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Interfacial tension between coexisting polymer solutions in mixed solvents and its correlation with bulk thermodynamics: phase equilibria (liquid/gas and liquid/liquid) for the system toluene/ethanol/PDMS

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Abstract

Vapor pressures, phase equilibria and interfacial tensions σ were measured for solutions of poly(dimethylsiloxane) (PDMS, $M_w = 75$ kg/mol and $M_n = 50$ kg/mol) in mixed solvents of toluene (TL) and ethanol (EtOH) at 30, 40, 50 and 60 °C. The experimental ternary phase diagrams can be modeled quantitatively from the determined concentration and temperature dependent binary interaction parameters χ_{ij} if the experimentally inaccessible composition dependence of $\chi_{EtOH/PDMS}$ is adjusted. The relations between σ and the equation of state of the system differ from that applying to single solvents. The exponents as well as the amplitude prefactors of the corresponding scaling laws (e.g. the dependencies of σ on the length of the tie lines or on the hump energy, i.e. on the intrusion into the two phase regime quantified in terms of Gibbs energies) change considerably with temperature. However, this variation can be reduced significantly by normalizing the independent variables. Dividing the length of the tie lines by the length for the corresponding *binary* subsystem proves more efficient than the distance of these tie lines from the critical point of the *ternary* system relative to the maximum distance of the binary subsystem. A combined normalization does not improve the situation. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Interfacial tension; Mixed solvents; Vapor pressures

1. Introduction

Out of the three topics named in the title, only liquid/liquid phase equilibria are frequently studied in the case of the present ternary systems solvent/precipitant/polymer. There also exists a limited number of publications on liquid/gas equilibria; such work is mostly restricted to the binary systems solvent/polymer and mainly provoked by the interest in Flory–Huggins interaction parameter χ that can be determined in this manner. Little has so far been reported [1] on the interfacial tension σ of phase separated polymer solutions in mixed solvents [2].

The present study comprises all three topics of research. It was undertaken to investigate to which extent it is possible to infer from the knowledge of the phase diagram

and of equilibrium vapor pressures of a particular system on the interfacial tension existing between the coexisting liquid phases. In order to cover the entire composition scale from the volatile components up to the pure polymer and to keep the measuring temperatures convenient, we have chosen poly(dimethylsiloxane) (PDMS) for that purpose. Toluene (TL) was the solvent and ethanol (EtOH) the precipitant.

This work could be carried out within reasonable time due to the development of different methods that give easier access to the required information. For the measurement of vapor pressures we have developed an automated method that also allows the measurement of partial pressures in the case of mixed solvents [3–6]. The determination of liquid/liquid equilibria is facilitated by an automated device for turbidimetric titration [7]. On the theoretical side, it is very helpful that the calculations for the ternary systems need not be performed in terms of the chemical potentials but can be obtained by a direct minimization of the Gibbs energy [8–12].

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2. Experimental

2.1. Substances

The polymer investigated was PDMS 50n (Wacker, Germany) with a number average molecular weight of 50 kg/mol (denoted in the abbreviation) and a weight average molecular weight of 75 kg/mol. Toluene was pro analysi grade and ethanol LiChrosolv grade (>99.9%). Both solvents were used without further purification. Solvent densities were measured with DMA 48 (Anton Paar GmbH, Graz, Austria). The carrier gas for the gas chromatographic analyses was helium 4.6 (Messer-Griesheim, Germany). Information on the temperature dependent densities of the different components is compiled in Table 1.

2.2. Interaction parameters

The techniques applied to obtain thermodynamic data for polymer solutions depend on the concentration range of interest. In order to gain full information, it is mandatory to combine different methods, like osmosis (OS) and light scattering (LS) for sufficiently low polymer concentrations, head-space gas chromatography (HSGC) for moderate concentrations [6] (typically 40–95 wt% of polymer), and inverse gas chromatography (IGC) [13] in the limit of the almost pure polymer melt. In the case of HSGC in combination with a thermal conductivity detector (TCD) it turned out essential to account for non-linear response of the gas chromatograph; corrections for the non-ideality of the equilibria vapor pressures were not required.

2.3. Phase diagrams

Turbidity measurements. Homogenous solutions of PDMS in toluene were prepared with concentrations up to 40 wt% polymer. In order to obtain cloud point curves, these mixtures were titrated using an automated device [7], which measures the turbidity as a function of the amount of non-solvent (EtOH) added.

