

Determination of χ from liquid-liquid phase data in ternary polymer systems (solvent/polymer/polymer) with hydrogen bonding

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Abstract. Two different models accounting for the dependences of χ and g interaction parameters on both temperature and composition have been applied to different ternary polymer systems (TPS) solvent(1)/polymer(2)/polymer(3). The analyzed TPS have consisted on ten different polymer mixtures in chloroform as common solvent that can specifically interact via hydrogen bond. Experimental ternary phase diagrams determined by liquid chromatography were taken from literature. The application of the two models to the experimental data have served to obtain χ_{ij} and g_{ij} interaction parameters for all the binary ij ($ij = 12, 13, 23$) interactions established between the three components of the system, with simplified mathematical procedures. The results have shown a fair agreement between the calculated and the literature values, at least when the model containing an empirical entropy correction is used. Moreover, the evaluated interaction parameters follow the expected behaviour as the content of the H-donor polymer in the mixture is raised and are also in good accordance with experimental viscometric data.

Keywords: modeling and simulation, interaction parameters, ternary polymer systems, hydrogen-bonding, rigid lattice theory

1. Introduction

An increasing interest in solving complex systems, such as polyblends [1], nanoparticles, composites or ternary polymer systems (TPS) formed by a mixture of three polymers, through the thermodynamic analysis of phase diagrams is clearly evidenced. For example, the curing of an epoxy in the presence of thermoplastics and additives is usually followed by the evolution of their phase diagrams as the curing process goes on. The classical procedure consists on writing the Gibbs free energy function of mixture and obtaining the corresponding chemical potentials, $\Delta\mu$, in each phase. Generally, the equations obtained for this kind of systems show a great complexity, and, in consequence, the values of the χ interaction parameters are usually unknown or

rarely known with any certainty. To circumvent this drawback, different approximations have to be introduced in order to simplify the mathematical solution.

It is now generally accepted that in order to obtain quantitative agreement between Flory-Huggins theory and experimental observations for most polymer systems, χ interaction parameter dependence on both temperature and composition must be considered [2–4]. Sometimes the g interaction parameter (mathematically related to χ) can be expressed as a more complex function than $1/T$ [5]. Other $g(T, \text{composition})$ functions can be theoretically derived in the framework of the rigid lattice model, as Staverman [6] and Koningsveld and Kleitjens [7], among others, have demonstrated. Nowadays it is

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accepted that the dependence of g on concentration mainly arises from the disparities in size and shape of the solvent molecules and the polymer segments. According to Staverman [6], it is possible to write the functionality of g as Equation (1):

$$g = \frac{D(T)}{1 - c\phi_2} \quad (1)$$

where c is a constant determined from Bondi studies [8–10] and $D(T)$ accounts for the temperature dependence in the form of Equation (2):

$$D(T) = a + \frac{b}{T} \quad (2)$$

On the other hand, $\chi \rightarrow g$, just when the volume fraction of component 2 $\phi_2 \rightarrow 1$, or at infinite dilution of solvent, which are the conditions fulfilled by the inverse gas chromatography technique [5], although, it is also used (Equation (3)) when analyzing the thermodynamics of the phase separation during polymerization of a thermoset system into a thermoplastic matrix [11, 12].

$$\chi = \frac{D(T)}{1 - c\phi_2} \quad (3)$$

Occasionally, and in order to adjust the experimental results, the interaction function, dependent on both temperature and composition, can be written [5, 13–15] as Equation (4):

$$g = \alpha + \frac{D(T)}{1 - \phi_2} \quad (4)$$

where α is an empirical entropy correction [5] given by Equation (5):

$$\alpha = \alpha_s + \frac{\alpha_H}{T} \quad (5)$$

Obviously, this new g value yields a different expression for χ , (Equation (6)) [15]:

$$\chi = \alpha + \frac{D(1 - c)}{(1 - c\phi_2)^2} \quad (6)$$

Moreover, an even more complex function to express the χ temperature and concentration dependence has been found (Equation (7)) [16]:

$$\chi(T, \phi_2) = (1 + c_1\phi_2 + c_2\phi_2^2)(D + d \ln T) \quad (7)$$

where c_i ($i = 1, 2$), D and d being adjustable parameters.

Usually, the use of any of the above expressions simplifies the χ evaluation, although unfortunately, the calculated values cannot be experimentally checked, especially in complex systems. Fortunately, there are more traditional and simple systems with well-known values of the interaction parameters that can be used to judge the validity of the approximations used in the more complex and actual systems. In this regard, in recent papers, dealing with compatibility between polystyrene copolymers and other polymers in solution via hydrogen bonding [17–19], the phase diagrams of the ternary polymer systems (TPS) have been obtained from experimental liquid chromatography data [20–22]. The achievement of χ values from liquid-liquid phase data has been considered a reliable method [16] and consists in solving the equations obtained by equating the chemical potentials in both phases in equilibrium, for all the components. To mathematically solve the equations, two of the most often used models for $\chi(T, \phi_2)$ have been applied. The validity of the theoretical results has been judged in the light of the experimental ones, measured by viscometry and liquid chromatography [18–20]. Moreover, the adequacy and reliability of the diverse χ models has also been tested from a basic thermodynamic viewpoint.

2. Theory

2.1. Chemical potentials and interaction parameters

In ternary solvent(1)/polymer(2)/polymer(3) systems with polydisperse polymers, the Gibbs free energy change upon mixing n_i mols of component i ($i = 1, 2, 3$) is given by Equation (8):

$$\frac{\Delta G^M}{RT} = n_1 \ln \phi_1 + \sum_{n=1, m_2}^{m_2} n_{2, x_n} \ln \phi_{2, x_n} + \sum_{n=1, m_3}^{m_3} n_{3, x_n} \ln \phi_{3, x_n} + n_1 \phi_2 g_{12} + n_1 \phi_3 g_{13} \quad (8)$$

whereas for monodisperse polymers (or with low polydispersity index) is given by Equation (9):

$$\frac{\Delta G^M}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1 \phi_2 g_{12} + n_1 \phi_3 g_{13} + \bar{x}_2 n_2 \phi_3 g_{23} \quad (9)$$

and the chemical potentials deduced from Equation (9) are then given by Equations (10) and (11):

$$\begin{aligned} \frac{\Delta \mu_1}{RT} &= \frac{1}{RT} \left(\frac{\partial \Delta G^M}{\partial n_1} \right)_{n_2, n_3, p, T} = \ln \phi_1 + \left(1 - \frac{V_1}{V_2} \right) \phi_2 + \left(1 - \frac{V_1}{V_3} \right) \phi_3 + \left[g_{12} - \frac{\phi_1 \phi_2}{1 - \phi_1} \frac{dg_{12}}{d\phi_2} \right] \phi_2 (1 - \phi_1) + \\ &\left[g_{13} - \frac{\phi_1 \phi_3}{1 - \phi_1} \frac{dg_{13}}{d\phi_3} \right] \phi_3 (1 - \phi_1) - \left[g_{23} + \phi_3 \frac{dg_{23}}{d\phi_3} \right] \phi_2 \phi_3 \frac{V_1}{V_2} = \\ &\ln \phi_1 + \left(1 - \frac{V_1}{V_2} \right) \phi_2 + \left(1 - \frac{V_1}{V_3} \right) \phi_3 + \chi_{12} \phi_2 (1 - \phi_1) + \chi_{13} \phi_3 (1 - \phi_1) - \varepsilon_{23} \phi_2 \phi_3 \frac{V_1}{V_2} \end{aligned} \quad (10)$$

$$\begin{aligned} \frac{\Delta \mu_2}{RT} &= \frac{1}{RT} \left(\frac{\partial \Delta G^M}{\partial n_2} \right)_{n_1, n_3, p, T} = \ln \phi_2 + \left(1 - \frac{V_2}{V_1} \right) \phi_1 + \left(1 - \frac{V_2}{V_3} \right) \phi_3 + \left[g_{12} + \phi_2 \frac{dg_{12}}{d\phi_2} \right] \phi_1 (1 - \phi_2) \frac{V_2}{V_1} - \\ &\left[g_{13} + \phi_3 \frac{dg_{13}}{d\phi_3} \right] \phi_1 \phi_3 \frac{V_2}{V_1} + \left[g_{23} - \frac{\phi_2 \phi_3}{1 - \phi_2} \frac{dg_{23}}{d\phi_3} \right] \phi_3 (1 - \phi_2) \frac{V_2}{V_1} = \\ &\ln \phi_2 + \left(1 - \frac{V_2}{V_1} \right) \phi_1 + \left(1 - \frac{V_2}{V_3} \right) \phi_3 + \varepsilon_{12} \phi_1 (1 - \phi_2) \frac{V_2}{V_1} - \varepsilon_{13} \phi_1 \phi_3 \frac{V_2}{V_1} + \chi_{23} \phi_3 (1 - \phi_2) \frac{V_2}{V_1} \end{aligned} \quad (11)$$

and by Equation (12):

$$\begin{aligned} \frac{\Delta \mu_3}{RT} &= \frac{1}{RT} \left(\frac{\partial \Delta G^M}{\partial n_3} \right)_{n_1, n_2, p, T} = \ln \phi_3 + \left(1 - \frac{V_3}{V_1} \right) \phi_1 + \left(1 - \frac{V_3}{V_2} \right) \phi_2 - \left[g_{12} + \phi_2 \frac{dg_{12}}{d\phi_2} \right] \phi_1 \phi_2 \frac{V_3}{V_1} + \\ &\left[g_{13} + \phi_3 \frac{dg_{13}}{d\phi_3} \right] \phi_1 (1 - \phi_3) \frac{V_3}{V_1} + \left[g_{23} + \phi_3 \frac{dg_{23}}{d\phi_3} \right] \phi_2 (1 - \phi_3) \frac{V_3}{V_1} = \\ &\ln \phi_3 + \left(1 - \frac{V_3}{V_1} \right) \phi_1 + \left(1 - \frac{V_3}{V_2} \right) \phi_2 - \varepsilon_{12} \phi_1 \phi_2 \frac{V_3}{V_1} + \varepsilon_{13} \phi_1 (1 - \phi_3) \frac{V_3}{V_1} + \varepsilon_{23} \phi_2 (1 - \phi_3) \frac{V_3}{V_1} \end{aligned} \quad (12)$$

where n_i , V_i and $\Delta \mu_i$ ($i = 1, 2, 3$) are mol numbers, molar volumes and chemical potentials, respectively. In Equations (10)–(12) the residual contributions to $\Delta \mu_i$ (the terms containing g_{12} , g_{13} and g_{23}) are ternary volume fractions ϕ_i ($i = 1, 2, 3$) functions representative of binary interaction parameters. Generally, two types of ternary functions can be considered, those of the form given in Equation (13):

$$\left[g_{ij} - \frac{\phi_i \phi_j}{1 - \phi_i} \frac{dg_{ij}}{d\phi_j} \right] \quad (13)$$

where ij represents the 1-2, 1-3 and 2-3 interactions, which are also called χ_{ij} because when they are transformed into binary functions (concretely, χ_{13}^{binary} is deduced from $\chi_{13}^{ternary}$ by making $\phi_2 = 0$), the classical Flory's interaction parameters are obtained, which are defined in $\Delta \mu_i^{binary}$ by Equation (14) [15]:

$$\chi_{ij} = g_{ij} - \phi_i \frac{dg_{ij}}{d\phi_j} = g_{ij} + \phi_i \frac{dg_{ij}}{d\phi_i} \quad (14)$$

