Solvent effects in the thermal decomposition reaction of ammonium carbamate: A computational molecular dynamics study of the relative solubilities of CO₂ and NH₃ in water, ethylene glycol, and their mixtures

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Abstract

The endothermic decomposition of ammonium carbamate has been proposed as a novel heat sink mechanism for aircraft thermal management [Johnson *et al.* SAE Technical Paper 2012-01-2190, 2012, doi:10.4271/2012-01-2190]. The products of the reversible decomposition are carbon dioxide and ammonia which need to be efficiently removed from the carrier fluid in order to better control the reaction and thus the heat transfer. Molecular dynamics simulations can provide insight into the transport properties of carbon dioxide and ammonia in the carrier fluid. In this work, extensive classical non-reactive molecular dynamics simulations were carried out to explore the solvent effects in the thermal decomposition reaction of ammonium carbamate by studying the temperature and concentration dependence of relative solubility and diffusivity of carbon dioxide and ammonia in water, ethylene glycol, and their mixtures at standard temperature and pressure and at the elevated temperature of the thermal decomposition reaction of ammonium carbamate. This comparative study shows that ammonia is more soluble than carbon dioxide in either water or ethylene glycol and that both carbon dioxide and ammonia are more soluble in ethylene glycol than in water. Our simulations of water - ethylene glycol mixtures show that increasing the molar fraction of ethylene glycol leads to increased solubility of carbon dioxide and ammonia in the mixture. Even though this is a non-reactive study, it is able to capture the general solubility trends. Accounting for the reactions of carbon dioxide and ammonia in the solution would further amplify the observed trends by amplifying the retaining of CO₂ and NH₃ in the solution. We present a low-cost computational procedure for relative solubility evaluation that can be used in a broader engineering design context.

Keywords: Molecular dynamics simulations, Carbon dioxide, Ammonia, Ammonium carbamate, Ethylene glycol, Solvent effects, Heat exchanger, Solubility, Volume expansion

PACS: 44.35.+c, 47.22.Mn, 47.45.Gx, 47.70.-n, 66.10.cg, 68.03Fg, 82.20.Yn

1. Introduction

The developments in modern aircraft and electronics pose ever increasing demands on thermal management applications and have prompted a heightened interest in the search of application-tailored phase change mechanisms and materials as heat sinks. Endothermic reactions represent novel opportunities for heat sinks and the implications and specific challenges they also present need further exploration. Ammonium carbamate has emerged as an expendable high energy density thermal management material in aircraft thermal management [1–4]. The reaction kinetics of the ammonium carbamate decomposition has proven to be elusive [5] and complex [6]. A Raman spectroscopy study on ammonium carbonate, ammonium

bicarbonate, ammonium carbamate, and ammonium chloride with sodium carbonate allowed for an estimate of the equilibrium constants and thermodynamic parameters and showed the carbamic acid to be unstable with respect to decomposition into carbon dioxide and ammonia. [7] The relative concentration of carbonate decreased with increase of temperature compared to the concentration of bicarbonate and carbamate. The relative stabilities and optimal geometries of H₂NCOO[−], H₂NCOOH, ⁺H₃NCOO[−] have been evaluated using *ab initio* restricted Hartree-Fock calculations and it has been established that the zwitterion was the most probable intermediate for the decomposition of carbamic acid into ammonia and carbon dioxide, and that the zwitterion is an unstable species. [7]

There has been a significant interest and focus on the CO₂ + NH₃ reaction for the purposes of post-combustion carbon dioxide capture and storage and ammonium carbamate is studied as a product or intermediate in the CO₂ capture in ammonia. All these studies help to provide better understanding of the reverse reaction, the decomposi-

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tion of ammonium carbamate as well. Ammonia scrubbing has been proposed and explored for CO₂ removal from flue gas [8–10]. A review paper by *et al.* [11] discussed the methods being considered and employed for separation, capture, and sequestration of CO₂, including in large geological formations, see also Benson and Cole [12]. Dissolution of carbon dioxide in brine is studied in connection with CO₂ sequestration in geological formations [13]. There is a large number of experimental [14–16] and theoretical investigations of carbon dioxide capture in ammonia. The reaction kinetics of absorption of CO₂ in aqueous ammonia solutions has been studied at a range of temperatures [16–21]. Jeon *et al.* [21] have experimentally shown that hydroxyl additives (including ethylene glycol) enhance the absorption rate of CO₂ in aqueous ammonia as well as reduce the volatility of ammonia. Zwitter-ion mechanism [22, 23] was proposed to describe the reaction CO₂ + NH₃ as a two-stage reaction. Choi *et al.* [24] experimentally investigated the role of temperature in the aqueous reaction CO₂ + NH₃ and observed that at 278 K, the dominant reaction becomes bicarbonation, while at 298 K the dominant reaction is carbamation. A review by Zhao *et al.* [25] presents an overview of the current understanding and the fundamental research in post-combustion capture of CO₂ in aqueous ammonia. Other solvents and mixtures are being considered for more efficient CO₂ capture. For example, Puxty *et al.* [26] experimentally compared the rate of CO₂ absorption in ammonia and monoethanolamine. More recently, ionic liquids are being explored as promising candidates for very efficient postcombustion CO₂ capture [10, 27–29] since the diffusivities of carbon dioxide in ionic liquids are one to two orders of magnitude less than in other liquid solvents [30]. The interest in carbon dioxide solubility in aqueous and non-aqueous solutions and mixtures is driven not only by the need to identify those solvents and mixtures providing enhanced capture but also by the need to consequently strip the captured gas in an efficient and controlled manner. [31, 32]

