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A segmental interaction model for liquid-liquid equilibria correlation and prediction

Application to the poly(vinyl alcohol)/water system

Eftychia Panagou[1], Jean Vidal[2], Grozdana Bogdanic[3,*]

[1] The National Technical University of Athens, Department of Chemical Engineering,
Athens, Greece
[2] Kozarceva 7, 10000 Zagreb, Croatia
[3] INA-Industrija nafte, d.d., Research and Development, 10000 Zagreb, Croatia

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Summary

A segmental interaction model containing the combinatorial, free-volume and energetic contributions to the excess Gibbs energy has been developed. The energetic contribution is based on the solution of segment concept. The model has been applied to the system poly(vinyl alcohol)/water between 330 and 420 K. The closed loop diagram, the lower and upper critical temperatures are correlated, using weakly temperature dependent UNIQUAC parameters.

Introduction

Many polymeric materials are produced in a solution. Therefore, reliable estimates of liquid-liquid equilibria (LLE) are necessary for prediction and optimization of process's performances.

In principle, LLE compositions may be calculated using any model for the Gibbs energy. Models relying on a group contribution approach, such as the UNIFAC model (1,2), have been applied to low molar mass compounds mixtures, but a special set of parameters has been necessary (3). Recently (4,5) such methods have been extended to polymer solutions LLE calculations, using parameters based on vapor-liquid equilibria (VLE), but only qualitative predictions have been obtained. Better results have been obtained using a group contribution lattice fluid equation of state (6).

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* Corresponding author

However, experimental evidence (7) shows that small structural changes, such as ortho or para substitution of halogen atom on an aromatic ring may induce large modifications in blends miscibility, and the usual definition of groups cannot take into account such effects. In the present work, as recently proposed (8), the groups will be defined as the segments, or monomer repeating units of polymers or copolymers, or as the solvent molecule. This is usually done when applying the mean field theory (9). Such definition of groups has also been applied by Chen (10), but, as underlined by the author, free-volume effects were not considered, therefore lower critical solution temperatures (LCST) could not be represented.

We present here the model and the results obtained for the poly(vinyl alcohol)/ water system.

This example has been chosen for two reasons:

a) Poly(vinyl alcohol) [PVAL] film has interesting practical properties, as for example: transparency, antielectrostatic behavior, good barrier properties and resistance to organic materials. It is used for general packaging application, to prevent oxidation of foods and the escape of flavor.

b) The PVAL/water system is strongly polar, and involves specific interactions (hydrogen bonds). It shows a closed loop phase diagram (11) between 330 and 420 K, and it is challenging to correlate the data, in order to evaluate the versatility of the model.

In the present illustration, the segments are the -CH_2-CHOH- [VAL] repeating unit of the polymer and the water molecule.

Description of the segmental interaction model

The model is derived from the entropic free-volume model proposed by Elbro et al. (12). The activity coefficients are given by the expression:

$$\ln\gamma_i = \ln\gamma_i^{entr\text{-}FV} + \ln\gamma_i^{resid} \qquad [1]$$

As in the original model, the combinatorial and the free-volume contributions are combined in a single term, the so-called entropic-FV part:

$$\ln\gamma_i^{entr\text{-}FV} = \ln\frac{\phi_i^{FV}}{x_i} + 1 - \frac{\phi_i^{FV}}{x_i} \qquad [2]$$

where ϕ_i^{FV} and x_i are the free-volume fraction and the molar fraction, respectively. The free-volume is defined as:

$$v_{F,i} = v_i - v_{w,i} \qquad [3]$$

where v_i and $v_{w,i}$ are the liquid molar volume and the van der Waals volume, respectively.

For the calculation of the residual term, $\ln\gamma_i^{resid}$, the mixture is considered as a solution of segments, and the molar fraction of each segment is calculated as:

$$X_k = \frac{\sum_{i}^{ncomp} x_i \, v_k^i}{\sum_{j}^{ncomp} \sum_{m}^{ng} x_j \, v_m^j} \qquad [4]$$

where x_i, x_j are the mole fractions of the components *i* and *j*. The summations are extended to the total number of components, *ncomp,* and to the total number of segments, *ng*. v_k^i and v_m^j are the numbers of segments *k* in the component *i*, and of segments *m* in the component *j*. Their values are equal to the number of repeating units for a homopolymer, and to one for the solvent. For a copolymer, the value of v_k^i is obtained from the molar mass of the copolymer, M_i, from the molar fraction, X_k^i, of each copolymer segment *k*, which characterizes the copolymer composition, and from the molar mass of each segment M_k:

$$v_k^i = \frac{M_i}{\sum_{m}^{ng} X_m^i \, M_m} X_k^i \qquad [5]$$

From the molar fractions X_k, the activity coefficients of the segments Γ_k in the mixture are calculated by applying a model of non ideality. We have used the residual term of the UNIQUAC model (13), and for a binary mixture the expression of $\ln \Gamma_l$ is:

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_{m}^{ng} \Theta_m \, \tau_{mk} \right) - \sum_{m}^{ng} \frac{\Theta_m \, \tau_{km}}{\sum_{l}^{ng} \Theta_l \, \tau_{lm}} \right] \qquad [6]$$

In this expression Q_k represents the surface parameters of the segments, derived from the van der Waals area (1, 14), and Θ_l, Θ_m their surface fractions.

$$\Theta_l = \frac{X_l Q_l}{\sum_m^{ng} X_m Q_m} \qquad [7]$$

The values of τ_{ij} are derived from the interaction parameters between segments, C_{ij} by the relation:

$$\tau_{ij} = \exp\left(-\frac{C_{ji}}{RT}\right) \qquad [8]$$

These interaction parameters may be linear function of the temperature and will be fitted on experimental data.

