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MOLECULAR THERMODYNAMICS FOR FLUIDS AT LOW AND HIGH DENSITIES. PART 2. PHASE EQUILIBRIA FOR MIXTURES CONTAINING COMPONENTS WITH LARGE DIFFERENCES IN MOLECULAR SIZE OR POTENTIAL ENERGY

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Molecular Thermodynamics for Fluids at Low and High Densities Part 2. Phase Equilibria for Mixtures Containing Components with Large Differences in Molecular Size or Potential Energy

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Abstract

The molecular-thermodynamic correlation presented in Part 1 for pure fluids is extended to mixtures; this extension is particularly useful for mixtures of components with large differences in molecular size or potential energy. The novel feature of this correlation is a separation of the high-density and low-density contributions to the residual Helmholtz energy; this separation allows use of separate mixing rules for each density regime, guided by theoretically-defined boundary conditions. Such flexibility is necessary to represent phase equilibria in highly asymmetric fluid mixtures such as water-hydrocarbon systems. Phase equilibria are correlated for a variety of binary and multicomponent mixtures, including a petroleum-reservoir fluid containing carbon dioxide and including a mixture of hydrogen and coal-derived liquids.

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SCOPE

Phase equilibria for fluid mixtures are necessary for efficient design and operation of separation processes. Molecular-thermodynamic correlations are widely used to calculate such equilibria. This work presents a new correlation, based on perturbed-hard-chain theory, for representation of phase behavior for mixtures containing components differing appreciably in molecular size or potential energy.

The correlation presented in Part 1 is for thermodynamic properties of pure fluids containing small or large molecules. The novel feature of that correlation is separation of low-density and high-density expressions for the residual Helmholtz energy. This separation allows flexibility for representing the properties of mixtures: separate mixing rules are chosen for each density region.

To illustrate applicability, phase equilibria are correlated for several binary mixtures over wide ranges of temperature and pressure. Attention is given to those mixtures which show large differences in size, shape and potential energy; such mixtures are of particular interest in the petroleum and related industries.

CONCLUSIONS AND SIGNIFICANCE

The expression for the Helmholtz energy, presented in Part 1, is extended to mixtures. A novel separation of low-density and high-density contributions to the Helmholtz energy allows separate mixing rules for each density region. This flexibility in mixing rules significantly improves representation of mixture phase behavior, especially for those mixtures whose molecules differ appreciably in size and potential energy.

Phase equilibria are correlated for a variety of binary mixtures of interest in the petroleum and related industries. Agreement between calculated and experimental results is good except in regions near the mixture critical point. For some classes of mixtures, parameters fit to binary phase equilibria can be expressed as generalized correlations; these correlations are useful to estimate parameters for other mixtures where experimental data are scarce.

For all mixtures, the second virial coefficient is a quadratic function of mole fraction. However, for highly asymmetric binary mixtures, such as water-hydrocarbon systems, the quadratic dense-fluid mixing rule is modified to permit separate correlation of each dilute region. Such a modification is necessary when large differences in potential energy lead to clustering.

Phase equilibria are calculated for several multicomponent mixtures using only pure-component and binary parameters. Calculated and experimental results agree well for a reservoir-fluid mixture and for a mixture of hydrogen and a coal-derived liquid.

Introduction

Phase equilibria for fluid mixtures are essential for efficient design and operation of chemical separation processes. Since it may be prohibitive to measure such equilibria at all conditions of interest, molecular-thermodynamic correlations are widely used to represent fluid-phase behavior over wide ranges of temperature, pressure and composition.

Most of the successful correlations for representation of mixture phase behavior are semitheoretical in nature. One particular class of semitheoretical correlations is derived from the dense-fluid theories of Prigogine (1957) and Flory (1970). These correlations include the perturbed-hard-chain (PHC) equation (Beret and Prausnitz, 1975; Donohue and Prausnitz, 1978) and the chain-of-rotators (COR) equation (Chien et al., 1983). These equations contain physically-significant molecular parameters that are obtained from pure-component thermodynamic data. Extension to mixtures is based on mixing rules to relate mixture averages to composition.

While the PHC and the COR equations are derived primarily for nonpolar fluids, both have been extended to include polar fluids. Gmehling et al.(1979) superimposed a chemical dimerization theory onto the PHC equation; Vimalchand and Donohue

(1985) and Vimalchand et al.(1985) extended the PHC equation to polar and quadrupolar fluids using the multipolar expansions of Gubbins and Twu (1978). Masuoka and Chao (1984) added a polar perturbation term to the COR equation.

In a manner similar to that of Vimalchand et al., this work extends the PHC theory to include both quadrupolar and dipolar fluids and their mixtures. However, the novel feature of this work is separation of high-density and low-density contributions to the residual Helmholtz energy. While this separation leads to improved correlation of pure-fluid thermodynamic properties as discussed in Part 1, the main advantage of the separation follows from extension to mixtures. Separate mixing rules are selected for each density region to meet theoretically-defined boundary conditions and to represent phase behavior for highly asymmetric mixtures.

As suggested by several authors (e.g. Mollerup, 1981; Whiting and Prausnitz, 1982; Wong and Johnston, 1984), density-dependent mixing rules improve representation of phase behavior in strongly nonideal fluid mixtures. Mathias and Copeman (1983) apply such mixing rules to the Peng-Robinson equation. Hu et al.(1984), Luedecke and Prausnitz (1985) and Mollerup (1983) have correlated phase behavior for several binary mixtures using an equation of the van der Waals form with density-dependent mixing rules. This work builds upon these previous developments using the PHC equation. The resulting correlation is applicable to a wide variety of mixtures containing fluids such as hydrogen, water, polymers and coal-derived liquids, in addition to the usual hydrocarbons, nitrogen, carbon dioxide and hydrogen sulfide.

Residual Helmholtz Energy for Mixtures

The expression for the residual Helmholtz energy presented in Part 1 is extended to mixtures. The molar residual Helmholtz energy for a mixture is the difference between the molar Helmholtz energy for that mixture and that for an ideal-gas mixture at the same temperature, volume and composition

$$\mathbf{a}^{r}(T,V,n_1,n_2...) = \mathbf{a}(T,V,n_1,n_2...) - \mathbf{a}^{IG}(T,V,n_1,n_2...) \qquad (1)$$

where n_1 is the mole number of component 1, etc.

The residual Helmholtz energy is given by the sum of a reference term and two perturbation terms

$$a^r = a^{ref} + a^{sv}(1-F) + a^{df} F \tag{2}$$

where a^{ref} is the contribution from the reference fluid and where a^{sv} and a^{df} are perturbation contributions in low-density and high-density regions, respectively. Function F provides a smooth interpolation between these two density regions.

Reference term a^{ref} includes contributions from repulsive intermolecular forces; it is calculated using a generalized form of the Carnahan-Starling equation (1972) shown by Eq. 7 of Part 1. To allow for softness of the spheres, the hard-core diameter is temperature-dependent (Eq. 10, Part 1), as suggested by Barker and Henderson(1967).

Separation of the perturbation term into high-density and low-density regions allows flexibility to choose separate mixing rules for each density region. Such flexibility is necessary to correlate phase behavior in highly asymmetric systems; it is this flexibility which allows us to relax the commonly-used quadratic mixing rule without violating the theoretically-determined composition dependence of the second virial coefficient.

The perturbation terms include contributions due to dispersion, polar and quadrupolar intermolecular forces. The low-density term a^{sv} is given by a virial expansion truncated after the second virial coefficient (Eq. 15, Part 1). Generalized expressions for dispersion, polar and quadrupolar contributions were obtained from experimental second virial coefficients.

The high-density term a^{df} is given by a perturbation series in reciprocal temperature. Expressions for dispersion contributions (Eq. 15, Part 1) are obtained from a generalization of computer-simulation data for Lennard-Jones molecules; polar and quadrupolar contributions follow from a multipolar expansion presented by Gubbins and Twu (1978).

Interpolation function F (Eq. 18, Part 1) is chosen to meet necessary boundary conditions; it is generalized using experimental vapor-pressure and density data for a large number of pure fluids.

The equation of state and the chemical potential are derived by differentiating Eq. 2 with respect to volume and mole number, respectively.

Each pure fluid is characterized by three molecular parameters v^*, $\varepsilon q/k$ and c; these parameters are characteristic of soft-core volume, dispersion potential energy and flexibility of a molecule; a characteristic temperature T^* is defined by $\varepsilon q/k$. [For polar fluids we also use reduced dipole moment $\tilde{\mu}$ and reduced quadrupole moment $\tilde{Q}$.] As discussed in Part 1, v^* and T^* are used to define a hard-core (temperature-dependent) volume $v^\dagger$. Values of parameters are determined by fitting pure-fluid vapor-pressure and/or density data. For polar fluids, reduced dipole and quadrupole moments are defined by Eqs. 14 and 15 of Part 1, respectively.

Reference Term

Reference term a^{ref} is calculated for mixtures by replacing pure-component parameters c and $v^\dagger$ in the generalized Carnahan-Starling expression (1972) given in Eq. 7 of Part 1 with the composition averages $<c>$ and $<v^\dagger>$. These averages are related to pure-component parameters using suitable mixing rules; these mixing rules are selected to meet two necessary boundary conditions. First, the expression for the entropy of mixing for an athermal mixture at high densities must reduce to the Flory-Huggins expression. Second, the composition dependence of the reference-term contribution to the second virial coefficient must be quadratic in mole fraction, as required by statistical mechanics (Prausnitz et al., 1986).

The physical significance of parameter c requires that the mixing rule for $<c>$ be linear in mole fraction x. Since reduced volume $\tilde{v}$ is per segment, we also use a linear rule for $v^\dagger$. Thus,

$$<c> = \sum_i x_i c_i \qquad (3)$$

$$<v^{\dagger}> = \sum_i x_i v_i^{\dagger} \tag{4}$$

To show that Eqs. 4 and 5 meet both boundary conditions, we first consider the entropy of mixing for an athermal mixture. The expression for the entropy of mixing arising from the reference term is

$$\frac{\Delta s^{mix}}{R} = -\sum_i x_i \ln \frac{x_i v_i^{pure}}{v} + <c> \frac{(3\tau/\tilde{v}-4)(\tau/\tilde{v})}{(1-\tau/\tilde{v})^2} - \sum_i x_i c_i \frac{(3\tau/\tilde{v}_i-4)(\tau/\tilde{v}_i)}{(1-\tau/\tilde{v}_i)^2} \tag{5}$$

where $\tau = \pi\sqrt{2}/6$; v_i^{pure} is the molar volume of pure i at the same pressure and temperature as those of the mixture and where v is the molar volume of the mixture; $<c>$ and $\tilde{v}$ are composition averages for parameter c and for reduced molar volume $\tilde{v} = v/<v^{\dagger}>$; c_i and $\tilde{v}_i$ are the corresponding pure-component quantities.

If we use Eq. 4 for $<c>$ and if we assume that the reduced densities of all the pure components and of the mixture are equal at high pressures (close-packed density), i.e.

$$\tilde{v} = \tilde{v}_i \quad \text{for } all \ i, \tag{6}$$

then, Eq. 5 becomes

$$\frac{\Delta s^{mix}}{R} = -\sum_i x_i \ln(x_i v_i^{pure}/v) \tag{7}$$

which is the Flory-Huggins expression.

To show that Eqs. 3 and 4 meet the second boundary condition, we calculate the contribution to the second virial coefficient from the reference term

$$B^{ref} = <c><v^{\dagger}>(2\pi\sqrt{2}/3) \tag{8}$$

Since both $<c>$ and $<v^{\dagger}>$ are linear in mole fraction, the composition dependence of B^{ref} is quadratic in mole fraction.

Second-Virial Perturbation Term

The expression for the low-density perturbation term a^{sv} is the sum of attractive contributions to the second virial coefficient. Since the mixture second virial coefficient must be quadratic in mole fraction, the mixture expression for a^{sv} becomes

$$a^{sv} = \frac{RT}{v}\sum_i\sum_j x_i x_j (B_{ij}^{disp} + B_{ij}^{\mu\mu} + B_{ij}^{QQ}) \tag{9}$$

where B_{ij}^{disp}, $B_{ij}^{\mu\mu}$ and B_{ij}^{QQ} are attractive contributions to the second virial coefficient due to dispersion, dipolar and quadrupolar forces, respectively.

Appendices I and II of Part 1 give pure-component $(i=j)$ expressions for each of the terms in Eq. 9. For the cross terms in Eq. 9 $(i \neq j)$, we must choose combination rules to calculate cross molecular parameters.

The cross parameters for the dispersion contributions are given by

$$c_{ij} = ½(c_i + c_j) \tag{10}$$

$$(cv^\dagger)_{ij} = (c_i v_j^\dagger + c_j v_i^\dagger) \tag{11}$$

$$T_{ij}^* = \frac{(c_i T_i^*)^{½}(c_j T_j^*)^{½}}{c_{ij}}(1 - k_{ij}^B) \tag{12}$$

where k_{ij}^B is an adjustable binary parameter which corrects the geometric mean assumption for T_{ij}^*. Parameter k_{ij}^B is fit to experimental second-virial cross coefficients for binary mixtures.

Combination rules for the dipolar and quadrupolar contributions are given in Appendix II. No additional binary parameters are introduced.

The upper diagram in Figure 1 shows calculated and observed second-virial cross coefficients for several methane-alkane binaries. Experimental values are reported by Dymond and Smith (1980). Second-virial cross coefficients are calculated using Eqs. 10 to 12 with binary parameters k_{ij}^B set to zero. For these binaries, agreement between calculated and experimental cross coefficients is good without use of any adjustable binary parameters.

The lower diagram in Figure 1 shows calculated and observed second-virial cross coefficients for several water-alkane binaries. Experimental data are from Dymond and Smith(1980) and Smith et al.(1983, 1984). Calculated and experimental values are in good agreement when one adjustable parameter is included for each binary. Fitted binary parameters are indicated in Figure 1.

Dense-Fluid Term

Dense-fluid expression $\mathbf{a}^{df}$ is the sum of terms representing high-density contributions due to dispersion, dipolar and quadrupolar forces. Each term is calculated using mixing rules to relate mixture composition averages to pure-component parameters. Mixing rules for the dispersion terms are similar to those of Donohue and Prausnitz (1978); mixing rules for polar terms follow the forms suggested by Gubbins and Twu (1978).

