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Thermodynamic Interactions of EVA Copolymer-Solvent Systems by Inverse Gas Chromatography Measurements

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ABSTRACT: The solubility parameter and the Flory–Huggins interaction parameter of two EVA (ethylene–vinyl acetate) copolymers, each one with different vinyl acetate content, are calculated by using inverse gas chromatography technique. The influence of the vinyl acetate percentage is analyzed and indicates that the polymer–solvent interactions are stronger in the case of the copolymer with the highest vinyl acetate percentage. The results also point to the fact that the most favorable solvents for the studied materials are the aromatic-type ones. Finally, from the calculated values of the polymer solubility parameter (16.3 MPa$^{0.5}$ for EVA 460 and 15.1 MPa$^{0.5}$ for EVA410, at 50°C), it can be noticed that the solubility parameter of the EVA copolymer with the largest vinyl acetate content is the closest to the solubility parameter of pure vinyl acetate. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Nowadays, polymers are ones of the most widely used materials as a consequence of their applicability in many fields. Among these materials, the ethylene–vinyl acetate copolymer (EVA) is gaining importance, mainly due to its wide range of applications in, for example, tyres and electronic cable industries or in photovoltaic cells coatings.[1]

The applicability of these EVA polymers is related to the vinyl acetate percentage, variable which also determines the way these materials are industrially obtained. Whenever the vinyl acetate content is higher than 70%, the EVA materials are manufactured by means of an emulsion process and their main applications are as adhesives. If the vinyl acetate percentage is between 30 and 40%, a dissolution process at moderate temperatures and pressures is required and, in this case, the obtained materials are mainly used as elastomers. Finally, whenever the vinyl acetate content is lower than 30%, EVA polymers are manufactured by means of high pressure processes, and their main applications are as modifiers.[2]

Focusing on the dissolution process, it is usually carried out with methanol as solvent, although other compounds like tetrahydrofuran (THF) could also be advisable.[3] On the other hand, in this kind of processes, one of the key points to be overcome is how to achieve an accurate separation between the final material and the solvent, with the aim of getting the EVA polymer as pure as possible. For this reason, it is crucial to thermodynamically characterize the compatibility between the EVA material and different solvents. This compatibility clearly depends on the nature of the solvent, but it might also depend on the vinyl acetate percentage of this EVA material.[4]

The analysis of the interactions between a polymer and a solvent is commonly carried out in terms of the Flory–Huggins parameter[5] and the weight-based solvent activity coefficient,[6] but also by comparing the solubility parameter of the solvent with the solubility parameter of the polymer.[7]

While in literature, several data showing the solubility parameter of a wide range of solvents can be easily found,[8,9] the solubility parameter of an EVA copolymer is not a common value, so it is important to determine it experimentally. Concerning the Flory–Huggins parameter and the weight-based solvent activity coefficient, because there is no any reference reporting these values for any kind of EVA polymer, they also have to be experimentally measured.

A polymer–solvent mixture is totally different from a conventional solvent–solvent mixture because there is a large difference in the size of the molecules of both compounds. So, the measurement of thermodynamic parameters of this kind of mixtures

is carried out by using nonconventional techniques, such as intrinsic viscosity,[10,11] swelling,[12,13] or inverse gas chromatography.[14,15] Among all these techniques, inverse gas chromatography (IGC) is one of the most widely used, because it gives a great deal of information with relatively simple measurements. In literature, this technique has been used with many different polymeric materials, always with good results.[16,17] Another important point is that it has been demonstrated that the obtained values with this technique (at solvent infinite dilution conditions) can be extrapolated to the overall composition range.[18]

This article reports the values of the weight-based solvent activity coefficient and Flory–Huggins parameter of the mixtures of two EVA copolymers with different solvents which could be adequate in an emulsion process. It also reports the solubility parameter of the two polymeric materials, calculated from the previous values. The main purpose of this work is to analyze the influence of the vinyl acetate percentage over these parameters; this is the first stage to model the EVA-solvent separation step, which is the final aim of the project in which our group is working.

