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Viscometric behaviour of polymer blends based on poly(vinylidene fluoride)

V. Soria, C.M. Gómez, P. Rodríguez, M.J. Parets, and A. Campos*

Departament de Química Física, Universitat de València, Burjassot, València, Spain

Abstract: The viscosity behavior of dilute dimethylformamide solutions of poly(vinylidene fluoride)-poly (methyl methacrylate) and poly(vinylidene fluoride)-polystyrene has been studied at 25 °C. The polymer concentration ranges are such that neither phase separation nor microgel formation occurs, although we are very close to theta conditions. The intrinsic viscosity and viscosity interaction parameter of the ternary mixtures have been calculated. The estimation of the compatibility of the above polymer pairs has been studied based on: a) specific viscosities; b) viscosity interaction parameters, according to Krigbaum and Wall formalism, and c) viscosity interaction parameters of a system formed by a dilute probe polymer in the presence of a matrix polymer and a small molecule solvent.

Key words: Poly(vinylidene fluoride) – intrinsic viscosity – polymer blend compatibility – polymer-solvent interaction

Introduction

Poly(vinylidene fluoride) (PVDF) is known to possess piro- and piezo-electric properties and has been extensively studied in the solid state to relate its structure to its properties [1]. A recent interest has arisen in enhancing these effects in new homo and copolymers blends based on PVDF. The study of this polymer and its blends in solution have been scarcely reported, perhaps due to several difficulties such as low increments of index of refraction dn/dc in dimethylformamide (DMF) and dimethylacetamide (DMAc), possible dehydrofluorination, presence of microgel and low solubility at room temperature in most solvents [2].

On the other hand, polymer-polymer compatibility has been extensively studied by several techniques such as differential scanning calorimetry, dynamic mechanical measurements, neutron scattering, inverse gas chromatography, electron microscopy and others [3]. Most of them are experimentally demanding and time-consuming, but offer an alternative method to study viscosity data for ternary solvent-polymer-polymer systems [4–11]. The intrinsic viscosity of the ternary mixture $[\eta]_m$ denotes the coil dimensions which can be altered by a contraction or expansion of the coil whether the interactions between unlike i–j polymer segments are attractive or not. Meanwhile, the interaction parameter b_m characterizes the overall interaction between the chainlike of both polymers, and can be used to determine polymer-polymer compatibility [5–8, 12].

In this report, we have performed a study on the viscosity behavior of mixtures of PVDF, with poly(methyl methacrylate) (PMMA) or polystyrene (PS) in a common solvent, such as DMF covering a whole composition range. The compatibility of the two mixtures of polymers in DMF is discussed by means of the difference between the experimental and theoretical interaction parameter between unlike polymer molecules, b_{AB}. This difference can be calculated by means of: a) the specific viscosities of the polymer mixture, or b) the viscosity interaction parameter of the ternary mixture.

Experimental

The PVDF used was Kynar homopolymer grade 720 with an average molecular weight Mw of 45 000 (Pennwalt). Commercial samples of PS (Mw = 82 800) and PMMA (Mw = 100 000) were characterized in benzene by light scattering. Polydispersity indexes as determined by GPC (with μ-styragel supports) ranged between 1.2 and 1.3. The solvent used in all experiments was DMF analytical-reagent grade (Merck, Darmstadt, FRG).

The viscosity measurements were made with a conventional Ubbelohde capillary viscometer from Schott-Geräte (FRG). The instrument determines elution times automatically. For each solution a 15-mL sample was loaded into the viscometer, which was then placed into a thermostated bath at 25 ± 0.01 °C. Measurements were initiated after approximately 5–10 min equilibration time and were continued until several elution time readings agreed to within 0.5%. The capillary sizes were selected so that kinetic energy corrections were minimal.

