

## Interaction Parameter ( $\chi$ ); Expansion Factor ( $\epsilon$ ); Steric Hindrance Factor ( $\sigma$ ); and Shielding Function $F(\xi)$ ; for the System PEA–Organic Solvents by Intrinsic Viscosity Measurements

Martha L. Cecopieri-Gómez<sup>\*,a</sup> and Joaquín Palacios-Alquisira<sup>b</sup>

<sup>a</sup> Instituto Mexicano del Petróleo, Research and Development Program in Molecular Engineering, Lázaro Cárdenas 152, Col. San B. Atepehuacán, 07730 México D. F., México

<sup>b</sup> Universidad Nacional Autónoma de México, Chemistry Faculty, Macromolecular Physicochemistry Department. "D" Building, Lab. 108, Cd. Universitaria, 04510 México D. F., México

Medidas viscosimétricas de PAE, poli(adipato de etileno), em benzeno, cloroformio e acetona a 30 °C foram utilizadas para determinar experimentalmente os parâmetros binários de interação de Flory ( $\chi_{ij}$ ), para esse material plastificante. Obtiveram-se valores de  $\chi_{1,2} = 0,1544 \pm 0,01$ ,  $\chi_{1,2} = 0,1631 \pm 0,01$ , e  $\chi_{1,2} = 0,1922 \pm 0,01$ , para o PAE em benzeno, cloroformio e acetona respectivamente, mediante correlação de dados de peso molecular (M) e viscosidade intrínseca  $[\eta]$  de acordo com o modelo hidrodinâmico de Stockmayer-Fixman (SF) para soluções poliméricas diluídas. O modelo permite também estimar o parâmetro constante,  $k_{\theta}$  para a combinação polímero (1) – solvente (2) no estado theta ( $\theta$ ) e o parâmetro de impedimento estérico ( $\sigma$ ). Neste trabalho reporta-se os valores para o parâmetro binário de interação de Flory, que apontam que os solventes utilizados, são termodinamicamente, bons solventes para o PAE. Adicionalmente, mediante a aplicação da teoria de Debye-Bueche aos dados experimentais de  $[\eta]$  e (M), estimaram-se os fatores de expansão ( $\epsilon$ ) e proteção ( $\xi$ ) e a profundidade de proteção (L), quantidades que confirmam que os solventes empregados são bons solventes para o sistema PAE.

In this work we present experimental data of the Flory binary interaction parameter,  $\chi$ , of poly(ethylene adipate) PEA, a plasticizer material. We have used the viscometric method for measuring dilute PEA solutions in good solvents: benzene, chloroform and acetone. A procedure based on the Stockmayer-Fixman, (SF), hydrodynamic solutions theory, allows us to evaluate some thermodynamic parameters *via* the intrinsic viscosity  $[\eta]$ , measured in several good solvents. This method also estimates the unperturbed parameter,  $k_{\theta}$ , and the steric hindrance parameter, ( $\sigma$ ), by viscosity measurements at constant temperature of 30°C. By correlation of the molecular weight (M) and intrinsic viscosity data, according to the Stockmayer-Fixman (SF) solution theory model, values of Flory binary interaction parameter  $\chi$ , equal to  $\chi_{1,2} = 0.1544 \pm 0.01$ ;  $\chi_{1,2} = 0.1631 \pm 0.01$ ; and  $\chi_{1,2} = 0.1922 \pm 0.01$ , for PEA in benzene, chloroform and acetone, respectively, were obtained. In addition we applied the Debye-Bueche theory, in order to estimate values of: expansion factor ( $\epsilon$ ), shielding factor ( $\xi$ ) and depth of shielding (L) for the system PEA-organic solvents, by  $[\eta]$  and (M) experimental data correlation. The results confirm that values obtained, correspond to "good solvents" for the PEA polymer.

**Keywords:** Flory binary interaction parameter, hydrodynamic properties of poly(ethylene adipate), Stockmayer-Fixman (SF) hydrodynamic model, Debye-Bueche solution theory, intrinsic viscosity

## Introduction

The Flory-Huggins theory includes the Flory interaction parameter  $\chi$ ,<sup>1,2</sup> to explain the polymeric solution properties.  $\chi$ , represents the polymer/solvent interaction, and it is a free energy parameter. The

importance of its determination for a given polymer/solvent pair, lies on the fact that, it serves as a miscibility criterion. Thus a low value of  $\chi$ , means thermodynamically speaking, a good solvent and  $\chi$  equal to 0.5, represents the theta state ( $\theta$ ) wherein polymer/solvent interactions disappear.

The Flory interaction parameter  $\chi$ , can be determined measuring solvent activity, which can be known by technical means such as: lowering the vapor pressure and

\* e-mail: mcecopie@imp.mx

the freezing point; light scattering; osmotic pressure; inverse gas chromatography and measurements of intrinsic viscosity  $[\eta]$ , the latter, has the advantage of information produced at the limiting case of infinite dilution.

