The solid–liquid equilibria in the system polyoxyethylene/phenol

Ivo Lapeš, Julius Pouchlý*, Ján Biroš and Josef Baldrian
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
162 06 Prague 6, Czechoslovakia
(*Received 22 March 1990; accepted 4 June 1990*)

The solid–liquid (S–L) phase diagram and the X-ray diffractogram of a mixture of polyoxyethylene ($M = 2000$) with phenol suggest the existence of a crystalline compound consisting of one molecule of phenol and two monomeric units of polyoxyethylene. The congruent melting point of this compound lies at 302.6 K. From an analysis of the phase diagram based on the theory of association equilibria, we have found that in the liquid phase: (1) the bond between phenol and polymer is very strong; (2) there exists a whole spectrum of association complexes containing different numbers of phenol molecules bound onto the macromolecule; and (3) the maximal number of bound phenol molecules is higher than in the crystalline compound.

(Keywords: polyoxyethylene; solid–liquid phase diagram; crystalline compound; polymer–solvent association)

INTRODUCTION

Our investigations of crystal–liquid phase equilibria in polymer/low-molecular-weight component systems now concern a mixture of polyoxyethylene (POE) and phenol. The solid–liquid (S–L) phase diagram obtained by the d.s.c. method indicates the existence of a crystalline compound comprising both components and having a congruent melting point (point C, *Figure 1*). The existence of the compound has been confirmed by wide-angle X-ray scattering measurements. In this study we analysed the phase diagram by employing the theory of association equilibria with the aim of obtaining at least qualitative conclusions regarding the interaction between phenol and polyoxyethylene in the liquid mixture.

THEORY

General background

Let us consider a mixture of a low-molecular-weight component A with a polymer B, in which a crystalline compound C having the composition $A_{i_C}B$ and a congruent melting point can be formed within a certain interval of composition and temperature. The components are completely miscible in the liquid phase. The L–S phase diagram indicates the dependence of the melting point of the crystalline component A, B or C on the composition of the equilibrium liquid mixture; for its individual branches limited by eutectic points E_1 and E_2 (*Figure 1*) the following conditions of phase equilibrium are valid:

$$\text{branch } AE_1 \qquad \mu_A^L = \mu_A^S \qquad (1a)$$

$$\text{branch } E_2B \qquad \mu_B^L = \mu_B^S \qquad (1b)$$

$$\text{branch } E_1CE_2 \qquad \mu_C^L = \mu_C^S \qquad (1c)$$

where μ_X^L and μ_X^S are the chemical potentials of component X ($X = A, B, C$) in the liquid mixture (L) or in the crystalline phase (S). Assuming that the heat of melting is independent of temperature, each of these equations can be rearranged to:

$$\mu_X^L - \mu_X^\circ = -\Delta H_{f,X}(1 - T/T_{f,X}^\circ) \qquad (X = A, B, C) \quad (2)$$

where μ_X° is the chemical potential of pure liquid component X at temperature T, $\Delta H_{f,X}$ is the molar heat of melting of component X and $T_{f,X}^\circ$ is the temperature of melting of component X in the absence of other components.

The difference $\mu_X^L - \mu_X^\circ$ should be expressed as a function of the composition of the liquid mixture at T. For this purpose, we use expressions obtained from the theory of association equilibria[1]. First, let it be assumed