The reaction of carbon dioxide and ammonia in solutions has proven to be a complex multistep process and the same is true for the reverse reaction of ammonium carbamate decomposition. Therefore, the goal of this work was to study the solvent effects in the thermal decomposition reaction of ammonium carbamate by employing classical non-reactive molecular dynamics simulations to quantify the solubility of carbon dioxide and ammonia in ethylene glycol, water, and their mixtures, the effects of temperature and carrier fluid composition, and to assess the suitability of ethylene glycol as a carrier fluid for the reaction of interest. This work focuses on an idealized and simplified situation as a first-approximation approach and further complexity can be added in future studies. Our approach does not take into account any reaction of the product gases and the carrier fluid but focuses, instead, at the solubility and diffusivity of the gases. The salt effects were also not the topic of this work as the experimental

Figure 1: Atomic structure of a single molecule of ethylene glycol.

setup of the reactive heat exchanger does not involve additives but the effect of contaminants should also be taken into account in the design of the experimental setup.

2. Simulation method and models

In this study, we use classical molecular dynamics (MD) simulations [33], in which each atom is modeled by the position of its nucleus, carries a partial electric charge, and its motion occurs in the potential field created by the rest of the atoms in the system. The interactions within a molecular system are approximated by intramolecular (bonded) interactions: bond stretching, bond bending, and torsions, and pairwise intermolecular (non-bonded) interactions: Lennard-Jones R^{-12} and R^{-6} interactions, and Coulomb interactions between any two charged particles. The set of parameters are usually called force field parameters and are either fitted to correctly reproduce some experimental properties (e.g. density and/or self-diffusion coefficient) or are derived from *ab initio* or density functional theory calculations of gas or condensed phase of the material being modeled.

2.1. Solvents: ethylene glycol and water

Figure 1 shows the molecular structure of ethylene glycol (EG) in a ball-and-stick representation as well as the atomic labels that were used in this work to specify atom types. The carbon atoms are shown in cyan and labeled CT, the oxygen atoms are shown in red and labeled OH, and all hydrogen atoms are white and labeled OH when they are in a hydroxyl group or HC when they are bonded to a carbon atom.

The performance of four different force fields with respect to predicting the structure of liquid ethylene glycol was evaluated by Saiz *et al.* [34]. In the study, the Lennard-Jones parameters for all models were the same while the partial charges were different and the results showed that the OPLS-based force fields reproduce more accurately the self-diffusion of ethylene glycol. Most recently, Szczerba *et*

al. [35] used AMBER force field to describe ethylene glycol intercalation in smectites and flexible SPC force field for water. An earlier work by Kaiser *et al.* [36] used OPLS-AA force field and these are the force field parameters adopted in this work, namely, OPLS/AMBER force field [37–40]. List of all parameters used to model ethylene glycol in this work is provided in Table 1. The bond stretch energy for each pair of bonded atoms is:

$$E_{\text{bond}} = k_r(r - r_{\text{eq}})^2; \quad (1)$$

the bond bend (angle) energy is:

$$E_{\text{angle}} = k_\theta(\theta - \theta_{\text{eq}})^2; \quad (2)$$

and the torsion energy for each dihedral angle φ is:

$$E_{\text{tor}} = \frac{V_1}{2}(1 + \cos \varphi) + \frac{V_2}{2}(1 - \cos 2\varphi) + \frac{V_3}{2}(1 + \cos 3\varphi) + \frac{V_4}{2}(1 - \cos 4\varphi), \quad (3)$$

where φ are the dihedral angles in the ethylene glycol molecule listed in Table 1. The non-bonded interaction are described by the Lennard-Jones and Coulomb interaction energy as follows:

$$E_{\text{non-bond}} = \sum_{i,j} 4\varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) - \sum_{i < j} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}, \quad (4)$$

where the mixing of the Lennard-Jones parameters is geometric: $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$ and $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ and $\epsilon_0 = 8.9 \times 10^{-12}$ F/m is the permittivity of free space.

