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Phase diagrams of the system tetrahydrofuran/γ-butyrolactone/poly(ether imide) and determination of interaction parameters

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The thermodynamic interactions in the ternary mixture tetrahydrofuran/γ-butyrolactone/poly(ether imide) (THF/γ-BL/PEI) are investigated from 30 to 50°C. This is a membrane-forming system with a high He-selectivity. Cloud point measurements show that the two binary polymer solutions THF/PEI and γ-BL/PEI exhibit miscibility gaps which close towards the centre of the ternary phase diagram where the mixtures become homogeneous (cosolvency). Vapour pressures were determined for the subsystem THF/γ-BL. For the theoretical calculations the Gibbs energy of mixing is formulated according to the Flory–Huggins theory and the interaction parameter $\chi_{\mathrm{THF}/\gamma\text{-}\mathrm{BL}}$ calculated from the vapour pressures. The adjustment of theoretical phase diagrams to the experimental data (cloud point curves, tie lines and critical points) gives access to $\chi_{\mathrm{THF/PEI}}$ and $\chi_{\gamma\text{-}\mathrm{BL/PEI}}$. For a satisfactory representation of the liquid–liquid demixing, a concentration dependent $\chi_{\mathrm{THF/PEI}}$ is required, whereas concentration independent values for $\chi_{\mathrm{THF}/\gamma\text{-}\mathrm{BL}}$ and $\chi_{\gamma\text{-}\mathrm{BL/PEI}}$ suffice. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: Flory–Huggins parameter; liquid–liquid demixing; ternary mixture)

INTRODUCTION

Poly(ether imide) (PEI) is known in the membrane field for its high He-selectivity. However, to be successful as a membrane, a complex asymmetric porous structure must be obtained. The integral asymmetric membrane has a thin selective top layer and a porous support with the same composition but which is only responsible for giving mechanical stability to the membrane. A thinner top layer promotes faster gas transport through the membrane. The porous structure is, in most cases, obtained by a process known as 'phase inversion'[1]. The polymer solution is cast on a substrate and subsequently immersed in a non-solvent bath. While permselectivity constitutes an inherent property of the polymer itself, the solvent/non-solvent system must be carefully chosen to give a suitable porous structure to the membrane. Recently, Peinemann *et al.*[2] reported an interesting solvent mixture to prepare PEI membranes: tetrahydrofuran (THF) and γ-butyrolactone (γ-BL). Both organic liquids are non-solvents for PEI, but some of their mixtures represent convenient cosolvents, i.e. they are completely miscible with the polymer. This allows the preparation of homogeneous solutions of PEI which—when immersed in water—form membranes with very good performance in He separation. To form a very thin top layer the quality of the solvent mixture must be poor but still good enough to keep the polymer in solution. This brings the system very close to the demixing conditions. If a very small amount of the more volatile solvent (THF) is lost by evaporation before immersion in water, phase separation starts and gives rise to the top layer. An immediate immersion in water promotes solvent–non-solvent exchange, continues the phase separation and gels the system, freezing the porous structure. The quality of the solvent mixture can be controlled by adjusting the THF/γ-BL proportion or sometimes by addition of another non-solvent, such as butanol, to the polymer solution. The limit conditions for optimization of membrane formation can therefore be much better controlled if more information on phase diagrams is available. In this paper, we investigate the thermodynamics of the system THF/γ-BL/PEI. The phenomenon of cosolvency is discussed on the basis of measured phase diagrams and vapour pressures.

