Next Chemical Engineering 2 (2026) 100049

Contents lists available at ScienceDirect

Next Chemical Engineering

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Research article

# Thermodynamic basis of heat-stable salt precipitation during industrial MDEA reclaiming

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ARTICLE INFO

*Keywords:*
Heat-stable salts
Amine degradation
Gas sweetening
Ionic strength
Salt precipitation
Vacuum distillation
Phase behavior

ABSTRACT

Heat-stable salt (HSS) accumulation in methyldiethanolamine (MDEA) solvents progressively impairs absorption performance, accelerates corrosion, and complicates solvent regeneration in industrial gas sweetening systems. In this study, an industrially contaminated MDEA solution from the Shurtan gas sweetening unit was subjected to vacuum distillation to examine precipitation behavior during reclaiming. Water removal induced solvent enrichment and visible salt precipitation, indicating a reclaiming-driven phase instability. To interpret this behavior, industrial sample observations were integrated with binary MDEA-$H_2O$ phase analysis and surrogate divalent electrolyte modeling. The binary solvent matrix remained thermodynamically stable over the investigated composition range, whereas electrolyte-containing systems exhibited marked contraction of the liquid stability region under water-depleted conditions. The calculated ionic strength increased from approximately 2.15 to 5.3 mol $L^{-1}$ during solvent enrichment, and a critical instability window of about 3.5-4.0 mol $L^{-1}$ was identified for the transition from stable liquid behavior to metastable and precipitation-prone regimes. These results indicate that precipitation during MDEA reclaiming is governed by the combined effects of ionic-strength amplification, dielectric suppression, and activity-driven crystallization. The study therefore provides a quantitative thermodynamic basis for defining solvent-enrichment limits during regeneration and for evaluating the potential of controlled crystallization as an HSS withdrawal strategy.

## 1. Introduction

Aqueous alkanolamine absorption remains one of the most established technologies for industrial acid-gas removal and carbon capture because of its process maturity, high separation efficiency, and compatibility with absorber–stripper operation. Among the available solvents, methyldiethanolamine (MDEA) is especially attractive for gas sweetening because of its favorable regeneration characteristics and selective performance in sour-gas systems [1,2].

Despite these advantages, the long-term operation of amine units inevitably leads to solvent degradation. Recent literature continues to identify solvent degradation as one of the major technical and economic limitations of amine-based capture systems because it reduces effective solvent capacity, increases regeneration duty, accelerates corrosion, promotes foaming, and causes cumulative solvent loss [3,4].

One of the most persistent consequences of degradation is the formation and accumulation of heat-stable salts (HSS). These species are produced when protonated amines react with acidic compounds that cannot be reversed in the normal regeneration cycle. As HSS accumulate, the circulating solvent departs from its intended composition and increasingly behaves as a concentrated mixed-solvent electrolyte. Industrial and review studies consistently associate HSS buildup with reduced amine efficiency, increased foaming tendency, corrosion, and the need for solvent reclaiming or partial replacement [4–6].

In practical MDEA systems, this contamination is not limited to one or two ionic species. Industrially degraded solvents may contain

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https://doi.org/10.1016/j.nxcen.2026.100049
Received 6 March 2026; Received in revised form 6 April 2026; Accepted 27 April 2026
Available online 29 May 2026
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degradation-derived organic acid anions, chloride- and sulfate-type contaminants, protonated amines, and dissolved metal species. Detailed industrial analysis of contaminated MDEA has shown that HSS-rich amine inventories often also contain measurable metal cations and other impurities that alter the physicochemical behavior of the solvent during reclamation [5].

Because of these operational consequences, solvent reclamation is an essential part of amine-process management. Several HSS control routes have been developed, including thermal or vacuum distillation, ion exchange, adsorption, electrosorption, solvent extraction, and electrodialysis. However, each method has trade-offs in selectivity, energy demand, impurity range, and industrial practicality. Adsorptive reclamation has been proposed as a simple route for HSS removal from lean MDEA, while electrodialysis has more recently been examined as a targeted desalination strategy for organic amine absorbents [6,7].

Although these technologies address impurity removal, they do not by themselves explain a related and practically important phenomenon: why precipitation occurs when contaminated MDEA is enriched during reclaiming. This point is especially relevant for solvent concentration or vacuum-treatment steps, where water is selectively removed while dissolved ionic species remain in the liquid phase. Under such conditions, the system cannot be interpreted using concentration alone.

The relevant thermodynamic variable is ionic strength, which depends on both concentration and ionic charge. Since ionic strength scales with the square of ionic charge, multivalent ions contribute disproportionately to electrostatic non-ideality relative to monovalent species [8]. This becomes particularly important in contaminated amine systems, where even moderate accumulation of multivalent or strongly interacting ions may sharply increase electrostatic density during solvent enrichment.

