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May 1995

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**Vapor-Liquid Equilibria for Solvent-Polymer Systems
from a Perturbed Hard-Sphere-Chain Equation of State**

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Vapor-Liquid Equilibria for Solvent-Polymer Systems from a Perturbed Hard-Sphere-Chain Equation of State

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Abstract

Vapor-liquid equilibria (VLE) for solvent-polymer mixtures at modest pressures are obtained from a perturbed hard-sphere-chain equation-of-state. This equation-of-state is the sum of a hard-sphere-chain term as the reference system and a van der Waals attractive term as the perturbation. The reference equation follows from the Percus-Yevick integral theory coupled with chain connectivity as described by Chiew. The effect of specific interactions, such as hydrogen bonding, is introduced through the proposal of Veytsman based on statistical distribution of hydrogen bonds between donor and acceptor sites suggested by molecular structure.

Calculated and observed vapor-liquid equilibria are presented for non-polar, polar and hydrogen-bonding solvent-homopolymer systems. Pure-component parameters (number of segments per molecule, segment-segment energy, and segment diameter) are obtained from pure-component properties: liquid density and vapor pressure data for normal fluids; and *pressure-volume-temperature* data for polymers. A binary energy interaction parameter must be obtained from limited VLE data for each binary system; this parameter appears to be independent of temperature and composition over a useful range. Theoretical correlations and predictions are in good agreement with experiment.

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Introduction

For process and product design, vapor-liquid equilibria (VLE) for solvent-polymer systems are necessary for a variety of applications including surface acoustic-wave vapor sensors (Ballantine and Wohltjen, 1989; Grate et al., 1992); recovery of organic vapors from waste-air streams using a polymeric membrane (Baker et al., 1987; Matsumoto et al., 1991); pervaporation (Maeda et al., 1991), and other polymeric membrane-separation processes; polymer devolatilization (High and Danner, 1990); vapor-phase photografting (Kubota et al., 1990); and for optimum formulation of paints and coatings (Napper, 1983). New experimental data and correlations are required for rational design.

Recently, we presented sixty-six isothermal data-sets for VLE in a variety of solvent-copolymer and solvent-homopolymer systems (Gupta and Prausnitz, 1995a). We observed an unusual effect in VLE for some copolymer+solvent systems where the solubility of an organic vapor in a copolymer was higher than that in either parent homopolymer (Gupta and Prausnitz, 1995b). This effect was attributed to "intramolecular repulsion" between unlike copolymer segments.

Polymer-solution phase behavior is more complex than that described by the incompressible-lattice Flory-Huggins theory, especially when the solvent is expanded or supercritical (i.e. at high temperatures). Hence, better theories are required to describe phase equilibria for compressible and highly non-ideal polymer solutions. For rational process and product design, we require correlations based on molecular thermodynamics. Previous efforts along these lines are reviewed by Danner and High (1993) and by Lambert et al. (1995).

Song et al. (1994a, 1994b, 1994c, 1995) have developed a perturbed hard-sphere-chain (PHSC) equation of state for calculating phase equilibria in solutions containing polymers, copolymers, and solvents. For binary polymer solutions, the PHSC theory can reproduce all types of observed liquid-liquid phase diagrams, including upper or lower critical solution temperatures (UCST or LCST), or both, including closed partial-miscibility loops (Song et al., 1994c). With some modifications (Hino and Prausnitz, 1995), the PHSC theory correlates experimental liquid-liquid equilibria of polymer-solvent and polymer-polymer systems, including spinodal and binodal curves and phase diagrams having a UCST, LCST, or both.

The PHSC equation of state is easily applied to represent vapor-liquid equilibria. In this work, we use the PHSC equation of state to correlate experimental data for vapor-liquid equilibria for polymers with solvents at modest pressures. Since the PHSC equation of state has parameters

that have clear physical significance, it provides a useful method for predicting thermodynamic properties outside the range of available data. We have correlated experimental data with the PHSC equation of state at one set of conditions and made predictions at other conditions; predictions were then compared with experimental data.

