Review

Phase equilibria for polymer systems

by

Y. IWAI†, T. FURUYA†, T. ISHIDAO† and Y. ARAI†

ABSTRACT

Phase equilibria for polymer systems such as (1) vapor-liquid equilibria, (2) liquid-liquid equilibria, (3) aqueous two-phase system, and (4) volume-phase transition of polymeric gel were reviewed. The authors first described solubilities of gases and vapors in molten polymers and showed that the UNIFAC-FV model is successful to predict the vapor-liquid equilibria. Furthermore, liquid-liquid equilibria of polymer-hydrocarbon solutions were discussed and it was shown that the UNIFAC-FV model with a modification is also useful to correlate the liquid-liquid equilibria. And the liquid-liquid equilibria of aqueous two-phase system and the partition of biomolecules were presented and the Flory-Huggins equation with a modification is found to be successful to correlate these phase equilibria. Finally, the volume-phase transition of polymeric gel and the concentrations between inside and outside the gels were described. The Flory-Huggins equation coupled with the rubber elasticity equation was found to be helpful to correlate these phase equilibria.

1. INTRODUCTION

In the chemical industry, it is very important to design appropriate separation equipment, because its cost is reported to be from about 40 to 60% of the total initial and running costs. To design such equipment, the knowledge of phase equilibria is necessary. There are not many data available for phase equilibria, and a successful correlation or prediction method has not yet been developed for polymer systems compared to low molecular weight component systems. In this review, the phase equilibria of mixtures containing low molecular weight components and polymers will be described.

2. VAPOR-LIQUID EQUILIBRIA

Vapor-liquid equilibria (VLE) at low pressures can be explained by Eq. (1).

\[ p_i = a_ip^*_i \]  

where \( p_i \) is the partial pressure, \( p^*_i \) is the saturated vapor pressure, and \( a_i \) is the activity in the liquid
phase for i-th component. Therefore, the VLE can be calculated from activity. Oishi and Prausnitz first applied a group contribution method to polymer solutions. They proposed the following expression for the activity of solute 1 in polymer 2.

\[
\ln a_1 = \ln a_1^c + \ln a_1^R + \ln a_1^{FV}
\]

where \(\ln a_1^c\) and \(\ln a_1^R\) are calculated with UNIFAC, which is a group contribution method, and \(\ln a_1^{FV}\) is calculated with the free volume derived by Flory.

Iwai et al. reexamined the free volume term and proposed a new free volume expression as follows.

\[
\ln a_1^{FV} = C_1 \left[ \ln \left( \frac{\bar{v}_r}{\bar{v}_{r,M}} \right) + \bar{v}_1 \left\{ \exp \left( 0.3\bar{v}_1 \right) \left(1.66 - 0.3\bar{v}_1\right) \right\} \right]
\]

where

\[
\bar{v}_r = (\bar{v} - 1) \exp \left[ -\left\{ 18 (\bar{v} - 1)^2 + 9 (\bar{v} - 1) + 2 \right\} / 6 (\bar{v} - 1)^2 \right]
\]

\[
\bar{v}_1 = \frac{v_1}{v_1^*}
\]

\[
\bar{v}_{r,M} = \left( \frac{v_1 w_1 + v_2 w_2}{v_1^* w_1 + v_2^* w_2} \right)
\]

The hard-core volume of molecule \(v_1^*\) and the external degrees of freedom of solute \(C_1\) can be calculated with the following equations.

\[
v_1^* = \frac{1}{M_1} \sum_k \nu_{k}^{(1)} V_k^*
\]

\[
C_1 = \sum_k \nu_{k}^{(1)} C_k
\]

where \(\nu_{k}^{(1)}\) is the number of group \(k\) in molecule \(i\), \(M_1\) is the molecular weight of component \(i\), \(V_k^*\) is the hard-core volume of group \(k\), and \(C_k\) is the external degrees of freedom of group \(k\). The solubilities of several solutes in polymers can be well predicted with the combination of the free volume term and UNIFAC as shown in Fig. 1. The free volume given by Eq. (4) can also be adopted.

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Fig. 1  Solubilities of m-xylene (1) in polystyrene (2): \(\circ\) Exp.; \(---\) Calc.
3. LIQUID-LIQUID EQUILIBRIA

Liquid-liquid equilibria (LLE) can be calculated by solving the following equations.

\[ \Delta \mu_1 = \Delta \mu_2 \]  \hspace{1cm} (9)

where \( \Delta \mu = \mu - \mu_{\text{pure}} \), and I and II denote liquid phases I and II, respectively. Only qualitative explanation can be given by the Flory-Huggins equation below the upper critical solution temperature (UCST).

