Phase Equilibrium Engineering of Supercritical Hydrogenation Reactors

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The general problem of phase equilibrium engineering of supercritical hydrogenation reactors is addressed. The conceptual design of process conditions is discussed, as well as procedures to determine the range of feasible operating conditions for two reaction problems: the hydrogenation of vegetable oils and the hydrogenolysis of fatty acid methyl esters. A group contribution equation of state is applied to predict the required phase equilibrium scenarios for solvent containing reactive mixtures.

Introduction

Hydrogenation is a major industrial chemical process. A wide variety of chemicals is obtained by catalytic hydrogenation; mostly heterogeneous solid catalysts are used (Rylander, 1985). When the compound to be hydrogenated and/or the reaction products are liquid at process conditions, the reaction rate is limited by the concentration of hydrogen on the catalyst surface. The low reaction rate is caused by the low solubility of hydrogen and the high mass-transfer resistance in the liquid phase, which leads to a depletion of hydrogen at the catalyst surface. In the presence of double bonds, this lack of hydrogen also gives rise to double-bond migration and *cis-trans*-isomerization. Figure 1 shows the typical hydrogen concentration profile of a gas–liquid catalyzed hydrogenation.

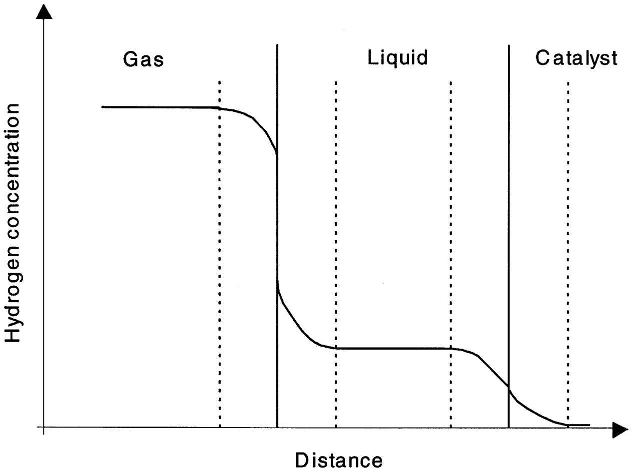

Figure 1. Hydrogen concentration profile in a classic gas–liquid catalyzed hydrogenation.

The favorable solvent and transport properties of supercritical fluids (SCF) make them an adequate medium for chemical reactions and offer great opportunities for process improvement (Savage et al., 1995; Baiker et al., 1999). The application of a suitable supercritical fluid to a gas–liquid hydrogenation process can bring all reactants and products into a homogeneous fluid phase. Under these conditions the problems of hydrogen solubility and gas–liquid mass-transfer resistance are removed and reaction rates are greatly increased. Härröd and Møller (1999) report increments in the supercritical hydrogenation rates of oils and derivatives of up to 1,000 times, compared to the traditional gas–liquid process. The main benefits of supercritical hydrogenation are process intensification (smaller reactors) and improved selectivity due to the independent control of temperature, pressure, and composition of the reactants at the catalyst surface. The superior heat and mass-transport properties of supercritical fluids, on the other hand, allow the use of continuous reactors in place of the traditional batch units. The low viscosity of the reaction medium improves the operation of the reactor and reduces the pressure drop; the low surface tension also assures a better wetting of the catalyst surface by the reaction mixture. The unique solvent properties of supercritical fluids guarantee, in principle, an easy separation from the reaction products.

Two typical heterogeneous catalytic hydrogenation processes are the production of margarine and shortenings from vegetable oils and that of fatty alcohols from alkyl esters.

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The hydrogenation of double bonds in fats and oils has the purpose of providing products with the desired melting profile and texture, according to their final use. The hydrogenated oil is more stable and less sensitive to oxidation. The classic process is carried out in batch reactors where the oil, hydrogen, and catalyst (nickel powder) are mixed intensively at temperatures between 373 K and 423 K.

The hydrogenation of alkyl esters to produce fatty alcohols for cosmetics and pharmaceutical applications is classically carried out at temperatures of 473–573 K, using a copper/chromium catalyst.

Recently, van den Hark (2000) and Macher (2001) have been able to overcome the hydrogen solubility and mass-transport problems of these processes by using supercritical propane as the reaction medium. Tremendous rate enhancement and a lower degree of *cis-trans*-isomerization were achieved in a continuous fixed-bed reactor, using commercial catalysts.

Phase Equilibrium Engineering

A supercritical catalyzed hydrogenation process requires the solid catalyst to be in contact with a single-phase reactive mixture at any time (batch reactor) or location (continuous reactor). This is a typical problem of what we call *phase equilibrium engineering*, that is, the systematic study and application of phase equilibrium tools to the development of chemical processes.

For each process there will be a set of specifications, which represent problem restrictions. In the case of catalytic hydrogenation of liquid substrates, these specifications are: (1) components of the reactive mixture, that is, reactants and products; (2) operating temperature, given by the reaction kinetics and catalyst; and (3) degree of conversion, fixed by the hydrogenation goal.

By applying phenomenological and modeling phase equilibrium engineering tools, it is possible to find the operating conditions that guarantee the existence of a single fluid phase in the reactor, at any time or location, subject to the preceding specifications. The solution to this problem requires the following process variables to be determined: (1) supercritical solvent; (2) operating pressure; and (3) solvent/feed ratio.

An adequate phase equilibrium predictive tool is necessary to explore the solvent properties and phase equilibrium behavior of the reactive mixture over a wide range of conditions.

The phase behavior of supercritical hydrogenation mixtures can be quite complex. Drastic changes in density and solubility with temperature, pressure, and composition can be expected, due to the presence of a near-critical or supercritical solvent in a mixture with a permanent gas (hydrogen) and heavy liquid components. The large difference in molecular size and volatility between these components is likely to give rise to liquid-phase split and multiphase behavior (Peters, 1994). The solubility of most gases falls with increasing temperature, while it rises for highly supercritical gases like hydrogen. It is then expected that the slope of a pressure–temperature phase diagram will change sign according to the relative amount of hydrogen/supercritical fluid present in the reactive mixture.

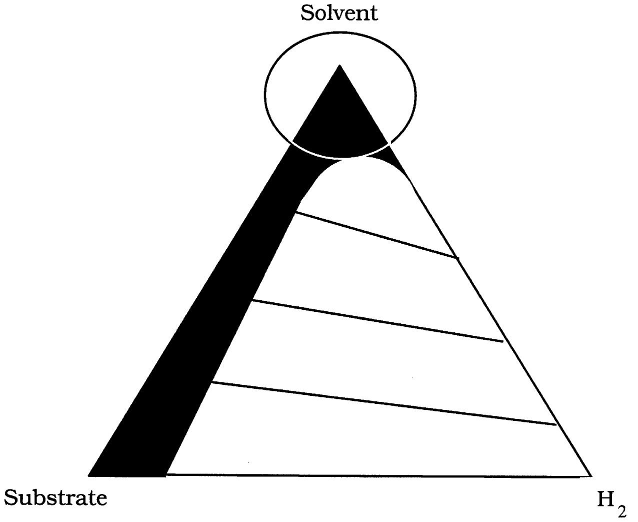

Figure 2. Type I phase diagram showing the feasible operating region for supercritical hydrogenation.

