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Modeling Phase Equilibria in Polymer–Solvent Systems for Process Design[1]

A. Anderko[2]

An excess Gibbs energy model is presented for calculating phase equilibria in multicomponent systems containing polymers and solvents. The model represents a combination of a physical contribution obtained from a lattice model and a chemical contribution that accounts for association and solvation effects. The lattice model is based on a revised version of Freed's lattice-field theory developed by Hu, Prausnitz, and co-workers. The model accurately represents solvent activities and liquid–liquid equilibria in binary and ternary polymer solutions over wide ranges of temperature and polymer molecular weight. It is capable of reproducing liquid–liquid equilibria with upper and lower critical solution temperatures as well as closed-loop and hourglass-shaped phase diagrams. Because of its numerical simplicity, a reasonably small number of binary parameters, and its applicability to multicomponent systems, the model can be useful for modeling industrial processes involving polymers.

KEY WORDS: excess functions; lattice model; liquid–liquid equilibria; polymer solutions; vapor–liquid equilibria.

1. INTRODUCTION

Modeling of polymer manufacturing processes requires the knowledge of phase equilibria in multicomponent systems containing polymers and solvents. Therefore, it is necessary to have an accurate excess Gibbs energy model that can be implemented in the environment of a process simulator. In particular, the optimum method should be capable of representing both vapor–liquid and liquid–liquid equilibria over wide ranges of temperature and polymer molecular weight. It should have a reasonably small number of adjustable binary parameters that are defined for polymer segments rather than whole molecules. Also, the model should make it possible to

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[2] Simulation Sciences Inc., 601 South Valencia Avenue, Brea, California 92621, U.S.A.

use information obtained from binary data to predict the phase behavior of multicomponent mixtures.

The majority of excess Gibbs energy models that can be used for the correlation of polymer solution data has been derived from the Flory–Huggins lattice model [1] by introducing empirical functions to represent the temperature and composition dependence of the Flory χ parameter [2–4]. An alternative approach is based on local-composition models for polymer solutions [5, 6]. In addition to the correlative G^{E} models, several group-contribution models have been developed for predicting solvent activities [9–11].

Significant progress in the lattice theory of macromolecules has been achieved by Freed and co-workers [7], whose theory is formally an exact solution of the Flory–Huggins lattice. Hu et al. [8] revised Freed's model to simplify its mathematical form and improve agreement with the phase behavior of an Ising lattice and molecular simulations for binary monomer + multimer mixtures. In this study, we combine the model of Hu et al. [8] with a chemical contribution to the excess Gibbs energy and apply it to the correlation of vapor–liquid and liquid–liquid equilibria.

2. MODEL

For binary systems, Hu et al. [8] obtained an expression for the Helmholtz energy of mixing:

$$\frac{A_{\mathrm{mix}}}{N_r kT}=\frac{\varphi_1}{r_1}\ln\varphi_1+\frac{\varphi_2}{r_2}\ln\varphi_2+g\varphi_1\varphi_2 \tag{1}$$

$$g=\frac{1.2}{9}\left(\frac{1}{r_1}-\frac{1}{r_2}\right)^2+2\varepsilon_r+\frac{\varepsilon_r}{r_1}\varphi_2+\frac{\varepsilon_r}{r_2}\varphi_1-\frac{3}{2}\,1.074\varepsilon_r^2\varphi_1\varphi_2 \tag{2}$$

where N_r is the total number of sites on the lattice, r_1 and r_2 are numbers of segments of molecules 1 and 2, respectively, and $\varepsilon_r=\varepsilon/kT$ is the reduced interaction energy between the segments of molecules 1 and 2. For an incompressible, close-packed system, the Helmholtz energy of mixing is equal to the Gibbs energy of mixing (i.e., $G_{\mathrm{mix}}=A_{\mathrm{mix}}$).