Perturbed Hard-Sphere-Chain (PHSC) Equation of State

In the PHSC theory, molecules are assumed to be attracting chains of spheres (segments) that are connected by covalent bonds (Song et al., 1994b). The total pressure, p , is given by

$$P = P_{\text{hard-sphere}} + P_{\text{chain-connectivity}} + P_{\text{vdW-attraction}} \quad (1)$$

where, $P_{\text{hard-sphere}}$ is due to hard-sphere repulsion; $P_{\text{chain-connectivity}}$ is due to covalent bonds between hard spheres; and $P_{\text{vdW-attraction}}$ is due to attractive van der Waal force between non-bonded hard-spheres.

The PHSC equation of state for pure fluids is (Song, 1994b)

$$\frac{P}{\rho k_B T} = 1 + r^2 b \rho g - (r-1)(g-1) - \frac{r^2 a \rho}{k_B T} \quad (2)$$

where $\rho = N/V$ is the number density (N is the number of molecules and V the volume), k_B is the Boltzmann constant, T is the absolute temperature, and g is the radial distribution function of hard spheres at contact; the best analytical expression for g is that from the Carnahan-Starling equation,

$$g = \frac{1 - \eta/2}{(1 - \eta)^3} \quad (3)$$

where reduced density η is

$$\eta = \frac{r b \rho}{4} \quad (4)$$

In Equation (2), the term $[1 + r^2 b \rho g - (r-1)(g-1)]$ represents the reference equation of state for hard-sphere chains and the last term is a van der Waals perturbation to take into account attractive forces. The three segment-based parameters in Equation (2), r , b , and a , all have a clear physical interpretation. The first parameter, r , represents the number of effective spheres per molecule. The second parameter, b , represents the second virial coefficient of hard spheres; it is an effective van

der Waals covolume. The third parameter, a , reflects the strength of the attractive forces between two non-bonded segments. In the PHSC theory, both b and a are temperature-dependent as given by the Song-Mason (1989) method

$$b(T) = \frac{2\pi}{3} d^3(T) = \frac{2\pi}{3} \sigma^3 F_b(k_B T/\epsilon) \quad (5)$$

$$a(T) = \frac{2\pi}{3} \sigma^3 \epsilon F_a(k_B T/\epsilon) \quad (6)$$

where ϵ and σ are pair-potential parameters; ϵ is the depth of the minimum in the pair potential and σ is the separation distance between segment centers at this minimum and d is the effective hard-sphere diameter. In Equations 5 and 6, $F_a(k_B T/\epsilon)$ and $F_b(k_B T/\epsilon)$ are two universal functions of the reduced temperature, $k_B T/\epsilon$. These are determined from experimental thermodynamic properties of argon and methane over the entire fluid ranges; they are represented by the relations

$$F_a(k_B T/\epsilon) = 1.8681 \exp[-0.0619(k_B T/\epsilon)] + 0.6715 \exp[-1.7317(k_B T/\epsilon)^{3/2}] \quad (7)$$

$$F_b(k_B T/\epsilon) = 0.7303 \exp[-0.1649(k_B T/\epsilon)^{1/2}] + 0.2697 \exp[-2.3973(k_B T/\epsilon)^{3/2}] \quad (8)$$

Derivation of the PHSC equation of state is readily extended to mixtures (Song et al., 1994a)

$$\frac{p}{\rho k_B T} = 1 + \rho \sum_{ij} x_i x_j r_i r_j b_{ij} g_{ij} - \sum_i x_i (r_i - 1) (g_{ii} - 1) - \frac{\rho}{k_B T} \sum_{ij} x_i x_j r_i r_j a_{ij} \quad (9)$$

where $x_i = N_i/N$ is the number fraction of molecules, r_i is the number of segments (tangent hard spheres) comprising component $i = 1, 2, \dots, m$, and g_{ij} is the ij pair radial distribution function of hard-sphere mixtures at contact. In Equation (9) no arbitrary mixing rules are required for $p_{\text{hard-sphere}}$ and $p_{\text{chain-connectivity}}$. However, a one-fluid theory of mixtures is assumed for calculating $p_{\text{vdW-attraction}}$.

