# Experimental Study of Dynamic Mass-Transfer Effects in Pervaporation

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Mass transport through dense polymeric membranes is generally described by the solution-diffusion model. According to this, the different transport steps are subdivided into the selective sorption of the permeating compounds in the polymer, the diffusion through the active layer and the desorption on the permeate side. The diffusive properties of the membrane are essentially influenced by membrane swelling due to the sorption of the permeating compounds. In the case of pervaporation, the permeate is evaporated causing a dry membrane surface on the downstream side. Hence, the degree of swelling varies within the active layer from a very expanded polymer lattice at the feed side to a very contracted chain structure at the permeate side (anisotropic swelling).

It is well-known that pervaporation membranes can exhibit a pronounced conditioning behavior (that is, a slow, time-dependent adaptation of the transport properties to rapidly changed process conditions). After startup of a pervaporation process, the steady-state regime of permeate flux and selectivity is attained with a certain delay. Depending on feed, membrane material, process conditions, and the initial state of the polymer (dry or preswollen), this conditioning time can last from minutes to several hours (Neel, 1991).

Although there is a general consensus that membrane conditioning has to be taken into account for determining steady-state separation characteristics and for startup procedures of technical plants, information on membrane characterization under transient conditions is scarcely available. Permeation experiments for the dehydration of ethanol and isopropanol with polyvinylalcohol (PVA) membranes (Ping et al., 1988) showed a rapid increase of the permeate flux when the vacuum was applied and the membrane was brought into contact with the liquid feed mixture. After reaching a maximum value, the permeate flux decreased to a steady-state value after 10 h. This behavior was explained by a solvent-induced crystallization of the PVA following the swelling-related wave at the beginning. Other authors (Bouma et al., 1995) relate the membrane conditioning to polymer relaxation, which controls the ability of the polymer to accommodate to changes in volume. These studies together with observed membrane conditioning in other experiments (Heintz et al., 1991; Vier, 1995) have in common that initially dry membranes have been employed and, therefore, all time-dependent effects can only be evaluated on this basis.

However, these investigations are not sufficient for answering questions regarding the way pervaporation membranes react to disturbances during operation. Since the membrane is already in a swollen state, conditioning times might be shorter than in the case of a dry membrane. A closer examination of this phenomenon seems interesting, since the economically most attractive application of pervaporation is the combination with other unit operations such as chemical reaction or distillation. Particularly in the case of a direct combination of distillation and pervaporation, the process dynamics of distillation columns (Jacobsen and Skogestad, 1994) might significantly interfere with the operation of the pervaporation unit. Dynamic permeation experiments can answer the question whether stability calculations for such processes should include models on a microscopic level for time-dependent membrane separation performance besides models for the technical pervaporation unit itself (such as permeate condenser, reheater sections, and vacuum vessel).

## Design of the Test Unit

The separation performance of pervaporation membranes is basically influenced by the parameters feed concentration $w_F$, feed temperature $T_F$, and permeate pressure $p_P$. The most pronounced response can be expected for the permeate flux. Accordingly dynamic experiments should be conducted as sketched in Figure 1.

All process parameters are kept constant for ensuring steady-state conditions. At $t_0$, one of the three parameters is rapidly changed to a different value causing the permeate flux to change with time delay. The flux $\dot{m}''_p$ might either directly approach the new value or show a peak before reaching steady state. A similar experimental technique has already been employed for the investigation of selectivities of gas separation membranes under unsteady-state boundary conditions (Beckmann and Shelekhin, 1991).

The construction of a test unit for dynamic experiments has to meet the following demands:

(1) Two separated feed cycles have to be installed for applying rapid concentration and temperature disturbances to

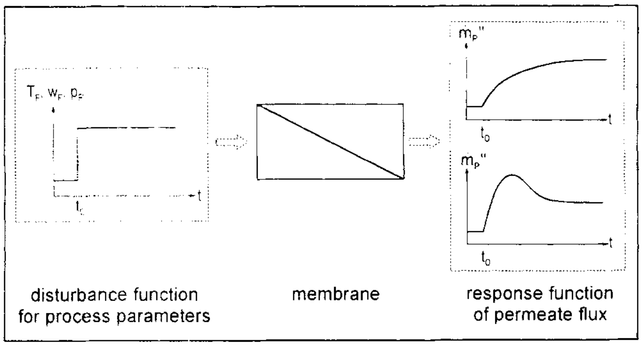

**Figure 1. Procedure of dynamic pervaporation experiments.**

the membrane (disturbances of the permeate pressure can be directly affected by the pressure controller).