EXPERIMENTAL

IGC—Calculations

According to IGC basis,[19] once the injected solvent has gone through the column, its specific retention volume (V_g) can be obtained from retention time measurements by means of eq. (1), where F is the flow rate of the carrier gas corrected to the column temperature, t_r is the retention time of the solvent, t_m is the retention time of a reference inert compound, W_s is the amount of polymer packed in the column, and j is a correction factor. Due to the carrier gas is compressible, the pressure drop along the column might cause an increase of the volume flow rate in the outlet (P_0) compared with the inlet value (P_i); therefore, a correction factor (j) is usually added [eq. (2)].[19]

$$V_g = \frac{j \cdot (t_r - t_m) \cdot F}{W_s} \quad (1)$$

$$j = \frac{3}{2} \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \quad (2)$$

The relation between the mass-based infinite dilution activity coefficient of the solvent, $(\Omega_i^\infty)_{IGC}$, and its retention volume (V_g), in a solvent (1)–polymer (2) mixture, is given by eq. (3),[19] where T is the temperature in K, R is the ideal gas constant, M_1 is the solvent molecular weight and f_1^0 is the standard fugacity of the solvent. This last parameter can be determined with the Virial EOS truncated after the second term; so, eq. (3) is transformed into eq. (4).

$$\ln(\Omega_1^\infty)_{IGC} = \ln\left(\frac{R \cdot T}{V_g \cdot M_1 \cdot f_1^0}\right) \quad (3)$$

$$\ln(\Omega_1^\infty)_{IGC} = \ln\left(\frac{R \cdot T}{V_g M_1 p_1^0}\right) - \frac{(B_{11} - V_1)p_1^0}{RT} \quad (4)$$

In this last equation, B_{11} is the solvent second term of the Virial EOS, p_1^0 is the solvent vapor pressure, and V_1 is the solvent molar volume.

In this work, molar volumes have been calculated according to a modification of Rackett model[20] using the value of the Rackett parameter which appears in literature[21]; the second terms of Virial EOS have been calculated with Tsonopoulos' correlation,[22] and the Antoine coefficients of the solvent vapour pressure values have been also taken from literature.[21]

From the values of infinite dilution activity coefficient, the Flory–Huggins interaction parameter (χ) can be calculated by using eq. (5),[23] where r is the ratio between molar volume of the polymer and the molar volume of the solvent, and ρ_1 and ρ_2 are the solvent and polymer densities, respectively.

$$\chi = \ln(\Omega_1^\infty)_{IGC} - \left(1 - \frac{1}{r}\right) + \ln\frac{\rho_1}{\rho_2} \quad (5)$$

Equivalent expressions have been used in literature,[24] because eq. (5) is directly derived from the combination of eq. (4) with the well-known Flory Equation[5] [eq. (6)], which allows calculating the activity of a solvent, in a polymer–solvent mixture.

$$\ln(a_1) = \ln(1 - \Phi_2) + \left(1 - \frac{1}{r}\right)\Phi_2 + \chi\Phi_2^2 \quad (6)$$

On the other hand, Hildebrand and Scout,[25] developed a regular solution model defining the solubility parameter of one compound i as the square root of its cohesive energy, which can be calculated from heat of vaporization values [eq. (7)].

$$\delta_1 = \left[\frac{\Delta_{vap}H_1 - RT}{V_1}\right]^{0.5} \quad (7)$$

The Flory–Huggins theory, modified by Blanks and Prausnitz,[7] allows establishing a relationship between the Flory–Huggins parameter (χ) and the solubility parameters of polymer (δ_2) and solvent (δ_1), eq. (8).

$$\chi = \chi_S + \chi_H = \chi_S + \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \quad (8)$$

In this last equation, χ_S is the entropic contribution to χ and χ_H is the enthalpic contribution to χ. The value of χ_S is usually kept constant and equal to 0.34,[7] while the enthalpic contribution is calculated from the solubility parameter values.

