Phase Separation in Polymer Solutions from a Born-Green-Yvon Lattice Theory

J. Luettmer-Strathmann and J. E. G. Lipson
Department of Chemistry
Dartmouth College, Hanover, NH 03755

Keywords: Born-Green-Yvon, lattice model, equation of state, liquid-liquid equilibria, polymer solutions, alkanes

1Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22–27, 1997, Boulder, Colorado, U.S.A.
Abstract

Phase separation in mixtures of polymers and alkanes is investigated with the aid of a recently developed lattice model, based on the Born-Green-Yvon (BGY) integral equation approach to fluids. The system-dependent parameters of the BGY lattice model for binary mixtures are deduced from those of its pure components, which in turn are determined from a comparison with experimental data. The lower critical solution temperatures (LCST’s) for polyethylene in various n-alkanes were predicted from the BGY lattice model and compared with experimental data. While the model underestimates the LCST’s for the smaller alkanes it reproduces the experimental values very well for the higher alkanes (decane through tridecane). The effect of the chain length of the polymer on the solubility is investigated for the case of decane as a solvent.

Introduction

In many polymer/solvent systems, phase separation occurs at a lower critical solution temperature (LCST) \[^1\]. For temperatures smaller than the LCST the polymer is soluble while a miscibility gap opens above the LCST which is closed again at an upper critical solution temperature (UCST). These lower critical solution temperatures are difficult to predict accurately from theory \[^2\]. \[^3\]. \[^4\]. In this work, we employ a recently developed lattice model \[^5\]. \[^6\]. \[^7\]. \[^8\] based on the Born-Green-Yvon (BGY) integral equation approach to fluids to investigate the miscibility of polyethylene in alkanes. The BGY lattice model provides a compact expression for the configurational part of the Helmholtz free-energy density which allows the calculation of the relevant thermodynamic properties of a mixture. In addition to the system-dependent parameters of the pure components, the lattice model for a binary mixture contains an energy parameter describing interactions between unlike molecules. In this work the interaction energy is approximated by the geometric mean of the energy parameters of the pure components, allowing the thermodynamic properties of the mixture to be predicted from those of the pure components. In the following sections we describe how the BGY lattice model is used to predict the LCST’s and corresponding coexistence curves for polyethylene in various alkanes, and then compare our results with experimental data.
Born-Green-Yvon lattice model for fluids

In the BGY lattice model, a molecule of species $i$ is assumed to occupy $r_i$ contiguous sites on a lattice having coordination number $z$ and a total of $N_0$ lattice sites. As in earlier work [7, 8], we set $z = 6$. The site-fraction $\phi_i$ is defined as $\phi_i = r_iN_i/N_0$, where $N_i$ is the number of molecules of component $i$ while $\phi_h = N_h/N_0$ is the fraction of empty sites or holes, where $N_h$ is the number of holes. Each molecule of species $i$ has $q_i z = r_i(z - 2) + 2$ interaction sites, leading to the definition of concentration variables $\xi_i = q_iN_i/(N_h + \sum_j q_j N_j)$ and $\xi_h = N_h/(N_h + \sum_j q_j N_j)$ which account for the nearest-neighbor connectivity of the molecules. The interaction energy associated with nonbonded nearest neighbors of the same species is $\epsilon_{ii}$, while $\epsilon_{ij}$ corresponds to interactions between unlike nearest neighbor segments. Using the Born-Green-Yvon integral equation approach, Lipson [5, 6] derived an expression for the dimensionless configurational Helmholtz free energy per lattice site $\hat{a} = \beta A/N_0$ of an $M$-component mixture

$$\hat{a} = \frac{\beta A}{N_0} = \sum_{i=h,1}^M \left( \frac{\phi_i}{r_i} \ln \frac{\phi_i}{r_i} + \frac{q_i z \phi_i}{2r_i} \left\{ \ln \left[ \frac{\xi_i}{\phi_i} \right] - \ln \left[ \xi_h + \sum_{j=1}^M \xi_j \exp(-\beta \epsilon_{ij}) \right] \right\} \right),$$

