition of the second liquid phase.

In addition to the VLL region a stable LLLE (see Fig. 2) is predicted at T = 393 K and P = 1.72 MPa, which has not been experimentally observed by Radosz[14]. Dahl et al.[15], however, also report a stable LLL region for the system at the above conditions.

Furthermore, Panagiotopoulos and Reid[16], who studied experimentally the system carbon dioxide–butanol–water observed in addition to extensive three-phase regions equilibrium between four phases. The very presence of a four-phase equilibrium region implies the existence of more than one three-phase region in the immediate vicinity of the four-phase point (a point of fixed pressure at constant temperature, according to the phase rule). There is one more case known to us for equilibrium between four fluid phases in a ternary mixture, that of the carbon dioxide–2-propanol–water system[12] at 313.15 K and 7.6 MPa.

Details of the calculations, following the steps of the algorithm of the phase identification procedure, the set of initial estimates for the LLL flash routine, and compositions of three equilibrium liquid phases as predicted and calculated by the model, are given in Appendix 2.

The three-phase VLL region at T = 448 K (supercritical butane) and P = 4.48 MPa, as predicted and calculated by the model, is shown in Fig. 3. In this particular case, new numerical values of the binary interaction parameters for the 2-butanol–water (as suggested in ref.[15]) have been used, because the mathematical form of the temperature dependency expression in the modified UNIFAC lead to “overcorrelating”, when extensive extrapolation with respect to temperature has taken place.

Carbon Dioxide–Acetone–Water

The economy of biotechnological production processes depends to a great extent on the cost of steps necessary for separating the products from the fermentation broth and

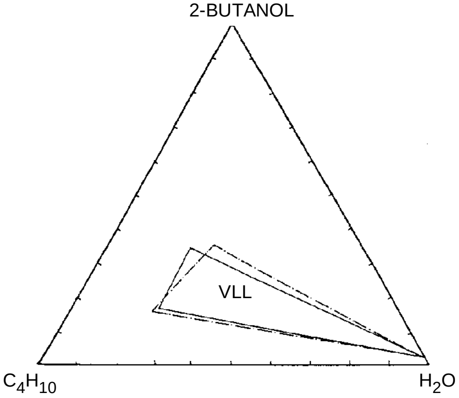

FIG. 3
Phase diagram of the C_4H_{10}–2-butanol–H_2O system at T = 449 K (supercritical C_4H_{10}) and P = 4.48 MPa and comparison between the model predictions (full lines) and experimental results (dashed lines) of Radosz[14]

from auxiliary substances like, for example, extraction solvents. Due to the high enthalpy of water, the thermal separation of such diluted solutions by distillation or crystallization is very energy-intensive and supercritical extraction with CO_2 can be a viable economic alternative.

Carbon dioxide–acetone–water is an excellent representative of the above class of systems with acetone being a model component for a low molecular weight, moderately polar extraction solvent.

The system has been studied experimentally by Panagiotopoulos and Reid[16] and Traub and Stefan[17]. We modelled the phase behaviour of the system at $T = 313.15$ K and four different pressures. At $T = 313.15$ K and $P = 4$ MPa there are three fluid phases in equilibrium (see Table IV, which gives the comparison between the theoretically predicted and experimentally measured compositions by Traub and Stefan[17]; whereas at $P = 10$ MPa (the CO_2–acetone binary system being above its critical pressure) only a two-phase region is found extending from the CO_2–H_2O side of the composition triangle to acetone concentrations of up to $x_{CO_2} \approx 0.43$ (not shown here).

Comparison between the model predictions and experimental results of Panagiotopoulos and Reid[16] at $T = 313$ K and three different pressures are given on the corresponding phase diagrams in Figs 4*a* – 4*c*.

In addition, the phase behaviour of the system ethylene–acetone–water has also been modelled with the new simulation technique, but due to a lack of space the results are not included.

