Energy Proceedings
Vol 34, 2023
ISSN 2004-2965

Effect of solvent on the thermal dissociation of TOAHCl through DFT and MD

Tianyu Sun, Yuan Ma, Chenglin Liu*, Jianguo Yu

National Engineering Research Center for Integrated Utilization of Salt Lake Resources,

East China University of Science and Technology, Shanghai 200273, PR CHINA

(*Chenglin Liu: liuchenglin@ecust.edu.cn)

ABSTRACT

The coupled reaction-extraction-crystallization process for CO_2 mineralization is a essential technology for CCUS. The thermal regeneration of organic amine hydrochlorides is a crucial technique to facilitate the industrialization of this process. In this study, DFT was used to calculate the geometry, charge distribution, infrared spectrum and solvation free energy of TOAHCl in different solvents. MD was used to examine the thermal dissociation of TOAHCl in non-polar solvents and calculate the RDF, MSD and diffusion coefficient during the dissociation. Through DFT and MD, effect of solvent on the thermal dissociation of TOAHCl was investigated. DFT calculations is consistent with experimental results. MD results show solvents can disperse reactants and products, enhance mass transfer.

Keywords: DFT, MD, thermal dissociation, tri-n-octylamine hydrochloride

NONMENCLATURE

Abbreviations

DFT	Density Functional Theory
TOAHCl	Tri-n-octylamine Hydrochloride
MD	molecular dynamics simulation
RDF	Radial Distribution Function
MSD	Mean Square Displacement

1. INTRODUCTION

Since the Industrial Revolution, human activities have increased the emission of greenhouse gases, leading to an enhanced greenhouse effect. According to the IPCC report, the global annual atmospheric CO_2 concentration reached 420.78 ppm[1] in 2022, which was the highest level in history. To cope with the climate challenge, many countries have been exploring effective CCS and CCUS technologies since 1980s to reduce CO_2 emissions and increase its utilization value.

CCUS technology has been developed so far, of which the chemical capture method is relatively mature[2]. The organic amine CO_2 chemical capture method can be combined with carbon mineralization technology, such as Coupled reaction-extraction-crystallization process to mineralize CO_2 with calcium chloride waste liquid[3] (Fig. 1). This technology is a very promising CCUS technology, which can not only solve the problem of calcium chloride waste liquid that needs to be disposed of urgently in many industries, but also fix a large amount of CO_2 and store it permanently. However, to promote the industrialization process of coupled reaction-extraction-crystallization, the research about the regeneration process of organic amine hydrochloride is the key factor.

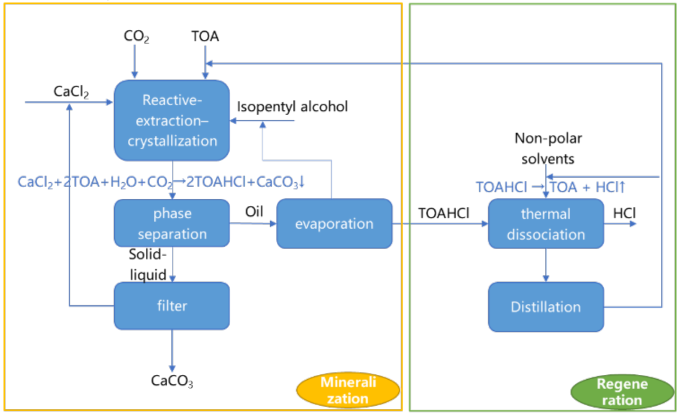

Fig. 1. reaction-extraction-crystallization coupled process

There are various regeneration technologies for organic amine hydrochloride, such as thermal dissociation[4], chemical regeneration[5], etc. Thermal dissociation can regenerate organic amines under certain conditions by heating, which is the most likely to achieve industrial application. Dong et al.[4] screened decalin as a thermal dissociation solvent for TOAHCl, which lowered the dissociation temperature to 180°C. The dissociation was carried out under nitrogen atmosphere to avoid the oxidation of TOA, and the regeneration rate could reach more than 99%. However,

---

This is a paper for International CCUS Conference 2023 (ICCUSC2023), April 14-15, 2023, Beijing, China.

decalin is an expensive solvent, and when used as a thermal dissociation solvent, it needs to be added to the system at a mass ratio of 5 times that of TOAHCl. The energy consumption of thermal dissociation and subsequent separation are both high, making it difficult to apply to industrial production. Therefore, it is still necessary to screen a cheaper and more accessible thermal dissociation solvent for industrial application.