THEORETICAL BACKGROUND

The Gibbs energy of mixing per mole of segments, $\Delta\bar{G}$, for polymer-containing systems with K components is often conveniently described by the Flory–Huggins equation[3,4]

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

The basic consideration is the subdivision of the system in lattice sites (fixed by the constant volume V_{segment}) and distributing the substances on that lattice. The number of lattice sites (N_i) occupied by one molecule i can be calculated by dividing its molar volume by V_{segment}. χ_{ij} is the Flory–Huggins

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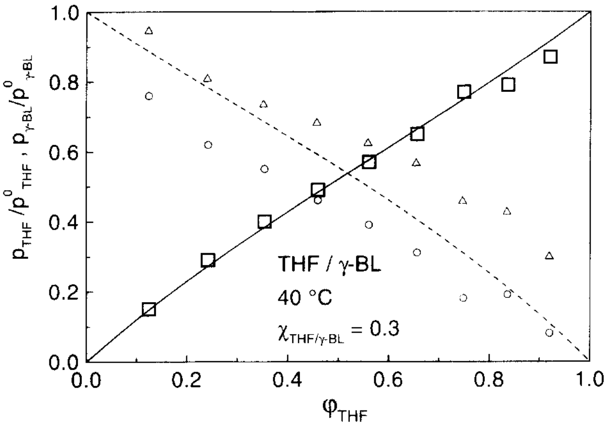

Figure 1 Reduced vapour pressures (over the mixture to that of the pure component, superscript 0) of tetrahydrofuran p_{THF} (squares) and of γ-butyrolactone $p_{\gamma\text{-BL}}$ (circles and triangles) at 40°C. The broken and solid lines are calculated with an interaction parameter $\chi_{THF/\gamma\text{-BL}} = 0.3$

interaction parameter describing the interaction between segments of components i and j.

In this paper, $\chi_{THF/\gamma\text{-BL}}$ is calculated from measured vapour pressures by means of a new fitting method[5] which is based on the fact that the free energy of the entire system (liquid and gas phase) becomes minimum under equilibrium conditions. The interaction parameters $\chi_{THF/PEI}$ and $\chi_{\gamma\text{-BL/PEI}}$ result from the theoretical evaluation of the observed liquid–liquid phase separation behaviour (cloud points and tie lines) of the ternary system THF/γ-BL/PEI; a procedure[6] not requiring chemical potentials is used for these calculations. It gives access to spinodals, binodals, tie lines and critical points using the Gibbs energy of mixing only, without the need to calculate the different derivatives with respect to composition.

The phenomenon of cosolvency, the mixture of two non-solvents being completely miscible with the solute[7,8], is bound to the interplay of the interactions between the components and can lead to rather spectacular effects[9,10]. One of the properties of interest is the intrinsic viscosity $[\eta]$ of polymers dissolved in mixed solvents which normally exhibits a maximum when plotted as a function of the composition of the solvent mixture[11–13]. Intrinsic viscosities can be obtained according to the Schulz–Blaschke equation[14]

$$\eta_{sp}/c = [\eta] + k_S[\eta]\eta_{sp} \qquad (2)$$

by plotting specific viscosity η_{sp} divided by the polymer concentration c as function of η_{sp}. The intercept gives $[\eta]$ and the slope divided by $[\eta]$ is the Schulz–Blaschke constant k_S.

EXPERIMENTAL

Materials

The solvent tetrahydrofuran (THF, content > 99.5%) was purchased from Merck (Darmstadt, Germany), γ-buty41 (γ-BL, content > 99%) and 1-methyl-2-pyrrolidone (NMP, content > 99%) from Fluka (Buchs, Switzerland). The poly(ether imide), poly(bisphenol A-*co*-4-nitrophthalic anhydride-*co*-1,3-phenylenediamine), is the commercial product ULTEM 1000 from General Electric Company. The chemical structure of PEI can be found in ref. [15]. The number-average molar mass M_n is 18 000 g mol^{-1}, as determined by osmosis (Osmomat 090, control unit 070/090, Gonotec, Berlin, Germany).

Densitometry

The densities of the solvents were measured at 30, 40 and 50°C with the DMA 48 Density Meter of Anton Paar GmbH, Graz, Austria. The density of PEI was determined at 30°C with a conventional pycnometer and water as auxiliary fluid.

Vapour pressures

The measurements with the system THF/γ-BL were performed at 40°C using a combination of a head-space sampler and an ordinary gas chromatograph as described in ref. [16].

