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On-line Nuclear Magnetic Resonance Spectroscopy in Reaction and Process Monitoring

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Nuclear Magnetic Resonance Spectroscopy (NMR)

In NMR Spectroscopy magnetic spin states of atomic nuclei are observed. ^{1}H atoms (protons) and ^{13}C atoms are the most frequently used nuclei for NMR spectroscopy. Providing a very strong magnetic field, different energy states of atomic nuclei can be discriminated. Nuclei in the ground state can be excited with electromagnetic energy in the radio frequency range of the electromagnetic spectrum.

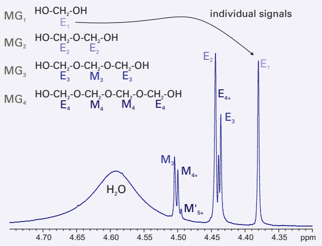


Figure 1: ^{1}H-NMR spectrum of 37.0 wt% formaldehyde in water at T = 298 K and p = 0.1 MPa (pH 5.0) obtained from one single NMR pulse within 3 seconds.

NMR spectra provide individual signals for individual nuclei - even for chemically similar species or from multicomponent mixtures, as can be seen, for example, in Fig. 1 for a mixture of formaldehyde and water.

Such mixtures contain a variety of poly(oxy-methylene) glycols, which are not stable as pure substances.

Engineering applications of NMR

In many engineering processes, complex multicomponent mixtures have to be handled, of which the properties are often only poorly understood. This is a conside-rable obstacle to process modeling and development. NMR spectroscopy is an excellent tool to study such mixtures, e.g., in

- reaction monitoring
- process monitoring

It can provide both qualitative and, for engineering tasks of outstanding importance, quantitative information.

Example: Formaldehyde containing solutions

Formaldehyde is one of the most important chemical intermediates. Due to its high reactivity, it is always handled in aqueous solutions, which usually also contain methanol. In these solutions, formaldehyde CH_2O is almost entirely chemically bound in its reaction products with the solvents (Fig. 2).

The information is, e.g., needed to develop predictive models of the physico-chemical properties of formaldehyde containing solutions but also in the design of reactors and separation equipment, like distillation and absorption columns.

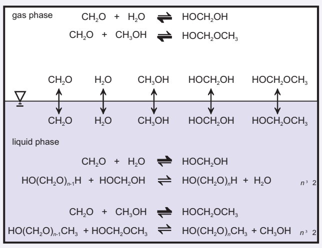
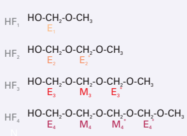


Figure 2: Vapor-liquid equilibrium of the chemically reactive system formaldehyde-water-methanol.

MG	methylene glycol
MG_n	poly(oxymethylene) glycol
HF	hemiformal
HF_n	poly(oxymethylene) hemiformal

NMR spectroscopy allows non-invasive investigations of these solutions and gives reliable information on the distribution of formaldehyde to the different species, both in equilibrium (Fig. 1) and in kinetically controlled processes (Fig. 3).



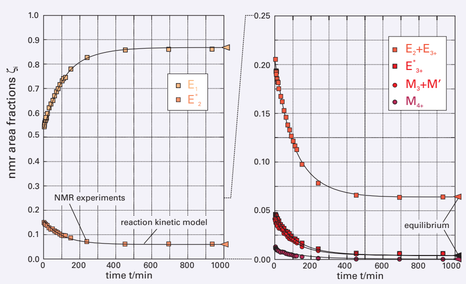


Figure 3: Reaction monitoring after dilution of a formaldehyde-methanol mixture with pure methanol, observed by on-line ^{1}H-NMR spectroscopy including results of thermodynamically consistent reaction kinetics (solid lines) and chemical equilibrium model (arrows).

NMR Techniques

In our group, techniques which allow to directly couple process engineering equipment with on-line NMR spectroscopy are being developed and applied. Investigations are carried out at pressures up to 3.0 MPa and temperatures up to 400 K. Routinely, ^{1}H-NMR and ^{13}C-NMR spectroscopy are used.