(1)

where $\beta = 1/(k_B T)$, $T$ is the temperature and $k_B$ is Boltzmann’s constant. Denoting the total volume of the lattice by $V = vN_0$, where $v$ is the volume per site, we obtain the Helmholtz free-energy density $A/VT$

$$A/VT = k_B \hat{a}/v + a_0,$$

(2)

where $a_0$ is a caloric background which is not discussed further in this work. All thermodynamic properties of a mixture can now be derived from the thermodynamic relation

$$d(A/VT) = (U/V)d(1/T) + \sum_{j=1}^M (\mu_j/T)d(\rho_j),$$

(3)

where $U$ is the internal energy of the system, and where $\rho_j = N_j/V = \phi_j/r_j v$ and $\mu_j$ are the number density and chemical potential of component $j$, respectively. The pressure $P$ and the chemical potentials $\mu_i$, for example, are given by

$$P = -\frac{1}{\beta v} \left[ \hat{a} - \sum_{j=1}^M \phi_j \left( \frac{\partial \hat{a}}{\partial \phi_j} \right)_{\beta,\phi_k \neq j} \right], \quad \mu_i = \frac{r_i}{\beta} \left( \frac{\partial \hat{a}}{\partial \phi_i} \right)_{\beta,\phi_k \neq i}.$$

(4)
It now becomes convenient to focus on molar quantities, so that \( \rho_j \) becomes the molar density of component \( j \), \( v \) denotes the volume of a mole of lattice sites, the energy parameters \( \epsilon \) are measured in J/mol, and \( k_B \) is replaced by the universal gas constant \( R \).

**Application to one-component fluids**

For the case of a one-component fluid, equations (1)–(4) are evaluated with \( M = 1 \), so that we can drop the subscripts other than \( h \). There are three system-dependent parameters which we determine from a comparison with experimental data: the number \( r \) of lattice sites occupied by a single molecule, the volume \( v \) per mole of sites, and the interaction energy \( \epsilon \).

To obtain parameters for the \( n \)-alkanes from pentane through tridecane we considered coexistence densities. The critical temperature \( T_c \) and the critical density \( \rho_c \) of a one-component fluid are determined by the following two conditions:

\[
\left( \frac{\partial \mu}{\partial \rho} \right)_T = 0, \quad \left( \frac{\partial^2 \mu}{\partial \rho^2} \right)_T = 0, \tag{5}
\]

For temperatures \( T \) smaller than \( T_c \) the coexistence densities \( \rho_{\text{vap}} \) and \( \rho_{\text{liq}} \) can be found from the conditions that pressure and chemical potential are equal in the vapor and the liquid phase, i.e.

\[
P(T, \rho_{\text{vap}}) = P(T, \rho_{\text{liq}}), \quad \mu(T, \rho_{\text{vap}}) = \mu(T, \rho_{\text{liq}}). \tag{6}
\]

We determined the parameters \( r, v, \) and \( \epsilon \) for a number of \( n \)-alkanes between methane and octane by comparing calculated liquid and vapor densities for temperatures between \( 0.5T_c \) and \( 0.9T_c \) (to avoid the critical region) with values tabulated by Vargaftik [9]. We then correlated the parameters with the chain length \( n \) of the alkanes, where we typically excluded the results for the lowest alkanes. The resulting expressions for the parameters as a function of chain length are given by

\[
rv/(L/mol) = 0.016n + 0.015, \tag{7}
\]

\[
r\epsilon/(J/mol) = -2150n - 3150, \tag{8}
\]

\[
\sqrt{r} = -0.877539 + 1.512447\sqrt{n} + 1.4651\left( \frac{1}{\sqrt{n}} + 0.58259 \right). \tag{9}
\]
The first of these equations, Eq. (7), reflects the fact that the hard core volume of the alkanes is expected to grow linearly with chain length, while Eq. (8) conveys a linear relationship between the interaction energy per mole and the chain length \( n \). Due to end effects, neither relation is expected to hold for very small \( n \). The last equation, Eq. (9), is motivated by the variation of the experimental [10] and calculated critical temperatures of the alkanes with chain length. In Table 1 we present the values of the system-dependent parameters for pentane through tridecane according to Eqs. (7)–(9). Calculated values for the coexistence densities of hexane along with values from Ref. [9] are presented in Fig. 1, while percent deviations between calculated and tabulated values for all alkanes considered in this work are presented in Fig. 2. The highest deviations seen in Fig. 2 are for vapor densities and are, in part, a result of the correlation of the parameters with chain length. The two figures show that our model gives a reasonable description of the coexistence densities outside the critical region.