Rearranging terms, eq. (9) is obtained so that the polymer solubility parameter can be determined from the slope of $[(\delta_1^2/2) - (\chi RT/2V_1)]$ vs. δ_1, by simply knowing the solubility parameter of several solvents.[26]

$$\left(\frac{\delta_1^2}{2} - \frac{\chi RT}{2V_1}\right) = \delta_2\delta_1 - \left(\frac{\delta_2^2}{2} + \frac{\chi_s RT}{2V_1}\right) \quad (9)$$

Finally, from the activity coefficient values at different temperatures, the values of the heats of vaporization of the solvent ($\Delta_{vap}H_1$) can be obtained [eq. (10)] by calculating the heats of solution $\Delta_s H_1$ [eq. (11)] and the partial molar heats of mixing $\Delta_{mix}\overline{H}_1^\infty$ [eq. (13)].[23]

$$\Delta_{vap}H_1 = \Delta_{mix}\overline{H}_1^\infty - \Delta_s H_1 \quad (10)$$

Table I. Experimental Results for EVA460 Polymer

EVA460 polymer	V_g (cm^3/g)			$(\Omega_i^\infty)^{IGC}$			χ		
Solvent	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
Metanol (MET)	86	57	41	45.51	44.01	40.14	2.62	2.58	2.47
Etanol (ET)	168	112	77	33.46	30.17	27.69	2.31	2.19	2.10
Butanol (BUT)	1463	906	559	18.31	15.56	14.09	1.73	1.56	1.45
n-Hexane (HEX)	139	103	76	11.55	11.14	11.13	1.07	1.01	1.00
Cyclohexane (CX)	305	224	163	6.00	5.64	5.51	0.57	0.50	0.47
Vinyl acetate (VA)	223	154	108	6.96	6.77	6.68	0.90	0.86	0.83
Toluene (TOL)	1535	1033	686	3.65	3.48	3.48	0.19	0.13	0.12
p-Xylene (XYL)	–	2763	1778	–	3.34	3.28	–	0.08	0.06
Tetrahydrofuran (THF)	293	210	153	4.51	4.35	4.27	0.42	0.37	0.34

$$\Delta_s H_1 = -R \left[\frac{\partial \left(\ln(V_g^\circ) \right)}{\partial (1/T)} \right] \quad (11)$$

$$V_g^\circ = V_g \left(\frac{273.15}{T} \right) \quad (12)$$

$$\Delta_{\mathrm{mix}} \overline{H}_1^\infty = R \left[\frac{\partial \left(\ln(\Omega_1^\infty) \right)}{\partial (1/T)} \right] \quad (13)$$

These values, derived from the experimentally determined activity coefficients, can be compared with the ones estimated using the Watson model[27] as a kind of consistency test, to check its goodness.

Materials

The polymeric materials used in this work are two random EVA copolymers, which differ in their molecular weight and in their vinyl acetate percentage. Both of them were supplied by REPSOL-YPF Company.[2] While EVA-1 (EVA460) has a vinyl acetate content of 33% (w/w), EVA-2 (EVA410) has a vinyl acetate content of 18% (w/w). The weight-average molecular weight and the number-average molecular weight are 61,040 and 18,580 for EVA460, and 42,460 and 14,010 for EVA410. Finally, the densities of the two polymeric materials, given by the supplier, are 956 kg/m^3 and 937 kg/m^3, respectively.

On the other hand, all the used solvents (Methanol, MET; Ethanol, ET; *n*-Butanol, BUT; *n*-Hexane, HEX; Cyclohexane, CX; Vinyl Acetate, VA; Toluene, TOL; *p*-Xylene, XYL and Tetrahydrofuran, THF) were analytical grade and were purchased from Aldrich. They were used directly, without any purification step.