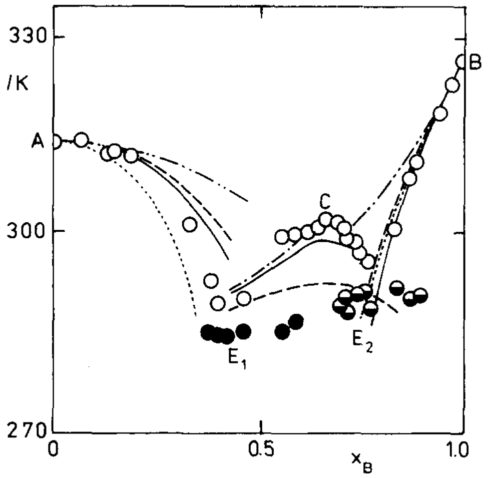

Figure 1 The solid–liquid phase diagram of the system phenol/polyoxyethylene ($M = 2000$). A, B and C denote the solid–liquid equilibria of pure phenol, of POE 2000, or of the crystalline compound; E_1 and E_2 give the approximate positions of eutectic points. The open circles represent melting of the single-crystalline component, and the half-full and full circles represent melting of the eutectic. Curves calculated from the theory for $m = 22$: (–··–) $\eta = 1$, (–––) $\eta = 10$, (———) $\eta = 100$ (in AE_1 and E_2B, $\eta \geqslant 100$), (–·–) $\eta = 1000$; for $m = 44$: (·····) $\eta \rightarrow \infty$. Finally, x_B is monomer mole fraction of POE

---

* To whom correspondence should be addressed

0032-3861/91/071309-04

that, along with simple molecules (unimers) A and B, complexes of the A_iB type also exist, which are due to bonds (e.g. hydrogen bonds) between molecules A and binding sites of the macromolecule B; if the polymer has m sites, then $0 < i \leqslant m$. Complexes and unimers are in mutual thermodynamic equilibrium. Later, we shall also examine the assumption that no complex other than $A_{i_C}B$ exists in the liquid phase.

The theory of association equilibria[1] gives us the following relations for the individual branches of the phase diagram:

branch AE_1
$$\ln(r_A p_A) + 1 - r_A(p_A + \nu_B) = -(\Delta H_{f,A}/R)(1/T - 1/T^{\circ}_{f,A}) \quad (3a)$$

branch E_2B
$$\ln(r_B p_B) + 1 - r_B(p_A + \nu_B) = -(\Delta H_{f,B}/R)(1/T - 1/T^{\circ}_{f,B}) \quad (3b)$$

branch E_1CE_2
$$\ln(r_C p_C) + 1 - r_C(p_A + \nu_B) = -(\Delta H_{f,C}/R)(1/T - 1/T^{\circ}_{f,C}) \quad (3c)$$

where r_A, r_B and r_C are the numbers of Flory–Huggins segments in molecules of the components A and B and of the complex C; hence,

$$r_C = i_C r_A + r_B \quad (4)$$

The concentrations are expressed as the moles of substance per mole of segments in the mixture; for the concentration of a general species or component X we have:

$$\nu_X = n_X \Big/ \sum_X r_X n_X \quad (5)$$

where n_X is the number of moles of substance X. In terms of the theory of association equilibria we distinguish the nominal concentrations of original components, i.e. the overall concentrations of components A and B in the liquid phase, irrespective of the formation of complexes, and the concentrations of species, i.e. the concentrations of complexes of a certain type or of unimers. The nominal concentrations of components A, B are denoted ν_A, ν_B. For the concentration of the complex species A_iB we introduce the symbol ν_{i1}; for the concentrations of unimer species A, B, the respective symbols are p_A, p_B; similarly, for the complex C we write p_C. For the nominal concentrations of components A, B we have:

$$r_A \nu_A + r_B \nu_B = 1 \quad (6)$$

The concentrations of unimer species p_A and p_B must be calculated from the nominal concentrations ν_A and ν_B. If the i binding sites of a macromolecule are mutually equivalent and independent, the bond between one molecule A and the given binding site of the polymer can be characterized by a single equilibrium constant η. In such a case, the equation of association equilibrium:

$$\nu_{i1} = \frac{m!}{i!(m-i)!} \eta^i p_A^i p_B \quad (7)$$

is valid, where the combinatorial factor indicates the number of possibilities of selecting i sites intended for occupation by the molecule A from m binding sites of the macromolecule. Hence we can substitute into the mass balances for components A and B and obtain the relations[1]:

