

Final Draft
of the original manuscript:

Fierro, D.; Scharnagl, N.; Emmler, T.; Boschetti de Fierro, A.; Abetz, V.:
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In: Journal of Membrane Science (2011) Elsevier

DOI: 10.1016/j.memsci.2011.09.006

Experimental determination of self-diffusivities through a polymer network for single components in a mixture

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Abstract

Diffusion models such as Vrentas & Duda diffusion theory and Wesselingh & Bollen multicomponent diffusion model have been used together with estimated tracer diffusion coefficients in order to provide a predictive method to calculate thermodynamic diffusion coefficients needed for transport simulation in polymer membrane processes. PFG-NMR measurements were carried out in order to estimate the tracer diffusion coefficients for solvent–solvent–polymer systems on free-standing crosslinked polymer films. The use of experimentally determined diffusivities for a set of finite solvent-solvent-polymer concentrations as well as of plausible assumptions in nanofiltration allows the estimation of the unclear parameters presented in the diffusion theories with the subsequent predictability for those systems.

Keywords: diffusion coefficient, diffusion theory, diffusion through polymer matrix, PFG-NMR, organic solvent nanofiltration

1. Introduction

Among membrane processes, organic solvent nanofiltration has gained significance in chemical technology and is used in a broad range of applications. The use of an increasing amount of solvents in a variety of industrial processes and the deficiencies associated to classical separation techniques stimulate the development of efficient new separation techniques which reduce the associated cost of materials and benefit the environment with lower energy consumption and higher recovery of residual substances.

Modeling of membrane processes is of high industrial importance, since it leads to the prediction of process performance and, ultimately, to prediction of process efficiency and profit. Modeling of ideal systems has been known for some years now and is widely described in the literature. However, modeling of real systems presents many obstacles, from deviation of substances from the ideal behavior to over simplification of the process in the model. Therefore, besides the expected deviations from the ideal behavior, which are accounted for by the appropriate factors, other considerations need to be taken into account. One of the main issues is that the feed solution in the membrane separation process is a mixture, and the diffusion of the mixture through the polymer membrane is different from the diffusion of the individual components in the mixture.

Based on a simple molecular model of liquids, Dullien established an equation capable to predict self-diffusion coefficients without the inclusion of any adjustable parameters [1]. Already in 1977 Vrentas and Duda revised the free volume theory in order correlate viscosities and tracer diffusion coefficients of simple liquids and polymeric materials [2, 3]. The free volume diffusion theory presented in these works is more general than the one from Fujita [4]. Although the Vrentas and Duda's theory overcomes some of the restrictions found in Fujita's theory, a term that relates the critical molar volume of a jumping unit of solvent to the one of the polymer jumping unit is introduced. The accuracy of the diffusion coefficient calculation is largely governed by the estimation of this ratio of critical molar volume of jumping units. Due to a vague definition and the consequently uncertain calculation of this ratio, the parameter is frequently adjusted from diffusion data [5-7]. The dependence of the calculation of the diffusivities on the aforementioned estimation causes great uncertainties in the extended version of the Vrentas and Duda diffusion theory for multicomponent systems

[6, 8, 9]. Based on the Maxwell-Stefan diffusion approach [10, 11] and the statistical model from Cohen and Turnbull [12], Wesselingh and Bollen [13] develop an extension of the binary free volume diffusion theory for multicomponent mixtures. This theory has the advantage of not relying on the estimation of the ratio of critical molar volume jumping units. However, it is based on a variety of assumptions that restrict the applicability of the theory for non-ideal systems.

With the scope of modelling the transport behavior in organic solvent nanofiltration processes, the purpose of the present work is to contribute to overcome the uncertainties of the estimation of the diffusivities presented in the available diffusion theories for multicomponent systems. Here, a method to effectively determine the diffusion behavior of a mixture of solvents in a crosslinked polymer network is proposed. For that purpose, the diffusion of each chemical through the polymer has been determined by pulse field gradient nuclear magnetic resonance spectroscopy (PFG-NMR) measurements. Determinations of the diffusion of pure chemicals have been compared to values reported in the literature, while determinations of the diffusion behavior of individual chemicals in a mixture could be used for describing the transport mechanism on real membrane applications.

2. Diffusion of small molecules through polymer matrices

Theoretical analysis of diffusion processes is an important step for a great number of applications. Different types of diffusion coefficients have to be considered in order to apply them under the proper conditions.

Tracer diffusion coefficients account for the mobility of a molecule in the absence of a concentration gradient. Techniques such as pulse field gradient NMR spectroscopy allow the measurement of tracer diffusion coefficients [14-28]. The term tracer diffusion coefficient is often called self-diffusion coefficient, mainly referring to the diffusion of a given molecule in its pure liquid [5].

The Fickian diffusion coefficient is the most often used diffusion coefficient in engineering calculations. It refers to the diffusion of molecules due to the presence of a concentration gradient. Therefore, without any other driving force, the molecules will move from a highly concentrated region to a region with lower concentration.

A third type of diffusion coefficient is the thermodynamic diffusion coefficient. This definition intends to express the rigorous driving force for mass transfer, i.e., it considers the

chemical potential gradient instead of the sole concentration gradient. A relationship between the Fickian diffusivity and the thermodynamic diffusion coefficient is expressed in equation 1.

$$\frac{D_{12}^F}{D_{12}} = 1 + \frac{d \ln \gamma_1}{d \ln x_1} \quad \text{Eq. 1}$$

where D_{12}^F is the mutual diffusion coefficient, between the solvent and the polymer, for diffusion processes with a concentration gradient driving force according to the Fick's law, whereas D_{12} is the thermodynamic diffusion coefficient. γ_1 and x_1 are the activity coefficient and the mole fraction of the solvent in the mixture, respectively.

For dilute solutions, the differences between all three diffusion coefficient definitions vanish. The oldest equation to describe this is the Einstein-Stokes equation (equation 2) [29, 30]. A more sophisticated one is the Wilke-Chang equation.[31] Due to its simplicity, one of the mostly used equations is the Dullien equation, a simple relationship of critical and specific volumes that is shown in equation 3[1].

$$D^{s-1} = \frac{kT}{6\pi\eta r} \quad \text{Eq. 2}$$

$$\bar{D} = \frac{1.124 \times 10^{-17} \text{ mol}^{2/3} V_C^{2/3} R T}{\eta MW V^*} \quad \text{Eq. 3}$$

For the prediction and correlation of multicomponent thermodynamic diffusion coefficients, Vrentas et al. proposed an extension for ternary systems of the Vrentas & Duda diffusion theory [6]. It is stated that this ternary extension can be reduced to the Fujita equation under proper conditions. Both versions of the freevolume theory suffer from not having predictive capabilities[5]. More recently, based on the Maxwell-Stefan diffusion approach and the statistical model from Cohen & Turnbull, Wesselingh and Bollen developed an extension of the free-volume diffusion theory for multicomponent mixtures. This approach allows the calculation of Maxwell-Stefan diffusivities for simple liquid mixtures[10-13].

2.1 Vrentas & Duda theory

Although the free volume model for molecular transport is based on a simplified version of molecular processes, there exists a significant amount of evidence that supports the use of the theory in the prediction and correlation of viscosities and tracer diffusion coefficients of simple liquids and polymeric materials[2]. According to the Vrentas & Duda free volume

diffusion model, the tracer diffusion coefficient for a diffusing solvent in a polymer is given by equation 4[2, 3].

$$\tilde{D}_t = \tilde{D}_1 e^{-\frac{E}{RT}} \exp\left(\frac{-\omega_1 \bar{V}_1^* - \xi_{12} \omega_2 \bar{V}_2^*}{\omega_1 \frac{K_{11}}{\lambda} (K_{21} - T_{g1} + T) + \omega_2 \frac{K_{12}}{\lambda} (K_{22} - T_{g2} + T)}\right) \quad \text{Eq. 4}$$

Here, \tilde{D}_1 is a constant pre-exponential factor for the solvent, E is the energy that a molecule needs to overcome attractive forces which hold it to its neighbors. ω_i are the mass fraction of each component. \bar{V}_1^* and \bar{V}_2^* refer to the specific critical hole free-volume required for a jump of a solvent and a polymer, respectively. These two critical hole free volume values can be estimated as the specific volume of the solvent and the polymer at 0 K, i.e., the conversion in mass units of the zero point molar volume V^c .

ξ is the ratio of the critical molar volumes of a jumping unit of solvent to the one of the polymer jumping unit. λ represents an overlap factor in order to account for the fact that the same free-volume is available for more than one molecule (this parameter should be between 0.5 and 1). K_{11}/λ and K_{21} are the free-volume parameters for the solvent referred to itself and to the polymer, respectively; K_{12}/λ and K_{22} are the parameters for the polymer and are related with the Williams-Landel-Ferry (WLF) constants[32, 33]. T_{g1} stands for the glass transition temperature of the solvent and T_{g2} for the one of the polymer.

