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Preferential solvation of a dicyanate ester monomer and poly(sulfone) in different organic solvents by size-exclusion chromatography[☆]

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Abstract

Preferential solvation parameters λ in the ternary systems solvent (1) – monomer (2) – polymer (3) were determined as a tool to measure the compatibility between the cyanate ester monomer Arocy B10 and poly(sulfone), PSF, in the presence of three organic solvents: tetrahydrofuran, dimethylformamide and dicloromethane. The λ parameter was measured by size-exclusion chromatography at different monomer-to-polymer ratios. The quantitative evaluation was rigorously made at polymer-diluted conditions. PSF was found to be preferentially solvated by the monomer. Concerning the solvent used, systems containing tetrahydrofuran showed the strongest solvation, the lowest λ values being those obtained in dicloromethane. These results were in accordance with the intrinsic viscosity values of the PSF–solvent systems. The variation of λ values with the Arocy B10 concentration is strongly dependent upon the nature of the solvent. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Solvation parameters; Polysulfone; Arocy B10; Bisphenol A dicyanate

1. Introduction

Cyanate esters are among the most attractive new thermostable polymers to which a lot of interest has been devoted over the past few years due to their high fracture toughness and high service tempera-

tures [1,2]. The practical use of these materials requires a good knowledge of the cure kinetics, the characterization of which is a current issue [3,4]. The fracture toughness of these matrices is commonly improved by incorporating modifiers, such as rubbers, although they affect the properties of the matrix. The advantage of using thermoplastics, however, is that they do not reduce the thermal and mechanical properties. In a previous work the curing of a dicyanate ester of bisphenol A (Arocy B10) with and without catalysts up to the gel point was analysed by liquid chromatography [5]. It would also be very interesting to investigate the compatibility of the modified systems composed by the Arocy B10 and a thermoplastic such as poly(sulfone), PSF,

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making use of the preferential adsorption phenomenon.

In this regard, it is well known that the behavior of polymers in mixed solvents is generally affected by the preferential solvation of one of the solvents by the polymer [6]. This is due to the difference in affinity of each solvent with regards to the polymer, and leads to composition variations of the mixed solvent in the vicinity of the macromolecule. The preferential solvation of polymers in binary solvent mixtures has been widely studied by different physicochemical [7,8] and spectroscopic techniques [9,10] as well as by size-exclusion chromatography (SEC) [11,12]. The latter allows obtaining the so-called vacancy peak, the height of which is proportional to the amount of injected polymer, providing a rapid and accurate determination of the preferential solvation parameter, λ [13]. Moreover, SEC has become one of the most widely used techniques for the evaluation of λ , especially in ternary polymer–solvent–solvent [14,15] or even in polymer–polymer–solvent systems [16,17]. In the latter case, the respective sizes in solution of the two polymers must be sufficiently different. In a previous work [18] we used this method to investigate the preferential binding of toxic agents, such as silicic acid and nicotine, to polymers in dilute aqueous solutions. In this paper we report the preferential solvation as a tool to measure the compatibility between the cyanate ester monomer Arocy B10 and PSF, in the presence of three organic solvents: tetrahydrofuran (THF), dimethylformamide (DMF) and dichloromethane (DCM). The quantitative evaluation of the λ parameter has rigorously been made at polymer-diluted conditions. The effect of changing the monomer-to-polymer ratio as well as of the chemical nature of the solvent on the compatibility between Arocy B10 and PSF has been investigated.

2. Experimental

2.1. Materials

The bisphenol A dicyanate (BADCy) monomer with the trade name Arocy B10, 99.5% purity (density 1.25 g/ml) (Fig. 1) was kindly supplied by Ciba-Geigy. The selected thermoplastic was a com-

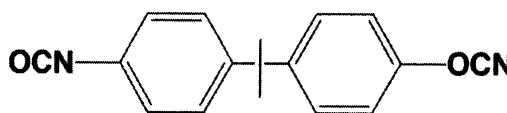


Fig. 1. Structure of Arocy B10.

mercial grade of PSF (Amoco UDEL P-1700) with number-average molecular mass ($M_n=38\,000$) and weight-average molecular mass ($M_w=63\,000$). All the organic solvents used, THF, DMF and DCM, were HPLC-grade from Scharlau (Barcelona, Spain).

2.2. Size-exclusion chromatography

The liquid chromatograph consisted of a model 590 solvent-delivery system and a U6K universal injector from Waters (Milford MA, USA). Detection was carried out with a refractive index (RI) detector Model 2410 from Waters. Data collection and handling were carried out using MILLENNIUM³² Chromatography Manager from Waters. The system was equipped with two μ Styragel columns (30 cm \times 0.78 cm I.D.) packed with highly crosslinked styrene–divinylbenzene copolymer of 10^3 and 100 \AA of nominal pore size from Waters. The mobile phase flow-rate was adjusted to 1.0 ml/min. The injection volume of samples was 100 μ l.

