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Representation of binodal curves for aqueous polymer solutions using a new local composition model

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Abstract

A new local composition model is used to reproduce the phase separation phenomena of aqueous polymer solutions. The energy parameters can be expressed by a quadratic function of temperature. Solutions of polyethylene glycol or polypropylene glycol in water are studied. The phase equilibria of these binary solutions are represented with sufficient accuracy.

Keywords: Model; PEG; Phase separation; Polymer; PP; Solvent

1. List of symbols

A_{21}, B_{21}, C_{21}	coefficients of Eq. (8)
A_{12}, B_{12}, C_{12}	coefficients of Eq. (9)
a_{21}, a_{12}	binary energy parameters
g^{E}	excess molar Gibbs free energy
M	molecular weight
n	degree of polymerization
p	exponent
R	universal gas constant
r_i	molecular size parameter of pure component i
T	absolute temperature
x_i	liquid-phase mole fraction of component i

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1.1. Greek letters

α, β	two liquid phases in equilibrium
γ_i	activity coefficient of component i
ρ_{12}	r_2/r_1
τ_{21}, τ_{12}	binary parameters are defined by Eqs. (4) and (5)
ϕ_i	segment fraction of component i
ϕ'_1, ϕ'_2	modified segment fractions of components 1 and 2 as defined by Eqs. (2) and (3)

2. Introduction

Several investigations have been carried out to represent phase separation in aqueous polymer solutions. Karlstroem [1] calculated a phase diagram with a lower critical solution temperature (LCST) for polyethylene oxide (PEO) in water using the Flory–Huggins theory, assuming that each segment of the PEO chain may exist in two forms due to the rotations around C–C and C–O bonds. Prange et al. [2] applied a quasi-chemical partition function to represent the thermodynamic properties of aqueous solutions of non-electrolytes, including linear polymers and cross-linked polymers. They considered that each polymer segment may possess three energetically different contact sites. Sites are distinguished into those that interact through dispersion forces and those that can participate in hydrogen bonds. Furthermore, these authors included a fluctuation correction, as proposed by de Pablo and Prausnitz [3], in their final equation to represent quantitatively upper or lower critical solution phenomena. Kim et al. [4] developed a blob calculation method of two-step renomalization for the asymmetric closed-loop diagrams of polymer–solvent mixtures in terms of blobs of polymers and a local composition model. The proposed model described only qualitatively a closed-loop diagram for polyethylene glycol (PEG-2290) and water mixtures. Matsuyama and Tanaka [5] introduced a simple model of solvation to describe lower critical solution points in polymer solutions. Their model predicted that physical bond formation between polymer segments and solvents can be the main cause of miscibility gaps. Hu et al. [6] revised Freed's lattice-field theory for binary polymer solutions and introduced a secondary lattice to account for highly oriented interaction between segments using the double-lattice theory. They reproduced co-existence curves for systems having an upper critical solution temperature (UCST) or an LCST or a miscibility loop with both UCST and LCST. Yu et al. [7] applied their chemical solvation model [8] to correlate binodal curves for the PEG and water and polypropylene glycol (PPG) and water systems by considering: (1) cross association due to the hydrogen bonds between polymer and water; (2) the Flory–Huggins equation for the entropy change; and (3) the NRTL equation for the interaction. These models are quite complicated.

Binodal curves have been calculated [9] for mixtures of small molecules over a wide temperature range using a new local composition model and better agreement was obtained between calculated and experimental values for aqueous systems with both LCST and UCST than when applying the chemical model of Yu and Nishiumi [8]. In this paper we apply our previous model [9] to the calculation of the phase equilibria of aqueous polymer solutions.

3. Solution model

Our model derives the excess Gibbs free energy g^E for binary mixtures as

$$\frac{g^E}{RT} = x_1 \ln\frac{\phi'_1}{x_1} + x_2 \ln\frac{\phi'_2}{x_2} - x_1 \ln(\phi_1 + \phi_2\tau_{21}) - x_2 \ln(\phi_2 + \phi_1\tau_{12}) \tag{1}$$

where the modified segment fractions ϕ'_1 and ϕ'_2, and the binary parameters τ_{21} and τ_{12}, related to the energy parameters a_{21} and a_{12}, are given by

