Phenoxy Resin: Characterization, Solution Properties, and Inverse Gas Chromatography Investigation of Its Potential Miscibility with Other Polymers
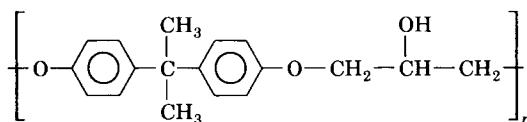
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Synopsis

A commercial sample of a copolymer of bisphenol-A and epichlorohydrin (Phenoxy) has been carefully fractionated in a dioxane/methanol mixture. Mark–Houwink constants in THF and the molecular weight distribution of the raw material have been obtained on the basis of the universal calibration procedure. Conformational magnitudes such as the characteristic ratio C_∞ or the steric factor σ have been determined from viscometric data at 63°C in a good (dioxane) and a θ-solvent (1,2-dichloroethane). Inverse gas chromatography was used to study phenoxy miscibility with a variety of polymers. Using different probes as model compounds, the partial molar enthalpy of mixing $\overline{\Delta H}_1^\infty$ at infinite dilution has been determined. Results were correlated with the reported miscibility of phenoxy with polyesters, polyethers, and polyoxides. A linear multiparametric correlation of $\overline{\Delta H}_1^\infty$ with polarizabilities, dipole moments, and hydrogen bond accepting powers provides for a comprehensive analysis of other miscible systems.

INTRODUCTION

A copolymer based on the reaction between bisphenol-A and epichlorohydrin is commercialized by Union Carbide under the trade name PKHH resin and is also known in the literature as phenoxy resin:

$$\left[O-\langle\bigcirc\rangle - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \langle\bigcirc\rangle - O - CH_2 - \underset{}{\overset{\overset{OH}{|}}{CH}} - CH_2 \right]_n$$

It has repeatedly proved its capacity to form miscible blends with a variety of other polymers, such as aliphatic[1] and aromatic[2,3] polyesters, polyethers and polyoxides,[4,5] polysulfones,[6] or poly(N-vinyl-2-pyrrolidone).[7] The hydroxyl groups which take part in every repetitive unit seem to be in the origin of such miscibility capacity, via the formation of specific interactions with other functional groups. The existence of such type of interactions and its influence on the miscibility of the above-mentioned mixtures have been shown by means of FT-IR.[8,9]

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However, as far as we know, little has been done in the domain of the solution characterization of such a polymer. Furthermore, no data are available in the literature about the Mark–Houwink constants, unperturbed dimensions and related magnitudes (C_∞, σ), ideal solvents, temperature coefficient of $\langle r^2 \rangle$, or other thermodynamic relationships with different kinds of solvents. Given our interest in mixtures of phenoxy with polymers such as polyethylene oxide (PEO), poly(vinyl methyl ether) (PVME), poly(butylene terephthalate) (PBT), etc., we have carried out an investigation on the solution properties of this polymer. Previously, a commercial sample of phenoxy has been carefully fractionated and characterized by a combination of GPC and viscometry. This route provides a good picture of the molecular weight distribution of the polymer.

Galin and Maslinko[10] have recently showed that inverse gas chromatography (IGC) can be used as a technique for studying polymer–solvent pairs which can be considered as model compounds of polymer–polymer systems. In our work, phenoxy, which has one of the highest capacities to miscibilize other polymers reported in the literature, has been used as a stationary phase in IGC experiments where the different probes have been selected as model compounds of other polymers miscible with phenoxy.

EXPERIMENTAL

Phenoxy was obtained from Quimidroga (Barcelona, Spain) and corresponds to the PKHH product of Union Carbide. The glass transition temperature of the commercial sample was 369 K. Solvents were commercial grade and were destilled before use. Densities of phenoxy were taken from Zoller.[11] Data of the different solvents were taken from different sources and have been given in previous works of this group in IGC.[12]

Ten fractions of the raw material were obtained by means of fractional precipitation in a dioxane/methanol mixture at 25°C. The fractionation in these conditions proceeded rapidly and without any separation problem.