At the same time, water removal changes the solvent environment itself. Mixed-solvent electrolyte studies have shown that phase behavior and speciation in such systems are strongly influenced by non-ideal interactions and solvent composition [9]. In parallel, ion-solvation studies indicate that decreasing solvent polarity and changing solvent reorganization can destabilize solvated ions and strengthen ion–ion interactions in liquid mixtures [10,11]. Therefore, as water is withdrawn from an MDEA–$H_2O$ medium, two effects intensify simultaneously: ionic strength rises, and dielectric screening becomes weaker.

From this perspective, precipitation during reclaiming should not be treated as a simple concentration effect. Instead, it is better understood as an activity-driven electrolyte instability, in which ionic activity increases nonlinearly because of the coupled effects of multivalent charge amplification and solvent dielectric suppression. This interpretation is consistent with the broader understanding that concentrated amine–electrolyte systems require rigorous thermodynamic treatment rather than dilution-based approximations [12,13].

The broader carbon-capture literature also shows that solvent absorption is only one part of a wider separation landscape that includes adsorption, cryogenic separation, and membrane-based technologies, with each route being constrained by feed composition, impurity content, required product purity, and process cost [14]. However, for industrial MDEA sweetening systems already in operation, reclaiming and solvent health management remain more immediately relevant than replacement by an entirely different capture platform. For such systems, understanding the thermodynamic onset of precipitation during solvent enrichment is directly valuable for operation and design.

Accordingly, the objective of the present study is to establish a thermodynamic framework for interpreting HSS precipitation during the reclaiming of contaminated industrial MDEA. An industrially degraded MDEA sample was subjected to vacuum concentration in order to reproduce reclaiming-induced water removal and directly observe salt precipitation. The industrial observations were then interpreted using a combined phase-behavior and activity-based framework. The binary MDEA–$H_2O$ system was used as the baseline solvent matrix, while a simplified divalent-electrolyte surrogate was employed to isolate the first-order effect of multivalent charge on ionic-strength amplification and contraction of the liquid stability region.

It should be emphasized that the surrogate electrolyte model is not intended to reproduce the full chemical complexity of actual industrial HSS species. Real contaminated MDEA systems may include formate, acetate, oxalate, sulfate, chloride, thiosulfate, protonated amines, and dissolved metals, all of which may shift the exact precipitation boundary through ion-specific interactions [4,5]. The purpose of the surrogate system is instead mechanistic: to identify how multivalent ionic charge and water depletion jointly destabilize the concentrated solvent phase.

The novelty of this work therefore lies not in restating classical electrolyte theory, but in linking industrial MDEA observations, vacuum-induced solvent enrichment, and activity-based thermodynamic interpretation to define a practically meaningful precipitation window for HSS-rich solvent reclaiming. In this way, the study provides a quantitative basis for defining enrichment limits during regeneration and for evaluating whether controlled crystallization can be used as a deliberate HSS withdrawal strategy.

## 2. Materials and methods

### 2.1. Industrial MDEA sample and study design

A contaminated methyldiethanolamine (MDEA) solvent sample was collected from the regeneration loop of an operating gas sweetening unit to investigate heat-stable salt (HSS) precipitation during solvent reclaiming. MDEA-based solvents are widely used for acid gas removal in natural-gas treatment, but prolonged operation under thermal and oxidative conditions promotes solvent degradation and the formation of HSS, which adversely affect solvent quality and plant operation [4,6,15]. HSS accumulation in industrial MDEA systems has been associated with reduced absorption efficiency, corrosion, foaming, and increased reclaiming demand [5,10]. On this basis, the present study was designed to combine direct experimental observation of precipitation from an industrial solvent with thermodynamic interpretation of electrolyte destabilization in concentrated MDEA media.

### 2.2. Vacuum concentration and isolation of precipitated solids

The contaminated industrial MDEA solution was subjected to vacuum distillation in order to remove water and progressively enrich the nonvolatile solvent and dissolved salt fraction. This treatment was intended to reproduce the enrichment conditions encountered during solvent reclaiming, where the concentration of dissolved ionic species increases as water is withdrawn. During concentration, visible solid formation occurred, indicating that the solution crossed from a stable liquid region into a precipitation-prone regime. The resulting solid residue was separated from the remaining concentrated liquid phase and treated as the HSS-rich precipitated fraction formed during industrial solvent treatment.

This procedure was selected because reclaiming by water removal is a recognized route for separating non-regenerable contaminants from amine solvents, even though conventional reclamation approaches such as thermal treatment, ion exchange, adsorption, solvent extraction, and electrodialysis differ in mechanism and process intensity [4,6,7,10]. In the present work, vacuum concentration was used primarily as an experimental route to induce solvent enrichment and to observe the onset of salt precipitation under controlled laboratory conditions.

### 2.3. Analytical characterization of the contaminated solvent and precipitated residue

The experimental workflow was structured to relate visible precipitation to the composition of the industrial MDEA matrix and to the presence of inorganic and degradation-derived salt-forming species. The contaminated solvent and the isolated solid fraction were therefore

analyzed using complementary methods for compositional interpretation. Chromatographic analysis was used to evaluate the degraded amine matrix and associated soluble contaminants, while elemental analysis by ICP–OES was used to assess the contribution of inorganic species and multivalent ions to the precipitated fraction.

