



APPLICATION OF FLORY–HUGGINS THEORY TO TERNARY POLYMER–SOLVENTS EQUILIBRIA: A CASE STUDY

E. FAVRE,* Q. T. NGUYEN, R. CLEMENT and J. NEEL
 LCPM, URA CNRS 494, BP 451, ENSIC 1, rue Gandville 54001 Nancy, France

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Abstract—The ternary equilibrium data of the following systems: benzene/heptane/NBR at 60°C (system 1), heptane/isooctane/PE at 25°C (system 2), ethanol/water/CA at 20°C (system 3) and ethanol/water/P(E-co-VAc) at 32°C (system 4), already reported in the literature, have been used and experimental results compared to predictions offered by the Flory–Huggins theory applied to ternary mixtures (one polymer and two liquids), with constant interaction parameters and negligible elastic contribution. Polymer–solvent interaction parameters have been determined from swelling in pure liquid, while liquid–liquid interaction parameters have been estimated from liquid–vapour equilibrium data curve fitting. It is shown that the Flory–Huggins theory offers reasonable prediction in the case of apolar liquids in an elastomeric matrix (system 1), while approximate isotherm patterns with significant discrepancies are obtained with apolar liquids in a thermoplastic (system 2). The equilibrium data of polar liquids in either homopolymer or copolymer (systems 3 and 4) can hardly be achieved by Flory–Huggins theory, even when a variable liquid–liquid interaction parameter is used. Implications in ternary diagram simulations and possible prediction improvements are discussed.

NOTATION

A	NRTL coefficient (–)
a	activity (–)
r	correlation coefficient (–)
V	molar volume ($\text{m}^3 \cdot \text{mol}^{-1}$)
VLE	vapour–liquid equilibria
α	non-randomness factor (NRTL equation) (–)
ΔG_E	excess free energy ($\text{J} \cdot \text{mol}^{-1}$)
ϕ	volume fraction (–)
χ	interaction parameter (Flory–Huggins theory) (–)

Subscripts

ns	non-solvent
p	polymer
s1	solvent 1
s2	solvent 2

INTRODUCTION

Polymer–solvents equilibria, reflecting molecular interactions, are of the utmost importance for processes involving polymer production and uses, and have received considerable attention in the past years [1]. Numerous studies have been reported for solutions consisting most often of a polymer swelled (or dissolved) in one of its good solvents [2] (i.e. binary solutions). Much less attention has been given, however, to the description of multicomponent polymer–solvents equilibria, despite the importance of these types of mixtures for several applications (porous materials production, membrane and chromatographic processes, etc.). This situation results from two major reasons: the lack of theories which

can be easily extended to multicomponent polymer–solvents mixtures, and their inherent mathematical difficulties.

Flory–Huggins theory [3] is one of the few theories which offers a rational method to describe multicomponent polymer–solvents equilibria; its validity and limitations for binary polymer–solvent mixtures have been already largely established [4], but the situation is far from clear in the case of ternary mixtures. Among the few studies devoted to ternary polymer–solvents systems [5–9], most of them make use of simulations based on Flory–Huggins equations, with various degrees of sophistication; interesting (but sometimes controversial [8]) conclusions could be drawn from these studies, concerning essentially the weight of each term of Flory–Huggins equation in the resulting ternary diagram pattern.

The applicability of the Flory–Huggins theory for ternary polymer–solvents systems, based on a comparison between predicted and experimental equilibrium data, cannot be pointed out by such purely numerical exercises. This work intends to achieve partly that purpose, based on a set of equilibrium data of four ternary systems (one polymer swelled by two liquids) already reported in the literature (Table 1); each of these systems is tentatively representative of a mixture category (i.e. apolar and polar components).

