Solubilities of CO2, CH4, H2, CO and N2 in choline chloride/urea

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Abstract

Solubilities of CO2, CH4, H2, CO and N2 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 CO2 is higher than that of CH4, H2, CO and N2, which indicates that ChCl/Urea may be used as a potential solvent for CO2 capture from the gas mixture. Solubility of CO2 in ChCl/Urea was fitted by Non-Random Two-Liquid and Redlich–Kwong (NRTL-RK) model, and solubility of CH4, H2, CO or N2 in ChCl/Urea was fitted by Henry's Law. The standard enthalpy, standard Gibbs energy and standard entropy of gases were calculated. Additionally, the CO2/CH4 selectivities in water, dry ChCl/Urea and aqueous ChCl/Urea were further discussed.

Keywords: Gas solubility; Choline chloride; Urea; CO2 separation

1. Introduction

CO2 capture plays an important role in the development of renewable energy and mitigating CO2 emission [1,2], for example, CO2 capture from flue gases (CO2/N2) in power station, CO2 removal from biosyngas (CO2/H2/CO) after gasification in order to further synthesis of renewable fuels, biogas (CO2/CH4) 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 CO2 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 CO2 separation [4,5]. Research work has been carried out to study the CO2 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 CO2, such as CH4, CO, H2, and N2, need to be studied further.

The present work aims to provide quantitative experimental information on the solubility of CO2, CH4, CO, H2, and N2 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 CO2/CH4 selectivities in water, dry ChCl/Urea and aqueous ChCl/Urea were further calculated.
2. Experimental section

Choline chloride (ChCl, mass fraction $\geq 99\%$) was produced by Sinopharm Chemical Reagent Co, Ltd, China. Urea (mass fraction $\geq 99\%$) 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 produced by Sinopharm Chemical Reagent Co, Ltd, China. Urea in the vapor phase, \text{HCO}_3^- was negligible. Therefore, it was assumed that only pure-gas exists in the vapor phase, i.e. $y = 1$.

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%, temperature and the volumes of gas reservoir and equilibrium cell, a magnetic stirrer and two pressure transducers. The experimental results 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 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:

$$P\varphi_{CO_2} = H_{CO_2}x_{CO_2}\gamma_{CO_2}$$

(1)

where $P$ is the pressure, $\varphi_{CO_2}$ 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:

$$H_{CO_2}(T, P) = H_{CO_2}(T)\exp\left(\frac{V_{CO_2}^\infty P}{RT}\right)$$

(2)

$$\ln H_{CO_2}(T) = c_1 + c_2/T$$

(3)

$$V_{CO_2}^\infty = c_3 + c_4T$$

(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 $V_{CO_2}^\infty$ 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:
\[ \ln \varphi = Z - 1 - \ln(Z - BP) - (A^2/B) \ln(1 + BP/Z) \] (5)

\[
P = \frac{RT}{(V-b)} - a/T^{1/2}V(V+b)
A^2 = a/\left(\frac{RT}{V}\right)^{2.5} = 0.42787T^{2.5}/P, T^{2.5}
B = b/RT = 0.0867T/P, T
Z = 1/(1-h) - (A^2/B)h/(1+h)
Z = PV/RT
h = BP/Z = b/V
\] (6)

where \(a, b, A, \) and \(B\) are parameters calculated from the critical temperature and pressure. The critical temperature and pressure of CO2 were obtained from NIST webbook with the values of 304.2 K and 7.38 MPa, respectively.

