

Determination of interaction parameters for highly incompatible polymers

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Experiments and calculations were performed for the ternary system cyclohexane/polystyrene/polyisobutylene (CH/PS/PIB) to study the possibilities of determining the Flory–Huggins interaction parameters $\chi_{PS/PIB}$ between these highly incompatible polymers. To that end $\chi_{CH/PIB}$ was determined (vapour pressure measurements and additional thermodynamic information) as a function of composition; $\chi_{CH/PS}$ and its concentration dependence could be taken from earlier experiments. Furthermore, the cloud point curve and some tie lines of the ternary system were measured. In the subsequent evaluation of these data, the phase diagram was calculated and $\chi_{PS/PIB}$ (as a function of concentration) adjusted until the theoretically calculated binodal line matches with the measured cloud points. The polymer/polymer interaction parameter thus obtained increases at 35°C from 0.416 in the limit of pure PS to 0.449 in the limit of pure PIB. This result agrees reasonably well with the prediction of the solubility parameter theory and is in good accord with information stemming from light scattering experiments in a ternary system under ‘optical theta conditions’. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

The predictability of phase diagrams for ternary systems composed of two incompatible polymers (indices A and B) dissolved in a common solvent (index 1) by means of reliable methods would be of great practical importance in many fields. This statement is particularly true for the preparation of membranes or, more generally, for the processing of polymer mixtures. Three major obstacles have so far impeded such calculations: (i) insufficient knowledge of the concentration dependence of the binary (Flory–Huggins) interaction parameters χ between the polymers and the solvent; (ii) no, or only very unreliable, information concerning the binary interaction parameters for highly incompatible polymers; (iii) the use of chemical potentials in the calculation of phase diagrams of multicomponent systems requiring manifold derivatives of the Gibbs energy of mixing and making it rather laborious to take account of concentration-dependent interaction parameters.

With items (i) and (iii) helpful progress has recently been made. Concerning (i), the combination of a head-space sampler with a conventional gas chromatograph for the determination of vapour pressures gives quick and reliable access^{1,2} to χ_{1A} and χ_{1B} as a function of composition. For (iii), the difficulties associated with the partial differentiation to obtain the chemical potentials for the components of multinary systems can be avoided³ using the Gibbs energy of mixing for the determination of the phase state in a direct manner. The situation with

item (ii) is still unsatisfactory: although several methods exist for the estimation of χ_{AB} (theoretical evaluation of tie-lines measured for the ternary mixtures⁴, inverse gas chromatography^{5,6}, light scattering of the ternary systems^{7,8}, ‘optical theta’ light scattering⁹), their results are often contradictory, in particular when the polymers A and B are highly incompatible.

The present work was undertaken for two reasons. One involved the testing of improvements in the calculation of phase diagrams for ternary systems resulting from the new approaches (i) and (iii). Another objective was examination of the possibilities for determination of χ_{AB} as a function of blend composition by comparing experimental and theoretical phase diagrams for systems of the type 1/A/B.

The present investigation was performed with 1 = cyclohexane (CH), A = polystyrene (PS) and B = polyisobutylene (PIB). The paper is organized in the following way. After a brief recollection of the theoretical background, experimental vapour pressure data are presented for solutions of PIB in CH and $\chi_{CH/PIB}$ is calculated as a function of the volume fraction φ of the polymer therefrom; the corresponding $\chi_{CH/PS}(\varphi_{PS})$ is taken from the literature. The phase diagram measured for the ternary system CH/PS/PIB is reported in the next chapter. This section is followed by the theoretical calculation of that phase diagram, using the information on $\chi_{CH/PIB}(\varphi_{PIB})$ and $\chi_{CH/PS}(\varphi_{PS})$ and adjusting $\chi_{PS/PIB}(\varphi_{PIB})$ until the experimental result is reproduced. Finally, the parameters obtained for the interaction between the highly incompatible PS and PIB are compared with information available in the literature.

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THEORETICAL BACKGROUND

In the subsequent approach it is, as usual, assumed that the thermodynamic behaviour of a complex mixture can be described using binary interaction parameters only, i.e. neglecting effects resulting from the environment of the intermolecular contact under consideration.

