

Evidence of ternary interaction parameters for polymer solutions in mixed solvents from headspace-gas chromatography

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Abstract

Partial vapor pressures of the volatiles have been measured for four solvent/precipitant/polymer systems at different temperatures. The high molecular weight compounds were polysulfone or polyethersulfone and the mixed solvent was either DMF/acetone or DMF/water. Systems containing the very powerful precipitant water exhibit a special phenomenon: Upon the addition of polymer to a mixed solvent of constant composition the partial vapor pressure of water increases by a factor of more than two before it falls to zero as the volume fraction of the polymer approaches unity. This particular situation cannot be modeled using binary interaction parameters only, in contrast to the results obtained with acetone as the precipitant. The present findings are used to discuss the necessity of ternary interaction parameters and possibilities for their calculation from known binary interaction parameters. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ternary interaction parameters; Headspace-gas chromatography; Polyethersulfone and polysulfone

1. Introduction

The question of whether it is possible to predict the thermodynamic behavior of multicomponent systems by means of the mere knowledge of the binary interaction parameters g_{ij} is of great theoretical interest and practical importance. Many attempts have therefore been made to find a conclusive answer [1–5]. Most of the past work was, however, restricted to the dilute regime and suffers from the fact that direct information on the interaction between a polymer and a precipitant (a liquid in which the polymer does not dissolve noteworthy, but takes up considerable amounts of solvent) is hard to obtain.

The latter restriction has meanwhile become less stringent thanks to the development of a method, that combines a headspace-sampler with a normal gas chromatograph [6–8]. This technique, so far applied to binary systems only, gives access to the partial vapor pressures of the components of mixed solvents in the presence of polymer (the different volatiles are separated in the GC). The additional knowledge on the chemical potentials of precipitants offers new possibilities to find an answer to the above question concerning the necessity of ternary interaction parameters.

For the present investigation we have chosen solutions of

a polysulfone and of a polyethersulfone in binary mixed solvents consisting of a good solvent and of a precipitant because of two reasons. Part of the information concerning the binary sub-systems has already been obtained in the course of a study on the effects of thermodynamic conditions during membrane formation on their performance [9,10] and an unexpected enrichment of the precipitant in the gas phase above the ternary mixtures at high polymer concentrations [11], which can be taken as an indication for the existence of ternary interactions.

2. Experimental part

2.1. Materials

The polysulfone (PSU 39w) and polyethersulfone (PES 49w) were both produced by BASF (Ludwigshafen, Germany) under the trade names Ultrason S 3010 and Ultrason E 6020 P. The numbers in the abbreviations given in brackets indicate their weight average molecular weight in kg/mol, as determined by light scattering experiments in *N*-methylpyrrolidone (NMP) at 30°C.

N,N-dimethylformamide (DMF) of absolute grade (stored under nitrogen atmosphere, in contact with molecular sieves) was purchased from Fluka (Neu-Ulm, Germany). It was used without further purification but kept under Argon after opening. The mass fraction purity of the DMF

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as determined by gas chromatography amounts to 0.999. Acetone (AC, for spectroscopy) was also supplied by Fluka and used without further purification.

2.2. Headspace-gas chromatography

Measurements have been carried out with an apparatus consisting of a headspace-sampler (Dani HSS 3950, Milano, Italy) and a normal gas chromatograph (Shimadzu GC 14B, Kyoto, Japan). This procedure gives access to the amounts of the volatiles in a constant volume of vapor phase, which is in thermodynamic equilibrium with the liquid. From these data it is possible to calculate the partial pressures of the volatiles. A detailed description of the machine and the method has already been given [6–8].

Samples of the different liquids (2.5 ml) were filled into crimp top vials (capacity 5 ml) and sealed with air-tight septa. In order to guarantee thermodynamic equilibrium, they were conditioned for 24 h at constant temperature inside the headspace-sampler before the analysis. The reproducibility of the experimental results was checked by means of at least five independent measurements for each sample and temperature; the experimental error in the vapor pressures is typically of the order of 1–3%—only for DMF it goes up to 6% as a result of its low volatility.

All measurements were performed within the homogeneous region of the different ternary systems known from the earlier experiments and theoretical analysis [10]. Keeping the composition of the low molecular weight compounds constant, the concentration of the polymer was varied within the range from 25 to 85 vol%. According to this procedure, the compositions of a sample series are located on a straight line in the corresponding phase diagram [11].

3. Theoretical background

The evaluation of experimental data is performed in terms of the well-known Flory–Huggins equation

$$\frac{\Delta \bar{G}}{RT} = \frac{\varphi_1}{N_1} \ln \varphi_1 + \frac{\varphi_2}{N_2} \ln \varphi_2 + \frac{\varphi_P}{N_P} \ln \varphi_P + g_{12} \varphi_1 \varphi_2 + g_{1P} \varphi_1 \varphi_P + g_{2P} \varphi_2 \varphi_P + g_{12P} \varphi_1 \varphi_2 \varphi_P \quad (1)$$

where index 1 stands for the solvent, index 2 for the precipitant, and index P for the polymer. For the calculation of N_i , the number of segments of component i , the smallest molar volume of the constituents is taken as the segmental volume. The possible ternary interaction parameters of the type iiP or iPP (i corresponding to 1 or 2) are, as usual, incorporated into the concentration dependence of the corresponding g_{iP} . Only ternary interactions between 1, 2 and P are dealt with explicitly in terms of g_{12P} .

The measured partial pressures of the volatiles in multinary mixtures were evaluated with respect to the interaction parameters by means of a minimization of the Helmholtz

energy of the system in thermodynamic equilibrium on a computer. This method [12] has already been applied to binary mixed solvents and to polymer solutions [8,10]. By means of this iteration procedure it is possible to find out whether a certain interaction parameter depends on the composition of the mixture, and—if this is actually the case—to establish the most adequate equation for its mathematical representation.