For extension to mixtures, we consider the perturbation terms due to dispersion forces, $\mathbf{a}^{(1)}$ and $\mathbf{a}^{(2)}$, introduced in Eq. 13 of Part 1. Appendix II discusses calculation for mixtures of the perturbation terms due to polar intermolecular forces.

The composition dependence of the dispersive terms is given by the following averages

$$\mathbf{a}^{(1)}(x) = \mathbf{a}^{(1)}(<cT^{*}v^{\dagger}>, <v^{\dagger}>) \tag{13}$$

$$\mathbf{a}^{(2)}(x) = \mathbf{a}^{(2)}(<cT^{*2}v^{\dagger}>, <v^{\dagger}>) \tag{14}$$

where $<v^{\dagger}>$ is given by Eq. 4. Mixing rules for $<cT^{*}v^{\dagger}>$ and $<cT^{*2}v^{\dagger}>$ are composition averages over molecular segments and surface area.

As in Part 1, a molecule is considered to be the sum of equisized segments; a molecule has r segments and an external surface area q. The soft-core volume per segment v^{*}_{seg} is the same for all segments; it is here set equal to 10 cm^3/mol. While this value is somewhat arbitrary, it follows from earlier work of Donohue (1978); the size of each segment is approximately equal to that of a methylene group in a long-chain hydrocarbon. The soft-core volumes per mole of molecules and per mole of segments are inter-related by

$$v^* = r\sigma^3 N_{av}/\sqrt{2} = r\, v^*_{seg} \tag{15}$$

where N_{av} is Avogadro's number and σ is the soft-core segment diameter. The hard-core volume $v^\dagger$ is defined by

$$v^\dagger = rd^3 N_{av}/\sqrt{2} \tag{16}$$

where d is the hard-core diameter calculated with Eq. 10 of Part 1.

The potential energy per molecule is given by $\varepsilon q/k$ where ε is potential energy per surface area and k is Boltzmann's constant. Characteristic temperature T^* is defined by

$$T^* = \varepsilon q/ck \tag{17}$$

While reduction of pure-component data yields the product $\varepsilon q/k$, for correlation of mixture data it is necessary to separate that product into its two factors.

Following Donohue and Prausnitz (1978), we write a general mixing rule

$$<cT^{*m}v^\dagger> = \sum_i \sum_j x_i x_j c_i \left[\frac{\varepsilon_{ij} q_i}{c_i k}\right]^m \frac{r_j d_{ij}^3 N_{av}}{\sqrt{2}} \tag{18}$$

where d_{ij} is given by

$$d_{ij} = ½(d_i + d_j) \tag{19}$$

and where ε_{ij} is given by

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{½}(1-k_{ij}) \tag{20}$$

Adjustable binary parameter k_{ij} corrects the geometric-mean assumption; k_{ij} is fit to binary phase-equilibrium data.

For alkanes, ε/k is chosen as 80 K. For other fluids, ε/k is determined using equilibrium data for a binary mixture whose second component is an alkane. Typically, the chosen value of ε/k is that which minimizes binary parameter k_{ij}. Table 1 lists values of ε/k for various hydrocarbon classes and for several other pure fluids.

For most binary mixtures, Eq. 18 is sufficient to represent phase behavior using a single adjustable parameter k_{ij}. However, for some highly asymmetric mixtures, it is advantageous to introduce a second adjustable parameter into the mixing rules in Eq. 18, as shown in Appendix I. The two binary parameters, denoted $k_{1(2)}$ and $k_{2(1)}$, adjust the geometric-mean assumption for ε_{ij} in separate concentration regions. When component 1 is infinitely dilute in component 2, only parameter $k_{1(2)}$ applies; at the opposite limit, when component 2 is dilute in 1, only parameter $k_{2(1)}$ applies. Parameter $k_{1(2)}$ is fixed by Henry's constant $H_{1(2)}$ and parameter $k_{2(1)}$ is fixed by Henry's constant $H_{2(1)}$; these Henry's constants are defined by

$$H_{1(2)} = \lim_{x_1 \to 0} \frac{f_1}{x_1} \quad \text{and} \quad H_{2(1)} = \lim_{x_2 \to 0} \frac{f_2}{x_2} \tag{21}$$

where f is fugacity. At intermediate concentrations, both parameters are required.

Appendix I gives modified mixing rules for Eq. 18 using two adjustable parameters. When the two parameters are equal ($k_{1(2)}=k_{2(1)}$), the mixing rule in Appendix I reduces to Eq. 18.

Interpolation Function

Function F is calculated for mixtures by replacing pure-fluid parameters with a composition average

$$F = 1 - \exp\left[-6\frac{<T^{*}(\varepsilon q/k)^{total}v^{\dagger}>}{T^{2}v}\right] \tag{22}$$

where $(\varepsilon q/k)^{total}$ is the sum of the dispersion, dipolar and quadrupolar contributions to the potential energy (Eq. 19, Part 1). The mixing rule used here is determined empirically by examining phase equilibria for a large number of binary mixtures

$$<T^{*}(\varepsilon q/k)^{total}v^{\dagger}> = \sum_i\sum_j x_i x_j\left(\frac{T_i^{*}+T_j^{*}}{2}\right)\left\{\frac{[(\varepsilon q/k)_i^{total}v_i^{\dagger}+(\varepsilon q/k)_j^{total}v_j^{\dagger}]}{2}\right\} \tag{23}$$

This mixing rule for interpolation function F uses only pure-component parameters;

no adjustable binary parameters are introduced.

Data Reduction

To calculate phase equilibria for fluid mixtures, it is necessary to fit adjustable binary parameters to experimental data for binary mixtures. In the correlation presented here, the resulting equation of state has one, two or three adjustable parameters depending upon the complexity of the mixture. These parameters can be determined independently using experimental second-virial cross coefficients and Henry's constants. However, for many binary mixtures of interest, reliable virial coefficients and Henry's constants are not available. Therefore, we have developed procedures to obtain binary parameters from various types of phase-equilibrium data that may be available for a particular mixture. The most common types of data include pressure-temperature-composition (P-T-x-y) data for equilibrium phases, bubble-point (P-T-x) data or dew-point (P-T-y) data.

Our regression method is based on the maximum-likelihood technique described by Anderson et al.(1979). The maximum-likelihood technique accounts for experimental uncertainties in both independent and dependent variables. The following estimates of experimental uncertainties are used for correlation of mixture data: temperatures ± 0.1 K, pressures ± 1.0 %, vapor-phase and liquid-phase mole fractions ± 0.01 and Henry's constants ± 3.0 %.

Asymmetric Binary Mixtures

To illustrate, Figure 2 shows calculated and observed vapor-liquid equilibria for the system hydrogen-hexane. Experimental phase equilibria of Nichols et al. (1957) are correlated using a single binary parameter for the dense fluid. The second-virial parameter k^B is set to zero.

Figure 3 shows calculated and observed phase equilibria for the system nitrogen-ammonia. Nitrogen and ammonia have similar molecular sizes but have large differences in potential energy. Nitrogen has a weak quadrupole moment; ammonia has a strong dipole moment. The phase equilibria for this mixture are correlated using two binary parameters: one for the second-virial cross coefficient and another for the dense-fluid region. The second-virial binary parameter k^B is fit to experimental second-virial cross coefficients reported by Lee et al. (1970). The dense-fluid parameter k_{ij} is correlated to vapor-liquid-equilibrium data from Reamer and Sage (1959).

Figure 4 presents vapor-liquid equilibria for the system carbon dioxide-ethane at 250 K. [At this temperature, both pure components are subcritical.] Figure 4 shows experimental data (solid points) on a y-x diagram; this system has an azeotrope near x_{CO_2}=0.7. For this binary mixture, the quadrupole moment of carbon dioxide has an important qualitative effect on calculated results. Following Vimalchand and Donohue (1985), we present calculations with and without quadrupolar effects, setting all binary parameters to zero. If we ignore the quadrupole moment of carbon dioxide (dashed line), the equation of state does not predict an azeotrope. Including the quadrupole moment (heavy line), an azeotrope is predicted with good agreement between calculated and observed results.

Table 2 summarizes typical correlation results for several binary systems. Average deviations in K-factors are reported for both components. A comprehensive tabulation of binary results and data references is deposited as supplementary material.

Aqueous Binary Mixtures

Water-hydrocarbon binaries represent an important class of asymmetric mixtures because such mixtures are of interest in many chemical and petroleum processes. However, strong polar effects in aqueous mixtures make the phase equilibria of these systems difficult to correlate.

Two adjustable binary parameters are used in the dense-fluid region to represent both water-rich and hydrocarbon-rich composition regions. To obtain good representation, the binary parameter for the water-rich end must be temperature-dependent.

Figure 5 shows calculated and experimental phase equilibria for the system methane-water. Experimental data for this system (Olds, et al., 1942; Sultanov, et al., 1971,1972) cover wide ranges of temperature and pressure. Observed and calculated vapor-liquid equilibria are in excellent agreement using binary parameters listed in Table 3.

Figures 6 and 7 show vapor-liquid and liquid-liquid equilibria for the system propane-water. Experimental and calculated results are shown at three temperatures. Figure 6 shows the solubility of water in the propane-rich phase. Below 370 K, there is a three-phase (vapor-liquid-liquid) region, indicated by dashed lines. At the lowest temperature shown (327.6 K), there is a transition from vapor-liquid to liquid-liquid equilibria near 20 bar. The middle isotherm (369.7 K) passes through a 3-phase critical point. The highest temperature (427.6 K) is beyond the liquid-liquid region; only vapor-liquid equilibria are observed.

For this difficult-to-fit binary system, calculated and experimental phase equilibria are in good agreement. Binary parameters are listed in Table 3. The virial parameter k^B is interpolated between the values listed in Figure 1; this interpolated value based on second-virial cross coefficients is in excellent agreement with k^B correlated to dense-fluid data.

Henry's Constants for Solutes in Polyethylene

The correlation presented here is useful for calculating phase behavior for mixtures containing high-molecular-weight fluids. To illustrate, the solubilities of several low-molecular-weight solutes in low-density polyethylene are calculated using binary parameters fit to experimental Henry's constants reported by Liu and Prausnitz (1976) and Maloney and Prausnitz (1976).

Figure 8 shows typical agreement between calculated and observed results. Pure-component parameters for polyethylene are given in Part 1. Fitted binary parameters (for the dense fluid) are reported in Table 4.

Ternary Mixtures

Phase equilibria are calculated for a ternary mixture using only pure-component and binary data. First, experimental and calculated phase-equilibrium results are presented for two binary systems: methane-tetralin and hydrogen-tetralin. Then, phase equilibria are calculated for the ternary system methane-hydrogen-tetralin.

Figure 9 shows K-factors as functions of temperature and pressure for the systems methane-tetralin and hydrogen-tetralin. For each binary, one adjustable binary parameter is obtained from data reduction; second-virial parameters k^B are set to zero. For the hydrogen-tetralin system, calculated and observed K-factors are in good agreement. However, for the methane-tetralin system at 623 K, the correlation overpredicts the apparent critical pressure.

Calculated and experimental vapor-liquid equilibria for the system methane-hydrogen (not shown) are in good agreement using a single binary parameter k_{12}=0.1431. [Temperatures corresponding to the vapor-liquid region for methane-hydrogen are significantly below those shown in Figure 9 for the tetralin binaries.]

Phase equilibria for the ternary system hydrogen-methane-tetralin are calculated at 462 K. Figure 10 shows calculated and experimental results at three pressures. K-factors for each component are plotted as functions of overall methane mole fraction on a tetralin-free basis. The left and right sections in Figure 10 give K-factors for methane and hydrogen in the ternary mixture. These K-factors are nearly independent of the relative amount of methane. However, in the center section, the K-factor of tetralin depends strongly on the methane content, as noted previously by Gray et al. (1983).

At the lowest pressure (51 bar), tetralin shows little preference for either methane or hydrogen. At higher pressures (101 and 253 bar), the tetralin K-factor is much larger in methane-rich mixtures than in hydrogen-rich mixtures, indicating that, as expected from second-virial-coefficient correlations, the vapor-phase solubility of tetralin is larger in dense methane than in dense hydrogen.

Equilibria in a Reservoir Fluid

Equations of state are commonly used to calculate phase equilibria for reservoir-fluid mixtures as needed for simulation of miscible-gas processes. Carbon dioxide is commonly used for reservoir injection; phase equilibria of carbon dioxide-rich mixtures are therefore of industrial importance.

Two examples are presented here for carbon dioxide-hydrocarbon mixtures. In the first example, binary parameters are correlated using solubility data for carbon dioxide in several heavy-hydrocarbon solvents (Gasem and Robinson, 1985). In the second example, phase equilibria are calculated for a 12-component synthetic oil mixture containing a significant amount of carbon dioxide. Such systems are valuable for testing correlation methods without introducing uncertainties due to incomplete characterization of real-oil mixtures.

Figure 11 shows calculated and experimental solubilities of carbon dioxide in four high-boiling alkane solvents at 100°C. Similar results are obtained at 50 and 150°C. One (high-density) adjustable binary parameter is used for each solvent. Table 5 lists generalized dense-fluid binary parameters k_{ij}. Since quadrupolar effects for carbon dioxide are explicitly taken into account, second-virial parameters k^B are set to zero for carbon dioxide-hydrocarbon binaries.

Figure 12 shows calculated and experimental phase equilibria for a 12-component synthetic-oil mixture at 322 K. Experimental flash data are reported by Turek et al.(1984). The feed composition of the oil is given in Table 6; overall mole fraction of carbon dioxide is 70 mole percent.

Calculated and experimental results are in good agreement from low pressures to the mixture bubble point (experimental: 115.1 bar, calculated 114.9 bar). Calculated K-factors for tetradecane are somewhat below experimental values; however, vapor-phase mole fractions for tetradecane are extremely small and perhaps subject to some experimental uncertainty.

The results in Figure 12 are calculated from flash calculations using the feed composition given in Table 6. Adjustable parameters for all binaries are given in Table 5. For all binaries, virial parameter k^B is set to zero.

