Investigation of Mixed Gas Sorption in Lab-Scale

Dr. Andreas Möller
Technical Necessity:

Application of porous Materials as Adsorbents

Fine cleaning of Gases (i.e. purification of H₂, natural gas, bio methane…)

Waste air treatment, respiratory protection, solvent recovery, removal of pollutants…)

Gas separation (i.e. Air separation…)

Modern and effective materials should have high sorption capacities, high selectivities, and a good kinetic performance.

For such applications, one must consider gas mixtures and their sorption properties in any case.
Characterization of Adsorbents

**Number of Samples**

- **Chemists**
  - BET
  - Pore volumes
  - Pore size distribution

- **Chemists/Physicists**
  - Pure component isotherms
  - Heat of adsorption

- **chemical Engineers**
  - Technical useable sorption capacity
  - Selectivity
  - Kinetic
  - Cycle stability

- **Engineers**
  - Optimization of process
  - Production

**Process Development**

- **Synthesis and first Characterization**
- **Determination of thermo-dynamic Data**
- **Basic process design, Shaping of Adsorbents**
- **Detailed process design, Application**
Characterization of Adsorbents

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**Detailed process design, Application**
- Engineers
  - Optimization of process
  - Production

**Number of Samples**
- Bench scale, Pilot and Production plants
- Optimi-
Why are Textural Properties not enough…?

Textural properties of adsorbents:

- BET-Surface
- Pore Size Distribution
- Micropore Volume

Textural properties allow only limited qualitative statements regarding:

- expected sorption capacity (Micropore volume)
- rough assessment of general sorption properties from pore size distribution

Textural properties do not allow quantitative statements regarding:

- sorption affinity
- selectivity
- no sufficient information of surface chemistry
Selectivity and Separation factor

Often different definition of selectivity (separation factor)!

**Thermodynamic selectivity and limit of selectivity** $(p \rightarrow 0) \alpha$

Difference of shape of isotherms and of loadings important [1]

$$\alpha_{CO_2,CH_4} = \frac{Y_{CH_4}}{Y_{CO_2}} \frac{X_{CO_2}}{X_{CH_4}}$$

$$\alpha_{CO_2,CH_4} (p \rightarrow 0) = \frac{H_{CO_2}}{H_{CH_4}}$$

$Y$... mole ratio in gas phase

$X$... mole ratio in adsorbed phase

$H$... Henry constants

**Sorbent selection parameter of Rege and Yang** [2]

$$S = \frac{\Delta q_{CO_2}}{\Delta q_{CH_4}} \alpha_{CO_2,CH_4}$$

$\Delta q$... difference in loading between adsorption and desorption

**Kinetic separation faktor** $\beta$

Difference of sorption rates important [3]

$$\beta_{CO_2,CH_4} = \frac{H_{CO_2}}{H_{CH_4}} \sqrt{\frac{D_{CO_2}}{D_{CH_4}}}$$

$H$... Henry constants

$D$... Diffusion coefficients

Dependence of partial and total adsorption amounts

**General:**

\[
n_{CO_2,CH_4,\text{total}} = FKT(Y_{CO_2}, Y_{CH_4}, p)
\]

Investigation along:

**THE READ LINE – Case A**

\[
n_{CO_2,CH_4,\text{total}}(p = \text{const.}) = FKT(Y_{CO_2}, Y_{CH_4})
\]

**THE BLUE LINE – Case B**

\[
n_{CO_2,CH_4,\text{total}}(Y_{CO_2}, Y_{CH_4} = \text{const.}) = FKT(p)
\]
Typical presentation of sorption capacities for binary mixtures

**Case A – variable gas composition**

\[ p = \text{const. (1 bar)}, \text{CO}_2, \text{CH}_4 \text{ on D55-1.5} \]

**Case B – variable pressure**

\[ Y = \text{const. (50:50)}, \text{CO}_2, \text{CH}_4 \text{ on D55-1.5} \]

**X-Y-Plot with statement to the composition of adsorbed phase at constant pressure**

**n-p-Plot with statement to the composition of amount of adsorbed at constant composition of the gas phase**
Mixture Equilibria - Basics

