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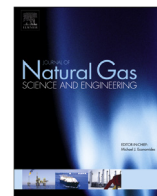
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Incorporating Pitzer equations in a new thermodynamic model for the prediction of acid gases solubility in aqueous alkanolamine solutions



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ABSTRACT

In gas sweetening, acid gases such as CO₂ and/or H₂S 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 H₂S and CO₂ 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 CO₂ and H₂S 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.

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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), H₂S and CO₂ 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).



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:

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

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:

$$\bar{m}_{\text{CO}_2} = m_{\text{CO}_2} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} \quad (2)$$

$$\bar{m}_{\text{H}_2\text{S}} = m_{\text{H}_2\text{S}} + m_{\text{HS}^-} + m_{\text{S}^{2-}} \quad (3)$$

$$\bar{m}_{\text{MDEA}} = m_{\text{MDEA}} + m_{\text{MDEAH}^+} \quad (4)$$

$$\bar{m}_w = m_w + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} + m_{\text{OH}^-} \quad (5)$$

The condition for liquid-phase electro-neutrality is:

$$m_{\text{MDEAH}^+} + m_{\text{H}^+} = m_{\text{OH}^-} + m_{\text{HS}^-} + 2m_{\text{S}^{2-}} + m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} \quad (6)$$

where \bar{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 \bar{m}_i of the components H₂O, MDEA, CO₂ and H₂S. 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:

$$a_i = m_i \gamma_i \quad (7)$$

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 H₂S and CO₂ (i.e., the product of the total pressure P and vapor phase mole fractions $y_{\text{H}_2\text{S}}$ and y_{CO_2}) above the aqueous solution and the extended Raoult's law for water.

$$k_{\text{H}_2\text{S}} \exp \left[\frac{\nu_{\text{H}_2\text{S}}^\infty (P - P_w^s)}{R_g T} \right] a_{\text{H}_2\text{S}} = y_{\text{H}_2\text{S}} P \phi_{\text{H}_2\text{S}} \quad (8)$$

$$k_{H,CO_2} \exp\left[\frac{v_{CO_2}^\infty (P - P_w^s)}{R_g T}\right] a_{CO_2} = y_{CO_2} P \phi_{CO_2} \quad (9)$$

$$P_w^s \phi_w^s \exp\left[\frac{v_w (P - P_w^s)}{R_g T}\right] a_w = y_w P \phi_w \quad (10)$$

where $k_{H,i}$ is Henry's constant of species i in water at temperature T , R_g is the universal gas constant, and P_w^s is the vapor pressure of water. v_w and v_i^∞ are the molar volume of liquid water and the partial molar volume of i at infinite dilution in water, respectively. ϕ_i and ϕ_w are the fugacity coefficient of component i and water, respectively, in the gaseous mixture that coexists with the liquid. ϕ_w^s is the fugacity coefficient of water in its saturation state, and a_i is the activity of species i in the liquid state.

3. Solubility prediction

A more theoretical approach for predicting the solubility of the dissolved species in amine aqueous solution could be established based on a fundamental and unified methodology through incorporating the ion-activities and principles of thermodynamics including Gibbs free energies. In Eq. (1), the ions constituting the soluble component ($Y_c Z_a$) are represented by “Y” and “Z”, and “c” and “a” are respectively the number of cations and anions in 1 mol of electrolyte, $e+$ and $e-$ are the valences for cation and anion, respectively.



$$-R_g T \ln(K_R) = \Delta_{\text{reac}} G^\circ \quad (12)$$

$$\Delta_{\text{reac}} G^\circ = \left\{ \sum \Delta_f G^\circ \right\}_{\text{products}} - \left\{ \sum \Delta_f G^\circ \right\}_{\text{reactants}} \quad (13)$$

The thermodynamic equilibrium constant, K_R , is related to the Gibbs free energy of reaction ($\Delta_{\text{reac}} G^\circ$) according to Eq. (12) and related to the standard Gibbs free energies of formation ($\Delta_f G^\circ$) according to Eq. (13). Thermodynamic principles and relationships can be used to incorporate the effect of temperature and process pressure on the equilibrium constants as will be discussed here below.

3.1. Effect of temperature

The equilibrium product, $K_R(T, P_o)$ at temperature T and reference pressure P_o (1 bar) can be calculated either from the Gibbs free energy change of reaction using Eq. (14) as described in Sheikholeslami (2004, 2005) and Alhseinat and Sheikholeslami (2012) or by using Eqs. (15)–(18) as described by Monnin (1999). Assuming the heat capacity is constant over the investigated temperature range then $K_R(T, P_o)$ is given by:

$$-R_g T \ln(K_R) = \Delta_r G^T = \frac{T}{298.15} \Delta_r G^{298} + \Delta_r H^{298} \left(1 - \frac{T}{298.15}\right) \quad (14)$$

$$\ln K_R(T, P_o) = A + B \ln T + \frac{C}{T} \quad (15)$$

With

$$A = \frac{\Delta_r S^\circ}{R_g} - \frac{\Delta_r C_p^\circ}{R_g} [1 + \ln T_o] \quad (16)$$

$$B = \frac{\Delta_r C_p^\circ}{R_g} \quad (17)$$

$$C = -\frac{\Delta_r H^\circ}{R_g} + \frac{T_o \Delta_r C_p^\circ}{R_g} \quad (18)$$

where $\Delta_r S^\circ$, $\Delta_r H^\circ$ and $\Delta_r C_p^\circ$ respectively refer to standard entropy, enthalpy and heat capacity changes of the reaction. T_o the reference temperature (298.15) (Monnin, 1999). Table 1 gives the thermodynamic standard properties for all species involved in R1–R6, and Table 2 gives the calculated change in thermodynamic properties for reactions R1–R6.

