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Multicomponent mass transport in organic solvent nanofiltration with solvent mixtures

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ABSTRACT

This work systematically investigates and models the retention behavior in organic solvent nanofiltration in solvent mixtures using a dense PDMS-based composite membrane. Experiments with n-alkanes as solutes with different chain lengths ($142–339 \, kg \, kmol^{-1}$) were performed. The transport of these solutes is comprehensively quantified not only in pure solvents such as toluene, isopropanol or methanol but also in binary mixtures of isopropanol/toluene and methanol/toluene. Depending on the solvent and on the ratio of these solvents in case of binary mixtures, considerable differences in the retention behavior of these solutes were discovered. Even negative retention could be observed.

Using model parameters from single solvent/solute mixtures, a Maxwell–Stefan model based on the assumption of a solution–diffusion transport mechanism was used to predict the solvent as well as the solute fluxes in multi-component mixtures. A good agreement between experimental data and model could be achieved with pure solvent fluxes and solvent fluxes in binary mixtures. However, predictions of solute retentions in solvent mixtures based on solutes/single solvent systems were insufficient and indicate a richer transport complexity in the binary solute/solvent/membrane system.

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1. Introduction

Over the last years, organic solvent nanofiltration (OSN) has become a viable alternative to the conventional thermal separation process. To use the full potential of OSN, a thorough understanding of the separation mechanism is essential. It is commonly understood that the membrane performance is influenced by solvent properties, solvent composition but also by solute properties [1–5]. Some authors have observed even negative retentions, where the larger solute molecule is enriched in the permeate [6,7].

An investigation with different single solvents (n-heptane, cyclohexane, xylene) and solutes (iron(III) acetylacetonat, 9,10-diphenylanthracene) in the range of $84–612 \, kg \, kmol^{-1}$ using a dense PDMS membrane was carried out by Tarleton et al. [8]. They observed the highest retention using xylene as solvent while the lowest retention was measured with n-heptane as solvent. Zwijnenberg et al. [9] studied the retention behavior of polyisobutylene (PIB) and polystyrene oligomers (PS) dissolved in n-hexane and toluene. They measured higher retentions of PIB and n-hexane as solvent compared with toluene as solvent using a PDMS membrane.

Previous studies investigated the influence of different solvent mixtures on the flux and on the retention. Geens et al. [10] studied for instance the retention behavior of raffinose (MW $504 \, kg \, kmol^{-1}$) with different membranes and diverse binary mixtures of water, methanol and ethanol. Different permeabilities depending on the solvent and on the solvent mixtures were found. They also observed different retentions of raffinose using varying compositions of the binary mixtures. A minimum in retention was found for instance while using a MPF-50 membrane and a water/methanol mixture at 25 wt% methanol.

Using the binary mixtures of methanol/toluene and ethyl acetate/toluene an increasing permeate flux with increasing toluene amount was observed by Silva et al. [11]. In this study a STARMEM™ 122 membrane showed no significant change in the retention of TOABr while using the mixture toluene/ethyl acetate. Only a slight increase was measured while using the binary mixture of methanol and toluene.

Recently, Schmidt et al. [12] published results using five different solutes (n-hexadecane, 2,2,4,4,6,8,8-heptamethylnonane, phenyldodecane, 2,6-diisopropylnaphthalene, triphenylphosphine) in binary and ternary mixtures of toluene, isopropanol and n-hexane. They observed a strong influence of the used solvent on the retention with two different membranes, namely STARMEM™ 122 (polyimide based) and Puramem™ 280 (silicone coated polyimide). Using the binary mixtures of n-hexane and isopropanol for example, a maximum of retentions was observed at 25 wt%

isopropanol. But only a small difference was measured regarding the retention of the five dissolved compounds using the same solvent or solvent mixtures [12].

The dependence of the retention on solute properties is studied for instance by Zheng et al. [13]. They measured the retention of linear alkyl acetates, branched alkyl acetates and cyclohexyl acetates dissolved in methanol. Three different membranes (STARMEM™ 122, STARMEM™ 240, and MPF-44) were used but the same trend could be seen: cyclic and branched molecules show a higher retention up to 88% compared to linear solutes (1%). The molecular shape apparently has a significant impact on the retention.

Even negative retentions were observed by Zeidler et al. [14], Darvishmanesh et al. [15] and in our previous work using organic solvents and a polymeric membrane. Zeidler et al. [14] investigated the retentions of two, three and four ring-type core substances with different functional groups dissolved in ethanol, n-heptane and tetrahydrofuran using a GMT-oNF-2 membrane (PDMS/PAN). A strong dependence of the retention on the used solvent was observed while even negative retentions were measured using ethanol as solvent. Negative retention was also observed by Darvishmanesh et al. [15]. They investigated the retention of STARMEM™ 122 with various dyes dissolved in six different solvents. The retentions of these dyes were strongly influenced by the solvent used. Using for instance n-hexane as solvent, negative retentions were observed up to −70%. Both authors based this observation on the difference of solubility parameters of solvent and solutes and on high interactions between solvent and membrane.

