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RESEARCH ARTICLE

Insight into thermal dissociation of tri-n-octylamine hydrochloride: The key to realizing CO₂ mineralization with waste calcium/magnesium chloride liquids

Chunhua Dong^{1,2} | Xingfu Song¹  | Jie Zhang¹ | Evert Jan Meijer² | Hang Chen¹ | Jianguo Yu¹

¹National Engineering Research Center for Integrated Utilization of Salt Lake Resources, East China University of Science and Technology, Shanghai, China

²Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands

Correspondence: Xingfu Song and Jianguo Yu, National Engineering Research Center for Integrated Utilization of Salt Lake Resources, East China University of Science and Technology, Shanghai 200237, China (xfsong@ecust.edu.cn; jgyu@ecust.edu.cn).

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Abstract

A thermal dissociation process (ideally, 100% atom utilization) to regenerate the amine extractant and to produce gaseous HCl which is the key to realizing the CO₂ mineralization with metal chloride waste liquids was investigated. Solvent effects on the thermal dissociation of tri-n-octylamine hydrochloride (TOAHCl) were predicted to be prominent via analyzing structure parameters, charge distribution, solvation free energy, apparent basicity, and N-H frequency with the help of molecular simulation and experiments. Inert solvents with low polarity such as decalin, dodecane were favorable in thermal dissociation experiments. In particular, decalin enhanced the dissociation most effectively which is in agreement with the prediction. In dilute solutions, the thermal dissociation kinetics was shown to be first order. The apparent reaction rate (3.0×10^{-4} – 1.5×10^{-2} min⁻¹) and activation energy (58.219–121.827 kJ/mol) differ a lot at 180–190°C in various solvents, confirming a strong solvent effect. A two-stage reaction scheme in dilute solutions has been proposed from the experimental study. The overall process is entropically driven, with the removal of HCl into gas phase from the solvated state. The work could offer a fundamental direction for the further actual process.

KEYWORDS

amine regeneration, decalin, entropically driven, kinetics, solvent effects, thermal dissociation

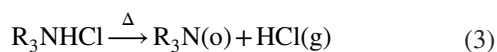
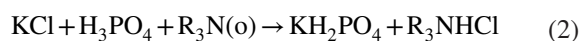
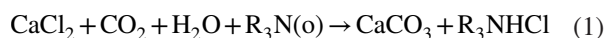
1 | INTRODUCTION

Since the beginning of the Industrial Revolution, anthropogenic activities have substantially increased the concentration of greenhouse gas CO₂ in atmosphere. Apart from green energy technologies and energy efficiency improvement technologies, carbon capture and storage (CCS) is a hot topic to relieve the CO₂ emission. Among the various CCS methods, mineralization by converting CO₂ to carbonate minerals offers

an attractive approach for the safe storage and effective utilization of CO₂. Some Mg²⁺/Ca²⁺-rich aqueous resources, such as seawater,^{1,2} salt lake brines,^{3,6} and industrial effluents^{7–10} have potential application in mineralization of CO₂.

Our research group has investigated a novel coupled reactive extraction-crystallization process systematically to realize the storage of CO₂ with the liquid wastes, such as distiller waste containing plentiful CaCl₂ from ammonia soda process^{7–9} and abandoned MgCl₂-rich brines^{3,5} after

the production of potassium fertilizer from salt lake. In the process, CaCl_2 , MgCl_2 were transformed to high-valued carbonates. The reaction for the coupled reactive extraction-crystallization process could be expressed with Equation (1), taking CaCl_2 , for example. In the process, water insoluble tertiary amines tri-*n*-octylamine (TOA) or N235 (a mixture of tertiary amines with 8-10 carbon atoms in each branch) are applied as the extractants of HCl, making the reaction occur constantly by increasing the pH of the aqueous phase through transferring HCl from aqueous phase to oil phase. The mechanism of CO_2 and HCl transformation has already been conformed.⁶ Regeneration of amine extractants from its hydrochlorides efficiently is crucial to realize the industrialization of the process.



Apart from the coupled process of CaCl_2 , the extraction technology for the production of compound fertilizers such as potassium dihydrogen phosphate (KH_2PO_4)¹¹⁻¹³ could also generate amine hydrochloride which is shown in Equation (2). The efficient regeneration of amine extractant is also a key point.

Harsh environmental protection laws enforcement poses a great challenge and strong economic motivation to develop the regeneration method. It is favored to separate HCl from amines, thereby lowering down the cost of waste treatment and making full use of resources. Considerable energy has to be introduced in terms of the strong binding interaction between amine and HCl. Either “pH swing” or “temperature swing” principle could be followed for regeneration of amine,¹⁴ which are applied in the following two ways accordingly. Neutralization by low-cost alkaline matter, such as lime slurry and ammonia solution is an effective and easy way, however, a sludge and the waste liquid that need to be disposed of are formed then.¹⁵⁻¹⁷ Besides, it involves consumption of reagents and loss of chloride values. Ideally, direct thermal dissociation of amine hydrochlorides is a promising technique with 100% atom utilization, in which amines could be recycled successfully although the energy consumption is still higher than the neutralization method. Moreover, quite appealing gaseous HCl could be produced. The equation can be shown as Equation (3). Coenen, Kosswig et al¹⁸⁻²⁰ had made extensive studies on the regeneration of tertiary amines from straight-chain to branched-chain through thermal dissociation of its chloride. Also, we have made some basic study on the thermal dissociation of solid TOAHCl.^{21,22} In comparison with branched-chain tertiary amine tris(2-ethylhexyl)amine

(TEHA), it is much difficult to regenerate straight-chain tertiary amine TOA by dissociation of their chlorides, with considerable higher temperature (with starting temperature of 170°C vs 100°C) and much longer time (with half-life of 47 and 2 minutes in certain conditions, respectively). The optimal temperature of dissociation of TOAHCl is as high as 215°C with the dodecane as the solvent.^{18,19,23} Eyal et al^{14,24-28} summarized the parameters for adjusting extractants’ properties (mainly basicity) such as inductive effect, solvent effect, the “temperature swing,” etc.

In our previous work, much stronger and cheaper amine extractant N235 (It was replaced by TOA for convenience in this paper and its feasibility was disclosed in Appendix S1) was used to accomplish the reactive extraction-crystallization process. Thus, solvent effects become fairly crucial that need to be studied deeply.