3.2. Effect of pressure

Effect of pressure on equilibrium can be calculated by integrating the following Eqs. (19) and (20) according to Alhseinat and Sheikholeslami (2012),

$$\left(\frac{\partial \ln K_R(T, P)}{\partial P}\right)_T = \frac{-\Delta V_r^\circ(T, P)}{R_g T} \quad (19)$$

and

$$\left(\frac{\partial \Delta V_r^\circ(T, P)}{\partial P}\right)_T = -\Delta K_r^\circ(T, P) \quad (20)$$

where ΔV_r° and ΔK_r° stand for the standard volume and compressibility changes of the reaction (Alhseinat and Sheikholeslami, 2012).

The integration of Eqs. (19) and (20) leads to the following expression (Alhseinat and Sheikholeslami, 2012; Monnin, 1999; Rushdi et al., 2000).

$$\ln K_R(T, P) = \ln K_R(T, P_o) - \frac{\Delta \bar{V}_r^\circ}{R_g T} (P - P_o) + \frac{\Delta \bar{K}_r^\circ}{2R_g} (P - P_o)^2 \quad (21)$$

where $\Delta \bar{V}_r^\circ$ is the standard molal volume change of the reaction and $\Delta \bar{K}_r^\circ$ is its standard molal compressibility change. The effect of $\Delta \bar{K}_r^\circ$ can be neglected at moderate pressures range.

3.3. Activity coefficients models

Activity coefficients of electrolytes dissolved in aqueous solutions are a special subject of study in the electrochemical literature (van der Stegen et al., 1999). There are several semi-empirical models in the literature that can be used to predict the activity coefficients of electrolytes dissolved in aqueous solution, most of them were discussed in Anderko et al. (2002). The activity coefficients are necessary for the calculation of the electrochemical potential, which is a very important parameter in determining the thermodynamic equilibrium (van der Stegen et al., 1999). Thus, reliable prediction of the activity coefficients is essential to achieve reliable predictions of the solubility of acid gases in aqueous amine solutions.

The Poisson–Boltzmann equation and the Debye–Hückel theory are the basis of a number of successful semi-empirical equations for a variety of thermodynamic properties (Loeche and Donohue, 1997). The more popular of these equations are discussed in references Loeche and Donohue (1997) and Anderko et al. (2002). Perhaps the most widely applied of these equations are those developed by Pitzer and coworkers since 1973 (Loeche and Donohue, 1997). Pitzer (Pitzer and Mayorga, 1973; Pitzer, 1975, 1991; Pitzer and Silvester, 1978; Pitzer and Kim, 1974) discusses the origin of these equations and their application in some detail.

Table 1

The thermodynamic standard properties for all species involves in R1–R6 at 298.15 K and 1 bar.

	$\Delta_f G^\circ$ (kJ/mol)	S° (J/mol K)	$\Delta_f H^\circ$ (kJ/mol)	C_p° (J/mol K)	\bar{V}° (cm ³ /mol)	\bar{K}° (cm ³ /MPa mol)
H ₂ O	–237.13 (Wagman et al., 1982)	69.91 (Wagman et al., 1982)	–285.83 (Wagman et al., 1982)	75.291 (Wagman et al., 1982)	18.068 (Barbero et al., 1982)	–
MDEA	–169.00 (Zhang and Chen, 2010)	–	–380.00 (Zhang and Chen, 2010)	380.90 (Zhang et al., 2002)	109.50 (Zhang et al., 2002)	–0.0008 (Zhang et al., 2002)
MDEA ⁺	–217.800 (Zhang and Chen, 2010)	–	–512.22 (Zhang and Chen, 2010)	198.80 (Zhang et al., 2002)	123.32 (Zhang et al., 2002)	–0.00087 (Zhang et al., 2002)
H ₂ S	–27.830 (Wagman et al., 1982)	121.0 (Wagman et al., 1982)	–39.700 (Wagman et al., 1982)	178.50 (Barbero et al., 1982)	39.920 (Barbero et al., 1982)	–
HS [–]	12.080 (Wagman et al., 1982)	62.80 (Wagman et al., 1982)	–17.600 (Wagman et al., 1982)	–92.000 (Barbero et al., 1982)	20.800 (Barbero et al., 1982)	–
S ^{2–}	85.800 (Wagman et al., 1982)	–14.60 (Wagman et al., 1982)	33.100 (Wagman et al., 1982)	–	–	–
CO ₂	–394.37 (Wagman et al., 1982)	117.6 (Wagman et al., 1982)	–393.51 (Wagman et al., 1982)	–	–	–
HCO ₃ [–]	–586.77 (Wagman et al., 1982)	91.200 (Wagman et al., 1982)	–691.99 (Wagman et al., 1982)	–	–	–
CO ₃ ^{2–}	–527.81 (Wagman et al., 1982)	–56.90 (Wagman et al., 1982)	–677.14 (Wagman et al., 1982)	–	–	–
OH [–]	–157.24 (Wagman et al., 1982)	–10.75 (Wagman et al., 1982)	–229.994 (Wagman et al., 1982)	–148.50 (Wagman et al., 1982)	–	–