THEORY

Based on a statistical thermodynamic development, Flory [3] derived a simple expression for the

*To whom all correspondence should be addressed.

description of sorption equilibrium between a polymer (p) and a liquid, usually called solvent (s):

$$\ln a_s = \ln \phi_s + \left(1 - \frac{V_s}{V_p}\right) \cdot \phi_p + \chi \cdot \phi_p^2. \quad (1)$$

This expression makes use of a single undetermined parameter, the polymer-solvent interaction parameter (χ). The molar volume of the polymer (V_p) is most often considered to largely overwhelm the solvent molar volume (V_s) so that equation (1) reduces to [9]:

$$\ln a_s = \ln \phi_s + \phi_p + \chi \cdot \phi_p^2. \quad (2)$$

Equation (2) corresponds to Flory-Huggins simplest expression and is often used in calculation for sake of simplicity; it has been proposed in order to determine the solvent-polymer interaction parameter χ , based on swelling a polymer sample in pure liquid (i.e. when $a_s = 1$) [13]. The use of equations (1) and (2) should be formally limited to non-crystalline, uncrosslinked polymers, showing a high chain flexibility (i.e. elastomers) and exhibiting moderate interaction with the solvent, so that the polymer-solvent mixture can be considered as a regular solution [11]. Despite these limitations, equation (2) has been already shown to give an excellent description of binary sorption isotherms, particularly in the case of an apolar solvent swelling an elastomer [14, 15].

Equation (1) can be readily extended to ternary mixtures (i.e. one polymer p, and two liquids s1 and s2), leading to the following non-linear equation system [1, 3]:

$$\begin{aligned} \ln a_{s1} = & \ln \phi_{s1} + (1 - \phi_{s1}) - \left(\frac{V_{s1}}{V_{s2}}\right) \cdot \phi_{s2} - \left(\frac{V_{s1}}{V_p}\right) \cdot \phi_p \\ & + ((\chi_{s1s2} \cdot \phi_{s2} + \chi_{s1p} \cdot \phi_p) \cdot (\phi_{s2} + \phi_p)) \\ & - \chi_{s2p} \cdot \left(\frac{V_{s1}}{V_{s2}}\right) \cdot \phi_{s2} \cdot \phi_p \end{aligned} \quad (3)$$

$$\begin{aligned} \ln a_{s2} = & \ln \phi_{s2} + (1 - \phi_{s2}) - \left(\frac{V_{s2}}{V_{s1}}\right) \cdot \phi_{s1} - \left(\frac{V_{s2}}{V_p}\right) \cdot \phi_p \\ & + \left((\chi_{s1s2} \cdot \phi_{s1} \cdot \frac{V_{s2}}{V_{s1}} + \chi_{s2p} \cdot \phi_p) \cdot (\phi_{s1} + \phi_p) \right) \\ & - \chi_{s1p} \cdot \left(\frac{V_{s2}}{V_{s1}}\right) \cdot \phi_{s1} \cdot \phi_p \end{aligned} \quad (4)$$

$$\phi_{s1} + \phi_{s2} + \phi_p = 1. \quad (5)$$

This system has already been used in order to predict polymer and solvents volume fractions and

thus simulate ternary diagrams; various authors could achieve that purpose by choosing an adequate numerical routine [5, 8]. These calculations demand the three molar volumes (V) and interaction parameters (χ) to be known. Simplifications similar to those proposed in equation (1) apply equally well: the polymer/solvent molar volume ratio (V_s/V_p) can be reasonably neglected and the interaction parameters χ can be taken as constants. Flory-Huggins simplest formulation for ternary systems is thus obtained.

Slightly more complicated equations can be derived, based on various sophistications; the two most often proposed include a supplementary term to equations (3) and (4) (reflecting either network elastic contribution [16] or ternary interactions [6]), or the use of one or several variable interaction parameters [6, 8]. One or both of these refinements have been used occasionally in order to possibly extend the theory application range, and for simulation purposes. The applicability of the former option is, however, strongly questioned [17], while the second is most often carried out on empirical grounds (i.e. a polynomial development of χ vs ϕ) [7, 9]; both these modifications complicate largely the numerical resolution of the system.

