# Negative retention of dyes in aqueous alcohol mixtures by nanofiltration membranes on the base of PTMSP and PMP

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One of the important goals of solvent resistance nanofiltration technique (SRNF) is to remove dissolved neutral or ionic dyes from hydroalcoholic mixtures. That requires selection of the optimal filtration modes in order to provide the best dye rejection by a polymer membrane and acceptable system productivity as well. This kind of optimization problems can be solved using appropriate mathematical model of the process taking into consideration gradual opening of the membrane pores with increasing applied pressure [1]. Such problems for nanoporous polymeric membranes based on poly (trimethylsilyl propyne) – PTMSP and poly (4-methyl-2-pentyne) – PMP are considered here in comparison between these two membranes. For both PTMSP and PMP-based membranes the flux is not detected at the alcohol concentration less than 45% [2] (in the case of aqueous ethanol solution) up to the pressure of several hundred atmospheres. The effect of negative rejection of a neutral dye (concentrating it in a permeate) was found in our experiments with "Oil Red" for both membranes.

The degree of the neutral dye retention $R$ depends on the effective distribution coefficient of a dye $\gamma_m/\alpha_m$ (the parameter $\alpha_m$ is not much different of 1): the lower $\gamma_m/\alpha_m$ the higher dye concentration in the permeate $C_p$, which can reach several of the feeding concentration $C_0$ (where $(Jh)_{\exp}$ is normalized flux through the membrane measured during an experiment, $\rho$ – mixture density) [3]:

$$R = 1 - \left(1 + \left(\frac{\gamma_m}{\alpha_m} - 1\right)\left(1 - \exp\left[-(Jh)_{\exp}\frac{\alpha_m}{D_m \rho}\right]\right)\right)^{-1} < 0 .$$

The diffusion coefficient $D_m$ of the solute molecules (in our case – neutral dye "Oil Red") can be obtained for example from the processing of diffusion experiments [4]. So, in fact, there are only two adjustable parameters in the theory: $\alpha_m$, which is usually very close to 1 and $\gamma_m$. Note that when using ion-exchange membranes (IEM) for the nanofiltration purification of water-alcohol mixtures from dyes, the negative values of the rejection coefficient can be observed as well, because of a positive adsorption of solute molecules inside the pores is typical for the IEM. It leads to the values $\gamma_m < 1$ [4] and therefore negative values of the potential of specific interactions of dye molecules with the membrane pore walls. The same phenomenon was observed in our experiments during nanofiltration (NF) of neutral dye – "Oil Red" by PTMSP and PMP-based membranes. It means that there is a positive specific adsorption of the dye in the membrane matrices.

The homogeneous model used here for nanofiltration of neutral dyes dissolved in water-alcohol mixture using nanoporous PMP and PTMSP-based membranes allowed quantitatively evaluate the behavior of the rejection coefficient as function of applied pressure/flux under given concentration of ethanol using only two fitting parameters. When using electrolyte solutions of ionic dyes, anyone should take into account the charge density of the membrane that leads to a more complex problem which requires numerical calculations applying analytical formulas which were derived in [3].

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