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OPENING OF THE PORES IN HYDROPHOBIC MEMBRANES DURING NANO-
FILTRATION OF AQUEOUS-ALCOHOL MIXTURES

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There is a lack of fluid flow through the membrane under considerable pressure drops depending on concentration of organic matter during nanofiltration of aqueous–alcohol mixtures (ethanol, butanol, propanol) through hydrophobic membranes based on poly (trimethylsilyl propyne) - PTMSP [1] and poly (4-methyl-2-pentyne) – PMP [2]. The effect is explained by the fact that membrane surface is hydrophobic, and in order to start the filtering process it is necessary to overcome the capillary pressure that arises in the membrane pores which have some characteristic distributions along the radius [3]. The resulting percolation threshold of the liquid is an important characteristic of the effectiveness of nanofiltration of aqueous–alcohol mixtures through polymer membranes. Weighing and volumetric methods which are usually used to determine this quantity are very time consuming. Therefore, the development of express methods for assessing the threshold of the liquid flow and optimize the precision experiments is an urgent task. In developing such procedures, dependence of capillary pressure or flow rate of liquid through the membrane pores on the wettability of the membrane material by this liquid can be used [4]. Through theoretical investigation three distribution laws for the pore radii are considered, i.e. normal-logarithmic law, exponential-power law and approximate triangular law. Originally the meniscus, which radius depends on the capillary radius, is formed in each capillary (pore), and the meniscus radius can be determined by the contact angle (wettability of the membrane material). We assume the Hagen-Poiseuille law for the liquid motion inside each membrane pore. The liquid flux through the membrane is a sum of individual fluxes through all opened pores and can be calculated by integrating over these pores. We found that the dependence of the liquid flux on the pressure difference is nonlinear for small pressure differences, and asymptotically tends to linear law at large pressure differences. So we are able to describe the behavior of the flux of aqueous-alcohol mixtures of different concentrations by varying the membrane pressure drop using our mathematical model without any fitting parameters.

In this work we also analyzed the wetting and the modifying effect of aqueous solutions of butanol in the concentration range $C = 0.15 \div 1.0$ M with respect to the PMP film. It was shown that the wetting tension isotherm has a maximum at $C = 0.125$ M, which appears to be associated with a decrease in the concentration of butanol in the solution which is in contact with the membrane surface, compared with the initial solution concentrations $C \geq 0.125$ M. Using method of Owens-Wendt-Kabli, we defined the polar and dispersion components of the specific surface free energy for the initial PMP membrane and studied their variation for the adsorption modification of the polymer by aqueous solutions of butanol. It was found that with increasing concentration of the modifying solution, first component decreases and second – increases to the constant values for $C \geq 0.125$ M. This result may be related to decompression of the surface layer of the PMP film, due to the inclusion of a polar liquid in the polymer.

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