(2) The unit must have control equipment to be operated fully automatically for longer time periods in order to reach steady-state conditions. That particularly requires a periodic measurement of the permeate flux and an automatic recycling of the permeate back into the feed loop to avoid any changes in the feed concentration.

(3) For a reliable mathematical modeling, a sufficient data density of permeate flux is necessary, especially for the ascending part of the response function. This requires special permeate condensers allowing the exact removal of small amounts of permeate.

As shown in Figure 2, the two feed cycles are each equipped with a feed vessel (10 L volume), a pump, and a thermostat. Both cycles are equipped with individual control devices and can be separately connected to the inlet of the membrane module. Since it is necessary to preclude any influence of polarization effects or concentration gradients on the dynamic measurement, the installed membrane test cells (two cells in parallel with an effective membrane area of 200 $cm^2$ per cell) possess a tangential feed inlet thus providing a turbulent flow through the feed channel inside. The permeate side is designed with respect to a minimization of permeate pressure drops. For the preconditioning of the membrane, the permeate condensation section (steady-state condensation section) consists of two condenser lines being operated alternately. During the operation of one condenser, the second one is automatically emptied and the permeate flux is measured gravimetrically with the permeate being subsequently recycled into the feed tank. Since a minimum amount of permeate is required for a reliable flux determination, smaller intervals between two measurements of $\Delta t \leq 5$ min. are impossible. Therefore, a second condensation section (dynamic condensation section) were added to the unit. Here the condensers are designed as double-jacket glass tubes with sufficient heat-transfer area. The permeate is removed by a piston placed in the center of the tube allowing the removal of small amounts with high accuracy.

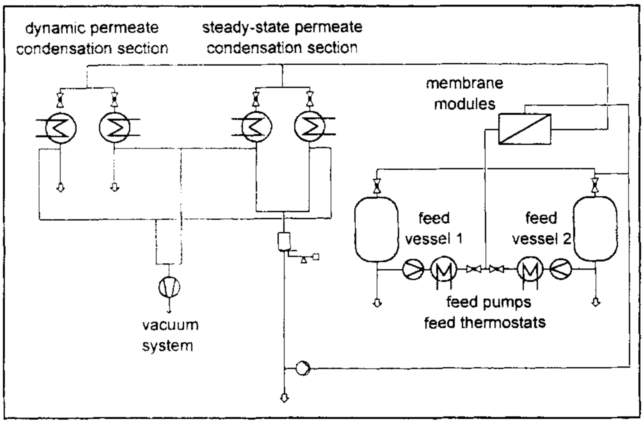

**Figure 2. Pervaporation unit.**

For the first dynamic test series, the dehydration of ethanol and isopropanol with different commercially available PVA/PAN membranes (Sulzer Chemtech GmbH, Germany; CM-CELFA Membrantrenntechnik AG, Switzerland) were chosen, since these applications reflect the state-of-the-art in pervaporation and additionally are interesting for the realization of combined pervaporation/distillation processes. The experiments were mainly restricted to the variation of feed concentrations due to several reasons. First, the data obtained during tests for varying feed temperatures revealed a significant influence of the heat storage capacity of the stainless steel test cells on the membrane performance, so that results are of questionable value for the interpretation of mass transfer under such transient conditions. With respect to process operation, variations of permeate pressure are of minor importance, since this parameter is decoupled from the rest of the process and, therefore, its stability is mainly a question of process control. Furthermore, the influence of variations of the permeate pressure on the driving force is much lower compared to the influence of feed temperature and concentration.

