PHASE SEPARATION OF POLYMER SOLUTIONS

THE CALCULATION OF THE CLOUDPOINT CURVE WITH A CONCENTRATION AND TEMPERATURE-DEPENDENT FREE ENERGY CORRECTION PARAMETER

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Abstract—The free enthalpy correction parameter g in the Flory-Huggins equation for the Gibbs free enthalpy of mixing in polymer solutions is considered generally as a concentration- and temperature-independent parameter. It has been extended here with linear concentration- and temperature-dependent terms. With these parameters, six different types of cloudpoint curves can be predicted. Using the experimental cloudpoint curve for solutions of poly(2,6-dimethyl-1,4-phenylene oxide) in toluene up to about 70 per cent by weight of polymer, a set of g -parameters is obtained, accounting for concentration and temperature dependence. With the parameters thus obtained, the melting point curve has been calculated which agrees very well with the experimental melting points for this system.

INTRODUCTION

LIQUID-liquid phase separation in polymer solvent systems have been described extensively by many authors.^(1,2) Depending upon the nature of the polymer and the solvent, cloudpoint curves have been reported with upper and lower critical solution points which may show a narrow or wide amorphous phase separation range.⁽³⁾ By assuming the original Flory-Huggins equation for the free enthalpy of mixing⁽¹⁾ (ΔG_m)* to be valid for all these systems, cloudpoint curves have been calculated but agreement with experimental curves was generally poor. Since then, refined theories have shown that the original Flory-Huggins interaction parameter χ does not have a constant value; it may depend upon the molecular weight of the polymer, the temperature or the total polymer concentration.⁽⁴⁾ There are some advantages⁽⁵⁾ in the use of weight fractions (w) rather than volume fractions ϕ in the Flory-Huggins equation, although the interaction parameter, then labeled as χ_w , will differ slightly from χ .⁽⁶⁾

By taking this into account, a better agreement for some specific polymer-solvent systems could be obtained. In the system poly(2,6-dimethyl-1,4-phenylene oxide)†-toluene, a cloudpoint curve has been measured which does not show a maximum up to 70 per cent of weight polymer.⁽⁷⁾ Next to this, a melting point curve could be measured on reheating demixed solutions, but never before liquid-liquid phase separation had occurred. Light scattering⁽⁸⁾ experiments with PPO-toluene solutions, performed according to the principles discussed by T. G. Scholte,^(6,9,10) indicate that

* The free enthalpy of mixing ΔG_m stands for Gibbs free energy change.

† PPO.

the monotonous rise of the cloudpoint curve as a function of polymer concentration is connected with an unusual dependence of the interaction parameter g upon temperature and polymer concentration, which must be due to polar interactions between the polymer segments and the toluene molecules.

Several authors have published theories which take into account the polar interaction between polymer molecules and the solvent.^(11,12) These theories are generally very complicated and require knowledge of numerous *a priori* unknown parameters. Heil and Prausnitz⁽¹³⁾ presented a semi-empirical equation for ΔG_m based on the local volume fraction concept of Wilson.⁽¹⁴⁾ This segment-interaction equation contains two adjustable parameters per binary mixture, determined from binary vapour pressure data. When these parameters are used to calculate ΔG_m vs w_1 curves for polymer-solvent systems at temperatures lower than the critical temperature, the cloudpoint curves obtained from the ΔG_m curves do not agree at all with most types of experimental cloudpoint curves. However, by extending the constant free enthalpy correction parameter with a linear concentration dependent term and assuming that both terms may be simple functions of temperature, different types of cloudpoint curves can be obtained. One of these types agrees with the system PPO-toluene. Using the experimental cloudpoint curve of PPO-toluene as a reference, a set of g parameters can be obtained which in turn can be used to calculate the melting point curve for this system.

THEORY

In order to calculate the equilibrium compositions of a demixed polymer-solvent system, the free enthalpy of mixing must be known.

The Gibbs free energy of mixing in a volume element ΔV is given as follows,^(1,5) in term of weight fractions:

$$\Delta G_m/RT = \left(w_0 \ln w_0 + \sum_i \frac{M_0}{M_i} w_i \ln w_i + g w_0 w \right) \frac{\rho \Delta V}{M_0} \quad (1)$$

w_0 = weight fraction of the solvent

M_0 = molecular weight of the solvent

w_i = weight fraction of the polymer component i

w = total weight fraction of the polymer

g = free enthalpy correction parameter

ρ = density of the solution

M_i = molecular weight of component i of the polymer

R = Universal Gas Constant.

g is a dimensionless quantity which characterizes the interaction energy per solvent molecule divided by kT (k = Boltzman constant) and which reaches the value 0.5 (for M_i infinitely large) at the critical concentration at which phase separation first appears.