Experimental Procedure

The EVA stationary phases used in this work were prepared by dissolving a weighted sample of the polymer in a suitable solvent and depositing the solution on a weighted amount of support (Chromosorb W/AW-DMCS 80-100 mesh). The employed solvents were cyclohexane, in the case of EVA460 material, and tetrahydrofuran, in the case of EVA410 material.

Once dissolved, each mixture was allowed to dry by slow evaporation in a rotavapor under vacuum, while being stirred to ensure homogeneous mixture; evaporation time was at less 8 h. The final amount of each polymer deposited in the support was determined by thermogravimetric analysis on a Seiko EXSTAR 6000 TG/DTA 6200 equipment. Each analysis was performed three times, and the average value was selected in each case. The obtained percentages were 11.45% (w/w) for EVA460 and 11.28% (w/w) for EVA410.

Afterwards, each coated support was packed into a $^1/_4$ in. nominal diameter column (1.92 m length for EVA460 and 2.00 m length for EVA410); both of them were installed in a VARIAN

Table II. Experimental Results for EVA410 Polymer

EVA410 polymer	V_g (cm^3/g)			$(\Omega_i^\infty)^{IGC}$			χ		
Solvent	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
Metanol (MET)	47	33	23	83.54	75.43	70.23	3.25	3.13	3.05
Etanol (ET)	93	62	43	60.83	54.44	49.18	2.93	2.81	2.69
Butanol (BUT)	765	522	328	35.01	27.03	23.97	2.40	2.13	2.00
n-Hexane (HEX)	111	85	64	14.46	13.47	13.24	1.31	1.23	1.19
Cyclohexane (CX)	241	180	135	7.59	7.00	6.60	0.83	0.74	0.67
Vinyl acetate (VA)	128	92	67	12.12	11.38	10.73	1.48	1.40	1.33
Toluene (TOL)	1056	720	493	5.31	5.00	4.85	0.59	0.51	0.47
p-Xylene (XYL)	–	1970	1286	–	4.69	4.54	–	0.44	0.40
Tetrahydrofuran (THF)	197	145	107	6.71	6.32	6.07	0.84	0.76	0.71
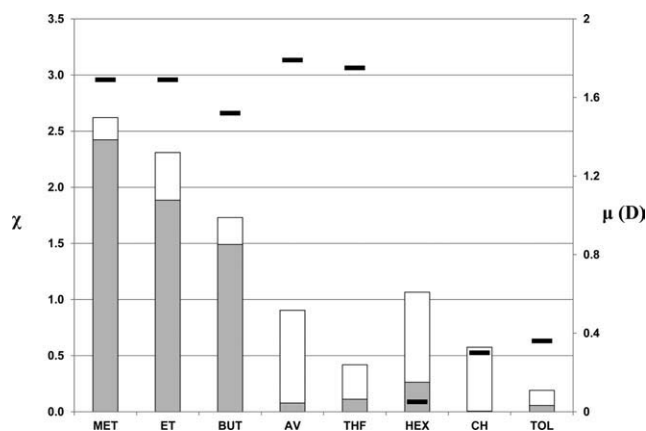
Figure 1. Flory–Huggins parameter for EVA 460—solvent pairs at 30°C (bars), related to the dipole moment of the solvent, μ (black horizontal lines). Each Flory–Huggins bar is divided into the enthalpic contribution (gray area) and entropic contribution (white area).

Figure 2. Flory–Huggins parameter for EVA 410—solvent pairs at 30°C (bars), related to the dipole moment of the solvent, μ (black horizontal lines). Each Flory–Huggins bar is divided into the enthalpic contribution (gray area) and entropic contribution (white area).

3800 gas chromatography, equipped with a thermal conductivity detector and an electronic flow controller.

All the measurements were carried out with a helium flow of 40 mL/min, as carrier gas, and air, as inert component, in a temperature range between 30 and 50°C.