Ethylene–Methyl Ethyl Ketone–Water

The system ethylene–methylene ethyl ketone (MEK)–water has been extensively studied by Elgin and Weinstock[18] and Yorizane et al.[19]. The latter reported the composi-

TABLE IV
VLLE predictions for the system CO_2–C_3H_6O–H_2O. Comparison between the calculated and measured compositions[16] (all composition data are mole fractions)

Component	Experimental			Calculated		
	$liquid_1$	$liquid_2$	vapor	$liquid_1$	$liquid_2$	vapor
			$T = 313.15$ K; $P = 4$ MPa			
CO_2	0.027	0.428	0.978	0.0436	0.4386	0.9823
C_3H_6O	0.099	0.430	0.019	0.1393	0.4653	0.0158
H_2O	0.874	0.142	0.003	0.8171	0.0961	0.0019

tions of the two liquid equilibrium phases only, as the vapour phase is considered pure ethylene (the mole fraction of MEK is at most 0.01 and the higher the temperature and pressure, the lower the concentration of MEK in the vapour tends to become). Considerations of water in the vapour are so small that they were not detected in gas chromatographic analysis.

We have modelled the phase behaviour of the system at two temperatures T_1 = 288.15 K and T_2 = 298.15 K. The first temperature lies outside the temperature range for which the numerical values for group interaction parameters in the modified UNIFAC parameter tables have been derived. Thus it is an interesting test for the capabilities of the MHV2 model to reproduce not only qualitatively but quantitatively as well the phase behaviour of the system at this temperature.