Viscometry of diluted solutions is an important technique in the study of polymeric solutions thermodynamic properties. W. H. Stockmayer in his publication,<sup>3</sup> proposed that unperturbed dimensions of polymeric chain, can be estimated from measurements of polymeric solution intrinsic viscosity  $[\eta]$  in non theta solvents, when hydrodynamic effects are negligible, and the expansion coefficient  $\alpha_{\eta}$ , can be known. Thus, a relative simple equation for  $[\eta]$ , was developed from which  $k_{\theta}$ , unperturbed parameter, can be estimated by plotting  $M^{1/2}$  vs.  $[\eta]M^{-1/2}$ ; from the slope of the straight line generated it is possible to estimate the Flory binary interaction parameter ( $\chi_{ij}$ ). The mathematical expression that relates  $M$  and  $[\eta]$ , is known as the Stockmayer-Fixman equation.<sup>4</sup>

As already mentioned,  $\chi$  is a measure of the interaction between any given solvent and a given polymer. It is a dimensionless free-energy parameter and contains both entropy and enthalpy terms:

$$\chi = \chi_s + \chi_H \quad (1)$$

where  $\chi_s$  = entropy term, temperature-dependent quantity.  
 $\chi_H$  = enthalpy term given by:

$$\chi_H = \left( \frac{V_1}{RT} \right) (\delta_2 - \delta_1)^2 \quad (2)$$

where  $V_1$  = molar volume of the solvent, ( $\text{cm}^3\text{mol}^{-1}$ ),  $R$  = universal gas constant, ( $\text{cal mol}^{-1} \text{K}^{-1}$ ),  $T$  = thermodynamic temperature, ( $\text{K}$ ),  $\delta_1$  and  $\delta_2$  = solubility parameters of the solvent and polymer, respectively, ( $\text{cal} / \text{cm}^3$ )<sup>1/2</sup>.

If we assume that the entropy contribution is negligible, the equation (1) is reduced to:

$$\chi = \left( \frac{V_1}{RT} \right) (\delta_2 - \delta_1)^2 \quad (3)$$

Equation (3) can be solved by the Newton-Rapson's successive approximations method, using as a first approximation for  $\delta_2$ , its experimental value or, the  $\delta_2$  value obtained by calculation, applying the Fedor's group contribution method.<sup>5, 6</sup>

On the other hand, Debye and Bueche, proposed a linear relation between  $[\eta]$  and  $M^{-1}$  through the equation (4), applied to describe the behavior of macromolecules in solution,<sup>7</sup>

$$[\eta] = F(\xi) N_1 \left( \frac{4\pi R_s^3}{3} \right) M^{-1} \quad (4)$$

where  $F(\xi)$ , is the shielding function defined as:

$$F(\xi) = 2.5 \left( \frac{1 + \left( \frac{3}{\xi} \right)^2 - (3/\xi)\cot\xi}{1 + \left( \frac{10}{\xi} \right)^2 \left[ 1 + \left( \frac{3}{\xi} \right)^2 - (3/\xi)\cot\xi \right]} \right) \quad (5)$$

where  $\xi$ , the shielding factor is given by:

$$\xi = R_s / L \quad (6)$$

being  $R_s$  = coil radius,  $L$  = shielding depth,  $N_1$  = constant parameter, specific for each system polymer/solvent.

## Experimental

Experimental methodology to estimate the thermodynamic parameters, is based on the measurement of intrinsic viscosity  $[\eta]$ , of diluted PEA solutions at 30 °C, in benzene, chloroform and acetone. For our purpose the mentioned polymer PEA, was obtained by the direct reaction of adipic acid and mono-ethylene glycol.<sup>6</sup>

### *Polymer synthesis and characterization*

PEA polymer was synthesized by solution polymerization technique; equimolar quantities (0.15 mol) of adipic acid and mono-ethylene glycol, Baker's Q.P. reactants, in 0.564 mol of toluene, Baker's G.R., as reaction media were added. *p*-toluenesulphonic acid was used as catalyst, (0.0031 mols) from Baker's G.R. The reaction was carried out at 94 °C, according to literature reported procedures, for synthesis of polyesters.<sup>8</sup>

During polymerization reaction time, samples were taken out to make available PEA polymer with different molecular weights. After 26 hours, total reaction time, final solution was allowed to cool at room temperature, and all samples were precipitated in enough amount of ethanol. After that, the precipitated polymers were filtered and dried in a vacuum oven, at no more than 30 °C, in order to eliminate non-solvent excess.

In order to get PEA polymer samples with low polydispersity index, samples obtained by the procedure described above, were purified using the precipitation technique by addition of a non-solvent. The pair solvent/non-solvent benzene/petroleum ether was used. All

purified samples were filtered through 0.5  $\mu\text{m}$  Millipore membranes; after that, residual non-solvent was eliminated in a vacuum oven.

To obtain absolute molecular weight values, number average molecular weight,  $M_n$ , of PEA samples was determined by cryoscopy characterization method, according to procedures described in literature.<sup>4,9</sup>

Also, we used GPC to characterize PEA polymers. The number average,  $M_n$ , weight average,  $M_w$ , and z average,  $M_z$ , molecular weights were obtained in a high pressure liquid chromatography apparatus, HPLC with refraction index detector, Waters 410, and Ultrastylagel linear columns, using THF as elution solvent at 1.0  $\text{mL min}^{-1}$ , 30  $^\circ\text{C}$  of temperature and 540-546 psi of pressure.<sup>6</sup> The universal calibration procedure was implemented, using polystyrene standards with weight average molecular weights,  $M_w$ , between 580-35,000 at the same experimental conditions.