3.3.1. Debye–Hückel theory

Debye–Hückel theories assume the ions to be charged species with a fixed diameter in a continuous dielectric medium (Loehe and Donohue, 1997). The original Debye–Hückel formulation is valid only for very low concentrations, i.e., below 0.001 m, due to assuming the ions to be point charges. The extended Debye–Hückel theory assigns a value to the ionic diameter and thus can be applied for concentrations up to 0.1 m. The Debye–Hückel limiting law gives the activity coefficients γ_i in terms of the ionic strength, I , which is defined by Eq. (22).

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (22)$$

where z_i is the charge on ion i , and m_i is the molality of ion i .

The activity coefficient can be calculated by the Debye–Hückel Limiting Law using Eq. (23)

$$\log \gamma_i = -A \cdot z_i^2 \cdot I^{1/2} \quad (23)$$

where $A = 0.509/(\text{mol kg}^{-1})^{1/2}$ for an aqueous solution at 25 °C. In general, A depends on the relative permittivity of the solvent and the temperature.

The activity coefficient may be estimated from the extended Debye–Hückel law using Eq. (24).

$$\log \gamma_i = \frac{-A \cdot z_i^2 \cdot I^{1/2}}{1 + b \cdot I^{1/2}} \quad (24)$$

where b is a measure of distance between ions. In the limit of small concentration $I^{1/2} \ll 1$, and, in the denominator of Eq. (24), $I^{1/2}$ can

be neglected; the extended Debye–Hückel Law tends to become the Debye–Hückel Limiting Law at low concentrations, Eq. (23).

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 et al. established very widely applicable equations for high concentrations up to 6 m, and discussed (Pitzer and Mayorga, 1973; Pitzer, 1991) the origin of these equations and their application in some detail (Loehe and Donohue, 1997). Below a brief description is presented of the Pitzer equations that have been used in this work.

3.3.2. Pitzer model

The Pitzer model can be considered as an extension of the Debye–Hückel model. The general formulation of the Pitzer model can be described by Eq. (25) which presents the total excess Gibbs energy. The first part of this equation corresponds to the Debye–Hückel model and is a function of ionic strength and the dielectric constant of the solvent (Hamrouni and Dhabbi, 2001). The second and the third terms are introduced to model the binary and ternary interactions which were neglected in the initial Debye–Hückel model. Pitzer introduced and formulated these two terms in order to describe the behavior of solutions at high concentrations (Hamrouni and Dhabbi, 2001).

$$\frac{G^{ex}}{n_w R_g T} = f(I) + \sum_i \sum_j \lambda_{ij} m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \quad (25)$$

where $f(I)$ is a function of ionic strength, expressing the effect of the long-range electrostatic forces; i , j and k are different anions (or cations), m_i denotes molality of the i th ion (moles per kilogram) and n_w is number of kilograms of water. λ_{ij} is a second virial coefficient which expresses the effect of the short-range forces between

Table 2

Calculated change in thermodynamic properties for reactions R1–R6 at 298.15 K and 1 bar.

	$\Delta_r G^\circ$ (kJ/mol)	$\Delta_r S^\circ$ (J/mol K)	$\Delta_r H^\circ$ (kJ/mol)	$\Delta_r C_p^\circ$ (J/mol K)	$\Delta_r \bar{V}^\circ$ (cm ³ /mol)	$\Delta_r \bar{K}^\circ$ (cm ³ /MPa mol)
R1	79.890	–80.66	55.836	–223.79	–18.068	–
R2	40.07	–58.2	22.100	–270.50	–19.120	–
R3	96.591	–77.4	50.700	–53.600	8.0600	–
R4	44.730	–96.31	–12.6500	–	–	–
R5	192.40	26.4	14.8500	–	–	–
R6	48.805	–	132.22	182.10	–13.820	0.00007

species i and j . λ_{ij} is dependent on the ionic strength. μ_{ijk} is the third virial coefficient which accounts for triple ion interactions; μ_{ijk} is independent of the ionic strength (Pitzer and Kim, 1974).

