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Liquid-liquid equilibrium of hydrogen bonding polymer solutions

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ABSTRACT

The liquid-liquid equilibrium (LLE) calculation for polymer solutions is essential for processes design of polymerization. The hydrogen bonding in polymer solutions leads to deviate remarkably from normal solutions behaviors. The perturbed hard-sphere-chain-association (PHSC-AS) equation of state (EoS) is applied to calculate the liquid-liquid equilibrium (LLE) of polymer mixtures with hydrogen bonding association such as self- and cross-association with various phase behaviors such as UCST, LCST and closed-loop of polymer solutions. In addition, the calculation results are compared with those obtained by the PC-SAFT EoS, which is known to be useful for calculating phase equilibria of polymer systems. PHSC-AS EoS shows a satisfactory performance for LLE calculation with similar accuracy compared to that with PC-SAFT EoS.

1. Introduction

Modeling of the phase behavior of polymer solutions is a crucial requirement to develop new polymer solution technologies and to design various polymer processes, such as purification, fractionation, devolatization and polymer production. In particular, the liquid-liquid equilibrium (LLE) calculation is essential for processes design of polymerization [1,2]. In general, LLE phase behaviors of polymer solutions show the various phase behaviors such as the upper critical solution temperature (UCST) due to energetic effect (i.e., the differences in intermolecular forces between the solvent and the polymer), the lower critical solution temperature (LCST) mainly attributed to equation-of-state or free volume effect (i.e., the compressibility disparity between compressible solvents and relatively dense polymers due to the difference of molecular size), UCST and LCST, and the closed-loop with the LCST lying below the UCST due to strong hydrogen bonding interaction [3,4]. Due to hydrogen bonding between the electron accepting site and the electron donating site in the functional groups, the polymer and solvent molecules can solvate or self-associate. It is well known that such association, especially a solvation (e.g., self- and cross-association), has a remarkable effect on the phase behavior of polymer solutions [5]. Due to those reasons, many researchers have been interested in developing an equation of state (EoS) that is

applicable to complex systems in which the component can have highly polar, of vast size, and many association sites to form the hydrogen bonding. However, numerous studies for polymer solution have been focusing on the vapor-liquid equilibrium (VLE) and LLE of non-associating polymer solutions [6–14]. Therefore, the modeling for polymer solutions with hydrogen bonding is still open for further research.

The calculation of phase equilibrium for associating polymer solutions is carried out rarely by few researchers [15]. Panayiotou and Sanchez [16] proposed a lattice-fluid associated solutions (LFAS) model and obtained the reasonable results for VLE calculation of PEO/chloroform and PPO/chloroform systems in which the cross-association between oxygen of -O- functional group in repeating unit of polymer and chloroform exists. The simplified Cubic-Plus-Association (CPA) EoS was applied by Kontogeorgis et al. [17] to VLE calculation for PVAC/1-propanol and showed more satisfactory results than that with Soave-Redlich-Kwong (SRK) EoS without association term. von Solms et al. [18] applied sPC-SAFT EoS to LLE calculation for HDPE/n-alkanol systems. Kouskoumvekaki et al. [19] applied sPC-SAFT EoS to VLE calculation for binary system of polyamide 6/water and for ternary systems of polyamide 6/water/ε-caprolactam. Kleiner et al. [20] extended PC-SAFT EoS to calculating phase equilibria of polydisperse associating copolymer-solvent systems (i.e., poly (ethene-co-acrylic acid)-ethene, poly (ethene-co-methacrylic acid)-ethene). Clark et al. [21] investigated the LLE with closed-loop type of poly (ethylene glycol) (PEG)/water mixtures. However, most research for associating polymer solutions are focused on their VLE calculation and do not extend the

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various LLE phase behaviors types for associating polymer solutions such as LCST, UCST, UCST and LCST, and the closed-loop.

The PC-SAFT EoS which has been used popularly to calculate the thermodynamic properties for polymer solutions has been used the complicated second order perturbation term to describe the attractive force between molecules. However, the attractive force in PHSC-AS EoS is expressed by the simplest van der Waals-type dispersion term. Despite the simplicity of dispersion term with van der Waals-type compared to SAFT-family EOS, the PHSC-AS EoS which combined the association term of SAFT model [22,23] to PHSC EoS [24,25], was successfully applied to describe the phase equilibria of associating polymer solutions such as pressure−volume−temperature (PVT), infinite dilution weight fraction activity coefficient (WFAC) and VLE, but showed a poor computational performance for LLE phase behaviors [26]. In this work, to obtain the satisfying results for LLE calculation, the PHSC-AS EoS using new estimation method for pure polymer parameters is applied to calculate LLE phase behaviors for associating polymer solutions with UCST, LCST, UCST and LCST, and closed-loop. In addition, the calculation results are compared with those obtained by the PC-SAFT EoS [27,28] which is known to be useful for calculating phase equilibria of polymer systems. PHSC-AS EoS shows a satisfactory performance for LLE calculation with similar accuracy compared to that with PC-SAFT EoS.