This complex behavior makes the phase equilibrium engineering of supercritical hydrogenation reactors a challenging problem from both an experimental and modeling point of view.

Solvent selection

The selection of a solvent that is able to bring the reactive mixture into a single fluid phase is a key step in the design of supercritical hydrogenation reactors.

In order to find an adequate solvent and operating conditions, it is necessary to determine the phase boundaries of a multicomponent reactive system containing hydrogen, solvent, substrate, and hydrogenation products.

Figure 2 represents a type I phase diagram for a ternary mixture of hydrogen, solvent, and a liquid substrate at a given temperature and pressure, showing only one partially miscible pair (substrate + hydrogen). The solvent shows complete miscibility with both hydrogen and substrate; this guarantees the existence of a homogeneous single-phase region around the solvent corner for all possible hydrogen/substrate ratios. Therefore, our goal is to find the solvent, pressure, and composition that reproduce this type of phase equilibrium diagram under the reaction conditions.

The critical temperature of the solvent is a key property for solvent selection. The solvent should have a critical temperature lower than the reaction temperature. In this way the complete miscibility of the pair solvent + hydrogen is assured. On the other hand, the critical temperature of the solvent should not be too low, compared to the reaction temperature, to achieve liquid-like densities and hence higher solvent capacity. Table 1 shows the critical temperature and pressure of solvents that have been proposed in the literature as supercritical reaction media.

Another important property to be evaluated is the solubility of reactants and products in the supercritical solvent. In

Table 1. Critical Properties of Potential Solvents for Chemical Reactions

Solvent	T_c (K)	P_c (MPa)
Ethylene	283.1	5.11
Xenon	289.8	5.87
Hexafluoroethane	293.0	3.06
Trifluoromethane	299.3	4.85
Chlorotrifluoromethane	302.0	3.86
Carbon dioxide	304.2	7.38
Ethane	305.5	4.88
Nitrous oxide	309.7	7.26
Sulfur hexafluoride	318.7	3.72
Propane	370.3	4.24
Hydrogen sulfide	373.5	9.0
Dimethyl ether	400.1	5.37
Ammonia	405.6	11.4
Pentane	470.2	3.37
1-Propanol	508.5	4.76
Methanol	513.7	7.99
Ethanol	516.6	6.38
1-Butanol	548.2	4.29
Benzene	562.1	4.89
Ethylendiamine	593.0	6.27
Pyridine	620.2	5.63
Water	647.3	22.11

the absence of specific solute–solvent interactions, the solubility will be higher for those compounds with higher vapor pressures. A problem that can be faced when dealing with high molecular-weight substrates, such as oils and fats, is the appearance of partial liquid miscibility.

It is known that carbon dioxide is not a good solvent for hydrocarbon substrates; liquid–liquid immiscibility has been reported by Schneider (1991) for hydrocarbons with more than eight carbon atoms. Therefore, the application of CO_2 as supercritical reaction medium is in principle limited to low molecular-weight substrates. The phase equilibrium diagrams shown in Figure 3 correspond to mixtures of triglycerides (tripalmitin and palm kernel oil) with different solvents, at a reduced temperature of 1.05. It becomes clear from the picture that carbon dioxide is not a good solvent for the supercritical hydrogenation of fats and oils, because the region of partial miscibility extends to very high pressures. However, other solvents, such as dimethyl ether (DME) and propane, achieve complete miscibility at moderate pressures. The final decision about solvent selection will also take into account other properties, such as solvent inertness, at the reaction conditions, environmental, and economical considerations.

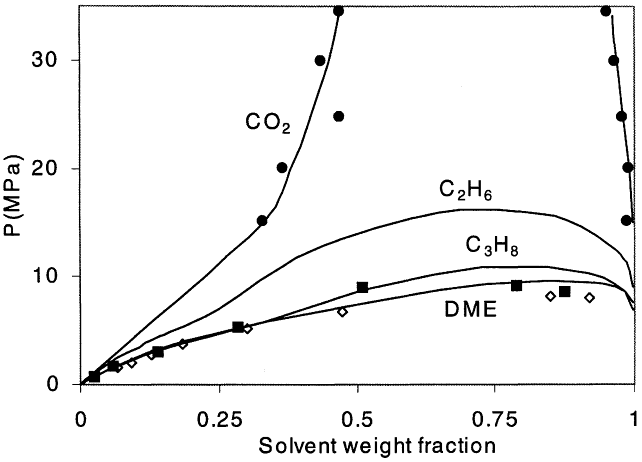

Figure 3. VLE and LLE of triglycerides with solvents at a reduced temperature of 1.05.

Experimental: ● Bharath et al. (1992); ■ Coorens et al. (1988); ◇ Florusse et al. (2002); —— GCA-EOS predictions.

Thermodynamic modeling

The thermodynamic model should be able to handle multicomponent asymmetric mixtures and to predict multiphase equilibrium conditions. The experimental information available in the literature on high-pressure phase equilibria of reactive mixtures is very scarce, which makes it difficult to determine the model parameters. An additional problem is faced with high molecular-weight substrates: pure component properties such as vapor pressure and critical properties are experimentally unattainable due to their low volatility and thermoliability.

All this makes group contribution methods an attractive option. These methods are particularly useful in modeling multicomponent natural products for which the exact molecular configuration is not always known. Using a few functional groups, for example, a natural fatty oil can be adequately represented by a pseudotriglyceride that has the same molecular weight and degree of unsaturation of the natural product (Bottini et al., 1999).

Many thermodynamic models have been proposed in the literature (Anderko, 2000) to represent the phase behavior of complex mixtures by the combination of cubic equations of state (EOS) with excess Gibbs energy models, according to Huron and Vidal (1979) mixing rules. Most of these models have been applied to calculate vapor–liquid equilibria (VLE), and only a few to liquid–liquid equilibria (LLE). The MHV2 (Dahl and Michelsen, 1990) and PSRK (Holderbaun and Gmehling, 1991) equations in particular have a predictive character given by the application of the modified (Larsen et al., 1987) and original (Fredenslund et al., 1975) UNIFAC model, respectively. Even though these models successfully extend the application of cubic equations of state to nonregular solutions, they share a major UNIFAC weakness: VLE and LLE calculations require different sets of group interaction parameters (Fredenslund and Sørensen, 1994).

