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Study and optimization of the hydrodynamic upstream conditions during recovery of a complex aroma profile by pervaporation

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Abstract

Using a coupled pervaporation-mass spectrometry set-up, the degree of concentration polarization of wine-must aroma compounds was determined in two different flow-cell configurations as a function of the hydrodynamic conditions over the membrane. It was found that for compounds of high sorption coefficient for the respective membrane polymer, concentration polarization might not be overcome, even under turbulent feed flow conditions, contrary to what was observed with compounds of low sorption coefficients. For the recovery of complex aroma mixtures comprising both, it is shown that the hydrodynamic feed flow conditions therefore represent a further degree of freedom for tailoring the permeate composition, and hence the product quality. As a consequence, under defined conditions, concentration polarization can be a desirable phenomenon with regard to the final product quality rather than being considered detrimental to the process efficiency.

Keywords: Pervaporation; Concentration polarization; Aroma recovery; Boundary layer

1. Introduction

In pervaporation, the dependence of the overall solute flux on the flow regime stems from the laminar boundary layer adjacent to the membrane surface where, at dilute concentration of the solute in the feed solution, transport occurs solely by diffusion [1]. As long as this diffusive flux is sufficiently fast, in comparison with the solute flux across the membrane, the boundary layer does not represent an additional transport resistance and the solute concentration at the membrane surface, $c_{i,\mathrm{bl}}$ is equal to that in the bulk, $c_{i,\mathrm{bulk}}$ (Fig. 1). However, if the diffusive flux across the liquid boundary layer is lower than the maximum achievable transmembranar flux at the respective feed bulk concentration $c_{i,\mathrm{bulk}}$, then the boundary layer detrimentally affects the overall transport of solute from the feed bulk to the permeate side of the pervaporation membrane because the membrane surface concentration of solute i will be lower than that of the bulk [2,3]. When the objective of the pervaporation process is the mere removal of components from the feed stream and the primary product is the retentate, such as in the separation of volatile pollutants from water [1,2], one will aim at minimizing the boundary layer resistance in order to maximize solute fluxes and, hence, removal efficiency. In the following it will be shown that if the principal product is the permeate whose composition determines its quality and hence economic value, such as is the case when recovering a complex aroma profile, it might be disadvantageous to straightforwardly minimize the boundary layer resistance.

Using as an example the recovery of a concentrated aroma profile, it will be demonstrated that in this case the hydrodynamic upstream conditions need to be optimized in view of maximizing the organoleptic quality of the aroma permeate rather than with the aim of minimizing the overall solute transport resistance. The respective studies, which will be presented in the following, were conducted using a coupled pervaporation-mass spectrometry (PV-MS) configuration which enables monitoring the perme-

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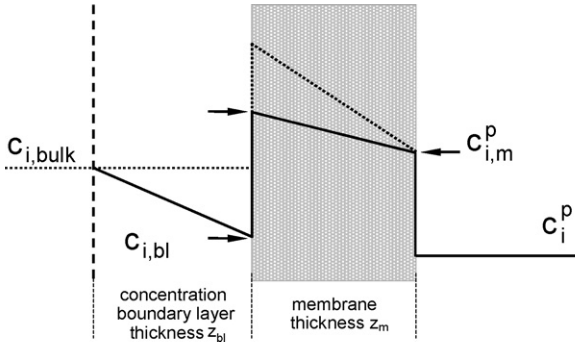

Fig. 1. Simplified scheme of the feed side concentration polarisation phenomenon and membrane mass transport, assuming a constant diffusion coefficient.

ation of solutes under actual pervaporation operating conditions in real-time and with a very high accuracy and time-resolution [4]. The method proved extremely useful for characterising the pervaporation under varying operating conditions as it reduces the experimental workload significantly.

2. Theory

2.1. Membrane mass transport

At steady-state, the flux across the boundary layer, $J_{i,\mathrm{bl}}$, and that across the membrane, $J_{i,\mathrm{m}}$, will be equal, yielding a defined overall flux $J_{i,\mathrm{ov}}$ such that $J_{i,\mathrm{bl}} = J_{i,\mathrm{m}} = J_{i,\mathrm{ov}}$. Assuming Fickian diffusion across both the concentration boundary layer and the membrane, it then follows that

$$J_{i,\mathrm{bl}} = k_{i,\mathrm{bl}}[c_{i,\mathrm{bulk}} - c_{i,\mathrm{bl}}] \tag{1}$$

$$J_{i,\mathrm{m}} = k_{i,\mathrm{m}} S_i [c_{i,\mathrm{bl}} - c^{\mathrm{p}}_{i,\mathrm{m}}] \tag{2}$$

$$J_{i,\mathrm{ov}} = k_{i,\mathrm{ov}}[c_{i,\mathrm{bulk}} - c_{i,\mathrm{perm}}] \tag{3}$$