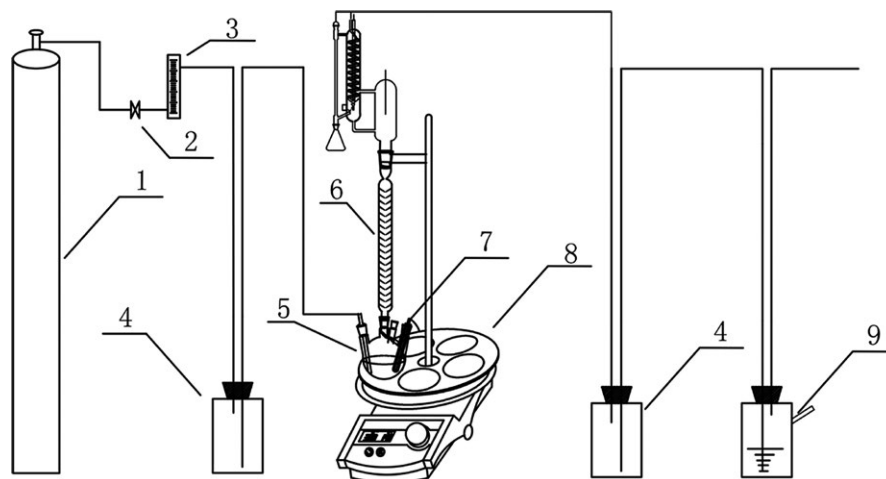
In the work, five types of solvents, that is, decalin (cycloalkane), *n*-dodecane (alkane), tetralin (with aromatic ring), diamyl ether (ether), and *n*-octanol (alcohol), were selected which were mentioned in references.^{14,24-28} Based on preexperiments, all the selected solvents have boiling point of more than 185°C (please see Appendix S2) but not so much. As it could not only inhibit significant solvent loss because of the relatively high boiling point but also keep the temperature in the boiling sump mixture below 250°C to prohibit the degradation of amines.²⁰ The solvent effect on thermal dissociation of TOAHCl was discussed both from molecular simulation and experimental aspects. A scheme for the process was proposed, during which the kinetics analysis was made and strong solvent dependence was confirmed quantitatively.

2 | EXPERIMENTAL AND CALCULATION DETAILS

2.1 | Materials and apparatus

Analytical reagent tri-*n*-octylamine (ie, TOA, purity $\geq 97.0\%$) was purchased from TCI (Shanghai) Development Co., Ltd., Shanghai, China. N235 was purchased from Shanghai Rare-earth Chemical Co., Ltd. Petroleum ether (point range, 60~90°C), hydrochloric acid of analytical grade (36%-38%, wt. %) were purchased from Shanghai Ling Feng Chemical Reagent Co. Ltd., Shanghai, China. Anhydrous ethanol (purity 99.5%, Shanghai Titan Scientific Co., Ltd.), sodium hydroxide (NaOH, purity 96.0%, Shanghai Ling Feng Chemical Reagent Co., Ltd.), silver nitrate (GR, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were used for titration. *N*-dodecane (purity $\geq 98.0\%$) was purchased from Aladdin Industrial Corporation (Shanghai). Decalin (GR, purity $\geq 99.5\%$), tetralin (CP, purity $\geq 98.0\%$), diamyl ether (purity $\geq 98.0\%$), and *n*-octanol (AR, purity $\geq 99.0\%$) were supported by Sinopharm Chemical Reagent Co., Ltd.

FIGURE 1 Schematic illustration of the device used in the thermal dissociation of TOAHCl in different solvents. (1-N₂ gas; 2-Relief Valve; 3- Gas Flowmeter; 4-Buffers; 5-Reactor; 6- Distillation column (with graham condenser); 7-Thermocouple; 8-StarFish Monoblock heater; 9-Gas washing bottle.)



A high precision low-temperature thermostat (Ningbo Tianheng Instrument Factory) and a homemade-jacked reactor were used to prepare TOAHCl. The dissociation experiments were performed in a four-necked round bottom flask (250 mL) reactor (the uses of the four necks are shown in Figure 1). The initial amount of HCl was determined by titration with NaOH solutions after solving the TOAHCl in ethanol. Before each experiment, gas tightness was checked. Then, certain amount of TOAHCl and solvents were added in the reactor and the reaction begins. A StarFish Parallel Reaction Station purchased from Radleys, UK surrounded with thermal insulation (not drawn in Figure 1) was used to control temperature. Besides, graham condensers were used on the top of distillation column to avoid the loss of solvents. The mixture was stirred with the magnetic stirrer. Then N₂ was introduced into the reactor bottom through a gas flowmeter. The inert carrier gas N₂ was used to accelerate the HCl formation and split-off and keep the amine from oxidation. During experiments, the conversion rate was determined indirectly by measuring the concentration of Cl⁻ in bottle 9 (with NaOH solutions in it) with AgNO₃ solutions. Thermal couple was put in a thermowell in case of corrosion. A series of experiments such as the ones at different kinds of solvents could be done simultaneously on the StarFish reactor, ensuring the other conditions same. And each set of experiments was repeated three time and the average values were shown in figures.

2.2 | Preparation of tri-n-octylamine hydrochloride

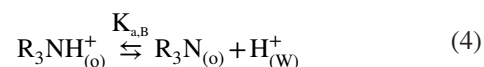
TOAHCl was prepared through dissolving 0.1 mol (about 35.4 g) TOA in 40-60 mL cold petroleum ether (about 0°C, in the jacketed reactor, isopropanol-water mixed solutions as the cooling medium) and adding 0.11-0.12 mol concentrated hydrochloric acid (9-10 mL) slowly in case of high local temperature. TOAHCl was obtained after three times

recrystallization from warm petroleum ether. Then the salts were filtrated using Buchner funnel, washing with ice-cold petroleum ether and drying overnight in gas phase at room temperature firstly²⁹ before at 50-60°C (melting point of TOAHCl is 73°C) in order to release the remaining petroleum ether.

2.3 | Characterization

The TOAHCl and HCl concentrations were analyzed by methods of aqueous (NaOH/water) acid-base titration and Mohr titration, respectively. Components of N235 were analyzed on gas chromatography (Agilent 7890, Palo Alto, California USA) combined with mass spectrometry (Agilent 5975C, USA), ie Agilent 7890/5975C GC/MSD.

Apparent basicity is used to indicate basic extractants' capability of combining with acid in solvents. Taking tertiary amine R₃N for example, the following Equation (4) exists.



Of which expression of K_{a,B} is shown as Equation (5),

$$K_{a,B} = \frac{[R_3N_{(o)}][H_{(w)}^+]}{[R_3NH_{(o)}^+]} \quad (5)$$

pK_{a,B} is used to present apparent basicity. The bigger pK_{a,B} value is, the stronger the amine becomes. Li³⁰ measured apparent basicity with the modified method. The solutions of amine in different solvents mix up with hydrochloric acid with the amine/HCl mole ratio of 2:1, ensuring the mole ratio of amine and its hydrochloride approaching to 1 as far as possible. Then Equation (6) can be obtained:

$$[R_3NH_{(o)}^+] = [R_3N_{(o)}] \quad (6)$$

Thus, pK_{a,B} is equal to pH of aqueous solutions. The pH values were measured by PHSJ-3F pH meter purchased from Shanghai INESA Scientific Instrument Co. Ltd, China.

Fourier-transform infrared spectra (FTIR) were carried out on a Nicolet 6700 instrument (Thermo Fisher Scientific, Waltham, Massachusetts USA), using liquid film method.