In this work the GCA-EOS model (Gros et al., 1996) is applied. This model is an extension of the group-contribution equation of state GC-EOS proposed by Skjold-Jørgensen (1984, 1988); in this model there are three contributions to the residual Helmholtz function: repulsive, attractive, and associative. A brief description of the GCA-EOS model is given in the Appendix. This model has proved to be successful in predicting phase equilibria of associating (Gros et al., 1996, 1997) and size-asymmetric mixtures (Bottini et al., 1999; Espinosa et al., 2000; Fornari et al., 2001). In particular VLE, LLE, and VLLE conditions are adequately predicted with a single set of parameters.

The systems studied in this work include the reactive mixtures found in the supercritical hydrogenation of vegetable oils and fatty acid methyl esters. In the hydrogenation of veg-

Table 2. GCA-EOS Binary Interaction Parameters

Group j	Group i	k_{ij}^*	k'_{ij}	α_{ij}	α_{ji}	N	SDV%	Ref.
H_2	CH_2/CH_3	1.0	0.0	11.846	11.846	63	1.263*	Rovetto et al., 2001
H_2	Triglyceride	1.0	0.0	−10.144	−10.144			
H_2	CH_2COO	1.0	0.0	−2.4526	−2.4526	60	3.801*	Rovetto et al., 2001
H_2	Methanol	1.1000	−0.3	0.00	0.00	42	7.98*	Liu et al., 1996; Wainwright et al., 1987
H_2	CH_2OH	1.8742	0.0	−5.7345	5.9028	30	1.43*	Breman et al., 1994
CH_2COO	CH_2OH	0.91	−0.2778	−16.044	−10.307	132	6.94**	Fernandez et al., 1987, 1985

Note: $\mathrm{SDV\%} = 100\sqrt{\sum_N ((z_{\mathrm{calc}} - z_{\mathrm{exp}})/z_{\mathrm{exp}})^2/N}$.

* z = Hydrogen solubility in the liquid phase.

**z = Alcohol composition in the vapor phase.

etable oils, reactive and product are both triglycerides, each with a different degree of unsaturation. The hydrogenation of fatty acid methyl esters, on the other hand, produces fatty alcohols and methanol according to the following reaction

$$RCOOCH_3 + 2\,H_2 \leftrightarrow RCH_2OH + CH_3OH$$

where R represents a hydrocarbon chain.

These reactive mixtures can be represented by the following functional groups: paraffin (CH_3 and CH_2), olefin ($CH{=}CH$), ester (CH_2COO), alcohol (CH_2OH), and triglyceride [$(CH_2COO)_2CHCOO$]. Methanol (CH_3OH) and hydrogen (H_2) are molecular groups.

The group-contribution attractive term of the GCA-EOS equation has four binary group-interaction parameters: two symmetrical parameters, k_{ij}^* and k'_{ij}, and two asymmetrical nonrandomness parameters, α_{ij} and α_{ji}. The values of these parameters were not available for the interactions between the ester and alcohol groups and between H_2 and most of the remaining functional groups, and had to be determined in this work.

Table 2 reports the binary interaction parameters obtained by fitting experimental high-pressure phase equilibrium data on binary systems. The table also includes the number of data points (N) and the reference to the experimental data. The mean standard deviations (SDV%) reported in this table for all hydrogen binaries correspond to the correlation of H_2 solubility in the liquid phase. For alcohol−ester mixtures isothermal bubble pressure calculations were performed, and the SDV% value given in Table 2 corresponds to the correlation of alcohol mole fraction in the vapor phase; a SDV% in pressure equal to 2.47 was obtained in this case.

The binary interaction parameters between H_2 and paraffin (CH_3 and CH_2) groups were already available in the original GC-EOS parameter table (Skjold-Jørgensen, 1988). However, these parameters, which were determined by fitting phase equilibrium data on mixtures of hydrogen with low to medium molecular weight hydrocarbons, were not able to give a good correlation of hydrogen solubility in high molecular-weight compounds. A new set of parameters was then required to extend the application of the model to long-chain molecules such as fatty oils. It is apparent that even in the presence of moderate dispersive energies the interaction parameters of the paraffin (CH_2 and CH_3) group have to be carefully evaluated in order to avoid degeneration of the predictions due to the large number of CH_2 groups in the mixture. The new set of parameters for the H_2−paraffin interaction are reported in the first row of Table 2 and should be applied to triglycerides and fatty oils. For low molecular-weight compounds the original H_2−paraffin interaction parameters (Skjold-Jørgensen, 1988) still apply.

The remaining sets of binary interaction parameters not included in Table 2 were taken from Skjold-Jørgensen (1988), Gros et al. (1997), and Espinosa et al. (2000).

There is only one associating group in the reactive mixtures under study, the alcohol group. The two association parameters of this group (energy $\epsilon/k = 2{,}700$ K and volume ($\kappa = 0.8621\ \mathrm{cm^3 \cdot mol^{-1}}$) were taken from Gros et al. (1997).

Finally, the size-related parameter of the GCA-EOS repulsive term, that is, the critical hard-sphere diameter (d_C), was determined from critical properties (T_c and P_c) or vapor pressure data on pure components, as discussed by Skjold-Jørgensen (1984). This information is not available for high molecular-weight triglycerides and fatty oils. Following the procedure proposed by Bottini et al. (1999), the d_C values of these compounds were determined by fitting experimental data on infinite dilution activity coefficients of alkanes in triglycerides. Table 3 reports the critical hard-sphere diameter of all compounds studied in this work.

Process operating conditions

The GCA-EOS model was applied to explore the feasible operating domain for the supercritical hydrogenation of fatty oils and esters. The equation was used to predict the fluid-phase equilibria of multicomponent mixtures containing hydrogen, solvent, reactants, and products. From these calculations, the process conditions (temperature, pressure, and solvent composition) that guarantee the operation of the reactor under a single fluid phase were found. The results discussed

Table 3. Critical Hard Sphere Diameters

Compound	d_c ($\mathrm{cm \cdot mol^{-1}}$)
Hydrogen	2.672
Propane	4.017
Tripalmitin	11.44
Sunflower oil	12.16
Methanol	3.610
Hexadecyl alcohol	7.341
Methyl palmitate	7.753

in the following sections correspond to the use of propane as supercritical solvent.

Supercritical Hydrogenation of Vegetable Oils

The hydrogenation of vegetable oils produces the partial saturation of double bonds in the fatty chains of the triglyceride molecules. Reactant and reaction products are both high molecular-weight triglycerides, and it is not expected that the fluid-phase behavior of the reactive mixture will change significantly with the extent of the reaction. Therefore, it is possible to select the process conditions by studying the phase behavior of a typical hydrogen–propane–triglyceride ternary system.