This combined analytical approach was adopted because industrial MDEA contamination commonly includes both degradation-derived organic acid anions and dissolved inorganic species, including metal-related contaminants, all of which can influence HSS formation and solvent performance [5,15,16]. The purpose of the analysis was not only to identify the deposited material, but also to support the subsequent thermodynamic interpretation that precipitation during reclaiming is governed by electrolyte enrichment rather than by solvent evaporation alone.

### 2.4. Surrogate electrolyte framework for charge-effect isolation

In addition to the industrial solvent sample, simplified model systems were considered to isolate the electrostatic effect of salt valence under water-depleted conditions. Calcium chloride ($CaCl_2$) was used as a surrogate divalent electrolyte in the MDEA–$H_2O$ medium in order to examine how multivalent charge amplifies ionic strength and promotes contraction of the liquid stability region. $CaCl_2$ was selected as a tractable model salt for charge-density analysis, rather than as an exact compositional substitute for real industrial HSS species.

This distinction is important because actual HSS in amine systems are chemically diverse and may include formate, acetate, oxalate, sulfate, chloride, thiosulfate, and related amine-associated ions formed from degradation or feed impurities [4,5]. Therefore, the $CaCl_2$ model was used only to isolate the first-order role of multivalent ionic charge and ionic-strength amplification, while acknowledging that ion-specific interactions in real industrial solvents may shift the precise precipitation boundary.

### 2.5. Separation of ionic-strength and water-depletion effects

To distinguish the effects of salt accumulation from those of solvent composition change, the thermodynamic interpretation was built around two independent variables: ionic strength and water fraction. Charge-related effects were isolated by comparing mono- and multivalent electrolytes at equivalent analytical concentration, whereas solvent-enrichment effects were examined by decreasing the water content of the MDEA-containing medium. This approach made it possible to evaluate the separate and combined roles of electrostatic amplification and dielectric suppression in precipitation behavior.

The binary MDEA–$H_2O$ system was treated as the baseline solvent matrix because mixed-solvent electrolyte systems require separation of solvent effects from electrolyte-specific interactions when phase behavior and speciation are interpreted thermodynamically [17]. The binary system was first examined as a salt-free reference case, after which the electrolyte-containing system was considered to determine how added ions modify liquid-region boundaries and promote crystallization under concentrated conditions.

### 2.6. Ionic-strength and activity-based thermodynamic interpretation

The thermodynamic analysis was formulated in terms of ionic strength and ionic activity rather than analytical concentration alone. Ionic strength, $I$, was defined as:

$$I = \frac{1}{2}\sum c_i z_i^2 \tag{1}$$

where $c_i$ is the concentration of ionic species $i$ and $z_i$ is its charge number. This formulation reflects the fact that electrostatic non-ideality increases with the square of ionic charge, so that multivalent ions contribute disproportionately to solution non-ideality relative to monovalent ions at the same molar concentration [8]. In mixed-solvent electrolyte systems, ionic strength is a key descriptor because phase equilibria, speciation, and solubility are strongly affected by long-range electrostatic interactions and solvent-dependent activity behavior [17].

To interpret the onset of precipitation during solvent concentration, solubility was considered on an activity basis. As water was removed from the MDEA–$H_2O$ medium, both the concentration of dissolved ions and the effective electrostatic density of the solution increased. At the same time, water depletion reduced solvent polarity and weakened ion solvation, which is expected to amplify interionic interactions in mixed-solvent environments [11,18]. Under such conditions, precipitation was interpreted as occurring when the ionic activity product exceeded the solubility limit of the electrolyte-containing system, rather than when concentration alone reached a simple threshold. This framework allowed the industrial observations and the model electrolyte analysis to be unified into a single interpretation of HSS precipitation during MDEA reclaiming.

## 3. Results and discussion

### 3.1. Precipitation observed during vacuum concentration of the industrial MDEA solvent

Vacuum treatment of the contaminated industrial MDEA sample led to progressive water removal and the appearance of visible solid precipitates in the concentrated solvent phase. This observation confirms that the industrial amine solution did not remain homogeneous throughout solvent enrichment, but instead crossed into a precipitation-prone regime as the aqueous fraction decreased. In practical terms, this indicates that the reclaiming step does not simply concentrate dissolved contaminants; it can also induce phase separation of HSS-rich solids once the solvent composition approaches a thermodynamically unstable region.

The formation of solids during treatment is consistent with the known behavior of degraded amine systems, in which HSS accumulation alters solvent chemistry, reduces absorption efficiency, and aggravates operational problems such as foaming, corrosion, and reclaiming difficulty [4,5,15,16]. In the present case, the experimental observation of precipitation served as the starting point for the thermodynamic analysis developed below. Rather than interpreting solid formation as a simple consequence of increased concentration, the following sections show that precipitation is more rigorously explained by the coupled effects of ionic-strength amplification and solvent-mediated destabilization.

