CO₂ Hydrate Formation Promoted by a Bio-friendly Amino Acid L-Isoleucine

Zhengwen Liu¹, Yanxian Zeng¹, and Weixing Wang*¹

¹ Key Laboratory of Enhanced Heat Transfer and Energy Conservation of the Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China.

*Corresponding author’s e-mail: cewxwang@scut.edu.cn

Abstract. We prove that L-isoleucine, a bio-friendly amino acid, can be used to greatly increased CO₂ uptake kinetics in the formation of CO₂ hydrate without stirring. As far as we know, L-Isoleucine is an accelerator that can effectively promotes the formation of CO₂ hydrate (the gravimetric capacity achieved to 331 mg g⁻¹ in 1000 min at a concentration of 0.2 wt%). We also provided a preliminary explanation for this promotion mechanism of L-isoleucine by comparing the structure-performance. Our results will provide a reference for exploring the promotion mechanism of CO₂ hydrate.

1. Introduction

Comparing with 1958, the level of CO₂ in the atmosphere has increased by 22% because of the increasing demand for fossil energy [1, 9]. In recent years, the World Climate Research Program (WCRP) has held a seminar on sea level change [10], gives progress since IPCC’s fifth assessment report, it also clearly pointed out that global average annual surface temperature (including land and sea) increased by 0.85 °C (0.65 ~ 1.06 °C) from 1880 to 2012, and the linear trend of global average sea level rise was 1.6 [1.2-2.2] mm a⁻¹ from 1902 to 1990 [16]. Therefore, carrying out carbon capture and storage (CCS) becomes extremely important.

Traditional CO₂ separation and recovery technologies include solvent absorption, membrane and low temperature methods [8, 13]. However, the above separation and recovery methods are difficult for large-scale industrial application due to large investment in equipment and complex process. The formation of hydrate to achieve CO₂ capture (HCCS) has been proved to be able to effectively reduce the concentration of CO₂ in emissions [25], however, HCCS has some disadvantages, such as low formation rate of CO₂ hydrate, which restricts its further industrial application. Therefore, how to improve the gas storage density, accelerate the formation rate and shorten the induction time of CO₂ hydrate are the key problems to be solved in large-scale application of HCCS [6].

For hydrate strengthening currently, there are mainly mechanical methods, including stirring, bubbling and spraying [3]; Static strengthening methods, including dry water, ice powder strengthening [12], porous medium technology, and chemical additives technologies. However, the mechanical method requires high equipment and requires a lot of energy to provide power, so it does not have good economic benefits in industrial production, so the chemical additive technology is considered to be the most likely to be widely used in industry.

The chemical additives with promoting effect are mainly divided into thermodynamic accelerant and kinetic accelerant, among which thermodynamic accelerant come from petrochemical products in general, such as THF, TBAB [14], etc. and for most kinetic accelerant are surfactants, such as sodium...
dodecyl sulfate (SDS)\cite{11,15}. However, most thermodynamic accelerators and surfactants are obtained from petrochemical process, they are not only harmful to the environment but also unsustainable. So in recent years, many researchers have focused on natural promoters, Cai, et al\cite{4}. reported a new type of CO$_2$ hydrate promoters, L-methionine. However, this finding solved the problems of surfactant accelerators, but L-methionine has an irritant odor, and hypertoxic chemicals, sodium cyanide are used in the production process. Therefore, from the perspective of environment friendly chemistry, we continue to research natural amino acid system promoters, and found a new natural amino acid, L-isoleucine. At the same time, we here also research the influence of structure-performance of CO$_2$ hydrates\cite{4}.

2. Experimental Section

2.1 Materials
L-norleucine (98 %), L-isoleucine (98 %), L-tert-leucine (98 %), and L-leucine (98 %) were purchased from Shanghai Bio Science & Technology, CO$_2$ (99.999 %) was purchased from Shengying Gas, PR China.

2.2 CO$_2$ hydrate formation in a static reactor
For CO$_2$ hydrate reactions, the amino acid solution (10.0 g) was added into a low-temperature and high-pressure reactor without agitation with a volume of 82 cm$^3$ (Kerui Instruments, Gongyi, Henan, PR China). Temperature of reaction system was adjusted by a programming thermal circulator (DWHW-10, Kerui Instruments, Gongyi, Henan, PR China). Measuring the temperature inside the container with a type K thermocouple (-250 to 200 °C, Tianyi Cekong, Henan, PR China). Using high precision gauge pressure transmitter to monitor CO$_2$ gas pressure (0–10 MPa, Tianyi Cekong, Henan, PR China).

