

# Thermodynamic modeling of aqueous systems containing amines and amine hydrochlorides: Application to methylamine, morpholine, and morpholine derivatives



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## ABSTRACT

A comprehensive thermodynamic model has been developed for calculating phase equilibria and speciation in aqueous mixtures containing neutralizing amines and corresponding amine hydrochlorides. The model has been designed to simulate the behavior of refinery overhead environments, in which the presence of amines in combination with hydrogen chloride may lead to the formation of potentially corrosive solid or concentrated aqueous amine hydrochloride phases. For this purpose, the previously developed Mixed-Solvent Electrolyte (MSE) model has been extended to calculate simultaneously solid–gas, solid–liquid, and vapor–liquid equilibria, liquid-phase chemical equilibria, and caloric properties. In the model, standard-state properties of individual species are calculated from the Helgeson–Kirkham–Flowers equation of state whereas the excess Gibbs energy includes a long-range electrostatic interaction term expressed by a Pitzer–Debye–Hückel equation, a virial coefficient-type term for interactions between ions and a short-range term for interactions involving neutral molecules. This framework accurately represents the properties of systems that range from weak electrolytes, such as amine–water mixtures, to strong electrolytes such as amine hydrochloride–water solutions. For amine hydrochlorides, the model is applicable up to the limit of solid or fused liquid hydrochloride phases. Model parameters have been developed for methylamine, morpholine, N-methylmorpholine, N-ethylmorpholine and their hydrochlorides. The model offers the possibility of understanding the formation of amine hydrochlorides in multicomponent mixtures containing amines, water, hydrogen chloride, and carbon dioxide.

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## 1. Introduction

Neutralizing amines are commonly used in many industrial applications to control corrosion. In particular, prominent applications include mitigating corrosion in refinery overhead systems [1–6] and in nuclear power plants [7–12]. In refining, various amines are added to neutralize hydrogen chloride, which results from the hydrolysis of alkaline earth chlorides that are found in crude oil. However, while the injection of amines reduces the risk of acid corrosion, it may lead to the formation of amine hydrochloride salts. Amine hydrochlorides may form either solid or concentrated aqueous phases, which may cause aggressive corrosion in refinery overheads. Thus, it is important to understand and to be able to

predict the conditions that lead to such phenomena. Because of the inherent difficulties in monitoring the phase behavior in actual refinery settings, a thermodynamic model that can realistically predict these phenomena can be of great value. However, the development of such a model is very challenging because refinery overhead systems are complex mixtures of hydrocarbons, water, acid gases, and amines.

A tremendous amount of research has been devoted in the literature to the thermodynamic behavior of amine systems that are used for CO<sub>2</sub> capture and acid gas removal applications. Much less work has been published on the behavior of amines in the context of corrosion control in refining. Although there is a substantial overlap in the amine mixture properties that are required for acid gas removal and for corrosion control, the fundamental difference lies in the fact that refinery corrosion control is inextricably linked with the presence of hydrogen chloride, which induces the formation of amine hydrochlorides. Thus, this study is focused

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on the properties of amine hydrochlorides as well as on those of the underlying amines.

The neutralizing amines that are used in the refining industry include primary alkyl amines (e.g., methylamine, ethylamine, propylamine, butylamine, cyclohexylamine, etc.), secondary alkyl amines (e.g., dimethylamine or diethylamine), tertiary alkyl amines (e.g., trimethylamine), alkoxy amines (e.g., 3-methoxypropylamine), cyclic ether amines (e.g., morpholine, N-methylmorpholine, N-ethylmorpholine, etc.), and alkanolamines (e.g., ethanolamine, diethanolamine, methyldiethanolamine, dimethylethanolamine, dimethylisopropanolamine, diglycolamine, etc.) Because of the differences in their molecular structure, these amines differ with respect to their volatility and their phase equilibria with water and hydrocarbons. Thus, their partitioning between the gas phase, hydrocarbon-rich liquid phase and aqueous phase differs widely. Also, the amines differ with respect to their propensity to form solid amine hydrochlorides or concentrated aqueous solutions containing amine hydrochlorides in an ionic form. Frequently, mixtures of amines are used, which additionally complicates the prediction of their behavior in refinery environments. Among the neutralizing amines, selected alkanolamines have been studied in great detail in the literature in conjunction with acid gas removal and CO<sub>2</sub> capture applications. In general, the other families of amines have been studied to a lesser extent.