UCST in the ideal (θ) solvent 1,2-dichloroethane was determined following the simplified method proposed by Cornet and Ballegooijen,[13] using the commercial sample. The cloud-point temperatures at different concentrations covering the range between 1 and 0.05% were located visually.

A Waters ALC 150 liquid chromatograph provided with a set of 500, 10^4, 10^5, and 10^6 Å μStyragel columns was used in GPC measurements. The solvent was THF at 25°C. The calibration was carried out with thirteen PS standards covering the range between 1.8×10^3 and 5×10^6 g/mol.

The gas chromatographic measurements were carried out on a Perkin-Elmer Sigma-3 chromatograph equipped with a flame ionization detector and connected to an Olivetti M-24 personal computer with appropriate software in order to yield high-precision retention data and to calculate the thermodynamic magnitudes derived from them. Other details about experimental devices and data reduction of this type of measurements have been given elsewhere.[12]

Viscosities were measured in Ubbelhode-type viscometers in the usual way.

TABLE I
Intrinsic Viscosities, Polydispersities as PS and $\overline{M}_v$ from Universal Calibration Procedure
of Different Phenoxy Fractions

Fraction	$[\eta]$ (dL/g)	$(\overline{M}_w/\overline{M}_n)$ as PS	$\overline{M}_v$
PH 1	0.876	1.52	89,200
PH 2	0.643	1.31	55,200
PH 3	0.528	1.30	40,000
PH 4	0.414	1.26	28,400
PH 5	0.354	1.22	22,000
PH 6	0.314	1.25	18,000
PH 7	0.313	1.41	18,600
PH 8	0.286	1.35	15,500
PH 9	0.205	1.29	10,400
PH 10	0.185	1.34	8,200

RESULTS AND DISCUSSION

Ten fractions of phenoxy were obtained by fractionating the commercial sample. Calculating the molecular weight distributions as if they were polystyrene samples, the polydispersity index ranged from 1.22 to 1.52 with an average value of 1.32. Table I gives these data together with the intrinsic viscosities in THF at 25°C and the viscosity-average molecular weights, calculated according to the classical adoptions of the universal calibration procedure. Data of Table I, used in a Mark–Houwink double logarithmic representation log[η] vs. log $\overline{M}_v$ gave the coefficients

$$K = 4.76 \times 10^{-4}, \quad a = 0.660 \quad (\text{THF}, 25°C; [\eta] \text{ in dL/g})$$

With these data, the chromatogram of the commercial sample provided the following average molecular weights:

$$\overline{M}_w = 50,700$$

$$\overline{M}_v = 43,000$$

$$\overline{M}_n = 18,000$$

Cornet and Ballegooijen[13] proposed a rapid semiempirical method which makes the usually tedious procedures for determining θ temperatures less tedious. The method can establish both θ temperatures and θ compositions. The method is based on the relationship between the interaction parameter χ and the volume fraction of the polymer at the incipient precipitation point, as derived by Napper.[14] This author concluded that the χ parameter is a practically linear function of the logarithm of the volume fraction of the polymer when $\phi_{pol} < 0.01$. The same range $10^{-5} < \phi_{pol} < 10^{-2}$ is commonly employed in cloud point titrations. Furthermore, all linear portions of the curves intersect at $\chi = 0.5$ for $\phi_{pol} = 1$, adopting the thermodynamic characteristics of a theta system for the pure polymer.[14] The method only requires
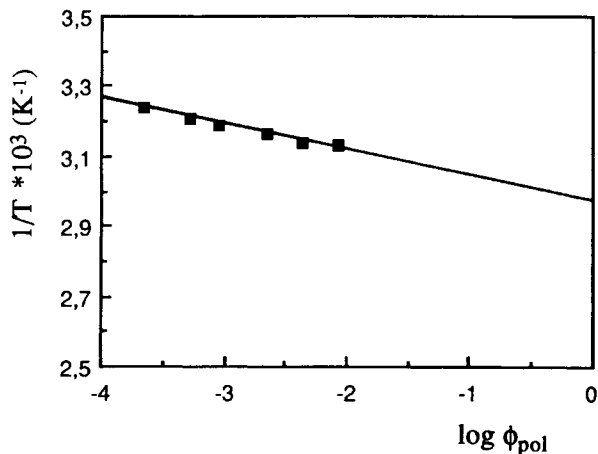
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Fig. 1.   Dependence of the inverse cloud-point temperatures T_p on the logarithm of the volume fraction of the polymer for phenoxy in 1,2-dichloroethane.