2.3 Calculation of CO$_2$ absorption
The capacity to absorb CO$_2$ is defined gravimetrically, that is the mass of CO$_2$ absorbed per unit mass in an aqueous solution at 273.2 K. The absorption capacity of CO$_2$ was calculated by the pressure reduction range in the reactor. Calculated the free volume of the container by subtracting the total volume of CO$_2$ hydrate, unreacted water and additives. Considering non-ideal factors, GASPAX v3.41 software (Horizon Technologies, USA) was used to calculate the gas absorption \cite{7,12}.

3. Results and discussion
Figure 1 shows the CO$_2$ hydrate kinetic curve during the reaction using L-isoleucine aqueous solutions with different concentrations (0.1 wt %, 0.2 wt %, 0.5 wt % and 1.0 wt %) and bulk water at 273.2 K. The induction time ($t_i$) and $t_{90}$ (the time to achieve 90% of the maximum gas storage) using the L-isoleucine aqueous solutions with different concentrations are presented in Table 1. The best performance of L-isoleucine was obtained at the concentration of 0.1 wt %, the gravimetric capacity reached up to 335 mg g$^{-1}$ (bulk water system under the same conditions is 50 mg g$^{-1}$), but the $t_{90}$ (the time to achieve 90% of the maximum gas storage) remained 155 min. L-isoleucine showed a mildly lower capacity (331 mg g$^{-1}$) but a shorter $t_{90}$ (131 min) at a higher concentration (0.2 wt %). When the concentration of L-isoleucine was increased to 1.0 wt %, the capacity significantly decreased to 290 mg g$^{-1}$. These results demonstrated that the L-isoleucine aqueous solution enhance the formation of CO$_2$ hydrate. In addition, the $t_i$ and $t_{90}$ using L-isoleucine aqueous solution with different concentrations in Table 1 also demonstrated that the dynamic driving force was higher at high concentration.
Figure 1. CO$_2$ uptake kinetics for bulk water and L-isoleucine aqueous solution at 273.2 K (initial pressure: 3.3 MPa).

Table 1. Summary of $t_i$ and $t_{90}$ time of CO$_2$ hydrate promoted by L-isoleucine

| Concentration | $t_i$ [min] | $t_{90}$ [min] |
|---------------|-------------|----------------|
| 0.1 wt%       | 71          | 155            |
| 0.2 wt%       | 28          | 131            |
| 0.5 wt%       | 16          | 93             |
| 1.0 wt%       | 10          | 59             |

The relationship between pressure-temperature (PT) and CO$_2$ hydrate formation in the presence of 0.2 wt % L-isoleucine and bulk water are shown in Figure 2. For the bulk water system (curve A), pressure changes linearly with temperature which indicating that there is no CO$_2$ hydrate formation of dissociation under bulk system. On the contrary, the PT curve of the system containing 0.2 wt % L-isoleucine (curve C) shows formation and subsequent dissociation of CO$_2$ hydrate, which can be seen by the sharp pressure drop during cooling and the rapid pressure rise during heating. In addition, the deviation from the phase equilibrium diagram of CO$_2$ hydrate (curve B) as the temperature of the sample continues to exceed 277 K, suggesting that CO$_2$ hydrate is metastable outside the acceptable pressure-temperature range due to the “self-preservation” effect of CO$_2$ hydrate which helps CO$_2$ hydrate keep stable for a period of time outside the stable range of pressure and temperature.
Figure 2. Pressure-temperature dependence during cooling and heating under CO₂ pressure: A) bulk water, B) phase equilibrium diagram of CO₂ hydrate[5] and C) 0.2 wt% L-isoleucine aqueous solution (temperature ramp: 2.0 K h⁻¹).

(a) CO₂ hydrate grew upward on the vessel wall (0.2 wt% L-isoleucine aqueous solution).
(b) CO₂ hydrate dissociate at room temperature.

Figure 3. Formation and dissociation of CO₂ hydrate.