Swelling experiments. The usual procedure (uptake of the low molecular weight liquid into a polymer film) cannot be applied for PDMS due its low viscosity at the temperatures of interest. For this reason, the liquid polymer and the non-solvent were vigorously mixed for several hours some 10 °C above the equilibrium temperature and then slowly cooled

to the desired temperature. After that, the stirring was stopped and the coexisting phases were allowed to separate macroscopically. The upper part (sol phase, not containing measurable amounts of polymer) was removed carefully with a pipette and the lower part was weighed to determine its composition.

Critical points. This information was obtained by means of the phase volume ratios observed for the minimum transgression of the limits of homogeneity as described in the literature [14].

Tie lines. PDMS solutions in toluene were titrated at constant temperature with EtOH to the desired composition of the ternary system inside the two-phase regime of the phase diagram. The turbid solutions were then heated for homogenizing and subsequently cooled with a rate of 0.1 °C/min. After keeping the solutions for at least two to three days at the equilibrium temperature, the fully transparent phases were quantitatively separated by means of a syringe. The volatile components of the two phases obtained in this manner were then removed by vacuum distillation, collected and analyzed (refractive index); the remaining polymers were weighed.

2.4. Interfacial tension

The coexisting phases required for these measurements were prepared as described in Section 2.3. A minimum volume of 2–3 ml of each phase is required (app. 1.5 ml for the interfacial tension measurement and app. 1 ml to determine the density). For practical reasons, a volume ratio of unity was chosen for all compositions. A spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg, Germany) served to determine the interfacial tension σ . The very small amount of the phase forming the droplet (lower density) can be most easily sampled by introducing the needle of the syringe into the polymer rich gel phase such that it penetrates the sol phase. The temperature control-sensor, located in the metal framework of the original setup by Krüss, proved to be insufficient for our purposes. During the rotation of the glass capillary T rises significantly (e.g. ≈ 1 °C at 4000 rpm) so that the demixed solution becomes homogenous. For this reason we have modified the original apparatus by introducing an additional Pt100-sensor into one of its glass windows and controlling the temperature by means of an external thermostat.

The interfacial tension was determined from the dependence of the thickness d of the cylinder-like droplet

Table 1
Densities of the different components as a function of temperature

	Abbrev.	Density ρ (g/cm) with ϑ (°C)
Poly(dimethylsiloxane)	PDMS 50n	$\rho_{\text{PDMS}} = 0.97/[1 + 9.2 \times 10^{-4}(\vartheta - 25) + 4.5 \times 10^{-7}(\vartheta - 25)^2]^a$
Toluene	TL	$0.8855 - 9.37 \times 10^{-4}\vartheta$
Ethanol	EtOH	$0.8073 - 8.83 \times 10^{-4}\vartheta$

^a Information supplied by Wacker-Chemie GmbH; D-84489 Burghausen.

on ω , the rotary velocity, according to the following relation

$$d^3 = \frac{k\sigma}{\omega^2} \quad (1)$$

k contains the calibration constant obtained by means of a wire of known dimension. This procedure has the advantage that experimental errors, especially at small or high rotary velocities, become obvious.

3. Theoretical background

3.1. Interaction parameters

For homogeneous polymer solutions in a single solvent, the activities a_1 of the volatile component can be determined from their vapor pressures p_1 as compared with p_1^0 , that of the pure liquid, according to the following relation

$$\ln \frac{p_1}{p_1^0} = \ln a_1 = \ln(1 - \varphi_P) + \left(1 - \frac{1}{N_P}\right)\varphi_P + \chi_{1P}\varphi_P^2 \quad (2)$$

where φ_P represents the volume fraction of the polymer and N_P , the number of polymer segments. The solvent quality is quantified by χ_{1P} , the (differential) Flory–Huggins interaction parameter. In many cases of practical interest, it is not necessary to correct for the non-ideality of the gas phase. Almost always, however, the interaction parameters do not only vary with temperature but also with composition and sometimes even with chain length [4–6].

Several theoretical relations reported in the literature [15–23] were tested with respect to their validity for the description of the results obtained with the present systems. Only the following equation proposed by Koningsveld and Kleintjens [17] proved to be reasonably applicable

$$\chi = \alpha + \frac{\beta(1 - \gamma)}{(1 - \gamma\varphi_P)^2} \quad (3)$$

and the series expansion of χ according to

$$\chi = \chi_0 + \chi_1\varphi_P + \chi_2\varphi_P^2 + \dots \quad (4)$$

served the purpose [15,16].