For pure polymers, the temperature dependencies of the viscosity can be expressed by the WLF equation as shown in equation 5. Consequently, the free volume parameters for polymers are related with the WLF constants as shown in equations 6 and 7. A set of polymer free volume parameters are provided in table 2[32-34].

$$\log\left(\frac{\eta_2(T)}{\eta_2(T_{g2})}\right) = \frac{-C_{12}^{WLF} (T - T_{g2})}{C_{22}^{WLF} - T_{g2} + T} \quad \text{Eq. 5}$$

$$K_{22} = C_{22}^{WLF} \quad \text{Eq. 6}$$

$$\frac{K_{12}}{\lambda} = \frac{\bar{V}_2^*}{2.303 C_{12}^{WLF} C_{22}^{WLF}} \quad \text{Eq. 7}$$

There are no feasible methods to model both the variation of the jumping activation energy E and the variation of the free volume with composition changes, therefore, E needs to be considered as a constant[5]. Nevertheless, there are several diffusion studies which assumed a negligible effect of the activation energy over the diffusion behavior under a reasonable temperature range [5, 6, 33, 35]. Rewriting equation 4, the Vrentas & Duda diffusion theory for binary systems is expressed as follows:

$$\tilde{D}_1 = \bar{D}_1 \exp\left(\frac{-\omega_1 \bar{V}_1^* - \xi_{12} \omega_2 \bar{V}_2^*}{\omega_1 \frac{K_{11}}{\lambda} (K_{21} - T_{g1} + T) + \omega_2 \frac{K_{12}}{\lambda} (K_{22} - T_{g2} + T)}\right) \quad \text{Eq. 8}$$

\bar{D}_1 is a constant diffusion pre-exponential factor when the jumping activation energy is considered equal to zero. This equation becomes similar to the one for self-diffusion coefficients when the proper conditions are considered, as presented in equation 9[12, 36].

$$\bar{D}_i = D_i \exp\left(-\lambda \frac{V_i^*}{V_f^*}\right) \quad \text{Eq. 9}$$

For the sake of simplicity, equation 8 can be rewritten with the introduction of the average hole free-volume per gram of mixture \bar{V}_{FH} as shown in equation 10. With the assumption of a negligible concentration dependence of the partial specific volumes of all components, equation 10 can be extended to a ternary solvent–solvent–polymer system as shown in equations 11 to 13 [6]:

$$\tilde{D}_1 = \bar{D}_1 \exp\left(\frac{-\omega_1 \bar{V}_1^* - \xi_{12} \omega_2 \bar{V}_2^*}{\bar{V}_{FH}/\lambda}\right) \quad \text{Eq. 10}$$

$$\bar{V}_{FH}/\gamma = \omega_1 \frac{K_{11}}{\lambda} (K_{21} - T_{g1} + T) + \omega_2 \frac{K_{12}}{\lambda} (K_{22} - T_{g2} + T)$$

$$\tilde{D}_1 = \bar{D}_1 \exp\left(\frac{-\omega_1 \bar{V}_1^* - \omega_2 \bar{V}_2^* \cdot \frac{\xi_{12}}{\xi_{22}} - \xi_{13} \omega_3 \bar{V}_3^*}{\bar{V}_{FH}/\lambda}\right) \quad \text{Eq. 11}$$

$$\tilde{D}_2 = \bar{D}_2 \exp\left(\frac{-\omega_1 \bar{V}_1^* \frac{\xi_{22}}{\xi_{12}} - \omega_2 \bar{V}_2^* - \xi_{23} \omega_3 \bar{V}_3^*}{\bar{V}_{FH}/\lambda}\right) \quad \text{Eq. 12}$$

$$\frac{\hat{V}_{FH}}{\lambda} = \omega_s \frac{K_{1s}}{\lambda} (K_{2s} - T_{g_s} + T) + \sum_{j=1}^2 \omega_j \frac{K_{1j}}{\lambda} (K_{2j} - T_{g_j} + T)$$

$$\frac{\hat{V}_{FH}}{\lambda} = \sum_{j=1}^3 \omega_j \frac{f_j}{\lambda} V_j^*$$

Eq. 13

where f_j is the fractional hole free volume of pure component j . With the use of equations 11-13 it is possible to predict the tracer diffusion coefficients for ternary systems.

The accuracy of the diffusion coefficient calculation is largely governed by the estimation of ξ_{1s} [37]. If binary data \bar{D}_i vs. ω_i for both solvent-polymer systems is available, a nonlinear regression of equation 10 to estimate the parameters \bar{D}_1 , \bar{D}_2 , ξ_{1s} , ξ_{2s} , f_1/λ and f_2/λ can be done. Consequently, equations 11 to 13 are used in order to complete the calculation of the ternary tracer diffusion coefficients.

By following the procedure proposed by Zielinski and Duda and further explored by Hong, it is possible to determine all the free-volume parameters on a pseudo-predictive basis with the only use of liquid viscosity data as a function of temperature [33, 38]. The parameter \bar{D} from the Vrentas & Duda diffusion theory can be estimated by merging the Dullien self-diffusivity equation [1] with the Vrentas & Duda equation simplified for a pure solvent. Later, the free volume parameters for a solvent i can be estimated by nonlinear regression of pure component viscosity and specific volume as a function of temperature.

$$\ln \left(\frac{1.124 \times 10^{-17} \text{ mol}^2 / \text{s} V_{C_i}^{2/3} R T}{\eta MW V_i^*} \right) = \ln(\bar{D}_i) - \frac{V_i^* / K_{1s} / \lambda}{(K_{2i} - T_{g_i}) + T}$$

Eq. 14

Afterwards, the computation of the ξ_{1s} parameters is needed. A linear correlation of the molar volume of polymer jumping unit with the glass transition temperature can be used to estimate the overlap factors as shown in equations 15 and 16. Although these equations have not been extensively tested, are only valid for molecules that move as a single unit and the results can change with variations in polymer properties (such as the degree of crosslinking), they offer a prediction capability for the theory [33]

$$\xi_{1s} = \frac{V_i^c}{V_{g_i}^*} = \frac{\hat{V}_i^* MW_{1j}}{\hat{V}_g^* MW_{2j}}$$

Eq. 15

$$\bar{V}_{sf} = \frac{0.0925 T_{gs} + 69.47}{10^6} (T_{gs} < 295 \text{ K})$$

Eq. 16

$$\bar{V}_{sf} = \frac{0.6224 T_{gs} + 86.95}{10^6} (T_{gs} \geq 295 \text{ K})$$

The accuracy of the diffusion coefficient calculation is largely governed by the estimation of the ratio of critical molar volume of jumping units. Due to the vague definition and the consequently uncertain calculation of ξ_{ts} , the parameters are frequently adjusted from the diffusion data[5-7]. However, ξ_{ts} has a broader meaning than simply being a correlative parameter used in free volume theory, since it signifies the extent to which the activation energy of shear viscosity and tracer diffusion are coupled, and whether there exists an apparent activation energy ceiling value for penetrant diffusion into polymers[4, 37, 39, 40]. From a theoretical point of view, ξ_{ts} can achieve any positive value, either greater or less than 1[41, 42]. However, experimental calculations suggest that the ξ_{ts} parameter should be less than 1[38, 43].

The above mentioned method is valid for noncrosslinked polymers. Nevertheless, it seems reasonable to expect that the theory can be extended to describe the tracer diffusion coefficient of solvent in amorphous crosslinked polymers. Vrentas et al. proposed an extension of the Vrentas & Duda diffusion theory for not-too-tightly-crosslinked polymers. An inspection of equations 4, 11, 12, 13 and 15 reveals the following considerations [44]:

- The energy of solvent migration and the jump distance for the solvent molecule are independent of the degree of crosslinking. Consequently, the constant pre-exponential diffusion factor of the solvents (D_0) and the molecular energy necessary to overcome attractive forces which hold it to its neighbors (E) are independent of the degree of crosslinking of the polymer.
- The solvent properties are independent of the degree of crosslinking. Namely, the specific critical hole free-volume required for a jump (V_1^*), the molecular weight of the solvent jumping unit (MW_{1f}) and the specific critical hole free-volume of the solvent ($\bar{V}_{FH1} = f_1 \cdot V_1^*$) are constant.

- The free volume configuration in the polymer (ξ) and the size of its jumping unit (MW_{sj}) are independent of the degree of crosslinking. As a result, $\xi_{1s} \cdot \bar{V}_s^*$ remains unaffected by the degree of crosslinking.
- The thermal expansion coefficient for the total specific volume of the polymer and the thermal expansion coefficient for the sum of the specific occupied volume and the specific interstitial free volume are assumed to be independent of the degree of crosslinking.

