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Phase equilibria of polymer solutions: modified perturbed hard-sphere-chain equation-of-state

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Abstract

We modified the perturbed hard-sphere-chain (PHSC) equation-of-state by introducing Chapman's equation into the bonding term of the reference equation. The proposed model successfully predicts the vapor/liquid equilibria (VLE) of pure fluids with three characteristic parameters obtained for each substance. We also extended the modified PHSC equation-of-state to describe the liquid/liquid equilibria (LLE) of polymer solutions. Characteristic parameters obtained from the pure substances were directly used to predict the LLE of polymer solutions. The calculated coexistence curves using the proposed model agree remarkably well with the experimental data. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Perturbation theory; Equation-of-state; Phase equilibria

1. Introduction

The equation-of-state theory gives us very useful information in investigating the properties of fluids, including mixtures of chain-like molecules. It contains all the information about a substance, and any equilibrium property can be obtained from any one of the fundamental equations-of-state by applying the appropriate thermodynamic relations. However, in the early pioneering days, the development of the fundamental equations-of-state was very slow and limited to a few pure fluids which have small molecular sizes and low molecular weights. Now, many theoretical approaches have been available for years, for predicting the non-ideal behavior of polymer solutions. Most of them can be considered either as generalized van der Waals or lattice-like models. These models currently give a correct qualitative behavior of the phase diagrams found in polymer systems.

The first qualitatively correct theory for the phase behaviors of polymer solutions was independently proposed by Flory [1] and Huggins [2] in 1941. The Flory–Huggins (F–H) theory considers a polymer molecule as a chain of r roughly spherical segments and the number of ways in which these polymer segments and solvent molecules can be arranged in a three-dimensional (3D) lattice in which the size of the each cells are all equal. However, this theory gives too narrow liquid–liquid coexistence curve when compared with experimental data for the polymer solution system. Moreover, the F–H polymer solution theory failed to describe a lower-critical-solution-temperature (LCST) at elevated temperatures. For more accurate description for the phase equilibrium of the polymer solutions, numerous studies on the modification of the lattice theory have been reported by Sanchez and Lacombe [3,4], Kleintjents and Koningsveld [5], and Hu et al. [6].

In recent years, there has been a continuing interest in the development of theoretically-based equations-of-state for chain-like molecules. The molecular description of these polymeric fluids is complicated, due to their asymmetric structure, etc. To understand chain fluids, it seems advantageous to develop ways of relating their behavior to simpler, more easily understood fluids. The hard-sphere-chain model provides an intuitively appealing starting point for the study of chain fluids [7]. Each molecule is modeled as a series of freely-jointed, tangent, hard spheres which interact through site–site potentials. The use of the hard-sphere-chain model simplifies the nature of the site–site interactions while retaining the essential geometric features of the chain, and allows one to explore the effects of molecular geometry and internal flexibility on the local structure of the fluid. At the same time, the hard chain system can serve as a reference fluid about which attractive interactions may be introduced as perturbations. In this sense, the hard-sphere-chain model can play an important role in the study of more realistic

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chain fluids analogous to that played by the hard-sphere monomer in the study of more complex monatomic fluids.

In 1994, Song et al. [8] proposed the perturbed hard-sphere-chain (PHSC) equation-of-state for the purpose of calculating the phase equilibria in solutions including solvents and polymers. However, in the description of compressibility factor for mixtures of hard-sphere chains, the PHSC equation-of-state somewhat overestimates the pressure when plotted against the reduced density η (packing fraction).

In this study, we excluded this shortcoming by introducing a modified form, previously proposed by Chapman et al. [9], into the bonding term of the reference equation. We extended the model to describe the liquid/liquid equilibria (LLE) of polymer/solvent mixtures. The proposed model is in good agreement with experimental results.

2. Theoretical consideration

2.1. Equation-of-state

2.1.1. Pure fluids

The PHSC equation-of-state consists of reference and perturbation terms [8] which have the dimensionless form of

$$\frac{P}{\rho \mathrm{k}T} = \left(\frac{P}{\rho \mathrm{k}T}\right)_{\mathrm{ref}} + \left(\frac{P}{\rho \mathrm{k}T}\right)_{\mathrm{pert}} \tag{1}$$

where P is the pressure, $\rho = N/V$ is the number density (N is the number of molecules and V is the volume), and k is the Boltzmann constant.