The water model used in this work was the rigid extended single point charge (SPC/E) pair potential [41] which reproduces very well the density and diffusion constant of water at 300 K [41, 42]. The bonds and the angle within the water molecules are kept rigid by employing the SHAKE algorithm [43] which does not compromise the transport properties of the simulated water as recent studies have shown that rigid models better reproduce the experimental diffusivity and thermal conductivity of water for the majority of the most popular water models [44, 45].

2.2. Decomposition products: Carbon dioxide and ammonia

The molecular structure of a carbon dioxide molecule is shown on the left of Figure 2. The usual color convention is followed where the carbon atom is shown in cyan and the oxygen atoms are red. Moulton *et al.* [46] computed the diffusivity of carbon dioxide in water at different temperatures and pressure. In a recent work,

Table 1: The values of the force field parameters for ethylene glycol used in this work are from OPLS-AA force field [36, 37]. The units are as follows: m [a.u.], q [e], σ [Å], ε [kcal/mol], k_r [kcal/(mol·Å²)], r_{eq} [Å], k_θ [kcal/(mol·rad²)], θ [°], V_i [kcal/mol], $i = 1, \dots, 4$.

Atoms	m	q	σ	ε
CT	12.01	0.145	3.500	0.066
HC	1.008	0.060	2.500	0.030
OH	15.999	-0.700	3.070	0.170
HO	1.006	0.435	0.0	0.0
Bonds	k_r	r_{eq}		
HO – OH	553.0	0.945		
CT – CT	268.0	1.526		
CT – HC	340.0	1.090		
CT – OH	320.0	1.410		
Angles	k_θ	θ		
CT – OH – HO	55.0	108.5		
CT – CT – HC	37.5	110.7		
HC – CT – HC	33.0	107.8		
CT – CT – OH	50.0	109.5		
HC – CT – OH	35.0	109.5		
Dihedral angles	V_1	V_2	V_3	V_4
OH – CT – CT – OH	9.066	0.0	0.0	0.0
HC – CT – CT – OH	0.0	0.0	0.468	0.0
HC – CT – CT – HC	0.0	0.0	0.318	0.0
CT – CT – OH – HO	2.674	-2.883	1.026	0.0
HC – CT – OH – HO	0.0	0.0	0.45	0.0

Figure 2: Atomic structure and atom labels of a carbon dioxide molecule (left) and an ammonia molecule (right).

Table 2: Non-bonded parameters for carbon dioxide.

Atoms	m [a.u.]	q [e]	σ [Å]	ε [kcal/mol]
C	12.010	0.6512	2.800	0.0559
O	15.999	-0.3256	3.028	0.1597

Table 3: Non-bonded parameters for ammonia.

Atoms	m [a.u.]	q [e]	σ [Å]	ε [kcal/mol]
N	14.0065	-1.02	0.17	3.42
H	1.008	0.34	0.0	0.0

Garcia-Ratés *et al.* [47] used molecular dynamics simulations to study the diffusion coefficients, ionic conductivity, and rotational relaxation of CO₂ in aqueous ionic solutions (brines). More recently, Criscenti and Cygan [48] used the flexible force field to compare the cation solvation in water and supercritical carbon dioxide. The solubility of carbon dioxide in 1-ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide was studied by means of molecular dynamics simulations [49] of the molar volume expansion vs. CO₂ mole fraction mixtures. In this work, we use the fully flexible force field developed by Cygan *et al.* [50] and based on the original carbon dioxide force field by Harris and Yung [51]. The bond parameters are: $k_r = 1008.963$ kcal/(mol·Å²) and $r_{eq} = 1.162$ Å, and the angle parameters are: $k_\theta = 108.0067$ kcal/(mol·rad²) and $\theta_{eq} = 180^\circ$. The non-bonded force field parameters for carbon dioxide used in this work are listed in Table 2.

The molecular structure of an ammonia molecule is shown on the right of Figure 2. The nitrogen atom is blue while the hydrogen atoms are white. Two sets of force field parameters are usually used for ammonia: OPLS all-atom (OPLS-AA) and TraPPE. OPLS-AA force field for ammonia was proposed by Rizzo and Jorgensen [38]. The TraPPE model of ammonia based on the 5-site model originally proposed by Impey and Klein [52], contains a fifth massless site carrying a negative charge and the bond lengths are rigid but the angles in the ammonia molecule are flexible [53]. The force field parameters for ammonia used in this work are from OPLS-AA [38] as follows, bond parameters: $k_r = 434.0$ kcal/(mol·Å²), $r_{eq} = 1.01$ Å, angle parameters: $k_\theta = 43.60$ kcal/(mol·rad²), $\theta_{eq} = 106.4^\circ$, and the non-bonded parameters are listed in Table 3.

3. Simulation systems and details

The relative solubilities of CO₂ and NH₃ were evaluated by considering the equilibrium volume expansion of simulation systems with added gas at different gas mole fraction under normal pressure of 1 atm which is the operational pressure of the proposed reaction heat exchanger.

