Continuous Solvent Stripping with a Modified Micro-structured Device

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Introduction

Chemistry in micro-flow lacks from feasible separation procedures devices, especially for distillation and rectification. To achieve a nearly complete separation of two fluids, the evaporation/condensation step must be performed repeatedly within long distillation columns close to equilibrium conditions. This process is characterized by two important values: the number of transfer units (NTU) and the height equivalent to one theoretical plate (HETP). For conventional distillation procedures the dimensions of NTU and HETP are by far out of the micro range[1]. Some devices and procedures were developed to overcome these scaling drawbacks, e.g. membrane or mesh supported distillation [2], with carrier gas co- or counter flow [3,4], or within micro capillaries [5]. As special device a fast rotating spiral (up to 5,000 rpm) was used to achieve good segregation of the of the gas and liquid phases by induced centrifugal forces [6]. Also a so-called zero gravity procedure, i.e. horizontal heat-pipe distillation is described in literature [7]. Nevertheless, a real application for distillation with microstructured devices is still missing [8]. Removing a volatile solvent from a reaction mixture with a rotary evaporator is a common and very often used separation procedure. Rotary evaporators allow continuous feeding with the reaction mixture and the subsequent stripping of the solvent. To transfer these advantages to the micro scale, an electrically heated falling film device is connected to an actively cooled microstructured counter part, separated by spacers which ensure a stable distance between the two parts. The condensation of the evaporated liquids is realized with a sustainable heat pipe system, which provides dynamic cooling temperatures depending on the heat to be dissipated [9].
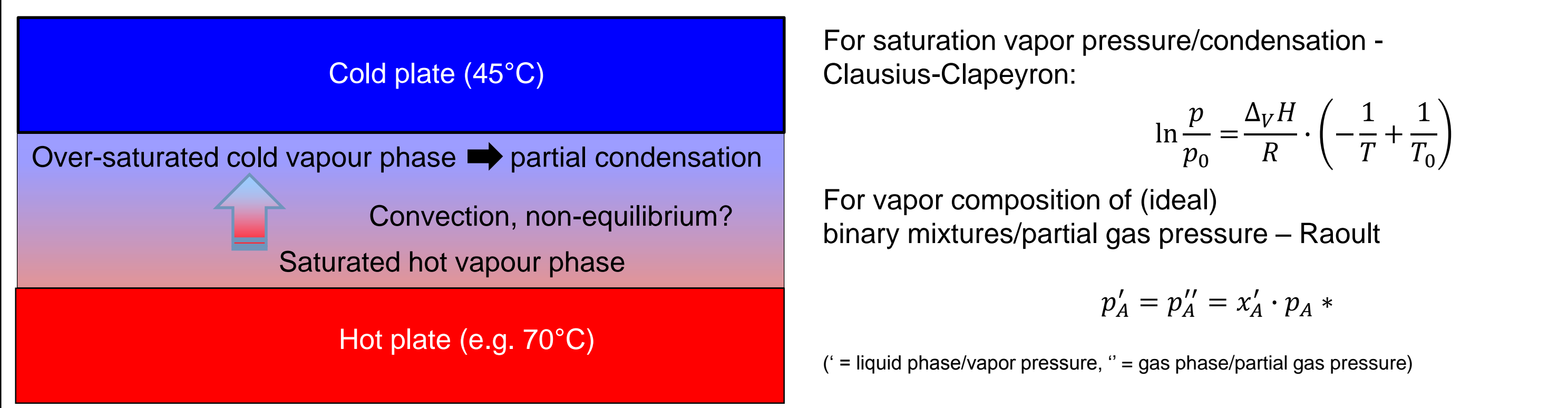
Design of the stripping device
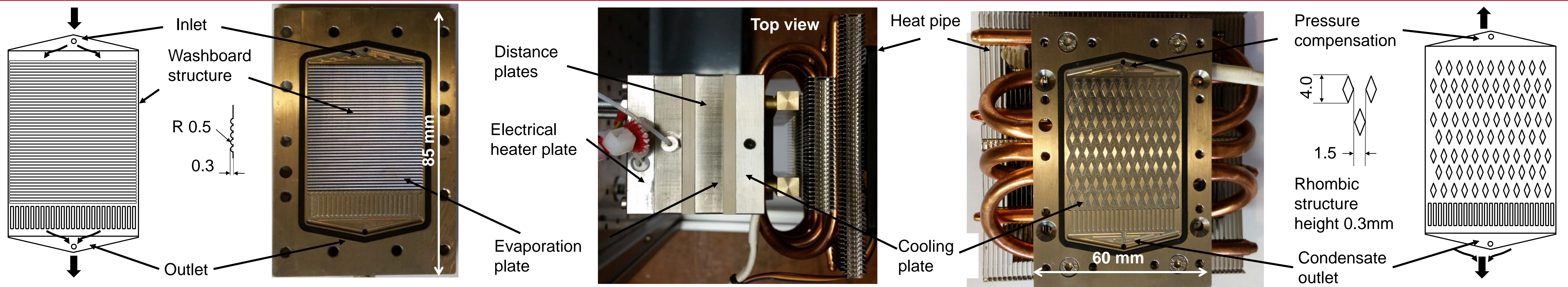
Wetting behaviour of the washboard structure
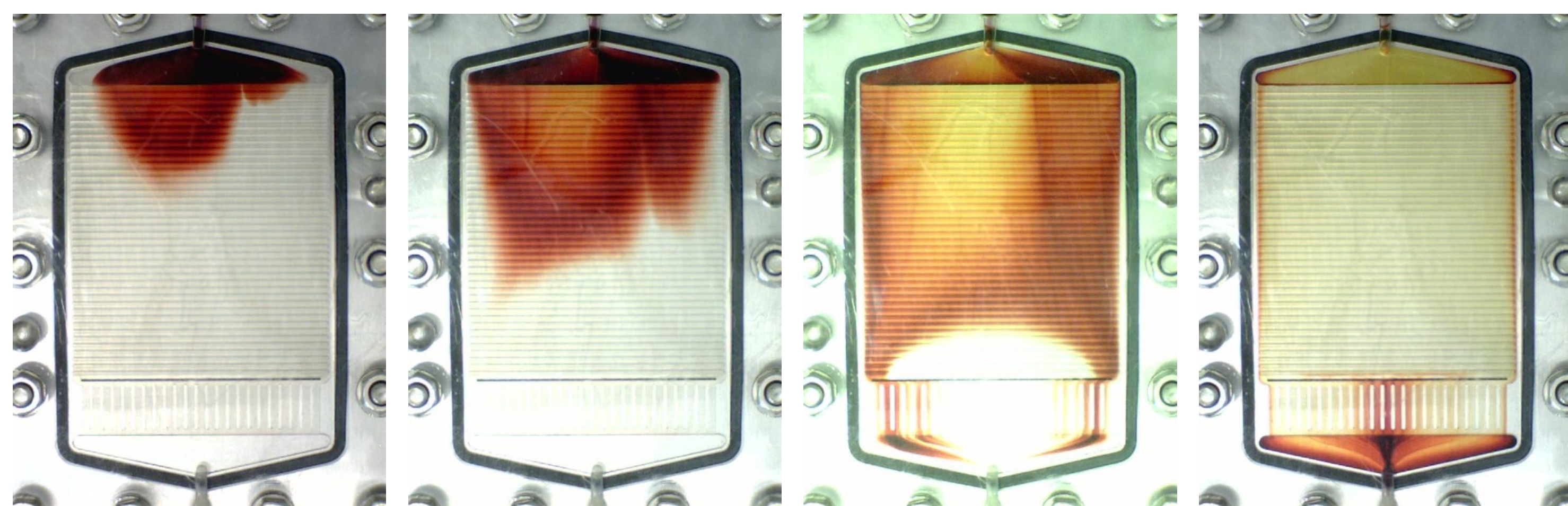
Washboard wetted with a 0.12 mol L^{-1} KSCN solution and subsequent feeding of a 0.04 mol L^{-1} FeCl$_3$ solution with a flow rate of 0.5 mL min^{-1} The colour change indicates the flow profile
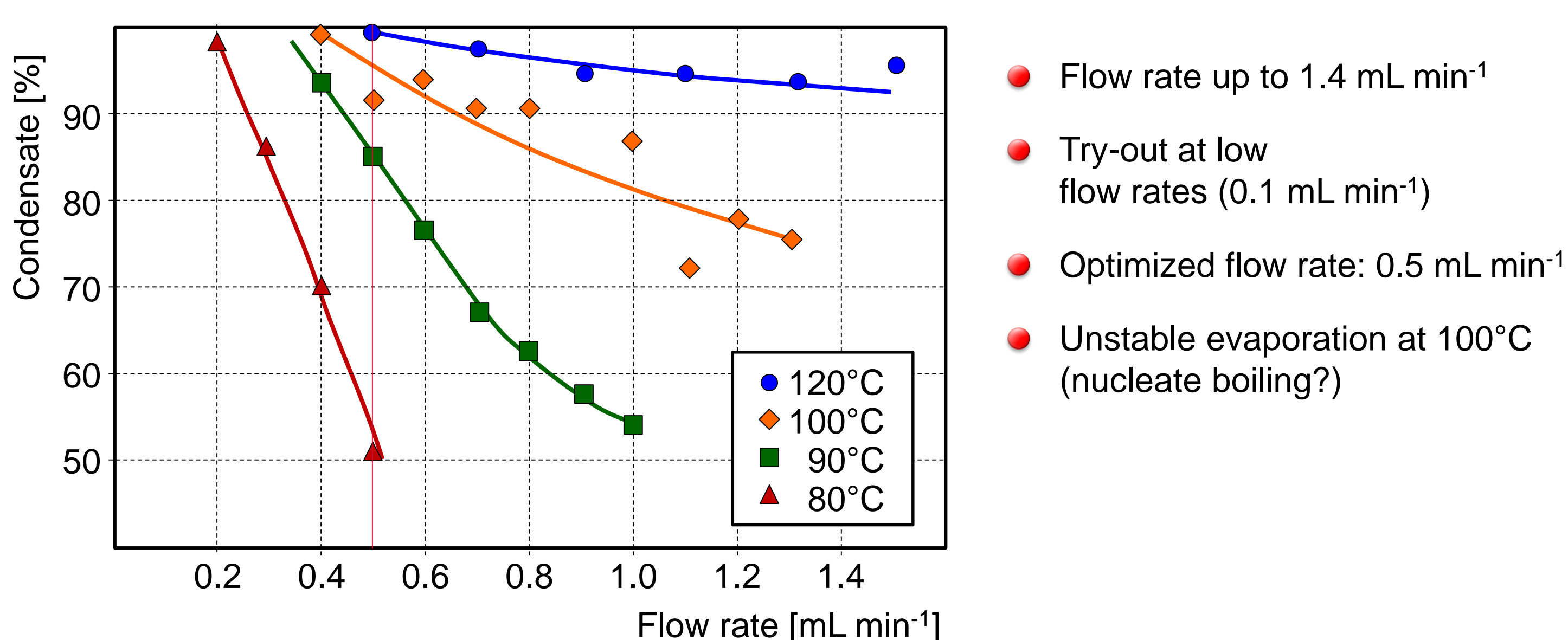
Equilibrium calculation