RESULTS AND DISCUSSION

Flory–Huggins Parameter and Solvent Activity Coefficient Values

Tables I and II show the measured values of the retention volumes (V_g), along with the calculated values of the mass-based infinite dilution solvent activity coefficients, $(\Omega_i^\infty)_{IGC}$, and the Flory–Huggins interaction parameters (χ), for the binary mixtures of both EVA460 and EVA410 polymers with different solvents, in the temperature range from 30 to 50°C.

As it can be observed in these two Tables, the specific retention volumes (V_g) are higher in the case of EVA460–solvent systems, while the solvent activity coefficients and Flory–Huggins parameters are lower. Taking into account that the lower the activity coefficient and Flory–Huggins parameter the higher the compatibility between a polymer and a solvent, this could indicate that an increase of vinyl acetate content (EVA460 is the copolymer with more vinyl acetate percentage) implies higher interactions between the EVA material and the studied solvents.

As it is described in literature,[26] values of the Flory–Huggins parameter below 0.5 (critical χ parameter for high molecular weight polymers) indicate that the solvent is adequate for the polymer, while values higher than 0.5 indicate that the solvent is not favourable. So, according to this criterion, the most adequate solvents for both polymers should be the aromatic-type compounds, as well as tetrahydrofuran; secondly, the most adequate solvent-type should be the aliphatic, being the alcohols the less compatible solvents. Regarding the temperature dependence, it can be noticed that both solvent infinite dilution activity coefficients and Flory–Huggins parameter decrease with temperature, which is in agreement with literature.[7,8,25]
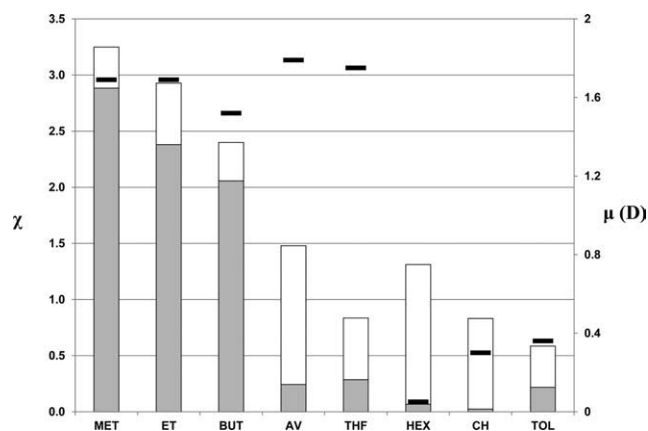
To further analyze the results of Tables I and II, it is important to take into consideration that the Flory–Huggins parameter includes two contributions: one entropic and one enthalpic. The entropic one is related to the free volume of the solvent, while the enthalpic one is related to the intermolecular forces between the polymer and the solvent. To investigate the relative importance of each contribution to the Flory–Huggins parameter, both of them were determined for each polymer–solvent pair. The enthalpic contribution was calculated following Blanks and Prausnitz assumption[7] [eq. (8)], once the solubility parameter of the polymer was obtained (see next section), while the entropic contribution was determined as the difference between the overall solubility and the enthalpic contribution; the results are presented in Figures 1 and 2. Figure 1 represent the overall Flory–Huggins parameter divided in its two contributions (entropic, χ_S, and enthalpic, χ_H), related to the dipole moment of the solvents, for EVA460–solvent pairs; Figure 2 represents the same for EVA410–solvent systems.