Intrinsic viscosity

The intrinsic viscosities were determined using Ubbelohde Micro-Viscometers, capillary No. I and Ic (Schott, Hofheim am Ts., Germany) at $T = 25$°C. The precision in efflux times was ± 0.1 s (Hagenbach corrections were applied) and temperature was controlled to ± 0.05°C. The solvent mixtures were prepared by weighing, the concentration range of PEI was 0 to 10 mg ml^{-1}.

Cloud points

The cloud points were visually detected by titration of homogeneous mixtures of THF/γ-BL/PEI with the pure solvents at constant temperature. To start in the one-phase region, homogeneous solutions with 30 wt% PEI were prepared, then the turbidimetric titration was carried out with one of the solvents. Afterwards, the other solvent was added until the system became homogeneous again. The procedure of titration and rehomogenization was repeated several times. The composition of the mixtures was determined by weighing.

Critical points

Either THF or γ-BL was added to a homogeneous ternary mixture until it became cloudy, as for the turbidimetric titration, then two further drops were added to guarantee macroscopic phase separation; in this manner the overall composition of the system was kept almost identical with that of the cloud point. After two clear phases had formed upon standing, the volumes of the coexisting phases were determined and their ratio plotted *versus* the content of PEI in the overall system. The critical concentration $w_{PEI,c}$ was then given by the point at which this ratio approaches unity[17,18]. The critical point is located on the cloud point curve at $w_{PEI,c}$.

Tie lines and swelling points

For the determination of the compositions of coexistent phases, mixtures within the two-phase area of the phase diagram were prepared. After stirring for 3 days the solutions were kept at 30°C for 1 day at rest to allow the formation of two macroscopic phases. After their separation the solvents were removed by vacuum distillation at temperatures up to 140°C and weighing of the remainder gave the amount of polymer. The solvents were condensed in a cooling trap and the composition of the solvent mixture was determined by measuring the refractive index at 25°C which depends linearly on the weight fraction in the binary solvent mixture (THF: $n_D^{25} = 1.4050$; γ-BL: $n_D^{25} = 1.4351$).

The swelling points represent the special case of a tie line in the binary subsystem polymer and one solvent, at conditions where the sol phase contains nearly no polymer. These data were obtained by immersing a polymer film in

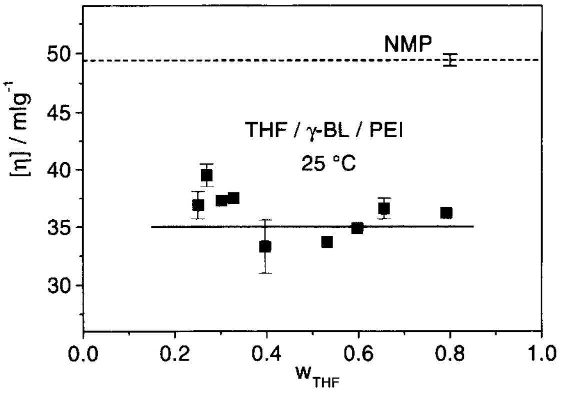

Figure 2 Intrinsic viscosity of poly(ether imide) (PEI) as a function of the weight fraction of THF in the solvent mixture at 25°C. The solid line gives the average value. For comparison, the value for the single solvent 1-methyl-2-pyrrolidone (NMP) is plotted as a broken line

the solvent and keeping this system at constant temperature for several days until the equilibrium of swelling is reached. Weighing the polymer again gave the amount of solvent in the gel phase.