$$\phi'_1 = \frac{x_1 r_1^p}{x_1 r_1^p + x_2 r_2^p} \tag{2}$$

$$\phi'_2 = \frac{x_2 r_2^p}{x_1 r_1^p} + x_2 r_2^p \tag{3}$$

$$\tau_{21} = \exp(-a_{21}/T) \tag{4}$$

$$\tau_{12} = \exp(-a_{12}/T) \tag{5}$$

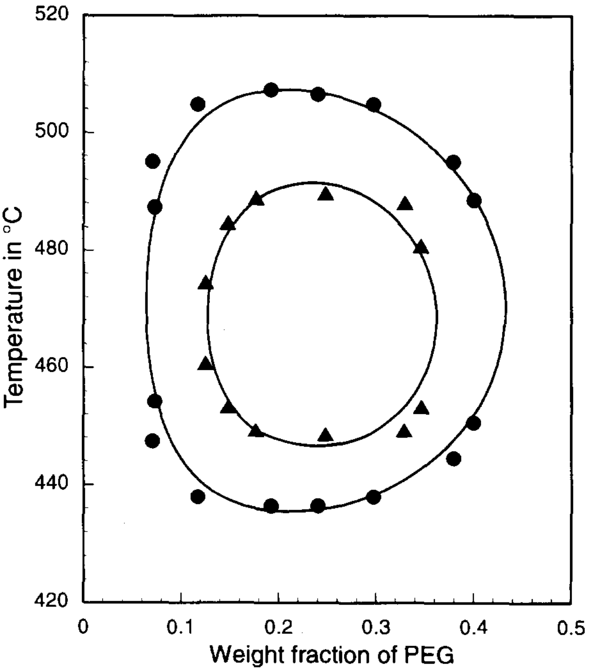

Fig. 1. Calculated coexistence curves for PEG + water mixtures. Experimental [10]: ●, $M_{PEG} = 2290$; ▲, $M_{PEG} = 2180$. ——, Calculated with quadratic temperature-dependent energy parameters.

The activity coefficients of both components are expressed by

$$\ln \gamma_1 = \ln \frac{\phi'_1}{x_1} + 1 - \frac{\phi'_1}{x_1} - \ln(\phi_1 + \phi_2 \tau_{21}) - \left(1 - \frac{\phi_1}{x_1}\right) + \phi_2\left(\frac{\tau_{21}}{\phi_1 + \phi_2 \tau_{21}} - \frac{\tau_{12}/\rho_{12}}{\phi_2 + \phi_1 \tau_{12}}\right) \tag{6}$$

$$\ln \gamma_2 = \ln \frac{\phi'_2}{x_2} + 1 - \frac{\phi'_2}{x_2} - \ln(\phi_2 + \phi_1 \tau_{12}) - \left(1 - \frac{\phi_2}{x_2}\right) + \phi_1\left(\frac{\tau_{12}}{\phi_2 + \phi_1 \tau_{12}} - \frac{\rho_{12}\tau_{21}}{\phi_1 + \phi_2 \tau_{21}}\right) \tag{7}$$

where $\rho_{12} = r_2/r_1$ and the subscripts 1 and 2 represent solute (polymer) and solvent (water).

In this work, the exponent p is taken as 2/3 and the energy parameters can be expressed by a quadratic function of the temperature