For each unlike pair of components ($i \neq j$), additional parameters, b_{ij} and a_{ij} , are needed for the mixture; b_{ij} is the second cross virial coefficient of hard-sphere mixtures and a_{ij} is the parameter reflecting attractive forces between two unlike non-bonded segments. Parameters b_{ij} and a_{ij} can be obtained by extending Equations 5 and 6 to mixtures:

$$b_{ij}(T) = \frac{2\pi}{3} d_{ij}^3(T) = \frac{2\pi}{3} \sigma_{ij}^3 F_b(k_B T/\epsilon_{ij}) \quad (10)$$

$$a_{ij}(T) = \frac{2\pi}{3} \sigma_{ij}^3 \epsilon_{ij} F_a(k_B T / \epsilon_{ij}) \quad (11)$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)(1 - \lambda_{ij}) \quad (12)$$

$$\epsilon_{ij} = (\epsilon_{ii} \epsilon_{jj})^{1/2} (1 - \kappa_{ij}) \quad (13)$$

where λ_{ij} and κ_{ij} are two adjustable binary parameters. Finally, g_{ij} is given by

$$g_{ij} = \frac{1}{1-\eta} + \frac{3}{2} \frac{\xi_{ij}}{(1-\eta)^2} + \frac{1}{2} \frac{\xi_{ij}^2}{(1-\eta)^3} \quad (14)$$

where

$$\eta = \frac{\rho}{4} \sum_i^m x_i r_i b_i \quad (15)$$

and

$$\xi_{ij} = \frac{\rho}{4} (b_i b_j / b_{ij})^{1/3} \sum_i^m x_k r_k b_k^{2/3} \quad (16)$$

In summary, each pure solvent or homopolymer is characterized by three molecular constants: r , segment number per molecule; σ , segment size; and ϵ , non-bonded segment pair interaction energy. These molecular constants are obtained from readily available pure-component data for thermodynamic properties such as vapor pressures, densities, and compressibilities (Song et al., 1994b). Pure-component parameters for 77 solvents and for 22 polymers have been collected by Song et al. (1995); these parameters were used here. For each unlike pair of segments, usually one and only rarely two binary parameters, (κ and λ) are needed for the mixture; these can be determined from limited experimental mixture properties.

Comparison with Experimental Data

The PHSC equation of state was applied to some of our data (Gupta and Prausnitz, 1995a) and to some data from literature. Pure-component molecular parameters were obtained from pure-component properties (Song et al. 1995). Binary interaction parameters (κ_{12} or λ_{12}) were regressed from experimental data at the highest available temperature because these data were of

highest accuracy; these binary parameters were then used to predict VLE at other conditions. In all the non-hydrogen-bonding cases, we found that $\kappa_{12}=0$ was sufficient to represent VLE. Isothermal results are presented as pressure versus weight fraction solvent in the polymer phase.

Benzene+polystyrene is a relatively simple system because polymer and solvent segments are similar in nature and there is no polar interaction. Figure 1 shows calculated and observed VLE. A single parameter ($\lambda_{12} = -0.024$) was determined from data at 60 °C; predictions were made at 45, 30, and 15 °C. For all four isotherms calculated VLE are in good agreement with experiment.

Figure 2 shows the effect of polymer molecular weight on VLE for pentane+polyisobutylene. It is well known that at higher polymer molecular weights (above 10,000), molecular weight does not have any significant influence on VLE (see for example Kun et al., 1993; Bonner and Prausnitz, 1974). However, at lower molecular weights, polymer molecular weight has some influence on VLE. At a given pressure, the solubility of pentane in low-molecular weight (1350) polyisobutylene is higher than that in high-molecular weight (2700) polymer (Figure 2). At fixed composition, an increase in polymer molecular weight causes a decrease in the entropy of mixing, resulting in lower miscibility.