In the case of binary polymer/non-solvents mixtures, a quantitative characterization is less comprehensive due to the normally large miscibility gap. The most straightforward information on the interaction parameter is obtained from φ_P^{swell} , the volume fraction of the polymer in polymer-rich phase for established swelling equilibrium according to

$$\chi_{2P}^{\text{swell}} = -\frac{\ln(1 - \varphi_P^{\text{swell}}) + \varphi_P^{\text{swell}}}{(\varphi_P^{\text{swell}})^2} \quad (5)$$

Due to the lack of additional data, this interaction parameter is for the present calculations taken to be identical with the integral interaction parameter g [3].

For the characterization of the mixed solvents, the measured partial vapor pressures of the two volatiles are

evaluated by means of a direct minimization of the Gibbs energy of mixing as described in the literature [24]. In this manner, one immediately obtains the integral interaction parameters required for the thermodynamic description of the ternary system.

3.2. Phase diagrams

The modeling of the critical conditions plus binodal and spinodal lines of the present ternary systems was again performed via the above-mentioned direct minimization of the Gibbs energy of the system. These calculations are based on the following expression

$$\frac{\Delta \bar{G}_m}{RT} = \sum_{i=1}^m \frac{\varphi_i}{N_i} \ln \varphi_i + \sum_{i=1}^{m-1} \sum_{j=i+1}^m g_{ij}\varphi_i\varphi_j \quad (6)$$

where the double bar indicates that the Gibbs energy refers to a mixture containing 1 mol of segments. φ_i are the volume fractions and g_{ij} the binary integral interaction parameters. For the polymer/solvent interaction, g is calculated from χ (resulting from the vapor pressure measurements) in the usual manner [3].

3.3. Interfacial tension

For the variation of the interfacial tension σ of binary mixtures with other parameters, like temperature, one often uses power laws of the following form

$$\sigma = \hat{\sigma}_x x^\alpha \quad (7)$$

where x may stand for $\tau = (T - T_c)/T_c$, the relative distance of the measuring temperature T to the critical temperature T_c of the system, for $\Delta\varphi$, the length of the tie line, or for ε , the so called hump energy, discussed in Section 4. In case of sufficient proximity of the system to the critical conditions, the power law exponent a of the above expression is independent of the chemical nature of the system, in contrast to $\hat{\sigma}_x$, the amplitude prefactor with respect to x , which may vary considerably [25,26].

The (reduced) hump energy ε is given by the area between the curve describing the Gibbs energy of mixing for the molecularly disperse, homogeneous system and the double tangent to this function, determining φ_P^I and φ_P^{II} , the composition of the macroscopically coexisting phases. For a binary mixture, this definition reads

$$\varepsilon = \frac{1}{RT} \int_{\varphi_P^I}^{\varphi_P^{II}} \left\{ \left[\frac{\bar{G}_m(\varphi_P^I) - \bar{G}_m(\varphi_P^{II})}{\varphi_P^I - \varphi_P^{II}} \right] \varphi_P + \bar{G}_m(\varphi_P^{II}) - \left[\frac{\bar{G}_m(\varphi_P^I) - \bar{G}_m(\varphi_P^{II})}{\varphi_P^I - \varphi_P^{II}} \right] \varphi_P^{II} - \bar{G}_m(\varphi_P) \right\} d\varphi_P \quad (8)$$

and Eq. (7) becomes

$$\sigma = \hat{\sigma}_p \varepsilon^\varphi \quad (9)$$

4. Results and discussion

The interpretation of the observed interfacial behavior requires experimental and theoretical knowledge on the phase diagram of the system. For this reason we have performed vapor pressure measurements on the binary subsystems solvent/polymer and solvent/precipitant to determine two of the three binary interaction parameters needed for the modeling of the demixing behavior. The third interaction parameter, describing the interaction between the precipitant and the polymer, was obtained from the measured phase diagram.

4.1. Interaction parameters

Fig. 1 shows how the reduced vapor pressure of toluene varies with the volume fraction of PDMS for the four temperatures indicated in this graph. The positions of the different isotherms indicate endothermal heats of dilution. Also depicted in this graph are the corresponding interaction parameters χ calculated from the measured p_{vap} by means of Eq. (2). In order to portray the entire available information on the composition dependence of interaction parameters we have included the χ_0 values resulting from osmotic pressure experiments [26] with dilute solutions (for which vapor pressure measurements are too inaccurate) and the χ_∞ values originating from IGC-measurements [13].

