



High-pressure gas solubility in multicomponent solvent systems for hydroformylation. Part I: Carbon monoxide solubility

Christina Vogelpohl, Christoph Brandenbusch, Gabriele Sadowski*

Technische Universität Dortmund, Department of Biochemical and Chemical Engineering, Laboratory of Thermodynamics, Emil-Figge-Strasse 70, D-44227 Dortmund, Germany

ARTICLE INFO

Article history:

Received 6 December 2012

Received in revised form 12 April 2013

Accepted 13 April 2013

Keywords:

Gas solubility
Carbon monoxide
PC-SAFT
High pressure
Solvent systems
Prediction

ABSTRACT

High-pressure gas-solubility data of carbon monoxide (CO) in various solvents like *n*-hexane, propylene carbonate, dimethylformamide, 1-dodecene, *n*-dodecanal and *n*/*iso*-tridecanal was measured for temperatures between 295 K and 364 K and pressures up to 17 MPa. The experiments were performed in a high-pressure variable-volume view cell applying the synthetic method. The binary systems investigated were correlated using the perturbed chain statistical associating fluid theory (PC-SAFT). A temperature-independent binary interaction parameter k_{ij} was fitted to solubility data. Based on this, to CO solubility in mixtures of *n*-dodecanal and 1-dodecene with various molar compositions of the two liquids (3:1, 1:1, 1:3) were predicted. CO-solubility measurements for these systems confirmed that PC-SAFT is able to accurately predict the ternary data based on the knowledge of the binary subsystems, only.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Economic and ecologic constraints become more and more driving forces for process intensification and optimization in the chemical industry. To improve the performance of established reactions or to make new products available that cannot be processed by already-existing processes, new strategies have to be developed and e.g. novel solvent systems have to be identified. An example for a classical chemical reaction undergoing such a process is the hydroformylation of olefins to aldehydes via reaction with synthesis gas. For this reaction, the Ruhrchemie/Rhône-Poulenc-Process (RRPP) is well established and understood but has certain limitations concerning the processing of long-chain olefins [1]. In order to extend this reaction to long-chain olefins, novel processing strategies such as the hydroformylation in thermomorphic multicomponent solvent (TMS) systems [2] are currently under investigation [3–13]. The desired approach for the hydroformylation in TMS is to carry out the reaction at high temperature in a single homogenous liquid phase. After reaction, the system is cooled down to a temperature where the system separates into two liquid phases. This allows for an effective catalyst recycling and product processing [2].

The concentration of synthesis gas consisting of carbon monoxide (CO) and hydrogen (H₂), which is used in this reaction, has a significant influence on the reaction rate and product composition

[14]. Synthesis gas is the gaseous reactant in hydroformylation reactions and thus indispensable. Further, the reaction can be initiated and controlled via the concentration of the two components CO and H₂. As published by Tijani and El Ali [12], H₂ is needed to activate the catalyst complex and has a positive effect on the reaction rate as well as on the *n*/*iso*-ratio (linear *n*-aldehyde is preferred) which is increasing with increasing partial pressure of H₂. On the other hand, a high partial pressure of H₂ leads to undesirable by-products [15]. Also CO is not only used as reactant during the hydroformylation, but also as part of the active catalyst complex. The partial pressure of CO is of high importance since high partial pressures of CO inhibit the hydroformylation reaction rate due to side reactions. These lead to a decrease in the effective concentration of active catalyst species and thus the reaction rate is decelerated [14]. Shahrarun et al. [11] and Bhanage et al. [14] identified a reaction-rate maximum at a specific partial pressure of CO for their investigated systems. The gas solubility generally depends on the solvent system and on the reaction conditions, e.g. temperature and pressure [16]. TMS systems typically consist of at least one polar and one apolar solvent. Schäfer et al. [10] and Schäfer and Sadowski [17] chose appropriate solvents that show the desired TMS-system attributes for the hydroformylation reaction, as miscibility at reaction temperature and phase separation at separation temperature. Propylene carbonate (PC) and dimethylformamide (DMF) were identified as polar solvents and alkanes, e.g. *n*-hexane, *n*-decane, or *n*-dodecane as apolar solvents. The solubility of synthesis gas in these solvent systems determines the quantity of the gas which is available for the hydroformylation reaction. That is why this information is required for choosing an appropriate TMS system

* Corresponding author. Tel.: +49 2317552635.

E-mail address: g.sadowski@bci.tu-dortmund.de (G. Sadowski).

Nomenclature

a	Helmholtz energy
ARD	average relative deviation
k_B	Boltzmann constant
k_{ij}	binary interaction parameter
m_i^{seg}	segment number
p	pressure
RD	relative deviation
T	temperature
x	mole fraction

Greek letters

u_i/k_B	dispersion-energy parameter
μ	dipole moment
σ_i	segment diameter

and for adjusting the reaction conditions from a thermodynamic point of view.

While often the gas solubility of H_2 or CO is only investigated in solvent systems [18,19], it is also influenced by the educt 1-dodecene as well as by the product n /iso-tridecanal (n -tridecanal is preferred) which are present in the hydroformylation reaction mixture at considerable amounts. For hydroformylation processes, synthesis-gas solubilities at pressures of up to 17 MPa and at temperatures between 323 K and 383 K are of particular interest.