2.4 | Quantum calculation details

In our work, we determined the structure parameters, Mulliken charge distribution, and solvation free energy of TOAHCl/TOA in various solvents, with the B3LYP exchange-correlation functional in conjunction with the 6-311++g(d, p) basis set on Gaussian 09 package.³¹ Structure parameters and Mulliken charge distribution could be obtained after geometry optimization of TOAHCl and TOA. The frequency of TOAHCl and TOA both in gas phase and different solvents were calculated to get the Gibbs free energy. Then, the Gibbs free energy difference between each solvent and gas phase was calculated to be the solvation free energy. The SMD³² model was employed when the solvents were included to finish the work.

3 | RESULTS AND DISCUSSIONS

3.1 | Solvent selection theoretically

3.1.1 | Molecular simulation of structure parameters and solvation free energy

Many studies³³⁻³⁵ have demonstrated that molecular properties including configuration geometries, charge distribution, spectroscopic properties can be affected to different extent by different solvents. Some main bond parameters, Mulliken charge distributions as well as dipole moment of TOAHCl in gas phase and different solvents are shown in Figure 2 and Table 1.

We can see from Table 1 that the equilibrium N-H1 distance of TOAHCl gets shorter when transferring from gas phase to solvents. Moreover, the distance decreases with the increase in permittivity of solvents, whereas H1-Cl distance shows the opposite trend, exhibiting more ion pair

characteristics. From Mulliken charge analysis, the same conclusion can be made. The chlorine atom gains an additional 0.064e, 0.080e, 0.117e, 0.133e, and 0.362e from R₃NH fragment when TOAHCl is moved from gas phase to solvents listed in Table 1. Based on the analysis above, the major charge rearrangement upon transferring TOAHCl from gas phase to solvents leads to an enhancement of the dipole moments of R₃NH and Cl groups. This strengthens the electrostatic interaction, thereby increasing the stability of TOAHCl. For the thermal dissociation process of TOAHCl, the electrons transferring from Cl to N is the essential step and it is advantageous if the TOAHCl is unstable. Thus, non-polar solvents are preferred.

Solvation free energy ΔG_{sol} is a crucial parameter in describing the solvent effects on chemical reactions. The stability of the substances can be represented by the absolute value of ΔG_{sol} : the larger of $|\Delta G_{\text{sol}}|$, the more stable of the substances. From Table 2, $|\Delta G_{\text{sol}}|$ values of reactants show an increase trend with the increase in polarity of solvents while values of products remain almost unchanged, indicating that the ion-pair-like reactants become more stable while the stabilities of products keep almost the same when transferred from nonpolar solvents to polar ones. We may suppose that the TOAHCl is least stable and dissociates most easily in decalin.

3.1.2 | Apparent basicity of TOA in various solvents

As seen from Figure 3, the apparent basicity of TOA in non-polar solvent (decalin, dodecane, diamyl ether, and tetralin) is lower than that of pure TOA and decreases with the decrease in TOA concentration (ie, increase in solvent concentration). Thereinto, decalin and dodecane weaken the basicity of TOA most effectively, consistent with the molecular simulation results in section 3.1.1. Whereas n-octanol could enhance the basicity of TOA and the apparent basicity increases with the decrease in TOA concentration. Thus, n-octanol seems not suitable for thermal dissociation.

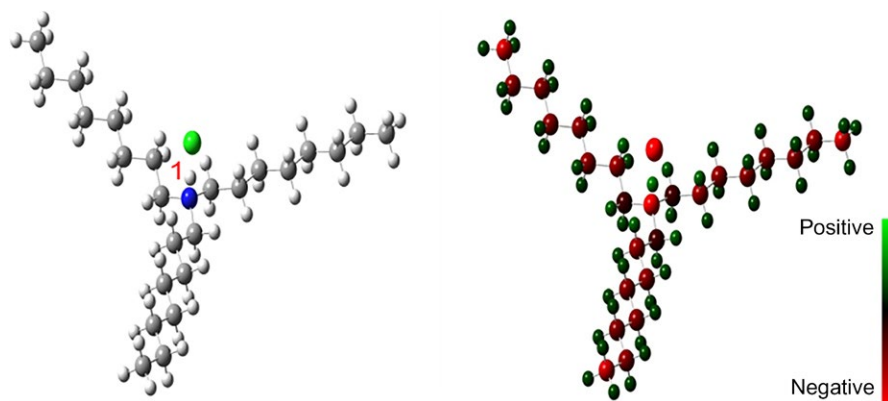


FIGURE 2 TOAHCl molecular geometry and the charge distributions

TABLE 1 Bond length, Mulliken population, and dipole moment of TOAHCl in different solvents

Solvent	Permittivity	$d_{(N-H)}$ (Å)	$d_{(H1-Cl)}$ (Å)	$q(R_3NH)$ (Å)	$q(Cl)$	Dipole moment (Debye)
Gas phase	1.000	1.112	1.805	0.481	-0.481	8.0893
n-dodecane	2.006	1.080	1.920	0.545	-0.545	10.1502
Decalin	2.196	1.077	1.933	0.561	-0.561	10.3831
Tetralin	2.771	1.071	1.966	0.598	-0.598	10.9775
Dibutyl ether	3.047	1.069	1.979	0.614	-0.614	11.2088
n-octanol	9.863	1.054	2.098	0.843	-0.843	13.3027

Dibutyl ether used in simulation with Gaussian09 was replaced with diamyl ether in experiment because they are both ethers and have almost the same permittivity, whereas diamyl ether has higher boiling point. R_3N represents TOA.

TABLE 2 Solvation free energy of TOAHCl and TOA in various solvents

Solvents	Solvation free energy (kJ/mol)	
	TOAHCl	TOA
Dodecane	89.898	57.366
Decalin	88.166	52.550
Tetralin	101.851	58.094
Dibutyl ether	101.198	54.618
n-octanol	124.587	56.455

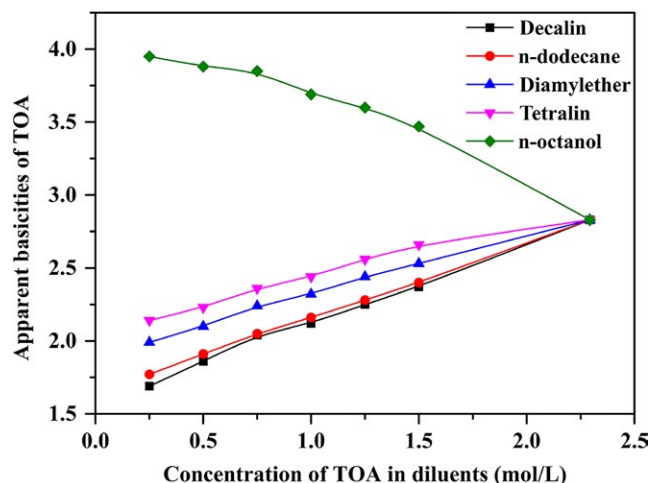
3.1.3 | Infrared spectra study

As is known, the nature of the dissociation of TOAHCl is to break the N-H bond. Thus, N-H stretching vibrations are sensitive markers of the chemical environment. Such vibrations are typically strongly infrared active and are assigned in the range between 2700 and 2300 cm^{-1} region, usually as the summation bands.^{22,36} Red shifts would be observed when electron cloud density moves to nitrogen atom, denoting the decrease in vibration force constant, that is, bond strength or bond energy. Thus the stability of the N-H would be weakened, and vice versa.^{37,38} From Figure 4, the peaks of wave number of N-H bond are 2340, 2350, 2450, 2450, and 2600 cm^{-1} in decalin, tetralin, dodecane, diamyl ether, and n-octanol, accordingly. Decalin, with the lowest N-H wave number should be the most effective solvent whereas n-octanol with the highest wave number stabilizes the TOAHCl most effectively.

