

Phase Splitting Rules of the Primary/Secondary Amine–Tertiary Amine Systems: Experimental Rapid Screening and Corrected Quasi-Activity Coefficient Model

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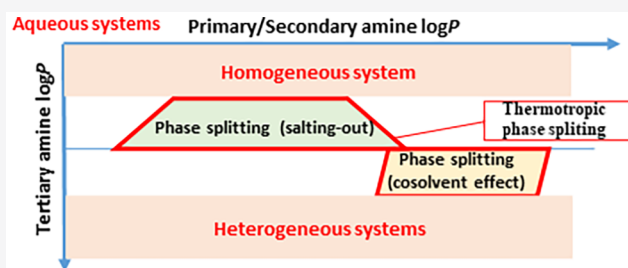
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ABSTRACT: Several phase splitting systems have shown potential in reducing regeneration energy consumption for large-scale CO₂ capture in the last decade. The development of new phase splitting systems currently depends on experimental screening. In this work, 90 sets of primary/secondary amine–tertiary amine anhydrous systems and 160 sets of primary/secondary amine–tertiary amine–water systems were used to investigate the phase splitting rules at the molecular level. The results show that the phase splitting behavior of the anhydrous system is directly affected by the carbamate solubility in the tertiary amine. The potential phase splitting system has a tertiary amine with proper lipophilicity. Among the aqueous systems, two different phase splitting zones were recognized: the salting-out effect zone with a lower amine log *P* and the cosolvent effect zone with a higher amine log *P*. Several thermotropic phase splitting systems are located at the edge of these two zones. The tertiary amine with more *tert*-amine groups and less hydroxyl groups would facilitate phase splitting. The primary/secondary amine with hydroxyl groups on the straight chain would facilitate phase splitting. A new parameter describing the primary amine/secondary amine as a nonelectrolyte is introduced to develop a new quasi-activity coefficient of the chemical–chemical aqueous system. This quasi-activity coefficient is applicable to the mono- or polyamine systems with different material ratios.



1. INTRODUCTION

Carbon dioxide (CO₂) emission reduction has attracted worldwide attention. Chemical absorption is one of the reliable technologies to capture CO₂. It has been commercialized since 1930s.^{1–3} Several alkanolamine aqueous systems, such as the monoethanolamine (MEA) aqueous system and methyldiethanolamine/piperazine (MDEA/PZ) aqueous system, have become the benchmark systems of CO₂ absorption. However, its large application in postcombustion capture is limited by high energy consumption and high degradation.⁴ During the last decades, some phase splitting absorbents have been developed and proved effective in reducing the regeneration energy consumption by concentrating CO₂ into one phase after absorption.^{5,6} The phase splitting absorbents are divided into chemical–physical systems and chemical–chemical systems.⁷ Some chemical–chemical systems show better performance by combining a primary/secondary amine with a fast absorption rate and a tertiary amine with a high absorption capacity.^{8,9}

Presently, the primary/secondary amine–tertiary amine aqueous system is one of the typical phase splitting chemical–chemical systems. Almost all of these systems are developed by experimental screening. Some lipophilic tertiary amines (octanol–water distribution coefficient of (log *P*) < 0) and hydrophilic tertiary amines (log *P* > 0) show different CO₂

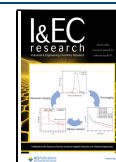
absorption behaviors.¹⁰ Almost all primary/secondary amine–hydrophilic tertiary amine–water systems remain homogeneous before and after CO₂ absorption. Some primary/secondary amine–lipophilic tertiary amine–water systems change from two phases into one phase during CO₂ absorption.^{11,12} Some systems change from one phase to two phases during CO₂ absorption, such as the triethylenetetramine (TETA)–diethylaminoethanol (DEEA)–water system,¹³ 2-((2-aminoethyl)-amino)ethanol (AEEA)–DEEA–water system,¹⁴ and diethylenetriamine (DETA)–*N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA)–water system.¹⁵ Some NMR studies and nonrandom two-liquid electrolyte model (NRTL) study show that the carbamates mainly exist in the CO₂-rich phase in the dissociation forms (RNH₂⁺, RNCOO[−]) rather than in the lean phase.^{16–18} The solubility difference of CO₂ absorption products (the carbamate formed from primary/secondary

