Prediction of diffusion in a ternary solvent-solvent-polymer blend by means of binary diffusion data: Comparison of experimental data and simulative results

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ABSTRACT: Multicomponent diffusion of solvents in polymeric systems is not completely understood, despite many scientific contributions to the topic. Literature scarcely offers measurement data on diffusion for model validation in such systems. In this work, the ternary systems consisting of poly(vinyl acetate) and the solvents toluene and methanol was investigated experimentally and numerically. By means of inverse micro Raman spectroscopy (IMRS) concentration gradients in drying thin films have been measured. Initial composition of the samples has been varied systematically in order to detect mutual influence of the solvents' diffusive behavior. It was shown that the mobility of the different species is increased in the presence of other solvents as predicted by theory. This experimental data is provided for model validation. A new expression to calculate the diffusion coefficients in ternary mixtures is proposed which only requires binary data. This expression is tested by means of a model-based simulation to predict the drying of ternary polymer solutions in terms of concentration profiles and residual solvent content. The results are in very good agreement with the experiments. Cross terms diffusion coefficients and thermodynamic factors were not found to be necessary for a satisfying prediction. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43899.

INTRODUCTION

In many industrial processes polymer solutions consisting of multiple solvents and a polymer are used in order to influence solubility or tailor rheological properties.[1] Multicomponent mass transport occurs in many different processes such as membrane manufacturing, coating processing and polymerization reactions.[2] For process design and estimation of drying times, mass transport inside the polymer phase has to be predictable. The mathematical framework to describe multicomponent diffusion is set up by the generalized Stefan–Maxwell equation (GSME) or a generalized form of Fick's law (GFL). Both equations are mathematically equivalent which renders preference a matter of choice.[3] For practical calculations the correct numerical values for the diffusion coefficients and their application are a much greater concern. Many different theories have been developed to calculate self-diffusion coefficients and compared in literature, discussing the effect of the thermodynamic factors (e.g., linking the self-diffusion coefficient to mutual diffusion coefficients by friction-based formalisms) and cross term diffusion coefficients.[4–6] In many cases, concerning prediction of

drying experiments both factors appear not to be of crucial importance as it was found that different approaches to both aspects lead to comparable results,[6] even though from a strictly physical point of view their implementation is necessary.[7] Some authors report better prediction of the mass transport including cross term diffusion coefficients.[8,9] The practical importance of these aspects still remains unclear.

The calculations are much more sensitive for the correct calculation of the main self-diffusion coefficients.[10,11] In contrast to mixtures of liquids, in the presence of polymers the (Fickian) diffusion coefficients change by many orders of magnitude with composition. This is the dominant factor in the modeling of drying processes for polymeric solutions. However, due to the fact that measurement data is not readily available, no universally accepted models to predict these transport parameters exist. Even in binary solutions pure prediction, for example, by Free Volume theory, fails to yield reliable results.[12,13] Accordingly parameters have to be fitted to measurement data.[9,10,12,14] In ternary polymer solutions shortage of measurement data is even worse. Reliable prediction is so far not possible without a

fit to ternary diffusion data, especially since simulations are very sensitive to the ratios of the molar volumes of the jumping units [see eq. (1)].[11] For polymer solutions consisting of two solvents and a polymer Vrentas et al.[15] proposed the following expression:

$$D_i = D_{0i} \cdot \exp\left(-\frac{\omega_i \hat{V}_i^* + \xi_{iP}/\xi_{jP} \cdot \omega_j \hat{V}_j^* + \xi_{iP}\omega_P \hat{V}_P^*}{\hat{V}^{FH}/\gamma_{lP}}\right) \quad (1)$$

Here D_{0i} is a pre-exponential factor, $\hat{V}^*$ denotes the critical hole free volume for a jumping step of the respective component, ω is its weight fraction. ξ is the ratio of the molar volume of the jumping units of the respective solvent to the polymer. The total hole free volume is denoted by $\hat{V}^{FH}$, while γ_{lP} is an overlap factor. According to eq. (1), addition of a second solvent "j" increases the mobility of a solvent "i." The mechanistic explanation for this behavior is the increase in Free Volume available for diffusion steps provided by the second solvent. This effect is generally accepted, but there is little knowledge about its exact magnitude. A practical application of this phenomenon is the removal residual solvent from coatings with drying air preloaded with a second solvent.[16] In case some of the parameters in eq. (1) are fitted to **binary** measurement data, the influence of addition of a second solvent depends on the choice of fitting parameters, which is not obvious or unambiguous. Different fit parameters have been used, for example, by Hong[12] and Arya and Vinjamur[10]. Lately, Ohashi proposed a modification of Free Volume theory using semiempirical quantum chemical calculations (*Shell-like Free Volume theory)* and offered an expansion for ternary systems.[17–19] This interesting new concept is yet to be vigorously tested and no final conclusions can be drawn yet. The inconclusive nature of the Free Volume theory and the lack of predictability of the parameters has led to the use of purely empirical expressions to calculate (binary) diffusion coefficients by some authors.[20,21]

$$\frac{D_i^V}{m^2/s} = \exp\left(-\frac{A_i + B_i \cdot X_i}{1 + C_i \cdot X_i}\right) \quad (2)$$