The activity coefficient equations are obtained by appropriate derivations from Eq. (25) which are described in detail in Pitzer and Mayorga (1973), Pitzer (1975, 1991) and Pitzer and Kim (1974). Eqs. (26) and (27) are used to obtain the ionic activity coefficients for cations M and anions X :

$$\begin{aligned} \ln(\gamma_M) = & z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) \\ & + \sum_c m_c \left(2\Phi_{Mc} + \sum_a m_a \psi_{Mca} \right) \\ & + \sum_{a < c} \sum_{a'} m_a m_{a'} \psi_{aa'M} + z_M \sum_c \sum_a m_c m_a C_{ca} \end{aligned} \quad (26)$$

$$\begin{aligned} \ln(\gamma_X) = & z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) \\ & + \sum_a m_a \left(2\Phi_{Xa} + \sum_c m_c \psi_{Xac} \right) \\ & + \sum_{c < c'} \sum_c m_c m_{c'} \psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca} \end{aligned} \quad (27)$$

The osmotic coefficient $\phi_{osmotic}$ which characterizes the deviation of solvent from ideal behavior can be calculated using Eq. (28).

$$\begin{aligned} (\phi_{osmotic} - 1) = & \frac{2}{\sum_i m_i} \left[\frac{-A_\phi I^{3/2}}{(1 + bI^{1/2})} + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}) \right. \\ & + \sum_{c < c'} \sum_{c'} m_c m_{c'} \left(\Phi_{cc'}^\phi + \sum_a m_a \psi_{cc'a} \right) \\ & \left. + \sum_{a < a'} \sum_{a'} m_a m_{a'} \left(\Phi_{aa'}^\phi + \sum_c m_c \psi_{caa'} \right) \right] \end{aligned} \quad (28)$$

The various terms in Eqs. (26)–(28) are defined as follows:

I is the ionic strength which is defined by Eq. (22).

The term F in Eqs. (26) and (27) is defined by Eq. (29)

$$\begin{aligned} F = & f^\gamma + \sum_c \sum_a m_c m_a B'_{ca} + \sum_{c < c'} \sum_{c'} m_c m_{c'} \Phi'_{cc'} \\ & + \sum_{a < a'} \sum_{a'} m_a m_{a'} \Phi'_{aa'} \end{aligned} \quad (29)$$

where f^γ is defined by Eq. (30)

$$f^\gamma = -A_\phi \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right] \quad (30)$$

where b is 1.2 and A_ϕ , which is the Debye–Hückel slope. The variation of the Debye–Hückel slope, A_ϕ , for the activity coefficient with temperature can be expressed by Eq. (31) (Møller, 1988).

$$\begin{aligned} A_\phi = & 3.6901531 \times 10^{-1} - 6.32100430 \times 10^{-4} T + \frac{9.1425359}{T} \\ & - 1.35143986 \times 10^{-2} \ln T + \frac{2.26089788 \times 10^{-3}}{T - 263} \\ & + 1.92118597 \times 10^{-6} T^2 + \frac{4.52586464 \times 10^1}{680 - T} \end{aligned} \quad (31)$$

where T is the absolute temperature in Kelvin.

The variables B_{MX} , B_{MX}^ϕ and C_{MX} which define the thermodynamic properties of single-salts solution are given below by

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} g(\alpha_2 I^{1/2}) \quad (32)$$

in which:

$$g(x) = 2 \left[1 - (1 - x)e^{-x} \right] / x^2 \quad (33)$$

$$g'(x) = -2 \left[1 - (1 + x + 0.5x^2)e^{-x} \right] / x^2 \quad (34)$$

$$B'(x) = \beta_{MX}^{(1)} g'(\alpha_1 I^{1/2}) / I + \beta_{MX}^{(2)} g'(\alpha_2 I^{1/2}) / I \quad (35)$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} \exp(-\alpha_2 I^{1/2}) \quad (36)$$

$$C_{MX} = \frac{C^\phi}{2|z_M z_X|^{1/2}} \quad (37)$$

The parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ , which define the variables B and C , are fitted from single-salt data (Plummer et al., 1988) and the literature values of these parameters are tabulated in Kuranov et al. (1996) and Kamps et al. (2000). For any salt containing a monovalent ion such as 1-1 (e.g. NaCl), 1-2 (e.g. Na₂SO₄) or 2-1 (e.g. CaCl₂) $\alpha_1 = 2$ and $\alpha_2 = 0$. For 2-2 (e.g. CaSO₄) electrolytes $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$. For 3-2 and 4-2 electrolytes $\alpha_1 = 2$ and $\alpha_2 = 50$ (Pitzer and Silvester, 1978).

The coefficient to C_{MX} , Z , in Eqs. (26)–(28) is defined by Eq. (38) below:

$$Z = \sum_i m_i |z_i| \quad (38)$$

The parameters Φ and ψ are determined from two-salt systems. Φ accounts for cation–cation and anion–anion interactions while the parameter ψ is defined for cation–cation–anion and anion–anion–cation interactions. Values of Φ_{ij} can be determined using Eqs. (39)–(46)

$$\Phi_{ij}^\phi = \theta_{ij} + I^E \theta'_{ij}(I) + {}^E \theta_{ij}(I) \quad (39)$$