To extend Eq. (1) to multicomponent mixtures, we recognize that Eq. (1) is formally similar to the Flory–Huggins model. The only difference is the composition dependence of the factor g. Therefore, the Helmholtz energy of mixing for a multicomponent system can be written in analogy to that from the multicomponent Flory–Huggins model [2] as

$$\frac{A_{\mathrm{mix}}}{N_r kT}=\sum_i\frac{\varphi_i}{r_i}\ln\varphi_i+\sum_i\sum_{j>i}g_{ij}\varphi_i\varphi_j \tag{3}$$

where the g_{ij} term is, in analogy with Eq. (2),

$$g_{ij}=\frac{1.2}{9}\left(\frac{1}{r_i}-\frac{1}{r_j}\right)^2+2\varepsilon_{r,ij}+\frac{\varepsilon_{r,ij}}{r_i}\varphi_j+\frac{\varepsilon_{r,ij}}{r_j}\varphi_i-\frac{3}{2}\,1.074\varepsilon_{r,ij}^2\varphi_i\varphi_j \tag{4}$$

The temperature dependence of ε_r is expressed as

$$\varepsilon_r=a_1+a_2/T+a_3\ln T \tag{5}$$

This form was proposed by Qian et al. [4] for the Flory–Huggins χ parameter by considering its enthalpy and entropy components. A similar reasoning can also be applied to the model considered in this study. Preliminary studies have shown that this form of the temperature dependence is superior to other forms of similar complexity, especially with respect to extrapolation to lower or higher temperatures. In addition to ε_r, a second adjustable parameter, c_r, is introduced to calculate the effective chain length of a polymer:

$$r_i=c_{r,i}v_i/v_{\text{ref}} \tag{6}$$

where v_i is the molar volume of the polymer and v_{ref} is a reference volume, which can be conveniently assumed to be equal to a solvent's molar volume. As a first approximation, the parameter c_r can be assumed to be equal to one, which leaves ε_r as the only adjustable parameter in Eqs. (3) and (4).

For systems with specific interactions, Veytsman [12] developed a simple technique for incorporating association and solvation effects into the lattice-fluid formalism. If specific interactions play a significant role in the mixture, the Gibbs energy of mixing is calculated as a sum of a physical and a chemical contributions:

$$G_{\text{mix}}=G_{\text{mix}}^{\text{phys}}+G^{\text{chem}} \tag{7}$$

where $G_{\text{mix}}^{\text{phys}}$ is defined by Eq. (3) and G^{chem} is given, for a close-packed lattice, by

$$\frac{G^{\text{chem}}}{N_rkT}=\sum_i^m\sum_j^n\frac{N_{ij}}{N_r}+\sum_i^m\frac{N_{\text{d}}^i}{N_r}\ln\frac{N_{i0}}{N_{\text{d}}^i}+\sum_j^n\frac{N_{\text{a}}^j}{N_r}\ln\frac{N_{0j}}{N_{\text{a}}^j},$$
$$i=1,\dots,m,\quad j=1,\dots,n \tag{8}$$

where N_{ij} is the number of bonds between a donor group i and an acceptor group j, N_{d}^i is the total number of donor sites of type i, N_{a}^j is the total number of acceptor sites of type j, $N_{i0}=N_{\text{d}}^i-\sum_j N_{ij}$, and $N_{0j}=N_{\text{a}}^j-\sum_i N_{ij}$.

The quantities N_{ij} are obtained by solving a set of mn simultaneous quadratic equations:

$$\frac{N_{ij}}{N_r}=\left(\frac{N_\mathrm{d}^i}{N_r}-\sum_k^n\frac{N_{ik}}{N_r}\right)\left(\frac{N_\mathrm{a}^j}{N_r}-\sum_k^m\frac{N_{kj}}{N_r}\right)\exp\left(\frac{-\Delta g_{ij}}{RT}\right),$$
$$i=1,\ldots,m,\quad j=1,\ldots,n \tag{9}$$

where the standard Gibbs energy of bond formation between a donor of type i and an acceptor of type j is related to the enthalpy Δh_{ij} and entropy Δs_{ij} of bond formation by $\Delta g_{ij}=\Delta h_{ij}-T\Delta s_{ij}$.

It is worthwhile to examine the effect of solvation on liquid–liquid equilibria predicted by the combined model. If the interaction parameter ε/k is independent of temperature, the physical contribution to the excess Gibbs energy can predict only an upper critical solution temperature because it is based on an incompressible, close-packed lattice model. This behavior may be changed by introducing association or solvation effects, which are accounted for by the G^chem contribution. In particular, strong solvation may give rise to a lower critical solution temperature. To verify