Each term of our proposed model for pure fluids, modified through introducing Chapman's equation into the bonding term, can be expressed as

$$\left(\frac{P}{\rho \mathrm{k}T}\right)_{\mathrm{ref}} = 1 + r^2 b\rho g(d^+) - (r-1)\rho \frac{\partial \ln g(d^+)}{\partial \rho} \tag{2}$$

$$\left(\frac{P}{\rho \mathrm{k}T}\right)_{\mathrm{pert}} = -\frac{r^2 a\rho}{\mathrm{k}T} \tag{3}$$

where r is the number of single hard spheres per chain molecule, which is the relative molecular size. a and b account for the attractive forces between two non-bonded segments and the second virial coefficient of hard spheres, respectively and both are temperature-dependent parameters inherited from two universal functions, $F_a(\mathrm{k}T/\varepsilon)$ and $F_b(\mathrm{k}T/\varepsilon)$ in the PHSC theory.

$$a(T) = \frac{2\pi}{3}\sigma^3 \varepsilon F_a(\mathrm{k}T/\varepsilon) \tag{4}$$

$$b(T) = \frac{2\pi}{3} d^3(T) = \frac{2\pi}{3}\sigma^3 F_b(kT/\varepsilon) \tag{5}$$

with

$$F_a(\mathrm{k}T/\varepsilon_{ii}) = 1.8681 \exp[-0.0619(\mathrm{k}T/\varepsilon_{ii})] + 0.6715 \exp[-1.7317(\mathrm{k}T/\varepsilon_{ii})^{3/2}] \tag{6}$$

$$F_b(\mathrm{k}T/\varepsilon_{ii}) = 0.7307 \exp[-0.1649(\mathrm{k}T/\varepsilon_{ii})^{1/2}] + (1 - 0.7303) \exp[-2.3973(\mathrm{k}T/\varepsilon_{ii})^{3/2}] \tag{7}$$

where d is the effective hard-sphere diameter, ε is the energy parameter and σ represents the size of the segment in a particular molecule. The complete form of the equation-of-state can be obtained by combining Eqs. (2) and (3)

$$\left(\frac{P}{\rho \mathrm{k}T}\right) = 1 + r^2 b\rho g(d^+) - (r-1)\rho \frac{\partial \ln g(d^+)}{\partial \rho} - \frac{r^2 a\rho}{\mathrm{k}T} \tag{8}$$

$g(d^+)$ is the radial distribution function and takes the form of Carnahan–Starling equation

$$g(d^+) = \frac{1 - \eta/2}{(1-\eta)^3} \tag{9}$$

where η is the packing fraction given by

$$\eta = \frac{rb\rho}{4}. \tag{10}$$

2.1.2. Extended equation for the polymer solutions

To extend the proposed model to the polymer solutions, the equation for pure fluids can be written as below

$$\frac{P}{\rho \mathrm{k}T} = 1 + \rho \sum_{ij}^{m} x_i x_j r_i r_j b_{ij} g_{ij}(d_{ij}^+) - \sum_{i}^{m} x_i (r_i - 1)\rho \frac{\partial \ln g_{ii}(d_{ii}^+)}{\partial \rho} - \frac{\rho}{\mathrm{k}T} \sum_{ij}^{m} x_i x_j r_i r_j a_{ij} \tag{11}$$

where $x_i = N_i/N$ is the number fraction of molecules, r_i is the number of hard spheres of species i, and $g_{ij}(d_{ij}^+)$ is the pair radial distribution function of hard-sphere mixtures which takes the form of Boublik–Mansoori–Carnahan–Starling (BMCS) equation [10]:

$$g_{ij}(\eta, \xi_{ij}) = \frac{1}{1-\eta} + \frac{3}{2}\frac{\xi_{ij}}{(1-\eta)^2} + \frac{1}{2}\frac{\xi_{ij}^2}{(1-\eta)^3} \tag{12}$$

where η and ξ_{ij} are

$$\eta = \frac{\rho}{4} \sum_{i}^{m} x_i r_i b_i \tag{13}$$

$$\xi_{ij} = \left(\frac{b_i b_j}{b_{ij}}\right)^{1/3} \frac{\rho}{4} \sum_{k}^{m} x_k r_k b_k^{2/3}. \tag{14}$$

