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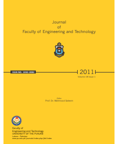

AN OVERVIEW OF THE THERMODYNAMIC MODELS FOR ACID GASES IN ELECTROLYTE SOLUTIONS

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Abstract:

Most of the thermodynamic models are structured with terms representing long range interactions or intermediate/short range interactions only. Thus for the proper thermodynamic presentation of electrolyte systems, all different types of interactions: ion-ion, ion-dipole, dipole-dipole, molecule-molecule should be taken into account. The potential energy caused by ion-ion interactions is inversely proportional to the separation between them. Electrostatic ion-ion interactions therefore are effective over a relatively long distance called as long range interactions. A review of the literature was conducted to find the available models, correlations: capable of describing the phase behavior and thermo physical properties of strong as well as weak electrolyte systems. In this work the comparative study for the models that has been used for describing the Phase behavior of acid gases and sulfur species in alkanolamine aqueous solutions, is presented. These kinds of models are of high interest for the absorption unit in the natural gas processing industry.

Key words: Electrolyte, Phase behavior, Acid gases, Rate constant, Acid-base neutralization approach.

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1. Introduction

The modeling of the phase equilibrium data and thermodynamic properties of electrolyte solutions are important for a variety of application in the chemical processes, electrochemical processes, petroleum industry and hydrometallurgical processes.

Although a couple of nice reviews on the modeling of electrolyte solutions are available in literature. Models for mixed-solvent solutions were review by Andrzej *et al.* [1]. Some of the empirical, semi-empirical and fundamental models are reviewed by Pitzer [2], Renon[3] Zemaitis et al [4], Loehe and Donohue [5], Friedman[6] Conway[7]. Although much advancement has been made in the area of thermodynamic properties than the understanding of physical principles.The substantial progress has been achieved and many practical, engineering oriented models are currently under development [1].

In this work emphasis is put on the comparative study for the models that has been used for describing the Phase behavior of acid gases and sulfur species in alkanolamine aqueous solutions. These kinds of models are of high interest for the absorption unit in the natural gas processing industry. Some times alkanolamines are not used alone due to many technical reasons, usually they are mixed with other solvents and diluted with water in sufficient concentrations to obtain the necessary basicity to react with acid gases. These reactions result into the formation of dissociated electrolytes into their constituent ions or sometime electrolytes as non dissociated components.

2. Dilute electrolyte solutions

A dilute electrolyte system can by defined as a system where long range interactions between ions have no influence on the structure of the solvent and other short range interactions between ions and molecules are negligibly small [8]. In 1923, Debye and Hückel [9] proposed first successful model for the electrostatic interactions between ions in aqueous solutions and this model become famous as Dielectric continuum model. But this model did not explain the interaction between water molecule and ion, it was also assumed that the solvent plays a role only due to its relative permittivity and its density.

Debye and Hückel [9] express the excess Helmholtz function for an ideal solution containing charged ions. It sounds like a contradiction to have an excess Helmholtz function for an ideal solution of charged ions, because ideal solution does not have excess terms [10].The molar excess Helmholtz function for the electrostatic interactions can be expressed by the equation:

$$-\frac{A^{E}}{RT} = -\frac{1}{3}\sum x_{i} z_{i}^{2} s\bar{k}\chi(\bar{k}a_{i}) \qquad (1)$$

where (a_i) is the nearest distance between ions. ($1/\bar{k}$) represent screening length thus ($\bar{k}a_i$) is dimensionless

$$s = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT} \tag{2}$$

where ε_0, is the dielectric constant under vacuum and ε_r is the relative permittivity, further information is available in reference [10]

$$\bar{k} = \left(\frac{e^2 N_A \sum n_i z_i^2}{nV\varepsilon_0\varepsilon_r kT} \right)^{1/2} \tag{3}$$

and

$$\chi = f(x) \tag{4}$$

3. Debye and Hückel extended law

The extended Debye and Hückel law represents a simplification of the original Debye-Hückel equation. A Gibbs energy function was derived from the Helmholtz function in equation (1) by replacing the molarity concentration unit with molality. The mass and volume of the ions are also considered as zero. This approximation represents a small error for dilute solutions and a more serious error for concentrated solutions because the density of the solution becomes equal to the density of pure water [11]