For the description of g_{ij} we use three different expressions. The series expansion reported by Redlich and Kister [13],

$$g_{ij}(\varphi_i) = b + c(2\varphi_i - 1) + d(2\varphi_i - 1)^2 + e(2\varphi_i - 1)^3 + \dots \quad (2)$$

where b , c , d and e are adjustable, the equation of Koningsveld and Kleintjens [14],

$$g_{ij}(\varphi_j) = \alpha + \frac{\beta}{1 - \gamma\varphi_j} \quad (3)$$

with the adjustable parameters α , β and γ , plus the relation of Wilson [15]

$$g_{ij} = -\frac{1}{N_i\varphi_j} \ln(1 - A_{ji}\varphi_j) - \frac{1}{N_j\varphi_i} \ln(1 - A_{ij}\varphi_i) \quad (4)$$

where A_{ji} and A_{ij} are adjusted.

Two theoretical expressions accounting for non-random mixing were also used. The so called NRTL [16]:

$$g_{ij} = \frac{\epsilon_i}{RTN_j} \frac{\exp(-a\epsilon_i/RT)}{\varphi_i + \varphi_j/N_j[\exp(-a\epsilon_i/RT)]} + \frac{\epsilon_j}{RTN_j} \frac{\exp(-a\epsilon_j/RT)}{\varphi_j/N_j + \varphi_i[\exp(-a\epsilon_j/RT)]} \quad (5)$$

in which ϵ_i , ϵ_j and a are adjustable parameters, and the following relation, based on the concept of quasi-chemical equilibria [17,18]

$$g_{qce} = g_{ij} \frac{-1 + \sqrt{1 + 4\alpha_\omega}}{2\alpha_\omega} \quad (6)$$

where the interaction parameter g_{qce} , accounting for the establishment of quasi-chemical equilibria, is calculated from the interaction parameter g_{ij} , referring to random mixing (e.g. Eqs. (2)–(4)), by means of the interchange energy ω according to [17,18]

$$\alpha_\omega = \varphi_i\varphi_j[\exp(2\omega/kT) - 1]. \quad (7)$$

Information on the binary interaction parameter g_{2P} (which is normally not directly accessible) can be obtained for one composition from swelling experiments with the binary mixtures and as a function of concentration by modeling the phase diagrams measured for the ternary systems. In the first case, it is possible to obtain the differential interaction parameter from the condition of equal chemical potentials of the solvent in the coexisting phases by means of φ_P^{swell} , the volume fraction of polymer for

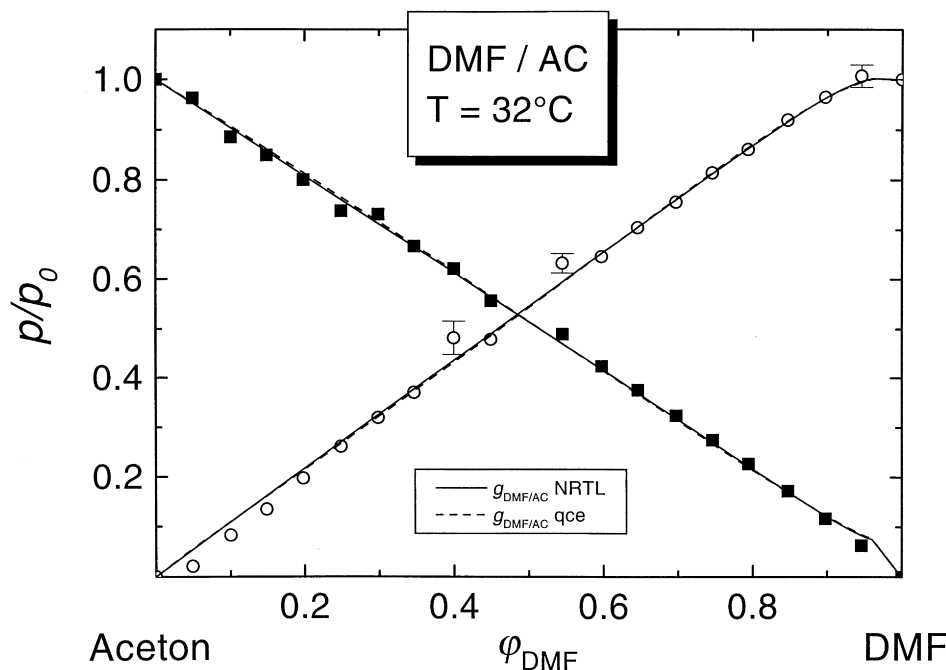


Fig. 1. Experimentally determined reduced partial vapor pressures of DMF and AC as a function of the volume fraction of DMF of the mixtures at 32°C and representation of these results by means of $g_{\text{DMF/AC}}$. Solid line: calculated according to Eq. (5); broken line: calculated according to Eqs. (4) and (6).

established swelling equilibrium [10]. Since this information refers to one composition of the binary system only and nothing is known on the concentration dependence of the differential interaction parameter we set it for the present purposes equal to the integral parameter g_{2P}^{swell} so that we can write

$$g_{2P}^{\text{swell}} = -\frac{\ln(1 - \varphi_P^{\text{swell}}) + \varphi_P^{\text{swell}}}{(\varphi_P^{\text{swell}})^2} \quad (8)$$

The modeling of the phase diagrams for the ternary systems has shown that g_{2P} is well described by

$$g_{2P}(\varphi_P) = k + l\varphi_P + m\varphi_P^2 \quad (9)$$

where the parameters k , l and m are adjusted.