For saturation vapor pressure/condensation - Clausius-Clapeyron

$$\ln\frac{p}{p_0} = \frac{\Delta_V H}{R}\cdot\left(-\frac{1}{T}+\frac{1}{T_0}\right)$$

For vapor composition of (ideal) binary mixtures/partial gas pressure – Raoult

$$p'_A = p''_A = x'_A \cdot p_A *$$

(' = liquid phase/vapor pressure, '' = gas phase/partial gas pressure)
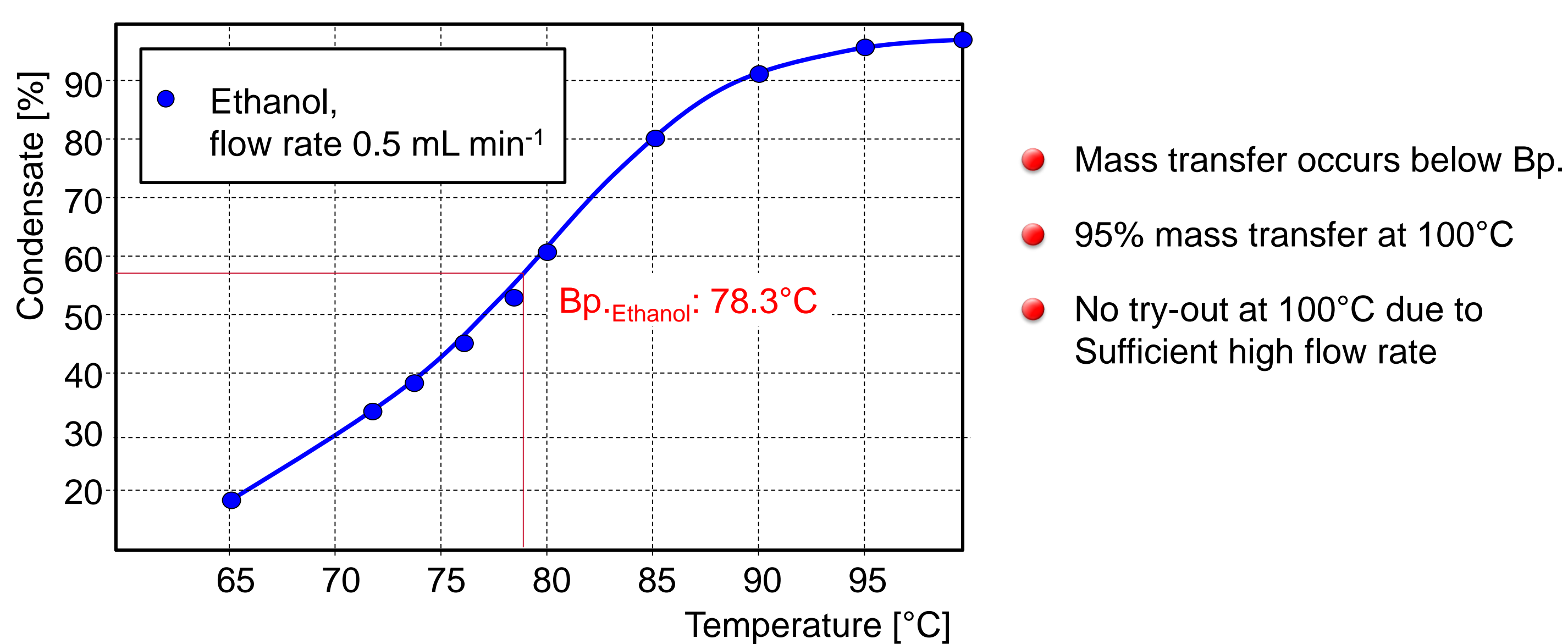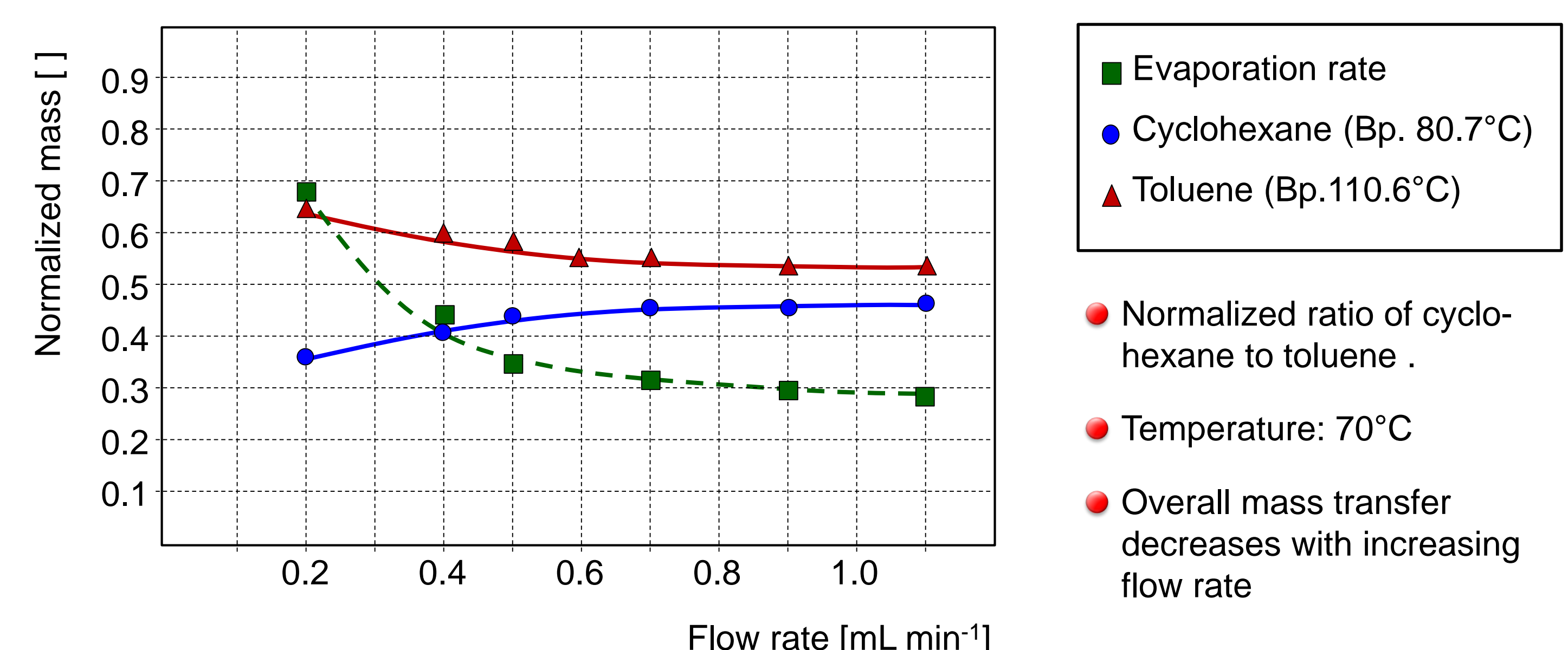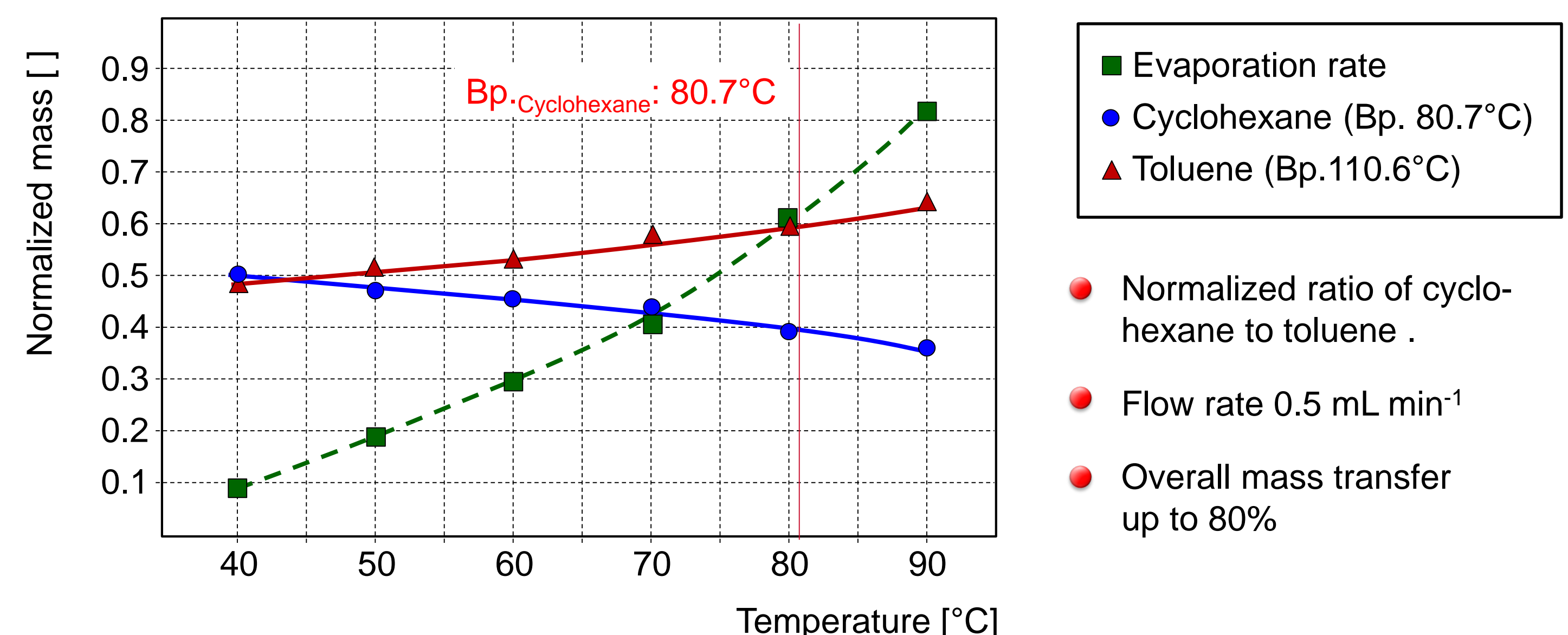
Assumption: evaporation of a 50/50 mol% binary solution of cyclohexane and toluene at 70°C. Condensation on the cooling plate at 45°C. The condensate does not have a 50/50 ratio, therefore, the partial pressures of liquid and gas phases are not equal. To achieve identical partial pressures, some toluene vapor has to be condensate as well as cyclohexane has to evaporated. The resulting set of non-linear equations of 2nd order can be solved by numerical calculation procedures.