Three sets of experiments were performed according to the three organic solvents studied. In all cases, the mobile phases, used as eluents, consisted in diluted solutions of the monomer Arocy B10 in the corresponding organic solvent, PSF always being the solute. The composition of the eluents was the following: 0.05, 0.10, 0.15, 0.17 and 0.20 g of B10/100 ml of solvent. The PSF concentrations of the injected solutions were in the range 0.015–2.500 g/100 ml of mobile phase.

The column was equilibrated overnight before injection of the analyte solution, which was prepared using the corresponding mobile phase as solvent. Eluents were always filtered and degassed through regenerated cellulose 0.45- μ m pore diameter filters from Micro Filtration Systems (Dublin, CA, USA).

2.3. Viscosities

An automatic AVS 440 Ubbelohde-type capillary

viscometer from Schott Geräte (Hofheim, Germany) at $(25.0 \pm 0.1)^\circ\text{C}$ was used to perform viscometric measurements. The stock solution was made by dissolving the polymer samples in the corresponding solvent up to a concentration of approximately 1.0% (w/v). At least six dilutions were obtained by adding the appropriate aliquots of solvent. Efflux time of the solvent was always above 100 s. To minimize drainage errors, a 12-ml sample, of each solution, was loaded into the viscometer and placed in the thermostated bath. Measurements started after an equilibration time of ~ 5 –10 min and were continued until several flow time readings agreed to within 0.5%. The elution time of each solution was then determined as the average of several readings. The dilution and measurements were stopped when the efflux time difference of the sample solution and pure solvent dropped below 10%. Kinetic energy corrections for this particular viscometer were not needed, as indicated by the viscometer calibration performed with different solvents. The evaluation of the intrinsic viscosity, $[\eta]$, was made by extrapolation to infinite dilution (zero solute concentration) of Huggins plots: $\eta_{\text{sp}}/c = [\eta] + bc$, i.e. η_{sp}/c vs. c , η_{sp} being the specific viscosity, c the concentration of the solution and b a viscosimetric parameter.

3. Theory

A ternary system solvent (1)–polymer (2)–polymer (3), where polymer (2) is much smaller in size than polymer (3), can be considered formed by two phases in equilibrium: the bulk solvent (or binary phase) constituted by the solvent (1)+the polymer (2), and the polymer (3) domain (or ternary phase). The notation used thereafter for the composition of the two phases will be as follows: ν_i ($i = 1, 2$) is the volume fraction of the component i in the bulk solvent [$\nu_1 + \nu_2 = 1$]; ϕ_i ($i = 1, 2, 3$) is the volume fraction of the component i in the domain of the polymer (3) coil [$\phi_1 + \phi_2 + \phi_3 = 1$]; u_i ($i = 1, 2$) is the volume fraction of the mixture (1)+(2) in the ternary phase defined as $u_i = \phi_i/(1 - \phi_3)$ [6,19,20].

In such a ternary system, the preferential solvation can be defined as the change, ϵ , in the volume fraction of the component i ($i = 1, 2$) in the ternary phase with respect to the composition of such a

component in the binary phase, the two phases being in thermodynamic equilibrium, i.e.:

$$\begin{aligned} u_1 &= \phi_1/(1 - \phi_3) = \nu_1 + \epsilon \quad \text{and} \\ u_2 &= \phi_2/(1 - \phi_3) = \nu_2 - \epsilon \end{aligned} \quad (1)$$

From this equation, a value of $\epsilon > 0$ indicates a positive preferential solvation of the component (3) by the component (1).

At diluted composition of the component (3), that is, when $\phi_3 \rightarrow 0$, $u_1 \rightarrow \phi_1$ and $\phi_1 = \nu_1 + \epsilon$, then $\epsilon = \phi_1 - \nu_1 = \Delta\nu_1$, the difference in the volume fraction of the component (1) between the ternary and the binary phase. In the same way, for the second component, $u_2 \rightarrow \phi_2$ and $\phi_2 = \nu_2 - \epsilon$, then $-\epsilon = \phi_2 - \nu_2 = \Delta\nu_2$, and therefore $\Delta\nu_1 = -\Delta\nu_2$.

Under such conditions, the preferential solvation coefficient λ will express the volume of the solvent (1) or of the polymer (2) preferentially adsorbed on the polymer (3) per unity of mass of such polymer (3), at infinite dilution. The expression for λ can be written as [6]:

$$\begin{aligned} \lambda &= \left(\frac{d\epsilon}{dc_3} \right)_{c_3 \rightarrow 0} = \left(\frac{d(\phi_1 - \nu_1)}{dc_3} \right)_{c_3 \rightarrow 0} \\ &\approx \left(\frac{\Delta\nu_1}{c_3} \right)_{c_3 \rightarrow 0} \end{aligned} \quad (2a)$$

for component (1) or, for component (2):

$$\lambda = \left(\frac{\Delta\nu_2}{c_3} \right)_{c_3 \rightarrow 0} \quad (2b)$$

where c_3 , is the polymer (3) concentration.

If preferential solvation of the polymer (3) by the solvent (1) takes place, $\phi_1 > \nu_1$ and $\lambda > 0$. In contrast, when the polymer (3) is preferentially adsorbed by the component (2), $\phi_2 > \nu_2$ and $\lambda < 0$.