$$p_A = \tfrac{1}{2}(\nu_A - m\nu_B - \eta^{-1}) + \tfrac{1}{2}[(\nu_A - m\nu_B - \eta^{-1})^2 + 4\eta^{-1}\nu_A]^{1/2} \quad (8a)$$

$$p_B = \nu_B(1 + \eta p_A)^{-m} \quad (8b)$$

Note that $\Delta H_{f,C}$ and $T^{\circ}_{f,C}$ in equation (3c) are related to the melting process of the crystalline compound, which gives rise to the pure liquid complex C. In a general case, this is a hypothetical process, because at equilibrium at least insignificant quantities of the other species must also be present in the liquid phase. As a consequence, $\Delta H_{f,C}$ and $T^{\circ}_{f,C}$ should usually be obtained by an extrapolation procedure.

Case of a very strong association in the liquid phase

To elucidate relations between the individual species in the liquid mixture, let us analyse the limiting case of a very strong association ($\eta \to \infty$).

In such a case it is suitable to divide the whole concentration range into two regions: (I) $\nu_A > m\nu_B$, (II) $\nu_A < m\nu_B$. The boundary between the two concentration regions corresponds to the composition of the complex A_mB and is given by the relation ensuing from the definition $\nu_A = m\nu_B$ and equation (6):

$$\nu_B = 1/(r_B + m r_A) \quad (9)$$

For the sake of simplicity, let it be assumed that the total number of sites m does not exceed the number of molecules of A per molecule of the crystalline compound C, so that:

$$i_C = m \quad (10)$$

The boundary between regions (I) and (II) then corresponds to the point C of the phase diagram, where $\nu_A = i_C \nu_B$ is valid, and—bearing in mind equation (4)—equation (9) becomes:

$$\nu_B = \nu_A/m = 1/r_C \qquad (\text{for } \nu_A = m\nu_B) \quad (11)$$

Concentration range (I). If the component A is present in excess ($\nu_A > m\nu_B$), for $\eta \to \infty$ virtually all binding sites of the polymer are saturated, and hence all molecules of B are transformed into the complex C. We then have:

$$p_A = \nu_A - m\nu_B \quad p_C = \nu_B \quad p_B \to 0 \quad \nu_{i1} \to 0 \qquad (\text{for } i < m)$$

For the branch AE_1 we obtain:

$$\ln[r_A(\nu_A - m\nu_B)] + [r_B + (m-1)r_A]\nu_B = -(\Delta H_{f,A}/R)(1/T - 1/T^{\circ}_{f,A}) \quad (12a)$$

and for the branch E_1C:

$$\ln(r_C \nu_B) + 1 - r_C[\nu_A - (m-1)\nu_B] = -(\Delta H_{f,C}/R)(1/T - 1/T^{\circ}_{f,C}) \quad (12b)$$

Both equations describe, in fact, the behaviour of the athermal Flory–Huggins mixture of component A present in concentration $\nu_A - m\nu_B$ and component C having concentration ν_B. Thus, if $\eta \to \infty$ is valid, the left-hand side of the phase diagram, i.e. the curve AE_1C, corresponds to a simple L–S diagram of the mixture of a low-molecular-weight component (A) and a polymeric compound (C).

Concentration range (II). If polymer B is the major component ($\nu_A < m\nu_B$), then virtually all molecules of component A are bound on macromolecules, so that

$p_A \rightarrow 0$. The probability that the chosen site of the polymer is occupied by a molecule of component A is $\nu_A/(m\nu_B) < 1$. The concentration of the complex A_iB is then given by the product of the nominal polymer concentration ν_B and the probability that the given macromolecule has i occupied and $(m-i)$ unoccupied sites:

$$\nu_{i1} = \frac{m!}{i!(m-i)!}\left(\frac{\nu_A}{m\nu_B}\right)^i\left(1-\frac{\nu_A}{m\nu_B}\right)^{m-i}\nu_B \qquad (13a)$$

