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Polymer-solvent interaction parameter for poly(4-hydroxystyrene) by IGC

E. G. Lezcano[1], **C. Salom**[1], **R. M. Masegosa**[2], **M. G. Prolongo**[1]

[1] E.T.S.I. Aeronáuticos, and [2] E.U.I.T. Aeronáutica, Universidad Politécnica,
E-28040 Madrid, Spain

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Summary

The polymer-solvent interaction parameter, χ_{12}, was determined for poly(4-hydroxystyrene) (P4HS) at 443 and 463 K, by inverse gas chromatography (IGC) using several probes. The partial molar heat of mixing at infinite dilution in the polymer was also calculated. The solubility parameter δ_2 of P4HS has been obtained by using the method developed by DiPaola-Baranyi and Guillet. Moreover using the equation-of-state theory the contact interaction energy, X_{12}, was also determined.The variation of the interaction parameters were correlated with the size and kinds of atoms present in the molecules.

Introduction

Inverse gas liquid chromatography has been recognized as an effective, simple technique for measurement of polymer-solvent interactions in molten polymers. It has been also used in the study of polymer blends.

Polymer blends have been of great interest in the last 20 years, mainly because of the difficulty of development new polymers and the ability to tailor properties by bending which in some cases yields synergistic behaviour. It is known that because of the low combinatorial entropy of mixing miscible blends result when there are specific interactions like hydrogen bonds between components. Recently we have been studying (1-5) miscible polymer blends formed by poly 4-hydroxystyrene, P4HS, and polymers with carbonyl or ether groups that make possible the hydrogen bond interaction with P4HS.

In particular we have determined the polymer-polymer interaction of several blends by IGC. In order to achieve such study we have need to determine previously the polymer-solvent interaction parameter for homopolymers using several solvents or probes of different chemical nature at the same temperature at which the blends were studied, that is in the molten state.

In this paper we report the polymer-solvent interaction parameter χ_{12} of P4HS with several solvents representing a number of chemical group families, to facilitate the correlation with probe characteristics. Moreover the study was carry out at two temperatures that allow to estimate a value for the solubility parameter. Finally the free volume contribution to χ_{12} was discounted, calculating the exchange energy parameter of Flory equation of state, X_{12}, in order to see if this parameter is determined only by the kinds of atoms and groups that interact, and not by the molecular size of components.

Experimental

Apparatus and Materials. All details about apparatus, materials column preparation and procedure were described previously (1).

Specific retention volumes, V_g, were calculated from the expression:

$$V_g = t_n \frac{F}{w} \left(\frac{3}{2}\right) \left[\frac{(P_i / P_o)^2-1}{(P_i / P_o)^3-1}\right] \left(\frac{P_o-P_w}{P_o}\right) \frac{273.15}{Tr} \qquad (1)$$

where t_n is the net retention time of each probe, w is the mass of the polymer in the column, P_i and P_o are the inlet and outlet pressures, F is the carrier gas flow rate at room temperature T_r and atmospheric pressure P_o, and P_w is the water vapour pressure at T_r. The values of V_g are usually extrapolated to zero flow rate to obtain V_g^o. In this work, V_g values were independent of the gas flow rate within the range 15-30 ml/min. Only a slight flow dependence was found at 443 K with probes that showed small retention times. Values of V_g^o were in the range 2-10 ml/g.

Results and discussion

From the Flory-Huggins treatment of solution thermodynamics, the reduced residual chemical potential of the solvent in the mixture (solvent + polymer) is defined as the solvent (1) polymer (2) interaction parameter, χ_{12} , which can be calculated from IGC experiments with the relationship (6)

$$\chi_{12} = \ln \frac{273.15\, R\, \upsilon_2}{V_g^o\, P_1^o\, V_1} - \left(1 - \frac{V_1}{M_2 \upsilon_2}\right) - \frac{P_1^o}{RT} (B_{11}-V_1) \qquad (2)$$

where ν_2 and M_2 refer to specific volume and molecular weight of the polymer. V_1 and P_1^o represent the probe molar volume in the liquid phase and saturated vapour pressure, respectively, and B_{11} is the second virial coefficient of the probe in the gas phase. All other symbols have the usual meanings.