RESULTS AND DISCUSSION

To determine the thermodynamic interactions between the two liquid solvents, vapour pressure measurements were carried out at 40°C. As can be seen in *Figure 1* the results are reasonable and well reproducible for THF within a wide range of conditions. For γ-BL, on the other hand, the measured vapour pressures are very sensitive to the slightest change in the experimental procedure. A possible reason for this may lie in the comparatively large difference in the size of the THF peak (very large) and of the γ-BL peak (very small). Since the sensitivity of the detector has to be increased when changing from the registration of THF to that of γ-BL, the tailing of THF becomes very important. For the above reasons, the theoretical evaluation neglects the data for γ-BL and refrains from using a concentration dependent $\chi_{\mathrm{THF}/\gamma\text{-BL}}$ for fitting the vapour pressures of THF. Introducing a concentration dependence for $\chi_{\mathrm{THF}/\gamma\text{-BL}}$ would improve the description of the experimental data but the curve for a constant $\chi_{\mathrm{THF}/\gamma\text{-BL}}$ suffices for a representation within experimental error. The lines in *Figure 1* are reduced vapour pressures calculated with $\chi_{\mathrm{THF}/\gamma\text{-BL}} = 0.3$. This value is taken for all further calculations independent of temperature.

The results of the viscometry are shown in *Figure 2*. Within the limits of experimental error the intrinsic viscosity is nearly independent of the composition of the solvent mixture. No maximum of $[\eta]$ as a function of solvent composition—indication for an enhanced solvent power of the mixture of the two poor solvents[11]—is discernible. The independence of the intrinsic viscosity of the solvent composition agrees with the low value of $\chi_{\mathrm{THF}/\gamma\text{-BL}}$. Furthermore, because of the low molar mass of the polymer sample, only a small increase is to be expected in any case. The scattering of the data is unusually large. The probable reason for that observation lies in the fact that changes in the solvent composition due to the preferential evaporation of the highly volatile THF cause changes in the composition of the mixed solvent and, due to the largely different viscosities of THF and γ-BL, also strong changes in flow times.

In order to obtain additional information on the solution behaviour of PEI in solvents of different thermodynamic quality, viscosity measurements were also performed with *N*-methyl pyrrolidone (NMP), which is reported in the literature[19] as a good solvent for PEI. In agreement with theoretical expectation the intrinsic viscosity of PEI in NMP is significantly higher than in any of the mixed solvents.

Figure 3 Figure 4 Figure 5 show the phase diagrams for the ternary system THF/γ-BL/PEI at three different temperatures. The discussion will first focus on cloud points and swelling points. There are two miscibility gaps located near the corners of the two pure solvents. Both binary subsystems, consisting of one solvent and the polymer, exhibit a two-phase range, whereas the centre of the ternary diagram is homogeneous. This phenomenon, termed cosolvency, has already been discussed by Gee[7] and

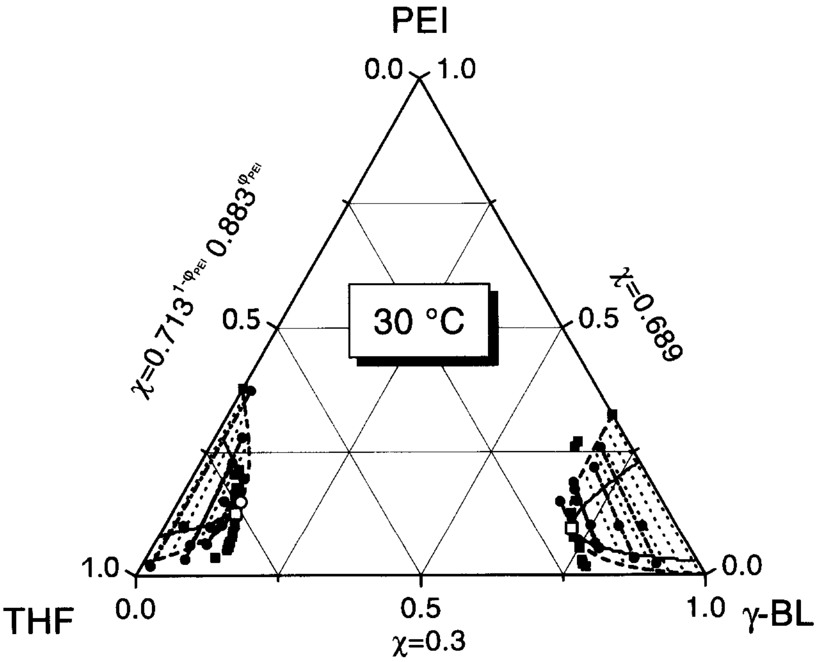

Figure 3 Phase diagram of the system THF/γ-BL/PEI at 30°C. Experimental data: cloud points (full squares); tie lines (full circles and dash-dotted lines); critical points (open squares). Calculated data: spinodals (solid lines); binodals (broken lines); tie lines (dotted lines); critical points (open circles)