An analytic description of $\chi(\varphi)$ turns out to be difficult due to the occurrence of extrema that cannot be modeled realistically by most theories [17–19,22,23]. The lines shown in Fig. 1 correspond to a series expansion up to the

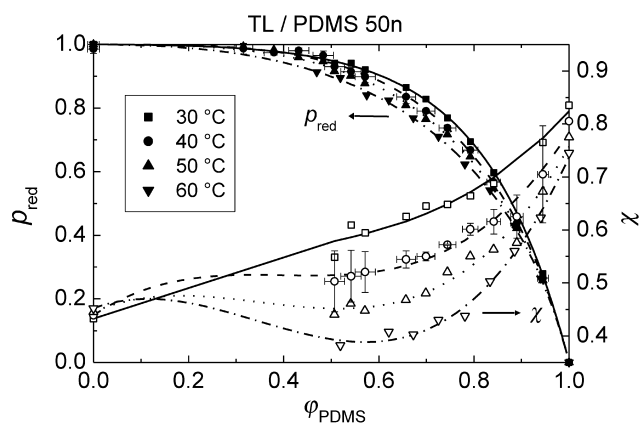


Fig. 1. Reduced vapor pressure (equilibrium vapor pressure p_{vap} of the solvent above the polymer solution, divided by the vapor pressure of the pure solvent) of TL as a function of the volume fraction of PDMS at the indicated temperatures (left scale), and Flory–Huggins interaction parameter χ as a function of composition calculated therefrom by means of the Eqs. (2) and (4) (right scale, $\chi_1 = 1/3$, χ_2 and χ_3 adjusted).

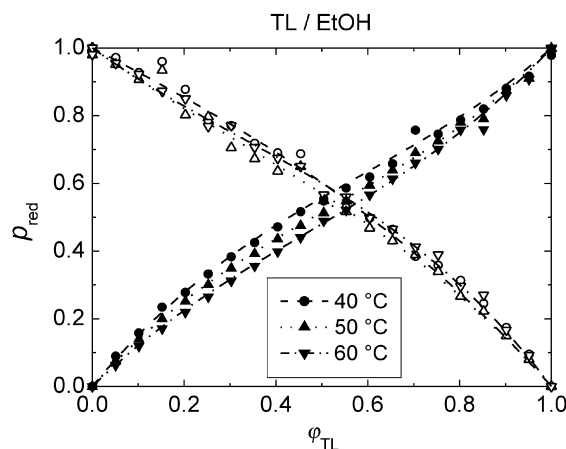


Fig. 2. Reduced vapor pressures for the binary system TL/EtOH as a function of the volume fraction φ of TL at the different, indicated temperatures.

third power, setting the coefficient of the second term equal to 1/3 in view of theoretical considerations [26].

Fig. 2 shows the reduced partial vapor pressures of the mixed solvent TL/EtOH as function φ_{TL} for three temperatures. The measured data are thermodynamically consistent within the normal experimental errors [27,28]. The corresponding Flory–Huggins interaction parameter were obtained by plotting $\ln(p_{\text{EtOH}}/p_{\text{TL}}) - (\ln(1 - \varphi_{\text{TL}}) + (V_{\text{EtOH}}/V_{\text{TL}})\varphi_{\text{TL}})$ as a function of φ_{TL}^2 (rearrangement of Eq. (2)), from the slope of these graphs which yields $\chi_{\text{TL}/\text{EtOH}}$ [29]. Within the range of composition of the mixed solvent that is of interest for the modeling of the phase diagram of the ternary system, the slope is constant, i.e. the interaction parameter can be considered constant. The corresponding data are collected in Table 2.

Swelling experiments can naturally supply information on the interaction parameters between the polymer and the precipitant for one concentration only. According to our modeling, this input is, however, insufficient to reproduce the experimental observations. It would predict complete miscibility of the components of this binary subsystem in contrast to reality. For this reason, we treat the parameter $\chi_{2\text{P}}$ concentration dependent using the relation reported by

Table 2

Parameters used for the modeling of the phase diagrams of the system TL/EtOH/PDMS 50n ($N_{\text{TL}} = 1.82$; $N_{\text{EtOH}} = 1.0$; SF: Shultz–Flory; KK: Koningsveld–Kleintjens)

T (°C)	30	40	50	60
N_{PDMS}	877.61	875.73	873.74	871.64
$g_{\text{TL}/\text{EtOH}}$ (SF) HS-GC	1.150	0.701	0.750	0.798
$g_{\text{TL}/\text{PDMS}}$ (KK) HS-GC	α 0.0	0.4264	0.3711	0.3020
	β 0.5789	0.1084	0.1054	0.1094
	γ 0.2556	0.6748	0.7249	0.7549
$g_{\text{EtOH}/\text{PDMS}}$ (KK)	α 0.0	0.0	0.0	0.0
	β 1.302	1.117	1.120	1.065
	γ 0.117	0.170	0.222	0.207