The polymer-solvent interaction parameter χ_{12} in eq. 2 is defined in terms of volume fractions. In more recent theories (7), segment fraction and "hard- core" volumes of components have been used, leading to the analogous expression (8):

$$\chi_{12}^* = \ln \frac{273.15\, R\, \upsilon_2^*}{V_g^o\, P_1^o\, V_1^*} - \left(1 - \frac{V_1^*}{M_2 \upsilon_2^*}\right) - \frac{P_1^o}{RT} (B_{11}-V_1) \qquad (3)$$

where the starred quantities differentiate the hard-core volumes of solvent and polymer from molar quantities; the vapour pressure P_1^o, were calculated from the Antoine equation, taking the Antoine´s constants from the Reid-Prausnitz-Sherwood compilation (9,10); the molar volumes of the probes, V_1, were calculated using Bensons´s method (9-11). Second virial coefficients were calculated from the Pitzer-Curl-Tsonopoulos correlation (10-12). The values of V_1^* were calculated by the usual way (7) from thermal expansion coefficient and density at 298 K. It was assumed that the hard -core parameters are independent of temperature. The density, thermal expansion coefficient and critical parameters for the solvents were taken from references (13,14). Data for the polymers were $\nu_2 = 0.862$ and 0.925 $cm^3.g^{-1}$ for P4HS and PCL, respectively. Thermal expansion coefficients were $\alpha_2 = 8.95.10^{-4}$ and $6.50.10^{-4}$ K^{-1} for P4HS and PCL respectively at 25 °C (10,11). Table 1 illustrates the derived data for P4HS at 443 and

463 K.

Table 1.- Values of V_1^* and interaction parameters χ_{12} and χ_{12}^* for solvent (1) + P4HS (2) at 443 and 463K

	T=298K	T=443K		T=463K	
SOLVENT (Code)	V_1^*(cm^{3}mol^{-1})	χ_{12}	χ_{12}^*	χ_{12}	χ_{12}^*
Acetone (ACT)	55.5	0.25	0.46	0.58	0.83
2-butanone (MEK)	68.9	0.52	0.69	0.62	0.82
3 pentanone (DEK)	82.2	1.08	1.22	0.76	0.94
Ethylacetate (EAC)	74.2	1.06	1.24	1.07	1.30
n-propylacetate (PAC)	88.1	1.22	1.38	1.10	1.28
n-butylacetate (BAC)	103.1	1.47	1.58	1.20	1.34
Tetrahydrofuran (THF)	63.8	0.21	0.33	0.27	0.42
Dioxane (DOX)	67.3	-	-	-0.03	0.07
Toluene (TOL)	84.7	2.20	2.29	2.22	2.37
Chlorobencene (ClBz)	82.1	-	-	1.99	2.06
1 propanol (1POL)	60.2	-	-	1.01	1.21
2 popanol (2POL)	61.0	0.96	1.12	0.84	1.05
Isobutylalcohol (IBOL)	74.9	-	-	1.10	1.21

As it can be seen a wide range of χ_{12} values were obtained for the selected solvents of different chemical nature. The highest χ_{12} values correspond to Tol and ClBz; they reflect an unfavourable interaction between probe and polymer. These results were not unexpected, because as it is well known (15) the P4HS shows self-association through OH-OH interaction and Tol and ClBz do not have the possibility of hydrogen bond interaction neither to break the P4HS self-association. Moreover, ClBz and Tol are reported as nonsolvents of P4HS in the temperature range 0-90°C (16). Otherwise, ketones an esters solvents have the carbonyl group C=O that makes feasible the hydrogen bond interaction with the OH group of P4HS, then they give lower χ_{12}, that seem so be correlated with the molecular size of the solvent. Actually, as it is illustrated on Table 1, within a given solvent family the value of χ_{12} increased with increasing the "hard-core" volume of the solvent.

The data for alcohols show the effects of the solvent self association. Even though the hydrogen bond interaction between OH groups of P4HS and alcohol is stronger than OH-C=O (15) the values of χ_{12} for alcohols are similar to those obtained with esters and ketones indicating that the self association of the solvent reduces the number of polymer solvent interactions. Thus 2-propanol is less self associated that 1-propanol and having the two molecules similar "hard-core" the former gives the lower χ_{12} value. Again, this results are in agreement with those reported (16) for dilute solution that show ketones esters and alcohols as solvents of P4HS. Dioxane and tethrahydrofurane give the smallest values of χ_{12}, these are ones of the best solvents reported for P4HS in dilute solution

(16). This can be explained considering these solvents do not present self association and have low V^* values.