As it can be seen, the larger contribution to the Flory–Huggins parameter of the most compatible solvents (the ones with the
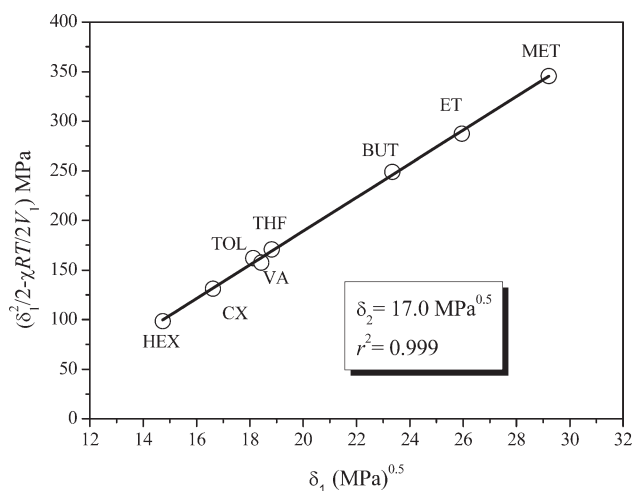
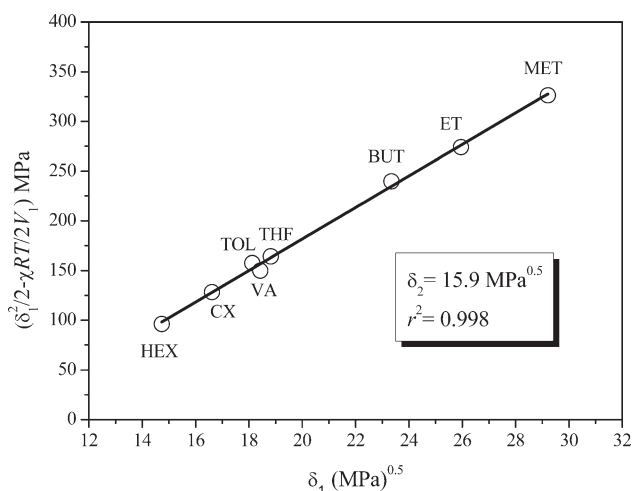**Figure 3.** Plot to calculate the EVA460 solubility parameter at 30°C.

Figure 4. Plot to calculate the EVA410 solubility parameter at 30°C.

Table III. Solubility Parameter Values

	Solubility parameter (MPa$^{1/2}$)	
Temperature (°C)	EVA460	EVA 410
30	17.0	15.9
40	16.6	15.5
50	16.3	15.1

are shown in Figures 3 and 4, as an example, while all solubility parameter values are shown in Table III.

The solubility parameter is derived from the cohesion energy of a compound[25] so it is expected to slightly decrease with temperature, as it can be observed in Table III. It can also be noticed that the solubility parameter values of EVA460 are higher than the ones of EVA410. This can be justified by the fact that, in the case of a polymer, the cohesion energy is related to the interactions between the polymer chains and, the higher the vinyl acetate content, the stronger the interactions, due to the increasing polarity. This can be further justified by the fact that a literature value[26] of $\delta_2 = 17.0$ MPa$^{1/2}$, obtained at 75°C, was found for an EVA with a vinyl acetate content of 40%.

On the other hand, it can also be observed that the obtained values for EVA460 material (the one with more vinyl acetate content) are closer to the solubility parameter values of pure vinyl acetate (18.4 MPa$^{0.5}$ at 30°C, 18.1 MPa$^{0.5}$ at 40°C and 17.8 MPa$^{0.5}$ at 50°C)[20] than the obtained values for EVA410 material. As previously said, the closer the solubility parameters of polymer and solvent are, the higher the compatibility; so it is logical that the more vinyl acetate the copolymer contains, the more compatible with pure vinyl acetate is.

lowest values of this parameter) is the entropic one. This indicates that the interactions between the polymers and the solvents happen to be due to entropic factors, independently of the polar (THF, AV) or nonpolar (HEX, CH, TOL) character of the solvent. On the other hand, in the case of alcohol-EVA mixtures, the enthalpic contribution represents more than 80%, may be due the ability of the alcohols to form hydrogen bonds; however, because the entropic contribution is practically negligible, they are not compatible at all with neither of the two EVA materials.