Binary mixtures of propane with high molecular-weight *n*-alkanes and triglycerides show type V fluid-phase behavior in the classification of Van Konynenburg and Scott (Straver et al., 1994) (see Figure 4). Partial liquid miscibility is found in these systems, and a three-phase liquid–liquid–vapor ($l_1 l_2 g$) region is bounded by the upper (UCST) and lower (LCST) critical endpoints. For the binary propane–tripalmitin this region extends between 349 K and 370 K (Coorens et al., 1988).

Figure 5 shows the GCA-EOS phase equilibrium predictions for the ternary system, hydrogen–propane–tripalmitin, at 360 K and 4 MPa. At these conditions a phase split in the three binaries—propane–tripalmitin, hydrogen–tripalmitin, and hydrogen–propane—is predicted. There is liquid–liquid ($l_1 l_2$) equilibrium in the binary propane–tripalmitin, with liquid phase l_2 being almost pure propane on molar basis. The addition of small quantities of hydrogen extends this liquid–liquid equilibrium region toward the hydrogen corner of the diagram. The saturation line of phase l_2 lies very close to the hydrogen–propane axis because the molar concentration of tripalmitin in this phase is negligible. A vapor phase is formed at higher concentrations of hydrogen, and there is a liquid–liquid–vapor surface ($l_1 l_2 g$) connecting the liquid–liquid ($l_1 l_2$) and the liquid–vapor ($l_1 g$ and $l_2 g$) equilibrium regions. Again the $l_2 g$ saturation line is almost coincident with the hydrogen–propane axis. The vertices of the $l_1 l_2 g$ triangle represent the compositions of the three coexisting phases at equilibrium.

The conditions shown in Figure 5 are not adequate for supercritical hydrogenation, because the one-phase region is limited to the liquid phase l_1, which has very low concentrations of hydrogen. This gives a situation similar to the traditional gas–liquid hydrogenation process.

In order to attain an adequate single-phase domain it is necessary to be above the propane–tripalmitin partial miscibility region. As shown in Figure 3, this region can be avoided by increasing the pressure.

Phase equilibrium calculations were carried out with the GCA-EOS model for ternary hydrogen (1)–propane (2)–tripalmitin (3) mixtures, at pressures of about 12 MPa and temperatures between 347 and 438 K. The results are shown in Figure 6. As expected, the mutual solubility between propane and tripalmitin increases by decreasing the temperature, and below 395 K the binary becomes completely miscible. At 347 K and 11.2 MPa the GCA-EOS model predicts partial miscibility in the binary H_2-propane, and the appearance of a two-phase liquid–liquid ($l_1 l_2$) and a three-phase liquid–liquid–vapor ($l_1 l_2 g$) region (see Figure 6b). The GCA-EOS predictions are in good agreement with recently measured experimental data on hydrogen–propane–tripalmitin mixtures (Rovetto et al., 2001). The experimental data points shown in Figure 6 represent saturated liquid conditions for three different isopleths. The filled circles in Figure 6a correspond to an isopleth with molar fractions of $x(1) = 0.1287$, $x(2) = 0.5215$, and $x(3) = 0.3498$, and that in Figure 6b to $x(1) = 0.0684$, $x(2) = 0.8618$, and $x(3) = 0.0698$. Liquid–liquid equilibria was experimentally determined at 347 K and 11.2 MPa for a mixture with $x(1) = 0.0693$, $x(2) = 0.8777$, and $x(3) = 0.053$ (represented by an empty square in Figure 6b). This experimental point lies very close to the liquid–liquid equilibrium region predicted by the GCA-EOS model.

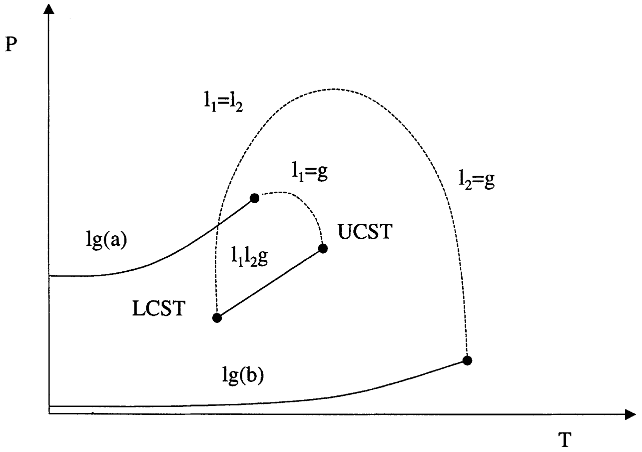

Figure 4. Type V phase diagram in the classification of van Konynenberg and Scott.

Figure 7 shows GCA-EOS phase equilibrium predictions for the hydrogen–propane–sunflower oil (molecular weight MW = 875; iodine number I = 134.3) system at 373 K and 12 MPa. As expected, the phase diagram is type I, with a one-phase region at high propane concentrations. Figure 7 also shows some experimental data measured by Schiemann (1993) at the same temperature and pressure, for mixtures with propane concentrations up to 50% molar. According to these experimental data, the addition of propane to a hydrogen–oil mixture produces a large increment in the solubility of hydrogen in the liquid phase, which is not followed by the GCA-EOS predictions. The experimental measurements of Rovetto et al. (2001) do not show these large solubility values, which raises doubts about the accuracy of the data reported by Schiemann.

Supercritical hydrogenation requires complete miscibility of the reactive mixture at the stoichiometric ratio H_2/oil fixed by product specification. It becomes clear from Figure 7 that the limits of the one-phase region change with the value of this ratio. Therefore, it is necessary to determine the one-phase boundary for each specific molar ratio of the reactants.

Figure 8 shows, for example, the homogeneous-phase limit for an equimolar reactive mixture at 373 K and 12 MPa. This limit is determined by the intersection of the binodal curve with the line representing a molar ratio for hydrogen/sunflower oil equal to one. The molar composition of this saturated phase is 81.7% of propane, and 9.15% each of H_2 and

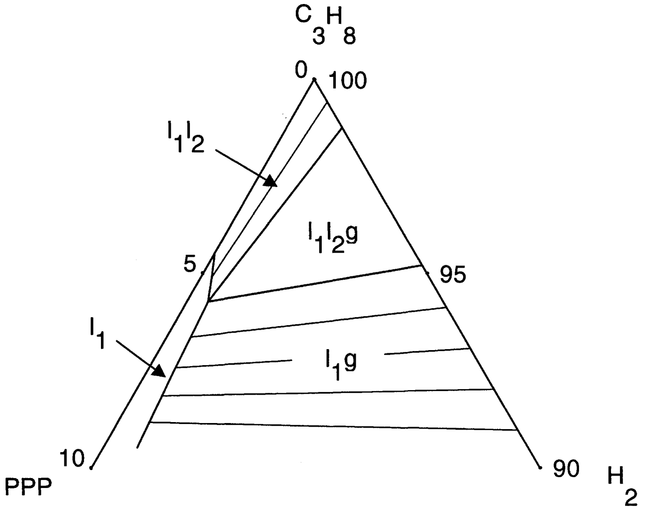

Figure 5. Immiscibility region in the ternary system hydrogen + tripalmitin (PPP) + propane at 360 K and 4 MPa.

sunflower oil. Therefore, it is necessary to feed more than 0.45 kg of propane/kg of oil to the reactor in order to assure a homogeneous fluid operation at 373 K and 12 MPa.