the use of a molecular weight fraction and different concentrations in the mixture with the solvent. Figure 1 shows the final representation of the experimental data where ϕ_{pol} is the volume fraction of the polymer in the mixture. The extrapolation at $\phi_{pol} = 1$ gives, according to the theoretical background of such method, the θ temperature of the system under study.

Figure 1 allows us to conclude that the upper critical solution temperature (UCST) of the system phenoxy/1,2-dichloroethane is $\theta = 63°C$.

With this result, the calculation of the different magnitudes which characterize the conformational properties of our polymer have been undertaken in two different ways. At 63°C viscometric measurements were determined in the previously determined θ conditions and in a good solvent (dioxane) at the same temperature.

Figure 2 summarizes the viscometric data in 1,2-dichloroethane at 63°C. A plot of $[\eta]_\theta/\overline{M}_v^{1/2}$ against $\overline{M}_v^{1/2}$ gives us an average value of the constant K_θ
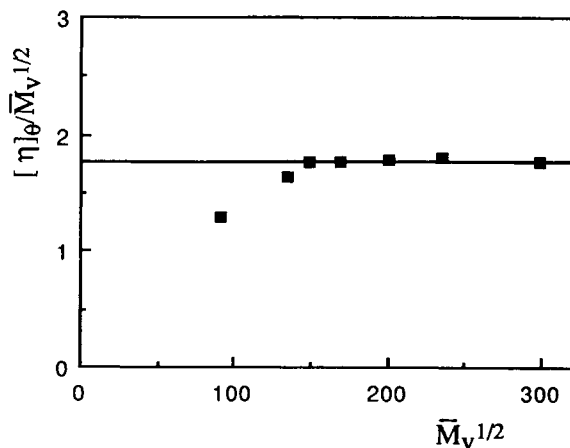

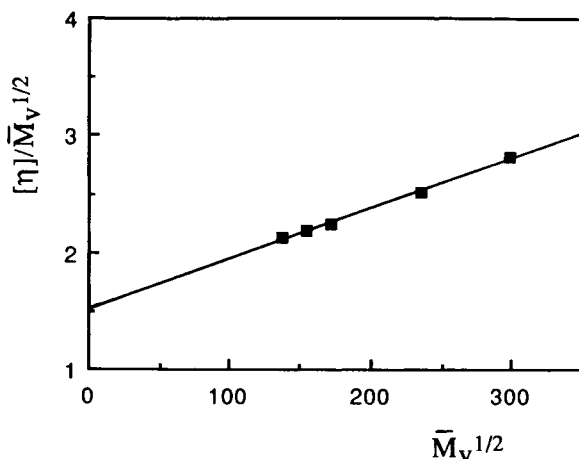Fig. 2.   Determination if K_θ from viscometric data in 1,2-dichloroethane at 63°C.

Fig. 3. Stockmayer–Fixman modified plot from viscometric data in dioxane at 63°C.

of the Fox–Flory equation in θ conditions:

$$[\eta]_\theta = K_\theta \cdot \overline{M}_v^{1/2} \tag{1}$$

The figure also shows that the plot deviates from the linearity at low molecular weights. This behavior is more or less general, and, for example, it has also been observed in a similar range of molecular weights for polymers with a chemical structure related to that of our phenoxy resins (PC/THF[15] and PAr/cyclohexane/dioxane[16]).