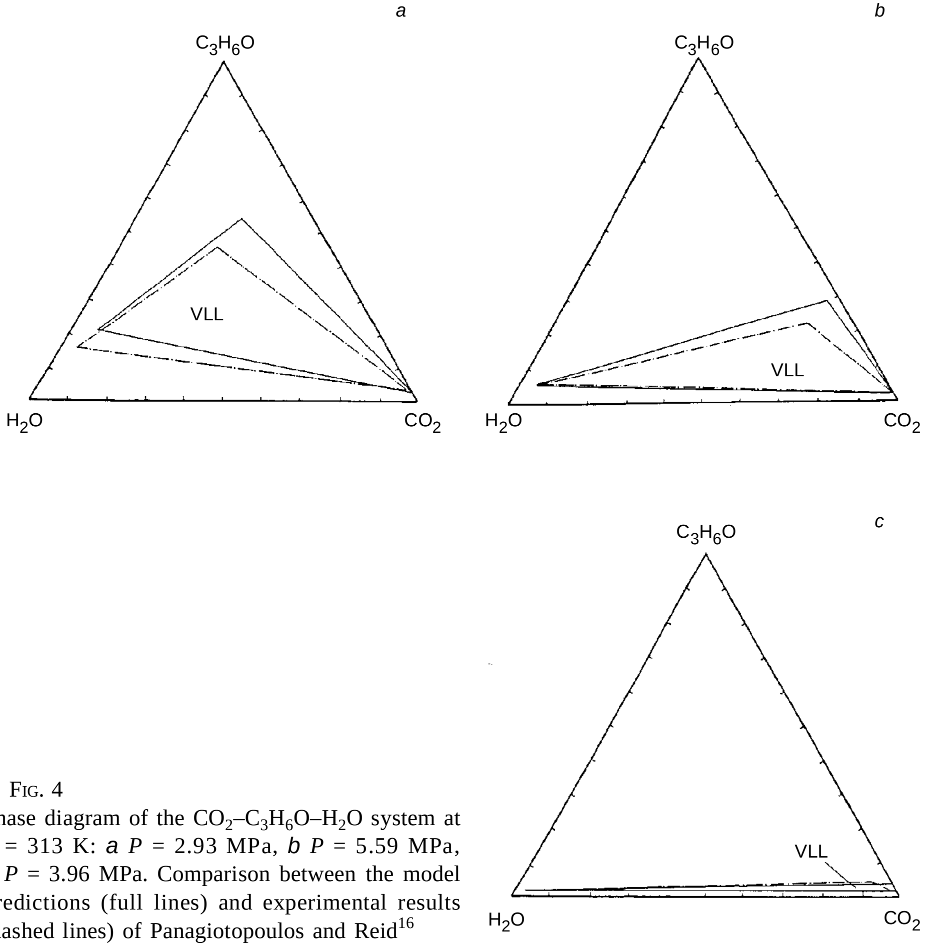

FIG. 4
Phase diagram of the CO_2–C_3H_6O–H_2O system at T = 313 K: *a* P = 2.93 MPa, *b* P = 5.59 MPa, *c* P = 3.96 MPa. Comparison between the model predictions (full lines) and experimental results (dashed lines) of Panagiotopoulos and Reid[16]

Comparison between the theoretically predicted and experimentally measured compositions is given in Table V. The model slightly overpredicts the extent of the three-phase region at T_1 = 298.15 K and P = 2.0265 MPa. However, the predictions improve considerably, both qualitatively and quantitatively with increasing pressure, the best being at the highest pressure at which Yorizane et al.[19] ran their experiments (last part of Table V).

TABLE V
VLLE predictions for the system C_2H_4–MEK–H_2O. Comparison between the calculated and measured compositions[19] (all composition data are mole fractions)

Component	Experimental		Calculated		
	liquid$_1$	liquid$_2$	liquid$_1$	liquid$_2$	vapor
		T = 288.15 K; P = 5.1676 MPa			
C_2H_4	0.0030	0.9115	0.0047	0.9549	0.9946
MEK	0.0323	0.0599	0.0200	0.0439	0.0050
H_2O	0.9647	0.0286	0.9753	0.0012	0.0004
		T = 298.15 K; P = 2.0265 MPa			
C_2H_4	0.0027	0.2016	0.0072	0.2207	0.9916
MEK	0.0613	0.6463	0.1140	0.6398	0.0071
H_2O	0.9360	0.1521	0.8788	0.1395	0.0013
		T = 298.15 K; P = 4.013 MPa			
C_2H_4	0.0033	0.4793	0.0059	0.5234	0.9930
MEK	0.0365	0.4742	0.0510	0.4372	0.0062
H_2O	0.9602	0.0465	0.9431	0.0394	0.0008
		T = 298.15 K; P = 5.2385 MPa			
C_2H_4	0.0036	0.7152	0.0053	0.7343	0.9915
MEK	0.0335	0.2690	0.0334	0.2530	0.0078
H_2O	0.9629	0.0158	0.9612	0.0127	0.0007

CONCLUSIONS

Studies on the phase behaviour of systems relevant to supercritical fluid extraction processes are essential for their technical and economic assessment. Furthermore, experimental studies are very expensive and time consuming. They can be considerably simplified if the results can be correlated by reliable mathematical models and if the measurements are automated to the greatest possible extent. The latter being crucial for the cases of new, unstudied as yet systems for which practically no experimental data are available.

The thermodynamic models applied in the present study, the MHV2 and RKS cubic EOS, demonstrate once again that a universally applicable equation does not exist. Although in theory binary parameters are sufficient for representation of multicomponent data (since the three- and many-body forces effects are distributed among the binary interaction effects to give an “effective” pair-potential), better results for specific mixtures are obtained when the parameters are based on multicomponent equilibrium data (see the CO_2–2-propanol–H_2O system, where the MHV2 model failed completely). Furthermore, as the size difference of the molecules of the components involved increases the results for the MHV2 model become progressively poorer.

On the other hand the new computational technique is general in nature and can be used with any of the available and appropriate thermodynamic models. It practically never fails to predict correctly which is the stable phase configuration and easily reproduces and provides a fair picture of the complete spectrum of fluid phase equilibria demonstrated by a system at a specified T and P. The technique is completely reliable, effective and efficient and can be successfully implemented in a process simulator for modelling and design of supercritical extraction processes involving strongly non-ideal mixtures.