An alternative procedure to determine the solvent requirement is to take the concentration of propane at the apex of the binodal curve (shown by the horizontal line $x^{\max}_{C_3H_8}$ in Figure 8) as the one-phase boundary. This gives a conservative solution, which guarantees homogeneity of the reactive mixture for all possible H_2/substrate ratios.

The following equation can be applied to calculate the solvent requirement R for the hydrogenation of vegetable oils. The propane/oil weight ratio given by Eq. 1 assures the homogeneous operation of the hydrogenation reactor, at any ratio H_2/oil

$$R = \frac{\text{weight}_{C_3H_8}}{\text{weight}_{\text{oil}}} = (1+MR)\frac{x^{\max}_{C_3H_8}}{\left(1-x^{\max}_{C_3H_8}\right)}\frac{MW_{C_3H_8}}{MW_{\text{oil}}}. \quad (1)$$

This equation was derived from the condition $x^{\max}_{C_3H_8} + x_{H_2} + x_{\text{oil}} = 1$ applied to the maximum propane molar fraction $x^{\max}_{C_3H_8}$ in the binodal curve. MR represents the molar ratio x_{H_2}/x_{oil} in the reactive mixture, and $MW_{C_3H_8}$ and MW_{oil} are the molecular weight of propane and oil, respectively.

In order to apply Eq. 1 it is necessary to determine the value of $x^{\max}_{C_3H_8}$ from phase equilibrium calculations. For the sunflower oil represented by a pseudotriglyceride molecule with five double bonds and a molecular weight of 875, the GCA-EOS model predicts $x^{\max}_{C_3H_8} = 0.9283$ at 373 K and 12 MPa. In this case Eq. 1 reduces to

$$R = 0.6510(1+MR). \quad (2)$$

On the hypothesis of complete conversion, a stoichiometric ratio $MR = 2.5$ will be required to hydrogenate half of the oil

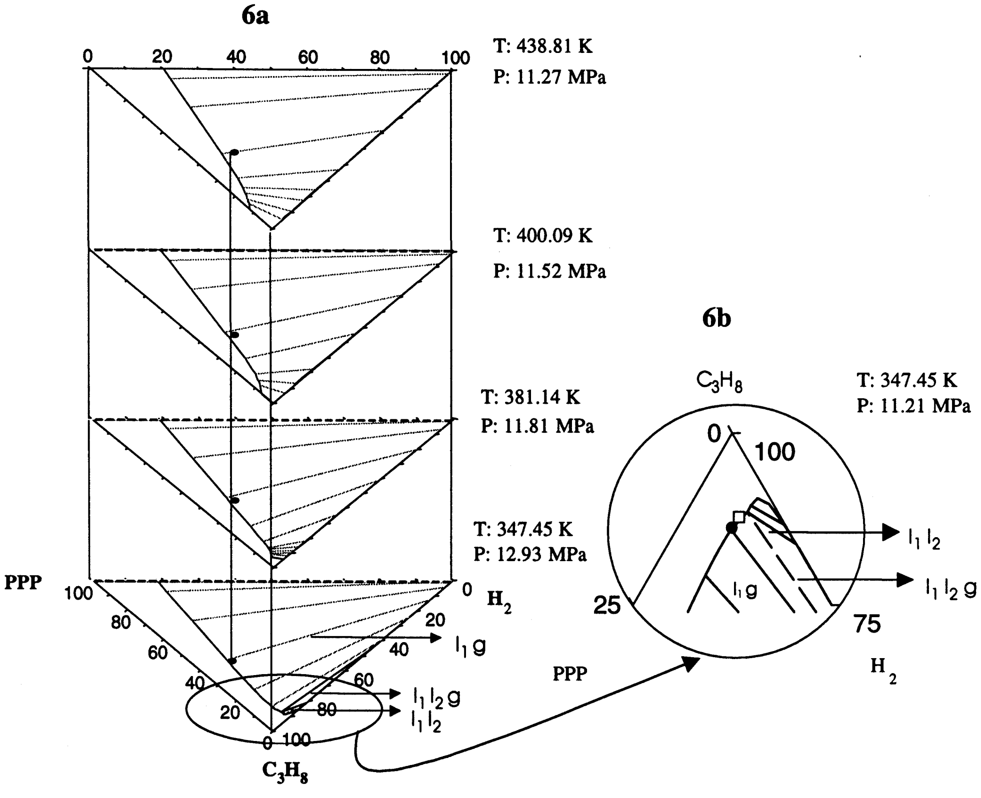

Figure 6. Effect of temperature on the phase behavior of the ternary system hydrogen + tripalmitin + propane.

Experimental data: □ (LLE), and ● (VLE) Rovetto et al. (2001).

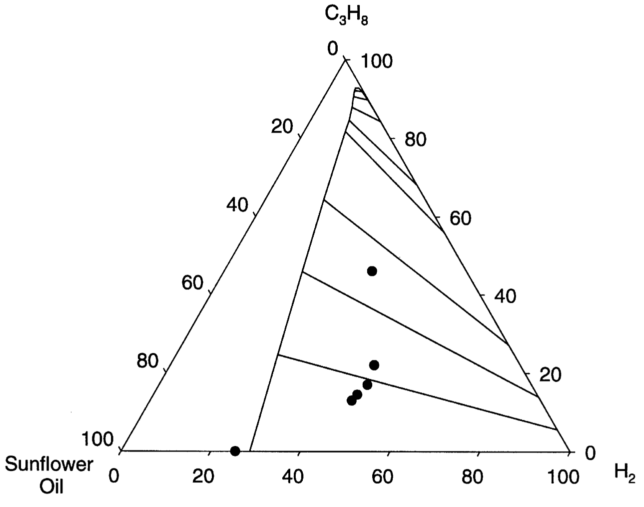

Figure 7. Ternary system hydrogen + propane + sunflower oil at 373 K and 12 MPa.

— GCA-EOS predictions; ● experimental data, Schiemann (1993).

double bonds. In this case, 2.3 kg of propane per kg of oil will be needed to assure the homogeneity of the reactive mixture at 373 K and 12 MPa.

Equation 1, together with GCA-EOS phase equilibrium predictions, can be applied to explore the domain of the operating conditions for the supercritical hydrogenation of fatty oils. An increase in pressure at constant temperature produces the enlargement of the one-phase region in the ternary hydrogen + propane + oil phase equilibrium diagram. The value of $x_{C_3H_8}^{max}$, and consequently the solvent requirement R calculated from Eq. 1, becomes lower at higher pressures. The curves in Figure 9 show the variation of R with pressure at three reaction temperatures. The solvent requirement decreases exponentially with pressure in the lower pressure range and goes to an asymptotic minimum at higher pressures. Therefore, for each reaction temperature there is a pressure range beyond which no significant reduction of the solvent requirement is achieved by a pressure increment. For a reaction temperature of 373 K, the optimum pressure range is around 12 MPa.