The discussion with respect to the ternary interaction parameters g_{12P} rests on the expression reported by Figueruelo [5].

$$g_{12P}(\varphi_1^*, \varphi_P) = g_{12}(\varphi_1^*) \frac{g_{1P}^0 g_{2P}^0}{1 - g_{1P}^0 (\partial g_{2P} / \partial \varphi_P) - g_{2P}^0 (\partial g_{1P} / \partial \varphi_P)} + \varphi_P g_{12}(\varphi_1^*) \frac{g_{1P}^0 (\partial g_{2P} / \partial \varphi_P) + g_{2P}^0 (\partial g_{1P} / \partial \varphi_P)}{1 - g_{1P}^0 (\partial g_{2P} / \partial \varphi_P) - g_{2P}^0 (\partial g_{1P} / \partial \varphi_P)} \quad (10)$$

This equation, which was established for dilute solutions of a polymer in a mixed solvent, relates g_{12P} to the three binary interaction parameters of the sub-systems. It is formulated for constant composition of the pure mixed

solvent, given by

$$\varphi_1^* = 1 - \varphi_2^* = \frac{\varphi_1}{\varphi_1 + \varphi_2} \quad (11)$$

The superscripts zero in Eq. (10) indicate that the interaction parameters refer to vanishing polymer concentration.

4. Results and discussions

The solvent component (index 1) was DMF in all cases. Two different precipitants (index 2), namely AC and water, have been used for PES as well as for PSU (index P). Partial vapor pressures were in all cases measured at least at three temperatures. In view of this large number of systems and temperatures, only the most interesting and typical results are presented in detail. More information is available on request. In the subsequent presentation, the material is grouped according to the nature of the precipitant since the choice of this component turned out to be the most important for the phenomena that are observed.

4.1. Systems containing acetone

4.1.1. Binary sub-systems

Fig. 1 shows how the reduced partial vapor pressures of DMF and AC vary with the composition of the binary mixed solvent at 32°C (the error bars, shown for representative data only, result from a statistical analysis of the experimental data and considering all errors occurring during the measurements). The composition dependencies of the binary interaction parameter, formulated in Eqs. (5) and

Table 1

Interaction parameters for DMF/AC, the components of the mixed solvent, as determined from their partial vapor pressures in the absence of polymer according to the cited relations; $g_{\text{DMF/AC}}^{0.5}$ is the interaction parameter for $\varphi_{\text{DMF}} = 0.5$

Interaction parameters for DMF/AC				
T (°C)		32	41	50
$N_{\text{DMF}}(N_{\text{AC}} = 1)$		1.0435	1.0391	1.0346
NRTL Eq. (5)	$g_{\text{DMF/AC}}^{0.5}$	0.2238	0.0539	0.1948
	ϵ_j/RT	7.1446	1.8402	3.3031
	ϵ_j/RT	0.0330	-0.7831	0.0025
	a	0.5955	0.5328	1.0515
Quasi-chemical equilibria Eq. (6), g_{ij} Eq. (4)	$g_{\text{DMF/AC}}^{0.5}$	0.2188	0.0631	0.1701
	A_{ji}	1.0160	0.9752	0.9694
	A_{ij}	-1.0117	-1.7695	-1.4337
	ϵ	1.5675	1.0000	0.8351

(6) in combination with Eqs. (4) and (7), represent the present data best. The observation that the parameters of these relations, collected in Table 1, do not change systematically with temperature results from the fact that different sets of parameters describe the experimental results with comparable accuracy. Equations assuming random mixing (Eqs. (2)–(4)) turned out to be inadequate.

The binary interaction parameters g_{IP} have already been reported [10]; the data for $g_{\text{AC/P}}$ obtained from swelling experiments and from modeling of the ternary phase diagrams are listed in Table 2.

4.1.2. Ternary systems

Out of the many measurements with mixtures of DMF, AC and PES or PSU, only that for PSU at one composition of the mixed solvent and at 32°C is shown graphically, since

Table 2

Concentration dependencies of $g_{\text{AC/P}}$ resulting from either the evaluation of the phase diagrams or from vapor pressures measured for the ternary systems, exemplified for DMF/AC/PSU 39w ($\varphi_{\text{AC}}^* = 0.232$) and DMF/AC/PES (49w) ($\varphi_{\text{AC}}^* = 0.341$) at 32°C

Interaction parameters AC/PSU and AC/PES		PSU 39w	PES 49w
Eq. (8) (swelling experiments)	$g_{2\text{P}}^{\text{swell}}$	0.80	0.74
Eq. (9) (modeling of the phase diagrams)	$g_{\text{AC/P}}^{0.5}$	0.93	0.98
	k	0.90	0.92
	l	-0.02	0.10
	m	0.16	0.05
Eq. (12) (vapor pressures, $b = 0$)	a	0.434	0.327
Eq. (13) (vapor pressures, $b^* \neq 0$)	$g_{\text{AC/P}}^{0.5}$	0.573	0.423
	b^*	-0.493	-0.547
	$\varphi_{\text{P}}^{\text{swell}}$	0.520	0.460

these results are typical. The corresponding primary data have already been reported [11]. For the sake of comparison, the parameters describing $g_{2\text{P}}(\varphi_{\text{P}})$ in the case of one PES system are also included in Table 2.

First we have checked whether the vapor pressures measured for the ternary systems can be calculated on the basis of Eqs. (8) and (9) by means of the parameters obtained from phase diagrams. Since these dependencies (cf. Fig. 2a) do not represent the findings with sufficient accuracy, we have formulated the two following relations:

$$g_{2\text{P}} = a + b\varphi_{\text{P}} \quad (12)$$

where a and b are adjusted to the measured vapor pressures, and

$$g_{2\text{P}} = g_{2\text{P}}^{\text{swell}} + b^*[\varphi_{\text{P}} - (2\varphi_{\text{P}}^{\text{swell}} - 1)] \quad (13)$$

which is obtained from Eq. (12) by substituting the parameter a using the information of the swelling experiments (accounting for the differences between differential and integral interaction parameters).