$$a_{21} = A_{21} + B_{21}T + C_{21}T^2 \tag{8}$$

$$a_{12} = A_{12} + B_{12}T + C_{12}T^2 \tag{9}$$

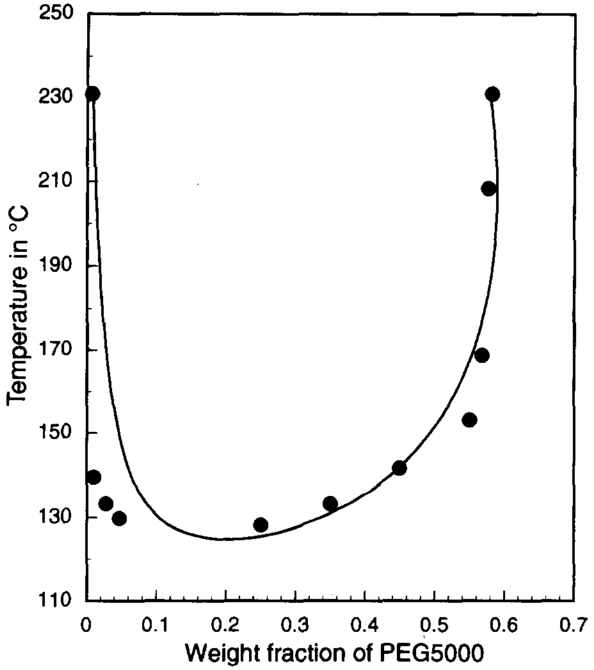

Fig. 2. Calculated coexistence curve of PEG + water mixture: ●, experimental [11], $M_{PEG} = 5000$; ——, calculated with quadratic temperature-dependent energy parameters.

4. Calculated results

Polymers were considered to be single components, although they generally have a molecular weight distribution. Binary mixtures PEG or PPG with water have been considered. The chemical formulae of PEG and PPG were taken as $H{-}(OCH_2CH_2)_n{-}OH$ and $H{-}(OCH_2CH(CH_3))_n{-}OH$. The degree of polymerization n was $n = (M_{PEG} - 18.0152)/44.0530$ for PEG, and $n = (M_{PPG} - 18.0152)/58.0798$ for PPG, where M_{PEG} and M_{PPG} are the molecular weights of PEG and PPG. In this work, $\rho_{12} = 1.0/n^{0.75}$ [7].

The mutual solubility points of the solutions of PEG or PPG with water are calculated by solving the thermodynamic equations of isoactivity for the components in equilibrated liquid phases

$$(x_1\gamma_1)^\alpha = (x_1\gamma_1)^\beta \tag{10a}$$

$$(x_2\gamma_2)^\alpha = (x_2\gamma_2)_\beta \tag{10b}$$

where α and β are the liquid phases.

Table 1 shows the coefficients of Eqs. (8) and (9) used in this work. Figures 1-3 compare the calculated results with the experimental values for the PEG + water and PPG + water systems. The quadratic temperature dependence of the energy

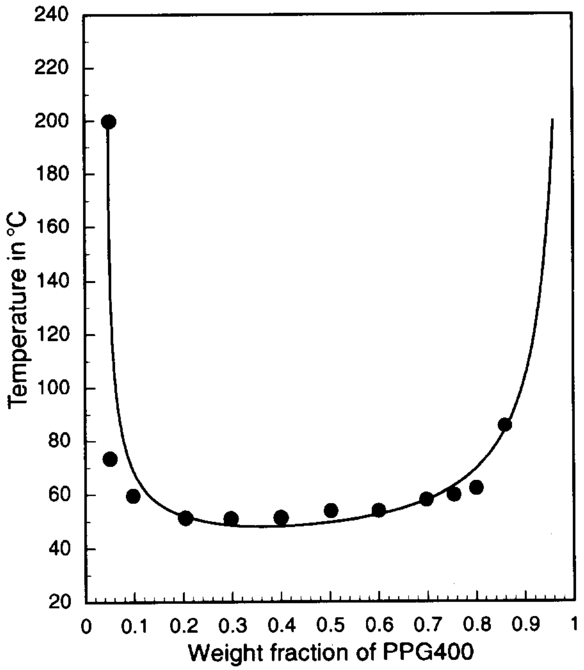

Fig. 3. Calculated coexistence curve for PPG + water mixture: ●, experimental [11], $M_{PPG} = 400$; ——, calculated with linearly temperature-dependent energy parameters.

Table 1
The values of model parameters

System (1 + 2)	Parameters	Ref.		Ref.
	A_{12} A_{21}	B_{12} B_{21}	C_{12} C_{21}	
PEG2180 + water	−1744.906	4.8422	−0.0032	10
	−94713.207	260.9218	−0.1718	
PEG2290 + water	−2067.589	5.6966	−0.0037	10
	−83697.768	230.9172	−0.1508	
PEG5000 + water	−163.392	0.7720	−0.0007	11
	6923.498	−30.7068	0.0494	
PPG 00 + water	−979.240	3.5618		11
	882.270	1.8719		

parameters gave a good representation of the experimental data, except for the PPE + water mixture, where the linear temperature dependence of the energy parameters led to improved correlated results. We may conclude that the present simple model can reproduce well the phase equilibria of the aqueous polymer mixtures studied.

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