The Non-Random Two-Liquid (NRTL) model was used to calculate the activity coefficient of CO2 in the liquid phase.

\[
\ln \gamma_1 = x_2^2 \left[ r_{12} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{r_{12} G_{12}}{(x_1 + x_2 G_{21})^2} \right] \] (7)

\[G_{12} = \exp(-\alpha r_{12}) \quad \text{and} \quad G_{21} = \exp(-\alpha r_{21})\] (8)

where \(\alpha\) was assumed to be 0.2, \(r_{12}\) and \(r_{21}\) are the binary interaction parameters and expressed as a function of temperature:

\[
\begin{align*}
\tau_{12} &= \tau_{12}^{(0)} + \tau_{12}^{(1)} / T \\
\tau_{21} &= \tau_{21}^{(0)} + \tau_{21}^{(1)} / T
\end{align*}
\] (9)

The \(H_{CO2}(T)\) was obtained from the extrapolation of experimental gas solubility and described as a function of the temperature (Eq. (3)). \(V_{\infty}^{CO2}\) was obtained from the fitting of CO2 solubility in the whole range by setting \(\tau_{12}\) and \(\tau_{21}\) to be zero. With the fixed \(H_{CO2}(T, P, \tau)\), \(\tau_{12}\) and \(\tau_{21}\) were fitted from the experimental CO2 solubility.

Li et al. [9] measured the CO2 solubility in ChCl/Urea at 313.15–333.15 K and pressure up to 13 MPa. The CO2 solubility measured in this work was correlated together with the data reported by Li et al. [9]. Fig. 1 shows the comparison on experimental data and model results. The overall average absolute relative deviation (AARD) is 0.43%. The AARD for the data measured in this work is 0.49% and for the data reported by Li et al. [9] is 0.40%. The parameters for NRTL model and Henry’s constant of CO2 are listed in Table 2.

3.2. Solubility of CH4, CO, H2, and N2

Solubilities of pure CH4, H2, CO and N2 in ChCl/Urea were measured at temperature ranging from 308.2 to 328.2 K and pressure ranging from 0.6 to 4.6 MPa. The experimental results are listed in Table 1. Comparing to the CO2 solubility, the solubility of other single gas (eg: CH4, H2, CO and N2) in ChCl/Urea is low. For example, at 328.2 K and 3.6 MPa, the mole fraction of CO2 is 0.156, and the mole fractions of CH4 and CO are 0.076 and 0.045, which decrease by 51% and 71%, respectively.

Due to the low solubility of CH4, CO, H2, and N2 in ChCl/Urea, the solubility of CH4, H2, CO and N2 can be represented with Henry’s law:

\[H_g(T) = \lim_{x_g \to 0} \left( \frac{P \phi_s}{x_g} \right)\] (10)

where \(\phi_s\) is the fugacity coefficient of gas (CH4, H2, CO and N2) in the vapor phase, \(H_g(T)\) is the Henry’s constant of gas in ChCl/Urea, and \(x_g\) is the mole fraction of gas in the liquid phase.

The \(\phi_s\) was calculated by RK model (Eqs. (5) and (6)), the critical temperature and pressure of each gas were illustrated in Table 3. The \(H_g(T)\) was obtained from the extrapolation of the experimental gas solubility. The calculated Henry’s constant are listed in Table 4.

The comparisons on experimental data and model results are shown in Figs. 2–5. The average absolute relative deviations for solubility of CH4, H2, CO and N2 are 0.14%, 0.087%, 0.074%, 0.11%, respectively. The solubility of CH4, H2, CO and N2 in ChCl/Urea increases linearly with increasing pressure, which indicates the physical absorption of these gases in ChCl/Urea. Both the mole fraction and molality of the five gases in ChCl/Urea at 318.2 K were compared, which is shown in Fig. 6. The sequence of the gas solubility is: CO2 > CH4 > H2 > CO > H2. In order to know the amounts of CO2 dissolving in 1 kg of ILs, the molalities of CO2 in ChCl/Urea and three conventional ILs ([bmim][Tf2N], [bmim][PF6] and [bmim][BF4]) are shown in Fig. 7. Within the investigated temperature and pressure, the molalities of CO2 in ChCl/Urea and [bmim][Tf2N] are higher than those in [bmim][PF6] and [bmim][BF4]. For example, at 318 K and 4 MPa, the molalities of CO2 are 2.8 mol/kg [bmim][Tf2N], 2.5 mol/kg ChCl/Urea, and 2.0 mol/kg [bmim][PF6] or [bmim][BF4].