Fig. 2a demonstrates that it is possible to predict the vapor pressures of the present ternary system in an approximate manner on the basis of the binary interaction parameters obtained from the independent measurements. From part b of this graph, it becomes obvious that the results can be modeled quantitatively within experimental error if $g_{\text{AC/PSU}}$ is fitted to the measured vapor pressures. The best agreement is obtained if one uses Eq. (12) and sets $b = 0$. In this context it appears worthwhile to note that the interaction between the precipitant and the polymer results more favorable from the vapor pressures of the ternary system than from swelling experiments with the binary sub-system (cf. Table 2). In conclusion of the valuation of the experiments with the mixed solvent DMF/AC it can be stated that there is no need to account for extra effects stemming from ternary interactions 1–2–P in this special case under consideration.

4.2. Systems containing water

4.2.1. Binary sub-systems

The thermodynamic properties of the mixed solvent consisting of DMF and water have already been reported [8], as well as the determination [10] of g_{IP} (by means of HS-GC and light scattering) and $g_{2\text{P}}$ (from swelling data and from modeling according to Eqs. (8) and (9)).

4.2.2. Ternary systems

Solutions of PES or PSU in the mixed solvent DMF/H₂O exhibit an outstanding feature [11]. The vapor contains considerably more precipitant than calculated along the usual thermodynamic lines. From Figs. 3 and 4, which present some results for PES and two constant compositions of the mixed solvent, it can be clearly seen that the partial vapor pressure of water increases markedly as the polymer concentration rises. At $\varphi_{\text{P}} \approx 0.85$ it becomes more than twice as large than in the absence of the polymer. This

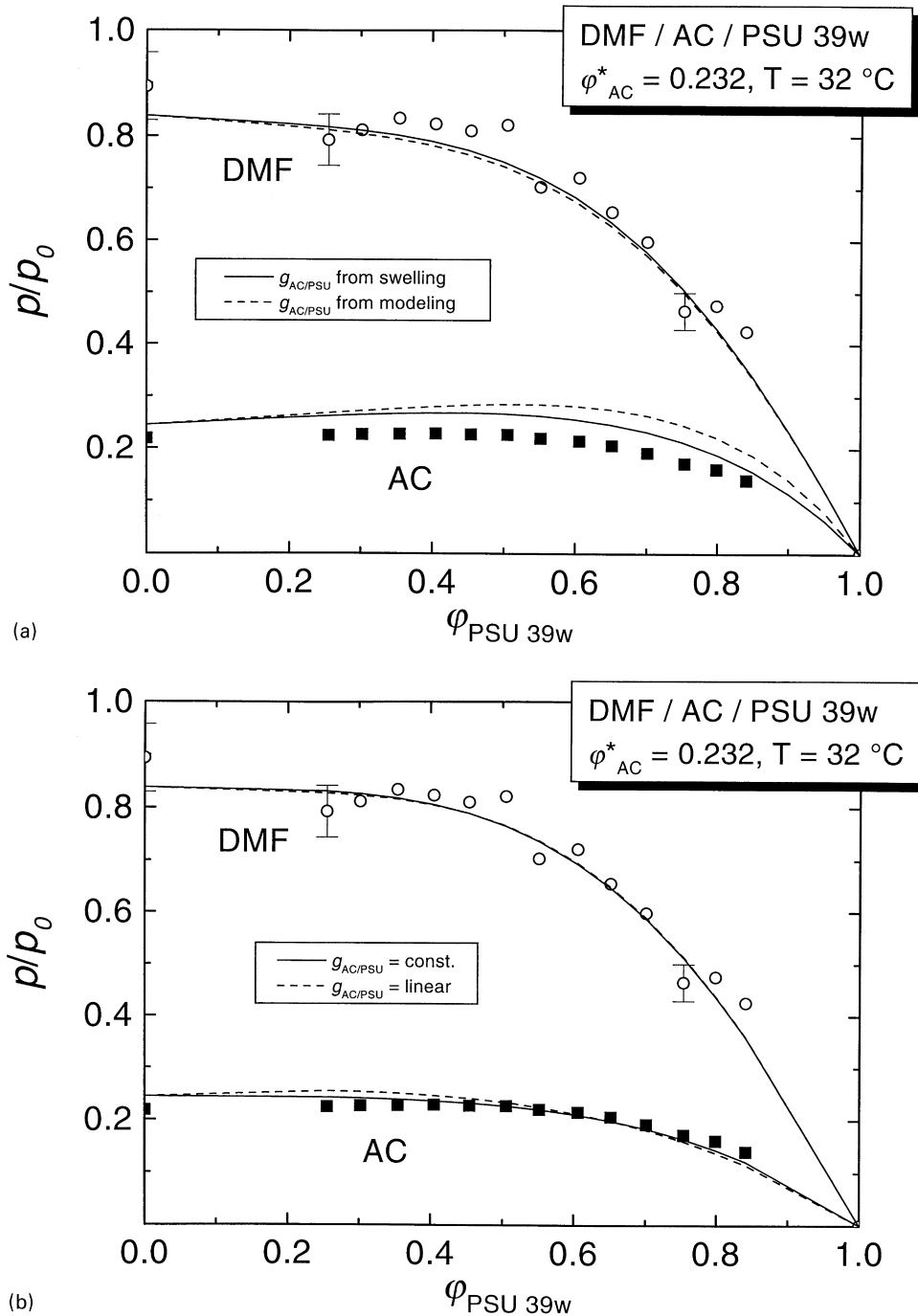


Fig. 2. Reduced partial vapor pressures of the volatiles for the system DMF/AC/PSU 39w at 32°C and at constant composition of the mixed solvent ($\phi_{\text{AC}}^* = 0.232$). The curves are calculated on the basis of the independently determined binary interaction parameters $g_{\text{DMF/PSU}}$ and $g_{\text{DMF/AC}}$ by means of different information concerning the interaction between the precipitant and the polymer. (a) Calculated with independently determined $g_{\text{AC/PSU}}$ —solid line: from swelling experiments; broken line: from modeling of the measured phase diagram. (b) Adjustment of $g_{\text{AC/PSU}}$ to the measured partial vapor pressures—solid line: $g_{\text{AC/PSU}} = \text{constant}$; broken line: linear dependence on polymer concentration according to Eq. (13).