3.2 | Thermal dissociation experiments

3.2.1 | Effect of solvent species

The experiments were carried out under conditions of 180°C, with solvent/TOAHCl mass ratio of 5:1 and high pure nitrogen flow rate of 300 mL/min. The result is shown in Figure 5.

**FIGURE 3** The apparent basicity of tri-n-octylamine (TOA) in different solvents versus concentration of TOA

As can be seen from Figure 5, decalin performs best both on rate and degree of reaction. The sequence of rate of thermal dissociation is in the order decalin > diamyl ether \approx dodecane > tetralin > no solvent > n-octanol.

Figure 6 was depicted by combination of Table 2 and Figure 5. From Figure 6 we can see that the instability of TOAHCl agrees well with the conversion rate instead of permittivity only (the more unstable TOAHCl is, the more easily the thermal dissociation process happens). The agreement between simulation and experimental results offers a solvent prediction method.

Compared with the N-H vibration prediction results in section 3.1.3, it shows a good agreement between the N-H wave number and the TOAHCl's stability except for tetralin. The reason why this abnormal phenomenon happens is still unclear.

The reaction happens mainly in the first 3 hours. After 8 hours, the conversion rate reaches up to 98.1% in decalin, whereas the values are 95.37% and 94.96% in diamyl ether and dodecane, respectively. In contrast, n-octanol as a polar solvent shows the negative performance due to its

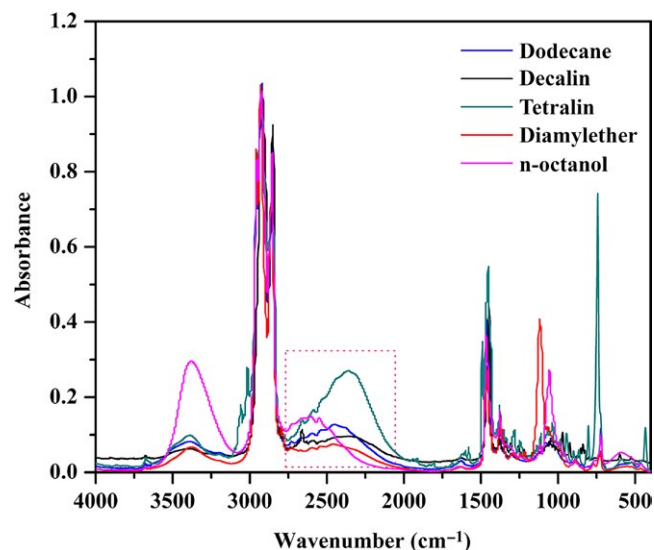


FIGURE 4 IR spectra of TOAHCl in different solvents with experimental method (N-H stretching vibration region in rectangle)

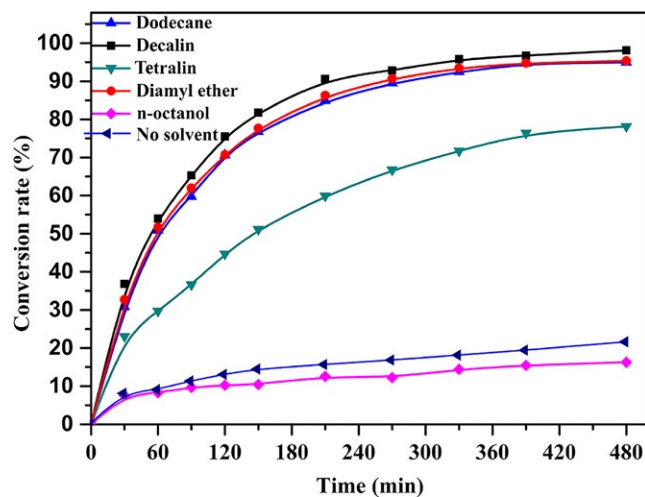


FIGURE 5 Effect of solvent types on thermal dissociation of TOAHCl

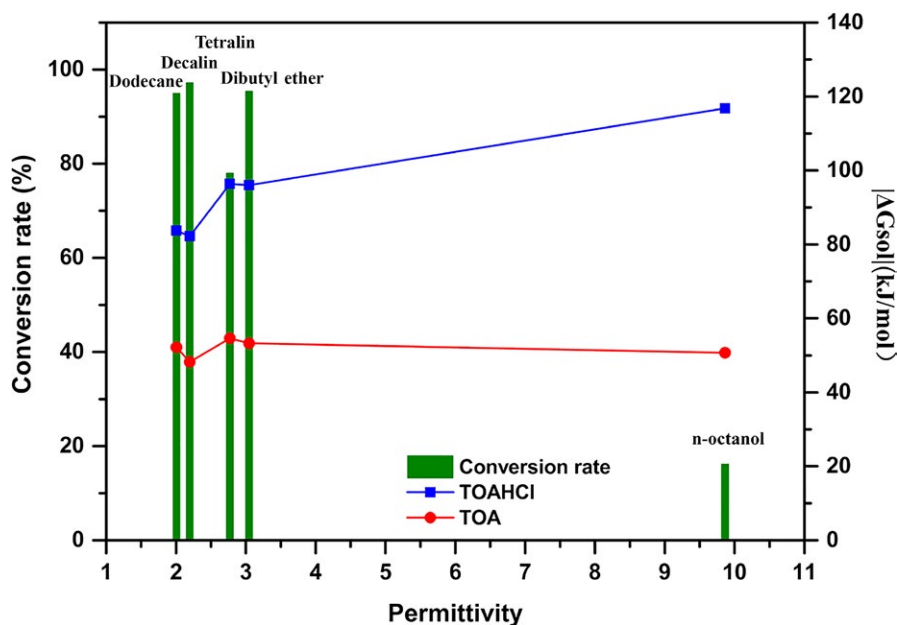


FIGURE 6 Conversion rate of thermal dissociation of TOAHCl (left vertical axis) and solvation free energy of tri-n-octylamine and TOAHCl (right vertical axis) in different solvents

capability of H-bond formation. TOAHCl most probably exists in n-octanol as solvated ions.³⁹ Worse still, alcohols might react with hydrogen chloride or hydrochloric acid at high temperature.²⁰ Thus, alcohols are not suitable in thermal dissociation of amine hydrochloride even though n-octanol was selected in our experiment. We chose it to make the study complete enough to figure out the general rules concerning the effect of solvent species. Meanwhile, we may conclude that alcohols, which play an indispensable role in the reactive-extraction crystallization coupled process of $\text{Ca}^{2+}/\text{Mg}^{2+}$ chlorides should be removed before thermal dissociation at relatively low temperature.