3.3. Thermodynamic properties calculation

Based on the Henry’s constant, other thermodynamic properties of gases in ChCl/Urea can be calculated as follows:

\[\Delta_{mol} H^\circ = R \left( \frac{\partial \ln (H_g(T, P)/P)}{\partial (1/T)} \right)\] (11)

\[\Delta_{mol} G^\circ = RT \ln \left( \frac{H_g(T, P)}{P} \right)\] (12)

<table>
<thead>
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<th>Table 3</th>
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<tr>
<td>The critical temperature and pressure of the gases.</td>
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</table>
\[
\Delta_{\text{sol}} S = \frac{\Delta_{\text{sol}} H - \Delta_{\text{sol}} G}{T}
\]

where \(\Delta_{\text{sol}} H\), \(\Delta_{\text{sol}} G\), and \(\Delta_{\text{sol}} S\) are the standard enthalpy, standard Gibbs free energy and standard entropy, respectively, and the standard state represents the state of \(P = 0.1\) MPa and \(T = 298.15\) K.

The calculated results are listed in Table 5. The magnitude of enthalpy for CO\(_2\) is the largest; the order follows: CO\(_2\) > CO > CH\(_4\) > N\(_2\) > H\(_2\). The value of enthalpy is negative, which shows than the dissolution of the gas is exothermic.

### 3.4. Gas selectivity

The gas selectivity is a key factor for CO\(_2\) separation. The ideal selectivity at certain temperature \((T)\) and pressure \((P)\) can be estimated from the solubility of pure gas. For the studied systems, the CH\(_4\) solubility is relatively high, and the CO\(_2\)/CH\(_4\) selectivity is quite important in the CO\(_2\) separation from biogas. Therefore, the ideal CO\(_2\)/CH\(_4\) selectivity was calculated as the following equation, and the CO\(_2\)/CH\(_4\) selectivity in water, pure ChCl/Urea and aqueous ChCl/Urea at were investigated.

\[
S_{CO_2/CH_4} = \left(\frac{x_{CO_2}}{x_{CH_4}}\right)_{P,T}
\]

The CO\(_2\) and CH\(_4\) solubility in water was retrieved from Aspen databank and shown in Fig. 8(a). Comparing to the CO\(_2\) solubility in ChCl/Urea, the CO\(_2\) solubility in water is low. For example, at 318 K and 1 MPa, the mole fraction of CO\(_2\) in ChCl/Urea is about 0.06 while mole fraction of CO\(_2\) in water is only 0.0036.

The CO\(_2\) solubility in aqueous ChCl/Urea has been measured and correlated in our previous work [7]. The water effect on the property of ChCl/Urea and CO\(_2\) solubility was

<table>
<thead>
<tr>
<th>T/K</th>
<th>(H_0/\text{MPa})</th>
<th>(\text{CO}_2)</th>
<th>(\text{CH}_4)</th>
<th>(\text{H}_2)</th>
<th>(\text{CO})</th>
<th>(\text{N}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>308.2</td>
<td>11.6</td>
<td>40.2</td>
<td>61.6</td>
<td>59.5</td>
<td>50.4</td>
<td></td>
</tr>
<tr>
<td>318.2</td>
<td>14.2</td>
<td>43.3</td>
<td>64.2</td>
<td>67.4</td>
<td>52.5</td>
<td></td>
</tr>
<tr>
<td>328.2</td>
<td>15.9</td>
<td>47.4</td>
<td>67.0</td>
<td>78.5</td>
<td>58.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 4

Henry's constants of gases in ChCl/Urea.

Fig. 2. Solubility of CH\(_4\) in ChCl/Urea. Symbols: □, 308.2 K; ○, 318.2 K; △, 328.2 K. Curves: correlations.

Fig. 3. Solubility of CO in ChCl/Urea. Symbols: □, 308.2 K; ○, 318.2 K; △, 328.2 K. Curves: correlations.

Fig. 4. Solubility of H\(_2\) in ChCl/Urea. Symbols: □, 308.2 K; ○, 318.2 K; △, 328.2 K. Curves: correlations.

