On the application of an association model to blends of phenoxy and ether-containing polymers

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An association model is used to predict phase behaviour in mixtures of poly(hydroxy ether) of bisphenol A (phenoxy) (PH) with poly(alkylene oxide)s, poly(vinyl alkyl ether)s, aromatic polyethers and related copolymers. Equilibrium constants and enthalpies corresponding to self-association of PH and interassociation of PH with the second component were calculated from a Fourier transform infra-red spectroscopy study of low molecular weight analogues in dilute solutions. Transferability of the association constants between model compounds and polymer blends, as well as model predictions of blend miscibility and phase diagrams, are discussed.

(Keywords: blends; association model; phase diagrams)

INTRODUCTION

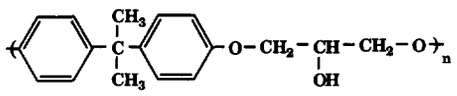
In some recent publications[1-3], Painter, Coleman and co-workers have proposed an association model to determine free energy changes and phase behaviour of binary polymer blends where specific interactions are present. The main equation of this model has the form of the classic Flory–Huggins relation, but with an added term to account for the strong intermolecular interactions:

$$\frac{\Delta G_m}{RT}=\frac{\Phi_A}{N_A}\ln\Phi_A+\frac{\Phi_B}{N_B}\ln\Phi_B+\Phi_A\Phi_B\chi+\frac{\Delta G_H}{RT} \quad (1)$$

In equation (1) N_A and N_B are the degrees of polymerization of polymers A and B, Φ_A and Φ_B are the volume fractions, and χ is the polymer–polymer interaction parameter, which only accounts for the 'physical' forces. The first and second terms correspond to the combinatorial entropy and can be neglected for high molecular weight polymers. The third term, unfavourable to the mixing, arises from non-hydrogen bonding or 'physical interactions', and can be estimated using group contributions proposed by Coleman *et al.*[4]. The $\Delta G_H/RT$ term can be calculated if one knows the molar volumes of the chemical repeat units, V_A and V_B, the equilibrium constants describing the association phenomena occurring in the blend and the corresponding association enthalpies. It is interesting to point out that, in terms of the model, B is a polymer capable of self-association. In most cases this self-association is in the form of dimers and multimers.

Painter, Coleman and co-workers have applied this model to a series of polymer blends, including poly(vinyl phenol) with polyacrylates[5], polymethacrylates[6], polyesters[5], polyethers[7] and poly(vinyl pyridine)[8], an amorphous polyurethane with polyethers[9,10], a copolymer of methacrylic acid and ethylene with polyethers[11,12], poly(vinyl pyridine)[13] and poly(ethyl oxazoline)[14] and polyamides with polyethers[15,16]. In other, more recent, papers they have corrected the original reference state[17], and have compared[18] their model with others based on a combinatorial method introduced by Veytsman[19] and extended and generalized by Panayiotou and Sanchez[20] and, finally, they have discussed the transferability of association constants between model compounds and the corresponding polymers[21].

Blends of poly(hydroxy ether) of bisphenol A (phenoxy) (PH):



with aliphatic[22] and aromatic[23] polyesters, polymethacrylates[24], polyoxides[25,26] and poly(vinyl ether)s[27] have been widely studied in recent years. These blends exhibit all sorts of phase behaviour, from completely miscible to completely immiscible, including some systems with lower critical solution temperature (*LCST*) type diagrams. For this reason, they are excellent systems to test the ability of the above-mentioned association model to predict their phase behaviours. In such blends, specific interactions are presumably not as strong as those formed with phenolic or carboxylic acid hydroxyl groups.

Phenoxy-containing systems present some difficulties for carrying out the necessary calculations of the association parameters introduced by Painter and Coleman. In blends with polyesters, a quantitative study of free and associated carbonyl groups is not feasible in the majority of cases. As far as the mixtures with

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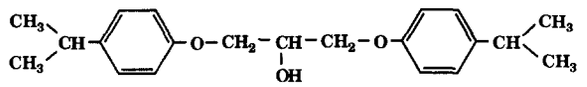
polyethers or poly(alkyl oxide)s are concerned, the ether asymmetric stretching band is not useful for this kind of study. Consequently, the only possible way is to use the hydroxyl stretching band. However, the strong PH self-association prevents a quantitative study of the 'free' hydroxyl band in the solid state. For this reason, it is necessary to dilute these self-associations using, for example, a non-polar solvent. Unfortunately, phenoxy is only miscible in solvents that form strong interactions with its hydroxyl groups (e.g. tetrahydrofuran, dioxane, chloroform, etc.). Thus, the only alternative is to use a low molecular weight analogue, soluble in non-polar solvents, to substitute phenoxy. Variations of the 'free' hydroxyl band absorbance with model compound concentration and frequency shifts will allow us to calculate association constants and enthalpies, respectively.

A recent paper by Coleman *et al.*[28] has stressed some of these problems in blends of phenoxy and aliphatic polyesters. Apart from the two constants generally used in describing the phenoxy self-association, they have introduced a third self-association constant which takes into account the association between the hydroxyl group of the phenoxy repeating unit and the aromatic ether group of the bisphenol-A moiety.

EXPERIMENTAL

Phenoxy resin was purchased from Union Carbide Co. The phenoxy resin analogue, 1,3-bis(4-(2-propyl) phenoxy)-2-propanol (IPPHP), was synthesized in our laboratory. The synthesis has been described previously[29].