Comparisons at other overall carbon dioxide concentrations give similar good results except near mixture critical conditions.

Hydrogen Solubility in Coal-Derived Liquids

The final example shows a correlation for the solubility of hydrogen in a middle distillate from the SRC-II process at several temperatures and pressures. Experimental data are reported by Harrison et al.(1985). The coal-derived liquid is considered to be a mixture of two pseudocomponents. One pseudocomponent corresponds to a saturated hydrocarbon and another corresponds to an aromatic hydrocarbon. To calculate hydrogen solubility in a mixture of these two pseudocomponents, three simplifying assumptions are necessary to determine pure-component parameters, relative amounts of each pseudocomponent and binary parameters.

First, pure-fluid parameters are estimated for each pseudocomponent using the generalized correlations presented in Appendix III of Part 1. The alkane correlation is used for the saturated component; the fused-ring correlation is used for the aromatic component. These correlations require the molecular weight of each component. Molecular weights for both pseudocomponents are estimated using the boiling-point characterization for the SRC-II middle distillate presented by Brinkman and Bowden (1982). The molecular weight of the alkane pseudocomponent is 183.3; that of the fused-ring pseudocomponent is 134.8.

Second, the relative amount of each pseudocomponent is estimated from the average molecular weight of the coal-derived liquid. Brinkman et al.(1985) report an average molecular weight 146.1 determined by mass spectrometry. Since the pseudocomponents have different molecular weights, the fraction of each is determined by matching the overall experimental molecular weight. On a hydrogen-free basis, the mole fractions of the alkane and the fused-ring pseudocomponents are 0.767 and 0.233, respectively.

Finally, binary parameters are estimated for binary pairs. Since the liquid-phase mole fraction of hydrogen is small, only one binary parameter is used for each hydrogen-hydrocarbon pair; virial parameters k^B and the hydrocarbon-hydrocarbon parameter are set to zero. The hydrogen-alkane binary parameter is estimated from Table 5 (k_{12}=0.06). The molecular weight of the aromatic corresponds roughly to that for tetralin. Therefore, the hydrogen-tetralin parameter used in Figure 9 is also used here (k_{12}=0.0133).

Figure 13 shows calculated (dashed lines) and experimental (symbols) solubilities for hydrogen in the SRC-II middle distillate. Agreement is good considering the simplifying assumptions that are required for performing calculations for this complex mixture.

Agreement between calculated and experimental results can be improved by correcting for decomposition and hydrogenation reactions. Harrison et al.(1985) correct their experimental results for the presence of volatile reaction products. The authors report an overall 5 % increase in the molecular weight of the coal-derived liquid following solubility measurements. (This increase in molecular weight results from the conversion of aromatics to saturates in the presence of hydrogen at high temperatures.) Assuming that this increase is a linear function of temperature, the relative amounts of each pseudocomponent are adjusted accordingly. As a result, the mole fraction of the alkane rises, leading to increased solubilities of hydrogen. The increased solubility is indicated by the solid lines in Figure 13.

This example illustrates the applicability of our correlation to provide quantitative estimates of hydrogen solubilities in complex mixtures. Further improvement requires more detailed experimental characterization of the complex hydrocarbon mixtures. Experimental procedures for such characterization are the subject of current research at Berkeley.

Conclusion

The correlation presented here uses an extended perturbed-hard-chain theory to calculate phase equilibria in mixtures. The extension takes into consideration the effect of hard-core softness as well as effects arising from dipole and quadrupole moments. More important, the extension considers separately contributions to the residual Helmholtz energy from low-density and high-density regions. This separation makes it easy to use density-dependent mixing rules: one mixing rule is used for the low-density region and another mixing rule is used for the high-density region. While the low-density mixing rule is always quadratic in mole fraction, the high-density mixing rule is arbitrary, dictated by the kind of mixture under consideration. For the high-density region, a quadratic mixing rule is satisfactory for most ordinary mixtures while a cubic mixing rule is necessary for those mixtures (e.g. water-hydrocarbons) where there is much deviation from randomness.

The correlation given here is entirely analytic, requiring no numerical integrations. It is therefore suitable for computer-aided process design. Computer programs are available upon request.

While the correlation presented here is applicable to a wide variety of fluid mixtures encountered in chemical technology, it has one significant limitation: it is not able to supply consistently reliable results in the critical region. That limitation is not peculiar to this correlation; that limitation, unfortunately, prevails in all correlations used in contemporary chemical engineering.

For significant advance in chemical engineering thermodynamics, our first priority should now not be to refine further existing equations of state in the high-density and low-density regions. Instead, primary attention should now be given toward establishing a useful, engineering-oriented equation of state that is reliable for correlating phase behavior of pure fluids and mixtures in the critical region as well as in regions remote from critical.

Acknowledgements

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Notation

Symbols

a	molar Helmholtz energy
$a^{(m)}$	binary combination of molecular parameters $cT^{*m}v^{\dagger}$
$A^{(m)}$	ternary combination of molecular parameters $cT^{*m}v^{\dagger}$
B	second virial coefficient
c	shape and flexibility parameter
d	hard-core (temperature-dependent) diameter
f	fugacity
F	interpolation function
$H_{i(j)}$	Henry's constant of solute i in solvent j
J	Integral of two-body radial distribution function
K	Integral of three-body radial distribution function
k	Boltzmann's constant
k^{B}	second-virial adjustable binary parameter
k_{ij}	dense-fluid adjustable binary parameter
$\hat{k}_{ij}$	average dense-fluid adjustable binary parameter
n	number of moles
P	absolute pressure
q	external molecular surface area
Q	molecular quadrupole moment
$\tilde{Q}$	reduced quadrupole moment in low-density region
$\hat{Q}$	reduced quadrupole moment in high-density region
r	number of segments per molecule
R	gas constant
Δs^{mix}	entropy of mixing
T	absolute temperature
$\tilde{T}$	reduced temperature, $\tilde{T}=T/T^{*}$
$\hat{T}$	characteristic temperature for high-density polar perturbation terms
T^{*}	characteristic temperature, $T^{*}=\varepsilon q/ck$
v	molar volume
$\tilde{v}$	reduced volume, $\tilde{v}=v/v^{\dagger}$
$\hat{v}$	characteristic volume for high-density polar perturbation terms
v^{*}	soft-core molar-volume parameter
v^{*}_{seg}	soft-core segment-volume parameter
$v^{\dagger}$	hard-core molar-volume parameter
v^{pure}	pure-component molar volume

V	total volume
x	mole fraction

Superscripts and Subscripts

df	dense-fluid contribution
$disp$	dispersive contribution
IG	ideal-gas contribution
i, j, k	component i, j or k
ij	interaction between components i and j
ijk	interaction between components i, j and k
m	integer in dense-fluid mixing rule
QQ	quadrupolar contribution
r	residual property
ref	reference term
sv	second-virial contribution
$\mu\mu$	dipolar contribution
μQ	dipolar-quadrupolar contribution

Greek Symbols

μ	molecular dipole moment
$\tilde{\mu}$	reduced dipole moment in low-density region
$\hat{\mu}$	reduced dipole moment in high-density region
ε	potential energy per unit surface area
σ	soft-core diameter
τ	hard-sphere packing factor (0.7405)

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Table 1. Potential energy per surface area for several hydrocarbon classes and other fluids. Values from analysis of binary phase-equilibrium data.

	ε/k, K
Hydrocarbon Class	
n-alkanes	80
n-alkylnaphthenes	90
n-alkylaromatics	110
Other Fluids	
Ethylene	100
Hydrogen	110
Nitrogen	50
Sulfur Dioxide	80
Carbon Dioxide	80
Water	80
Ammonia	60
Acetone	80
Hydrogen Sulfide	120

Table 2. Typical agreement between calculated and experimental K-factors for some illustrative binary systems.

System		T, K	P, bar	Avg. % Dev.	
(1)	(2)			K_1	K_2
hydrogen	methane	116-172	34-275	7.72	5.16
hydrogen	decane	462-583	19-255	3.24	4.74
methane	tetralin	462-665	20-253	3.20	5.01
methane	water	311-573	27-980	5.90	3.23
hydrogen sulfide	pentane	278-444	1-69	4.93	7.41
hydrogen sulfide	propylcyclohexane	311-478	2-116	4.01	9.67
carbon dioxide	toluene	311-477	3-153	3.36	5.48
carbon dioxide	hexadecane	463-664	20-51	8.48	10.43
nitrogen	ammonia	278-378	34-310	5.88	3.48
nitrogen	benzene	348-398	62-307	1.31	5.99

Table 3. Binary parameters for two water(1)-hydrocarbon(2) binary mixtures.

Binary Parameter	Component (2)	
	Methane	Propane
$k^{B\dagger}$	0.250	0.330
$k_{1(2)}$	0.3722	0.3657
$k_{2(1)}$	$0.1759-49050/T^2$ T in K	$0.1186-41890/T^2$ T in K

† from second-virial-coefficient data

Table 4. Binary parameters for five solutes in polyethylene.

Solute	$100k_{12}$
Ethylene	0.05
Sulfur Dioxide	5.38
Acetone	2.69
Benzene	1.94
Octane	0.00

Table 5. Binary parameters for several binary systems.

	$100k_{12}$						
Component	CH_4	C_2H_6	C_3H_8	N_2	H_2S	CO_2	H_2
n-alkanes							
CH_4	-	1.0	1.7	3.0	3.5	3.0	15.0
C_2H_6	1.0	-	0.2	4.0	4.0	3.5	12.0
C_3H_8	1.7	0.2	-	5.0	4.5	4.0	10.0
C_4H_{10}	2.2	0.5	0.1	5.5	4.7	4.4	8.5
C_5H_{12}	2.7	0.7	0.2	5.5	5.0	4.6	7.5
C_6H_{14}	3.0	0.8	0.3	5.5	5.2	4.8	6.5
C_7H_{16}	3.3	0.9	0.4	5.5	5.4	5.0	6.0
C_8H_{18}	3.6	1.0	0.5	5.5	5.6	5.2	6.0
$C_{10}H_{22}$	4.0	1.2	0.5	5.5	5.8	5.4	6.0
$C_{16}H_{34}$	4.8	1.2	0.5	5.5	6.0	5.9	6.0
$C_{20}H_{42}$	5.0	1.2	0.5	5.5	6.0	6.0	6.0
$C_{30}H_{62}$	5.0	1.2	0.5	5.5	6.0	6.0	6.0
n-alkylcyclohexanes	3.0	1.5	0.7	9.0	3.0	3.0	0.0
n-alkylbenzenes	4.0	2.0	1.5	9.5	0.0	4.0	4.5

Table 6. Overall feed composition for 12-component synthetic oil.

Component	Mole Percent
Carbon Dioxide	69.520
Nitrogen	0.456
Methane	10.130
Ethane	0.851
Propane	1.195
Butane	1.798
Pentane	1.305
Hexane	0.966
Heptane	1.482
Octane	1.505
Decane	9.196
Tetradecane	1.596

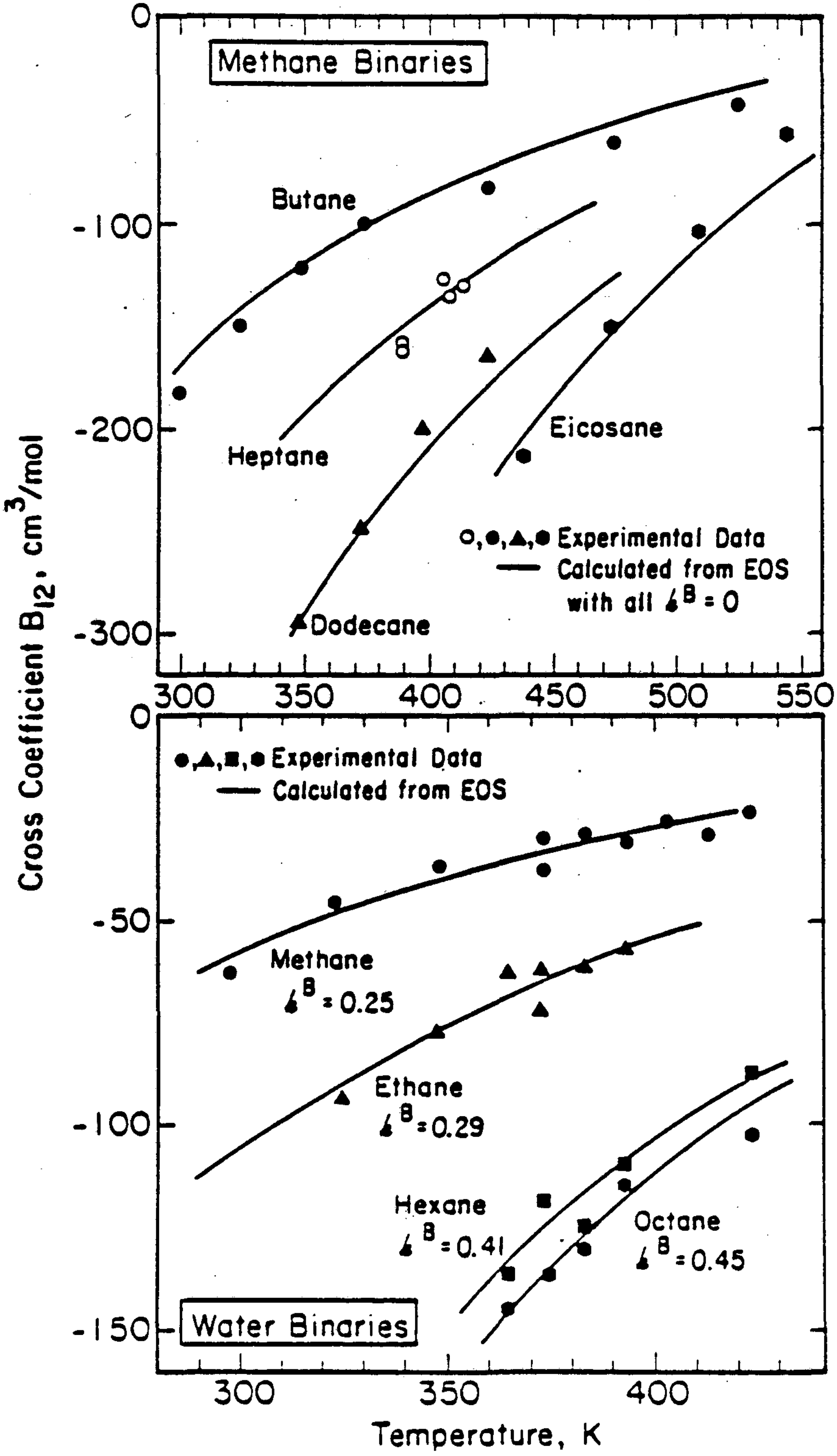

Figure 1. Second-virial cross coefficients for asymmetric mixtures.

