A critical comparison of diffusion coefficient measurements in polymer-solvent systems measured by means of gravimetric sorption experiments and spectroscopic methods

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Introduction

The diffusion coefficient of solvents in polymeric systems is a required parameter to describe the drying process of polymeric solutions. Although the drying process is an important step during the production of polymeric films, only few reliable diffusion data are available in literature.

In this work, the diffusion coefficient of methanol in the binary system methanol-polyvinyl acetate was investigated experimentally with three different methods. Diffusion coefficients at different solvent concentrations were determined from: (i) Pulsed-Field-Gradient NMR spectroscopy (PFG NMR) (self-diffusion), (ii) sorption experiments in a magnetic suspension balance (mutual diffusion) and (iii) drying experiments analyzed by means of Inverse-Micro-Raman-Spectroscopy (IMRS) (mutual diffusion). The results were compared and led to different diffusion coefficients.

Experimental Methods

The self-diffusion coefficient of methanol in the binary system methanol-polyvinyl acetate was measured by pulsed field gradient nuclear magnetic resonance on a Bruker DRX-200 spectrometer equipped with a Diff30 probe for different temperatures and solvent contents. Spin-bearing molecules are marked by a gradient pulse and move within the diffusion time along the direction of the field gradient. The NMR signal is an average over all spins and will be reduced by the divergence of phases. For free self-diffusion the logarithmic signal attenuation is proportional to the squared gradient amplitude, gradient pulse duration and gyromagnetic ratio, as well as to the diffusion time and the diffusion coefficient D. The magnetic field gradient amplitude was varied linearly and the signal attenuation was detected. Keeping the other parameters fixed the diffusion coefficient can be calculated from the slope of the attenuation plot.

Another method to determine diffusion coefficients of solvents in polymeric systems is to investigate the sorption/desorption behaviour with a magnetic suspension balance. By plotting the ratio of the current mass and the mass at sorption equilibrium M_t/M_{eq} vs. the square root of the experimental time, the diffusion coefficient can be calculated from the initial slope of the sorption curve [1]. By repeating these experiments at stepwise increasing (or decreasing) solvent activities

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in the sorption cell, the concentration-dependent diffusion coefficient of the solvent in the polymer can be obtained.

A new approach to determine the mutual diffusion coefficients of solvents in polymers is applied. By Inverse-Micro-Raman-Spectroscopy (IMRS) the local solvent concentration profiles within a polymeric film are measured during the drying process. The diffusion coefficients are determined by fitting simulation results to the measured data [2]. To simulate the drying process of a polymeric solution, the mass transport in the gas phase, the sorption equilibrium at the phase interface and the diffusive mass transport in the film have to be taken into account. For a binary polymer-solvent-system one obtains a strongly non-linear partial differential equation. To solve the equation a VISUAL BASIC program using FORTRAN routines and numerical libraries from NAG (Numerical Algorithms Group) was developed [2]. The only unknown parameter - the concentration-dependent diffusion coefficient of the solvent in the film - can be determined by fitting calculated to measured solvent content profiles.

Results

The determined diffusion data from PFG NMR spectroscopy and the data correlated to drying experiments predict a continuous increase of the diffusion coefficient with increasing solvent concentration. The data from initial sorption kinetics show a decreasing mutual diffusion coefficient with increasing solvent content, what has been observed before by other authors for different solvent-polymer systems [3]. In literature, theses differences are described by a thermodynamic factor [4], to match NMR self-diffusion data to sorption balance mutual diffusion data. Astonishingly, the mutual diffusion coefficient determined from the IMRS measurements does not show any decrease at higher solvent contents. Furthermore, the diffusion coefficient determined from sorption kinetic measurements cannot predict the measured solvent concentration profiles during the drying process of the polymeric films by means of IMRS measurements. Therefore the question arises, whether the determination of diffusion data from sorption kinetics is possible without consideration of additional assumptions. In this work, we provide new diffusion data and discuss the impact on current diffusion theories. Measurements for additional polymer-solvent-systems and an advanced theoretical discussion will be topic of further investigations.

Acknowledgement

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