Binary interaction parameters

On the basis of the Flory–Huggins theory, the Gibbs energy of mixing per mole of segments, $\Delta\bar{G}$, is formulated as

$$\frac{\Delta\bar{G}}{RT} = \sum_{i=1}^K \frac{1}{N_i} \varphi_i \ln \varphi_i + \sum_{i=1}^{K-1} \sum_{j=i+1}^K g_{ij} \varphi_i \varphi_j \quad (1)$$

N_i is the number of segments of a molecule of type i in a mixture of K components, φ is the fraction of segments of a certain component in the system (in good approximation the volume fraction) and g_{ij} are the binary (integral) interaction parameters between the components i and j .

In the case of a polymer/solvent system N_1 is set at unity and the above relation reduces to

$$\frac{\Delta\bar{G}}{RT} = \varphi_1 \ln \varphi_1 + \frac{\varphi_2}{N_2} \ln \varphi_2 + g \varphi_1 \varphi_2 \quad (2)$$

Interaction parameters are normally determined by means of the chemical potential of the solvent μ_1 , i.e. the Gibbs energy of dilution $\Delta\bar{G}_1$, given by

$$\frac{\Delta\bar{G}_1}{RT} = \frac{\Delta\mu_1}{RT} = \ln(1 - \varphi_2) + \left(1 - \frac{1}{N_2}\right) \varphi_2 + \chi \varphi_2^2 \quad (3)$$

χ represents the well known Flory–Huggins parameter, measuring the Gibbs energy of dilution, i.e. the chemical potential of the solvent. Different symbols for the interaction parameters in equations (2) and (3) are used in order to make clear that the numerical values differ even for identical solutions and conditions in case these parameters depend on composition.

In the region of moderate to high polymer concentrations χ is usually calculated from the vapour pressure p_1 of the solvent according to

$$\frac{\Delta\bar{G}_1}{RT} = \frac{\Delta\mu_1}{RT} \approx \ln \frac{p_1}{p_1^0} \quad (4)$$

where p_1^0 is the vapour pressure of the pure component. The data thus obtained are normally complemented^{1,2} by information stemming from osmosis or light scattering on the dilute side and from inverse gas chromatography close to the composition of the pure polymer.

Differential and integral interaction parameters can be converted into each other by means of the relation

$$g = \frac{1}{\varphi_1} \int_0^{\varphi_1} \chi d\varphi_1 \quad (5)$$

In some cases it is a good approximation to describe χ and g as a function of polymer concentration by either a series expansion

$$\chi = \sum_{i=0}^{\infty} \chi_i \varphi_2^i \quad \text{equivalent to} \quad g = \sum_{i=0}^{\infty} \frac{\chi_i}{i+1} \frac{1 - \varphi_2^{i+1}}{1 - \varphi_2} \quad (6)$$

or by the expression¹⁰

$$\chi = \alpha + \frac{\beta(1 - \gamma)}{(1 - \gamma\varphi_2)^2} \quad \text{equivalent to} \quad g = \alpha + \frac{\beta}{(1 - \gamma\varphi_2)} \quad (7)$$

In the context of a study on the interrelation between interaction parameters and interfacial tensions, a simplified version¹¹, containing two adjustable parameters only by setting $\alpha = 0$, has been found to be very useful; in the present contribution it will be applied to the polymer blend, where it reads

$$\chi_{AB} = \frac{p(1 - q)}{(1 - q\varphi_B)^2} \quad \text{equivalent to} \quad g_{AB} = \frac{p}{(1 - q\varphi_B)} \quad (8)$$

Calculation of phase diagrams for ternary systems

A new procedure³, not requiring chemical potentials, is used for that purpose. It starts from equation (1) ($K = 3, g_{ij}$ depending on composition) and allows the determination of spinodals, binodals, tie lines plus critical points¹² using the Gibbs energy of mixing only. By means of ‘test tie lines’ the extension of the unstable region is determined first. Then one selects a point inside this range to calculate the corresponding tie line from the condition that the Gibbs energy of mixing for the total system must become a minimum as the coexisting phases assume their equilibrium composition. Repetition of this procedure yields the binodal line. These computations are performed on an ordinary personal computer by means of standard minimization programs.

Since information on the composition dependence of g_{ij} was exclusively obtained from measurements of the binary systems in the case of the polymer solutions, one has to find a way to account for the concentration influences in ternary mixtures. With the present study all g_{ij} required for ternary systems were calculated by substituting φ_j in equations (6)–(8) by $\varphi_j/(\varphi_i + \varphi_j)$ since it is assumed¹³ that g_{ij} depends only on the components i and j . In equations (6) and (7) the indices ij have been omitted, as is usual for binary systems. The other possible choice, namely using the above relations unmodified, leads to physically meaningless results as will be shown later.

