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Incorporating Pitzer equations in a new thermodynamic model for the prediction of acid gases solubility in aqueous alkanolamine solutions

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In gas sweetening, acid gases such as CO_2 and/or H_2S are usually removed by "chemical" absorption through aqueous amine solutions such as N-Methyldiethanolamine (MDEA) solution. Reliable prediction of equilibrium properties (vapor–liquid equilibrium and species distribution) is needed for a rigorous design of such absorption processes. Information on energy requirements can also be obtained from a reliable vapor–liquid equilibrium thermodynamic model. The currently used methods for correlating/predicting the simultaneous solubility of H_2S and CO_2 in aqueous MDEA solutions require accurate experimental solubility data of single and mixed gases which, in general, confine their applicability in the experimental region. The purpose of this paper is to develop a new theoretical thermodynamic model based on incorporating thermodynamic relationships that correlates the equilibrium and solubility constants to the Gibbs free energy of reaction, leading to an enhanced predictive capability of the model. In this work the Pitzer model is used to account for activity and specific ion interactive forces. This will allow taking into account the effect of the presence of all cations and anions such as thermally stable salts, dissolved organic species and amine degradation products that are usually encountered in absorption units. The suggested model has been verified through comparison with literature data for CO_2 and H_2S absorption. The presented model can be a very powerful tool that could be of significant importance in the design of amine absorption processes as well as in simulations of the operating variables for optimization of gas sweetening systems.

1. Introduction

Acid gases such as hydrogen sulfide and carbon dioxide are major impurities in natural, refinery, and synthesis gases. Chemical absorption by aqueous solutions of amines such as N-Methyldiethanolamine (MDEA) solution is one of the most effective industrial methods for the removal of these acid gases from gaseous effluents (Speyer et al., 2012, 2009). Availability of accurate acid gas solubilities in the solvent is essential for any modeling of absorption processes. A number of models such as Kent–Eisenberg (KE), Modified Kent–Eisenberg (M-KE), Deshmukh and Mather model, Electrolyte-NRTL, Extended Debye–Hückel (E-DH), Pitzer and Li–Mather models were proposed to correlate solubility data (Benamor and Aroussi, 2013). Kent and Eisenberg (1976) modeled the solubility of acid gases and their mixtures in MEA and DEA aqueous solutions. In this model equilibrium constants of carbamate formation and protonation of the amines have been considered to be only temperature-dependent. The KE model is an empirical model and, therefore, it cannot properly predict the solubility of acid gases in aqueous amine solutions in a wide range of temperature, pressure and amine concentrations. The NRTL model (Chen and Evans, 1986) and the model of Deshmukh and Mather (Deshmukh and Mather, 1981) are based on sound thermodynamic principles. Non-idealities of the solution are taken into consideration by considering long and short range interactions between the different species present in the solution. The NRTL model used a combination of Debye–Hückel theory and the electrolyte-NRTL equation to calculate the activity coefficients. The Deshmukh and Mather model is much simpler to handle than the NRTL model. It employs the Guggenheim equation to represent activity coefficients. The Kent and Eisenberg model is the simplest among all mentioned models. The non-idealities present in the system are lumped together and represented by constant values (Benamor and Aroussi, 2013). Unfortunately, there are still significant limitations in models currently in use to predict acid gas solubilities in amine solutions. These limitations are mainly caused by the use of

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empirical approaches, in which crude assumptions have been introduced. In the best scenario these models are mainly useful to correlate experimental data.

To enhance the reliability of solubility predictions of acid gases in aqueous amine solutions, the following can be done: Firstly, implementation of sound thermodynamic relations to account for the equilibrium constants rather than just correlating the experimental data at specific conditions. Application of thermodynamically reliable equations will account for the effect of temperature and pressure on equilibrium constants and solubilities. Secondly, the activity coefficients of the species present in the aqueous phase and the fugacity coefficients of the species present in the vapor phase must be considered. The Debye–Hückel and the extended Debye–Hückel theory are the basis of a number of successful semi-empirical equations for a variety of thermodynamic properties (Loehe and Donohue, 1997). Pitzer and coworkers established very widely applicable equations for calculating the activity coefficients of individual species in aqueous media at high concentrations. In his publications (Pitzer and Mayorga, 1973; Pitzer, 1991) the origin of these equations and their application are discussed in some detail. To consider the deviation of real gas phase behavior from the ideal gas state, the Virial (George Hayden and O'Connell, 1975), PR (Peng and Robinson, 1976) or SRK (Soave, 1972) equations of state (EOS) can be used to calculate the fugacity-coefficients of the components in the gas phase.