with $k_{i,\mathrm{bl}}$ is the liquid boundary layer mass transfer coefficient, $k_{i,\mathrm{m}}$ the membrane mass transfer coefficient, $k_{i,\mathrm{ov}}$ the overall mass transfer coefficient, $c_{i,\mathrm{bulk}}$, $c_{i,\mathrm{bl}}$, $c^{\mathrm{p}}_{i,\mathrm{m}}$, $c_{i,\mathrm{perm}}$ the concentration of solute i in the bulk, at the membrane surface in the liquid boundary layer, at the membrane downstream surface, and in the permeate, respectively, S_i is the sorption coefficient of i. Henry-type sorption was assumed based on the experimental evidence that the sorption coefficients were previously found to be independent of the solute concentration in this range of feed concentrations of interest [5]. Combining Eqs. (1)–(3) and assuming vacuum conditions that allow considering the solute concentration in the permeate concentration negligible under the operating conditions, one yields

$$k_{i,\mathrm{ov}} = \frac{1}{(k_{i,\mathrm{m}} S_i / k_{i,\mathrm{bl}}) + 1} k_{i,\mathrm{m}} S_i \tag{4}$$

$$\Leftrightarrow \frac{1}{k_{i,\mathrm{ov}}} = \frac{1}{k_{i,\mathrm{bl}}} + \frac{1}{k_{i,\mathrm{m}} S_i} = \frac{1}{k_{i,\mathrm{bl}}} + \frac{z_{\mathrm{m}}}{L_i} \tag{5}$$

with L_i is the membrane permeability, and z_{m} is the membrane thickness. Eq. (5) is so-called "resistance-in-series model". Combining Eqs. (3) and (5) and assuming both the permeate concentration of i as well as a possible permeate concentration boundary layer negligible, one obtains an overall flux equation that accounts for liquid boundary layer effects during mass transport of solute i:

$$\begin{aligned} J_i &= k_{i,\mathrm{ov}} c_{i,\mathrm{bulk}} \\ &= \frac{1}{(D_{i,\mathrm{m}}/D_{i,\mathrm{w}}) S_i (z_{\mathrm{bl}}/z_{\mathrm{m}}) + 1} \frac{D_{i,\mathrm{m}} S_i}{z_{\mathrm{m}}} c_{i,\mathrm{bulk}} \end{aligned} \tag{6}$$

with $D_{i,\mathrm{w}}$ and $D_{i,\mathrm{m}}$ is the diffusion coefficient of i the liquid feed (aqueous solution) and the membrane, respectively, z_{bl} is the liquid boundary layer thickness.

For modelling the effect of the liquid concentration boundary layer on the overall mass transport of solute i, Eqs. (1) and (2) can be combined to yield

$$\Pi_i = \frac{c_{i,\mathrm{bl}}}{c_{i,\mathrm{bulk}}} = \frac{1}{(D_{i,\mathrm{m}}/D_{i,\mathrm{w}}) S_i (z_{\mathrm{bl}}/z_{\mathrm{m}}) + 1} \tag{7}$$

which is a convenient measure for the degree of concentration polarisation of solute i (Π_i), since it relates the solute concentration in the bulk feed to that in the liquid boundary layer at the membrane surface based on intrinsic parameters. It is pointed out that Eq. (7) is only valid within the frame of the assumptions made.

2.2. Liquid concentration boundary layer mass transport

The boundary layer mass transfer coefficient is commonly described by dimensionless mass transfer correlations of the form

$$\begin{aligned} Sh &= \frac{k_{i,\mathrm{bl}} d_{\mathrm{h}}}{D_{i,\mathrm{w}}} = \frac{d_{\mathrm{h}}}{z_{\mathrm{bl}}} = a\, Re^{\mathrm{b}}\, Sc^{\mathrm{c}} \left(\frac{d_{\mathrm{h}}}{L}\right)^{\mathrm{d}} \\ &= a \left(\frac{v d_{\mathrm{h}}}{\upsilon}\right)^{\mathrm{b}} \left(\frac{\upsilon}{D_{i,\mathrm{w}}}\right)^{\mathrm{c}} \left(\frac{d_{\mathrm{h}}}{L}\right)^{\mathrm{d}} \end{aligned} \tag{8}$$

with $k_{i,\mathrm{bl}}$ is the mass transfer coefficient of i the liquid concentration boundary layer, d_{h} the characteristic length of the flow duct, here the hydraulic diameter of the flow channel, $D_{i,\mathrm{w}}$ the solute diffusion coefficient in the bulk liquid, z_{bl} the concentration boundary layer thickness, L the flow channel length, Sh the Sherwood number, Re the Reynolds number and Sc is the Schmidt number.

For the flow in tubular channels, empirical correlations have been proposed for the laminar flow as

$$Sh_{\mathrm{lam}} = \frac{d_{\mathrm{h}}}{z_{\mathrm{bl}}} = 1.62 \left[Re\ Sc \left(\frac{d_{\mathrm{h}}}{L}\right)\right]^{0.333} \tag{9}$$

and for the turbulent flow as

$$Sh_{\mathrm{turb}} = \frac{d_{\mathrm{h}}}{z_{\mathrm{bl}}} = 0.023 Re^{0.8}\, Sc^{0.333} \tag{10}$$

according to Gekas and Hallström [6]. Cussler [7] gives the factor 0.026 instead of 0.023 in Eq. (10). Further information on parameters used in these empirical correlations is given elsewhere [8].