Published and reliable data for solubilities of synthesis gas, CO or H_2 in the above-mentioned systems is rather limited. This is especially true when high temperatures and pressures are concerned. To the best of our knowledge, synthesis-gas solubility data in the solvents of interest in this work are not available in literature at all. Neither gas-solubility data for synthesis gas, CO or H_2 in 1-dodecene or n /iso-tridecanal have been published yet. The only available data related to hydroformylation systems is solubility data of H_2 or CO in alkanes, PC or DMF [18,20–27], whereas solubility data of CO in DMF and in PC as well as H_2 in PC, only concerns pressures up to 3 MPa or less (e.g. Khan et al. [24]).

Within this work, the gas solubility of CO in PC, DMF, 1-dodecene, n -dodecanal and n /iso-tridecanal at temperatures between 301.8 K and 364.0 K and at pressures up to 17 MPa were measured. In a subsequent paper gas-solubility data of synthesis gas will be presented. To minimize the experimental effort and to allow for further process optimization, the experimental data also needs to be modeled. It is worthwhile to use a physically-based equation of state (EOS) as a thermodynamic model for describing gas solubility, especially when the application of Henry constants is no longer sufficient. Actually, Srivatsan et al. [27] and Park et al. [26] compared solubility data of CO and H_2 in alkanes like n -decane with modeling results obtained using the Peng–Robinson EOS and Soave–Redlich–Kwong EOS. But often these models are not accurate enough as far as predictions in multicomponent systems or over a wide temperature and pressure range are concerned. For those purposes, SAFT-like models yield better modeling results. SAFT modeling of H_2 solubility in heavy alkanes can be found e.g. in the work of Florusse et al. [28]. Ghosh et al. [29] tested the predictive and correlative capability of PC-SAFT to model gas solubilities of (beside other gases) CO and H_2 in hydrocarbons. Tran et al. [30] and Le Thi et al. [31] combined the PC-SAFT model with a group contribution method to model H_2 /hydrocarbon mixtures and H_2 /alkane binary systems.

In this work, also PC-SAFT [32] will be utilized to model the measured gas solubilities. This model was chosen because of its wide applicability in high-pressure modeling as well as for correlation and prediction of highly asymmetric binary and multicomponent

Table 1

Materials used for experiments.

Material	Supplier	Purity (%)
n -hexane	Merck KGaA	>96
1-dodecene	Sigma Aldrich	>99
PC	Sigma Aldrich	>99
DMF	Merck KGaA	>99
n -dodecanal	Merck KGaA	>98
n /iso-tridecanal	BASF SE	>90
CO	Messer Group GmbH	>98

mixtures [33–39]. The application of PC-SAFT will allow in subsequent works the prediction of systems with more than one gas (e.g. H_2 and CO) in TMS as well as in systems also containing the hydroformylation product and educt, respectively.

2. Materials and methods

2.1. Materials

All substances in this work were used without further purification as purchased from suppliers listed in Table 1. The aldehydes were flushed with nitrogen to avoid oxidation.

2.2. Gas-solubility measurements

Gas-solubility measurements were performed in a high-pressure variable-volume view cell (HPVVV) (NWA GmbH, Lörrach, Germany) with a variable volume from 30 mL to 60 mL ($T_{max} = 373$ K, $p_{max} = 40$ MPa) which was used in our research group before [33,40,41]. The view cell is equipped with two sapphire windows to allow for the observation of the phase behavior under high pressure during the experiments. One sapphire is fixed to the front of the cell whereas the back sapphire piston is movable by applying a back pressure through a hydraulic press. For a quick equilibration, a magnetically coupled stirrer was used. The temperature was measured directly in the cell by a Pt-100 thermocouple (standard deviation (STD) 0.1 K). The temperature was controlled within ± 1 K by two heating jackets. The pressure was measured directly inside the cell by a WIKA GmbH (C-10) pressure transducer ($p_{max} = 60$ MPa, $T_{max} = 373$ K) and also in the hydraulic part of the view cell. The HPVVV enabled to evacuate the view cell. For this purpose, the front sapphire piston was fixed by a simple flat washer avoiding movements during the evacuation. The movable back sapphire piston was also fixed during the evacuation. However, it was kept movable when the gas-solubility measurements started and the change of cell volume was needed. Temperature and pressure were monitored and recorded by a computer running Lab View instrumentation software. Fig. 1 shows a schematic representation of the experimental setup.

At the beginning of each experiment, the view cell was evacuated using a Vacuubrand PC 3004 VARIO vacuum pump (Wertheim, Germany) and heated to the desired temperature. After achieving a constant vacuum, the degassed liquid solvent(s) was transferred into the view cell. The mass of the liquid was determined by differential weighing. The uncertainty of the molar composition of CO in the investigated liquid based on the uncertainty of the differential weighing results in a STD of below 0.0001%. The compressed CO was added to the view cell by a 260D syringe pump (Teledyne ISCO, Axel Semrau GmbH & Co. KG, Sprockhövel, Germany) ($p_{max} = 56$ MPa). The mass of the gas introduced into the cell was determined from the volume change of the syringe pump and the density at the given temperature and pressure calculated by certified software GERG2008 provided by Kunz and Wagner [42]. The cell was afterwards pressurized by reducing the volume of the cell to a pressure where a single phase was observed inside the view

Download English Version:

<https://daneshyari.com/en/article/230605>

Download Persian Version:

<https://daneshyari.com/article/230605>

[Daneshyari.com](https://daneshyari.com)