The hard-sphere diameters have the additivity which allows

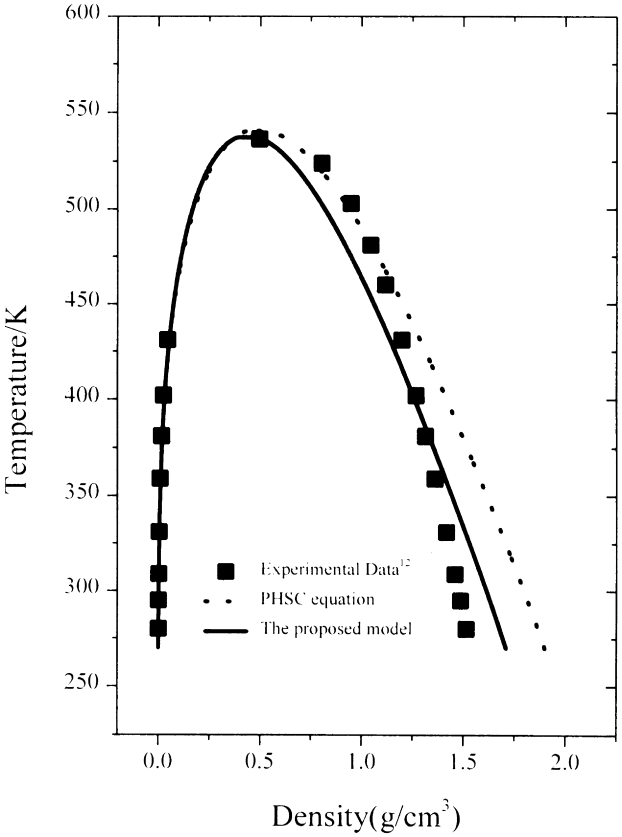

Fig. 1. Vapor/liquid equilibria for saturated acetone. The dotted line and the solid line are those calculated by the PHSC equation-of-state and the proposed model, respectively. The solid squares are experimental data by Smith and Srivastava [12].

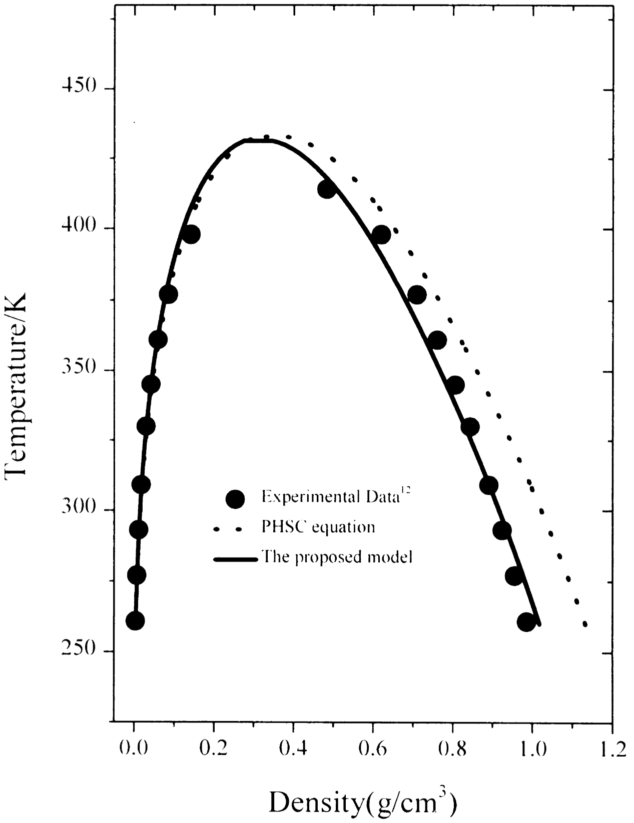

Fig. 2. Vapor/liquid equilibria for saturated diethyl ether. The dotted line and the solid line are those calculated by the PHSC equation-of-state and the proposed model, respectively. The solid circles are experimental data by Smith and Srivastava [12].