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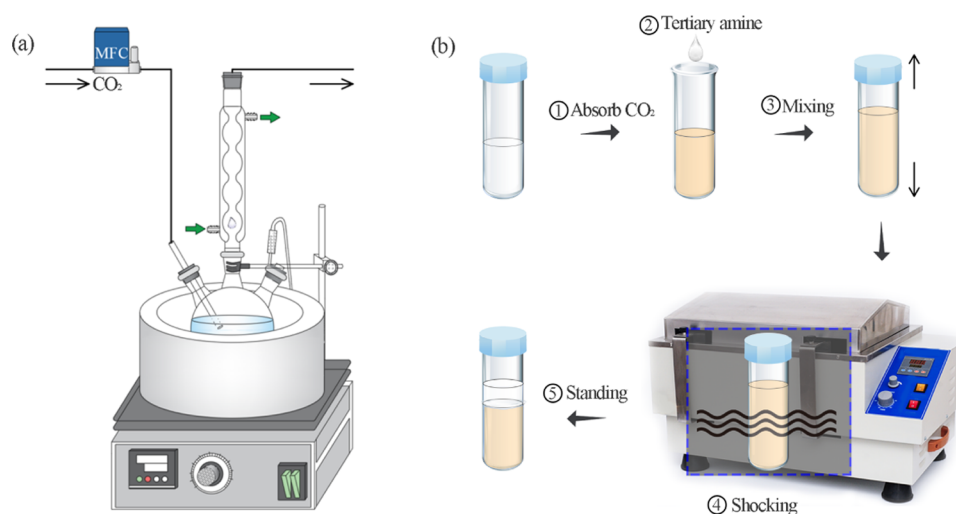


Figure 1. Experimental devices: (a) rapid screening device and (b) flow chart of carbamate solubility experiment.

amine) in tertiary amine and water is considered to affect the phase splitting.^{19,20} Although the phase splitting behavior is believed to be related to the molecular structure of amines, the quantitative relationships at the molecular level for the primary/secondary amine–tertiary amine aqueous system are still not understood.

Some phase splitting rules have been investigated over the chemical–physical aqueous systems.^{19,21} The salting-out effect referring to the electrolyte–nonelectrolyte system is introduced to study the phase splitting mechanism of the primary/secondary amine–organic solvent–water system (the chemical–physical aqueous system).^{21,22} The quantitative structure–property relationship (QSPR) work for predicting the organic solvent–water distribution coefficient of the product ions shows that the interactions between the organic solvent and the carbamate are highly relevant to the volume of organic solvents (V_s), the maximum electrostatic potential value on the solvent molecular surface (ESP^+), and the surface/volume value of organic solvents (S/V_s).²³ On the basis of this QSPR work,^{23,24} a phase splitting prediction figure based on the organic solvent–water distribution coefficient of anions and cations and a quasi-activity coefficient ($\ln \gamma'$) model derived from the Debye and McAulay equation are obtained for the chemical–physical aqueous system. These studies provide a molecular basis for designing new phase splitting chemical–physical aqueous systems, including monoamine or polyamine systems with different material ratios.

Would the rules of chemical–physical aqueous systems^{5,6} also apply to the chemical–chemical aqueous systems? In the chemical–physical aqueous systems, the physical solvents have poor solubility of electrolyte and proper hydrophilicity ensuring that the system is homogeneous before CO₂ absorption but heterogeneous after CO₂ absorption. The tertiary amines may play the same role in the chemical–chemical aqueous system at the beginning of the CO₂ absorption. With the CO₂ absorbing, tertiary amines turn to react with CO₂ and water to form protonated amines, which dissolve into the water phase. Similar to the chemical–physical aqueous systems, the initial phase splitting of the primary/secondary amine–tertiary amine–water system is caused by the solubility difference of carbamate in water and in the organic solvent.^{25,26} The quasi-activity coefficient may also apply to the chemical–chemical aqueous systems in theory.

To further get a clear understanding of the phase splitting rules of the primary/secondary amine–tertiary amine–water systems, 160 sets of primary/secondary amine–tertiary amine–water systems and 90 sets of primary/secondary amine–tertiary amine systems were rapidly screened in this work. Several phase behaviors related to the amine molecules were analyzed. The saturated solubility of carbamate in tertiary amines was investigated. A new density functional theory (DFT) parameter describing the effect of primary/secondary amines was introduced to correct $\ln \gamma'$. The new $\ln \gamma'$ was proven effective in predicting the phase splitting behaviors of the primary/secondary amine–tertiary amine–water systems caused by the salting-out effect. Some new phase splitting systems were predicted by calculation and verified experimentally.