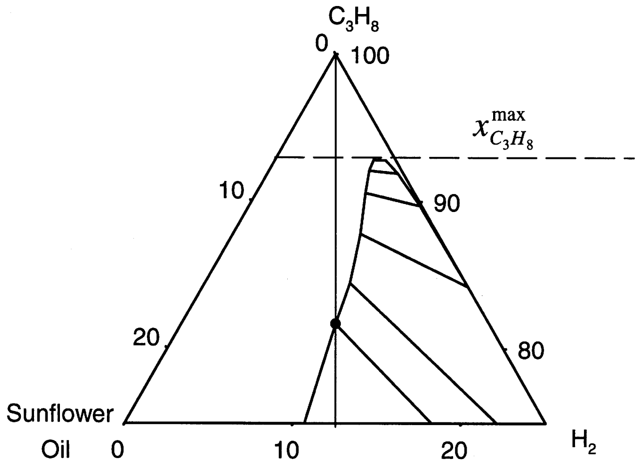

Figure 8. Propane requirement for the homogeneous hydrogenation of sunflower oil.

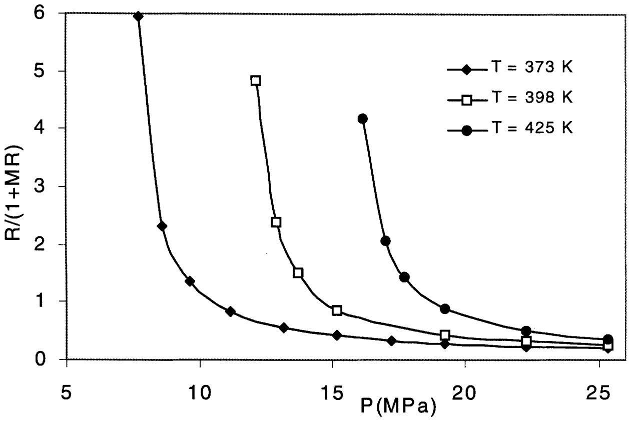

Figure 9. Feasible operating conditions for the supercritical hydrogenation of sunflower oil.

Supercritical Hydrogenolysis of Fatty Acid Methyl Esters

The hydrogenation of fatty acid methyl esters (FAME) yields fatty alcohols (FOH) and methanol (MeOH) as reaction products. Reactants and products are compounds of different chemical natures, and it is expected that the phase behavior of the reactive mixture will change with the extent of the reaction. This situation will require the phase equilibrium conditions to be studied along the reaction path.

There are no phase equilibrium experimental data available in the literature for the reaction mixtures studied in this work. The only information found in the literature are the vapor–liquid equilibrium data measured by Brands (2000) on the binary systems butane + methyl palmitate and butane + hexadecyl alcohol. Figures 10 and 11 show good agreement between the GCA-EOS predictions and the experimental data of Brands (2000).

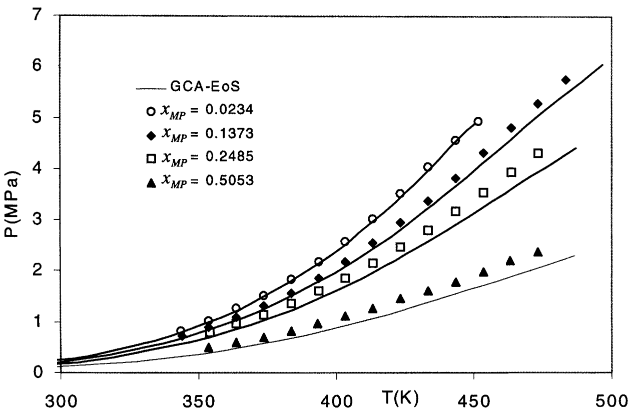

Figure 10. VLE of butane + methyl palmitate.

— GCA-EOS predictions; experimental data: Brands (2000).

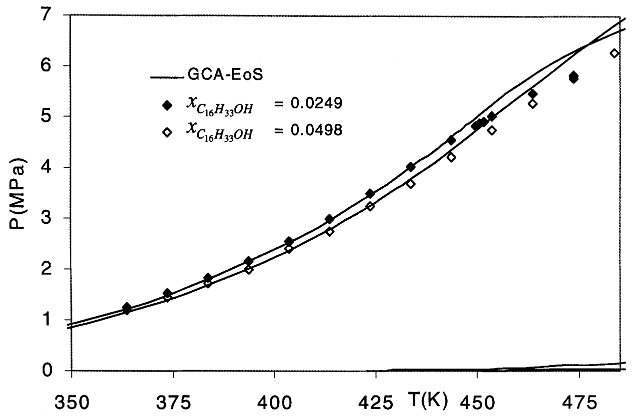

Figure 11. VLE of butane + hexadecyl alcohol.

— GCA-EOS predictions; experimental data: Brands (2000).

Based on the good representation of these binary phase equilibria, the GCA-EOS was used to predict the phase behavior of the multicomponent reactive mixture. Five components are present in this reaction mixture: hydrogen, propane, methyl palmitate, hexadecyl alcohol, and methanol.

Figure 12 shows the pressure–temperature phase envelopes predicted by the GCA-EOS model for a reactive mixture having an initial molar composition of 15.4% hydrogen + 2% methyl palmitate + 82.6% propane. Each curve in Figure 12 corresponds to a given reaction conversion (ϵ), with values ranging from 0 to 1. Van der Hark et al. (2000) used the same feed composition (which has an excess of hydrogen with respect to the stoichiometric requirement) in their experimental work. These measurements were carried out in a fixed-bed reactor at 553 K. The two points in Figure 12 represent the inlet and outlet reactor conditions in the van den Hark et al. experiments. These conditions lie in the single-phase region predicted by the GCA-EOS, which is in agreement with the experimental observation.

Figure 12 shows a three-phase liquid–liquid–vapor region predicted by the GCA-EOS for the isopleth of complete conversion ($\epsilon = 1$). This region extends over a very small area, between 370.8 and 370.9 K and 11.5 and 11.6 MPa. Peters (1994) describes the existence of partial liquid miscibility in mixtures of propane with *n*-alcohols having more than 18 carbon atoms. The GCA-EOS predictions are then in close agreement with this experimental evidence.