Results and discussion

The dependence of viscosity η of dilute polymer solutions on concentration c can be described by the Huggins equation [13] as follows:

$$\eta(c) = \eta_s(1 + [\eta]c + k_H[\eta]^2c^2) , \tag{1}$$

where η_s is the viscosity of the pure solvent, $[\eta]$ the intrinsic viscosity of the polymer, and k_H the dimensionless Huggins viscosity constant, independent of the molecular mass, and strongly dependent on the solvent purity [14].

Equation (1) can be rearranged in the form:

$$\frac{\eta(c) - \eta_s}{\eta_s c} = [\eta] + k_H[\eta]^2 c . \tag{2}$$

By denoting $\frac{\eta(c) - \eta_s}{\eta_s} = \eta_{sp}$ as the specific viscosity and $b = k_H[\eta]^2$ an interaction parameter which denotes the binary interactions between the polymer segments [15], Eq. (2) can be rewritten as:

$$\frac{\eta_{sp}}{c} = [\eta] + bc . \tag{3}$$

Expression (3) can be extended to a ternary polymer system solvent-polymer(A)-polymer(B) following the method proposed by Krigbaum and Wall [16] and discussed in detail by Kragg and Bigelow [17]:

$$\left(\frac{\eta_{sp}}{c}\right)_m = [\eta]_m + b_m c = \sum_i [\eta]_i \frac{c_i}{c} + \left(\frac{\sum_i b_{ii}^{1/2} c_i}{c^{1/2}}\right)^2 , \tag{4}$$

where subscript m refers to the ternary system, $i = A, B$ to each of the polymer components, and $c = c_A + c_B$ is the total concentration of polymer. Equation (4) has been developed without accounting for interactions between unlike polymer segments.

From Eq. (4), the intrinsic viscosity of the mixture of polymers in a common solvent for non interacting system is:

$$[\eta]_m = \sum_i [\eta]_i \frac{c_i}{c} = [\eta]_A w_A + [\eta]_B w_B \tag{5}$$

$w_i = c_i/c$ (i = A, B) being the weight fraction of polymer.

The parameter b_m summarizes the global interactions between all the segments in a polymer chain, no interactions between unlike i–j segments are included:

$$\begin{aligned} b_m &= \left[\sum_i b_{ii}^{1/2} \frac{c_i}{c}\right]^2 \\ &= b_{AA} w_A^2 + b_{BB} w_B^2 + 2b_{AA}^{1/2} b_{BB}^{1/2} w_A w_B \\ &= b_{AA} w_A^2 + b_{BB} w_B^2 + 2b_{AB} w_A w_B , \end{aligned} \tag{6}$$

where b_{AB} is a complex interaction parameter in which hydrodynamic and thermodynamic interactions as well as possible existing associations are included.

In the present context, b_{AB} parameter corresponds to the geometric mean of each polymer-solvent interaction parameter, $b_{AB} = (b_{AA} b_{BB})^{1/2}$, frequently used [5, 10, 17, 18], instead of the arithmetic mean, $b_{AB} = (b_{AA} + b_{BB})/2$, suggested by other authors [6, 7].

Hence, Tables 1 and 2 collect experimental values of the reduced viscosities at arbitrary

Table 1. Experimental values of the reduced viscosity $(\eta_{sp}/c)_m$ at different weight fractions of PMMA w_B for DMF-PVDF(A)-PMMA(B) at 25 °C

w_B	$(\eta_{sp}/c)_m$ (dL g^{-1})	c_A (g dL^{-1})	c_B (g dL^{-1})
0.000	0.9728	0.400	0.000
	1.0002	0.501	0.000
	1.0272	0.600	0.000
	1.0843	0.815	0.000
	1.1632	1.100	0.000
0.107	1.043	0.629	0.075
	1.014	0.504	0.060
	0.983	0.360	0.043
	0.960	0.280	0.033
0.236	0.946	0.577	0.178
	0.917	0.462	0.143
	0.898	0.385	0.119
	0.871	0.231	0.071
0.474	0.759	0.411	0.371
	0.734	0.319	0.287
	0.721	0.260	0.234
	0.710	0.210	0.189
	0.637	0.159	0.144
0.793	0.520	0.157	0.600
	0.512	0.126	0.480
	0.508	0.105	0.400
	0.500	0.063	0.240
0.910	0.441	0.070	0.707
	0.432	0.048	0.485
	0.425	0.036	0.369
	0.424	0.027	0.274
1.000	0.3395	0.000	0.300
	0.3405	0.000	0.500
	0.3415	0.000	0.700
	0.3423	0.000	0.860