In this expression A_i, B_i, and C_i are empirical parameters, obtained by a fit to measurement data at the respective temperature. X_i is the solvent loading, defined as mass of solvent per mass polymer. The temperature dependence of diffusion coefficients is not described by eq. (2) but has been included by an Arrhenius-type expression with temperature dependent coefficients.[20] Equation (2) can be transformed to Free Volume theory assuming constant temperature,[22] allowing the calculation of the coefficients from tabulated Free Volume parameters. However, there is no direct physical meaning to its parameters. In this work we propose a strategy to calculate ternary diffusion coefficients from binary data, based on eq. (2). The focus of this article is the concentration dependence of the diffusion coefficients, whereas temperature dependence is not our objective. Readers interested in this aspect are referred to specialized studies.[20,23,24]

To validate models to predict multicomponent mass transport, measurement data is still a necessity. Often integral measurement data such as mass loss during drying of polymer films are used to validate diffusion models.[8,25,26] However, this information does not allow differentiating between the different solvents and is much more suitable for binary polymer solutions than in the ternary case. Studies with FTIR-analysis[27,28] of drying experiments for example offer this information, but local data within the samples, that is, the concentration profiles, remain inaccessible. Inverse micro Raman spectroscopy (IMRS) allows the distinction of different species and offers local data. The measurement technique has been intensely tested and refined by Schabel et al.,[29] Ludwig et al.,[30] Scharfer et al.,[31] Poggendorf et al.,[32] Arya et al.,[33] and Siebel et al.[34] among others. It has been used in binary and a few ternary systems of various material systems, including toluene-PVAc,[14] methanol-PVAc,[14] toluene-methanol-PVAc,[29] p-xylene-tetrahydrofuran-poly (styrene),[9] ethylbenzene-tetrahydrofuran-poly(methyl mathacrylate),[9] Dichloromethane-Cellulose triacetate (TAC),[21] and methanol-water-Nafion membranes.[31] These works have led to a better understanding of mass transport phenomena in polymeric systems and are suitable for the derivation of transport parameters. In the work of Schabel, Free Volume parameters improving prediction in the ternary system toluene-methanol-PVAc have been determined by bringing predicted concentration profiles with eq. (1) and measurement data into accordance.[14] The results were additionally verified by a measurement routine proposed by Schabel[35] to obtain ternary diffusion data with a magnetic suspension balance. However, the data presented is far from exhaustive.

In this work the same ternary system has been investigated in more detail, both experimentally and numerically. Toluene is known to exhibit diffusional limitation in PVAc at low solvent loadings, whereas the effect is orders of magnitude less strong for methanol[21,36] as a result of the molecule sizes of the solvents. With careful calibration of the multicomponent systems, Raman measurements have been performed during drying of multicomponent samples varying initial composition. The results offer insight in the relevant transport phenomena and will be discussed in terms of diffusive behavior. A new expression to calculate solvent diffusivity in the ternary mixtures is proposed and used to predict the drying process. This data is compared with measurement data.

EXPERIMENTAL

The experiments were carried out using poly(vinyl acetate) (Carl Roth GmbH + Co. KG, Karlsruhe, Germany, catalogue nr. 9154.1) with a molecular weight of 55,000–70,000 g/mol. For sample preparation the polymer was dried at least 48 h at vacuum and $T = 25\,°C$. Toluene was obtained from Merck KGaA (Darmstadt, Germany, catalogue nr. 1.08326.1001), whereas Methanol (catalogue nr. 4627.2) was obtained from Carl Roth GmbH + Co. KG, Karlsruhe. Data on densities and refractive indices which are necessary for analysis were taken from literature and are given in Supporting Information Table 1S.

