

# **Experimental investigation on multicomponent mass transport during drying of ternary and quaternary polymer solutions**

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Polymer solutions consisting of one polymer and several solvents are used in many manufacturing processes, e.g. membrane production and optical foils. After coating, the subsequent drying step has impact on the functionality of the final product. Despite this practical relevance, multi-component diffusion in these systems is not yet understood. The main reason is that it has been almost impossible to determine local solvent concentrations in multicomponent systems. Therefore no experimentally validated theoretical descriptions of multicomponent diffusion exist. Inverse Micro Raman Spectroscopy (IMRS) allows the in-situ measurement of solvent concentrations in thin films during drying with a high spatial resolution of 1 to 2  $\mu\text{m}$  and high accuracy.

In this work, ternary and quaternary mixtures of polyvinyl acetate (PVAc) and the solvents toluene, methanol and dichloromethane were investigated by means of IMRS as a model system. Compared to gravimetric methods, spectroscopic measurements have the advantage that changes in solvent loadings can be detected for all solvents separately. Therefore it is possible to investigate multicomponent systems. Prior to the measurements extensive calibration has been performed to receive reliable data.

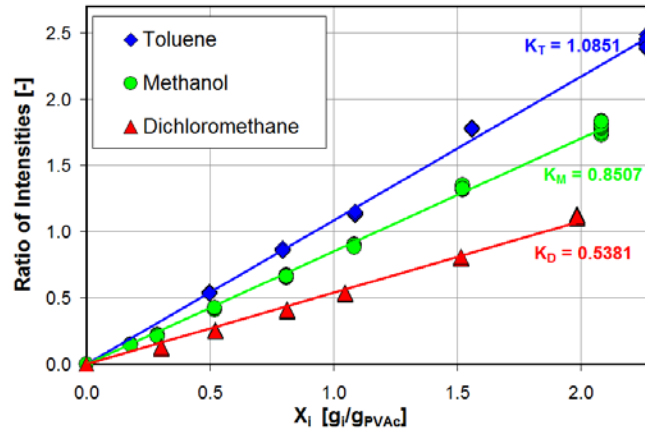


Fig. 1: Calibration curves for the material system dichloromethane, methanol, toluene and polyvinyl acetate from quaternary samples.

During the experiments spectra of a drying sample are taken at different times and locations. From these measurements the local concentrations of the solvents can be calculated with high accuracy. Scans through the sample show the internal gradients. This is depicted in figure 2 for a sample with initial solvent loading of 0.9 kg (solvent) / kg (polymer) for both dichloromethane and methanol and 0.2 kg (solvent) / kg (polymer) for toluene. This information is crucial for better understanding of the underlying mass transport phenomena in multi component systems. From literature it is well known that different species mutually influence the diffusive behavior of each other. Therefore the initial composition and its implications on the drying process will be discussed.