$$\Phi_{ij} = \theta_{ij} + {}^E \theta_{ij}(I) \quad (40)$$

$$\Phi'_{ij} = {}^E \theta'_{ij}(I) \quad (41)$$

$${}^E \theta_{ij}(I) = \left(\frac{|z_i z_j|}{4I} \right) [J(x_{ij}) - 0.5J(x_{ii}) - 0.5J(x_{jj})] \quad (42)$$

$${}^E \theta'_{ij} = \left(\frac{-{}^E \theta_{ij}}{I} \right) + \left(\frac{|z_i z_j|}{8I^2} \right) \cdot [x_{ij} J''(x_{ij}) - 0.5x_{ii} J''(x_{ii}) - 0.5x_{jj} J''(x_{jj})] \quad (43)$$

$$x_{ij} = 6|z_i z_j| A_\phi I^{0.5} \quad (44)$$

$$J(x) = x \left[4 + 4.581x^{-0.7237} \exp(-0.0120x^{0.528}) \right]^{-1} \quad (45)$$

$$f''(x) = \frac{4 + [4.581x^{-0.7237} \exp(-0.0120x^{0.528})] [0.006336x^{0.528} + 1.7237]}{[4 + 4.581x^{-0.7237} \exp(-0.012x^{0.528})]^2} \quad (46)$$

In the above equations m_i denotes molality of the i th ion (moles per kilogram) where the subscripts M , c and c' refer to cations and the subscripts X , a and a' to anions. The summation index, c , denotes the sum over all cations in the system while the double summation index, $c < c'$, denotes the sum over all distinguishable pairs of dissimilar cations. Similar definitions apply to the summation indices for anions X , a and a' . B and f represent measurable combinations of the second virial coefficients λ . C and ψ represent measurable combinations of the third virial coefficients μ (Hamrouni and Dhahbi, 2001). The terms ${}^E\theta_{ij}$ and ${}^E\theta'_{ij}$ account for electrostatic mixing effects of unsymmetrical cation–cation and anion–anion pairs (Pitzer, 1975). Values of ${}^E\theta_{ij}$ and ${}^E\theta'_{ij}$ depend only on ion charge and total ionic strength and are zero when ij cation or anion pairs have the same charge (Plummer et al., 1988).

Pitzer ion interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, θ , ψ and C^ϕ are functions of temperature. The values of the binary interaction parameters as function of temperature are given in Kuranov et al. (1996) and Kamps et al. (2000).

Three separate Matlab programs have been written for calculating the anion and cation activity coefficients and the osmotic coefficient in the aqueous amine stream using Eqs. (22)–(46). These programs can be used to calculate the activity coefficient and osmotic pressure for any solution with known initial composition.

4. Results and discussion

The objective of this work is to predict the solubility of acid gases using an improved thermodynamic model. The model is based on a set of equations for chemical equilibria, phase equilibria, charge, and mass balances. Non-ideality in the liquid and gas phases was taken into account by using the Pitzer model to calculate the activity coefficients and using the PR equation of state to calculate the fugacity coefficients.

4.1. Model validation

To assess the validity of the model for CO_2 and H_2S solubilities prediction, a comparison was made with the available data reported by Lemoine et al. (2000) and Huttenhuis et al. (2007) as

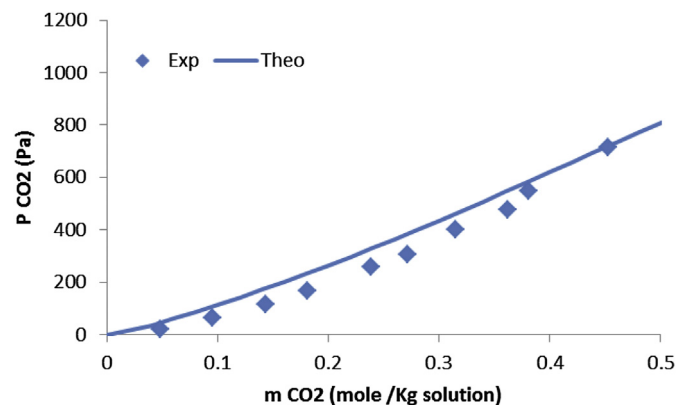


Fig. 1. Comparison between predicted P_{CO_2} and the data of the data of Lemoine et al. (2000) at 298 K and 23.63 wt. % of MDEA ($R^2 = 0.985$).

shown in Figs. 1 and 2 and Fig. 3, respectively. In Fig. 1 the data of Lemoine et al. were obtained for CO_2 solubilities in 23.63 wt.% MDEA aqueous solutions at 298 K, and in Fig. 2 the data were obtained for H_2S solubilities at temperatures of 313.15 K in 2.5 (mol/kg H_2O) MDEA solution. The data of Huttenhuis et al. were obtained for H_2S solubilities at 298.15 K in an 8.39 m MDEA solution. An overall good agreement between experimental and predicted values was obtained. The deviations between the experimental and predicted data can be due to systematic experimental errors as explained in Lemoine et al. (2000). It should be noted that rigor of the simulation is of secondary importance in the current paper as the novelty of the paper and hence “primary” importance is to introduce our fundamental and realistic approach of using new theoretical thermodynamic model based on incorporating theoretical thermodynamic relationships that correlates the equilibrium and solubility constants to the Gibbs free energy of reactions and using of Pitzer model.