behavior can be understood qualitatively on the basis of the largely different binary interaction parameters g_{1P} and g_{2P} . The precipitant interacts so unfavorably with the polymer (as compared with the solvent) that it is increasingly preferring the gas phase over the liquid phase as the polymer concentration rises in order to avoid these contacts.

The quantitative discussion of the measured reduced vapor pressures of the volatiles shown in Fig. 3 is at first exclusively based on binary interaction parameters again. The different curves shown in Fig. 3a testify that it is impossible to account for the preferential evaporation of water, neither by using g_{ij} values that reproduce the phase diagram

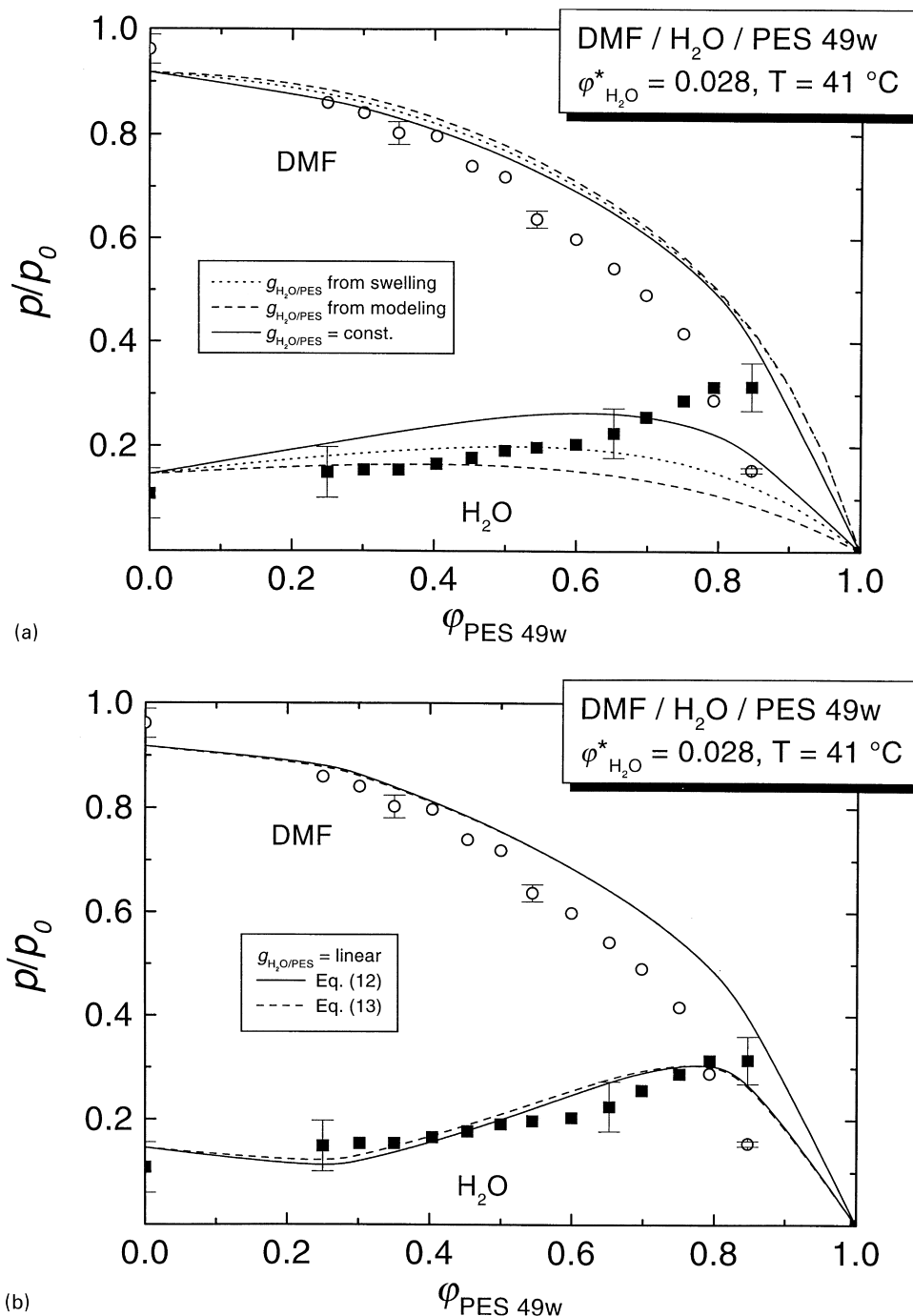


Fig. 3. Reduced partial vapor pressures of the volatiles for the system DMF/H₂O/PES 49w at 41°C and at constant composition of the mixed solvent ($\phi_{\text{H}_2\text{O}}^* = 0.028$). The curves are calculated on the basis of the independently determined binary interaction parameters $g_{\text{DMF}/\text{PES}}$ and $g_{\text{DMF}/\text{H}_2\text{O}}$ by means of different information concerning the interaction between the precipitant and the polymer. (a) solid line: $g_{\text{H}_2\text{O}/\text{PES}} = \text{constant}$, adjusted to the measured partial vapor pressures; broken line: $g_{\text{H}_2\text{O}/\text{PES}}$ from the modeling of the measured phase diagram; dotted line: $g_{\text{H}_2\text{O}/\text{PES}}$ from swelling experiments. (b) $g_{\text{H}_2\text{O}/\text{PES}}$ adjusted to the measured partial vapor pressures—solid line: linear dependence on polymer concentration according to Eq. (12); broken line: linear dependence on polymer concentration according to Eq. (13).

