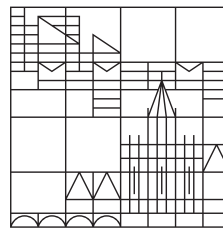# Condensation and evaporation of Hexane in nanoporous alumina membranes

Bachelor Thesis

by

Hermann Böttcher

at the

Universität
Konstanz

Mathematisch-Naturwissenschaftlichen Sektion
Fachbereich Physik

1. Evaluated by   Prof. Dr. Georg Maret
2. Evaluated by   Prof. Dr. Pierre-Etienne Wolf

Constance, 2018

Contents

List of Figures

List of Tables

1 Introduction

1.1 Error sources

1.1.1 Temperature fluctuations

1.1.2 Pressure gauge resolution

1.1.3 Knowledge of the absolute pressure

As to compute the saturated vapor pressure of hexane.

2 Theory

3 Experimental

3.1 Computing the isotherms

To compute the isotherms from the recorded data the experiment needs to the conducted not only with a membrane inside of the cell, but also with an empty cell. From here on, the following indices shall be used:

$$1 \longrightarrow \text{no membrane}$$
$$2 \longrightarrow \text{membrane.}$$

Furthermore, the variables P_i, $\dot{P}_i$, V_i, T_i, n_i and $\dot{n}_i$, $i \in \{1, 2\}$, refer to the values measured inside of the cell, in explanation the red marked part of the system in **??**. The raw isotherms of the two experiments are shown in **??**. The plateaus of the yellow curve with membrane inside the cell of the plot versus time correspond to the dips of the time derivative of the pressure of the versus pressure plot. This can be explained by the hexane condensing inside the membrane's pores at a given pressure due to which the continuing matter flow into the cell does not yield an increase of pressure.
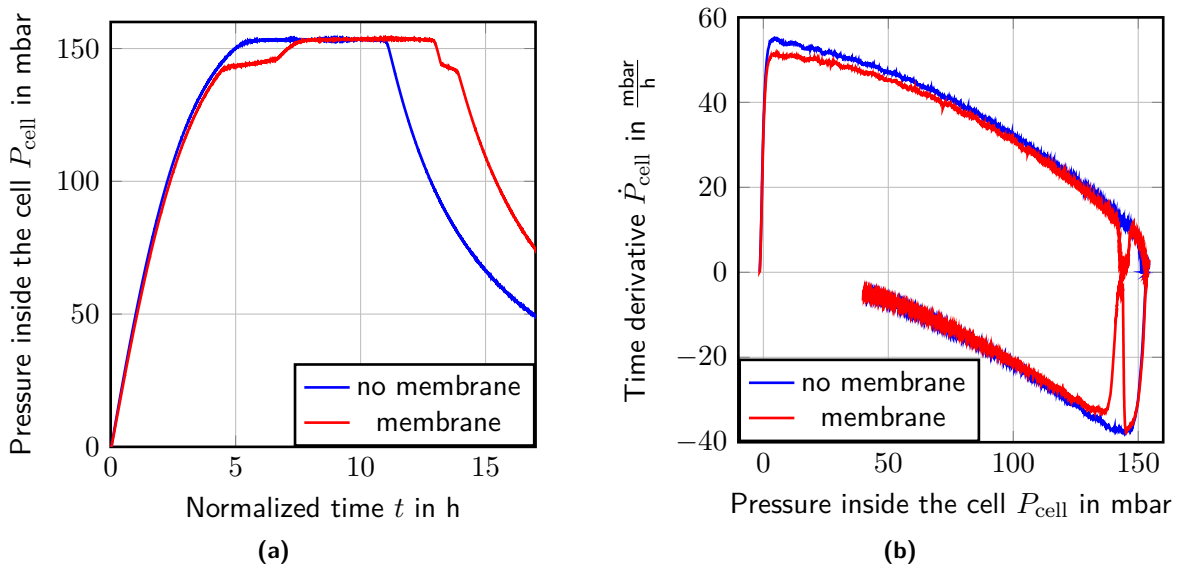
Figure 3.1 Raw volumetric isotherm data recorded with the experimental setup as explained in **??** for one cycle without a membrane inside the cell and one with a membrane inside the cell. (a) shows the pressure values over time making the condensation and evaporation plateaus of absorption and desorption of hexane within the membrane's pores visible. (b) is the pressure loop which is relevant for the computation of the isotherms. Again, the before mentioned plateaus are visible as dips in the time derivative of the pressure.