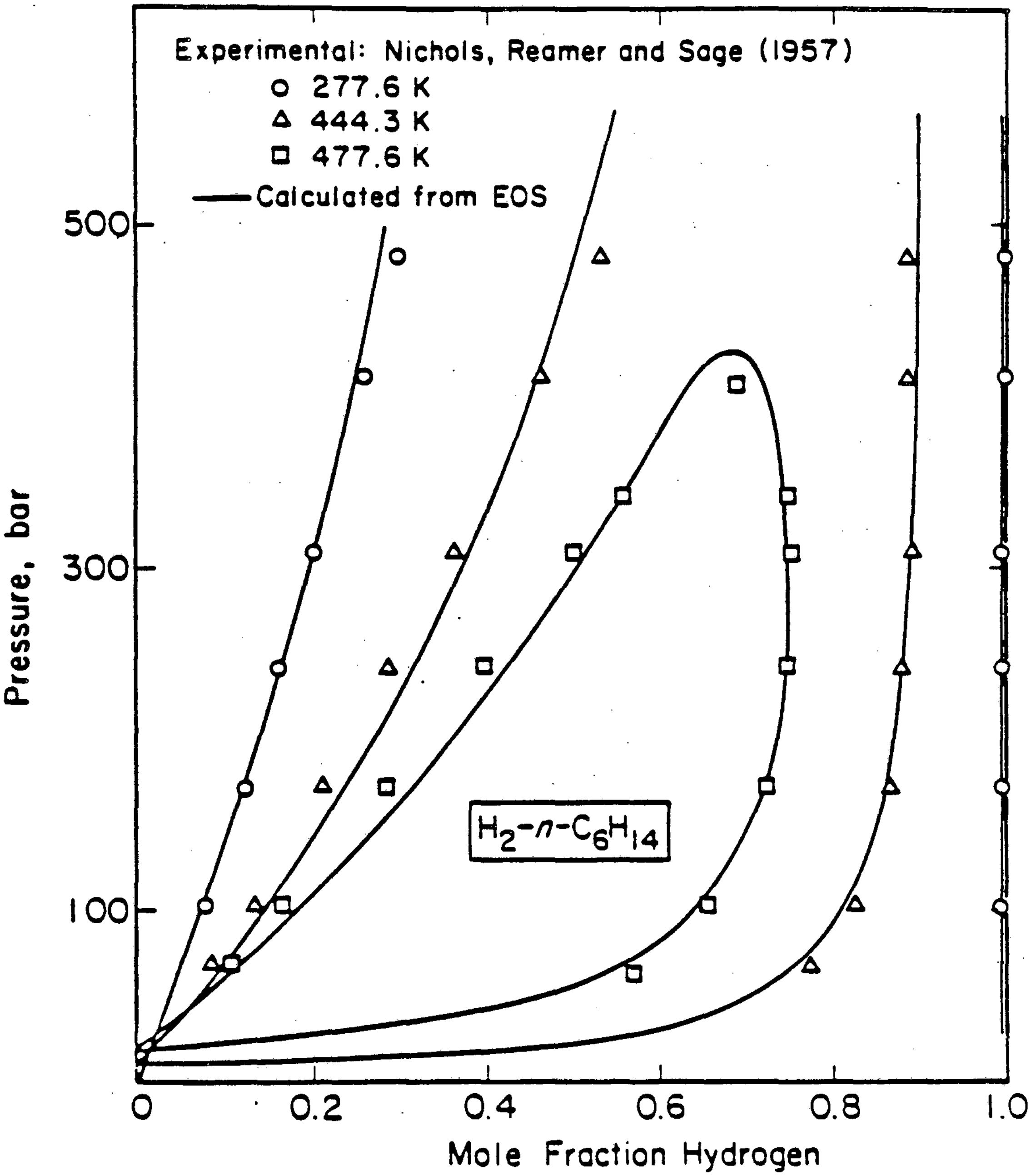

Figure 2. Vapor-liquid equilibria for the system hydrogen-*n*-hexane. Binary parameters: $k^B=0$, $k_{12}=0.065$.

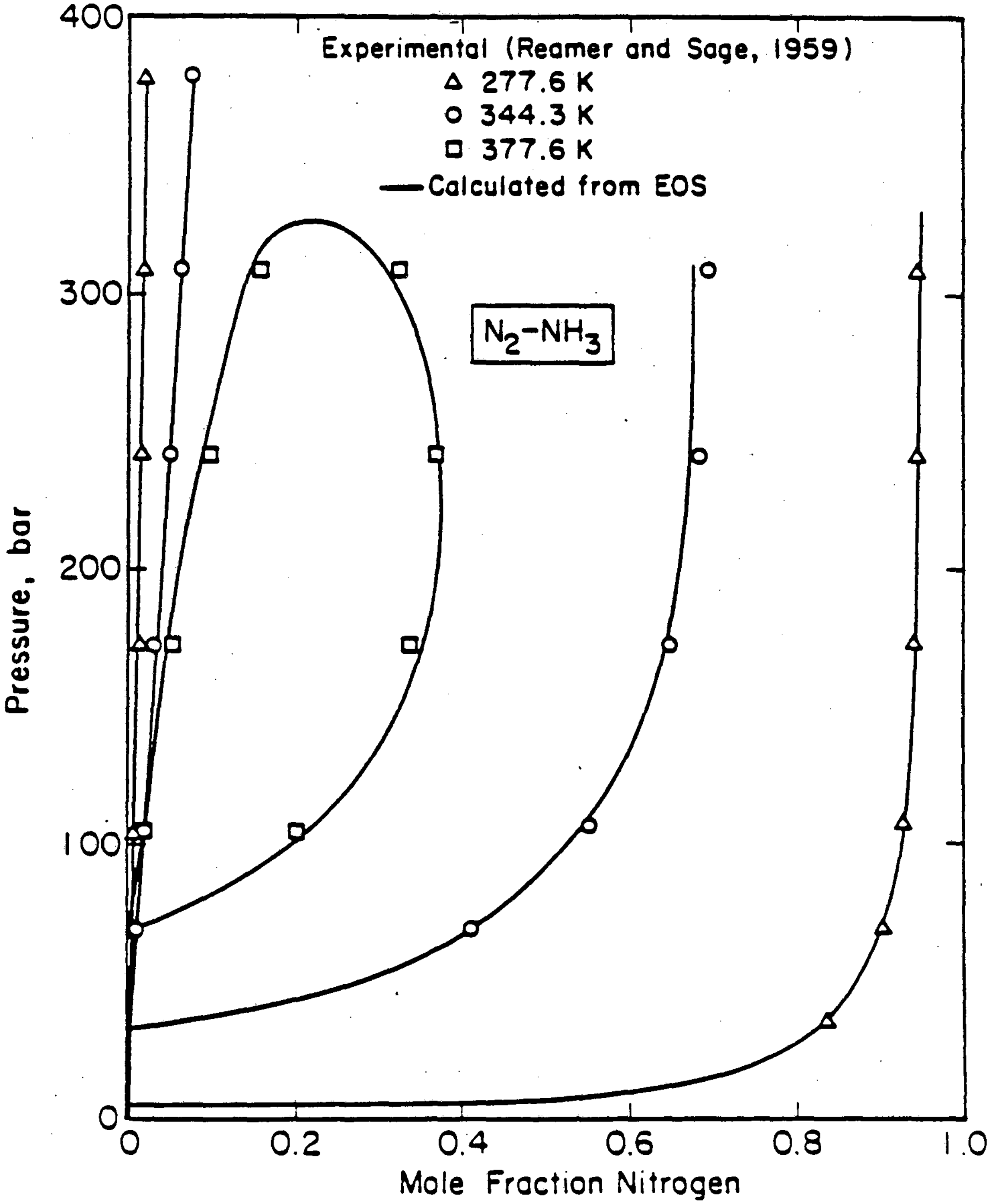

Figure 3. Vapor-liquid equilibria for the system nitrogen-ammonia. Binary parameters: k^B=0.21, k_{12}=0.0256.

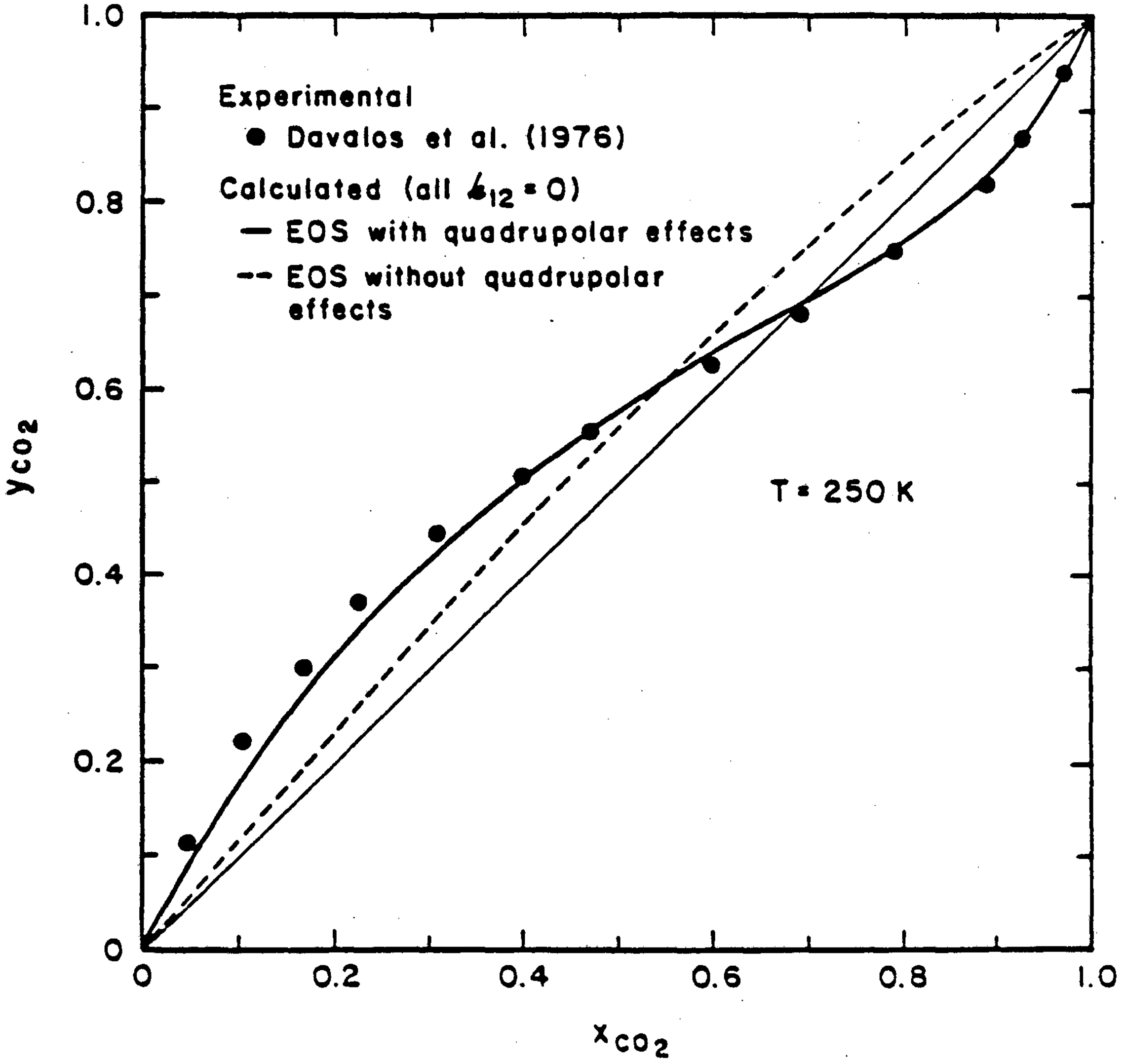

Figure 4. Comparison of equation-of-state results with and without quadrupolar effects for the system carbon dioxide-ethane. All binary parameters set to zero.