The other functions types adopt the following functionality shown by Equation (15):

$$g_{ij} + \phi_j \frac{dg_{ij}}{d\phi_j} \quad (15)$$

also named ε_{ij} , because when they are transformed into binary functions, the parameters defining $\Delta\mu_i^{binary}$ are obtained by Equation (16) [15, 23]:

$$\varepsilon_{ij} = g_{ij} + \phi_j \frac{dg_{ij}}{d\phi_j} = g_{ij} - \phi_j \frac{dg_{ij}}{d\phi_i} \quad (16)$$

The interconversion between χ_{ij} and ε_{ij} for binary polymer systems (BPS) is achieved at constant temperature [24] through different dependences on component j concentration, χ_{13}^{binary} expressed as volume fraction ϕ_j by Equations (17)–(20):

$$\chi_{ij} = \chi_{ij}^{(0)} + \chi_{ij}^{(1)}\phi_j + \dots = \sum_{n=0}^m \chi^{(n)}\phi_j^n \quad (17)$$

$$\chi_{ij} = g_{ij} - \phi_i \frac{dg_{ij}}{d\phi_j} = g_{ij} - (1-\phi_j) \frac{dg_{ij}}{d\phi_j} \quad (18)$$

$$\chi_{ij} = -d[(1-\phi_j)g_{ij}] \quad (19)$$

$$g_{ij} = \frac{1}{1-\phi_j} \int_{\phi_j}^1 \chi_{ij} d\phi_j \quad (20)$$

Finally, the substitution of Equation (20) into Equation (17) yields Equation (21):

$$g_{ij} = \left(\chi_{ij}^{(0)} + \frac{\chi_{ij}^{(1)}}{2} + \dots \right) + \left(\frac{\chi_{ij}^{(1)}}{2} + \frac{\chi_{ij}^{(2)}}{3} \right) \phi_j + \dots = \sum_{n=0}^m \frac{\chi^{(n)}}{n+1} \frac{1-\phi_j^{(n+1)}}{1-\phi_j} \quad (21)$$

which allows to evaluate g_{ij} parameters from experimental χ_{ij} values.

2.2. Models for interaction parameters dependences on concentration and temperature in BPS

2.2.1. Model a1

In the literature is possible to find g_{ij} values as a function of temperature and composition according to Equation (22) [5, 15]:

$$g_{ij} = \alpha_{ij} + \frac{D_{ij}}{1 - c_{ij}\phi_j} \quad (22)$$

where α_{ij} and c_{ij} are constants for a given system and temperature interval, and $D_{ij}(T)$ (Equation (2)), being a and b parameters with entropic and enthalpic character, respectively [4]. According to Equation (18), the corresponding χ_{ij} values are given by Equation (23):

$$\chi_{ij} = \alpha_{ij} + \frac{D_{ij}(1 - c_{ij})}{(1 - c_{ij}\phi_j)^2} \quad (23)$$

and according to Equation (16) the corresponding ε_{ij} should be as given by Equation (24):

$$\varepsilon_{ij} = \alpha_{ij} + \frac{D_{ij}}{(1 - c_{ij}\phi_j)^2} \quad (24)$$

There are other models describing the g dependences with temperature and composition for binary polymer systems. In general it is accepted that the main reason for the g dependence on concentration arises from the disparity in size and shape between the solvent molecules and the polymer segments. Therefore, and according to Staverman [6], the g function can be written as given by Equation (25):

$$g_{ij} = \frac{D_{ij}}{1 - c_{ij}\phi_j} \quad (25)$$

with D_{ij} and c_{ij} as previously defined. However, when this set of equations is applied to the experimental results, is necessary to introduce a new fitting empirical parameter, α_{ij} . At high ϕ_j values, calculated and measured binodals, spinodals and χ_{ij} vs. ϕ_j curves show that the empirical α_{ij} parameter depends on temperature (Equation (26)):

$$\alpha_{ij} = m + nT \quad (26)$$

where the parameter n may assume any sign and the relation can only describe the behaviour within a rather limited range of temperatures. As a consequence, it is arrived again at the Equation (22) with α_{ij} dependence with T .

2.2.2. Model a2

Other models allow to express the g_{ij} interaction parameters in BPS by using a less number of fitting parameters, according to Equation (27):

$$g_{ij} = \frac{D_{ij}}{c_{ij}(1-\phi_j)} \ln(1-c_{ij}\phi_j) \quad (27)$$

with D_{ij} and c_{ij} as defined in Equation (22). Now, the χ_{ij} values attained are given by Equation (28):

$$\chi_{ij} = \frac{D_{ij}}{1-c_{ij}\phi_j} \quad (28)$$

This expression has been recently used to thermodynamically analyze the phase separation occurring during the polymerization of a thermoset epoxy system into a thermoplastic matrix [11, 12, 25]. According to this model and taking into account Equation (27) the following ε_{ij} value is obtained as shown by Equation (29):

$$\varepsilon_{ij} = \frac{D_{ij}}{c_{ij}} \ln(1-c_{ij}\phi_j) \frac{\phi_i + \phi_j}{\phi_i^2} - \frac{\phi_j}{\phi_i} \frac{D_{ij}}{1-c_{ij}\phi_j} \quad (29)$$

as well as by Equation (30):

$$\phi_i^2 \varepsilon_{ij} = \frac{D_{ij}}{c_{ij}} \ln(1-c_{ij}\phi_j) - \phi_i \phi_j \frac{D_{ij}}{1-c_{ij}\phi_j} = \int_{\phi_j}^1 \chi_{ij} d\phi_j - \phi_i \phi_j \chi_{ij} \quad (30)$$

which relates ε_{ij} and χ_{ij} in binary polymeric systems [11, 12, 25].

2.3. Models for interaction parameters dependences on concentration and temperature in TPS

The g_{ij} values derived with the different models for BPS have no reasons to change when ternary solvent/polymer/polymer systems are considered. In fact, in the Gibbs free energy of mixing, g_{ij} represents the energy interchanged by one contact i - j (1-2, 1-3 and 2-3) independently of the presence of a third component (see Equation (8)). To prove this fact, next the corresponding expressions for the 1-2 interaction, as an example, will be derived.

2.3.1. Model b1

First of all and recalling the **a1** model, the following expressions shown by Equations (31)–(34) hold in BPS:

$$g_{12} = \alpha_{12} + \frac{D_{12}}{1-c_{12}\phi_2} \quad (31)$$

$$\frac{dg_{12}}{d\phi_2} = \frac{c_{12}D_{12}}{(1-c_{12}\phi_2)^2} \quad (32)$$

$$\chi_{12} = g_{12} - \phi_1 \frac{dg_{12}}{d\phi_2} = \alpha_{12} + \frac{D_{12}(1-c_{12})}{(1-c_{12}\phi_2)^2} \quad (33)$$

$$\varepsilon_{12} = g_{12} + \phi_2 \frac{dg_{12}}{d\phi_2} = \alpha_{12} + \frac{D_{12}}{(1-c_{12}\phi_2)^2} \quad (34)$$

whereas for a TPS and recalling Equations (13), (31) and (32), Equation (33) yields Equation (35):

$$\chi_{12} = g_{12} - \frac{\phi_1 \phi_2}{1-\phi_1} \frac{dg_{12}}{d\phi_2} \quad (35)$$

or Equation (36):

$$\chi_{12} = \alpha_{12} + \frac{D_{12}(1-\phi_1-c_{12}\phi_2)}{(1-\phi_1)(1-c_{12}\phi_2)^2} \quad (36)$$

On the other hand, from Equations (16), (31) and (32) Equation (37) can be obtained:

$$\varepsilon_{12} = g_{12} + \phi_2 \frac{dg_{12}}{d\phi_2} = \alpha_{12} + \frac{D_{12}}{(1-c_{12}\phi_2)^2} \quad (37)$$

which is the same expression as Equation (34) since ε is identical both in BPS and in TPS, although by using their respective binary and ternary volume fractions, ϕ , in the corresponding calculations.

In TPS with two phases (α and β) present in equilibrium the following conditions, given by Equation (38) hold:

$$\begin{aligned} \Delta\mu_1^\alpha &= \Delta\mu_1^\beta \\ \Delta\mu_2^\alpha &= \Delta\mu_2^\beta \\ \Delta\mu_3^\alpha &= \Delta\mu_3^\beta \end{aligned} \quad (38)$$

that applied to the present model leads to Equations (39)–(41):

$$\begin{aligned}
 & \ln \phi_1^\alpha + \left(1 - \frac{V_1}{V_2}\right) \phi_2^\alpha + \left(1 - \frac{V_1}{V_3}\right) \phi_3^\alpha + \left[\alpha_{12} + \frac{D_{12}(1 - \phi_1^\alpha - c_{12}\phi_2^\alpha)}{(1 - \phi_1^\alpha)(1 - c_{12}\phi_2^\alpha)^2} \right] \phi_2^\alpha (1 - \phi_1^\alpha) + \\
 & \left[\alpha_{13} + \frac{D_{13}(1 - \phi_1^\alpha - c_{13}\phi_3^\alpha)}{(1 - \phi_1^\alpha)(1 - c_{13}\phi_3^\alpha)^2} \right] \phi_3^\alpha (1 - \phi_1^\alpha) - \left[\alpha_{23} + \frac{D_{23}}{(1 - c_{23}\phi_3^\alpha)^2} \right] \frac{V_1}{V_2} \phi_2^\alpha \phi_3^\alpha = \\
 & \ln \phi_1^\beta + \left(1 - \frac{V_1}{V_2}\right) \phi_2^\beta + \left(1 - \frac{V_1}{V_3}\right) \phi_3^\beta + \left[\alpha_{12} + \frac{D_{12}(1 - \phi_1^\beta - c_{12}\phi_2^\beta)}{(1 - \phi_1^\beta)(1 - c_{12}\phi_2^\beta)^2} \right] \phi_2^\beta (1 - \phi_1^\beta) + \\
 & \left[\alpha_{13} + \frac{D_{13}(1 - \phi_1^\beta - c_{13}\phi_3^\beta)}{(1 - \phi_1^\beta)(1 - c_{13}\phi_3^\beta)^2} \right] \phi_3^\beta (1 - \phi_1^\beta) - \left[\alpha_{23} + \frac{D_{23}}{(1 - c_{23}\phi_3^\beta)^2} \right] \frac{V_1}{V_2} \phi_2^\beta \phi_3^\beta
 \end{aligned} \tag{39}$$