In this paper, effect of solvent on the thermal dissociation of TOAHCl was investigated by DFT and MD, which helped us to experimentally screen the most suitable thermal dissociation solvent for TOAHCl.

2. METHODOLOGY

2.1 Experimental reagents and instruments

TOA (≥95%) was purchased from Shanghai Macklin Biochemical Co., Ltd. Decalin (GR, ≥99.5%), tetralin (CP, ≥98.0%), n-octanol (AR, ≥99.0%), hydrochloric acid (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. n-undecane (GR, ≥99%), n-dodecane (GR, ≥99%), n-pentadecane (GR, ≥99%), n-hexadecane (GR, ≥99%), was purchased from Shanghai Titan Scientific Co.,Ltd. The thermal dissociation experiments refered to Dong[6].

2.2 Computational Methods

The calculation consists of two parts. First, the geometry, charge distribution, infrared spectrum and solvation free energy of TOAHCl in different solvents were calculated by DFT. Then, the thermal dissociation of TOAHCl in non-polar solvents and RDF, MSD and diffusion coefficient during the dissociation were calculated by MD.

DFT calculations were performed by Gaussian 16[7], with hybrid density functional B3LYP-D3[8], basis set 6-311++G(d,p)., The SMD[9] implicit solvent model was used to account for the solvent in these calculations.

MD described the dissociation process of TOAHCl by including TOA, HCl and solvent at different temperatures and compositions. 50 ion pairs and different quantities of solvent molecules optimized by Gaussian 16 were placed into a box using the Amorphous Cell calculation module of MS, the charges of each atom were obtained by DFT calculations. The MD results are carried out by Materials Studio 2020[10] through employing the Forcite modules and consistent force field COMPASS III in the Forcite module. The initial temperature was set to 373 K, initial density was set to 1.0g/cm^3.

The AC construction was relaxed by NPT Ensemble, temperature was set to 373 K, pressure was set to 101325 Pa (TOAHCl is in liquid form under this condition), initial velocities was set as random, the simulation time step was set to 1 fs, using Nosé thermostat/Berendsen barostat. The COMPASS III force field is used to compute the forces and interactions between particles. The van der Waals and electrostatic forces were obtained using atom based summation, the cutoff distance for calculating van der Waals and electrostatic forces was set to 18.5 Å, relaxation lasted until the system reaches equilibrium, which means that the system energy had dropped to the lowest and the system density had also approached the real value.

Then we performed 500 ps NVT ensemble at different temperatures and compositions to describe the dissociation process of TOAHCl.

2.3 Solvation free energy

The formula for calculating the solvation free energy of the solvent is:

$$\Delta G_{sol}(T) = \sum(\varepsilon_0 + G_{corr})_{solvent} - \sum(\varepsilon_0 + G_{corr})_{gas} \qquad (1)$$

where ε_0 represents the total electronic energy, and G_{corr} represents the Gibbs free energy correction term.

2.4 Radial distribution function

This parameter describes the ratio of the density of specific atoms within *r* distance to the total density. Therefore, it shows the change of density around a given particle, as follows:

$$g_{\alpha\beta}(r) = \frac{V}{N_\alpha N_\beta}\left(\sum_{i=1}^{N_\alpha} \frac{n_i\beta(r)}{4\pi r^2 \Delta r}\right) \qquad (2)$$

where N_α and N_β represent the total number of *α* and *β* atoms; *V* represents the volume of the simulation box; and $n_i\beta(r)$ is similar to the number of particles *β* at the spherical distance *r* from particle *α*.