Table 2. Experimental values of the reduced viscosity $(\eta_{sp}/c)_m$ at different weight fractions of PS, w_B for DMF-PVDF(A)-PS(B) at 25 °C

w_B	$(\eta_{sp}/c)_m$ (dL g^{-1})	c_A (g dL^{-1})	c_B (g dL^{-1})
0.000	0.9728	0.400	0.000
	1.0002	0.501	0.000
	1.0272	0.600	0.000
	1.0843	0.815	0.000
	1.1632	1.100	0.000
0.173	1.052	0.633	0.132
	1.018	0.507	0.106
	1.000	0.422	0.088
	0.935	0.249	0.052
0.359	0.945	0.506	0.283
	0.910	0.379	0.213
	0.877	0.243	0.136
	0.865	0.193	0.108
0.516	0.883	0.424	0.452
	0.858	0.339	0.362
	0.836	0.242	0.259
	0.819	0.145	0.155
0.768	0.733	0.176	0.582
	0.718	0.141	0.465
	0.713	0.117	0.388
	0.691	0.070	0.233
1.000	0.5540	0.000	0.490
	0.5592	0.000	0.605
	0.5685	0.000	0.811

Table 3. Intrinsic viscosity $[\eta]_m$ and interaction parameter b_m (Eq. (4)) as a function of w_B for the polymer mixtures, PVDF-PMMA and PVDF-PS, dissolved in DMF.

polymer mixture	$[\eta]_m$ (dL g^{-1})	b_m (dL^2 g^{-2})	w_B
PVDF-PMMA	0.864	0.272	0.000
	0.892	0.209	0.107
	0.815	0.164	0.236
	0.662	0.119	0.474
	0.481	0.048	0.793
	0.411	0.037	0.910
	0.338	0.005	1.000
PVDF-PS	0.864	0.272	0.000
	0.863	0.249	0.173
	0.811	0.163	0.359
	0.776	0.110	0.516
	0.660	0.091	0.768
	0.532	0.047	1.000

selected weight fractions for the ternary systems DMF-PVDF(A)-PMMA(B) and DMF-PVDF(A)-PS(B), respectively. The plot of $(\eta_{sp}/c)_m$ against c at every w_B (Eq. (4)) yields a straight line with intercept and slope equal to $[\eta]_m$ and b_m experimental data, respectively. The results obtained by the linear least-squares treatment are collected in Table 3.

Most viscometric studies of polymer-polymer compatibility are based on the difference between the experimental (E) and theoretical (T) values of $[\eta]_m$. In order to visualize the deviation of $[\eta]_m^E$ from $[\eta]_m^T$ (Eq. 5), Fig. 1 shows the plot of both magnitudes against w_B for the mixture of polymers PVDF-PMMA (Part a) and PVDF-PS (Part b) in DMF. There is a slight increase of $[\eta]_m^E$ from the theoretical values by supposing an additivity of $[\eta]_m$. This positive deviation reflects an increase of the effective hydrodynamic specific volume which suggests expansion of the coil due to favorable polymer(A)-polymer(B) interactions. A similar trend is observed for the experimental b_m values, denoting an increase of the binary