Experiment: $\frac{C_{toluene}}{C_{cyclohexane}} = 0.667$ Calculation: $\frac{C_{toluene}}{C_{cyclohexane}} = 0.568$ ➡ thermodynamic equilibrium not achieved

Stripping of ethanol – proof of principle

- Mass transfer occurs below Bp.
- 95% mass transfer at 100°C
- No try-out at 100°C due to Sufficient high flow rate

- Flow rate up to 1.4 mL min^{-1}
- Try-out at low flow rates (0.1 mL min^{-1})
- Optimized flow rate: 0.5 mL min^{-1}
- Unstable evaporation at 100°C (nucleate boiling?)

Stripping of a binary mixture of cyclohexane / toluene

- Normalized ratio of cyclo-hexane to toluene .
- Flow rate 0.5 mL min^{-1}
- Overall mass transfer up to 80%

- Normalized ratio of cyclo-hexane to toluene .
- Temperature: 70°C
- Overall mass transfer decreases with increasing flow rate

Summary

- Microfluidic devices are suitable for performing continuous evaporation of volatile substances , e.g. products, solvents or the excesses of reactive substances

- Stripping of solvents (VOC) allows to remove them from a non-volatile matrix, e.g. a complete removal of ethyl acetate from an Ionic Liquid (not shown here) or to concentrate target molecules from large volume.

- A distillation in its true sense, i.e. the separation of substances with small differences of their boiling points, could not be performed sufficiently.

References
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