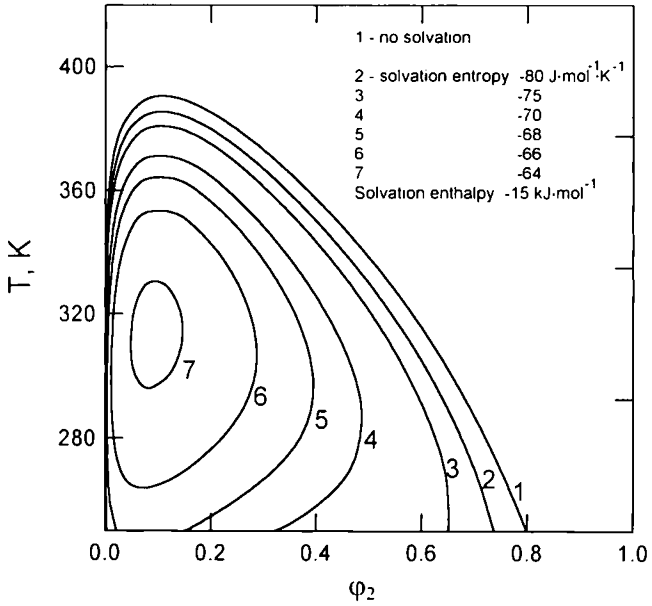

Fig. 1. Liquid–liquid coexistence curve calculated for a mixture of a solvent ($r_1 = 1$) and a polymer ($r_2 = 100$) with and without solvation. The solvation entropy is varied, while the solvation enthalpy is kept at a constant value of -15 kJ · mol^{-1}. The parameter ε/k is equal to 120 K over the whole temperature range.

this, liquid–liquid equilibrium was calculated for a binary system composed of monomers and 100-mers that are capable of solvation as the only possible specific interaction [i.e., $m = n = 1$ in Eqs. (8) and (9)]. For simplicity, the number of solvation (either acceptor or donor) sites was assumed to be equal to the number of repeat units (i.e., $N_d^1 = r_1 N_1$ and $N_a^1 = r_2 N_2$). In this case, only one quadratic equation [Eq. (9)] has to be solved for N_{11}. The effect of solvation is illustrated in Fig. 1, which shows the different shapes of the miscibility gap when the entropy of solvation is varied from −80 to −64 J · mol^{-1} · K^{-1}. The solvation enthalpy is kept at a constant value of −15 kJ · mol^{-1}, which is typical for hydrogen bonds of intermediate strength. As shown in Fig. 1, solvation causes the appearance of a closed-loop miscibility gap. The immiscible region rapidly shrinks as the solvation becomes stronger.

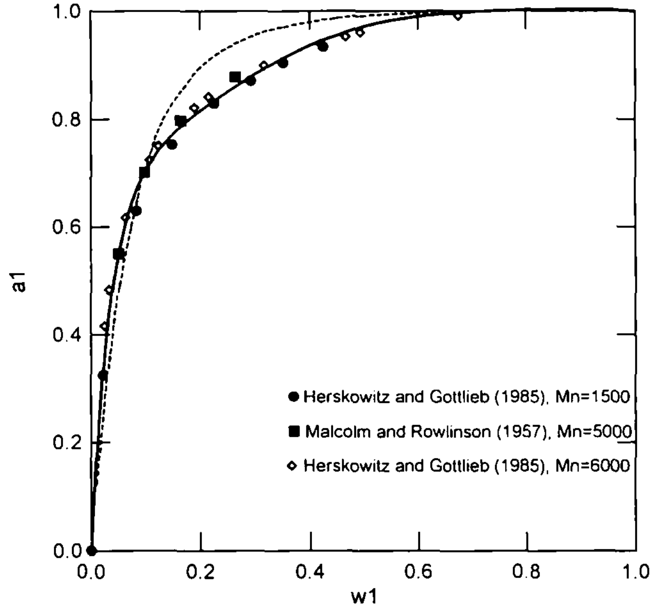

Fig. 2. Solvent activity calculated for the system water(1)–polyethylene glycol(2) at $T = 333.15$ K (data from Malcolm and Rowlinson [13] and Herskowitz and Gottlieb [14]). The solid line shows the activity obtained when the solvation effects are taken into account with the following model parameters: $\Delta h^0 = -10.411$ kJ · mol^{-1}, $\Delta s^0 = -27.31$ J · mol^{-1}, $\varepsilon_r = 0.7140$, and $c_r = 0.5335$. The temperature range for the correlation is $293.15 \leq T \leq 338.15$ K and the molecular weight range is $1500 \leq M_n \leq 6000$. The dashed line shows the results obtained when the solvation is neglected.

