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Thermodynamic Study of PVAc – Solvent and PE – Solvent Diluted Solutions

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The objective of this work is to develop a thermodynamic study of poly-vinyl acetate (PVAc) – methanol (MET), polyethylene (PE) – cyclohexane (CX) and polyethylene – *p*-xylene (p-XYL) mixtures by means of Intrinsic Viscosity (IV) technique, with the aim of obtaining the Flory Huggins polymer-solvent interaction parameter. As it can be seen, the higher is the value of viscous-average molecular weight of the polymeric materials (Mw), the higher is the IV. From the Intrinsic Viscosity data, the Flory-Huggins parameters of the studied couples were calculated following the Stockmayer-Fixman procedure. The obtained parameter, at 60 ºC, of both PE – CX and PVAc – MET pairs is lower than 0.5 which, according to Flory Huggins theory, implies that, at polymer infinite dilution, the polymer and the solvent are completely compatible. However, the Flory Huggins parameter PE – p-XYL couple is higher than 0.5 so this couple is not completely compatible.

1. Introduction

Polyvinyl acetate (PVAc) is a highly employed thermoplastic amorphous polymer, which is commonly obtained by free radical polymerization of vinyl acetate. Additionally, polyethylene (PE) is a thermoplastic crystalline polymer which is typically obtained from ethylene polymerization.

The main applications of PVAc are as an adhesive for several porous materials like paper of wood (Harper and Petrie, 2003), while PE is basically employed in cable isolations, pipe structures or recipients manufacture (Brydson, 1999) and, recently, it residues have been used in hydrogen production (Moghadam, 2013). Additionally, the monomers of these two homopolymers can also constitute a copolymer, named ethylene – vinyl acetate copolymer, which is widely applied in tyres manufacture or as photovoltaic cells coverage (Brydson, 1999).

Among other procedures, this copolymer is industrially produced in a solution process, at temperatures around 60ºC and with methanol as solvent, although other impurities, such as cyclohexane or *p*-xylene, can be present in the media after the reaction has taken place (Brydson, 1999). For this reason, it is crucial to thermodynamically characterize the polymer-solvent mixtures.

A frequent approximation to model these copolymer (such as EVA) – solvent systems is to split the polymeric material into its correspondent homopolymers and to determine the homopolymer - solvent binary interaction parameters. Because in literature the thermodynamic data of PE – solvent and PVAc – solvent systems at the temperatures of interest are seldom found, in this article we have experimentally obtained them.

One of the widely used theories to determine the polymer solvent interaction parameters is the Flory Huggins theory (Flory, 1941). As stated by this theory, in a polymer (subscript 2) – solvent (subscript 1) mixture, the solvent activity can be calculated by means of Eq(1). In this equation, a_1 is the activity of the solvent, ϕ_2 is the polymer volumetric fraction, and χ is the Flory-Huggins polymer-solvent interaction parameter.

Although originally this parameter was assumed to be composition independent, nowadays it is well establish that its value changes with the relative amount of solvent in the mixture (Wolf, 2003). So, it is important to determine its value both at solvent infinite dilution and polymer infinite dilution. In this study we are focusing on

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determining the Flory Huggins parameter at polymer infinite dilution as we have previously obtained the values at solvent infinite dilution.

At polymer infinite dilution, this parameter can be experimentally determined by means of Intrinsic Viscosity (IV) measurements. The Intrinsic Viscosity (IV) of a polymer – solvent mixture (denoted as [η]) is defined as the viscosity of an infinite diluted solution and its value is related to the Flory-Huggins parameter by plotting the Stockmayer-Fixman (Stockmayer and Fixman, 1963) relationship ($[\eta]/M_w^{1/2}$ vs $M_w^{1/2}$), Eq(2)), where M_w is the viscous-average polymer molecular weight, r is the ratio between the molar volume of the polymer and the molar volume of the solvent, ϕ_2 is the polymer volumetric fraction, $[\eta]_\theta$ is the IV under theta conditions V_1 is the solvent molar volume, v_2 is the polymer specific volume, ϕ_0 is the Flory universal constant (equal to 2.8E23 if the IV units are $mL.g^{-1}$) , N_A is the Avogadro number and K_0 is the unperturbed dimension of the polymer in the studied solvent.