In a recent theory, Huggins⁽¹¹⁾ suggests g to be dependent upon temperature and concentration; the concentration dependence can be approximated by a polynomial in w_1 , the polymer weight fraction. This concept has also been followed by Koningsveld,⁽¹⁵⁾ leading to the following expression for g :

$$g = \sum_{j=0}^n g_j w_1^j \quad (j = 0, 1, 2 \dots n) \quad (2)$$

In this formula, each coefficient g_j may be a temperature function of the form:⁽¹⁵⁾

$$g_j = g_{j,1} + g_{j,2}/T + g_{j,3}T + g_{j,4} \ln T. \quad (3)$$

If in a polymer-solvent system no polar or hydrogen bonding is to be expected, $n = 0$ in Eqn. (2) and g is independent of w_1 . If in those cases the temperature dependence of g also is not very marked, experimental values are in reasonable agreement with calculated values, this being true for systems like polyethylene-diphenylether and several others.⁽¹⁶⁾

Delmas *et al.*⁽¹⁷⁾ succeeded in describing the occurrence of a lower and upper critical solution point by using the second and third term of Eqn. (3) as a temperature function of g . Which terms must be taken depends upon the kind of polymer-solvent system considered.

From ultracentrifuge, light scattering and critical miscibility measurements performed with polymer solutions in which polar bonding exists between the polymer segments and the solvent molecules, χ_w is found to be dependent upon w_1 and T .^(5,18)

A. TYPES OF CLOUDPOINT CURVES OBTAINED WITH A LINEAR CONCENTRATION AND TEMPERATURE DEPENDENCE OF g

To account for the interaction energy due to polar bonding, use can be made of Eqn. (2) in which we have limited ourselves to $n = 1$.

This means that

$$g = g_0 + g_1 w_1 \quad (4)$$

while both g_0 and g_1 may be a temperature function again. As it is known that polar interaction depends strongly upon temperature, the temperature dependency has been taken as follows:

$$g_j = g_{j,1} + g_{j,3} T \quad (5)$$

in which $g_{j,1}$ can be negative or positive.

With Eqns. (4) and (5), ΔG_m versus w_1 curves can be calculated at each temperature. From double tangent points of these ΔG_m versus w_1 curves, the binodal curve is found.

In general, polymer-solvent systems are treated as quasi-binary systems and although the cloudpoint curve is not the same as the binodal in those cases, for polymers with a rather narrow molecular weight distribution these curves are comparable. The following six types of cloudpoint curves can now be obtained:

- I. If $g_0 \neq f(T)$ and $g_1 = 0$, the cloudpoint curve will show a distinct maximum at values of $w_1 < 0.1$ and will have a narrow amorphous phase separation range (Fig. 1a).

An example of this kind is polyethylene-diphenylether.⁽¹⁶⁾

- II. If $g_0 \neq f(T)$ and $g_1 \neq f(T)$, the cloudpoint curve will show a very broad amorphous separation range; the maximum of the curve is not well defined (Fig. 1b).

An example of this kind is cellulosediacetate-benzylalcohol.⁽¹⁹⁾

FIG. 1. Different types of cloudpoint curves calculated with $g_0 = g_0 + g_1 w_1$ and $g_k = g_{k.1} + g_{k.3} T$. w_1 = polymer concentration expressed in weight fractions. For further explanation, see text.

III. If $g_0 \neq f(T)$ and $g_1 = f(T)$, the cloudpoint curve will show a broad amorphous separation range with a maximum for $w < 0.3$ (Fig. 1c).

An example of this kind may be ethylene-vinyl acetate (Elvax-40)-Caprolactam.⁽²⁰⁾

IV. If $g_0 = f(T)$ and $g_1 = 0$, the cloudpoint curve will show a broad maximum at values of w_1 between 0.05 and 0.20 (Fig. 1d).