These potentially applicable options lead to numerous variants of Flory-Huggins equations (Table 2), the validity and application range of which are still largely unknown. A clear picture should be best pointed out by gradually increasing the mathematical complexity of the equations (i.e. number of parameters and variables) when applied to a given polymer-solvents ternary system, thus indicating the degree of sophistication required; unfortunately, to our knowledge, such an exercise has not been reported. The work described hereafter intends to achieve, to some extent, that purpose and check the validity of equations (3) and (4); the simplest option (no supplementary term and constant interaction parameters) will be used in a first step, based on the following procedure.

(1) Interaction parameters will be determined from polymer swelling in pure solvent (for χ_{s1p} and χ_{s2p}) and from liquid-vapour equilibrium curve-fitting (for χ_{s1s2}).

(2) Knowing interaction parameters, molar volumes V and experimental solvents volume fractions ϕ , a theoretical solvent activity value can be calculated through equations (3) and (4), leading to a predicted solvent sorption isotherm.

Table 1. References and characteristics of equilibrium data of polymer-solvents ternary mixtures used for this work

System	Solvents	Polymer	T (°C)	Reference
1	Benzene (s1) Heptane (s2)	Nitrile butadiene rubber (NBR)	60	[10]
2	Heptane (s1) Isocotane (s2)	High-density polyethylene Exxon 45% crystallinity (PE)	25	[11]
3	Ethanol (s1) Water (s2)	Cellulose acetate Eastman E-398-3 39% acetyl content (CA)	20	[9]
4	Ethanol (s1) Water (s2)	Poly(ethylene-co-vinyl acetate) Dupont Elvax-70 37% wt VAc content (P(E-co-VAc))	32	[12]

Table 2. Summary of different previously reported Flory–Huggins ternary systems expressions used for simulation purposes

χ_{sp}	χ_{nsp}	χ_{s1s2}	Supplementary term	Reference
Constant	Constant	Variable	No	[5]
Constant	Constant	Variable	Yes*	[6]
Constant	Constant	Variable	No	[7]
Variable	Constant	Variable	No	[8]
Constant	Constant	Variable	No	[9]

*Supplementary term of Pouchly type.

Comparison of predicted vs experimental isotherm will enable the validity of Flory–Huggins theory to be evaluated.

RESULTS AND DISCUSSION

Determination of χ_{sp} interaction parameters

Polymer–solvent interaction parameters have been determined with equation (2) applied to results obtained from swelling a polymer sample in a pure liquid (i.e. $a = 1$), through [9]:

$$\chi_{sp} = -\left(\frac{\ln(1 - \phi_p) + \phi_p}{\phi_p^2}\right). \quad (6)$$

Results are shown in Table 3. From their respective χ_{sp} values, the liquids investigated can be classified as good, fair, and non-solvents [18]; it can be shown that this study will be concerned with a full range of solvent properties. Slightly different χ_{sp} values would have been obtained from the literature [18–20], depending on the polymer origin and the experimental χ_{sp} determination method (e.g. heat of mixing, gas chromatography, osmotic pressure); this fact has already been largely discussed [18] and leads to the conclusion that the polymer–solvent interaction parameter is essentially an adjustable parameter. In our case, determination of χ_{sp} from swelling experiment is best suited because it is more representative of the effective sorption range, and can be easily achieved at any temperature; thus, it does not need to be extrapolated, contrarily to the inverse gas chromatography method, for instance [9].

Determination of χ_{s1s2} interaction parameters

The determination of liquid–liquid interaction parameters (χ_{s1s2}) can be performed in a similar way.

Table 3. Solvent volume fractions (ϕ_s) determined by polymer samples swelled in pure liquid and corresponding solvent/polymer interaction parameters (χ_{sp}) [equation (6)]

System	Solvent	ϕ_s	χ_{sp}	Solvent type
1	Benzene	0.720	0.619	Good
	Heptane	0.089	1.815	Poor
2	Heptane	0.262	1.104	Poor
	Isooctane	0.139	1.498	Poor
3	Ethanol	0.194	1.284	Poor
	Water	0.191	1.293	Poor
4	Ethanol	0.173	1.356	Poor
	Water	0.005	4.347	Non solvent