Fig. 1 provides a schematic interpretation of the sequence leading from solvent concentration to solid formation. During vacuum treatment, selective removal of water enriches the residual MDEA phase in dissolved HSS-related species and metal ions, causing a simultaneous rise in ionic strength and decline in solvent-mediated stabilization. As the liquid becomes progressively more water-depleted, electrostatic interactions are amplified, ion solvation weakens, and the concentrated amine matrix approaches a thermodynamically unstable regime in which precipitation becomes favorable. In this sense, the figure is not merely illustrative; it defines the mechanistic framework for the analysis that follows, linking the observed macroscopic precipitation event to electrolyte enrichment, non-ideal solution behavior, and activity-driven phase separation.

### 3.2. Ionic-strength amplification as the first-order driver of destabilization

The ternary phase analysis shows that precipitation in concentrated MDEA systems is governed more fundamentally by electrostatic amplification than by simple binary solubility limits. Under water-depleted conditions, stability boundaries correlate more closely with ionic strength than with molar concentration.

For a symmetric monovalent electrolyte, Eq. (1) reduces to

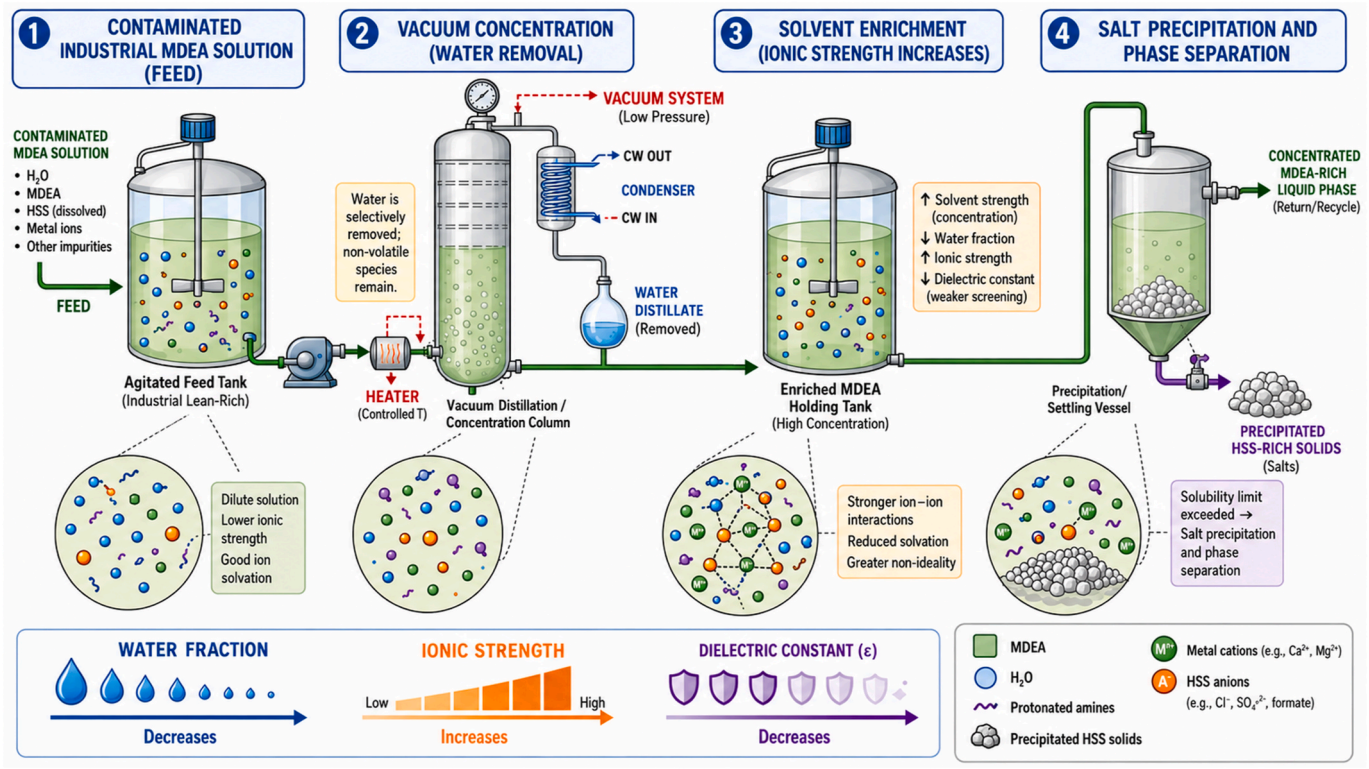



**Fig. 1.** Schematic representation of the separation and precipitation process observed during vacuum-induced concentration of the industrial MDEA solution.

$$I = c$$

whereas for a symmetric divalent electrolyte,

$$I = 4c$$

Thus, at identical analytical concentration, a divalent electrolyte generates approximately fourfold higher ionic strength. This amplification mechanism is central to explaining why multivalent HSS species destabilize concentrated amine solvents much more effectively than monovalent analogues. In the model comparison, this behavior is illustrated through the NaCl/$CaCl_2$ contrast shown in Fig. 2.

