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Lower and upper critical solution temperatures of binary polymeric solutions

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ABSTRACT

The phase behavior of binary polymeric solutions such as lower and upper critical solution temperatures has an important role in many polymeric processes. For theoretical investigation on the prediction of these temperatures, a substantial number of data points on binary polymeric solutions were collected from literature and used to present a reliable calculation routine through chemical engineering thermodynamic modeling approach. The thermodynamic model of Compressible Regular Solution was used. The minimization of errors and predefined objective function was done by applying Particle Swarm Optimization technique. An efficient and accurate empirical correlation employing some quantitative structure–property relationship concept through statistical modeling was developed. To develop the statistical model, the connectivity indices of polymer and solvent were used as the independent variables of the model. Four statistical parameters were defined as auxiliary criteria to evaluate the models and convergence of calculations. In addition, attempts were made to develop and correlate the connectivity indices (topological descriptors) of polymer and solvent to the lattice fluid theory parameters of Sanchez-Lacombe Equation of State. The reliability and accuracy of proposed approaches were discussed in-details and the results were compared to the available experimental data. Desirable agreements between calculated and experimental data were found in thermodynamic model as demonstrated by a maximum Individual Absolute Relative Deviation of 5%. An averaged IARD of 4.3% was obtained for the empirical model. The new correlation predicts connectivity indices of components with acceptable accuracy.

1. Introduction

The lower critical solution temperature (LCST) is the temperature below which components of a mixture are completely miscible for all compositions [1,2]. On the other side, a temperature above which the miscibility of components for all compositions will be observed is referred as upper critical solution temperature (UCST) [3]. UCST and LCST can be observed in partially miscible polymeric solutions and depends on the operating pressure and solution component compositions [2,4]. The spinodal and binodal curves [5] have shared minimum (critical point) and maximum respectively at LCST and UCST.

In polymeric processes such as polymerization and membrane fabrication [6–9], any knowledge on phase behaviors vs. solution composition and operating pressure is highly valuable and plays an important role. While the experimental data on LCST and UCST are available, however still accurate and reliable approach or model to correlate these critical solution temperatures (CST) data is rarely found [6–9]. The research works in literature to model and correlate LCST and/or UCST data include [10]; phase equilibrium data based calculation [11], empirical correlations [12,13], the quantitative structure–property relationship (QSPR) models and etc. [10,14–18].

To develop more accurate and predictive models for LCST and/or UCST, here, the compressible regular solution theory and lattice fluid theory were used for thermodynamic modeling. In addition,

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the connectivity indices of polymer and solvent were used to develop a reliable empirical model. Attempts were made to correlate the connectivity indices of selected components to the lattice fluid scaling parameters. The evolutionary based algorithm of particle swarm optimization was used for minimization of errors. The details of modeling, calculations and the obtained results are illustrated in following paragraphs.

2. Thermodynamic modeling of UCST and LCST

2.1. Model development

Various miscibility behaviors can be observed in binary polymeric solutions such as showing only one LCST, only one UCST, both LCST and UCST simultaneously, cases in which the LCST and UCST regions have overlapped which are computationally more complicated. For current work, we considered systems that only show one LCST or one UCST, and other cases might be investigated in a future work. The LCST and/or UCST is the point where spinodal and binodal (coexistence) curves cross, in where there's a shared minima for the case of LCST and a shared maximum for the later.

The binodal curve, itself, represent the local thermodynamic equilibrium of two phases at contact, thus one may write the equilibrium criteria for component "*i*" at two phases as presented by Eq. (1) [2,5,19], where μ_i is the chemical potential of component *i* and superscripts *l* and *r*, refer to polymer lean and polymer rich phases respectively.

$$\mu_i^l = \mu_i^r \tag{1}$$

The spinodal condition requires that the second derivative of Δg_{mix} , with respect to the composition (in terms of volume fraction), at constant temperature and pressure, to be positive as presented by Eq. (2) [5,18,20];

$$\frac{\partial^2 \Delta g_m}{\partial \phi_i^2} \geq 0 \approx \frac{\partial^2 \Delta g_m}{\partial \phi_i^2} = 0 \tag{2}$$

In addition, applying material balance, in the form of volume fraction of the two components, one obtains Eq. (3), which must be holding on this point (and any point).

$$\phi_1^r + \phi_2^r = 1 \quad , \quad \phi_1^l + \phi_2^l = 1 \tag{3}$$

These set of equations must be solved simultaneously to find the corresponding temperature (LCST/UCST) in a trial and error procedure and by an initial guess, which is a kind of optimization problems that $\left|\Delta\mu_i^l - \Delta\mu_i^r\right| \rightarrow 0$ is used as main optimizing criteria (in which$\Delta\mu_i = \mu_i - \mu_i^0$ andμ_i^0 refers to standard state of the chemical potential of component "*i*"). For optimization purpose, Particle Swarm Optimization (PSO) Technique was used [21,22].