Iwai et al. correlated the solubility curves of the cyclopentane (1)-polystyrene (2) system. The chemical potentials, empirically modified, was proposed.

\[ \Delta \mu_1 / RT = \ln \phi_1 + (1 - r_1 / r_2) \phi_2 + p \cdot V^*_{1} \left[ 3 T \ln \left( (v_1^{1/3} - 1) / (v_2^{1/3} - 1) \right) + (1/v_1 - 1/v) + (V^*_{1} \theta^2 / v)(\theta - b \phi_1 \phi_2) \right] \chi_{12} \]  \hspace{1cm} (10)

where \( r \) is the number of segments per molecule, \( V^* \) is the molar hard-core volume, \( \theta \) is the surface fraction. The similar expression for \( \Delta \mu_2 / RT \) can be derived. The interaction parameter \( \chi_{12} \) was assumed to be a function of the volume fraction of polystyrene.

\[ \chi_{12} = a \exp (b \phi_2) \]  \hspace{1cm} (11)

The parameters \( a \) and \( b \) seemed to be a function of temperature and molecular weight of polystyrene as follows to correlate the solubility curves.

Fig. 2 Cloud points for cyclopentane (1)-polystyrene (2) systems: ○ Exp.; —— Calc.

Fig. 3 Cloud points for cyclopentane (1)-polystyrene (2) systems: ○ Exp.; —— Calc.
The correlation results are good as shown in Fig. 2.

The quantitative representation for liquid-liquid equilibria above the lower critical solution temperature (LCST) is more difficult. Iwai et al. have attempted to correlate the LLE above LCST for the cyclopentane-polystyrene system using the UNIFAC-FV model with a modification and fairly good results have been obtained as shown in Fig. 3.

4. AQUEOUS TWO-PHASE SYSTEM

Aqueous two-phase system is one of the most interesting topics for study in the field of liquid-liquid equilibria containing polymers. Usually, dextran (DEX) and poly (ethylene glycol) (PEG) are used as water-soluble polymers. As the polymers possess the molecular weight distribution, the effect of the molecular weight distribution as well as the average molecular weight on LLE becomes very important. In recent years, therefore, experimental LLE data of aqueous two-phase systems containing the molecular weight distribution measurement are reported. The Flory-Huggins model have been used to calculate the liquid-liquid equilibria for the system containing DEX, PEG, and water. However, the Flory-Huggins model is not suitable for such systems that exhibit specific interactions such as hydrogen bonding. To correlate LLE of polymer solutions quantitatively, the Flory-Huggins interaction parameter is not constant in many cases and it depends on the composition and polymer molecular weight.

Furuya et al. have attempted to modify the Flory-Huggins equation empirically. To take into account of deviations from random mixing caused by specific interaction such as hydrogen bonding, the exponent is empirically introduced to the interaction term of the conventional Flory-Huggins equation. A modified Flory-Huggins model can give the chemical potential difference of mixing:

\[ \Delta \mu_i = k_B T (1 - \phi_i) + m_i \sum_j (\phi_j/m_j) + m_i \sum_j \chi_{ij} \alpha_{ij} \phi_i^{(\alpha_{ij} - 1)} \phi_j^{\alpha_{ij}} - m_i \sum_k \phi_k \phi_k^{\gamma_k} (\alpha_{jk} + \alpha_{kj} - 1) \]

where \( \phi_i \) and \( m_i \) denote the volume fraction and the ratio of the molar volume of component \( i \) to a reference volume, respectively. The interaction parameters \( \chi_{ij} \) are empirically expressed as a function of dextran molecular weight by the following equation.

\[ \chi_{ij} = \chi_{ij0} + \alpha_{ij} \log (M_i/M_j) + b_{ij} [\log (M_i/M_j)]^2 \]

Further, the \( \Gamma \) distribution function was used to express the molecular weight distribution of DEX (see Fig. 4). And the Laguerre-Gauss quadrature method was used to choose pseudo-components of DEX in application of a continuous thermodynamic approach. As shown in Fig. 5, the modified Flory-Huggins equation coupled with the continuous thermodynamic approach can correlate the LLE in fairly good agreement with experimental data. For design of a separation process using aqueous two-phase system, the partition coefficients, \( K_p \), are also needed as fundamental knowledge. For example, the partition coefficients of three hydrolytic enzymes, \( \alpha \)-amylase, \( \beta \)-amylase and glucoamylase, in the DEX-PEG-water aqueous two-phase system are shown in Fig. 6. As shown in
Fig. 4 Molecular weight distribution of DEX in top and bottom phases for DEX T 40-PEG 4000-water system: Exp. ○ Feed, △ Top, □ Bottom; ——— Calc.