$$\begin{aligned}
 & \ln \phi_2^\alpha + \left(1 - \frac{V_2}{V_1}\right) \phi_1^\alpha + \left(1 - \frac{V_2}{V_3}\right) \phi_3^\alpha + \left[\alpha_{12} + \frac{D_{12}}{(1 - c_{12}\phi_2^\alpha)^2} \right] \phi_1^\alpha (1 - \phi_2^\alpha) \frac{V_2}{V_1} - \\
 & \left[\alpha_{13} + \frac{D_{13}}{(1 - c_{13}\phi_3^\alpha)^2} \right] \phi_1^\alpha \phi_3^\alpha \frac{V_2}{V_1} + \left[\alpha_{23} + \frac{D_{23}(1 - \phi_2^\alpha - c_{23}\phi_3^\alpha)}{(1 - \phi_2^\alpha)(1 - c_{23}\phi_3^\alpha)^2} \right] \phi_3^\alpha (1 - \phi_2^\alpha) \frac{V_2}{V_1} = \\
 & \ln \phi_2^\beta + \left(1 - \frac{V_2}{V_1}\right) \phi_1^\beta + \left(1 - \frac{V_2}{V_3}\right) \phi_3^\beta + \left[\alpha_{12} + \frac{D_{12}}{(1 - c_{12}\phi_2^\beta)^2} \right] \phi_1^\beta (1 - \phi_2^\beta) \frac{V_2}{V_1} - \\
 & \left[\alpha_{13} + \frac{D_{13}}{(1 - c_{13}\phi_3^\beta)^2} \right] \phi_1^\beta \phi_3^\beta \frac{V_2}{V_1} + \left[\alpha_{23} + \frac{D_{23}(1 - \phi_2^\beta - c_{23}\phi_3^\beta)}{(1 - \phi_2^\beta)(1 - c_{23}\phi_3^\beta)^2} \right] \phi_3^\beta (1 - \phi_2^\beta) \frac{V_2}{V_1}
 \end{aligned} \tag{40}$$

$$\begin{aligned}
 & \ln \phi_3^\alpha + \left(1 - \frac{V_3}{V_1}\right) \phi_1^\alpha + \left(1 - \frac{V_3}{V_2}\right) \phi_2^\alpha - \left[\alpha_{12} + \frac{D_{12}}{(1 - c_{12}\phi_2^\alpha)^2} \right] \phi_1^\alpha \phi_2^\alpha \frac{V_3}{V_1} + \\
 & \left[\alpha_{13} + \frac{D_{13}}{(1 - c_{13}\phi_3^\alpha)^2} \right] \phi_1^\alpha (1 - \phi_3^\alpha) \frac{V_3}{V_1} + \left[\alpha_{23} + \frac{D_{23}}{(1 - c_{23}\phi_3^\alpha)^2} \right] \phi_2^\alpha (1 - \phi_3^\alpha) \frac{V_3}{V_1} = \\
 & \ln \phi_3^\beta + \left(1 - \frac{V_3}{V_1}\right) \phi_1^\beta + \left(1 - \frac{V_3}{V_2}\right) \phi_2^\beta - \left[\alpha_{12} + \frac{D_{12}}{(1 - c_{12}\phi_2^\beta)^2} \right] \phi_1^\beta \phi_2^\beta \frac{V_3}{V_1} + \\
 & \left[\alpha_{13} + \frac{D_{13}}{(1 - c_{13}\phi_3^\beta)^2} \right] \phi_1^\beta (1 - \phi_3^\beta) \frac{V_3}{V_1} + \left[\alpha_{23} + \frac{D_{23}}{(1 - c_{23}\phi_3^\beta)^2} \right] \phi_2^\beta (1 - \phi_3^\beta) \frac{V_3}{V_1}
 \end{aligned} \tag{41}$$

The terms in brackets are the corresponding χ_{ij} and ε_{ij} values ($ij = 12, 13, 23$) in phases α or β , according to the **b1** model, that is, taking into account Equations (36) and (37).

$$g_{12} = \frac{D_{12}}{c_{12}(1 - \phi_2)} \ln(1 - c_{12}\phi_2) \tag{42}$$

2.3.2 Model b2

Similarly and according to the **a2** model, in PBS the generic Equations (27)–(29) should read for the 1-2 interaction as shown by Equations (42)–(44):

$$\chi_{12} = \frac{D_{12}}{1 - c_{12}\phi_2} \tag{43}$$

$$\varepsilon_{12} = \frac{D_{12} \ln(1 - \phi_2)}{c_{12}} \frac{\phi_1 \phi_2}{\phi_1^2} - \frac{\phi_2}{\phi_1} \frac{D_{12}}{1 - c_{12}\phi_2} \tag{44}$$

whereas for a TPS yields Equation (45):

$$\chi_{12} = g_{12} - \frac{\phi_1\phi_2}{1-\phi_1} \frac{dg_{12}}{d\phi_2} = \frac{D_{12}}{c_{12}} \frac{\ln(1-\phi_2)}{1-\phi_2} \left\{ 1 - \frac{\phi_1\phi_2}{(1-\phi_1)(1-\phi_2)} \right\} + \frac{D_{12}}{1-c_{12}\phi_2} \frac{\phi_1\phi_2}{(1-\phi_1)(1-\phi_2)} \quad (45)$$

and Equation (46):

$$\varepsilon_{12} = g_{12} + \phi_2 \frac{dg_{12}}{d\phi_2} = \frac{D_{12}}{c_{12}} \frac{\ln(1-c_{12}\phi_2)}{(1-\phi_2)^2} - \frac{\phi_2 D_{12}}{(1-\phi_2)(1-c_{12}\phi_2)} \quad (46)$$

It is easy to prove that Equation (45) transforms into Equation (43) for BPS when $\phi_3 = 0$ and $\phi_1\phi_2/[(1-\phi_1)(1-\phi_2)] = 1$; and Equation (46) into Equation (29) if $\phi_3 = 0$.

Finally, the substitution of χ_{12} and ε_{12} values derived with the **b2** model into Equations (10)–(12) when equilibrium condition holds (Equation (38)), yields for each component of the TPS Equations (47) and (48):

$$\begin{aligned} & \ln \phi_1^\alpha + \left(1 - \frac{V_1}{V_2} \right) \phi_2^\alpha + \left(1 - \frac{V_1}{V_3} \right) \phi_3^\alpha + \\ & \left[\frac{D_{12}}{c_{12}} + \frac{\ln(1-\phi_2^\alpha)}{1-\phi_2^\alpha} \right] \left\{ 1 - \frac{\phi_1^\alpha\phi_2^\alpha}{(1-\phi_1^\alpha)(1-\phi_2^\alpha)} \right\} + \frac{\phi_1^\alpha\phi_2^\alpha}{(1-\phi_1^\alpha)(1-\phi_2^\alpha)} \frac{D_{12}}{1-c_{12}\phi_2^\alpha} \left] \phi_2^\alpha (1-\phi_1^\alpha) + \right. \\ & \left. \left[\frac{D_{13}}{c_{13}} + \frac{\ln(1-\phi_3^\alpha)}{1-\phi_3^\alpha} \right] \left\{ 1 - \frac{\phi_1^\alpha\phi_3^\alpha}{(1-\phi_1^\alpha)(1-\phi_3^\alpha)} \right\} + \frac{\phi_1^\alpha\phi_3^\alpha}{(1-\phi_1^\alpha)(1-\phi_3^\alpha)} \frac{D_{13}}{1-c_{13}\phi_3^\alpha} \right] \phi_3^\alpha (1-\phi_1^\alpha) - \\ & D_{13} \left[\frac{\ln(1-c_{23}\phi_3^\alpha)}{c_{23}(1-\phi_3^\alpha)^2} - \frac{\phi_3^\alpha}{(1-\phi_3^\alpha)(1-c_{23}\phi_3^\alpha)} \right] \frac{V_1}{V_2} \phi_2^\alpha \phi_3^\alpha = \\ & \ln \phi_1^\beta + \left(1 - \frac{V_1}{V_2} \right) \phi_2^\beta + \left(1 - \frac{V_1}{V_3} \right) \phi_3^\beta + \\ & \left[\frac{D_{12}}{c_{12}} + \frac{\ln(1-\phi_2^\beta)}{1-\phi_2^\beta} \right] \left\{ 1 - \frac{\phi_1^\beta\phi_2^\beta}{(1-\phi_1^\beta)(1-\phi_2^\beta)} \right\} + \frac{\phi_1^\beta\phi_2^\beta}{(1-\phi_1^\beta)(1-\phi_2^\beta)} \frac{D_{12}}{1-c_{12}\phi_2^\beta} \left] \phi_2^\beta (1-\phi_1^\beta) + \right. \\ & \left. \left[\frac{D_{13}}{c_{13}} + \frac{\ln(1-\phi_3^\beta)}{1-\phi_3^\beta} \right] \left\{ 1 - \frac{\phi_1^\beta\phi_3^\beta}{(1-\phi_1^\beta)(1-\phi_3^\beta)} \right\} + \frac{\phi_1^\beta\phi_3^\beta}{(1-\phi_1^\beta)(1-\phi_3^\beta)} \frac{D_{13}}{1-c_{13}\phi_3^\beta} \right] \phi_3^\beta (1-\phi_1^\beta) - \\ & D_{23} \left[\frac{\ln(1-c_{23}\phi_3^\beta)}{c_{23}(1-\phi_3^\beta)^2} - \frac{\phi_3^\beta}{(1-\phi_3^\beta)(1-c_{23}\phi_3^\beta)} \right] \frac{V_1}{V_2} \phi_2^\beta \phi_3^\beta \end{aligned} \quad (47)$$