System-dependent parameters for polyethylene (PE) were determined from a com-
Figure 2: Percent deviations between values for the coexistence densities as provided in Ref. [9] and as calculated from Eqs. (3) with system-dependent parameters given in Table 1.

![Percent deviations between values for the coexistence densities as provided in Ref. [9] and as calculated from Eqs. (3) with system-dependent parameters given in Table 1.](image)

**Table 1: System-dependent parameters for the pure components.**

| name         | molmass | $r$        | $v$ (mL/mol) | $\epsilon$ (J/mol) | LCST(K) |
|--------------|---------|------------|--------------|---------------------|---------|
| n-Pentane    | 72.146  | 9.505229   | 9.994499     | -1462.353           | 260.4   |
| n-Hexane     | 86.172  | 10.35107   | 10.72353     | -1550.565           | 371.2   |
| n-Heptane    | 100.198 | 11.22030   | 11.31877     | -1622.060           | 435.9   |
| n-Octane     | 114.224 | 12.10191   | 11.81632     | -1681.552           | 484.0   |
| n-Nonane     | 128.250 | 12.99011   | 12.24009     | -1732.088           | 522.8   |
| n-Decane     | 142.276 | 13.88162   | 12.60660     | -1775.729           | 555.5   |
| n-Undecane   | 156.302 | 14.77453   | 12.92766     | -1813.933           | 583.7   |
| n-Dodecane   | 170.328 | 15.66765   | 13.21193     | -1847.756           | 608.6   |
| n-Tridecane  | 184.354 | 16.56028   | 13.46595     | -1877.987           | 630.8   |
| PE           | 140262.0| 15890.72   | 9.621464     | -1988.320           |         |
| PE           | 85000.0 | 9629.90    | 9.621934     | -1988.458           |         |
| PE           | 50000.0 | 5663.81    | 9.623040     | -1988.729           |         |
Figure 3: Percent deviations between experimental [11, 12] and calculated (cf. Eq. (4)) values of the densities of polyethylene at given temperature and pressure.

The representation of the experimental data was virtually identical in the three cases. and the resulting values for the parameters, as presented in Table 1, show that for long chain polymers $\epsilon$ and $v$ are indeed independent of the molecular mass [11, 12] of the polymer. We determined system-dependent parameters for PE from a comparison between experimental and calculated pressures using three different molecular masses for the polymer. The representation of the experimental data was virtually identical in the three cases. The deviations are generally smaller than 0.3% but reach up to 1% for the lowest pressures.
Phase separation in binary solutions

To discuss phase separation in binary mixtures, it is convenient to introduce the total molar density \( \rho = \rho_1 + \rho_2 \) and the mole fraction \( x = \rho_2/\rho \) of component 2. The thermodynamic field conjugate to the mole fraction \( x \) is the difference of the chemical potentials \( \mu = \mu_2 - \mu_1 \). In terms of these variables, the conditions for a point \( T_c, P_c, x_c \) on the critical line of a binary mixture take the form [13]:

\[
\left( \frac{\partial \mu}{\partial x} \right)_{T,P} = \left( \frac{\partial \mu}{\partial x} \right)_{T,\rho} - \rho^2 \left( \frac{\partial \mu}{\partial \rho} \right)_{T,x} \left/ \left( \frac{\partial P}{\partial \rho} \right)_{T,x} \right. = 0, \tag{10}
\]

\[
\left( \frac{\partial^2 \mu}{\partial x^2} \right)_{T,P} = 0. \tag{11}
\]