If we specify $i = 0$ in this equation, we obtain:

$$p_B = \nu_B(1 - \nu_A/m\nu_B)^m \qquad (13b)$$

and for $i = m$ we have:

$$p_C = \nu_B(\nu_A/m\nu_B)^m \qquad (13c)$$

By substituting (13b) and (13c) into (3b) and (3c) we obtain for the branch E_2B:

$$\ln(r_B\nu_B) + m\ln(1 - \nu_A/m\nu_B) + r_A\nu_A = -(\Delta H_{f,B}/R)(1/T - 1/T^\circ_{f,B}) \qquad (14a)$$

and for the branch CE_2:

$$\ln(r_C\nu_B) + m\ln(\nu_A/m\nu_B) + 1 - r_C\nu_B = -(\Delta H_{f,C}/R)(1/T - 1/T^\circ_{f,C}) \qquad (14b)$$

In the predominant part of the concentration range (i.e. with the exception of the close surroundings of points B and C), the dominant term on the left-hand side of both these equations is the second term, proportional to the number of sites m, and thus also to the degree of polymerization of component B.

At the point C, common to the branches E_1C and E_2C, both branches have a common limit $T = T^\circ_{f,C}$ also for $\eta \rightarrow \infty$, as can be seen by substituting from equation (11) into (12b) and (14b). On the other hand, it can be demonstrated that the derivative of the left-hand side of equation (12b) with respect to the volume fraction ϕ_B becomes $r_C^2/(r_Ar_B)$ at the point C, while the analogous value ensuing from equation (14b) is $-r_C^2/(r_Ar_B)$. Hence, the curve E_1CE_2 is continuous at the point C, but its derivative has a discontinuity for $\eta \rightarrow \infty$. It can be shown by means of a general argument that, if any common dependence of the Gibbs energy on composition is used, the curve E_1CE_2 has a 'rounded' maximum, which at the point C has a continuous first derivative equal to zero; for our model with $\eta \rightarrow \infty$, however, the curve has a pointed shape at the maximum.

For the sake of comparison, let us now consider a case where, along with unimer molecules A or B, only the complex C can exist in the melt, so that $\nu_{i1} = 0$ $(0 < i < m)$. It is easy to see that in the limit $\eta \rightarrow \infty$ the same relations are valid in the range $\nu_A > m\nu_B$ as in the case discussed earlier. A different situation arises of course if $\nu_A < m\nu_B$, so that $p_A \rightarrow 0$. Mass balance then gives:

$$p_B = \nu_B - \nu_A/m \qquad (15a)$$

$$p_C = \nu_A/m \qquad (15b)$$

By substituting into equations (3b) and (3c) we obtain for the branch E_2B:

$$\ln[r_B(\nu_B - \nu_A/m)] + r_A\nu_A = -(\Delta H_{f,B}/R)(1/T - 1/T^\circ_{f,B}) \qquad (16a)$$

and for the branch CE_2:

$$\ln(r_C\nu_A/m) + 1 - r_C\nu_B = -(\Delta H_{f,C}/R)(1/T - 1/T^\circ_{f,C}) \qquad (16b)$$

Unlike relations (14a) and (14b) the left-hand sides of these equations do not contain any term proportional to the degree of polymerization; on the other hand, however, the expressions $\Delta H_{f,B}$ and $\Delta H_{f,C}$ on the right-hand sides are molar enthalpic changes proportional to the length of the polymer chain. Hence, the decrease in the melting point should be very small in both branches under consideration. This can also be expected for the simple phase diagram of two crystallizing high-molecular-weight components that form an athermal Flory–Huggins mixture. It can indeed be demonstrated that equations (16a) and (16b) describe the behaviour of such a mixture consisting of components B and C with concentrations given by relations (15a) and (15b).