From the above considerations, the introduction of crosslinking into the polymer affects the tracer diffusion coefficient only through the specific critical hole free-volume of the polymer \bar{V}_{FHs} . Furthermore, from the last assumption, the following volumetric relationship is valid:

$$\frac{\bar{V}_{FHs}(T, X)}{\bar{V}_{FHs}(T, 0)} = \frac{V_s^*(0, X)}{V_s^*(0, 0)} = \frac{V_s^*(T, X)}{V_s^*(T, 0)} = \frac{V_s^*(T, X)}{V_s^*} = \varrho \quad \text{Eq. 17}$$

Here, $V_s^*(T, X)$ is the specific volume of the pure polymer at a temperature T and a degree of crosslinking X . The effect of crosslinking on the free volume of the polymer is represented by ϱ . Lastly, for polymers without strong crosslinking, equations 11, 12, 13 are expressed as follows:

$$\bar{D}_1 = \bar{D}_1 \exp \left(\frac{-\omega_1 \bar{V}_1^* - \omega_2 \bar{V}_2^* \frac{\xi_{1s}}{\xi_{2s}} - \xi_{1s} \omega_s \bar{V}_s^*}{\bar{V}_{FH}/\lambda} \right) \quad \text{Eq. 18}$$

$$\bar{D}_2 = \bar{D}_2 \exp \left(\frac{-\omega_1 \bar{V}_1^* \frac{\xi_{2s}}{\xi_{1s}} - \omega_2 \bar{V}_2^* - \xi_{2s} \omega_s \bar{V}_s^*}{\bar{V}_{FH}/\lambda} \right) \quad \text{Eq. 19}$$

$$\frac{\bar{V}_{FH}}{\lambda} = \sum_{\substack{j=1 \\ \text{solvents}}}^s \omega_j \bar{V}_{FHj} + \omega_s V_s^*(T, X) = \sum_{\substack{j=1 \\ \text{solvents}}}^s \omega_j \frac{f_j}{\lambda} V_j^* + \omega_s \frac{\lambda_0}{\lambda} V_s^* \varrho \quad \text{Eq. 20}$$

2.2 Wesselingh & Bollen method

Based on the Maxwell-Stefan diffusion approach[10, 11] and the statistical model from Cohen & Turnbull[12], Wesselingh and Bollen[13] developed an extension of the binary free volume diffusion theory for multicomponent mixtures. This approach allows the calculation of Maxwell-Stefan (thermodynamic) tracer diffusivities for simple liquid mixtures. Wesselingh

and Bollen proposed three mixing rules which allow the estimation of the tracer diffusion coefficients with the use of effective tracer friction coefficients ($\zeta_{tr,eff}$).

The first mixing rule assumes a linear mixing of the free volume of pure components as shown in equation 21[45]. The second mixing rule considers spherical molecules, and the free volume is considered as a function of the surface fraction (equation 22). The third mixing rule considers the density of the mixture instead of the density of the single compounds. The density of the mixture is assumed as a linear mixing of the compounds, as shown in equation 23. To achieve the calculation of the tracer friction factors, it is assumed that a compressed substance is arranged on a cubic lattice, with a lattice distance close to the molecular diameter (d).

$$V_M^F = \sum_{i=1}^{\text{all comp.}} x_i V_i^F \quad \text{Eq. 21}$$

$$a_i = \frac{(V_i)^{\frac{2}{3}}}{\sum_{j=1}^n x_j (V_j)^{\frac{2}{3}}} \quad V_i^{FF} = \frac{a_i}{x_i} V_M^F \quad \text{Eq. 22}$$

$$\zeta_{tr,i}^0 = 2 N_A \sqrt{3 k T \rho^{-C} d_i} \quad \text{Eq. 23}$$

$$\rho^{-C} = \sum_{i=1}^{\text{all comp.}} \frac{x_i M W_i}{V_i^C} \quad d_i = 2 \sqrt{\frac{V_i^C}{4/3 \pi N_A}}$$

Here, V_M^F is the total free volume of the mixture of polymer-solvent(s) and V_i^F are the single compound free volumes. a_i represents the surface fractions of single compounds in the mixture. V_i represents the molar volume of the solvents and the molar volume of the polymer chain unit. V_i^{FF} are the surface weighted free volumes which represent the free volume of a pseudo-pure solution. $\zeta_{tr,i}^0$ is the tracer friction coefficient pre-exponential factor. V_i^C is the compressed molar volume, and ρ^{-C} is the compressed specific volume of the mixture.

According to the free volume theory, the tracer friction factor of a molecule which is assumed to be diffusing through an otherwise stagnant mixture of all components can be estimated as shown in equations 24 and 25. The method shown below allows the calculation of the tracer diffusivities of substances in a mixture. Note that, for a single substance, the tracer diffusion coefficient for a mixture reduces to the self-diffusion coefficient presented in equation 9[2, 13, 46, 47].

$$\zeta_{in,eff} = \zeta_{in,t}^0 \exp\left(\lambda \frac{V_t^C}{V_{FF}^C}\right) \quad \text{Eq. 24}$$

$$\bar{D}_1 = \frac{R T}{\zeta_{in,t}^0} \quad \text{Eq. 25}$$

$$\bar{D}_i = \bar{D}_1 \exp\left(-\lambda \frac{V_t^C}{V_{FF}^C}\right)$$

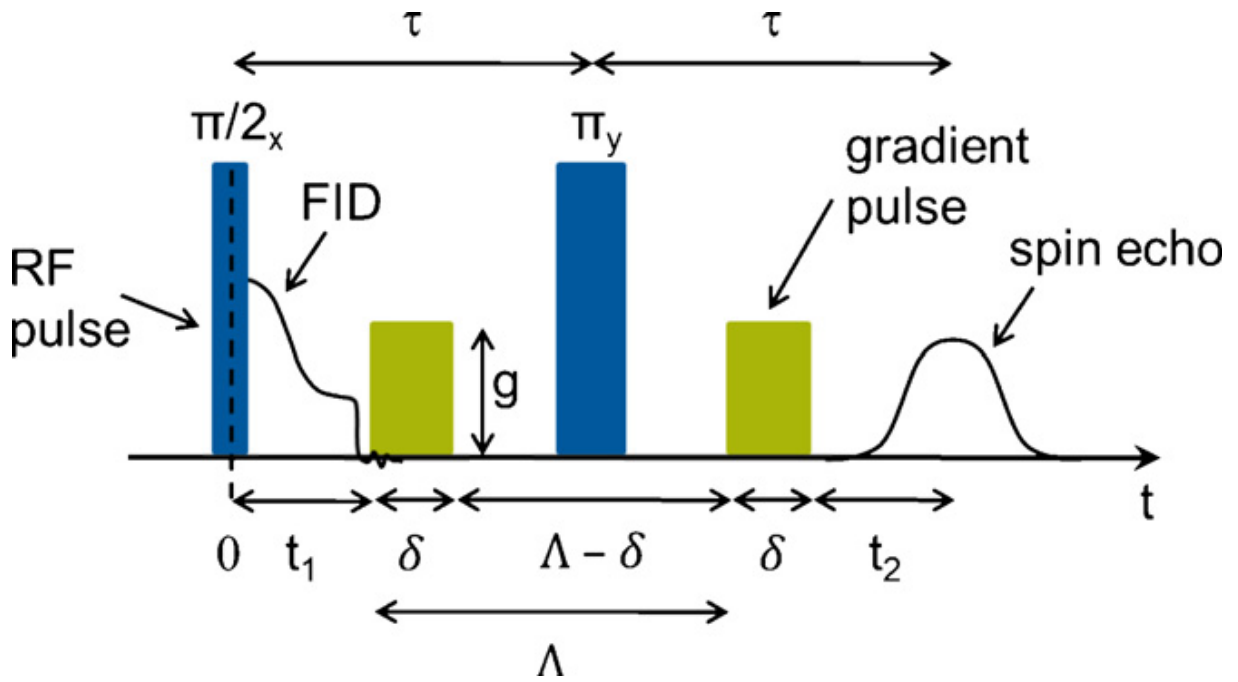


Fig. 1. Schematic representation of spin-echo sequence in PFG-NMR measurements.

3. Experimental Methods

3.1 Materials

Freestanding polydimethylsiloxane (PDMS) films were obtained by solution casting of a high molecular weight PDMS, curing agent, solvent (hydrocarbon) and platinum catalyst which allows the polymer to thermally crosslink. The PDMS films were prepared according to the procedure published elsewhere [48] Solvents with synthesis grade were used as received. Here, mixtures of ketones and glycols were chosen as model systems in order to investigate

the diffusion behavior of organics when they pass through a membrane in organic solvent nanofiltration applications. Mixtures of ketones and glycols were prepared for different glycol concentrations, i.e., 5 wt %, 10 wt % and 15 wt %. The selected ketones were methyl ethyl ketone (MEK) and diethyl ketone (DEK). The used glycols were tetraethylene glycol dimethyl ether (TEGDME) and polyethylene glycol dimethyl ether 250 (PEGDME). The PEGDME was obtained from Fluka[®] and the rest of the solvents from MERCK[®]. Density and viscosity values of the ketones were estimated by ASPEN[®] Properties, whereas, the values for the glycols are found elsewhere[49].