Experimentally, turbidity appeared at lower molar concentrations in divalent systems than in monovalent analogues (see Fig. 3). However, when the threshold was re-expressed in terms of ionic strength, the instability boundary became nearly charge-independent. This indicates

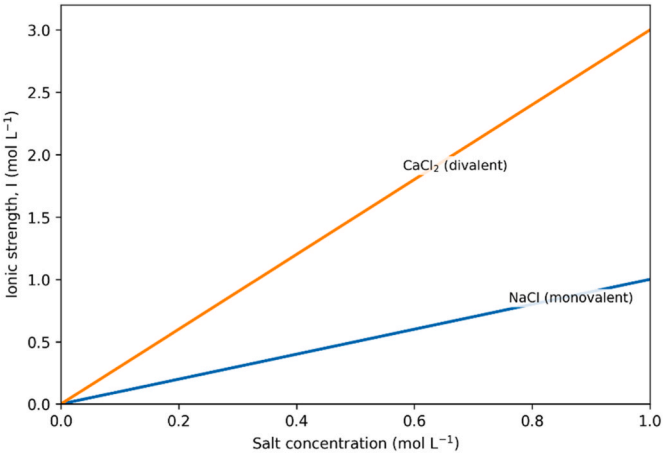



**Fig. 2.** Ionic strength as a function of salt concentration for monovalent (NaCl) and divalent ($CaCl_2$) electrolytes.

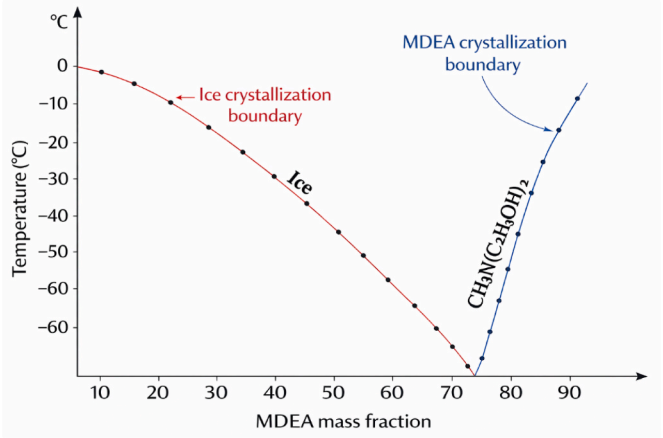



**Fig. 3.** Binary phase diagram of the MDEA–$H_2O$ system calculated in this work and used to establish the baseline phase stability of the salt-free solvent matrix.

that electrostatic density, rather than concentration alone, controls destabilization in concentrated MDEA systems.

The physical origin of this amplification is linked to the compression of the ionic atmosphere. According to Debye–Hückel theory, the electrostatic screening length decreases as ionic strength rises [19]:

$$\kappa^{-1} = \left(\frac{\varepsilon_r \varepsilon_0 k_B T}{2 N_A e^2 I}\right)^{1/2} \quad (2)$$

where $e$ is the elementary charge, $N_A$ is Avogadro's number, $k_B$ is the Boltzmann constant, $T$ is temperature, $\varepsilon_r$ is the relative dielectric constant of the medium, and $\varepsilon_0$ is the permittivity of free space ($\approx 8.854 \times 10^{12}\ F/m$). As $I$ increases, $\kappa^{-1}$ decreases, meaning that ions interact over shorter distances but with stronger local electrostatic correlations.

The consequence is important for industrial interpretation:

precipitation thresholds should not be read on a concentration basis alone. Two solutions with similar molar salt content may exhibit very different stability if one contains a higher proportion of multivalent ions. Thus, electrostatic density, not merely concentration, is the relevant first-order variable controlling destabilization in reclaimed MDEA systems.

### 3.3. Binary MDEA–$H_2O$ phase behavior: the solvent matrix remains intrinsically stable

To distinguish electrolyte-induced precipitation from intrinsic solvent behavior, the binary MDEA–$H_2O$ system was first examined as the baseline phase-stability reference. The binary phase diagram shows conventional crystallization boundaries associated with water-rich and MDEA-rich limits, but no anomalous splitting or abrupt instability. This demonstrates that the solvent matrix itself remains thermodynamically continuous over the investigated composition range.

From a thermodynamic viewpoint, binary liquid–solid equilibrium may be written generically as

$$\mu_i^{(l)} = \mu_i^{(s)} \tag{3}$$

where $\mu_i^{(l)}$ and $\mu_i^{(s)}$ are the chemical potentials of component $i$ in the liquid and solid phases, respectively [20]. In the absence of electrolytes, deviations from ideality are governed primarily by solvent–solvent interactions and hydrogen bonding, not by long-range Coulombic effects. Consequently, although the dielectric constant decreases as the organic fraction increases, water depletion alone does not produce abrupt precipitation in the binary system.