$b_{ij}(T)$ to be expressed as

$$b_{ij}(T) = \frac{2\pi}{3} d_{ij}^3(T) = \frac{1}{8}(b_i^{1/3} + b_j^{1/3})^3. \tag{15}$$

To describe the coexistence curve of binary polymer solutions, we introduce two adjustable model parameters into energy and size parameters:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}(1 - k_{ij}) \tag{16}$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}(1 - \lambda_{ij}) \tag{17}$$

$a_{ij}(T)$, which explains the attractive forces between species i and j, can be expressed as

$$a_{ij}(T) = \frac{2\pi}{3} \sigma_{ij}^3 \varepsilon_{ij} F_{ij}(\mathrm{k}T/\varepsilon_{ij}) \tag{18}$$

where $F_{ij}(\mathrm{k}T/\varepsilon_{ij}) = \sqrt{F_a(\mathrm{k}T/\varepsilon_{ii})F_a(\mathrm{k}T/\varepsilon_{jj})}$.

With the segment-basis variables such as $\rho_r = N_r/V$ and $\phi_i = N_i r_i/V$, where $N_r = \sum_i^m N_i r_i$ is the total number of segments in the system of which the total volume is V, Eq. (11) can be transformed into

$$\frac{P}{\rho_r \mathrm{k}T} = \rho_r \sum_{ij}^{m} \phi_i \phi_j b_{ij} g_{ij}(d_{ij}^+) + \sum_{i}^{m} \frac{\phi_i}{r_i} - \sum_{i}^{m} \phi_i \left(1 - \frac{1}{r_i}\right) \rho \frac{\partial \ln g_{ii}(d_{ii}^+)}{\partial \rho} - \frac{\rho_r}{\mathrm{k}T} \sum_{ij}^{m} \phi_i \phi_j a_{ij}. \tag{19}$$

2.2. Thermodynamic functions

2.2.1. Helmholtz energy

The Helmholtz energy can be calculated from the pressure-explicit equation-of-state [11]:

$$\frac{A}{N_r \mathrm{k}T} = \sum_{i}^{m} \frac{\phi_i}{r_i} \frac{A_i^0}{N_i \mathrm{k}T} + \int_0^{\rho_r} \left(\frac{P}{\rho_r \mathrm{k}T} - \frac{N}{N_r}\right) \frac{\mathrm{d}\rho_r}{\rho_r} + \sum_{i}^{m} \frac{\phi_i}{r_i} \ln\left(\frac{\phi_i}{r_i} \rho_r \mathrm{k}T\right). \tag{20}$$

The calculation procedure and the final result are given

$$\begin{aligned}\frac{A}{N_r\mathrm{k}T} = {} & \sum_i^m \frac{\phi_i}{r_i}\frac{A_i^0}{N_i\mathrm{k}T} + \rho_r \sum_{ij}^m \phi_i\phi_j b_{ij} W_{ij} \\ & - \frac{\rho_r}{\mathrm{k}T}\sum_{ij}^m \phi_i\phi_j a_{ij} \\ & - \sum_i^m \phi_i\left(1-\frac{1}{r_i}\right)\int_0^{\rho_r}\frac{\partial \ln g_{ii}(d_{ii}^+)}{\partial\rho_r}\mathrm{d}\rho_r \\ & + \sum_i^m \frac{\phi_i}{r_i}\ln\left(\frac{\phi_i}{r_i}\rho_r\mathrm{k}T\right) \qquad (21)\end{aligned}$$

$$\begin{aligned}\frac{A}{N_r\mathrm{k}T} = {} & \sum_i^m \frac{\phi_i}{r_i}\frac{A_i^0}{N_i\mathrm{k}T} + \rho_r \sum_{ij}^m \phi_i\phi_j b_{ij} W_{ij} \\ & - \sum_i^m \phi_i\left(1-\frac{1}{r_i}\right)Q_{ii} - \frac{\rho_r}{\mathrm{k}T}\sum_{ij}^m \phi_i\phi_j a_{ij} \\ & + \sum_i^m \frac{\phi_i}{r_i}\ln\left(\frac{\phi_i}{r_i}\rho_r\mathrm{k}T\right) \qquad (22)\end{aligned}$$

where

$$W_{ij} = \frac{1}{\rho_r}\int_0^{\rho_r} g_{ij}\,\mathrm{d}\rho_r = \frac{I_1}{\eta} + \frac{3}{2}\frac{\xi_{ij}}{\eta^2}I_2 + \frac{1}{2}\frac{\xi_{ij}^2}{\eta^3}I_3 \qquad (23)$$

$$\begin{aligned}Q_{ii} & = \int_0^{\rho_r}\frac{\partial \ln g_{ii}(d_{ii}^+)}{\partial\rho_r}\mathrm{d}\rho_r \\ & = -\ln(1-\eta) + \frac{3}{2}\frac{\xi_{ii}}{(1-\eta)} + \frac{1}{4}\frac{\xi_{ii}^2}{(1-\eta)^2} \qquad (24)\end{aligned}$$

with

$$I_n = -I_{n-1} + \frac{1}{n-1}\frac{\eta^{n-1}}{(1-\eta)^{n-1}}, \qquad I_1 = -\ln(1-\eta). \qquad (25)$$