Experimental liquid–vapour equilibrium data are used in order to determine χ_{s1s2} by curve-fitting volume fraction vs activity data for one of the liquid components of the mixture; the latter values can be calculated by the NRTL method for liquid mixtures, in compliance with thermodynamic tables recommendations [21]. Given the fact that both liquids are volatile, contrarily to a binary polymer–solvent system, the two following equations can be used in order to assess χ_{s1s2} [3]:

$$\ln a_{s1} = \ln \phi_{s1} + \left(1 - \frac{V_{s1}}{V_{s2}}\right) \cdot \phi_{s2} + \chi_{s1s2} \cdot \phi_{s2}^2 \quad (7)$$

$$\ln a_{s2} = \ln \phi_{s2} + \left(1 - \frac{V_{s2}}{V_{s1}}\right) \cdot \phi_{s1} + \chi_{s1s2} \cdot \frac{V_{s2}}{V_{s1}} \cdot \phi_{s1}^2 \quad (8)$$

The thermodynamic parameters employed and the corresponding results obtained by equations (7) and (8) are summarized in Table 4. None of the liquid mixtures investigated exhibits partial miscibility, and two of them are quasi ideal (mixtures 1 and 2). It can be seen that despite the fact that application of equations (7) or (8) should theoretically lead to the same liquid–liquid interaction parameter value, slight differences are obtained (the largest difference being obtained, surprisingly, with system 1), reflecting the non-validity of regular solutions assumptions in each case. For similar reasons, the curve-fit efficiency decreases from apolar to polar mixtures; the use of variable interaction parameters (e.g. a polynomial development of χ versus ϕ) is usually proposed in order to improve fit efficiency in this case [7, 9].

It appears at this stage that the determination of χ_{s1s2} liquid–liquid interaction parameter can be problematic, given the restricted applicability of the

Table 4. NRTL vapour–liquid equilibria parameters of solvent mixtures [21]

System	Solvents	NRTL parameters	χ_{s1s2}	r
1	Benzene (s1)	$A_{12} = 977.7520$	−0.911 (1)	0.999
	Heptane (s2)	$A_{21} = -452.4296$	1.371 (2)	0.967
		$\alpha = 0.2969$		
2	Heptane (s1)	$A_{12} = 430.8604$	0.152 (1)	0.999
	Isooctane (s2)	$A_{21} = -362.9476$	−0.162 (2)	0.999
		$\alpha = 0.3092$		
3	Ethanol (s1)	$A_{12} = -411.351$	3.55 (1)	0.980
	Water (s2)	$A_{21} = 1403.5$	3.37 (2)	0.988
		$\alpha = 0.1803$		
4	Ethanol (s1)	$A_{12} = -7910.2216$	3.51 (1)	0.981
	Water (s2)	$A_{21} = 10026.3367$	3.35 (2)	0.985
		$\alpha = 0.0103$		

Liquid–liquid interaction parameters (χ_{s1s2}) are noted (1) for equation (7) and (2) for equation (8). r is the corresponding curve-fit correlation coefficient.

Flory–Huggins equation to liquid mixtures. The situation is further complicated by the fact that alternative χ_{s1s2} determination methods have been proposed, based on excess free energy data (ΔG_E). For instance [3]:

$$\chi_{s1s2} = \frac{1}{x_1 \cdot \phi_{s2}} \left(x_1 \cdot \ln \left(\frac{x_1}{\phi_{s1}} \right) + x_2 \cdot \ln \left(\frac{x_2}{\phi_{s2}} \right) + \frac{\Delta G_E}{RT} \right) \quad (9)$$

and [9]:

$$\chi_{s1s2} = \left(\frac{\Delta G_E}{RT \cdot \phi_{s1} \cdot \phi_{s2}} \right). \quad (10)$$

Each of these methods leads to slightly different χ_{s1s2} values. This can be seen in Fig. 1, where the variation law of ethanol–water χ_{s1s2} parameter, determined through different methods, is compared. The implications of χ_{s1s2} variation on equilibrium data prediction efficiency will be discussed later.