An average value of $K_\theta = 1.77 \times 10^{-3}$ dL mol$^{1/2}$ g$^{-3/2}$ is consequently proposed, which together with the well-founded value of the hydrodynamic constant in θ solvents

$$\Phi = 2.5 \times 10^{21}$$

gives us a

$$(K_\theta/\Phi)_{1,2\text{-DCE}} = 7.08 \times 10^{-25} \text{ mol}^{3/2} \text{ g}^{3/2} \text{ cm}^3$$

which will be compared with that obtained in a good solvent. This ratio allows the calculation of other conformational magnitudes.

Figure 3 has been drawn with viscometric data of different fractions in dioxane at 63°C. Once again, the lower molecular weight deviates from linearity, as was also the case of the PC/THF system. In this system, Berry et al.[15] observed that extrapolations from high molecular weights provided K_θ values which were higher than those obtained with low molecular weights. These discrepancies reflect the nonlinearity of α^3 with the excluded volume parameter z. Another source of error in the determination of K_θ has been explained by Kamide et al.[17] on the basis of the polydispersity of the samples. Kamide et al.[17] proposed the use of $\overline{M}_v$ in order to minimize the effect of polydispersity. It is reasonable to disregard this type of effects in our samples, given the polydispersity and the use of the recommended average molecular weight.

Using the modified Stockmayer–Fixman plot[18]

$$[\eta]/M^{1/2} = K_\theta + 0.346\Phi\big(v_{sp,2}^2/V_1N_A\big)(1 - 2\chi)M^{1/2} \qquad (2)$$

Figure 3 allows us to calculate from the intercept and the slope

$$K_\theta = 1.52 \times 10^{-3}\,\text{dL mol}^{1/2}\,\text{g}^{-3/2}$$

$$\chi = 0.237$$

using the dioxane molar volume $V_1 = 89.37$ cm^3/mol and the specific volume of the polymer $v_{sp,2} = 0.7738$ cm^3/g.

In good solvents, such as dioxane, the hydrodynamic constant is

$$\Phi = 2.1 \times 10^{21}\,\text{dL mol}^{-1}\,\text{cm}^{-3}$$

and the ratio

$$(K_\theta/\Phi)_{\text{dioxane}} = 7.26 \times 10^{-25}\,\text{mol}^{3/2}\,\text{g}^{3/2}\,\text{cm}^3$$

From the ratio K_θ/Φ, it is possible to calculate the so-called characteristic ratio C_∞

$$C_\infty = (K_\theta/\Phi)^{2/3}\, M_0/\bar{l}^2 \qquad (3)$$

where M_0 is the molecular weight per bond and $\bar{l}$ is the bond average length. $\bar{l}$ has been calculated taking into account the molecule models proposed by Williams and Flory[19] for poly(ethylene terephthalate) and by Berry et al.[15] for polycarbonate. Following these criteria in the phenoxy molecule

$$\bar{l} = 2.91 \times 10^{-8}\,\text{cm}$$

and

$$M_0 = 47.33$$

Consequently,

$$C_\infty = 4.47\ (\pm 0.03)$$

according to the data of K_θ/Φ in 1,2-dichloroethane and dioxane.

The steric factor σ can be calculated as

$$\sigma^2 = C_\infty\,(1 + \cos\theta)/(1 - \cos\theta) \qquad (4)$$

where $\theta = 109.5°$C, if the phenoxy molecule is considered as a freely-rotating chain. Using the C_∞ average value

$$\sigma = 1.49$$

If we compare these values of σ and C_∞ with others compiled in the literature, they correspond to a flexible chain, where this character arises

mainly from the presence of the fragment $—C(CH_3)_2—$ which facilitates the rotation of the chain. This σ value is clearly lower than that of 2.2 for polystyrene or other vinyl polymers.