Regarding the system with and empty cell, it is clear that the ideal gas law can be used to compute the flow rate of hexane (compare **??**). By solving for the amount of matter

$$n_1 = \frac{P_1 V_1}{R T_1},$$

taking into account that the temperature of the cell is regulated at T_1 and the volume V_1 is constant, the flow of matter becomes

$$\dot{n}_1 = \frac{V_1}{RT_1} \cdot \dot{P}_1.$$

Furthermore, the flow of matter for the system with a membrane inside the cell can be interpreted as the sum of the flow into the membrane $\dot{n}_2^{\text{mem}}$ and the flow into the system volume excluding the membrane $\dot{n}_2^{\text{cell}}$. This can be rewritten yielding

$$\dot{n}_2^{\text{mem}} = \dot{n}_2 - \dot{n}_2^{\text{cell}},$$

where $\dot{n}_2^{\text{cell}}$ obeys ideal gas law. Using the fact that the flow through the PFEIFFER valve only depends on the pressure difference $\Delta P_i = P_i^{\text{tank}} - P_i^{\text{cell}}$, assuming that $P_1^{\text{tank}} = P_2^{\text{tank}}$ leads to

$$\begin{aligned}
\dot{n}_2^{\text{mem}}(P_2) &= \dot{n}_1(P_2) - \dot{n}_2^{\text{cell}}(P_2) \\
&= \frac{V_1}{RT_1} \cdot \dot{P}_1(P_2) - \frac{V_2}{RT_2} \cdot \dot{P}_2(P_2)
\end{aligned} \tag{3.1}$$

?? shows the computation steps visually using the respective plots versus time.
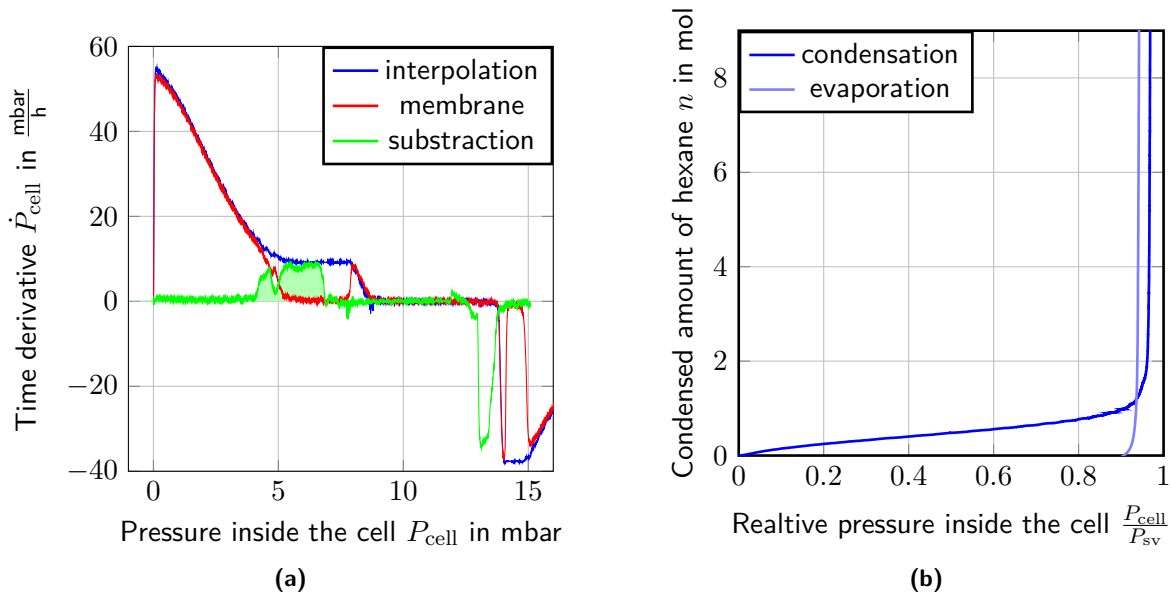
Figure 3.2 (a) shows the raw data of the isotherm with membrane and interpolation of the reference isotherm without membrane. Also, the substraction of the latter (compare integrand of eq. (3.1)) is plotted where the area to be integrated for the absorption and desorption isotherm is shaded light green. The integration according to eq. (3.3) results in the isotherm displayed in (b).