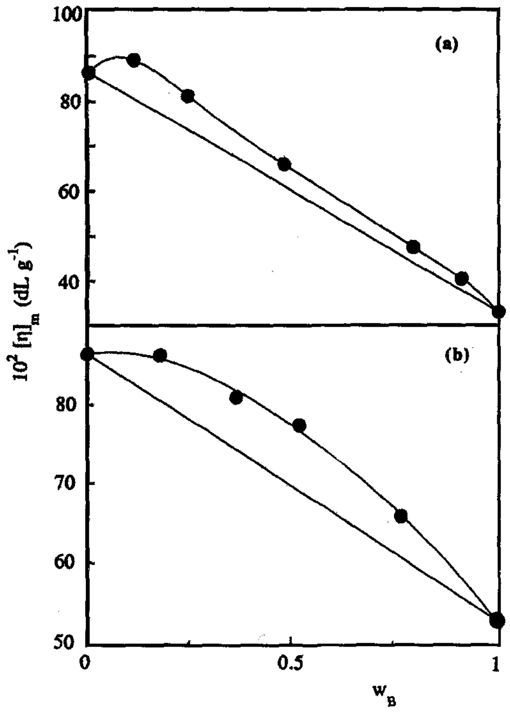

Fig. 1. Comparison between experimental (●) and theoretical (——) (Eq. (5)) intrinsic viscosities $[\eta]_m$ as a function of the weight fraction of PMMA or PS, w_B, for DMF-PVDF-PMMA (part a) and DMF-PVDF-PS (part b)

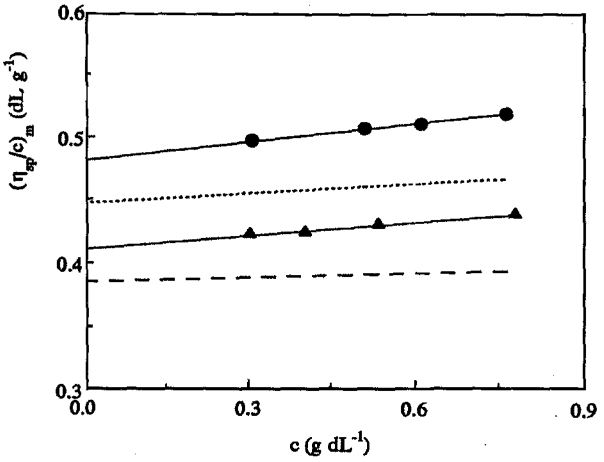

Fig. 2. Plot of the reduced viscosity $(\eta_{sp}/c)_m$ against the total polymer concentration c for DMF-PVDF-PMMA. Experimental and theoretical (Eq. (4)) values for $w_B = 0.793$: (●) and (····); and for $w_B = 0.910$: (▲) and (– – –), respectively

interactions between polymer segments [15]. The increase of both parameters, $[\eta]_m$ and b_m, with respect to the theoretical ones suggests compatibility between both polymers. Nevertheless, these methods employing viscosity-composition plots are purely empirical, and hence should be dealt with caution. As a rule, $[\eta]_m$ decrease [5, 6] with a decrease of b_m, however there are some exceptions: see for instance from $w_2 = 0.27$ to 0 in Fig. 1B and from $w_2 = 0.23$ to 0 in Fig. 1C of ref. [6].

Therefore, according to Krigbaum and Wall [16] comparison of the experimental and theoretical (Eq. (6)) values of b could give accurate information on interactions between polymer pairs. That is, the sign of $\Delta b = b^E_{AB} - b^T_{AB}$ sheds light on the degree of polymer–polymer compatibility. In this way, $\Delta b > 0$ refers to attractive interaction between polymer segments and compatibility, whereas $\Delta b < 0$ is found for solutions of systems containing incompatible polymers.

