Bericht zur Max-Buchner-Forschungsarbeit

„Reinforcing Efficient Azeotrope Separation with Outperforming Nanomembranes (REASON)“ (MBFSt-Kennziffer: 3724)

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1. Aufgabenstellung und Zielsetzung

According to the United Nations, the global energy consumption has grown by 50% over the last 30 years, while a quarter of the current demand accounts for transportation. Given the interest in alternative energy sources, the use of biofuels is particularly on the rise as they are readily compatible with the conventional combustion engines. However, the production of biofuels, such as alcohols, is coupled to the problem of chemical separation that is predominantly done by fractional distillation. As the latter is known to get less effective at low alcohol concentrations and to fail at breaking azeotropic mixtures, separation of the aqueous azeotropes is a crucial step in reaching fuel grade. The energy efficiency of the dehydration can be vastly improved by implementing membrane technologies, and recent advances in nanostructured graphitic materials allowing for rapid and selective permeation of water molecules offer intriguing opportunities for pervaporation and vapor permeation processes. The ‘REASON’ project aimed at exploring whether ultrathin water-permeable carbon nanomembranes (CNMs) are able to selectively remove water from alcohols.

2. Durchgeführter Arbeitsplan

CNMs are nanometer-thick materials which are synthesized from adsorbed aromatic molecules via electron irradiation. In this work, we have examined two types of oligophenyl precursors with different head groups and addressed the impact of molecular structure on the transport properties of CNMs [1]. While CNMs from terphenylthiol (TPT) on gold were well documented, a new method has been developed to prepare nanomembranes from terphenyl carboxylic acid (TPC). TPC has been found to react with electrochemically deposited silver in aqueous solutions resulting in free-standing CNMs of extended lateral dimensions (Fig. 1a). There has been no difference observed between TPC and TPT membranes with respect to permeation of water indicating that electron-induced carbonization is insensitive to the precursor molecules.

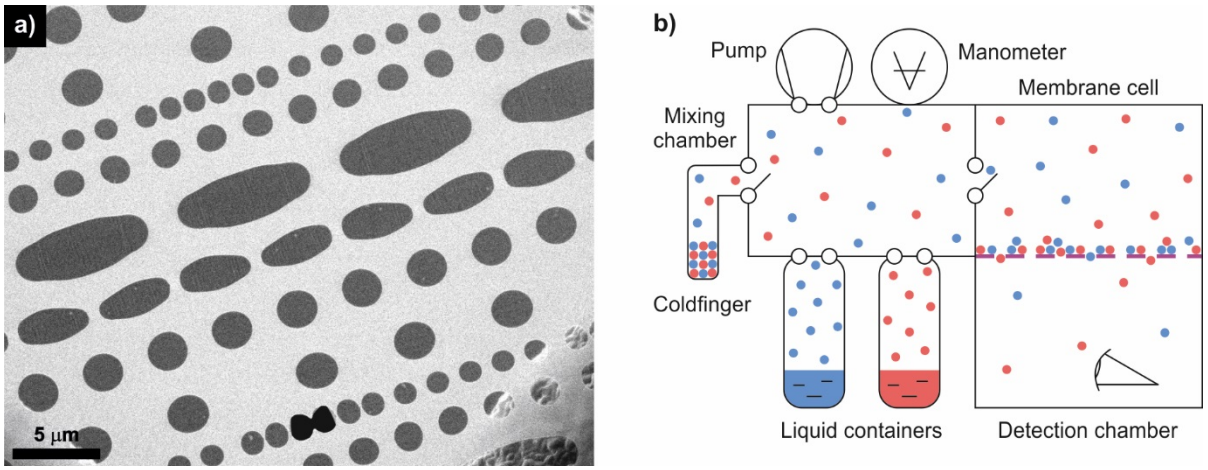

Figure 1. a) Helium ion micrograph of a large area TPC CNM suspended over a TEM grid [1]. b) Schematic of the ACP measurements with vaporous mixtures [2].

In order to study separation performance of the nanomembranes concerned, we have introduced an original experimental approach – Adsorption Controlled Permeation (ACP) – which is based on measuring permeation rates in microscopic samples with the help of a reference nanoaperture [2]. More specifically, a suspened nanomembrane is placed between a sensitive mass-spectrometric detector and a gaseous reservoir of variable atmosphere (Fig. 1b). The ACP method allows for quantifying transmembrane fluxes under well-defined feed conditions and enables experiments with vaporous mixtures. Within the 'REASON' project, we have designed a model aqueous azeotrope consisting of 60 mol % heavy water and 40 mol % propanol. The mixture is prepared *in situ* and has been proven to behave as a positive azeotrope at room temperature [3].