Table 4: Number of gas molecules (CO₂ or NH₃) in the simulation systems to obtain the gas molar fraction (X_{gas} , first row).

X_{gas}	1%	5%	10%	20%	30%	40%
In WAT	41	202	440	1012	1716	2700
In EG	20	102	225	518	879	1350

The prepared neat solvent systems consisted of 4096 water molecules and 2048 ethylene glycol molecules, respectively. To those neat solvent systems, a different number of gas molecules was added to achieve molar fraction X_{gas} of 1 %, 5%, 10%, 20%, 30% CO₂ with additional 40 % mole fraction of NH₃ as shown in Table 4. In addition, the equilibrium volume expansion in 2%, 3%, and 4% mole fraction of carbon dioxide in neat water was also considered. A number of water-ethylene glycol systems were built corresponding to different ethylene glycol mole fractions and, here, we report the results for two mixtures, ethylene glycol mole fraction of 10 % and 75 %. The corresponding simulation systems were built using Packmol [54] by arranging 4096 water molecules and 480 EG molecules in a random manner in the simulation box to achieve $X_{EG} = 10$ % and 512 water molecules and 1536 EG molecules for $X_{EG} = 75$ %. All simulation systems were equilibrated for 100 ps under constant volume and temperature (300 K or 333 K), followed by 200 ps simulation time at constant pressure of 1 atm and constant temperature, and a final equilibration at constant volume and temperature for another 100 ps. The timestep of integration of the Newton’s equations of motion was 0.001 ps. A snapshot of the simulated system was output every 500 simulation steps or every 0.5 ps. The equilibrium volume of the system was computed from the simulation box size at the end of the equilibration for each system. Periodic boundary conditions were used in all three dimensions to model bulk properties. The cut-off for the non-bonded interactions was 8 Å smoothed over an additional angstrom [55]. Particle Mesh Ewald summation was used to account for the long-range Coulomb interactions beyond the cutoff. All simulation systems were built using Packmol [54] and all MD simulations were carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [55].

4. Results and discussion

4.1. Equilibrium volume and volume expansion

The equilibrium volume of the simulation systems after the addition of CO₂ or NH₃ was compared to the original equilibrium volume of the neat solvent as a measure of the solubility of carbon dioxide and ammonia in pure water and pure ethylene glycol. The volume expansion of the liquid phase is defined as follows [56]:

$$\frac{\Delta V}{V_0} = \frac{V - V_0}{V_0}, \quad (5)$$

Figure 3: Equilibrium molar volume expansion at different CO_2 (filled symbols) and NH_3 (open symbols) mole fraction in water (circles) and ethylene glycol (triangles) at 300 K. The lines are provided as a guide to the eye.

where V_0 is the equilibrium molar volume of the neat solvent system and V is the equilibrium molar volume of the liquid with added CO_2 or NH_3 . The results for the equilibrium volume expansion at 300 K are shown in Figure 3. Here and in what follows, all volumes are per-molecule. Figure 3 shows that both CO_2 and NH_3 are more soluble in ethylene glycol (EG) than in water, especially at higher mole fractions. Furthermore, NH_3 is more soluble than CO_2 in either water or ethylene glycol and the solubility of CO_2 in water decreases at higher CO_2 concentrations. Our simulations of the CO_2 mole fractions of 20% and 30% showed spontaneous phase separation in the water - carbon dioxide system into water and CO_2 phase.

The solubility of carbon dioxide in water-ethylene glycol mixtures was also explored and Figure 4 compares the molar volume expansion when adding carbon dioxide to two water-EG mixtures, 10% mole fraction EG and 75% mole fraction EG, with pure water and pure ethylene glycol. The results confirmed that the solubility of CO_2 increases with the increase of the ethylene glycol mole fraction as it is clear from Figure 4.

Figure 5 shows the temperature dependence of the equilibrium molar volume expansion of carbon dioxide and ammonia dissolved in pure water and pure ethylene glycol. A decrease in the solubility of ammonia was observed at the ammonium carbamate reaction temperature (333 K) compared to the ammonia solubility at 300 K both in water and ethylene glycol. This effect has been observed experimentally [57, 58]. In the case of carbon dioxide, however, the solubility in water decreases drastically at higher CO_2 concentrations (above 10% mole fraction where the phase separation was observed) at the temperature of the decomposition reaction. Thus, the results of our simulations

Figure 4: Equilibrium molar volume expansion as a function of CO_2 mole fraction in water - ethylene glycol mixtures of increasing EG mole fraction at 300 K. The lines are provided as a guide to the eye.

show that for the purposes of thermal management where the goal is to drive the reaction toward the thermal decomposition of ammonium carbamate and to efficiently remove the product gases, ethylene glycol is a poor choice of carrier fluid. Using a mixture of water and ethylene glycol would decrease the solubility of the product gases and may help with their removal. Screening of other solvents in which both CO_2 and NH_3 are less soluble as candidate carrier fluids for the thermal decomposition reaction of ammonium carbamate could be the subject of future work.