Δb can be expressed as a function of the experimental and theoretical specific viscosities by assuming that the experimental and theoretical $[\eta]_m$ are the same for every mixture of polymers:

$$\Delta b = \frac{(\eta_{sp})^E_m - (\eta_{sp})^T_m}{2c_A c_B} , \qquad (7)$$

or without any prior hypothesis by means of the b_m parameters through:

$$\Delta b = \frac{b^E_m - b^T_m}{2w_A w_B} . \qquad (8)$$

In order to check the validity of the above assumption made to obtain Eq. (7), that is, $[\eta]^T_m c = [\eta]^E_m c = [\eta]_A c_A + [\eta]_B c_B$, Figs. 2 and 3 show a plot of $(\eta_{sp}/c)_m$ experimental and theoretical (Eq. (4)) values against c for DMF-PVDF-PMMA and DMF-PVDF-PS, respectively at different w_B. The experimental intrinsic viscosities show an increase of about 10% with respect to the theoretical ones showing the inaccuracy of Eq. (7). Moreover, for DMF-PVDF-PS at $w_B = 0.516$, $\Delta[\eta]_m = [\eta]^E_M - [\eta]^T_m = 0.084 > 0$, while for $\Delta b = b^E_m - b^T_m = -0.03 < 0$ both increments have an opposite sign, therefore the increase of $[\eta]_m$ is not a good criterion to describe the compatibility of polymers. This notwithstanding, it seems interesting to analyze the Δb values obtained through Eq. (7) and recently used by Shih and Beatty [7] to study the miscibility of blends of polycarbonate and poly(hexamethylene sebacate).

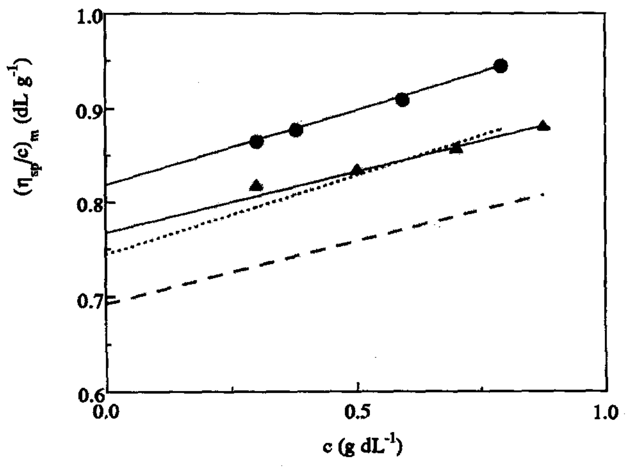

Fig. 3. Plot of the reduced viscosity $(\eta_{sp}/c)_m$ against the total polymer concentration c for DMF-PVDF-PS. Experimental and theoretical (Eq. (4)) values for $w_B = 0.359$: (●) and (···); and for $w_B = 0.516$: (▲) and (– – –), respectively

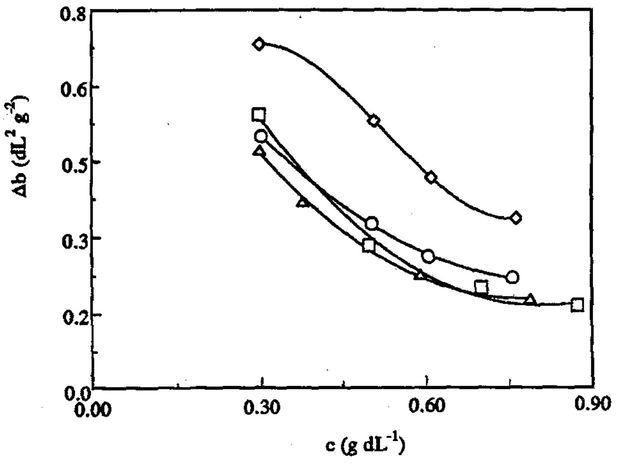

Fig. 5. Plot of Δb (Eq. (7)) against the total polymer concentration c for DMF-PVDF-PS at different blend compositions, w_B: (◇) 0.173; (△) 0.359; (□) 0.516; and (○) 0.768