## Results and Discussion

In conventional dehydration experiments, the alcohol/water mixture is fed to the membrane at ambient temperature with the feed being subsequently heated up to the required process temperature. Thus, the time-dependence of the permeate flux due to membrane conditioning is overlapped by startup effects. The alternative procedure is a preheating of the mixture before contacting the membrane. Experiments showed that in this case the membrane structure is irreversibly damaged as a consequence of a fast and strong swelling process. This damage becomes apparent by high permeate fluxes and low selectivities. The third possibility is a "drying" of the membrane by feeding pure alcohol at process temperature.

Figure 3 shows the permeate flux for a PVA membrane (CMC-CA-01, CM-CELFA Membrantrenntechnik AG, Switzerland), which was contacted with pure isopropanol at $T_F = 90°C$ and $p_P = 30$ mbar for 5 days. At $t_0$, the water content was increased to 13 wt. %. The flux increased to a first plateau before approaching the steady-state value of about 1 $kg/m^2h$. The permeate quality was determined to be constant at around 99 wt. % water.

After a return to pure isopropanol, the membrane was allowed to deswell for 4 h. After this period, a second experiment with a stepwise change of feed concentration to $\Delta w_{F,H_2O} = 15$ wt. % was started. The response function depicted in Figure 4 shows a direct asymptotic behavior without any plateau in the ascending part.

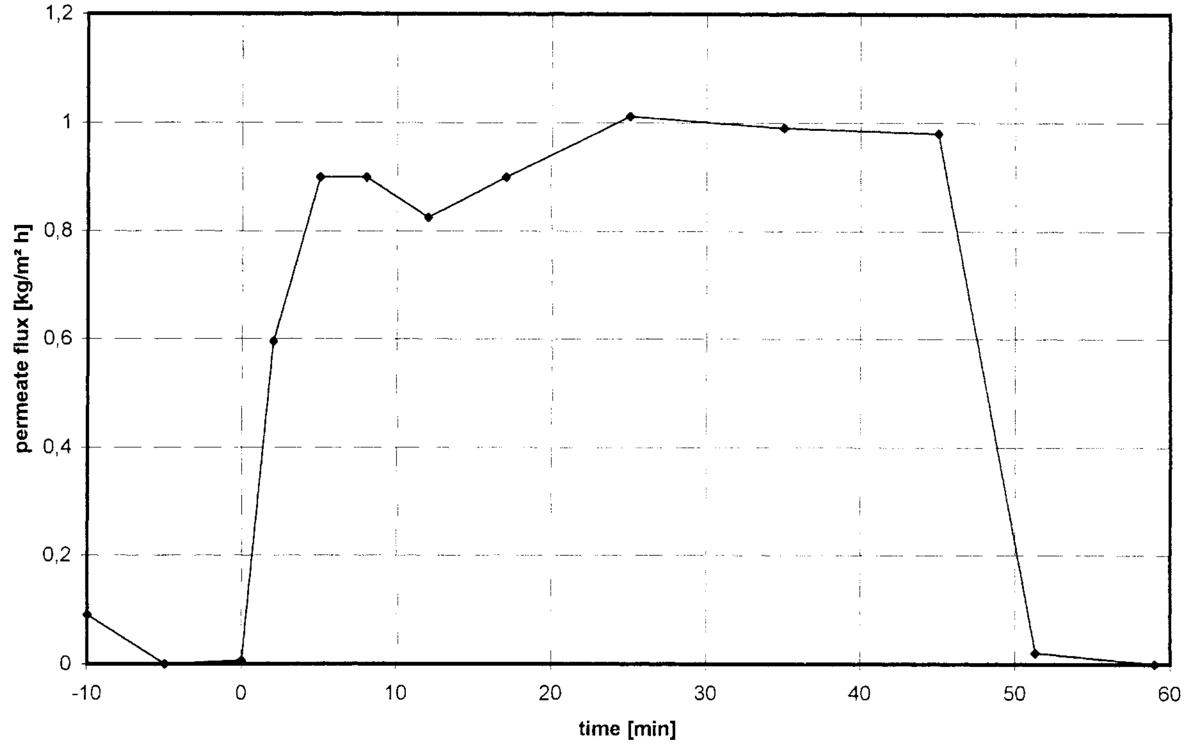

**Figure 3. Permeate flux response for $\Delta w_{F,H_2O} = 13$ wt. %.**

Isopropanol/water, $T_F = 90°C$ and $p_P = 30$ mbar after contact with isopropanol contact for five days.