2.2.2. Chemical potentials

The chemical potential is defined

$$\mu_k = \left(\frac{\partial A}{\partial N_k}\right)_{T,V,N_{i\neq k}} \qquad (26)$$

and the Helmholtz energy can be rewritten

$$\begin{aligned}\frac{A}{N_r\mathrm{k}T} = {} & \left(\frac{\phi_1}{r_1}\frac{A_1^0}{N_1\mathrm{k}T} + \cdots + \frac{\phi_k}{r_k}\frac{A_k^0}{N_k\mathrm{k}T} + \cdots + \frac{\phi_m}{r_m}\frac{A_m^0}{N_m\mathrm{k}T}\right) \\ & + \rho_r[\phi_1^2 b_{11}W_{11} + \cdots + (2\phi_1\phi_k b_{1k}W_{1k} + 2\phi_2\phi_k b_{2k}W_{2k} \\ & + \cdots + \phi_k^2 b_{kk}W_{kk} + \cdots + 2\phi_m\phi_k b_{mk}W_{mk})] \\ & - \left[\phi_1\left(1-\frac{1}{r_1}\right)\int_0^{\rho_r}\frac{\partial\ln g_{11}}{\partial\rho_r}\mathrm{d}\rho_r + \cdots + \phi_k\left(1-\frac{1}{r_k}\right)\right. \\ & \times\int_0^{\rho_r}\frac{\partial\ln g_{kk}}{\partial\rho_r}\mathrm{d}\rho_r + \cdots + \phi_m\left(1-\frac{1}{r_m}\right) \\ & \left.\times\int_0^{\rho_r}\frac{\partial\ln g_{mm}}{\partial\rho_r}\mathrm{d}\rho_r\right] - \frac{\rho_r}{\mathrm{k}T}[\phi_1^2 a_{11} + \cdots + (2\phi_1\phi_k a_{1k} \\ & + \cdots + \phi_k^2 a_{kk} + \cdots + 2\phi_m\phi_k a_{mk}) + \cdots + \phi_m^2 a_{mm}] \\ & + \left[\frac{\phi_1}{r_1}\ln\left(\frac{\phi_1}{r_1}\rho_r\mathrm{k}T\right) + \cdots + \frac{\phi_k}{r_k}\ln\left(\frac{\phi_k}{r_k}\rho_r\mathrm{k}T\right)\right. \\ & \left. + \cdots + \frac{\phi_m}{r_m}\ln\left(\frac{\phi_m}{r_m}\rho_r\mathrm{k}T\right)\right] \qquad (27)\end{aligned}$$

$$\begin{aligned}\frac{\mu_k}{\mathrm{k}T} = {} & \frac{\mu_k^0}{\mathrm{k}T} + 2r_k\rho_r\sum_i^m \phi_i b_{ik}W_{ik} + \rho_r\sum_{ij}^m \phi_i\phi_j b_{ij}\left(N_r\frac{\partial W_{ij}}{\partial N_k}\right) \\ & - (r_k-1)\int_0^{\rho_r}\frac{\partial\ln g_{kk}}{\partial\rho_r}\mathrm{d}\rho_r - \sum_i^m \phi_i\left(1-\frac{1}{r_i}\right) \\ & \times\left[r_k\frac{\partial}{\partial\phi_k}\int_0^{\rho_r}\frac{\partial\ln g_{ii}}{\partial\rho_r}\mathrm{d}\rho_r\right] - \frac{2r_k\rho_r}{\mathrm{k}T}\sum_i^m \phi_i a_{ik} \\ & + \ln\left(\frac{\phi_k}{r_k}\rho_r\mathrm{k}T\right) + 1 \qquad (28)\end{aligned}$$

where

$$N_r\frac{\partial W_{ij}}{\partial N_k} = \left(\frac{\partial W_{ij}}{\partial\eta}\right)\left(N_r\frac{\partial\eta}{\partial N_k}\right) + \left(\frac{\partial W_{ij}}{\partial\xi_{ij}}\right)\left(N_r\frac{\partial\xi_{ij}}{\partial N_k}\right) \qquad (29)$$

with

$$N_r\frac{\partial\eta}{\partial N_k} = \frac{\rho_r}{4}r_k b_k. \qquad (30)$$

3. Results and discussion

The proposed model has three characteristic parameters: Number of single hard spheres per chain molecule r, a segment size σ, and a non-bonded segment pair interaction energy ε. To describe the LLE of fluid mixtures, we