Other polymers and low molecular weight compounds used in this work were supplied by Aldrich Chemical Co. Their purity was at least 98% and they were used without further purification.

Infra-red spectra were obtained on a Nicolet 5DXC spectrometer. In all cases, a minimum of 64 scans with an accuracy of 2 cm^{-1} were signal-averaged and the spectra were stored on a magnetic disc system.

For liquid samples, an adequate Beckman cell with KBr windows and variable thickness was used. Two different optical paths were used for studying the self-association of IPPHP and the interassociation between IPPHP and other compounds (0.1 and 1 mm, respectively).

Solutions of IPPHP in cyclohexane, carbon tetrachloride and toluene at concentrations between 0.05 and 0.5 mol l^{-1} were prepared for the self-association study. The interassociations between IPPHP and the other model compounds were investigated by taking the i.r. spectra of the IPPHP + analogue solutions in cyclohexane. To ensure that the hydrogen bonding between IPPHP and the corresponding analogue was the dominant intermolecular interaction in the mixture, 0.01 mol l^{-1} was selected as the IPPHP concentration. The concentrations of the other analogues were between 0.05 and 0.5 mol l^{-1}.

In order to obtain the enthalpy–i.r. frequency shift correlation for IPPHP, we used a 0.01 mol l^{-1} solution of IPPHP, mixing it with a series of small molecule bases: ethyl acetate, 1,4-dioxane, tetrahydrofuran, pyridine and *N*,*N*-dimethylacetamide at concentration 0.2 mol l^{-1}. The correlation between Δv and Δh for these bases with different small hydrogen-bonding donors (e.g. *t*-butanol, phenol, hexafluoroisopropanol) has been established previously by Drago *et al.*[30].

All model compound solutions and polymer films were within an absorbance range where the Beer–Lambert law is obeyed (<0.6 absorbance units).

All calculations have been made using recent versions of the Miscibility Guide & Phase Calculator (MG&PC) software package[3], kindly provided by the authors.

RESULTS AND DISCUSSION

Estimation of self- and interassociation constants and enthalpies

As mentioned before, two groups of parameters are required in order to estimate the free energy of mixing for a polymer blend using the Painter–Coleman equation (1). The first group defines the association equilibria between polymers by means of the equilibrium constants for the self-association of polymer B and for the interassociation between A and B. We also need their respective association enthalpies which measure the evolution of the constants with temperature. In the second set, characteristic parameters of each polymer (molecular weight and molar volume of the specific repeating unit, solubility parameter δ and degree of polymerization) are required. This set can be easily calculated from group contributions, but association parameters have to be estimated from a Fourier transform i.r. (*FT*i.r.) study of the appropriate polymer blend or an analogue mixture.

Neither phenoxy resin nor polyethers contain carbonyl groups, the most useful bands to carry out a quantitative study of bonded groups. For this reason, and in order to determine association constants, we followed the procedure applied by Coggeshall and Saier[31] in a study of self-associations of alcohols and phenols and their interassociations with some hydrogen-bonding acceptors. They found that two equilibrium constants are required to describe most alcohol self-associations, one describing the formation of dimers K_2 and the other describing the formation of higher multimers K_B.

We employed three different 'non-polar' solvents (cyclohexane, carbon tetrachloride and toluene) to explore the influence they have on the determination of equilibrium constants. First of all, observing the free hydroxyl zone, we found important differences in the IPPHP spectrum depending on the solvent used. In toluene, IPPHP shows one band at 3590 cm^{-1}; in carbon tetrachloride, one band at 3605 cm^{-1} with a shoulder centred at 3590 cm^{-1}; and in cyclohexane, two separated bands at 3610 and 3590 cm^{-1}. The band which appears at higher wavenumber can be ascribed to 'free' hydroxyl groups and the second one to intramolecular hydrogen bonded hydroxyls[32]. These last interactions can only be formed if the molecule adopts some specific conformations that can be favoured or hindered by the solvent. This fact can explain the differences between spectra obtained in different solvents. A similar behaviour has been observed by Coleman *et al.*[33] in studying solutions of 3,3,4,4,4-penta fluorobutan-2-ol as a model compound of an alternating copolymer of vinyl alcohol and tetrafluoroethylene.

Another solvent effect that has been observed is the different intermolecular 'associated' hydroxyl bands (broad band at 3500–3540 cm^{-1}) obtained in solutions with the same IPPHP concentrations but different solvents. In the light of this difference, we can affirm that the IPPHP tendency to self-associate depends on the solvent used: this is maximal in cyclohexane, intermediate in carbon tetrachloride and minimal in toluene. Doubtless, this is caused by the different ability of these solvents to interact with IPPHP.