In Figure 2, one binary parameter ($\lambda_{12} = -0.061$) was determined from VLE data for the higher-molecular-weight polymer; equilibria were then predicted for the system with lower-molecular-weight polymer.

VLE for benzene+poly(ethylene oxide) are shown in Figure 3. One binary parameter ($\lambda_{12} = -0.026$) was obtained from the data at 70 °C; VLE were predicted for 45.8 °C. It is gratifying that the PHSC theory correctly predicts that the VLE line at 45.8 °C isotherm has a different curvature than that at 70 °C.

Figure 4 shows VLE for chloroform+polystyrene. Here, pressure versus weight fraction solvent shows more curvature than that in Figure 1. This curvature is due to higher polarity of chloroform as compared to benzene. Here, one parameter ($\lambda_{12} = -0.0234$) was determined using 50 °C data; VLE were predicted at 25 °C. At both temperatures, the PHSC theory is in good agreement with experiment.

Figure 5 shows VLE in another polar system, chloroform+polybutadiene. One binary parameter ($\lambda_{12} = -0.016$) was regressed from the 25 °C data; predicted VLE at 0 °C agree well with experiment.

As suggested by Figures 1-5, one binary parameter appears to be sufficient to represent VLE over a range of composition, temperatures, and molecular weight. For these systems, when represented by the Flory-Huggins theory, Flory binary parameter (χ) depends upon composition, temperature and polymer molecular weight (Danner and High, 1993).

However, the equations discussed above are not applicable when there is hydrogen bonding between components. We have extended the PHSC equation of state to such systems.

Systems with Specific Interactions (Hydrogen Bonding)

The system chloroform+poly(vinyl acetate) exhibits hydrogen bonding; each chloroform molecule has one proton donor site and each vinyl acetate segment of the polymer has two proton acceptor sites. For this system, Figure 6 shows results using the PHSC equation of state. Two binary parameters ($\kappa_{12} = -0.043$; $\lambda_{12} = 0.0112$) are needed to fit data at 60 °C. Correlation at 60 °C is in good agreement with experimental data; however, prediction at 45 °C does not match the data well, giving an error of 5 to 10%.

The PHSC equation of state (Equation 1) does not account for strong attractive forces due to hydrogen bonding. The PHSC theory accounts only for weak attraction due to van der Waals forces as a perturbation to the dominating repulsive forces. To account for hydrogen-bonding interaction, Equation 1 was modified to

$$P = P_{\text{hard-sphere}} + P_{\text{chain-connectivity}} + P_{\text{vdW-attraction}} + P_{\text{hb}} \quad (17)$$

where p_{hb} is due to attractive hydrogen bonding interaction, which can be calculated from the volume derivative of the Helmholtz free energy due to hydrogen bonding (A_{hb})

$$P_{\text{hb}} = - \left(\frac{\partial A_{\text{hb}}}{\partial V} \right)_{N_{\text{a}}, T} \quad (18)$$

The hydrogen-bonding Helmholtz energy is found from a proposal of Veytsman (Veytsman, 1990; Panayiotou and Sanchez, 1991; Gupta et al., 1992) and further improvement by Gupta and Johnston (1994) using local-segment density. The derivation was based on the combinatorial expression for distributing hydrogen bonds between given donor and acceptor sites. The equation for A_{hb} (Gupta and Johnston, 1994) is

$$\frac{A_{hb}}{RT} = \sum_k \sum_l N_{kl} \left[1 + \frac{F_{kl}^0}{RT} + \ln \frac{N_{kl} r N}{N_{k0} N_{0l}} - \ln(g_{ij} \eta) \right] + \sum_k N_d^k \ln \frac{N_{k0}}{N_d^k} + \sum_l N_a^l \ln \frac{N_{0l}}{N_a^l} \quad (19)$$

where N_{kl} is the number of kl hydrogen bonds; and F_{kl}^0 , is the standard Helmholtz energy of hydrogen bonding given by

$$F_{kl}^0 = E_{kl}^0 - T \cdot S_{kl}^0 \quad (20)$$

where E_{kl}^0 and S_{kl}^0 are standard energy and entropy-of-hydrogen-bonding parameters, respectively. N_{k0} , is the number of unbonded donor sites and N_{0l} is the number of unbonded acceptor sites given by

$$N_{k0} = N_d^k - \sum_{l=1}^m N_{kl} \quad (21)$$

$$N_{0l} = N_a^l - \sum_{k=1}^n N_{kl} \quad (22)$$

where N_d^k is the total number of k donor sites, and N_a^l is the total number of l acceptor sites in the system.