Infrared spectroscopy (IR), nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) were used as identification techniques. The absorption bands shown on the PEA IR spectrum, correspond to PEA signals reported in literature<sup>6</sup> (see Table 1) and the  $^1\text{H NMR}(\text{CDCl}_3)$  spectra signals registered were  $\delta$  1.65 (t,  $\text{CH}_2-\text{CH}_2$ ), 2.3 (t,  $\text{COO}-\text{CH}_2$ ), 4.3 (dt,  $\text{CH}_2-\text{CH}_2-\text{O}$ ).

**Table 1.** Main absorption bands registered in the IR spectra, from PEA polymer

GROUPS	BANDS ( $\text{cm}^{-1}$ )
-OH (polymeric)	3400-3200, (3450)
-CH <sub>2</sub> -	2925, (2956)
-CO-O-	1735, (1738)
R-CO-OR	1190, (1174)
-(CH <sub>2</sub> ) <sub>4</sub> -O-	724-734, (740)

The DSC melting points of all polymer samples were in the range of 51.8-53.2  $^\circ\text{C}$ , these values are in good agreement with the melting point reported for PEA in the literature (47-65  $^\circ\text{C}$ ).<sup>10</sup>

### Viscometry

The viscosity measurements of PEA diluted solutions

were carried out in a capillary Ubbelohde viscosimeter. Since the apparatus gives results independent of the amount of solution fed into the instrument, the measure of a series of concentrations can be carried out through successive dilutions.

Viscometry determinations were carried out in a controlled temperature bath, regulated at  $30 \pm 0.2$   $^\circ\text{C}$ . To eliminate the need of correction to the observed data, draining times over 100 seconds were recorded, as well as relative viscosity values in the range of 1.1 to 1.3, according to the ASTM D 446-89 a, and ASTM D 2857-87 standards.<sup>11,12</sup>

### Sample preparation

0.1 g of dry solid PEA purified polymer, were weighted in 10 mL flasks. In our study, eight polymer samples were evaluated, whose molecular weights were between 3,500 and 10,500  $\text{g mol}^{-1}$ , corresponding to the number average molecular weights ( $M_n$ ).

Solvent filtered through Millipore membranes with a pore size of 0.5  $\mu\text{m}$  ( $5 \times 10^{-7}$  m), was added to each flask without reaching the gauging mark, and 24 hours were waiting to allow complete dissolution. The solutions were filtered again, and filled to the flask's gauging mark with filtered solvent. In this process benzene, chloroform and acetone were used as solvents.

Table 2, shows some of the physical chemistry parameters of the solvents used in this study.

### Intrinsic viscosity evaluation

In determining the PEA solutions draining time, methodology stated by ASTM standards was used,<sup>11,12</sup> carrying out successive dilutions in an Ubbelohde 0C viscosimeter (0.36  $\text{mm} \pm 2\%$  capillary diameter). By the consecutive addition of 2.0 mL of solvent used, the following concentration values of 0.01; 0.00833; 0.00714 and 0.00625 g PEA  $\text{mL}^{-1}$  were obtained. After each solvent addition, to make sure the temperature in the viscosimeter reached thermal equilibrium (30  $^\circ\text{C}$ ), a waiting time of 10 minutes was given. In all cases the draining time

**Table 2.** Physical chemical properties of solvents and polymer used in this study

SOLVENTS	Density at 20 $^\circ\text{C}$ , $\rho^{19}$ ( $\text{g cm}^{-3}$ )	Molecular weight, $M^{19}$ ( $\text{g mol}^{-1}$ )	Molar volume at 30 $^\circ\text{C}$ , $V_1^{17}$ ( $\text{mL mol}^{-1}$ )	Solubility parameter, $\delta^{20}$ ( $\text{cal cm}^{-3}$ ) <sup>1/2</sup>	Dielectric constant at 25 $^\circ\text{C}$ , $\epsilon^{18}$	Dipolar moment, DIPM <sup>18</sup>
$\text{C}_6\text{H}_6$	0.8794	78.12	88.91	9.2	2.274	0.0
$\text{CHCl}_3$	1.4984 [15 $^\circ\text{C}$ ]	119.37	80.49	9.3	4.806 (at 20 $^\circ\text{C}$ )	1.1
$(\text{CH}_3)_2\text{CO}$	0.792	58.09	73.53	9.9	20.7	2.9
PEA	1.20	3,500 - 10,500	2910.66 - 8750.0	10.01	---	---

determinations were recorded three times using an electric chronometer with 0.01 seconds reproducibility.

#### Data treatment

Draining times can be changed to viscosity data by applying the relations shown in Table 3.

The viscosity data as a concentration function were extrapolated at infinite dilution applying the Huggins's equation (7).

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \quad (7)$$

where  $k'$  is a polymer constant, in a given solvent.