nor if $g_{\text{H}_2\text{O}/\text{P}}$ is adjusted by a constant. In all cases the partial vapor pressure of water is predicted considerably too small at high polymer concentration and consequently that of DMF by far too large. The adjustment of $g_{\text{H}_2\text{O}/\text{P}}$ on the basis of Eqs. (12) and (13) (cf. Table 3) shifts the vapor pressures calculated for water markedly towards the

measured values, whereas that of DMF remain rather unchanged (cf. Fig. 3b). However, a closer look at the data range of $g_{\text{H}_2\text{O}/\text{P}}$ reveals that this interaction parameter starts negative at low polymer contents and becomes positive with rising polymer concentration. This feature and the extremely large range of values (from ca. -20 to $+20$) are

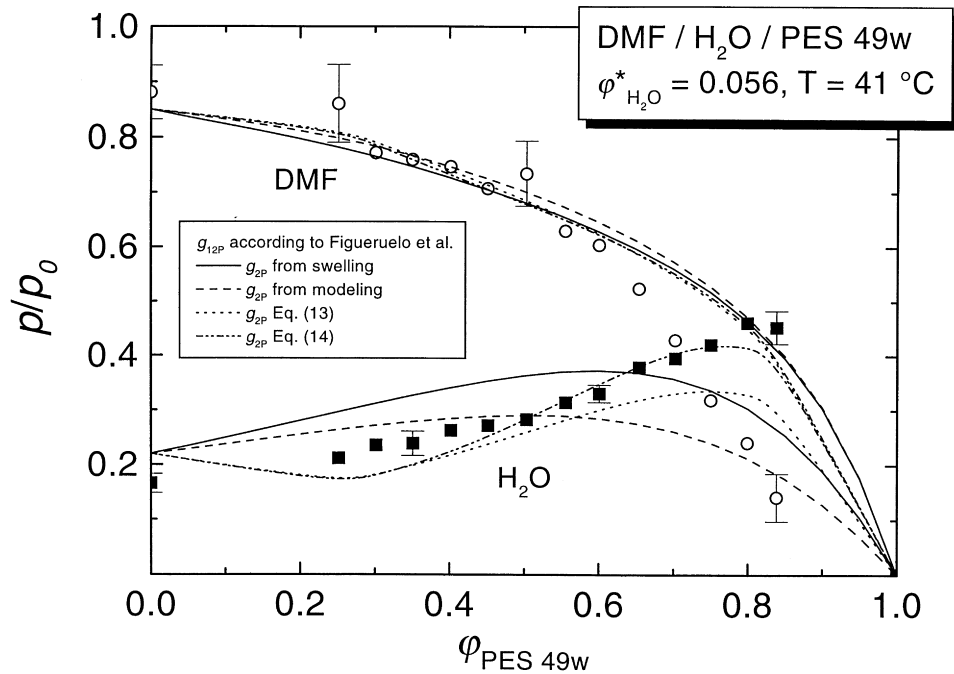


Fig. 4. Reduced partial vapor pressures of the volatiles for the system DMF/H₂O/PES 49w at 41°C and at constant composition of the mixed solvent ($\varphi_{\text{H}_2\text{O}}^* = 0.056$). The curves are calculated on the basis of binary and ternary interaction parameters; $g_{\text{DMF/PES}}$ and $g_{\text{DMF/H}_2\text{O}}$ stem from independent measurements and $g_{\text{DMF/H}_2\text{O/PES}}$ is calculated according to Eq. (10) by means of different information concerning the interaction between the precipitant and polymer. Solid line: $g_{\text{H}_2\text{O/PES}}$ from swelling experiments; broken line: from modeling of the measured phase diagram; dotted line: linear dependence on polymer concentration according to Eq. (13); dash-dotted line: linear dependence on polymer concentration according to Eq. (14).

physically not meaningful and constitute a further indication that binary interaction parameters do not suffice for the description of the present system.

For that reason we have investigated whether it is possible to account for the observed preferential expulsion of water from the liquid phase by means of ternary interaction

Table 3

Concentration dependencies of $g_{\text{H}_2\text{O/P}}$ resulting from either the evaluation of the phase diagrams or from vapor pressures measured for the ternary systems, exemplified for DMF/H₂O/PSU 39w ($\varphi_{\text{H}_2\text{O}}^* = 0.014$) and DMF/H₂O/PES 49w ($\varphi_{\text{H}_2\text{O}}^* = 0.028$) at 41°C

Interaction parameters H ₂ O/PSU and H ₂ O/PES		PSU 39w	PES 49w
Eq. (8) (swelling experiments)	g_{2P}^{swell}	4.03	2.70
Eq. (9) (modeling of the phase diagrams)	$g_{AC/P}^{0.5}$	2.45	2.22
	k	2.45	2.15
	l	0.00	0.13
	m	0.00	0.00
Eq. (12) (vapor pressures, $b = 0$)	a	3.36	3.21
Eq. (12) (vapor pressures, $b \neq 0$)	$g_{AC/P}^{0.5}$	-16.50	-7.25
	a	-37.10	-18.40
	b	41.20	22.30
Eq. (13) (vapor pressures)	$g_{AC/P}^{0.5}$	-0.02	-5.88
	b^*	8.43	19.50
	φ_P^{swell}	0.99	0.97

parameters. Figs. 4 and 5 show the results for two different possibilities to model g_{12P} .

