



In situ measurement of liquid-liquid equilibria by medium field nuclear magnetic resonance



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ABSTRACT

A new method for non-invasive measurement of liquid-liquid equilibria (LLE) using a compact medium field nuclear magnetic resonance (NMR) spectrometer is presented. Mixing of all components, phase separation, and analysis of the composition of the coexisting phases is performed in situ in an NMR glass tube. Thus, the experimental effort is reduced and errors caused by sampling are eliminated. Furthermore, calibration of the analysis method is not necessary as quantitative information is obtained directly from the NMR spectra. The proposed method for studying LLE in situ can be swiftly conducted in standard chemical laboratories as medium field NMR spectrometer do not require dedicated laboratory infrastructure but enable convenient handling and fast analysis of the samples. In the present work, four non-reactive ternary solvent systems with closed miscibility gap (toluene + acetone + water, diethyl ether + acetone + water, diethyl ether + methanol + water, and acetonitrile + ethanol + cyclohexane) and one reactive ternary system (water + acetic acid + acetic anhydride) were investigated at a temperature of 22.0 °C using ¹H medium field NMR spectroscopic measurements. For comparison, the composition of the coexisting phases is also examined for one non-reactive system (acetonitrile + ethanol + cyclohexane) using ¹³C medium field NMR spectroscopy as well as spatially resolved spectroscopy in a conventional high field NMR spectrometer. The comparison of the results of the present work to literature data shows that the new proposed method enables swift and reliable investigations of LLE.

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1. Introduction

For process design reliable data on physico-chemical properties are essential. For many processes such as extraction processes or processes with decanter information on the liquid-liquid equilibrium (LLE) is required. Typically, tie lines of the LLE, i.e. the composition of the different coexisting phases, are determined using small thermostated batch vessels [1,2]. A known component mixture is stirred until the equilibrium is reached. Then the phases are separated and a sample is taken from each phase. Subsequently the composition of these samples is analyzed using ex situ analysis methods such as liquid or gas chromatography. This procedure has to be carried out for each tie line, which is time-consuming and prone to experimental errors. Furthermore, in many cases the samples cannot be reused after analysis, which may cause problems if only small amounts of substances are available.

In this work, we present a method to investigate LLE in situ with quantitative NMR spectroscopy. The equilibration, separation of the phases, and analysis of the composition of each phase are carried out directly in the NMR sample tube avoiding most of the problems mentioned above.

NMR spectroscopy is an analytic tool with a wide range of applications in chemistry, biology, and chemical engineering [3,4]. NMR spectroscopy has a high chemical resolution and enables to resolve even chemically similar substances. It is a non-invasive analysis method and facilitates the analysis of complex fluid mixtures in situ without sampling.

The basic idea of the method presented in this work is to equilibrate the two phases in the NMR sample tube and adjust the position of the tube in the NMR spectrometer such that first one and then the other phase is measured. This approach requires no sampling thus eliminating sampling errors and facilitating studies of hazardous substances. Contrarily to optical spectroscopy, no previous calibration is needed for quantitative analysis by NMR spectroscopy.

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The ability to obtain quantitative results without calibration is an important feature of NMR spectroscopy as it reduces the experimental effort significantly and enables the analysis of mixtures containing components, which are not available as pure substances or which cannot be isolated e.g. intermediates. In comparison to typically used setups, the sample volume required for the in situ LLE analysis method is much lower and the sample can be reused for measuring several tie lines simply by adding the desired components. Thus, this method can also be applied if only small amounts of the involved components are available.

The preliminary tests that are necessary to determine the required mixing and settling time of the investigated LLE system can easily be carried out with this in situ analysis method simply by repeating the measurement procedure with the same mixture. Besides, it is possible to obtain the composition of a mixture within seconds because of the short total acquisition time of ^1H NMR spectroscopy. Thus, reactions taking place in the different coexisting phases can directly be monitored with the in situ LLE analysis method presented in this work.

In principal, two different types of NMR spectrometers are applicable for the proposed in situ LLE analysis method: high and medium field NMR spectrometer. High field NMR spectrometer have been used in many cases for quantitative investigations and monitoring of reactions and processes by several groups [5–10], listing only a few examples. As described above, the easiest way to analyze the composition of different phases in an NMR sample tube is to change the location of the sample tube within the spectrometer (sample shifting method). However, in commercially available standard NMR probe heads the location of the sample tube cannot be changed significantly. To overcome this obstacle, Leclerc et al. [11] developed a home-built probe head enabling a precise displacement of the sample tube within the NMR active volume. They demonstrated the applicability of this probe head for studying LLE using the system water + toluene as an example. However, only qualitative results and no exact composition of the two coexisting phases were determined. The composition of different phases can also be analyzed in situ in the sample tube using a gradient based spatially selective NMR spectroscopy method (slicing method) as described in Refs. [12–15]. Here, the sample tube does not have to be shifted inside the NMR spectrometer. So far only Mantel et al. [16] have applied spatially selective NMR methods to study liquid phase boundaries, however, without quantifying the concentration of the coexisting phases.