Polymer Solubility Parameter for P4HS

According to the solubility parameter theory (17) the polymer(2) - solvent (1) interaction parameter, χ_{12}, is related to the difference between the solubility δ, of the two components through:

$$\chi_{12} = \frac{V_1}{RT}(\delta_1-\delta_2)^2 + \chi_s \tag{4}$$

The eq. 4 implies the hypothesis that the enthalpic contribution, $\chi_H = V_1/RT\ (\delta_1 - \delta_2)^2$, is always positive. Although in these systems, (P4HS + solvents) are present hydrogen bond interactions, it is not expected that they would be exothermic at the temperature of study (443-463 K), taking into account the quite high positive values of χ_{12} obtained. This can be explained considering that the polymer-solvent hydrogen bonds interactions are formed mainly by means of through the rupture of the hydrogen bonds of P4HS (self association). Then it seems to be feasible the application of eq. 4 to get the solubility parameter of P4HS. The solubility parameter is defined:

$$\delta = \left(\frac{\Delta Ev}{V}\right)^{1/2} = \left[\frac{(\Delta Hv - RT)}{V}\right]^{1/2} \tag{5}$$

where ΔE_v and ΔH_v are the molar energy and molar enthalpy of vaporization respectively, and V represents the molar volume; χ_s is an entropy correction term, absent in the original theory but necessary for polymer systems (17). Solubility parameters for volatile liquids are calculated from liquid density and molar heat vaporization data, at the same temperature. Rearrangement of Eq. 4 gives:

$$\frac{\delta_1^2}{RT} - \frac{\chi_{12}}{V_1} = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left[\left(\frac{\delta_2^2}{RT}\right) - \left(\frac{\chi_s}{V_1}\right)\right] \tag{6}$$

According to Eq. 6 a plot of the left-hand side against δ_1 should yield a straight line with a slope $2\delta_2/RT$ and using the value of δ_2 from slope the entropic component χ_s can be estimate from the intercept. Eq. 7 was used in several opportunities with gas chromatographic data measured on different polymers (18-20). In all the cases it has been possible determine the value of δ_2 with reliability, including those where the solute probes belonged to several and very different families.

To obtain δ_1 from Eq.5 it is necessary to calculate ΔHv. The specific retention volume, V_g, of a probe can be related to the solution thermodynamic properties such us the partial molar heat of mixing ΔH_1^∞ and the heat of solution, ΔH_s^∞, of the probe at infinite dilution through:

$$\Delta H_1^\infty = R\ [\partial \ln(a_1 / w_1)^\infty / \partial\ (1/T)] \tag{7}$$

where $\ln\ (a_1/w_1)^\infty$ is the weight fraction activity coefficient, given by

$$\ln(a_1 / w_1)^{\infty} = \chi_{12} + \ln\frac{v_1}{v_2} + \left(1 - \frac{V_1}{M_2 v_2}\right) \tag{8}$$

$$\Delta H_s^{\infty} = -R\ [\partial \ln Vg / \partial(1/T)] \tag{9}$$

From Eq. 7 and 9 we obtain ΔH_v^{∞} according to

$$\Delta H_v^{\infty} = \Delta H_1^{\infty} - \Delta H_s^{\infty} \tag{10}$$

Experimental retention volumes, derived weight fraction activity coefficients and χ_{12} parameters for several probes in P4HS at T>Tg (170,190 °C) have been used in order to calculate δ_1 according to Eq. 5 and Eq 10.

Table 2 summarizes ΔH_1^{∞}, ΔH_s^{∞} for the probes in P4HS in the temperature range 443-463 K and also the values of δ_1 at both temperatures. The molar enthalpy of vaporization decreases and polar volumes increases when temperature increases therefore δ_1 parameters are lower at T = 463 K.

According to Eq. 6 a plot of $(\delta_1^2/RT - \chi_{12}/V_1)$ vs. δ_1 is shown in figure 1 at 443 K and 463 K. By means a least squares analysis and from the slope we obtain δ_2 = 8,32 cal $^{1/2}$. cm$^{-3/2}$ and = 7.45 cal$^{1/2}$.cm$^{-3/2}$ for P4HS at 443 K and 463 K respectively. The values of χ_s obtained from the intercept are negative at both temperatures and not strongly dependent on temperature.

The results of χ_{12} can be extrapolated at T = 298 K fitting an equation of the form $\chi_{12} = \alpha + \beta/T$ and assuming that this relationship remains valid at lower temperatures. Using the δ_1 values for the solutes at 298 K and literature values (21) for V_1,

Table 2.- Partial molar heats of mixing, heats of solution, solute solubility parameters of several solvents in P4HS.

SOLVENT	ΔH_1^{∞} (kcal.mol^{-1})	$-\Delta H_1^{\infty}$ (kcal.mol^{-1})	δ_1(cal.cm^{-3})$^{1/2}$	
			T=443 K	T=463 K
Acetone	-7.40	13.04	7.01	6.80
2-butanone	-1.47	9.04	7.65	7.44
3-pentanone	5.81	1.34	6.87	6.68
Ethylacetate	-1.06	7.27	6.47	6.29
n-propylacetate	2.00	4.96	6.46	6.30
n-butylacetate	5.28	2.85	6.68	6.54
2-propanol	0.59	6.12	7.64	7.37
Tetrahydrofurane	-1.71	7.69	7.10	6.94