2.5 Mean square displacement/Diffusion coefficient

The motion and vibration of each molecule can be expressed by MSD, defined as follows:

$$MSD = (|\overline{r}_i - \overline{r}_{i0}|^2) = \frac{1}{N}\sum_{i=1}^{N}\left(\left|\overline{R}_i(t) - \overline{R}_i(t_0)\right|^2\right) \qquad (3)$$

$\overline{R}_i(t)$ is similar to the position of atom at t; $\overline{R}_i(t_0)$ introduces the initial position of particle; *N* represents the total number of particles. The MSD curve can be used to study the motion and behavior of molecules at different process stages.

The diffusion rates of all the above systems are directly calculated by using the MSD of the target molecules, as shown in the following equation:

$$6Dt = MSD \qquad (4)$$

D and *t* represent diffusion coefficient and simulation time, respectively.

3. *RESULTS AND DISCUSSION*

3.1 DFT calculations

In this section, geometry, Mulliken charge distribution, infrared spectrum and solvation free energy of TOAHCl in differdent solvents were calculated.

3.1.1 Molecular simulation of structure parameters

Some chemical reactions have significant solvent effects, which can be reflected by the changes in molecular geometry, charge distribution and infrared spectrum[11,12]. By comparing the relevant properties of substances in different solvents, we can simply analyze and predict the chemical properties and stability of molecules. By DFT calculation, the N-H bond distance and Mulliken charge distribution of TOAHCl in gas phase and different solvents were obtained. Some main bond parameters, Mulliken charge distributions of TOAHCl in gas phase and 41 different solvents are shown in Fig.2, Fig.3 and Table 1(not all solvents listed in the table).

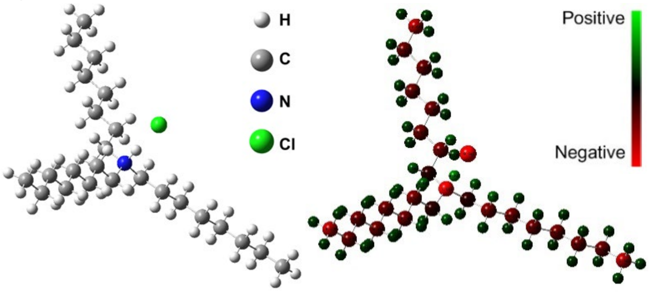

Fig. 2. TOAHCl molecular geometry/ charge distributions

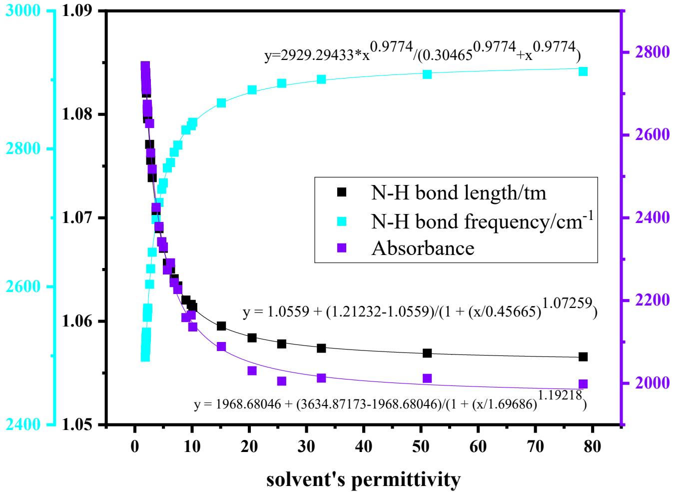

Fig. 3 N-H parameters of TOAHCl in different solvents by SMD

The polarity of the solvent can be characterized by permittivity. As shown in Table 1 and Fig.3, when transferring from gas phase to solvents, the N-H bond length in TOAHCl gradually decreases from 1.10509(gas phase) to 1.06163(n-octanol), the H-Cl bond length gradually increases, and both show more ion pair characteristics with the increase of the permittivity of the solvent. this variation can be synthesized by formulating Eq:

$$d_{(N-H)} = 1.0559 + \frac{0.15642}{1 + (\frac{P}{0.45665})^{1.07259}} \tag{5}$$

P represent permittivity.