We have completed our study on the phenoxy resin with the determination by means of IGC of some thermodynamic relationships of our polymer with different solvents, specially selected in order to cover a wide range of functional chemical groups. The study has had two different objectives. First, IGC allows us to illustrate the different interactions of the phenoxy resin with the different functional groups contained in different solvents. Second, these solvents can be used as model compounds for explaining the well-founded capacity of this polymer to be miscible with a wide range of different polymers.

From the pioneering work of Freeman and Rowlinson,[20] it has been recognized that polymer solutions can exhibit two critical temperatures, upper critical solution temperature (UCST) and lower critical solution temperature (LCST). The critical conditions can be resumed by means of the well-known Flory–Huggins interaction parameter, whose physical meaning has been conveniently redefined by modern polymer solution theories. With the consequence of these new theories, the interaction parameter χ^* can be understood as a residual free energy parameter which exhibits a parabolic dependence on the temperature. The two critical temperatures correspond to the points where χ^* reaches the χ^*_{crit} value. Between these two points, χ^* passes through a minimum which gives the maximum of solubility in the solvent.

Inverse gas chromatography provides valuable information of the dependence of χ^* with temperature. Starting with the specific retention volume V_g^0, calculable[12] from the retention time of a solvent in a column packed with the polymer, it is possible[12] to calculate the state-equation χ^* parameter as

$$\chi^* = \ln\left(273.16 \cdot R \cdot v^*_{sp,2}/P_1^0 \cdot V_g^0 \cdot V_1^*\right) - 1 - \left[(B_{11} - V_1^*)/RT\right] \cdot P_1^0 \quad (5)$$

where V_1^* is the characteristic molar volume of the solvent, $v^*_{sp,2}$ the characteristic specific volume of the polymer, P_1^0 the solvent vapor pressure, and B_{11} its second virial coefficient. The specific retention volumes were measured between 120 and 160°C. Linear variations to $\ln V_g^0$ vs. $1/T$ were observed within this temperature range. These experimental points were extrapolated to lower temperatures in order to have interaction parameters in a wider range, more adequate for further IGC studies of the miscibility of phenoxy with poly(ethylene oxide) and poly(vinyl methyl ether).[21]

Figures 4–6 summarize the χ^*–T behavior of different phenoxy/solvent pairs studied by IGC in the range 90–150°C. The curves can be interpreted in all cases as parts of the general parabolic behavior mentioned before. It is important to realize that in IGC systems we are in a range of concentrations of $\phi_{solvent} \rightarrow 0$, in precisely the opposite range to that in which the critical conditions are satisfied. However, two important aspects can be inferred from these diagrams. First, the value of the χ^* parameter; high values such as these of n-decane or tetradecane correspond to very poor solvents for phenoxy. In the opposite range, low values as for bis(2-methoxyethyl) ether or dimethyl formamide (DMF) reflect the good solubility capacities of such solvents for
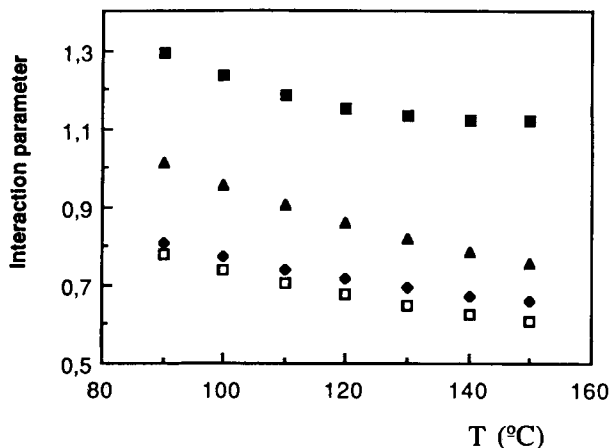
Fig. 4. Interaction parameter vs. temperature from IGC measurements with the probes:
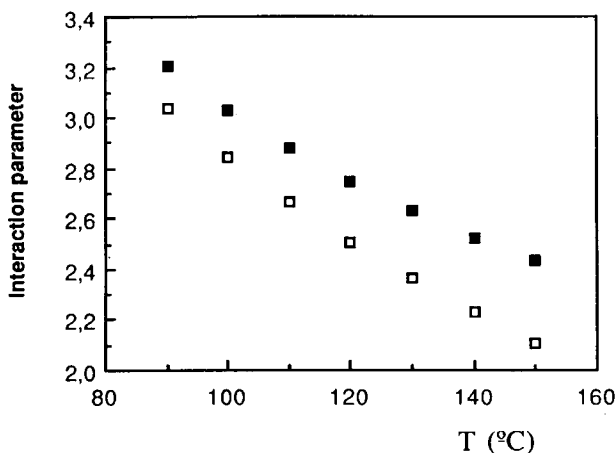(□) chlorobenzene; (◆) 1,2-dichloroethane; (■) n-propanol, (△) toluene.