According to Conesa et al. [49], the PEGDME 250 from Fluka[®] is a mixture of ethylene glycol dimethyl ethers with different chain lengths – between 3 and 9 – but is often considered as a pseudo pure compound. Therefore, a pseudo chain unit value of 5.723 was found, which corresponds to a molecular weight of 298.21 g/mol.

3.2 PFG-NMR diffusion measurements

A standard pulse field gradient based on spin-echo sequence (PFG-NMR) allows measurements of the tracer diffusion coefficient when a series of NMR spectra are taken when the overall gradient strength (\vec{G}) is progressively incremented[50, 51]. A schematic representation of the PFG-NMR measurement could be found elsewhere and is shown in figure Fehler! Verweisquelle konnte nicht gefunden werden.[52-54]. The resulting signal intensity of the PFG spin echo experiment is given in equation 26. Here, the attenuation of the obtained echo intensity is dependent on the strength of the gradient.

$$I_t = I_t^0 \exp\left(-\vec{D}_t \left(2\pi \cdot \gamma \cdot \vec{G}_t \cdot \delta\right)^2 \left(A \cdot \frac{\delta}{3}\right) 10^4\right) \quad \text{Eq. 26}$$

Here, I_t is the measured peak intensity and I_t^0 is the maximum peak intensity. \vec{D}_t is the tracer diffusion coefficient, also known as translational diffusion coefficient. γ represents the gyromagnetic ratio (4258 Hz/G). δ corresponds to the duration of the gradient and Λ is the diffusion time which corresponds to the time between the onsets of subsequent gradient pulses. \vec{G}_t is the gradient strength. The calculation of the desired tracer diffusion coefficient is done by fitting the obtained PFG-NMR data with an exponential decay.

$$-\ln\left(\frac{I_t}{I_t^0}\right) = \vec{G}_t^2 \gamma^2 \delta^2 \left(A \cdot \frac{\delta}{3}\right) 10^4 \quad \text{Eq. 27}$$

Diffusion measurements were made on a Bruker Avance 300 NMR spectrometer, equipped with a BGI II gradient unit and a water cooled Bruker Diff 30 probe. The temperature of the sample (25 °C) was calibrated using methanol. The temperature change of the sample during the repeated measurements was found to be at ± 0.1 °C. During the course of the experiment the temperature was thoroughly checked. To calibrate the gradient system water (self diffusion coefficient at 25 °C is 2.30×10^{-9} m²/s) and deuterated water (1.87×10^{-9} m²/s) were used. The calibration coefficient for the gradient system was determined at 115.656 G/mm. For the fitting of the measurements the program SIMFIT (supplied with Bruker Topspin 1.4) was used.

Polymer samples of around 1.5 mm · 1.5 mm · 5 mm were swollen in the desired solvents over night at room temperature. Each swollen piece was then placed into an NMR tube containing a small amount of the solvent or mixture of solvents in order to maintain a constant concentration for the duration of the measurement. Later, the sample is directly transferred into the magnet where a time of 30 min was allowed for stabilization at the desired temperature of 25°C.

For the measurements of both ethylene glycol dimethyl ethers (EGDMEs) the diffusion time (Δ) was 200 ms, for all the rest the diffusion time was 20 ms. The gradient pulse (Δt) was set to 1 ms in all the measurements. The gradient strength was increased in 20 steps from 20 to 240 G/cm depending on the substance, for both EGDMEs the maximum value corresponds to 200 G/cm, for all the rest up to 160 G/cm. For every step, the data was acquired 16 times. Additionally, every measurement was done 7 times and the signal intensity was averaged between different sample points.

From the results obtained by PFG-NMR measurements, due to the presence of the Wirbelstrom effect and a nonlinearity of the sender, an inaccuracy in the diffusivities values due to convection up to 10 % is expected. Specially, a bigger difference for substances with high proton density due to radiation damping is expected.

3.3 Swelling experiments

In order to investigate concentration of the permeants inside the polymer, polymer pieces were immersed in different solvents for 8 hours and their dry and wet weights were compared. Hence, a polydimethylsiloxane film was prepared according to the recipe used in the preparation of the composite membranes (recipe is not shown). Afterwards, cubic pieces of 5

mm length were cut and weighted (M_{dry}). The preweighted dry PDMS pieces were immersed in pure solvents or mixture of solvents. After a minimum of 8 hours, the pieces were removed from the solution and the excess of liquid was wiped out. To avoid possible evaporation, the wet pieces were weighted (M_{wet}) as fast as possible. The solvent uptake (SU) and the swelling degree in % (SD) of the polymer are calculated with equations 27 and 28.

$$SU = (M_{wet} - M_{dry}) \quad \text{Eq. 27}$$

$$SD = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100 \quad \text{Eq. 28}$$

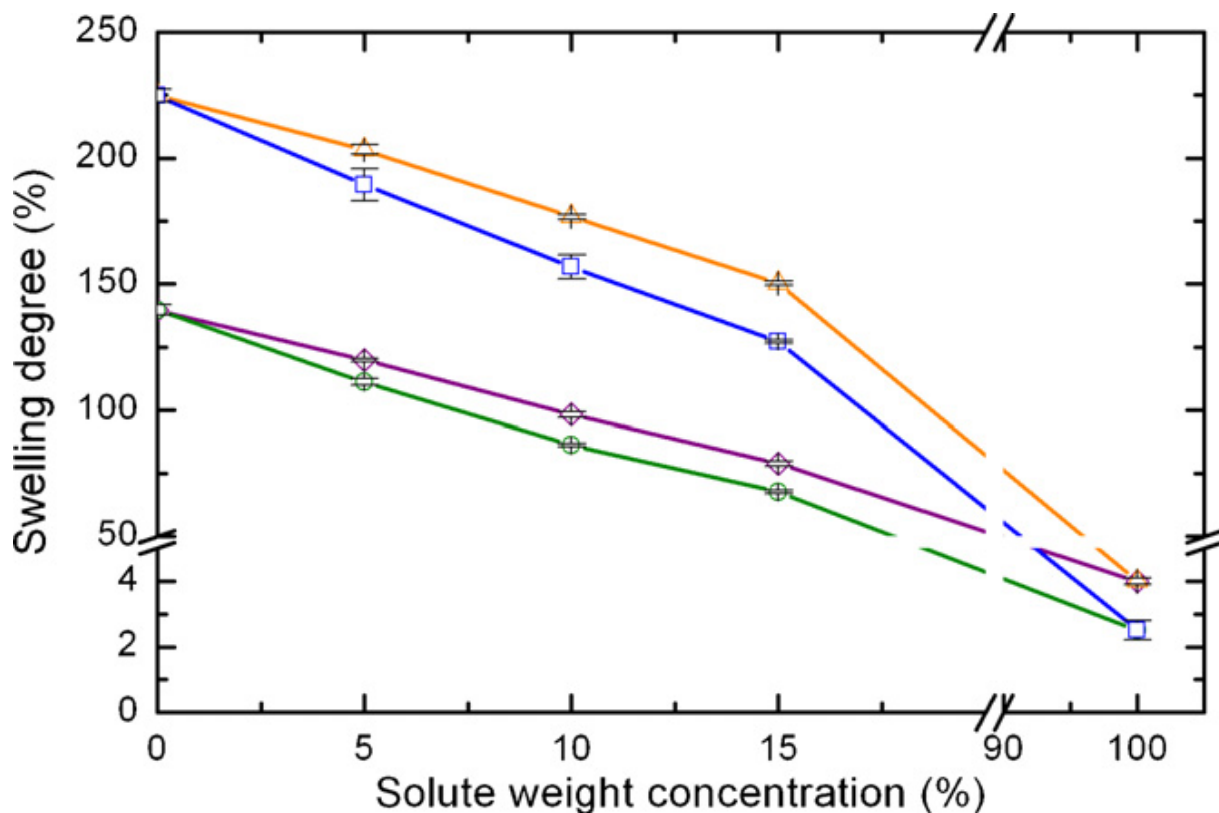


Fig. 2. Polymer swelling degree as a function of solute (TEGDME or PEGDME) concentration in binary mixtures.

♦ MEK/TEGDME, ○ OMEK/PEGDME, Δ DEK/TEGDME, λ DEK/PEGDME.

Assuming that the concentration inside the polymer sample is equal to the one in the surroundings and neglecting, for the sake of simplicity, any selectivity in of the interactions between the different solvents and the polymer matrix, the information of the solvent uptake is used to calculate the weight fraction of a solvent inside the polymer with equation 29. The weight fraction of the polymer in the ternary solvent-solvent-polymer is calculated by equation 30.

$$\omega_{i,Pol} = \frac{\omega_{i,FS}(SU)}{M_{urec}} \quad \text{Eq. 29}$$

$$\omega_{Pol} = \frac{M_{dry}}{M_{urec}} \quad \text{Eq. 30}$$

where $\omega_{i,Pol}$ is the weight fraction of a solvent i in the ternary system (solvent–solvent–polymer), $\omega_{i,FS}$ represents the weight fraction of a solvent i in the binary solvent–solvent free solution. The previous assumption is based on the consideration that after 8 hours the system reaches equilibrium. Therefore, at both polymer interfaces the solvent activities are equal to the ones in the free solution.