The activity coefficients of the segments Γ^i_k in the pure components must also be evaluated. For a solvent or a homopolymer, they are equal to one and for a copolymer they are calculated using equation [6], where the surface fractions will be obtained from the mole fractions of the segments in the pure copolymer, X^i_k.

Finally, the activity coefficients of the components, solvent, homopolymer or copolymer, are obtained by the relation

$$\ln \gamma_i^{resid} = \sum_k \nu_k^i \left(\ln \Gamma_k - \ln \Gamma_k^i\right) \qquad [9]$$

which has been proposed by Wilson and Deal (15) and succesfully applied in the UNIFAC method (1,2) to the evaluation of activity coefficients of low molar mass compounds. However, for such a purpose, the definition of groups is different; they are small structural units, like CH, OH, C=O, etc.

It should be underlined that the term ln Γ^i_k in equation [9] takes into account the internal repulsion effect in copolymers (9,16).

Correlation of the experimental data

The procedure requires the densities of the solvent and of the polymer at the temperature of the mixture, the van der Waals volumes for the calculation of the free volume-combinatorial contribution, and the molecular surface parameters of the segments for the application of the UNIQUAC model. The densities are estimated using the DIPPR data bank (17) for the solvent and the Polymer Solution Handbook (18) for the Tait equation parameters. The van der Waals volumes and molecular surface parameters are calculated through additive group contributions (1, 14).

The UNIQUAC interaction parameters are determined from the experimental data of Rehage (11). The activities of each component (polymer or solvent), a^I_i or a^{II}_i in the two phases I and II in equilibrium are the same, and their values, calculated by the model should be as close as possible. Therefore we have minimized the following objective function:

$$O.F. = \sum_{nexp} \sum_{ncomp} \left(a_i^I - a_i^{II}\right)^2 \qquad [10]$$

where the summations are extended to the number of experimental tie lines, *nexp*, and to the number of components, *ncomp*. The optimization program used in the parameter estimation is a modified Levenberg-Marquard algorithm (19).

Results and discussion

It should be noted that the experimental data (11) in the middle of the closed loop diagram are not available. Also the molecular weight distribution of the polymer has not been described. Therefore the polymer has been considered as monodisperse (M_n = M_w = 140000 g/mol). The experimental values of the upper and lower critical temperature (UCST and LCST) have not been included in our data base. We did not take into account the small content of vinyl acetate units in PVAL, which is usually obtained through hydrolysis of poly(vinyl acetate). In spite of these approximations, it can be seen from Figure 1 that the model gives an excellent agreement with the experimental closed loop diagram.

Both LCST and UCST are represented with parameters that are weakly temperature dependent:

$$\left.\begin{aligned} \Delta U_{\left(\mathrm{VAL},\ \mathrm{H_2O}\right)} &= 827.10 + 4.98\left(T - 340\right)\ \mathrm{J/mol} \\ \Delta U_{\left(\mathrm{H_2O},\ \mathrm{VAL}\right)} &= -\ 351.82 + 7.40\left(T - 340\right)\ \mathrm{J/mol} \end{aligned}\right\} \qquad [11]$$

As we did not use any experimental data, such as, for example VLE data at temperatures higher than 430 K, the parameters values should not be extrapolated in a high temperature range.

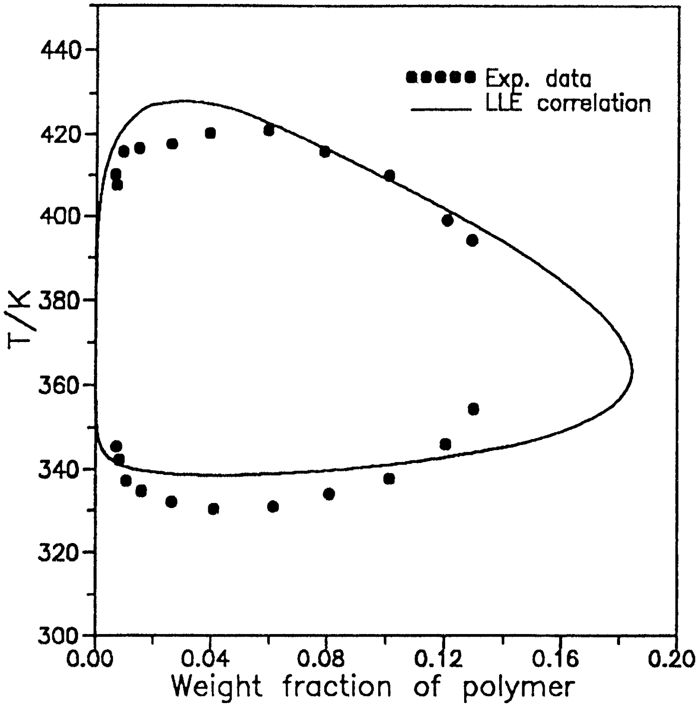

Figure 1. Correlation of LLE for PVAL/water system. Experimental data: Rehage, (11).

It should be mentioned that the results show that the values of the activity of the polymer in the phases in equilibrium are very low, while that of the solvent are very close to one, and that the inflection points of the Gibbs energy of mixing curve as a function of molar fractions, $G^M(x)$ (limits of the spinodal curve) are not visible; this phenomenon has been discussed previously for another model (20).

Previous application of the model (8) were related to the LCST prediction of moderately polar systems [poly(styrene-co-*n*-butylmethacrylate) in methyl ethyl ketone], and the present work shows that the extension to a system with strong specific interactions is possible. The main limitation is probably the immediate proximity of the critical point of the solvent, where the excess volume of the solution cannot be described.

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