3. RESULTS AND DISCUSSION

The model has been applied to correlate vapor-liquid and liquid-liquid equilibria in systems containing polymers and solvents. First, the usefulness of the chemical contribution was verified by correlating solvent activities in the system water + polyethylene glycol (PEG), which exhibits strong hydrogen bonding. The results are illustrated in Fig. 2. If the chemical contribution is neglected and only ε_r and c_r are regressed, the shape of the solvent activity versus composition curve cannot be correctly reproduced (cf. the dashed curve in Fig. 2). On the other hand, the data can be very accurately correlated using the chemical contribution (cf. the solid curve in Fig. 2). Only one solvation equilibrium has been taken into account (i.e., $m = n = 1$, $N_d^1 = r_1 N_1$, and $N_a^1 = r_2 N_2$). With four adjustable parameters (i.e., the enthalpy and entropy of solvation and temperature-independent ε_r and c_r parameters), the solvent activities are accurately

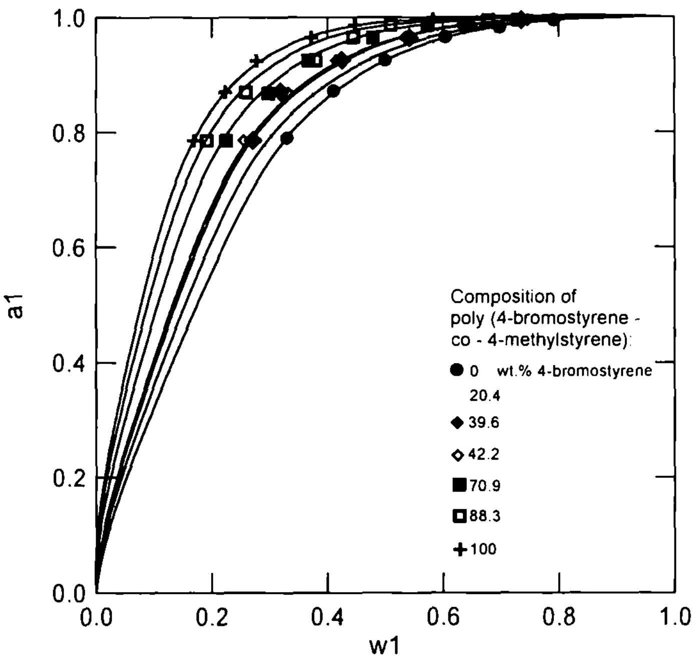

Fig. 3. Solvent activity calculated for the system toluene(1) + poly(4-bromostyrene-co-4-methylstyrene)(2) at $T = 294.15$ K (data from Corneliussen et al. [15]). The model parameters for the pair toluene + poly(4-bromostyrene) are $\varepsilon_r = 0.2708$ and $c_r = 1$ and those for the pair toluene + poly(4-methylstyrene) are $\varepsilon_r = 0.1573$ and $c_r = 1$.

reproduced for temperatures ranging from 293.15 to 338.15 K and molecular weights of PEG ranging from 1500 to 6000. It should be noted that the use of only solvation equilibria (without self-association) is an oversimplification of physical phenomena in this system. However, it is entirely sufficient to represent the data within experimental uncertainty.

It is important that the model be applicable to systems containing copolymers as well as homopolymers. To verify the model's performance for copolymers, solvent activities have been computed for the system toluene + poly(4-bromostyrene–co-4-methylstyrene). No chemical contribution is necessary for this system. The interaction parameters ε_r have been regressed from the data for two binary systems containing homopolymers: toluene + poly-4-bromobenzene and toluene + 4-methylstyrene. The parameters c_r have been set equal to 1. In this way, the interaction parameters for the segment pairs toluene–4-bromostyrene and toluene–4-methylstyrene have been obtained. The interaction parameters between the 4-bromostyrene and the 4-methylstyrene segments have been assumed to be equal to zero. These parameters have then been used to predict