EXPERIMENTAL

Materials

Cyclohexane (p.a., Merck, Darmstadt, Germany) was kept over a molecular sieve of 3 Å. The weight average molecular mass of the polystyrene sample PS 233 (PSS; Mainz, Germany) used for vapour pressure measurements is 233 kg mol⁻¹; its molecular non-uniformity (M_w/M_n) – 1 is < 0.01 according to the suppliers and as checked by g.p.c. The sample PS 330, utilized for the determination of phase diagrams and tie lines, was purchased from Pressure Chemical Company (Pittsburgh, PA, USA); its weight average molecular mass is 330 kg mol⁻¹ and its non-uniformity is less than 0.1 according to the producer. Polyisobutylene was fractionated¹⁴ from a technical product (Oppanol B15, BASF, Ludwigshafen, Germany); according to light scattering and g.p.c. measurements the sample PIB 87

used for the present measurements has a weight average molecular mass of 87 kg mol^{-1} and a non-uniformity of 0.24.

For the theoretical calculations presented in the next section, the volume of CH was taken as that of a segment (i.e. $N_{\text{CH}} \equiv 1$); the following values then result for the polymers: $N_{\text{PS } 330} = 3000$ and $N_{\text{PIB } 87} = 780$

Vapour pressures

The measurements with the system CH/PIB were performed at 35 and at 45°C using a combination of a head-space sampler and an ordinary gas chromatograph in the same manner and under identical experimental conditions as already described for the system CH/PS^{1,2}.

Cloud points

The entrance into the two-phase region was determined visually at constant temperature. This was done by evaporating solvent at a given constant ratio of the two polymers until the solution becomes cloudy. Despite this primitive procedure, the reproducibility of the cloud points is surprisingly high, namely better than $\pm 0.1 \text{ wt}\%$.

Tie lines

The composition of coexisting phases was determined by cooling a given homogeneous ternary system slowly down to the equilibrium temperature and keeping it there until the phases have become totally clear (minimum time required for that purpose is one week). Samples of these phases were then taken out by means of a syringe and analysed with respect to the solvent content by total evaporation of the volatile part and with respect to the polymers by means of g.p.c. using u.v and r.i. detectors and calibrating with the pure components.

RESULTS AND DISCUSSION

Polymer/solvent interaction parameters

The parameters describing the concentration dependence of the differential interaction parameters χ for the binary solvent-containing systems are collected in Table 1 for cyclohexane/polystyrene^{1,2} and in Table 2 for cyclohexane/polyisobutylene; in the latter case information from the literature concerning low polymer concentrations (osmosis¹⁵) and very high polymer concentration (inverse gas chromatography¹⁶) is taken

Table 1 Parameters for the analytical description of $g(\phi_{\text{PS}})$ for the system cyclohexane/polystyrene 233 resulting from vapour pressure measurements^{1,2} and represented by equation (7)

T (°C)	α	β	γ
35	0.20	0.53	0.44
45	0.05	0.65	0.33

Table 2 Parameters for the analytical description of $g(\phi_{\text{PIB}})$ for the system cyclohexane/polyisobutylene 87 resulting from vapour pressure measurements and represented by equation (6)

T (°C)	χ_0	χ_1
35	0.44	0.32
45	0.45	0.29

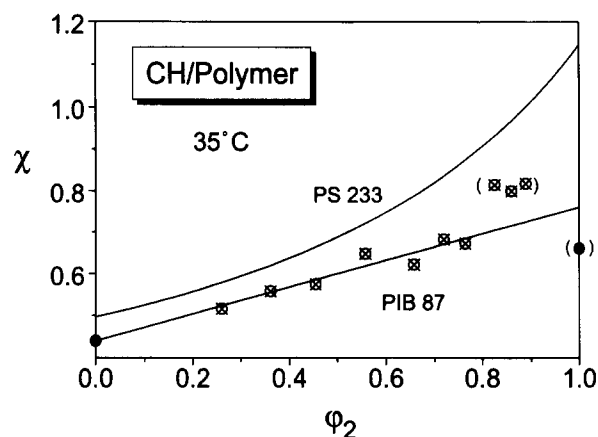


Figure 1 Polymer/solvent interaction parameters of the systems cyclohexane/polystyrene (taken from the literature^{1,2}) and of cyclohexane/polyisobutylene (see text) at 35°C

