Determination of diffusion coefficients of water in polymeric films for blood glucose test strips

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Introduction

The number of people worldwide suffering from diabetes is growing rapidly. For the patients a good control of the blood glucose level is essential for successful therapy. Therefore regular self-monitoring is an important part of the treatment of diabetics. Single use biosensor strips are the number one device used by the patients to measure their blood glucose level. One common type of sensor applies an amperometric measurement principle where an enzymatic reaction is followed by an electrochemical reaction to detect glucose. The enzyme is immobilized in a polymer matrix and coated on a polymer carrier as a thin film.

It is of great interest to develop a better understanding of the drying and rehydration of these sensor films in order to improve performance and handling of the test strips. Knowing the characteristics of water transport within the film would make predictions of water uptake possible. The aim of this study is to determine the diffusion coefficient of water in the matrix from drying experiments.

Drying curves were measured gravimetrically in a drying channel for different temperatures and air velocities. The mass transfer model for drying of thin films was then fitted to the measured curves. With known sorption equilibrium and defined mass transfer in the gas phase the diffusion in the film can be simulated. The diffusion coefficient of water in the film was determined by this method as a function of solvent content and temperature.

Experimental

The matrix for immobilization of the enzyme and mediator on the electrodes consists of polymers, silica, salts, and additives such as surfactants. The solvent is water. Solids were

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dispersed or dissolved in water and combined during sample preparation. For the drying experiments the enzyme was replaced by a substitute protein.

Drying curves were measured gravimetrically in a drying channel (Figure 1). Dry air was heated to the desired temperature. A heated drying channel ensured a constant air temperature throughout the channel. The velocity of the air flow was adjusted and was measured with a hot-wire anemometer directly in front of the plate where the film was dried. Flow rates ranged from 0.2 m/s to 0.5 m/s The air temperature was also measured in front of the plate. Temperatures ranged from 30°C to 50°C.
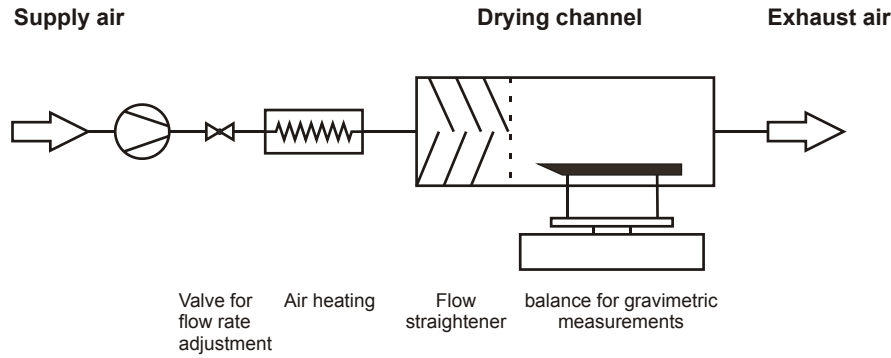
Figure 1 Schematic drawing of the drying channel

A film of the sample containing protein, mediator, and matrix was coated on the aluminum plate in the channel and the mass was recorded during the drying process.

Numerical simulation of the drying process

The mass transfer in the gas phase and in the film as well as the phase equilibrium for the film are required for simulation of the drying process. The molar rate of evaporation at the surface of the coating was calculated using the Stefan-Maxwell equation.

$$\dot{n}_1 = \widetilde{\rho}_g \beta_{1g} \ln \frac{1 - \widetilde{y}_{1,\infty}}{1 - \widetilde{y}_{1,0}} \tag{1}$$

with

$\widetilde{\rho}_g$ molar density of the gas phase

β_{1g} mass transfer coefficient of water in the gas phase

$\widetilde{y}_{1,\infty}$ mole fraction of water in the gas phase (bulk)

$\widetilde{y}_{1,0}$ mole fraction of water in the gas phase at the interface

The mass transfer coefficient in the gas phase was calculated locally using the correlation for a flat plate in laminar flow with an offset between the concentration boundary layer and the hydrodynamic boundary layer. The moving drying front due to faster drying at the upstream end of the film was taken into account.