The first of the two equations defines the spinodal while the second one implies that, for given pressure, the critical point is an extremum of the spinodal in the \( T-x \) plane. Hence, lower and upper critical solution temperatures (LCST’s and UCST’s) correspond to the minimum and maximum of their spinodals, respectively. For temperatures \( LCST < T < UCST \), the mixture phase separates into two phases of different mole fractions \( x_I \) and \( x_{II} \). For a given pressure \( P \), the coexisting phases satisfy

\[
\mu(T, P, x_I) = \mu(T, P, x_{II}), \quad \mu_1(T, P, x_I) = \mu_1(T, P, x_{II}). \tag{12}
\]

For typical solutions of polymers in alkanes, the mole fractions \( x \) are very small numbers so that it is more convenient to employ mass fractions \( c \):

\[
c = \frac{M_2 x}{(M_2 x + M_1 (1 - x))}, \tag{13}
\]

where \( M_1 \) and \( M_2 \) are the molecular masses of component 1 and 2, respectively.

When the BGY lattice model is applied to binary mixtures, Eqns. (1)–(4) are evaluated with \( M = 2 \). The total molar density \( \rho = \rho_1 + \rho_2 \) and the mole fraction \( x = \rho_2/\rho \) of the mixture are related to the site fractions \( \phi_1 \) and \( \phi_2 \) by

\[
\rho = \frac{1}{v} \left( \frac{\phi_1}{r_1} + \frac{\phi_2}{r_2} \right), \quad \frac{1}{x} = 1 + \frac{\phi_1 r_2}{r_1 \phi_2}. \tag{14}
\]

In addition to the energy parameters \( \epsilon_{11} \equiv \epsilon_1 \) and \( \epsilon_{22} \equiv \epsilon_2 \), and the numbers of segments \( r_1 \) and \( r_2 \), which are determined directly by the pure components of the mixture, values need to be supplied for the interaction energy \( \epsilon_{12} \) and the volume \( v \) of
a mole of lattice sites. For the energy parameter $\epsilon_{12}$ we employ Berthelot’s geometrical mean combining rule [13]:

$$\epsilon_{12} \equiv -\sqrt{\epsilon_1 \epsilon_2}.$$  

(15)

To find a value for $v$, we take advantage of the fact that the BGY model for the pure polymer depends more strongly on the product $rv$ than on the values of the number of segments $r$ and the volume $v$ separately. Hence, for a mixture of an alkane and polyethylene, we assign the value $v_1$ of the alkane to the mixture, and rescale the segment length of the polymer, i.e.

$$v \equiv v_1, \quad r_2 \rightarrow (r_2v_2)/v_1.$$  

(16)

When parameters $v$ and $r_2$, given by Eq. (16), are used to compare experimental and calculated $PVT$ data for pure polyethylene over the whole temperature and pressure range, it is seen that the new parameters diminish the overall agreement between experiment and theory. However, for the lowest pressures the description of the $PVT$ surface is improved over that using the original parameters, and becomes excellent for the highest alkanes. This is important since we are going to investigate phase separation of polyethylene solutions at atmospheric pressure.

To determine the lower critical solution temperatures for mixtures of polyethylene and the various alkanes discussed in the previous section, we employed the parameters presented in Table 1, where the highest molecular-mass parameters were used for polyethylene, together with Eqs. (13) and (16). We then solved Eqn. (10) numerically to find the spinodal curve for atmospheric pressure $P = 0.1$MPa. The LCST was identified as the minimum of the spinodal curve as a function of $x$. All calculated LCST’s are included in Table 1, and the values for the $n$-alkanes between pentane and tridecane are compared with experimental values [2, 4, 14, 15] in Fig. 4. These results show that while the BGY lattice model with the parameters of Table 1 somewhat underestimates the LCST’s for the shorter chains, it gives a very good description of the data for the higher alkanes.

