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Research paper

# Solubilities of $CO_2$, $CH_4$, $H_2$, CO and $N_2$ in choline chloride/urea

Yujiao Xie [a,*], Haifeng Dong [b], Suojiang Zhang [b], Xiaohua Lu [c], Xiaoyan Ji [a,**]

[a] *Energy Engineering, Division of Energy Science, Luleå University of Technology, 97187 Luleå, Sweden*
[b] *Beijing Key Laboratory of Ionic Liquids Clean Process, State Key Laboratory of Multiphase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, 100190 Beijing, China*
[c] *Key Laboratory of Material and Chemical Engineering, Nanjing Tech University, 210009 Nanjing, China*

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**Abstract**

Solubilities of $CO_2$, $CH_4$, $H_2$, CO and $N_2$ in choline chloride/urea (ChCl/Urea) were investigated at temperatures ranging from 308.2 to 328.2 K and pressures ranging from 0.6 to 4.6 MPa. The results show that the solubilities of gases increase with increasing pressure and decreasing temperature. The solubility of $CO_2$ is higher than that of $CH_4$, $H_2$, CO and $N_2$, which indicates that ChCl/Urea may be used as a potential solvent for $CO_2$ capture from the gas mixture. Solubility of $CO_2$ in ChCl/Urea was fitted by Non-Random Two-Liquid and Redlich–Kwong (NRTL-RK) model, and solubility of $CH_4$, $H_2$, CO or $N_2$ in ChCl/Urea was fitted by Henry's Law. The standard enthalpy, standard Gibbs energy and standard entropy of gases were calculated. Additionally, the $CO_2/CH_4$ selectivities in water, dry ChCl/Urea and aqueous ChCl/Urea were further discussed.


*Keywords:* Gas solubility; Choline chloride; Urea; $CO_2$ separation

## 1. Introduction

$CO_2$ capture plays an important role in the development of renewable energy and mitigating $CO_2$ emission [1,2], for example, $CO_2$ capture from flue gases ($CO_2/N_2$) in power station, $CO_2$ removal from biosyngas ($CO_2/H_2/CO$) after gasification in order to further synthesis of renewable fuels, biogas ($CO_2/CH_4$) purification to be used as transportation fuels, as well as hydrogen purification [3]. Currently, amine-based technology is widely used, while amines are corrosive and suffer high solvent loses as well as high energy penalty. Therefore, it is necessary to explore high efficient solvent in order to develop an energy effective and environmentally benign $CO_2$ separation technology.

In recent years, deep eutectic solvent was proposed and considered as a new type of ionic liquids (ILs). Among this type of ILs, the solvent of choline chloride/Urea (ChCl/Urea) with cheap price, easy synthesis as well as bio-degradation has shown great potential to be used as liquid absorbents for $CO_2$ separation [4,5]. Research work has been carried out to study the $CO_2$ solubility and the thermophysical properties of ChCl/Urea [6–13]. However, the available knowledge is still limited towards the application. For example, the vapor–liquid equilibria of the gases other than $CO_2$, such as $CH_4$, CO, $H_2$, and $N_2$, need to be studied further.

The present work aims to provide quantitative experimental information on the solubility of $CO_2$, $CH_4$, CO, $H_2$, and $N_2$ in ChCl/Urea. The solubilities of pure gases were measured at 308.2, 318.2 and 328.2 K and at pressures up to 4.5 MPa. The measured gas solubility was fitted by semi-empirical models. The Henry's constant, the standard Gibbs energy, the standard enthalpy and standard entropy of the gases were obtained. The ideal $CO_2/CH_4$ selectivities in water, dry ChCl/Urea and aqueous ChCl/Urea were further calculated.

* Corresponding author.
** Corresponding author.
*E-mail addresses:* yujiao.xie@ltu.se (Y. Xie), xiaoyan.ji@itu.se (X. Ji).

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## 2. Experimental section

Choline chloride (ChCl, mass fraction ≥ 99%) was produced by Sinopharm Chemical Reagent Co, Ltd, China. Urea (mass fraction ≥ 99%) was produced by Xilong Chemical Reagent Co, Ltd, China. The chemicals were analytical reagent (A. R.) grade and used as received. The mixture of choline chloride and urea (ChCl/Urea) was synthesized according to procedure reported in our previous work [7]. The ChCl/Urea was all based on the molar ratio of 1:2 (choline chloride:urea). The water content in ChCl/Urea (1:2) was 1200 ± 100 ppm, which was determined by Karl Fischer titration analysis. The $CO_2$, $CH_4$, CO, $H_2$, and $N_2$ were received from Beijing Bei Temperature Gas Factory, and the mole fraction of all the gases is ≥99.9%.

The gas solubility apparatus consists of a gas reservoir, an equilibrium cell, a magnetic stirrer and two pressure transducers. The experimental procedures were the same as that reported in our previous work [7], no detailed descriptions were repeated here. The uncertainties of the gas solubility measurements consist of the system errors of pressure, temperature and the volumes of gas reservoir and equilibrium cell. The precision of pressure transducers was 0.075%, the accuracies of temperature and volume measurements were 0.1 K and 0.5 ml, respectively. The overall uncertainty for the measured solubility of gas was estimated to be within ±1%.

## 3. Results and discussions

For the system studied in this work, the vapor pressure of ChCl/Urea is negligible. Therefore, it was assumed that only pure-gas exists in the vapor phase, i.e. $y = 1$.

### 3.1. Solubility of $CO_2$

The solubility of $CO_2$ was measured at temperature ranging from 308.2 K to 328.2 K and pressure ranging from 0.6 MPa to 4.6 MPa. The experimental results are listed in Table 1 and depicted in Fig. 1. Within the investigated temperature and pressure ranges, the solubility of $CO_2$ increases with increasing pressure and decreasing temperature. The mole fraction of $CO_2$ was up to 0.195 at 308.2 K and 4.4 MPa.