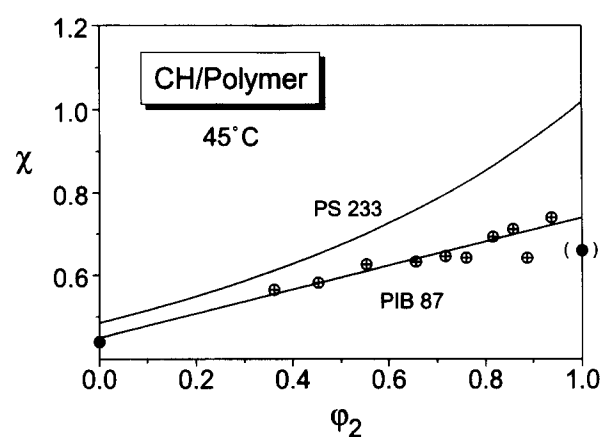


Figure 2 Same as Figure 1 but at 45°C

into consideration; earlier investigations in the intermediate range¹⁷ have yielded markedly lower χ values than the present vapour pressure measurements. Possible reasons for these deviations are discussed in ref. 18. Figure 1 shows $\chi(\phi_2)$ for both systems at 35°C and Figure 2 at 45°C.

Phase diagram of the ternary system

Cloud point curves of the system CH/PS/PIB at 35°C and at 45°C are depicted in Figure 3. The retraction of the two-phase region observed upon heating indicates endothermal mixing. The present results agree well in shape and extension of the miscibility gap with data reported in the literature⁷ for slightly different molar masses¹⁹ (PS 53.6 kg mol^{-1} and PIB 154 kg mol^{-1}).

Polymer/polymer interaction parameters

Knowing the interaction parameters $g_{\text{CH/PS}}$ and $g_{\text{CH/PIB}}$ as a function of polymer concentration from independent measurements, one can calculate the phase diagram for the ternary system CH/PIS/PIB as described, if information concerning $g_{\text{PS/PIB}}$ and its concentration dependence is available. In the present context the question is reversed and one asks what $g_{\text{PS/PIB}}(\phi_{\text{PIB}})$ has to look like in order to reproduce the experimentally measured cloud point curve. In order to keep things simple and to avoid an overinterpretation of the experimental data, the two-parameter composition

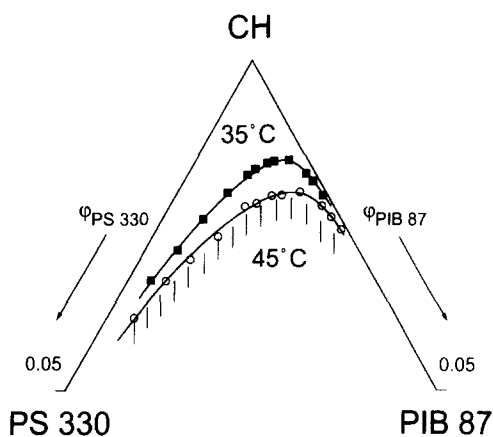


Figure 3 Visually determined cloud point curves of the ternary system cyclohexane/polystyrene/polyisobutylene for the indicated temperatures; the compositions are given in volume fractions and the two-phase region is indicated by small vertical dashes. The solid lines serve as a guide for the eye only

Table 3 Parameters for the analytical description of $g(\varphi_{\text{PIB}})$ for the interaction between polyisobutylene and polystyrene resulting from the calculation of the phase diagrams of the system CH/PS 330/PIB 87 and represented by equation (8)

T (°C)	p	q
35	0.416	0.073
45	0.388	0.052

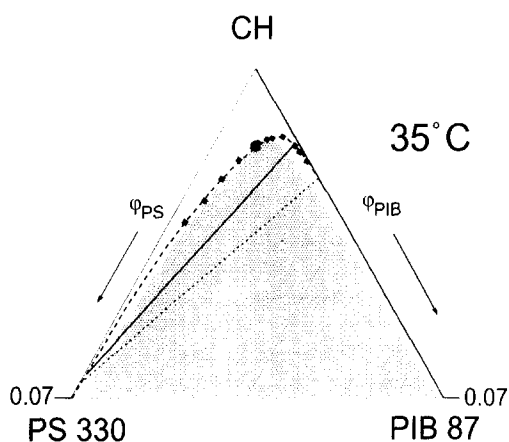


Figure 4 Theoretically calculated unstable area (shaded), tie line (dotted), binodal line (broken), and critical point (full circle) of the ternary system cyclohexane/polystyrene/polyisobutylene at 35°C; also depicted are the cloud points (full squares) shown in Figure 3 and an experimentally determined tie line (full line); the compositions are given in volume fractions