Phase equilibrium was calculated according to the Flory-Huggins model for pure polymer – solvent systems.

$$\ln a_1 = \ln \phi_1 + \phi_S + \chi_{1,S} \phi_S^2 \tag{2}$$

with

a_1 water activity in the gas phase

ϕ_i volume fraction of water (1) or solid (S)

$\chi_{1,S}$ Flory-Huggins interaction parameter

The model was found to be suitable to describe the measured values for the complete mixture of the reagent. The interaction parameter $\chi_{1,S}$ was fitted to measured data and was found to be a function of water content in the film but independent of temperature.

The mass transfer in the film was calculated with Fick's law of diffusion. The shrinkage of the film was taken into account by a moving coordinate system [1].

$$j_i^P = -D_{1S}^P \frac{1}{\hat{V}_S} \frac{\partial X_1}{\partial \zeta} \tag{3}$$

with $D_{1S}^P = D_{1S}^V \phi_S^{\,2}$

D_{1S}^P diffusion coefficient in polymer based coordinate system

$\hat{V}_S$ specific volume of the solid

X_1 solvent content in the film [kg_{water}/kg_{solid}]

ζ coordinate perpendicular to coating surface in polymer based coordinate system

During the drying process the plate and the film cool down due to the evaporation of solvent. The calculation of the temperature in the film was included in the simulation. Film and plate temperature were assumed to be equal and uniform over the complete plate.

The diffusion coefficient was fitted to the measured drying curves. An exponential approach was used to describe the dependency of the diffusion coefficient on the water content in the film. An equation using an Arrhenius approach for the activation energy was used to describe temperature dependency.

$$D_{1S} = \exp\left(\frac{A + B \cdot X_1}{C + X_1} \right) \cdot \exp\left(-\frac{E_a}{\tilde{R}} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right) \tag{4}$$
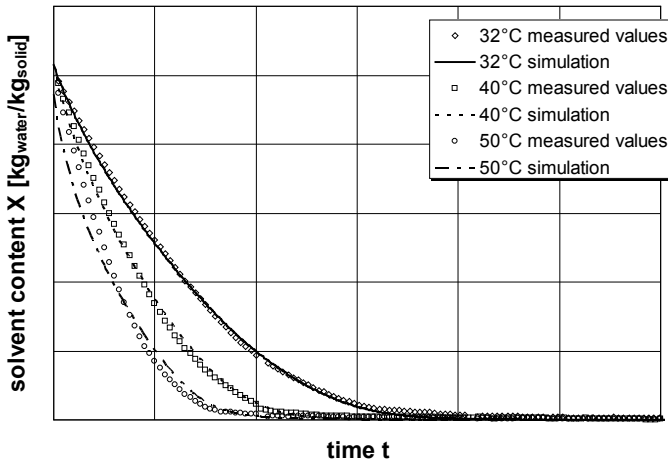
with

$\tilde{R}$ universal gas constant

T temperature [K]

The parameters A, B and C as well as the activation energy E_a were fitted to experimental data. Simulation was done using a numerical simulation program. The implemented FORTRAN solver is specialized to solve the non-linear differential equations occurring in heat and mass transfer problems in thin films.

Results and Discussion

The measured drying curves for different air temperatures are shown in Figure 2. With increasing temperature the drying process accelerates due to increasing vapor pressure of the solvent. Also the diffusion in the film is expected to be faster at higher temperatures. The influence of different air velocities is predominantly seen in the first stage of the drying process. The drying rate

increases with increasing flow rate. Later in the drying process when the solvent content decreases the drying becomes more and more controlled by the diffusion in the film which is independent of air flow.

Figure 2 Measured and simulated drying curves for different air temperatures

Comparison with the simulation shows that the drying process is influenced by mass transfer within the film from the beginning of the drying process. The drying kinetics can be described by a solvent content and temperature dependent diffusion coefficient of water in the film. The parameters *A*, *B* and *C* in equation were fitted to one drying curve at 40°C and 0.4 m/s air velocity and proved to be consistent for different air velocities and film thicknesses. The activation energy E_a was fitted to describe all measured temperature variations. Figure 2 compares the gravimetrically measured and the simulated drying curves.
The results show that the mass transport in the complex multi-component film can be modeled by an approach for diffusion in thin polymer films.
The findings of this study will be useful for predicting drying and rehydration processes of the biosensor films.

References
[1]   R. Saure, G.R. Wagner, and E.-U. Schlünder. Drying of solvent-borne polymeric coatings: I. modeling the drying process. *Surface and Coatings Technology*, 99(3):253 – 256, 1998.