



Phase equilibria of binary mixture of carbon monoxide and water at elevated temperatures and pressures



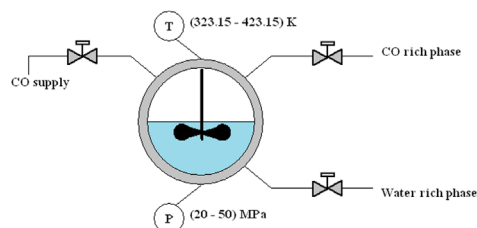
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HIGHLIGHTS

- Phase equilibria of CO and water.
- Measurements at high pressures and elevated temperatures.
- Mathematical correlation with van der Waals EOS and Adachi–Sugie mixing rule.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work reports the measurement and mathematical correlation of phase equilibrium data for the binary system composed of carbon monoxide and water at temperatures up to 423.15 K and pressures up to 50 MPa. This data, although crucial when designing high pressure technologies, is not available in the literature. The experimental data were collected using a high pressure view cell. Mathematical correlation was performed using an online available programme tool Phase Equilibria (2000) with van der Waals cubic equation of state and a mixing rule proposed by Adachi and Sugie. The combination of EOS and mixing rule are found to be in good agreement with experimental data.

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1. Introduction

The knowledge about the behaviour of gases in liquids dependent on temperature and pressure is essential in designing separation or synthesis processes. These data provide the designer with the necessary information to determine the needed parameters for the process and to establish an economical and efficient production plant.

Increase of interest in recent years in phase equilibria of binary mixtures of carbon monoxide and water at elevated temperatures and pressures is a consequence of both limited data available in the literature and increased implementation of high pressure technologies (e.g. supercritical water reforming of biomass, where, besides hydrogen, carbon monoxide and water are among the main products (Xu et al., 1996; Antal and Xu, 1998)).

A mixture of carbon monoxide and hydrogen is known under the term of synthesis gas and it was used since 1920s to obtain different compounds: Fischer Tropsch synthesis of olefins, waxes and gasoline; oxosynthesis of alcohols; ammonia production in the presence of water with water-gas shift reaction as an intermediate reaction step (Spath and Dayton, 2003). Water-gas shift reaction is

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also applied for hydrogen production (Lei et al., 2005). In previous years synthesis gas was largely obtained from natural gas, mineral oil or coal with the use of water steam (Baerns et al., 2006). In recent years new processes of obtaining synthesis gas from biomass were developed (Van Bennekom et al., 2011; Hashaikeh et al., 2006), particularly due to greater awareness of the impact of fossil fuels on the environment and of their limited stock in traditional deposits in Asia, Arabian and Mexican Gulf.

Carbon monoxide is separated from gas mixtures by absorption or distillation. During low temperature distillation CO is obtained as the more volatile component, while during high temperature distillation it is flushed with methane (Baerns et al., 2006). As single component it is mostly used for production of acetic and formic acids and for production of carbon dioxide in the presence of water with metal oxides as catalysts (Laine and Severino, 1990; Lopez Agudo et al., 1992). Some compounds used for polyurethane production are also obtained from carbon monoxide. At high pressure CO forms complex compounds with Co and Rh which act as homogeneous catalysts in processes such as hydroformulation of olefins (Cornils and Hermann, 2002). Carbon monoxide with water and acetylene is used for the production of acrylic acid which is further used to obtain polyacrylate (Baerns et al., 2006). Preparation of Schiff's bases from nitroarenes or aldehydes (Macho et al., 2004) is carried out in the presence of carbon monoxide and water. The CO–H₂O mixture is also used as reagent during catalytic synthesis of hydrogen peroxide in the presence of oxygen (Ma et al., 2004, 2006).

There are some data on the solubility of carbon monoxide in water reported in the literature (Gillespie and Wilson, 1980), but they are limited either to low temperatures or low pressures. The aim of this work was to fill up the gap of missing data as phase equilibria information for the mentioned system at elevated temperatures and pressures is demanded by engineers for process design.

Experimental data on phase equilibrium of binary mixtures of carbon monoxide and water were obtained in the pressure range from 20 MPa to 50 MPa and temperatures from 323.15 K to 423.15 K at an increment of 25 K.

2. Materials and methods

2.1. Experimental setup and operation

CO was supplied by Messer Slovenia. Water of miliQ quality was obtained in an in-house purifying facility.