Quantitative measurements of the absorbance of the isolated free hydroxyl band as a function of the IPPHP concentration at 25°C have been made for the three solvents investigated. Absorptivity coefficients (ε) can be determined from the usual extrapolations of I/cl in the limit $c=0$, where l is the path length and c the concentration. The experimental fraction of isolated hydroxyl groups f_m^{OH}, at any given concentration, is then simply $I/c\varepsilon l$. Data of f_m^{OH} for IPPHP/cyclohexane solutions are given in *Table 1*. These data can be used (*Figure 1*) in an iterative least-squares fitting procedure to directly obtain the best fit to an equation[28] relating the fraction of free monomers to the dimensionless equilibrium constants K_2 and K_B. The constants so obtained (10.4 and 18.6) can be easily scaled to the phenoxy repeating unit after taking into account the differences in the molar volumes of the model (IPPHP, 0.2988 l mol^{-1}) and the phenoxy specific repeat unit

Table 1 Fraction of free monomer data for IPPHP/cyclohexane mixtures

Free monomer fraction	IPPHP volume fraction
0.819	0.0105
0.813	0.0106
0.772	0.0128
0.752	0.0172
0.681	0.0205
0.649	0.0248
0.599	0.0293
0.529	0.0365
0.454	0.0477
0.399	0.0660
0.333	0.0873
0.267	0.1222

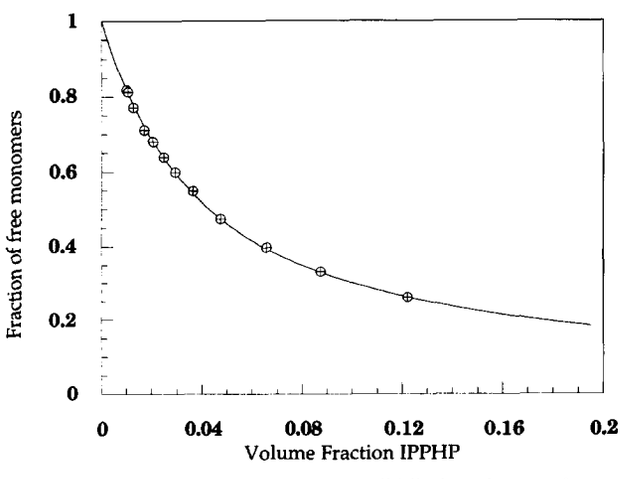


Figure 1 Results of a least-squares fit (solid line) to the experimental fraction of free monomers *versus* concentration. IPPHP/cyclohexane at 25°C

(0.2166 l mol^{-1}) by means of the expression:

$$K^* = K^{model}\left(\frac{V^{model}}{V^*}\right) \quad (2)$$

The corresponding values, taking the phenoxy molecule as a reference, were 14.4 and 25.6.

A similar procedure was applied with the solutions of IPPHP in toluene and carbon tetrachloride. Since these results confirm that the highest self-association occurs in cyclohexane, we decided to use this solvent in the calculation of the interassociation constant and enthalpy. It is necessary to emphasize the influence of the solvent in the obtained parameter set and, therefore, in the predictive character of the model.

In their paper about phenoxy/aliphatic esters blends, Coleman *et al.*[28] calculated K_2 and K_B using solutions of 2-propanol in cyclohexane. In order to obtain a best fit in calculating K_A, they introduced a third self-association constant K_E, which quantifies the interaction between the hydroxyl group and the ether group attached to the phenoxy aromatic ring. As a test of the consistency between our data and those of ref. 28 we have used their K_2 and K_B values and our experimental data of IPPHP in cyclohexane in an attempt to calculate the third self-association constant K_E using another possibility of the software package. After scaling their K_2 and K_B constants to the IPPHP molar volume (equation (2), the new values being 8.5 and 15.5), the best fit reproducing our experimental results gave a dimensionless K_E value of 2.2 (referred to the IPPHP molecule). Rescaling to the phenoxy repeating unit, the resulting K_E value was 3.0, in good agreement with the value of 2.9 they obtained from a similar study of dilute solutions of 2-propanol and phenyl methyl ether. We do not include the least-squares fitting graph because of its similarity with *Figure 1*.

Interassociation constants (K_A) describing hydroxyl–aliphatic ether interactions were obtained from data of the 'free' OH band absorbance at one fixed IPPHP concentration and varying that of the other analogue compound. We used diethylene glycol diethyl ether (DEGDEE, three ether groups per molecule) as model compound of polyethers. The Coggeshall and Saier[31] methodology, also described by Yang *et al.*[34], involves the calculation of an association constant K_a (in l mol^{-1}) from the following equation:

$$K_a = \frac{1 - f_m^{OH}}{f_m^{OH}[c_A - (1 - f_m^{OH})c_B]} \quad (3)$$

where c_B and c_A are the concentrations in mol l^{-1} of IPPHP and ether groups of DEGDEE. The value of K_a so obtained is concentration dependent. Although this is not a general result, such a dependence was also observed by Coggeshall and Saier[31]. Extrapolation at zero concentration gives a reliable value of the interassociation constant (see *Figure 2*). The interassociation constant has to be changed from the concentration-based equilibrium value (K_a) to the dimensionless parameters (K_A) defined in the model. This change is made by dividing K_a by the molar volume of the PH repeating unit (0.2166 l mol^{-1} at 25°C). The corrected equilibrium constant K_A was 3.4.