Let us compare the left-hand sides of equations (14a) and (16a), or (14b) and (16b); they differ in the term $(m-1)\ln(\nu_A/m\nu_B)$ or $(m-1)\ln(1-\nu_A/m\nu_B)$ respectively. These terms characterize the difference in combinatorial entropy ensuing from the fact that in the former case the binding sites are completely independent of each other, while in the latter case they are fully cooperative. If each side may exist in two states, i.e. a free and an occupied one, a macromolecule containing m independent sites may exist in one of 2^m occupancy states; such a situation is adequately described by equations (14a) and (14b). In the model leading to equations (16a) and (16b), however, the state of one binding site determines the state of all sites of the macromolecule, so that the number of possible occupancy states of the macromolecule is only 2. The additional combinatorial entropy thus arising in independent sites has the consequence that the decrease in the melting point in the branches E_2B and CE_2 is much larger than that observed with a mixture of two inert polymer components.

EXPERIMENTAL

Polyoxyethylene (POE 2000) manufactured by Fluka was kept in a desiccator and used without purification. Phenol produced by Polskie Odczynniki Chemiczne, Gliwice, was redistilled *in vacuo* before use. The solutions were prepared by introducing weighed amounts of the components into 2 ml ampoules in which they were sealed and homogenized. The individual samples (3–10 mg) were closed in hermetic aluminium vessels in a dry-bag under a stream of dry nitrogen.

The temperatures of the maximum of the melting endotherm measured in a Perkin–Elmer DSC-2 apparatus at a heating rate of 1.25 K min^{-1} were taken as the melting temperatures. The apparatus was calibrated to the melting temperatures of water and indium.

The X-ray measurements were carried out on a wide-angle diffractometer with Cu K_α radiation filtered by Ni.

RESULTS AND DISCUSSION

The diffractogram of a system melting at the point C of the phase diagram (*Figure 1*) is not a superposition of diffractograms of pure components A and B, but differs qualitatively from them (*Figure 2*), which confirms the existence of a crystalline compound. In *Figure 1*, the

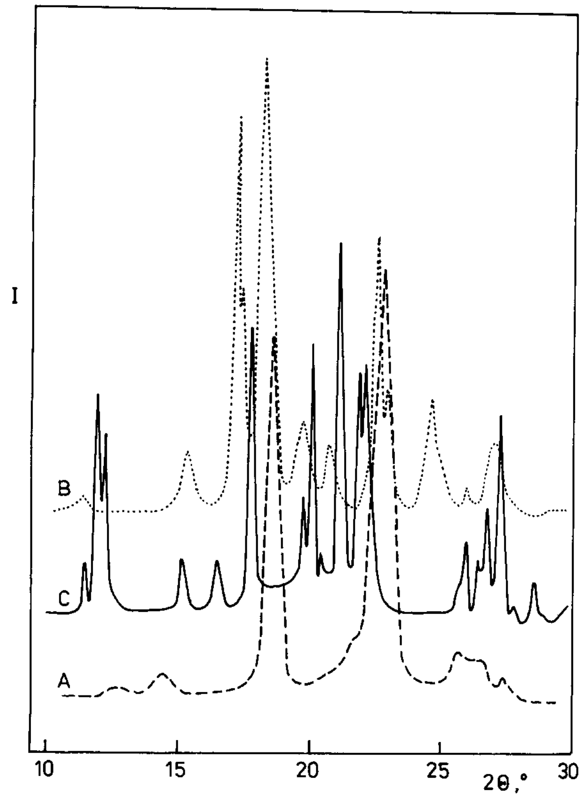

Figure 2 X-ray diffractograms for (A) phenol, (B) polyoxyethylene ($M = 2000$) and (C) crystalline compound. The diffraction angle is 2θ

monomer mole fraction $x_B = 2/3$ corresponds to the local maximum of C; hence, in the crystalline compound C there is one phenol molecule per two monomeric POE units. Consequently, for our POE sample having degree of polymerization $p = 44$, $i_C = 22$.