In polar solvents such as water, methanol and n-octanol, TOAHCl can be considered to exist in the form of $TOAH^+$ and Cl^- ion pairs. From the Mulliken charge distribution analysis, the same conclusion can be drawn. Based on the above analysis, it can be known that the charge rearrangement in the process of TOAHCl from gas phase to solvents mainly leads to the gradual decrease of N-H bond length, which improves the stability of TOAHCl. For the thermal dissociation process of TOAHCl, its essence is proton transfer from N to Cl, so the lower the stability of TOAHCl, the more favorable for the thermal dissociation reaction. TOAHCl in gas phase has the lowest stability, but thermal dissociation without solvents will cause TOA and HCl to re-collide in air and form TOAHCl. The experimental results (Fig.10) show that under 180 °C, 300ml/min N_2 flow rate and 8h thermal dissociation rate can only reach about 20%, therefore, solvent is needed to stabilize TOA. Thus thermal dissociation in non-polar solvents are preferred.

Table 1 Bond length, Mulliken charge of TOAHCl in different solvents

Solvents	Permit tivity	$d_{(N-H)}$ (Å)	$d_{(H-Cl)}$ (Å)	q(N)	q(H)	q(Cl)
gas phase		1.10509	1.85564	-0.601	0.295	-0.646
n-undecane	1.991	1.08265	1.93959	-0.609	0.334	-0.733
n-dodecane	2.006	1.08243	1.94044	-0.609	0.334	-0.734
n-pentadecane	2.033	1.08214	1.94178	-0.609	0.335	-0.735
n-hexadecane	2.040	1.08205	1.94214	-0.609	0.335	-0.735
decalin	2.196	1.08032	1.95018	-0.610	0.338	-0.742
tetralin	2.771	1.07555	1.97497	-0.612	0.347	-0.762
dibutyl ether	3.047	1.07388	1.98403	-0.613	0.350	-0.769
chloroform	4.711	1.06767	2.02356	-0.616	0.361	-0.795
n-octanol	9.863	1.06163	2.06713	-0.620	0.372	-0.822
acetone	20.493	1.05839	2.09875	-0.622	0.378	-0.836
methanol	32.613	1.05739	2.10642	-0.623	0.379	-0.841
water	78.355	1.05656	2.10649	-0.623	0.380	-0.841

3.1.2 Infrared spectra

The thermal dissociation reaction of TOAHCl is essentially the breakage of the N-H bond, the strength of the N-H bond can be expressed by the N-H bond frequency, and the bigger the value, the more stable TOAHCl is in the solvent. [13]

Fig. 3, 4, and Table 2 show the infrared spectra and the specific values of the N-H bond frequency of TOAHCl in different solvents. The SMD implicit solvent model generally reproduces the infrared spectral peak shape of TOAHCl well.The N-H stretching vibration frequency is positively correlated with the permittivity of the solvents, which can be synthesized by formulating Eq:

$$F_{(N-H)} = \frac{2929.29433 \times P^{0.9774}}{0.3129 + P^{0.9774}} \tag{6}$$

That means lower permittivity solvent is more suitable for thermal dissociation of TOAHCl.