The solubility of $CO_2$ in ChCl/Urea was represented with the following equation:

$$P\varphi^{v}_{CO_2} = H_{CO_2} x_{CO_2} \gamma^{*}_{CO_2} \quad (1)$$

where $P$ is the pressure, $\varphi^{v}_{CO_2}$ is the fugacity coefficient of $CO_2$ in the vapor phase, $H_{CO_2}$ is the Henry's law constant, $x_{CO_2}$ is the $CO_2$ mole fraction in the liquid phase, and $\gamma^{*}_{CO_2}$ is the activity coefficient of $CO_2$ in the liquid phase at the infinite dilution reference state.

The Henry's law constant of $CO_2$ was expressed by:

$$H_{CO_2}(T,P) = H_{CO_2}(T)\exp\left(\frac{V^{\infty}_{CO_2} P}{RT}\right) \quad (2)$$

Table 1
Solubilities of $CO_2$, $CH_4$, $H_2$, CO and $N_2$ in ChCl/Urea.

| | 308.2 K | | 318.2 K | | 328.2 K | |
|---|---|---|---|---|---|---|
| | *P*/MPa | *x* | *P*/MPa | *x* | *P*/MPa | *x* |
| $CO_2$ | 0.651 | 0.050 | 0.706 | 0.044 | 0.692 | 0.042 |
| | 1.527 | 0.095 | 1.661 | 0.092 | 1.691 | 0.088 |
| | 2.453 | 0.137 | 2.618 | 0.127 | 2.544 | 0.118 |
| | 3.445 | 0.174 | 3.527 | 0.168 | 3.577 | 0.156 |
| | 4.376 | 0.195 | 4.504 | 0.188 | 4.499 | 0.175 |
| $CH_4$ | 0.585 | 0.014 | 0.548 | 0.013 | 0.550 | 0.012 |
| | 1.274 | 0.029 | 1.268 | 0.028 | 1.270 | 0.026 |
| | 2.042 | 0.049 | 2.001 | 0.044 | 2.031 | 0.041 |
| | 2.782 | 0.068 | 2.818 | 0.063 | 2.790 | 0.059 |
| | 3.570 | 0.089 | 3.618 | 0.081 | 3.590 | 0.076 |
| $H_2$ | 0.688 | 0.012 | 0.683 | 0.011 | 0.673 | 0.010 |
| | 1.563 | 0.027 | 1.560 | 0.025 | 1.566 | 0.024 |
| | 2.544 | 0.043 | 2.545 | 0.041 | 2.543 | 0.039 |
| | 3.578 | 0.059 | 3.566 | 0.057 | 3.552 | 0.054 |
| | 4.553 | 0.073 | 4.559 | 0.071 | 4.565 | 0.068 |
| CO | 0.704 | 0.012 | 0.732 | 0.011 | 0.708 | 0.009 |
| | 1.627 | 0.027 | 1.576 | 0.023 | 1.591 | 0.020 |
| | 2.525 | 0.042 | 2.527 | 0.038 | 2.581 | 0.032 |
| | 3.515 | 0.060 | 3.490 | 0.053 | 3.582 | 0.045 |
| | 4.505 | 0.076 | 4.539 | 0.068 | 4.561 | 0.056 |
| $N_2$ | 0.709 | 0.014 | 0.689 | 0.013 | 0.704 | 0.012 |
| | 1.599 | 0.031 | 1.588 | 0.030 | 1.590 | 0.027 |
| | 2.531 | 0.049 | 2.531 | 0.046 | 2.571 | 0.043 |
| | 3.536 | 0.068 | 3.537 | 0.065 | 3.564 | 0.060 |
| | 4.539 | 0.086 | 4.536 | 0.082 | 4.545 | 0.076 |

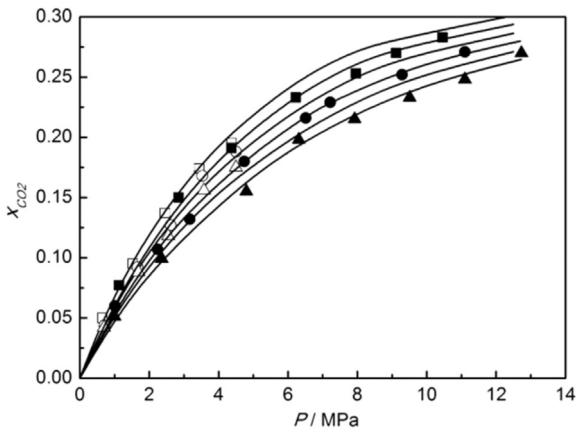


Fig. 1. Solubility of $CO_2$ in ChCl/Urea. Symbols: this work □, 308.2 K; ○, 318.2 K; △, 328.2 K. Li et al. [9] ■, 313.15 K; ●, 323.15 K; ▲, 333.15 K. Curves: –, correlations.

$$lnH_{CO_2}(T) = c_1 + c_2/T \quad (3)$$

$$V^{\infty}_{CO_2} = c_3 + c_4 T \quad (4)$$

where $H_{CO_2}(T,P)$ is the Henry's law constant of $CO_2$ at system temperature and pressure, $H_{CO_2}(T)$ is the Henry's law constant of $CO_2$ at zero pressure, and $V^{\infty}_{CO_2}$ is the infinite dilution partial volume of $CO_2$ in solvent.

The Redlich–Kwong (RK) equation of state was used to calculate the fugacity of $CO_2$ in the vapor phase. The fugacity coefficient of $CO_2$ was calculated as:

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