Association enthalpies can be calculated if one knows values of the corresponding constants at different temperatures. However, in our case the low cyclohexane

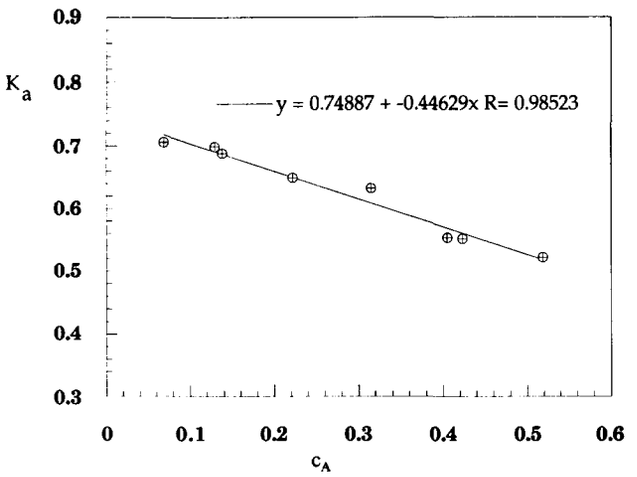


Figure 2 Experimental dependence of K_a (calculated according to equation (3) and experimental fraction of free monomers) *versus* concentration. IPPHP/DEGDEE mixtures in cyclohexane at 25°C

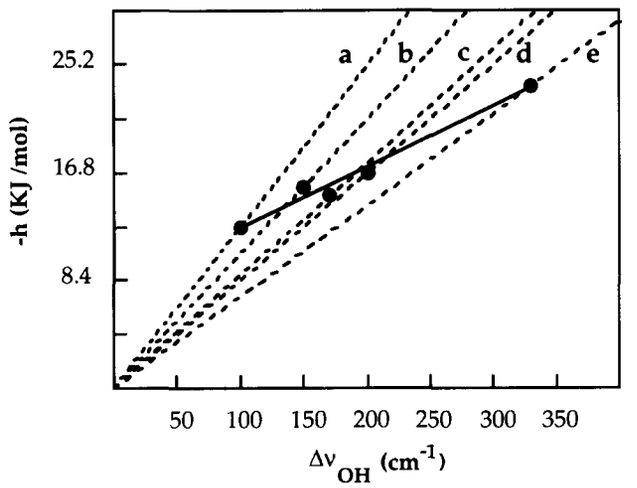


Figure 3 Enthalpies and spectral shifts of IPPHP with basic compounds. (a) Ethyl acetate; (b) dioxane; (c) tetrahydrofuran; (d) dimethyl acetamide; (e) pyridine

boiling point gives a narrow temperature range in which to work without risk of solvent loss. For this reason, we decided to make an indirect estimation based on the frequency shifts in the IPPHP i.r. spectrum. This method was used in other systems[35] with similar results to those of direct estimation. Using different low molecular weight bases it is possible to obtain linear correlations between i.r. frequency shifts and enthalpies in their mixtures with hydroxyl-containing compounds (the broken lines in *Figure 3*). After measuring the i.r. frequency shifts for mixtures of IPPHP with these low molecular weight bases it is possible to locate experimental points in the different broken lines. These experimental points provide an enthalpy *versus* frequency shift correlation (*Figure 3*) for the hydroxyl band of IPPHP.

$$-h\ (\text{kJ mol}^{-1}) = 7.90 + 0.0468\ \Delta\nu_{OH}(\text{cm}^{-1}) \quad (4)$$

The non-zero intercept of the acid lines, such as the IPPHP line, has been discussed previously[30].

In the self-association constant estimation, we found that 'associated' hydroxyl band frequency shift varies from 60 cm^{-1} at low IPPHP concentration to 140 cm^{-1} at high IPPHP concentrations. The first value was taken as the shift corresponding to dimer formation, which is favoured at low alcohol concentration. The second value was ascribed to multimer formation, which is favoured at high concentrations. In mixtures of IPPHP with DEGDEE a shift of 100 cm^{-1} was found, without relevant changes with concentration variations. After substituting these shifts in equation (4), we obtained the enthalpies corresponding to each association. Results are given in *Table 2*. Incidentally, K_A and h_A are not very different from those obtained by Coleman *et al.*[28] for the interaction between the hydroxyl group and an aromatic ether.

An important question remaining, before entering into the simulation of phase diagrams and other thermodynamic properties, is the so-called transferability of the constants and enthalpies obtained from analogue compound studies to the simulation of polymer blend properties. Coleman *et al.*[21] have recently reported that there are appreciable differences between interassociation constants depending on the system employed. Constants calculated with the aid of low molecular weight analogues are higher than those calculated with solutions of one polymer and an analogue compound of the other. These are higher than constants calculated with copolymers containing both repeating units and, in the lowest level, we have the constants directly calculated with polymer blends. This behaviour has been found, for instance, in blends of poly(vinyl phenol) and polyacrylates[21]. As mentioned previously, the only way to calculate interassociation parameters in phenoxy/polyether blends is through the use of model compounds. In the following discussion we will present some arguments that could support our present approach, despite the experimental evidence mentioned above[21].

In the frequently cited paper about phenoxy/aliphatic ester blends, Coleman *et al.*[28] obtained the appropriate interassociation constant K_A and the corresponding enthalpy between ester and hydroxyl groups. As mentioned previously, they used three self-association constants for phenoxy, calculated with the aid of cyclohexane solutions of 2-propanol and solutions of 2-propanol and methyl phenyl ether in the same solvent. K_A was obtained by adjusting *FT*i.r. data of blends of PH and polycaprolactone (PCL) at different temperatures. From these data K_A and h_A were stated to be 7.9 and -16.30 kJ mol^{-1} at 25°C.