Fig. 5 Calculated and experimental LLE for DEX 140-PEG 4000-water aqueous two-phase system: ○ Exp.; Calc. ——— Conventional, =—— Modified.

Fig. 6 Calculated and experimental partition coefficients of hydrolytic enzymes for DEX T 500-PEG 4000-water aqueous two-phase system: ○ α-amylase, △ β-amylase, □ glucoamylase; Calc. ——— α-amylase, ——— β-amylase, ——— glucoamylase.

5. VOLUME-PHASE TRANSITION OF GEL

Several gels were expected to be applied as a size-selective extraction solvent because gels change their volumes upon small changes in the external conditions such as temperature and solvent as shown in Fig. 7. The volume change of the gels is described by the Flory-Huggins formula. However, the equation of Tanaka et al. is necessary to take into account temperature dependence and concentration dependence of the Flory-Huggins interaction parameter \( \chi \). Further, it is assumed that concentrations of solutions inside and outside the gel are equal.

To understand the interaction between gel network and solvent, equilibrium concentrations of solution inside and outside the gel are also very important. Mukae et al. and Ishidao et al. have recently reported swelling volume of poly (N-isopropylacrylamide) (NIPA) gel in alcohol-water mixtures and solvent concentration in aqueous solution inside and outside the gel. Moreover,
Ishidao et al.\textsuperscript{24} measured the poly (ethylene glycol) (PEG200, 1000, 6000, 20000 and 50000) concentrations inside and outside NIPA gel in aqueous PEG solutions. It has been observed that the concentrations inside and outside the gel are much different from each other as shown in Fig. 8.

At swelling equilibrium, the chemical potential difference of the solvent $i$ ($i = 1, 2$) in both gel and solution phases should be identical.\textsuperscript{20}

\begin{equation}
\Delta \mu_i = \Delta \mu_i^S + v_i \pi_{el},
\end{equation}

where superscripts $S$ and $G$ denote solution and gel phases respectively, $v_i$ is the molar volume of solvent $i$, and $\pi_{el}$ is the osmotic pressure by rubber elasticity. In order to consider the effect of hydrogen bonding, they suggested that the volume fraction of gel network should be separated to be

\begin{equation}
\phi_s^G = \phi_{sG}^G + \phi_s^G,
\end{equation}

where subscripts $3$, $M$ and $S$ denote polymer, and the main chain and side chain of network, respectively. The effective volume fraction of side chain is described as follows empirically by use of volume of side chain in dried gel, $V_s$.

\begin{equation}
\phi_s^G = (V_s / V)[\beta \omega + \exp (\beta \omega (V / V_o) + \beta \omega)]
\end{equation}

that is, $\phi_s^G$ was empirically expressed as a function of the solvent concentration in gel phase $w_i^G$, and the gel volume $V$ because the contact fraction between side chains and solvent molecules depends on the strength of their interaction and the gel volume. The chemical potential difference obtained for the swelling equilibrium of a gel is finally shown as follows.

\begin{equation}
\ln \phi_i^S - m_1 [(\phi_i^S / m_1) + \phi_s^S] + m_1 \chi_{12} (\phi_i^S)^2
= \ln \phi_i^G - m_1 [(\phi_i^G / m_1) + \phi_s^G + (\phi_s^G / m_3)] + m_1 (\chi_{12} \phi_s^G + \chi_{13} \phi_s^G) + m_1 (\chi_{12} \phi_s^G + \chi_{13} \phi_s^G)
- m_1 (\chi_{12} \phi_s^G + \chi_{13} \phi_s^G + \chi_{23} \phi_s^G) + 1
- (v_1 \nu / N)[(V_o / 2 V) - (V_o / V)^{1/3}].
\end{equation}

At the volume phase transition, the free energies of mixing for polymeric gel are identical at both shrunk (I) and swollen (II) states.\textsuperscript{20}
As shown in Figs. 7 and 8, the present correlation seems to be successful.

6. CONCLUSIONS

Some topics on phase equilibria for polymer systems have been described. The UNIFAC-FV model was successful to predict the solubilities of gases and vapors in molten polymers. Furthermore, the UNIFAC-FV model with a modification was also useful to correlate the LLE of polymer-hydrocarbon solutions. And the modified Flory-Huggins equation coupled with the continuous thermodynamic approach was successful to correlate the LLE data for the aqueous two-phase systems. Finally, the volume-phase transition of the gel and the concentrations between inside and outside the gels were correlated by the Flory-Huggins equation coupled with the rubber elasticity equation by taking into account the solvent concentration dependence of volume fraction of side chain inside the gel.

REFERENCES