The great decrease in the melting point in the branches CE_2 and E_2B allows us to deduce (cf. the end of the 'Theory' section) that a whole spectrum of A_iB complexes, where $i \leqslant m$, coexists in the liquid phase. This is why equations (8a) and (8b) combined with equations (3a)–(3c) were used in theoretical calculations. First, the theoretical form of branches AE_1 and E_2B was calculated for various values of the association constant η (in this approximation, they were temperature-independent) and for the maximal number of binding sites m. In the calculation, $r_A = 1$ was chosen, so that r_B was given by the ratio of molar volumes V_B/V_A: $r_B = 0.457P$. The melting points of pure components and the molar heats of melting were substituted by the values measured by us: $T^\circ_{f,A} = 314.0$ K, $T^\circ_{f,B} = 327.0$ K, $\Delta H_{f,A} = 11.36$ kJ mol^{-1} and $\Delta H_{f,B} = 7.5P$ kJ mol^{-1}. [Note that, in terms of the usual theories, the heat of melting of the polymer should be replaced by the value that holds for an infinitely thick equilibrium crystal; in the case of POE, $\Delta H_f(\infty) = 8.7P$ kJ mol^{-1} is considered to be the best value[2]. In our paper under preparation[3] we show that in the case of POE crystals with extended chains better results are obtained by using the experimental ΔH_f value. Moreover, the difference between E_2B curves calculated using the one or the other ΔH_f value is almost negligible.] For the given x_2, the melting points calculated for $m = i_C = 22$ decrease with increasing η, as follows from a comparison of the curves in *Figure 1*. However, curves calculated for $\eta \geqslant 100$ coincide. Experimental points in the AE_1 branch lie below this limiting curve. We therefore also carried out a calculation for $m = 2i_C = 44$; this value fits the assumption that complex formation in the liquid phase is conditioned by the hydrogen bond between the hydroxyl group of phenol and the oxygen atom in the POE molecule, and that each monomeric POE unit is then able to bind the phenol molecule. In the branch AE_1 the melting temperatures thus calculated are lower than the experimental values. In the branch BE_2 the difference between curves calculated for $m = 22$ and $m = 44$ is small and probably does not exceed the experimental error.

At least in the surroundings of the maximum, the course of the branch E_1CE_2 can be adequately described by using curves calculated from equation (3c) for $m = 22$ and $\eta \geqslant 1000$, if $T^\circ_{f,C}$ and $\Delta H_{f,C}$ have been adjusted ($T^\circ_{f,C} = 302.4$ K, $\Delta H_{f,C} = 23.9P$ kJ mol^{-1}). For the sake of comparison, we have added curves calculated for lower values of the binding constant η and the same $T^\circ_{f,C}$ and $\Delta H_{f,C}$.

Obviously, the safest starting point for further interpretation is the branch AE_1. From its behaviour it can be inferred that in the liquid state the binding of phenol to POE is very strong and that, basically, all monomeric units ($m = 44$) can enter into an interaction with phenol. The difference between a curve calculated under such an assumption and the experiment can be attributed to the influence of several factors: (a) effect of the difference in expansivity of the low- and high-molecular-weight components in the sense of the Flory–Patterson–Prigogine equation-of-state theory; (b) mutual interference of phenol molecules bound at adjacent sites; and (c) self-association of phenol.

A complete quantitative analysis would require, in the first place, the introduction of the dependence of η on temperature and, secondly, taking into account the factors mentioned above. For the given database, the number of corresponding parameters would of course be too high.

REFERENCES

1 Pouchlý, J. *Collect. Czech. Chem. Commun.* 1969, **34**, 1236
2 Buckley, C. P. and Kovacs, A. J. *Prog. Colloid Polym. Sci.* 1975, **58**, 44
3 Lapeš, I., Baldrian, J., Biroš, J. and Pouchlý, J. in preparation