Experimental determinations similar to those described above for IPPHP/DEGDEE solutions in cyclohexane, have been made in our laboratory with mixtures of IPPHP and diethyl adipate (DEA). DEA is an analogue compound of aliphatic polyesters. For IPPHP/DEA mixtures, K_A (in terms of the PH repeating unit) was 4.1 and a shift of 80 cm^{-1} was observed in the hydroxyl band, giving an enthalpy of -11.3 kJ mol^{-1} using

Table 2 Summary of association parameters for phenoxy blends with polyesters and polyethers

Interaction	K (at 25°C)	h(kJ mol^{-1})
Self-association		
dimer formation	14.4	−10.45
multimer formation	25.6	−14.21
Interassociation		
with polyethers	3.4	−12.54
with linear polyesters	4.1	−11.29

equation (4). Both data are given at the standard temperature (25°C) and are summarized in *Table 2*. It is interesting to point out the similar values of constants and enthalpies obtained from IPPHP/ether and IPPHP/ester mixtures. Both are clearly lower than those representing poly(vinyl phenol)/polyacrylate mixtures[21].

Reported *FTi.r.* data[28] of the fraction of free carbonyl groups in a PH/PCL blend have been obtained at higher temperatures, above the thermal transitions of the blend. We have selected 75°C as a comparison temperature. New values of our constants K_2, K_B and K_A may be calculated at 75°C with the constants and enthalpies at 25°C (*Table 2*) and the Van t'Hoff equation expressing the temperature dependence of the equilibrium constants. The new values were 7.9, 11.3 and 2.2, respectively. With these values we have tried to reproduce experimental results of free carbonyl fractions of different PH/PCL blends, reported by Coleman *et al.*[28]. *Figure 4* compares experimental and calculated data using our constants at 75°C. The agreement is similar to that obtained by Coleman *et al.* using their values and including a third constant for the self-association of phenoxy. If we use the least-squares analysis provided in the MG&PC software package[3] and fix our self-association constants at 75°C, allowing K_A to vary, the best fit is obtained for only a slightly different value of $K_A = 2.25$. Similar results are obtained when comparing experimental and simulated data at 195°C. In this case the best fit is attained with $K_A = 0.80$, compared with a value of 0.70 calculated with our constant and enthalpy at 25°C.

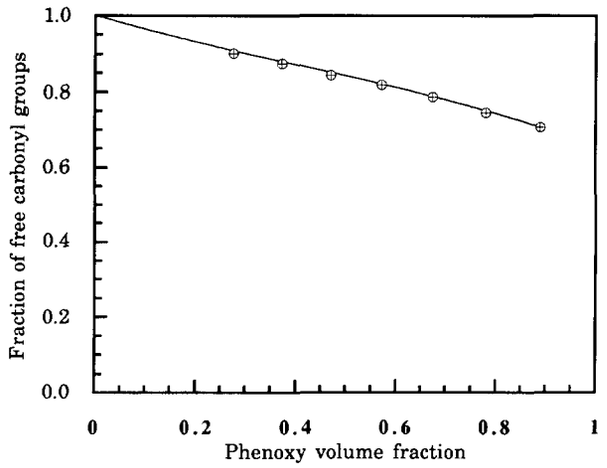


Figure 4 Comparison between experimental results for PH/PCL blends at 75°C[28] and the theoretical simulations using the constants and enthalpies reported in this work

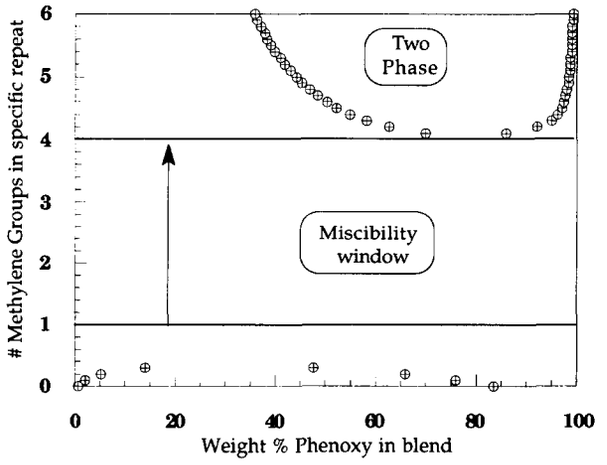


Figure 5 Miscibility window at 200°C for phenoxy blends with a homologous series of poly(alkylene oxide)s

Given the similar values of constants and enthalpies in IPPHP/ester and IPPHP/ether mixtures, the results summarized above seem to support a tentative analysis of the possibilities of the association model in describing phenoxy/polyether blends, with constants and enthalpies calculated by using model compounds. So we have calculated miscibility windows and phase diagrams in phenoxy/ether-containing polymers, using the constants and enthalpies summarized in *Table 2*.

Predicting phase behaviour

Using an identical procedure to that described by Serman *et al.*[7], the MG&PC software package[3] and the parameters given in *Table 2*, we present in *Figure 5* the miscibility window for phenoxy blends with poly(alkylene oxide)s. We have made the calculations at 200°C, a temperature at which the liquid state of the mixtures is ensured. The poly(alkylene oxide) series starts with the ether group and continues by adding methylene groups to form poly(methylene oxide) (PMO, one methylene group), poly(ethylene oxide) (PEO, two methylene groups), poly(trimethylene oxide) (PTrO), poly(tetrahydrofuran) (PTHF), poly(pentamethylene oxide) (P5O) and poly(hexamethylene oxide) (P6O). In all cases the polyoxides had 5000 repeating units and phenoxy 200.