After the "drying" of the membrane by repeated circulation, with pure isopropanol for five days, a third experiment with a stepwise increase to 22 wt. % water was performed. The feed temperature was set to 70°C in order to obtain an identical steady-state flux. A time-dependent permeation rate similar to the one shown in Figure 3 was observed. Figure 5

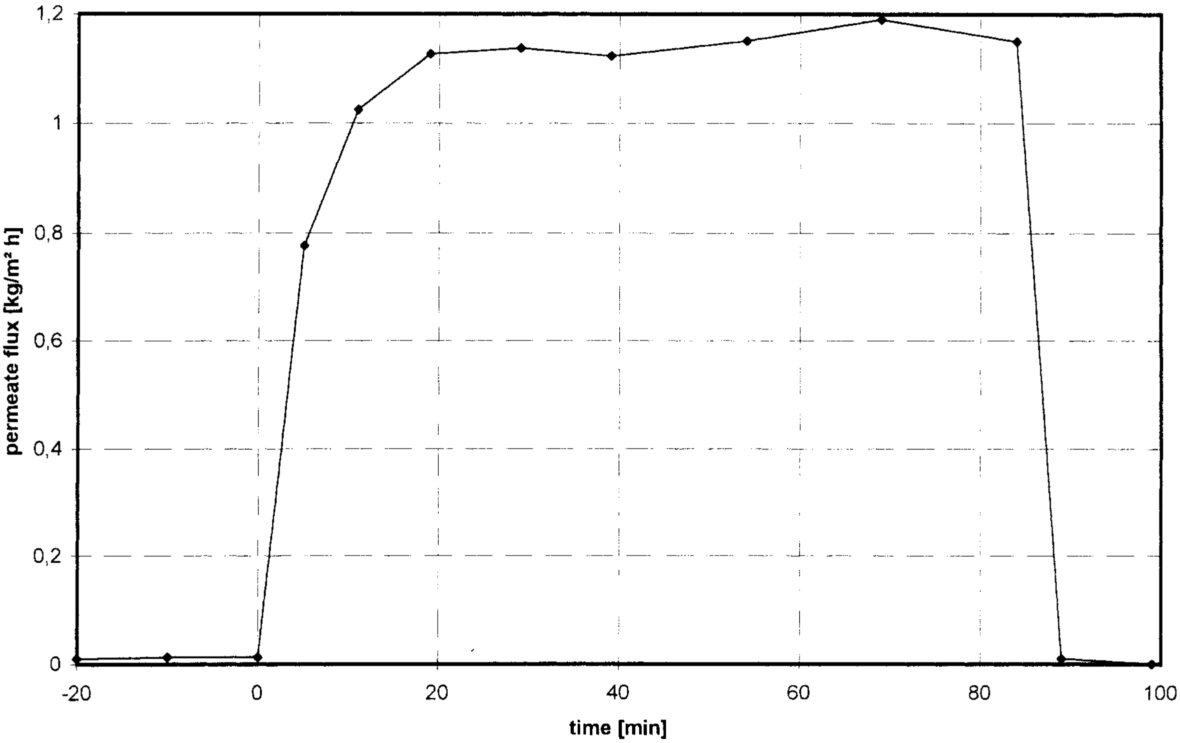

**Figure 4. Permeate flux response for $\Delta w_{F,H_2O} = 15$ wt. %.**

Isopropanol/water, $T_F = 90°C$ and $p_P = 30$ mbar after contact with isopropanol contact for 4 h.

