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# Characterisation and modelling of transient transport through dense membranes using on-line mass spectrometry

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## ABSTRACT

This work presents a methodology for characterising solute transport through pervaporation membranes or, more generally, through dense membranes, in the whole transient regime. A real-time characterisation of transport through dense membrane is obtained by using on-line mass spectrometry (MS) monitoring, which allows to acquire the concentration of solutes in the permeate compartment with time intervals of 2 s (and shorter if required). Time-dependent diffusion coefficients,  $D(t)$ , were calculated for the whole operation period, including the initial transient period. Based on these values it is possible to infer about the relevance of solute–membrane interactions and rearrangement of the membrane structure due to the presence of permeant solutes. Finally, based on the information acquired, a mathematical model was developed in order to obtain solute concentration profiles inside the membrane and their evolution along time.

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## 1. Introduction

Mass transport through dense membranes is most commonly studied under steady-state conditions, when constant permeate flux of solutes and solvent is observed. The study of the transient period of mass transport, although more complex, has attracted the attention of researchers because it may offer a route for a better understanding of the membrane under study and how it interacts with the permeating species. Mass transport in pervaporation but also in organic solvent nanofiltration [1], gas and vapour permeation, is usually described by the solution–diffusion model [2–5]. Therefore, estimation of diffusion coefficients during the time-course of the transient transport process is critical. This issue is relatively simple when the permeating species do not induce major alterations in the structure of the membrane, as is the case of most gases when permeating through polymeric membranes, but it becomes rather complex when the permeating species have very high affinity to the membrane, causing swelling and rearrangements in the membrane structure [6], which impact in their flux and selectivity.

The most common technique used to characterise mass transport through dense membranes is the time-lag method, originally conceived by Daynes in 1920 [7], in order to study mass transfer through an elastomeric material. This method was refined and extended by authors as Barrer and Crank, and applied to a large variety of materials. Rutherford and Do published an excellent review of the most significant work developed with this technique up to 1997 [8]. The time-lag permeation method is a flexible and powerful technique that can give both equilibrium (sorption coefficient) and transport properties (diffusivity and permeability) in a single experiment [9]. Nevertheless, the standard mathematical analysis used with this technique assumes that the concentration of the permeating compounds is null inside the membrane at the downstream side and that the diffusion coefficient is constant throughout the transient permeation period. Therefore, the calculated diffusion coefficient does not account for possible material rearrangements that permeating solutes may cause during the initial stage of the transient regime [10–12]. Some authors [13–15] calculated concentration-dependent diffusion coefficients from transient sorption data. These studies were performed by changing and monitoring solute concentration at the upstream face of the membrane, in order to determine the plasticisation parameters of a penetrant, which diffusivity is assumed to depend exponentially with its concentration. However, the treatment of data is established assuming a Fickian diffusion process with a constant diffusion coefficient.

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Most time-lag work has been performed with mono-component gas systems, where data is obtained by an accurate recording of pressure in the receiving compartment but, more recently, several papers have been published using on-line mass spectrometry in order to characterise the simultaneous permeation of multiple species [10,11,14–16]. On-line mass spectrometry (MS) is a suitable monitoring tool for characterising the whole transient regime of permeation of mixtures of compounds through dense films, because it allows for determining permeate compositions and partial pressures, fluxes and selectivities in real-time [17]. Bowen et al. [10] measured constant diffusion rates of different compounds in zeolite membranes using the time-lag analysis through transient responses in the permeate, monitored with a quadrupole mass spectrometer. A similar technique was used by Tanaka et al. [11] to measure the diffusion coefficient in polymeric membranes.

The challenge still relies on the development and validation of an on-line mass spectrometry technique able to acquire composition data in the permeate compartment with a minimal time interval. Ideally, one data-point per second would allow studying systems that undergo a fast change during the initial transient stage of species penetration in the membrane [17,18]. Additionally, the transport of vapours through dense membranes introduces a degree of complexity which results from the non-constancy of the diffusion coefficient along the time-course of permeation during the transient period [8,9] due to the progressive increase of concentration of the permeating species inside the membrane. This increase in concentration may lead to membrane swelling and rearrangement of the polymer material with impact on the permeation process and, ultimately, the diffusion coefficient of these species.

The changes occurring in a membrane during the whole transient regime depend on its internal structure and impact directly on the diffusion of the permeating species through the membrane. Therefore, the study of the whole transient regime may contribute for the fundamental understanding of structure–transport relationships in dense membranes. The design, development and fabrication of new and improved membranes for specific applications will directly benefit from this knowledge.