Therefore, the binary system establishes two key conclusions. First, the MDEA–$H_2O$ solvent matrix is intrinsically stable over the relevant concentration range. Second, the precipitation observed experimentally must arise from the presence of electrolytes superimposed on this otherwise stable binary solvent background. This provides the thermodynamic justification for shifting the interpretation from concentration-driven precipitation to electrolyte-controlled phase destabilization.

### 3.4. Ternary electrolyte-containing system: water depletion and dielectric suppression

Once the binary solvent baseline was established, the electrolyte-containing ternary system was examined to determine how multivalent ions shift phase behavior. In contrast to the binary MDEA–$H_2O$ system, the ternary $CaCl_2$–MDEA–$H_2O$ phase diagram shows contraction of the liquid stability region and the appearance of hydrate crystallization domains. This demonstrates that water depletion alone is insufficient to induce precipitation; instead, multivalent ions promote solid formation through ionic-strength amplification and reduced dielectric screening.

The solvent-mediated electrostatic contribution can be interpreted through the inverse dependence of Coulombic interaction on the dielectric constant [11,17,21]:

$$U_{ij}(r) \propto \frac{z_i z_j e^2}{4\pi\varepsilon_0\varepsilon_r r} \tag{4}$$

where $r$ is the interionic distance. As $\varepsilon_r$ decreases with increasing MDEA fraction, electrostatic attraction between oppositely charged ions becomes stronger, ion solvation weakens, and clustering becomes more favorable. This is fully consistent with mixed-solvent electrolyte theory and ion-solvation studies showing that local solvation structure in liquid mixtures does not depend on bulk dielectric constant alone, but is strongly affected by solvent reorganization and composition near the ion.

It should be emphasized that $CaCl_2$ was used only as a simplified surrogate electrolyte to isolate the role of multivalent charge and ionic-strength amplification in shifting phase boundaries. In actual industrial MDEA systems, HSS are chemically more diverse and may include formate, acetate, oxalate, sulfate, chloride, and thiosulfate species associated with protonated amines and dissolved metals. Therefore, the present results should not be interpreted as implying strict quantitative universality across all HSS chemistries; rather, they identify ionic strength as the dominant first-order descriptor of phase destabilization, while ion-specific effects may shift the exact precipitation boundary.

It is important to reiterate that $CaCl_2$ was used here only as a surrogate divalent electrolyte to isolate the general effect of multivalent charge. Real industrial HSS in MDEA systems are chemically more diverse and typically include formate, acetate, oxalate, sulfate, chloride, and thiosulfate associated with protonated amines and dissolved metals. These anions differ in hydration structure, size, and specific interaction with the MDEA–$H_2O$ matrix. Accordingly, the present ternary diagram should not be interpreted as quantitatively universal for all HSS chemistries. Its value lies in identifying the dominant first-order mechanism: multivalent charge compresses the liquid stability region and makes the solvent much more sensitive to water depletion.

### 3.5. Ionic activity, non-ideality, and the onset of precipitation

The calculated ionic strength increased monotonically as water was removed from the solvent, rising from approximately 2.15 mol $L^{-1}$ at high water fraction to about 5.3 mol $L^{-1}$ at the most concentrated condition considered. Within this enrichment pathway, a transition window of approximately 3.5–4.0 mol $L^{-1}$ was identified, corresponding to the shift from stable liquid behavior to metastable and precipitation-prone domains.

At this stage, thermodynamic interpretation must be expressed in terms of ionic activity rather than concentration. For species $i$,

$$a_i = \gamma_i c_i \tag{5}$$

where $a_i$ is activity, $c_i$ is concentration, and $\gamma_i$ is the activity coefficient [22]. Under concentrated conditions, deviations from ideality become significant.

A first estimate of activity-coefficient growth may be obtained using the extended Debye–Hückel equation [23]:

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} \tag{6}$$

where $A$ and $B$ are solvent-dependent electrostatic parameters and $a_i$ is an ion-size parameter. In dilute systems this relation captures the growth of non-ideality with ionic strength, although at elevated ionic strength the limiting Debye–Hückel law becomes inadequate.

For more concentrated electrolyte systems, Pitzer-type formalism is more appropriate because it supplements long-range electrostatic terms with short-range specific interactions [9]:

$$\ln \gamma_i = \ln \gamma_i^{DH} + \sum_j m_j \lambda_{ij} + \sum_j \sum_k m_j m_k \mu_{ijk} \tag{7}$$

where $\ln \gamma_i^{DH}$ represents the Debye–Hückel long-range term, $\lambda_{ij}$ accounts for short-range binary interactions, $\mu_{ijk}$ represents higher-order interaction terms, and $m_j$ is the molality of interacting species.