As the temperature of the system is regulated ($T = T_1 = T_2 = \text{const.}$) and because $V = V_1 \approx V_2$ since $V_{\text{mem}} \ll V_1$, equation eq. (3.1) yields

$$n_2^{\text{membrane}} = \frac{V}{RT} \int_0^{t_2} \left(\dot{P}_1(t_1') - \dot{P}_2(t_2') \right) \, dt_2'. \tag{3.2}$$

Important at this point is the dependency of $\dot{P}_1(t_1)$ on t_1 while the integration is over t_2.

As the experimental setup yields discreet values at given time intervals Δt, the data evaluation makes use of a sum rather than an integration.

$$n = \frac{V}{RT} \sum \left(\dot{P}_1(P_1 = P_2) - \dot{P}_2(P_2) \right) \cdot \Delta t \tag{3.3}$$

yields the molar amount of hexane condensed inside the membrane. Figure **??** shows the result of the integration eq. (3.3) for membrane 296d. It is a absorption and desorption isotherm for hexane

Hermann Böttcher

inside the porous alumina membrane. The bulk condensation and evaporation is not visible, as it is also recorded with the reference isotherm without membrane inside the cell.

Moreover, the plots

$$i \quad \text{over} \quad j, \quad i \in \{n, LF, FF\}, \quad j \in \{P_{\text{cell}}, P_{\text{rel}}, D_{\text{kelvin}}\} \tag{3.4}$$

are of interest, where

$$P_{\text{rel}} = \frac{P_{\text{cell}}}{P_{\text{sv}}^{\text{exp}}}, \tag{3.5}$$

with the saturated vapor pressure P_{sv}.

$$LF = \frac{n}{n_{\text{max}}} \tag{3.6}$$

is the liquid fraction of hexane condensed inside the pores of the membrane using the total maximum amount of condensed hexane n_{max} and last,

$$FF = \frac{V_{\text{hex}}^{\text{cond}}}{V_{\text{mem}}} \tag{3.7}$$

with the volume of condensed hexane $V_{\text{hex}}^{\text{cond}}$ and the membrane's volume V_{mem}, is the filled fraction of the membrane. Its maximum corresponds to the porosity of the membrane. For the computation please refer to section 3.1.2.

For the computation of the introduced physical sizes, the saturated vapor pressure P_{sv} must be determined.

3.1.1 Determination of the saturated vapor pressure

As the bulk condensation plateau shows a slight drift (compare figure **??**), using the maximum measured pressure P_{cell} does not yield the saturated vapor pressure P_{sv} but a higher value. In addition, depending on the contamination of the system by air or degassing grease, the measured value for P_{sv} shifts due to the partial pressures. To probe the reproducibility of an isotherm loop including the grade of contamination, the maximum measured pressure for different membranes is compared. As the system is opened to replace the membrane in between the isotherms, each cycle is independent. For the change of membrane process please read **??**. The result of the experiment is that $P_{\text{sv}}^{\text{exp}}$ fluctuates by

$$\delta P_{\text{sv}}^{\text{exp}} = \pm 0.5 \,\text{mbar}. \tag{3.8}$$

As the relevant plateau of condensation and evaporation inside the pores of the membrane occur at about