2. EXPERIMENTAL AND COMPUTATIONAL SECTION

2.1. Experiments. **2.1.1. Materials.** Methanolamine (MEA, GR, 99%), 3-aminopropan-1-ol (3AP, AR, 99%), 2-(2-aminoethoxy)ethanol (DEA, GR, 99%), isopropanolamine (IPA, GR, >99%), 2-amino-1-butanol (2AB, GR, 99%), 1-propanamine (PA, GR, 99%), 1-butylamine (BA, GR, 99%), isobutylamine (IBA, GR, 98%), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, GR, 98%), *N,N,N,N*-tetramethylethylenediamine (TMEEA, GR, 99%), diethylaminoethanol (DEEA, GR, 98%), 1-dimethylamino-2-Propanol (1DMA2P, GR, 98%), 3-dimethylamino-1-propanol (3DMA1P, GR, 99%), 2-(dimethylamino)-ethanol (DMEA, GR, 99%), *N*-methyldiethanolamine (MDEA, GR, 99%), triethanolamine (TEA, GR, 99%), triethylamine (GR, 99%), dimethylaminocyclohexane (DMCHA, GR, 98%), *N,N*-butyldimethylamine (DMBA, GR, >98%), *N,N*-diethylaniline (NNDEA, GR, 99%), *N,N*-dimethylbenzylamine (NNDMBA, GR, >98%), *N,N*-dimethylaniline (NNDMA, GR, 99%), *N,N*-dipropyl-1-propanamine (TPA, GR, ≥98%), *N,N,N',N'*-tetramethyl-1,3-propanediamine (TMPDA, GR, >99%), and 4-amino-1-butanol (4AB, GR, ≥98%) were purchased from Adamas, Shanghai Titan, and TCI. CO₂ (>99%) was purchased from Chengdu Dongfeng Gas Co., Ltd., China.

2.1.2. CO₂ Absorption. All the CO₂ absorptions were carried out in a rapid screening device at atmospheric pressure (Figure 1a). A total of 20 g of absorbent was added to a 50 mL three-

necked round-bottom flask. The magnetic stirring rate was set to 200 r/min. A thermostatic water bath (DF101S, Hangzhou-jingfei Co., ± 1 K) was used to control the temperature. CO₂ was injected into the reactor at a flow rate of 500 mL/min through a mass flowmeter (MFC, Beijing Sevenstar Electronics Co., Ltd., China). The phase behavior of the system was observed every 5 min during the CO₂ absorption. The reaction was terminated at 30 min. Then, the reaction device was let to stand for 2 h at the reaction temperature. The final phase behavior of the system was recorded. In the 90 sets of the anhydrous systems, the mass ratio of the primary/secondary amine and tertiary amine was set to 1:1. In the 160 sets of the aqueous systems, the mass ratio of the primary/secondary amine and tertiary amine and water was set to 1:2:1.

2.1.3. Solubility Determination of CO₂ Absorption Products. The solubility determination experiments were carried out as shown in Figure 1b. In the anhydrous system, the primary/secondary amine reacts with CO₂, eq 1. The ion pairs ([R₁R₂NH₂⁺][R₁R₂NCOO[−]]) are the products of CO₂ absorption. Due to the high viscosity of liquid or solid products, it is hard to completely transfer the products. The CO₂ absorption for solubility determination was carried out in a 50 mL centrifuge tube. A total of 10 g of primary/secondary amine was fully reacted with CO₂ at 313 K for 30 min to obtain the carbamate. By titrating the product at different times, the system was confirmed to achieve absorption saturation at 30 min (S-Section 1.1). Then, 5 g of tertiary amine was added to the centrifuge tube as a solvent. The centrifuge tube was preshaken. Then, it was fully shaken in a constant-temperature oscillator (SHA-B, Yinggong Co., ± 0.5 K) at 313 K for 24 h. After fully mixing, the centrifuge tube was let to stand for 12 h. The upper phase (tertiary amine phase) was collected and titrated to determine the solubility of the product in the tertiary amine (S-Section 1.2). If the system was still homogeneous at the mass ratio, the addition amount of the tertiary amine would be adjusted. If the system was still homogeneous at the mass ratio of tertiary amine to primary/secondary amine lower than 1:10, the CO₂ absorption product was considered miscible with tertiary amine in any proportion.



2.2. Computational Section. **2.2.1. DFT Calculation and Descriptor Generation.** All the molecules (carbamate anions, protonated amine ions, and neutral molecules) were geometry-optimized at the functional level of M062X and the basis set of 6-311++G(d, p) with Gaussian software. The D3 version of Grimme's empirical dispersion with the original D3 damping function was added.^{27,28} All calculations were performed with implicit solvent effects using the integral equation formalism–polarizable continuum model (IEF-PCM). All of the ionic and molecular descriptors were calculated with Materials Studio and Multiwfn²⁹ (the calculation details are shown in S-Section 2).

The interaction region index (IRI) is a simple real-space function, which can clearly reveal the chemical bonds and weak interactions between atoms and molecular fragments.³⁰ In combination with Multiwfn and VMD software, various types of interactions are allowed to be visualized at the same time. The molecular surface electrostatic potential (ESP) is analyzed (S-Section 2.2 and S-Section 4). The molecular polarity index (MPI)³¹ was calculated with Multiwfn to directly measure the polarity of the system by analyzing the distribution characteristics of ESP.