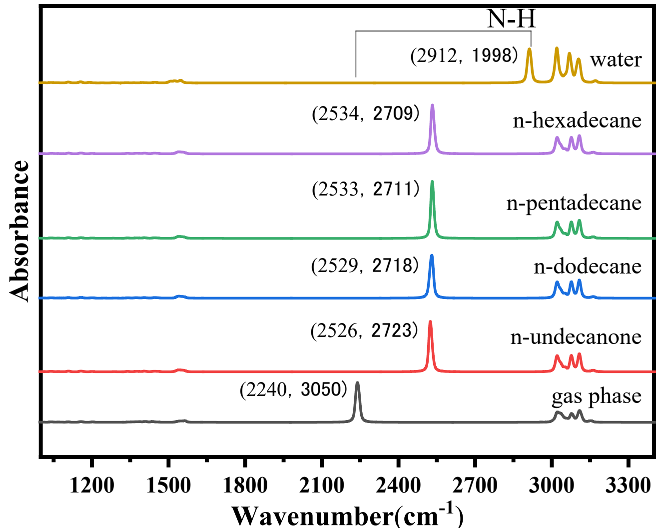

Fig. 4 IR spectra of TOAHCl in different solvents with SMD

Table 2 N-H bond frequency and ΔG_{sol} of TOAHCl in different solvents

Solvents	Permittivity	N-H/cm^{-1}	ΔG_{sol}/(kJ/mol)
gas phase		2239.8318	
n-undecane	1.991	2526.0146	-86.80953
n-dodecane	2.006	2528.9386	-85.06095
n-pentadecane	2.0333	2533.0842	-83.79283
n-hexadecane	2.0402	2534.2133	-83.54078
decalin	2.196	2558.3514	-83.09708
tetralin	2.771	2626.1008	-96.64991
dibutyl ether	3.0473	2650.0303	-95.92002
chloroform	4.7113	2741.3827	-124.64036
n-octanol	9.8629	2833.3653	-119.1872
acetone	20.493	2885.4397	-135.68584
methanol	32.613	2900.7929	-131.19886
water	78.3553	2912.1058	-56.28022

3.1.3 Solvation free energy

The solvation free energy ΔG_{sol} is an important parameter to describe the solvation effect of chemical reactions. The stability of the solute in the solvent can be expressed by ΔG_{sol}, and the smaller the value, the more stable the solute is in the solvent. From Fig.5, it can be seen that TOAHCl has the largest ΔG_{sol} in long-chain aliphatic hydrocarbons (n-undecane, n-dodecane, n-pentadecane, n-hexadecane) and decalin, respectively, indicating that TOAHCl is the most unstable in these solvents. The thermal dissociation experimental results are basically consistent with the stability of TOAHCl, that is, the worse the stability of TOAHCl, the higher the conversion rate of thermal dissociation. It is worth noting that unlike the parameters shown in Fig.4, ΔG_{sol} of TOAHCl in different solvents does not monotonically decrease with the increase of the permittivity of the solvents, but first decreases with the increase of the solvent permittivity, and then increases after a significant turning point at acetone solvent. TOAHCl has the smallest ΔG_{sol} in acetone, meaning that it is most stable in acetone, while TOAHCl becomes unstable again in solvents with higher permittivity than acetone , such as methanol, water. The possible reason is that TOAHCl cannot dissolve in the corresponding solvent, which leads to a higher ΔG_{sol}. In summary, when screening suitable thermal dissociation solvents (generally non-polar solvents with low permittivity), suitable thermal dissociation solvents can be preliminarily screened by comparing ΔG_{sol} of TOAHCl in solvents.

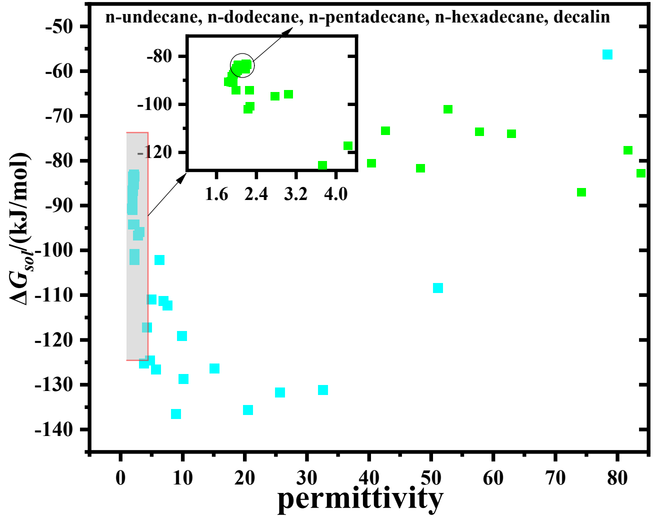

Fig. 5 solvation free energy of TOAHCl in different solvents

3.2 MD calculations

The dissociation process of TOAHCl and solvents with different concentrations at different temperatures were simulated by MD.