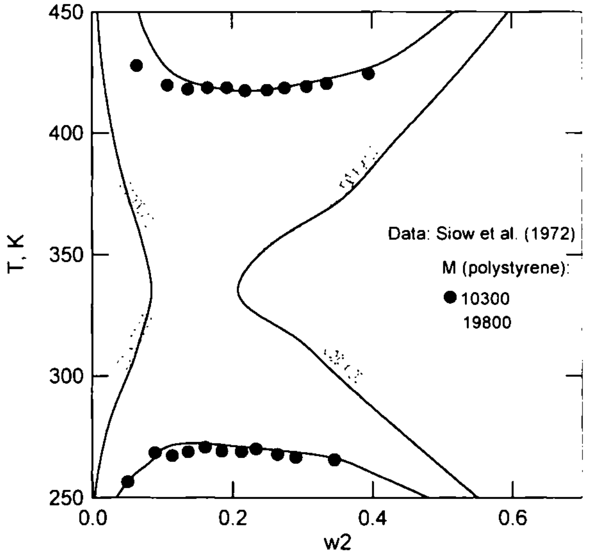

Fig. 4. Liquid–liquid equilibria calculated for the system acetone(1) + polystyrene(2) for two molecular weights of polystyrene (i.e., $M_n = 10{,}300$ and 19,800; data from Siow et al. [16]). The regressed model parameters are $\varepsilon_r = -4.100 + 212.8/T + 0.6475 \ln T$ and $c_r = 0.668$.

solvent activities for systems containing copolymers with different compositions. As shown in Fig. 3, the results are very satisfactory.

The model is also capable of reproducing liquid–liquid equilibria with good accuracy. This is illustrated in Fig. 4 for the system acetone + polystyrene. This system shows an upper and lower critical solution point or an hourglass-shaped miscibility gap depending on the molecular weight of the polymer. It should be noted that the model is based on a close-packed lattice, and as a result, it does not reproduce the compressibility effects that usually cause the lower critical solution temperatures (LCST). Therefore, it is necessary to introduce a sufficiently flexible, empirical temperature dependence for the energetic parameter ε_r. As shown in Fig. 4, the LCST phase behavior can be accurately reproduced using Eq. (5) to fit the temperature dependence of ε_r. Also, the model correctly reproduces the effect of molecular weight on the transition between an hourglass-shaped diagram and one with two separate miscibility gaps. Thus, the phase behavior of this system can be modeled over a wide temperature range with four binary parameters: c_r and the three parameters that determine the

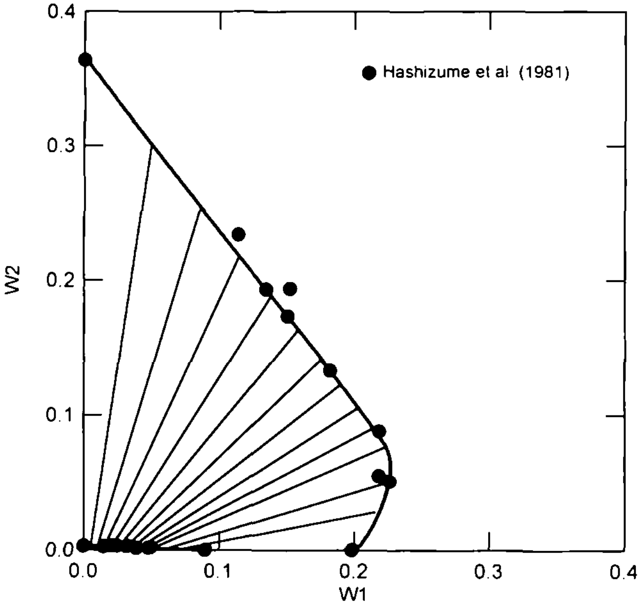

Fig. 5. Liquid–liquid equilibria calculated for the system polystyrene (1; $M_n = 42{,}800$) + polystyrene(2; $M_n = 107{,}000$) + cyclohexane(3) at $T = 287.15$ K (data from Hashizume et al. [17]). The model parameters are $\varepsilon_{r,12} = 0.137196$, $\varepsilon_{r,13} = 0.2925$, $\varepsilon_{r,23} = 0.2925$, $c_{r1} = 0.5811$, $c_{r2} = 0.5811$, and $c_{r3} = 1$.

temperature dependence of ε_r. Also, the model accurately represents the liquid–liquid behavior of model polydisperse systems as illustrated in Fig. 5 for a system composed of cyclohexane and two nearly monodisperse polystyrene fractions. This indicates that the model can be applied to more complex systems containing polydisperse polymers. In a forthcoming study, the model will be applied to ternary and multicomponent polymer solutions and blends containing polydisperse polymers.

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