**Table 3.** Viscosity nomenclature for dissolutions

Common name	Recommended name	Symbol and Equation
Relative viscosity	Viscosity relation	$\eta_r = \eta / \eta_0$ $^{\circ} t / t_0$
Specific viscosity	—	$\eta_{sp} = \eta_r - 1$ $= (\eta - \eta_0) / \eta_0$ $^{\circ} (t - t_0) / t_0$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp} / c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = (\ln \eta_r) / c$
Intrinsic viscosity	Limit viscosity number	$[\eta] = \lim_{c \rightarrow 0} (\eta_{sp} / c)$ $= \lim_{c \rightarrow 0} [(\ln \eta_r) / c]$

Concentration values ( $c$ ), [g/dl] were plotted *versus* reduced viscosity values ( $\eta_{sp}/c$ ) [dl/g], adjusting them to the linear behavior described in equation (7). The intrinsic viscosity  $[\eta]$ , was obtained from the origin ordinate, and from the slope of the straight line, the Huggins's constant,  $k'$  is known.

The unperturbed dimensions of linear flexible macromolecules dissolved in good or poor solvents, can be determined from intrinsic viscosity and molecular weight data, according to the theory for polymeric diluted solutions, if the hydrodynamic effects are negligible and the viscometry expansion factor  $\alpha_{\eta}$ , is available.

$\alpha_{\eta}$ , is defined as:

$$\alpha_{\eta}^3 = [\eta]/kM^{1/2} = [\eta]/[\eta]_0 \quad (8)$$

The fact that  $k$  corresponds to  $k_{\theta}$ , is derived from equation (8). Starting from the experimental data,  $k_{\theta}$  can be obtained by adjustment to the thermodynamic model that best describes the intrinsic viscosity  $[\eta]$  variation, versus molecular weight  $M$ . Several models have been proposed:<sup>4,6</sup>

Flory-Fox-Schaeffgen, (FFS)

$$[\eta]^{2/3} M^{-1/3} = k_{\theta}^{2/3} + 0.858 k_{\theta}^{2/3} \Phi_0 B M / [\eta] \quad (9)$$

Kurata-Stockmayer, (KS)

$$[\eta]^{2/3} M^{-1/3} = k_{\theta}^{2/3} + 0.363 \Phi_0 B g(\alpha_{\eta}) M^{2/3} [\eta]^{-1/3} \quad (10)$$

$$\text{where } g(\alpha_{\eta}) = 8\alpha_{\eta}^3 / (3\alpha_{\eta}^2 + 1)^{3/2} \quad (10a)$$

Stockmayer-Fixman, (SF)

$$[\eta] / M^{1/2} = k_{\theta} + 0.51 \Phi_0 B M^{1/2} \quad (11)$$

$$\text{where } B = 2\nu^2 \left( \frac{1}{2} - \chi \right) / N_A V_1 \quad (11a)$$

$$0.51 \Phi_0 = k_{\theta} C_1 \quad (11b)$$

$$k_{\theta} = \left( \Phi_0 / 6^{3/2} \right) A^3 \quad (11c)$$

where  $\nu$  = polymer specific volume. ( $\text{cm}^3 \text{g}^{-1}$ ),  $V_1$  = molar volume of the solvent ( $\text{cm}^3 \text{mol}^{-1}$ ),  $\chi$  = Flory interaction parameter,  $N_A$  = Avogadro's number ( $\text{mol}^{-1}$ ),  $C_1$  = Numeric constant, theoretically<sup>13</sup> evaluated as 1.55,  $\Phi_0$  = Viscosity constant or Flory constant. It is a function related to the hydrodynamic behavior of macromolecules in solution. There are several theoretical values, they are resumed in Table 4.<sup>14</sup>  $k_{\theta}$  = Uperturbed parameter ( $\text{mL g}^{-1}$ ), it contains the steric hindrance contribution in factor A. See equation (12).

**Table 4.** Flory constant for linear flexible chains, according to several theories<sup>14</sup>

THEORIES	$\Phi_0 \times 10^{-23} (\text{mol}^{-1})$
KRAG	2.87
ZIMM	2.84
HEARST	2.82
FIXMAN-PYUN (Order 0)	2.68
(1 <sup>st</sup> . Order)	1.81
(2 <sup>nd</sup> . Order)	2.66
HEARST-TAGAMI	2.19

According to equation (12), factor A contains in addition: the steric hindrance parameter  $\sigma$ , the bond length among the main chain atoms  $l$ , the bond angle  $\vartheta$ , and the average molar mass formula  $Mu$ , for the chain structural unit.

$$A = \left[ \left( \frac{1 - \cos \vartheta}{1 + \cos \vartheta} \right) \frac{\sigma^2 l^2}{Mu} \right]^{0.5} \quad (12)$$

The equation (12) leads to  $\sigma$  estimation, starting from viscosity measurements, known  $k_\theta$  from equation (11), substituted in equation (11c)

From the slope of SF equation (11), and the equation (11a), it is possible to estimate the  $\chi_{ij}$  the Flory binary interaction parameter, from expression (13):<sup>15</sup>

$$m = 1.02\Phi_0\nu^2(0.5 - \chi_{ij})/N_A V_1 \quad (13)$$

where  $m$  = slope SF equation (11),  $\Phi_0$  = Flory constant =  $2.84 \times 10^{23} \text{ mol}^{-1}$ ,  $\nu$  = specific volume of polymer =  $1/\rho$ ,  $\rho$  = polymer density ( $\text{g cm}^{-3}$ ),  $\nu^2 = (1/1.2)^2 = 0.6944 (\text{cm}^3 \text{g}^{-1})^2$ ,  $N_A$  = Avogadro's number =  $6.025 \times 10^{23} \text{ mol}^{-1}$ ,  $V_1$  = molar volume of solvent ( $\text{cm}^3 \text{mol}^{-1}$ ).