The goal of the present work is to study the behaviour of ternary systems solvent (1)–monomer (2)–polymer (3) at diluted concentrations of the component (3) by SEC. As Berek et al. [13], showed, since the magnitude of the vacancy peak is proportional to the amount of injected polymer and its elution volume corresponds to that of one of the components of the mixture, the quantitative evaluation of the preferential solvation parameter for ternary systems becomes possible. Keeping Eq. (2) in mind, the following procedure has to be carried out.

3.1. Calibration of refractive index detector response

In order to calibrate the detector, several binary mixtures of components (1)+(2) of known concentration were injected in such an eluent. The difference in the composition of component (1) between the injected solution ϕ_1^i [simulating the volume fraction of (1) in a ternary phase, ϕ_1] and the eluent mixture ϕ_1^e [simulating the volume fraction of (1) in the bulk solvent or binary phase, ν_1] will be $\phi_1^i - \phi_1^e = \phi_1^o - \nu_1^o = \Delta\nu_1^o$. This magnitude is related to the height of the obtained peak, h_{cal} .

In the same way, the phenomenon for component (2) will be expressed as $\phi_2^i - \phi_2^e = \phi_2^o - \nu_2^o = \Delta\nu_2^o$, and this excess of component (2) will be related to the corresponding h_{cal} , obviously with opposite sign.

The plot of $\Delta\nu_1^o$ (or $\Delta\nu_2^o$) versus h_{cal} , will give a calibration curve for the detector response.

3.2. Evaluation of λ

Subsequent injection of a solution formed by the polymer (3) and components (1) and (2) at the same composition than the eluent mixture will give a vacancy peak [21–23] due to the preferential solvation of (3) by either (1) or (2). If polymer (3) is preferentially solvated by monomer (2), the bulk solvent in the vicinity of the injected polymer (3) will be poorer in (2) [or richer in (1)], then a vacancy peak with a height $h_{\text{probe}} < 0$ and proportional to the amount of (2) adsorbed on (3) will be obtained. Taking into account the proportionality between $\Delta\nu_2^o$ and h_{cal} , we can write the following relationship:

$$\frac{\Delta\nu_2^o}{\Delta\nu_2} = \frac{h_{\text{cal}}}{h_{\text{probe}}} \quad \text{i.e.} \quad \Delta\nu_2 = \frac{\Delta\nu_2^o}{h_{\text{cal}}}(h_{\text{probe}}) \quad (3)$$

where the quotient is the slope of the calibration curve $\Delta\nu_2^o$ versus h_{cal} .

Since in the calibration, an excess of (2) gives an $h_{\text{cal}} > 0$ and a defect ($\Delta\nu_2^o < 0$) yields an $h_{\text{cal}} < 0$, the slope ($\Delta\nu_2^o/h_{\text{cal}}$) will be always positive. As $h_{\text{probe}} < 0$, the value of λ obtained through Eq. (2b) will be negative.

On the contrary, if component (3) is preferentially solvated by (1), and in a similar treatment, λ will be

positive. This criteria of signs will enable us to elucidate, for a given system, if the polymer is preferentially adsorbed by the monomer or by the solvent.

4. Results and discussion

Keeping in mind this theoretical background, the preferential solvation parameter for each solvent (1) in the ternary systems solvent–Arocy B10–PSF was obtained as follows.

(1) For a given binary eluent [a fixed (1)+(2) composition], the injection of diverse binary phases of Arocy B10 concentrations ranging from 0.0125 to 1.2% (w/v) provided us with the elution volume, V_e , of component (2), necessary to recognize the vacancy peak in the elution profile of the ternary systems. The heights of the Arocy B10 peak (positive or negative depending on the Arocy B10 concentrations, greater or lower than that of the eluent composition, respectively) were then plotted versus the concentration. A good linear correlation allowed us to perform the subsequent representation $\Delta\nu_2^o$ versus h_{cal} , the slope of which supplied the ($\Delta\nu_2^o/h_{\text{cal}}$) value.

(2) Ternary solutions containing PSF at different concentrations ranging from 0.0125 to 2.5% in the binary eluent specified in (1) were then injected. The heights of the vacancy peaks corresponding to Arocy B10 provided the h_{probe} value for each ternary solution. Therefore, the $\Delta\nu_2$ values for all PSF concentrations were easily calculated by means of Eq. (3).

(3) Plotting ($\Delta\nu_2/c_3$) versus c_3 , the preferential solvation parameter λ for PSF at this given eluent composition was obtained at infinite dilution [see Eq. (2b)].

(4) By repeating steps 1–3 at several eluent compositions, the values of λ for different ternary systems were then obtained.

This procedure has been performed for the three solvents studied, THF, DMF and DCM. Next, we proceed to show the obtained results for each system.