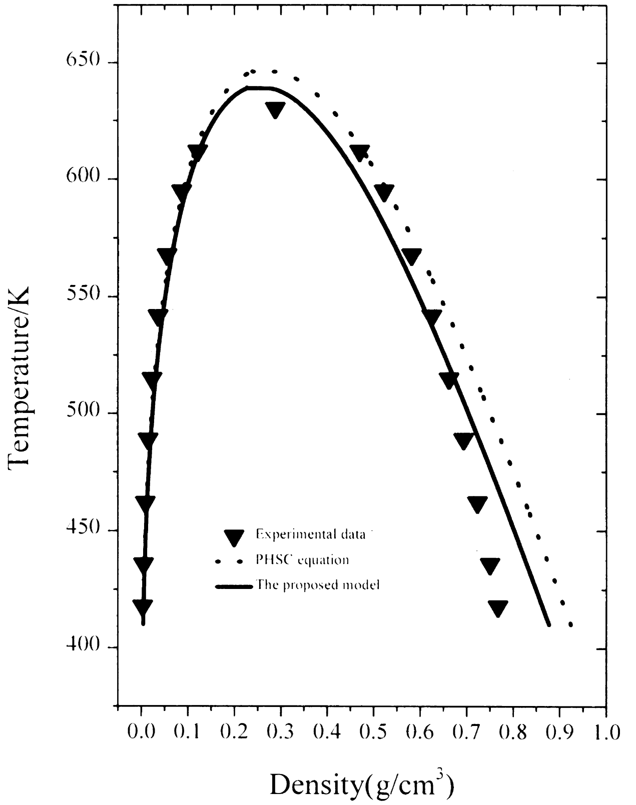

Fig. 3. Vapor/liquid equilibria for saturated cyclohexane. The dotted line and the solid line are those calculated by the PHSC equation-of-state and the proposed model, respectively. The solid down-triangles are experimental data by Smith and Srivastava [12].

introduced two binary adjustable parameters such as k_{12} and λ_{12} into energy and size terms.

Fig. 1 shows the vapor/liquid coexistence curve for saturated acetone. Solid squares are experimental data reported by Smith and Srivastava [12], the dotted and solid lines are the predicted values by the PHSC equation and the proposed model, respectively. The values of three characteristic parameters for acetone are $r = 3.578$ Å, $\sigma = 3.006$ Å, and $\varepsilon/k = 245.1$. These parameters are determined by fitting experimental data of fluid densities for pure saturated acetone. Near the critical region, the proposed model agrees very well with the critical point of the saturated acetone. However, the PHSC equation overestimates it. At higher density region ($\eta > 0.4$), the modified PHSC equation-of-state predicts VLE of the saturated acetone better than that of the PHSC equation.

Fig. 2 is the phase diagram which represents the VLE of saturated diethyl ether. Solid circles are experimental data reported by Smith and Srivastava [12], the dotted and solid lines are predicted values by the PHSC equation and the proposed model, respectively. The values of three characteristic parameters for diethyl ether are $r = 3.735$ Å, $\sigma = 3.485$ Å and $\varepsilon/k = 226.8$. Near the critical region, our proposed model passes the experimental critical point. However, the PHSC equation overestimates about 20 K. In the higher density region ($\eta > 0.4$), our proposed model describes the experimental data of VLE for the saturated diethyl ether better than that of the PHSC equation.