The first three polymers in the series are theoretically miscible at the temperature considered. Blends of PH with PTHF (four CH_2 groups) seem to be on the edge of miscibility. In fact, a simulation of the spinodal phase diagram shows two phase-separated regions at temperatures above 240°C (*LCST*) and below 0°C (upper critical solution temperature, *UCST*). In a similar simulation for PH blends with P5O and P6O, the two phase regions merge to form the classic hourglass-shaped phase diagram typical of immiscible polymer blends. In summary, the results of these calculations indicate that phenoxy should be miscible with linear aliphatic polyoxides containing one to four methylene groups in the chemical repeating unit.

Experimentally, only PEO is known to be miscible with PH[25,26]. This fact agrees with the result of our calculation. On the contrary, PMO/PH blends should be theoretically miscible, but in a recent work we have found evidence of immiscibility for this blend[36]. This failure cannot be ascribed to minor errors in the parameter determination. The unfavourable term of the Painter–Coleman equation for this blend is the smallest in the family because of the similar solubility parameters of PH and PMO. The favourable term is the largest, because ether groups are more concentrated in PMO than in the other members of the series. In our opinion, the failure of this system could be attributed to structural differences between PMO and the other polyoxides. PMO is highly crystalline, has a high melting point, is resistant to most solvents and has been found to be miscible only with poly(vinyl phenol)[37]. This could suggest a certain degree of self-association[37] which might be reflected in an interassociation constant (K_A) smaller than that for the other polyoxides. No experimental studies have been carried out for blends of PH with the other polyoxides of this family, impeding the verification of the other theoretical predictions.

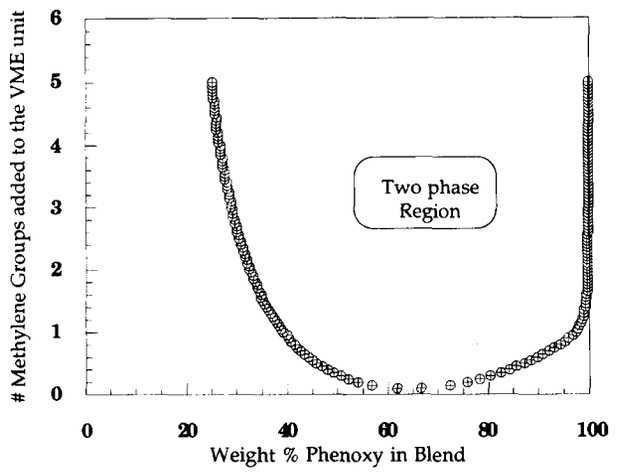


Figure 6 Miscibility window at 100°C for phenoxy blends with a homologous series of poly(vinyl ether)s

Using the same parameter set, *Figure 6* shows the miscibility window for blends PH/poly(vinyl alkyl ether). In this case, calculations were made at 100°C, given the amorphous character and low glass transition temperatures (T_gs) of this series. In this case poly(vinyl methyl ether) (PVME) was taken as a reference and the number of repeating units were 1000 and 200 for polyether and phenoxy, respectively. Consequently, PVME corresponds to zero methylene groups added to the specific repeat unit. As shown in the figure, this first member of the series is in the limit of miscibility, the rest of the family being predicted to be immiscible. These predictions agree quite well with the reported experimental behaviour[27] for blends of phenoxy with PVME and poly(vinyl ethyl ether).

In *Figure 7* we have simulated the spinodal phase diagram for the PH/PVME blend. It exhibits two phase-separated zones above 190°C (*LCST*) and below 40°C (*UCST*). The *LCST* prediction agrees quite well with the experimental cloud point curve[27]. The *UCST* has not been confirmed experimentally, but it should appear very close to the T_gs of the blend and the hypothetical phase separation could be kinetically hindered.

Another aliphatic polyoxide having a pendent methyl group is poly(1,2-propylene oxide). It is important to point out that, for the model we are using, this polymer and PVME are completely equivalent

$$-(-CH_2-CH(CH_3)-O-)_n- = -(-CH_2-CH(O-CH_3)-)_n-$$

because polymer parameters (δ, V_m, M_w) are the same for both polymers. Conversely, experimental trends in miscibility are different: poly(propylene oxide) has been reported to be completely immiscible with PH[25], while PVME forms miscible blends from 0 to 160°C[27]. Small changes in association parameters or in the solubility parameters of the polymers can give a completely immiscible diagram for both blends, indicating that differences between both systems can be explained attending to the experimental error in the parameter determination. In fact, using the K_A and h_A values obtained by Coleman *et al.*[28] from mixtures of 2-propanol and methyl phenyl ether, the phase behaviour for phenoxy and poly(propylene oxide) mixtures exhibited an hourglass-type diagram which would prevent miscibility in equimolar mixtures.

Other ether-containing polymers can be handled using the same methodology. For instance, poly(4-methoxy styrene) is a polyether in which the ether group is located between a methyl and an aromatic ring, a similar situation to that of the ether groups in the phenoxy repeating unit. In fact, the third self-association parameters (K_E and h_E) introduced by Coleman *et al.*[28] for phenoxy correspond to the same type of interaction. Taking values of $K_A = 2.9$ (at 25°C) and $h_A = -13.4$ kJ mol^{-1}, we have simulated the theoretical spinodal phase diagram for a mixture of PH/P4MS, each polymer having 500 repeating units. The blend should be miscible up to 300°C (*Figure 8*). However, blends prepared in our laboratory by solution–precipitation and by casting from different solvents showed, in all cases, two T_gs located in the same position of the pure components.