4.1. THF–Arocy B10–PSF system

Fig. 2 shows the complete procedure for the determination of preferential solvation of PSF in the

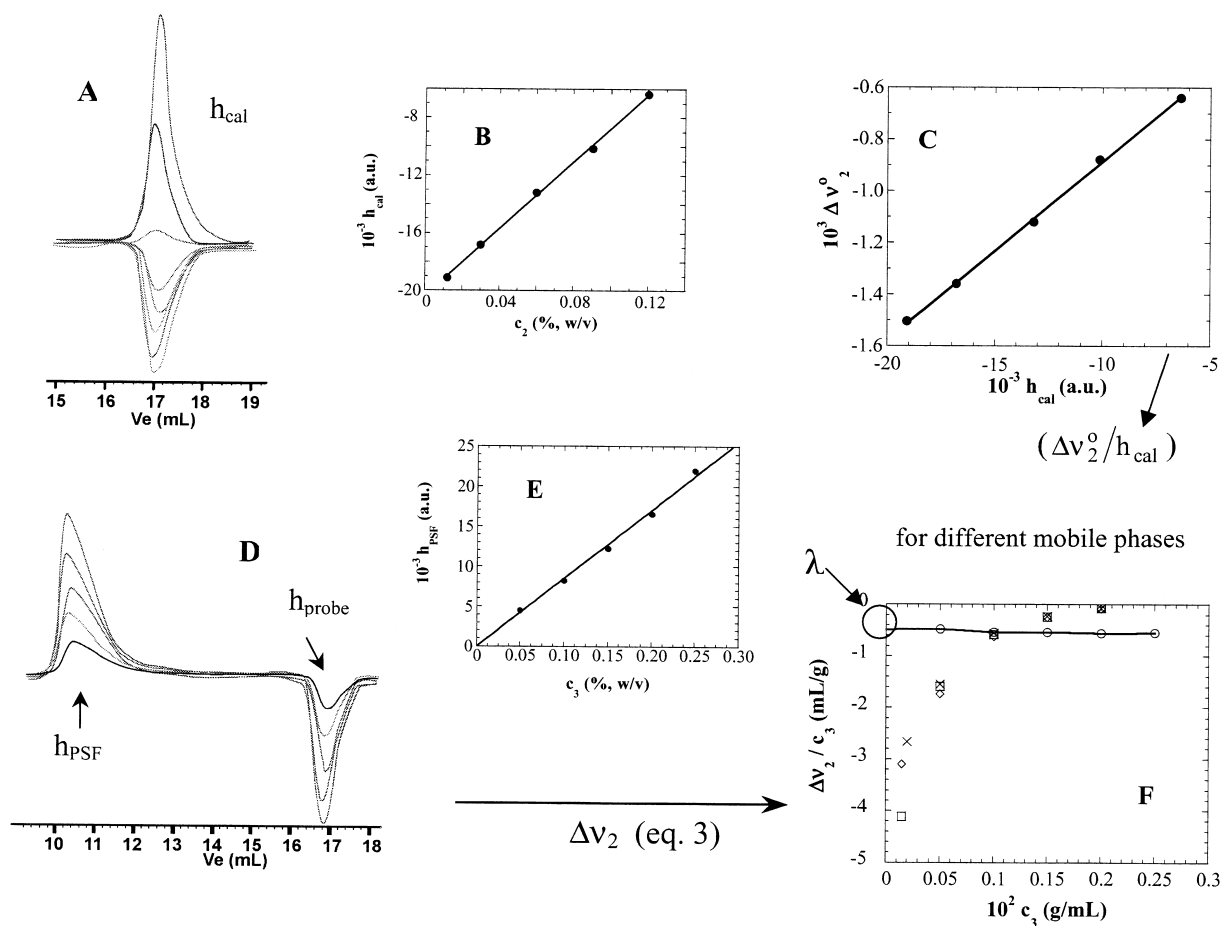


Fig. 2. Ternary system: THF–Arocy B10–PSF. (A) Positive and negative signal deflections from refractive index detector on injection of different B10 solutions. Baseline corresponds to a mobile phase composition of 0.20% solution of Arocy B10 in THF. (B10 concentrations: 0.005, 0.03, 0.06, 0.09, 0.12, 0.25, 0.36 and 0.60%, w/v). SEC conditions are described in the text. (B) Dependence of the height of the Arocy B10 peak on its concentration. (C) Calibration graph for the deflection peaks obtained from different B10 solutions. (D) Chromatograms of PSF in THF–B10 (0.20%) at different polymer concentrations (0.05, 0.10, 0.15, 0.20 and 0.25%, w/v). Mobile phase: B10 at 0.20% in THF. (E) Dependence of the height of the PSF peak on polymer concentration. (F) Change in the volume fraction of B10 per gram of polymer ($\Delta v_2/c_3$) as a function of the PSF concentration, c_3 for different mobile phase compositions: \times , 0.10; \square , 0.15; \diamond , 0.17 and \circ , 0.20% of Arocy B10.

