

Molecular Mechanism of Liquid-Liquid Phase Separation in the Amine-CO₂-H₂O System

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Abstract

Some amine-water mixtures have lower critical solution temperatures (LCSTs) and can be separated into two phases by increasing the temperature. Hydrogen bonding (HB) is considered to play an important role in such phase transitions [1]. Recently, biphasic amine absorbents have attracted increased interest, since some biphasic systems show the potential for reducing the energy of the CO₂ capture process [2]. However, the molecular mechanism of liquid-liquid phase separation in the amine-CO₂-H₂O system is not understood and remains to be elucidated.

Aqueous amine solutions absorb CO₂ by the formation of (1) carbamate or (2) bicarbonate anions as follows [3-6]:



The ionic species produced by CO₂ absorption drastically change the solvation structure, which makes the phase separation phenomena more complicated. To explore the molecular mechanisms, in this study, we investigated the effects of CO₂ absorption on phase separation in amine-water systems by systematically changing the molecular formula of the amine. For this purpose, we used various amines, including newly synthesised amines [7], and computational chemistry methods [8-10].

Figure 1 shows the phase diagrams measured for (CH₃)₂N(CH₂)_nN(CH₃)₂-H₂O systems, where tertiary diamines were investigated by varying the alkyl chain length (n = 5,6,7). From the phase diagrams, we can determine the phase separation temperature for a certain amine mass fraction. For example, if we prepare 30 wt% aqueous diamine solutions (n = 5,6,7) and increase the temperature, the solutions start to separate into amine-rich and water-rich phases at ~350, 330, and 305 K. These measurements revealed that the LCST is sensitive to the alkyl chain length between the two amino groups. This fact can be explained in terms of the incomplete HB networks around the hydrophobic domain,

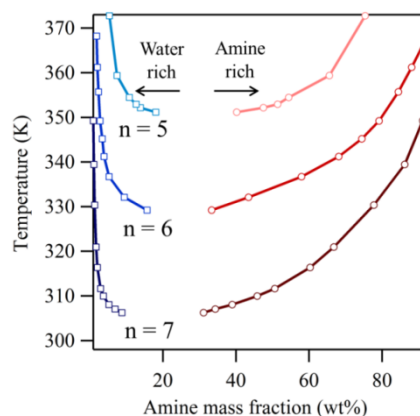


Figure 1. Phase diagrams of (CH₃)₂N(CH₂)_nN(CH₃)₂-H₂O systems.

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i.e., the alkyl chain.

We also experimentally demonstrated that under isothermal conditions, some aqueous amine solutions separate into amine-rich and water-rich phases, which is triggered by the absorption of CO₂. At the same time, the phase separation induces a transition in the CO₂ absorption rate, as seen in Figure 2. Chemical analysis showed that the neutral amine, which is a reactant in reaction (2), exists predominantly in the amine-rich phase. On the other hand, the protonated amine, which is a product of reaction (2), as well as the bicarbonate are dissolved in the water-rich phase. It should be noted that the reactants of reaction (2), i.e., $R^1R^2R^3N$ and H₂O, are separated while both products (HCO₃⁻ and $R^1R^2R^3NH^+$) are dissolved in the same phase in this case, which explains the reduction in the CO₂ absorption rate after the phase transition.

To gain insight into the mechanisms underlying these phenomena, we analysed the molecular interactions in these systems using molecular dynamics, density functional theory, and solvation models [8-10]. Figure 3 shows snapshots of molecular dynamics simulations for a diamine-water system at a fixed temperature and a pressure of 100 kPa (isothermal-isobaric ensemble). The results indicate that the phase separation occurs below the LCST in the presence of CO₂, because the ions formed by CO₂ absorption disrupt the water HB networks.

Furthermore, results of calorimetric measurements revealed that the phase separation process absorbs energy from its surroundings, in other words, the liquid-liquid phase separation is an endothermic process. Consequently, heat of CO₂ absorption can be significantly reduced in such systems as shown in Table 1.

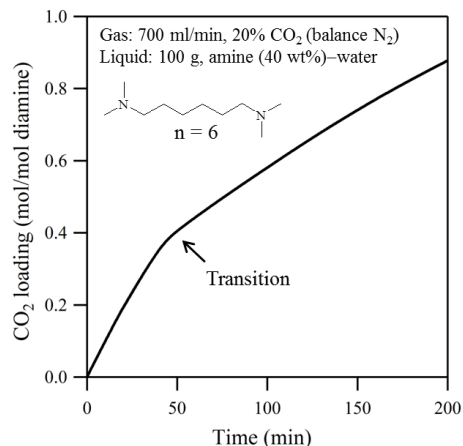


Figure 2. Time profile of CO₂ absorption in an aqueous diamine ($n = 6$) solution at 313 K.

Table 1. Heat of CO₂ absorption in (CH₃)₂N(CH₂)₆N(CH₃)₂-H₂O system^a measured at 313 K.

CO ₂ -loading range (mol/mol diamine)	Heat of absorption (GJ/ton CO ₂)
0.0–1.9	1.2
0.4–0.9	0.86

^a 35 wt%.

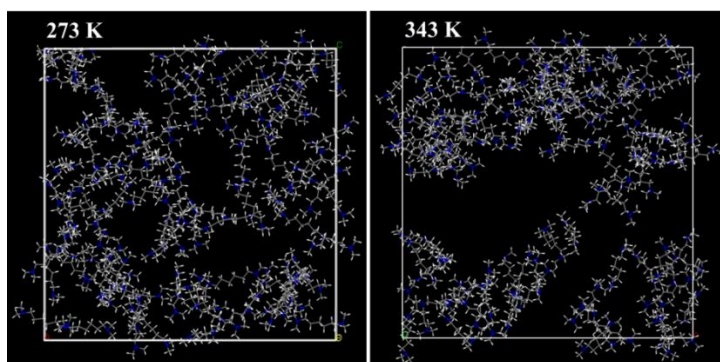


Figure 3. Snapshots of molecular dynamics simulation for system of 90 diamine ($n = 6$) and 3440 water (hidden) molecules.

Keywords: Biphasic amine absorbent; CO₂-induced phase separation; Hydrogen bonding; Thermal energy storage

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