4. Results and Discussion

Swelling degrees of free standing polymer pieces were measured according to section 3.3 whereas the results are shown in figure 2.. Here, the swelling degree is used as an indication of the crosslinking degree of the polymer network as well as of the affinity between the permeating molecules and the polymeric matrix, i.e., it is also an estimation of the interaction parameters. For both MEK and DEK, the swelling degree decreases when the EGDME concentration increases. In addition, the swelling degree for ternary systems containing DEK is around 2 times higher than the one corresponding to MEK under the same conditions of solute concentration. Later, the weight fraction of each compound in a ternary system is calculated according to equations 29 and 30. The weight concentration obtained for solvent-polymer systems is as follows: MEK 58.3 wt %, DEK 69.2 wt %, TEGDME 3.9 wt % and PEGDME 2.4 wt %. Because there are no variations of the crosslinking degree between the studied systems, one can conclude that PDMS has the highest affinity towards DEK and the lowest towards the glycol molecule with the longest chain (i.e., PEGDME).

The diffusion coefficients of pure substances were measured with PFG-NMR according to the process previously described at 25 °C, and the results are summarized in table 1. The goodness of the experimental results was checked by comparing experimental data with data reported in literature for self diffusion coefficient of a variety of alcohols, ketones and hydrocarbons (results are not shown). It can be observed from the experimental self-diffusivities presented in table 1 that, for the ketones and the EGDMEs, as expected, the self-diffusion coefficients of smaller molecules are higher than the ones of bigger molecules due to the facility of the smaller molecules to move through other molecules of the same substance.

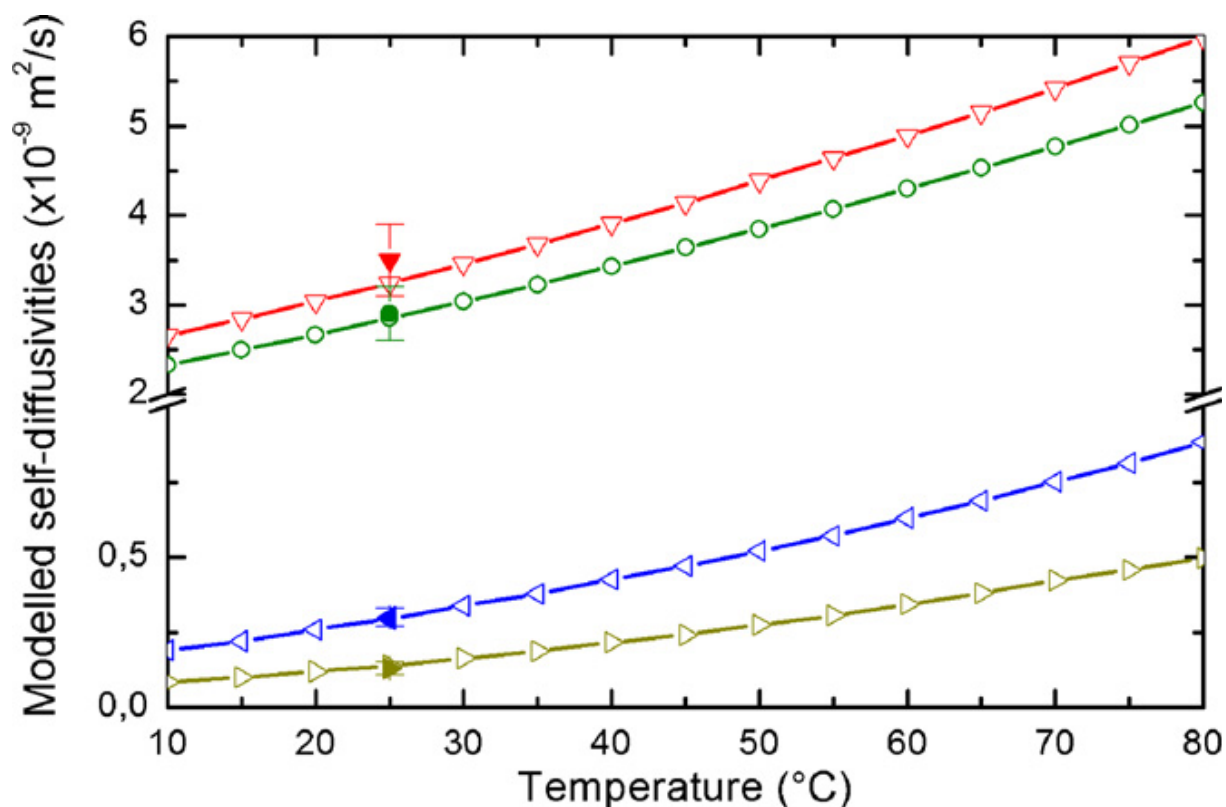


Fig. 3. Self-diffusion coefficients for ▼ MEK, O DEK, ◀ TEGDME, ▶ PEGDME as a function of temperature. Filled symbols correspond to experimental data at 25 °C as shown in Table 1.

Table 1. Measured solvents self-diffusion coefficients at 25 °C with PFG-NMR.

Substance	\bar{D} (10^{-9} m ² /s)
MEK ^{a)}	3.5 ± 0.4
DEK	2.9 ± 0.3
TEGDME	0.30 ± 0.03
PEGDME	0.13 ± 0.02

a) Reported as 3.58×10^{-9} m²/s in the literature [55]

Self-diffusion coefficients of pure substances can be estimated with the use of the Dullien equation. Figure 3 Fehler! Verweisquelle konnte nicht gefunden werden. shows the self-diffusion coefficient as a function of temperature. As expected from the experimental results, when the self-diffusion of similar substances are compared (i.e., MEK/DEK and

TEGDME/PEGDME), the self-diffusivities of smaller substances are higher than the ones corresponding to bigger molecules, i.e., MEK has more mobility than DEK and TEGDME more than PEGDME.

When modeled values of the self-diffusion coefficient (figure 3) and the experimental values obtained by PFG-NMR measurements (table 1) are compared, all the measurements lead to similar modeled values within the expected errors.

A merge of the Dullien equation with the pure solvent simplified version of the Vrentas & Duda diffusion equation allows the calculation of the necessary free volume parameters for each solvent. Figure 4 shows the quality of the viscosity regression (viscosity data as reported by Conesa et al. [49]), whereas table 2 presents the regressed values of the Vrentas & Duda free volume parameters. For the estimation of free volume diffusion parameters a curve fitting method based on the steepest decent method minimizing the sum of square errors was used.

Table 2. Diffusion and free-volume parameters calculated from the Vrentas & Duda diffusion theory.

Substance	\bar{D} (10^{-8} m ² /s)	$K_{gr} - T_{gr}$ (K)	K_{gr}/λ (10^{-7} m ³ /kg·K)
PDMS ^(a)	–	-81.0	9.32
MEK ^(b)	30.97	56.3	5.49
DEK ^(b)	24.98	49.2	5.86
TEGDME ^(b)	2.01	-139.1	12.66
PEGDME ^(b)	3.20	-120.5	8.62
Ethylene glycol ^(a)	88.20	-139.38	7.50

a) From Hong[33]; b) Curve fitting.