eluent formed by Arocy B10 at 0.2% in THF. Fig. 2A displays the detector response on injection of diverse THF–Arocy B10 compositions. In all cases the Arocy B10 monomer elutes at 17 ml and the peak is either positive or negative according to the injected composition, i.e. at c_2 values greater than the baseline (0.2%), the direction of the signal shows an increase, whereas for $c_2 < 0.2\%$, the signal decreases in the relative transmittance. The good linear correlation shown in Fig. 2B allows us to plot the corresponding calibration curve (Fig. 2C). When size

exclusion is the main factor governing the separation mechanism in liquid chromatography, the first peaks correspond to macromolecular species whereas the last peak or ‘vacancy peak’ reveals the existence of preferential interaction of the polymer by one of the remaining components. Indeed, the elution profiles of PSF in an eluent formed by 0.2% of Arocy B10 in THF (Fig. 2D) show two peaks: the first one (at $V_e = 10.3$ ml), positive, corresponds to the solvated polymer, and its height (h_{PSF}) linearly increases with increasing polymer concentration (see Fig. 2E). From

Table 1

Calibration equations for the THF–Arocy B10–PSF system at different compositions of the binary eluent THF–Arocy B10

B10 (%)	h_{cal} vs. c_2^a	$\Delta\nu_2^o$ vs. h_{cal}	h_{PSF} vs. c_3^a
0.05	$h_{\text{cal}} = -5660 + 110\,214\,c_2$ ($r = 0.9966$)	$\Delta\nu_2^o = 9.03 \cdot 10^{-6} + 7.62 \cdot 10^{-8} h_{\text{cal}}$ ($r = 0.9975$)	$h_{\text{PSF}} = 83\,597\,c_3$ ($r = 0.9992$)
0.10	$h_{\text{cal}} = -10\,125 + 94\,772\,c_2$ ($r = 0.9983$)	$\Delta\nu_2^o = 5.55 \cdot 10^{-6} + 8.42 \cdot 10^{-8} h_{\text{cal}}$ ($r = 0.9985$)	$h_{\text{PSF}} = 80\,659\,c_3$ ($r = 0.9974$)
0.15	$h_{\text{cal}} = -17\,065 + 138\,710\,c_2$ ($r = 0.9953$)	$\Delta\nu_2^o = 2.21 \cdot 10^{-4} + 5.71 \cdot 10^{-8} h_{\text{cal}}$ ($r = 0.9953$)	$h_{\text{PSF}} = 80\,935\,c_3$ ($r = 0.9997$)
0.17	$h_{\text{cal}} = -14\,413 + 87\,979\,c_2$ ($r = 0.9984$)	$\Delta\nu_2^o = 1.11 \cdot 10^{-4} + 9.07 \cdot 10^{-8} h_{\text{cal}}$ ($r = 0.9988$)	$h_{\text{PSF}} = 59\,089\,c_3$ ($r = 0.9936$)
0.20	$h_{\text{cal}} = -20\,372 + 116\,150\,c_2$ ($r = 0.9994$)	$\Delta\nu_2^o = 1.98 \cdot 10^{-4} + 6.88 \cdot 10^{-8} h_{\text{cal}}$ ($r = 0.9994$)	$h_{\text{PSF}} = 84\,928\,c_3$ ($r = 0.9968$)

^a Concentrations are expressed as % (w/v); r is the correlation coefficient.

the height of the second peak (h_{probe}), negative, which appears at the elution volume of Arocy B10 in THF, and using the slope of the calibration curve (Fig. 2C), $\Delta\nu_2$ is readily calculated through Eq. (3). After plotting $(\Delta\nu_2/c_3)$ versus c_3 (Fig. 2F, circles), the preferential solvation parameter λ for PSF at this given eluent composition is determined at infinite dilution [according to Eq. (2b)]. The sign of the λ value obtained at this mobile phase composition, -0.5 ml/g, indicates that the polymer is preferentially solvated by Arocy B10.

Experiments were also carried out at different eluent compositions: 0.05, 0.1, 0.15 and 0.17% of Arocy B10 in THF. In all cases the elution profiles of the binary mixtures showed positive and negative peaks at 17 ml. The chromatograms obtained by injection of the ternary systems showed a positive peak between 10 and 10.5 ml and a negative peak at 17 ml, with the exception of the system THF–Arocy B10 (0.05%) where no vacancy peaks were observed. Table 1 shows the relationships between

concentration and height of the peaks as well as the calibration equations used to obtain the plots $(\Delta\nu_2/c_3)$ versus c_3 for all the eluent compositions. These plots (shown in Fig. 2F) yielded negative λ values in all cases except for the eluent THF–Arocy B10 (0.05%) (where $\lambda=0$). It is noteworthy that a new calibration curve per eluent composition was carried out prior to injecting the PSF in the binary solvent–Arocy B10 mixture. The fact that all points $(h_{\text{cal}}, \Delta\nu_2^o)$ corresponding to the five eluents can be linearly fitted in a common curve $(\Delta\nu_2^o = 6.27 \cdot 10^{-5} + 8.60 \cdot 10^{-8} h_{\text{cal}}; r = 0.99388)$ would probably imply the universal response of the detector and the goodness of the experimental measurements, at least in the concentration range assayed.