$$\ln(a_1) = \ln(1-\phi_2) + \left(1-\frac{1}{r}\right)\phi_2 + \chi\phi_2^2 \tag{1}$$

$$[\eta]\Big/M_w^{1/2} = K_0 + 0{,}51B\phi_0 M_w^{1/2}$$

$$K_0 = [\eta]_\theta\Big/M_w^{1/2} \qquad B = \frac{\upsilon_2^2(1-2\chi)}{V_1 N_A} \tag{2}$$

The viscous-average polymer molecular weight, M_w, can be directly determined form Intrinsic Viscosity values with the well-known Mark-Hawking relationship (Brandrup and Immergut, 2005), Eq(3). In this equation, a and K are constants that can be taken from literature for determined polymer-solvent system.

$$[\eta] = K \cdot M_w^a \tag{3}$$

This technique has only one drawback to be overcome: the polymer and the solvent must be miscible each other in the composition range studied. For this reason, the selected pairs to study in this work are PE – cyclohexane, PE – *p*-xylene and PVAc – methanol.

2. Experimental section

2.1 Materials

All the polymeric materials were purchased from Aldrich in pellet-type form. The density values of the three PE materials are 920 $kg.m^{-3}$ (PE1), 906 $kg.m^{-3}$ (PE2) and 925 $kg.m^{-3}$ (PE3). The average density of the three PVAc materials is 1180 $kg.m^{-3}$. On the other hand, all the employed solvents (cyclohexane, CX, *p*-xylene, p-XYL, and methanol, MET) were analytical grade and were also obtained from Aldrich. They were used directly, without any purification step.

2.2 Intrinsic Viscosity Determination

The IV of each polymer-solvent mixture was determined by measuring the flow time through a capillary viscosimeter of five solutions. The most concentrated solution of each series was prepared by adding 200-300 mg of polymer over approx. 60 g of pure solvent, and then shaking until the polymer completely dissolved. The rest of solutions were prepared from the first one by adding pure solvent. Flow time measurements were carried out in a JP – Selecta Ubbelohde 0b type of capillary viscosimeter. Once prepared, each solution of the series was transferred into the viscosimeter, which was immersed in a water bath, thermo-stated at $T \pm 0.01$ºC. The solutions were allowed to equilibrate at the adequate temperature before starting the measurement. The accuracy of the measurements was 10^{-2} s. Each flow time was measured 5 times and the average value was taken; from the flow times, relative and specific viscosities were determined.

The IV of a polymer-solvent mixture, [η], can be calculated, from the previously described flow time measurements, with Huggins, Eq(4) and Kraemer, Eq(5) expressions (Huggins, 1942 and Kraemer, 1938).

$$\frac{\eta_{sp}}{c_2} = [\eta] + K_H [\eta]^2 c_2 \tag{4}$$

$$\frac{\ln(\eta_r)}{c_2} = [\eta] + K_K [\eta]^2 c_2 \tag{5}$$

In these equations, c_2 is the concentration of polymer solution, K_H is the Huggins coefficient, and K_K is the Kramer coefficient; relative viscosity (η_r) is the ratio between the flow time of the polymer solution through the viscosimeter, and the flow time of the pure solvent through the apparatus; finally, specific viscosity (η_{sp}) is defined as relative viscosity minus one, and represents the viscosity increasing due to the polymer. So, the Intrinsic Viscosity ([η]) can be determined as the common intercept of the Kraemer and Huggins relationships, using η_r and η_{sp} experimentally measured.

3. Results and discussion

3.1 Viscous-average molecular weight

To determine the viscous-average molecular weight of the polymeric materials (three PE samples with different molecular weight and three PVAc samples also with different molecular weight), Intrinsic Viscosity measurements of the systems PE – *p*-xylene at 75 °C and PVAc – methanol at 53 °C were carried out. Under these conditions, the Mark Hawking constants are a = 0.63 and K = 0.135 for PE – *p*-xylene system and a = 0.59 and K = 0.0366 for PVAc – methanol system (Brandrup and Immergut, 2005).
These IV (Huggins and Kraemer equations) plots are shown in Figure 1. On the other hand, the Intrinsic Viscosity values, as well as the M_w data, are summarized in Table 1. In all cases, good regression coefficients were obtained; this indicates the validity of the obtained values.