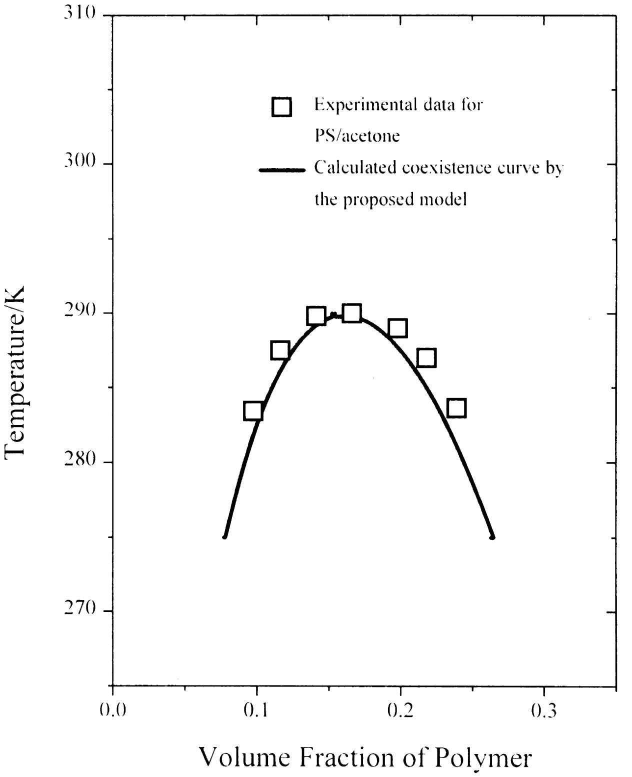

Fig. 4. Liquid/liquid equilibria for polystyrene/acetone. The solid line is that calculated by the proposed model. The open squares are experimental data by Zeman et al. [13].

Fig. 3 shows the VLE of saturated pure cyclohexane. Solid down-triangles are experimental data reported by Smith and Srivastava [12], the dotted and solid lines are predicted values by the PHSC equation and the proposed model, respectively. The values of three characteristic parameters for cyclohexane are $r = 3.689$ Å, $\sigma = 3.434$ Å, and $\varepsilon/k = 248.5$. In the entire density region, the proposed model predicts VLE of the saturated cyclohexane remarkably well. However, the PHSC equation still overestimates the experimental data. All characteristic parameters obtained from the pure substances were directly used in the calculation of the liquid/liquid coexistence curves for the following polymer/solvent systems.

Fig. 4 shows cloud point data for binary polystyrene (PS)/acetone system which shows a upper critical-solution-temperature (UCST) behavior. The open squares are the experimental data reported by Zeman et al. [13] and the solid line is the calculated coexistence curve by the proposed model. The values of three characteristic parameters for polystyrene are $r/M = 0.01203$ mol/g, $\sigma = 5.563$ Å, and $\varepsilon/k = 726.8$. The binary model parameters have the value of $k_{12} = 0.2106$ and $\lambda_{12} = 0.1865$. From the values of binary model parameters, we can infer

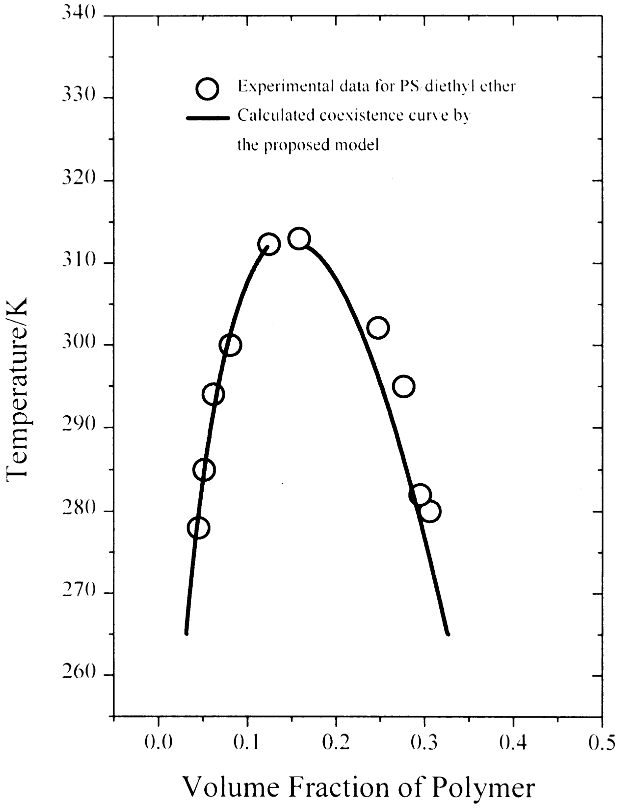

Fig. 5. Liquid/liquid equilibria for polystyrene/diethyl ether. The solid line is that calculated by the proposed model. The open circles are experimental data by Zeman et al. [13].