Application of Flory–Huggins theory to experimental results

Since volume fractions, interaction parameters and solvents molar volumes are known, the application of equation (3), in order to calculate Flory–Huggins predicted equilibrium values, is now possible, provided that polymer molar volume (V_p) influence is neglected. Figures 2–5 compare the experimental to the predicted solvent volume fractions for the four investigated systems. Since the application of equations (7) and (8) could not lead to a single χ_{s1s2} interaction parameter value, the two values appearing in Table 4 have been compared for systems 1 and 2. Significant differences are obtained only for system 1; the influence of liquid–liquid interaction being dependent on the product $\chi_{s1s2} \cdot \phi_s$ [equations (3) and (4)], this result seems logical. In fact, system 1 showed the largest difference between the two χ_{s1s2} values (Table 4), as well as the largest solvent volume fraction values ϕ_s (Table 3).

It can be seen that a reasonable agreement between predicted and experimental equilibrium data is

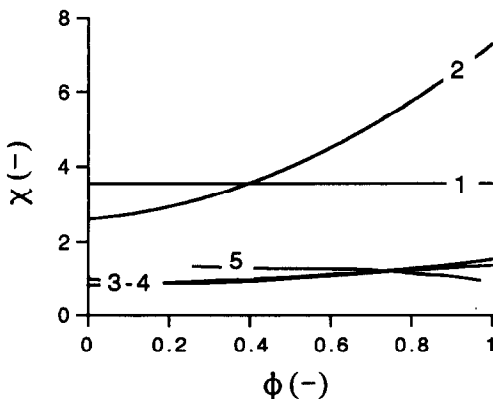


Fig. 1. Variation of χ_{s1s2} vs ethanol volume fraction (ϕ) for ethanol–water mixture at 25°C, according to different authors and determination methods. (1) Equation (7) with constant χ_{s1s2} (VLE data); (2) equation (7) with quadratic development of χ_{s1s2} vs ϕ (VLE data); (3) equation (9) (ΔG_E data) [9]; (4) equation (10) (ΔG_E data) [7]; (5) equation (10) (ΔG_E data) [9].

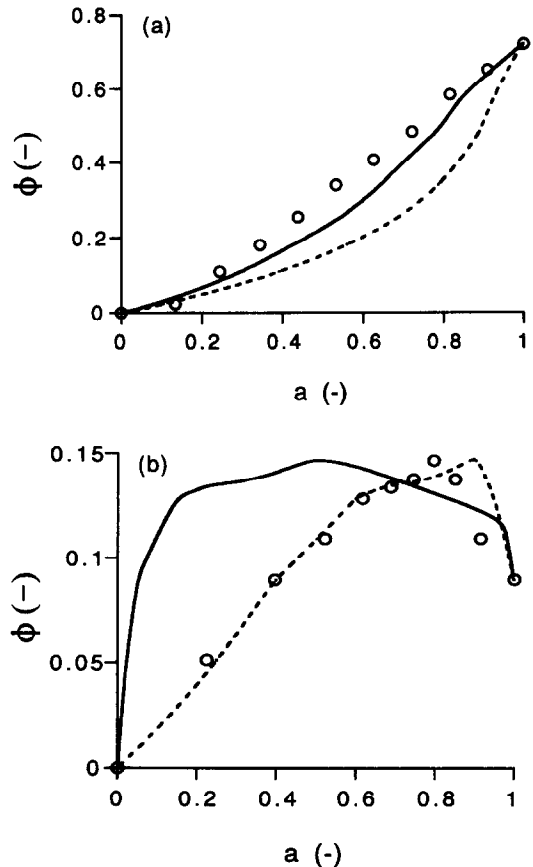


Fig. 2. Comparison between experimental (O) and predicted (lines) solvent volume fractions for system (1). ϕ : Solvent volume fraction in polymer; a: solvent activity in liquid mixture (calculated by NRTL). —: $\chi_{s1s2} = -0.911$; ---: $\chi_{s1s2} = 1.371$; (a) benzene; (b) heptane.

obtained for mixture 1 (Fig. 2), providing the liquid–liquid interaction parameter determined from a given solvent activity–volume fraction VLE data is used for the same solvent isotherm prediction (i.e. χ_{s1s2} determined from benzene data for benzene isotherm, χ_{s1s2} determined from heptane data for heptane isotherm). Even the bell-shaped pattern of heptane isotherm, resulting from liquid–liquid interactions (i.e. the high sorption level of benzene facilitates sorption of heptane) can be reasonably predicted (Fig. 2(b)). This result confirms the fact that sorption of apolar liquid mixtures in elastomers can be quite well depicted by the Flory–Huggins theory, even under drastic simplifications; an additional conclusion is the importance of χ_{s1s2} parameter values for correct predictions to be achieved.