2. Theoretical background

For the two phases (I and II) under LLE phase equilibria, they must satisfy the thermodynamic condition, i.e., the equality of activities for species in both phases. At given absolute temperature T and total pressure P, the activity of species i in two phases is to be equal as following;

$$\left(x_i \frac{\overline{\phi}_i(T,P)}{\phi_i^o(T,P)}\right)^I = \left(x_i \frac{\overline{\phi}_i(T,P)}{\phi_i^o(T,P)}\right)^{II} \tag{1}$$

where $\overline{\phi}_i$ and ϕ_i^o are the fugacity coefficients of i in the mixture and in the pure state, respectively. The fugacity coefficient of component i in the mixture and in the pure state can be calculated from the PHSC-AS EoS which is described in literature [29,30] in detail. In terms of the Helmholtz free energy, PHSC-AS and PC-SAFT EoS can be expressed briefly as

$$A = mA^{hs} + A^{chain} + A^{disp} + A^{assoc} \tag{2}$$

where A^{hs}, A^{chain}, A^{disp}, and A^{assoc} account for hard-sphere repulsive interactions, chain connectivity, attractive interactions, and association (i.e. hydrogen bonding), respectively. In PHSC-AS, the dispersion term with van der Waals-type is used, and the complicated second order dispersion term based on perturbation theory of Barker and Henderson is used in PC-SAFT EoS.

In the mixture, pair-potential parameters σ_{ij} and ε_{ij} between unlike segments can be obtained by conventional combining rules:

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_i + \sigma_j\right) \tag{3}$$

$$\varepsilon_{ij} = \left(1 - k_{ij}\right)\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{4}$$

where k_{ij} is the adjustable binary interaction parameter. The association parameters, $\varepsilon^{A_iB_j}$ and $\kappa^{A_iB_j}$ are defined as [31].

$$\varepsilon^{A_iB_j} = \left(\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}\right)/2 \tag{5}$$

$$\kappa^{A_iB_j} = \sqrt{\kappa^{A_iB_i}\kappa^{A_jB_j}}\left[\frac{\sqrt{\sigma_i\sigma_j}}{(\sigma_i + \sigma_j)/2}\right]^3 \tag{6}$$

3. Results and discussion

To adequately describe the phase behavior of a mixture with EoS, the molecular parameters for the pure compounds are required. In general, the pure parameters for polymer are obtained from fitting PVT data of pure molten-polymer. In previous work [26], this method was applied to calculate the various phase behaviors of polymer solutions such as PVT, VLE, WFAC and LLE with PHSC-AS and PC-SAFT EoS, and showed a poor performance for LLE phase behavior calculation with PHSC-AS EoS. When pure-polymer parameters are adjusted only to liquid-density data, it is known that adjusted parameters often take on unreasonable values, which leads to unsatisfying descriptions of phase equilibria for polymer mixtures [32,33]. The simultaneous regression method of both pure-polymer PVT data and binary phase equilibria data is used by Sadowski's group [32,34] to estimate pure-polymer parameters, and they mentioned that pure-component parameters obtained by this method are suitable for different mixtures.

Therefore, in this work, to obtain the satisfying results for LLE calculation, the simultaneous regression method of both pure molten-polymer and VLE data is applied to the estimation for pure molecular parameters of PHSC-AS and PC-SAFT EoS. Both models for associating polymer require five pure compound parameters which are three parameters (the number of effective segment per molecule $r_i/\overline{M_w}$, segmental diameter σ_i and interaction energy ε_i/k) from reference terms and two association-based parameters (association energy parameter $\varepsilon^{A_iB_j}$ and association volume parameter $\kappa^{A_iB_j}$) from association term. The pure polymer parameters estimated by simultaneously fitting PVT data [35−38] of pure molten-polymer and binary VLE data are reported in Table 1, and the liquid densities correlated by PHSC-AS and PC-SAFT EoS show a little bit large deviation with the average absolute relative deviation (ARD) value of 2.92% and 1.69%, respectively, over a wide temperature range of 303 K−527 K and pressure range of 1−2001 bar.

The estimated pure polymer parameters are used to calculate VLE and LLE for polymer/solvent systems in which the strong interaction such as hydrogen association between polymer and solvent exists. Then, the cross-association (i.e., $\varepsilon^{A_iB_j}/k$, $\kappa^{A_iB_j}$) between self-associating polymers (i.e., PVAL, PVPh) and solvents (i.e., alcohols, propanamine, water) is defined by mixing rule (i.e., Eqns. (4) and (5)). Then the associating molecules are characterized by different association types [23]; two-site (2B type) for alcohols, PVAL and PVPh, and three-site (3B type) for water and propanamine. Although PEO, PPO, PVAC and PVME are not self-associating compounds (that is, it is not able to apply their association to mixing rule), there are cross-association interactions between oxygen (of functional group -O- and -COO in repeating unit of polymer) and hydrogen (of the hydroxyl group of alcohol, amine and water). The cross-association parameters (ε^{AB}/k and κ^{AB}) for these non-self-associating polymers are estimated from fitting VLE data and are considered as temperature-independent parameters. The cross-association and binary interaction parameter are simultaneously regressed through the calculation process shown in Fig. 1. The calculated results for VLE from both PHSC-AS and PC-SAFT show a similar ARD error of about 4.6% (see Table 2).

As can be seen in Table 2, both models shows a good agreement with experimental vapor pressure over broad temperature range from 293 K to 383 K.