Recently, we reported negative retention of three different linear carboxylic acids (MW=228–340 kg mol^{-1}) and of n-alkanes with different chain lengths (MW=142–339 kg mol^{-1}) dissolved in pure isopropanol and methanol while positive retention was found using pure toluene and n-hexane as solvents. In general, this study discussed the influence of solvent and solute properties on the retention using four different solvents and solutes. Here, positive as well as negative retentions were observed depending on the used solvent [16].

For the mathematical description of nanofiltration processes with organic solvents, the solution–diffusion model (SDM) or extensions of this model are commonly used. [17,18].

Peeva et al. [19] measured the flux and retention of TOABr with different concentrations dissolved in toluene. They found a good agreement between the experimental and calculated data using the SDM. Silva et al. [11] compared a pore flow model and the solution–diffusion model in their publication. Both, the flux of the binary mixtures of toluene/ethyl acetate and the flux of the mixtures of toluene/methanol are well represented by the solution–diffusion model.

The solution–diffusion model is often extended with convective contribution based for instance on imperfections in the membrane. Furthermore, some authors use the Maxwell–Stefan equation, to avoid simplifying assumptions which are included in the solution–diffusion model. Dijkstra et al. [20] compared this extended solution–diffusion model with a Maxwell–Stefan equation. They found a good agreement with both models between the measured fluxes through dense PDMS/PAN membranes of different binary mixtures of pentane, decane and dodecane and calculated data. The Maxwell–Stefan flux model was also used by Hesse et al. [21] for the prediction of different single solvents fluxes and fluxes of solvent mixtures. They showed very good agreement between the calculated data and the experimental data for the measured fluxes but also for the partial fluxes of ethyl acetate and isopropanol in various compositions. Schmidt et al. [22] used a phenomenological permeation model based on the solution–diffusion model with imperfection and extended this model with diffusive and convective coupling fluxes. A good agreement between simulated and experimental data was reported for retention experiments with different solutes dissolved in binary but also in ternary solvents mixtures.

Straatsma et al. [23] also use the Maxwell–Stefan model to model the retention of glucose, different single salt solutions (NaCl, CaCl$_2$, Na$_2$SO$_4$) and ternary ion mixtures of these salts. Here, the experimental results are described well by this model. They also reported that negative Na$^+$ retention can be represented by the model. However, in such aqueous electrolyte systems, the negative retentions of some ions stem from the coupling of the ionic species and the requirement of electro neutrality.

The rigorous characterization of mass transport behavior of solute mixtures in binary solvent is yet unexplored and will be addressed here. Thus this study experimentally investigates the retention behavior of mixtures of n-alkanes with different chain lengths in binary solvent mixtures of toluene/isopropanol and toluene/methanol. A Maxwell–Stefan model is used to describe solvent as well as solute mixture fluxes showing positive as well as negative retentions. We will report potentials and limitations of extracting model parameters from single solvent/solute mixtures and predicting binary solvent/solute mixtures.

2. Theoretical background

Several models have been developed to describe the permeation of organic solvents through dense polymeric membranes. Of these all, the solution–diffusion model presented in 1965 by Lonsdale and Merten [24] is the most commonly used and widely accepted for this purpose. The concept of this model conceives the transport as consecutive three separate steps. First, the permeating component dissolves in the membrane. Once dissolved in the polymer network, the dissolved penetrant molecules diffuse through the membrane and, in a third step, desorb from the membrane at the side of the lower chemical potential. Accordingly, different components are separated due to differences in sorption and diffusion.

Wijmans and Baker [25] gave an excellent review about the experimentally observed phenomena and their description using the solution–diffusion model. Relevant for our contribution is that the apparent pressure difference between feed and permeate sides give rise to differences in chemical potential of all components in the mixture. Assuming thermodynamic equilibrium between the components in the fluid phase and the membrane, the chemical potential in the fluid phase is sufficient to quantify the driving force. Recently, Ogieglo et al. [26] proved the validity of the solution–diffusion model through ellipsometry measurements comparing static pressure and non-equilibrium measurements with hexane permeation through PDMS. The regular solution–diffusion model assumes that the dissolved penetrant molecules in the polymer matrix diffuse independently of each other making any cross-coupling terms superfluous. To describe the transport of solutes in organic solvents and the effect of negative retention, the before mentioned cross-coupling term should be taken into account, as also reported in previous works [20,23,27,28].

Therefore, we suggest this using the generalized Maxwell–Stefan equation (Eq. (1)). Using this fundamental equation also mutual cross-coupling effects are taken into account by considering the individual species in a mixture. Here the friction forces on the right side of this equation are described by $\zeta_{i,j}$ as diffusive friction coefficient between different components i,j or as mutual friction coefficient $\zeta_{i,M}$ between molecules i and membrane M. This friction force has to be equal to the driving forces F_i at a steady