Thus the molar excess Gibbs energy function in simplified form is

$$-\frac{g^E_{Ext.D.H}}{RT} = -x_i M_i \frac{4}{3} A I^{3/2} \chi(BaI^{1/2}) \tag{5}$$

Where x_i is the mole fraction and M_i is molar mass in kg.mol^{-1} of water. a is the ionic size parameter. I is the ionic strength on the molality scale in mol.kg^{-1}. A is Debye-Hückel parameter. B can be written as:

$$B = \left(\frac{2e^2 N_A d_o}{\varepsilon_0 \varepsilon_r kT} \right)^{1/2} \tag{6}$$

The extended Debye-Hückel law usually gives good results for activity coefficients up to an ionic strength of about 0.1 molal. Above this concentration, short range interactions apparently give a significant contribution to the deviation from ideality[11].

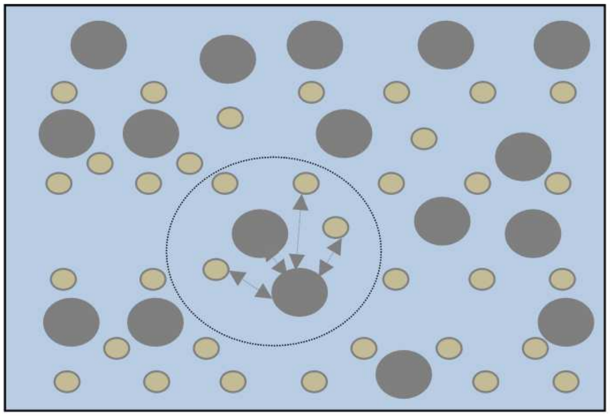

Figure 1: Pictorial view of a solution that represent the theory of Debye and Hückel in an electrolyte solution, where anions(○) shows attractions towards cations(●) and cations shows attractions towards anions, this pictorial view is in unit time and attractions of ions change with time and distance.

4. Debye-Hückel limiting law

The Debye-Hückel limiting law is a simplified form of original Debye-Hückel theory.

$$-\frac{g^E_{Ext.D.H\,(limiting\,law)}}{RT} = -x_i M_i \frac{4}{3} A I^{3/2} \tag{7}$$

The performances of the Debye-Hückel limiting law, the Debye-Hückel extended law, and Debye-Hückel equation are illustrated in reference [12], while calculating the activity coefficients of aqueous hydrochloric acid solutions. However the Debye-Hückel limiting law works well for the systems at infinite dilution. Furthermore the Debye-Hückel theory can only be used at low ionic strength.

5. Strong electrolyte solutions

For strong electrolyte solutions activity coefficient models and the equation of states have been developed for the last 70 years. They are further divided on the basis of dielectric constant of ions and molecules. For example some models consider ions as distinct particles while solvent is referred to have dielectric constant contributing to the electrolyte part [13]. Non primitive models are those which regard both solute and solvent as distinct particles, EOS are the examples of these types of models. [14].

Extended UNIQUAC proposed by Thomsen (1997) [12] has been successfully used to present the ternary VLE data of the system containing n-PM-H_2O-CH_4[73]. Furthermore CPA-EoS proposed by Kontogeorgis *et al.*, 1996 [15] without association so called SRK has been successfully employed for mercaptan-hydrocarbon systems[74]. Both models are discussed in detail in their respective articles. Herein few models for the electrolyte solutions especially used for the representation of CO_2 and H_2S solubility in alkanolamine-water solutions are presented.

6. Models based on the equilibrium constants

Mason and Dodge (1936) [16] were the first who attempt the thermodynamic modeling of the systems containing acid gases in alkanolamine aqueous solutions. Since then, the representation of these systems was carried out using different approaches. A large proportion are based upon Gibbs free energy, equilibrium constants.

The models based on the equilibrium constants are apparently the first one developed to represent the absorption of acid gases by alkanolamine aqueous solutions. In these models the concentrations of the species produced by the absorption are calculated with equilibrium constant values that incorporate activity coefficient calculations. The models presented by Van Krevelen et al. (1949) [17], Atwood et al. (1957) [18], Kent and Eisenberg (1976) [19] and the model of Posey et al. (1996) [20] are of significant importance.