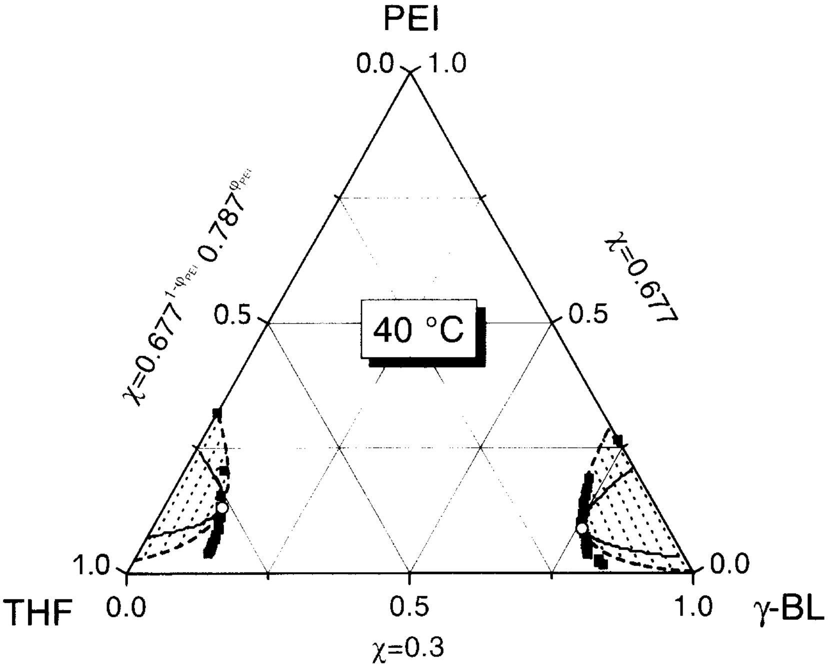

Figure 4 Phase diagram for THF/γ-BL/PEI at 40°C

Scott[8]. Cosolvency can be observed when there is an unfavourable interaction between the two solvents ($\chi_{THF/\gamma\text{-}BL} > 0$) and when the two χ-values for the polymer interacting with the solvents are not too large. Under these conditions the system is homogeneous in the centre of the ternary phase diagram since the demixed state would be associated with more unfavourable contacts between the two solvents.

The two-phase region on the THF side of the ternary diagram is smaller than that on the γ-BL side and both miscibility gaps show a similar temperature dependence: both become smaller as T is raised, but on the γ-BL side the effect is larger.

The critical weight fraction of PEI was determined at 30°C as described before. The corresponding plot is shown in *Figure 6*. Since there are two miscibility gaps, there also exist two critical points and so the determination was carried out on both sides of the phase diagram. $w_{PEI,c}$ is higher on the THF side than on the γ-BL side.

The compositions of coexistent phases were determined at 30°C. As can be seen in *Figure 3* the end points of the tie lines are not exactly located on the cloud point curve. This observation is related to the polydispersity of the PEI. In the case of polydisperse polymers, the cloud point curve and coexistence curve differ[20,21].