$$\begin{aligned}
 & \ln \phi_2^\alpha + \left(1 - \frac{V_2}{V_1}\right) \phi_1^\alpha + \left(1 - \frac{V_2}{V_3}\right) \phi_3^\alpha + \\
 & D_{12} \left[\frac{\ln(1 - c_{12} \phi_2^\alpha)}{c_{12}(1 - \phi_2^\alpha)^2} - \frac{\phi_2^\alpha}{(1 - \phi_2^\alpha)(1 - c_{12} \phi_2^\alpha)} \right] \phi_1^\alpha (1 - \phi_2^\alpha) \frac{V_2}{V_1} - D_{13} \left[\frac{\ln(1 - c_{13} \phi_3^\alpha)}{c_{13}(1 - \phi_3^\alpha)^2} - \frac{\phi_3^\alpha}{(1 - \phi_3^\alpha)(1 - c_{13} \phi_3^\alpha)} \right] \phi_1^\alpha \phi_3^\alpha \frac{V_2}{V_1} + \\
 & \left[\frac{D_{23}}{c_{23}} \frac{\ln(1 - \phi_3^\alpha)}{1 - \phi_3^\alpha} \left\{ 1 - \frac{\phi_2^\alpha \phi_3^\alpha}{(1 - \phi_2^\alpha)(1 - \phi_3^\alpha)} \right\} + \frac{\phi_2^\alpha \phi_3^\alpha D_{23}}{(1 - \phi_2^\alpha)(1 - \phi_3^\alpha)(1 - c_{13} \phi_3^\alpha)} \right] \phi_3^\alpha (1 - \phi_2^\alpha) \frac{V_2}{V_1} = \\
 & \ln \phi_2^\beta + \left(1 - \frac{V_2}{V_1}\right) \phi_1^\beta + \left(1 - \frac{V_2}{V_3}\right) \phi_3^\beta + \\
 & D_{12} \left[\frac{\ln(1 - c_{12} \phi_2^\beta)}{c_{12}(1 - \phi_2^\beta)^2} - \frac{\phi_2^\beta}{(1 - \phi_2^\beta)(1 - c_{12} \phi_2^\beta)} \right] \phi_1^\beta (1 - \phi_2^\beta) \frac{V_2}{V_1} - D_{13} \left[\frac{\ln(1 - c_{13} \phi_3^\beta)}{c_{13}(1 - \phi_3^\beta)^2} - \frac{\phi_3^\beta}{(1 - \phi_3^\beta)(1 - c_{13} \phi_3^\beta)} \right] \phi_1^\beta \phi_3^\beta \frac{V_2}{V_1} + \\
 & \left[\frac{D_{23}}{c_{23}} \frac{\ln(1 - \phi_3^\beta)}{1 - \phi_3^\beta} \left\{ 1 - \frac{\phi_2^\beta \phi_3^\beta}{(1 - \phi_2^\beta)(1 - \phi_3^\beta)} \right\} + \frac{\phi_2^\beta \phi_3^\beta D_{23}}{(1 - \phi_2^\beta)(1 - \phi_3^\beta)(1 - c_{13} \phi_3^\beta)} \right] \phi_3^\beta (1 - \phi_2^\beta) \frac{V_2}{V_1}
 \end{aligned} \tag{48}$$

and Equation (49):

$$\begin{aligned}
 & \ln \phi_3^\alpha + \left(1 - \frac{V_3}{V_1}\right) \phi_1^\alpha + \left(1 - \frac{V_3}{V_2}\right) \phi_2^\alpha - D_{12} \left[\frac{\ln(1 - c_{12} \phi_2^\alpha)}{c_{12}(1 - \phi_2^\alpha)^2} - \frac{\phi_2^\alpha}{(1 - \phi_2^\alpha)(1 - c_{12} \phi_2^\alpha)} \right] \phi_1^\alpha \phi_2^\alpha \frac{V_3}{V_1} + \\
 & D_{13} \left[\frac{\ln(1 - c_{13} \phi_3^\alpha)}{c_{13}(1 - \phi_3^\alpha)^2} - \frac{\phi_3^\alpha}{(1 - \phi_3^\alpha)(1 - c_{13} \phi_3^\alpha)} \right] \phi_1^\alpha (1 - \phi_3^\alpha) \frac{V_3}{V_1} + D_{23} \left[\frac{\ln(1 - c_{23} \phi_3^\alpha)}{c_{23}(1 - \phi_3^\alpha)^2} - \frac{\phi_3^\alpha}{(1 - \phi_3^\alpha)(1 - c_{23} \phi_3^\alpha)} \right] \phi_2^\alpha (1 - \phi_3^\alpha) \frac{V_3}{V_1} = \\
 & \ln \phi_3^\beta + \left(1 - \frac{V_3}{V_1}\right) \phi_1^\beta + \left(1 - \frac{V_3}{V_2}\right) \phi_2^\beta - D_{12} \left[\frac{\ln(1 - c_{12} \phi_2^\beta)}{c_{12}(1 - \phi_2^\beta)^2} - \frac{\phi_2^\beta}{(1 - \phi_2^\beta)(1 - c_{12} \phi_2^\beta)} \right] \phi_1^\beta \phi_2^\beta \frac{V_3}{V_1} + \\
 & D_{13} \left[\frac{\ln(1 - c_{13} \phi_3^\beta)}{c_{13}(1 - \phi_3^\beta)^2} - \frac{\phi_3^\beta}{(1 - \phi_3^\beta)(1 - c_{13} \phi_3^\beta)} \right] \phi_1^\beta (1 - \phi_3^\beta) \frac{V_3}{V_1} + D_{23} \left[\frac{\ln(1 - c_{23} \phi_3^\beta)}{c_{23}(1 - \phi_3^\beta)^2} - \frac{\phi_3^\beta}{(1 - \phi_3^\beta)(1 - c_{23} \phi_3^\beta)} \right] \phi_2^\beta (1 - \phi_3^\beta) \frac{V_3}{V_1}
 \end{aligned} \tag{49}$$

Again, the terms in brackets correspond to the χ_{ij} and ε_{ij} ($ij = 12, 13, 23$) interaction parameters in phases α or β derived with **b2** model.

It is interesting to note that both **b1** (Equation (39) or (40)) and **b2** (Equation (47) or (48)) models lead to the following expressions shown by Equations (50) and (51) when $\phi_3 = 0$ and $\phi_1 + \phi_2 = 1$, that is, in binary conditions:

$$\ln \phi_1^\alpha + \left(1 - \frac{V_1}{V_2}\right) \phi_2^\alpha + \chi_{12}^\alpha (\phi_1^\alpha)^2 = \ln \phi_1^\beta + \left(1 - \frac{V_1}{V_2}\right) \phi_2^\beta + \chi_{12}^\beta (\phi_1^\beta)^2 \tag{50}$$

$$\ln \phi_2^\alpha + \left(1 - \frac{V_2}{V_1}\right) \phi_1^\alpha + \varepsilon_{12}^\alpha (\phi_1^\alpha)^2 \frac{V_2}{V_1} = \ln \phi_2^\beta + \left(1 - \frac{V_2}{V_1}\right) \phi_1^\beta + \varepsilon_{12}^\beta (\phi_1^\beta)^2 \frac{V_2}{V_1} \tag{51}$$

that are those obtained for BPS [23, 25], evidencing the reliability of the models in spite of the mathematical complexity.

The advantage of using $\chi(T, \phi)$ and $\varepsilon(T, \phi)$ from models is the important reduction of the number of unknowns when mathematically solving the Equations (10)–(12). Once equilibrium compositions of each component in both phases are known (ϕ_i^α and ϕ_i^β), the system of equations has 12 unknowns to determine, namely: $g_{ij}^\alpha, g_{ij}^\beta, (dg_{ij}/d\phi_j)^2, (ij = 12, 13, 23)$. However, if model **b1** is applied, in Equations (39)–(41) remain only 9 unknowns: α_{ij}, D_{ij} and $c_{ij} (ij = 12, 13, 23)$. The reduction is more drastic if model **b2** is applied, since only 6 unknowns remain in the Equations (47)–(49): D_{ij} and $c_{ij} (ij = 12, 13, 23)$. In order to solve such systems, an additional number of equations must be generated,

6 in the case of **b1** model and 3 in the **b2** one, as it will be explained in the following.

3. Results and discussion

First of all, let us describe the TPS for which the calculations have been focused. They are ten polymer(2)/polymer(3) mixtures in CHCl₃ as solvent (component(1)), namely: polystyrene (PS)/poly(vinyl pyridine) (PVPy), poly(styrene-co-methacrylic acid) (PSMAA-3)/PVPy, PSMAA-6/PVPy, PSMAA-7/PVPy, poly(styrene-co-vinyl phenol) (PSVPh-2)/PVPy, PSVPh-4/PVPy, PSVPh-7/PVPy, PS/poly(vinyl pyrrolidone) (PVP), PSMAA-3/PVP and PSVPh-2/PVP; where the number following MMA or VPh indicates the percentage (% in weight) of comonomer in the corresponding copoly-

Table 1. Experimental compositions in equilibrium, $\phi_i^\gamma (i = 1, 2; \gamma = \alpha, \beta)$, from the binodal curve and randomly generated, u_i^γ and v_i^γ through **b1** model (Equations (39)–(41)), for different ternary solvent(1)/polymer(2)/polymer(3) systems