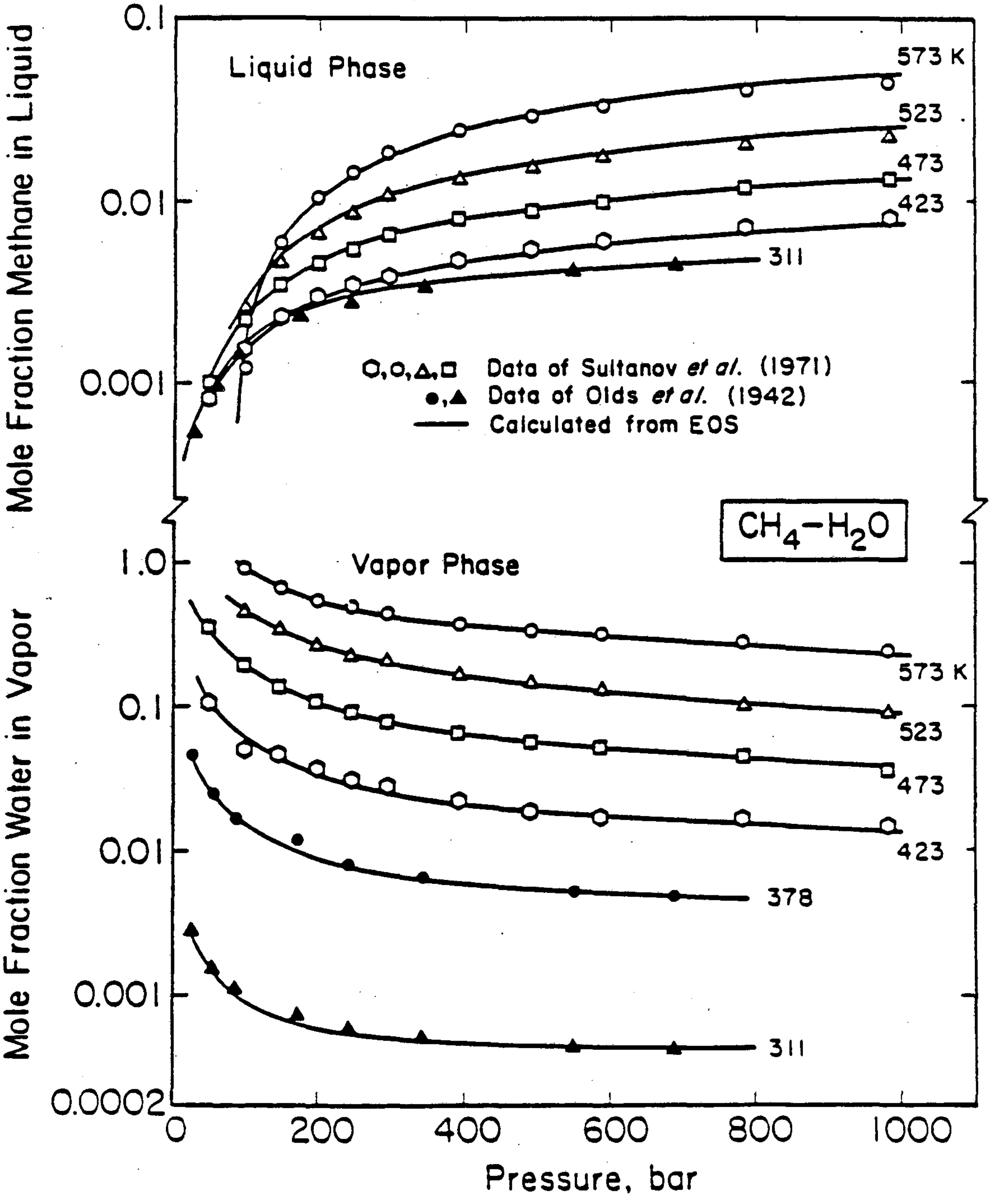

Figure 5. Vapor-liquid equilibria for the system methane-water. Liquid-phase isotherm at 378 K not shown for clarity. Binary parameters listed in Table 3.

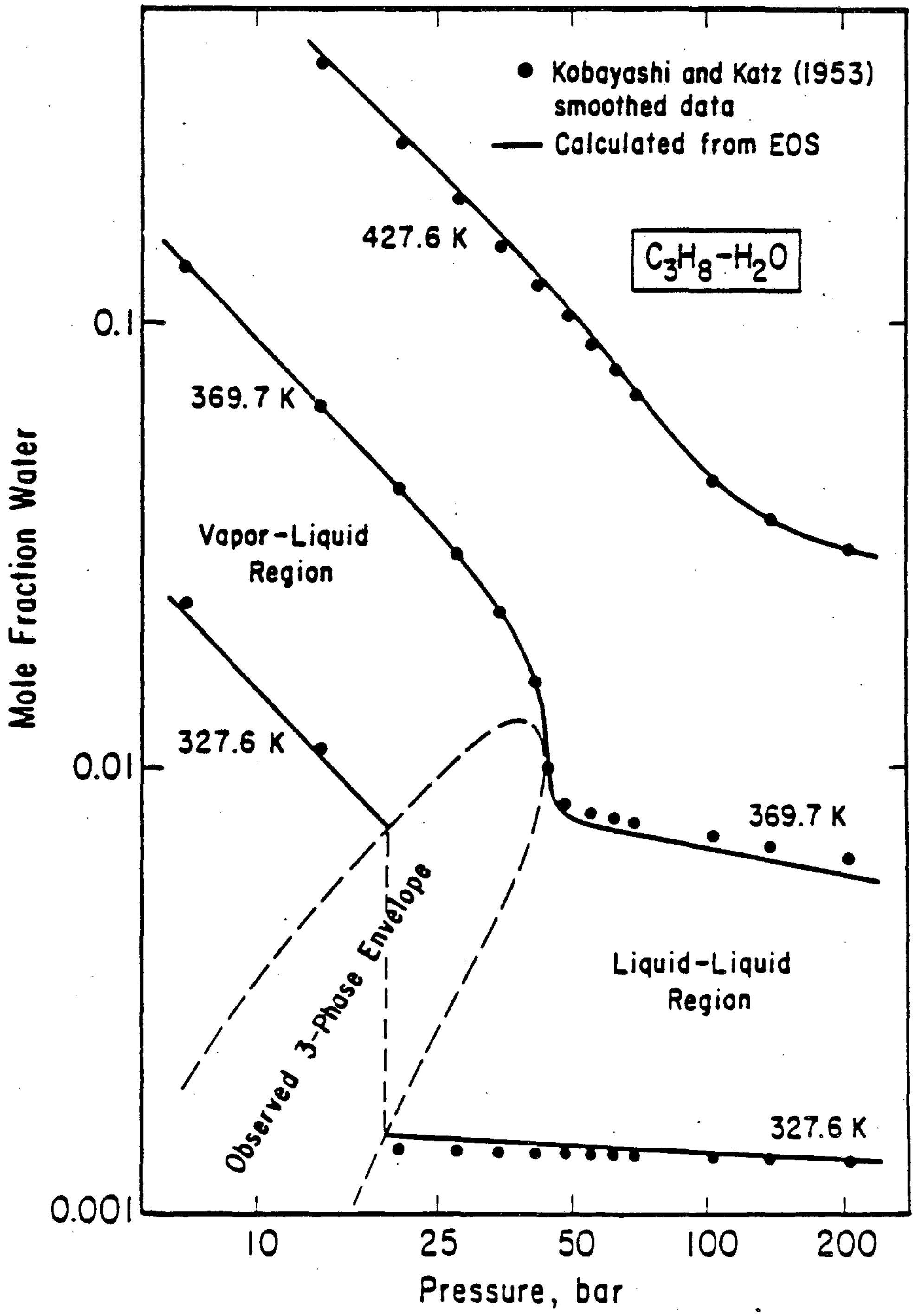

Figure 6. Phase equilibria for the system propane-water at three temperatures. Solubility of water in propane. Binary parameters listed in Table 3.

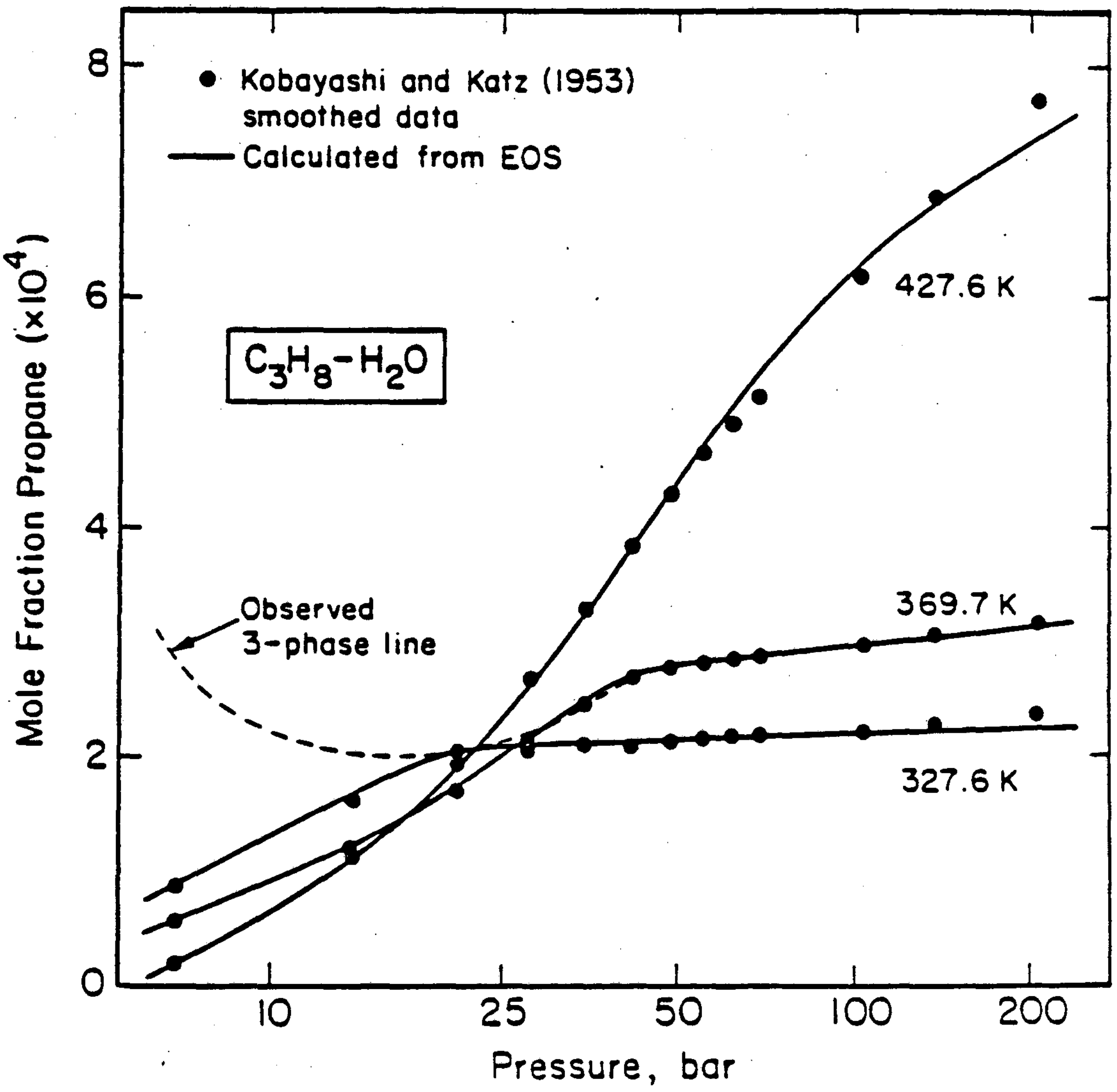

Figure 7. Phase equilibria for the system propane-water at three temperatures. Solubility of propane in water. Binary parameters listed in Table 3.

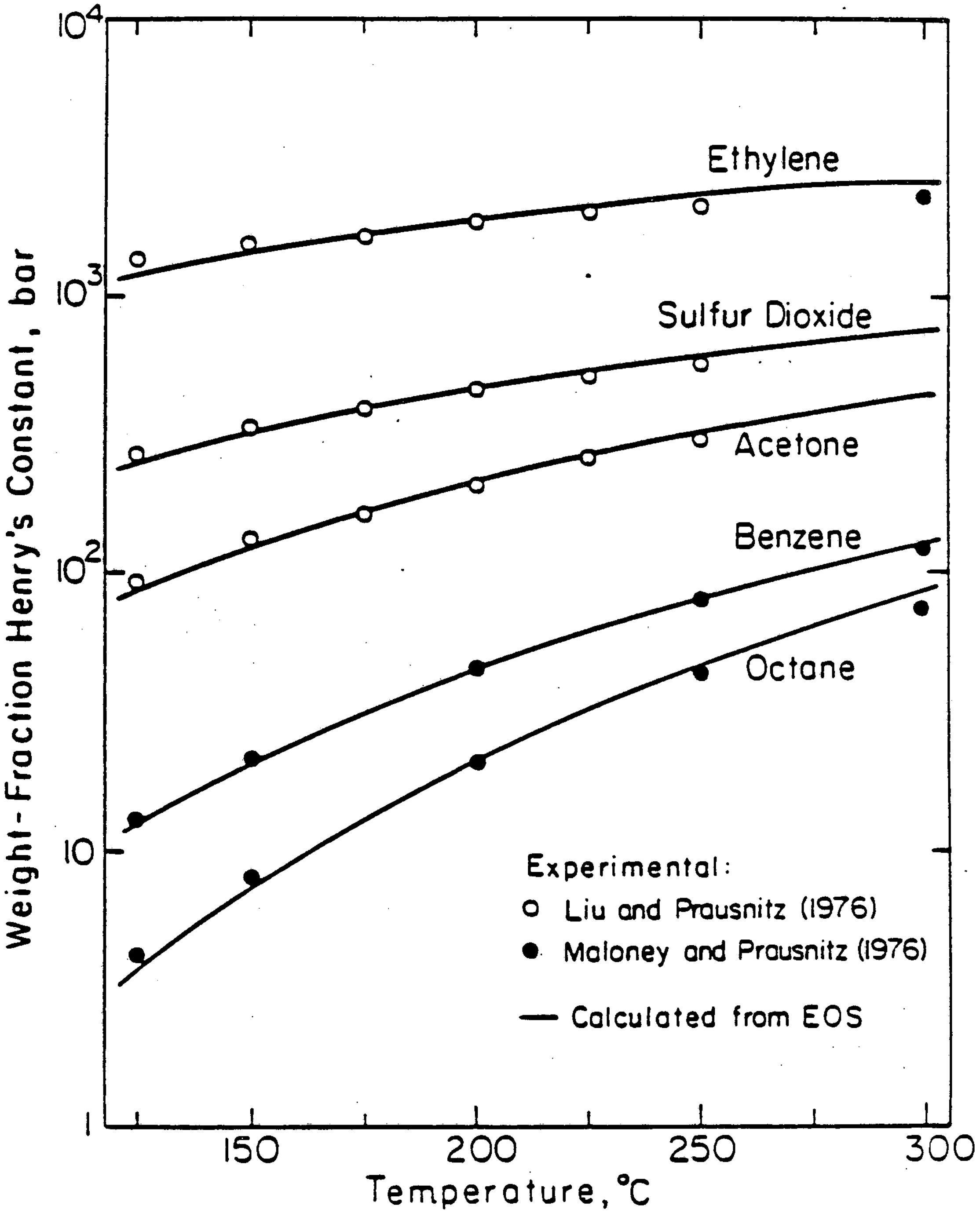

Figure 8. Weight-fraction Henry's constants for solutes in low-density polyethylene. Binary parameters listed in Table 4.

