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A lattice-fluid model for the determination of the water/polymer interaction parameter from water uptake measurements

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ABSTRACT:

The Flory-Huggins (FH) theory is commonly used for a thermodynamic analysis of the phase behavior in ternary nonsolvent/solvent/polymer systems to describe membrane formation, in general. Actually three precisely and independently determined interaction parameters have to be known. Particularly the nonsolvent/polymer interaction parameter is difficult to determine, although it considerably affects the size and location of the miscibility gap in a ternary phase diagram. In a recent publication [J. Membrane Sci., 265 (2005) 1], it was found that the values for the water/polymer interaction parameters obtained by a fit of ternary polymer solution data are significantly smaller than values determined on the basis of the Flory-Huggins model from water vapor sorption on the solid membrane polymer. To resolve the discrepancy, a lattice fluid model is introduced which assumes for the water-swollen polymer a state between glass-like and rubber-like (GRP model). The contributions of each of the boundary cases to the mixed state depend on the original stiffness of the pure components, indicated by the glass transition temperature of the pure polymer, and the relative amount of penetrant in the polymer matrix, initiating a plasticization of the polymer. The plasticization then causes an increase of chain mobility and, therefore, a continuous transfer from the glass-like to the rubber-like state. Using this approach a Flory water/polymer interaction parameter can be calculated which is in excellent accordance with respective values obtained by the more elaborated fitting technique of experimental cloud points of ternary systems for the investigated systems.

KEYWORDS: Thermodynamics, membrane formation, nonsolvent/polymer interaction parameter, equilibrium water uptake,

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1. Introduction

Generally the Flory-Huggins (FH) theory [1] is used to determine the interaction parameter χ_{13} of a nonsolvent/polymer mixture which is one of the three essential parameters to describe the thermodynamic behavior of a ternary nonsolvent(1)/solvent(2)/polymer(3) (NS-S-P) system [2-4]. The free energy of mixing, ΔG_M , of the three-component mixture can be formulated in form of Tompa's extension [5,6] based on the classical FH model as

$$\frac{\Delta G_M}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + \chi_{12}(u_2)n_1\phi_2 + \chi_{23}(\phi_3)n_2\phi_3 + \chi_{13}n_1\phi_3 \quad (1)$$

where R is the gas constant, T is the absolute temperature, n_i and ϕ_i are the number of moles and the volume fraction of components i , and χ_{ij} are the i/j interaction functions, respectively.

Using equation (1), Altena and Smolders [3] and also Yilmaz and McHugh [7] analyzed thermodynamic aspects of NS-S-P systems, and especially, the effects of variations in the interaction parameter value on the phase diagram characteristics. It was shown that precisely determined interaction parameters (concentration independent) or interaction parameter functions (concentration dependent) are a strong prerequisite for any application of equation (1). Literature data [3] document that the nonsolvent/polymer interaction parameter, assumed as concentration independent, considerably affects the size and the location of the miscibility gap in the ternary phase diagram. The common way to determine χ_{13} experimentally is an equilibrium uptake experiment of nonsolvent in a thin film of polymer. The FH theory is then used to calculate a value for the parameter on the basis of the amount of sorbed nonsolvent. The basic relation is obtained by deriving an expression for $\Delta\mu_1$, the excess chemical potential of component 1 in the binary nonsolvent(1)/polymer(3) system. The relation can be obtained from eq. (1) by assuming $n_2 = 0$ and calculating the first derivative of the Gibbs free energy of mixing with respect to n_1 , i.e., $\Delta\mu_1 = \left[\partial(\Delta G_M) / \partial n_1 \right]_{T,P,n_3}$. Usually one introduces the volume fraction of penetrant $\phi_1 = V_1 / (V_1 + V_3) = n_1 v / (n_1 v + r n_3 v)$ where V_i is the volume of component i , which can also be expressed with the help of the molar volume v of a lattice segment. This segment volume is assumed to be equal to the molar volume of the penetrant and of a polymer segment, i.e. $v = v_1 = V_1 / n_1 = V_3 / (r n_3)$ where the ratio of molar volumes $r = v_3 / v_1$, represents the number of segments per polymer chain. If $\phi_3 = 1 - \phi_1$ is the volume fraction of the polymer, one obtains the well-known FH relation as function of ϕ_1

$$\Delta\mu_1 / RT = \ln(\phi_1) + (1 - 1/r)(1 - \phi_1) + \chi_{13}(1 - \phi_1)^2 = \Delta\mu_{1,g} / RT = \ln(a_{1,g}) \quad (2)$$

This equation also applies for a phase equilibrium with a pure nonsolvent vapor phase (index g). $\Delta\mu_{1,g}$ and $a_{1,g}$ are the chemical potential differences and vapor phase activity of the nonsolvent, respectively. Because the model behind equation (2) is strictly speaking only valid for *rubbery polymers*, we will refer to it in the following as *RP-model*.

Alternatively, χ_{13} values have been determined in ternary solution systems with several other experimental techniques such as light scattering [8] and intrinsic viscosity [9]. In the recent work [10], we have compared values for the water/polymer interaction parameter determined *directly* from vapor sorption measurements and *indirectly* by thermodynamic modeling of experimental cloud point data (*fitting technique*) for some ternary systems frequently used for membrane formation. Differences between both, the direct and the indirect method, are significant and outside of the standard deviations of the experimental techniques. Interestingly, it was found that the discrepancies in the nonsolvent/polymer interaction parameters are a function of hydrophilicity/hydrophobicity of the investigated polymers. We considered the ternary fit results as the data with the most relevance for the membrane formation process but the results of this fitting approach could not be interpreted theoretically.

The complete disagreement of χ_{13} -values, obtained by the two different methods, especially for hydrophobic polymers, requires a new concept of interpretation on the basis of a modified theoretical approach for describing nonsolvent/polymer mixtures.

The objective of this study is to formulate a thermodynamic model applicable to calculate the water/polymer interaction parameter based on equilibrium water uptake techniques such as swelling or vapor sorption measurements. Both techniques are identical in the physical basis. In our derivation we generalize the lattice theory similar as in the derivation, which results in the FH equation, but we take into account that the polymer is in a glassy state. In the model development it will be shown that, the combinatorial contribution (entropy) of polymer segments in the glassy state is zero but that there exists an entropic part of the Gibbs free energy of the system due to the number of possible arrangements of penetrant molecules in the free volume of the polymer bulk. The resulting lattice model can be applied to calculate the water/polymer interaction parameter from equilibrium water uptake measurements. Applying this model the values of the water/polymer interaction parameter from different experiments agree much better than the respective values derived from the thermodynamic modeling of the ternary systems and the values derived from the FH equation (2). But in the simplest version of the new model, this agreement for polymers with high chain stiffness is limited to the range of low water volume fractions. For an even more generally applicable model, we believe, it is necessary to consider in addition a partial 'plasticization' of the polymer through the nonsolvent resulting in an increased segmental motion of the originally glassy polymer chains. The so modified lattice model can then be applied to calculate the water/polymer interaction parameter from equilibrium water uptake measurements. In the result, the obtained values of the water/polymer interaction parameter agree much better with the values derived from the thermodynamic modeling of the ternary systems, presented in our previous work [10] than the values obtained from the traditional FH equation (2).

2. Lattice fluid models for a penetrant(1)/glassy polymer(3) system

A solid polymer phase is ordinarily designated as a glass if it is non-crystalline and if it exhibits at a certain higher temperature a second-order transition, often referred to as the *glass transition* [11]. It was found that the specific volume of those polymers diminishes linearly with the temperature until the glass transition temperature T_g . Below this temperature the reduction continues but at a smaller rate. The difference between the volume observed at absolute zero temperature and the volume measured at the transition temperature was considered the space, which, in the amorphous solid, is available for oscillations [12].