ϕ_1^α	ϕ_2^α	ϕ_1^β	ϕ_2^β	u_1^α	u_2^α	u_1^β	u_2^β	v_1^α	v_2^α	v_1^β	v_2^β
CHCl ₃ /PS/PVPy											
0.9607	0.0297	0.9753	0.0042	0.9630	0.0298	0.9733	0.0042	0.9606	0.0297	0.9708	0.0042
0.9678	0.0194	0.9761	0.0074	0.9701	0.0194	0.9741	0.0074	0.9677	0.0194	0.9716	0.0074
0.9559	0.0378	0.9781	0.0013	0.9582	0.0379	0.9761	0.0013	0.9558	0.0378	0.9736	0.0013
CHCl ₃ /PSMMA-3/PVPy											
0.7993	0.1745	0.9523	0.0072	0.8012	0.1749	0.9503	0.0072	0.7992	0.1745	0.9479	0.0072
0.8552	0.1182	0.96	0.0096	0.8573	0.1185	0.9580	0.0096	0.8551	0.1182	0.9556	0.0096
0.9290	0.0486	0.9578	0.0181	0.9312	0.0487	0.9558	0.0181	0.9289	0.0486	0.9534	0.0180
CHCl ₃ /PSMMA-6/PVPy											
0.7917	0.1734	0.9112	0.0204	0.7936	0.1738	0.9093	0.0204	0.7916	0.1734	0.9070	0.0203
0.8240	0.1409	0.9078	0.0317	0.8260	0.1412	0.9059	0.0316	0.8239	0.1409	0.9036	0.0316
0.8803	0.0723	0.8982	0.0482	0.8824	0.0725	0.8963	0.0481	0.8802	0.0723	0.8941	0.0480
CHCl ₃ /PSMMA-7/PVPy											
0.7670	0.2087	0.9047	0.0097	0.7668	0.2092	0.9028	0.0097	0.7669	0.2087	0.9006	0.0097
0.8680	0.0925	0.8995	0.0371	0.8701	0.0927	0.8976	0.0370	0.8679	0.0925	0.8954	0.0369
0.9541	0.0241	0.9644	0.0134	0.9564	0.0242	0.9624	0.0134	0.9540	0.0241	0.9600	0.0133
CHCl ₃ /PSVPh-2/PVPy											
0.9009	0.0843	0.9643	0.008	0.9031	0.0845	0.9623	0.0080	0.9008	0.0843	0.9599	0.0080
0.9369	0.0463	0.9656	0.0109	0.9392	0.0464	0.9636	0.0109	0.9368	0.0463	0.9618	0.0109
0.9541	0.0241	0.9644	0.0134	0.9564	0.0242	0.9624	0.0134	0.9540	0.0241	0.9600	0.0133
CHCl ₃ /PSVPh-4/PVPy											
0.8833	0.0814	0.9443	0.0056	0.8854	0.0816	0.9423	0.0059	0.8832	0.0814	0.9400	0.0056
0.9238	0.0445	0.9442	0.0161	0.9260	0.0446	0.9422	0.0161	0.9237	0.0445	0.9399	0.0160
CHCl ₃ /PSVPh-7/PVPy											
0.9211	0.0646	0.9671	0.0051	0.9233	0.0648	0.9651	0.0051	0.9210	0.0646	0.9627	0.0051
0.9397	0.0446	0.9629	0.0138	0.9420	0.0447	0.9609	0.0138	0.9396	0.0446	0.9585	0.0137
CHCl ₃ /PS/PVP											
0.9212	0.0675	0.9511	0.0155	0.9234	0.0677	0.9491	0.0155	0.9211	0.0675	0.9467	0.0154
0.9349	0.0498	0.9522	0.0189	0.9372	0.0499	0.9502	0.0189	0.9348	0.0498	0.9478	0.0188
CHCl ₃ /PSMMA-3/PVP											
0.8277	0.0891	0.8990	0.0024	0.8297	0.0893	0.8971	0.0024	0.8276	0.0891	0.8949	0.0024
0.8741	0.0467	0.8904	0.0208	0.8735	0.0468	0.8885	0.0208	0.8713	0.0467	0.8863	0.0207
CHCl ₃ /PSVPh-2/PVP											
0.8370	0.0927	0.9016	0.0067	0.8390	0.0929	0.8997	0.0067	0.8369	0.0927	0.8975	0.0067
0.8781	0.0447	0.8985	0.0169	0.8802	0.0448	0.8966	0.0169	0.8780	0.0447	0.8944	0.0168

mers. The supplier, characterization and physico-chemical properties of all the chemicals used have been recently described, as well as the experimental ternary phase diagrams determined by liquid chromatography with SEC columns [17]. These diagrams have served to obtain all the phase compositions for each component through the tie-lines joining the two phases in equilibrium at the binodal or cloud-point isotherm as explained elsewhere [17, 20–22].

Next, following the methods and procedure described in the Theory section, the volume fractions ϕ_i^γ ($i = 1, 2, 3; \gamma = \alpha, \beta$) have been determined for all the phases equilibria of the above TPS and are compiled in Table 1. As mentioned above, Equations (39)–(41) generated through the model **b1** contain 9 unknowns: α_{ij} , D_{ij} and c_{ij} ($ij = 12, 13, 23$) and in order to solve the system, 6 additional

equations should be written. These additional equations are analogous in form to Equations (39)–(41) but with new compositions randomly generated, that differ from the original ones by a quantity no larger than $\pm 0.5\%$. To do this, the original compositions in phase α (ϕ_i^α) are multiplied by the function $(1+0.005 \text{ Random})$ [26] and those in phase β (ϕ_i^β) by $(1-0.005 \text{ Random})$. Therefore, a new set of compositions, namely u_i^γ ($i = 1, 2, 3; \gamma = \alpha, \beta$) are obtained. The third set, v_i^γ ($i = 1, 2, 3; \gamma = \alpha, \beta$), is generated by multiplying the original compositions by the function $(1-0.005 \text{ Random})$. Summarizing, the 9 equations are: the (39)–(41) ones formed with ϕ_i^γ , 3 with u_i^γ (compositions very close to ϕ_i^γ and with unknowns concentration dependent assumed to remain invariants) and 3 more with v_i^γ (also very close to ϕ_i^γ with unknowns also invariant). It must be remarked that u_i^γ and v_i^γ are randomly generated,

Table 2. Interaction parameters evaluated from Equations (39)–(41) for different ternary polymer systems

ϕ_1^α	χ_{12}^α	χ_{12}^β	χ_{13}^α	χ_{13}^β	χ_{23}^α	χ_{23}^β	ϵ_{23}^α	ϵ_{23}^β	g_{12}^α	g_{12}^β	g_{13}^α	g_{13}^β	g_{23}^α	g_{23}^β
CHCl ₃ /PS/PVPy														
0.9607	0.5319	0.5870	0.5533	0.5418	0.1204	0.1559	0.1526	0.2150	0.5020	0.5045	0.5607	0.5612	0.1551	0.2153
0.9678	0.5760	0.5560	0.5350	0.5810	0.0043	0.0035	0.0003	0.0005	0.5760	0.5770	0.4530	0.4520	0.0003	0.0005
0.9559	0.5545	0.5000	0.5322	0.5667	0.0870	0.0930	0.0887	0.1086	0.5540	0.5550	0.5260	0.5250	0.0900	0.1022
0.9597	0.4965	0.4737	0.5350	0.5470	0.0162	0.1395	0.0480	0.4340	0.4630	0.4670	0.5640	0.5650	0.0490	0.4407
0.9645	0.5570	0.6400	0.4650	0.5801	0.0120	0.0120	0.0120	0.0120	0.6440	0.6420	0.4020	0.3980	0.0120	0.0120
CHCl ₃ /PSMMA-3/PVPy														
0.7993	0.6500	0.6910	0.2240	0.6330	0.0130	0.0130	0.0110	0.0120	1.1200	0.7520	0.1310	0.1160	0.0110	0.0120
0.8552	0.6390	0.6530	0.4970	0.5220	-0.0830	-0.0740	-0.0430	-0.0335	1.0805	0.7665	0.0970	0.0920	-0.0440	-0.0341
0.9290	0.7120	0.6690	0.3560	0.5340	-0.0410	-0.0420	-0.0510	-0.0520	0.9090	0.6910	0.1380	0.9534	-0.0520	-0.0530
CHCl ₃ /PSMMA-6/PVPy														
0.7917	0.6630	0.8430	0.2860	0.4950	0.0810	0.0530	0.0520	0.0044	1.0610	0.9230	0.2320	0.2060	0.0520	0.0041
0.8240	0.5740	0.5730	0.5800	0.6110	-0.0780	-0.0670	-0.0630	-0.0330	0.5720	0.5720	0.5650	-0.5610	-0.0640	-0.0340
0.8803	0.6800	0.6980	0.5670	0.6400	-0.0041	-0.0041	-0.0045	-0.0047	0.8113	0.8010	0.2670	0.2600	-0.0074	-0.0048
CHCl ₃ /PSMMA-7/PVPy														
0.7670	0.6800	0.6890	0.4310	0.4370	-0.1280	-0.1720	-0.1440	-0.2140	0.7000	0.6910	0.4500	0.4500	-0.1500	-0.2230
0.8680	0.5650	0.6540	0.5820	0.6010	-0.0390	-0.0310	-0.0270	-0.0002	0.5700	0.5700	0.5260	0.4220	-0.0280	-0.0002
CHCl ₃ /PSVPh-2/PVPy														
0.9009	0.5410	0.5700	0.7751	0.7722	0.1160	0.0221	-0.0680	-0.0690	0.4901	0.5003	0.8242	0.8244	-0.0690	-0.0690
0.9369	0.6010	0.6692	0.4041	0.5253	-0.0191	-0.0173	-0.0142	-0.0086	0.7392	0.7261	0.3111	0.3074	-0.0140	-0.0087
0.9541	0.6441	0.6683	0.4490	0.4970	-0.0044	-0.0043	-0.0022	-0.0022	0.7480	0.7440	0.2960	0.2931	-0.0022	-0.0021
CHCl ₃ /PSVPh-4/PVPy														
0.9238	0.7550	0.7582	0.5140	0.5981	-0.1280	-0.2318	-0.5170	-0.6800	0.7620	0.7611	0.5932	0.5881	-0.5260	-0.6911
CHCl ₃ /PSVPh-7/PVPy														
0.9211	0.5820	0.5670	0.5050	0.5402	-0.2291	-0.2493	-0.2603	-0.2653	0.5590	0.5622	0.4651	0.4643	-0.2641	-0.2702
0.9397	0.5840	0.6192	0.4571	0.5403	-0.0370	-0.0391	-0.0392	-0.0423	0.6661	0.6592	0.3772	0.3743	-0.0402	-0.0420
CHCl ₃ /PS/PVP														
0.9212	0.5921	0.6961	0.5903	0.5900	0.3391	0.2762	0.2991	0.1830	0.7862	0.7623	0.5881	0.5882	0.3042	0.1850
0.9349	0.6470	0.6581	0.5542	0.5271	0.3072	0.3051	0.3011	0.2912	0.6760	0.6742	0.5703	0.5724	0.3052	0.2851
CHCl ₃ /PSMMA-3/PVP														
0.8277	0.7001	0.6362	0.4741	0.5603	-0.1771	-0.1652	-0.1461	-0.0290	0.6342	0.6333	0.3920	0.3853	-0.1481	-0.0291
0.8714	0.7382	0.7753	0.4480	0.4751	-0.0007	-0.0003	0.0027	0.0033	0.8461	0.8311	0.3250	0.3233	0.0028	0.0033
CHCl ₃ /PSVPh-2/PVP														
0.8370	0.7270	0.7510	0.3490	0.3951	-0.0172	-0.0101	0.0015	0.0152	0.9370	0.8752	0.3060	0.3021	0.0015	0.0154
0.8781	0.7641	0.7893	0.4622	0.4971	-0.0072	-0.0076	-0.0103	-0.0107	0.8261	0.8172	0.2953	0.2931	-0.0103	-0.0108

therefore their equations should not be lineal combinations of those formed with ϕ_i^γ . Both composition sets, u_i^γ and v_i^γ , have been also included in Table 1. Note that the values corresponding to component 3 have been omitted given by Equation (52):

$$\sum_{i=1}^3 \phi_i = \sum_{i=1}^3 u_i = \sum_{i=1}^3 v_i \quad (52)$$

Once solved the 9 equations system, the α_{ij} , D_{ij} and c_{ij} ($ij = 12, 13, 23$) values are obtained being then possible to evaluate the 14 interaction parameters for each compositions set. In Table 2 are gathered the obtained results with **b1** model for all the studied systems.