APPENDIX 1

VLLE Predictions for the System CO_2–2-Propanol–H_2O with the New Technique

Details of the Phase Identification and Calculation Procedures[2]

To illustrate the logic behind the phase identification procedure and the performance of its algorithm, an example of an initial feed composition $\boldsymbol{z}$ is chosen for which the system exhibits a three-phase VLL equilibrium. All other possible cases in the thermodynamic composition space (e.g. mixture overall compositions for which the system exhibits either a two-phase vapour–liquid or liquid–liquid equilibria) will be correctly identified by the phase identification procedure, too. However, due to a lack of space such example is not presented here.

Furthermore, all converged results of the corresponding two-phase flash calculations, involved in the algorithm of the identification procedure, are presented in the form of tables to facilitate the reading.

1. For an initial feed composition $\boldsymbol{z}$ = (0.42 CO_2; 0.2 2-propanol; 0.38 H_2O) at T = 323.15 K and P = 9.4 MPa, the thermodynamic stability check locates three zeros of the functional $\Phi(\boldsymbol{y})$, two "liquid" and a "vapour". One of the liquid zeros has a negative k^*, the other – a positive k^*, while the vapour one has a negative k^* and hence the system with the above overall composition is classified as unstable.

The two liquid zeros and the feed form the "liquid" group and they are arranged in an ascending order so that the first zero is classified as a "heavy" liquid zero (lean in the most volatile component CO_2); $\boldsymbol{y}^*_{L_{HL}}$ = (0.0700; 0.0300; 0.9000) and the last as a "light" zero, rich in the most volatile component; $\boldsymbol{y}^*_{L_{LTL}}$ = (0.3964; 0.2956; 0.3080).

The vapour group contains the only vapour zero of the functional: $\boldsymbol{y}^*_V$ = (0.9476; 0.0384; 0.0140).

2. LL and LV flashes are run. They require initial estimates for the K values, which are estimated as follows:

– for the vapour–liquid flash calculations:

$$K_m = \boldsymbol{y}^*_V / \boldsymbol{y}^*_L, \quad m = 1,2,\ldots,M,$$

where M is the total number of liquid zeros (in this case M = 3);

– for the liquid–liquid flash calculations the K values are defined as a combination between the three liquid zeros.

3. An LV (split A) and an LL (split B) solution, among all in the two respective groups of step *2*, with the lowest Gibbs energy are selected. They are called "initial" splits and are given below.

Component	Split A		Split B	
	liquid	vapour	$liquid_1$	$liquid_2$
CO_2	0.2505	0.9097	0.0328	0.5042
2-Propanol	0.2463	0.0661	0.0191	0.2394
H_2O	0.5032	0.0242	0.9481	0.2564
	Phase split β = 0.2571		Phase split β = 0.8213	

4. The LV solution (split A) has a lower Gibbs energy than the LL solution (split B). The latter is dropped from further consideration.

To determine whether the LV split is stable or unstable its L phase is flashed into (LL)′ using the following set of initial estimates for the *K* values:

$$K_i = \boldsymbol{y}^*_{i_{\mathrm{LTL}}}/\boldsymbol{y}^*_{i_{\mathrm{HL}}}, \quad i = 1,2,\ldots,N_{\mathrm{c}} \ .$$

If the phase split of the converged solution is inside the physically accepted bounds $0 \le \beta \le 1$, the system is classified as VLL. Otherwise, the system is a stable VL. The converged equilibrium compositions of the (LL)′ split are given below.

Component	L	L_1'	L_2'
CO_2	0.2505	0.0290	0.2827
2-Propanol	0.2463	0.0200	0.2793
H_2O	0.5032	0.9510	0.4380

Since the phase split $\beta = 0.8729$ the system is diagnosed as a three-phase VLL.