4.2. DMF–Arocy B10–PSF system

Typical chromatograms obtained by injection of different PSF concentrations in the eluent formed by Arocy B10 at 0.2% in DMF are shown in Fig. 3A.

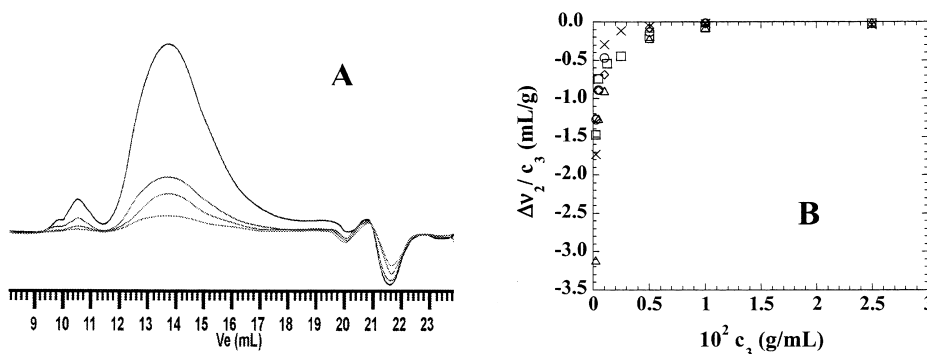


Fig. 3. Ternary system: DMF–Arocy B10–PSF. (A) Chromatograms of PSF in DMF Arocy B10 0.20% at different polymer concentrations (0.025, 0.05, 0.10 and 0.50%, w/v). Mobile phase: Arocy B10 at 0.20% in DMF. SEC conditions are described in the text. (B) Change in the volume fraction of B10 per gram of polymer $(\Delta\nu_2/c_3)$ as a function of the PSF concentration, c_3 , for different mobile phase compositions: Δ , 0.05%; \times , 0.10%; \square , 0.15%; \diamond , 0.17% and O , 0.20% of Arocy B10.

Table 2

Calibration equations for the DMF–Arocy B10–PSF system at different compositions of the binary eluent DMF–Arocy B10

B10 (%)	h_{cal} vs. c_2^a	$\Delta\nu_2^0$ vs. h_{cal}	h_{PSF} vs. c_3^a
0.05	$h_{\text{cal}} = -3514 + 69\,038 c_2$ ($r = 0.9998$)	$\Delta\nu_2^0 = 7.96 \cdot 10^{-6} + 1.16 \cdot 10^{-7} h_{\text{cal}}$ ($r = 0.9998$)	$h_{\text{PSF}} = 29\,914 c_3$ ($r = 0.9999$)
0.10	$h_{\text{cal}} = -4428 + 61\,684 c_2$ ($r = 0.9986$)	$\Delta\nu_2^0 = 2.18 \cdot 10^{-4} + 1.29 \cdot 10^{-7} h_{\text{cal}}$ ($r = 0.9986$)	$h_{\text{PSF}} = 30\,821 c_3$ ($r = 0.9947$)
0.15	$h_{\text{cal}} = -9382 + 61\,237 c_2$ ($r = 0.9979$)	$\Delta\nu_2^0 = 3.06 \cdot 10^{-5} + 1.30 \cdot 10^{-7} h_{\text{cal}}$ ($r = 0.9979$)	$h_{\text{PSF}} = 31\,288 c_3$ ($r = 0.9996$)
0.17	$h_{\text{cal}} = -8504 + 47\,212 c_2$ ($r = 0.9984$)	$\Delta\nu_2^0 = 8.19 \cdot 10^{-5} + 1.69 \cdot 10^{-7} h_{\text{cal}}$ ($r = 0.9988$)	$h_{\text{PSF}} = 29\,218 c_3$ ($r = 0.9975$)
0.20	$h_{\text{cal}} = -13\,468 + 71\,270 c_2$ ($r = 0.9989$)	$\Delta\nu_2^0 = 5.02 \cdot 10^{-5} + 1.19 \cdot 10^{-7} h_{\text{cal}}$ ($r = 0.9823$)	$h_{\text{PSF}} = 29\,251 c_3$ ($r = 0.9949$)

^a Concentrations are expressed in % (w/v); r is the correlation coefficient.

Two positive peaks followed by a negative one constitute the elution profile of this ternary system. The height of the peak eluted at 14 ml shows a good linear correlation with polymer concentration (see Table 2, last column). The first one ($V_e = 10.2$ ml) could be due to the chemical reaction between the amide group of the solvent and the sulfone groups of the polymer yielding a macromolecule with a molar mass higher than that of PSF. The size of the complex and the participation of the polymer are consistent with the DMF self-association and the linear increase of the height of this peak with the PSF concentration, respectively. The negative vacancy peaks corresponding to the defect of Arocy B10 in the bulk solvent (or the excess of Arocy B10 in the vicinity of the macromolecule) are located at 21 ml, which is coincident with the elution volume obtained in the elution profiles of the binary DMF–Arocy B10 mixture.