2.1. Lattice-fluid model for a glassy polymer (GP model)

For the following model derivation, we assume that the state of the investigated polymer at the beginning is a glass. In this state the polymer chains are fixed on their location at least in comparison with the typical time constants of individual jump events of diffusing water molecules from one hole of the free volume to another. On the other hand, according to the free volume theory characterizing the excluded volume of a glassy polymer system, there is "free" space between atoms of the polymer chain, which can be occupied by small penetrant molecules. However, due to their size and shape, these penetrants can only "see" a subset of the total free volume, termed as the "accessible free volume". In this way accessible free volume depends on both, polymer and penetrant, whereas the total free volume depends only on the polymer. The situation is illustrated schematically in Figure 1 on a lattice where it is assumed that the polymer chain consists of segments, which have the same volume as a penetrant particle.

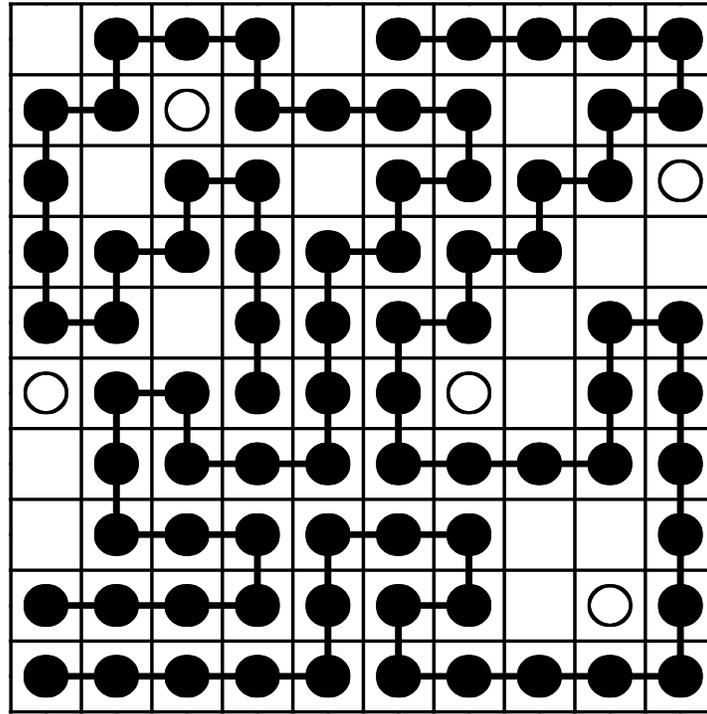


Figure 1. Segments of a polymer molecule located in the lattice and penetrant molecules distributed within (schematically).

This accessible free volume consists of the empty lattice sites and the sites occupied by the penetrant. For a corresponding lattice model, the primary statistical mechanical problem is to determine the number of combinatorial configurations available for the system (see e.g. [13,14]). From the assumption of the glassy state, it follows that there is only one conformation for the polymer chain. This situation is different to the case of a polymer solution. Furthermore it is assumed for the thermodynamic model that also during the diffusion of penetrants through the polymer bulk, the conformation of the polymer chains does not change and remains as before (One should have in mind that diffusion is in reality only possible by rearrangement of polymer segments, i.e. by the opening of temporary diffusion channels. Therefore the zero-entropy is describing the extreme case of a completely stiff, i.e. ultra-glassy polymer, in which strictly speaking no diffusion could occur.). Therefore the number of possible conformations does not vary and is equal to one ($\Omega = 1$). It results that the entropy change during the penetration is zero, $S_{3^*} = k \ln(\Omega) = 0$.

Entropy of mixing: It is assumed that N_1 penetrant molecules are randomly distributed on a lattice of $M = (N_1 + N_3 + N_0)$ sites where N_3 is the number of polymer segments and N_0 is the number of empty lattice sites. The volume of each lattice site is v , which is called the hard-core volume. The total volume of the lattice is $V = M \times v$. It means also that each penetrant molecule occupies a single lattice site as does a polymer segment (see Figure 1). They are virtually identical in size, spatial configuration, and external force field. Moreover it has to be assumed that the migration of penetrant molecules into empty sites can be done without any energy restriction. It means that all spaces are continuous and available for penetrant molecules.

Assuming a glassy state for the polymer, the N_3 polymer sites are frozen. Then, the N_1 penetrant molecules can be distributed only on a part of the lattice, i.e. the $N_1 + N_0$ sites, representing the accessible free volume. This assumption is supported by MD simulations which indicate that local segmental rearrangements, permitting diffusive jumps, do occur

roughly every nanosecond while the overall arrangement of larger chain segments is certainly stable over much longer times. The accessible fractional free volume of the polymer can be expressed as $\phi_{FV} = (N_1 + N_0)v / (N_1 + N_3 + N_0)v$, a quantity which can be estimated for polymers, e.g. by group contribution methods (see below). The total number Ω of ways of arranging N_1 penetrant molecules on the lattice comprising $N_1 + N_0$ sites is

$$\Omega = \frac{(N_1 + N_0)!}{N_1! N_0!} \quad (3)$$

If $N_0 = 0$, i.e. all empty sites are occupied by penetrant, only one arrangement exists, $\Omega = 1$. According to Boltzmann's relation, the entropy is given by $S = k \ln \Omega$. With the introduction of Sterling's approximation, $\ln N! = N \ln N - N$, it results for the factorials equation (4):

$$S = k[(N_1 + N_0) \ln(N_1 + N_0) - N_1 \ln N_1 - N_0 \ln N_0] \quad (4)$$

This value is also equal to the entropy of mixing $\Delta S_M = (S_1 + S_3) - (S_{1*} + S_{3*})$ of the pure penetrant ($S_{1*} = 0$) and the pure polymer ($S_{3*} = 0$). One can find a similar expression applied in the entropy theory of Gibbs and Di Marzio to predict the glass transition [11,12]. By rearranging, introducing the number of moles n_i for all components i , and the volume fractions $\phi_i = V_i / V = n_i v / (n_1 + n_3 + n_0)v$, equation (4) can be written as

$$\frac{\Delta S_M}{R} = -n_1 \ln\left(\frac{n_1}{n_1 + n_0}\right) - n_0 \ln\left(\frac{n_0}{n_1 + n_0}\right) \quad (5a)$$

or

$$\frac{\Delta S_M}{R} = -n_1 \ln\left(\frac{\phi_1}{\phi_{FV}}\right) - n_0 \ln\left(\frac{\phi_0}{\phi_{FV}}\right) \quad (5b)$$

where ϕ_1 is the volume fraction of the penetrant on the lattice $\phi_1 = n_1 v / [(n_1 + n_3 + n_0)v]$. In experiments the penetrant is sorbed in the polymer sample. If swelling of the sample is excluded, ϕ_1 can be approximated from the mass m_1 of sorbed penetrant per mass of polymer m_3 and the respective densities by $\phi_1 \approx V_1 / V_3 = (m_1 / m_3)(\rho_3 / \rho_1)$. $\phi_0 = n_0 v / (Mv)$ is the volume fraction of empty sites, which can be expressed by $\phi_0 = \phi_{FV} - \phi_1$.

Enthalpy of mixing: The mixing enthalpy is calculated by considering the interaction energies of penetrant molecules and polymer segments. ω_{11} , ω_{33} , and ω_{13} are the energies associated with pair contacts of (1,1), (3,3), and (1,3). z is the number of next neighbors on the lattice. In addition the probability p_i is considered which represents the average fraction of neighbors of type i for a given lattice site. This probability is given by

$$p_i = \frac{n_i v}{(n_1 + n_3 + n_0)v} \quad (6)$$

where the denominator represents the total volume of the lattice. To proceed, it is considered that N_1 penetrant molecule and N_3 polymer segment of hard core v are placed on the lattice. Under the assumed hard core state, the total volumes occupied by each pure component, $V_{i,hc}$, and the mixture, V_{hc} , are simply given by $V_{i,hc} = N_i v$ and $V_{hc} = (N_1 + N_3)v$. According to the definition of reduced properties typically used in equation of state (EOS) theories, the actual volume V_i , $i=1, 3$, occupied by the pure compressible fluids at any temperature T and pressure P is related to the hard core volumes through the reduced densities $\tilde{\rho}_1$ and $\tilde{\rho}_3$, respectively:

$$\tilde{\rho}_i(T, P) = \frac{V_{i, hc}}{V_i} = \frac{N_i v}{V_i} = \frac{\rho_i}{\rho_i^*} \quad (7a)$$

where ρ_i is the T - and P - dependent mass density and $\rho_i^* = M_{s,i} / N_0 v$ is the hard-core density, given by the ratio of the segment molecular weight $M_{s,i}$ (g/mol) and hard core volume (N_0 is Avogadro's number). The reduced density $\tilde{\rho}_i$ is simply a measure of the fractional occupied volume or, equivalently, one minus the "fractional free volume". Likewise, the total volume V occupied by the mixture at T and P is related to the mixture reduced density $\tilde{\rho}_M$ and the total hard core volume V_{hc} :

$$\tilde{\rho}_M(T, P) = \frac{V_{hc}}{V} = \frac{(N_1 + N_3)v}{V} = \frac{\rho_M}{\rho_M^*} \quad (7b)$$

where ρ_M and ρ_M^* are the mixture density and the mixture hard-core density, respectively.