On the basis of experimental data for the liquid–liquid phase separation of the present system, interaction parameters can be determined by fitting calculated phase diagrams to the experimental data. For this purpose $\chi_{THF/PEI}$ and $\chi_{\gamma\text{-}BL/PEI}$ were treated as fit parameters (independent of the concentration of PEI) and varied until the calculated critical points were situated on the experimental cloud point curve. The resulting $\chi_{THF/PEI}$ and $\chi_{\gamma\text{-}BL/PEI}$ values are given in

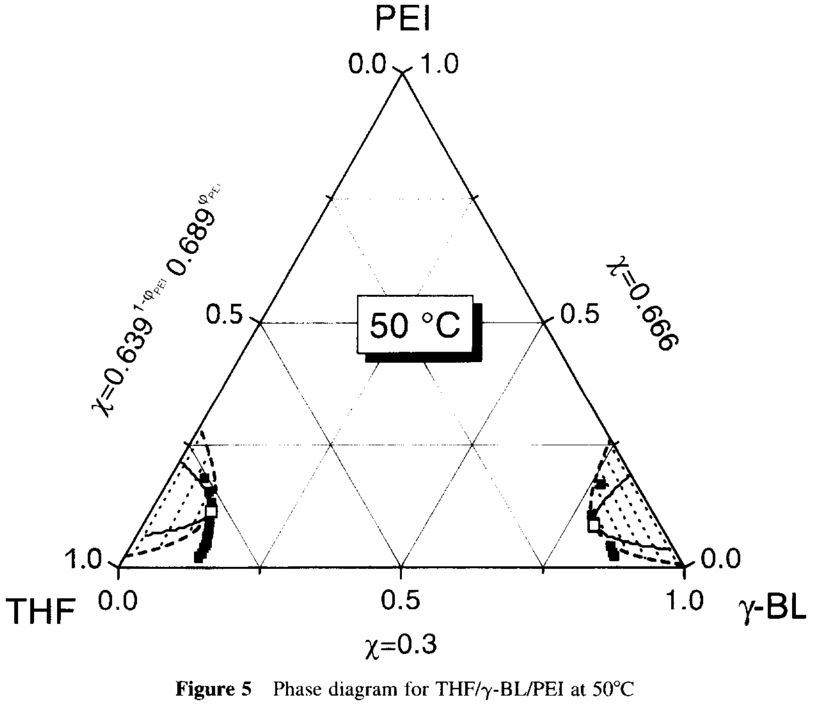

Figure 5 Phase diagram for THF/γ-BL/PEI at 50°C

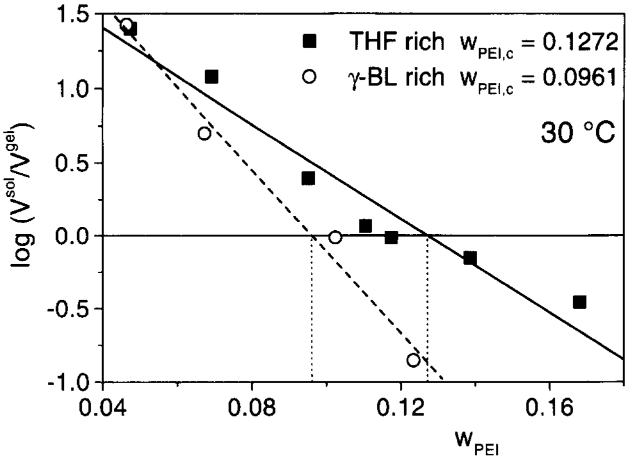

Figure 6 Phase volume ratio of sol and gel phase—for an approximately constant, very small distance to overall compositions near the cloud point curve—as a function of the weight fraction of poly(ether imide) w_{PEI} at 30°C. The full squares refer to the miscibility gap on the THF side of the ternary diagram and the open circles to that on the γ-BL side. The critical content of PEI is indicated by dotted lines

Table 1 and plotted *versus* the inverse of *T* in *Figure 7* as non-solid lines. Even the small value of 0.3 for the interaction parameter describing the interaction between the two solvents suffices to cause the effect of cosolvency.