2.2.2. Quasi-Activity Coefficient Calculation. The quasi-activity coefficient of the amine–organic solvent–water system (chemical–physical aqueous system) is shown in eq 2.²⁴

$$\ln \gamma' = \frac{(ze)^2 c}{2r_{\pm} kT} (\epsilon_0 - \epsilon) \sqrt{\frac{V_s}{ESP_s^+ \left(\frac{S}{V}\right)_s}} - b \quad (2)$$

In eq 2, the first part was derived from the Debye and McAulay equation. z is the charge of ion. e is elementary charge (1.6×10^{-19} C). r_{\pm} is the average ionic radius. c is the molar concentration of salt in the aqueous solution (mol/L). k is the Boltzmann constant (1.380649×10^{-23} J/K). The second part could be expressed as the dielectric decrease. The dielectric decrease could be partially expressed as the static dielectric constant difference. ϵ_0 is the dielectric constant of pure water of 78.36, and ϵ is the dielectric constant of organic solvents. The third part of eq 2 is the DFT parameter developed based on the QSPR study.^{23,24} V_s is the volume of organic solvents, ESP_s^+ is the maximum electrostatic potential value on the solvent molecular surface, $(S/V)_s$ is the surface/volume value of organic solvents. b varying in different types of systems is used to compare $\ln \gamma'$ with 0 in accordance with the thermodynamic convention.

$$\frac{1}{r_{\pm}} = x_1 \frac{1}{r_+} + x_2 \frac{1}{r_-} \quad (3)$$

The average ionic radius (r_{\pm}) is calculated according to eq 3. r_+ is the cation radius, r_- is the anion radius, x_1 is the cation mole fraction, and x_2 is the anion mole fraction. In the system, the molar ratio of carbamate anions to protonated amines is 1:1. x_1 and x_2 are set to 0.5. The ion radius (eq 4) is the sum of the distance from the farthest atom to the geometry center of the anion or cation (d) and the van der Waals radius of the atoms (r_{atom}).



























$$r = d + r_{\text{atom}} \quad (4)$$

Here, the quasi-activity coefficient of primary/secondary amine–tertiary amine–water (chemical–chemical aqueous system) derived from the chemical–physical aqueous system is shown in eq 5.

$$\ln \gamma' = \frac{(ze)^2 c}{2r_{\pm} kT} (\epsilon_0 - \epsilon) \sqrt{\frac{V_s}{ESP_s^+ \left(\frac{S}{V}\right)_s}} \times [(N_{\text{HBD}} + N_{\text{HBA}})(ESP_A^+/ESP_W^+)] - b \quad (5)$$

The first three parts of eq 2 are reserved. Here, tertiary amines are regarded as the organic solvent to calculate the second and third parts. The fourth part is proposed to describe the interaction between the primary/secondary amine (regarded as the solvent) and the CO₂ absorption product of the tertiary amine (regarded as the solute). N_{HBD} is the number of hydrogen bond donors of the primary/secondary amine. N_{HBA} is the number of hydrogen bond receptors of the primary/secondary amine. ESP_A^+ is the maximum electrostatic potential value on the molecular surface of the primary/secondary amine, and ESP_W^+ is the maximum electrostatic potential value on the water molecular surface. All the parameters used for the $\ln \gamma'$ calculation are listed in S-Table 2.

Table 1. Summary of Phase Splitting Behaviors of the System

											
	$\log P$	DGA	DEA	MEA	3AP	4AB	IPA	2AB	PA	IBA	BA
		-1.5	-1.43	-1.31	-1.12	-1.1	-0.96	-0.43	0.48	0.73	0.97
	-1.11	1	1	1	1	1	1	1	1	1	1
TEA											
	-0.72	1	1	1	1	1	1	1	1	1	1
MDEA											
	-0.4	1	1	1	1	1	1	1	1	1	1
DMEA											
	-0.1	1	1	1	1	1	1	1	1	1	1
3DMA1P											
	0.02	1	1	2	1	1	1	1	1	1	1
1DMA2P											
	0.3	1	1	2	1	1	1	1	1	1	1
DEEA											
	0.3	2	1*	2	2	2	1*	1	1	1	1
TMEEA											
	0.43	2	2	2	2	2	2	1*	1	1	1
TMPDA											
	0.54	2	2	2	2	2	2	1*	1	1	1
PMDETA											
	1.45	3	3	3	3	3	3	2	2	2	2
Triethylamine											
	1.7	3	3	3	3	3	3	2	2	1	1*
DMBA											
	1.98	3	3	3	3	3	2	2	2	2	1*
NNDMBA											
	2.01	3	3	3	3	2	2	2	1*	1	1
DMCHA											
	2.31	3	3	3	3	3	3	3	3	3	3
NNDMA											
	2.79	3	3	3	3	3	3	3	3	3	3
TPA											
	3.31	3	3	3	3	3	3	3	3	3	3
NNDEA											