Fig. 5. Solubility of N\(_2\) in ChCl/Urea. Symbols: □, 308.2 K; ○, 318.2 K; △, 328.2 K. Curves: correlations.
studied. It was found that the trace water significantly decrease the viscosity of ChCl/Urea while the influence on CO2 solubility is weak.

Fig. 8(b) shows the CO2/CH4 selectivity in water, pure ChCl/Urea and aqueous ChCl/Urea at 318 K and 1 MPa. It can be seen that the CO2/CH4 selectivity in pure ChCl/Urea is only 2.6. With the increase of water content, the CO2/CH4 selectivity increase rapidly. When the mass fractions of water in aqueous ChCl/Urea are in the range from 50% to 100%, the CO2/CH4 selectivity keeps constant, and around 20. The addition of water influences the interaction between cation/anion of ILs, and the amount of water influences the interaction between water molecule and ILs molecule. As a consequence, the gas solubility in aqueous ChCl/Urea is influenced. In the investigation, it is found the water influence on the CO2 solubility is not significant, while the CH4 decreases with adding water in ChCl/Urea. Thus, the CO2/CH4 selectivity increases.

The CO2 solubility in aqueous ChCl/Urea (w_{water} > 0.5) is higher than that in water, while the CO2/CH4 selectively is kept. The higher CO2 solubility will result in a lower amount of scrubbing solvent, and thus reduce the capital cost of the separation process. Therefore, the aqueous ChCl/Urea could be used as a potential solvent for CO2 separation from the gas mixture.

3.5. Thermal stability

Fig. 9 shows the thermogravimetric (TG) curves of ChCl/Urea and aqueous ChCl/Urea at heating rate of 10 °C/min in

Table 5

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<th>Thermodynamic properties of gases in ChCl/Urea at the standard state.</th>
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<tr>
<td>D_{mol}H (kJ mol(^{-1}))</td>
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<tr>
<td>--------------------------------</td>
</tr>
<tr>
<td>CO2</td>
</tr>
<tr>
<td>CH4</td>
</tr>
<tr>
<td>H2</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>N2</td>
</tr>
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</table>

Fig. 8. (a), solubility of gases in water at 318.2 K. Symbols: ■, CO2; •, CH4, (b), the CO2/CH4 selectivity in water, dry ChCl/Urea and aqueous ChCl/Urea at 318 K and 1 MPa. (w_{water} is the mass fraction of water in the aqueous ChCl/Urea).
nitrogen atmosphere. It can be seen that the ChCl/Urea starts the decomposition at about 140 °C (413 K). The mixture of (ChCl/Urea + 0.1 H2O) shows a 10% mass loss when the temperature reaches 100 °C (373 K), which could be attributed to the loss of free water and the dehydration of water. As water influences the interaction between ChCl/Urea molecules, the mixture of (ChCl/Urea + 0.1 H2O) continues decomposing after 100 °C (373 K). The thermal stability of ChCl/Urea decreases in the presence of admixtures of water, while there is only water loss at temperature below 100 °C (373 K). In the CO2 separation process, the solvent could be regenerated by the air blowing at room temperature.

4. Conclusion

The solubilities of CO2, CH4, CO, H2, and N2 in ChCl/Urea were investigated at temperatures ranging from 308.2 to 328.2 K and pressures ranging from 0.6 to 4.6 MPa. It showed that the solubility of CO2 was higher than the other four gases. Solubility of CO2 in ChCl/Urea was represented by NRTL-RK model, while solubility of CH4, H2, CO and N2 in ChCl/Urea were correlated by Henry's Law. Besides the gas solubility, the idea gas selectivity was investigated. It is found that the CO2/CH4 selectivity in aqueous ChCl/Urea increases with the increase of water content when wwater <0.5. With further increase, the CO2/CH4 selectivity keeps constant. Compared to high pressure water scrubbing, the aqueous ChCl/Urea will decrease the amounts of required solvent, lower the energy use and the capital cost of the separation process. This work provides a design basis for the further industrial application of CO2 separation using ChCl/Urea-based solvent.

Conflict of interest

There is no conflict of interest.

Acknowledgement

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