$$P_{\text{plateaus}} = 140 \,\text{mbar}, \tag{3.9}$$

$\delta P_{\text{sv}}^{\text{exp}}$ translates to an error of about

$$\delta P_{\text{rel}} \leq \pm 0,005. \tag{3.10}$$

3.1.2 Porosity

Equation eq. (3.3) gives the molar amount of hexane n_{hex} condensed inside the membrane's pores. Furthermore, for the given pressures $0 \,\text{mbar} \, to \, 160 \,\text{mbar}$ hexane in its liquid form can be regarded as incompressible and therefore the hexane's volume be computed via

$$V_{\text{hex}} = n_{\text{hex}} \cdot V_{\text{mol,hex}}.$$

. The thickness l_{pore} of the membrane is easily determinable via MEB views since its magnitude is micrometers. Finally, the area A_{mem} of the measured samples is derived from a photo taken using binoculars.

Using these information the porosity ϕ of a given membrane is given by

$$\phi = 1 - \frac{V_{\text{hex}}}{V_{\text{mem}}}, \tag{3.11}$$

with the membrane's volume

$$V_{\text{mem}} = A_{\text{mem}} \cdot l_{\text{pore}}.$$

3.1.3 Light transmission evaluation

As mentioned in **??**, the light transmission setup is independent from the volumetric measurements and also the evaluations do not depend on each other. The light transmission is rather a tool to check on the theory of evaporation and condensation within the membrane using a different approach.

To compute the transmission coefficient of a membrane, it is measured in dry state using the same transmission setup as during the volumetric experiment yielding $T_{\text{mem}}^{\text{dry}}$. Then, the first measured intensity value I_0 of a given isotherm is assigned to the dry coefficient as at this point no hexane is condensed inside of the membranes pores yet. From there on, each intensity measurement is translated to a transmission coefficient according to

$$T(t) = T_{\text{mem}}^{\text{dry}} \cdot \frac{I_0}{I(t)}. \tag{3.12}$$

The aquired physical size can be interpreted as explained in the following section 3.1.3.1.

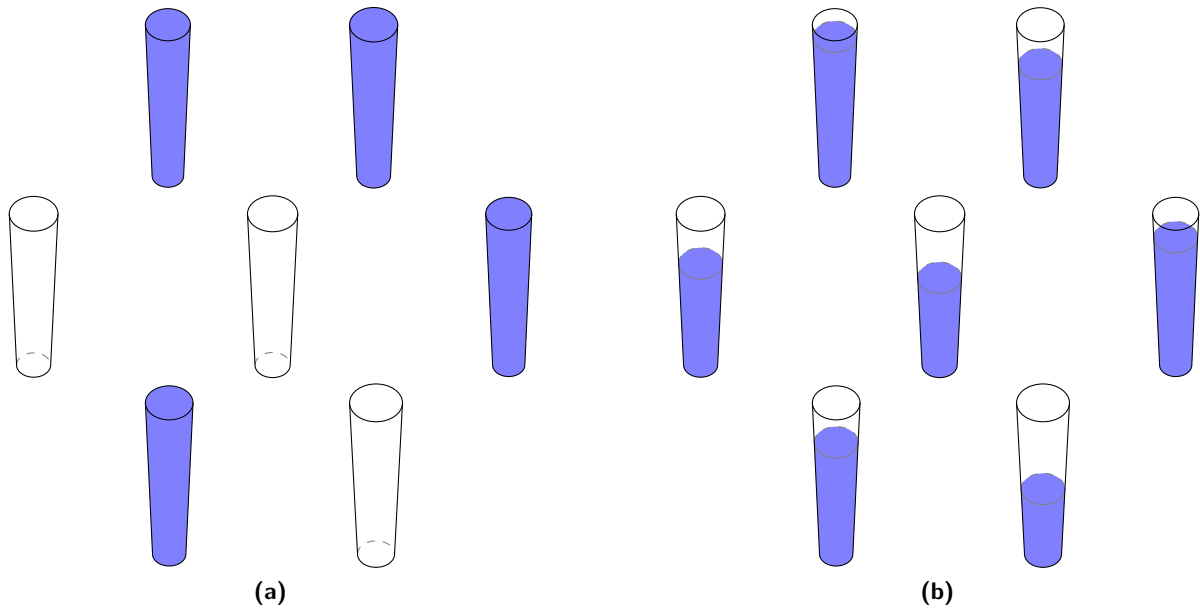### 3.1.3.1 Light transmission interpretations