3.2.1 Radial distribution function

The RDF of N and Cl atoms in TOAHCl at 273, 373, 393, 413, 433, and 453 K were obtained, denoted as $g_{N-Cl}(r)$. Fig.6 shows that there is a characteristic peak at 5 Å distance between N and Cl atoms that decays significantly with temperature, which originates from the hydrogen bond formed between N in TOA and H in HCl after TOAHCl dissociated. Decay trend of this peak indicating that the stability of hydrogen bond decreases with increasing temperature, leading to an increase in distance between N and Cl atoms, and HCl molecules start to escape from the system continuously, showing a tendency of dissociation. In addition, in the presence of solvents (Fig.7), $g_{N-Cl}(r)$ is much lower than in the absence of solvent, which indicates that solvent can disperse reactants and products well and enhance mass transfer.

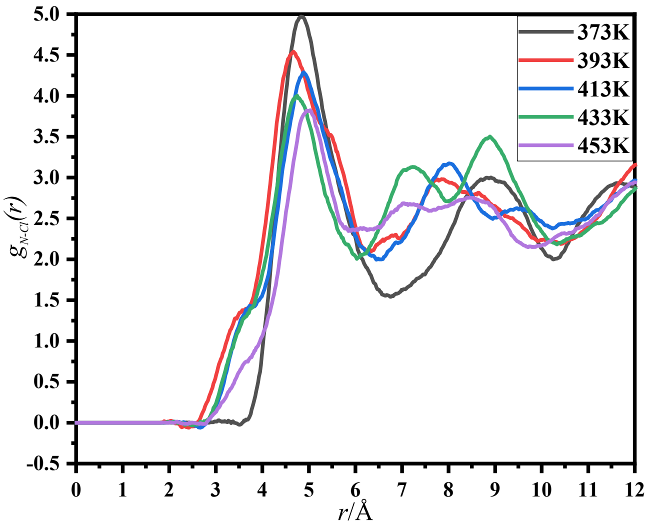

Fig. 6 RDF-TOAHCl(100%)

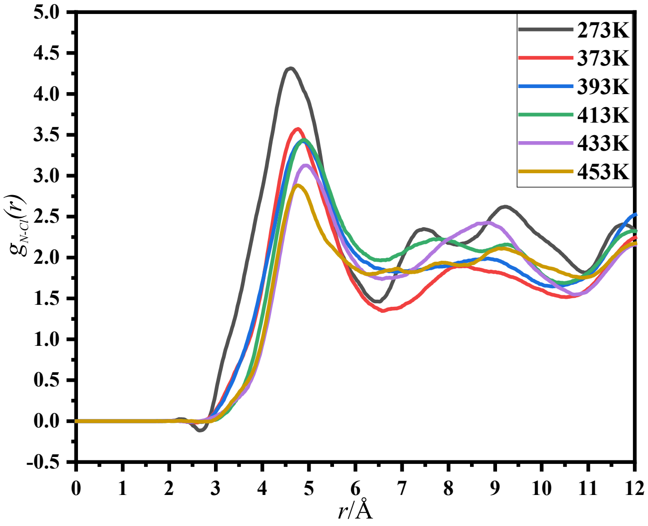

Fig. 7 RDF-TOAHCl(20%)+n-undecanone(80%)

3.2.2 Mean square displacement/Diffusion coefficient

The MSD of Cl atoms in different concentrations of TOAHCl and n-undecane at 273, 373, 393, 413, 433, and 453 K were obtained. Fig.8 shows that TOAHCl is very stable at 273 K while Cl atoms hardly move at all. The experiment also proved that TOAHCl forms a solid white crystal at 0°C, and atoms in the system only vibrate slightly at fixed positions. With increasing temperature, the diffusion coefficient (slope) of Cl atoms increases significantly with increasing temperature, due to the increase of thermal motion of Cl atoms, which enhances the diffusion ability of Cl atoms. This is also consistent with the thermal dissociation process of TOAHCl at different temperatures. With increasing temperature, the hydrogen bond between N atom in TOA molecule and H atom in HCl molecule becomes more and more unstable, leading to HCl molecule dissociating and escaping from the system more easily.