Typical presentation of sorption capacities for binary mixtures

Case A – variable gas composition

Case B – variable pressure

\[ p = \text{const. (1 bar), } \text{CO}_2, \text{CH}_4 \text{ on D55-1.5} \]

\[ Y = \text{const. (50:50), } \text{CO}_2, \text{CH}_4 \text{ on D55-1.5} \]

- **n-Y-Plot** with statement to the partial loading at constant pressure

- **n-p-Plot** with statement to the composition of amount of adsorbed at constant composition of the gas phase
Relationship between loading – mole fraction – selectivity

1. Calculation of **mole fractions of adsorbed phase** from partial loading
2. Calculation of **mole fraction of gas phase** from partial pressures
3. Calculation of **selectivity**
4. Check **plausibility with help of limit for selectivity** (for IAST-Calculations)

\[
X_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{CH_4}} \quad Y_{CO_2} = \frac{p_{CO_2}}{p_{CO_2} + p_{CH_4}}
\]

\[
\alpha_{CO_2,CH_4} = \frac{Y_{CH_4} \cdot X_{CO_2}}{Y_{CO_2} \cdot X_{CH_4}} \quad \alpha_{CO_2,CH_4}(p \to 0) = \frac{H_{CO_2}}{H_{CH_4}}
\]

**Limit of selectivity** can be used to check the results of IAST-Calculations (only for models with Henry range)

Often **Limit of selectivity** do not reflect the **selectivity** for the real separation process, therefore a **single consideration is not enough**
Mixture Equilibria - Models

Models for mixture data

- Extended langmuir-like equations [1]
- IAS-Theory [2]
- VS-Model [3]

Requirements:
- Knowledge of pure component isotherms

- Multi Component-Langmuir (MCLAI)
- Multi Component-Sips (MCSIPS)
- Multi Component-DSLAI (MCDSLAI)

\[ q_i = q_{m,i} \frac{(b_ip_i)^{x_i}}{1+\sum (b jp_j)^{x_j}} \] MCSIPS

\[ \frac{A \cdot \pi}{RT} = \int_0^{p_i} \frac{n}{p} dp = \text{const.} \]

\[ n = \text{Isotherme}(p_{io}) \]

Mixture Equilibria - Models

Models for mixture data

- Extended langmuir-like equations
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- IAS-Theory
  - IAST with Langmuir
  - IAST with Toth
  - IAST with DSLAI

- VS-Model
  - VS-Modell with Wilson

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\[
q_i = q_{m,i} \frac{(b_i p_i)^{x_i}}{1 + \sum (b_j p_j)^{x_j}}, \quad \text{MCSIPS}
\]

\[
\frac{A \cdot \pi}{RT} = \int_0^{p_o} \frac{n}{p} dp = \text{const.}
\]

\[
n = \text{Isotherme}(p_{io})
\]

predictive calculations with dynaSim possible
Calculations of mixture data with dynaSim – Recommendations for pure components

1. Fitting of pure component data at **same temperature for all components**
2. All data as table - **pressure / bar** (mbar) and **adsorbed amount / mmol g⁻¹**
3. **All components** must be fitted with **same isotherm model**

TYP I: Langmuir, SIPS, Toth, DSLangmuir, DSLangmuirSIPS

Typ II: (Freundlich)

Typ IV, V: DSLangmuirSIPS, (DSLangmuir), (SIPS)
Mixture Equilibria - Calculations

Calculations of mixture data with dynaSim – fitting of pure components

1) Copy equilibrium data from EXCEL

2) Choice of a suitable isotherm model

3) Fitting the Model to get model parameter

Example: CO$_2$, CH$_4$ on NaMSX at 40°C
Mixture Equilibria - Calculations

Calculations of mixture data with dynaSim – fitting of pure components

1) Check of coefficient of determination $R^2$

2) Eventually choice of an another model

3) Parameter for mixture equilibria available
Calculations of mixture data with dynaSim – fitting of pure components
Calculations of mixture data with dynaSim – fitting of pure components
Mixture Equilibria - Calculations

Calculations of mixture data with dynaSim – calculation of mixture data

1) Choice of a isotherm model for mixture
2) Input of parameter from pure component isotherms
3) Choice of calculation type (\(p=\text{const.}\) or \(Y=\text{const.}\))