4.2. Temperature and concentration dependence of CO_2 and NH_3 diffusivity in water - ethylene glycol mixtures

After equilibration at pressure of 1 atm and room temperature (300 K) or the reaction temperature (333 K), classical MD simulations were performed for 1 nanosecond in NVE ensemble for all systems and the simulation results were used to compute the diffusivities of carbon dioxide and ammonia in the solutions from the mean squared displacement (MSD) of the center of mass of all gas molecules of each type as follows:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle, \quad (6)$$

where $\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle$ is the mean squared displacement averaged over all gas molecules of each type and over all time origins. The computed diffusion coefficients of carbon dioxide and ammonia in pure ethylene glycol and pure water and in two mixtures, i.e. 10% and 75% molar fraction of ethylene glycol, at room temperature, are listed in Table 5. The values for 20% and 30% CO_2 are in parentheses

Figure 5: Equilibrium molar volume expansion at different CO_2 (left) and NH_3 (right) mole fraction in water (circles) and ethylene glycol (triangles) at 300 K (filled symbols) and 333 K (open symbols). The lines are provided as a guide to the eye.

Table 5: Values of the computed diffusion coefficients (in $\times 10^{-5} \text{ cm}^2/\text{s}$) of CO_2 and NH_3 in water - ethylene glycol mixtures at different gas mole fractions (X_{gas}) at 300 K. The first row lists the mole fraction X_{EG} (%) of ethylene glycol (EG) in the solvent mixture. The first column lists the values of the gas mole fraction in the solution.

$X_{\text{EG}} \rightarrow$	0%		10%	75%	100%	
X_{gas}	CO_2	NH_3	CO_2	CO_2	CO_2	NH_3
1%	2.92	3.41	1.64	0.09	0.05	-
5%	2.52	2.66	1.77	0.15	0.10	0.07
10%	2.91	2.54	1.89	0.23	0.14	0.13
20%	(7.28)	2.81	3.52	0.43	0.28	0.25
30%	(26.52)	3.29	8.68	0.67	0.49	0.42
40%		3.79				0.83

since phase separation was observed during the simulation and the computed diffusivities do not correspond to diffusion in water but rather in the gas phase. The computed values for the diffusivities of CO_2 in neat water are comparable with the ones obtained by Moulton *et al.* [46] using the SPC/E water model even though the force field models used for carbon dioxide were different.

Additionally, Figure 6 compares the diffusivities on CO_2 and NH_3 in neat water and neat ethylene glycol at 300 K (left panel) and 333 K (right panel). Higher diffusivities are observed for both gases in water than in ethylene glycol. An increase of the diffusivity at elevated temperature was observed. For the case of carbon dioxide molar fraction in water above 20%, when spontaneous phase separation was observed in our simulations, the diffusivity of CO_2 increases dramatically because of the phase separation. Thus the computed values for the diffusion coefficients do not correspond to diffusivity in water but rather

in the gas phase and, therefore, cannot be compared with the values computed for diffusion in the condensed phase. At low concentrations, the diffusivity of CO_2 is somewhat higher than the diffusivity of NH_3 in ethylene glycol, while in water both gases show similar diffusivities. Furthermore, the concentration dependence of the diffusivity of ammonia in both water and ethylene glycol is very weak at least to the extent of the concentrations that were considered in this study. Thus, even though the simulations did not account for the recombination reaction of carbon dioxide and ammonia, nor the reaction of the gases with the solvent, the computed diffusivity trends support the observations and conclusions made in the previous section when the equilibrium volume expansion was considered, namely, that in comparison to ethylene glycol, water is a better carrier fluid for the purposes of promptly removing the product gases of the thermal decomposition reaction of ammonium carbamate.

5. Conclusions

An extensive set of molecular dynamics simulations was carried out with the purpose of studying the liquid volume expansion and diffusion coefficients of the products of the thermal decomposition of ammonium carbamate, carbon dioxide and ammonia, in water and ethylene glycol at standard conditions and at the elevated temperature of the decomposition reaction. Solvent mixtures of water and ethylene glycol were also considered. The goal of this study was to compare the solvent compositions for the purposes of using the mixtures as carrier fluid in a heat exchanger utilizing the endothermic decomposition reaction of ammonium carbamate. The modeling and simulation results

Figure 6: Diffusion coefficients (D_0) of CO_2 (circles) and NH_3 (squares) in neat water (open symbols) and ethylene glycol (filled symbols) at 300 K (left) and 333 K (right).