An important restriction in most applications of on-line NMR spectroscopy in process engineering is to work completely without deuterated solvents, which are either simply not affordable or not allowable, as they induce isotope effects.

Quantitative flow NMR in process engineering

- fast and direct sample transfer using flow probes (Fig. 4)
- automation (Fig. 5)
- no calibration required as peak areas in NMR spectra are direcly proportional to number of nuclei
- extended pressure and temperature range presetly up to 30 bar and up to 130 °C
- high spectral resolution
- non-invasive analytical technique
- fast (minute range)

NMR flow cell

h = 50 mm
d = 3 mm
V_{total} = 120 µl
V_{active} = 95 µl
T_{max} = 400 K
p_{max} = 30 bar

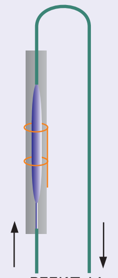


Figure 4: Typical flow cell used for on-line NMR experiments

On-line NMR coupling

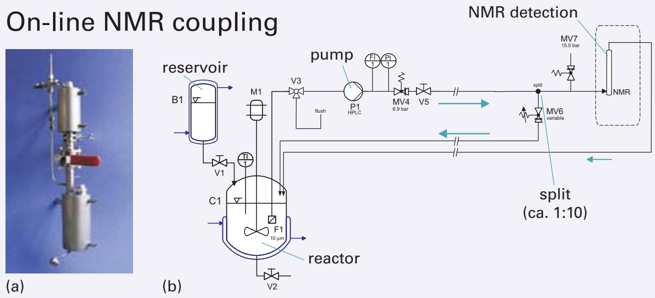


Figure 5: (a) Stainless steel reaction vessel (50 ml reservoir, 100 ml reaction compartment, magn. stirred) for moderate pressures as an example.
(b) Set-up for on-line NMR measurements from a reaction vessel. B1: tempered reservoir, C1: tempered reaction vessel, M1: stirrer motor, V1: activation valve, V2: outlet valve, F1 inlet filter, V3: (tee) purging valve, P1: fully tempered dosing pump, MV4: backpressure regulator (membrane valve), V5: shut off valve, MV6: variable back pressure regulator for split adjustment, MV7:

Infrastructure

A typical laboratory infrastructure with vented cabins is required next to the NMR for engineering process monitoring by on-line NMR spectroscopy. Additionally the NMR should ideally be shielded to ferromagnetic dust and tools.

Our laboratory offers two accessible vented cabins for large scale devices and a mobile cabin for laboratory size reactors next to the NMR (Fig. 6).

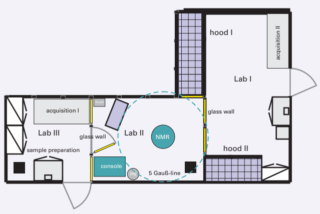


Figure 6a: Plan of three neighbouring NMR laboratories at ITT. Lab I: two accessible vented cabins (h = 3.30 m) for large scale devices, Lab II: NMR magnet, mobile vented cabin, Lab III: acquisition and probe preparation.

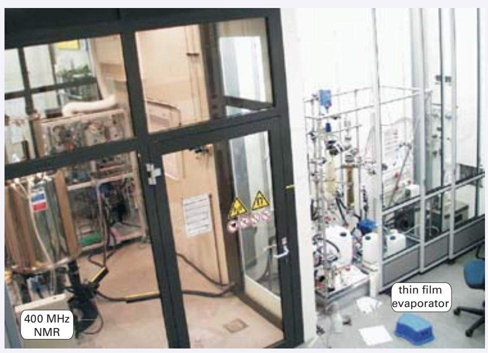


Figure 6b: NMR laboratory at ITT (University of Stuttgart): Direct coupling of thin film evaporator (right) with 400 MHz NMR spectrometer (left). For safety reasons both laboratories are separated by a transparent wall.