



Liquid-liquid equilibrium in binary and ternary mixtures containing formaldehyde, water, methanol, methylal, and poly(oxymethylene) dimethyl ethers



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ARTICLE INFO

Article history:

Received 21 March 2016

Received in revised form

6 May 2016

Accepted 14 May 2016

Available online 20 May 2016

Keywords:

Poly(oxymethylene) dimethyl ethers

Liquid-liquid equilibrium

UNIFAC

Medium-field NMR

ABSTRACT

Poly(oxymethylene) dimethyl ethers (OME) are an interesting class of oxygenated fuel components and solvents for the absorption of carbon dioxide. The chemical structure of OME_n is $\text{H}_3\text{C}-\text{O}-(\text{CH}_2\text{O})_n-\text{CH}_3$ with $n \geq 2$ and the IUPAC names are methoxy(methoxymethoxy)methane ($n = 2$), 2,4,6,8-tetraoxanonane ($n = 3$), and 2,4,6,8,10-pentaoxaundecane ($n = 4$). This work studies the liquid-liquid equilibrium (LLE) in the binary systems (water + methylal), (water + OME_2), (water + OME_3), and (water + OME_4) and the ternary systems (water + methanol + OME_2), (water + methanol + OME_3), (formaldehyde + water + OME_2), (formaldehyde + water + OME_3), and (water + methylal + OME_2) in the temperature range 280 K – 340 K. The systems were studied by gas chromatographic- and titrimetric analysis of samples that were drawn from the coexisting liquid phases, as well by in situ analysis with a medium-field NMR spectrometer. The LLE was modeled by extending a UNIFAC-based activity coefficient model of the system (formaldehyde + water + methanol + methylal) from the literature. One new structural group is introduced to represent the OME.

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1. Introduction

Poly(oxymethylene) dimethyl ethers (OME) are attractive oxygenated fuels [1–3] and physical solvents for the absorption of carbon dioxide from natural gas [4]. The chemical structure of OME is $\text{H}_3\text{C}-\text{O}-(\text{CH}_2\text{O})_n-\text{CH}_3$ with $n \geq 2$. When mixed to diesel fuel, OME reduce the soot formation during the combustion process [1,2]. OME are also considered as safe fuels in direct oxidation fuel cells [5,6].

OME can be produced in a non-aqueous environment from trioxane and methylal [7–9]. Methylal can formally be seen as an OME of chain length $n = 1$. The reactants trioxane and methylal are produced in intermediate process steps from methanol via the formaldehyde route [10,11]. The direct synthesis of OME from formaldehyde and methanol in aqueous solutions is an interesting short-cut towards the OME [12,13]. In this synthesis route, methylal and water are formed as coupled products. As water is present in this reaction

system, the knowledge of the liquid-liquid equilibrium (LLE) in systems of (formaldehyde + water + methanol + methylal + OME) is essential for a reliable process design.

The binary LLE of the system (water + methylal) was investigated in the early work of Bourgom [14]. Albert et al. [15] also investigated the LLE in the binary system (water + methylal) and extended the results to the ternary system (water + methanol + methylal). Kuhnert et al. [16] investigated the LLE in the ternary system (formaldehyde + water + methylal). In the literature, there is only little information on the LLE in systems containing OME with $n \geq 2$. Dai et al. [17] studied the LLE in the ternary system (water + OME_2 + 1-butanol). However, no information on the binary system (water + OME_2) is given.

Kuhnert et al. [16] developed a UNIFAC-based activity coefficient model of the system (formaldehyde + water + methanol + methylal), which is able to describe the LLE in a wide range of conditions. The main field of application of the model was however the calculation of the vapor-liquid equilibrium (VLE). The model is based on the pioneering work of Maurer [18] and has been extended over the years [15,19–23]. The model takes into account the inherently reactive nature of aqueous- and methanolic formaldehyde solutions, where

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formaldehyde is bound in the oligomers poly(oxymethylene) glycols and poly(oxymethylene) hemiformals [24–26].

In the present work, experimental LLE data are provided for the binary systems (water + methylal), (water + OME₂), (water + OME₃) and (water + OME₄) and the ternary systems (water + methanol + OME₂), (water + methanol + OME₃), (formaldehyde + water + OME₂), (formaldehyde + water + OME₃) and (water + methylal + OME₂). Except for the system (water + methylal), LLE data were previously not available. The systems were studied by gas chromatographic (GC)- and titrimetric analysis of samples that were drawn from the coexisting liquid phases, as well as by in situ analysis using a medium-field NMR spectrometer. For describing the LLE, the UNIFAC-based activity coefficient model from Kuhnert et al. [16] was extended to model OME-containing systems by introducing the CH₂O repetition unit of OME as a new structural group.