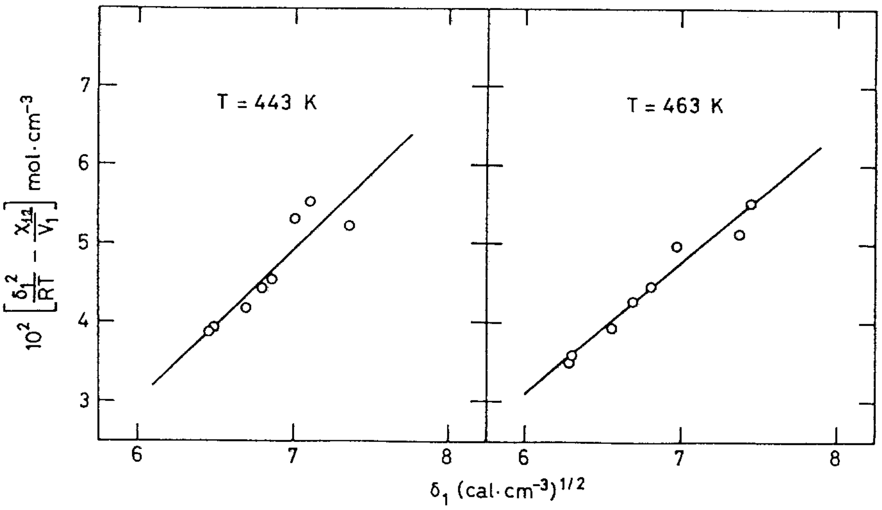

Figure 1. Estimation of solubility parameter for P4HS at 443 K and 463 K

at the same temperature, the value of δ_2 = 11.4 cal$^{1/2}$ cm$^{-3/2}$ for P4HS at 298 K is obtained. This value is in agreement with the value of δ_2 = 10.6 - 11.0 cal$^{1/2}$ cm$^{-3/2}$ proposed by Coleman and Painter at 298 K (22).

Equation of state theory: Prigogine-Flory Exchange interaction parameter X_{12}

The Prigogine-Flory theory (7) has proved very useful for polymer-solvent systems as well as for polymer mixtures.

The Gibbs mixing function, ΔG_M, according to this theory is composed of three contributions: combinatorial entropy, interactional exchange energy and free volume. Derivating the expression for the non combinatorial part of ΔG_M, for a polymer-solvent system, we get the residual chemical potential of the solvent $\Delta\ \mu_1^R$ / RT at infinite dilution in the polymer:

$$\frac{\Delta\mu_1^R}{RT} = \chi_{12}^* = \frac{V_1^*}{\tilde{V}_2}\frac{X_{12}}{RT} + \frac{P_1^*V_1^*}{RT}\left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}_2} - 3\tilde{T}_1 \ln\left(\frac{\tilde{V}_2^{1/3}-1}{\tilde{V}_1^{1/3}-1}\right)\right] \qquad (11)$$

Here the starred quantities are constant reduction parameters and $\tilde{V}_1;\tilde{V}_2$ are the reduced volume of solvent and polymer respectively. The reduced magnitudes are the basic quantities characterizing a liquid in the Prigogine theory. Eq. 11 includes a free volume term and the interactional or contact energy term (6, 7, 23) which is characterized by the X_{12} parameter having the dimensions of pressure. As can be seen in eq. 11, the elimination of the free volume contribution to χ_{12} leads to the X_{12} parameter. Table 3 collects the values of X_{12} for P4HS/solvent systems.

Table 3.- Exchange interaction parameters, X_{12}, for solvent (1) + P4HS (2) at 443 and 463 K.

Solvent	X_{12}(J.cm^{-3})	
	443 K	463 K
Acetone	20	53
2-butanone	37	47
3-pentanone	66	49
Ethylacetate	64	69
n-propylacetate	63	58
n-butylacetate	70	59
Tetrahydrofurane	19	26
Dioxane	--	-5
Toluene	133	145
Chlorobenzene	--	132
1-propanol	--	105
2-propanol	91	89
Isobutylalcohol	--	86

It is noteworthy that values found for the exchange interaction parameter X_{12}, appear to be determined by the kinds of atoms and groups belonging to the molecules of the components and not by molecular size or shape. Within the first group consisting of ketones and esters groups a mean value of X_{12} around 60 J.cm^{-3} reflect the solvent carbonyl-hydroxyl polymer interaction. For the alcohols-polymer pairs values of X_{12} are larger ($\simeq$ 90 J.cm^{-3}). The worst interactions correspond to toluene and chlorobenzene, because they can not interact with P4HS through hydrogen-bonding. Finally molecules with an ether as chemical group, give the best interaction, irrespective of their polar character.

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