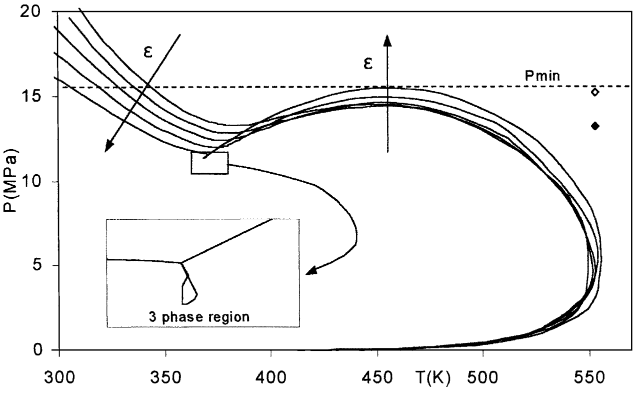

Figure 12. Phase envelopes for the hydrogenolysis of methyl palmitate.

Conversion range: $0 \leq \epsilon \leq 1$. Experimental conditions, van der Hark et al. (2000): ◇ inlet (15 MPa, 553 K); ◆ outlet (13 MPa, 553 K).

Each isopleth plotted in Figure 12 represents the phase limit between the two-phase and the one-phase regions. From these curves it is possible to find, for a given temperature and conversion, the minimum pressure required to assure complete miscibility in the reactive mixture. In the range of typical hydrogenation temperatures, these minimum pressures increase with increasing conversion. This means that the reaction products (hexadecyl alcohol and methanol) are less soluble in the supercritical phase than the reactants. This behavior was also experimentally observed by van den Hark et al. (2000).

The isobar indicated as Pmin in Figure 12 corresponds to the minimum operating pressure that guarantees a one-phase condition in the reactive mixture, at any temperature and conversion.

Following this same procedure, the value of Pmin can be computed for different feed compositions. Figure 13 shows the results of these calculations for mixtures with propane mole fractions between 0.7 and 0.9, and H_2/substrate molar ratios (MR) in the range of 1 to 10. The shaded lower surface corresponds to the feed mixture ($\epsilon = 0$), and the upper surface corresponds to the composition of the reaction products ($\epsilon = 1$). For all feed compositions in the temperature range of interest, Figure 13 shows that the limiting pressure Pmin is always given by the surface of the reaction products. Therefore, the reactor operating conditions should be established from the reactive mixture at complete conversion.

Figure 14 shows the projection of the products surface ($\epsilon = 1$) of Figure 13 on the plane Pmin vs. propane mole fraction. The surface named *operating region* is bounded by a curve tangent to the lines of constant MR. Any point inside this region represents single-phase conditions for every temperature, conversion, and molar ratio. From this diagram it is easy to select the correct operating pressure and the amount of solvent required to guarantee a homogenous reactive mixture. For example, an operating pressure of 15.7 MPa, will require more than 85% molar of propane to assure a single-phase reactive mixture in the reactor.

Conclusions

The problem of phase equilibrium engineering of supercritical hydrogenation reactors is formulated and applied to the hydrogenation of vegetable oils and fatty acid methyl esters, with supercritical propane as the reaction medium. The GCA-EOS model is able to describe the phase equilibrium behavior of the reactive mixtures and to predict vapor–liquid, liquid–liquid, and vapor–liquid–liquid boundaries using a single set of parameters. Therefore, the GCA-EOS model is an adequate predictive tool to determine the limits of homogeneity of the reactive mixtures for supercritical hydrogenation. A general expression is given to determine the amount of propane required to hydrogenate fatty oils under homogeneous conditions, as a function of the stoichiometric hydrogen/oil feed ratio. The concept of minimum pressure for

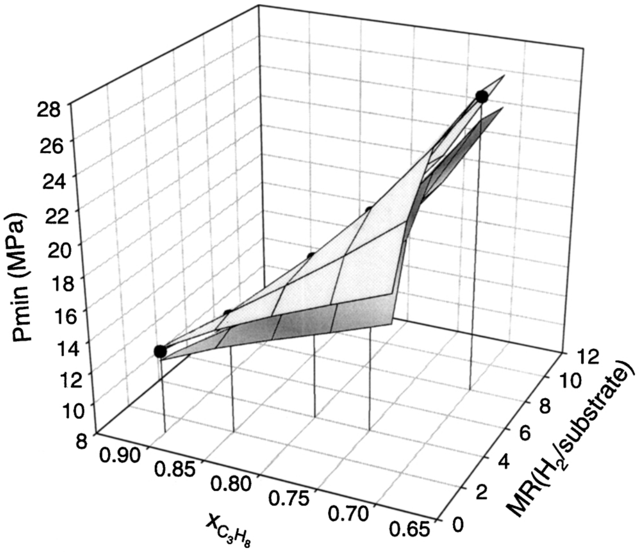

Figure 13. Minimum operating pressures for the supercritical hydrogenolysis of methyl palmitate.

Lower surface: $\epsilon = 0$; upper surface: $\epsilon = 1$.

complete miscibility is presented and applied to the selection of feasible operating conditions for the hydrogenolysis of fatty esters.

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Notation

A = Helmholtz function
d = hard-sphere diameter
g = attractive energy per segment–segment interaction
k = binary interaction parameter (with subscripts) or Boltzmann constant
M = number of association sites
MR = molar ratio hydrogen/substrate in the reactive mixture
MW = molecular weight

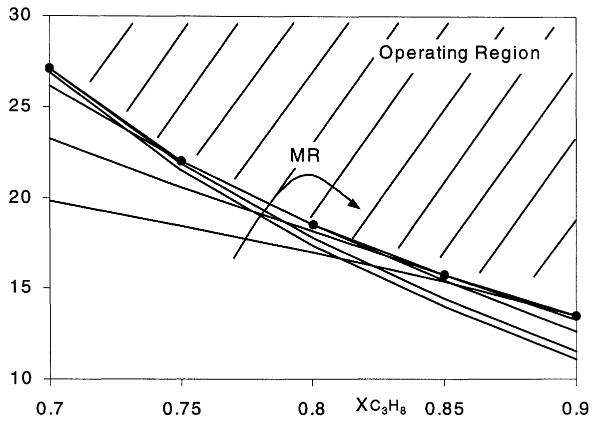

Figure 14. Feasible operating region for the supercritical hydrogenation of methyl palmitate.

n = number of moles
NC = number of components
NG = number of functional groups
NGA = number of associating groups
q = number of surface segments per mole
R = solvent requirement (Eq. 1) or universal gas constant
T = absolute temperature
V = total volume
x = mole fraction
X = fraction of nonbonded sites
Y = auxiliary function
z = coordination number

Greek letters

α = nonrandomness parameter
Δ = difference or association strength (with superscripts)
ϵ = energy of association
κ = volume of association
λ = average length, surface or volume
ν = number of times a group is contained in a molecule
π = number pi
θ = surface fraction
ρ = density
τ = exponential nonrandomness factor