In keeping with the spirit of the well-known FH theory and assuming random mixing (mean field approximation), an equally simple expression can be derived for the change in interaction energy upon mixing. In the mixed state, the total interaction energy is obtained by counting the number of pair-wise interactions of all type contacts. The N_1 penetrant molecules on the lattice have total interaction energy as follow:

$$H_1 = \frac{1}{2} z N_1 \tilde{\rho}_M (\omega_{11} \phi_1 \tilde{\rho}_1 + \omega_{13} \phi_3 \tilde{\rho}_3) \quad (8)$$

where the factor $\frac{1}{2}$ corrects the double counting of this procedure. In the same way the interaction energy for the polymer is obtained as follows:

$$H_3 = \frac{1}{2} z N_3 (\omega_{13} \phi_1 \tilde{\rho}_1 + \omega_{33} \phi_3 \tilde{\rho}_3) \quad (9)$$

If we consider the sorption process as a mixing process of pure penetrant with interaction energy $H_1^* = \frac{1}{2} z N_1 \omega_{11} \tilde{\rho}_1$ and the pure glassy polymer with $H_3^* = \frac{1}{2} z N_3 \omega_{33} \tilde{\rho}_3$, a mixture is characterized by the change in interaction energy:

$$\Delta H_M = (H_1 + H_3) - (H_1^* + H_3^*) = \frac{z}{2 \tilde{\rho}_1} N_1 \phi_3 (2 \tilde{\rho}_1 \tilde{\rho}_3 \omega_{13} - \tilde{\rho}_1 \tilde{\rho}_1 \omega_{11} - \tilde{\rho}_3 \tilde{\rho}_3 \omega_{33}) \quad (10)$$

Note that, alternatively, Equation (10) can be rewritten in a more transparent form that all interaction energies collaborate in an analogous parameter to the well-defined FH interaction parameter χ :

$$\Delta H_M = k T N_1 \phi_3 \chi_{13}^* \quad (11)$$

with

$$\chi_{13}^* \equiv \frac{z}{k T} \left[\alpha \omega_{13} - \frac{1}{2} (\beta \omega_{13} + \gamma \omega_{33}) \right] \quad (11a)$$

where $\alpha \equiv \tilde{\rho}_3$, $\beta \equiv \tilde{\rho}_1$, and $\gamma \equiv \tilde{\rho}_3^2 / \tilde{\rho}_1$. As can be seen from the last equation, χ_{13}^* has a similar shape as the original FH-parameter. If $\alpha = \beta = \gamma = 1$, i.e. the reduced densities are 1, the parameter agrees with the "original" FH-parameter.

Free energy of mixing: The Gibbs free energy of mixing in the GP model is easily obtained by combining equations (5) and (11) expressed for moles of penetrant. It is:

$$\Delta G_M = \Delta H_M - T \Delta S_M = RT \left[\chi_{13}^* n_1 \phi_3 + n_1 \ln \left(\frac{\phi_1}{\phi_{FV}} \right) + n_0 \ln \left(\frac{\phi_0}{\phi_{FV}} \right) \right] \quad (12)$$

The Equation (12) describes the thermodynamic behavior of the binary penetrant(1)/polymer(3) mixture in a glassy state only. The last two first terms represent entropy contributions to the free energy of mixing and include configurational and combinatorial contributions, while the first term originates from energetic contributions like in

the FH theory. Assuming phase equilibrium with the vapor phase of the nonsolvent, in analogy to the derivation of equation (2) for the FH- or RP-model, the following relation for the chemical potential of component 1 can be derived from (12) by derivation with respect to n_1 and considering the replacement of free volume sites by penetrant ($n_1 + n_0 = n_{FV} = \text{const.}$)

$$\frac{\Delta u_1}{RT} = \ln a_1 = \ln\left(\frac{\phi_1}{\phi_0}\right) + (1 - \phi_1)^2 \chi_{13}^* \quad (13)$$

which is then valid specifically for *glassy polymers*, and which we will call therefore the *GP-model*.

2.3 Extension to a *partially glassy and partially rubbery polymer matrix (GRP model)*

The GP model represents, according to the definition, the thermodynamic state of a penetrant/polymer system where the polymer chains are completely inflexible and this stiffness will not be influenced by the sorption of the penetrant. In general such a condition will be only fulfilled if the quantity of penetrant in the polymer matrix is very small. Mainly hydrophobic polymers are candidates, which will meet these requirements completely. However it can not be expected that the GP model can also describe polymer/nonsolvent systems for hydrophilic membrane polymers. Therefore in order to extend the approach described in section 2.2, it is assumed in the following that the status of the wetted polymer sample can be considered as a superposition of a glassy state (section 2.2) and a rubber-like state (FH state, see introduction), in general. We consider the polymer sample partly as a glass and partly (through the interaction with water) as a rubber. The ratio of glassy and rubbery contributions will be assumed to be depending on the stiffness of the dry polymer sample (characterized e.g., by the glass temperature) and the quantity of sorbed penetrant. The glass temperature T_{gM} of a polymer-penetrant mixture can be estimated, based on caloric data [15] according to

$$T_{gM} = \frac{x_1 \Delta C_{p1} T_{g1} + x_3 \Delta C_{p3} T_{g3}}{x_1 \Delta C_{p1} + x_3 \Delta C_{p3}} \quad (14)$$

where T_{gM} and T_{gi} are the glass transition temperatures of the mixture and the pure component i , respectively. ΔC_{pi} is the incremental change in heat capacity at T_{gi} , and $x_i = N_i / (N_1 + N_3)$ represents the mole fraction defined on the basis of the repeat unit for the polymer (see Table 1). All the ΔC_{pi} parameters necessary for application of eq. (14) can be estimated by calculations using the concept of group contributions (see Table 1). Equation 14 establishes a relation between the stiffness of the polymer, expressed by the glass temperature of the pure polymer, and the state of sorption, expressed by the mole fraction of sorbed penetrant on the one hand and the glass transition temperature of the mixed system, on the other hand. It should be mentioned that this relation was verified for compatible mixing systems like compatible polymer/polymer blends or single-phase polymer/plasticizer systems. Polymer/water systems fulfill this requirement as long as the mixture represents a single-phase system.

On basis of the change in T_g by the penetrant sorption (in comparison to the T_{g3} of the pure polymer) a plasticization factor β can be defined according to

$$\beta = \frac{T_{gM} - T_{g3}}{T - T_{g3}} \quad \text{for } T_{gM} > T \text{ and } \beta = 1 \text{ for } T_{gM} \leq T \quad (15)$$

which should be a measure for the relative amount of “rubber-like regions” in the polymer at the measurement temperature T in the sorbed state. Per definition the β values vary between 0 and 1 for a completely glass-like and a completely rubber-like state, respectively, if both states are present. However β -values higher than 1 can be indicating a completely rubber-like state. Then the evaluation of data is carried out due to the FH theory. The so

defined plasticization factor leads to a quantification in the contribution of the glass-like and the rubber-like states in mixed state systems, and takes in account the differences of the original chain stiffness of the investigated polymer and the quantity of penetrant sorbed into the polymer at the equilibrium.