Van Krevelen et al. (1949) [17] has developed a model for calculating partial pressure of H_2S, CO_2 and NH_3 in aqueous solutions while fixing the value of activity coefficient to 1. They calculate the equilibrium constant by solving the system of equations through material balance and ionic strength values, while using the following correlation:

$$I = \frac{1}{2}\sum_j C_j z_j^2 \tag{8}$$

The limitation of this model is that the ionic strength is a single parameter dependent, which is not sufficient to determine the dependency of equilibrium constants on concentration. Furthermore this approach is assumed valid for the whole concentration range. Danckwerts and Mcneil (1967) [21] further modified this model for CO_2-H_2O-alkanolamine systems.

Atwood et al. (1957) [18] expressed the equilibrium constant in terms of the ionic strength of the solution from the activity coefficient of ionic species and assumed the same value of activity coefficient for all ionic species. However this hypothesis is valuable only at low ionic strength or whether only cations or anions are present in significant quantities. Klyamer et al. (1973) [22] generalized this approach for single gas solubility (CO_2) in alkanolamine aqueous solution by fixing the value of activity coefficient equal to unity. Kent and Eisenbeg (1976) [19] used similar approach like Van Krevelen et al. (1949) [17] for the presentation of solubility of CO_2 and H_2S in aqueous solution of MEA and DEA. *i.e* the vapor pressure of the acid gas species is related to the free acid gas concentration in the liquid phase ionic equilibria. The simplicity of this model makes it more important for real industrial application. It is also based on the apparent equilibrium constants and the Henry's constant as a function of temperature.

Lee et al. (1976) [23] point out that partial pressure of acid gas calculated with Van Krevelen model comes up with an error of 100%. Posey et al. (1996) [20] observe that that model proposed by Kent and Eisenbeg (1976) [20] provides good modeling results only for the acid gas loading higher then 0.1. Later on Hu and Chakma (1990) [24, 25] modified the Kent and Eisenbeg (1976) [19] model, while presenting the solubility of carbon dioxide and hydrogen sulfide in DGA (Diglycolamine) and AMP (2-amino, 2-methyl, 1-propanol) aqueous solutions. In this model they proposed the equilibrium constant in terms of Amine and acid gas concentrations, with more adjustable parameters. Li and Shen (1993) [26] proposed another correlation for equilibrium constant as a function of liquid loading of acid gas and molality of amine. Haji-Suliman et al. (1998) [27] also proposed a correlation of equilibrium constant for Carbamate formation and Protonation of amine at infinite dilution. Abu-Arabi and al-Muhtaseb (2000) [28] also proposed some correlations for the calculation of equilibrium constant of ionic and molecular species in acid gas-water-amine systems, which are well explained with equations in reference [29]. Park et al. (2002) [30] used the original correlation of equilibrium constants in Kent and Eisenbeg model while presenting the solubility of CO_2 in MEA, DEA, AMP and mixtures of amine. However Posey et al. (1996) proposed more simple model for the absorption of acid gases in amine aqueous solutions while neglecting the formation of species like CO_3^{-2}, S^{-2}, OH^- and H_3O^+.

7. Models based on Debye and Hückel approach

The Debye and Hückel (1923) [31] equation has been discussed earlier where a Gibbs energy function was derived from the Helmholtz function in equation (3-61) with some simplifications in the expression. Edward et al. (1975) [32] and Deshmukh and Mather (1981) [33] apply Debye and Hückel approach for the presentation of vapor-liquid equilibria of weak electrolyte systems.

Edwards et al. (1978) [32] calculate the fugacity of molecular species with a correlation, *i.e*

$$\ln f_m = \left(\frac{B_m P}{RT} \right) \tag{9}$$

here B_m is the second order virial temperature dependent coefficient. The chemical equilibrium has been expressed in terms of equilibrium constants and calculated with Guggenheim and Turgeon's equation (1955) [34] while taking into account all the ion-ion, ion-molecule, and molecule-molecule interactions

$$g^{Ex} = g^{SRI} + g^{DH} \tag{10}$$

Where g^{SRI} short range interaction, can be written as

$$\frac{g^{SRI}}{RT} = \sum_{i \neq 0} \sum_{j \neq 0} m_i m_j \left[M_s A_{ij} - \frac{M_s}{2} \right] \tag{11}$$

where, m_i and m_j are the molalities of component i and j. M_s is molar mass of the solvent; A_{ij} is the binary interaction parameter. The long range interaction presented by Debye and Hükel (1923) can be written as