As shown in Figure 3 (a), the liquid migrates from the bulk to the porous structure and the CO₂ hydrate grows on the reactor wall as a porous structure because of the capillary force, so L-isoleucine may act as dispersants to prevent hydrate particles from agglomerating and forming a rigid hydrate film at the liquid-gas interface, which significantly hinder further hydrate formation. The CO₂ hydrate formed by surfactant system produces a lot of persistent foam when degassing, while the CO₂ hydrate formed by using L-isoleucine aqueous solution dissociates without foaming upon degassing (Figure 3(a)), which suggesting that the L-isoleucine aqueous solution may hold considerable potential to be applied in practical.

We further studied the effect of isomerism of amino acid on the CO₂-hydrate-formation kinetics. Figure 4 shows the CO₂ hydrate formation kinetic curve using different amino acids aqueous solutions (containing 0.2 wt % L-norleucine, L-isoleucine, L-tert-leucine and L-leucine) at 273.2 K. With the same concentration of 0.2 wt %, the L-norleucine aqueous solution and the L-isoleucine aqueous solution exhibit good formation kinetics and high capacities while the L-tert-leucine aqueous solution and the L-leucine aqueous solution inhibit the formation of CO₂ hydrate. As expected, not each amino acid can promote the formation of CO₂ hydrates equally. For the L-norleucine aqueous solution, the gravimetric capacity reached up to 350 mg g⁻¹ in 1000 min, the t₉₀ was 41 min.
Figure 4. CO\textsubscript{2} uptake kinetics for the aqueous solution of L-norleucine, L-isoleucine, L-tert-leucine and L-leucine at 273.2 K (initial pressure, 3.3 MPa).

To better illustrate the promoting effect of the 0.2 wt % L-norleucine aqueous solution and the 0.2 wt % L-norleucine aqueous solution, the molecule structure was presented in Table 2. All these amino acids have the alpha carbon bonded to a hydrogen atom, carboxyl group, and amino group. The "R" group varies among amino acids and determines the differences. We speculate that the promoting effect of amino acids probably stem from the “R” group which can be considering into two main aspects: (1) the main-chain length; (2) the amount of methyl group bonded to γ-carbon.

Hydrophobicity increases with the number of carbon atoms in the hydrocarbon chain. As shown in Figure 4 and Table 2, L-norleucine with a longer alkyl chain and no methyl group compared with L-tert-leucine and L-leucine shows a promoting effect in the formation of CO\textsubscript{2} hydrate. In our early works, we also demonstrated that 2-aminoheptanoic acid with a longer alkyl chain (one more methylene group) compared with L-norleucine shows an inhibiting effect in the formation of CO\textsubscript{2} hydrate\cite{4}. Hence, there is an optimal alkyl chain length in hydrophobic amino acids enhancing the CO\textsubscript{2} hydrate formation. For L-isoleucine, there is a methyl group bonded to the β-carbon, which is differ from L-tert-leucine (two methyl group bonded to the β-carbon) and L-leucine (zero methyl group bonded to the β-carbon). Therefore, we assume that the promoting effect of L-isoleucine is closely related to the amount of methyl group bonded to the β-carbon of the amino acids.

Table 2. Structural formula of amino acid

| Name          | Molecular structure | Capacity \[mg g\textsuperscript{-1}\] | \(t\textsubscript{90}\) [min] |
|---------------|---------------------|--------------------------------------|-----------------------------|
| L-norleucine  | ![Molecular structure of L-norleucine] | 350                                  | 40                          |
| L-isoleucine  | ![Molecular structure of L-isoleucine]   | 331                                  | 131                         |
| L-tert-leucine| ![Molecular structure of L-tert-leucine] | 42                                   | 587                         |
4. Conclusions

To sum up, we have proved that L-isoleucine can significantly increase the CO$_2$ hydrate formation kinetics, and the gravimetric capacity of it can up to 331 mg g$^{-1}$ at a concentration of 0.2 wt%. We also proposed that the structure-performance of L-isoleucine from a sufficiently long hydrophobic carbon chain length and the number of methyl groups bonded to the $\beta$-carbon. These will provide a reference for exploring the promotion mechanism of CO$_2$hydrate.

Acknowledgements

The authors acknowledge the support from the National Natural Science Foundation of China (21676107 and 21176093).

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