TOAHCl dissociates only 78.14% in tetralin, nearly 20% lower than that in decalin mainly owing to the aromatic ring. Kertes et al^{29,40} pointed out that the substantial solvation power of aromatic hydrocarbons via π -electrons of aromatic ring, in comparison with the aliphatic hydrocarbons, brings about a relatively strong solute-solvent interaction. And that results in a shielding of the dipole moment of the amine hydrochloride ion pair, thereby increasing the compatibility with solvent molecules. Furthermore, the ion pair is stabilized by the above effect. Thus, the solvents containing the aromatic ring(s) are improper. Diamyl ether with higher permittivity does almost the same good

performance as dodecane may because of diamyl ether's lower boiling point (compared with dodecane) which is just a little higher than the experimental temperature. In that case, the solutions almost boil and more solvent vapors besides N₂ participating in carrying HCl.

Based on the analysis in section 3.1 and 3.2.1, we chose decalin as the most suitable solvent currently due to its best performance at a relatively low temperature. Besides, it is the most stable one among the listed solvents.⁴¹⁻⁴³ Thus, decalin was used in following experiments.

3.2.2 | Effect of nitrogen flow rate

Studies^{44,45} have been done for the closed and open system, showing that the release of HCl is crucial to break the reaction equilibrium of dissociation of amine hydrochloride to realize the thermal dissociation process of amine hydrochlorides. With different flow rates of N₂, Figure 7 was drawn as follows, which shows the substantial influence. 300 mL/min was selected as the optimum after a trade-off although the higher the better if just the thermal dissociation rate is considered. Other conditions were 180°C, with decalin/TOAHCl mass ratio of 5:1.

3.2.3 | Effect of temperature

Heating temperature is an important factor in thermal dissociation process. However, the energy consumption will be quite large and the amine may degrade if the temperature is too high. We did a set of experiments at different temperatures with the initial decalin/TOAHCl mass ratio of 5:1, high pure nitrogen flow rate of 300 mL/min. The result is depicted in Figure 8.

The strong temperature dependence of the thermal dissociation of TOAHCl in decalin could be read from the curves. Conversion rate plunges from 99.7% to only 20.8% as the temperature drops from 190°C to 150°C after 8 hours heating. For endothermic reaction, the best temperature is the one that the system (including the equipment and materials) could endure. Herein, 190°C was chosen as the optimal temperature, just a little bit higher than the boiling point of decalin.

3.2.4 | Effect of solvent concentration

It is manifest from Figure 9 that solvent concentration has a significant effect on thermal dissociation process. As the concentration of solvent increases, thermal dissociation rate becomes much quicker and the degree of conversion becomes higher. It happens as mentioned above mostly because more solvent molecules could disperse the produced TOA and HCl molecules more thoroughly and inhibit the recombination of them more efficiently according to "cage effect" raised by

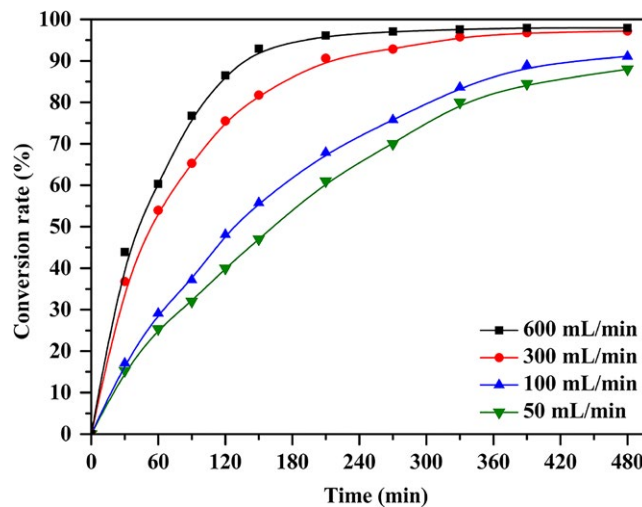


FIGURE 7 Effect of N₂ flow rate on thermal dissociation of TOAHCl

Franck and Rabinowitch^{46,47} so that the HCl could escape from the solutions once the thermal dissociation happens. However, the handling capacity will decline in the meantime. Therefore, it is important to choose a proper concentration of solvent in terms of the balance between dissociation efficiency and handling capacity or energy consumption, namely, the conversion rate should be high enough while the amount of solvents should not be too large. According to Figure 9, there is a significant conversion rate increase from 4:1 to 5:1. However, the increase from 5:1 to 10:1 is moderate whereas the energy consumption would be roughly doubled. Hence, decalin/TOAHCl mass ratio of 5:1 could be the optimal concentration currently.

3.3 | Reaction mechanism analysis

3.3.1 | Kinetic analysis

According to the work of Gibson et al.,^{44,45} the dissociation of amine hydrochloride in dilute chlorobenzene follows the first-order reaction principle in open system. Besides, under certain high N₂ flow rate, the external diffusion could be ignored as far as possible. Thus, it is reasonable to assume that HCl could escape the system once formed in dilute enough solutions. Let A represent TOAHCl_(solv). For first-order reaction, the following expression holds: $d(C_A)/dt = -kC_A$. Integrating and applying the initial condition, we get Equation (7).

$$\ln \left(\frac{C_A}{C_{A_0}} \right) = -kt \quad (7)$$

The equation could be transformed to the conversion rate form as Equation (8).