An example of this kind is polystyrene-toluene.⁽¹⁸⁾

V. If $g_0 = f(T)$ and $g_1 \neq f(T)$, the cloudpoint curve will show a broad amorphous separation range with a maximum for $w_1 > 0.7$ (Fig. 1e). This combination of g values is not very likely and experimental examples have not been reported.

VI. If $g_0 = f(T)$ and $g_1 = f(T)$, the cloudpoint curve will show a broad amorphous separation range with a maximum for w_1 between 0.3 and 0.7 (Fig. 1f).

An example of this kind is PPO-toluene.⁽⁷⁾

The cloudpoint curves I to VI represent the main types. Since many combinations of values for g_0 and g_1 are possible, the maxima of the cloudpoint curves may shift to higher or lower values of w_1 and the height of the maximum may change to higher or lower temperatures. By introducing proper values for g_0 and g_1 , the ΔG_m curves as a function of w_1 at each temperature can be calculated for any particular system.

B. CALCULATION OF THE THERMODYNAMIC POTENTIALS

If phase separation occurs, the following conditions must be obeyed⁽²⁾

$$\begin{aligned}\Delta\mu_0' &= \Delta\mu_0'' \\ \Delta\mu_1' &= \Delta\mu_1''\end{aligned}\tag{6}$$

$\Delta\mu_0'$ = (chemical potential of the solvent in phase 1) — (chemical potential of the pure solvent)

$\Delta\mu_0''$ = the same in phase 2

$\Delta\mu_1'$ = (chemical potential of the polymer in phase 1) — (chemical potential of the polymer in the pure state)

$\Delta\mu_1''$ = the same in phase 2.

Introduction of Eqn. (4) in (1) and differentiation of (1) with respect to the number of moles of each component, assuming $\rho\Delta V/M_0 = 1$, gives the expressions for the thermodynamic potentials:

$$\frac{\Delta\mu_0}{RT} = \ln(1 - w_1) + \left(1 - \frac{M_0}{M_n}\right) w_1 + (g_0 + 2g_1 w_1 - g_1) w_1^2 \quad (7)$$

$$\frac{\Delta\mu_1}{RT} = \frac{M_0}{M_n} \ln w_1 + (1 - w_1) \frac{M_0}{M_n} - (1 - w_1) + (g_0 + 2g_1 w_1) (1 - w_1)^2. \quad (8)$$

The factor $(g_0 + 2g_1 w_1 - g_1)$ is to be compared with the correction parameter χ in the original Flory-Huggins equations for $\Delta\mu_0$.

If g_0 and g_1 are known as functions of T , $\Delta\mu_0$ and $\Delta\mu_1$ can be calculated with Eqns. (7) and (8).

C. CALCULATION OF THE MELTING POINT CURVE

If in PPO-toluene solutions liquid-liquid phase separation has taken place, the concentrated phase will crystallize after a certain time.⁽⁷⁾ Differential scanning calorimetry has shown that liquid-liquid phase separation always precedes crystallization and that the degree of crystallinity is very small. When a demixed solution is heated again, it will become homogeneous at its melting point.

At this temperature for each composition, the following expression is valid:⁽²¹⁾

$$\Delta\mu_{f,u} = \Delta H_u^0 \frac{\Delta T T_m}{(T_m^0)^2} \quad (9)$$

$\Delta\mu_{f,u}$ = chemical potential of melting of 1 mole of polymer segments

ΔH_u^0 = enthalpy of melting of 1 mole of polymer segments

T_m = melting temperature of the solution

T_m^0 = melting point of the pure polymer

ΔT = $T_m^0 - T_m$.

Since

$$-\Delta\mu_{f,u} = \Delta\mu_{1,u} \quad (10)$$

the melting point curve can be calculated with Eqns. (8), (9) and (10) once the parameters necessary to determine $\Delta\mu_1$ and further ΔH_u^0 and T_m^0 are known.

The agreement of the calculated and measured melting point curves has been used as a check on the validity of the parameters obtained for g .

RESULTS

The calculations were based on the system PPO-toluene; the PPO used is characterized by $\bar{M}_n = 25,000$ and $\bar{M}_w = 49,000$. Although this system is in fact a multi-component one, it has been treated as a quasi-binary system. The thermodynamic quantities have been calculated for M_0 grams of solution, this means that the factor $\rho\Delta V/M_0 = 1$ in all calculations.