5. To determine the composition distribution into the equilibrium phases an VLL flash is run. It requires a set of initial composition estimates, which are obtained in the following way:

5a. The V phase of the initial LV split is flashed into $(LV)^\sim$ using the following initial estimates for the *K* values:

$$K_i = \boldsymbol{y}^*_{i_{\mathrm{V}}}/\boldsymbol{y}^*_{i_{\mathrm{LTL}}}, \quad i = 1,2,\ldots,N_{\mathrm{c}} \ .$$

Component	Feed	$(LV)^\sim$	Flash
	V	$L^\sim$	$V^\sim$
CO_2	0.9097	0.0311	0.9107
2-Propanol	0.0661	0.0187	0.0662
H_2O	0.0242	0.9502	0.0231

5b. The liquid $\tilde{\mathrm{L}}$ phase of the converged $\tilde{\mathrm{L}}\tilde{\mathrm{V}}$ solution of step *5a* is flashed into (LL)″ using the following intial estimates for the *K* values:

$$K_i = \boldsymbol{y}^*_{i_{\mathrm{LTL}}} / \boldsymbol{y}^*_{i_{\mathrm{HL}}}, \quad i = 1,2,\ldots,N_{\mathrm{c}} \ .$$

Component	Feed	(LL)″	Flash
	$\tilde{\mathrm{L}}$	L_1''	L_2''
CO_2	0.0311	0.0322	0.3210
2-Propanol	0.0187	0.0196	0.2681
H_2O	0.9502	0.9482	0.4109

The intial estimates for the three-phase VLL flash calculations are: $\boldsymbol{x}_{\mathrm{L}_1''}, \boldsymbol{x}_{\mathrm{L}_2''}, \boldsymbol{y}_{\tilde{\mathrm{V}}}$.

6. An VLL flash is run. The initial composition estimates are so close to the true solution that the three-phase flash calculation converges very quickly and steadily in less than four iteration.

Initial estimates and converged results for the VLLE flash calculations.

Component	Initial estimates			Calculated[a]		
	liquid$_1$	liquid$_2$	vapor	liquid$_1$	liquid$_2$	vapor
CO_2	0.0322	0.3210	0.9107	0.0317	0.2945	0.9005
2-Propanol	0.0196	0.2681	0.0662	0.0200	0.2716	0.0733
H_2O	0.9482	0.4109	0.0231	0.9483	0.4339	0.0262

[a] See also the upper part of Table II.

APPENDIX 2

LLL Predictions for the System C_4H_{10}–2-Butanol–H_2O

T = 393 K, P = 1.72 MPa

Details of the Phase Identification and Calculation Procedures of the New Technique[2]

The possibility of an LLLE for a given system is indicated by the fact that no vapour zeros of the functional are found and that the liquid zeros of $\Phi(\boldsymbol{y})$ are (eventually) more than two.

1. For an intial feed composition $\boldsymbol{z}$ = (0.1 C_4H_{10}; 0.4 2-butanol; 0.5 H_2O) no vapour zeros of the functional $\Phi(\boldsymbol{y})$ are found.

2. Liquid–liquid flashes are run (split A and split B), of which split A has lower Gibbs energy than split B. The former is called the initial split.

Component	Split A		Split B	
	liquid$_1$	liquid$_2$	liquid$_1$	liquid$_2$
C_4H_{10}	0.0002	0.1398	0.0305	0.3887
2-Butanol	0.0181	0.5523	0.3753	0.5026
H_2O	0.9817	0.3079	0.5942	0.1087
	Phase split β = 0.7149		Phase split β = 0.1941	

3. A (LL)′ flash is run on the L_1 phase of the initial split. The following results are obtained.

Component	L_1	L_1'	L_2'
C_4H_{10}	0.0002	0.0002	0.2913
2-Butanol	0.0181	0.0181	0.5543
H_2O	0.9817	0.9817	0.1544

The phase split $\beta = 2.68 \,.\, 10^{-6}$ is inside the physically accepted bounds and the system is diagnosed as a three-phase LLL.