The selected mixture model must include the pure component isotherm model!

i.e.: with SIPS only the Multicomponent-SIPS approach is available
Calculations of mixture data with dynaSim – calculation of mixture data

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Static versus Dynamic Methods

**Static-volumetric Method**

- Sorption in closed chamber
- Measurement of pressure drop
- Pure component isotherms, **mixed gas sorption hard to realize**
  - Standard characterization (BET, Pore volume, pure component isotherms)

**Dynamic Method**

- Sorption in an open system at constant pressure
- Time resolved measurement of effluent gas composition
- **Mainly for mixed gas sorption**, pure component data only with some approaches possible
- Technical processes in „Labscale“
  - Investigations to technical relevant parameters (**selectivity**, sorption kinetic, regenerability, cycle stability …)
- Dosing and **mixing of a predefined gas mixture** in V1 by circulation pump
- Switch to **adsorption chamber V2 and continuous mixing** by circulation pump
- Recording of pressure drop and **analysis of gas phase** after achievement of equilibrium
- Calculation of partial loading based on **mass balance**

→ **Precalculations necessary for a desired equilibrium point**

Headspace Method (HS):

- **Special case** of a static-volumetric setup
- Higher sample throughput as classical volumetry
- Primarily for vapor mixtures suitable

Principle:

- Regeneration under $N_2$ at 150 °C (AC)
- Sometimes preloading with component 1 (i.e. $H_2O$)
- Loading of HS-Vial with sample and VOC **(with µl-Syringe)**
- **Equilibration for several days** in tempered bath
- **Analysis of gas phase** via GC and performing of a mass balance

→ **Precalculations necessary for a desired equilibrium point**

Flow plot of a setup for the dynamic method

- Flow through the regenerated sample with a predefined gas mixture
- Measurement of equilibrium data at a specified pressure and gas composition
  
  → Advantage over static volumetry, no precalculations necessary

A.Möller et al., *Adsorption*, 2016, 23(2-3), 197-209
# Measurement Methods - Overview

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Balancing of breakthrough experiments

\[ n_{\text{adsorbed}} = \int \dot{n}_{\text{in}}(t) \, dt - \int \dot{n}_{\text{out}}(t) \, dt \]

\[ n_{\text{adsorbed}} = \int \dot{V}_{\text{in}}(t) \frac{y_{\text{in}}(t)}{V_m} \, dt - \int \dot{V}_{\text{out}}(t) \frac{y_{\text{out}}(t)}{V_m} \, dt \]

- Widely used approach and simplification for high diluted systems:
  \[ \dot{V}_{\text{out}}(t) = \dot{V}_{\text{in}}(t) = \text{const.} \]

Small changes in concentration minimize this error.
Measurement Methods – Dynamic Technique

- **binary mixture:**
  - CO$_2$/He (non-adsorbable carrier gas)
    - Pure component equilibria
  - CO$_2$/CH$_4$ (adsorbable carrier gas)
    - Preloading of sample with pure CH$_4$
    - Incomplete Determination of the system
      (evaluation mostly simple)
    - Partial loading for CO$_2$ (mixture sorption data)

- **ternary mixture:**
  - CO$_2$/CH$_4$/He (non-adsorbable carrier gas)
    - Displacement of less adsorbed component
      - Partial Desorption, Role-Up Effects
      - Complete Determination (evaluation complex)
  - CO$_2$/CH$_4$/N$_2$ (adsorbable carrier gas)
    - Preloading of sample with pure N$_2$
    - Partial loading for CO$_2$ and CH$_4$
    - Incomplete ternary mixture data
Planning of a Mixture Measurement

- **Calculation of mixture data** desired (Y/N)?
  - Pure component isotherms necessary
- Definition of total flow, measurement temperature etc.
  - **Sample must be under „thermodynamic control“** (always)
- Is a **complete determination of the system** desired?
  - **determination of all partial loadings**, diluting with Helium-carrier gas (Y/N)
- Which **concentration range** is relevant?
  - Calibration of suitable analytic technique (always)
  - Check if any approach is valid, i.e. constant gas velocity …(always)
- Sample preparation and definition of preparation conditions
  - Temperature, carrier gas (always)
- Build up of a measurement routine
  - pressurization, Helium or Adsorptive 1 (**Helium for complete determination**) (always)
- Evaluation of the experiment
Task: Investigation of a binary system