In this work, a new theoretical thermodynamic model will be developed based on incorporating theoretical thermodynamic relationships that correlates the equilibrium and solubility constants to the Gibbs free energy of reactions. For the first time, the effect of temperature and pressure will be incorporated through fundamental thermodynamic equations. The Pitzer model and the PR EOS will be used to account for activity coefficients and fugacity coefficients, respectively. The application of the Pitzer model will allow considering the effect of ion-specific interactive forces that results from the presence of heat stable salts, dissolved organic and amine degradation products that are usually encountered in absorption units.

2. Theory and framework of our model

In this section the N-Methyldiethanolamine (MDEA), H_2S and CO_2 system has been used as an example to demonstrate the model framework. The following assumptions have been made: (i) the volatility of the amine has been neglected; (ii) in the liquid phase, hydrogen sulphide and carbon dioxide are dissolved in the liquid phase not only in neutral, but also in non-volatile ionic form. The following reversible chemical reactions (chemical equilibrium) are taken into account: (i) the auto-protolyses of water (R1), the formations of hydrosulfide (bisulfide) and sulfide (R2, R3), (ii) the formation and dissociation of bicarbonate (R4 and R5), (iii) the protonation of MDEA (R6).

$$H_2O \underset{K_{R1}}{\Leftrightarrow} H^+ + OH^- \tag{R1}$$

$$H_2S \underset{K_{R2}}{\Leftrightarrow} HS^- + H^+ \tag{R2}$$

$$HS^- \underset{K_{R3}}{\Leftrightarrow} H^+ + S^{2-} \tag{R3}$$

$$CO_2 + H_2O \underset{K_{R4}}{\Leftrightarrow} H^+ + HCO_3^- \tag{R4}$$

$$HCO_3^- \underset{K_{R5}}{\Leftrightarrow} H^+ + CO_3^{2-} \tag{R5}$$

$$MDEAH^+ \underset{K_{R6}}{\Leftrightarrow} H^+ + MDEA \tag{R6}$$

The chemical reaction equilibrium constants (K_{R1}–K_{R6}) will be calculated from the Gibbs free energy of reaction. Then the effect of temperature and pressure will be taken into account as will be explained in detail later.

The condition for chemical equilibrium for a chemical reaction R (=1, …, 6) is:

$$K_R(T,P) = \prod_i a_i^{V_{i,R}} \tag{1}$$

where K_R (T, P) is the chemical reaction equilibrium constant for reaction R, a_i is the thermodynamic activity of species i in the liquid phase, and $\nu_{i,R}$ is the stoichiometric coefficient of species i in reaction R.

Applying mass conservation equations on carbon dioxide, hydrogen sulfide, MDEA, and water result in:

$$\overline{m}_{CO_2} = m_{CO_2} + m_{HCO_3^-} + m_{CO_3^{2-}} \tag{2}$$

$$\overline{m}_{H_2S} = m_{H_2S} + m_{HS^-} + m_{S^{2-}} \tag{3}$$

$$\overline{m}_{MDEA} = m_{MDEA} + m_{MDEAH^+} \tag{4}$$

$$\overline{m}_W = m_W + m_{HCO_3^-} + m_{CO_3^{2-}} + m_{OH^-} \tag{5}$$

The condition for liquid-phase electro-neutrality is:

$$m_{MDEAH^+} + m_{H^+} = m_{OH^-} + m_{HS^-} + 2m_{S^{2-}} + m_{HCO_3^-} + 2m_{CO_3^{2-}} \tag{6}$$

where $\overline{m}_i$ is the amount of substance i in the liquid feed. The speciation, i.e., the “true” composition of the liquid phase (the amount of substance m_i of all species present) is obtained by solving this set of equations for a given temperature, pressure and stoichiometric amounts of substances $\overline{m}_i$ of the components H_2O, MDEA, CO_2 and H_2S. This speciation is required to determine the composition of the vapor phase.

The activity of species i is normalized according to Henry's law on the molality scale:

$$a_i = m_i \gamma_i \tag{7}$$

where m_i and γ_i are the molality and the molality-based activity coefficient of solute species i. The activity coefficients of all species are calculated with a modification of Pitzer's equation for the excess Gibbs energy of aqueous electrolyte solutions as will be discussed in more detail later in this paper.

For the vapor phase, the model applies the extended Henry's law on the molality scale to describe the partial pressure of H_2S and CO_2 (i.e., the product of the total pressure P and vapor phase mole fractions y_{H_2S} and y_{CO_2}) above the aqueous solution and the extended Raoult's law for water.

$$k_{H,H_2S} \exp\left[\frac{v^{\infty}_{H_2S}(P - P^s_w)}{R_g T}\right] a_{H_2S} = y_{H_2S} P \varphi_{H_2S} \tag{8}$$