Another well known aromatic ether is poly(2,6 dimethyl phenylene oxide) (PPO). In this case, we do not have constant and enthalpy values for ether between two aromatic rings. If, in a first test, we use the same constant as in the case of P4MS, the blend PH/PPO has even more possibilities to be miscible (the PPO solubility parameter is closer to PH than that of P4MS). In spite of the blend transparency (due to very similar refractive indexes), the blend showed the two T_gs of the pure components. It is reasonable to think that the tendency

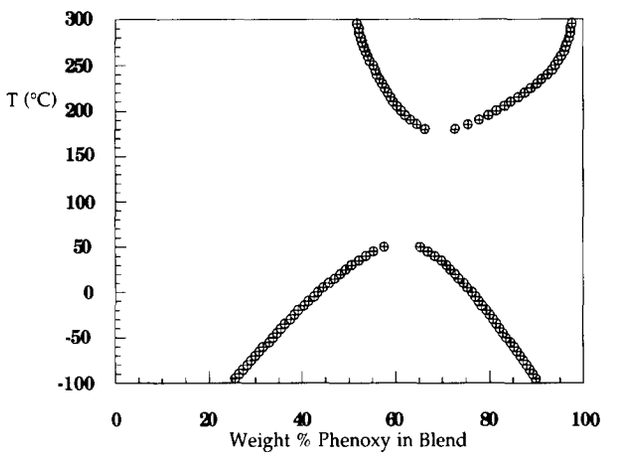


Figure 7 Calculated spinodal phase diagram for PH/PVME blends between −100 and 300°C

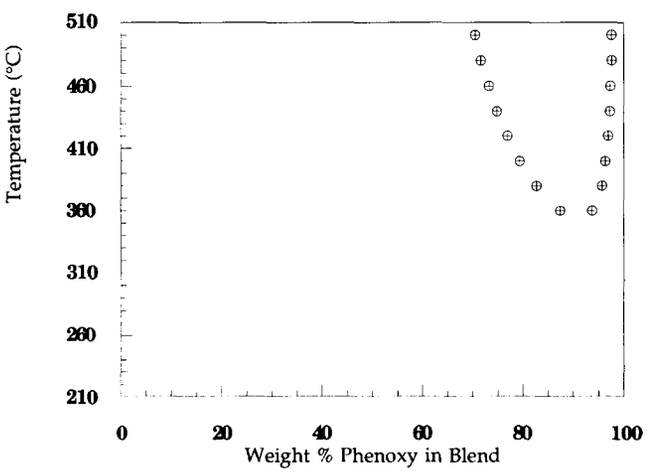


Figure 8 Calculated spinodal phase diagram for PH/P4MS blends between 200 and 500°C

of this ether group to form specific hydrogen bonds is severely restricted in this case by steric factors. Similar arguments can be proposed in the case of a halogenated poly(alkylene oxide) as poly(epichlorohydrin) (PECH). In spite of its similar solubility parameter (PECH, 10.1; PH, 10.2) neither PECH nor its copolymers with ethylene oxide are miscible[25] with phenoxy.

Finally, in a recent paper, Qipeng *et al.*[38] have considered blends of phenoxy with different copolymers of ethylene oxide (EO) and propylene oxide. These copolymers exhibited *LCST*-type phase diagrams with up to 66% of EO in the copolymer, although data at high EO content must be considered with caution given the degradability of such materials at the high temperatures reported as phase separation temperatures. Perhaps the more confident result is that of the copolymer containing 22% of EO units, which showed an *LCST* diagram at about 60°C. Our constant K_A and enthalpy h_A predict phase separation at very high temperatures, in agreement with the results discussed previously about poly(propylene oxide) blends. The values of Coleman *et al.*[28] ($K_A = 2.9$ and $h_A = -13.7$ kJ mol^{-1}) gave a phase diagram at about 140°C. However, the extremely low values of the molecular weights of the copolymer employed could enhance the role of its hydroxyl terminal groups in association equilibria, which have not been taken into account in our analysis.

CONCLUSIONS

In this work, we have applied the Painter–Coleman association model to different phenoxy–ether-containing polymers. In this type of system, where a quantitative study of the carbonyl stretching band is not possible and the self-associated component is not soluble in inert solvents, the use of model compounds in dilute solutions is the only way to estimate the parameter set necessary to apply the model. We have pointed out that solvents described as inert can have an influence on the parameters obtained and, therefore, on the predictions. Cyclohexane seems to be a good solvent for such experiments, as has been reported by other authors[28].

In spite of the well documented arguments[21] against the transferability of the constants between model compounds and polymer blends, reasonable phase behaviour predictions have been obtained with the constants determined via model compounds. A possible explanation of this apparent contradiction could arise from the low value of the interactions involved in the systems under study. For instance, the K_A constants in IPPHP/DEGDEE and IPPHP/diethyl adipate mixtures are one order of magnitude lower than that of the poly(vinyl phenol)/polyacrylate blends employed in testing the transferability of the constants. This lower value could result in a less determinant effect on the thermodynamic properties when the use of constants determined from polymer blends or model compounds is compared.