Although the agreement of calculated and measured data is satisfactory for the γ-BL side of the phase diagram, the calculated tie lines for the THF-rich mixtures are shorter than the experimentally determined ones. Therefore, it can be concluded that the concentration dependence of $\chi_{THF/PEI}$ must be taken into account for realistic modelling, where $\chi_{THF/PEI}$ has to increase towards the PEI corner. Since no information on the composition dependence of $\chi_{THF/\gamma\text{-}BL}$ is available, the simplest possibility to account for composition influences was chosen, namely a linear dependence of $\chi_{THF/PEI}$ on φ_{PEI} on a semi-logarithmic scale, resulting in

$$\chi_{THF/PEI} = \left[\chi_{THF/PEI}(\varphi_{PEI} = 0)\right]^{1-\varphi_{PEI}}\left[\chi_{THF/PEI}(\varphi_{PEI} = 1)\right]^{\varphi_{PEI}} \qquad (3)$$

This second variant of evaluation with a concentration dependent $\chi_{THF/PEI}$ has three fit parameters: $\chi_{THF/PEI}(\varphi_{PEI} = 0)$, $\chi_{THF/PEI}(\varphi_{PEI} = 1)$ and $\chi_{\gamma\text{-}BL/PEI}$. The experimental data were now fitted so that the critical points are located on the cloud point curve and that the swelling point THF/PEI coincides with the calculated binodal. The resulting interaction parameters are given in *Table 1* and plotted in *Figure 7*. The agreement of measured and calculated spinodals, binodals and critical points can be seen in *Figures 3–5*. The tie lines are well described by this set of parameters, whereas there is still some deviation between the cloud point curve and the calculated binodal, supposedly caused by the polydispersity of PEI.

Summarizing, for a given value of 0.3 for $\chi_{THF/\gamma\text{-}BL}$ the remaining interaction parameters were determined by adjusting calculated phase diagrams to experimental data according to two different variants as mentioned before. Variant 1 is based on three concentration independent interaction parameters with the two adjustable parameters $\chi_{THF/PEI}$ and $\chi_{\gamma\text{-}BL/PEI}$. In variant 2 $\chi_{THF/PEI}$ is allowed to depend linearly on the volume fraction of PEI, i.e. there are three adjustable parameters: $\chi_{THF/PEI}(\varphi_{PEI} = 0)$, $\chi_{THF/PEI}(\varphi_{PEI} = 1)$ and $\chi_{\gamma\text{-}BL/PEI}$.

In variant 1 the concentration independent $\chi_{THF/PEI}$ turns out to be practically independent of temperature, in agreement with the fact that the miscibility gap on the THF side does not change very much with *T*, whereas $\chi_{\gamma\text{-}BL/PEI}$ decreases with *T*, like the two-phase area on the γ-BL side. The immiscible area on the γ-BL side has a bigger extension than that on the THF side and so $\chi_{\gamma\text{-}BL/PEI}$ is larger than $\chi_{THF/PEI}$.

In variant 2 $\chi_{THF/PEI}$ increases with φ_{PEI}, but the concentration dependence of $\chi_{THF/PEI}$ becomes less pronounced with rising temperature, i.e. the difference between $\chi_{THF/PEI}(\varphi_{PEI} = 0)$ and $\chi_{THF/PEI}(\varphi_{PEI} = 1)$ decreases at higher temperatures. Both $\chi_{THF/PEI}(\varphi_{PEI} = 0)$ and $\chi_{THF/PEI}(\varphi_{PEI} = 1)$ decline markedly as *T* is raised. The size of the concentration dependent $\chi_{THF/PEI}$ does not correlate with the extension of the miscibility gap in an obvious manner, since the increase of $\chi_{THF/PEI}$ with φ_{PEI} enhances the tendency to mixing: the larger the difference between $\chi_{THF/PEI}(\varphi_{PEI} = 0)$ and $\chi_{THF/PEI}(\varphi_{PEI} = 1)$, the larger $\chi_{THF/PEI}$ must be to keep the extension of the miscibility gap constant. This is the reason why the concentration dependent $\chi_{THF/PEI}$ values of variant 2 are larger than the concentration independent values of variant 1, and even larger than $\chi_{\gamma\text{-}BL/PEI}$. The increase of the concentration dependence with decreasing *T* requires a pronounced *T*-dependence of $\chi_{THF/PEI}$ for appropriate modelling. The introduction of a concentration dependence for $\chi_{THF/PEI}$ also changes the adjusted value of $\chi_{\gamma\text{-}BL/PEI}$. It

