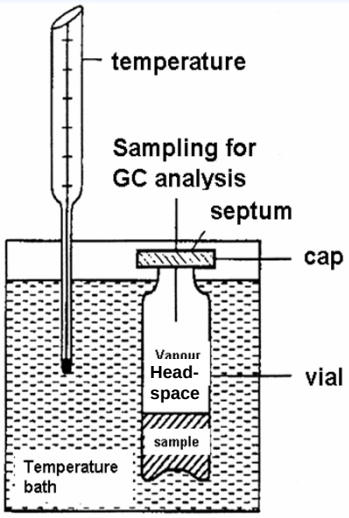
Head Space Gas Chromatography (HS-GC)

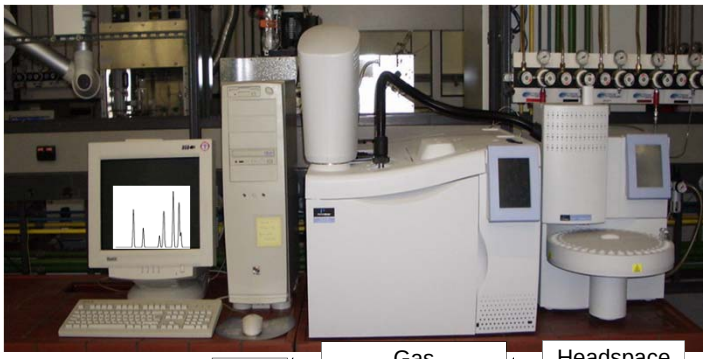
Motivation

- HS-GC can be used for gas/vapour phase analysis above simple or complex liquid and solid mixtures with high accuracy
- Measurements of vapour-liquid equilibria (VLE) can be measured at finite compositions
- Competitive solubility of several gases can be examined (e.g. absorption isotherms)

Experimental setup



- The liquid or solid sample is put into a sealed vial
- Thermodynamic equilibrium is established between the sample and the gas/vapour above it
- The gas phase (*headspace*) is analysed by GC with regard to volatile compounds
- Perfect control of the gas/vapour sampling
  - Temperature control in vials
  - Shaking for faster equilibration
  - Pneumatic sampling for reproducible injection
- Key value: peak area



Data reduction

Way 1 (2-component solvent + nonvolatile entrainer):

- Calibration of detector for the binary liquid mixture of volatiles
- HS-GC analysis for solutions of known composition (x_i) to obtain vapour composition (y_i)
- VLE data (e.g., activity coefficient) from g^E-models or EOS

$$\gamma_i = \frac{y_i P}{x_i P_{0i}^{LV}}; \qquad P = \sum_i x_i \gamma_i P_{0i}^{LV}$$

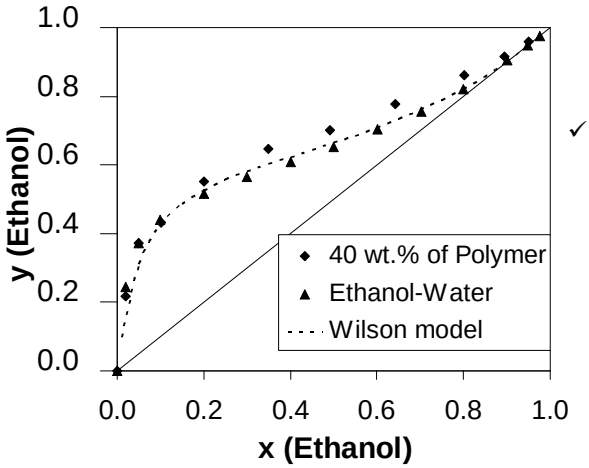
Way 2 (multicomponent systems):

- HS-GC analysis of solutions (x_i) and pure volatiles (x_i=1)
- Peak area is proportional to the partial pressure, $A_i = kP_i$
- VLE data directly from the measurements:

$$\gamma_i = \frac{P_i}{x_i P_{0i}^{LV}} = \frac{A_i}{x_i A_{0i}}$$

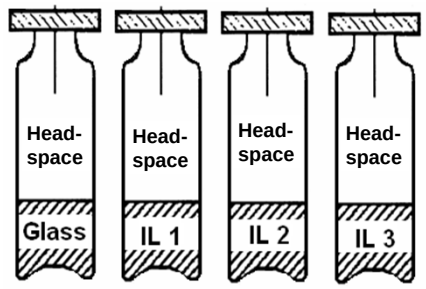
Examples

Hyperbranched polyether as entrainer for the extractive distillation of the ethanol-water mixture

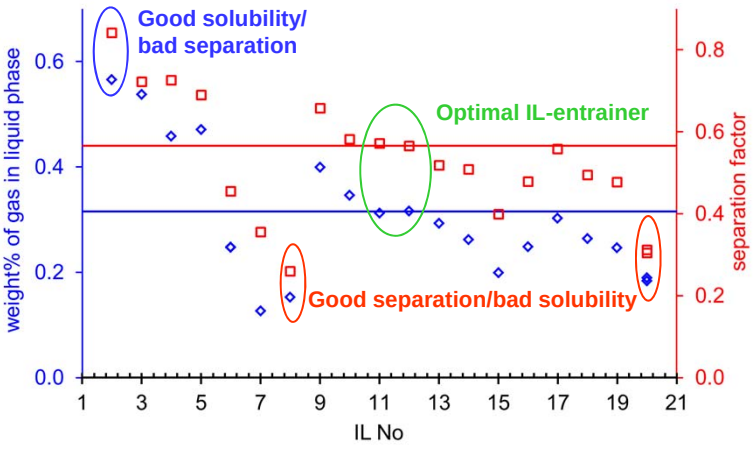


✓ Azeotrope is broken by the polymer

Solvent screening for a propene-propane separation



- 5 ml of IL + 0.05 g of propene+propane mixture of fixed composition in each vial (equal volume of the gas phase!)
- Analysis of the headspace by HS-GC
- Decrease of the propene content in the headspace is a measure of separation
- Decrease of a sum of the peak areas of propene+ propane is a measure of solubility



✓ An optimal entrainer (i) converts the low-boiling propene to the high-boiler shifting the separation factor below 1 and (ii) dissolves propene so effectively that the separation factor is ~0.6

Contact: liudmila.mokrushina@fau.de

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG
TECHNISCHE FAKULTÄT