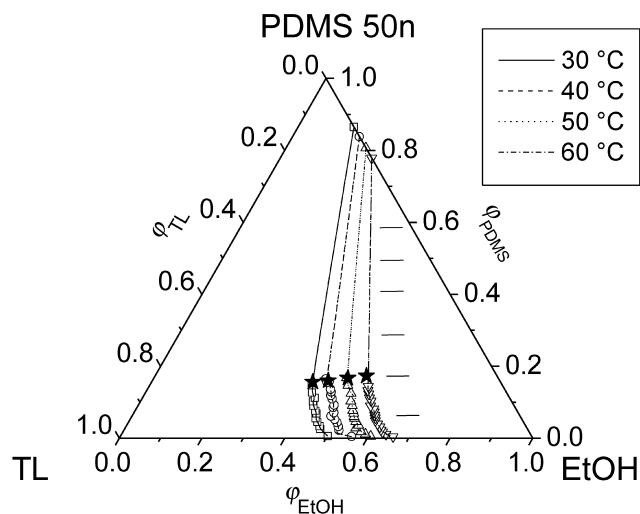


Fig. 3. Cloud points (open symbols) and critical points (full stars) measured for the system TL/EtOH/PDMS at the indicated temperatures; also shown are the swelling points of the polymer in the precipitant. The lines are guides for the eye only.

Koningsveld and Kleintjens setting α of Eq. (3) equal to zero and adjusting the parameters β and γ .

4.2. Phase diagrams

The regions of incomplete miscibility of the polymer and the components of the mixed solvent as determined from cloud point measurements and swelling experiments at different temperatures can be seen in Fig. 3. The fact that the extension of the two-phase region decreases with rising temperature testifies UCSTs. As expected from the position of the critical points, the tie lines are slightly rotated counterclockwise with respect to the lines passing the PDMS corner, as shown in Fig. 4 for one temperature. This

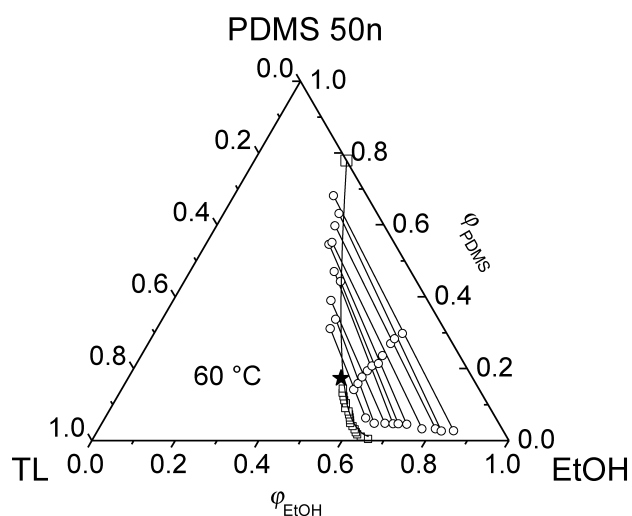


Fig. 4. Tie lines of the system TL/EtOH/PDMS at 60 °C. Also shown are the cloud point curve (open squares) and the critical point (full star) under these conditions. The results for the other temperatures look qualitatively very similar.

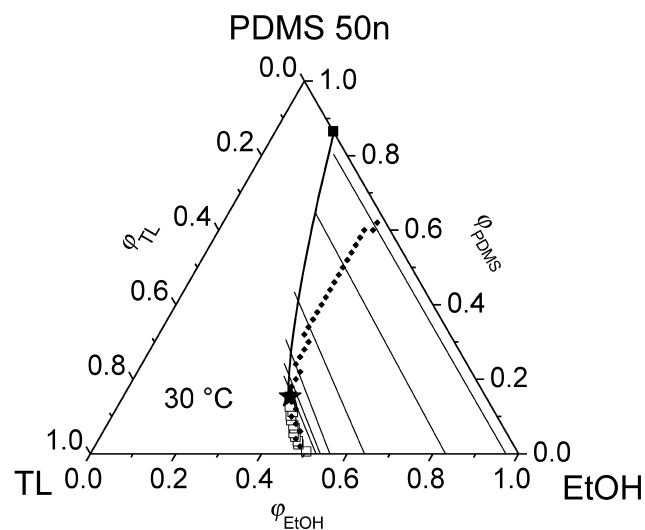


Fig. 5. Spinodal curve (dotted line) and some tie lines calculated for 30 °C for the system TL/EtOH/PDMS as described in the text by means of Eq. (4) on the basis of the interaction parameters collected in Table 2. Also shown are measured cloud points, the critical point (full star) and the swelling point of the binary subsystem (full square).

means that the mixed solvent behaves ‘normal’ i.e. the solvent prefers the gel phase and the precipitant the sol phase. The slight but systematic displacement of the ends of the individual tie lines from the cloud point curve hardly exceeds the experimental uncertainty and could be due to the polydispersity of the present PDMS sample.