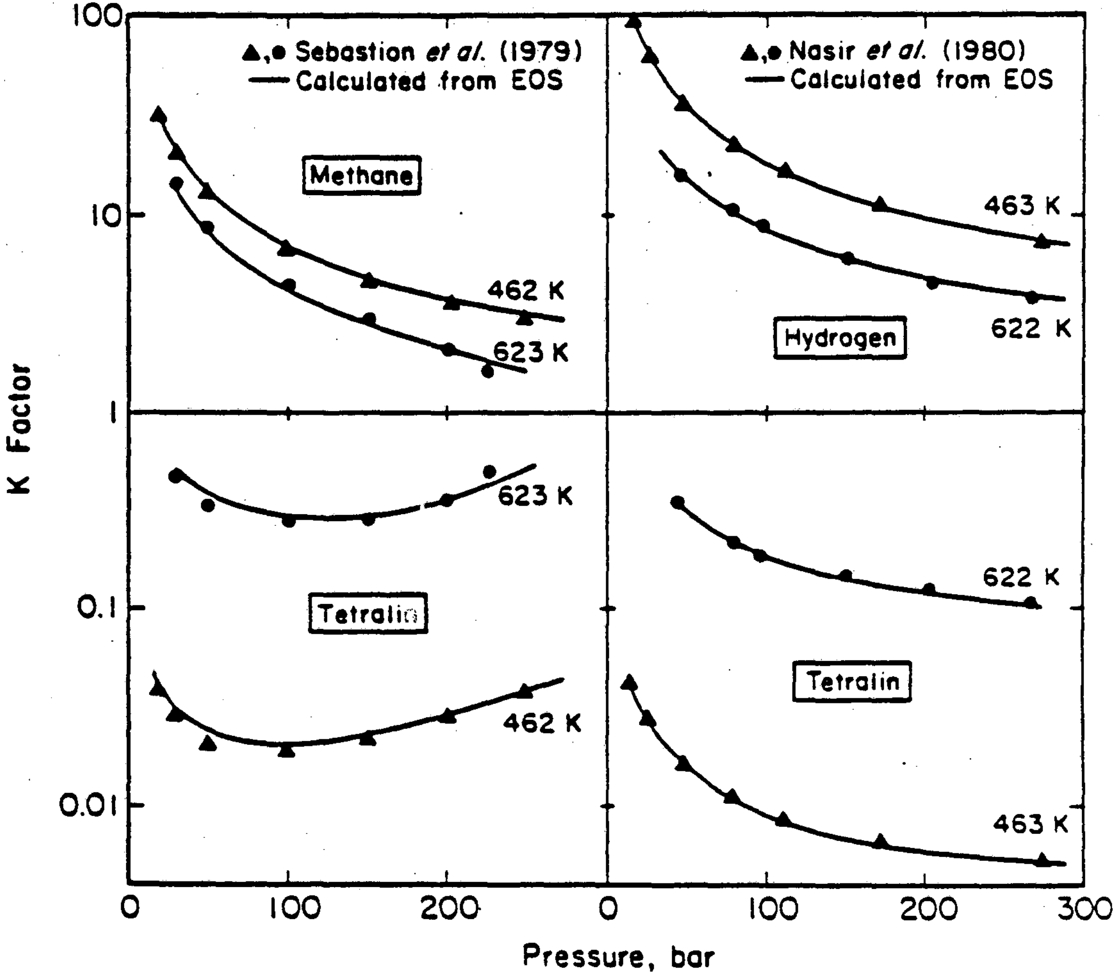

Figure 9. K factors for methane(1)-tetralin(3) and hydrogen(2)-tetralin(3). Binary parameters: all $k^B = 0$, $k_{13} = 0.0461$, $k_{23} = 0.0133$.

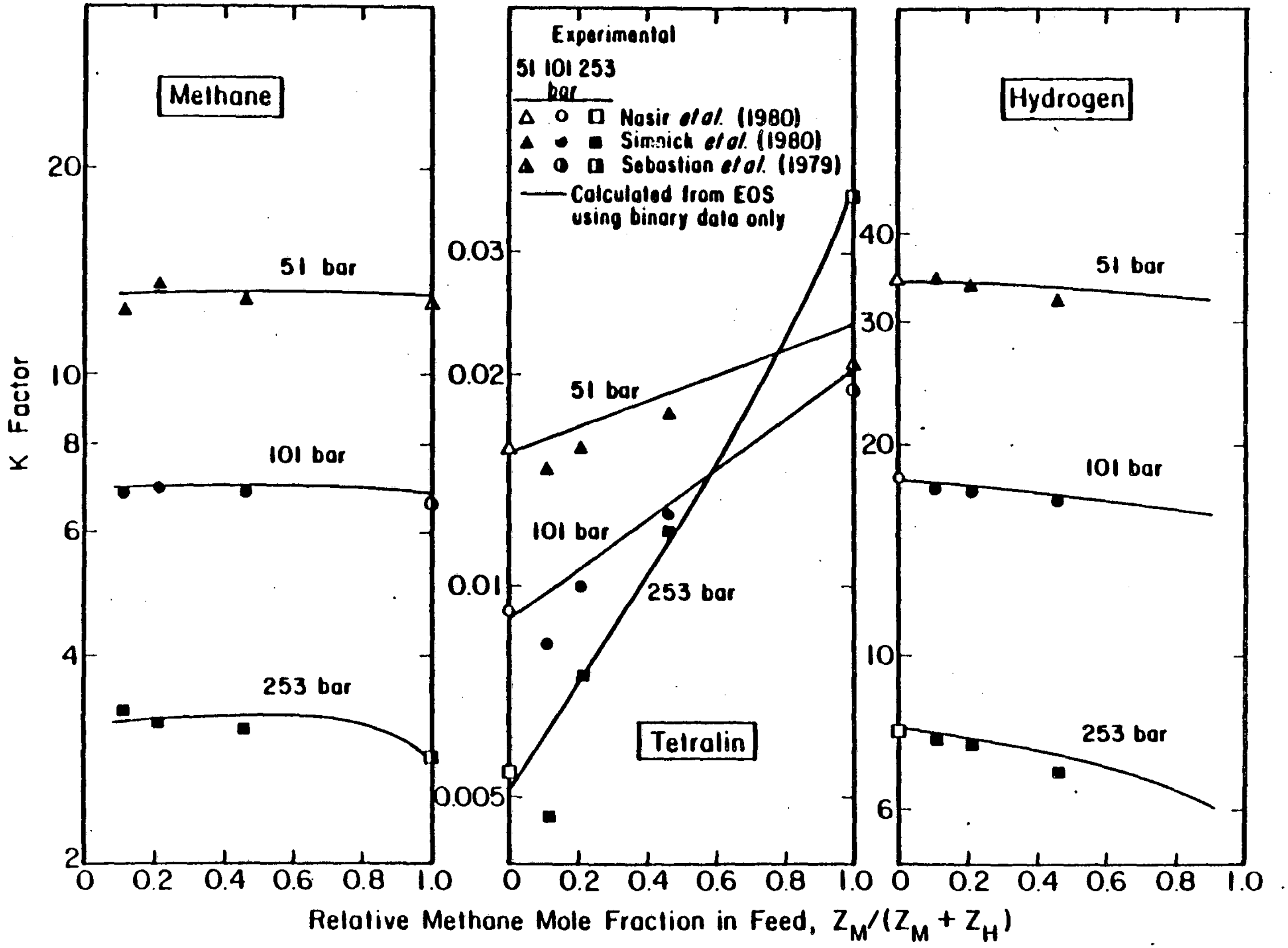

Figure 10. Equilibrium flash calculations for the system hydrogen(1)-methane(2)-tetralin(3) at 462 K.

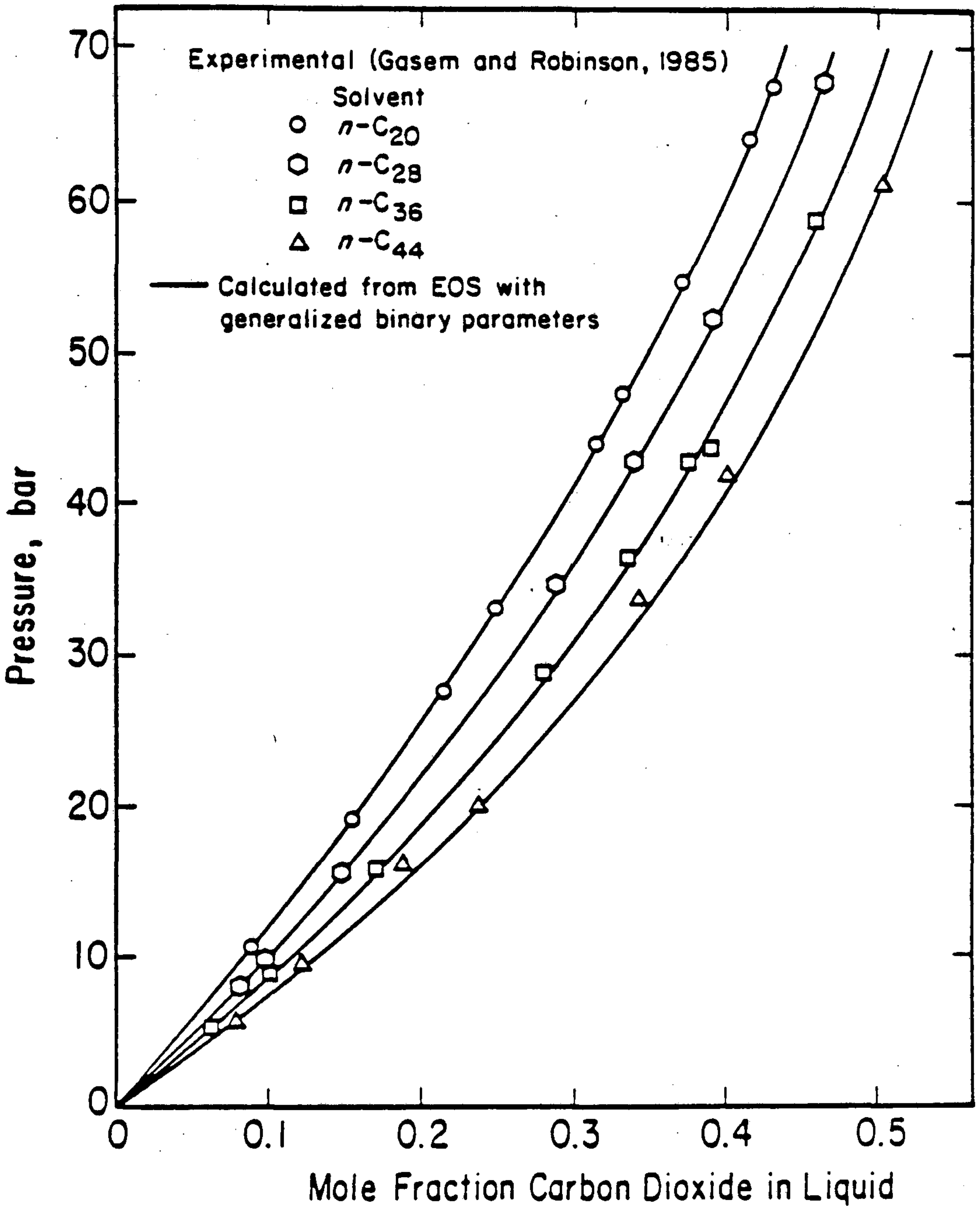

Figure 11. Solubility of carbon dioxide in high-boiling normal paraffins at 100°C. Similar results are obtained at 50 and 150°C. Calculated using binary parameters from Table 5.

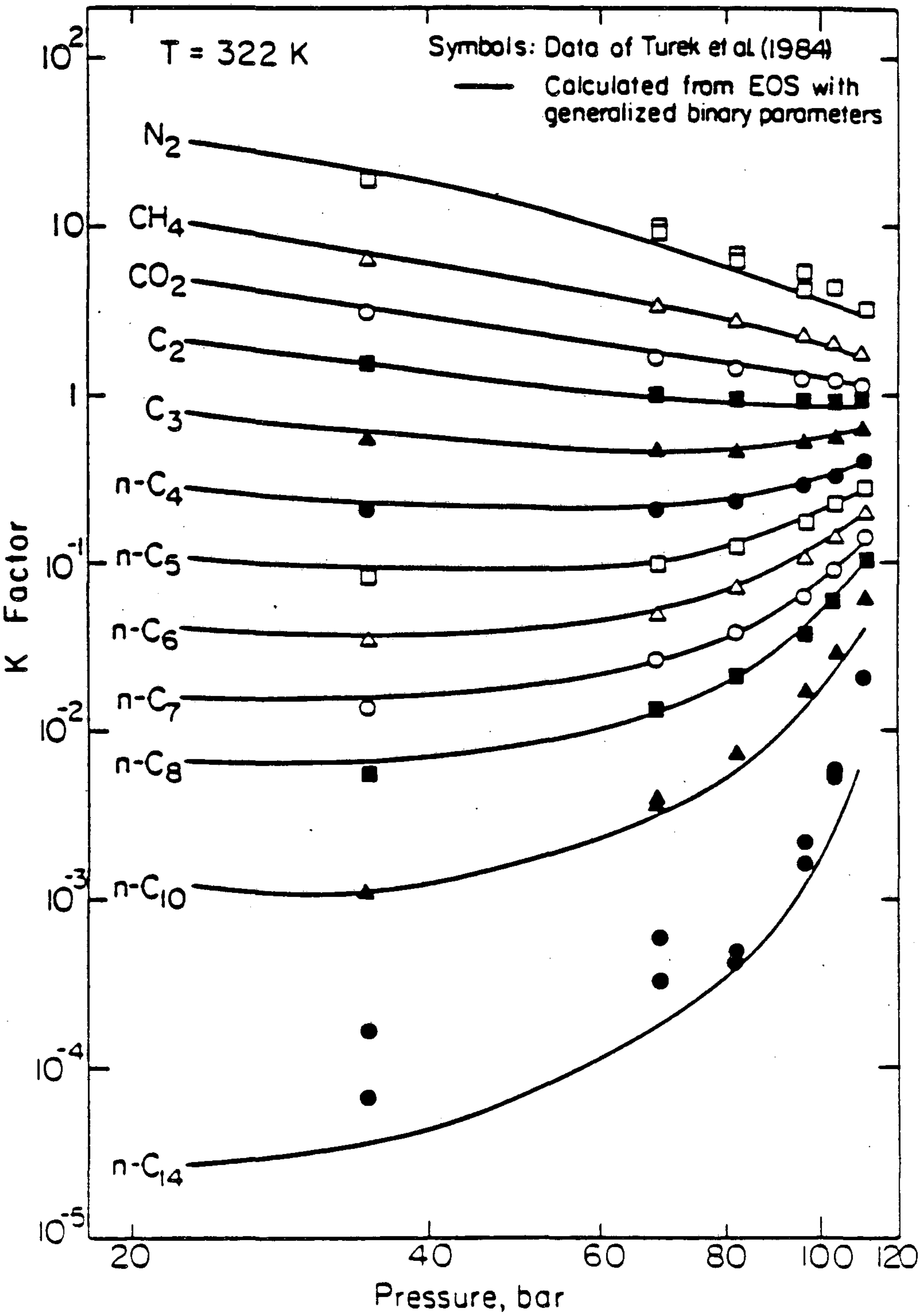

Figure 12. K factors for 12-component synthetic oil with 70 mole percent carbon dioxide. Calculated using binary parameters from Table 5.