Precipitation occurs when the ionic activity product exceeds the solubility product constant [24]:

$$K_{sp} < \prod_i a_i^{\nu_i} \tag{8}$$

Substituting Eq. (5) gives

$$K_{sp} < \prod_i (\gamma_i c_i)^{\nu_i} \tag{9}$$

Thus, even if concentrations increase gradually, the activity product

may rise superlinearly because $\gamma_i$ also increases nonlinearly as ionic strength rises and dielectric screening weakens. The instability condition may therefore be written as

$$\prod_i (\gamma_i c_i)^{\nu_i} \geq K_{sp} \tag{10}$$

This explains why precipitation boundaries in the ternary diagram align more naturally with ionic-strength contours than with analytical concentration lines. According to Eq. (4), decreasing water fraction lowers $\varepsilon_r$, while Eq. (1) shows that solvent enrichment raises $I$. Their coupled effect on activity-coefficient growth may be summarized schematically as

$$\gamma_i = f(I, \varepsilon_r) \tag{11}$$

This coupling creates a narrow metastable region beyond which the system transitions abruptly into precipitation. In process terms, this provides a quantitative basis for defining solvent-enrichment limits during industrial MDEA reclaiming and for evaluating whether crystallization can be controlled as a deliberate HSS withdrawal strategy rather than treated solely as an undesirable fouling event.

This result (Fig. 5) is one of the most important quantitative outcomes of the study because it provides an operationally meaningful instability threshold (see Fig. 4). Below this interval, the contaminated MDEA solution remains in a stable liquid regime despite progressive concentration. Within the 3.5–4.0 mol $L^{-1}$ range, however, the system enters a narrow metastable region in which relatively small changes in water content, local supersaturation, or heterogeneous nucleation conditions may trigger crystallization. Beyond this window, the probability of bulk precipitation increases sharply.

This behavior demonstrates why analytical concentration alone is insufficient for process interpretation. The observed transition does not occur because the salt content crosses a simple concentration boundary, but because ionic activity increases superlinearly as ionic strength rises and dielectric screening weakens. In this sense, the instability window is better understood as an activity-controlled threshold than as a concentration-controlled one. The quantitative agreement between the enrichment trajectory and the ternary phase-boundary contraction further supports this interpretation.

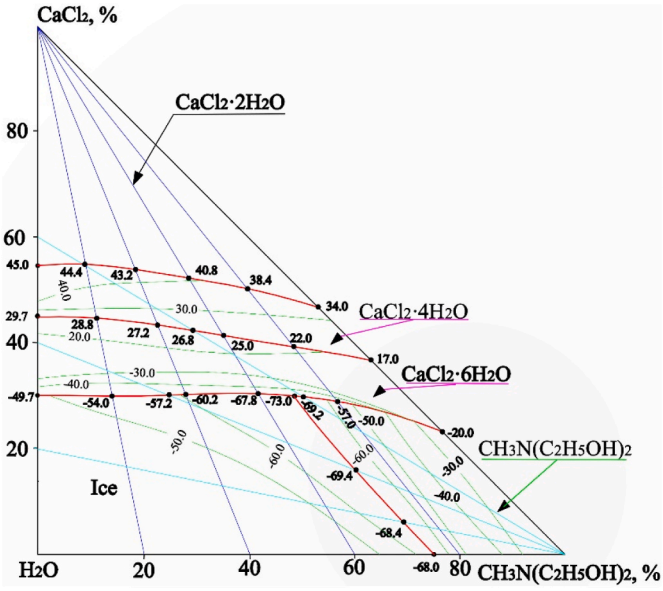



**Fig. 4.** Ternary phase diagram of the $CaCl_2$–MDEA–$H_2O$ system calculated in this work to illustrate contraction of the liquid stability region and the onset of hydrate crystallization under multivalent electrolyte loading.

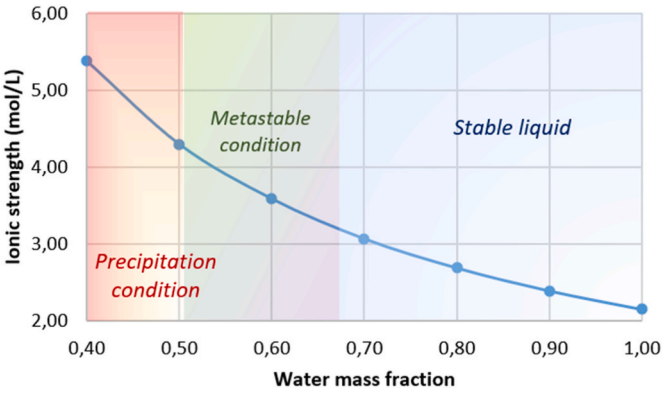



**Fig. 5.** Ionic strength evolution as a function of water mass fraction during vacuum-induced solvent enrichment.

### 3.6. Activity-based interpretation of precipitation in concentrated MDEA systems

The thermodynamic significance of the results becomes clearer when precipitation is interpreted on an activity basis. Under concentrated conditions, the relevant precipitation criterion is not the analytical concentration of dissolved ions, but the ionic activity product. As ionic strength increases, activity coefficients also increase because electrostatic interactions become stronger and less efficiently screened. At the same time, water depletion reduces the dielectric constant of the MDEA–$H_2O$ medium, further destabilizing solvated ions and enhancing short-range electrostatic correlation [11,17,18].