The goal of this work is to develop an adequate methodology for characterising solute transport through pervaporation membranes or, more generally, through dense membranes, in the whole transient regime. What really matters is the impact of the solute local concentration on the membrane itself and, ultimately, on the ease/difficulty of solute movement (diffusion) across the membrane. To the best of our knowledge there is no way to measure experimentally the solute local concentrations inside the membrane during short transient periods. Experimental approaches such as Raman confocal microscopy could give the required spatial resolution but not within the required time-scale. Therefore, there are not techniques allowing for obtaining local solute concentrations during the fast transient periods under study. The approach followed in this study is based on the ability to obtain permeation data with time intervals as short as 2 s. Considering the extremely high quality of the data obtained (with not observable scatter) this data can be further interpolated, making possible to obtain a “continuum” of permeation data (and a “continuum” of  $D(t)$  experimental values). The approach followed in this work is therefore supported on the assumption that, although the diffusion coefficient does not depend intrinsically from time, this dependence accommodates all possible effects that impact on the diffusion coefficient values.

A real-time characterisation of transport through dense membrane is obtained by on-line MS monitoring in terms of the solute partial pressures and fluxes. With these experimental parameters, together with the sorption coefficients of the solutes in the membranes under study, a mathematical model is developed in order to estimate the permeating solutes concentration profiles across the membrane, along time. The characterisation of the

transient regime was carried out in this work for evaluating the changes that occur in the membrane material when exposed to penetrating solutes. Time-dependent diffusion coefficients,  $D(t)$ , were calculated, supported on the on-line MS monitoring technique, where each increment of time was as short as 2 s.

Two case-studies were selected, corresponding to different systems, using permeating solutes with different affinities towards the membranes under study. The dehydration of solvents, in this case of isopropanol, was selected because it is the most relevant industrial application of pervaporation processes, with important economical savings when compared to conventional distillation processes [19–21]. This system was also selected because, due to the character of the membrane (ceramic, hybrid silica-based, HybSi<sup>®</sup>), minimal changes are expected to occur in the membrane structure during permeation [22–23]. The second case-study selected involves the recovery of aromas from dilute aqueous streams, in this case of dilute ethyl acetate in water. A modified silicon–rubber composite membrane (polyoctylmethylsiloxane–polyetherimide, POMS–PEI) is used in this organophilic pervaporation process and a higher degree of polymer rearrangement is anticipated.

## 2. Experimental

### 2.1. Materials

The components used to prepare the feed solutions were isopropanol (99.8% Merck, Germany), ethyl acetate (99.5%, Merck, USA) and deionised water. Two different types of dense membranes were used, a tubular Hybrid Silica selective ceramic membrane HybSi<sup>®</sup> (Pervatech, The Netherlands) and a modified silicon–rubbery composite membrane of polyoctylmethylsiloxane supported on a porous structure of polyetherimide POMS–PEI (GKSS, Germany). These membranes were selected to be used, respectively, in the dehydration of solvents [24] and in the recovery of a representative aroma compound from wine-must [17,25]. These membranes were used for isopropanol dewatering and for ethyl acetate recovery. The properties of these membranes are listed in Table 1.

### 2.2. Experimental set-up

The pervaporation–condensation system used was coupled on-line to a mass spectrometer using the experimental setup represented in Fig. 1.

The set-up for isopropanol dewatering includes a tubular stainless steel pervaporation cell (Pervatech, The Netherlands) connected to a condenser. The feed vessel was a water jacketed vessel in which the temperature of water was controlled by a controlling bath (model CW 05G, JeioTech, Korea). The pervaporation module and the permeate circuit (to the condenser) was covered with a heating tape connected to a temperature controller (CB100, from RKC Instruments Inc., Japan). A rotary vane pump (DUO 2.5, Pfeiffer Vacuum, Germany) assured vacuum conditions in the permeate circuit and the downstream pressure was measured by a pressure gauge consisting of a capacitance manometer, model 600 Barocel, and a transducer power supply model 1575 (BOC Edwards, UK). The condenser was a glass U-shape

**Table 1**  
Properties of the membranes used in this work.

Active layer	Support	Active layer thickness $\times 10^6$ (m)	Internal diameter (m)	Effective active area (m <sup>2</sup> )
HybSi	Alumina	0.15–0.20	$2 \times 10^{-3}$	$7.5 \times 10^{-3}$
POMS–PEI	PEI	10.0	–	$1.0 \times 10^{-2}$

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