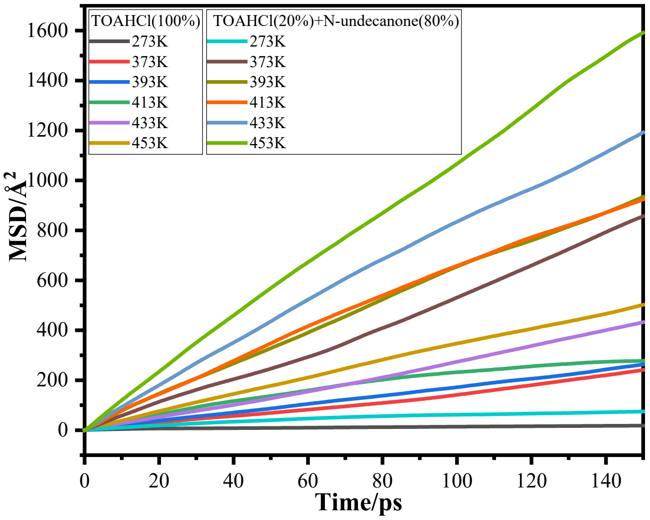

Fig. 8 MSD of Cl in different TOAHCl systems

The diffusion coefficient of HCl molecules in different concentrations of TOAHCl and n-undecane (solvent) at 273, 373, 393, 413, 433, and 453 K were obtained. The function relationship between diffusion coefficient and temperature is shown in the Fig.9. It can be seen that the diffusion coefficient of HCl molecules increases gradually with increasing temperature, and also increases rapidly with increasing solvent concentration, indicating that solvent greatly enhances mass transfer, making HCl molecules easier to escape from the system, reducing the probability of contact between TOA and HCl, thus promoting reaction progress.

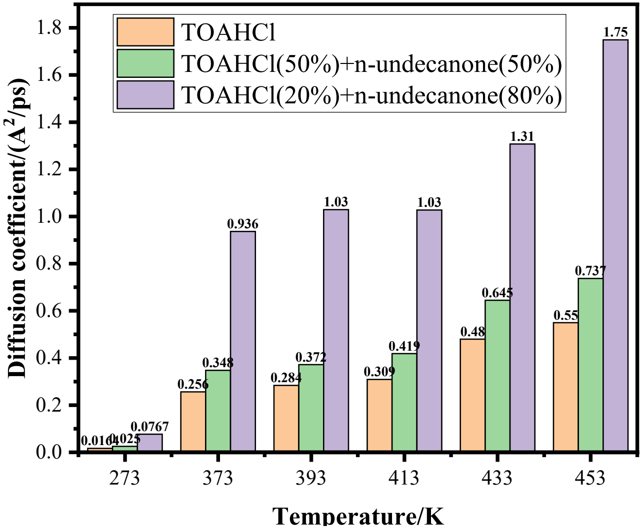

Fig. 9 Diffusion coefficient of HCl in various systems

3.3 experiments results

The thermal dissociation experiments were carried out under this condition: temperature set to 180 °C, N_2 flow rate set to 300 mL/min, and solvent:TOAHCl mole ratio of 5:1. A part of experiment results were from Dong[4].The experiment results are showing in Fig.10.

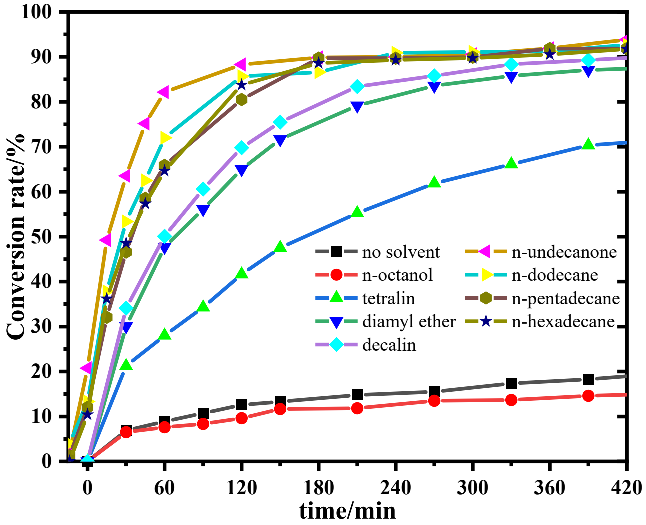

Fig. 10 conversion rate of TOAHCl in various systems

The experimental results basically validate the relationship between the magnitude of the permittivity and the ease of dissociation by DFT.