The consequence is a superlinear rise in ionic activity during solvent enrichment. Even if dissolved salt concentration increases gradually, the corresponding activity product can increase much more sharply because both ionic strength and activity coefficients rise together. This explains why precipitation boundaries in the ternary system align more naturally with ionic-strength contours than with analytical concentration lines. It also explains why multivalent salts are especially problematic in industrial amine systems: they accelerate not only ionic-strength growth but also activity-coefficient amplification.

Accordingly, the experimental precipitation observed after vacuum concentration of the industrial solvent is best understood as an activity-driven electrolyte instability. This interpretation integrates the industrial observation, the binary solvent baseline, the surrogate ternary phase diagram, and the enrichment-pathway calculations into a single mechanistic framework. The central implication is that reclaiming-induced precipitation is governed by the coupled action of (i) multivalent ionic charge, (ii) solvent dielectric suppression, and (iii) nonlinear activity growth.

### 3.7. Process implications for industrial MDEA reclaiming

From a process-engineering perspective, the results show that salt precipitation during reclaiming should not be viewed only as an undesirable fouling event. Instead, it can also be interpreted as a thermodynamically structured phase-separation phenomenon that may be either avoided or deliberately used, depending on the reclaiming objective.

Three practically relevant regimes may therefore be defined. In the stable liquid region, solvent concentration can proceed without visible salt deposition, which is desirable when the operational goal is to preserve flowability and avoid uncontrolled scaling. In the metastable region, the solution becomes highly sensitive to fluctuations in local supersaturation, temperature, and nucleation conditions, indicating a sharply increasing risk of unplanned precipitation. In the precipitation region, further solvent enrichment can promote deliberate crystallization of salt-rich phases, which may then be separated from the liquid solvent by solid–liquid separation.

This gives the thermodynamic analysis direct operational value. Vacuum regeneration can be operated below the identified ionic-strength threshold when the objective is to minimize salt deposition inside process equipment. Conversely, it may be driven beyond that threshold under controlled conditions if the process is designed to intensify HSS withdrawal by targeted crystallization. Thus, the present results do not merely explain why precipitation occurs; they also provide a quantitative basis for defining solvent-enrichment limits during industrial MDEA reclaiming.

## 4. Conclusions

This study demonstrates that precipitation during industrial MDEA regeneration is governed by electrolyte destabilization under solvent enrichment rather than by solvent freezing alone. As the water mass fraction decreased from 1.0 to 0.4, the calculated ionic strength increased from approximately 2.15 to 5.3 mol $L^{-1}$, and a critical instability window of about 3.5–4.0 mol $L^{-1}$ was identified for the transition from stable liquid behavior to metastable and precipitation regimes. The binary MDEA–$H_2O$ system remained continuous and thermodynamically stable over the investigated composition range, whereas the ternary electrolyte system exhibited pronounced contraction of the liquid region and multiple hydrate crystallization domains. In the model comparison, $CaCl_2$ generated approximately threefold higher ionic strength than NaCl at the same analytical concentration, confirming the strong destabilizing role of multivalent ions. These results indicate that ionic strength is a dominant first-order descriptor of precipitation risk during reclaiming, while the exact boundary may still depend on ion-specific HSS chemistry. From a process standpoint, the findings provide a quantitative basis for defining solvent-enrichment limits during regeneration to either avoid uncontrolled precipitation or promote controlled HSS removal by targeted crystallization.

A limitation of the present study is that $CaCl_2$ was used as a surrogate divalent electrolyte and therefore does not reproduce the full structural and chemical diversity of industrial HSS anions. Future work should include comparative phase-behavior measurements with representative organic and inorganic HSS salts, including formate, acetate, oxalate, and sulfate species, to quantify ion-specific shifts in the precipitation boundary.

Overall, the present study contributes to a better understanding of phase behavior in contaminated amine solvents and offers a thermodynamic basis for predicting precipitation risks in industrial gas treating systems.

## Availability of data and materials

The data used in this study were compiled from publicly available literature sources. The curated dataset and processed data supporting the findings of this work are available from the corresponding author upon reasonable request.

## Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this manuscript, the author(s) used ChatGPT to improve the grammar and stylistic quality of the English language. After using this tool, the author(s) carefully reviewed and edited the content as necessary and take full responsibility for the final version of the published article.

## CRediT authorship contribution statement

**Jonibek Norkulov:** Investigation, Resources. **Rakhmatullo Muradov:** Investigation, Methodology, Validation. **Ruzimurod Juraev:** Conceptualization, Data curation. **Kakhramon Turayev:** Methodology, Resources, Software, Visualization. **Abbos Elmanov:** Formal analysis, Funding acquisition. **Fazliddin Meylikov:** Investigation, Methodology. **Oybek Valiev:** Resources, Software. **Isomiddin Hamraev:** Validation, Visualization. **Rustam Bozorov:** Data curation, Investigation, Methodology. **Adham Norkobilov:** Methodology, Writing – original draft, Writing – review & editing. **Olim Abdurakhmonov:** Supervision, Writing – original draft.

## Declaration of competing interest

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.

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