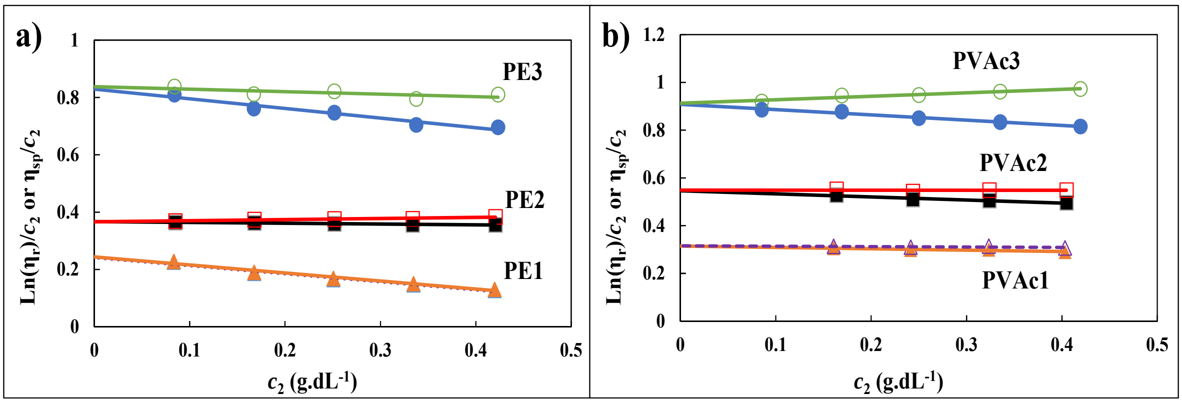

Figure 1. Huggins and Kraemer plots of PE – p-xylene systems at 75 °C (a) and PVAc – methanol systems at 53 °C (b)

Table 1. M_w determination of the polymeric materials

Parameter	Polymer					
	PE-1	**PE-2**	**PE-3**	**PVAc-1**	**PVAc-2**	**PVAc-3**
IV (dL.g^{-1})	0.243	0.367	0.833	0.315	0.547	0.910
Mw (kg.kmol^{-1})	3800	7300	26900	94400	240500	569200

3.2 Intrinsic Viscosity values at 60 °C

The Intrinsic Viscosity values, as well as the Huggins and Kraemer constants of the studied systems at 60 °C are summarized in Table 2.
Figures 2, 3 and 4 show the Huggins and Kraemer plots for the studied systems. In all cases, good regression coefficients were reached, except for the system PE3 – CX. This can be related to the fact that experimentally was quite difficult to completely dissolve this couple.

As it could be expected, the higher the molecular weight is, the higher the Intrinsic Viscosity values are, The systems where the lower influence of molecular weight on IV is less noticeable is PE – p-XYL because, as seen in Figure 3, the IV of PE2 (Mw = 7300 g.mol^{-1}) with this solvent is practically equal to the IV of p-XYL with PE3 (Mw = 26900 g.mol^{-1}).

Apart from the Intrinsic Viscosity value, a good criterion to ascertain if a solvent will be suitable for a determined polymer is the difference between Huggins and Kraemer constants. The closer this difference to 0.5, the more compatible the polymer and the solvent are. According to this criterion, all couples are compatible (at low polymer compositions) except PE3 – CX and PE1 – p-XYL and PE2 – p-XYL. This is in agreement with was experimentally observed as these systems were the most difficult to completely dissolve.

Table 2. Intrinsic Viscosity values

System	IV (dL.g^{-1})	K_H	K_K	$K_H - K_K$
PE-1 - CHX	0.138	-1.248	-1.663	0.415
PE-2 - CHX	0.423	0.650	0.100	0.550
PE-3 - CHX	0.848	-0.591	-0.962	0.371
PE-1 – *p*-XYL	0.201	-3.203	-3-414	0.211
PE-2 - *p*-XYL	0.465	-0.604	-0.932	0.328
PE-3 - *p*-XYL	0.415	-0.196	-0.606	0.410
PVAc-1 - MET	0.327	-0.287	-0.686	0.399
PVAc-2 – MET	0.510	0.360	-0.145	0.505
PVAc-3 - MET	0.938	0.168	-0.266	0.434