The  $k_\theta$  value can be obtained from the origin ordinate in the same equation (11); its value represents the  $k$  constant in the theta state or unperturbed state.

Like it was defined by Flory, the theta condition refers to the ideal state of a polymeric system, and it represents the condition under which, the effect of the excluded volume apparently disappears and the polymeric chain behaves as an entity moving at random.

In expression (11), if  $k_\theta = 0$ , this means that hydrodynamic volume defined as the product  $[\eta] M$ , is proportional to the square of molecular weight ( $M^2$ ) being the proportionality constant, equivalent to:  $0.51\Phi_0 B$ .

On the other hand, the Debye-Bueche theory considers the partially draining coil as a sphere that is more or less permeable, within which a number of smaller beads are homogeneously distributed. The beads correspond to the monomeric units. The drag which one bead produces on the others is calculated, and this resistance is then expressed in terms of a length  $L$ , which corresponds to the distance from the surface of the coil to where the flow rate of the solvent is reduced to  $1/e$  times, what it is at the surface of this coil.

The shielding ratio or "shielding factor"  $\xi$ , is given by equation (6).  $\xi$ , also can be obtained from the shielding function  $F(\xi)$ , derived by Debye and Bueche theory, and shown in equation (5).  $F(\xi)$  is related to  $[\eta]$  by expression (4).

Coil macromolecules tend however, to occur in the form of ellipsoids. With ellipsoid-shaped coils,  $R_s$  corresponds to the major rotational axis of the ellipsoid. For such coils, a simple empirical relationship between shielding factor  $\xi$ , and the quantity  $\varepsilon$ , expansion factor, has been found when the coils are flexible. The relationship is  $\xi \varepsilon = 3$ . The effect of the solvent on the coil expansion is described by  $\varepsilon$ . Thus, equation (6) becomes:

$$L = R_s \varepsilon / 3 \quad (14)$$

$\varepsilon$ , can be calculated starting from the expression (15):

$$a_\eta = 0.5(1 + 3\varepsilon) \quad (15)$$

where  $a_\eta$ , corresponds to the Mark-Houwink-Sakurada (MHS) constant, which values were reported for PEA-organic solvent systems in a previous work.<sup>16</sup>

## Results and Discussion

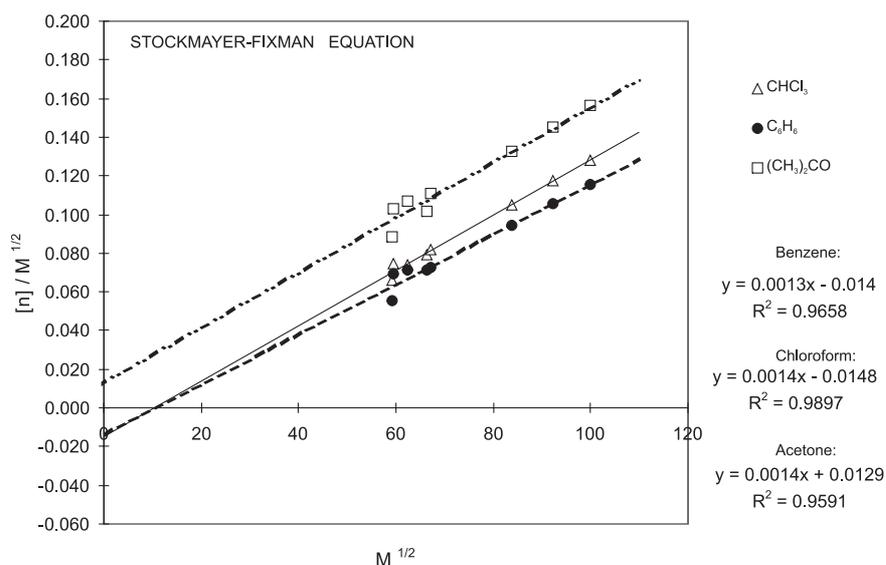
From each of the evaluated samples, Table 5 shows the molecular weight values determined by cryoscopy and HPLC techniques.<sup>4,9</sup> It presents  $[\eta]$  values for each of the polymer solutions, obtained by using the extrapolation method to zero concentration or infinite dilution. Table 5 also presents the  $M^{1/2}$  and  $[\eta]/M^{1/2}$  data, necessary for latter calculations.<sup>16</sup>