Fig. 5. Interaction parameter vs. temperature from IGC measurements with the probes:
(□) n-decane, (■) n-tetradecane.

our resin. The second important aspect is the χ^*-T behavior. Solvents where χ^* is decreasing with T correspond to systems leaving the UCS temperature, as is the case of 1,2-dichloroethane in the range 90–150°C. Dioxane seems to be in the minimum of its parabolic dependence, showing its maximum of solubility in this range. Other solvents such as dimethyl formamide (DMF) or bis(2-methoxyethyl) ether leave the maximum of solubility towards their LCST. Of course, this analysis is restricted by the χ^* value and by the fact that we are in the other extreme of the critical conditions. However, qualitative conclusions similar to those explained above give a first insight into the quality of different solvents for phenoxy.

Galin and Maslinko[10] have recently demonstrated that the specific retention volumes V_g^0, measured by IGC and their related magnitudes, the partial molar enthalpies of mixing at infinite dilution, can be used as a tool for predicting
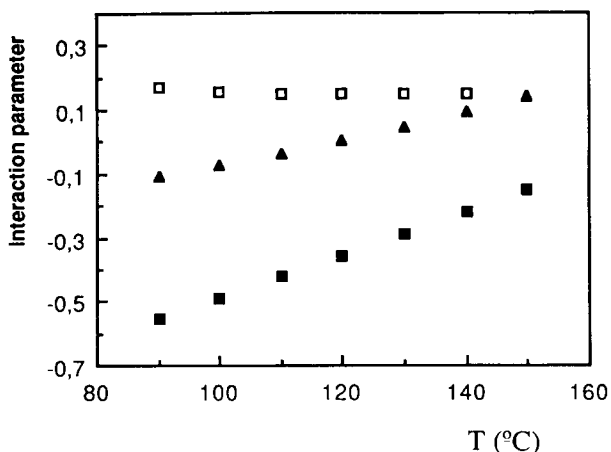
Fig. 6. Interaction parameter vs. temperature from IGC measurements with the probes: (□) dioxane; (▲) bis(2-methoxy ethyl) ether; (■) dimethyl formamide.

polymer 1/polymer 2 miscibility in systems where the solvent is a model compound for polymer 2.

The activity coefficients at infinite dilution Ω_1^∞ based on weight fractions can be derived from the corresponding V_g^0 values according to

$$\ln \Omega_1^\infty = \ln\left(273.16R/P_1^0 V_g^0 M_1\right) - P_1^0/RT(B_{11} - V_1) \tag{6}$$

where M_1 is the molecular weight of the solvent. Experimental values of the partial molar heat of mixing at infinite dilution $\overline{\Delta H_1^\infty}$ may be directly obtained:

$$\overline{\Delta H_1^\infty} = R \cdot \partial \ln \Omega_1^\infty / \partial(1/T) \tag{7}$$

Figure 7 shows linear variations of $\ln \Omega_1^\infty$ vs. $1/T$. The average value of $\overline{\Delta H_1^\infty}$ for each solvent can be determined by least square analysis of the above mentioned plots. Table II summarizes $\overline{\Delta H_1^\infty}$ experimental values for the different solvents investigated. This table illustrates the capacity of this type of analysis. $\overline{\Delta H_1^\infty}$ becomes negative in solvents like ethers and esters reflecting, in a qualitative way, the preference of the phenoxy resin for this type of interaction. A similar analysis has been carried out by Galin and Maslinko[10] in the case of poly(vinylidene fluoride).