Approximate predictions only could be obtained for mixture 2 (Fig. 3), despite the fact that the liquid mixture equilibrium is correctly described by Flory–Huggins binary equations (Table 4). As PE is a semi-crystalline polymer, a poorer efficiency of Flory–Huggins theory can result; in fact, it can be shown that even for binary PE mixtures (i.e. PE swelled by one solvent) the Flory–Huggins theory

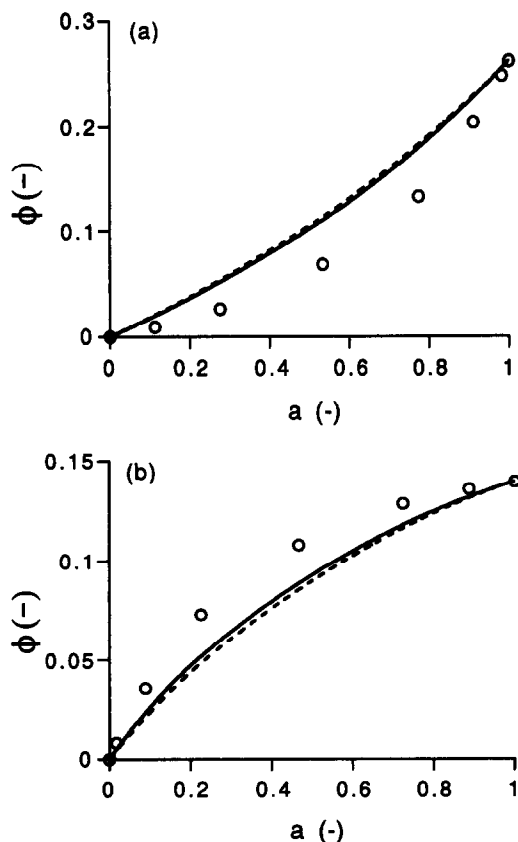


Fig. 3. Comparison between experimental (○) and predicted (lines) solvent volume fractions for system (2). ϕ : Solvent volume fraction in polymer; a : solvent activity in liquid mixture (calculated by NRTL). —: $\chi_{s1s2} = 0.152$; ---: $\chi_{s1s2} = -0.162$; (a) heptane; (b) isooctane.

with constant interaction parameter is of poor relevance [11]. Thus, an improvement in prediction efficiency for such systems relies not on more representative χ_{s1s2} values, but more likely on either variable polymer solvent interaction parameters, or adequate elastic contribution expressions. The best formulation taking into account this last effect is, however, still uncertain [22] and further work is needed in order to point out the exact origin of the observed discrepancies.

Application of equations (3) and (4) to systems 3 and 4 gives very poor equilibrium data predictions (Figs 4 and 5); this statement is especially true for water, whose high polarity makes it hardly compatible with regular solutions assumptions. The influence of the different previously determined χ_{s1s2} values (Fig. 1) is minor, despite the fact that these values range on almost one order of magnitude. The use of complicated χ_{s1s2} expressions does not seem to significantly improve prediction efficiency in this case; this result confirms one of the conclusions drawn from numerical simulations, stating that χ_{s1s2} variations have little influence on equilibrium predictions [8]. Again, the observed discrepancies can be attributed either to non-constant polymer-solvent interaction parameters, or to significant elastic contributions; the latter is less likely, given the limited

Table 5. Prediction efficiency of Flory-Huggins theory for different solvent isotherms of Figs 2-5

System	Solvent	Average error (%)
1	Benzene	15.6
	Heptane	7.4
2	Heptane	22.8
	Isooctane	34.0
3	Ethanol	34.4
	Water	87.0
4	Ethanol	35.6
	Water	164.1

The lowest average error is given for each isotherm.

swelling exerted by the solvents, particularly for system 4. Thus, for ternary systems including polar liquid mixtures, the difficulties inherent to realistic χ_{s1s2} value determination are not the sole problem to be circumvented, if quantitative equilibrium predictions are expected.