**Table 5.** Intrinsic viscosity of PEA solutions at 30 °C

Solvent	M (g mol <sup>-1</sup> )	$[\eta]$ (mL g <sup>-1</sup> )	$M^{1/2}$	$[\eta]/M^{1/2}$
C <sub>6</sub> H <sub>6</sub>	3500	3.30	59.16	0.0558
	3550	4.12	59.58	0.0691
	3900	4.46	62.45	0.0714
	4400	4.71	66.33	0.0710
	4500	4.87	67.08	0.0726
	7000	7.91	83.66	0.0946
	8500	10.01	92.19	0.1086
	10000	11.56	100.00	0.1156
CHCl <sub>3</sub>	3500	3.90	59.16	0.0659
	3550	4.46	59.58	0.0749
	3900	4.60	62.45	0.0737
	4400	5.24	66.33	0.0790
	4500	5.51	67.08	0.0821
	7000	8.78	83.66	0.1050
	8500	10.80	92.19	0.1172
	10000	12.85	100.00	0.1285
(CH <sub>3</sub> ) <sub>2</sub> CO	3500	5.25	59.16	0.0887
	3550	6.13	59.58	0.1029
	3900	6.68	62.45	0.1070
	4400	6.75	66.33	0.1018
	4500	7.42	67.08	0.1106
	7000	11.09	83.66	0.1326
	8500	13.37	92.19	0.1451
	10000	15.65	100.00	0.1565

Figure 1 shows a plot of  $M^{1/2}$  versus  $[\eta]/M^{1/2}$ , according to Stockmayer-Fixman equation (11), taking the information presented in Table 5. Figure 1 also shows the linear equations generated for: PEA-benzene, PEA-chloroform, PEA-acetone systems, from where the unperturbed parameter  $k_\theta$ , values were obtained directly.

From Figure 1, for the benzene and chloroform systems, we found that the value of  $k_\theta$  parameter is coincident and



**Figure 1.** Stockmayer-Fixman model applied to  $[\eta]$  data, for PEA-organic solvents systems at 30°C.

it takes the value of  $14.8 \times 10^{-3}$  (mL g<sup>-1</sup>), its absolute value is small and very close to zero, this value approaches closely to the value obtained in acetone solvent, where the unperturbed parameter is  $k_{\theta} = 12.9 \times 10^{-3}$  (mL g<sup>-1</sup>). Furthermore, considering the solvents physicochemical properties, acetone is more polar than benzene and chloroform, the values of their dielectric constant ( $\epsilon$ ) and their dipolar moment (DIPM) confirm this (see Table 2).

Starting from equation (13) the Flory interaction parameter,  $\chi_{ij}$  was obtained for three organic solvent-PEA systems, by using the slopes of the SF equation for each polymer-solvent system presented in Figure 1, from which:

$$\chi_{i,j} = 0.5 - 2.99V_1m \quad (16)$$

and  $\chi_{C_6H_6-PAE} = 0.5 - 2.99(88.91)(0.0013) = 0.1544$ ;  
 $\chi_{CHCl_3-PAE} = 0.5 - 2.99(80.49)(0.0014) = 0.1631$ ;  
 $\chi_{(CH_3)_2CO-PAE} = 0.5 - 2.99(73.53)(0.0014) = 0.1922$ .

All these  $\chi_{ij}$  values are small, this indicates that solvents considered in the analysis are good solvents for PEA polymer, since  $\chi_{ij} < 0.5$ .

Combining equations (11), (11c) and (12), the steric hindrance parameter ( $\sigma$ ) was estimated, taking  $\vartheta = 109.5^\circ$  (bond angle);  $l = 1.54 \text{ \AA}$  (bond length); and  $M_u = 172$  (molecular weight of structural unit, repeated in PEA polymer)  $-\text{OCH}_2\text{CH}_2\text{OCO}(\text{CH}_2)_4\text{CO}-$ .

As we know, the steric hindrance parameter measures the hindrance to rotation about the main chain bonds, so it is an indicator of the thermodynamic flexibility of the coiled molecules. The steric hindrance parameter varies with the polarity of the polymer and solvent. For PEA polymer in benzene, chloroform and acetone solvents, small

values of  $\sigma$ , were calculated, (see Table 6). Since in our case no substituents are present in the main chain, hence we can expect high chain flexibility and rotation about the main chain bonds of the PEA polymer.

From MHS equation for PEA in solution at 30 °C, the constant  $a = a_{\eta}$ , corresponds to 1.133 in benzene; 1.111 in chloroform and 0.967 in acetone.<sup>16</sup> The  $a$  constant, is related to the way the molecule holds in solution.<sup>21</sup> This parameter is really a measure of the interactions between the polymer and solvent, its value increases when the coil expands in good solvents, so  $a$  value varies from 1.8 to 2.0 for a rigid polymer of extended chain at its maximum length with constant diameter. In our case values of  $a$  close to 1.0 were calculated, these values correspond to a linear polymer, that in solution makes up coils, considering free draining characteristics without excluded volume.<sup>7,10</sup>

The expansion factor ( $\epsilon$ ), for the PEA molecules in the three solvents, was estimated according to the equation (15), knowing  $a$  from the MHS equation.<sup>16</sup>

The expansion factors  $\epsilon$ , calculated in this work, are in the order of 0.4, which indicates that as  $\epsilon$  increases, the  $a$  parameter can take values higher than 1, this condition corresponds to an unbranched coil with free draining.