Fig. 5 shows the phase diagram calculated from the binary interaction parameters reported in the previous section (Table 2) neglecting the polymolecularity of PDMS. This modeling naturally does not account for the dislocation of the tie lines but otherwise describes the experimental findings very satisfactorily and thus constitutes a reliable basis for the discussion of the dependence of the interfacial tension on the composition of the mixed solvent.

4.3. Interfacial tension

The discussion of the scaling behavior for ternary systems is considerably less straightforward than with binary ones. For this reason we examine several options for a correlation of the interfacial tension with other thermodynamic quantities. The critical exponents and amplitude prefactors of the different attempts resulting there from are collected in Table 3.

4.3.1. Correlation with tie lines

The dependence of σ on $\Delta\phi$, the length of the tie line in terms of volume fractions, is most evident, because both quantities can be directly measured. The corresponding evaluation is shown in Fig. 6 for different temperatures. This graph demonstrates the lack of a general scaling law beyond doubt. In view of the additional thermodynamic variable

Table 3
Critical exponents and amplitude prefactors

Scaling law	ϑ (°C)	Amplitude prefactor	Critical exponent
$\sigma(\Delta\varphi)$	30	3.398	3.00 mean-field, 3.88 Ising
	40	0.593	4.153
	50	0.711	2.008
	60	0.984	2.221
$\varepsilon(\Delta\varphi)$	30	0.092	5.00 mean-field, 6.81 Ising
	40	0.173	3.801
	50	0.123	5.505
	60	0.043	5.345
$\sigma(\Delta\varepsilon)$	30	152.770	0.6 mean-field, 0.57 Ising
	40	13.786	1.219
	50	26.900	0.762
	60	36.615	0.915
$\sigma(\delta)$	30	0.673	0.984
	40	0.649	1.303
	50	0.837	1.369
	60	0.888	1.713
$\sigma(\delta/\Delta\varphi_0)$	30	1.273	1.834
	40	1.167	1.036
	50	1.685	1.036
	60	1.705	1.036

(composition of the mixed solvent) this result is, however, not too surprising.

4.3.2. Correlation with hump energies

According to theoretical considerations, the interfacial tension should also be correlated with the so called reduced hump energy ε . This quantity measures the difference between the curve describing the reduced Gibbs energy of mixing as a function of composition for the (hypothetical) homogeneous mixtures and the double tangent to this curve, determining the composition of the phases that coexist under equilibrium conditions. The definition of ε is illustrated for the ternary systems of present interest in Fig. 7. Because of the fact that the calculation of the hump

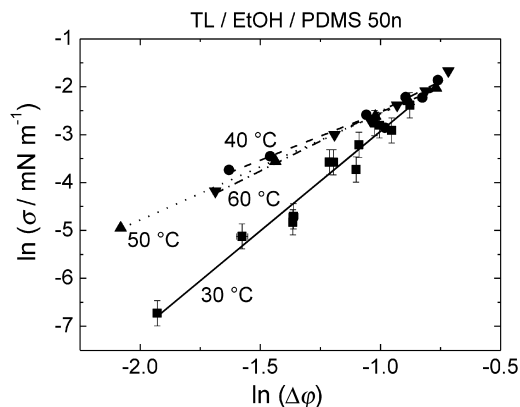


Fig. 6. Natural logarithm of the interfacial tension σ for the system TL/EtOH/PDMS as a function of $\ln(\Delta\varphi)$, where $\Delta\varphi$ is the length of the tie line. The measuring temperatures are indicated.

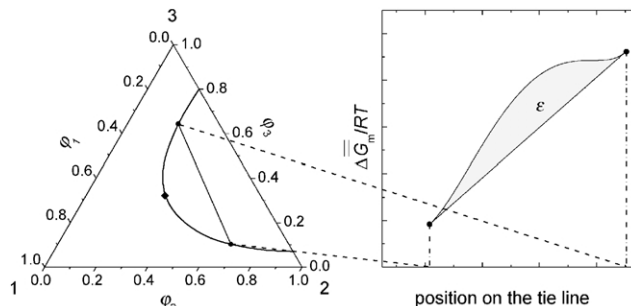


Fig. 7. Scheme demonstrating how the reduced hump energy ε is calculated in the case of ternary systems. A given over-all composition inside the miscibility gap fixes position and length of the tie line (left part), by definition ε signifies the area between the curve representing the composition dependence of the (hypothetically) homogeneous mixture as one moves along the tie line from one coexisting phase to the other (right part: upper curve) and the straight line representing the corresponding (equilibrium) two phase state (right part: straight line).

energy must proceed along the tie line, we also indicate in this graph how the reduced Gibbs energy of mixing under these boundary conditions. Mathematically, this requirement means that the Gibbs energies must be treated as a function of two variables (φ_p and φ_l) instead of one (φ_p) such that all points are situated on the tie line. The numerical integration method was preferred over the analytical method by means of Eq. (8).