3. Ergebnisse

Fig. 2a illustrates the results of our ACP studies with homologous n-alkanols [3]. As evidenced, the flow rate of anhydrous alcohols in CNMs depends much on the molecular size revealing a rather narrow pore size distribution. While no permeation has been detected for propanol and butanol, the flux for smaller methanol molecules is almost of the same order of magnitude as for water ones. To improve the performance, we have produced composite membranes by placing two CNMs on one another and found a substantial drop in the transport rate of both methanol and ethanol. However, the permeation rate of water vapor in the double-layer stacks has been found to remain as high as in the single-layer membranes. The enhanced selectivity is reflective of a tight interlayer spacing in the composites acting as a bottleneck for permeating species.

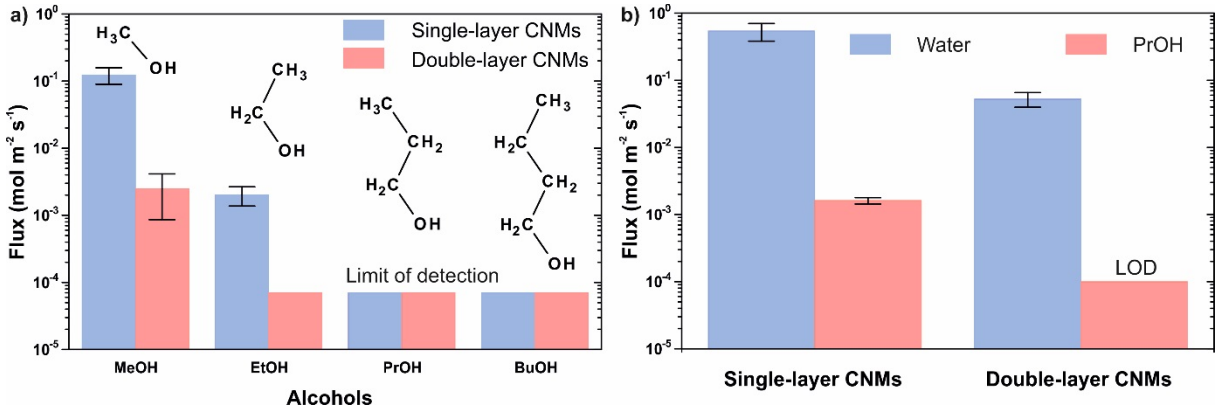

Figure 2. a) Transmembrane flux of pure alcohols in single- and double layer CNMs under saturation vapor pressure [3]. b) Transmembrane flux of D_2O and C_3H_7OH in single- and double layer CNMs upon exposure to the azeotropic mixture [3].

The separation performance has been further tested upon exposing the membranes to the model azeotrope (Fig. 2b). The single-layer nanomembranes have been found to preferentially transmit water molecules with a separation factor of 330. Extrapolating to larger areas, the transport rate measured would correspond to a record value of 35 kg m^{-2} h^{-1} which outperforms the mass flow characteristics of the state-of-the-art membranes. Despite the fact that the double-layer CNMs have exhibited better separation entirely retaining propanol molecules, the flux of water in the stacks has been also suppressed. The observed effect has been attributed to the disruption of hydrogen-bonded water networks by bulky organic solutes. We have performed additional experiments with isopropanol which allowed for gradual variation of the molar composition in the vaporous mixtures and conducting ACP measurements as a function of concentration. The permeation rate of water has been revealed to decrease by a few orders of magnitude as the molar fraction of the alcohol increased from 0.4 to 0.8 [2]. A kinetic model has been elaborated to explain the experimental data.

4. Fazit

In the framework of the ‘REASON’ project, we have studied the performance of free-standing CNMs with regards to water-alcohol separation. Electron-induced carbonization has been established as a generic route for preparing ultrathin microporous CNMs from aromatic precursors. Adsorption Controlled Permeation has been introduced as a new method for exploring transport properties in nanoscale membranes, including model azeotropic mixtures. CNMs have been demonstrated to be suitable for breaking aqueous azeotropes, whereas our findings have also disclosed the impact of hydrogen-bonding on the fast water permeation in nanochannes. For the first time, molecular transport has been studied in free-standing bilayer CNMs, and the stacking has been proven to be promising in terms of engineering nanostructured membranes. However, our research has confirmed the previous theoretical predictions that the less water in the solution, the slower its permeation. We have proposed a phenomenological model to account for intermolecular rearrangements, and our simulations have agreed well with the experimental data. The results obtained foresee challenges in applying nanomaterials to dehydration of organic solvents. While water-selective membranes can be effectively used to concentrate alcohols, alcohol-selective membranes might be more practical at the final stages of upgrading.

5. Literatur

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