dependence of $g_{\text{PS/PIB}}$ formulated in equation (8) was assumed to be valid. In order to adjust the theoretical phase diagram to the experimental one, the parameters p and q in equation (8) were varied until the calculated binodal line becomes identical to the experimental cloud points. Furthermore the polymer/solvent interaction parameters determined by means of a polystyrene sample of a somewhat lower molar mass than that used for the phase establishment of the phase diagram are taken for the calculations since they can be expected to be identical within experimental error.

For optimum modelling of the ternary phase diagram

the polymer/polymer interaction parameter must assume the values and concentration dependencies calculated for the parameters given in Table 3. The reliability of these data can be estimated from the first visible discrepancy between theory and experiment which show up as p and q are varied by ± 0.002 . The results of the theoretical calculation using the data of Table 3 for $g_{\text{PS/PIB}}$ are shown in Figure 4, together with the measured cloud points of Figure 3 and an experimentally determined tie line.

Figure 4 demonstrates that even the simple two-parameter equation (8) for $g_{\text{PS/PIB}}$ suffices to describe the phase diagrams. If suitable p and q values are chosen, the calculated binodal line coincides, within experimental error, with the measured cloud point curve. The unstable area is marked by points at those compositions where the test tie lines have indicated instability. The slope of the calculated tie line (broken) and that of the measured one (solid) match well. Some slight discrepancies that remain may be due either to the polymolecularity of the samples, not accounted for theoretically, or to experimental difficulties in measuring the composition of the coexisting phases.

In the following, we examined how the polymer/polymer interaction parameters at 35°C resulting from the present modelling (0.416 in the limit of pure PS and 0.449 in the limit of pure PIB) compare with data reported in the literature.

The present findings are totally at variance with the $\chi_{\text{PS/PIB}}$ values calculated from light scattering data obtained with different representatives of the ternary system if the concentration dependence of the polymer/solvent interaction parameters is ignored²⁰. From experiments with solutions of the blend of PS 3880/PIB 992 in CH at temperatures ranging from 25 to 40°C, the authors report even negative values. A similar statement holds true if $\chi_{\text{PS/PIB}}$ is calculated from knowledge of the composition of phases that coexist in the ternary system using concentration-independent polymer/solvent interaction parameters.

On the other hand, the agreement of the present results with $\chi_{\text{PS/PIB}}$ values calculated from the solubility parameter theory using increments (group molar attraction constants given by Hoy²¹) is quite reasonable; one obtains 0.374 for 35°C and 0.363 for 45°C. Furthermore, the new findings are also in good accord with the data resulting from light scattering measurements under 'optical theta' conditions⁹. For $\varphi_{\text{PS}} = 0.593$ the authors report a value (recalculated for the molar volume of CH as the segment molar volume instead of $100 \text{ cm}^3 \text{ mol}^{-1}$) of $\chi_{\text{PS/PIB}} = 0.452$ as compared with $\chi_{\text{PS/PIB}} = 0.410$ and $g_{\text{PS/PIB}} = 0.429$ following from the present approach for that composition of the blend. From literature data obtained via light scattering measurements¹⁹ one calculates $\chi_{\text{PS/PIB}} = 0.422$, again for 35°C and a blend composition of $\varphi_{\text{PS}} = 0.593$ in the limit of vanishing total polymer concentration.

The other possibility that was mentioned in the theoretical section – using equations (6)–(8) unmodified – leads to $p = 0.412$ and $q = 5$ for 35°C. This implies a divergence of $g_{\text{PS/PIB}}$ at $\varphi_{\text{PIB}} = 0.2$ and negative $g_{\text{PS/PIB}}$ values at higher contents of PIB. Such a large value for q is physically senseless and this possibility for the description of the composition dependence can be ruled out for the description of the present ternary mixture.

In conclusion it can therefore be stated that the theoretical modelling of an experimentally determined phase diagram of a ternary system consisting of two polymers and a common solvent using accurately measured polymer/solvent interaction parameters and adjusting the polymer/polymer interaction parameter constitutes a promising method to obtain otherwise scarcely available information on the interaction between two highly incompatible macromolecules.

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