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Fluid Phase Equilibria 231 (2005) 77–83

FLUID PHASE EQUILIBRIA

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Extension of the NRTL and NRF models to multicomponent polymer solutions: Applications to polymer–polymer aqueous two-phase systems

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Received 23 June 2004; received in revised form 8 November 2004; accepted 11 January 2005

Abstract

The modified NRTL (nonrandom two-liquid) model for multisolvent, single polymer solutions proposed by Chen [C.C. Chen, Fluid Phase Equilib. 83 (1993) 301–312] and the modified NRF (nonrandom factor) model for single solvent, single polymer solutions, proposed by Zafarani-Moattar and Sadeghi [M.T. Zafarani-Moattar, R. Sadeghi, Fluid Phase Equilib. 202 (2002) 413–422] have been used for the representation of the excess Gibbs energy of multicomponent polymer solutions. The models represent a synergistic combination of the Flory–Huggins description for the configurational entropy of mixing molecules of different sizes and the NRTL or NRF theory for the local composition contribution from mixing solvents and segments of polymers. These models have been applied for the correlation of the phase behavior of some polymer–polymer aqueous two-phase systems. The results show that the models can accurately correlate a series of the liquid–liquid equilibrium phase diagrams of aqueous two-phase systems at different polymer molecular weights.

Keywords: Excess Gibbs energy; NRTL; NRF; Aqueous two-phase systems; Liquid–liquid equilibrium; Polymer solutions

1. Introduction

Aqueous solutions of two incompatible polymers such as polyethylene glycol (PEG) and dextran (DEX) form liquid–liquid two-phase systems, in which each aqueous phase is rich with respect to one of the phase-forming polymers. These polymer–polymer aqueous two-phase systems provide a powerful method for separating mixtures of biomolecules by extraction [1–4].

The thermodynamics of polymeric solutions has been studied extensively. Principal models for phase equilibrium calculations are those of Flory [5] and Huggins [6], who developed an expression based on lattice theory to describe the nonidealities of polymer solutions and of Edmond and Ogston [7], who modeled nonidealities with a truncated osmotic virial expansion based on McMillan–Mayer theory [8]. These models have been extended and applied to aqueous two-phase systems by others [2,7,9–15]. Local composition models UNIQUAC, UNIFAC, NRTL and NRF have also been used to describe the thermodynamics of polymer solutions. Among these local composition models, only the UNIQUAC model [16] can be used for the modeling of the phase equilibrium of polymer solutions without further modification. Kang and Sandler [17,18] and Hartounian et al. [19] used the UNIQUAC solution model to deal with the phase behavior of polymer–polymer aqueous two-phase systems. The UNIFAC model [20] was extended to polymer solutions by Oishi and Prausnitz [21]. Tan and Shen [22] used the polymer UNIFAC model to represent the LLE phase diagrams of polymer–polymer aqueous two-phase systems. Two different versions of the NRTL model [23] have been used for polymer solutions. Chen [24] developed a segment-based local composition model for multisolvent, single polymer solutions, which uses a combination of the Flory–Huggins expression for the entropy of mixing molecules of different sizes and the

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doi:10.1016/j.fluid.2005.01.003

NRTL equation for weak local physical interactions between solvent and segments of polymer chains. More recently, Wu et al. [25] developed the modified NRTL model for the representation of the Helmholtz energy of polymer solutions. They used a slightly different version of the NRTL equation; and for the entropic contribution, the truncated Freed [26] correction to the Flory–Huggins expression as first correction was used. Later, Wu et al. [27] further extended their polymer NRTL model to describe the LLE of PEG–DEX aqueous two-phase systems.

Recently, Haghtalab and Vera [28] developed an NRF model for electrolyte solutions. It was shown [28–30] that the model consistently produces better results than the NRTL model and reproduces the experimental value from the dilute region up to saturation. In our previous paper [31], the NRF model was extended to single solvent, single polymer solutions and applied to correlate the solvent activity of some polymer solutions. It was shown [31] that the model consistently produces better results than the polymer NRTL, Flory–Huggins and UNIQUAC models and reproduces the experimental value from the dilute region up to saturation. The polymer NRF model [31] consists of two contributions due to the configurational entropy of mixing, represented by the Flory–Huggins relation, and to the enthalpic contribution, represented by local compositions through nonrandom factors.

In this work, the modified NRTL model for multisolvent, single polymer solutions [24] and the modified NRF model for single solvent, single polymer solutions [31] have been further developed for the representation of the excess Gibbs energy of multicomponent polymer solutions. To obtain the necessary expression for excess Gibbs energy for polymer solutions we considered two contributions. The modified NRTL and NRF equations were used for weak local physical interactions between solvents and segments of polymer chains (the local composition contribution). The Flory–Huggins expression for the configurational entropy of mixing was used as an entropic contribution to the excess Gibbs energy. The applicability of the developed models has been tested using experimental liquid–liquid equilibrium phase diagrams of some polymer–polymer aqueous two-phase systems.

2. Outline of the thermodynamic model

As in our previous work [31], we assumed that the excess Gibbs energy of a polymer solution can be expressed as the sum of the configurational entropy of mixing (entropic contribution), $G^{\text{EX,Config.}}$, and the local composition contribution,$G^{\text{EX,LC}}$:

$$G^{\text{EX}} = G^{\text{EX,Config.}} + G^{\text{EX,LC}} \tag{1}$$

Therefore, the activity coefficient of component I (polymers or solvents) in a polymer solution can also be considered as the sum of two contributions:

$$\ln \gamma_I = \ln \gamma_I^{\text{Config.}} + \ln \gamma_I^{\text{LC}} \tag{2}$$

In this work, the Flory–Huggins expression was used for the entropic contribution and the modified NRTL and modified NRF equations were used for the local composition contribution to the excess Gibbs energy.

2.1. Entropic contributions to the excess Gibbs energy

The Flory–Huggins equation for the configurational entropy of mixing of multicomponent polymer solutions can be written as:

$$\frac{G^{\text{EX,Config.}}}{RT} = \sum_I n_I \ln \frac{\phi_I}{x_I} \tag{3}$$

therefore

$$\ln \gamma_I^{\text{Config.}} = \ln\left(\frac{\phi_I}{x_I}\right) + 1 - \frac{\phi_I}{x_I} \tag{4}$$

where

$$\phi_I = \frac{r_I n_I}{\sum_J r_J n_J} \tag{5}$$

In these relations, n_I, x_I and r_I are the number of moles, the mole fraction and the number of segments of the component I. Following Chen [24] we assume that the molar volume of all segments and solvents are constant, thus for the solvents $r_I = 1$.

2.2. Local composition contributions to the excess Gibbs energy

Following Chen [24], for the modification of the NRF and NRTL models to polymer solutions the local composition concept is applied to the individual segments and solvent molecules, not the polymer chain. This approach reflects the vision that each segment should exert unique local physical interaction characteristic with its immediate neighboring solvent species or segments. This unique physical interaction of the segments determines the most favorable local environment around a segment. Following the NRTL derivation, the effective local mole fractions X_{ji} and X_{ii} of species j and i, respectively, in the immediate neighborhood of a central species i are related by

$$\frac{X_{ji}}{X_{ii}} = \left(\frac{X_j}{X_i}\right) G_{ji} \tag{6}$$

where

$$X_i = \frac{x_I r_{i,I} \sigma_I}{\sum_J \sum_j x_J r_{j.J}} \tag{7}$$

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{8}$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \tag{9}$$