The samples were prepared by adding the solvents to polymer pellets. To reduce solvent losses due to evaporation, solvents with lower volatility were added first. Subsequently the polymer solutions were stirred 48 h to guarantee homogeneous distribution of the various components in the sample.
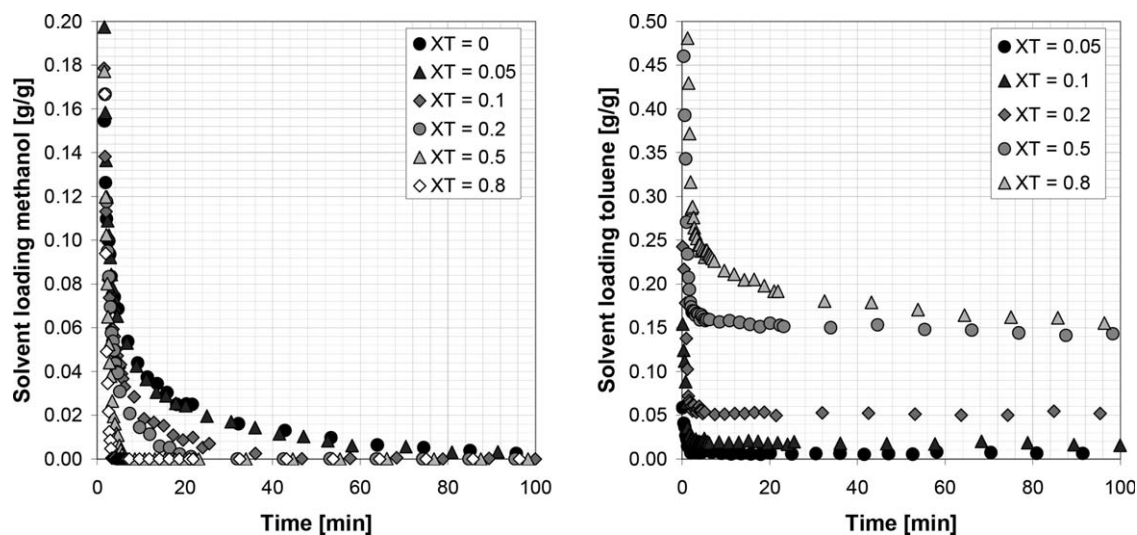
Figure 1. Isothermal integral drying curves in the ternary system methanol-toluene-PVAc under variation of the initial toluene loading at an air velocity of $u = 0.2$ m/s and a temperature of 20 °C. The left diagram shows the results for the methanol loading, whereas the right diagram depicts the toluene loading. The initial solvent loading of methanol was kept constant at 1.5 g/g.

The measurement set-up was described in detail in previous works including schematics of the inverse micro Raman spectrometer.[29,30] The experimental procedure consists of casting the polymer solution with the desired solvent loadings by an automated knife coating procedure on an impermeable glass substrate (0.12 by 0.12 m², thickness 150 μm) and subsequent drying in a drying channel with well-defined boundary conditions in the gas phase.[34] By temperature-controlling the substrate, the drying air and the drying channel, isothermal conditions are guaranteed. All experiments have been performed at a uniform temperature of 20 °C. During the drying process, Raman spectra are measurement at different positions in the film (from the bottom to the top) with an oil immersion objective. By repeating this procedure, solvent loading profiles through the film at different times are measured from which integral drying curves can be obtained by averaging the local data. The measurement time is approximately 1 s per measured spectrum. Accordingly a concentration profile is obtained in about 5–20 s depending on the chosen spatial resolution. In order to calculate concentrations (in terms of mass loadings) a calibration procedure described by Scharfer was employed.[31] For correct analysis the Raman spectra of the components have to be clearly distinguishable. The Raman spectra of the pure components are given in a previous publication.[34] For analysis the region of 2750–3150 cm^{-1} has been used. Calibration has been performed with ternary samples in order to guarantee correct spectral analysis of the ternary samples. The calibration curves are shown in Figure 1S in Supporting Information.

RESULTS AND DISCUSSION

Results of Drying Experiments
Both methanol and toluene show diffusive limitations during drying in binary mixtures with PVAc as a result of their low diffusion coefficients at low solvent loadings.[14] In this work small amounts of toluene were added to a binary methanol-PVAc solution with an initial solvent loading of 1.5 g/g [defined as

g(Methanol)/g(Polymer)]. The toluene loading was increased in small steps from 0 (binary case) up to 0.8 g/g. This corresponds to a toluene mass fraction of 0%$_w$ to 24%$_w$. The results of the experiments are shown as integral drying curves in Figure 1. The data has been obtained by averaging measured concentration profiles. The results are given in tabular form in Supporting Information Table 2S for model validation. Strictly speaking quantitative comparison of these experiments is only possible in case the dry film thickness is identical. This requirement is not easy to fulfill in case of high toluene loadings, since the viscosity of the polymer solution changes significantly. Up to toluene loadings of 0.2 the film thickness is 30 ± 3 μm, whereas the dry film thicknesses of the experiments with toluene loadings of 0.5 and 0.8 is higher (40 ± 1 μm) without restriction of the general observations.

