Diffusion in quaternary polymer solutions—Model development and validation

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A B S T R A C T

Multicomponent diffusion in polymer solutions is a complex and not yet completely understood phenomenon. Available studies are so far almost exclusively limited to ternary systems containing a polymer and two solvents. In this work measurement data in form of isothermal drying curves in quaternary systems, consisting of the polymer poly(vinyl acetate) (PVAC) and the solvents dichloromethane, methanol and toluene obtained by inverse micro-Raman spectroscopy (IMRS) is presented. The measurements show that the diffusive behaviour is a function of the overall composition of the mixture, as additional solvents accelerate diffusion. Since no numerical model for such systems has been validated in literature, a framework for the simulation of mass transfer processes in quaternary systems has been developed. The shrinking of the film due to evaporation is taken into account by a transformation of the frame of reference. The concentration-dependent diffusion coefficients are calculated by an expression only requiring binary data, previously only tested in ternary systems, enabling predictions in uncharacterized multicomponent systems. Cross-term diffusion is neglected. The numerical model, validated by the measurement data, is able to predict the experimental results reliably for varying initial conditions.

1. Introduction

The diffusion in multicomponent polymeric systems is so far not completely understood, even though such systems are commonly used in many industrial applications. The use of solvent mixtures offers various advantages compared to pure solvents, e.g. the tailoring of rheological properties of coating solutions and improved solubility of non-volatiles [1]. During the subsequent drying process, multicomponent mass transport influences drying paths and residual solvent contents, both being critical parameters for product quality. Even though the mathematical framework to describe mass transport in such systems has been set up [2], reliable predictions concerning drying paths, drying times and residual solvent contents for process design in multicomponent systems are not yet possible.

The behaviour of binary polymer solutions is much better understood and has been investigated intensely in the past, giving rise to many studies concerning experimental measurement [3–5], theoretical description [6,7] and numerical modelling [8–11] of mass transport phenomena. In these systems, temperature [12–14] and the strong concentration-dependence [15] of the diffusion coefficients are well-studied topics. It is known that mutual diffusion coefficients increase with increasing temperature and, in the limit of low solvent contents,

increasing solvent content in the mixture. Both effects are significant, leading to changes of the numerical values of the transport coefficients up to several orders of magnitude. Accordingly correct description of mass transport can only be possible if these effects are taken into account appropriately. Study of mass transport in multicomponent systems is more complex, as additional effects might occur (i. e. cross-term diffusion) and experimental setups have to be more advanced in order to distinguished different species. Measurement of the diffusion coefficients and their concentration dependence gets increasingly complicated, which is supposedly one of the reasons investigation in multicomponent systems is mostly restricted to ternary systems with very few exceptions [16,17]. It is generally accepted that the addition of solvents increases the self-diffusion coefficient of any species in the mixture but the exact magnitude of this effect is often not known. Measurement data can for example be obtained by Raman spectroscopy [18–20], gravimetric film drying experiments [8] or by advanced sorption experiments [3].

Many existing publications concentrate on implantation of different theoretical descriptions of the cross-term diffusion coefficients and thermodynamic factors, which link self-diffusion coefficients to mutual diffusion coefficients by friction laws, rather than on the exact values of the diffusion coefficients [21–23]. The connection of self-diffusion

coefficients to mutual diffusion coefficients causes some concern, since there is no clarity which strategy is best and how friction factors should be determined [8,24]. One additional limitation of existing theories is that the number of parameters required for calculations grows much more rapidly than the number of components in the system, when cross-term diffusion coefficients are taken into account [2]. Even though the necessity of taking cross-term diffusion into account to fulfill the Onsager Reciprocal Relations (ORR) has been shown [22], from a practical point of view there is no clear evidence that these effects have to be considered to achieve satisfying results [19,20].

For correct prediction of mass transport processes the correct calculation of the (main) self-diffusion coefficients has been reported to be the most important aspect [20]. In binary systems Free Volume theory has caught much attention in the last decades. The diffusion coefficients can be in principle predicted, even though fit of one or more of parameters leads to significantly better results [19,25–27]. Literature also offers a ternary expansion of the Free Volume expressions [28]. In this case a fit of the binary parameters leads to some ambiguity of concerning the fitted parameters, as different fit parameters have been chosen by different authors [19,25,27]. To our knowledge, the Free Volume formalism has so far not been applied to quaternary mixtures. A newer approach is Shell like Free Volume Theory, predicting diffusion coefficients from pure component data and semi-empirical quantum chemical calculations [7,29,30]. This rather recent development requires more testing before conclusions can be drawn. Data availability is still limited even though a collection of parameters has been published [30]. To overcome these problems for practical applications we lately proposed a new expression to calculate the diffusion coefficient solely from binary data, which showed promising results in the ternary system methanol-toluene-poly(vinyl acetate) [20]:

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

Here the concentration-dependence of the diffusion coefficient D_i^V is described by the solvent loading (in terms of mass solvent per mass polymer) and three empirical parameters (A_i, B_i, C_i). These parameters can be fitted to binary measurements of the solvent-polymer combination in question. The addition of either solvent has the same impact according Eq. (1) concerning diffusion of a given species, namely increase of the diffusion coefficient. However each solvent has a distinct diffusional behaviour. The specific implications of this approach have been discussed in more detail in our previous work [20].