presented in this paper confirm that addition of hydroxyl groups, i.e. ethylene glycol, to aqueous solutions increases the solubility of carbon dioxide. This study points to the observation that compared to water, ethylene glycol is not as well suited to be a carrier fluid for the thermal decomposition reaction of ammonium carbamate. Addition of water could improve the properties of ethylene glycol as a carrier fluid by decreasing the solubility of the product gases and assisting with their removal. Alternatively, a different solvent or mixture can be a suitable carrier fluid in which either both ammonia and carbon dioxide are less soluble or their solubility decreases rapidly at higher gas mole fractions within the temperature range of the decomposition reaction. Thus, this study underlines that molecular dynamics simulations offer a powerful low-cost tool in fast throughput and engineering design that can be useful in a broader context of solvent screening for better solubility and heat transfer control beyond the more specific thermal decomposition reaction of ammonium carbamate.

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Disclosure Statement

To the best of the authors' knowledge, there are no conflicts of interest between the authors or their respective institutions and the International Journal of Heat and Mass Transfer.

References

- [1] J.E. Schmidt, D.S. Dudis, D.J. Miller, Expendable high energy density thermal management material: Ammonium Carbamate, *J. Thermophys. Heat Transfer*, 26 (2012) 345-351.
- [2] D. Johnson, S. Patnaik, J. Ervin, An integrated chemical reactor - heat exchanger based on ammonium carbamate, in: *Proceedings of the SAE 2012 Power Systems Conference*, SAE International, Phoenix, 2012.
- [3] N. Niedbalski, D. Johnson, S. Patnaik, D. Banerjee, Study of a multi-phase hybrid heat exchanger-reactor (HEX reactor): Part I - Experimental characterization, *Int. J. Heat Mass Transf.* 70 (2014) 1078-1085.
- [4] N. Niedbalski, D. Johnson, S. Patnaik, D. Banerjee, Study of a multi-phase hybrid heat exchanger-reactor (HEX reactor): Part II - Numerical prediction of thermal performance, *Int. J. Heat Mass Transf.* 70 (2014) 1086 -1094.
- [5] B. Claudel, L. Boulamri, A new model of gas-solid kinetics: The case of ammonium carbamate formation and decomposition, *Thermochim. Acta*, 126 (1988) 129-148.
- [6] B.R. Ramachandran, A.M. Halperin, E.D. Glendening, Kinetics and mechanism of the reversible dissociation of ammonium carbamate: Involvement of carbamic acid, *J. Phys. Chem. A*, 102 (1998) 3934-3941.
- [7] N. Wen, M.H. Brooker, Ammonium carbonate, ammonium bicarbonate, and ammonium carbamate equilibria: A Raman study, *J. Chem. Phys.* 99 (1995) 359-368.
- [8] H. Bai, A.C. Yeh, Removal of CO_2 greenhouse gas by ammonia scrubbing, *Ind. Eng. Chem. Res.* 36 (1997) 2490-2493.
- [9] A. Yeh, H. Bai, Comparison of ammonia and monoethanolamine solvents to reduce CO_2 greenhouse emissions, *Sci. Total Environ.* 228 (1999) 121-133.
- [10] J.D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, R.D. Srivastava, Advances in CO_2 capture technology: The U.S. Department of Energy carbon sequestration program, *Int. J. Greenhouse Gas Control* 2 (2008) 9-20.
- [11] C.M. White, B.R. Strazisar, E.J. Granite, J.S. Hoffman, H.W. Pennline, Separation and capture of CO_2 from large stationary sources and sequestration in geological formations, coalbeds, and deep saline aquifers, *J. Air Waste Manag. Assoc.* 53 (2003) 645-715.
- [12] S.M. Benson, D.R. Cole, CO_2 sequestration in deep sedimentary formations, *Elements* 4 (2008) 325-331.
- [13] J. Rosenqvist, A.D. Kilpatrick, B.W. Yardley, Solubility of car-