In case of toluene loading 0 g/g (which corresponds to the binary case) Figure 1 (left) shows that the methanol loading reduces very fast at short times as long as the activity of methanol is high and no diffusive limitation hinders evaporation (constant rate period). After about 5 min the rate of methanol evaporation is reduced and becomes increasingly smaller as the activity of methanol approaches lower values and the diffusion coefficient decreases (falling rate period). After about 100 min the methanol loading approaches zero and the drying process is finished. Adding *toluene* (0.05, 0.1, and 0.2 g/g) affects the drying path of *methanol*. At a given time the methanol loading is lower in case of samples with higher toluene loading during the falling rate period. This effect is very small in case of an initial toluene loading of 0.05 g/g, but becomes increasingly significant with increasing toluene loading. This behavior can be explained mechanistically by increase of Free Volume for diffusional steps of methanol in the presence of toluene. For the initial solvent loadings of toluene of 0.5 and 0.8 g/g, methanol evaporates completely with a constant rate without encountering any diffusive limitation. In this case, after the complete evaporation of methanol, the drying process reduces to a binary problem. This
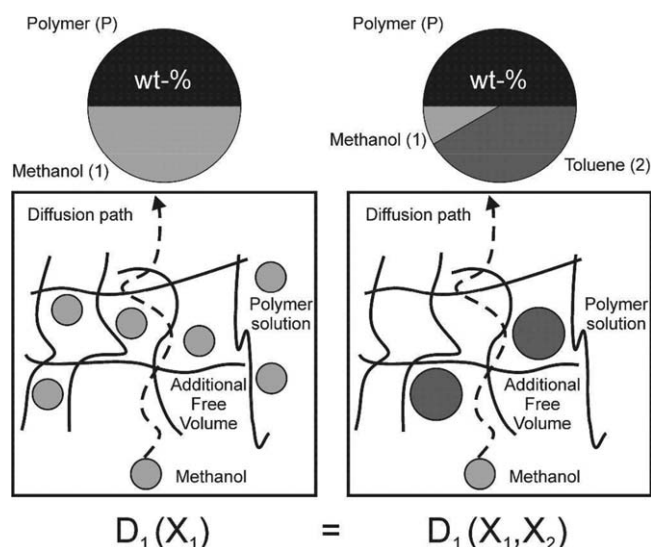
Figure 2. Diffusion according to the ideal additive solvent content model. Two situations are depicted at the same total solvent content: A binary mixture of methanol and polymer (left) and a ternary mixture of methanol, toluene, and polymer (right). In both cases eq. (3) predicts the same diffusion coefficient for the component methanol. The diffusion coefficient is dependent on the sum of solvent loadings but independent of the ratio of the local solvent contents.

specific situation has been previously under investigation in the work of Schabel (2003).[35]

However, for a detailed understanding the current toluene loading is more relevant than its initial solvent loading, as the exact value of the diffusion coefficient is dependent on the current composition. Figure 1 (right) shows the toluene loadings as a function of time during the same drying experiments. Toluene does not evaporate completely from the film during 100 min of measurement time in all cases. Only a very short constant rate period can be observed for toluene. At very low initial toluene loadings drying at constant rate is only possible due to the increase of toluene diffusion speed in the presence of methanol. After that the diffusive limitation of toluene leads to almost constant solvent loadings at increasingly high values with increasing initial toluene content. The much lower diffusion coefficient of toluene at low solvent loadings (compare Figure 2) and the low activity which favors the evaporation of methanol hinder significant changes of the toluene loadings in the falling rate period. Figure 1 (right) shows that the diffusion speed of the remaining methanol molecules is increased at any time in all experiments, since toluene is always present.