Let us now discuss the values of the interaction parameters, starting by those determined with the model **b1** (listed in Table 2). The analysis will be done on the χ_{ij}^γ ($ij = 12, 13, 23; \gamma = \alpha, \beta$) and ϵ_{ij}^γ values since they are better known than the g_{ij}^γ parameters [24, 27–29]. In Figure 1, the dependence of the binary χ_{12}^α and χ_{12}^β parameters with the binary compositions $\phi_2^\beta = \phi_2/(1-\phi_3)$ is plotted for the system $\text{CHCl}_3/\text{PS}/\text{PVPy}$, as an example. For the sake of comparison, Figure 1 also shows some χ_{12} values of CHCl_3/PS from the literature [30]. The observed behaviour is the typical trend for good solvents and it seems that no disagreement takes place between experimental and theoretical values, neither with the values $\chi_{12}^0 = 0.51, 0.53$ [24] or with $g_{12}^0 = 0.543, 0.720$ [24], where the superscript 0 means infinite dilution. Similar χ_{13}^α and χ_{13}^β values (Table 2) are found at any composition (a narrow composition range), just slightly larger than those

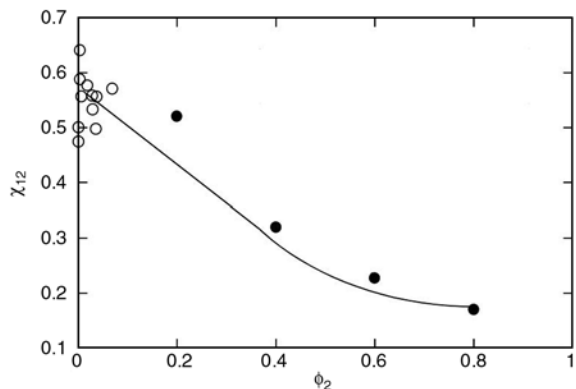


Figure 1. Dependence with composition of χ_{12} interaction parameters evaluated in this paper (o) and literature ones (•) [30], for the $\text{CHCl}_3(1)/\text{PS}(2)$ system

found in the literature: $\chi_{13} = 0.35, 0.44$ [24]. Regarding the χ_{23} and ϵ_{23} values, they appear always lower than experimental, as expected [14, 19].

The χ_{ij}^γ and ϵ_{ij}^γ values for the systems $\text{CHCl}_3/\text{PSMAA-x}/\text{PVPy}$ with three different MAA contents are also gathered in Table 2, showing similar behaviours to those above discussed with pure PS as component 2 but with some differences which deserve to be commented. Since no appreciable changes in the values of $\chi_{12}^\alpha, \chi_{12}^\beta, \chi_{13}^\alpha, \dots$ at the diverse compositions have been found, it should be more illustrative to use mean values for the parameters; which are listed in Table 3. As seen, χ_{12}^α and χ_{12}^β values smoothly increase with the MAA content in the copolymer, in agreement with the behaviour followed by their intrinsic viscosities, $[\eta_2]$ [17], shown in Figure 2a. The χ_{13}^α and χ_{13}^β values

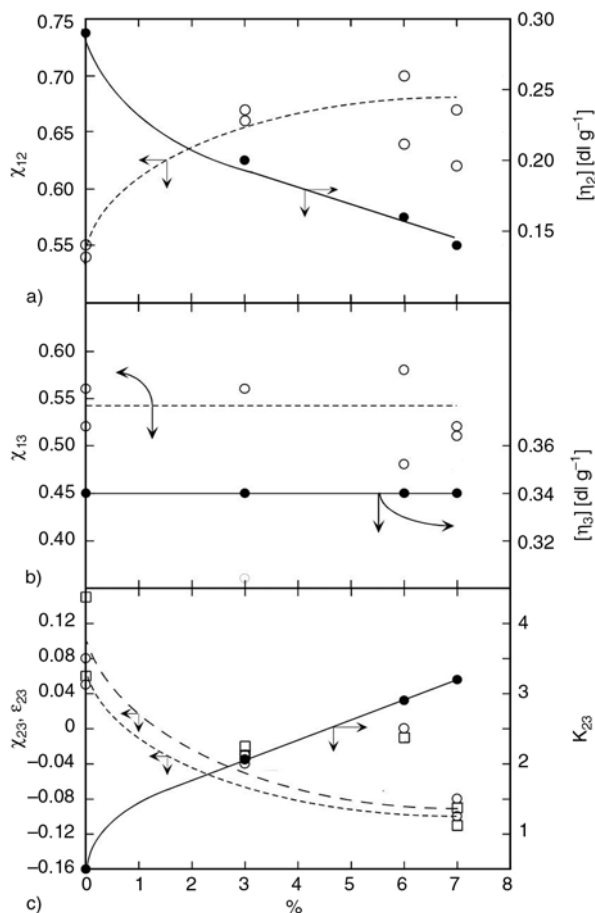


Figure 2. Variation with MAA content (in %) of different magnitudes for the $\text{CHCl}_3(1)/\text{PSMAA-x}(2)/\text{PVPy}(3)$ systems: (a) mean interaction parameters $\bar{\chi}_{12}$ from Table 3 (o, ----) and $[\eta_2]$ (•, —); (b) mean interaction parameters $\bar{\chi}_{13}$ from Table 3 (o, ----) and $[\eta_3]$ (•, —); and (c) $\bar{\chi}_{23}$ (o, ----), ϵ_{23} (□, —) and K_{23} viscometric parameter (•, —) from [17]

practically do not change with MAA content and are smaller than the χ_{12} ones, probably due to the weak hydrogen bonds that can be established between CHCl_3 and PVPy because of the slight acid character of CHCl_3 [31]. Dependences with MAA content of χ_{13}^α , χ_{13}^β and $[\eta_3]$ are shown in Figure 2b. As it can be seen, χ_{13} values range between 0.48 and 0.58 and $[\eta_3]$ values do not change with component 2 nature, which seems to indicate that this component has no influence on the 1-3 interactions. Finally, in Figure 2c strong χ_{23} or ϵ_{23} dependences on copolymer PSMAA composition are observed. The calculated values even reach negative figures, typical of stable blends [14, 27], as the MAA content is raised, probably due to hydrogen bond specific interactions between MAA (H-donor) and PVPy (H-acceptor). Moreover, for these systems, the χ_{23} values can be evaluated through $\chi_{23} = \chi_{\text{PS-PVPy}}\phi_{\text{PS}} + \chi_{\text{MAA-PVPy}}\phi_{\text{MAA}}$ with ϕ_{PS} and ϕ_{MAA} standing for the respective volume fractions of PS and MAA in the copolymer [32]. As $\chi_{\text{PS-PVPy}}$ displays positive values and decreases with rising MAA content in the copolymer, the term $\chi_{\text{PS-PVPy}}\phi_{\text{PS}}$ will also decrease. On the other hand, $\chi_{\text{MAA-PVPy}}$ will have negative values, decreasing with rising MMA content as it does the term $\chi_{\text{MAA-PVPy}}\phi_{\text{MAA}}$. Since both terms work in the same direction, the χ_{23} values will decrease with rising MAA content in the copolymer, as seen in Figure 2c and in Table 3. The parallel increase of the K_{23} viscometric parameter [17], also plotted in Figure 2c, confirms the increasing stability of the polymer mixtures as the MMA content goes up. Finally, ϵ_{23} values in these systems are small and positive in agreement with recently published ones [19].

Table 3 also gathers values of the interaction parameters calculated for $\text{CHCl}_3/\text{PSVPh-y}/\text{PVPy}$ systems at three different VPh contents. χ_{12}^α and χ_{12}^β

values smoothly increase with the VPh content, except for the PSVPh-7 where they slightly decrease. In any case, the increase in χ_{12} is in agreement with the decreasing $[\eta_2]$, as shown in Figure 3a. Figure 3b depicts the χ_{13}^α and χ_{13}^β dependences with VPh content and shows that χ_{13} values remain practically constant (between 0.48 and 0.60), as in the preceding analyzed systems. Again, it seems that the component 2 nature plays scarce if any influence on 1-3 interactions. Finally, Figure 3c shows the χ_{23} or ϵ_{23} dependences on copolymer composition. As can be seen, decreasing χ_{23} or ϵ_{23} and increasing K_{23} values when rising the VPh content are the normal behaviours. However, the viscosity values and the ternary phase diagram (figure 2 in ref. [17]) were anomalous in the system $\text{CHCl}_3/\text{PSVPh-7}/\text{PVPy}$, in which a diminution of stability (stable zones outside the binodal) accounts probably due to self-associations competing with inter-associations. The anomalous K_{23} decrease in the PSVPh-7 is also reflected in χ_{23} or ϵ_{23} values here calculated, as corroborated in Figure 3c.