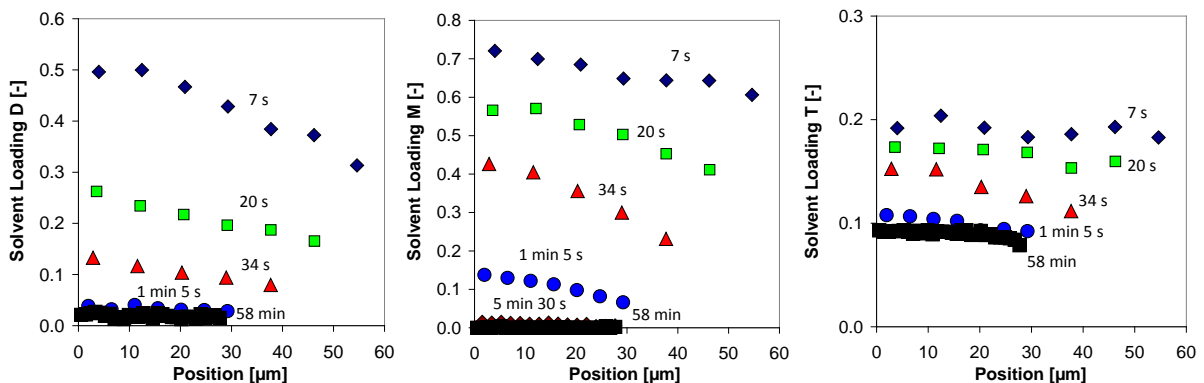


Fig. 2: Gradients measured at different times during drying of a quaternary polymer solution on a flat plate in laminar flow at  $T = 20^{\circ}\text{C}$  and air velocity  $u = 0.2 \text{ m/s}$  for

dichloromethane (left), methanol (middle) and toluene (right) with a dry film thickness of 26  $\mu\text{m}$ .

Over time the solvent loading for all components decreases due to drying. For both dichloromethane and toluene the solvent loading remains at a certain, almost constant residual solvent content even for very long drying times. This phenomenon known as skinning effect is caused by diffusive limitations in the sample when the solvent loadings are low. From these data integral drying curves as shown in figure 3 can be calculated by averaging the profiles.

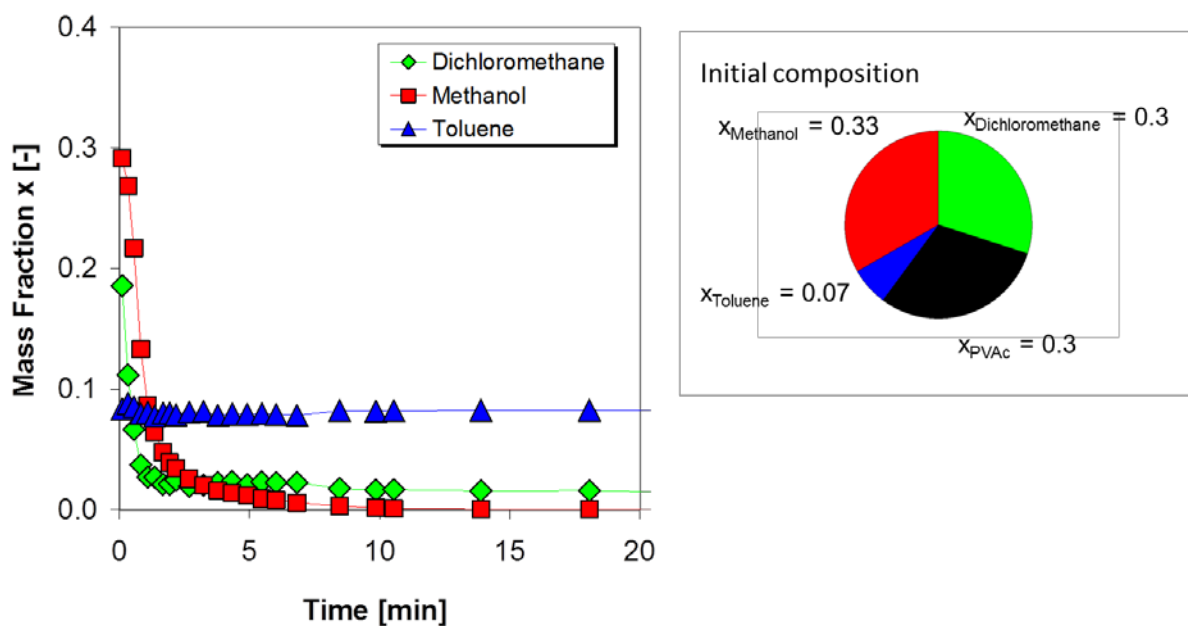


Fig. 3: Integral drying curves of three solvents during the drying of a quaternary sample on a flat plate in laminar flow at  $T = 20$   $^{\circ}\text{C}$  and air velocity  $u = 0.2$  m/s. The initial composition of the sample is shown in terms of mass fractions in the right diagram.