MODEL-BASED SIMULATION OF TERNARY DRYING EXPERIMENTS

In this work, we propose an expanded equation, with the aim to calculate (mutual) diffusion coefficients in ternary systems only from **binary** data. This expression is deducted from eq. (2)[20,21] and expanded for ternary mixtures by adding the all solvent contents using the following term:

$$\frac{D_i^V}{m^2/s} = \exp\left(-\frac{A_i + B_i \cdot (X_i + X_j)}{1 + C_i \cdot (X_i + X_j)}\right) = \exp\left(-\frac{A_i + B_i \cdot X_{total}}{1 + C_i \cdot X_{total}}\right) \quad (3)$$

Here A_i, B_i, and C_i are empirical parameters as in eq. (2). X_{total} is the sum of the solvent loadings X_i and X_j. This new expression ("Ideal additive solvent content model") takes the most important effect into account that the Free Volume is increased by the presence of other solvents, not differentiating between the various species. In contrast to Free Volume theory [eq. (1)], in this case all parameters are fitted to binary data, leaving no room for ambiguity. Parameter A_i controls the value of the diffusion coefficient in the limit of low solvent loadings, whereas the parameters B_i and C_i are determining in the limit of high solvent loadings. Equation (3) implies that increase of solvent loading has the same effect, no matter which component is added. The underlying model assumption is depicted in Figure 2.

We, therefore, expect this expression to be increasingly applicable in cases of similar solvents (i.e., comparable molecular weight and shape). To identify exact restrictions of applicability concerning parings of solvents further tests have to be performed. In terms of the Free Volume theory eq. (3) implies that all solvents have the same contribution to the available Free Volume, while the required Free Volume for a diffusional step is different for all components. In the limit of zero solvent loading of the second solvent this expression equals the binary case. However, despite its compelling simplicity, eq. (3) has the drawback of predicting that the diffusion coefficient of component "i" is the same at infinite solvent content, regardless whether component "i" or "j" is added in excess. This is justified by the fact that the diffusion coefficients in the film phase are usually not relevant for the drying process in the limit of high solvent loadings (as the mass transport in the gas phase is the limiting factor) and that the diffusion coefficient in liquid mixtures "all fall into a narrow range around 0.7 cm^2/s,"[3] rendering the error negligible. In principle eq. (3) can also be used considering volume fractions as concentration measure, but the temperature dependence of the volumes renders the use of mass-based concentration more practical in view of future non-isothermal applications. The diffusion coefficients of the solvents used in this work as calculated according to eq. (3) are depicted in Figure 3. The binary parameters (A_i, B_i, C_i) have been determined by Siebel[34] at 20 °C by means of analysis of Raman measurements. They are calculated from concentration profiles measured during binary drying experiments and are therefore are mutual in nature. More details about the procedure can be found in the cited publication. The parameters are tabulated in Supporting Information Table 3S.

Both concentration dependent diffusion coefficients show typical behavior in the binary case (i.e., without addition of a second solvent). High diffusion coefficients at high solvent loadings and a sharp decline toward zero solvent loadings. At high solvent loadings (above solvent loading i of 1 g/g) the influence of the second solvent is small. This is due to the fact that the relative change of diffusion coefficient with changing solvent content is small in this region. However, at solvent loadings i approaching zero the relative effect of a second solvent is
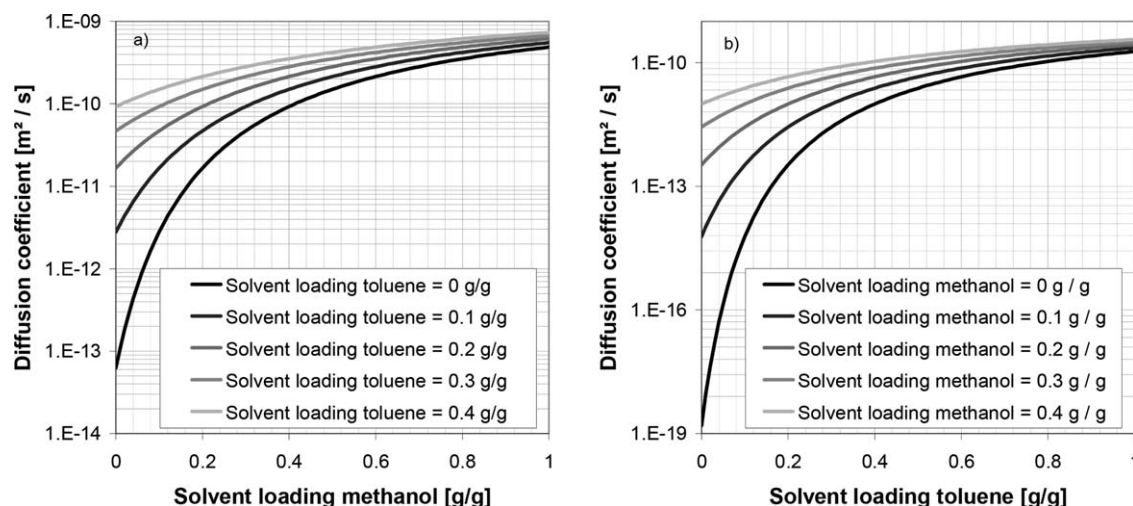
Figure 3. Diffusion coefficients of methanol (a) and toluene (b) in PVAc calculated according to eq (3). Parameters have been determined by a fit to binary drying experiments at 20 °C (Supporting Information Table 3S). The array parameter is the solvent loading of a second solvent.

increasingly strong. The difference is generally larger in case of systems with stronger concentration dependence of the diffusion coefficient (in this example for toluene).