To extend the GP-model, expressed in eq. (12), for the systems composed of a partially plasticized polymer matrix due to the sorption of nonsolvent the following relation for the Gibbs free energy of mixing can be derived:

$$\frac{\Delta G_M}{RT} = \frac{\Delta H_M}{RT} - \frac{T\Delta S_M}{RT} = \chi_{13}^* n_1 \phi + \beta \left[n_1 \ln(\phi_1) + n_3 \ln(\phi_3) \right] + (1 - \beta) \left[n_1 \ln\left(\frac{\phi_1}{\phi_{FV}}\right) + n_0 \ln\left(\frac{\phi_0}{\phi_{FV}}\right) \right] \quad (16)$$

In comparison to eq. (12), it can be seen that the enthalpic part is the same as in the RP- and GP models, but the entropic or configurational part is now a superposition of the well-known contributions corresponding to the case of polymer solutions, i.e. rubbery polymers (see derivations of the FH-model) and the entropy of mixing part for the glassy state (see eq. (5)). The extent of the two contributions is determined by the plasticization factor β , given by eq. (15). The so extended model does also match the RP- or FH-model and the GP-model for $\beta = 1$ and $\beta = 0$, respectively. It should be valid for *glassy and rubbery polymers*, and is therefore named the *GRP-model*. The postulated equation for the Gibbs free energy of polymer/penetrant mixture should result in a considerably better description for the thermodynamic behavior of polymer/nonsolvent systems and should lead to reliable polymer/nonsolvent interaction parameters. For the chemical potential of penetrant species, the following expression is obtained after some algebra,

$$\frac{\Delta\mu_1}{RT} = \ln a_1 = \beta \left[\ln(\phi_1) + (1 - \phi_1) \right] + (1 - \beta) \left[\ln\left(\frac{\phi_1}{\phi_0}\right) \right] + (1 - \phi_1)^2 \chi_{13}^* \quad (17)$$

Equation (17) should allow a determination of the interaction parameter χ_{13}^* for the penetrant/polymer interaction also in the common case where the polymer is in a partially glassy state. Similar to eq. (16), the two first terms on the right side represent entropy contributions to $\Delta\mu_1$ while the last term originates from energetic contributions.

3. Experimental Section

3.1. Materials

The polymers used for swelling measurements are the following: poly(ether imide) (PEI), type Ultem[®] 1000 (General Electric, USA) as well as polysulfone (PSF), type Ultrason[®] S3010 and poly(ether sulfone) (PES), type Ultrason[®] E6020, (both BASF, Germany). Cellulose acetate (CA) containing 39.8 wt.-% acetyl content, M_n : 30 kDa (data of supplier) was purchased from Sigma-Aldrich, Germany. The polymers were dried before use for 4h at 100°C. All other chemicals were obtained from Sigma-Aldrich and applied as purchased. Characteristic data of the polymers like density and molecular weight used for calculations are listed in Table 1. Table 1 also contains the characteristic data of PMMA extracted from the literature [19, 20].

Table 1: Characteristic data of the investigated polymers and parameters used for calculation of the plasticization factor β in the GRP model

Code	MW [kDa]	Density [gcm ⁻³]	MW “repeat” unit [Da]	ϕ_{FV} ²⁾	Water uptake ³⁾ [mg _{water} mg _{polymer} ⁻¹]	$\Delta C_{pi}(T_{g3})$ ^{2,4)} [Jmol ⁻¹ K ⁻¹]	T_{g3} [K]	T_{gM} [K]	β (at 293K)
PSU	39	1.24	442.5	0.156	0.0056	84.9	455 ²⁾ /460	444	0.11
PEI	32.8	1.287	592.6	0.130	0.0141	85.6	493 ²⁾ /488	432	0.29
PES	49	1.37	464.6	0.151	0.0174	29.1	484 ²⁾ /498	373	0.63
CA	30 ¹⁾	1.31	408.4	0.189	0.1626	66.7	402 ²⁾ /463	249	1.00
PMMA	139.5	1.19	400.5	0.162	0.0282[19]	37.1	334 ²⁾ /392	3100	0.86

1) data of the supplier

2) calculated by Synthia

3) measured by swelling measurements

4) Water values were taken from Johari et.al. [21] ($\Delta C_{pi}(T_{g3}) = 34.9$ Jmol⁻¹K⁻¹; $T_{g3} = 138$ K)

3.2. Preparation of polymer films

The polymer was dissolved in dichloromethane (except CA, dissolved in acetone) at room temperature (22°C) under stirring to achieve a clear polymer solution with a polymer concentration of 20 wt.%. After that the solution was degassed by keeping it for a longer time at room temperature. This solution was applied to film formation using a knife with a slit thickness of 300 μ m. Then solvent was evaporated at room temperature (about 1 h) and the glass plate with the “dry” polymer film was given in an ethanol bath until the polymer film was detached from the plate. Finally the ethanol-wetted film was intensely rinsed with water and dried at room temperature following drying in an oven for 48 h at 60°C.

3.3. Equilibrium water uptake measurements

The polymer films (about 30 cm² = 0.2-0.3 g) were immersed in water at room temperature and swollen for the desired time, shortly contacted with tissue to remove adherent water and weighed until a constant wetted weight was reached (about 4 to 5 days). Then the swollen films were dried at 100°C until a constant weight of polymer mass was obtained.

3.4. Calculation of fractional free volume ϕ_{FV}

The fractional free volume values ϕ_{FV} , given in Table 1, were estimated with a quantitative structure property relationship (QSPR) using an atomistic model representation of the repeat unit of the single membrane polymers. The computer program *Synthia* of Accelrys Inc. [21] was used to calculate the van der Waals (vdW) volumes V_{vdW} of the polymer chain out of

group contributions. With the specific volume of the polymer V_{sp} , determined from the experimental number density, the fractional free volume was estimated according to the Bondi method as $\phi_{FV} = 1 - 1.3V_{vdW} / V_{sp}$. Here the universal “packing coefficient”, equal to 1.3, is used to convert the vdW volume of the repeat unit in the occupied volume. The plausibility of this approach for all the polymers and in relation to transport of various gases has been discussed in the literature [26]. We consider the values for fractional free volume values ϕ_{FV} , reported in Table 1 as a useful estimate for the modeling calculations.

3.5. Phase diagrams

The phase diagrams of the ternary systems were calculated by employing the FH equation under phase equilibrium conditions. The interaction parameters nonsolvent/solvent and solvent/polymer as well as cloud point data used in the calculations and for fitting, have been obtained from well-documented references or were determined in own experiments [10]. The interaction parameters of the water/polymer systems were adjusted to the cloud point data of the ternary system. More details on the different experimental and theoretical methods used for the description of the phase behavior have been given elsewhere [10].

4. Result and Discussion

4.1. Activity of penetrant

In the glassy state, polymers behave differently to the rubbery state. As a matter of fact, the mobility of the polymer chains greatly decreases below the glass transition temperature T_g , being even considerably slower than the motion of small molecule diffusion jumps. Polymer chains can only vibrate within a limited range in the form of local segmental motion. If the temperature T of the experiment is below the glass transition of a pure polymer, T_{g3} , the motion depends on the penetrant concentration in the polymer and whether the system under these conditions is effectively in a glassy or rubbery state. The effect of penetrant plasticization in the polymer depresses the glass-transition temperature to T_{gM} , and increases the domain of local segmental motion. Therefore at $T > T_{gM}$, the system is partly glassy state and partly rubbery state in which their proportions are proportional to the defined plasticization factor β . **Figure 2** depicts schematically for a hypothetic case the types of entropy or conformational contributions to the chemical potential μ_1^c in the different discussed models.