Similar results have been attained for systems including the H-acceptor PVP as component 3, namely: $\text{CHCl}_3/\text{PS}/\text{PVP}$, $\text{CHCl}_3/\text{PSMAA-3}/\text{PVP}$ and $\text{CHCl}_3/\text{PSVPh-2}/\text{PVP}$, as it can be seen in Table 3. The χ_{12}^α and χ_{12}^β values slightly increase when rising the H-donor comonomer content in both copolymers, in correspondence with the expected decrease of $[\eta_2]$ [17], as shown in Figure 4. Similar evolutions with MMA or VPh content to the previously discussed systems are also followed by the χ_{12}^α , χ_{23}^α , ϵ_{12}^α , ϵ_{23}^α parameters. These magnitudes decrease up to small negative values with increasing H-donor comonomer content, whereas the K_{23} viscometric parameters increase, as also seen in Figure 4. As a summary, the results in Table 2, obtained through the **b1**

Table 3. Interaction parameters mean values from Table 2 data

System	$\bar{\chi}_{12}^\alpha$	$\bar{\chi}_{12}^\beta$	$\bar{\chi}_{13}^\alpha$	$\bar{\chi}_{13}^\beta$	$\bar{\chi}_{23}^\alpha$	$\bar{\chi}_{23}^\beta$	$\bar{\epsilon}_{23}^\alpha$	$\bar{\epsilon}_{23}^\beta$
$\text{CHCl}_3/\text{PS}/\text{PVPy}$	0.54	0.55	0.52	0.56	0.05	0.08	0.06	0.15
$\text{CHCl}_3/\text{PSMMA-3}/\text{PVPy}$	0.66	0.67	0.36	0.56	-0.04	-0.03	-0.03	-0.02
$\text{CHCl}_3/\text{PSMMA-6}/\text{PVPy}$	0.64	0.70	0.48	0.58	0.00	0.00	-0.01	-0.01
$\text{CHCl}_3/\text{PSMMA-7}/\text{PVPy}$	0.62	0.67	0.51	0.52	-0.08	-0.10	-0.09	-0.11
$\text{CHCl}_3/\text{PSVPh-2}/\text{PVPy}$	0.60	0.62	0.54	0.60	0.03	0.00	-0.03	-0.03
$\text{CHCl}_3/\text{PSVPh-4}/\text{PVPy}$	0.76	0.76	0.51	0.60	-0.13	-0.23	-0.52	-0.68
$\text{CHCl}_3/\text{PSVPh-7}/\text{PVPy}$	0.58	0.59	0.48	0.54	-0.14	-0.14	-0.15	-0.15
$\text{CHCl}_3/\text{PS}/\text{PVP}$	0.62	0.68	0.57	0.56	0.32	0.29	0.30	0.24
$\text{CHCl}_3/\text{PSMMA-3}/\text{PVP}$	0.72	0.71	0.46	0.52	-0.09	-0.08	-0.07	-0.01
$\text{CHCl}_3/\text{PSVPh-2}/\text{PVP}$	0.74	0.77	0.41	0.45	-0.01	-0.01	0.00	0.07

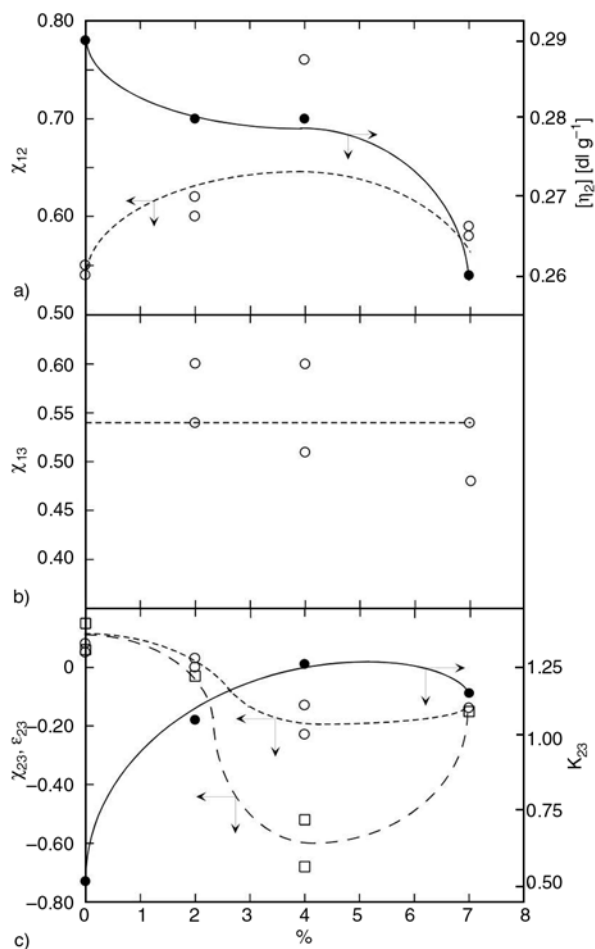


Figure 3. Variation with MAA content (in %) of different magnitudes for the $\text{CHCl}_3(1)/\text{PSVPh-y}(2)/\text{PVPy}(3)$ systems: (a) mean interaction parameters $\bar{\chi}_{12}$ from Table 3 and $[\eta_2]$; (b) mean interaction parameters $\bar{\chi}_{13}$ from Table 3; and (c) $\bar{\chi}_{23}$, ϵ_{23} and K_{23} viscometric parameter from [17]. Symbols as in Figure 2

model (Equations (39)–(41)) seem to be satisfactory and even values as $g_{13} = 0.46_3$ for the $\text{CHCl}_3/\text{PVPy}$ system [24] or $g_{12} = 0.54_3, 0.72_0$ for the CHCl_3/PS system [24] are fairly reflected in the corresponding data of Table 2. In conclusion, it can be quoted that the **b1** approach is a good enough procedure to describe and calculate the interaction parameters.

On the other hand, the molar volumes, V_i , necessary to apply the **b2** model (Equations (47)–(49)) were deduced from data on specific volumes and molar masses of the components and were previously reported [17]. The application of model **b2** leads to 6 unknowns (D_{ij} and c_{ij} with $ij = 12, 13, 23$) and therefore, 6 equations are necessary to deduce them: 3 of them are generated with the original compositions ϕ_i^γ and the other three by applying

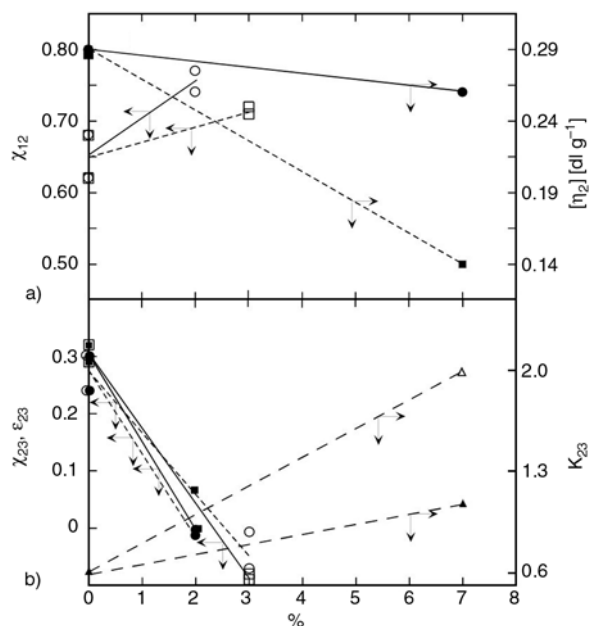


Figure 4. (a) Variation with component 2 nature and composition of χ_{12} interaction parameters for $\text{CHCl}_3(1)/\text{PSMAA-x}(2)/\text{PVP}(3)$ (\square , ----) and $\text{CHCl}_3(1)/\text{PSVPh-y}(2)/\text{PVP}(3)$ systems (\circ , ----), as well as $[\eta_2]$ intrinsic viscosities from [17] for $\text{CHCl}_3(1)/\text{PSMAA-x}(2)/\text{PVP}(3)$ (\blacksquare , ----) and $\text{CHCl}_3(1)/\text{PSVPh-y}(2)/\text{PVP}(3)$ systems (\bullet , —); (b) Variation with component 2 composition and nature of χ_{23} (squares, —) and ϵ_{23} (circles, ----) interaction parameters and K_{23} viscometric parameters from [17] (triangles, ----) for $\text{CHCl}_3(1)/\text{PSMAA-x}(2)/\text{PVP}(3)$ (empty symbols) and $\text{CHCl}_3(1)/\text{PSVPh-y}(2)/\text{PVP}(3)$ (filled symbols) systems

randomly generated compositions u_i^γ . In Table 4 are gathered ϕ_1^α (the remaining ϕ_i^γ values have been already given in Table 1) and u_i^γ values. Once solved the 6 equations system, it is possible to obtain the 14 interaction parameters for each composition set of any system, which are compiled in Table 5. As before, mean values of χ_{12}^γ , χ_{13}^γ , χ_{23}^γ , and ϵ_{23}^γ , ($\gamma = \alpha, \beta$) have been gathered in Table 6. For the system $\text{CHCl}_3/\text{PS}/\text{PVPy}$ the χ_{12}^α mean values seem to be acceptable, but the χ_{12}^β ones are extremely low and incomprehensible. Similar behaviours follow the χ_{13}^α and χ_{13}^β values, that is, very low values becoming strongly negative as the H-donor comonomer content raises. The χ_{13} small positive values for the systems $\text{CHCl}_3/\text{PVPy}$ or CHCl_3/PVP are not supported by literature results, and the strongly negative ones neither can be explained by the weakly H-donor character of CHCl_3 [31]. The obtained values seem to be the

Table 4. Experimental compositions in equilibrium, ϕ_1^α , from the binodal curve and randomly generated, u_i^γ ($i = 1, 2, 3$; $\gamma = \alpha, \beta$), through **b2** model (Equations (47)–(49)) for different ternary polymer systems