The constant rate period (CRT) and the falling rate period (FRP) are clearly visible in Fig. 2. After about 2 minutes the drying is limited by the mass transport within the film. It can be noted that the solvent toluene, even though it has the lowest initial solvent loading, has the highest residual solvent loading due to its low vapor pressure and low diffusion coefficients.

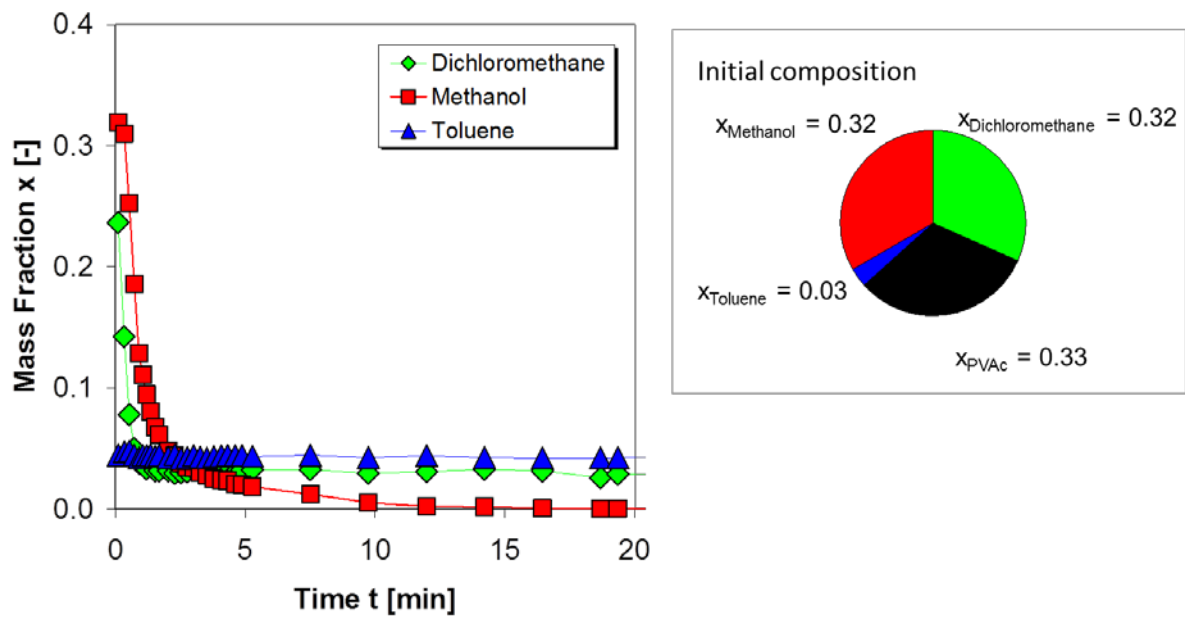


Figure 4: Integral drying curves of three solvents during the drying of a quaternary sample on a flat plate in laminar flow at  $T = 20 \text{ }^\circ\text{C}$  and air velocity  $u = 0.2 \text{ m/s}$ . The initial composition of the sample is shown in terms of mass fractions in the right diagram.

Figure 4 shows such an experiment with an even lower initial mass fraction of toluene of only 3 wt%. During drying the toluene mass fraction is almost constant and exhibits the highest residual solvent content. Consequently, even in cases of very low toluene mass fractions, this component cannot be neglected in a theoretical description. By comparison of Fig. 3 and Fig. 4 the influence of the initial solvent content on the residual content can be seen. To explain this behavior in detail, the underlying mass transfer phenomena have to be understood. Mass transfer mechanisms and the concentration dependent diffusion coefficients have to be known for the modeling of the process. Therefore experiments have been performed under variation of temperature and air velocity. With this information a better understanding of the underlying mass transport phenomena can be obtained and a verified numerical model will be developed.