3. RESULTS AND DISCUSSION

3.1. Phase Splitting Behavior of Different Systems. In this work, 10 monoamines and 16 tertiary amines (including 24 amines for rapid screening and 2 amines from prediction results) were selected. A total of 90 sets of primary/secondary amine–tertiary amine anhydrous systems and 160 sets of primary/secondary amine–tertiary amine–water systems were studied. The phase behaviors during the CO₂ absorption are shown in Table 1. All the tertiary amines and primary amines are listed in Table 1 in the ascending order of the log *P* value.

All the experiments were carried out at 313 K and 1 atm. The phase behaviors of the anhydrous system (the mass ratio of the primary/secondary amine and tertiary amine at 1:1) were marked in different background colors: the heterogeneous systems before and after CO₂ absorption are marked in gray, the homogeneous systems with no phase splitting behavior are marked in green, the homogeneous systems with a liquid–liquid phase splitting behavior during CO₂ absorption are marked in blue, the homogeneous systems with a solid–liquid phase splitting behavior during CO₂ absorption are marked in orange, and the homogeneous liquid systems before CO₂ absorption and only solid phase after CO₂ absorption are marked in red. The phase behaviors of the aqueous system (the mass ratio of the primary/secondary amine, tertiary amine, and water of 1:2:1) were marked in numbers: 1 represents homogeneous systems with no phase splitting behavior with CO₂ absorption; 2 represents the homogeneous system with a liquid–liquid phase splitting behavior with CO₂ absorption; and 3 represents the heterogeneous system before and after CO₂ absorption. The red line represents the boundary between the phase splitting aqueous systems and other aqueous systems. Some systems (marked with *) are homogeneous at 313 K but heterogeneous at 333 K after CO₂ absorption.

Table 2. Carbamate Solubility (g/100 g Tertiary Amine)^a

	DGA	DEA	MEA	3AP	4AB	IPA	2AB
TEA	x	x	x	x	x	x	x
MDEA	x	x	x	x	x	x	x
DMEA	x	x	x	x	x	x	x
3DMA1P	x	x	7.49	x	x	x	x
1DMA2P	x	x	1.77	x	x	x	x
DEEA	x	x	2.29	x	x	x	x
TMEEA	3.26	2.67	1.35	2.01	5.02	2.24	x
TMPDA	4.15	3.41	1.14	3.07	3.30	4.25	3.70
PMDETA	2.67	5.33	1.87	1.3	4.23	2.60	6.52

^ax: the carbamate is miscible with tertiary amines at the mass ratio of primary/secondary amine to tertiary amine in the range of 2:1–10:1. The phase behaviors of the anhydrous system (the mass ratio of primary/secondary amine to tertiary amine at 1:1) were marked in different background colors: the heterogeneous systems before and after CO₂ absorption in gray, the homogeneous systems with no phase splitting behavior in green, and the homogeneous system with a liquid–liquid phase splitting behavior during CO₂ absorption in blue.

3.1.1. Anhydrous Systems. In anhydrous systems, only the primary/secondary amine participates in the CO₂ absorption. The solubility of the primary/secondary amine carbamate in tertiary amine is believed to be related to the phase splitting behaviors in the anhydrous systems. Here, 63 sets of carbamate solubility were investigated and are listed in Table 2. All the carbamates of the primary/secondary amines in Table 2 are in the liquid form. The CO₂ absorption products of PA, IBA, and BA (log *P* of the primary/secondary amines > 0) are in the solid form. This leads to a solid–liquid phase splitting or solid phase change. Due to the poor transfer performance caused by the high viscosity of these solid products, it is hard to measure the carbamate solubility.

These carbamate solubilities are in good agreement with the phase splitting behaviors (Table 1). The carbamates from PA, IBA, and BA are solid, while other primary/secondary amine carbamates are liquid. Due to the different properties of the carbamates, liquid–liquid phase splitting, liquid–solid phase splitting, and a solid phase were observed.⁵ The carbamate with a higher polarity may lead to the phase splitting behavior in the tertiary amines with a lower polarity. The polarity of tertiary amines generally decreases with the log *P* increasing. Therefore, the system with a tertiary amine of higher log *P* is more prone to show phase splitting. Due to the molecular interaction between MEA and tertiary amine with no hydroxyl, MEA-TMEEA, MEA-TMPDA, and MEA-PMDETA show a heterogeneous phase before and after CO₂ absorption.