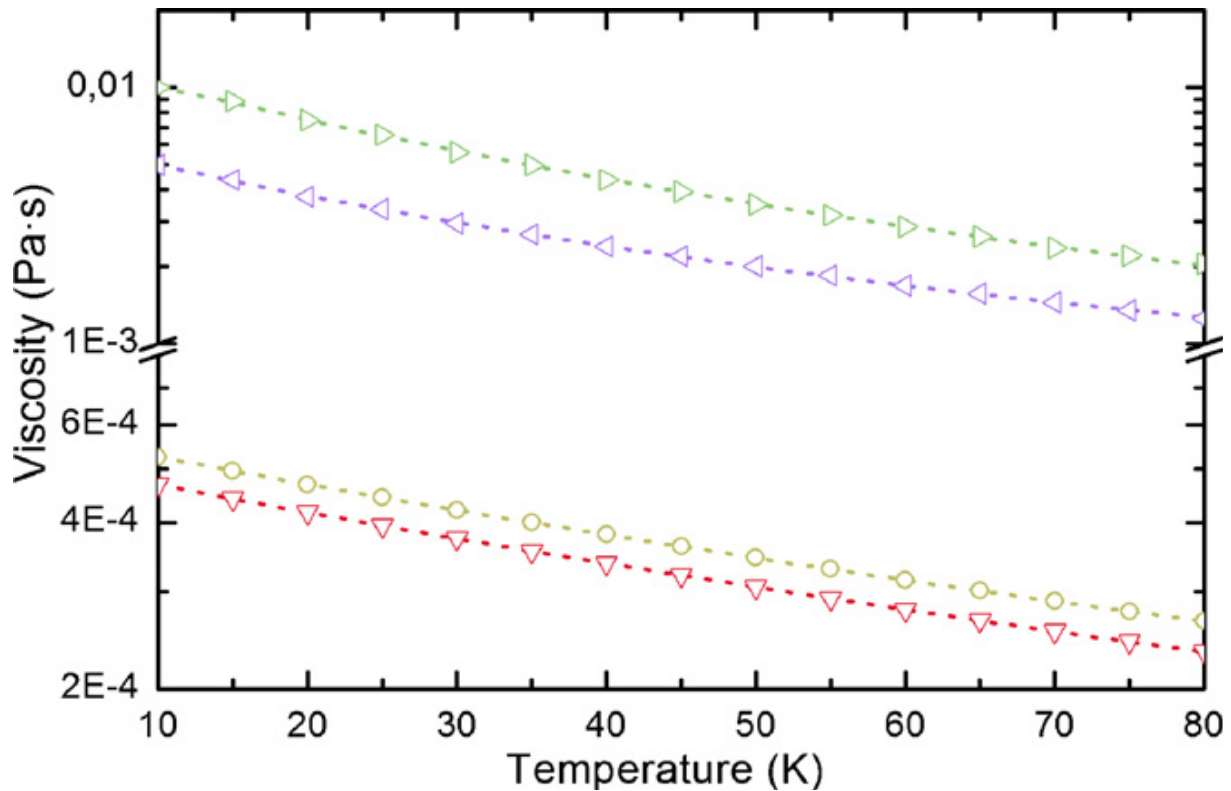


Fig. 4. Solvent viscosity as a function of temperature. The broken lines correspond to simulated data and the symbols represent experimental data with the following identification: ▼ MEK, ○ DEK, ◀ TEGDME, ▶ PEGDME.

As expected, the diffusion pre-exponential factor and $K_{gr} - T_{gr}$ increase and K_{gr}/λ decreases when the molecular weight decreases if both EGDMEs are compared [7]. Tracer diffusion coefficients for ternary solvent-solvent-polymer systems were measured by PFG-NMR spectroscopy. The results are summarized in table 3.

The measured solvent tracer diffusion coefficients for binary solvent-polymer mixtures are lower than the corresponding self-diffusion coefficients. As expected, the mobility of the molecules is diminished inside the polymer network. Additionally, the tracer diffusivities are lower for big molecular sizes than for small ones, that is, the tracer diffusion coefficient of MEK and TEGDME are higher than the DEK or PEGDME tracer diffusivities, respectively. For both comparisons, a lower mobility inside the polymer network is expected for the big molecules than for small ones – with a similar chemical potential – because of the existence of less possible configurations inside the lattice. It should be remarked that the tracer diffusion coefficients of DEK are lower than the ones of MEK, despite the fact that the swelling degrees of the DEK systems are higher than the ones of MEK systems.

Table 3. Tracer diffusion coefficients for binary solvent-polymer systems and ternary solvent-solvent-polymer systems as a function of EGDME concentrations.

Binary system		Tracer diffusion coefficients ($10^{-9} \text{ m}^2/\text{s}$)		
MEK/PDMS	MEK	2.2 ± 0.2		
DEK/PDMS	DEK	2.0 ± 0.2		
TEGDME/PDMS	TEGDME	0.27 ± 0.03		
PEGDME/PDMS	PEGDME	0.13 ± 0.01		
Ternary system		Tracer diffusion coefficients ($10^{-9} \text{ m}^2/\text{s}$)		
		5 wt %	10 wt %	15 wt %
MEK/TEGDME/PDMS	MEK	2.1 ± 0.2	2.0 ± 0.2	1.9 ± 0.2
	TEGDME	1.0 ± 0.1	0.8 ± 0.1	0.79 ± 0.09
MEK/PEGDME/PDMS	MEK	2.1 ± 0.2	1.9 ± 0.2	1.6 ± 0.2
	PEGDME	0.70 ± 0.07	0.56 ± 0.06	0.44 ± 0.05
DEK/TEGDME/PDMS	DEK	1.9 ± 0.2	1.8 ± 0.2	1.6 ± 0.2
	TEGDME	0.9 ± 0.2	0.85 ± 0.09	0.68 ± 0.08
DEK/PEGDME/PDMS	DEK	2.0 ± 0.2	1.8 ± 0.2	1.6 ± 0.2
	PEGDME	0.73 ± 0.07	0.67 ± 0.07	0.54 ± 0.05

For ternary systems, it is expected that the presence of slow diffusive substances (i.e., EGDME) decreases the diffusivity of high diffusive substances (i.e., MEK/DEK) due to dragging effects. Therefore, the tracer diffusivities of both MEK and DEK should be less than those found in the ketone/PDMS mixtures. Additionally, the swelling induced in the polymer by the presence of the ketones facilitates the mobility of the low diffusive substances inside the polymer network. Contrary, the tracer diffusion coefficient of EGDME/PDMS systems should be the lower limit of the corresponding ternary ketone/EGDME/PDMS system.

The tracer diffusion coefficients are simulated by the use of the Vrentas & Duda diffusion theory or the Wesselingh & Bollen model. In addition to the free volume parameters estimated from previous sections, the Vrentas & Duda model requires the estimation of the ratio between critical molar volume of a jumping unit of a substance to the one of the jumping unit of the polymer ϕ^* . This factor is defined by equation 15 and the calculation is completed with the experimental correlation¹⁶. However, the estimation of the critical molar volume of the polymer jumping unit still remains uncertain and inaccurate. Therefore, this parameter is

often estimated by diffusion data regression as previously discussed. A set of ξ parameters calculated by equations 15-16 and estimated from diffusion data are summarized in table 4.

Table 4. Critical molar volume ratio between jumping units in a binary mixture.

Substance	ξ a)	ξ b)	ξ c)
MEK	0.779	1.193	0.806
DEK	0.955	1.209	0.807
TEGDME	2.289	0.770	0.510
PEGDME	3.022	0.950	0.640

a) Estimated by equations 15 and 16; b) Calculated by diffusion data regression for a noncrosslinked polymer; c) Calculated by diffusion data regression for a crosslinked polymer.

The values shown in the column denoted by the superscript “b” in table 4 represent the critical molar volume ratio between jumping units regressed from the Vrentas & Duda diffusion theory without any consideration of crosslinks in the polymer. The results show an overestimation of both MEK and DEK parameters. Besides showing a good correlation of the tracer diffusion data, the parameters for both ketones are higher than 1.0, differing from experimental calculations found elsewhere [38, 43]. Nevertheless, parameters higher than 1.0 are often used for correlating purposes because the free volume theory allows it without any boundary [41, 42].

Additionally, the values found for TEGDME and PEGDME are lower than the ones estimated by equations 15-16. From equation 15, a decrease of the ratio of critical molar volume of jumping units indicates that the permeant molecule is moving in sections rather than as a whole molecule. The later is especially true for large molecules which have difficulties to arrange themselves inside the lattice. Therefore, ξ parameters for the EGDMEs are expected to be lower than the ones calculated by equations 15-16.

In order to take into account any effect of the degree of crosslinking, the ratio between critical molar volume of jumping units and the free volume crosslinking parameter were solved together by nonlinear regression of the available diffusion data. The results are presented in table 4 in the column denoted by the superscript “c”. The estimated ξ parameter for MEK is close to the one estimated by equations 15 and 16. The results corresponding to DEK indicate a segmental movement of the solvent inside the polymer, with a main unit similar to the one of the MEK (i.e., one ethyl group of DEK is moving separately from the rest of the molecule).

The regressed TEGDME and PEGDME values correspond to 22.3 % and 21.2 % of the values estimated by equations 15 and 16. Therefore, the movement of each EGDME molecule across the polymer can be assumed to take place in approximately 5 sections. For these results, the corresponding crosslink factor from the Vrentas & Duda diffusion theory is 0.643.

An inspection in the Vrentas & Duda theory reveals that if the polymer crosslinking is not considered, the λ parameter should increase to compensate the term corresponding to the free volume per kilogram of mixture, which is higher for noncrosslinked polymers than for crosslinked ones. Therefore, the observed differences between columns “b” and “c” in table 4 are expected. To qualify the goodness of the regression, a graph of measured tracer diffusivities versus simulated ones for a crosslinked polymer is presented in figure 5, while the insert corresponds to the correlation for a noncrosslinked polymer.

For both approaches of the Vrentas & Duda diffusion theory (i.e., for crosslinked and noncrosslinked polymers), the simulation of tracer diffusion data describes well the values from the PFG-NMR spectroscopy measurements, as can be concluded from the fact that the modeled values describe the diffusion behavior for all the systems and concentrations within the experimental errors.