The evaluation of the present data according to the described procedure yields a picture which is very similar to that of the correlation between σ and $\Delta\varphi$. Again, critical exponents and amplitude prefactors vary with temperature as shown in Fig. 8.

4.3.3. Other correlations

The reason why the scaling laws established for binary systems fail lies in the fact that a certain thermodynamic quality of mixed solvents can be realized by infinitely many combinations of chemically different solvents and non-solvents. It would therefore be recommendable to search for independent variables that account in an adequate manner for the particularities of the components of a mixed solvent.

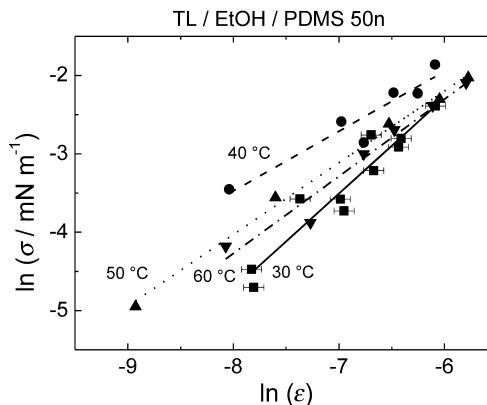


Fig. 8. Correlation between the interfacial tension σ and the reduced hump energy ε for different temperatures.

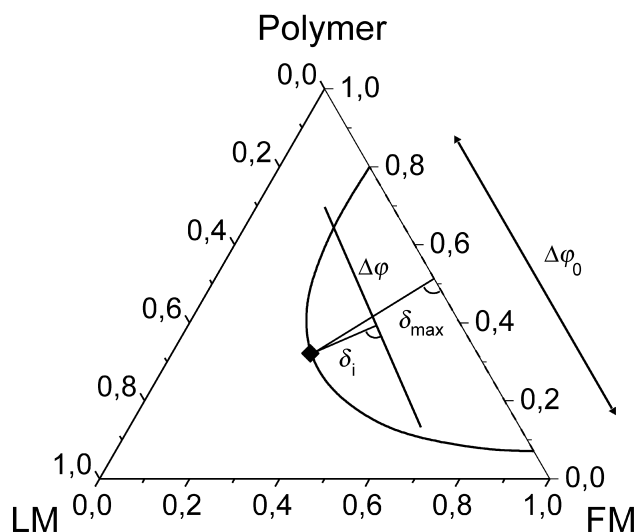


Fig. 9. Scheme displaying options for the normalization of the thermodynamic conditions in phase separated solutions of polymers in mixed solvents. One option uses δ_{\max} , the distance of the critical point (full square) from tie line of the binary subsystem precipitant/polymer, the other one employs $\Delta\varphi_0$, the length of the tie line of this subsystem, for that purpose.

Two possibilities are visualized in Fig. 9. The most obvious option consists in the normalization of $\Delta\varphi$ to $\Delta\varphi_0$, the length of the tie line of the binary subsystem non-solvent/polymer; it accounts explicitly for the strength of the precipitant. A less evident but promising alternative introduces the ratio of δ , the distance of the tie lines from the critical point of the ternary system, and δ_{\max} , the maximum distance corresponding to the binary subsystem precipitant/polymer as a new variable. This choice does not only account for the thermodynamic quality of the precipitant, but also for that of the solvent via its fraction that is required to realize critical conditions. Furthermore, it can automatically reproduce the correct limiting behavior [26]. The interfacial tension becomes σ_{2P} (value for the binary subsystem) as δ_i/δ_{\max} approaches unity and tends to zero as δ_i/δ_{\max} vanishes (critical conditions for the ternary system). Such a correlation should consequently be at least helpful for a reliable interpolation of experimental results.