$$\ln(1 - x_A) = -kt \quad (8)$$

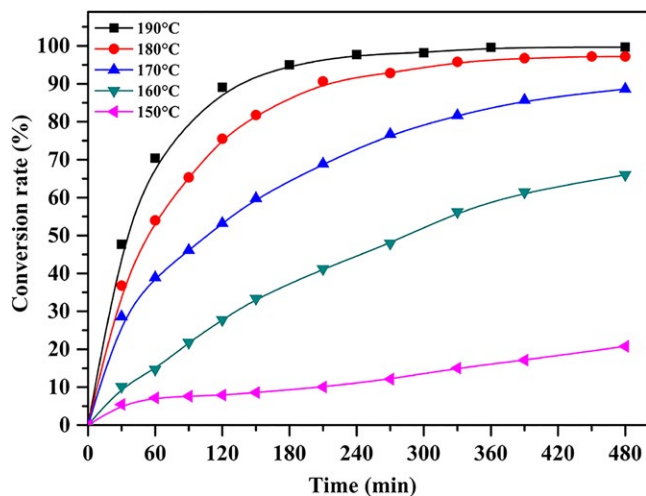


FIGURE 8 Effect of temperature on thermal dissociation of TOAHCl

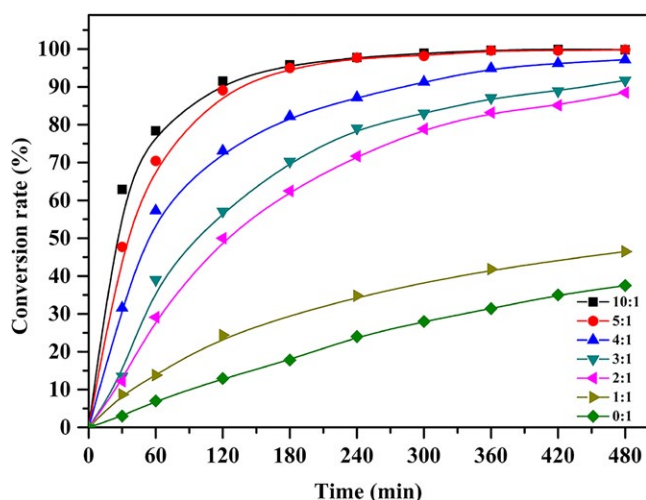


FIGURE 9 Effect of concentration of solvent on thermal dissociation of TOAHCl. (represented by decalin/TOAHCl mass ratio)

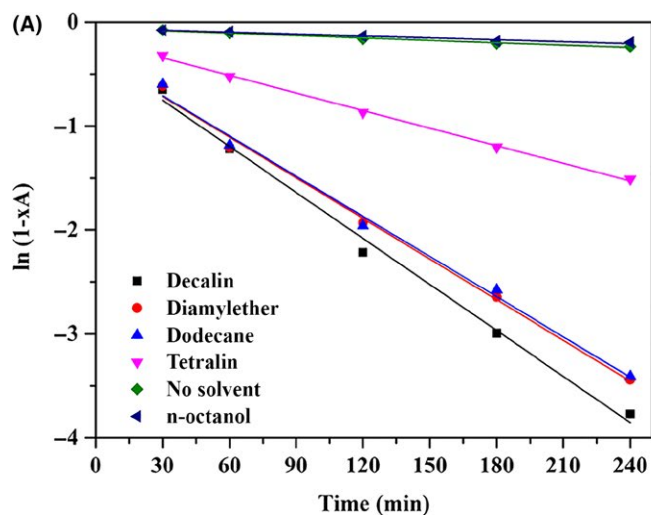


Figure 10 shows a plot of $\ln(1-x_A)$ versus t for each solvent under two different temperatures, 190°C and 180°C (for the dissociation of TOAHCl in different solvents at 190°C please see the Appendix S3). The dataset for each condition is well-correlated to a linear fit, consistent with a first-order process. From Equation (8) we know that the slope equals to $-k$. All the reaction rate constants are listed in Table 3.

Seen from Table 3, the conspicuous solvent effect could be found for the dissociation of TOAHCl. Difference of order of magnitude exists for different solvents in k . As is known, the interaction among the product TOA with low polarity is weaker than that among the reactant TOAHCl with high polarity. Thus, nonpolar solvents with weak intramolecular interaction favor such kind of reactions. The difference of intramolecular interaction among each component of solutions leads to instability, namely, the ideal mixture would be formed if the interactions are similar.⁴⁸

Based on Arrhenius Equation (9), activation energy E_a could be considered as a constant if the temperature varies in a narrow range. Thus, the E_a could be calculated from the slope of $\ln(k)-1/T$ based on Equation (10).

$$k = Ae^{-E_a/RT} \quad (9)$$

$$\ln(k) = -\frac{E_a}{RT} + \ln(A) \quad (10)$$

First-order fitting and the values of apparent reaction rates at different temperatures in Figure 8, please see Figure 11 and Table 4 accordingly. However, sometimes the straight line bends when the temperature increases which happens in our work, as shown in Figure 12. In this case, modified Equation (11) with three parameters raised by Van't Hoff's student Kooij where the B , m , and E_a need to be determined through experiments. For us, we applied another form of

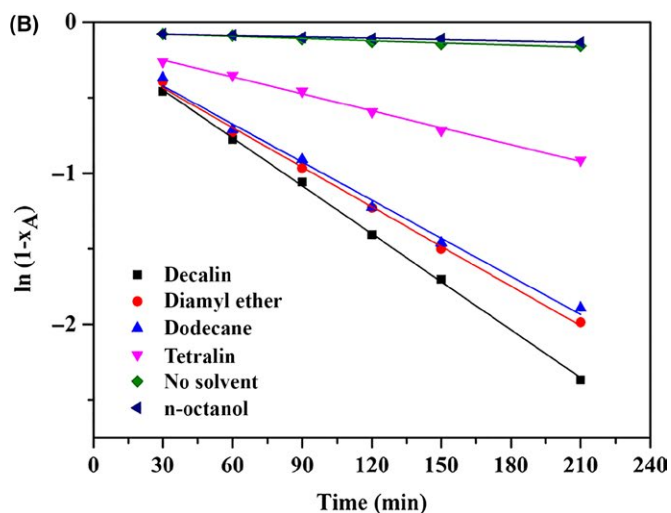


FIGURE 10 First-order fitting plot as a function of time at 190°C (A) and 180°C (B) under open conditions

TABLE 3 Kinetics parameters k and E_a for thermal dissociation of TOAHCl in dilute solutions

Solvent	$k \times 10^4$ (min^{-1})		E_a (kJ/mol)	R^2	
	190°C	180°C		190°C	180°C
Decalin	147.7	105.8	58.219	0.9924	0.9993
n-dodecane	129.0	80.2	74.653	0.9941	0.9975
Diamyl ether*	130.5	87.5	69.754	0.9912	0.9920
Tetralin	56.4	37.3	72.152	0.9979	0.9957
No solvent	7.6	4.7	83.670	0.9781	0.9445
n-octanol	6.0	3.0	121.827	0.9655	0.9655

*The temperature is 187°C for the one with asterisk due to the low boiling point of diamyl ether.

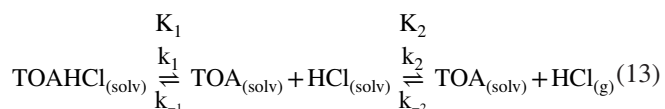
Arrhenius Equation (12) to calculate E_a at the temperature between 180°C and 190°C, which should be reasonable for this temperature range. The results were also listed in Table 3. As for activation energy E_a , the values differ not so largely except for n-octanol. In n-octanol, complex mechanism might exist because its strong solvation power that the proton from solvents may join the reaction.

$$k = BT^m \exp\left(-\frac{E_a}{RT}\right) \quad (11)$$

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{RT}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (12)$$

3.3.2 | Reaction scheme

Inspired by the work of Gibson et al.,^{44,45} a possible reaction scheme for the thermal dissociation of TOAHCl in decalin was proposed below as Equation (13).