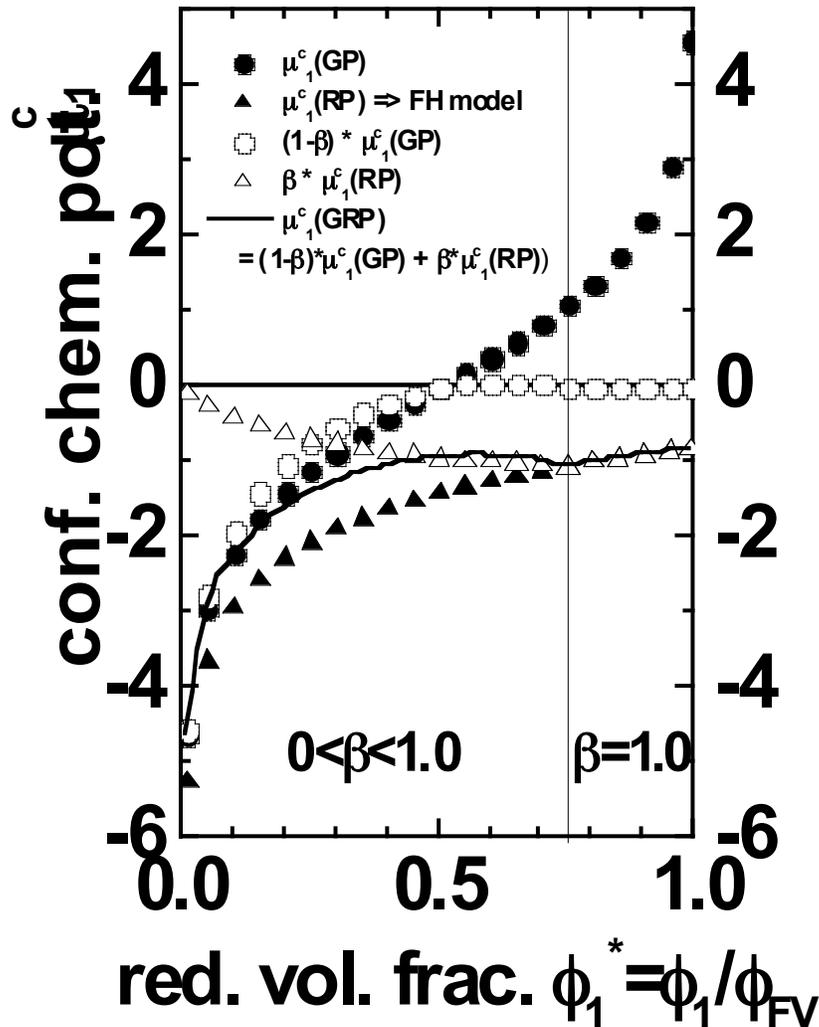


Figure 2. Schematical representation of the entropic (conformational) part μ_1^c of the chemical potential of penetrant 1 in a glassy (GP model, eq. 13 $\phi_{FV} = 0.2$), a rubbery (RP model, eq. 2), and a glassy/rubbery mixture state (GRP model, eq. 17). For the GRP calculation a linear increase of the plasticization factor $\beta = (4/3)\phi_1^*$ was assumed up to a loading of $\phi_1^* \leq 0.75$ and a rubbery state $\beta = 1.0$ for higher values $0.75 < \phi_1^* \leq 1.0$.

For the RP (or FH) model which describes the thermodynamic behavior of the solvent/polymer mixture in the rubbery or solution state the conformational contribution has been plotted as closed triangles. It is a smooth increasing function with loading. The corresponding part with respect to the GP model (closed circles) goes for small occupation of free volume sites (as the RP model) to minus infinity, describing an infinite driving force to attract penetrant particles. At half coverage of the free volume sites $\phi_1^* = \phi_1 / \phi_{FV} = 0.5$, the entropy of mixing in the GP model

has a maximum, and correspondingly $\mu_1^c(\phi_1^* = 0.5) = 0$. For larger coverage, there exists an increasing “repulsing force” to attract further penetrant particles into the remaining free volume sites. The GRP model assumes that, in an initially purely glassy polymer, during sorption of penetrants an increase in “rubbery” domains with coverage occurs. For the GRP calculation, shown in Figure 2, a linear increase of the plasticization factor $\beta = (4/3)\phi_1^*$ was assumed up to a loading of $\phi_1^* \leq 0.75$. For higher coverage of the free volume $0.75 < \phi_1^* \leq 1.0$ the system was assumed in a totally rubbery state ($\beta = 1.0$). The “rubbery” and “glassy” contribution to $\mu_1^c(\phi_1^*)$ for the GRP model (thick line) are given as open symbols. As can be seen from Figure 2, the $\mu_1^c(\phi_1^*)$ -curve agrees for small coverage with values for the GP model, and for higher loading, i.e. increasing plasticization, it approaches values of the “rubbery” model. For loadings higher as 0.75, the curve for GRP model agrees with the RP model. In a first application of the developed model water vapor sorption data of the investigated polymers [10] were evaluated with respect to changes in the T_{gM} according to equation (14). Data are presented in Figure 3.

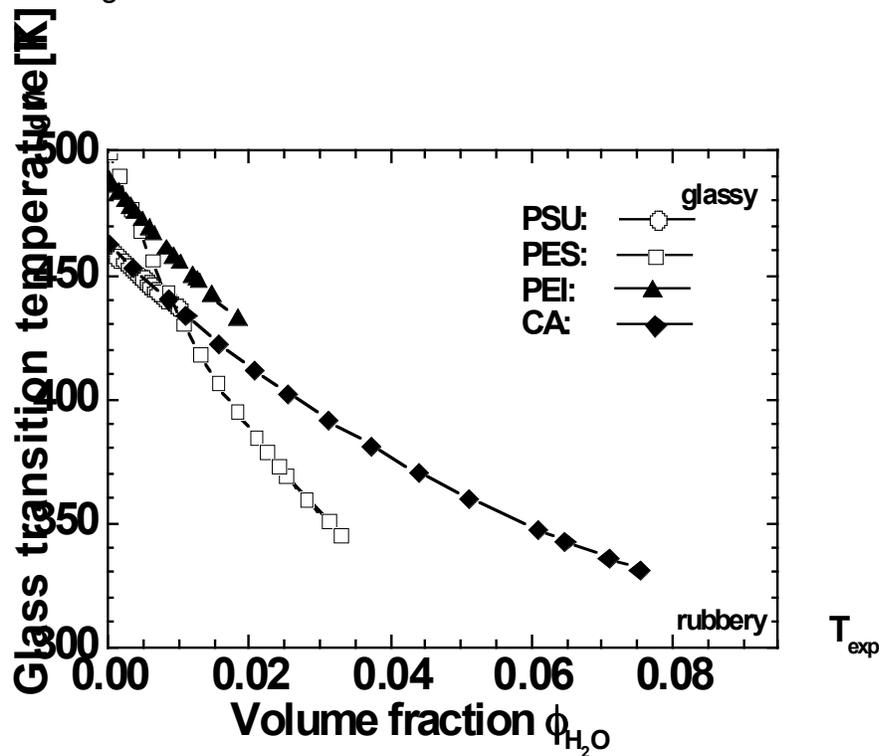


Figure 3: Variation of T_g in a polymer/water mixture in dependence on the amount of sorbed water for polymers with different chain stiffness

Due to the chain stiffness of the individual polymer in a penetrant-free state the curves start at different locations at the y-axis and T_{gM} is continuously decreasing with increasing penetrant contents. The polymers PSU and PEI and partially also PES absorb only a relatively small amount of water and are thus remaining glassy even at their maximum water uptake. In difference CA absorbs considerably more water, reaching already a rather rubbery state at the maximum measured water contents. Insofar the evaluation of data from water uptake measurements using swelling experiments (water activity=1) for CA can be carried out by applying the FH model and a reasonable accordance with the data from the fit technique can be expected while the data of all other polymers should be in disagreement. However such a

data evaluation with the FH model should be also connected with marginal up to considerable errors for CA if sorption data in the low water vapor activity range are processed. Here a more glassy state is taken in account.

For each measured sorption value a plasticization factor can be calculated (equation (15)) and subsequently a water/polymer interaction parameter (equation (17)). These data are pictured in dependence on the plasticization factor for the different polymers in Figure 4. The variation of the plasticization factor for the different polymers results from different water vapor activities during the sorption measurement.