A summary of average errors offered by Flory-Huggins theory for each system is shown in Table 5. A rough conclusion is that the strategy investigated throughout this work (constant interaction parameters determined by either swelling or liquid-vapour equilibrium curve-fitting; negligible elastic contribution) offers a reasonable prediction efficiency

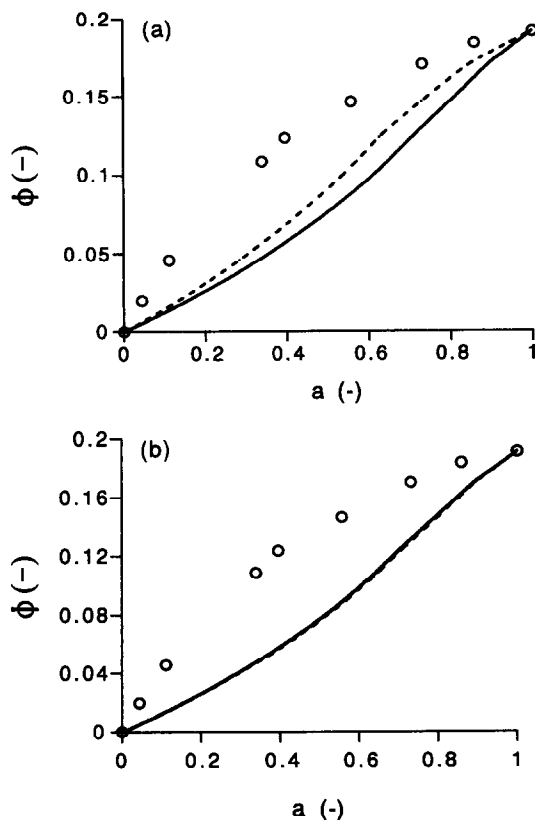


Fig. 4. Comparison between experimental (○) and predicted (lines) solvent volume fractions for system (3). ϕ : Solvent volume fraction in polymer; a : solvent activity in liquid mixture (calculated by NRTL). —: χ_{s1s2} from VLE (3.55); ---: χ_{s1s2} from ΔG_E ; (a) ethanol; (b) water.

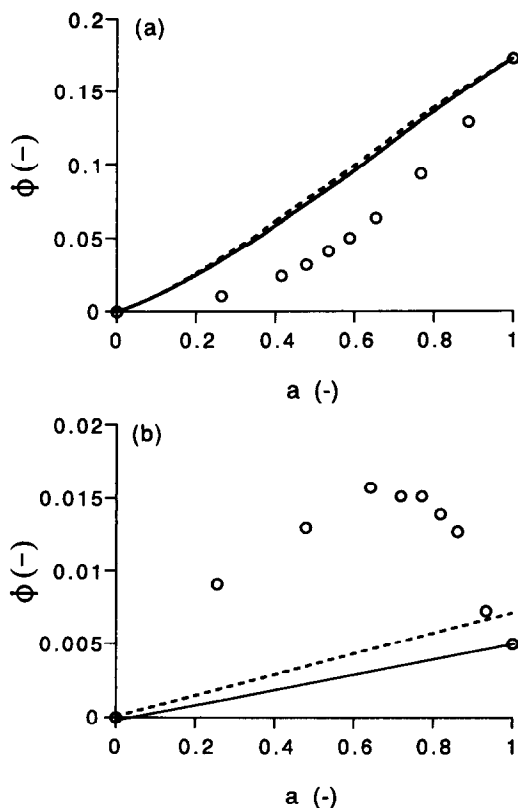


Fig. 5. Comparison between experimental (○) and predicted (lines) solvent volume fractions for system (4). ϕ : Solvent volume fraction in polymer; a : solvent activity in liquid mixture (calculated by NRTL). —: χ_{s1s2} from VLE (3.51); ---: χ_{s1s2} from ΔG_E ; (a) ethanol; (b) water.