The influence of the chain length of the polymer on its solubility is illustrated in Fig 5. The symbols indicate experimental data by Kodama and Swinton [4] for three polyethylene samples of different molecular masses in decane. We calculated the coexistence curves for polyethylene in decane for three comparable molecular masses (see Table 1) using the coexistence conditions Eqs. (12). Shown in Fig. 5, as a function of the mass fraction $c$, are the differences between the coexistence temperatures and the
Figure 4: Lower critical solution temperatures for polyethylene in \( n \)-alkanes at \( P = 0.1 \text{MPa} \). The symbols represent experimental data for Marlex-50 by Orwoll and Flory [2] (open circles), for Kodama and Swinton’s [4] longest chain polymer PE Type 2 (open squares), extrapolated values to \( M \to \infty \) by Hamada et al. [14] (open diamonds), and values collected by Charlet and Delmas [15] (open triangles). The filled diamonds on the solid line indicate values calculated with the aid of Eqns. (14) and (16) and the values presented in Table I together with Eqns. (15) and (16).
Figure 5: Coexistence curves for polyethylene in n-decane at $P = 0.1\text{MPa}$ as a function of the mass fraction $c$. The symbols correspond to experimental data by Kodama and Swinton [4] and the lines represent values calculated according to Eqn. (11) with the aid of the parameters in Table 1 and Eqns. (15) and (16).  

For the experimental data, the LCST ($T = 557.6\text{K}$) of PE Type 2 has been subtracted from the coexistence temperatures, while the predicted LCST ($T = 555.7\text{K}$) of PE with molecular mass 140262 has been subtracted from the calculated values.
calculated and experimental values of the LCST of the longest chain, respectively. Since the experimental data in the paper by Kodama and Swinton \cite{4} were not tabulated but presented in a graph the comparison is not exact. It appears, however, that the effect of changing molecular mass on the coexistence temperatures of polyethylene in decane is predicted well by the BGY lattice model.

**Conclusion**

With the aid of the system-dependent parameters for the pure components as well as the geometric mean approximation for the interaction energy, the BGY lattice model has been shown to predict LCST’s for solutions of polyethylene in alkanes in very good agreement with experimental data. The theory also captures the effect of changing polymer molecular mass on solubility. In current work, we are investigating the influence on miscibility of polymer and solvent architecture.

**Acknowledgements**

The authors would like to thank D. J. Lohse for supplying $PVT$ data on polyethylene. The research is supported by the National Science Foundation through grant DMR-9424086 and by the Camille and Henry Dreyfus foundation.

**References**

\[1\] P. L. Freeman and J. S. Rowlinson, Polymer, 1 (1960) 20–26.

\[2\] R. A. Orwoll and P. J. Flory, J. Am. Chem. Soc., 89 (1967) 6822–6829.

\[3\] D. Patterson and G. Delmas, Trans. Faraday Soc., 65 (1969) 708–724.

\[4\] Y. Kodama and F. L. Swinton, The British Polymer Journal, 10 (1978) 191–200.

\[5\] J. E. G. Lipson, Macromolecules, 24 (1991) 1334–1340.

\[6\] J. E. G. Lipson, J. Chem. Phys., 96 (1992) 1418–1425.

\[7\] J. E. G. Lipson and S. S. Andrews, J. Chem. Phys., 96 (1992) 1426–1434.

\[8\] J. E. G. Lipson and P. K. Brazhnik, J. Chem. Phys., 98 (1993) 8178–8185.
[9] N. B. Vargaftik, *Tables on the Thermophysical Properties of Liquids and Gases*, second ed. (Hemisphere Publishing Corp., Washington D.C., 1975).

[10] D. Ambrose and C. Tsonopoulou, J. Chem. Eng. Data, 40 (1995) 531–546.

[11] D. J. Walsh, W. W. Graessley, S. Datta, D. J. Lohse, and J. L. Fetters, Macromolecules, 25 (1992) 5236–5240.

[12] R. Krishnamoorti, W. W. Graessley, G. T. Dee, D. J. Walsh, L. J. Fetters, and D. J. Lohse, Macromolecules, 29 (1996) 367–376.

[13] J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures*, third ed. (Butterworths, London, 1982).

[14] F. Hamada, K. Fujisawa, and A. Nakajima, Polymer J., 4 (1973) 316–322.

[15] G. Charlet and G. Delmas, Polymer, 22 (1981) 1181–1189.