The number of hydrogen bonds N_{kl} between donor group k and acceptor group l is determined by minimizing the Gibbs energy with respect to all kl hydrogen bonds

$$\frac{N_{kl} r N}{N_{k0} N_{0l}} = \eta \cdot g_{ij} \cdot \exp\left(\frac{-G_{kl}^0}{RT}\right) \quad (23)$$

where

$$G_{kl}^0 = E_{kl}^0 - T \cdot S_{kl}^0 + P \cdot V_{kl}^0 \quad (24)$$

and V_{kl}^0 is a hydrogen-bonding-volume parameter. At modest pressures, the contribution from PV_{kl}^0 is negligible.

In summary, each type of hydrogen bond requires two parameters, E_{kl}^0 and S_{kl}^0 . These are obtained by fitting the extended PHSC model to experimental data.

Comparison with Experimental Data for Hydrogen-Bonding Systems

The extended PHSC equation of state (Equation 17) was applied to VLE for chloroform+poly(vinyl acetate) shown in Figure 7. Two hydrogen-bonding parameters ($E_{12}^0/R = -1705$ K; and $S_{12}^0/R = -4.64$) were obtained from data at 60 °C; these were used to predict VLE at 45 °C. At both temperatures calculated results are in excellent agreement with experiment. Using two binary parameters in both cases, results shown in Figure 7 are much better than shown in Figure 6.

Results similar to those in Figure 7 are shown in Figure 8 for VLE in the hydrogen-bonding system chloroform+poly(ethylene oxide). VLE in this system is shown in Figure 8. Two hydrogen bonding parameters ($E_{12}^0/R = -1303$ K; $S_{12}^0/R = -2.78$) were regressed from data at 60 °C. Predicted VLE at 5.53 °C compares very well with experiment. Extended PHSC equation of state provides good prediction even though the molecular weight at 60 °C (5×10^6) is much larger than that at 5.53 °C (308).

The hydrogen-bonding-energy (E_{12}^0) and entropy (S_{12}^0) parameters obtained in Figure 7 and 8 are of the same order as those reported for hydrogen bonding by Pimentel and McClellan (1960).

Conclusions

The perturbed hard-sphere-chain (PHSC) equation of state can represent vapor-liquid equilibria of homopolymer solutions. Correlations and predictions are in good agreement with the experimental data. It appears that, as suggested by theory, binary parameter λ_{12} is independent over useful ranges of concentration, temperature, and polymer molecular weight. For many binary systems $\kappa_{12} = 0$.

Using Veytsman's method, contributions from hydrogen bonding are incorporated into an extended PHSC theory with good results for poly(ethylene oxide) and poly(vinyl acetate) with chloroform.