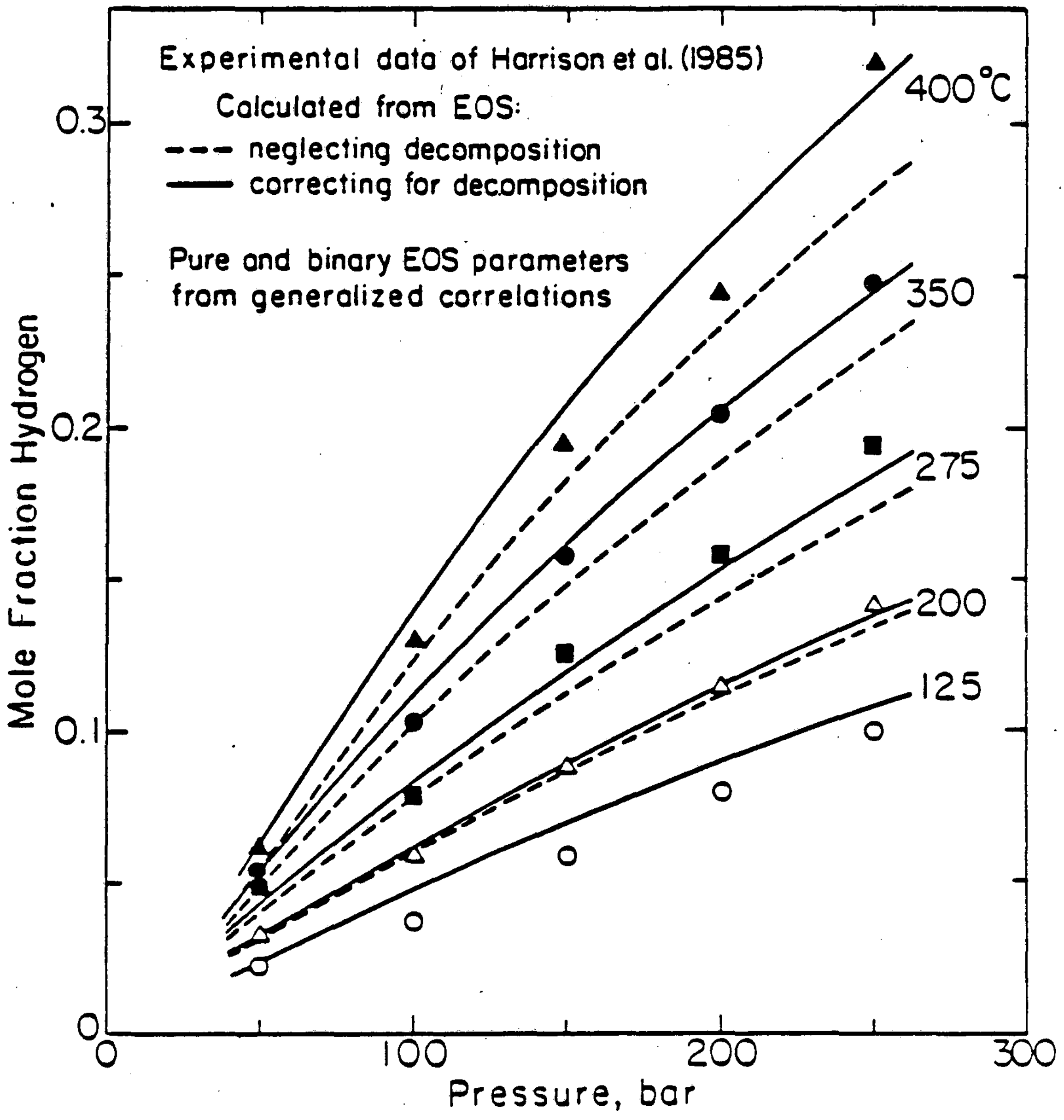

Figure 13. Solubility of hydrogen in a middle distillate from the Solvent-Refined-Coal II Process.

APPENDIX I

Modified Dense-Fluid Mixing Rules for Highly Asymmetric Mixtures

This appendix describes a modification of the generalized mixing rule given in Eq. 18 for the nonpolar perturbation terms $\mathbf{a}^{(1)}$ and $\mathbf{a}^{(2)}$. This modification is useful for representing phase behavior for mixtures containing components with very large differences in potential energy. Two adjustable binary parameters are introduced allowing flexibility to correlate separately the dilute region of each component in a binary mixture.

The two adjustable parameters $k_{1(2)}$ and $k_{2(1)}$ adjust the geometric mean assumption for ε_{ij} in the two Henry's constant limits (see Eq. 21). When the two parameters are equal to one another, the modified mixing rule reduces to Eq. 18.

The modified mixing rule is cubic in mole fraction

$$<cT^{*m}v^{\dagger}> = \sum_i \sum_j \sum_k x_i x_j x_k A_{ijk}^{(m)} \tag{I-1}$$

where $A^{(m)}$ represents a particular combination of molecular parameters. The order of the subscripts on $A^{(m)}$ is important for selecting the correct sequence of parameters.

For the two simplest cases, when $i=j=k$,

$$A_{iii}^{(m)} = c_i \left[\frac{\varepsilon_{ii} q_i}{c_i k} \right]^m \frac{r_i d_{ii}^3 N_{av}}{\sqrt{2}} \tag{I-2}$$

and when $i \neq j \neq k$,

$$A_{ijk}^{(m)} = \tfrac{1}{2} a_{ij}^{(m)} (1-\hat{k}_{ij}) + \tfrac{1}{2} a_{jk}^{(m)} (1-\hat{k}_{jk}) \tag{I-3}$$

where $\hat{k}_{ij}$ is an average of the two binary parameters

$$\hat{k}_{ij} = \tfrac{1}{2}(k_{i(j)} + k_{j(i)}) \tag{I-4}$$

and where $a_{ij}^{(m)}$ represents the parameter combination

$$a_{ij}^{(m)} = c_i \left[\frac{(\varepsilon_{ii} \varepsilon_{jj})^{1/2} q_i}{c_i k} \right]^m \frac{r_j d_{ij}^3 N_{av}}{\sqrt{2}} \tag{I-5}$$

The order of the subscripts in Eq. I-5 is important since $a_{ij}^{(m)} \neq a_{ji}^{(m)}$.

For the $A_{ijk}^{(m)}$ terms which have two identical subscripts, individual terms are defined such that only $k_{1(2)}$ contributes to $H_{1(2)}$ and only $k_{2(1)}$ contributes to $H_{2(1)}$. The following expressions are chosen to meet these conditions

$$A_{iij}^{(m)} = \tfrac{1}{2}[a_{ii}^{(m)} + a_{ij}^{(m)}(1-k_{j(i)})] \tag{I-6a}$$

$$A_{iji}^{(m)} = \tfrac{1}{2}[a_{ij}^{(m)} + a_{ji}^{(m)}](1-k_{j(i)}) \tag{I-6b}$$

$$A_{jii}^{(m)} = \tfrac{1}{2}[a_{ii}^{(m)} + a_{ji}^{(m)}(1-k_{j(i)})] \tag{I-6c}$$

where all a_{ij} are defined by Eq. I-5.

APPENDIX II

Expressions for Polar Contributions to Attractive Perturbation Terms in Mixtures

Appendix II of Part 1 gives expressions for multipolar contributions to low-density and high-density perturbation terms. This appendix extends those expressions to mixtures. The composition dependence of the low-density term is chosen to meet the boundary condition that the second virial coefficient is quadratic in mole fraction; the composition dependence of the high-density term follows from the forms suggested by Gubbins and Twu (1978). The high-density expressions presented here differ slightly from those presented earlier by Vimalchand and Donohue(1985).

Low-Density Contributions

Equation 9 gives the expression for the low-density perturbation term due to polar and nonpolar contributions; Eqs. 10-12 give cross parameters as needed for B_{ij}^{disp}. To calculate B_{ij}^{QQ} and $B_{ij}^{\mu\mu}$ from the expressions given in Appendix II of Part 1, cross parameters are needed for reduced dipole and quadrupole moments; these are

$$\tilde{\mu}_{ij}^{2} = \frac{\mu_i \mu_j}{c_{ij} T_{ij}^{*} v_{ij}^{*}} \left[\frac{N_{av}}{k\sqrt{2}}\right] \tag{II-1}$$

$$\tilde{Q}_{ij}^{2} = \frac{Q_i Q_j}{c_{ij} T_{ij}^{*} v_{ij}^{*5/3}} k \left[\frac{N_{av}}{\sqrt{2}}\right]^{5/3} \tag{II-2}$$

where the cross soft-core volume is defined

$$v_{ij}^{*} = \left[\frac{(v_i^{*})^{1/3} + (v_j^{*})^{1/3}}{2}\right]^{3} \tag{II-3}$$

The product cv^{*} is defined in a manner analogous to that for the nonpolar expression

$$(cv^{*})_{ij} = \tfrac{1}{2}(c_i v_j^{*} + c_j v_i^{*}) \tag{II-4}$$

These cross parameters are substituted directly into the expressions for pure fluids given in Part 1. No adjustable binary parameters are introduced.

High-Density Contributions

Expressions for the high-density polar contributions in pure fluids are extended to mixtures using forms given by Gubbins and Twu (1978). These forms are derived from two-body and three-body radial distribution functions. Hence, two-body mixing rules are quadratic mole-fraction averages over pure-component parameters and three-body mixing rules are cubic mole-fraction averages over pure-component parameters.

To simplify the mixture expressions, we define characteristic parameters for both two-body and three-body interactions. The two-body characteristic parameters are defined by

$$\hat{T}_{ij} = \frac{(\varepsilon_{ii}\varepsilon_{jj})^{1/2} q_i}{c_i k} \tag{II-5}$$

$$\hat{v}_{ij} = r_j \left[\frac{\sigma_i + \sigma_j}{2}\right]^3 N_{av}/\sqrt{2} \tag{II-6}$$

Two-body dipole and quadrupole moments are defined by

$$\hat{\mu}^2_{ij} = \frac{\mu_i \mu_j}{c_i \hat{T}_{ij} \hat{v}_{ij}} \left[\frac{N_{av}}{k\sqrt{2}}\right] \tag{II-7}$$

$$\hat{Q}^2_{ij} = \frac{Q_i Q_j}{c_i \hat{T}_{ij} \hat{v}_{ij}^{5/3}} k \left[\frac{N_{av}}{\sqrt{2}}\right]^{5/3} \tag{II-8}$$

$$(\hat{\mu}\hat{Q})_{ij} = \frac{\frac{1}{2}(\mu_i Q_j + \mu_j Q_i)}{c_i \hat{T}_{ij} \hat{v}_{ij}^{4/3}} k \left[\frac{N_{av}}{\sqrt{2}}\right]^{4/3} \tag{II-9}$$

These two-body expressions are used to defined characteristic parameters for three-body interactions:

$$\hat{T}_{ijk} = (\hat{T}_{ij}\hat{T}_{ki}\hat{T}_{jk})^{1/3} \tag{II-10}$$

$$\hat{v}_{ijk} = (\hat{v}_{ij}\hat{v}_{jk})^{1/2} \tag{II-11}$$

$$\hat{\mu}_{ijk} = (\hat{\mu}_{ij}\hat{\mu}_{ki}\hat{\mu}_{jk})^{1/3} \tag{II-12}$$

$$\hat{Q}_{ijk} = (\hat{Q}_{ij}\hat{Q}_{ki}\hat{Q}_{jk})^{1/3} \tag{II-13}$$

As discussed in Appendix II of Part 1, the perturbation expansions for contributions due to dipolar and quadrupolar intermolecular forces are replaced by Padé approximants. For a mixture, the expression for dipole-dipole interactions is

$$\mathbf{a}^{\mu\mu} = \mathbf{a}_{\mu\mu}^{(2)}\left[- \frac{\mathbf{a}_{\mu\mu}^{(3)}}{\mathbf{a}_{\mu\mu}^{(2)}}\right]^{-1} \tag{II-14}$$

where

$$\frac{\mathbf{a}_{\mu\mu}^{(2)}}{RT} = -\frac{2.9619}{T^2 v}\sum_i \sum_j x_i x_j c_i \hat{T}_{ij}^2 \hat{v}_{ij} \hat{\mu}_{ij}^4 J^{\mu\mu}\left(\frac{T}{\hat{T}_{ij}}, \frac{v}{\hat{v}_{ij}}\right) \tag{II-15}$$

$$\frac{\mathbf{a}_{\mu\mu}^{(3)}}{RT} = -\frac{43.596}{T^3 v^2}\sum_i \sum_j \sum_k x_i x_j x_k c_i \hat{T}_{ijk}^3 \hat{v}_{ijk}^2 \hat{\mu}_{ijk}^6 K^{\mu\mu\mu}\left(\frac{T}{\hat{T}_{ijk}}, \frac{v}{\hat{v}_{ijk}}\right) \tag{II-16}$$

where J and K are integrals of two-body and three-body radial distribution functions. Expressions for these integrals are given by Gubbins and Twu (1978) and are included in supplementary material for Part 1.