Fig. 10 shows the evaluation of the measured interfacial tensions with respect to $\Delta\varphi/\Delta\varphi_0$, the reduced length of the tie lines. The variation of these correlations with temperature is considerably less pronounced than with $\Delta\varphi$ (Fig. 6). This result can be tentatively interpreted in terms of a much more pronounced temperature influence on the thermodynamic quality of the precipitant as compared with that of the solvent. Nevertheless, it appears impossible to formulate a common scaling law for all temperatures, because of a noticeable trend of the scaling exponents with T , which is beyond experimental error.

The idea to account for the particularities of a given mixed solvent by means of the normalized distance of the tie line from the critical point of the ternary system (Fig. 9) is

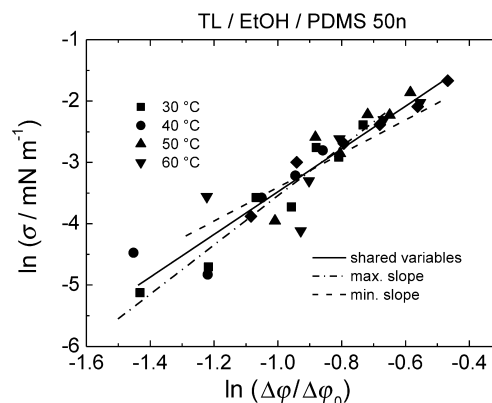


Fig. 10. Correlation between σ and the normalized length of the tie line $\Delta\varphi/\Delta\varphi_0$ (Fig. 9) for the system TL/EtOH/PDMS for different temperatures. The corresponding dependence $\sigma(\Delta\varphi)$ is shown in Fig. 6.

checked by means of Fig. 11. This graph demonstrates that this approach is considerably inferior to the previous option.

For this reason we have also examined whether a combination of the two possibilities discussed above would give better results. To this end we choose the product $\Delta\varphi\delta/\Delta\varphi_0\delta_{\max}$ as the independent variable for the evaluation shown in Fig. 12. The different isotherms obtained in this manner are considerably more dispersed than those shown in Fig. 10. The critical exponent, on the other hand, turns out to be almost independent of temperature. This result should, however, not be overvalued in view of all experimental uncertainties and the insignificant differences in the quality of correlation.

5. Conclusions

The present study on the interfacial tension between coexisting phases of polymer solutions in mixed solvents has made evident that the scaling laws established for polymer solutions in single solvents do in the general case not remain valid because of the presence of a further

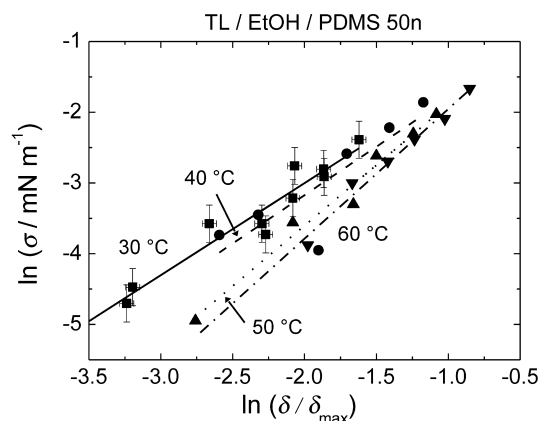


Fig. 11. Correlation between σ and the normalized distance δ/δ_{\max} of the tie line from critical point of the ternary system (Fig. 9) for the system TL/EtOH/PDMS for different temperatures.

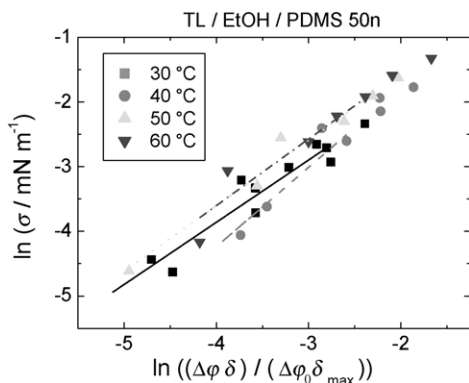


Fig. 12. Correlation between σ and $(\Delta\varphi\delta)/(\Delta\varphi_0\delta_{\max})$, i.e. dependence of the interfacial tension on a variable that simultaneously accounts for the strength of the precipitant ($\Delta\varphi_0$) and for the thermodynamic quality of the solvent (δ_{\max}).

(chemically different) component. Different attempts to account for this observation (which has to be expected from phenomenological thermodynamic considerations) were reported. However, none of them has resulted in a truly universal description of σ on temperature and composition. The best representation of the experimental data could be achieved in terms of the reduced length of the tie lines. To which extent this finding is generally applicable or a specificity of the system under investigation must remain open until further experimental evidence with thermodynamically widely different systems is available.

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