To obtain proper values for g_0 and g_1 , ΔG_m curves were calculated at different temperatures starting for example, with $g_0 = 500 \text{ cal mol}^{-1}$ and $g_1 = 1500 \text{ cal mol}^{-1}$.

From the tangent points of these ΔG_m vs w_1 curves, a cloudpoint curve was obtained which in general had one common point with the measured cloudpoint curve of PPO-toluene. For that temperature and concentration, the values of g , $\Delta\mu_0$ and $\Delta\mu_1$ were known. The same was done taking other values for g_0 and g_1 until, for a set of four concentrations, the appropriate values for g , $\Delta\mu_0$ and $\Delta\mu_1$ were known. Since Eqns. (4) and (5) must be obeyed, from these four values of g , $\Delta\mu_0$ and $\Delta\mu_1$ the four unknown parameters could be obtained, leading to

$$g_0 = \frac{566.0 - 6.7 (T - 273)}{RT} \quad (11)$$

and

$$g_1 = \frac{1251.8 - 0.7 (T - 273)}{RT}. \quad (12)$$

FIG. 2. $\Delta G/RT$ versus weight per cent polymer; curves calculated with Eqns. (1) and (4) making use of Eqns. (11) and (12).

FIG. 3. $\Delta\mu_0/RT$ versus weight per cent polymer; curves calculated with Eqns. (7), (11) and (12) for $\rho\Delta V/M_0 = 1$.

FIG. 4. $\Delta\mu_1/RT$ versus weight per cent polymer; curves calculated with Eqns. (8), (11) and (12) for $\rho\Delta V/M_0 = 1$.

With these values and Eqns. (1) and (4), the $\Delta G/RT$ values have been calculated at temperatures between 278°K and 373°K. The results are shown in Fig. 2.

By drawing tangent lines along the $\Delta G/RT$ versus w_1 curves, the thermodynamic potentials $\Delta\mu_0$ and $\Delta\mu_1$ at the concentrations of the tangent points can be obtained graphically. The calculated results for $\Delta\mu_0$ and $\Delta\mu_1$ as a function of w_1 , obtained from Eqns. (7) and (8), are represented in Fig. 3 and 4. The complete cloudpoint curve obtained from Fig. 2 is shown in Fig. 5, together with the experimental cloudpoints. Hence the system PPO-toluene can be described as a type VI cloudpoint curve with g_0 and g_1 both functions of T .

FIG. 5. Calculated and experimental cloudpoint and melting point curves. — Calculated cloudpoint curve, --- calculated melting point curve, × experimental cloudpoints, ○ experimental melting points.

To check the validity of the parameters g_0 and g_1 , the melting point curve was calculated with Eqns. (8), (9) and (10). ΔH_u^0 values between 6 and 15 cal gram⁻¹ have been reported.⁽²²⁾ In Fig. 5, the calculated melting point curve is shown obtained by taking $\Delta H_u^0 = 9$ cal gram⁻¹, $T_m^0 = 513$ K and making use of (11) and (12).

DISCUSSION

It is well known that the g factor in many polymer solvent systems is concentration-dependent. In this paper the effect upon ΔG_m , $\Delta\mu$ and the cloudpoint curve of a linear concentration dependence of g , in combination with a simple temperature dependence, has been discussed. It should be realized, however, that in many polymer solvent systems, g may also depend upon molecular weight of the polymer and the temperature dependence may be of a different kind. Since these two effects are in general not very pronounced, most polymer solvent systems with a not too broad molecular weight distribution can be quantitatively described according to types I to VI. If g contains

FIG. 6. $\Delta G/RT$ versus weight per cent polymer. $\times$ Light scattering results for $T = 45^\circ$, $\circ$ calculated results with Eqns. (1), (4), (11) and (12).

a concentration dependent term, it is not equal any more to the constant χ_w term of Flory-Huggins. Following the equations of Flory-Huggins, the factor χ_w is equal to $g - (1 - w) (\partial g / \partial w)$. If $(1 - w) (\partial g / \partial w)$ outweighs g then χ_w will become negative, which has indeed been found in several systems.⁽²³⁾ Since the calculation of $\Delta \mu_0$ is very sensitive to the value of $(\partial g / \partial w)$ and, as in many polymer solvent systems $(1 - w) (\partial g / \partial w)$ has been neglected, it is to be expected that in general the agreement of the calculated and the experimental cloudpoint curves would be poor.