For a mixture, the expression for quadrupole-quadrupole interactions is

$$\mathbf{a}^{QQ} = \mathbf{a}_{QQ}^{(2)}\left[1 - \frac{\mathbf{a}_{QQ}^{(3)}}{\mathbf{a}_{QQ}^{(2)}}\right]^{-1} \tag{II-17}$$

where

$$\frac{\mathbf{a}_{QQ}^{(2)}}{RT} = -\frac{12.440}{T^2 v}\sum_i \sum_j x_i x_j c_i \hat{T}_{ij}^2 \hat{v}_{ij} \hat{Q}_{ij}^4 J^{QQ}\left(\frac{T}{\hat{T}_{ij}}, \frac{v}{\hat{v}_{ij}}\right) \tag{II-18}$$

$$\begin{aligned}\frac{\mathbf{a}_{QQ}^{(3)}}{RT} &= \frac{2.6113}{T^3 v}\sum_i \sum_j x_i x_j c_i \hat{T}_{ij}^3 \hat{v}_{ij} \hat{Q}_{ij}^6 J^{QQQ}\left(\frac{T}{\hat{T}_{ij}}, \frac{v}{\hat{v}_{ij}}\right) \\ &+ \frac{77.716}{T^3 v^2}\sum_i \sum_j \sum_k x_i x_j x_k c_i \hat{T}_{ijk}^3 \hat{v}_{ijk}^2 \hat{Q}_{ijk}^6 K^{QQQ}\left(\frac{T}{\hat{T}_{ijk}}, \frac{v}{\hat{v}_{ijk}}\right)\end{aligned} \tag{II-19}$$

Dipole-quadrupole contributions are expressed using only the second-order term

$$\frac{\mathbf{a}^{\mu Q}}{RT} = -\frac{8.8858}{T^2 v}\sum_i \sum_j x_i x_j c_i \hat{T}_{ij}^2 \hat{v}_{ij} (\hat{\mu}\hat{Q})_{ij}^2 J^{\mu Q}\left(\frac{T}{\hat{T}_{ij}}, \frac{v}{\hat{v}_{ij}}\right) \tag{II-20}$$

For use here, constants reported by Gubbins and Twu (1978) for the above integrals must be multiplied by $\sqrt{2}$ wherever reduced density appears; this follows since reduced density in this work is based on a close-packed molecular volume.

Supplementary Material

APPENDIX III

Correlation of Binary Parameters to Phase Equilibria for Binary Mixtures

This appendix presents binary interaction parameters correlated to phase equilibria for binary mixtures. Table III-1 presents binary parameters for several systems. Ranges of temperature and pressure are indicated; the quality of fit is given in percent average absolute deviations (%AAD) in independent and dependent variables as calculated using the maximum-likelihood method. Deviations are given for liquid-phase mole fraction ($\Delta x / x$), vapor-phase mole fraction ($\Delta y / y$) and pressure ($\Delta P / P$). Temperature deviations are not given since, in all cases, they are negligibly small.

For each of the binaries listed in Table III-1, virial parameters k^B are set to zero.

Table III-1. Regression results for correlation of binary parameters to phase-equilibrium data.

1^{st} Component	2^{nd} Component	k_{12}	Temperature Range, K	Pressure Range, bar	%AAD $\Delta x / x$	%AAD $\Delta P / P$	%AAD $\Delta y / y$	Data Source
methane	ethane	0.0123	144-283	7-55	2.37	0.24	1.87	(1)
	propane	0.0153	278-344	7-90	2.58	0.42	1.72	(2)
	butane	0.0202	144-258	2-97	4.99	0.61	0.27	(3)
	pentane	0.0290	311-444	1-155	1.63	0.35	2.03	(4)
	hexane	0.0314	183-423	10-101	4.55	0.56	3.02	(5)
	heptane	0.0328	278-511	14-138	2.47	0.41	1.84	(6)
	octane	0.0381	223-423	10-71	3.37	0.18	0.23	(7)
	decane	0.0436	348-423	10-101	2.49	0.19	0.14	(8)
	decane	0.0366	310-511	3-259	3.69	1.06	1.09	(9)
	hexadecane	0.0510	300-475	0	-	3.01	-	(10)
	eicosane	0.0506	325-475	0	-	2.18	-	(11)
	dotriacontane	0.0585	343	16-66	0.49	1.08	-	(12)
	benzene	0.0494	421-501	20-243	3.23	0.77	5.44	(13)
	toluene	0.0461	422-543	20-250	3.82	2.53	2.32	(13)
	propylbenzene	0.0226	314-473	19-379	1.44	4.98	1.41	(14)
	butylbenzene	0.0366	343-373	10-61	1.06	0.32	-	(15)
	cyclohexane	0.0353	311-444	14-207	1.34	1.62	0.70	(16)
	ethylcyclohexane	0.0010	311-478	4-207	1.88	1.92	0.31	(17)
	propylcyclohexane	0.0273	314-473	15-300	0.99	3.34	0.93	(14)
	tetralin	0.0461	462-665	20-251	3.20	0.33	2.24	(18)

Table III-1 (cont). Regression results for correlation of binary parameters to phase-equilibrium data.

1st Component	2nd Component	k_{12}	Temperature Range, K	Pressure Range, bar	%AAD $\Delta x/x$	%AAD $\Delta P/P$	%AAD $\Delta y/y$	Data Source
ethane	propane	0.0013	255-355	3-45	1.16	0.42	1.64	(19)
	butane	0.0068	235-397	7-48	1.05	0.19	0.65	(20)
	pentane	0.0160	278-444	3-55	4.03	0.56	1.33	(21)
	hexane	-0.0192	339-450	2-69	10.19	1.43	1.85	(22)
	heptane	0.0086	2[illegible]-426	7-83	2.10	0.50	0.69	(23)
	octane	0.0137	273-373	4-53	1.92	0.73	0.67	(24)
	decane	0.0114	278-478	3-103	3.79	0.77	0.51	(25)
	hexadecane	0.0112	300-475	0	-	3.24	-	(10)
	eicosane	0.0071	333	5-61	0.59	3.33	-	(26)
	benzene	0.0197	293-533	21-70	0.67	0.95	1.85	(27)
	toluene	0.0182	313-473	6-99	1.28	2.99	0.90	(28)
	propylbenzene	0.0233	313-473	5-130	1.59	3.26	0.82	(28)
	cyclohexane	0.0132	233-516	7-83	2.60	1.67	5.07	(29)
	methylcyclohexane	0.0078	313-473	6-91	0.63	3.88	0.93	(28)
	propylcyclohexane	0.0168	313-473	8-118	0.55	3.45	0.40	(30)
propane	butane	0.0047	353-403	21-34	0.31	0.34	1.71	(31)
	pentane	0.0131	344-444	4-38	0.49	1.08	1.40	(32)
	hexane	0.0027	353-473	17-41	0.36	1.86	1.12	(33)
	heptane	0.0044	353-513	21-48	1.83	1.88	4.13	(34)

Table III-1 (cont). Regression results for correlation of binary parameters to phase-equilibrium data.

1^{st} Component	2^{nd} Component	k_{12}	Temperature Range, K	Pressure Range, bar	%AAD $\Delta x / x$	%AAD $\Delta P / P$	%AAD $\Delta y / y$	Data Source
propane	octane	0.0038	371-531	7-54	0.15	2.49	-	(35)
	decane	0.0017	278-511	2-41	0.41	1.84	0.42	(36)
	hexadecane	0.0072	300-475	0	-	5.78	-	(11)
	benzene	0.0188	344-478	1-52	2.51	1.67	0.99	(37)
	propylbenzene	0.0150	313-473	3-70	0.47	1.48	1.04	(30)
	cyclohexane	0.0090	313-473	3-53	0.34	0.78	0.77	(30)
	propylcyclohexane	0.0070	313-473	4-70	0.39	1.85	0.67	(30)
nitrogen	methane	0.0287	140-180	7-47	1.89	0.44	2.65	(38)
	ethane	0.0162	200-290	7-132	5.28	0.90	5.39	(39)
	propane	0.0513	143-353	14-138	4.24	0.57	2.18	(40)
	butane	0.0637	311-412	16-235	7.66	0.80	4.74	(41)
	pentane	0.0539	277-378	8-208	5.03	0.71	1.50	(42)
	hexane	0.0890	311-444	17-276	6.48	0.84	1.14	(43)
	heptane	0.0548	305-400	70-277	9.15	0.96	0.66	(44)
	decane	0.0492	311-411	17-285	5.24	0.26	0.29	(45)
	hexadecane	0.1288	463-623	20-205	5.69	0.22	0.35	(46)
	benzene	0.0893	348-398	62-307	1.87	0.28	0.35	(47)
	toluene	0.1052	313-473	29-329	5.70	0.52	1.00	(48)
	propylcyclohexane	0.0905	314-473	20-300	3.46	0.34	0.30	(14)

Table III-1 (cont). Regression results for correlation of binary parameters to phase-equilibrium data.

1st Component	2nd Component	k_{12}	Temperature Range, K	Pressure Range, bar	%AAD $\Delta x/x$	%AAD $\Delta P/P$	%AAD $\Delta y/y$	Data Source
hydrogen sulfide	methane	0.0352	278-344	14-124	8.33	0.46	3.94	(49)
	ethane	0.0446	200-283	1-28	3.24	1.14	2.83	(50)
	propane	0.0583	219-344	1-28	3.98	1.39	3.62	(51)
	pentane	0.0453	278-444	1-69	3.77	0.72	3.30	(52)
	heptane	0.0535	311-478	1-81	7.15	1.25	1.86	(53)
	decane	0.0470	278-444	1-97	6.27	0.65	0.14	(54)
	toluene	-0.0059	311-478	2-116	9.83	0.60	1.04	(53)
	methylcyclohexane	0.0281	311-478	3-95	10.60	1.02	2.00	(55)
	ethylcyclohexane	0.0399	311-478	2-111	6.29	1.33	1.58	(56)
	propylcyclohexane	0.0221	311-478	2-116	4.11	0.69	0.69	(56)
carbon dioxide	methane	-0.0323	230-270	15-71	3.94	0.64	3.16	(57)
	ethane	0.0344	223-293	6-40	1.53	1.12	3.60	(58)
	propane	0.0414	278-344	7-55	3.08	0.48	0.98	(59)
	butane	0.0496	311-411	4-70	4.15	0.39	1.39	(60)
	pentane	0.0375	278-378	2-83	11.14	1.25	1.63	(61)
	hexane	0.0457	313-393	8-110	4.10	0.60	1.42	(62)
	heptane	0.0275	310-477	2-106	3.78	0.77	1.84	(63)
	decane	0.0419	278 511	7-103	5.82	0.75	0.76	(64)
	hexadecane	0.0600	463-664	20-51	9.04	0.38	1.75	(65)

Table III-1(cont). Regression results for correlation of binary parameters to phase-equilibrium data.

1st Component	2nd Component	k_{12}	Temperature Range, K	Pressure Range, bar	%AAD			Data Source
					$\Delta x/x$	$\Delta P/P$	$\Delta y/y$	
carbon dioxide	octadecane	0.0374	396-463	11-61	3.34	0.13	-	(66)
	octadecane	0.0374	535-673	10-62	6.36	0.28	0.53	(66)
	eicosane	0.0599	323-373	6-68	3.97	0.18	-	(67)
	octacosane	0.0563	348-423	8-96	3.24	0.17	-	(67)
	hexatriacontane	0.0602	373-423	5-59	2.67	0.09	-	(67)
	tetratetracontane	0.0628	373-423	6-61	3.00	0.12	-	(67)
	benzene	0.0231	313-393	6-133	3.51	0.54	0.25	(68)
	toluene	0.0349	311-477	3-153	4.36	0.66	0.46	(69)
	propylbenzene	0.0417	313-473	11-194	5.35	1.99	0.96	(14)
	butylbenzene	0.0394	273-293	10-51	10.57	1.24	-	(70)
	cyclohexane	0.0183	473-533	20-101	4.25	0.93	6.13	(71)
	methylcyclohexane	0.0204	311-477	4-136	7.00	1.79	3.20	(55)
	ethylcyclohexane	0.0331	311-478	2-156	7.69	1.44	1.28	(17)
	propylcyclohexane	0.0552	313-473	10-176	6.27	2.32	2.79	(14)

Table III-1 (cont). Regression results for correlation of binary parameters to phase-equilibrium data.

1^{st} Component	2^{nd} Component	k_{12}	Temperature Range, K	Pressure Range, bar	%AAD			Data Source
					$\Delta x / x$	$\Delta P / P$	$\Delta y / y$	
hydrogen	methane	0.1431	116-172	34-159	8.84	0.27	3.89	(72)
	ethane	0.1411	227-283	16-266	9.47	0.44	5.70	(73)
	propane	0.1198	223-348	14-207	4.75	0.42	3.27	(74)
	butane	0.0821	355-389	43-95	2.85	0.59	3.71	(75)
	hexane	0.0112	276-478	34-621	7.71	0.59	2.22	(76)
	heptane	0.0540	424-499	25-196	2.37	0.72	4.03	(77)
	decane	0.0626	462-583	19-255	3.69	0.33	1.34	(78)
	hexadecane	0.0562	462-664	20-254	6.97	0.45	0.51	(79)
	benzene	0.0436	339-433	5-689	3.15	0.11	0.25	(80)
	cyclohexane	-0.0005	339-394	7-690	2.92	0.15	0.09	(80)
	tetralin	0.0133	423-622	17-273	1.59	0.17	0.28	(81)
hexane	benzene	0.0156	277-294	0.05-0.17	0.014	0.062	-	(82)
hexane	cyclohexane	0,0033	274-299	0.04-0.16	0.02	1.02	-	(82)
benzene	cyclohexane	0.0171	276-295	0.04-0.15	0.01	0.62	-	(82)

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