Polymers Solubility Parameters

The solubility parameters of the two PVA materials were calculated from the slope of the plot of $[(\delta_{12}/2) - (\chi RT/2V_1)]$ vs. δ_1 [eq. (9)]. In both cases high regression coefficients were obtained ($r^2 > 0.995$). The values of this parameter are important due to, nowadays, they are considered to be a criterion which indicates the capacity of a polymer to be dissolved into a solvent because the closer the solubility parameters of a polymer and solvent are the better the solubility is. The above mentioned plots for EVA460 and EVA410 copolymers, respectively, at 30°C,

Heat of Vaporization of the Solvents

From the values of the activity coefficient of the solvents at several temperatures, the values of their heats of vaporization ($\Delta_{vap}H_1$) were calculated [eqs. (10)–(13)] and compared with the ones estimated with Watson model.[26] The results are summarized in Table IV. As it can be observed, the difference

Table IV. Experimentally Derived and Estimated Enthalpy Values

	EVA460 polymer					EVA410 polymer				
Solvent	$\Delta_s H_1$ (kJ/mol)	$\Delta_{mix}H_1^{\infty}$ (kJ/mol)	$\Delta_{vap}H_{1,exp}$ (kJ/mol)	$\Delta_{vap}H_{1,Watson}$ (kJ/mol)	Dev (%)	$\Delta_s H_1$ (kJ/mol)	$\Delta_{mix}H_1^{\infty}$ (kJ/mol)	$\Delta_{vap}H_{1,exp}$ (kJ/mol)	$\Delta_{vap}H_{1,Watson}$ (kJ/mol)	Dev (%)
MET	−32.7	5.1	37.7	36.7	2.7	−30.7	7.1	37.7	36.7	2.7
ET	−34.6	7.7	42.3	41.6	1.8	−33.7	8.7	42.3	41.6	1.8
BUT	−41.8	10.7	52.5	52.0	0.9	−37.0	15.5	52.5	52.0	0.9
HEX	−27.3	1.5	28.8	30.6	−6.0	−25.2	3.6	28.8	30.6	−6.0
CX	−28.2	3.5	31.7	32.2	−1.5	−26.0	5.7	31.7	32.2	−1.5
VA	−32.3	1.7	34.0	33.7	1.0	−29.0	5.0	34.0	33.7	1.0
TOL	−35.4	2.0	37.3	37.3	0.2	−33.6	3.7	37.3	37.3	0.2
XYL	−39.7	1.5	41.2	41.2	0.0	−38.5	2.7	41.2	41.2	0.0
THF	−29.2	2.2	31.4	31.2	0.6	−27.4	4.1	31.4	31.2	0.6

between the experimental and estimated values is always lower than 6%.

CONCLUSIONS

The mass-based infinite dilution solvent activity coefficients and Flory–Huggins interaction parameters have been experimentally determined for binary mixtures of several solvents with two EVA copolymers with different vinyl acetate content. The obtained values of these parameters are clearly lower for EVA460 mixtures (the copolymer with more vinyl acetate percentage) than for EVA410 mixtures, pointing to the fact that an increase of vinyl acetate content implies higher interactions between the EVA material and the solvent. The results also indicate that the most adequate solvents for both polymers (the ones whose mixtures with any of the polymers have the smallest Flory–Huggins parameter) are the aromatic-type compounds, as well as tetrahydrofuran.

From the calculated values of the entropic and enthalpic contributions to the Flory–Huggins parameter it can be noticed that, in the case of the most compatible solvents, the polymer–solvent interaction is mainly due to entropic effects, independently of the polar character of the solvent. On the contrary, for polymer–alcohol mixtures, the main contribution to the Flory–Huggins parameter is the enthalpic one. The influence of the temperature over this parameter shows that it tends to diminish with increasing temperature, which is in agreement with literature.

Finally, the solubility parameters of the two EVA copolymers were also determined. The obtained value for EVA460 material, the one with the most vinyl acetate percentage, is closest to the solubility parameter of the pure vinyl acetate.

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