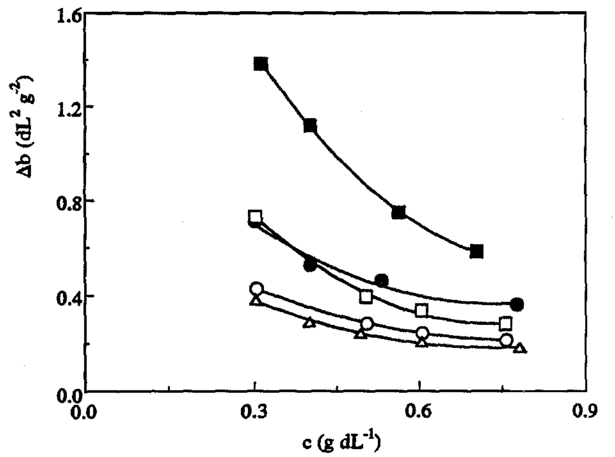

Fig. 4. Plot of Δb (Eq. (7)) against the total polymer concentration c for DMF-PVDF-PMMA at different blend compositions, w_B: (■) 0.107; (□) 0.236; (△) 0.474; (○) 0.793; and (●) 0.910

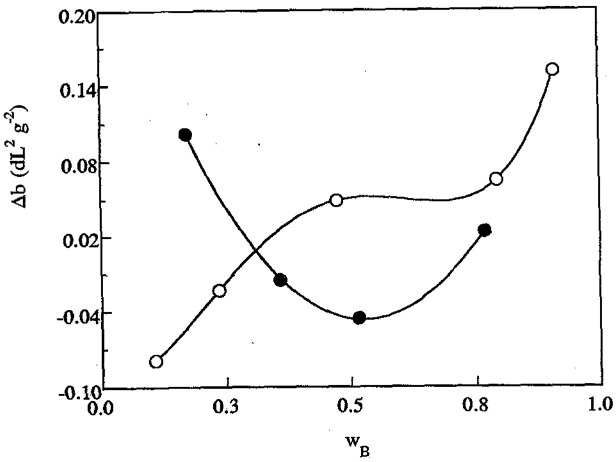

Fig. 6. Plot of Δb (Eq. (8)) against the total polymer concentration c for DMF-PVDF-PMMA (○) and DMF-PVDF-PS (●)

Figures 4 and 5 show a plot of Δb (from Eq. (7)) against c at different w_B for DMF-PVDF-PMMA and DMF-PVDF-PS, respectively. Δb is a function of c and w_B, and increases as c decreases when compared at the the same w_B. The values of Δb are positive at all mixture compositions and concentrations, denoting miscibility. But the most striking features is that $\Delta b = b_m^E - b_m^T$ is a function of c, when b_m^E and b_m^T are obtained from the slope $(\eta_{sp}/c)_m$ against c in a concentration range where the plot is linear, and so Δb should be independent of c. The error comes from the way of calculating Δb in Eq. (7) by assuming that $[\eta]_m^E = [\eta]_m^T$, a hypothesis that is not always true, as corroborated in Figs. 2 and 3. In fact, if we consider $[\eta]_m^E \neq [\eta]_m^T$, Eq. (7) can be written as:

$$\Delta b = \frac{([\eta]_m^E - [\eta]_m^T)c + (b_m^E - b_m^T)c^2}{2c_A c_B}$$

$$= \frac{([\eta]_m^E - [\eta]_m^T)1/c + (b_m^E - b_m^T)}{2w_A w_B},$$

Table 4. Intrinsic viscosity of polymer A at one fixed c_B concentration, $[\eta]_{A,c_B}$, interaction parameter b_{AB} and increment of the interaction parameter Δb for DMF-PVDF/PMMA and DMF-PVDF/PS at 25 °C

System	c_B (g dL^{-1})	$[\eta]_{A,c_B}$ (dL g^{-1})	b_{AB} (dL^2 g^{-2})	Δb (dL^2 g^{-2})
DMF-PVDF/PMMA	0.80	0.8283	0.247	0.210
	0.48	0.8590	0.281	0.244
	0.29	0.8437	0.221	0.184
DMF-PVDF/PS	0.82	0.8009	0.395	0.282
	0.50	0.8553	0.442	0.328
	0.32	0.8478	0.408	0.295

and Δb depends on $1/c$ through the increment of viscosities.