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References

- Baker, R. W.; Yoshioka, N.; Mohr, J. M.; Kahn, A. J. Separation of Organic Vapors from Air. *J. Membr. Sci.* **1987**, *31*, 259.
- Ballantine, D. S., Jr.; Wohltjen, H. Surface Acoustic Wave Device for Chemical Analysis. *Anal. Chem.* **1989**, *61*, 704A-715A.
- Bawn, C. E. H.; Wajid, M. A. High Polymer Solutions. Part 7. Vapour Pressure of Polystyrene Solutions in Acetone, Chloroform and Propyl Acetate. *Trans. Faraday Soc.* **1956**, *52*, 1658.
- Bonner, D. C.; and Prausnitz, J. M. Thermodynamic Properties of Some Concentrated Polymer Solutions. *J. Polym. Sci.* **1974**, *21*, 51-73.
- Booth, C.; Devoy, C. J. Thermodynamics of Mixtures of Poly(ethylene oxide) and Benzene. *Polymer* **1971**, *12*, 309.
- Booth, C.; Gee, G.; Jones, M. N.; Taylor, W. D. Studies in the Thermodynamics of Polymer-Liquid Systems Part II. A Reassessment of Published Data. *Polymer* **1964**, *5*, 353.
- Danner, R. P.; High, M. S. Handbook of Polymer Solution Thermodynamics, DIPPR, AIChE, New York, 1993.
- Gupta, R. B.; Johnston, K. P. Hydrogen Bonding Lattice Fluid Model with a Local Segment Density. *Fluid Phase Equilibria* **1994**, *99*, 135-151.
- Gupta, R. B.; Panayiotou, C. G.; Sanchez, I. C.; Johnston, K. P., Theory of Hydrogen Bonding in Supercritical fluids. *AIChE J.* **1992**, *38*, 1243.
- Gupta, R. B.; Prausnitz, J. M. Vapor-Liquid Equilibria of Copolymer+Solvent and Homopolymer+Solvent Binaries: New Experimental Data and Their Correlation. in press *J. Chem. Eng. Data* **1995a**.
- Gupta, R. B.; Prausnitz, J. M. Vapor-Liquid Equilibria of Copolymer+Solvent Systems: Effect of "Intramolecular Repulsion." submitted to *Fluid Phase Equilibria* **1995b**.

- Grate, J. W.; Klusty, M.; McGill, R. A.; Abraham, M. H.; Whiting, G.; Andonian-Haftvan, J. The Predominant Role of Swelling-induced Modulus Changes of the Sorbent Phase in Determining the Responses of Polymer-Coated Surface Acoustic Wave Vapor Sensor. *Anal. Chem.* **1992**, *64*, 610-624.
- High, M. S.; Danner, R. P., Prediction of Solvent Activities in Polymer Solutions. *Fluid Phase Equil.* **1990**, *55*, 1-15.
- Hino, T.; Song, Y.; Prausnitz, J. M. Liquid-liquid Equilibria and Theta Temperatures in Homopolymer-Solvent Solutions from a Perturbed Hard-Sphere-Chain Equation of State. submitted to *J. Polym. Sci. Polym. Phys. Ed.*, **1995**.
- Kubota, H.; Yoshino, N.; Ogiwara, Y. Vapor Phase Photografting on Low-Density Film In Binary Monomer System. *J. Appl. Polym. Sci.* **1990**, *39*, 1231.
- Kun, W.; Yifeng, C.; Jinyan, F.; Hu, Y. Vapor-Liquid Equilibria for Mixtures of Toluene and Polystyrene with Different Molecular Weights. *Chinese J. of Chem. Eng.* **1993**, *1*, 65-73.
- Lambert S. M.; Song, Y.; Prausnitz, J.M. Equation of State for Polymer Systems. in Sengers, ed., in press **1995**.
- Maeda, Y.; Tsuyumoto, M.; Karakane, H.; Tsugaya, H. Separation of Water-Ethanol Mixture by Pervaporation Through Hydrolyzed Polyacrylonitrile Hollow Fibre Membrane. *Polym. J.* **1991**, *23*, 501-511.
- Malcolm, G. N.; Baird, C. E.; Bruce, G. R.; Cheyne, K. G.; Kershaw, R. W.; Pratt, M. C. Thermodynamics of Polyether Solutions. *J. Polym. Sci., Part A-2* **1969**, *7*, 1495.
- Matsumoto, K.; Ishii, K.; Kuroda, T.; Inoue, K.; Iwama, A. Membrane Process for Organic Vapor Recovery from Air. *Polym. J.* **1991**, *23*, 491-499.
- Napper, D.H. Polymeric Stabilization of Colloidal Dispersions. London: Academic Press, Inc., **1983**.
- Noda, I.; Higo, Y.; Ueno, N.; Fujimoto, T. Semi-dilute Region for Linear Polymers in Good Solvents. *Macromolecules* **1984**, *17*, 1055.
- Panayiotou, C. G. Thermodynamics of Associated Solutions. Mixtures of 1-Alkanols. *Fluid Phase Equilibria* **1990**, *56*, 171-188.
- Panayiotou C.; Sanchez, I. C. Hydrogen Bonding in Fluid: an Equation-of-State Approach. *J. Phys. Chem.* **1991**, *95*, 10090-10097.
- Panayiotou, C. P.; Vera, J. H. Thermodynamics of Polymer-Polymer-Solvent and Block Copolymer- Solvent Systems. I. Experimental Systems. *Polym. J.* **1984**, *16*, 89.
- Pimentel, G. C.; McClellan, A. L. The Hydrogen Bond, W.H. Freeman and Company, San Francisco, **1960**.
- Song, Y.; Lambert, S. M.; Prausnitz, J. M. Equation of State for Mixtures of Hard-Sphere Chain Including Copolymers. *Macromolecules* **1994a**, *27*, 441-448.
- Song, Y.; Lambert, S. M.; Prausnitz, J. M. A Perturbed Hard-Sphere-Chain Equation of State for Normal Fluids and Polymers. *Ind. Eng. Chem. Res.* **1994b**, *33*, 1047-1057.