Activated Carbon, CO\textsubscript{2} (25%), CH\textsubscript{4} (75%), complete determination at 5 bar

1. Weighting the sample and sample preparation at 120°C, He-flow 200 ml min\textsuperscript{-1} (STP)
2. Definition of partial pressures: 1,25 bar CO\textsubscript{2}; 3,75 bar CH\textsubscript{4}; 5 bar He; $\Sigma$10 bar
3. Gas flows: 1l min\textsuperscript{-1} (STP) He, 0,75 l min\textsuperscript{-1} (STP) CH\textsubscript{4}, 0,25 l min\textsuperscript{-1} (STP) CO\textsubscript{2}
4. Pressurization with Helium up to 10 bar
5. Start of measurement by simultaneous dosing of CO\textsubscript{2} and CH\textsubscript{4} in Helium
6. Recording of effluent gas composition via MS (all components!)
7. After breakthrough, regeneration of sample for determination of activated mass
Result of an Experiment with a Gas Mixture

Task: Investigation of a binary system
Activated Carbon, CO₂ (25%), CH₄ (75%), complete determination at 5 bar

Result:
Breakthrough curve with “Role-Up”
Effect
- Includes all partial loadings
- Reference on p₃CO₂=0,25 bar and P₃CH₄=3,75 bar
- Mole ratios: y₃CO₂=0,25; y₃CH₄=0,75
- Helium will not be considered!

Integration of areas:
- n(CO₂); n(CH₄); n(total); α
Sequence of several breakthrough curves on Activated Carbon D 55-1.5

**Conditions:**
- 20 °C, 2 L min\(^{-1}\)
- 10 bar (pressurization with N\(_2\))
- Concentrations:
  - 5 % CO\(_2\) - 80 % CO\(_2\) in N\(_2\)

**Procedure:**
- Start further breakthroughs after equilibrium before
- **Integration** and **summation** results in partial loading data of CO\(_2\)
- Volume ratio and total pressure defines the partial pressure of CO\(_2\)

→ **Mixed isotherm data of CO\(_2\) in N\(_2\)**
Measurement Method – Dynamic Technique

Measured partial loading data for CO\textsubscript{2} on Activated Carbon D 55-1.5 at 10 bar

- Dynamic measured data (red)
- IAST-Model (Ideal Adsorbed Solution Theory) based on pure component isotherms (lines)
- Mixture of CO\textsubscript{2} and N\textsubscript{2} shows ideal behavior on AC

Determination of partial loading data of CO\textsubscript{2} on AC D 55-1.5 by performing sequentially experiments along constant total pressure.

$$n_{CO_2,N_2,\text{total}}(p = \text{const.}) = FKT(Y_{CO_2}, Y_{N_2})$$
Assumption of **non-adsorbable** Gas, i.e. Helium as carrier gas will lead to pure component equilibria.

Other, **adsorbable gases** results in mixture sorption data.
An Incomplete Determined System…

5% CO₂ 95% N₂ at 40°C, 5 bar, 2000 ml min⁻¹ on D 55/1.5

Thermodyn. Model (Multi component-SIPS)
- $Y_{CO₂} = 0.05$
- $Y_{N₂} = 0.95$
- $P_{total} = 5\text{ bar}$
- $\alpha_{Model} = 15.7$

Dynamic Experiment (Determination of on partial loading)
- $n_{CO₂} = 0.57\text{ mmol g}^{-1}$
- $n_{N₂} = \text{not determined}$
- $\alpha_{Experiment} = \text{not determined}$

System is only **incomplete determined**. Model is confirmed by experiment.
A Complete Determined System...