Krigbaum and Wall [16] calculated Δb values exclusively from b experimental and theoretical data and the same procedure has been used more recently by Chee [6] to obtain Δb values independent of c.

Figure 6 shows a plot of Δb (Eq. (8)) against w_B for DMF-PVDF-PMMA and DMF-PVDF-PS. Δb is independent of c in contrast to the values plotted in Figs. 4 and 5, and takes positive and negative values. In DMF as solvent, Δb values for PVDF-PMMA change from negative to positive at $w_B = 0.3$, thus the polymer mixture is more compatible when increasing the amount of PMMA. Nevertheless, for PVDF-PS there is a range of incompatibility for $w_B = 0.32$–0.75. The compatibility range of PVDF and PMMA in DMF as solvent is wider than with PS as expected due to the higher polarity of PMMA.

Other methods to calculate b, and thus Δb, can be found in the literature. One of them was proposed by Dondos and Benoit [10] and is based on the following procedure: consider a system formed by a polymer(A) (PVDF for instance) in a dilute solution of a "solvent" formed by polymer(B) (PMMA or PS) in solvent (DMF). Then a plot of $\eta_{sp,A}/c_A$ against c_A at different c_B gives straight lines from the intercept of which the intrinsic viscosity of polymer A at one fixed c_B concentration, $[\eta]_{A,c_B}$ can be obtained. Moreover, $[\eta]_{A,c_B}$ can be related to the interaction parameter b_{AB} through [5]: $[\eta]_{A,c_B} = [\eta]_A + c_B(b_{AB} - [\eta]_A [\eta]_B)$, an expression that allows us to calculate for each $[\eta]_{A,c_B}$ a value of b_{AB}. But these $[\eta]_{A,c_B}$ values have been obtained for $c_A \rightarrow 0$ and hence $w_B \rightarrow 1$, so we should obtain a unique value of Δb independent of c_B.

Table 4 summarizes values of $[\eta]_{A,c_B}$, b_{AB} and Δb for PVDF(A)/PMMA(B)-DMF and PVDF(A)/PS(B)-DMF. The method proposed by Dondos and Benoit [10] yields to an average Δb value of 0.213 and 0.302 for PVDF(A)/PMMA(B)-DMF and PVDF(A)/PS(B)-DMF ternary systems, respectively. These values are in good quantitative accord with the ones obtained by extrapolation of $w_B \rightarrow 1$ in Fig. 6.

Conclusions

The viscosity study of ternary solutions formed by two pairs of polymers PVDF-PMMA and PVDF-PS in a common solvent DMF sheds light on the compatibility of both polymer pairs. The binary polymer-solvent mixtures appear very close to theta conditions, however, no microgel formation has been observed. The intrinsic viscosity and viscometric interaction parameter of the ternary mixtures show a positive deviation from the linear dependence of the "ideal" values on the assumption of additivity denoting, at first sight, compatibility. A more in-depth analysis of polymer-polymer compatibility based on comparison between theoretical and experimental b_{AB} reflects that: a) positive Δb values as a function of w_B are found when this increment is calculated from specific viscosities; b) positive and negative Δb values independent of w_B are obtained from a comparison of b_m parameters, and c) a Δb value in good accord with the one previously found is obtained by applying the method proposed by Dondos and Benoit.

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Author's address:

Prof. Agustín Campos
Departament de Química Física
Universitat de Valencia
46100 Burjassot, Valencia, Spain