FIG. 7. χ as a function of weight per cent polymer. $\times$ Light scattering results for $T = 45^\circ$, $\circ$ calculated results for $T = 45^\circ$.

In the system PPO-toluene, polar interactions occur between the benzene rings in PPO and toluene. This kind of interaction also takes place with other solvents like chloroform, nitrobenzene etc., in general with those solvents with a dipole moment or with solvents that can be polarized easily.

Our experiments indicate that solvents with a large dipole moment are very good solvents for PPO. If the solvent molecules do not have a dipole moment and cannot be polarized, or if the polar interaction between the solvent molecules themselves is strong, the system PPO-solvent behaves like one described as type I or II, at rather

FIG. 8. Free enthalpy correction parameter g versus weight per cent polymer. $\times$ Light scattering results for $T = 45^\circ$, $\circ$ calculated results for $T = 45^\circ$.

high temperatures. With light scattering experiments, quantitative values for the thermodynamic parameters of PPO-toluene have been obtained⁽⁸⁾ for concentrations up to $w_1 = 0.245$. Figure 6 shows the $\Delta G/RT$ curves for $T = 45^\circ$ calculated with the parameters obtained from light scattering, together with the calculated curve obtained above. Figures 7 and 8 represent the g and χ values respectively. Light scattering experiments for polar systems are difficult to interpret since light scattering theory has not been adapted for corrections necessary for the attractive forces of the polymer segments with the solvent molecules. From Figs. 7 and 8, it can be concluded that for $w_1 > 0.1$ the calculated values for χ_w and g agree qualitatively. For low concentrations, the light scattering results deviate strongly from the newly calculated values.

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Résumé—On considère généralement que le paramètre g , de correction d'enthalpie libre dans l'équation de Flory–Huggins, pour l'enthalpie libre de mélange de Gibbs des solutions de polymères, est indépendant de la concentration et de la température. On lui a ajouté ici des termes dépendant linéairement de la concentration et de la température. Avec ces paramètres, on peut prévoir six types différents de courbes de point de louche. En utilisant la courbe expérimentale du point de louche pour des solutions de poly(diméthyl 2,6-oxyde de phénylène-1,4) dans le toluène, jusqu'à environ 70 pour cent en poids de polymère, on obtient un ensemble de paramètres G tenant compte de l'influence de la température et de la pression. Avec les paramètres ainsi obtenus on a calculé une courbe de point de fusion qui coïncide très bien avec les points de fusion expérimentaux de ce système.

Sommario—La correzione entalpica parametrica libera g nell'equazione Flory–Huggins per l'entalpia libera Gibbs per la miscela in soluzioni polimere che vengono considerate generalmente come concentrazione e parametro indipendente di temperatura. E stato esteso qui con concentrazione lineare e termini dipendenti di temperatura. Con questi parametri, sei tipi diversi di curve di punti nuvolosi possono essere predetti. Usando i punti nuvolosi sperimentali per soluzione di poli (2,6-dimetil-1,4-fenilene ossidato) in toluene fino a circa 70 per cento secondo peso di polimeri, un gioco di parametri- g è ottenuto, essendo, responsabile per la concentrazione e di-endenza di temperatura. Con i parametri anzi ottenuti, la curva del punto di fusione è stato calcolata e questo è in accordo buonissimo con i punti di fusione sperimentali per questo sistema.

Zusammenfassung—Der Korrekturparameter der freien Enthalpie g in der Flory–Huggins Gleichung für die Gibbs'sche freie Mischungsenthalpie in Polymerlösungen wird im allgemeinen als ein von der Konzentration und der Temperatur unabhängiger Parameter betrachtet. Er wurde hier mit linearen Konzentrations- und Temperatur-abhängigen Termen erweitert. Mit diesen Parametern lassen sich sechs verschiedene Arten von Trübungspunktkurven voraussagen. Wenn man die experimentelle Trübungspunktkurve für Lösungen von Poly(2,6 dimethyl 1,4 phenylenoxid) in Toluol bis zu etwa 70 Gewichtsprozent des Polymeren zugrundegelegt, erhält man einen Satz von g -Parametern, der die Konzentrations- und Temperaturabhängigkeit wiedergibt. Mit den so erhaltenen Parametern wurde die Schmelzpunktkurve berechnet, die sehr gut mit den experimentellen Schmelzpunkten dieses Systems übereinstimmt.