In order to predict the possibility of corrosion in refinery overheads, it is necessary to construct a thermodynamic model for multicomponent mixtures that include water, amines, amine hydrochlorides, hydrogen chloride, carbon dioxide, and hydrocarbons. In general, such mixtures may form multiphase systems, including a gas phase, a hydrocarbon-rich liquid phase, an aqueous phase and solid amine hydrochloride phases. A conceptual scheme of the phases, species, and phase equilibria in such systems is shown in Fig. 1. In this figure, the amines are denoted as RNH<sub>2</sub> for simplicity. Thus, a comprehensive model must simultaneously reproduce:

- (i) Vapor–liquid equilibria for mixtures of amines with water, which is necessary to predict the partitioning of amines between the vapor and aqueous phases;
- (ii) Vapor–solid equilibria for amine hydrochlorides, which determines the possibility of precipitation of amine hydrochlorides from the gas phase;

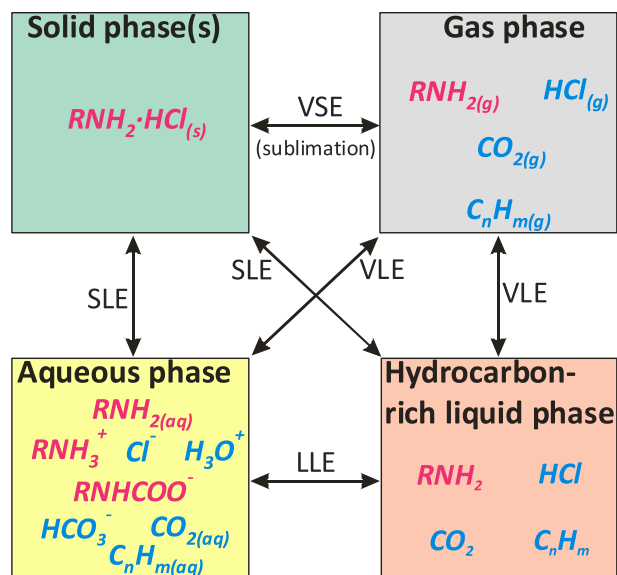


Fig. 1. A conceptual scheme of the phases, species, and phase equilibria that may appear in conjunction with the application of neutralizing amines.

- (iii) Solid–liquid and solid–liquid–vapor equilibria for amine hydrochlorides in water, which influence the transition between solid amine hydrochlorides and concentrated amine hydrochloride solutions, the latter being of particular interest for predicting conditions that are conducive to corrosion;
- (iv) Speciation in the aqueous phase involving the equilibrium between molecular and ionized forms of the amines, dissociation of acid gases and formation of carbamate ions in the presence of CO<sub>2</sub>;
- (v) Partitioning of amines and acid gases between the gas phase and the hydrocarbon-rich liquid phase, which influences the availability of the amines and HCl in the aqueous phase.

Also, it should be noted that substantial overlap exists between the neutralizing amines used in refinery overheads and those used for water treatment in nuclear steam generating systems. In the latter case, the phase behavior and speciation at high temperatures are of particular interest while the formation of amine hydrochlorides is not expected. Thus, it is possible to develop a model that simultaneously addresses the refinery overhead and power plant conditions.

In order to develop a thermodynamic model that satisfies conditions (i–v), we extend the previously developed Mixed-Solvent Electrolyte (MSE) computational framework of Wang et al. [13–15]. This framework was designed for the simultaneous calculation of phase and chemical equilibria in systems containing strong and weak electrolytes in aqueous, non-aqueous and mixed solvents. In particular, it was shown to be applicable to electrolyte solutions up to the fused salt limit [13] and to reproduce acid–base equilibria in environments dominated either by water or by other protic solvents [16,17]. Furthermore, it was applied to systems containing acid gases in wide temperature and pressure ranges [18,19], salt solutions with complex solid–liquid–vapor equilibria [20] and ionic liquid mixtures [21]. However, the amine hydrochlorides that are of interest here constitute a somewhat different class of systems for thermodynamic modeling. On the one hand, they form strong electrolytes. On the other hand, they have relatively low melting points and are much more volatile than the majority of salts or ionic liquids. Thus, the model needs to reproduce vapor–solid as well as vapor–liquid and vapor–liquid–solid equilibria in systems containing amine hydrochlorides.

In this study, we focus on phase and chemical equilibria in mixtures containing water, amines and their corresponding hydrochlorides, HCl, and CO<sub>2</sub>. The behavior of amine – hydrocarbon mixtures (especially the partitioning of amines between aqueous and hydrocarbon phases) requires a separate study. The amines that have been selected for this study include methylamine and three cyclic ether amines, i.e., morpholine, N-methylmorpholine, and N-ethylmorpholine. These amines represent primary (methylamine), secondary (morpholine) and tertiary (N-methyl- and N-ethylmorpholines) amines and span a relatively wide range of volatilities. The available experimental data are analyzed and a comprehensive set of parameters is developed to model the thermodynamic behavior of vapor – liquid – solid mixtures that can range from weak electrolyte systems, such as the amine – water – CO<sub>2</sub> mixtures, to strong, yet volatile electrolyte solutions containing amine hydrochlorides.

## 2. Thermodynamic model

### 2.1. Solution speciation and phase equilibria

To model the behavior of both amines and amine hydrochlorides, the hydrolysis (or protonation) of the amine is of key importance. For methylamine, the hydrolysis reaction can be written as

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