4. CONCLUSIONS

In this paper, effect of solvent on the thermal dissociation of TOAHCl was investigated by DFT and MD:

The relevant parameters of TOAHCl in 41 solvents were calculated by DFT and fitted to Eqs. (5) and (6) for the N-H bond length and N-H bond frequency versus permittivity obtained.

The frequency of N-H bond, ΔG_{sol} of TOAHCl in different solvents is consistent with experimental results, which can be used as a theoretical reference for solvent screening.

MD results show TOAHCl shows a tendency of dissociation with increasing temperature and the concentration of non-polar solvent. Non-polar solvents can disperse reactants and products, enhance mass transfer.

ACKNOWLEDGEMENT

Thanks to the support of ECUST-JINGHAO SALT CHEMICAL Joint Research Center of Calcium Carbon Cycle.

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

REFERENCE

[1] IPCC-Intergovernmental Panel on Climate Change. https://www.ipcc.ch/

[2] Federica Raganati, Francesco Miccio, and Paola Ammendola. Adsorption of Carbon Dioxide for Post-combustion Capture: A Review. Energy & Fuels 2021;35(16): 12845-12868.

[3] Li Y., Song X., Chen G., Sun Z., Xu Y., Yu J. Preparation of calcium carbonate and hydrogen chloride from distiller waste based on reactive extraction-crystallization process. Chemical Engineering Journal 2015;278:55-61.

[4] Dong C., Song X., Zhang J., Chen H., Meijer E.J., Yu J. Selecting solvents for intensification of thermal dissociation of tri-n-octylamine hydrochloride by calculating infrared spectra from ab initio molecular dynamics. Chemical Engineering Journal 2019;377:120120.

[5] Sarangi K, Padhan E, Sarma P V R B, Park K H, Das R P. Removal/recovery of Hydrochloric Acid Using Alamine 336, Aliquat 336, TBP and Cyanex 923. Hydrometallurgy 2006;84(3–4):125–129.

[6] Dong C., Li Y., Song X., Chen G., Sun Z., Xu Y., Yu J., Insight into Thermal Dissociation of Tri-n-octylamine Hydrochloride: The Key to Realizing CO2 Mineralization with Waste Calcium/Magnesium Chloride Liquids, Energy Science & Engineering 2018, 6 (5), 437-447.

[7] Frisch M.J. et al. Gaussian 16, Revision C.01. Wallingford CT: Gaussian Inc.; 2016.

[8] Daniel G. A. Smith, Lori A. Burns, Konrad Patkowski, and C. David Sherrill. Revised Damping Parameters for the D3 Dispersion Correction to Density Functional Theory. J. Phys. Chem. Lett. 2016; 7 (12):2197-2203.

[9] Marenich A.V., Cramer C.J., Truhlar D.G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. J Phys Chem B 2009;113:6378-6396.

[10] BIOVIA, Dassault Systèmes. Materials Studio, Release 2020. San Diego: Dassault Systèmes; 2020.

[11] Wong M.W., Wiberg K.B., Frisch M.J. Solvent Effects. 3.Tautomeric Equilibria of Formamide and 2-pyridone in the Gas Phase and Solution: an ab initio SCRF Study. J Am Chem Soc 1992;114(5):1645–1652.

[12] Tomasi J., Persico M. Molecular Interactions in Solution: An Overview of Methods Based on Continuous Distributions of the Solvent. Chemical Reviews 1994;94(7):2027–2094 .

[13] Weng S.F . Fourier Transform Infrared Spectroscopy Analysis. 2nd ed . Beijing: Chemical Industry Press ;2010 .