- bon dioxide in aqueous fluids and mineral suspensions at 294 K and subcritical pressure, *Appl. Geochem.* 27 (2012) 1610-1614.
- [14] Y.-F. Diao, X.-Y. Zheng, B.-S. He, C.-H. Chen, X.-C. Xu, Experimental study on capturing CO₂ greenhouse gas by ammonia scrubbing, *En. Conv. Manag.* 45 (2004) 2283-2296.
 - [15] W. Conway, X. Wang, D. Fernandes, R. Burns, G. Lawrence, M. Maeder, Comprehensive kinetic and thermodynamics study of the reaction of CO₂(aq) and HCO₃ with monoethanolamine (MEA) in aqueous solution, *J. Phys. Chem. A* 115 (2011) 14340-14349.
 - [16] X. Wang, W. Conway, D. Fernandes, R. Burns, G. Puxty, M. Maeder, Kinetics of the reversible reaction of CO₂(aq) with ammonia in aqueous solution, *J. Phys. Chem. A* 115 (2011) 6405-6412.
 - [17] P. Derks, G. Versteeg, Kinetics of absorption of carbon dioxide in aqueous ammonia solutions, *En. Procedia* 1 (2009) 1139-1146.
 - [18] J. Liu, S. Wang, B. Zhao, H. Tong, C. Chen, Absorption of carbon dioxide in aqueous ammonia, *En. Procedia* 1 (2009) 933-940.
 - [19] F. Qin, S. Wang, A. Hartono, H.F. Svendsen, C. Chen, Kinetics of CO₂ absorption in aqueous ammonia solutions, *Int. J. Greenhouse Gas Control* 4 (2010) 729-738.
 - [20] J. Liu, S. Wang, G. Qi, B. Zhao, Kinetics and mass transfer of carbon dioxide absorption into aqueous ammonia, *En. Procedia* 4 (2011) 525-532.
 - [21] A.-B. Jeon, J.-B. Seo, H.-D. Lee, S.-K. Kang, K.-J. Oh, Absorption kinetics of carbon dioxide into aqueous ammonia solution: Addition of hydroxyl groups for suppression of vaporization, *Kor. J. Chem. Eng.* 30 (2013) 1790-1796.
 - [22] M. Caplow, Kinetics of carbamate formation and breakdown, *J. Am. Chem. Soc.* 90 (1968) 6795-6803.
 - [23] P. Danckwerts, The reaction of CO₂ with ethanolamines, *Chem. Eng. Sci.* 34 (1979) 443-446.
 - [24] B.G. Choi, H.S. Park, G.H. Kim, Y.M. Jung, K.B. Yi, J.-N. Kim, W.H. Hong, Analysis of CO₂-NH₃ reaction dynamics in an aqueous phase by PCA and 2D IR COSY, *J. Ind. Eng. Chem.* 18 (2012) 98-104.
 - [25] B. Zhao, Y. Su, W. Tao, L. Li, Y. Peng, Post-combustion CO₂ capture by aqueous ammonia: A state-of-the-art review, *Int. J. Greenhouse Gas Control* 9 (2012) 355-371.
 - [26] G. Puxty, R. Rowland, M. Attalla, Comparison of the rate of CO₂ absorption into aqueous ammonia and monoethanolamine, *Chem. Eng. Sci.* 65 (2010) 915-922.
 - [27] C. Cadena, J.L. Anthony, J.K. Shah, T.I. Morrow, J.F. Brennecke, E.J. Maginn, Why is CO₂ so soluble in imidazolium-based ionic liquids?, *J. Am. Chem. Soc.* 126 (2004) 5300-5308.
 - [28] D.M. D'Alessandro, B. Smit, J. Long, Carbon dioxide capture: Prospects for new materials, *Angew. Chem. Int. Ed.* 49 (2010) 6058-6082.
 - [29] J.F. Brennecke, B.E. Gurkan, Ionic liquids for CO₂ capture and emission reduction, *J. Phys. Chem. Lett.* 1 (2010) 3459-3464.
 - [30] M.B. Shiflett, A. Yokozeki, Solubilities and diffusivities of carbon dioxide in ionic liquids: [bmim][PF₆] and [bmim][BF₄], *Ind. Eng. Chem. Res.* 44 (2005) 4453-4464.
 - [31] J. Li, C. You, L. Chen, Y. Ye, Z. Qi, K. Sundmacher, Dynamics of CO₂ absorption and desorption with co-solvent polyethylene glycol, *Ind. Eng. Chem. Res.* 51 (2012) 12081-12088.
 - [32] C. Guo, S. Chen, Y. Zhang, G. Wang, Solubility of CO₂ in non-aqueous absorption system of 2-(2-aminoethylamine)ethanol + benzyl alcohol, *J. Chem. Eng. Data* 59 (2014) 1796-1801.
 - [33] M. Allen, D. Tildesley, *Computer simulations of liquids*; Oxford Science, Oxford, 1987.
 - [34] L. Saiz, J.A. Padró, E. Guàrdia, Structure of liquid ethylene glycol: A molecular dynamics study with different force fields, *J. Chem. Phys.* 114 (2001) 3187-3199.
 - [35] M. Szczerba, Z. Kłapyta, A. Kalinichev, Ethylene glycol intercalation in smectites. Molecular dynamics simulation studies, *Appl. Clay Sci.* 91 (2014) 87-97.
 - [36] A. Kaiser, O. Ismailova, A. Koskela, S. Huber, M. Ritter, B. Cosenza, W. Bengler, R. Nazmutdinov, M. Probst, Ethylene glycol revisited: Molecular dynamics simulations and visualization of the liquid and its hydrogen-bond network, *J. Molec. Liquids* 189 (2014) 20-29.