5% CO₂ 15% CH₄ in He at 20°C, 5 bar, 2500 ml min⁻¹ (STP) on D 55/1.5

Thermodyn. Model (Multi component-SIPS)

\( Y_{CO_2} = 0.25 \)
\( Y_{CH_4} = 0.75 \)
\( P_{total} = 1 \) bar
\( \alpha_{Model} = 3.53 \)

Dynamic experiment (determination of all partial loadings)

\( n_{CO_2} = 0.86 \) mmol g⁻¹
\( n_{CH_4} = 0.71 \) mmol g⁻¹
\( \alpha_{Experiment} = 3.63 \)

System is complete determined, good agreement confirmed ideal behavior.
Measurements of Vapor Mixtures…

1% EtOH 2,5% H₂O (approx. 80% RH) in N₂ at 25°C, 1 bar, 4000 ml/min on NaMSX

Thermodyn. Model (IAST-DSLAI)

\[ Y_{\text{EtOH}} = 0.322 \]

\[ Y_{\text{H₂O}} = 0.678 \]

\[ P_{\text{total}} = 0.033 \text{ bar} \]

\[ \alpha_{\text{Model}} > 20000 \]

Dynamic experiment (determination of all partial loadings)

\[ n_{\text{EtOH}} = \text{ca. 0 mmol g}^{-1} \]

\[ n_{\text{H₂O}} = 12.9 \text{ mmol g}^{-1} \]

\[ \alpha_{\text{Experiment}} = \text{not determined} \]

Very high selectivity of model confirmed by experiment
Measurements of Vapor Mixtures…

1% EtOH 2,5% H₂O (approx. 80% RH) in N₂ at 25°C, 1 bar, 4000 ml/min on D 55/1.5

Thermodyn. Model (IAST-DSL AISIPS)

\[ Y_{\text{EtOH}} = 0.286 \]
\[ Y_{\text{H₂O}} = 0.714 \]
\[ P_{\text{total}} = 0.035 \text{ bar} \]
\[ \alpha_{\text{Model}} = 2.9 \]

Dynamic experiment (determination of all partial loadings)

\[ n_{\text{EtOH}} = 3.82 \text{ mmol g}^{-1} \]
\[ n_{\text{H₂O}} = 3.11 \text{ mmol g}^{-1} \]
\[ \alpha_{\text{Experiment}} = 3.1 \]

Deviation between model and experiment \(\rightarrow\) no prediction, experiment necessary!
Comparable Measurements of Mixtures

15% Propane 45% Propylene in He at 25°C, 5 bar, 1000 ml/min on A1, A2, A3

Sample: A1

\[ Y_{\text{Propane}} = 0.25 \]
\[ Y_{\text{Propylene}} = 0.75 \]
\[ n_{\text{Propane}} = 0.03 \text{ mmol g}^{-1} \]
\[ n_{\text{Propylene}} = 0.06 \text{ mmol g}^{-1} \]
\[ \alpha_{\text{Propylene}} = 0.67 \]

Sample: A2

\[ Y_{\text{Propane}} = 0.25 \]
\[ Y_{\text{Propylene}} = 0.75 \]
\[ n_{\text{Propane}} = 0.2 \text{ mmol g}^{-1} \]
\[ n_{\text{Propylene}} = 1.7 \text{ mmol g}^{-1} \]
\[ \alpha_{\text{Propylene}} = 2.83 \]

Sample: A3

\[ Y_{\text{Propane}} = 0.25 \]
\[ Y_{\text{Propylene}} = 0.75 \]
\[ n_{\text{Propane}} = \text{ca. 0 mmol g}^{-1} \]
\[ n_{\text{Propylene}} = 2.1 \text{ mmol g}^{-1} \]
\[ \alpha_{\text{Propylene}} = \text{not determined} \]

Selectivity

Statements on selectivity also possible without modeling from pure component data

Determination of sorption capacities and selectivities, recording of kinetic behavior
Equilibria of mixtures and selectivities are important for applications.

Knowledge of such data are highly valuable and of great interest.

However much more difficult to measure as pure component equilibria.

There is a lack of data in literature.

Mixture equilibria can not calculated by textural properties but partial predictive from pure component isotherms based on classical thermodynamic Models.

Predictions have some limits! Number of components, vapors, non-ideal systems...

Investigation of mixture sorption by dynamic method easy possible and should be favored (sequential experiments possible).

We can support you and offer commercial measurement capabilities.
Thank you for your attention!

Please visit our website for further information

www.dynamicsorption.com

via E-Mail on

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