The rich phase of these phase splitting anhydrous systems has quite a high viscosity. The water from the flue gas accumulates in the absorbent during CO₂ absorption. These will hinder further application of the anhydrous systems. With water accumulation, some tertiary amines would react with CO₂. The viscosity of the rich phase will decrease. The system will transform into an aqueous system. The phase splitting behavior of some systems may disappear eventually.

3.1.2. Aqueous Systems. The amines with a higher log *P* value may not be miscible with water. In total, 40 sets of systems with the hydrophilic tertiary amine (log *P* < 0) are homogeneous. The systems with the tertiary amine with a suitable lipophilicity (0 < log *P* < 2.01) tend to facilitate the formation of two phases.⁵ A total of 30 sets of systems with strong lipophilic tertiary amines (log *P* > 2.01) are heterogeneous.

The aqueous systems with the phase splitting behaviors are distributed in two different zones in Table 1: **Zone 1** with the tertiary amine log *P* ranging from −0.1 to 0.54 and the primary/secondary amine log *P* ranging from −1.5 to −0.43 and **Zone 2** with the tertiary amine log *P* ranging from 1.45 to 2.01 and the primary/secondary amine log *P* ranging from −0.96 to 0.97. The phase splitting mechanisms of **Zone 1** and **Zone 2** are different.³² In **Zone 1** (the lower log *P* zone), the tertiary amine (0 < log *P* < 0.54) may both be miscible with water and primary/secondary amine; most phase splitting behaviors in this zone can be explained by the salting-out effect. In salting-out theory, the solubility of the salt is the key factor affecting the phase behaviors of the system. The phase splitting of these systems is caused by the solubility difference of the carbamate in the tertiary amine and water.^{33,34} The phase behavior demarcation line of **Zone 1** is also consistent with the zone of the carbamate solubility in the tertiary amine, as shown in Table 2. In **Zone 2** (the higher log *P* zone), the tertiary amines with a log *P* greater than 1.45 are insoluble in water. However, due to the higher log *P* value of the primary/secondary amines, the

systems are homogeneous before CO₂ absorption. After CO₂ absorption, some carbamates of primary/secondary amines are formed, and then, the equilibrium of the original system is destroyed. In this case, the phase splitting behaviors should be attributed to the cosolvent effect.^{35,36}

It is worth noting that some aqueous systems (DEA-TMEEA, IPA-TMEEA, 2AB-TMPDA, 2AB-PMDETA, BA-DMBA, BA-NNDMBA, and PA-DMCHA) do undergo phase splitting at 333 K rather than at 313 K. The IBA-DMBA aqueous system is hard to be recognized as phase splitting at 333 K due to the IBA-CO₂ carbamate decomposing. The systems with a small solubility of the liquid carbamate in anhydrous systems (DEA-TMEEA, IPA-TMEEA, 2AB-TMPDA, and 2AB-PMDETA) and the systems with the solid carbamate in anhydrous systems (BA-DMBA, BA-NNDMBA, PA-DMCHA, and IBA-DMBA) could undergo phase splitting at a ratio of primary/secondary amine, tertiary amine, and water of 1:4:1. Theoretically, with more solvent (the tertiary amine), the product of CO₂ absorption may dissolve more. However, the phase splitting behavior occurs in those systems with more tertiary amine. A more complicated interaction among those components or thermotropic phase splitting theory may help to understand better the phase splitting mechanism.

3.2. Effect of the Amine Structure on Phase Splitting Behavior.

3.2.1. Tertiary Amine Structure. The molecular structure of the tertiary amine shows a major effect on phase splitting. In the process of CO₂ absorption, the tertiary amines can act as proton acceptors. The formed protonated amines may coordinate with water. The tertiary amines in the CO₂ lean phase gradually transfer into the CO₂-rich phase in the ionic forms with CO₂ absorption. As the tertiary amine containing only one *tert*-amine group is easily protonated, the phase splitting behavior may be unstable. The protonation degree of the tertiary amine may be affected by steric hindrance and electronic properties. Complete protonation of the tertiary amines with multiple *tert*-amine groups may barely occur or only occur at the terminal of CO₂ absorption. Therefore, the tertiary amines with multiple *tert*-amine groups show stronger phase splitting ability. A similar phenomenon has been reported that the rich-phase volume of the DETA-DEEA system was much larger than that of the DETA-PMDETA system.³⁷ Among all systems in Table 1, seven PMDETA (with three *tert*-amine groups) systems and six TMEEA (with two *tert*-amine groups) systems show phase splitting behaviors. With the exception of DEEA and IDMA2P, other systems with tertiary amines of only one *tert*-amine group remain homogeneous during CO₂ absorption.