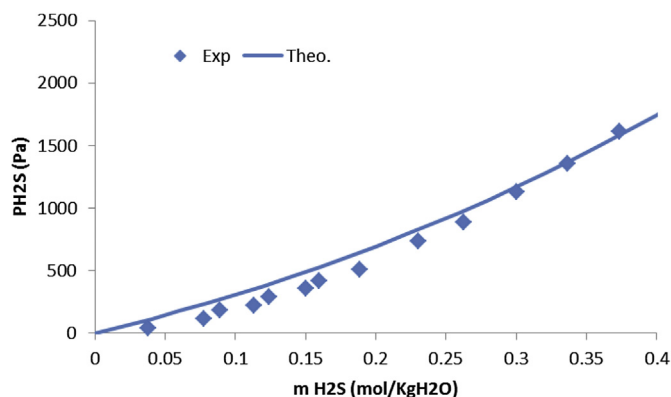


Fig. 2. Comparison between predicted $P_{\text{H}_2\text{S}}$ and the data of Lemoine et al. (2000) at 313.15 K and 2.5 m of MDEA ($R^2 = 0.9986$).

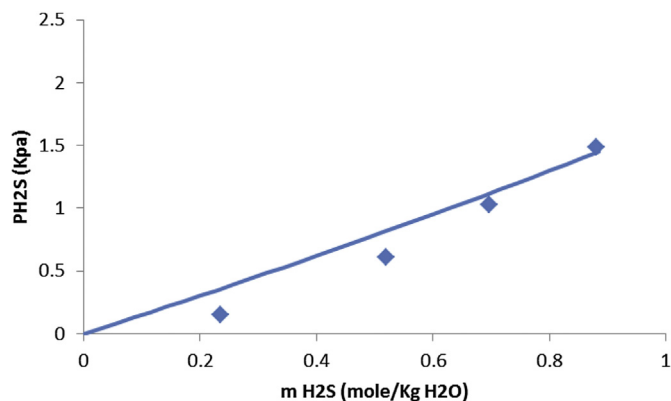


Fig. 3. Comparison between predicted $P_{\text{H}_2\text{S}}$ and the data of Huttenhuis et al. (2007) at 298.15 K and 8.39 m of MDEA ($R^2 = 0.989$).

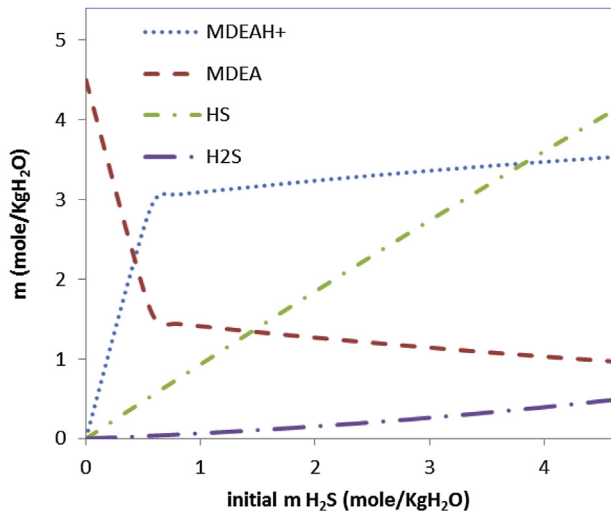


Fig. 4. Species concentration profile for aqueous solution of $[H_2S + MDEA + H_2O]$ at 313.15 K ($\bar{m}_{MDEA} = 4.5 \text{ mol (kg water)}^{-1}$).

4.2. Speciation prediction

The concentrations of the different species in the H_2S and aqueous MDEA system were evaluated using the model. Fig. 4 gives the predicted speciation of ($MDEA^+$, H_2O , and H_2S) solution at $\bar{m}_{MDEA} = 4.5 \text{ mol (kg water)}^{-1}$ and 313.15 K.

It was found that at the simulated conditions most of the H_2S absorbed into the solution is in the form of HS^- with a small amount in the form of H_2S . As the loading increase, the concentration of $MDEA^+$ increases and the concentration of MDEA decreases. However, the will change in the MDEA and $MDEA^+$ concentrations will be limited once the entail H_2S concentration exceeds 6 m.

4.3. Effect of process temperature

The effect of temperature on the solubility of acid gases has been examined as well. As can be seen in Fig. 5, increasing system temperature up to 383.15 K decreases the solubility of acid gases. However, further increase of the system temperature above 383.15 K decreases the partial pressure of H_2S . Increasing the temperature has affected the reaction equilibrium as can be seen in Fig. 6.