This qualitative analysis can be extended to other solvents. Experimental values of $\overline{\Delta H_1^\infty}$ can be correlated with probe polarizabilities P, dipole moments μ, and Taft's β empirical parameter which measures the probe hydrogen bond accepting power, through the general equation

$$\overline{\Delta H_1^\infty} \text{ (kcal/mol)} = aP + b\mu + d\beta \tag{8}$$

Data of P, μ, and β of the different solvent employed are also given in Table II.[10,22,23,24] Figure 8 shows $\overline{\Delta H_1^\infty}$ experimental values confronted with calculated values for the different phenoxy/solvent systems, according to the
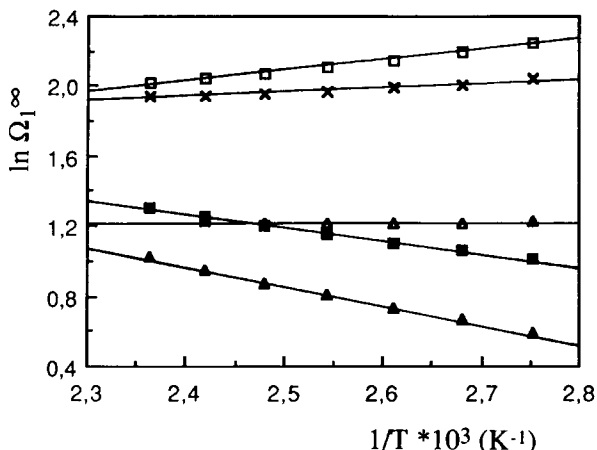
Fig. 7. Temperature dependence of the weight-fraction activity coefficients of different probes: (□) toluene; (▲) dimethyl formamide; (×) *n*-butanone; (△) dioxane; (■) bis(2-methoxy ethyl) ether.

best fit

$$\overline{\Delta H}_1^{\infty} \ (\text{kcal/mol}) = 0.145 \ P \ (\text{cm}^3 \times 10^{-24}) - 0.25 \ \mu \ (D) - 1.63 \ \beta$$

The data summarized in Figure 8 may be characterized, at first sight, as a random scatter. The correlation coefficient is worse than that obtained by Galin and Maslinko[10] in their similar analysis of the poly(vinylidene fluoride) (PVF$_2$). Whether or not the correlation is correct obviously depends on the accuracy of the $\overline{\Delta H}_1^{\infty}$ measurements and on the reliability of the β literature data. In spite of these shortcomings at the experimental level, this correlation has allowed to rationalize the PVF$_2$ miscibility with a variety of polyesters and, as may be seen further on, it can be used, in a qualitative way, to illustrate phenoxy miscibility with other different polymers.

TABLE II

Polarizability P, Dipole Moment μ, and Hydrogen Bond Accepting Power β of Pure Solvents and Partial Molar Heat of Mixing $\overline{\Delta H}_1^{\infty}$ of the Various Solute–Phenoxy Systems