Figure 3.3 Disorder between neighboring pores during absorption (a) and desorption (b). Important is the larger degree of disorder upon the absorption process. Upon condensation pores fill immediately when the spinodal pressure $P_{\text{sp}}(d_{\text{min}})$ is reached, where d_{min} is the radius of the opening at the small end. The evaporation is continuous at equilibrium pressure $P_{\text{eq}}(d)$ and empties each pore simultaneously while the diameter d is large enough.

Firstly, a completely filled membrane should always yield a higher transmission coefficient T than in its dry state according to the theory of index matching explained in **??**. This fact serves as a tool to optically detect membranes that do not fill completely due to constrictions.

Hermann Böttcher

Furthermore, due to the disorder created by pore filling and emptying, the transmission drops during the processes. Phenomena occurring on the volumetric measurements can therefore be interpreted corresponding to the measured transmission coefficient.

Last, an often observed phenomenon is that the transmission drops to lower values for the condensation than for evaporation of a given isotherm. **??** shows an isotherm of membrane 292d (open pores) where this is the case. A possible interpretation is the degree of disorder caused inside the membrane by the respective process. As the membrane contains pores open on both ends, the condensation takes place at spinodal pressure $P_{\mathrm{sp}}(d_{\mathrm{pore}})$. Due to the distribution of pore sizes, funnelization, corrugation and constrictions, the pores fill at different pressures $P_{\mathrm{sp}}^1 \neq P_{\mathrm{sp}}^2$. At a given pressure

$$P_{\mathrm{sp}}^1 < P < P_{\mathrm{sp}}^2,$$

where P_{sp}^1 shall correspond to the smallest pore diameter found on the membrane and P_{sp}^2 the largest one, the state of the membrane regarding filled and empty pores is assumed to be comparable to figure fig. 3.3 (a). The hexane evaporates at equilibrium pressure P_{eq}, though. That means that, assuming the same pore size distribution, funnelization, corregation and constrictions, the pores empty continuously. The theoretical state of the membrane is visualized in fig. 3.3 (b).

The difference is that during the condensation process neighboring pores can be in very different states meaning empty and filled, while for evaporation the pores only show different levels of liquid during most of the process. As a result, the absorption of hexane creates a higher grade of disorder than the desorption and therefore causes a more significant drop of the transmission coefficient (compare fig. 3.4(a)).

The occurrence of the small peak in between two dips of the evaporation transmission cannot be explained by this theory. Moreover, the later analysed membranes of wafer 295 and 296 yield a more even dip distribution (compare fig. 3.4(c) and fig. 3.4(b)) and upon reducing the pore diameter of 295 using ALD, the membranes even show the inverse behaviour (**??**).