when elastomers swelled by apolar solvents are concerned; less efficient predictions are observed for similar mixtures swelling a semi-crystalline polymer, while unrealistic patterns are obtained for polar liquid mixtures. This gradation in prediction efficiency suggests that the Flory–Huggins theory should be used with caution as soon as non-elastomeric matrices or polar mixtures are concerned.

CONCLUSION

Despite the fact that it is commonly used for simulation purposes, the validity and limitations of the Flory–Huggins theory when applied to polymer–solvents ternary mixtures are still largely unknown. This work intended to sketch out the prediction efficiency attainable by the Flory–Huggins theory when applied to different categories of ternary systems. It has been shown that reasonably good predictions (i.e. in the range of 10%) could be achieved by the Flory–Huggins theory, in the case of elastomers swelled by apolar liquids, even under drastic simplifications (constant interaction parameters, no elastic contributions, negligible polymer molar volume influence). This statement, which remains to be generalized by further studies on other systems, would largely facilitate numerical

simulations of such mixtures; in fact, χ_{sp} values can quite often be obtained in extensive tabulations [18–20]. A new guideline pointed out by this work is the importance of χ_{s1s2} value, which can be taken as constant, providing it is determined from reliable vapour–liquid equilibrium data. Fortunately, these can be easily assessed for apolar mixtures [23].

Sorption isotherms of apolar liquids in a semi-crystalline polymer (system 2) have been shown to be only approximately predicted under the same conditions; since liquid–vapour equilibria are equally well represented by Flory–Huggins theory, the observed discrepancies probably result from either the non-constancy of polymer–solvent interaction parameters, or the existence of a significant elastic contribution.

For polar liquids (systems 3 and 4), largely unrealistic predictions are obtained, which cannot be improved by using a variable liquid–liquid interaction parameter. These limitations of the Flory–Huggins theory should be borne in mind for studies devoted to the simulation of ternary systems including polar solvents. The low swelling extent achieved by liquids in one of the presently investigated systems (system 4) probably gives rise to very weak network elastic contributions. Thus, the poor prediction efficiency observed is likely to result essentially from variable polymer–solvent interaction parameters in the latter case.

All in all, the major conclusion of this work remains the fact that, if quantitative predictions are looked for, Flory–Huggins' simplest equation validity remains restricted, almost exclusively, to ternary systems consisting of one elastomer swelled by two apolar liquids; interestingly, a similar statement was recently drawn from binary systems examination [15]. Furthermore, attention should be focused on variable polymer–solvent (χ_{sp}), rather than liquid–liquid (χ_{s1s2}) interaction parameters; it is striking that the usual practice for simulation purposes most often makes use of the contrary (Table 2). Given the complications arising with Flory–Huggins theory when applied to polar solvents (i.e. highly variable interaction parameters), it can be questioned whether this approach remains realistic for simulation purposes. It is uncertain that reliable predictions for ternary systems could be performed, even at the expense of highly complicated expressions; such an evaluation would demand both the binary and ternary solvent polymer equilibria to be known on a complete activity range. Unfortunately, examples fulfilling these conditions are scarce in the literature [6].

Prausnitz already stated that lattice-based theories are no longer useful, as soon as interaction parameters depend on composition [24]; however, theories taking into account non-random polymer–solvent mixing rules lead to extremely complicated expressions, even for binary systems [25]. In that event, alternative approaches, based ideally on theories already proven to apply to polar liquid mixtures (e.g. Uniquac method), would possibly be of value, in order to circumvent the problems associated with polar liquid–polymer equilibria; however, apart from pioneering studies restricted to multicomponent

polymer-liquid apolar mixtures [26], no systematic research of this type has yet been addressed. It is hoped that the conclusions drawn from the present work will stimulate research in this area.

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