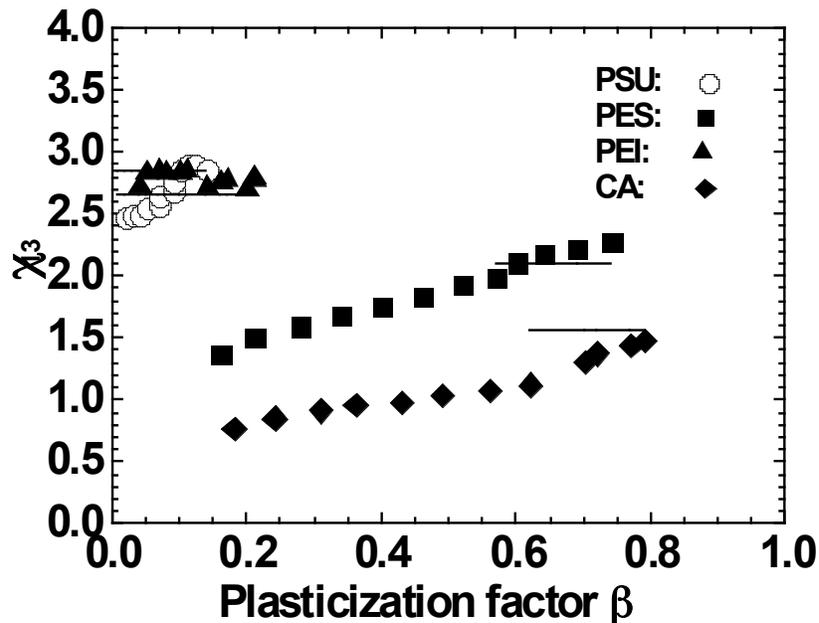


Figure 4: Dependency of the water/polymer interaction parameter calculated with the GRP model (eq. 17) for different polymers on their plasticization state. Different plasticization states are realized by variation of water vapor activity during sorption experiments. The lines indicate the averaged parameter value obtained from the fit of ternary LLE systems (see Table 4 in Ref. [10]).

The data reveal the expected constancy of the interaction parameter within the statistical scattering of the applied methodology for the two most hydrophobic polymers (PSU, PEI) with a low water uptake. For these polymers the developed model seems to be an excellent frame for data evaluation. The averaged interaction parameters calculated from the water uptake at different activities during the sorption measurement are in good coincidence with the cloud point data fit as discussed later. In the case of polymers with higher water sorption (CA, PES) a marginal increase of the interaction parameter with the amount of sorbed water is observed which is converging towards a nearly constant value at higher water activities. At high water activities the water/polymer interaction parameter (plateau range) is in reasonable accordance with the value of the mentioned fit technique whereas at low water activities the glassy part of the model is overestimated resulting in lower values for interaction parameter. Experimental data of sorption measurement were checked with data referred in the literature for CA [27-29] and PES [30-32] but the results of evaluation are identical (not shown here). Therefore the experimental data basis is not the reason for the inconstancy of the interaction parameters for highly water-absorbing polymers. Further investigations are necessary to identify the reason(s).

4.2. Interaction parameter of penetrant/polymer according to the different models

Data of equilibrium water uptake were analyzed by the RP, GP, and GRP model to obtain water/polymer interaction parameters for different polymers (PSU, PEI, PES, CA and PMMA). The results of the calculation are listed in Table 2.

Table 2: Experimental volume fraction of water from equilibrium water uptake measurements and resulting water/polymer interaction parameters calculated by use of different models.

Polymer	ϕ_1 [ref.]	χ_{13}^*	χ_{13}^*	χ_{13}^*
		(FH/RP model)	(GP model)	(GRP model)
PSU	0.0069 ¹⁾	4.0	3.1	3.2
	0.002-0.009 ²⁾ [10]	3.6 ± 0.2	2.6 ± 0.2	2.7 ± 0.2
PEI	0.0181 ¹⁾	3.1	2.3	2.6
	0.002-0.015 ²⁾ [10]	3.4 ± 0.1	2.7 ± 0.1	2.8 ± 0.1
PES	0.0238 ¹⁾	2.9	2.0	2.4
	0.006-0.030 ²⁾ [10]	2.6 ± 0.1	1.4 ± 0.1	2.2 ± 0.1
CA	0.0878 ¹⁾	1.4	0.1	1.35
	0.015-0.090 ²⁾ [10]	1.8 ± 0.1	0.4 ± 0.1	1.4 ± 0.1
PMMA	0.0336 ¹⁾ [19]	2.8	1.7	2.6
	0.003-0.018 ²⁾ [20]	3.2 ± 0.2	2.3 ± 0.3	2.7 ± 0.1

1) swelling measurement

2) sorption measurement

As expected and according to the earlier statement, the value of χ_{13} obtained through the RP, GP, and GRP model are different for each polymer. In general the data of the GP model are lower than the data of RP model whereas the data of the GRP model are in between. GP and GRP models are converging at low water sorption capacity and high chain stiffness, i.e. for the investigated hydrophobic polymers (PSU, PEI). Oppositely, for polymers showing higher water sorption (CA), these models are diverging from each other while the GRP model is approaching the RP model. It is clear that the convergence of GRP and RP models is connected with the formation of a solution (rubber like) state. Hydrophilic polymers with a higher water sorption capacity behave more rubber-like than glassy polymers.

A comparison between data of swelling and sorption measurement reveals marginal differences in water/polymer interaction parameter if the interaction parameters calculated from sorption measurement consider the high water vapor region. Nevertheless the application of a data set from sorption measurements allows determining a mean value, which has a higher relevance in comparison to the single-point evaluation of swelling measurements which is often influenced by the incomplete removal of adhered water. However both techniques result in reliable water/polymer interaction parameters.

The data of the water/polymer interaction parameters determined by the GRP model can be related to the values obtained by fitting techniques, the water/polymer interaction parameter with the highest relevance for membrane formation. The comparison of both approach are shown in Figure 5.

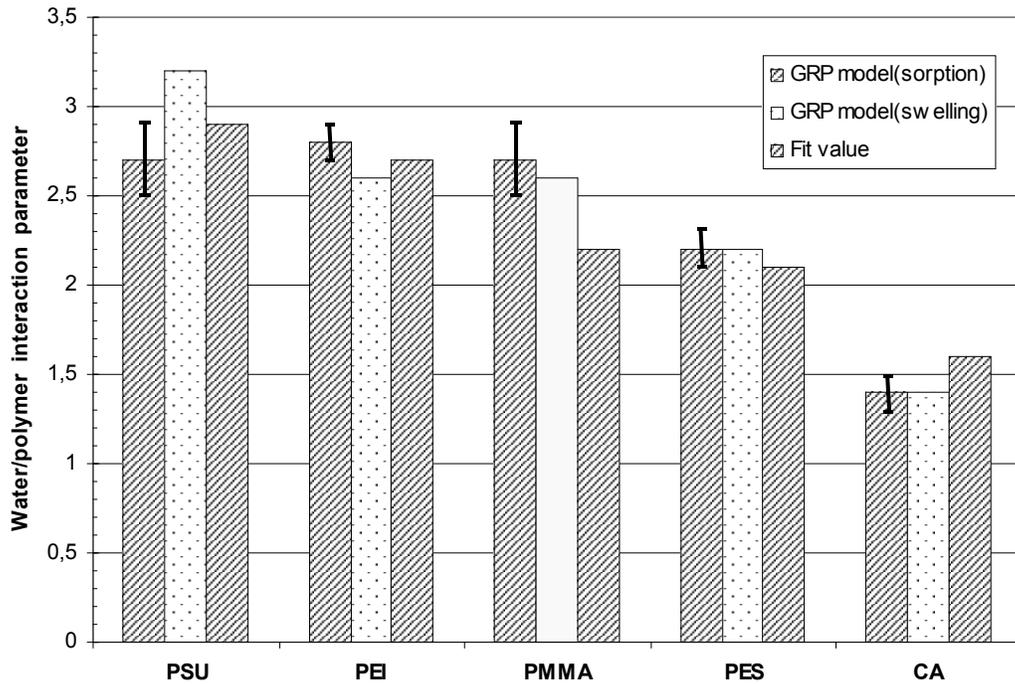


Figure 5: Comparison of the water/polymer interaction parameters from equilibrium water uptake measurements (GRP model evaluation) to data calculated by cloud point fit technique.