The hydroxyl group, easy to form hydrogen bonds with water, always shows strong hydrophilicity. Generally, the more the hydroxyl groups in tertiary amines, the lower their log *P*. The MPI results in S-Figure 5 show that the molecular polarity increases with the number of the hydroxyl groups. In addition to the PMDETA and TMPDA, MPI results show almost the same tendency with log *P*. Therefore, the system with the hydroxyl groups barely undergoes phase splitting. Among the 29 sets of phase splitting systems, 27 sets have no hydroxyl group on the tertiary amine, while the other 2 sets have only one hydroxyl group on the tertiary amine.

3.2.2. Primary/Secondary Amine Structure. In Table 1, all primary/secondary amines could form the phase splitting system with a proper tertiary amine. Different molecular structures of primary/secondary amines will lead to different hydrophilicity values, which is reflected on the log *P* value. The

hydrophilicity of the primary/secondary amine affects the phase splitting behavior. The hydroxyl groups are both hydrogen bond donors and hydrogen bond receptors. They promote the CO₂ absorption products (R₁R₂NH₂⁺, R₁R₂NCOO[−]) reacting with water.²³ In addition, the ESP analysis (in S-Section 4) shows that the presence of hydroxyl groups may increase the maximum ESP area (ESP⁺) and the minimum ESP area (ESP[−]). The consequent coordination between amines and H₂O would promote the phase splitting. Then, the primary/secondary amine systems (log *P* < 0) in Zone 1 are ascribed with the salting-out effects.

The PA, BA, or IBA (with no hydroxyl group) systems with the tertiary amines of a lower log *P* (−0.4 < log *P* < 0.54) are homogeneous after CO₂ absorption. The carbamates of PA, BA, and IBA (log *P* > 0) are solid in these anhydrous systems. Due to the lipophilicity of PA, BA, and IBA and the hydrophilicity of the carbamates, some phase splitting systems appear in Zone 2.

Here, Zone 1 and Zone 2 are recognized based on 250 sets of rapid screening experiments. The basic rules of the phase splitting behavior are discussed. Due to the limit of the number of samples, the boundaries are not accurate enough. The zones and the boundaries could be further improved by further accumulating experimental and computational data.

3.3. Quasi-Activity Coefficient (ln γ') of the Primary/Secondary Amine–Tertiary Amine–Water System.

To establish an extended quasi-activity coefficient equation for the primary/secondary amine–tertiary amine–water system, the interaction between the primary/secondary amine and tertiary amine was further analyzed. The chemical absorption component of the tertiary amine may participate in the reaction to produce protonated amine, and it changes from nonelectrolyte to electrolyte. Then, partial primary/secondary amine and partial tertiary amine could be attributed as nonelectrolytes. As discussed in Section 3.2.2, the salting-out effect is affected by the primary/secondary amine structure, another factor describing the primary/secondary amine as nonelectrolytes which may help to correct the origin quasi-activity coefficient for chemical–chemical aqueous systems.

The interaction between the primary/secondary amine and the protonated tertiary amine was calculated by the IRI method (S-Section 5). The hydroxyl groups of the primary/secondary amines may form hydrogen bonds with the primary/secondary amines or the ions. In the previous QSPR study, the hydrogen bond donor of the solvent is positively correlated with the log *P* of the anion.²³ Therefore, the number of hydrogen bond donors and hydrogen bond receptors of the primary/secondary amine molecule is introduced as the descriptor. In addition, the maximum ESP of the primary/secondary amine shows a positive correlation with the attraction of the ions (Section 3.2.2 and S-Section 4). The descriptor ESP_A⁺/ESP_W⁺ is introduced into the equation. A new parameter β (eq 6) is proposed to describe the primary/secondary amines as the nonelectrolyte in eq 5.

$$\beta = (N_{\text{HBD}} + N_{\text{HBA}}) \times (\text{ESP}_A^+ / \text{ESP}_W^+) \quad (6)$$

A total of 65 sets of monoamine systems in Table 1 and 12 sets of polyamine systems^{13,15,16,33,38,39} were calculated according to the new ln γ' equation (eq 5). All parameters used for the calculation are listed in S-Table 2, and the calculated values of ln γ' are listed in S-Table 3. The charge of polyamines is set to 2. According to the ln γ' based on the salting-out effect, the phase splitting prediction diagram of primary/secondary amine–tertiary amine–water system is proposed, as shown in Figure 2. The value of constant *b* applicable to the systems is obtained as

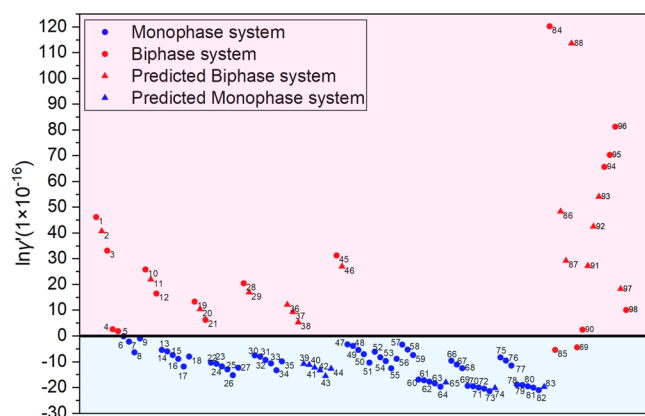


Figure 2. Phase splitting prediction diagram of primary/secondary amine–tertiary amine–water systems based on the quasi-activity coefficient $\ln \gamma'$.