The dissociation step (K_1) involves breaking up the tight ion pair of solvated hydrochloride salt. The second step (K_2), the conversion from solvated HCl to gaseous phase which was entropically powered, was thought to be the thermodynamic driver (ie, controlling step). Moreover, the second process could be considered to be almost irreversible in open system with high flow rate of N_2 . The rate constant k we calculated was the apparent rate constant.

4 | CONCLUSIONS

A 100% atom utilization process to regenerate amine extractant and to produce HCl gas which is the key to realizing the CO_2 mineralization with metal chloride waste liquids was investigated. The main conclusions could be summarized as follows.

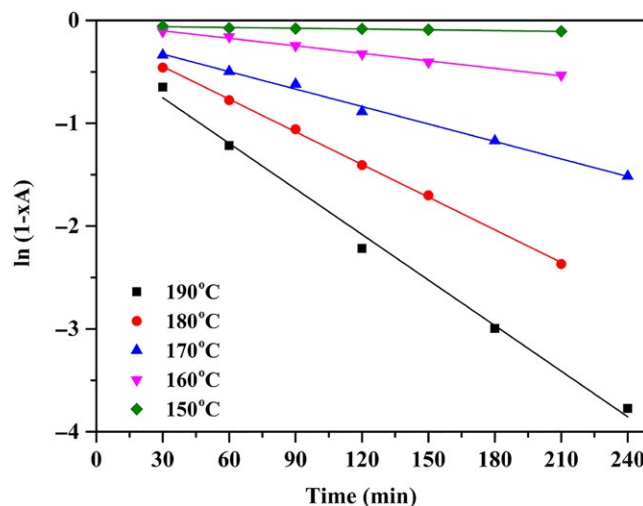


FIGURE 11 First-order fitting plot as a function of time for thermal dissociation of TOAHCl in decalin at different temperatures

TABLE 4 Apparent reaction rate k for thermal dissociation of TOAHCl in decalin at different temperatures

Temperature, °C	Reaction rate $k \times 10^4$ (min^{-1})	R^2
190	147.7	0.9924
180	105.8	0.9993
170	56.6	0.9937
160	24.4	0.9949
150	2.5	0.9357

- The solvent effect is prominent. In contrast of structure parameters, charge distribution, solvation free energy, apparent basicity, and N-H frequency with the help of molecular simulation and experiments, the solvents for thermal dissociation of TOAHCl were compared theoretically. Inert solvents of low polarity without aromatic ring such as decalin, dodecane, and diamyl ether are favorable. Particularly, decalin shows the best performance at a relatively low temperature.
- For dilute solutions, the thermal dissociation exhibits first-order kinetics. The apparent reaction rates and activation energy vary in various solvents a lot, confirming a strong solvent effect.

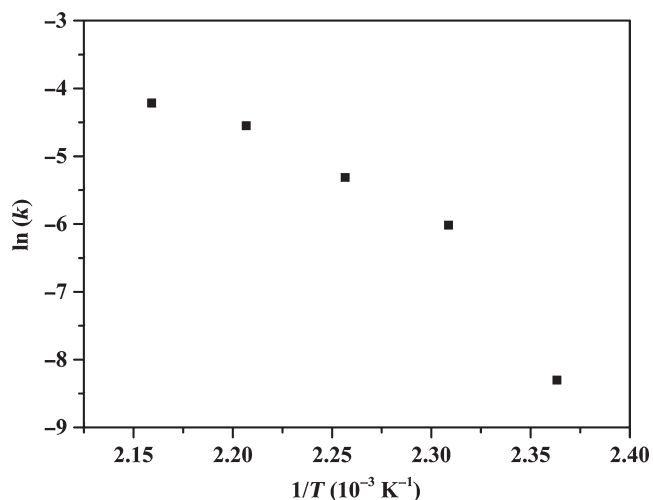


FIGURE 12 Plot of $\ln(k)$ as a function of $1/T$

- The overall two-stage process is entropically driven, with the removal of HCl into gaseous phase from the solvated state.
- Strong temperature effect exists. Degradation during the process need to be investigated deeply to direct the selection of proper solvent such as dodecane and other inert solvents with higher boiling point.
- The investigation of degradations of amine extractants and solvents which are crucial for further real production is in progress and not included in the paper.

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CONFLICT OF INTEREST

None declared.

ORCID

Xingfu Song  <http://orcid.org/0000-0001-6558-8288>

REFERENCES

1. Wang W, Liu X, Wang P, Zheng Y, Wang M. Enhancement of CO_2 mineralization in Ca^{2+} -/ Mg^{2+} -rich aqueous solutions using insoluble amine. *Ind Eng Chem Res.* 2013;52:8028-8033.
2. Liu X, Wang W, Wang M, Wang P. Experimental study of CO_2 mineralization in Ca^{2+} -rich aqueous solutions using tributylamine as an enhancing medium. *Energy Fuels.* 2014;28:2047-2053.
3. Chen G, Song X, Dong C, Sun S, Sun Z, Yu J. Mineralizing CO_2 as $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ using abandoned MgCl_2 based on a coupled reaction-extraction-alcohol precipitation process. *Energy Fuels.* 2016;30:7551-7559.
4. Chen P, Tang S, Yue H, Liu C, Li C, Liang B. Lithium enrichment of high Mg/Li ratio brine by precipitation of magnesium via combined CO_2 mineralization and solvent extraction. *Ind Eng Chem Res.* 2017;56:5668-5678.
5. Chen G, Song X, Xu Y, Yu J. Effects of NO_3^- and SO_4^{2-} ions on the coupled reaction-extraction-crystallization process of MgCl_2 and CO_2 . *Ind Eng Chem Res.* 2017;56:7100-7108.
6. Chen G, Song X, Sun S, Xu Y, Yu J. Solubility and diffusivity of CO_2 in n-butanol+N235 system and absorption mechanism of CO_2 in a coupled reaction-extraction process. *Front Chem Sci Eng.* 2016;10:480-489.
7. Li Y, Song X, Chen G, Sun S, Xu Y, Yu J. Extraction of hydrogen chloride by a coupled reaction-solvent extraction process. *Front Chem Sci Eng.* 2015;9:479-487.
8. Li Y, Song X, Sun S, Xu Y, Yu J. Extraction equilibrium of hydrochloric acid at low concentrations between water and N235 in isoamyl alcohol solution: experiments and simulation. *J Chem Eng Data.* 2015;60:3000-3008.
9. 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. *Chem Eng J.* 2015;278:55-61.
10. Dong C, Song X, Li Y, Liu C, Yu J. Impurity ions effect on CO_2 mineralization via coupled reaction-extraction-crystallization process of CaCl_2 waste liquids. *J CO₂ Util.* 2018. <https://doi.org/10.1016/j.jcou.2018.05.023>
11. Chen H, Sun Z, Song X, Yu J. Efficient extraction of phosphoric acid with a trialkyl amine-based solvent mixture. *J Chem Eng Data.* 2016;61:438-443.
12. Jiang C, Zheng S, Zheng Y, Wang Z. Preparation of potassium dihydrogen phosphate by triethylamine-isoamyl alcohol organic solvent extraction. *Inorg Chem Ind.* 2014;2:44-46 (in Chinese).
13. Liu Y, Li J, Li Y, Duan X. Preparation of potassium dihydrogen phosphate by extraction method. *Inorg Chem Ind.* 2007;39:24-26 (in Chinese).
14. Eyal AM, Baniel A. Recovery and concentration of strong mineral acids from dilute solutions through LLX. I: review of parameters for adjusting extractant property and analysis of process options. *Solvent Extr Ion Exch.* 1991;9:195-210.
15. Kang H, Zhou X, Dong L, Feng T. Synergetic extraction of phytic acid from HCl extract of rapeseed meal with alamine 336 and N-octanol dissolved in sulfonated kerosene. *Ind Eng Chem Res.* 2011;50:8658-8664.
16. Sarangi K, Padhan E, Sarma PVRB, Park KH, Das RP. Removal/recovery of hydrochloric acid using alamine 336, aliquat 336, TBP and cyanex 923. *Hydrometallurgy.* 2006;84:125-129.
17. Agrawal A, Kumari S, Ray BC, Sahu KK. Extraction of acid and iron values from sulphate waste pickle liquor of a steel industry by solvent extraction route. *Hydrometallurgy.* 2007;88:58-66.
18. Coenen A, Kosswig K, Hentschel B, Ziebarth J. Method of manufacturing hydrogen chloride from solutions of amine hydrochlorides. US 4230681, 1980.
19. Coenen A, Maria L, Kosswig K, Balzer D. Method for preparing ammonia and hydrogen chloride from ammonium chloride. US 4305917, 1981.