Shielding depth  $L$  has been considered a measure of the solvent free draining penetration in a coiled molecule, its value can be interpreted in terms of the hydrodynamic behavior of the macromolecules in solution. Values of  $L$  higher than  $0.5R_s$  are typical of free draining coils. Using equation (14), shielding depth  $L$  was estimated for PEA samples with 4500 molecular weight in the solvents considered here; taking as  $R_s$  values, the rotating major axis of the ellipsoid that describes the coil (see Table 6)

and the data correspond to 1.3 times the minor rotating axis (equivalent to the radius of gyration) of the particle.

According to Table 6, the systems studied have low  $L$  values, this is an indication of the small draining effect of the solvent molecules in PEA polymer. A physical interpretation of the shielding depth  $L$ , is related to the amount of solvent molecules penetrating into the inner part of the polymeric coil, in that sense, the estimated shielding depth  $L$  is only 0.14 $R_s$ , for  $C_6H_6$ , 0.135 $R_s$  for  $CHCl_3$ , 0.103 $R_s$  for  $(CH_3)_2CO$ .

In this work, it was used the gyration radius as 17.31 Å for the PEA polymer particles in benzene; 18.05 Å for the PEA dissolved in chloroform, and 19.92 Å for the PEA coils, in acetone solution. These values were estimated experimentally by means of viscometry and correspond to PEA polymer with 4500 [g mol<sup>-1</sup>] molecular weight.<sup>6</sup>

From equation (5) it was possible to estimate the shielding function  $F(\xi)$ , the ratio  $\xi = R_s/L = 3/\varepsilon$ , was

considered in our calculation.

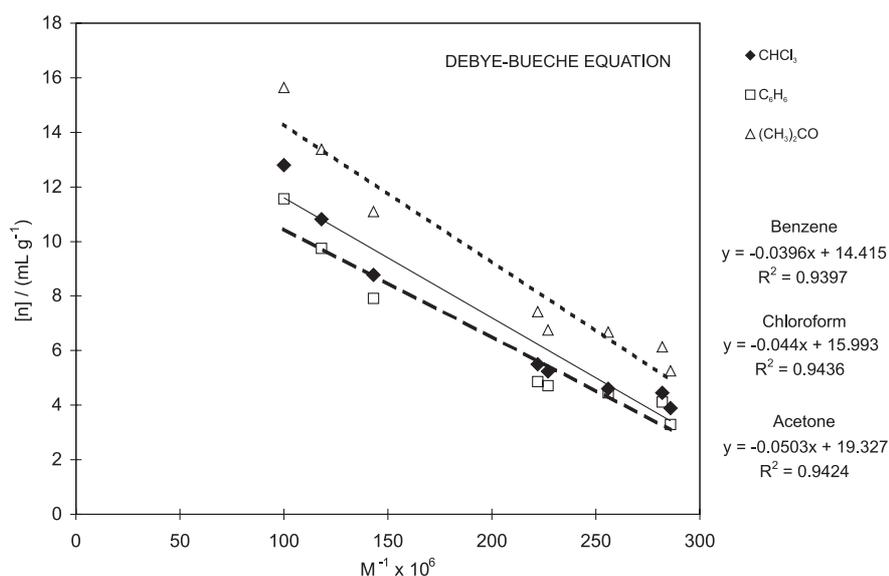
In Figure 2 a plot that shows the variation of molecular weight ( $M^{-1}$ ) versus  $[\eta]$  experimental values, is presented, according to equation (4) from the Debye and Bueche theory. By knowing the slope of the straight line generated for each PEA-solvent system, it is possible to determine the  $N_1$  value.

In Table 6, we resume the thermodynamic quantities calculated from the application of the extrapolation graphic method proposed by Stockmayer-Fixman, to correlate  $M$  and  $[\eta]$  polymeric solutions data. It was then possible to estimate the  $k_\theta$  unperturbed parameter, the  $\chi$  Flory interaction parameter, the  $B$  parameter and the ( $\sigma$ ) steric hindrance parameter from SF model, and by the Debye-Bueche theory application it was possible to estimate the expansion factor ( $\varepsilon$ ), shielding function  $F(\xi)$ , and shielding depth ( $L$ ), for PEA systems in benzene, chloroform and acetone.

**Table 6.** Results from Stockmayer-Fixman model and Debye-Bueche theory, applied to PEA solutions

PARAMETER	$C_6H_6$	$CHCl_3$	$(CH_3)_2CO$
SF MODEL			
$K_\theta$ (mL g <sup>-1</sup> )	$14.8 \times 10^{-3}$	$14.8 \times 10^{-3}$	$12.9 \times 10^{-3}$
$B$	$8.96 \times 10^{-27}$	$9.64 \times 10^{-27}$	$9.65 \times 10^{-27}$
$\sigma$ (Steric hindrance parameter)	$5.50 \times 10^{-8}$	$5.50 \times 10^{-8}$	$5.25 \times 10^{-8}$
DEBYE-BUECHE THEORY			
$\varepsilon$ (Expansion factor)	0.422	0.4073	0.3113
$\xi$ (Shielding factor)	7.11	7.40	9.64
$F(\xi)$ (Shielding function)	- 10.7486	- 8.29	- 2.5
$R_s$ (Major rotational axis)* [Å]	22.50	23.45	25.89
$L$ (Shielding depth) [Å]	14.7% of $R_s=3.166$	13.58% of $R_s=3.185$	10.38% of $R_s=2.688$

\* Gyration radius.