4. To obtain excellent initial estimates for the LLL flash a (LL)″ flash is run on the L_2' phase and the following results are obtained.

Component	L_2'	L_1''	L_2''
C_4H_{10}	0.2913	0.0846	0.2898
2-Butanol	0.5543	0.5144	0.5541
H_2O	0.1544	0.4010	0.1561

The initial estimates for the three phase LLL flash calculations are: $\boldsymbol{x}_{L_1'}, \boldsymbol{x}_{L_1''}, \boldsymbol{x}_{L_2''}$.

5. An LLL flash is run. The comparison between the initial composition estimates and the converged results are shown in the following table.

Initial estimates and converged results for the LLLE flash calculations.

Component	Initial estimates			Calculated		
	liquid$_1$	liquid$_2$	liquid$_3$	liquid$_1$	liquid$_2$	liquid$_3$
C_4H_{10}	0.0002	0.0846	0.2898	0.0002	0.0894	0.2819
2-Butanol	0.0181	0.5144	0.5541	0.0181	0.5211	0.5572
H_2O	0.9817	0.4010	0.1561	0.9817	0.3895	0.1609

SYMBOLS

a	cubic EOS mixture parameter, kPa m^6 mol^{-2}
b	van der Waals volume, m^3 mol^{-1}
f_i	fugacity, component *i*, kPa
g	molar Gibbs energy, J mol^{-1}
$k_i(\boldsymbol{y})$	function of the chemical potential difference, defined by Eq. (*1a*)
k_{ij}	binary interaction parameter, cubic EOS
k^*	a number, corresponding to $\boldsymbol{y}^*$
K_i	equilibrium factor, component *i*
LCST	lower critical solution temperature, K
LLG	liquid–liquid–gas
LLLG	liquid–liquid–liquid–gas

M	total number of “liquid” zeros of $\Phi(\boldsymbol{y})$
n	number of moles
N_c	number of components
P	pressure, Pa
$q(\alpha)$	function defined by Eqs (*4*), (*4a*) and (*6*)
$\boldsymbol{R}$	universal gas constant, kPa $\mathrm{m^3\,mol^{-1}\,K^{-1}}$
T	temperature, K
$u = v/b$	parameter, Eqs (*4a*), (*5*) and (*5a*)
UCEP	upper critical end point
UCST	upper critical solution temperature, K
v	mixture molar volume, $\mathrm{m^3\,mol^{-1}}$
v^*	molar volume corresponding to $\boldsymbol{y}^*$, $\mathrm{m^3\,mol^{-1}}$
$\boldsymbol{y}$	mole fraction vector, Eq. (*1*)
$\boldsymbol{y}^*$	zero of the functional $\Phi(\boldsymbol{y})$ for the initial system
$\boldsymbol{x}$	mole fraction vector, equilibrium compositions
$\boldsymbol{z}$	mole fraction vector, initial system
α	$= a/b\boldsymbol{R}T$, equation of state mixture parameter, Eqs (*4*) to (*8*)
β	phase split, two-phase flash
$\Phi(\boldsymbol{y})$	functional, defined by Eq. (*1*)
ϕ_i	fugacity coefficient, component i

Superscripts

crit	critical
E	excess
$*$	corresponding to a zero of the functional $\Phi(\boldsymbol{y})$
$(')$, $('')$	indicates the sequence of LL flashes run by the Identification procedure
$(')$, $(\sim)$	indicates the sequence of LV flashes run by the Identification procedure

Subscripts

ii	corresponding to the pure component
HL	“heavy” liquid
L	liquid
LTL	“light” liquid
mix	corresponding to the mixture
V	vapour

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