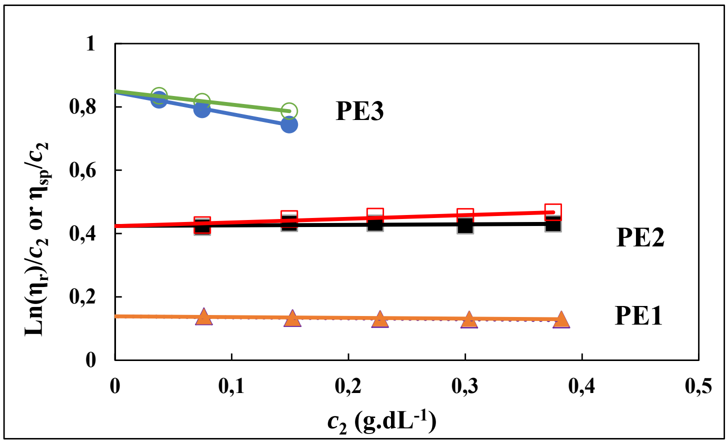

Figure 2. Huggins and Kraemer plots for polyethylene – cyclohexane systems

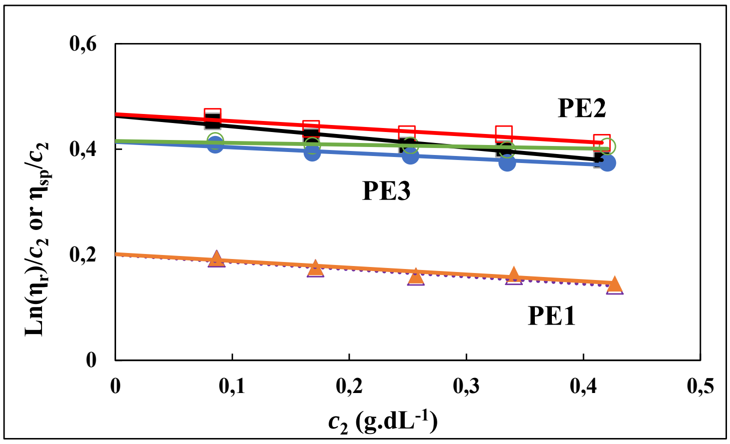

Figure 3. Huggins and Kraemer plots for polyethylene - p-xylene systems

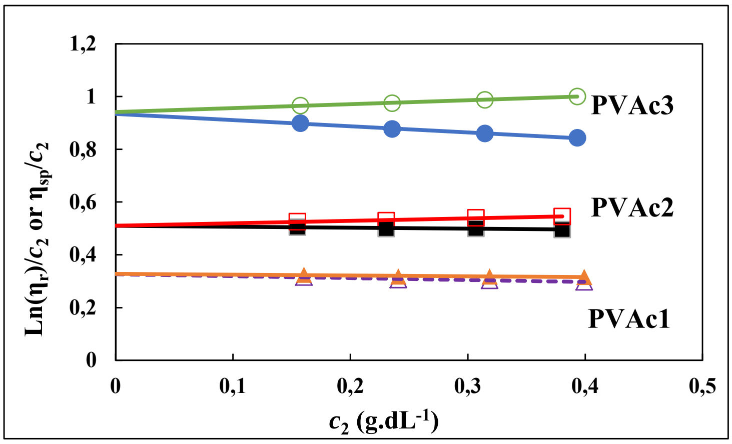

Figure 4. Huggins and Kraemer plots for polyvinyl acetate - methanol systems

3.3 Flory Huggins parameters

Having obtained the viscous-average molecular weight of the materials, the Stockmayer-Fixman plots ($[\eta]/Mw^{1/2}$ vs $Mw^{1/2}$) were carried out, as it can be seen in Figure 5, for each polymer – solvent pair. The plots were done at 60 °C for the three mixtures but also at 75 °C for PE – CX mixture and at 53 °C for PVAc – MET mixture. From the slopes, it could possible to obtain the Flory Huggins parameter (χ) for each couple, while the K0 values were calculated from the intercepts. These data are summarized in Table 3.
To obtain the Flory Huggins parameter, it was necessary to calculate the specific volumes (v_2) of the polymers and the molar volumes of the solvents (V_1). The first data were determined from the densities of the polymeric materials (906 kg.m^{-3} for PE and 1180 kg.m^{-3} for PVAc), while the second data were calculated from the solvent densities at different temperatures (NIST, 2014).