20. Coenen A, Kosswig K, Prominski G. Process for obtaining gaseous hydrogen chloride from dilute, aqueous hydrochloric acid. US 4115530, 1978.
21. Dong C, Song X, Zhang J, Liu D, Meijer EJ, Yu J. Thermodynamics and kinetics analysis of thermal dissociation of tri-n-octylamine hydrochloride in open system: A DFT and TGA study. *Thermochim Acta*. 2018. <https://doi.org/10.1016/j.tca.2018.05.017>
22. Dong C, Song X, Meijer EJ, Chen G, Xu Y, Yu J. Mechanism studies on thermal dissociation of tri-n-octylamine hydrochloride with FTIR, TG, DSC and quantum chemical methods. *J Chem Sci*. 2017;129:1431-1440.
23. Yuan L. Research on technology of hydrogen chloride and ammonia manufacture by decomposition of ammonium chloride based on organic amine. Nanjing University of Technology, 2012 (in Chinese).
24. Eyal AM, Hazan B, Bloch R. Recovery and concentration of strong mineral acids from dilute solutions through LLX. II. Reversible extraction with branched-chain amines. *Solvent Extr Ion Exch*. 1991;9:211-222.
25. Eyal AM, Hazan B, Bloch R. Recovery and concentration of strong mineral acids from dilute solutions through LLX. III. A "temperature swing" based process. *Solvent Extr Ion Exch*. 1991;9:223-236.
26. Baniel A, Eyal A. Process for the recovery of HCl from a dilute solution thereof. US 2010/0093995 A1, 2010.
27. Baniel A, Eyal A. Process for the recovery of HCl from a dilute solution thereof and extractant composition for use therein. 2011/0028710 A1, 2011.
28. Eyal A, Baniel A. Extraction of strong mineral acids by organic acid-base couples. *Ind Eng Chem Process Des Dev*. 1982;21:334-337.
29. Kertes AS. Solubility and activity of high-molecular amine hydrochlorides in organic solvents. *J Inorg Nucl Chem*. 1965;27:209-217.
30. Li Z. Mechanism study on complex extraction of carboxylic acid with tri-n-octylamine. Tsinghua University, 2001. (in Chinese)
31. Frisch MJ, Trucks GW, Schlegel HB, et al. Gaussian 09, Version A.02, 2009.
32. Marenich AV, Cramer CJ, Truhlar DG. 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.
33. Tomasi J, Persico M. Molecular interactions in solution: an overview of methods based on continuous distributions of the solvent. *Chem Rev*. 1994;94:2027-2094.
34. Wang Y. Quantum-chemical studies of solvent effect. Sichuan University, 2006 (in Chinese)
35. Wong MW, Wiberg KB, Frisch MJ. 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;114:1645-1652.
36. Bernadette C, Sandorfy C. Hydrogen bonding in the amine hydrohalides: I. General aspects. *Can J Chem*. 1958;36:1181-1206.
37. Larkin P. *Infrared and Raman Spectroscopy: Principles and Spectral Interpretation*, 1st edn. Cambridge, MA: Elsevier Inc; 2011.
38. Weng S. *Fourier Transform Infrared Spectrum*, 2nd edn. Beijing: Chemical Industry Press; 2010 (in Chinese).
39. Mulliken RS. Molecular compounds and their spectra. III. The interaction of electron donors and acceptors. *J Phys Chem*. 1952;56:801-822.
40. Kertes AS, Grauer F. Thermodynamics of solvent extraction processes effect of diluent on the enthalpy of formation of tri-n-octylammonium chloride. *J Inorg Nucl Chem*. 1978;40:1781-1782.
41. Aguado J, Serrano DP, Vicente G, Sánchez N. Enhanced production of r-olefins by thermal degradation of high-density polyethylene (HDPE) in decalin solvent: effect of the reaction time and temperature. *Ind Eng Chem Res*. 2007;46:3497-3504.
42. Chae K, Violi A. Thermal decomposition of decalin: an ab initio study. *J Org Chem*. 2007;72:3179-3185.
43. Gollis MH, Belenyessy LI, Gudzinowicz BJ, Koch SD, Smith JO, Wineman RJ. Evaluation of pure hydrocarbons as jet fuels. *J Chem Eng Data*. 1962;7:311-316.
44. Gibson EK. Amine hydrochloride salts: a problem in polyurethane synthesis. University of Glasgow, 2007.
45. Gibson EK, Winfield JM, Adam D, et al. The solvation and dissociation of 4-benzylaniline hydrochloride in chlorobenzene. *Ind Eng Chem Res*. 2014;53:4156-4164.
46. Franck J, Rabinowitch E. Some remarks about free radicals and the photochemistry of solutions. *Trans Faraday Soc*. 1934;30:120-130.
47. Rabinowitch E. The collision [sic] mechanism and the primary photochemical process in solutions. *Trans Faraday Soc*. 1936;32:1381-1387.
48. Hu Y, Lv R, Liu G, Hei E. *Physical Chemistry*, 5th edn. Beijing: Higher Education Press; 2007. (in Chinese).

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