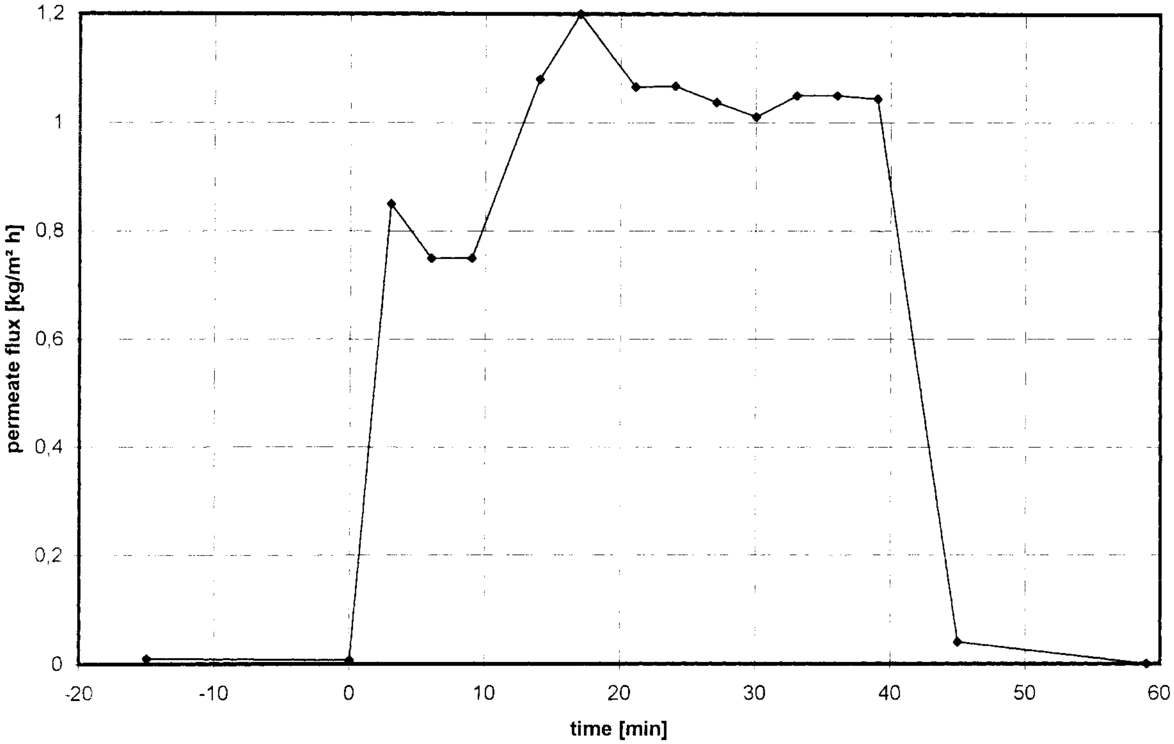

**Figure 5. Permeate flux response for $\Delta w_{F,H_2O} = 22$ wt. %.**

Isopropanol/water, $T_F = 70°C$ and $p_P = 30$ mbar after contact with isopropanol contact for five days.

shows again a plateau at a value of approx. 80% of the steady-state flux. This reaction of the membrane to varying times for deswelling was confirmed in a number of test series. Obviously, it takes longer than a few hours to restore an unswollen polymer structure similar to that of a dry membrane although the flux decreases fast to almost zero. This