It shows a reasonable accordance between χ_{13} values from both, GRP model prediction from simple water uptake and the more laboriously obtained fit value for ternary systems consisting of water, polymer and several organic solvents. This result indicates that the GRP model represents a useful evaluation tool for the determination of nonsolvent/polymer interaction parameters from equilibrium uptake measurements.

Finally the nonsolvent/polymer interaction parameter, evaluated with the GRP model for water/PES will be used for the construction of the ternary phase diagram of the system water/NMP/PES, the membrane-forming system with the most available experimental data. This is an example using well defined solvent/nonsolvent and solvent/polymer interaction parameter functions [8,33] as well as cloud points [8,34]. The calculations of characteristic lines (binodal, spinodal and tie lines) and the critical point (open circle) are pictured in Figure 6. The full points represent the experimentally determined cloud points.

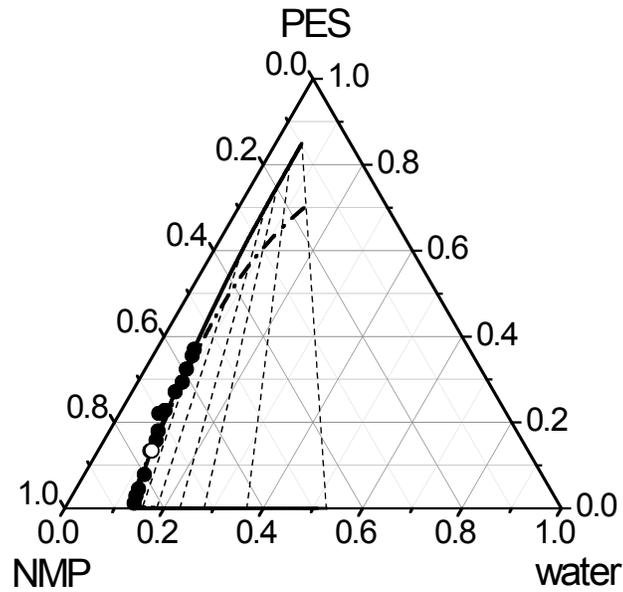


Figure 6: Phase diagram of water/NMP/PES system calculated according to equation (1). The parameters used are $\chi_{12} = 0.718 + 0.669\phi_2$, $\chi_{23} = 0.3 + 0.63\phi_3$, and $\chi_{13} = 2.2$. The last one has been obtained from the GRP model on the basis of the water uptake experiment. (full line, bold: binodal; dotted line, bold: spinodal; dotted line, normal: tie line; open circle: critical point; full circle: experimental cloud points [8,34])

As can be seen the calculated data of the binodal are practically identical with the experimentally determined cloud points up to a high polymer concentration without introducing a ternary interaction parameter (χ_{123}) as suggested first by Pouchly et al. [6] as correction term for thermodynamic models of NS-S-P systems. This correction term (χ_{123}) was also applied for the ternary system, discussed here, by Li [35]. Due to this result it is questionable whether ternary interaction parameters are principally necessary if precisely determined binary interaction parameter were applied in the calculation. In the past the precision in the nonsolvent/polymer interaction parameter was the most limiting factor for the calculation of characteristic lines/points of the ternary phase diagram. With the new evaluation technique relatively precise water/polymer interaction parameter are available and the binodal calculation is in complete accordance with the experimental cloud points (Figure 6). Therefore, if any ternary interaction parameter is present the numeric value is very low and in the precision of the experimental method and is negligible.

5. Conclusions

Generally, the FH theory (RP model) is used to model the thermodynamic behavior of ternary NS-S-P systems describing the phase inversion process during membrane formation. For its application three different interaction parameters or their interaction functions have to be known precisely. The nonsolvent/polymer interaction parameter χ_{13} has crucial importance because of its strong influence on the size and location of the miscibility gap, but it is difficult to determine this parameter experimentally. Considerably different values of water/polymer interaction parameters are reported from different experiments for some water/polymer systems. The question is: Is this a consequence of the precision of the experimental methods or of the data evaluation? In order to answer this question, theoretical considerations of the thermodynamic state during equilibrium water uptake measurements, the usually applied

technique for experimental investigations, are made here in the framework of the FH theory leading to the following conclusions:

- The application of the FH theory (RP model, eq. (2)) is limited to polymer/penetrant systems with a high mobility of the polymer chains (prerequisite per definition), i.e. it requires a rubber-like or solution state. This prerequisite is only fulfilled if the amount of sorbed penetrant is high and/or if the chain stiffness is low. Therefore, the application of the RP model for data evaluation of water swelling measurements is only correct if the polymer is hydrophilic and if it has absorbed a high amount of water resulting in high chain flexibility. It is principally incorrect, however to use this theoretical frame in general for the analysis of water swelling measurements including hydrophobic polymers with high chain stiffness and low water uptake.
- The situation of water swelling measurements for highly hydrophobic polymers can be accurately described if in the derivation of the FH equation the polymer is considered as an extreme glass (no chain mobility, i.e. zero configuration entropy). Under this assumption a “glassy polymer” model (GP), eq. (13), was derived leading to an equation applicable for the evaluation of equilibrium water uptake measurements in highly hydrophobic polymers. This model fails however, as expected, if data of hydrophilic polymers are analyzed.
- As a potential solution for all types of polymers the GRP model, eq. (17), was proposed which is based on a partially glass-like and partially rubber-like state (plasticization factor) to describe water-swollen polymers. The contributions of each of the “border cases” to the “mixed” state depend on the original stiffness of the pure components, indicated by the T_g -value, and the relative amount of penetrant in the polymer matrix, initiating a plasticization of the polymer connected with a reduction of the glass temperature. Lowering the T_g initiates an increase of chain mobility and, therefore, a continuous transfer from the glass-like to the rubber-like state if the equilibrium sorption capacity and the chain stiffness of the water-free polymer allow this. Using this approach the water/polymer interaction parameter can be calculated. Resulting data are in reasonable accordance with respective values obtained by the more elaborated fitting technique of experimental cloud points of ternary systems. Additionally, in contrast to the fitting technique, the proposed GRP model has a theoretical basis. However further developments are necessary to find out the reasons for some remaining inconsistencies like the inconstancy of interaction parameters in the low water vapor activity region.
- The reconstruction of ternary phase diagrams based on the FH theory results in an excellent accordance of the calculated binodal and the experimental cloud points over a wide concentration range without introducing of a ternary interaction parameter if precisely determined binary interaction parameters are available. This requires to employ the herein described data evaluation on nonsolvent equilibrium uptake data. It can be done on basis of the GRP model to determine the nonsolvent/polymer interaction parameter correctly.

In summary, the investigation verifies that simple water uptake measurements can be used for a precise determination of reliable nonsolvent/polymer interaction parameters if the physical state of this mixture, in particular the chain mobility, is taken in account. The GRP model, developed in analogy to the well-known FH model, is a suitable and simple theoretical basis for data processing and interpretation.