Alternatively, tracer diffusion coefficients for ternary mixtures can be estimated by the Wesselingh & Bollen model. Multicomponent mixtures are treated as pseudo-pure substances in this model, in order to extend the self-diffusion equations to be used in the estimation of tracer diffusivities. It should be remarked that in the model developed by Wesselingh & Bollen, the overlap factor which considers that the same free-volume is available for more than one molecule (λ) was arbitrary set to be 0.70 [13]. The results obtained by the Wesselingh & Bollen model with a λ parameter equal to 0.70 are shown in figure 6.

For most of the cases, an underestimation of the tracer diffusivities of EGDMEs (up to 30 %) as well as an overestimation of the ones corresponding to the ketones have been found. However, if the λ factor remains equal for all the substances, but is shifted between 0.50 and 1.00 – which are the theoretical boundaries – the values of the tracer diffusion coefficients move in block, as shown in figure 7.

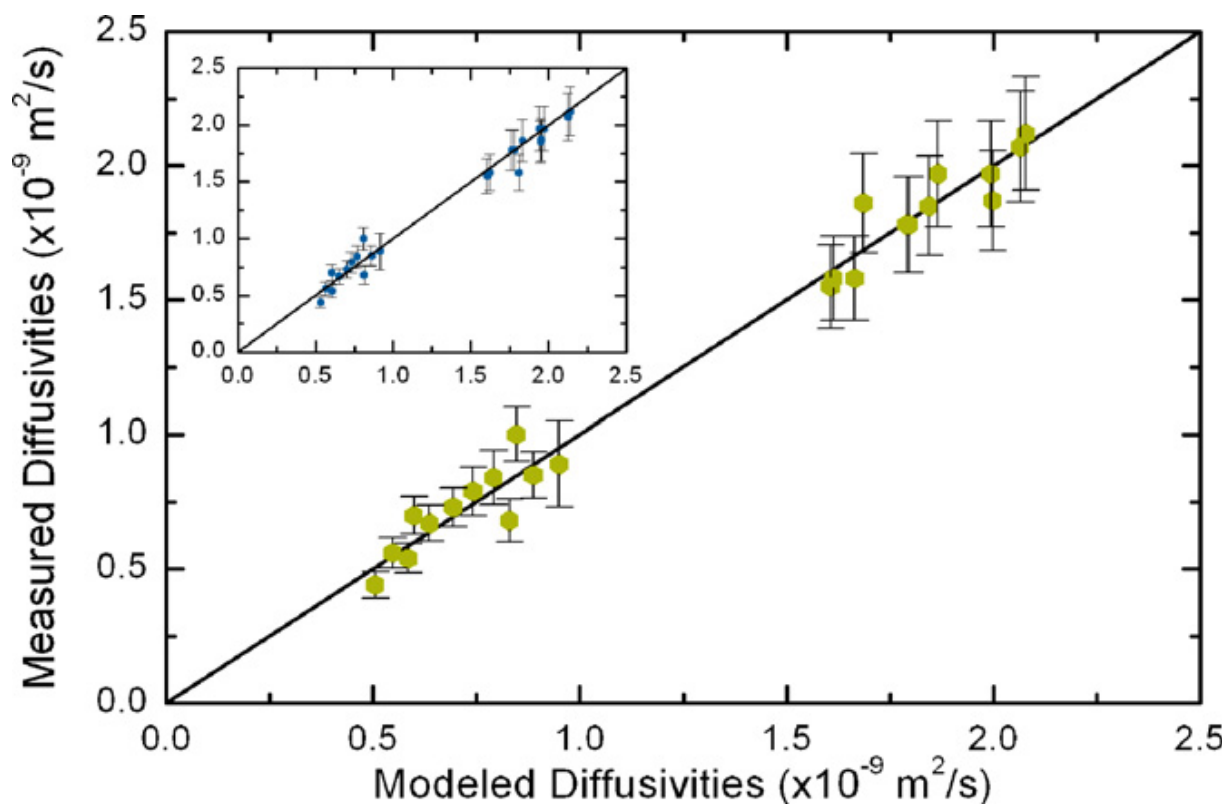


Fig. 5. Correlation between experimental PFG-NMR diffusion data and simulated data from the Vrentas & Duda diffusion theory for crosslinked polymers (the insert corresponds to noncrosslinked polymers).

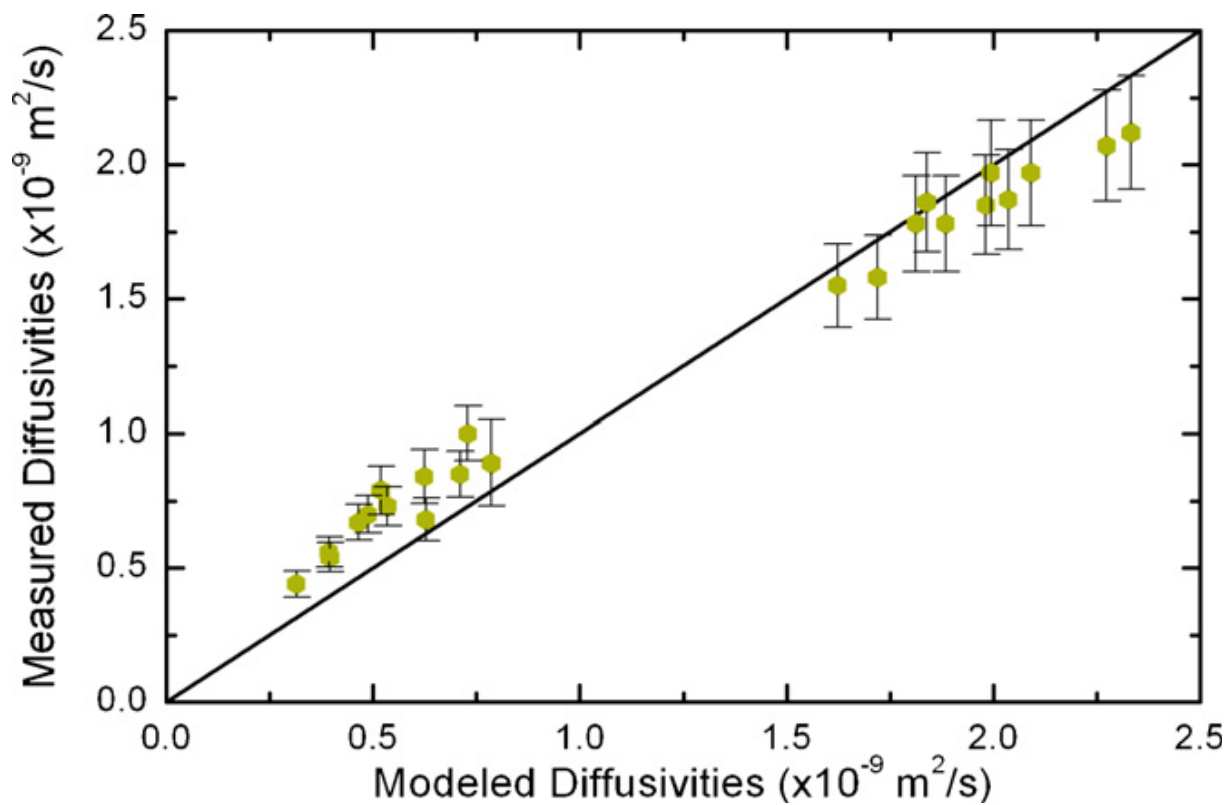


Fig. 6. Correlation between experimental PFG-NMR diffusion data (measured diffusivities) and simulated data from the Wesselingh & Bollen diffusion model (modelled diffusivities).

An inspection of different λ parameters reveals the best fit value to be 0.69.

Nonetheless, the free volume overlap factor for pure substances can be estimated by equation 31, which is known as the first application of the free volume theory. Therefore, nonlinear regressions of pure viscosity data as well as diffusivity data allow the estimation of the overlap factor of pure substances. The regressed values are shown in table 5.

$$\eta_i = \eta_0 \exp\left(\lambda_i \frac{V_i^F}{V_F}\right) \quad \text{Eq. 31}$$

Table 5. Critical molar volume ratio between jumping units in a binary mixture.

Substance	λ ^{a)}	η_0 (10^{-5} Pa·s)	λ ^{b)}
MEK	0.950	3.922	0.750
DEK	0.823	4.427	0.725
TEGDME	0.685	6.692	0.650
PEGDME	0.760	6.767	0.750

a) Estimated by equation 31; b) Estimated by nonlinear regression of tracer diffusion data.

By comparison, the free-volume overlap factors calculated by regression of diffusion data (column $\lambda^{(b)}$ in table 5) show lower values compared to the ones estimated by viscosity regression (column $\lambda^{(a)}$ in table 5). This difference may be explained by the fact that the presence of an “i” permeant inside the polymer diminishes the availability of a molecule of permeant “j” to occupy a specific place from the total free-volume. Therefore, the λ parameter calculated by regression of diffusion data tends to account not only for the competition between molecules of the same substance to occupy a specific lattice place but also for competition between molecules of both substances (i.e., “i” and “j”). This is not the case for the λ parameter estimated by viscosity regression, since the later one is calculated with equation 31 which describes only the viscosity of pure substances. A correlation between experimental and simulated tracer diffusivities when the λ parameters are estimated from diffusion data regression is shown in figure 7.