Equations (2) and (3) have been used in the simulative framework described by Saure[37] and Schabel[14] to predict the drying behavior of polymer solutions, which has been expanded to the ternary case.[38] The calculation includes a full description of the gas phase mass transfer, phase equilibrium and diffusion in the film. The phase equilibrium in ternary solutions can be calculated with the Flory Huggins theory.[35,39] The vapor liquid equilibrium (VLE) data used in the simulation is given in Supporting Information Table 4S. The mass transport in the gas phase has been calculated according to Ameel.[40] The shrinking of the film due to evaporation is taken into account by using an alternative frame of reference.[41] The diffusion in the film is described by the generalized form of Fick's law, assuming that all cross term diffusion coefficients are zero without use of thermodynamic factors. The set of partial differential equations describing the process is solved by a Fortran solver taken from the NAG-library. The solver is embedded in a modified Visual Basic for Applications (VBA) code which has been successfully validated in a number of previous works.[14,42,43] The criteria for successful prediction are correct calculation of the **solvent loading** in the film and good agreement of the **concentration profiles**. Simulation of the film drying with eq. (2) is expected to predict the process poorly since mutual influence of the solvents regarding diffusion is not taken into account. We present the results as a means to clarify the enhancing nature of the second solvent regarding diffusion. With eq. (3) a much more precise prediction of the drying curves is expected. In both cases only data for the binary system is necessary to predict the drying process in the ternary system. Figure 4 exemplarily shows simulative results with eqs. (2) and (3) in comparison to measurement data [other examples employing eq. (3) are given in Figures 3S–6S in Supporting Information]. The sample had an initial solvent content of 1.5 g/g of methanol and 0.2 g/g of toluene. In order to improve clarity of the different drying

regimes, a logarithmic scaling for the same data has been chosen in Figure 4 (right).

The results show that at shorts times both variations of the simulation show good accordance with the measured data for methanol. This indicates that the phase equilibrium and the mass transfer in the gas phase are described correctly in the simulation. At these high solvent loadings the diffusion coefficient is high (as seen in Figure 3) and the simulated results are not dependent of the diffusion coefficient in the liquid phase. Therefore an almost constant mass flux is calculated at short simulated times. For better understanding the evaporation rates of both solvents predicted with the model based simulation are depicted in Figure 2S in Supporting Information for various initial solvent loadings, in which the transposition from the constant rate period to the falling rate period after about one minute is clearly seen by the change of the mass flux. From this moment on, the diffusion coefficient in the polymer solution affects the simulative result. As depicted, the deceleration of the drying due to the diffusive limitation is described accurately by the simulation with eq. (3). After drying times of more than about one minute the two simulations diverge increasingly concerning the methanol loading. Simulation with eq. (2) calculates a much stronger diffusion limitation for the transport of methanol as the influence of the toluene is not considered. This results in a prediction of methanol loadings which are much too high. Simulation of eq. (3) on the other hand takes the influence of toluene on the methanol mobility into account (e.g., the diffusion coefficient of methanol is increased by factor 30 after 10 min drying time). This results in much more accurate predictions of the methanol loading at drying times longer than two minutes. After about 5 min of drying time the methanol loading is predicted slightly too low, which indicates that the influence of toluene is slightly overestimated by this model of the diffusion coefficient. Even though it should be noted that the absolute methanol loading is smaller than 0.02 g/g after 5 min and therefore close to the resolution limit of the measurement set-up, this behavior could be a result of the increasing
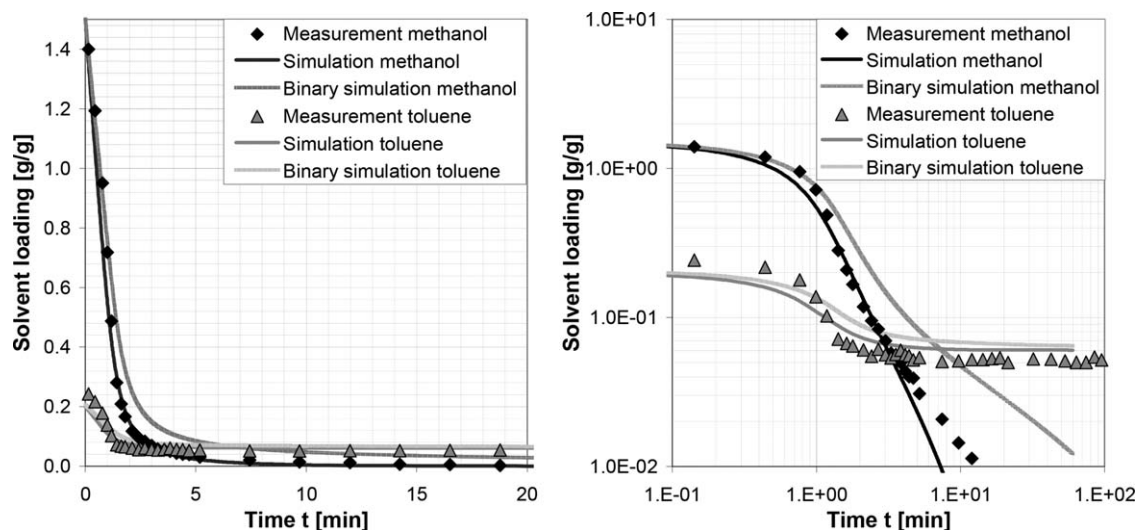
Figure 4. Simulative results in the system methanol-toluene-PVAc in comparison to an isothermal drying experiment at 20 °C and $u = 0.2$ m/s with initial solvent loadings of 1.5 and 0.2 g/g. The diffusion coefficients of the solvents have been calculated according to eq. (3) ("Simulation results") and without taking the mutual influence into account ("Binary simulation") according to eq. (2).