25.7×10^{-16} . The system with a $\ln \gamma'$ value higher than 0 will undergo phase splitting, while the system with a $\ln \gamma'$ value lower than 0 would be homogeneous after CO_2 absorption. The equation is in good agreement with the existing experimental results with only two abnormal systems (Nos. 85, 89).

Similar to the original quasi-activity coefficient in eq 2, some systems under a low concentration may have some systematic errors. When the concentration of water in the system increases (the salt concentration decreases), some unexpected products may be produced, such as bicarbonate or little tricarbonates. These unexpected products may lead to boundary errors in the system.^{24,40} The outlier systems, Nos. 85 and 89, are abnormal at a low concentration. However, the same system can be accurately predicted at a higher concentration. To further verify the accuracy of the equation, a tertiary amine with two tertiary amine groups (TMPDA) and a primary amine with one hydroxyl group (4AB) were selected. For polyamine systems, three sets of polyamine systems were selected for verification. All the predicted results of 21 sets of systems are consistent with experimental results.

In general, the new quasi-activity coefficient for the primary/secondary amine–tertiary amine–water system (chemical–chemical aqueous system) can be calculated by eq 7. It is applicable to the prediction of some new systems with phase splitting behaviors caused by the salting-out effect. It can be applied to both monoamine and polyamine systems with different material ratios.

$$\ln \gamma' = \frac{(ze)^2 c}{2r_{\pm} kT} (\epsilon_0 - \epsilon) \sqrt{\frac{V_s}{\text{ESP}_s^+ \left(\frac{s}{V}\right)_s}} \times [(N_{\text{HBD}} + N_{\text{HBA}}) (\text{ESP}_A^+ / \text{ESP}_W^+) - 25.7 \times 10^{-16}] \quad (7)$$

4. CONCLUSIONS

In this work, 160 sets of primary/secondary amine–tertiary amine–water systems and 90 sets of primary/secondary amine–tertiary amine systems were rapidly screened. Some primary/secondary amines with no hydroxyl group may form solid carbamates with CO_2 . The carbamate solubility in the tertiary amine is highly related to the phase behaviors of these anhydrous systems.

Among all aqueous systems, several phase behaviors are observed: the homogeneous systems with a hydrophilic tertiary

amine ($\log P < 0$), the potential phase splitting systems with a properly lipophilic tertiary amine ($0 < \log P < 2.01$), and the heterogeneous systems with a strong lipophilic tertiary amine ($\log P > 2.01$). Two different phase splitting zones are recognized: in the lower amine $\log P$ zone (a lower tertiary amine $\log P$ and a lower primary/secondary amine $\log P$), phase splitting may be caused by salting-out effect and in the higher amine $\log P$ zone (a higher tertiary amine $\log P$ and a higher primary/secondary amine $\log P$), phase splitting may be attributed to the cosolvent effect. Several thermotropic phase splitting systems are located at the edges of the two zones.

The design rules of aqueous phase splitting systems caused by salting-out effects were proposed. The tertiary amine with more *tert*-amine groups and less hydroxyl groups facilitates phase splitting. The primary/secondary amines with hydroxyl groups on the straight chain facilitate phase splitting. A new factor describing the primary amine/secondary amine as a non-electrolyte is introduced for the development of a quasi-activity coefficient of a chemical–chemical aqueous system. The system with a quasi-activity coefficient higher than 0 will show phase splitting, while the system with a quasi-activity coefficient lower than 0 may show no phase splitting. The quasi-activity coefficient model has a good predictability. It is applicable to the mono- or polyamine systems with different material ratios.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.2c00533>.

CO_2 absorption of amines with different reaction times; titration experiments; comparison diagrams before and after the experiments of solubility determination and CO_2 absorption; $\ln \gamma'$ calculation details; molecule optimization; charge and spin set for the ions; ESP calculation and descriptor generation; parameters used for the $\ln \gamma'$ calculation; MPI calculation; MPI of tertiary amines; ESP analysis of different primary/secondary amines; IRI calculation; and interaction between the primary/secondary amine, protonated amines, and bicarbonate ions (PDF)

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Notes

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