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REFERENCES

1 Painter, P. C., Park, Y. and Coleman, M. M. *Macromolecules* 1988, 21, 66
2 Painter, P. C., Park, Y. and Coleman, M. M. *Macromolecules* 1989, **22**, 570
3 Coleman, M. M., Graf, J. F. and Painter, P. C. 'Specific Interactions and the Miscibility of Polymer Blends', Technomic Publishing, Lancaster, PA, 1991
4 Coleman, M. M., Serman, C. J., Bahwagar, D. E. and Painter, P. C. *Polymer* 1990, **31**, 1187
5 Coleman, M. M., Lichkus, A. M. and Painter, P. C. *Macromolecules* 1989, **22**, 586
6 Serman, C. J., Painter, P. C. and Coleman, M. M. *Polymer* 1991, **32**, 1049
7 Serman, C. J., Xu, Y., Painter, P. C. and Coleman, M. M. *Polymer* 1991, **32**, 516
8 Painter, P. C., Graf, J. F. and Coleman, M. M. *Macromolecules* 1991, **24**, 5630
9 Coleman, M. M., Skrovanek, D. J., Hu, J. and Painter, P. C. *Macromolecules* 1988, **21**, 59
10 Coleman, M. M., Hu, J., Park, Y. and Painter, P. C. *Polymer* 1988, **29**, 1659; erratum: *Polymer* 1989, **30**, 766
11 Lee, J. Y., Painter, P. C. and Coleman, M. M. *Macromolecules* 1988, **21**, 346
12 Coleman, M. M., Lee, J. Y., Serman, C. J., Wang, Z. and Painter, P. C. *Polymer* 1989, **30**, 1298
13 Lee, J. Y., Painter, P. C. and Coleman, M. M. *Macromolecules* 1988, **21**, 954
14 Lichkus, A. M., Painter, P. C. and Coleman, M. M. *Macromolecules* 1988, **21**, 2636
15 Hu, J., Painter, P. C., Coleman, M. M. and Krizan, T. D. *J. Polym. Sci., Polym. Phys. Edn* 1990, **28**, 149
16 Bhagwagar, D. E., Painter, P. C., Coleman, M. M. and Krizan, T. D. *J. Polym. Sci., Polym. Phys. Edn* 1991, **29**, 1547
17 Veytsman, B. A. and Painter, P. C. *J. Chem. Phys.* 1993, **99**, 9272
18 Painter, P. C., Veytsman, B. A. and Coleman, M. M. *J. Polym. Sci. Part A: Polym. Chem.* 1994, **32**, 1189
19 Veytsman, B. A. *J. Chem. Phys.* 1990, **94**, 8499
20 Panayiotou, C. and Sanchez, I. C. *J. Chem. Phys.* 1991, **95**, 10090
21 Coleman, M. M., Xu, Y. and Painter, P. C. *Macromolecules* 1994, **27**, 127
22 Harris, J. E., Goh, S. H., Paul, D. R. and Barlow, J. W. *J. Appl. Polym. Sci.* 1982, **27**, 839
23 Robeson, L. M. and Furtek, A. B. *J. Appl. Polym. Sci.* 1979, **23**, 645
24 Chiou, J. S. and Paul, D. R. *J. Appl. Polym. Sci.* 1991, **42**, 279
25 Robeson, L. M., Hale, W. F. and Merriam, C. N. *Macromolecules* 1981, **14**, 1644
26 Iriarte, M., Espi, E., Etxeberria, A., Valero, M., Fernandez-Berridi, M. J. and Iruin, J. J. *Macromolecules* 1991, **24**, 5546
27 Uriarte, C., Eguiazabal, J. I., Llanos, M., Iribarren, J. I. and Iruin, J. J. *Macromolecules* 1987, **20**, 3038
28 Coleman, M. M., Yang, X. and Painter, P. C. *Macromolecules* 1992, **25**, 4414
29 Espi, E. and Iruin, J. J. *Macromolecules* 1991, **24**, 6458
30 Drago, R. S., O'Bryan, N. and Vogel, G. C. *J. Am. Chem. Soc.* 1970, **92**, 3924
31 Coggeshall, N. D. and Saier, E. L. *J. Am. Chem. Soc.* 1951, **73**, 5414
32 Kuhn, L. P. *J. Am. Chem. Soc.* 1952, **74**, 2492
33 Coleman, M. M., Yang, X., Zhang, H., Painter, P. C. and Scherer Jr, K. V. *J. Polym. Sci: Part A: Polym. Chem.* 1993, **31**, 2039
34 Yang, X., Painter, P. C., Coleman, M. M., Pearce, E. M. and Kwei, T. K. *Macromolecules* 1992, **25**, 2156
35 Kwei, T. K., Pearce, E. M., Ren, F. and Chen, J. P. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 1597
36 Fernández-Berridi, M. J., Valero, M., Martinez de Ilarduya, A., Espi, E. and Iruin, J. J. *Polymer* 1993, **34**, 38
37 French, R. N., Machado, J. M. and Lin-Vien, D. *Polymer* 1992, **33**, 765
38 Qipeng, G., Jinyu, H. and Tinalu, C. *Polym. Commun.* 1990, **31**, 115