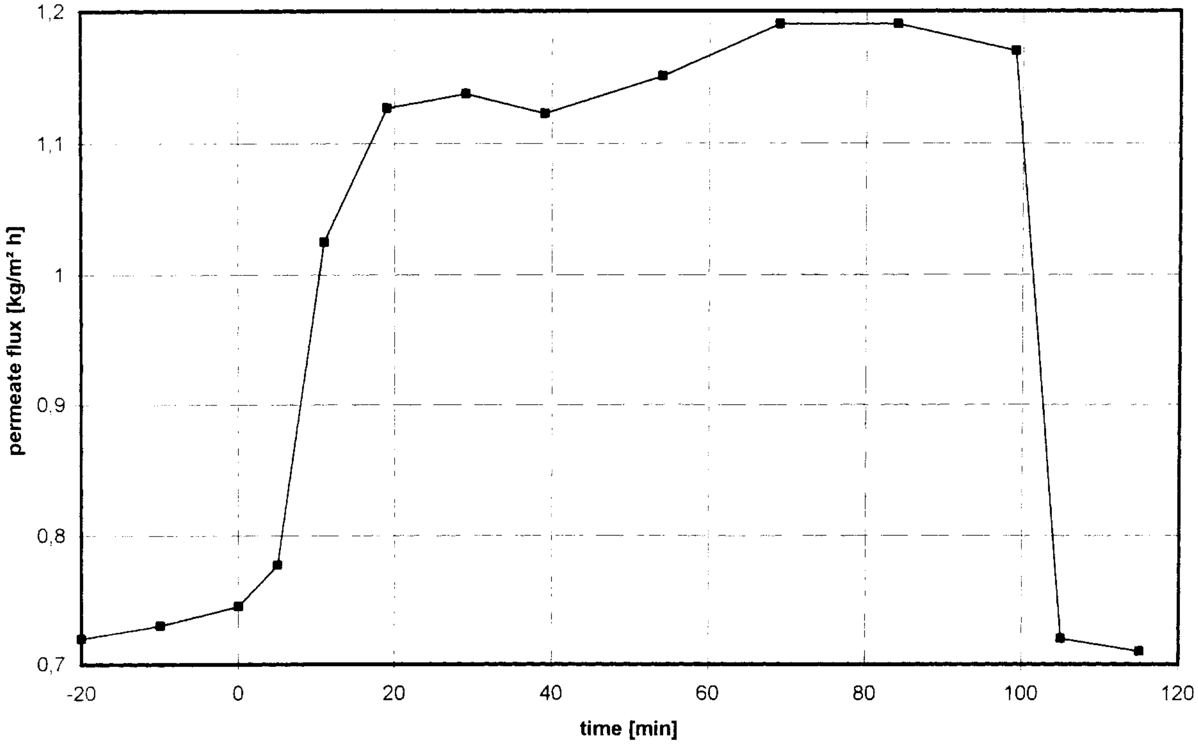

**Figure 6. Permeate flux response for $\Delta w_{F,H_2O} = 7 \rightarrow 14$ wt. %.**

Isopropanol/water, $T_F = 90°C$ and $p_P = 30$ mbar.