Table 3. Flory Huggins parameter and K_0 value for the studied pairs at 60°C

Couple	K_0 (mL.g^{-1})	χ
PE – CX at T = 60 °C	0.183	0.065
PE – *p*-XYL at T = 60 °C	0.526	0.825
PE – *p*-XYL at T = 75 °C	0.331	0.281
PVAc – MET at T = 53 °C	0.091	0.495
PVAc – MET at T = 60 °C	0.090	0.495

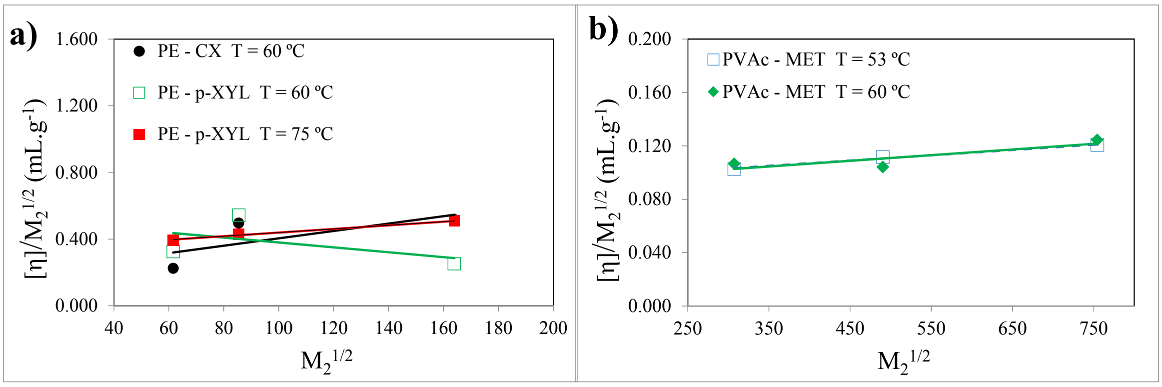

Figure 5. Stockmayer-Fixman plots of PE – p-xylene and PE – cyclohexane mixtures (a) and PVAc – methanol mixture (b)

As it can be noticed in Table 3, the Flory Huggins parameter for PE – CX and PVAc – MET pairs is lower than 0.5. According to Flory Huggins model, this implies that, in the studied composition interval, the polymer and the solvent are completely compatible. On the other hand, the Flory Huggins parameter PE – *p*-XYL couple is higher than 0.5 so this couple is not completely compatible. This is in agreement with what experimentally was observed and has previously commented.

Regarding the K_0 values, it can be also noticed that the higher value correspond to PE – p-XYL couple. This parameter is known as unperturbed dimension and is a measurement of the dimensions of the polymer random coil in a solvent media and in theta estate (an estate in which polymer-solvent interactions and balanced with polymer-polymer interactions). The higher this value, the less importance of polymer-solvent interactions compared with polymer-polymer interactions.

In Figure 2 it can be noticed that the Stockmayer-Fixman plot is quite accurate for PVAc – Methanol couple, although it is not for the other two pairs. However, the Flory Huggins parameters obtained for PE- CX and PE – p-XYL pairs at 60 ºC, are in between the expected interval, as they are in agreement with the values of this parameter at lower temperatures (Brandrup and Immergut, 2005).

4. Conclusions

Intrinsic Viscosity measurements have been carried out for polyethylene – cyclohexane, polyethylene – p-xylene and polyvinyl acetate – methanol systems have been carried out with the aim of obtaining the Flory Huggins parameters by means of the Stockmayer – Fixman procedure. To perform this it was previously necessary to determine the viscous-average molecular weight of the employed polymer, what was done by means of Mark Hawking relationship with Mark Hawking parameters taken from literature. These molecular weights were accurately obtained as, in all cases, good adjustment parameters were achieved.

The Flory Huggins results indicate that, in the studied composition interval, the most compatible pairs are polyethylene – cyclohexane and polyvinyl acetate – methanol, as the Flory Huggins parameter is below 0.5. This is supported by means of the Intrinsic Viscosity and K_0 obtained values.

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