glass transition temperature with decreasing solvent content (for the specific material the glass transition temperature is about 20 °C at methanol loadings of about 0.05 g/g as measured by Schabel[38]).

Because of the low initial solvent content of toluene, only a very short constant rate period can be observed for toluene. In case of toluene, the very low values in the falling rate period are in the vicinity of the resolution of the measurement set-up. However no significant deviations of simulative and experimental results are observed for both simulations. The simulations with eqs. (2) and (3) are very similar in this case since the solvent loading of methanol is too small after about 5 min to have

a large impact on the diffusion of toluene. Both simulations calculate toluene loadings which are slightly too high. Arya and Vinjamur, as well as Alsoy et al. have reported the same finding for the low volatile component.[6,9] We attribute this to underestimation of the influence of methanol on the main term diffusion coefficient.

In case of a correct description of the drying process not only the integral data but also local data has to be predicted accurately. The averaged data seen Figure 4 is derived from concentration profiles, which are depicted as calculated with eq. (3) in Figure 5. The time delay of the measurements described in the experimental section is taken into account by the simulation.
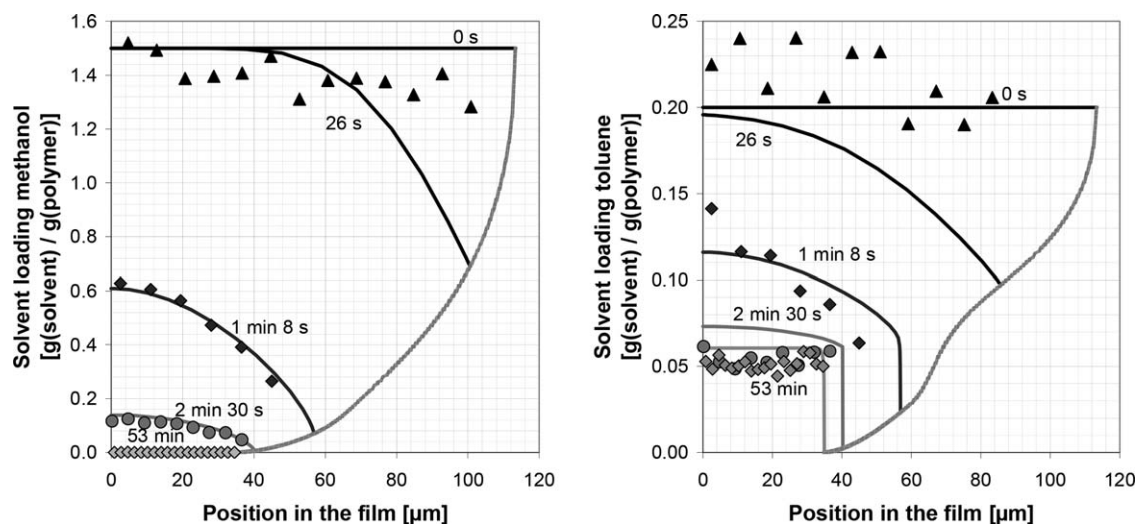