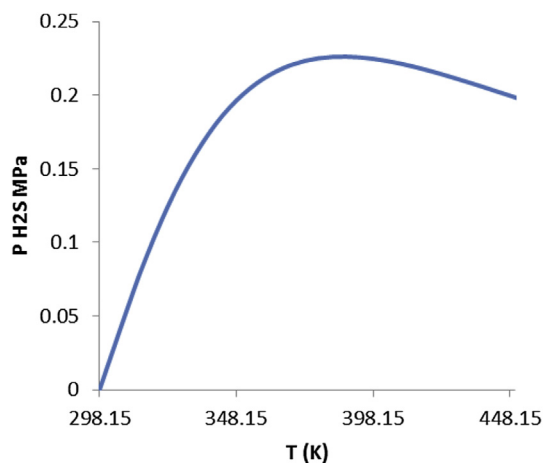


Fig. 5. Effect of temperature change on H_2S partial pressure in initial 8.39 m MDEA and various H_2S loadings from 0 to 3.1 m.

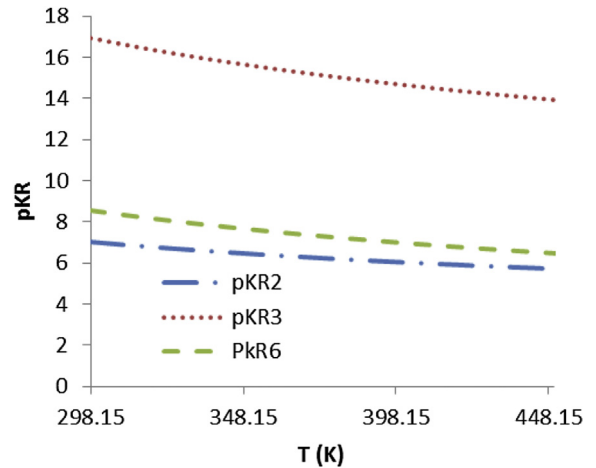


Fig. 6. Equilibrium constant for R2, R3 and R6 versus temperature.

Fig. 7 shows the effect of temperature change on the concentrations of $MDEA^+$ and MDEA at an initial MDEA concentration of 8.39 m. As can be seen from Fig. 7, as the temperature of the system increases, the concentration of $MDEA^+$ in the system decreases and the concentration of MDEA increases. This decrease of $MDEA^+$ decreases the solubility of H_2S , and contributes to increase the partial pressure of H_2S as a consequence of the temperature increase.

4.4. Effect of solution pH

Fig. 8 shows the effect of the pH of the solution on the solubility of H_2S . As can be seen from Fig. 8, increasing of the system pH increases the solubility of H_2S in the amine solution. Increasing the pH of the solution shifts the reaction to dissolved more H_2S and produced more HS^- and S^{2-} .

4.5. Effect of process pressure on solubility

Also the effect of the process pressure has been studied. As can be seen in Fig. 9, increasing of the process pressure increases the

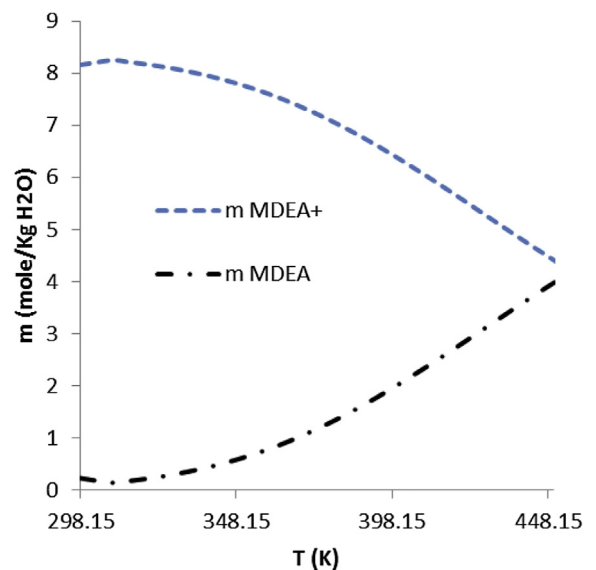


Fig. 7. Effect of temperature change on the concentration of $MDEA^+$ and MDEA at initial 8.39 m MDEA.

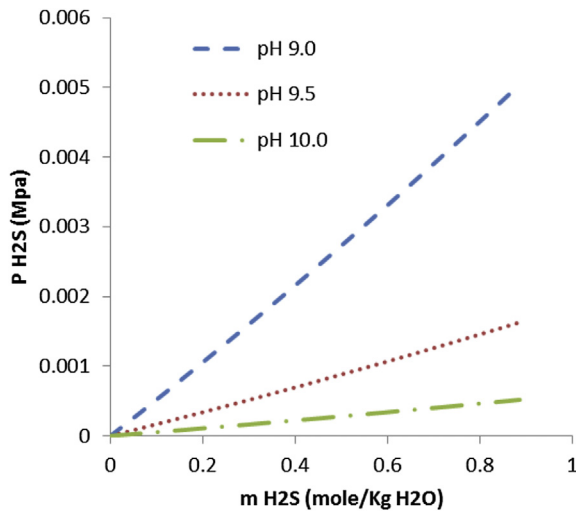


Fig. 8. Effect of solution pH on H₂S solubility in 8.39 m MDEA solution.