Song, Y.; Lambert, S. M.; Prausnitz, J. M. Liquid-Liquid Phase Diagrams for Binary Polymer Solutions from a Perturbed Hard-Sphere-Chain Equation of State. *Chem. Eng. Sci.* **1994c**, *49*, 2765-2775.

Song, Y.; Hino, T.; Lambert, S. M.; Prausnitz, J. M. Liquid-liquid equilibria for polymer solutions and blends, including copolymers. Submitted to *Fluid Phase Equilibria* **1995**.

Song, Y.; Mason, E. A. Statistical-Mechanical Theory of a New Analytical Equation of State. *J. Chem. Phys.* **1989**, *91*, 7840-7853.

Veytsman, B. A. Are Lattice Models Valid for Fluids with Hydrogen Bonds? *J. Phys. Chem.* **1990**, *94*, 8499.

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- Figure 5.** VLE for chloroform+1,4 cis-polybutadiene solutions. Polymer molecular weight, 0.25×10^6 ; points, experimental data from Booth et al., 1964; lines, calculation using PHSC equation-of-state parameters: $\kappa_{12} = 0$, $\lambda_{12} = -0.016$.
- Figure 6.** VLE for chloroform+poly(vinyl acetate) solutions. Two binary parameters evaluated from VLE at 60 °C cannot predict VLE at 45 °C because of hydrogen bonding. Polymer molecular weight, 0.19×10^6 ; points, experimental data from Gupta and Prausnitz, 1995a; lines, calculation using PHSC equation-of-state parameters: $\kappa_{12} = -0.043$, $\lambda_{12} = 0.0112$.
- Figure 7.** VLE for chloroform+poly(vinyl acetate) solutions. Two hydrogen-bonding parameters obtained at 60 °C predict good VLE at 45 °C. Polymer molecular weight, 0.19×10^6 ; points, experimental data from Gupta and Prausnitz, 1995a; lines, calculation using PHSC equation-of-state parameters: $\kappa_{12} = 0$, $\lambda_{12} = 0$; $E^{\circ}_{12}/R = -1705$ K, $S^{\circ}_{12}/R = -4.64$.
- Figure 8.** VLE for chloroform+poly(ethylene oxide) solutions. At 60 °C, polymer molecular weight, 5×10^6 ; experimental data from Gupta and Prausnitz, 1995a; at 5.53 °C, polymer molecular weight, 308, experimental data from Malcolm et al., 1969; lines, calculation using PHSC equation-of-state parameters: $\kappa_{12} = 0$, $\lambda_{12} = 0$, $E^{\circ}_{12}/R = -1303$ K, $S^{\circ}_{12}/R = -2.78$.

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