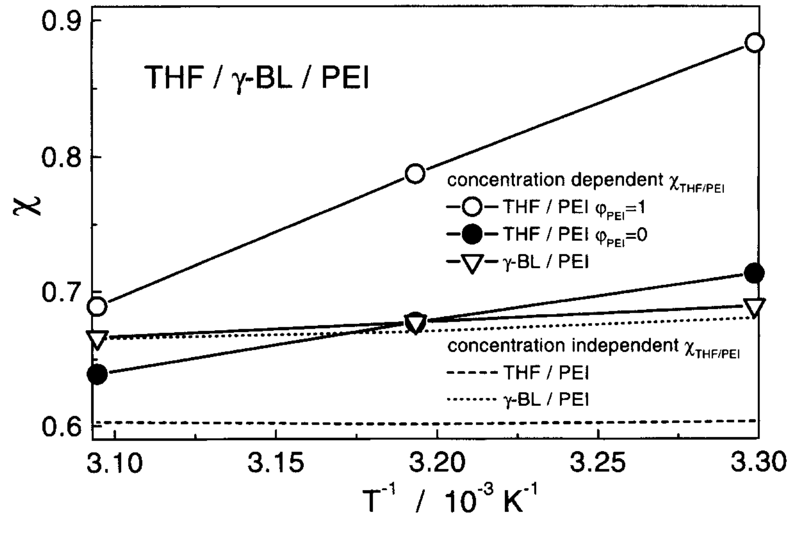

Figure 7 Temperature dependence of the interaction parameters adjusted with concentration independent parameters (dotted and broken lines) or with the concentration dependence of $\chi_{THF/PEI}$ formulated in equation (3) (solid lines and symbols)

Table 1 Physico-chemical properties of the substances and interaction parameters

	30°C	40°C	50°C
ρ_{THF} (kg m^{-3})	876.6	865.6	854.2
$\rho_{\gamma\text{-BL}}$	1119.3	1109.6	1100.1
ρ_{PEI}		13000.0	
M_{THF} (kg mol^{-1})		0.07212	
$M_{\gamma\text{-BL}}$		0.08609	
M_{PEI}		18.0	
V_{Segment} (10^{-5} m^3 mol^{-1})	8.2272	8.3318	8.4430
$\chi_{\mathrm{THF}/\gamma\text{-BL}}$		0.3	
Concentration independent $\chi_{\mathrm{THF/PEI}}$			
$\chi_{\mathrm{THF/PEI}}$	0.603	0.601	0.603
$\chi_{\gamma\text{-BL/PEI}}$	0.680	0.670	0.665
Concentration dependent $\chi_{\mathrm{THF/PEI}}$			
$\chi_{\mathrm{THF/PEI}}$ $\varphi_{\mathrm{PEI}} = 0$	0.713	0.677	0.639
$\chi_{\mathrm{THF/PEI}}$ $\varphi_{\mathrm{PEI}} = 1$	0.883	0.787	0.689
$\chi_{\gamma\text{-BL/PEI}}$	0.689	0.677	0.666

shifts to slightly higher values and its temperature dependence increases compared to variant 1.

OUTLOOK

The present experimental and theoretical results demonstrate that the phase separation behaviour of solutions of PEI in THF and γ-BL can be well described on the basis of the Flory–Huggins theory. This modelling allows the calculation of unstable and metastable regions in the phase diagram. The findings represent a starting point for more demanding studies of the processes required to prepare high performance separation membranes made of PEI. The thermodynamic description of the ternary system THF/γ-BL/PEI constitutes the basis of further research with quaternary and quinternary mixtures (butanol and water are added as auxiliary components) used in practice during the preparation of the membranes.

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