The theoretical curves of Fig. 4 are based on a relation reported in the literature [5]. According to this approach (Eq. (10)), developed for dilute polymer solutions in a mixed solvent, the ternary interaction parameter is composed of the three binary interaction parameters. For g_{2P} we have used the relations of the previous section (Eqs. (8), (9), (12) and (13)) again and additionally introduced the following expression

$$g_{2P} = g_{2P}^{\text{swell}} + b^*[\varphi_P - (2\varphi_P^{\text{swell}} - 1)] + c^*[\varphi_P^2 - \varphi_P^{\text{swell}}(3\varphi_P^{\text{swell}} - 2)] \quad (14)$$

which constitutes the extension of Eq. (13) by one adjustable parameter modeling a curvature in $g_{2P}(\varphi_P)$.

From the results of these calculations, plotted in Fig. 4, it becomes obvious that a linear concentration dependence of g_{2P} (Eq. (13)) reproduces $p/p_0(\text{H}_2\text{O})$ at least qualitatively and that the adjustment of two parameters (Eq. (14)) describes the situation reasonably well. But still the calculated partial vapor pressures $p/p_0(\text{DMF})$ is by far too large for high polymer concentrations, as with the neglect of ternary interaction parameters in the last section. One possible reason for the failure of Eq. (10) could lie in the fact that it was established for dilute solutions and is therefore inapplicable to the present situation.

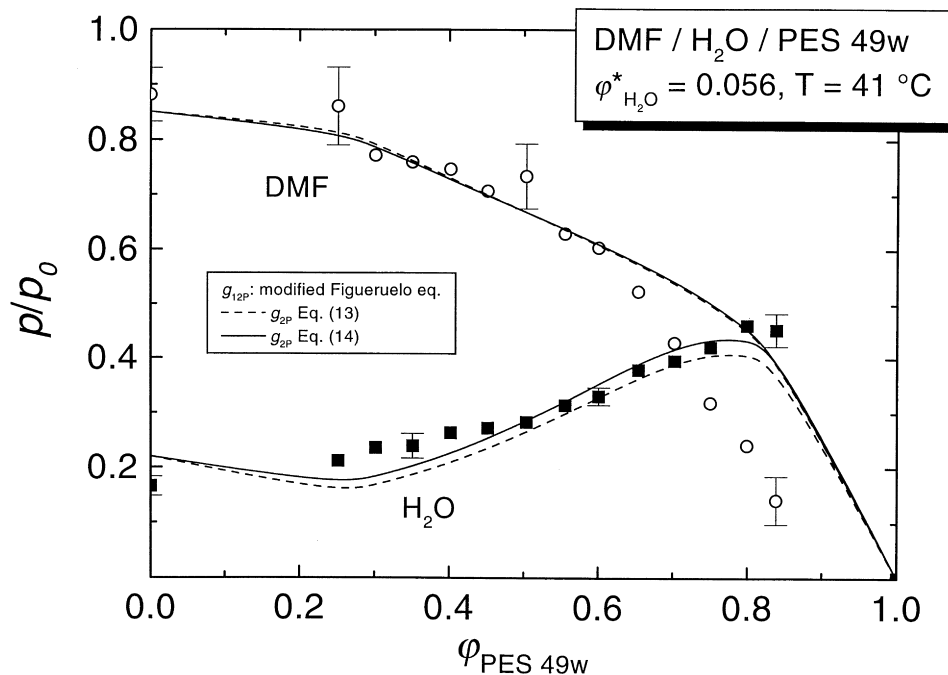


Fig. 5. Reduced partial vapor pressures of the volatiles for the system DMF/H₂O/PES 49w at 41°C and at constant composition of the mixed solvent ($\phi_{\text{H}_2\text{O}}^* = 0.056$). The curves are calculated on the basis of binary and ternary interaction parameters; $g_{\text{DMF/PES}}$ and $g_{\text{DMF/H}_2\text{O}}$ stem from independent measurements and $g_{\text{DMF/H}_2\text{O/PES}}$ is calculated according to Eq. (17) by means of different information concerning the interaction between the precipitant and polymer. Solid line: linear dependence on polymer concentration according to Eq. (14); broken line: linear dependence on polymer concentration according to Eq. (13).