| Solvent	$(\overline{\Delta H}_1^{\infty})_{\text{exptl}}$ (kcal/mol)	$P \times 10^{24}$ (cm^3)	μ (D)	β
Chlorobenzene	0.75	12.34	1.71	0.07
Acetonitrile	0.19	4.44	3.94	0
1,2-Dichloroethane	0.53	8.34	1.40	0
n-Propanol	0.84	6.90	3.09	0.95
Benzene	1.31	10.40	0	0.10
n-Decane	4.62	19.1	0	0
Toluene	1.17	12.34	0.37	0.11
Dioxane	-0.13	8.56	0.42	0.37
Dimethyl formamide	-2.16	7.85	3.86	0.69
Bis(2-methoxy ethyl) ether	-1.46	13.8	1.97	0.55
Tetradecane	3.81	26.0	0	0
Ethyl acetate	-0.31	8.83	1.78	0.45
Butanone	0.54	8.24	2.70	0.48
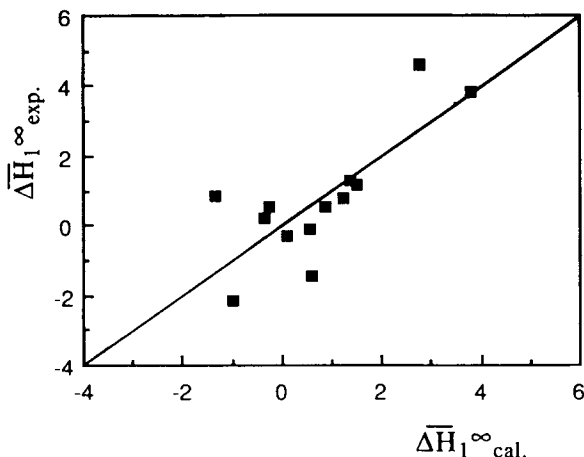
Fig. 8. $\overline{\Delta H}_1^{\infty}$ experimental vs. calculated values for the various phenoxy-probe mixtures according to the multiparametric correlation given in the text.

This equation allows us to infer some interesting new conclusions. For instance, in the case of N-methyl pyrrolidone [model solvent of poly(N-vinyl pyrrolidone)], P (cm$^3 \times 10^{-24}$) = 10.56, μ (D) = 4.09, and β = 0.72,[10]

$$\left(\overline{\Delta H_1^{\infty}}\right)_{calcd} = -0.66$$

in good agreement with the well-established miscibility of phenoxy with poly(N-vinyl pyrrolidone). In a similar way $(\overline{\Delta H_1^{\infty}})_{calcd} = -0.28$ for the system phenoxy/tetramethylene sulfone. Given the negative values of phenoxy with ethers and sulfones, the reported miscibility of our resin with a poly (ether sulfone)[6] is not surprising.

Another interesting analysis derives from the study of different phenoxy/ester systems carried out by Harris et al.[1] These authors have studied the polymer/polymer miscibility of phenoxy with different aliphatic polyesters, finding that, in spite of the apparently well-founded interactions between the hydroxyl group of phenoxy and the carbonyl of the polyesters, not all polyesters are miscible with phenoxy. We can plot the miscibility, measured as the value of the interaction parameter, against the proportion of ester linkages in the polyester repeat unit structure, expressed as CH_x/COO, where x may have values 0, 1, 2, or 3, depending on the substitution. In this plot the interaction parameter tends to a maximum negative value indicating maximum interaction as the CH_x/COO ratio tends toward the optimum value 4. If we apply our multiparametric correlation equation to the series methyl acetate, ethyl acetate, and butyl acetate, the corresponding $(\overline{\Delta H_1^{\infty}})_{calcd}$ values are -0.0081, -0.31, and 0.71. A cyclic ester like γ-butyrolactone, with a CH_x/COO ratio of 3 also shows a $(\overline{\Delta H_1^{\infty}})_{calcd}$ value of -0.68. Values of P, μ, and β are also available for dimethyl formamide and dimethyl acetamide. The respective $(\overline{\Delta H_1^{\infty}})_{calcd}$ values are -0.95 and -0.78 indicating a tendency which would be in agreement with the immiscibility of phenoxy with nylon-6, with a higher $CH_x/amide$ group ratio.

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CONCLUSION

Solution characterization data of the phenoxy resin was presented both in good and ideal solvents. In spite of the experimental uncertainties appearing in Figure 8, the correlation allows us to rationalize some of the experimental data reported in phenoxy/polymer systems. Perhaps a more complete experimental work with a large series of probes or with a different polymer of recognized good miscibility with other polymers (e.g., PVC) might be a plausible way of continuing this type of study which may provide a new insight into the field of polymer–polymer miscibility.

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