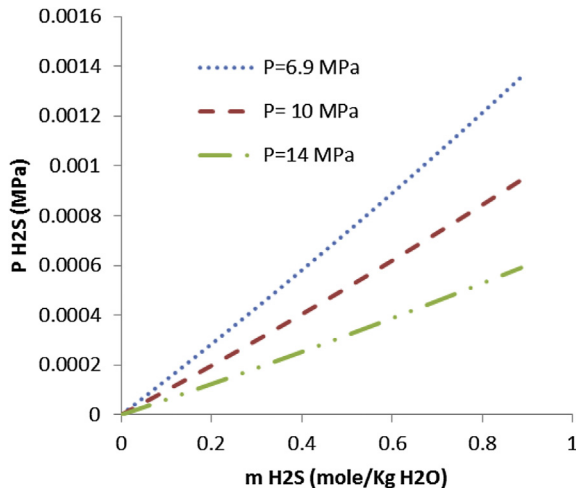


Fig. 9. Effect of process pressure on H₂S solubility in 8.39 m MDEA solution.

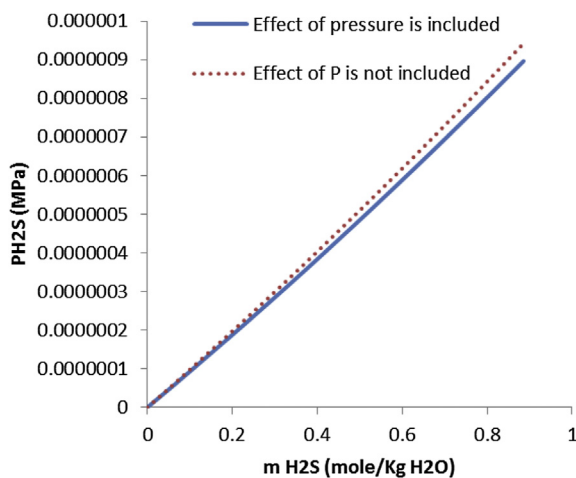


Fig. 10. The effect of including process pressure (69 MPa) in the thermodynamic equilibrium constants' calculation at H₂S solubility at constant temperature 25 °C and initial 8.39 m MDEA.

solubility of H₂S. The effect of the process pressure on the thermodynamic equilibrium constant has been included and evaluated in Fig. 10. Interestingly, the effect of process pressure increased as the initial concentration of H₂S increased, which indicates that at high H₂S loading the effect of process pressure on the equilibrium constants should not be ignored.

5. Conclusions

In this paper, a new thermodynamic model was proposed to predict the solubility of acid gases in the amine absorption processes. The fundamental equations of Gibbs free energy of reaction have been used to calculate the thermodynamic equilibrium constants of all reactions involved in the acid gas absorption system. The effect of process pressure and temperature was incorporated theoretically in this model. The non-ideality in the liquid phase was taken into account by using the Pitzer model to calculate the activity coefficients for all species present in the liquid phase. The non-ideality in the gas phase was taken into account by using the PR equation of state to calculate the fugacity coefficient for all species present in the gas phase.

The model has been positively validated through comparison with experimental data. The effects of process temperature, pressure, and pH on the H₂S solubility in MDEA amine solutions were evaluated. This model forms the basis for an adequate assessment of the effect of the presence of multiple dissolved species that also may occur in real amine absorption processes. Also this model could be further developed to a user-friendly program, able to give an accurate prediction of acid gas solubilities at actual process conditions, allowing the optimization of the process accordingly.

Acknowledgments

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Nomenclature

A_p	interaction parameter Pitzer model (–)
B, B', B''	interaction parameter Pitzer model (–)
C, C''	interaction parameter Pitzer model (–)
f^o	interaction parameter Pitzer model (–)
G	standard Gibbs free energy
I	ionic strength, mol/kg
K_R	thermodynamic solubility product
P	process pressure, bar
P_0	reference pressure, 1 bar
R_g	the universal gas constant
T	temperature, K
V	volume of the dissolution reaction
\bar{V}	molal volume of dissolution reaction
z_i	ionic charge of component i
Z	modified ionic strength, mol/kg

Greek letter

α_1, α_2	interaction parameter Pitzer model (–)
Δ	denote the difference between two values
$\Delta_r C_p^o$	standard heat capacity change of reaction
$\Delta_f G^o$	standard Gibbs free energy change of formation
$\Delta_{\text{reac}} G^o$	standard molar Gibbs free energy change of reaction
ΔH_{reac}	enthalpy change of reaction
$\Delta_r H^o$	standard enthalpy change of reaction
ΔK_p^o	standard compressibility change of reaction
$\Delta \bar{K}_p^o$	standard molal compressibility change of reaction
$\Delta_r S^o$	standard entropy change of reaction

ΔV_r^0	standard volume change of reaction
$\Delta \bar{V}_r^0$	standard molal volume change of reaction
γ	activity coefficient
Φ, Φ', Φ^p	Interaction parameter Pitzer model (–)
$\phi_{osmotic}$	Pitzer osmotic coefficient
λ_{ij}	the second virial coefficient
μ_{ijk}	third virial coefficient
Ψ	interaction parameter Pitzer model (–)

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