Chemical potential, μ_i in Eq. (1) (for $\left|\Delta\mu_i^l - \Delta\mu_i^r\right| \rightarrow 0$) can be calculated by using activity coefficient models such as Flory-Huggins theory and its extensions (such as Lattice Cluster Theory) [2]. These models require binary interaction parameters, which must be calculated or experimentally measured and this limits their application [23]. It must be noted that using a model which needs only pure component properties, is of the much interest [5]. Thus, thermodynamic model of Compressible Regular Solution theory (CRS) was considered in this paper for development of Model. The main equations of this theory for a binary solution are given by Eqs. (4)–(6) [20,24–26] where V_i accounts for molar volume of component "*i*".

$$\frac{\Delta g_{mix}}{kT} = \frac{\phi_1\tilde{\rho}_1}{N_1 v_1}\ln\phi_1 + \frac{\phi_2\tilde{\rho}_2}{N_2 v_2}\ln\phi_2 + \phi_1\phi_2\tilde{\rho}_1\tilde{\rho}_2\left(\delta_{1,0}-\delta_{2,0}\right)^2 + \phi_1\phi_2\left(\tilde{\rho}_1-\tilde{\rho}_2\right)\left(\delta_{1,0}^2-\delta_{2,0}^2\right) \tag{4}$$

$$\Delta\mu_1 = \ln\phi_1 + 1 - \phi_1 - \left(\frac{\tilde{\rho}_2/N_2 v_2}{\tilde{\rho}_1/N_1 v_1}\right)\phi_1 + \frac{\left(\tilde{\rho}_1\delta_{1,0}-\tilde{\rho}_2\delta_{2,0}\right)^2}{RT}\phi_2 V_1 \tag{5}$$

$$\Delta\mu_2 = \ln\phi_2 + 1 - \phi_2 - \left(\frac{\tilde{\rho}_1/N_1 v_1}{\tilde{\rho}_2/N_2 v_2}\right)\phi_1 + \left(\frac{\tilde{\rho}_1/N_1 v_1}{\tilde{\rho}_2/N_2 v_2}\right)\frac{\left(\tilde{\rho}_1\delta_{1,0}-\tilde{\rho}_2\delta_{2,0}\right)^2}{RT}\phi_1\phi_2 V_1 \tag{6}$$

The pure component properties are needed for the activity coefficient calculations using CRS theory, which can be obtained by group contribution methods (GCM) [20,24–26]. Group contribution methods, themselves, can be regarded as some QSPR method for estimation and calculation of physicochemical properties of interest. The solubility parameter values at temperature *T* in CRS model requires the estimation of the solubility parameter at 298 K through some group contribution methods (as given by$\delta_i^2(T) = \delta_i^2(298)[\rho_i(T)/\rho_i^0(T)]$), here the van Krevelen GCM was used [24]. In addition, the reduced density (hard core density) were calculated from the modified Sanchez-Lacombe Lattice Fluid model (SL-EOS) [27] (given as $\tilde{\rho} = 1 - \exp[-\tilde{\rho} - \tilde{P}/\tilde{T} - \tilde{\rho}^2/\tilde{T}]$) using an iterative root seeking technique [28] and the Constantinou and Gani group contribution method for evaluation for the scaling parameters (ρ^*,T^*,P^*) [24,25,27]. In addition, the coefficients of thermal expansion for each component were calculated through the modified SL-EOS model [27]. For calculation of$N_i v_i$ in CRS model (N_i represents number of hard cores in lattices of volumev_i), one might use$N_i v_i = Mw/\rho^*$ equality, where *Mw* is the molecular weight of components (for polymer the repeating units). In this case, Eq. (2) simplifies to Eq. (8) considering $\phi_1 = 1 - \phi_2$ as dependent composition [5];

$$\alpha_i = -\frac{\rho^*\left(\tilde{P}+\tilde{\rho}^2\right)}{\rho T^*\tilde{T}}\cdot\left(\tilde{T}\left(\exp\left[\tilde{\rho}+\frac{\tilde{P}}{\tilde{T}}+\frac{\tilde{\rho}^2}{\tilde{T}}\right]-1\right)-2\tilde{\rho}\right)^{-1} \tag{7}$$

$$\frac{\partial^2 \Delta g_m}{\partial \phi_2^2} = \frac{1}{\phi_1} + \left(\frac{1}{\phi_1}\right)\left(\frac{\tilde{\rho}_2 N_1 v_1}{\tilde{\rho}_1 N_2 v_2}\right) - 2\frac{\left(\tilde{\rho}_1\delta_{1,0}-\tilde{\rho}_2\delta_{2,0}\right)^2}{RT}V_1 \tag{8}$$

Using these equations, the temperature of interest, i.e. LCST and/or UCST, can be searched employing an appropriate optimization technique [22].

2.2. Method of calculations

Particle Swarm Optimization (PSO) technique was used in this work for determination of temperature which satisfies the thermodynamic modeling criteria. In thermodynamic modeling, the CRS model, itself, requires no optimization and calculation as this model is straightforward [5], however, finding the temperature of interest i.e. LCST and/or UCST, requires solution of a set of equations as described in previous section, which is an optimization problem. In this case, the number of variables in PSO is 1 (temperature) [22],