2. Experiments

2.1. Chemicals

Table 1 gives information on the used chemicals, the suppliers and the purities. Ultrapure Milli-Q water was produced with a water purification system from Merck. Aqueous formaldehyde solution was prepared by dissolving paraformaldehyde in water at elevated temperatures, as described in previous work [12].

2.2. LLE measurement with sampling

2.2.1. Experimental procedure

Most of the LLE data reported in the present work were measured by a standard method using thermostated double-jacketed glass vessels. The vessels were filled with known amounts of substances (determined gravimetrically) so that a liquid two-phase system was obtained. The total mass of each mixture was approximately 20 g. The heterogeneous mixtures were stirred for one hour with a magnetic stirrer. The stirrer was turned off and the phases were settled over night. It was checked in preliminary experiments that the equilibrium is established. The temperature of the mixture was measured with a Pt 100 resistance thermometer (accuracy: ± 0.05 K). The experiments were carried out at temperatures from 280 K to 340 K, which is expected to be the relevant temperature range for the OME production process. A sample from the top phase was drawn with a syringe through a septum on the top of the vessels. A sample from the bottom phase was drawn with a syringe through a septum at the bottom of the vessels. The liquid-liquid phase interface was never penetrated in the experiments. The experiments were carried out at atmospheric pressure. The reproducibility of the results was checked by a triple measurement of at least one tie line for each system. The relative deviation did not exceed the analysis error.

2.2.2. Analysis

The mass fractions of methanol, methylal and the OME in the coexisting phases were analyzed with a GC using 1,4-dioxane as internal standard and a flame ionization detector. The chromatographic method was the same as described in previous work [12]. The relative errors for the mass fractions are less than 2%. This was checked by the analysis of test samples that were prepared gravimetrically. The overall mass fraction of formaldehyde was measured by the sodium-sulfite titration method with hydrochloric acid as titer. The relative error for the overall mass fraction of formaldehyde is less than 2% [12,19]. The consistency of the results was checked in some cases by the additional analysis of the mass fraction of water by Karl Fischer titration. The sum of mass fractions was between 0.98 g/g and 1.02 g/g in these tests. The reported mass fractions are those determined by GC and formaldehyde titration.

2.3. In situ LLE measurement

The LLE of all binary systems and the ternary system (water + methylal + OME₂) were additionally measured using a medium-field NMR spectrometer (Magritek Spinsolve Carbon, ¹H-frequency: 42.5 MHz). A conventional NMR tube was filled with known amounts of substances (determined gravimetrically) so that a liquid two-phase system was obtained. The tube was shaken manually for five minutes and the phases were settled in the NMR tube with a centrifuge. The NMR tubes were put in the spectrometer. The mixtures were equilibrated for 15 min in the spectrometer. The temperature of the mixture in the tube remained constant at 301.35 K. This was checked with a Pt 100 resistance thermometer (accuracy: ± 0.05 K). Experiments with equilibration times up to 2 h did not yield different results for the equilibrium compositions of both phases. The experiments were carried out at atmospheric pressure.

After equilibration, ¹H-spectra of the top- and bottom phase, respectively, were acquired by adjusting the height of the NMR tube within the spectrometer. Hence, no samples had to be drawn from the two-phase system. The ¹H-spectra were acquired with the following parameters: acquisition time = 6.4 s with 32 k data points, relaxation delay = 30 s, pulse width = 90°. A number of 32 scans was recorded and averaged. For each component one characteristic quantifiable peak was chosen and integrated. The peak areas were normalized with respect to the number of underlying H-atoms and the mole fractions of each component are calculated as the ratio of the normalized peak area of the component to the sum of the normalized peak areas of all components. The NMR spectra, the peak assignment and information on the peak integration are given in the [Supplementary Information](#). The relative error of this method is less than 2% at mass fractions of methylal and OME >0.4 g/g, less than 7% at mass fractions from 0.4 g/g to 0.2 g/g, and less than 10% below. This was checked by the analysis of test samples that were prepared gravimetrically.

Table 1
Sample table.

Chemical name	Source	Purity	Analysis method
formaldehyde ^a	Carl Roth	≥0.95 g/g	–
methanol	Sigma-Aldrich	≥0.999 g/g	–
methylal (= dimethoxymethane)	Sigma-Aldrich	≥0.99 g/g	–
OME ₂ (= methoxy(methoxymethoxy)methane)	BASF SE	≥0.985 g/g	GC
OME ₃ (= 2,4,6,8-tetraoxanonane)	BASF SE	≥0.985 g/g	GC
OME ₄ (= 2,4,6,8,10-pentaoxaundecane)	BASF SE	≥0.985 g/g	GC

^a Obtained in solid polymeric form as paraformaldehyde.

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