The phase equilibrium of the CO–H₂O binary mixture was measured in a view cell with variable volume (Fig. 1) manufactured by NWA (Lörrach-D). The view cell has a maximum volume of 60 mL and operates at pressures up to 70 MPa and temperatures up to 523.15 K. The cell is equipped with a stirrer, electrical heater and has two outlets, one for the sampling of the upper phase and the other for the lower phase.

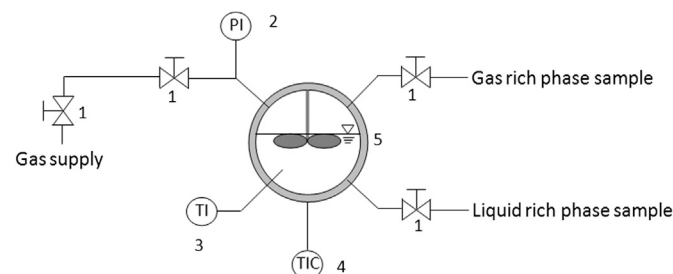


Fig. 1. Schematic representation of the variable volume view cell apparatus. 1–high pressure valve, 2–pressure indicator, 3–temperature indicator, 4–temperature control, 5–high pressure view cell with stirrer.

30 mL of water were introduced into the view cell using a syringe. Then carbon monoxide was introduced directly into the cell from the gas bottle. Afterwards the mixture was heated to the desired temperature and the desired pressure was set by modifying the internal volume of the cell. The mixture was stirred for half an hour, left to settle for one hour and then samples were collected from both upper and lower phase. The samples were introduced in a flash separator set at atmospheric pressure which was placed in an ice-salt trap ($T \approx 267$ K) to avoid the loss of water by evaporation. After sampling the ice-salt trap was removed in order to allow the gas to escape from the liquid. The amount of liquid after separation was determined gravimetrically. The volume of gas was determined volumetrically by using a U-tube connected to the flash separator. The gas released from the sample displaced the fluid in the U-tube. Using the difference in volume the amount of gas dissolved in the sample was determined. The working method is already described in detail in our previous works (Knez et al., 2008; Ilić et al., 2009). During sampling the temperature in the system remained unchanged and the pressure dropped for a maximum of 0.5 MPa. The pressure values presented in the article were taken as an average of the values before and after sampling. Each point was measured at least three times and the average value was calculated. The average errors (AARD) during measurements were 3.68%.

2.2. Thermodynamic modelling

Since Henry's law does not provide satisfactory results for this system because of the high pressure employed during measurements (Sedlbauer et al., 2002; Majer et al., 2008), the experimental data have been correlated using a cubic equation of state, van der Waals (Eq. (1), with Adachi–Sugie mixing rule.

$$P = \frac{RT}{v-b_m} - \frac{a_m}{v^2} \quad (1)$$

where P is pressure, T is temperature, R is gas constant, v is volume, and a_m and b_m represent cohesion parameter and, respectively, co-volume parameter of a cubic equation of state.

As our binary system includes water, which is strongly polar, a conventional mixing rule does not offer reasonable results (Adachi and Sugie, 1986). Therefore a mixing rule derived from local composition concepts is a suitable choice. For example Huron and Vidal developed in 1979 a mixing rule for NRTL equation that yields accurate results for such non-ideal mixtures (Huron and Vidal, 1979). Here we use a mixing rule developed by Adachi and Sugie by modification of a Redlich–Kister mixing rule (Adachi and Sugie, 1986). The proposed mixing rule has the following expression (Adachi and Sugie, 1986):

$$a_m = \sum x_i a_i + \sum \sum x_i x_j [A + B(x_i - x_j) + C(x_i - x_j)^2 + D(x_i - x_j)^3] \quad (2)$$

where x_i and x_j represent the molar fraction of component i and j , respectively. A , B , C and D are parameters in Redlich–Kister mixing rule and a_i is a cohesion parameter of a cubic equation of state pertaining to component i .

Adachi–Sugie mixing rule is used for parameter a_m , while a linear mixing rule is used for the co-volume parameter b_m .

Eq. (2) may be reduced to a more conventional form:

$$a_m = \sum \sum x_i x_j a_{ij} \quad (3)$$

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2} \quad (4)$$

Binary interaction parameter k_{ij} is obtained by Eq. (5):

$$k_{ij} = l_{ij} + m_{ij}(x_i - x_j) \quad (5)$$

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