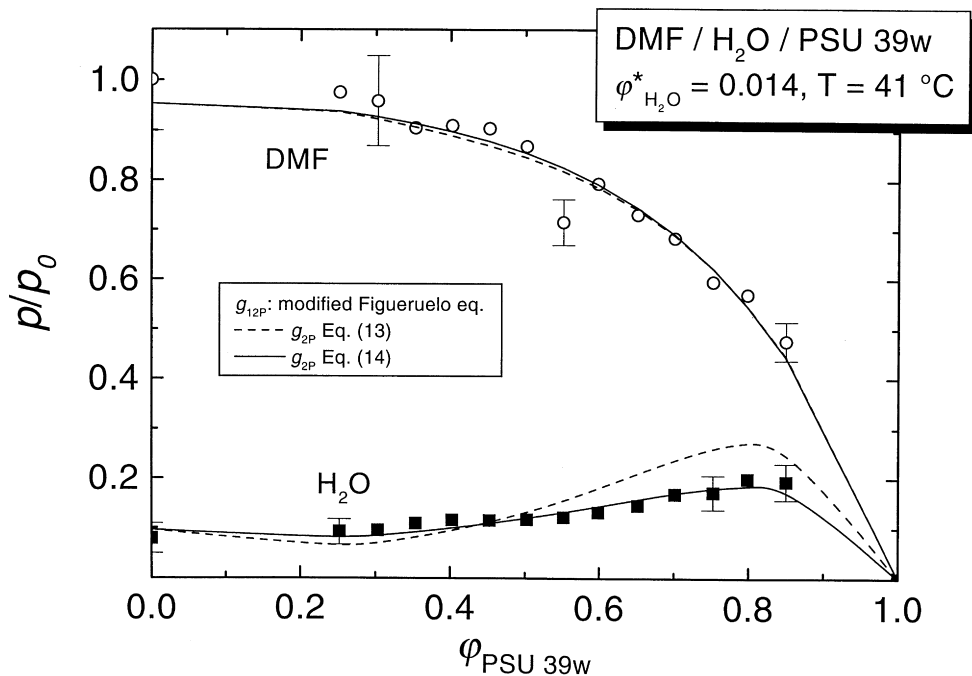


Fig. 6. Reduced partial vapor pressures of the volatiles for the system DMF/H₂O/PSU 39w at 41°C and at constant composition of the mixed solvent ($\phi_{\text{H}_2\text{O}}^* = 0.014$). The curves are calculated on the basis of binary and ternary interaction parameters; $g_{\text{DMF/PSU}}$ and $g_{\text{DMF/H}_2\text{O}}$ stem from independent measurements and $g_{\text{DMF/H}_2\text{O/PSU}}$ is calculated according to Eq. (17) by means of different information concerning the interaction between the precipitant and the polymer. Solid line: linear dependence on polymer concentration according to Eq. (14); broken line: linear dependence on polymer concentration according to Eq. (13).

In order to get rid of that restraint, Eq. (10) is slightly modified. We maintain the assumption that g_{12P} is a function of the three binary interaction parameters of the subsystems, according to

$$g_{12P} \propto g_{12}g_{1P}g_{2P} \quad (15)$$

and also formulate the concentration dependence of g_{12P} as in the original work [5], with the only difference, that the last term is no longer restricted to the dilute regime

$$g_{12P}(\varphi_1^*, \varphi_P) = g_{12P}^0(\varphi_1^*) + \varphi_P \left(\frac{\partial g_{12P}}{\partial \varphi_P} \right) \quad (16)$$

Inserting Eq. (15) and its derivations into Eq. (16) yields the following expression for the dependence of the ternary interaction parameters on polymer concentration

$$g_{12P}(\varphi_1^*, \varphi_P) = g_{12}(\varphi_1^*) [g_{1P}^0 g_{2P}^0 + \varphi_P (g_{1P}(\partial g_{2P} / \partial \varphi_P) + g_{2P}(\partial g_{1P} / \partial \varphi_P))] \quad (17)$$

The evaluation of the present data on the basis of Eq. (17) and of the polynomials formulated for g_{2P} in the Eqs. (13) and (14) yields the results shown in Fig. 5. From this graph it becomes obvious that the agreement between experiment and theory has not improved significantly, at least for the present system.

In order to check whether this statement is a particularity of PES or more general, we have also evaluated the results of solutions of PSU in the mixed solvent DMF/H₂O by means of Eqs. (10) and (17). The original version for the ternary interaction parameter again turned out to be insufficient, whereas the modified version reproduces the experimental results quite accurately (cf. Fig. 6) if Eq. (14) is used for the concentration dependence of g_{2P} .

In a common valuation of all results presented here it can be stated that ternary interaction parameters as formulated in Eq. (10) are at least for the systems with very powerful precipitants incapable to describe the vapor pressure data. Some generalization according to Eq. (17) seems to be useful for mixtures with low content of precipitant (DMF/H₂O/PSU) or weaker precipitants, while systems with high water concentrations (DMF/H₂O/PES) still lack adequate theoretical description. Only a speculative explanation can be offered for these findings. Reasoning on the basis of a pronounced preference of both polymers for DMF leads to the following plausible situation: the larger solvent content of the mixed solvent in the case of PSU guarantees a sufficient surplus of this component; even at very high polymer concentration it is therefore possible to establish many favorable contacts to the polymer without large entropy costs. With PES, on the other hand, the DMF concentration in the mixed solvent is considerably less and this depletion requires the expulsion of a larger fraction of water into the vapor phase in order to facilitate a larger number of highly advantageous 1–P contacts. In

terms of interaction parameters, this would mean that ternary interaction parameters, as formulated in Eq. (10) or (17), do no longer suffice to describe this particular situation.

One aspect of the above results deserves further comment, namely the fact that the vapor pressures of water are modeled with reasonable accuracy for the system DMF/H₂O/PES, in contrast to that of DMF, which emerges by far too large. Since the Gibbs–Duhem equation is forcedly obeyed during the theoretical evaluation of primary data, there remain two obvious possibilities to explain that finding. The more likely of them is an inadequate formulation of the ternary interaction parameters. The other option consists in experimental errors of the partial vapor pressures at high concentrations of PES, which are however, rather improbable in view of the agreement between experiment and theory for the systems DMF/AC/PES, DMF/AC/PSU, and DMF/H₂O/PSU.

5. Conclusions

Measured partial vapor pressures of the volatiles for polymer solutions in mixed solvents in combination with known phase diagrams plus the theoretical evaluation of these data demonstrate beyond doubt that systems exist for which binary interaction parameters do not suffice to describe their thermodynamic behavior.

In a first valuation of the present results we conclude that one condition that brings the necessity of ternary interaction parameters into play consists in a very pronounced preference of the polymer for the solvent, in combination with an insufficient supply of this component due to the composition of the mixed solvent. It is self-evident that additional experimental material is required to obtain a more detailed understanding of the observed phenomena. Above all it will be necessary to vary the binary interaction parameters systematically. One special combination that leads to the phenomenon of cosolvency appears particularly interesting in that context. For systems exhibiting that behavior the interaction between the components turns a mixture of two liquids, which are both non-solvents for the polymer under consideration, into a thermodynamically good solvent [19,20].

On the basis of the then available broader information concerning special effects reflecting the immediate neighborhood of molecules in systems composed of three or more components it will be worthwhile to start a new attempt for the theoretical calculation of multinary interaction parameters from pair interactions.

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