High field NMR spectrometers have the disadvantage that cryogenically cooled super-conducting magnets are required to install high magnetic field strengths of 5 T and more. Thus, high field NMR spectrometers are large and expensive and they need a dedicated laboratory infrastructure such as a vibration free location, constant supply with cryogenic media, and climatisation. In recent years, benchtop NMR spectrometers employing small permanent magnets with high stability and homogeneity of the magnetic field have been developed. These medium field NMR spectrometers have typically magnetic field strengths of 1–1.5 T (corresponding to proton Larmor frequencies of 42.5–60.0 MHz) [17,18]. Furthermore, compared to high field NMR spectrometers, medium field NMR spectrometers have significantly lower investment costs. Without the need of cryogenic media and their small size they are flexible and easily applicable in every day laboratories so that they can be placed for example directly inside a fume hood next to a reactor [19,20]. The lower magnetic field strength and less homogeneity of the magnetic field, however, entail lower sensitivity and chemical resolution compared to high field NMR spectrometers [21]. Nevertheless, it is possible to receive quantitatively evaluable spectra from medium field NMR spectroscopic measurements. Another limitation of the medium field NMR

spectrometers being on today's market is the absence of a temperature control for the sample inside. There are workarounds for this problem e.g. by mounting a dewar inside the bore of the magnet, which insulates the NMR sample tube and enables thermostatisation of the sample without evoking a magnetic field drift of the permanent magnet [20,22]. The problem of thermostating the sample, however, is not in the scope of this paper as this restriction does not limit the usefulness of the proposed method in general. In recent years, several groups have employed medium field NMR spectroscopy to investigate and monitor reactions [22–24] and processes [25–27]. To our knowledge, however, medium field NMR spectroscopy has not been used yet to determine physico-chemical properties of multicomponent systems such as phase equilibria.

Therefore, we apply in this work the in situ sample shifting method in combination with medium field NMR spectroscopy to study the composition of the coexisting phases in four non-reactive (toluene + acetone + water, diethyl ether + acetone + water, diethyl ether + methanol + water, and acetonitrile + ethanol + cyclohexane) and one reactive ternary system (water + acetic acid + acetic anhydride). Thereby, we address the question whether the accuracy of the measurement of LLE using medium field NMR spectroscopy can compete with common LLE measurements using ex situ analysis. For comparison one non-reactive ternary system (acetonitrile + ethanol + cyclohexane) is also examined using the sample shifting method with ^{13}C medium field NMR spectroscopy and a slicing method with ^1H high field NMR spectroscopy.

The LLE data from the present work are correlated using standard models for the Gibbs excess energy (UNIQUAC and NRTL). Furthermore, the experimental results are compared to experimental data from literature. In this context, the data are also depicted with the slope curve method (SCM) first described by Burger et al. [28] to get more detailed information about the characteristics of the investigated LLE systems. The SCM offers the possibility to rate the quality of measured phase compositions in ternary systems more detailed than in Gibbs ternary diagrams by just comparing the binodal curve. Thus the SCM is a appropriate tool to get an overview of the LLE data and assess the applicability of the system for an extraction process.

2. Experimental section

2.1. Chemicals

Table 1 gives information on the used chemicals, the suppliers and the purities. All purities listed here were adopted from the supplier. All chemicals were used without further purification. Ultrapure water was produced using a Milli-Q integral water purification system from Merck Millipore (Merck, Darmstadt, Germany). During the analysis carried out in the present work no significant amounts of side components were detected.

Table 1
Sample table.

Chemical name	Source	Grade	Purity
Cyclohexane	Sigma-Aldrich	Chromasolv	≥ 0.999 g/g
Diethyl ether	Sigma-Aldrich	ACS reagent	≥ 0.995 g/g
Acetic anhydride	Sigma-Aldrich	ReagentPlus	≥ 0.990 g/g
Deuterium oxide	Sigma-Aldrich	–	≥ 0.999 g/g
Acetonitrile	Carl Roth	Rotisolve	≥ 0.999 g/g
Acetic acid	Carl Roth	Rotipurán	≥ 0.998 g/g
Methanol	Carl Roth	Anhydrous	≥ 0.998 g/g
Ethanol	Merck	Uvasolv	≥ 0.999 g/g
Toluene	Merck	Uvasolv	≥ 0.999 g/g
Acetone	Merck	Uvasolv	≥ 0.999 g/g

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