Figure 5. Simulated methanol (left) and toluene (right) profiles in the system methanol-toluene-PVAc in comparison to isothermal measurement data at 20 °C and $u = 0.2$ m/s with initial solvent loadings of 1.5 g (methanol)/g(polymer)$^{-1}$ and 0.2 g (toluene)/g(polymer)$^{-1}$ at different drying times. The diffusion coefficients of the solvents have been calculated according to eq. (3). The diagrams show four measured profiles at 26 s (*black triangles*), 1 min and 8 s (*dark gray diamonds*), 2 min and 30 s (*gray circles*), and 53 min (*light gray diamonds*). The *lines* in the respective colors depict the correlating simulated, time corrected profiles. Additionally the initial profile at 0 s is shown (constant solvent loading). The *shaded line* depicts the calculated solvent loading at the surface of the film at any time during the simulation.

This is done by a time-correction of the simulated profiles. The values calculated at the bottom of the film are given for slightly shorter times than the values at the top of the film, corresponding to the exact times of the corresponding measurement data. This ensures that a perfect prediction results in match of calculated and measured profiles. The times specified in the diagram are the averaged time of the calculated profile. For both solvents the accuracy of the predicted profiles increases at longer drying times. From 1 min onward virtually no difference between measured and predicted concentrations is visible. At shorter times comparison of measurement data and simulative data is expected to be less accurate because the error in determining the starting time of the experiments has a comparatively large impact. At times longer than 53 min the methanol has evaporated completely, accordingly the diffusion problem becomes binary. The model has been shown to work in this case with the given parameters in a previous study.[34]

At other initial solvent contents the quality of the predicted results is comparable as seen in Figures 3S–6S in Supporting Information. Accordingly, we conclude that eq. (3) is suitable to predict drying experiments in this ternary system, both in methanol and toluene rich solutions independent of the initial composition of the sample. With solvent combinations of more similar nature (such as alkanes of comparable molecular weight) calculation with this expression is expected to yield even better results. The agreement of prediction and measurement indicates that the numerical values of the diffusion coefficients are accurate over the whole covered concentration range. In contrast to the findings in other systems in literature,[9] thermodynamic factors and cross term diffusion are not required to describe the process in this system.

CONCLUSIONS

In this work, we provide measurement data of drying experiments in the system methanol-toluene-PVAc. The results clearly show the interaction between different solvent species during diffusive processes, meaning that the effect cannot be neglected for process design applications. As predicted by Free Volume theory, presence of other solvent species increases the mobility of a solvent. At a certain critical initial toluene loading, methanol does not encounter any diffusive limitation in the film before complete evaporation. Accordingly, low boiling components can be removed from the film by addition of another high boiling component which acts as diffusion enhancer. On the other hand, the high boiling components with low diffusion coefficients (such as toluene in the system under investigation) cannot be removed from a sample by changing the initial composition of the solution, but only by thermal activation. Knowledge of such effects can be used in the design of precursor solutions in combination of a subsequent drying process.

The experimental results can be predicted calculating the diffusion coefficient in ternary systems only using binary data. The simulative results show that the diffusion coefficients calculated with eq. (3) are sufficient to describe the drying behavior of this ternary mixture. We conclude that the chosen ideal additive solvent content model [eq. (3)] could provide an applicable way to calculate diffusion coefficients in ternary mixtures for practical applications. No cross term diffusion coefficients are necessary in this specific system to achieve satisfying results, leading to the conclusion that their influence is negligible. Thermodynamic factors are not required as well. The main factor controlling the mass transport in the film and therewith the drying path are the numerical values of the main term diffusion coefficients. This enables the prediction of the drying behavior of ternary systems solely relying on binary input data. However, general applicability of eq. (3) is so far unclear and requires further investigation. No solvents with differences in molecular mass of more than factor 3 were tested. It is to be expected that diffusional behavior of solvents with extremely differing properties is not well-described by the ideal additive solvent content model. A more complex expression taking different contributions to the available free volume into account might be necessary in this case. Also no experiments below the glass transition temperature of the mixtures were performed. Since the simulative framework is based on Fickian kinetics, eq. (3) has not been tested in situation where Fick's law of diffusion is not valid. A correct prediction with the chosen approach cannot be expected in such situations. We therefore propose further investigation on these findings in other material systems employing eq. (3) to identify the boundaries and limitations of this approach.

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