ϕ_1^α	u_1^α	u_2^α	u_3^α	u_1^β	u_2^β	u_3^β
CHCl ₃ /PS/PVPy						
0.9607	0.9611	0.0297	0.0092	0.9720	0.0042	0.0238
0.9678	0.9682	0.0194	0.0124	0.9728	0.0074	0.0198
0.9559	0.9563	0.0378	0.0059	0.9748	0.0013	0.0239
CHCl ₃ /PSMMA-3/PVPy						
0.7993	0.7996	0.1746	0.0258	0.9491	0.0072	0.0437
0.8552	0.8556	0.1182	0.0262	0.9568	0.0096	0.0337
0.9290	0.9294	0.0486	0.0220	0.9546	0.0180	0.0274
CHCl ₃ /PSMMA-6/PVPy						
0.7917	0.7920	0.1735	0.0345	0.9081	0.0203	0.0716
0.8240	0.8243	0.1410	0.0347	0.9047	0.0316	0.0637
0.8803	0.8807	0.0723	0.0470	0.8952	0.0480	0.0568
CHCl ₃ /PSMMA-7/PVPy						
0.7670	0.7673	0.2088	0.0239	0.9016	0.0097	0.0887
0.868	0.8684	0.0925	0.0391	0.8965	0.0370	0.0666
CHCl ₃ /PSVPh-2/PVPy						
0.9009	0.9013	0.0843	0.0144	0.9610	0.0080	0.0310
0.9369	0.9373	0.0463	0.0164	0.9623	0.0109	0.0268
0.9541	0.9545	0.0241	0.0214	0.9611	0.0134	0.0255
CHCl ₃ /PSVPh-4/PVPy						
0.8833	0.8837	0.0814	0.0349	0.9411	0.0558	0.0533
0.9238	0.9242	0.0445	0.0313	0.9410	0.0160	0.0429
CHCl ₃ /PSVPh-7/PVPy						
0.9211	0.9215	0.0646	0.0139	0.9638	0.0051	0.0311
0.9397	0.9410	0.0446	0.0153	0.9596	0.0138	0.0266
CHCl ₃ /PS/PVP						
0.9212	0.9216	0.0675	0.0109	0.9479	0.0154	0.0367
0.9349	0.9353	0.0498	0.0149	0.9490	0.0188	0.0322
CHCl ₃ /PSMMA-3/PVP						
0.8277	0.8280	0.0891	0.0828	0.8960	0.0024	0.1016
0.8741	0.8718	0.0467	0.0815	0.8874	0.0207	0.0919
CHCl ₃ /PSVPh-2/PVP						
0.8370	0.8373	0.0927	0.0699	0.8986	0.0067	0.0948
0.8781	0.8785	0.0447	0.0768	0.8955	0.0168	0.0877

most appropriate, since these magnitudes use to display small positive [19] or negative [14, 26] values in blends. However, as seen before and as expected, they do not become more negative with increasing the H-donor content of copolymer neither follow the expected viscometric behaviour [17]. As a summary, obtained results from **b2** model (Equations (47)–(49)) are unsatisfactory, in sharp contrast with those determined with the **b1** model (Equations (39)–(41)). Probably, the main reason for these results is the fact that the α parameter is used in the **b1** model but ignored in the **b2** approach. As a conclusion, the obtained interaction parameters through the **b1** approach are considerably better than those coming from **b2** approach, in spite of the need of an additional fitting parameter

in the former, an aspect long supported for binary solvent/polymer systems [33].

4. Conclusions

Two theoretical approaches to calculate χ_{ij} or ϵ_{ij} and g_{ij} interaction parameters in ternary polymer systems with specific interactions have been proposed. The validity of both models has been checked and assessed by comparison between the calculated values and those experimentally obtained through ternary phase diagrams. In general, the values calculated with model **b1** (Equations (39)–(41)) show a fair agreement with the experimental ones found in the literature. Moreover, in the systems where the component 2 is a

Table 5. Interaction parameters evaluated from Equations (47)–(49) for different ternary polymer systems

Φ_1^α	χ_{12}^α	χ_{12}^β	χ_{13}^α	χ_{13}^β	χ_{23}^α	χ_{23}^β	ϵ_{23}^α	ϵ_{23}^β	g_{12}^α	g_{12}^β	g_{13}^α	g_{13}^β	g_{23}^α	g_{23}^β
CHCl ₃ /PS/PVPy														
0.9607	0.5066	0.0727	0.1146	0.3439	0.0247	0.0249	0.0022	0.0035	0.0160	0.0018	0.0050	0.0101	0.6549	1.1110
0.9678	0.4405	0.2228	-0.0466	-0.0637	0.0452	0.0056	0.0006	0.0008	0.0141	0.0053	0.0489	0.0504	0.1614	0.2074
0.9559	0.4485	-0.0297	0.0291	0.0834	0.0211	0.0254	0.0015	0.0037	0.0209	0.0070	0.0021	0.0040	0.4158	1.0347
CHCl ₃ /PSMMA-3/PVPy														
0.7993	0.5489	0.0623	-0.4608	-2.3319	-0.0419	-0.0282	0.0005	0.0007	0.1124	0.0032	0.8730	0.9370	0.1301	0.1944
0.8552	0.5388	0.0889	-0.2358	-0.9588	0.1793	0.2316	0.0007	0.0008	0.0665	0.0037	1.1279	1.1377	0.1712	0.1970
0.9290	0.4674	0.1402	-0.1137	-0.1975	-0.0402	-0.0408	0.0003	0.0003	0.0207	0.0054	0.2416	0.2426	0.0750	0.0810
CHCl ₃ /PSMMA-6/PVPy														
0.7917	0.5747	0.1232	-0.0364	-0.1013	0.1183	0.2574	0.0001	0.0002	0.1410	0.0127	0.2740	0.2904	0.0289	0.0592
0.8240	0.5888	0.0755	-0.1061	-0.2283	0.2525	0.4653	0.0002	0.0003	0.0592	0.0071	0.6076	0.6366	0.0450	0.0795
0.8803	0.2396	0.0053	-0.5110	-0.6165	-0.0978	-0.0971	0.0019	0.0022	0.0015	0.0003	1.0170	1.0323	0.5283	0.5881
CHCl ₃ /PSMMA-7/PVPy														
0.7670	0.5175	0.0680	-0.0431	-0.1317	0.0307	0.1838	0.0003	0.0011	0.1346	0.0051	0.3673	0.4094	0.0630	0.2482
0.8680	0.3650	0.0359	-0.3033	-1.2969	0.0549	0.0626	0.0033	0.0101	0.1650	0.0032	0.0342	0.0741	0.6810	1.5535
CHCl ₃ /PSVPh-2/PVPy														
0.9009	0.4118	0.0591	-0.1178	-0.3544	0.1823	0.3546	0.0001	0.0002	0.0324	0.0021	0.3460	0.3590	0.0390	0.0746
0.9369	0.3796	0.0249	-0.1983	-0.3770	0.1993	0.2840	0.0001	0.0002	0.0074	0.0008	0.3552	0.3621	0.0526	0.0741
0.9541	0.1806	0.0182	-0.1404	-0.1830	0.1018	0.1023	0.0003	0.0003	0.0017	0.0005	0.1773	0.1774	0.1267	0.1240
CHCl ₃ /PSVPh-4/PVPy														
0.8833	0.4600	-0.0683	-0.5441	-1.9430	-0.0001	-0.0001	0.0000	0.0000	0.0524	0.0034	0.0670	0.1006	0.0176	0.0181
0.9238	0.4175	0.0056	-0.3700	-0.5203	-0.0053	-0.0014	0.0005	0.0008	0.0025	0.0003	0.5899	0.6017	0.1280	0.1967
CHCl ₃ /PSVPh-7/PVPy														
0.9211	0.5636	0.1174	-0.0030	-0.0076	0.0039	0.0064	0.0000	0.0000	0.0410	0.0030	0.0076	0.0079	0.0109	0.0210
0.9397	0.5512	0.2829	-0.0206	-0.0346	0.0225	0.0338	0.0000	0.0000	0.0342	0.0103	0.0384	0.0392	0.0004	0.0006
CHCl ₃ /PS/PVP														
0.9212	0.4279	0.0270	0.0201	0.1283	0.0527	0.0647	0.0022	0.0045	0.0117	0.0012	0.0016	0.0055	0.6125	1.3915
0.9349	0.3065	0.0748	-0.0421	-0.0592	0.0234	0.0246	0.0013	0.0019	0.0123	0.0032	0.0782	0.0811	0.3676	0.5789
CHCl ₃ /PSMMA-3/PVP														
0.8277	0.4470	0.0055	-0.8054	-1.5043	-0.0680	-0.0633	0.0008	0.0009	0.0451	0.0006	0.8576	0.9010	0.2037	0.2388
0.8714	0.2230	0.0042	-0.2872	-0.3460	-0.0414	-0.0415	0.0006	0.0006	0.0026	0.0004	0.7975	0.8069	0.1536	0.1655
CHCl ₃ /PSVPh-2/PVP														
0.8370	0.4245	0.0515	-0.0503	-0.0911	0.1362	0.1861	0.0000	0.0001	0.0496	0.0033	0.2941	0.3037	0.0126	0.0168
0.8781	0.2576	0.0033	-0.6400	-0.7908	0.2147	0.2542	0.0013	0.0014	0.0026	0.0003	0.9441	0.9600	0.4402	0.4900

Table 6. Interaction parameters mean values from Table 5 data

System	$\bar{\chi}_{12}^\alpha$	$\bar{\chi}_{12}^\beta$	$\bar{\chi}_{13}^\alpha$	$\bar{\chi}_{13}^\beta$	$\bar{\chi}_{23}^\alpha$	$\bar{\chi}_{23}^\beta$	$\bar{\epsilon}_{23}^\alpha$	$\bar{\epsilon}_{23}^\beta$
CHCl ₃ /PS/PVPy	0.47	0.11	0.03	0.12	0.03	0.04	0.00	0.00
CHCl ₃ /PSMMA-3/PVPy	0.52	0.10	-0.27	-1.16	0.03	0.05	0.00	0.00
CHCl ₃ /PSMMA-6/PVPy	0.47	0.07	-0.22	-0.32	0.09	0.21	0.00	0.00
CHCl ₃ /PSMMA-7/PVPy	0.44	0.05	-0.17	-0.71	0.04	0.12	0.00	0.01
CHCl ₃ /PSVPh-2/PVPy	0.32	0.03	-0.15	-0.30	0.16	0.25	0.00	0.00
CHCl ₃ /PSVPh-4/PVPy	0.44	0.04	-0.46	-1.23	0.00	0.00	0.00	0.00
CHCl ₃ /PSVPh-7/PVPy	0.56	0.20	-0.01	-0.02	0.01	0.02	0.00	0.00
CHCl ₃ /PS/PVP	0.37	0.05	-0.01	0.03	0.04	0.04	0.00	0.00
CHCl ₃ /PSMMA-3/PVP	0.34	0.01	-0.55	-0.93	-0.05	-0.05	0.00	0.01
CHCl ₃ /PSVPh-2/PVP	0.34	0.03	-0.35	-0.44	0.18	0.22	0.00	0.00

copolymer, the χ_{13} values practically do not change with the copolymer content (MMA or VPh) denoting that the chemical nature of this component has no influence on the 1-3 interactions. On the contrary, strong χ_{23} or ϵ_{23} dependences on copolymer composition are observed. The calculated values

even reach negative figures, typical of stable blends, as the comonomer content is raised, probably due to hydrogen bond specific interactions between the H-donor (PSMAA or PSVPh) and the H-acceptor (PVPy or PVP), in correspondence with the experimental viscometric data. However, the

obtained results from **b2** model (Equations (47)–(49)) are quite unsatisfactory, in sharp contrast with those determined with the **b1** model, most probably due to the fact that the later model contains an empirical entropy correction (α parameter) that is ignored in the other approach. Therefore, as a main conclusion, it can be quoted that the **b1** approach is a good enough mathematical procedure to describe and calculate interaction parameters, at least for the TPS here compared and for all the phase compositions assayed.

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