The first phenomenom could be explained by the pores being less flawed talking corrugations and funneling. The latter assumption is backed by the fact, that the transmission drops of 295d are of smaller magnitude than those of 296b. While both are open pore membranes, membrane 295d is only half as thick as 296b, meaning the pores are only half as long and therefore the influence of the funneling aspect is reduced respectively by half.
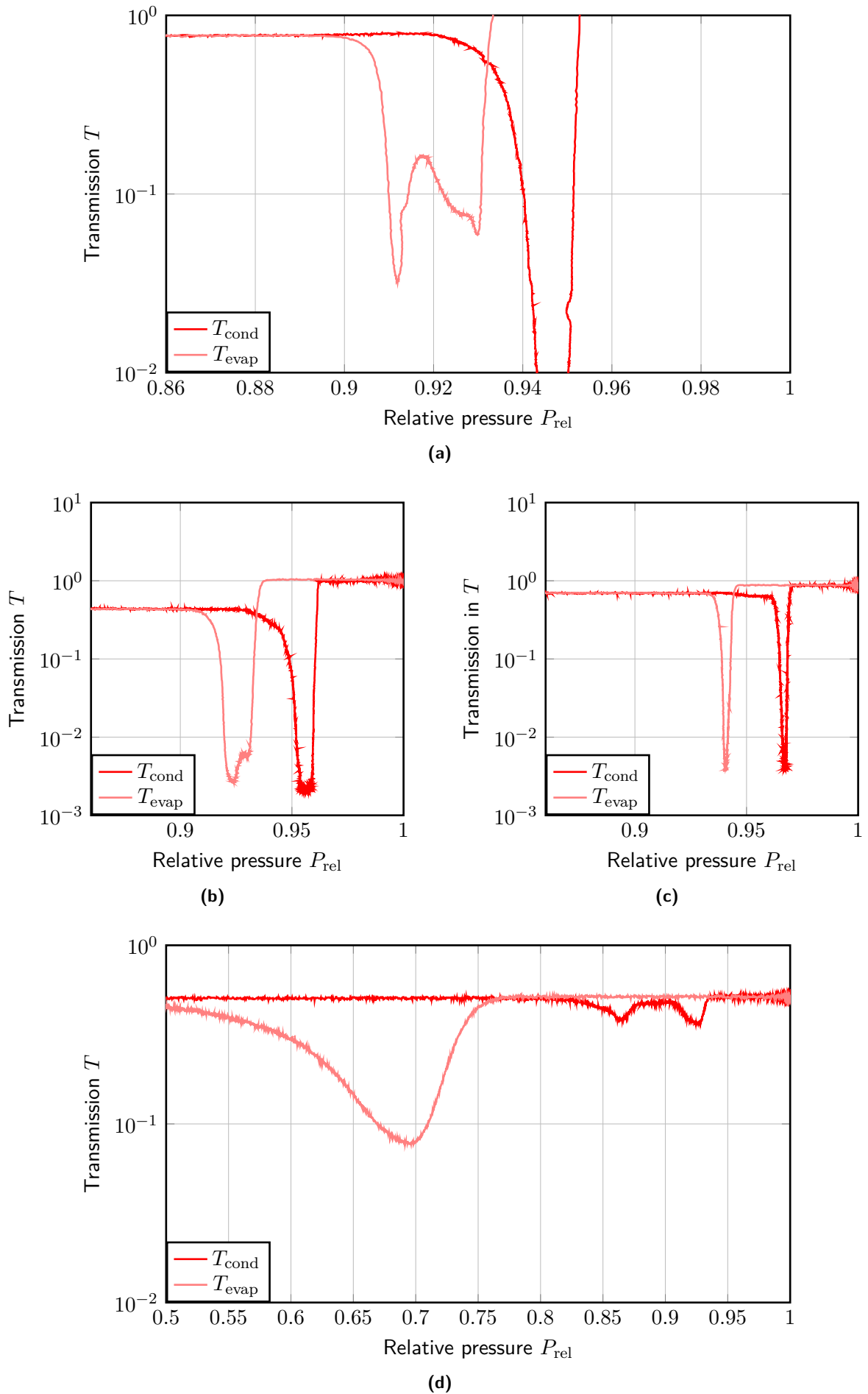
The second one remains unclear though.

Figure 3.4 P_{rel} transmission isotherms of the membranes 292d (a), 296b (b), 295d (c), and 295f 200ALD (d). All membranes have open pores. Unlike the isotherm of membrane 292d, the transmission drops of condensation and evaporation are of the same magnitude. The magnitudes of condensation and evaporation dip are reversed in respect to membrane 292d for membrane 295f 200ALD.

4 Test

Bibliography

[Cd15]   Universität Konstanz: Corporate Design Manual. Universtät Konstanz, (2015)

Hermann Böttcher