Superscripts and subscripts

assoc = association
att = attractive
fv = free volume
res = residual
$\sim$ = total value
$*$ = reference value
$'$ = first temperature-dependent coefficient
$''$ = second temperature-dependent coefficient
c = critical
max = maximum value

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Appendix

There are three contributions to the residual Helmholtz function (A^{res}) in the GCA-EOS model: free volume (A^{fv}), attractive (A^{att}), and associative (A^{assoc})

$$A^{res} = A^{fv} + A^{att} + A^{assoc}. \tag{A1}$$

The free-volume contribution is represented by the extended Carnahan−Starling equation for mixtures of hard spheres developed by Mansoori and Leland (1972)

$$\begin{aligned}(A/RT)^{fv} &= 3(\lambda_1\lambda_2/\lambda_3)(Y-1)\\ &\quad + \left(\lambda_2^3/\lambda_3^2\right)\left(-Y+Y^2-\ln Y\right) + n\ln Y, \end{aligned}\tag{A2}$$

with

$$Y = \left(1 - \frac{\pi\lambda_3}{6V}\right)^{-1} \tag{A3}$$

and

$$\lambda_k = \sum_i^{NC} n_i d_i^k, \tag{A4}$$

where n_i is the number of moles of component i, NC is the number of components in the mixture, n is the total number of moles, V is the total volume, and d_i is the hard-sphere diameter per mol of species i.

The following generalized expression gives the temperature dependence of the hard-sphere diameter

$$d_i = 1.065655 d_{ci}\left\{1 - 0.12\exp\left[-2T_{ci}/(3T)\right]\right\}, \tag{A5}$$

where d_{ci} and T_{ci} are, respectively, the critical hard-sphere diameter and critical temperature of component i. The value of d_{ci} can be determined from the critical properties

$$d_{ci} = \left(0.08943 RT_{ci}/P_{ci}\right)^{1/3}, \tag{A6}$$

or it can be calculated by fitting data on the vapor pressure of species i (Skjold-Jørgensen, 1984). For high molecular-weight compounds (for which T_c and P_c are unknown and vapor pressure data are unavailable), the d_{ci} value can be determined by fitting experimental data on infinite dilution activity coefficients of alkanes in compound i (Bottini et al., 1999).

The attractive contribution to the Helmholtz energy accounts for dispersive forces between functional groups, through a density-dependent, local-composition expression based on the NRTL model (Renon and Prausnitz, 1968)

$$(A/RT)^{\text{att}} = -\frac{z}{2}\sum_{i}^{NC} n_i \sum_{i}^{NG} \nu_j^i q_j \sum_{k}^{NG} \times \left(\theta_k g_{kj} \tilde{q} \tau_{kj}/RTV\right) \Big/ \sum_{l}^{NG} \nu_l \hat{o}_{lj}, \quad \text{(A7)}$$

with

$$\tilde{q} = \sum_{i}^{NC} n_i \sum_{j}^{NG} \nu_j^i q_j \quad \text{(A8)}$$

$$\theta_j = \left(q_j/\tilde{q}\right) \sum_{i}^{NC} n_i \nu_j^i \quad \text{(A9)}$$

$$\tau_{ij} = \exp\left(\alpha_{ij} \Delta_{ij} \tilde{q}/RTV\right) \quad \text{(A10)}$$

$$\Delta g_{ij} = g_{ij} - g_{jj}, \quad \text{(A11)}$$

where z is the coordination number (set equal to 10), υ_j^i is the number of groups of type j in molecule i, q_j is the number of surface segments assigned to group j, $\tilde{q}$ is the total number of surface segments, θ_k is the surface fraction of group k, g_{ij} is the attractive energy between segments of groups i and j, and α_{ij} is the nonrandomness parameter.

The attractive energy, g_{ij}, is calculated from the energy between like-group segments by the following combination rule:

$$g_{ij} = k_{ij}\left(g_{ii} g_{jj}\right)^{1/2}, \quad \text{(A12)}$$

where the binary interaction parameter k_{ij} is symmetrical ($k_{ij} = k_{ji}$). Both the attractive energy between like segments and the binary interaction parameter are temperature dependent

$$g_{jj} = g_{jj}^*\left[1 + g'_{jj}\left(T/T_j^* - 1\right) + g''_{jj} \ln\left(T/T_j^*\right)\right] \quad \text{(A13)}$$

$$k_{ij} = k_{ij}^*\left\{1 + k'_{ij} \ln\left[2T/\left(T_i^* + T_j^*\right)\right]\right\} \quad \text{(A14)}$$

where T_i^* is an arbitrary but fixed reference temperature for group i; g_{jj}^*, g'_{jj}, and g''_{jj} are pure-group energy parameters, and k_{ij}^* and k'_{ij} are binary group interaction parameters.

The association contribution to the Helmholtz function is calculated with a group-contribution expression (Gros et al., 1996) based on Wertheim's theory (1984a,b; 1986a,b) of associating fluids

$$\frac{A^{\text{assoc}}}{RT} = \sum_{i=1}^{NGA} n_i^{\text{assoc}} \left[\sum_{k=1}^{M_i}\left(\ln X^{(k,i)} - \frac{X^{(k,i)}}{2}\right) + \frac{1}{2} M_i\right] \quad \text{(A15)}$$

where NGA represents the number of associating groups, n_i^{assoc} the number of moles of associating group i, M_i the number of associating sites assigned to group i, and $X^{(k,i)}$ the mole fraction of group i not bonded at site k. The number of moles of associating group i is

$$n_i^{\text{assoc}} = \sum_{m=1}^{NC} \upsilon_m^{i,\text{assoc}} n_m \quad \text{(A16)}$$

where $\upsilon_m^{i,\text{assoc}}$ represents the number of times associating group i is present in molecule m, and n_m is the total number of moles of species m; the summation includes all NC components in the mixture.

The mole fraction of group i not bonded at site k is determined from the following expression

$$X^{(k,i)} = \left[1 + \sum_{j=1}^{NGA} \sum_{l=1}^{M_j} \rho_j^{\text{assoc}} X^{(l,j)} \Delta^{(k,i,l,j)}\right]^{-1} \quad \text{(A17)}$$

The value of $X^{(k,i)}$ depends on the molar density of associating group j ($\rho_j^{\text{assoc}} = n_j^{\text{assoc}}/V$) and the association strength $\Delta^{(k,i,l,j)}$ between site k of group i and site l of group j

$$\Delta^{(k,i,l,j)} = \kappa^{(k,i,l,j)}\left[\exp\left(\epsilon^{(k,i,l,j)}/kT\right) - 1\right] \quad \text{(A18)}$$

where the association parameters are the energy (ϵ) and volume (κ) of association. In mixtures containing alcohols and/or water, association effects can be computed by a single hydrogen-bonding hydroxyl group characterized by the following parameters: energy of $\epsilon/k = 2{,}700$ K and volume $\kappa = 0.8621$ cm^3/mol (Gros et al., 1997).

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