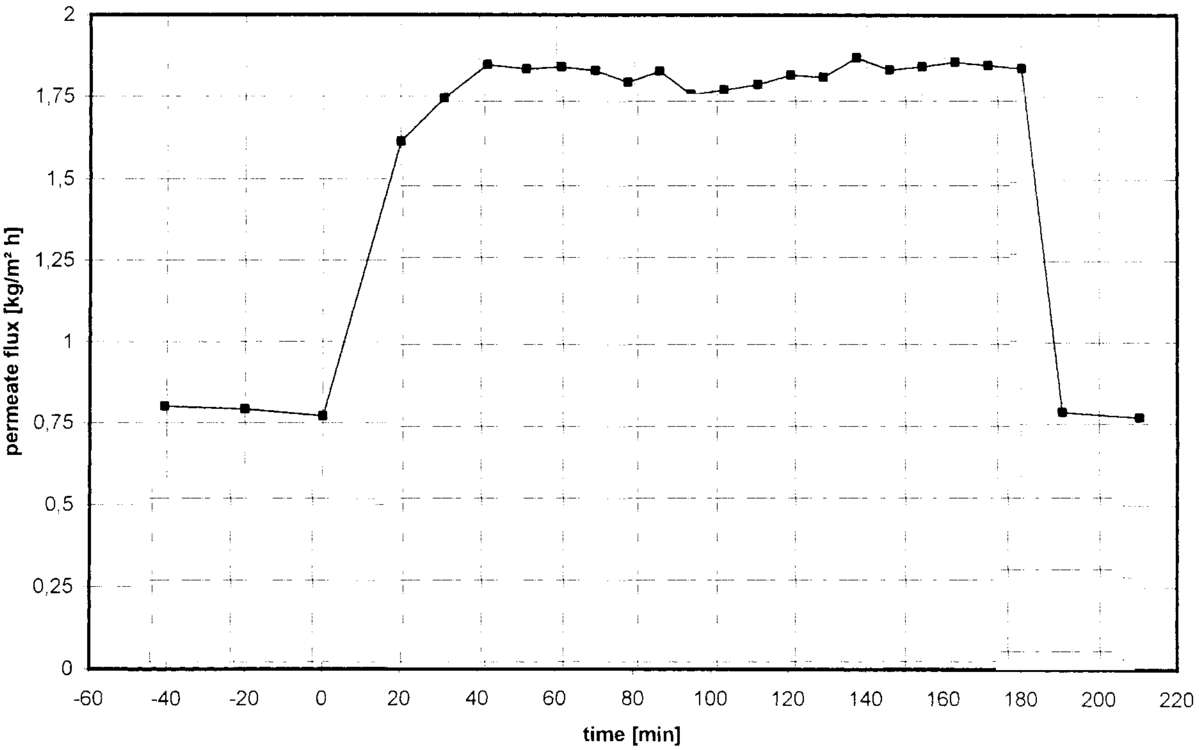

**Figure 7. Permeate flux response for $\Delta w_{F,H_2O} = 12 \rightarrow 20$ wt. %.**

Ethanol/water, $T_F = 90°C$ and $p_P = 30$ mbar.

leads to the conclusion that the time-dependence of the permeate flux for a preswollen membrane is not as distinct as that of a dry membrane. During operation at a constant water content in the feed, the flux response was always similar to that observed in Figure 4. A stepwise variation from 7 to 14 wt. % water did not exhibit any plateau; instead, it exhibited a straight asymptotic approach (see Figure 6). Qualitatively, the behavior is identical for other systems: Figure 7 shows the flux response to a concentration variation from 12 to 20 wt. % water in the case of ethanol dehydration with a different membrane (PERVAP 1001, Sulzer Chemtech GmbH, Germany). The ascending part shows an asymptotic behavior whereas the response to the reestablishment of the initial concentration of 12 wt. % water is without delay. As in the case of isopropanol/water, the permeate concentration increased from 91 wt. % to approx. 95 wt. % water without any remarkable time-dependence.

It should be pointed out that the observed plateaus are definitely caused by the membrane performance and not by any dynamic behavior of the experimental setup. Since the experimental procedure itself was standardized, the same plateaus would have to be detected in all test series. The straight asymptotic characteristics for the preswollen membrane however exclude the possibility of misinterpretations by any data glitch.

From these first dynamic tests, some conclusions can be drawn: Time-dependence can be observed for the permeate flux rather than for the permeate concentration. Furthermore, it appears that the sorption process for solvent uptake takes longer than the release of the solvent, since only a rapid increase of the feed concentration causes a time-dependent membrane flux whereas a rapid decrease leads directly to steady-state fluxes. The results of the experiments suggest a complex interaction between permeating compounds and polymer. Accordingly, it seems worthwhile to continue with dynamic experiments in that area. This would require equipment for fast on-line measurement in order to increase the data density of flux in the interesting range of the response function.

However, with respect to their technical relevance the dynamic effects are of little importance: The adaption time was always lower than approx. 40 min. with the flux reaching about 70–80% of its final value after a very short time span. For smaller concentration variations (such as $\Delta w = 5$ wt. %), the time dependence even vanished. Experimental data for defined disturbances of feed temperature and permeate pressure have still to be collected, but the response functions can be expected to be qualitatively similar.

## Conclusions

The experimental results show that the conditioning behavior of, at least, commercial dehydration membranes during operation is clearly overrated—the time-dependence of the permeate flux on sudden changes in feed concentration is not as distinct as described in literature. Thus, the mass transfer through PVA membranes can be regarded as "pseudo steady-state" with sufficient precision when looking at the dynamics of hybrid processes for solvent dehydration. However, in addition to steady-state techniques for the determination of sorptive and diffusive properties, dynamic experiments can be a tool for membrane development as it reveals a deeper insight into the transport phenomena through pervaporation membranes. That would require a refinement of the experimental procedure presented to increase the data density for a more detailed investigation and modeling of these phenomena.

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