Nomenclature and abbreviation

Abbreviation

PSU	polysulfone
PEI	poly(ether imide)
PES	poly(ether sulfone)
CA	cellulose acetate
PMMA	poly(methyl methacrylate)
GP	glassy polymer
RP	rubbery polymer
GRP	glassy and rubbery polymer
FH	Flory-Huggins
NS-S-P	nonsolvent/solvent/polymer

Nomenclature

a	activity
f	coefficient
G	Gibbs free energy (J mole^{-1})
g	interaction function
k	Boltzman constant ($1.381 \times 10^{-23} \text{ mol}^{-1}$)
n	number of moles
m	mass (g)
R	gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
T	absolute temperature (K)
T_g	glass transition temperature (K)
u	volume fraction in binary system
z	coordination number
v	hard core volume (cm^3)
x	mole fraction
C	heat capacity ($\text{J g}^{-1} \text{ K}^{-1}$)

N	number of molecules/polymer segments
N_0	Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$)
p	probability
P	pressure (Pa)
V	volume (cm^3)
ρ	density (g cm^{-3})
$\tilde{\rho}$	reduced density
ρ^*	hard-core density
M	molecular weight
M_s	segment molecular weight
β	plasticization factor
α, β, γ	constants
v	molar volume ($\text{cm}^3 \text{ mole}^{-1}$)
χ	interaction parameter
ϕ	volume fraction
$\Delta\mu$	chemical potential differences
H	enthalpy (J)
S	entropy (J K^{-1})
Ω	the number of arrangements
ω	energy of formation

Index

0	empty lattice site
1	nonsolvent
2	solvent
3	polymer
M	mixture
g	gas
FV	accessible free volume

hc hard core

vdW van der Waals

sp specific

References

- [1] P.J. Flory, Principle of polymer chemistry, Cornell University, Ithaca, N.Y., 1953.
- [2] M.H.V. Mulder, T. Franken and C.A. Smolders, Preferential sorption versus preferential permeability in pervaporation, *J. Membrane Sci.*, 22 (1985) 155.
- [3] F.W. Altena and C.A. Smolders, Calculation of liquid-liquid phase separation in a ternary system of a polymer in a mixture of a solvent and a nonsolvent, *Macromolecules*, 15 (1982) 1491.
- [4] O. Rodriguez, F. Fornasiro, A. Arce, C.J. Radke and J.M. Prausnitz, Solubilities and diffusivities of water vapor in poly(methylmethacrylate), poly(2-hydroxyethylmethacrylate), poly(N-vinylpyrrolidone) and poly(acrylonitrile), *Polymer*, 44 (2003) 6323.
- [5] H. Tompa, Polymer solution, Butterworth, London, 1956.
- [6] J. Pouchly, A. Zivny and K.Solc, Thermodynamic equilibrium in the system macromolecular coil-binary solvent, *J. Polym. Sci.: Part C, Polym. Symp.*, 23 (1968) 245.
- [7] L. Yilmaz and A.J. McHugh, Analysis of nonsolvent-solvent-polymer phase diagrams and their relevance to membrane formation modeling, *J. Appl. Polym. Sci.*, 31 (1986) 997.
- [8] L. Zeman and G. Tkacik, Thermodynamic analysis of a membrane-forming system water/N-methyl-2-pyrrolidone/polyethersulfone, *J. Membrane Sci.*, 36 (1988) 119.
- [9] Z. Li and C. Jiang, Determination of the nonsolvent/polymer interaction parameter χ_{13} in the casting solutions, *J. Membrane Sci.*, 174 (2000) 87.
- [10] M. Karimi, W. Albrecht, M. Heuchel, M.H. Kish, J. Frahn, Th. Weigel, D. Hofmann, H. Modaress and A. Lendlein, Determination of water/polymer interaction parameter for membrane-forming systems by sorption measurements and fitting techniques, *J. Membrane Sci.*, 265 (2005) 1.
- [11] J.H. Gibbs and E.A. Di Marzio, Chain stiffness and the lattice theory of polymer phases, *J. Chem. Phys.*, 28 (1958) 373.
- [12] E.A. DiMarzio, C. Castellano and A. Yang, Glass temperature depression of polymers by use of mixed solvents: A colligative property, *J. Polym. Sci.: Part B: Polym. Phys.*, 34 (1996) 535.
- [13] J.M. Prausnitz, R.N. Lichtenthaler and E.G. de Azevedo, Molecular thermodynamics of fluid-phase equilibria, 3th ed., PTR: Prentice Hall, 1999.
- [14] I.C. Sanchez and R.H. Lacombe, Statistical thermodynamics of polymer solutions, *Macromolecules*, 11 (1978) 1145.
- [15] P.R. Couchman and F.E. Karasz, A classical thermodynamic discussion of the effect of composition on glass-transition temperature, *Macromolecules*, 11 (1978) 117.
- [16] C. Barth and B.A. Wolf, Quick and reliable routes to phase diagrams for polyethersulfone and polysulfone membrane formation, *Macromol. Chem. Phys.*, 201 (2000) 365.
- [17] M.E. Rezac and B. Schöberl, Transport and thermal properties of poly(ether imide)/acetylene-terminated monomer blends, *J. Membrane Sci.*, 156 (1999) 211.

- [18] C.A. Smolders, A.J. Reuvers, R.M. Boom and I.M. Wienk, Microstructures in phase-inversion membranes. Part 1. Formation of macrovoids, *J. Membrane Sci.*, 73 (1992) 259.
- [19] J.Y. Lai, S.F. Lin, F.C. Lin and D.M. Wang, Construction of ternary phase diagrams in nonsolvent/solvent/PMMA systems, *J. Polym. Sci., Part B, Polym. Phys.*, 36 (1998) 607.
- [20] O. Rodriguez, F. Fornasiero, A. Arce, C.J. Radke and J.M. Prausnitz, Solubilities and diffusivities of water vapor in poly(methylmethacrylate), poly(2-hydroxyethylmethacrylate), poly(vinylpyrrolidone) and poly(acrylonitrile), *Polymer* 44 (2003) 6323.
- [21] G.P. Johari, A. Hallbrucker and E. Mayer, The glass transition of hyperquenched water, *Nature* 330 (1987) 552.
- [22] M. Heuchel, M. Böhning, O. Hölck, M.R. Siegert and D. Hofmann, Atomistic packing models for experimentally investigated swelling states induced by CO₂ in glassy polysulfone and poly(ether sulfone), *J. Polym. Sci. Part B: Polym. Phys.*, 44 (2006) 1874.
- [23] K. Kneifel and K.V. Peinemann, Preparation of hollow fiber membranes from polyetherimide for gas separation, *J. Membrane Sci.*, 65 (1992) 295.
- [24] M Scandola and G. Ceccorulli, Viscoelastic properties of cellulose derivatives: 1. Celulose acetate, *Polymer* , 26 (1985) 1953
- [25] Polymer User Guide, Synthia Section, Version 4.0.0, Molecular Simulations, San Diego 1996.
- [26] A. Bondi, Physical properties of molecular crystals, liquids and glasses, Wiley, New York, 1968.
- [27] P.P. Roussis, Diffusion of water vapor in cellulose acetate: 1. Differential transient sorption kinetics and equilibria, *Polymer*, 22 (1981) 768.
- [28] L. Perrin, Q.T. Nguyen, D. Sacco and P. Lochon, Experimental studies and modeling of sorption and diffusion of water and alcohols in cellulose acetate, *Polymer Int.*, 42 (1997) 9.
- [29] H. Gocho, H. Shimizu, A. Tanioka, T.-J. Chou and T. Nakajima, Effect of acetyl content on the sorption isotherm of water by cellulose acetate: comparison with the thermal analysis results, *Carbohydrate Polymer*, 41 (2000) 83.
- [30] V.B. Singh, J.A. Barrie and D.J. Walsh, Sorption of water in polyethersulfone/poly(ethylene oxide) blends, *J. Appl. Polym. Sci.*, 31 (1986) 295.
- [31] B.T. Swinyard, P.S. Sahoo, J.A. Barrie and R. Ash, The transport and sorption of water in polyethersulfone, polysulfone, and polyethersulfone phenoxy blends, *J. Appl. Polym. Sci.*, 41 (1990) 2479.
- [32] K.A. Schult and D.R. Paul, Water sorption and transport in a series of polysulfones, *J. Polym. Sci.: Part B: Polym. Phys.*, 34 (1996) 2805.
- [33] R.M. Boom, Membrane formation by immersion precipitation: The role of a polymeric additive, Thesis, University of Twente, Enschede, The Netherlands, 1992.

- [34] W.W.Y. Lau, M.D. Guiver and T. Matsuura, Phase separation in polysulfone/solvent/water and polyethersulfone/solvent/water systems, *J. Membrane Sci.*, 59 (1991) 219.
- [35] S.G. Li, Preparation of hollow fiber membranes for gas separation, Thesis, University of Twente, Enschede, The Netherlands, (1994).