**Figure 2.** Molecular weight variation ( $M^{-1}$ ), versus intrinsic viscosity  $[\eta]$ , according to Debye-Bueche theory.

## Conclusions

The Stockmayer-Fixman model, represents an experimental alternative to estimate the Flory binary interaction parameter of polymer-solvent systems, providing molecular weight and intrinsic viscosity data in good solvents.

The values obtained for the Flory binary interaction parameters  $\chi_{ij}$ , from the Stockmayer-Fixman equation, according to the thermodynamic theory, corroborates that evaluated solvents are good solvents for the poly(ethylene adipate), since, thermodynamically speaking, a small value of  $\chi < 0.5$ , indicates a good solvent.

It can be established that solvents considered in the analysis, are good solvents. Additionally, according to calculated  $\chi$  values for the PEA solutions, the dissolution power of organic solvents used in this work is very similar and it increases according to the following order: acetone < chloroform < benzene.

The SF model also allows the unperturbed parameter  $k_{\theta}$ , direct estimation provided that solvents used are good solvents for the polymer. This is quite convenient when the hydrodynamic behavior of a polymer in the unperturbed state needs to be known.

The use of Debye-Bueche theory, gives more expanded information on solvents behavior as it allows the estimation of quantities as  $\epsilon$ ,  $\xi$ , and  $L$ , contributing to verify the results obtained by means of the Stockmayer-Fixman theory.

## References

1. Flory, P. J.; *J. Chem. Phys.* **1942**, *10*, 51.
2. Huggins, M. L.; *Ann. N. Y. Acad. Sci.* **1942**, *1*, 43.
3. Stockmayer W. H.; *J. Polym. Sci. Part C* **1963**, *1*, 137.
4. Rabek J. F.; *Experimental Methods in Polymer Chemistry*, Wiley & Sons: New York, 1980, ch. 2.
5. Fedors R.F.; *Polym. Eng. Sci.* **1974**, *14*, 147.
6. Cecopieri-Gómez M. L.; *M.Sc. Dissertation*, Universidad Nacional Autónoma de México, Facultad Química, México, 1998.
7. Elias H. G.; *Macromolecules*, Plenum Press: New York, 1995, vol. I, ch. 9.
8. Allen, G.; Bevington, J. C.; *Comprehensive Polymer Science*, Ed. Pergamon Press: N.Y., 1989, ch. 17.
9. Mc Caffery, E.; *Laboratory Preparation for Macromolecular Chemistry*, Ed. Mc. Graw Hill Book Co.: New York, 1970.
10. Pethrick, R. A.; *Polymer Year Book 3*, Institute of Chemical Physics, USSR, Academy of Science, Harwood Academy Publishers: Moscow, 1986.
11. D 446-89; *Standard Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers*, Annual Book of ASTM Standards, vol. 05.01, Dec. 1989.
12. D 2857-87; *Standard Practice for Diluted Solution Viscosity of Polymers*, Annual Book of ASTM Standards, vol. 08.01, Oct., 1987.
13. Chee, K.; *Polymer* **1987**, *28*, 977.
14. Yamakawa, H.; *Modern Theory of Polymer Solutions*, Ed. Harper and Row: New York, 1971, ch. 6.
15. Azim, A.; Azim, A.; Huglin, M. B.; *Polymer* **1984**, *25*, 803.
16. Cecopieri-Gomez, M. L.; Palacios-Alquisira, J.; *Rev. Soc. Quim. Mex.* **2001**, *45*, 82.
17. David, L. R., ed.; *CRC Handbook of Chemistry and Physics*, 74<sup>th</sup> ed., CRC Press: Ann Arbor, 1993-1994.
18. Reid, R. C.; Prausnitz, J. M.; Poling, B. E.; *The Properties of Gases and Liquids*, 4<sup>th</sup> ed., Mc. Graw Hill, Book Co.: New York, 1987.
19. *The Sigma-Aldrich Library of Chemical Safety Data*, Sigma-Aldrich Corp.: Milwaukee, Wisconsin, USA., 1988, (Sigma: 314-771-5765; Aldrich: 414-273-3850).
20. Burrell, H.; Immergut B. In *Polymer Handbook*, Brandrup, J.; Immergut, E. H., eds., IV-341, Interscience Publish: N. Y., 1966.
21. Seymour, R. B.; Carraher, CH. E.; *Polymer Chemistry*, 2<sup>nd</sup> ed., Marcel Dekker Inc.: New York, 1988, ch. 3.

Received: November 5, 2004

Published on the web: April 26, 2005