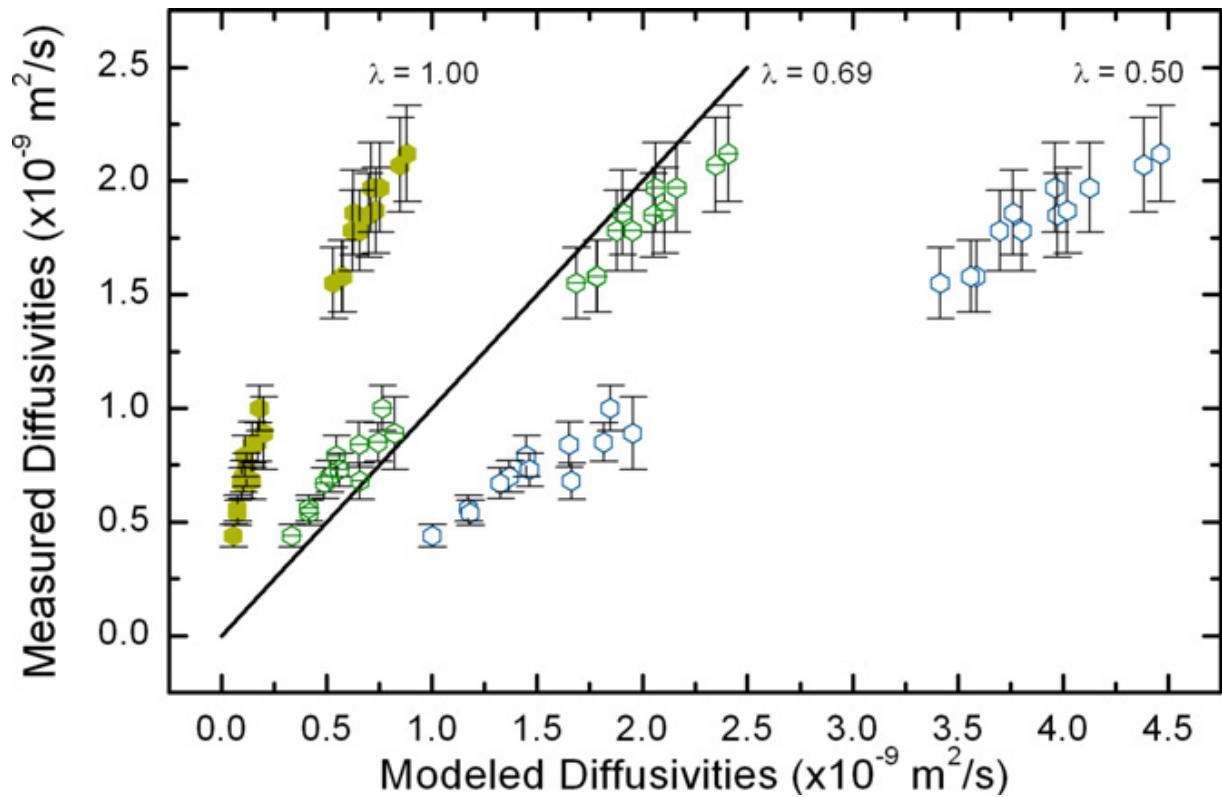


Fig. 7. Correlation between experimental PFG-NMR diffusion data and simulated data from the Wesselingh & Bollen diffusion model. The filled, struck and open symbols correspond to $\lambda = 1.0$, $\lambda = 0.69$ and $\lambda = 0.5$, respectively.

Even though the employed model introduces an additional fit parameter into the simulation with the consequent loss of prediction capability, it is evident from the results presented in figure 8 **Fehler! Verweisquelle konnte nicht gefunden werden.** that there is a good agreement between the experimental and the simulated values of the tracer diffusivities. Therefore one can infer that the assumptions of the model are supported by the experimental results.

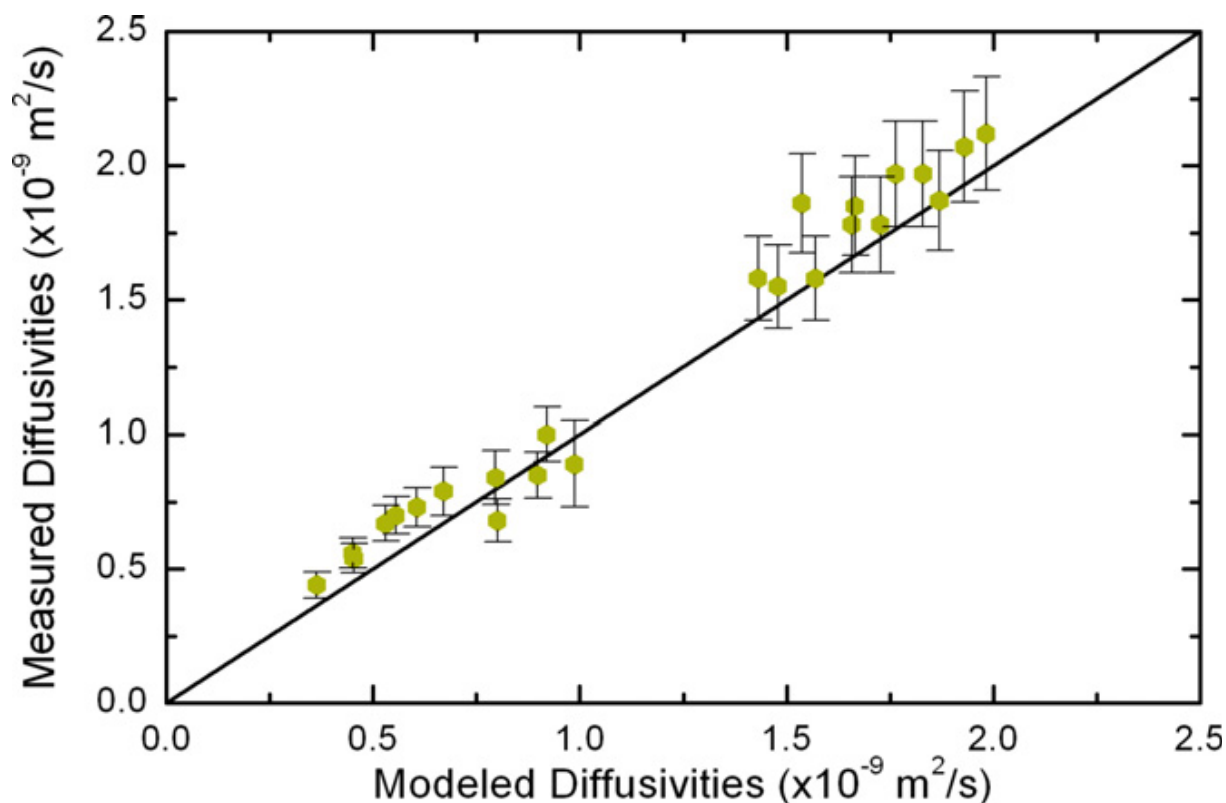


Fig. 8. Correlation between experimental PFG-NMR diffusion data and simulated data from the Wesselingh & Bollen diffusion model when the free volume overlap factor is regressed from experimental ternary diffusivities.

4. Conclusions

Tracer diffusion coefficients were successfully estimated for solvent–solvent–polymer systems by PFG-NMR measurements on free-standing crosslinked polymer films. The PFG-NMR results were later correlated with available diffusion models (i.e., Vrentas & Duda diffusion theory and Wesselingh & Bollen multicomponent diffusion model) in order to provide a predictive method to calculate thermodynamic diffusion coefficients needed for transport simulation in polymer membrane processes. Both models estimate the diffusion coefficients with the use of the polymer free volume theory. In this work, we have taken advantage of experimentally determined diffusivities as well as of plausible assumptions to overcome the lack of a method to calculate a set of theoretically unclear parameters needed along the employed theories.

The Wesselingh & Bollen model shows, for a set of mixtures and concentrations, a good representation of the experimental data with the use of a pure predictive method. While the model describes the value of the diffusion coefficients in the right order of magnitude and tendency, an inverse tendency is observed when the values corresponding to the good solvent are slightly overestimated and the ones corresponding to the bad solvent are underestimated.

For complex mixtures, the here developed modeling method shows a great and fast representation of the diffusivities once the concentration of the solvents inside the membrane has been estimated experimentally.

Acknowledgements

The collaboration of Dr. M. F. J. Dijkstra is highly appreciated. The authors thank the German Federal Ministry of Education and Science (BMBF) for financial support via the project “Organophile Nanofiltration für die nachhaltige Produktion in der Industrie” (01R/05111).

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