 - [37] W. Damm, A. Frontera, J. Tirado-Rives, W. Jorgensen, OPLS all-atom force field for carbohydrates, *J. Comput. Chem.* 18 (1997) 1955-1970.
 - [38] R.C. Rizzo, W.L. Jorgensen, OPLS all-atom model for amines: Resolution of the amine hydration problem, *J. Am. Chem. Soc.* 121 (1999) 4827-4836.
 - [39] O.V. de Oliveira, L.C.G. Freitas, Molecular dynamics simulation of liquid ethylene glycol and its aqueous solutions, *J. Molec. Struct.: THEOCHEM* 728 (2005) 179-187.
 - [40] V. Hornak, R. Abel, A. Okur, B. Strickbinder, A. Roitberg, C. Simmering, Comparison of multiple Amber force fields and development of improved protein backbone parameters, *Proteins: Structure, Function, and Bioinformatics* 65 (2006) 712-725.
 - [41] H.J.C. Berendsen, J.R. Grigera, T.P. Straatsma, The missing term in effective pair potentials, *J. Phys. Chem.* 91 (1987), 6269-6271.
 - [42] P. Mark, L. Nilsson, Structure and dynamics of the TIP3P, SPC, and SPC/E water models at 298 K, *J. Phys. Chem. A* 105 (2001) 9954-9960.
 - [43] J.-P. Ryckaert, G. Ciccotti, H. Berendsen, Numerical integration of the cartesian equations of motion of a system with constraints: Molecular dynamics of *n*-alkanes, *J. Comput. Phys.* 23 (1977) 327-341.
 - [44] T.W. Sirk, S. Moore, E.F. Brown, Characteristics of thermal conductivity in classical water models, *J. Chem. Phys.* 138 (2013) 064505.
 - [45] E.K. Iskrenova, S.S. Patnaik, Transport properties of water and sodium dodecyl sulfate, *ASME J. Nanotechnol. Eng. Medicine* 4 (2013) 031001.
 - [46] O.A. Moulton, I.N. Tsimpanogiannis, A.Z. Panagiotopoulos, I.G. Economou, Atomistic molecular dynamics simulations of CO₂ diffusivity in H₂O for a wide range of temperatures and pressures, *J. Chem. Phys. B* 118 (2014) 5532-5541.
 - [47] M. Garcia-Ratés, J.-C. de Hemptinne, J.B. Avalos, C. Nieto-Draghi, Molecular modeling of diffusion coefficient and ionic conductivity of CO₂ in aqueous ionic solutions, *J. Phys. Chem. B* 116 (2012) 2787-2800.
 - [48] L.J. Criscenti, R.T. Cygan, Molecular simulations of carbon dioxide and water: Cation solvation, *Environ. Sci. Technol.* 47 (2013) 87-94.
 - [49] T. Lourenço, M. Coelho, T. Ramalho, D. van der Spoel, L. Costa, Insights on the solubility of CO₂ in 1-ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide from the microscopic point of view, *Environ. Sci. Technol.* 47 (2013) 7421-7429.
 - [50] R.T. Cygan, V.N. Romanov, E.M. Myshakin, Molecular simulation of carbon dioxide capture by montmorillonite using an accurate and flexible force field, *J. Chem. Phys. C* 116 (2012) 13079-13091.
 - [51] J.G. Harris, K.H. Yung, Carbon dioxide's liquid-vapor coexistence curve and critical properties as predicted by a simple molecular model, *J. Chem. Phys.* 99 (1995) 12021-12024.
 - [52] R. Impey, M. Klein, A simple intermolecular potential for liquid ammonia, *Chem. Phys. Lett.* 104 (1984) 579-582.
 - [53] L. Zhang, J.I. Siepmann, Development of the TraPPE force field for ammonia, *Coll. Czech. Chem. Comm.* 75 (2010) 577-591.
 - [54] L. Martínez, R. Andrade and E.G. Birgin and J.M. Martínez, PACKMOL: A package for building initial configurations for molecular dynamics simulations, *J. Comput. Chem.* 30 (2009) 2157.
 - [55] S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, *J. Comput. Phys.* 117 (1995) 1-19.
 - [56] J. de la Fuente Badilla, C. Peters, J. de Swaan Arons, Volume expansion in relation to the gas-antisolvent process, *J. Supercrit. Fluids* 17 (2000) 13-23.
 - [57] I. Short, A. Sahgal, W. Hayduk, Solubility of ammonia and hydrogen sulfide in several polar solvents, *J. Chem. Eng. Data* 28 (1983) 63-66.
 - [58] M.I. Pownceby, D.H. Jenkins, R. Ruzbacky, S. Saunders, Sol-

ubilities of ammonia and ammonium chloride in ammoniated and nonammoniated methanol and ethylene glycol between 298 K and 353 K, J. Chem. Eng. Data 57 (2012) 1449-1455.