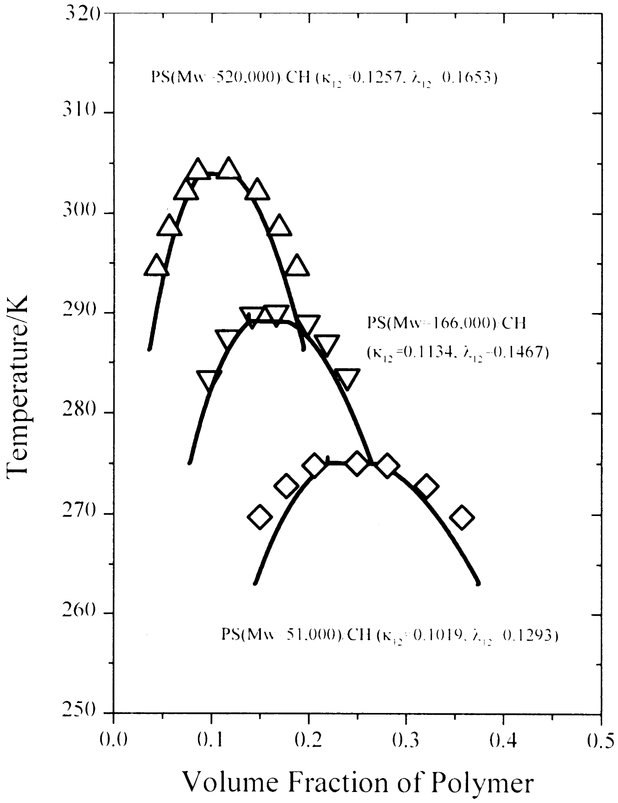

Fig. 6. Liquid/liquid equilibria for polystyrene/cyclohexane. The solid lines are those calculated by the proposed model. The open symbols are experimental data by Opstal et al. [14].

that the PHSC equation-of-state theory overestimates ε_{12} and σ_{12} by about 21 and 19%, respectively. The calculated coexistence curve shows a slightly narrow values compared with the experimental data. It still predicts the critical point remarkably well.

Fig. 5 represents a cloud point curve of the PS/diethyl ether system which shows a UCST behavior. The open circles are the experimental data reported by Zeman et al. [13] and the solid line is the calculated coexistence curve by the proposed model. Binary model parameter values for our proposed model are $k_{12} = 0.1845$ and $\lambda_{12} = 0.1558$. The PHSC equation-of-state theory overestimates the energy and size parameters by about 18 and 16%, respectively. The proposed model slightly overestimates the experimental critical point and shows a slight deviation from the experimental data in the higher polymer composition region.

Fig. 6 shows a phase diagram of PS/cyclohexane which represents a UCST behavior. Open up-triangles (PS $M_w = 520\ 000$), open down-triangles (PS $M_w = 166\ 000$), and open diamonds (PS $M_w = 51\ 000$) are experimental data reported by Opstal et al. [14]. The solid lines are the calculated coexistence curves for the each system. As shown in Fig. 6, it is apparent that the deviations between the experimental data and the calculated values from the proposed model decreases with the molecular weight of PS. Each system shows slight deviations from the experimental data, however describes the critical points very well. Binary model parameter values for PS with molecular weights of 51 000, 166 000, and 520 000 are $k_{12} = 0.1019$ and $\lambda_{12} = 0.1293$, $k_{12} = 0.1134$ and $\lambda_{12} = 0.1467$, and $k_{12} = 0.1257$ and $\lambda_{12} = 0.1653$, respectively. In each system, energy and size parameters, ε_{12} and σ_{12}, are overestimated by about 10–13% and 13–17%, respectively. Further, the values of k_{12} and λ_{12} increase with molecular weight of PS.

4. Conclusion

We successfully described the phase equilibria of several fluids, such as saturated pure fluids and binary polymer/solvent systems using the proposed model. Three characteristic parameters for each substance were determined from the properties of pure saturated fluids. Using these characteristic parameters, the LLE of the given polymer/solvents systems were predicted. Calculated coexistence curves show good agreement with the experimental data. The proposed model can explain the non-ideal behaviors of polymer solutions by performing a simple modification on the PHSC equation-of-state.

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