The change in the volume fraction of Arocy B10

per polymer gram ($\Delta\nu_2/c_3$) with the PSF concentration, for all eluents is shown in Fig. 3B. As can be seen, the variation of ($\Delta\nu_2/c_3$) with c_3 is similar to that exhibited in the THF–Arocy B10–PSF system. The λ values obtained at infinite dilution of polymer for every eluent composition will be discussed below. Again, the negative sign of λ means that PSF is preferentially solvated by the Arocy B10 monomer.

4.3. DCM–Arocy B10–PSF system

Fig. 4A shows chromatograms recorded for the DCM–Arocy B10–PSF system at different polymer concentrations in the mobile phase formed by B10 at 0.2% in DCM. Positive peaks due to the polymer appear at 15 ml, and their heights are linearly dependent on the polymer concentration injected (the corresponding equations are collected in Table 3, last column). The height of the negative vacancy peaks

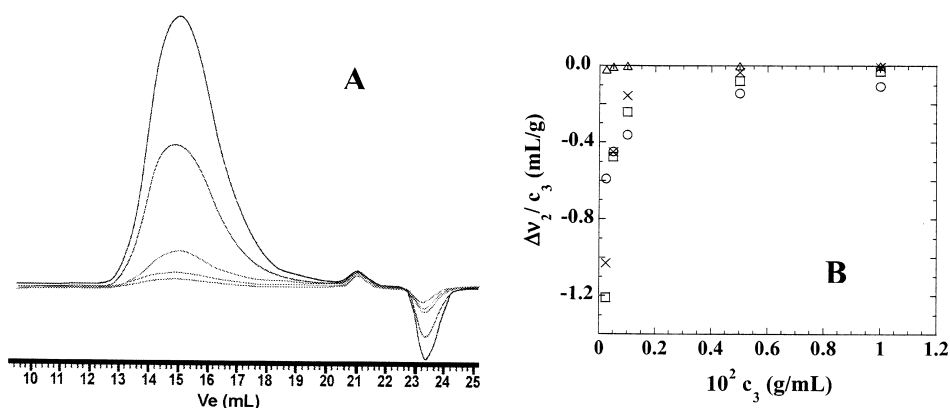


Fig. 4. Ternary system: DCM–Arocy B10–PSF. (A) Chromatograms of PSF in DCM–Arocy B10 0.20% at different polymer concentrations (0.025, 0.05, 0.10, 0.50 and 1.00%, w/v). Mobile phase: Arocy B10 at 0.20% in DCM. HPLC conditions are described in the text. (B) Change in the volume fraction of B10 per gram of polymer ($\Delta\nu_2/c_3$) as a function of the PSF concentration, c_3 , for different mobile phase compositions: Δ , 0.05, \times , 0.10; \square , 0.15 and O , 0.20% of Arocy B10.

Table 3

Calibration equations for the DCM–Arocy B10–PSF system at different compositions of the binary eluent DCM–Arocy B10

B10 (%)	h_{cal} vs. c_2^a	$\Delta\nu_2^o$ vs. h_{cal}	h_{PSF} vs. c_3^a
0.05	$h_{\text{cal}} = -4656 + 100\,270\,c_2$ ($r = 0.9999$)	$\Delta\nu_2^o = 2.78 \cdot 10^{-5} + 7.98 \cdot 10^{-8} h_{\text{cal}}$ ($r = 0.9999$)	$h_{\text{PSF}} = 37\,958\,c_3$ ($r = 0.9993$)
0.10	$h_{\text{cal}} = -8699 + 103\,940\,c_2$ ($r = 0.9976$)	$\Delta\nu_2^o = 1.25 \cdot 10^{-4} + 7.66 \cdot 10^{-8} h_{\text{cal}}$ ($r = 0.9976$)	$h_{\text{PSF}} = 38\,971\,c_3$ ($r = 0.9991$)
0.15	$h_{\text{cal}} = -14\,310 + 94\,471\,c_2$ ($r = 0.9997$)	$\Delta\nu_2^o = 1.25 \cdot 10^{-5} + 8.46 \cdot 10^{-8} h_{\text{cal}}$ ($r = 0.9998$)	$h_{\text{PSF}} = 41\,133\,c_3$ ($r = 0.9996$)
0.20	$h_{\text{cal}} = -14\,758 + 82\,628\,c_2$ ($r = 0.9998$)	$\Delta\nu_2^o = 1.69 \cdot 10^{-4} + 9.67 \cdot 10^{-8} h_{\text{cal}}$ ($r = 0.9994$)	$h_{\text{PSF}} = 39\,885\,c_3$ ($r = 0.9993$)

^a Concentrations are expressed in % (w/v); r is the correlation coefficient.

of Arocy B10 ($V_e = 21–23$ ml) together with their calibration curve (also listed in Table 3) have been used to obtain the corresponding $\Delta\nu_2$ value for each polymer concentration and then, $(\Delta\nu_2/c_3)$ versus c_3 plotted, as shown in Fig. 4B. Again, the extrapolation at $c_3 \rightarrow 0$ gives negative λ values which denotes that PSF is preferentially adsorbed by Arocy B10 as in the preceding systems.