In this work the mass transfer in *quaternary* PVAc solutions was under experimental and numerical investigation. In contrast to our previous works dichloromethane was added additionally to methanol and toluene as a third solvent. The mass transport was observed during the isothermal drying of thin films by inverse micro-Raman spectroscopy. Since literature does not offer any numerical model to describe the mass transport in a quaternary system, a suitable mathematical framework has been developed. With the employed simulation strategy and an expansion of Eq. (1) we predict the multicomponent mass transport only from data fitted to binary measurements. The prediction is compared to the measurement data in order to validate the model.

2. Experimental

The polymer used in this study is poly(vinyl acetate) obtained from Carl Roth GmbH + Co. KG, Karlsruhe, Germany (nr. 9154.1) with a molecular weight of 55,000–70,000 g mol^{-1}. The glass transition temperature of the polymer was found to be T_g = 32–34 °C experimentally [19]. Toluene was obtained from Merck KGaA (Darmstadt, Germany, catalogue number 1.08326.1001), whereas Methanol (catalogue number 4627.2) and Dichloromethane (catalogue number 6053.1) were obtained from Carl Roth GmbH + Co. KG, Karlsruhe.

The material data required for the analysis of the performed experiments are summarized in Table 1S. Before sample preparation the polymer was dried for 48 h at vacuum and room temperature. Subsequently the solvents were added at the desired mass fractions in reverse order of their volatility to reduce solvent losses.

The measurement setup including schematic illustrations is described in detail in previous works [31,32]. The sample is cast on a glass substrate by a knife coating process in a drying channel with adjustable air flow. The temperature of the drying channel, drying air and substrate is controlled in order to guarantee isothermal conditions during the experiments. During drying Raman spectra are recorded at different positions in the film. This is done by shifting the focus of the measurement setup from the bottom of the sample to the top of the film repeatedly and thereby measuring concentration profiles ("depth scans"). Recording and data processing of this procedure takes about 1 s per measured spectrum. In the beginning of the experiments, the drying process is very dynamic and large spatial intervals are chosen (10 μm). At later stages of drying the spatial interval is reduced down to 1 μm. Accordingly, the acquisition of a full concentration profile requires approximately 10–30 s.

During the subsequent data processing the measured spectra are expressed as a superposition of the pure component spectra as described in our previous works ([33], [20]). The weighing factors of the superposition are then used to calculate concentrations of the solvents (in terms of mass loadings defined as g(solvent) ·g(polymer)$^{-1}$) from the measured spectra by means of a calibration procedure described in detail by Scharfer et al. [34]. Residual solvent contents as they are shown in this work are calculated by averaging the solvent loadings within each concentration profile. For correct analysis the Raman spectra of the components have to be clearly distinguishable. Fig. 1S shows the normalized Raman spectra for different components used in this work. In order to yield high accuracy of the concentration measurements extensive testing of the calibration procedure has been conducted, as it has so far only been used in binary [3] and ternary [20,34,35] systems. Calibration samples of the binary, ternary and quaternary samples were used under systematic variation of concentrations, resulting in more than 1000 measurement points for each calibration constant. For the calibration samples with well-known composition were prepared, by adding the polymer and one of the solvents with the desired mass loading in glass bottles. Solvent loadings from 0.1 up to 2.3 g g^{-1} were used, covering the whole concentration range of the experiments. After the polymer has completely dissolved in the solvent, potential material loss is detected by differential weighing. Directly before the acquisition of the spectra, random but measured amounts of the other solvents are added. The spectra are then used for calibration by plotting the ratio of intensities of the spectrum of respective solvent to that of the polymer determined by a least square fit over the actual solvent loading. The slope of the curve represents the calibration constant for the component in question.

3. Results and discussion

3.1. Multicomponent calibration

According to theory the ratio of intensity of the spectra of two components in a solution is only dependent on the mass ratio of these components in case no strong interactions with further components occur [36]. Calibration curves for any solvent-polymer combination are expected to be independent of the amount of other solvents in the solution. This theoretical prediction has already been confirmed in various ternary systems [24,26,34,35]. Fig. 1 shows the calibration curves for the three different solvents used in this work in mixture with PVAc under variation of composition determined by the aforementioned procedure.

The calibration curves of all components exhibit a constant slope. As predicted, for each component the ratio of intensity of a specific solvent