As seen from Figs. 2F, 3B and 4B, in the three systems assayed, the plots of the variation of $(\Delta\nu_2/c_3)$ with c_3 follow a similar trend, that is, λ values approach zero at high polymer concentrations and sharply decrease as c_3 decreases, reaching always negative values. However, and from a quantitative viewpoint, the preferential solvation coefficients (obtained from the intercepts of these plots) are different depending on the organic solvent used. In order to discuss these values, Fig. 5 shows the variation of λ as a function of the Arocy B10

composition. Although in all solvents the PSF is preferentially solvated by the monomer, this variation depends on the chemical nature of the solvent. Indeed, in THF, the absolute value of λ increases with the Arocy B10 concentration up to a maximum of 0.15% and then decreases, reaching a value similar to that obtained in the other two solvents. In contrast, in DMF and DCM λ slightly decreases with c_2 . The comparison of data in the three solvents reveals the strongest solvation for the THF systems and the lowest λ values for DCM. These results can be related to the thermodynamic quality of the different solvents with PSF. In effect, a good agreement has been found between the preferential solvation and the intrinsic viscosity values $[\eta]$ obtained for the PSF–solvent systems: $[\eta]_{\text{PSF}}^{\text{THF}} < [\eta]_{\text{PSF}}^{\text{DMF}} < [\eta]_{\text{PSF}}^{\text{DCM}}$. This means that the effective specific volume of the macromolecule [24] increases when changing from THF to DCM; in other words, as the macromolecule is more solvated by DCM, it finds more difficulty in interacting with another molecule leading to a weaker solvation by the Arocy B10 monomer.

Finally, the best compatibility found between PSF and Arocy B10 in THF is also consistent with scanning electron microscopy (SEM) measurements. After release of the solvent by annealing the samples in a stove at 60°C for 1 h, the SEM revealed more homogeneous mixtures when they were prepared in THF (data not shown). On the contrary, the most heterogeneous sample was obtained in DCM. It is noteworthy that the two kinds of experiments are not performed under similar conditions. However, although the solvent has been removed, the SEM results are an indication of the compatibility of the ternary system, because there is a reminiscence of the presence of the solvent left. Such a phenomenon is called ‘solvent history dependence’ and it is often observed in biological systems [25].

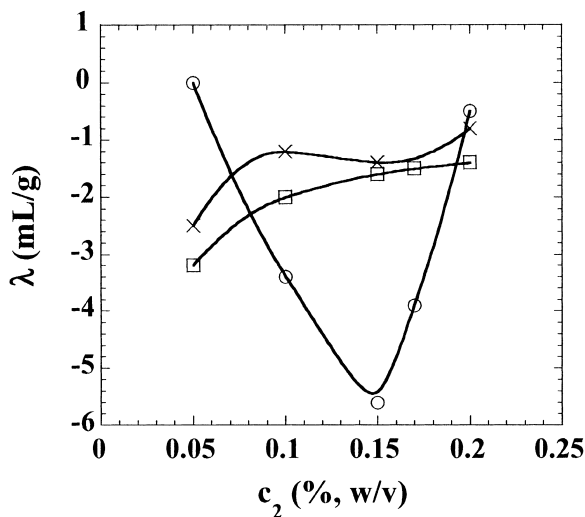


Fig. 5. Dependence of the preferential interaction parameter, λ , on Arocy B10 concentration in \circ , THF; \square , DMF; \times , DCM.

5. Conclusions

The compatibility between the cyanate ester monomer Arocy B10 and PSF in the presence of different organic solvents has been mainly studied by SEC. From the analysis of the vacancy peaks obtained for PSF in solvent–Arocy B10 mixtures, accurate information regarding the preferential solvation parameter, λ , at polymer-diluted conditions has been obtained. The results show that whatever the solvent was, PSF is preferentially adsorbed by Arocy B10. A quantitative comparison of the solvation for the different solvents reveals that the compatibility between Arocy B10 and PSF is enhanced in THF whereas the lowest λ values are obtained in DCM. The effect of the concentration of the cyanate ester monomer on the adsorption on PSF also depends on the type of solvent: in the presence of THF, the absolute values of λ increase with Arocy B10 concentration up to 0.15% (w/v) and then decrease. In DCM and DMF the preferential solvation parameter slightly decreases with the monomer concentration, achieving similar values for all the three solvents at the highest c_2 assayed. Regarding the behaviour respect to the polymer concentration, at high c_3 values λ approaches zero, and decreases as c_3 does.

The best compatibility between Arocy B10 and PSF has been found in tetrahydrofuran, which seems to be related to the thermodynamic quality of this solvent with PSF. Indeed, the intrinsic viscosity values $[\eta]$ obtained for the PSF–solvent systems reveals a smaller effective specific volume of the macromolecule in THF, and as a consequence, the interaction with the Arocy B10 would result favoured. Assessment of this phenomenon deserves further investigation. Work is continuing to acquire additional viscometry data on ternary systems. Preliminary scanning electronic microscopy measurements seem to be also in accordance with these results.

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