$$\frac{g^{D.H}}{RT} = -\frac{2}{3} A I^{1/2} \tau \sum_j Z_j^2 n_j \tag{12}$$

Where I is the ionic strength, Z_i is the charge number of species j, $\tau(x)$ is the function of mole fraction and can be written as,

$$\tau(x) = \frac{3}{x^3} \left[\ln(1+x) + \frac{x^2}{2} - x \right] \tag{13}$$

Deshmukh and Mather (1981) [33] further extend the work of Edwards et al. (1975) [32] for the presentation of CO_2 and H_2S solubility in MEA aqueous solutions. This model includes phase equilibrium between an aqueous liquid and a gas as well as chemical equilibrium in the aqueous phase. In this model regression of binary interaction parameters (ionic-ionic and molecular-ionic) is performed on the equilibrium data of acid gases / MEA/ H_2O systems. The equilibrium constants relative to deprotonation of amine and formation of carbamate ions has been adjusted. The activity of water is considered as unity and interactions concerning the species present in small quantities are considered as negligibly small. The total number of interaction parameters is six plus parameters in equilibrium constant expressions. Later on Charkravarty et al. (1985) [35] and Weiland et al. (1993) [36] apply Deshmukh and Mather (1981) model for the representation of acid gas solubility in MEA, DEA, DGA/ MDEA aqueous solutions. Furthermore Weiland et al. (1993) take into account the formation CO_3^{-2} ions, and point out the sensitivity of interaction between $MDEAH^+$ ions and CO_2 or H_2S molecules.

8. Models based on Pitzer and Clegg-Pitzer equations

Pitzer (1973) [37] further extend the model of Guggenheim by reducing theoretical parameters and introduced a 3rd order virial equation to account for the interaction between ionic solutes. This model also accounts for binary interaction parameters, which are dependent on ionic solution strength. This virial extension in Debye Hückel equation so called Pitzer equation is mostly used for electrolyte solutions. Later on this model was applied successufully by Kuranov et al. (1996) [38], Silkenbaumer (1998) [40] and Pérez-Salado Kamps et al (2001) [39] for CO_2 and H_2S solubility in alkanolamine-water solutions. The excess Gibbs energy in Pitzer equation can be expressed as:

$$\frac{g^{Ex}}{n_w RTM_w} = \frac{g^{Ex}_{D.H}}{n_w RTM_w} + \frac{g^{Ex}_{Virial}}{n_w RTM_w} \tag{14}$$

where Debye and Hückel equation presents long-range interactions between ions and the virial term presents the short range interactions between molecular solutes and ions.

$$\frac{g^{Ex}_{Virial}}{n_w RTM_w} = \sum_i \sum_j m_i m_j \lambda_{ij} + \sum_i \sum_j m_i m_j m_k \tau_{ijk} \tag{15}$$

Where λ_{ij} and τ_{ijk} are the coefficients of 2nd order and 3rd order virial equations. However the Pitzer equation does not count for interactions between solvent molecules with other species. This model does not work well for the representation of thermodynamic properties of mixed solvents. Clegg and Pitzer (1992) [41] extended original Pitzer equation for a large number of ionic species.

$$\frac{g^{Ex}}{n_w RTM_w} = \frac{g^{Ex}_{D.H}}{n_w RTM_w} + \frac{g^{Ex}_{S}}{n_w RTM_w} \tag{16}$$

Herein the short range interaction G_S^{Ex} , the Margules term is considered up to quarternary components.

$$\frac{g_S^{Ex}}{RT} = \sum_i \sum_j a_{ij} x_i x_j + \sum_i \sum_j \sum_k a_{ijk} x_i x_j x_k + \sum_i \sum_j \sum_k \sum_l a_{ijkl} x_i x_j x_k x_l \tag{17}$$

Li and Mather (1996) [42] successfully apply Clegg-Pitzer equation with some modifications for the presentation of CO_2 solubility in MEA and MDEA aqueous solutions. In their hypothesis they consider amine and water both as solvent with an assumption that quantity of HCO_3^{-2} present in liquid phase is not negligible.

9. Models based on NRTL-Electrolyte equations

The electrolyte NRTL activity coefficient model has been developed by Chen et al. (1982) [43] by extending the work of Renon and Praustnitz (1968) [44]. The electrolyte NRTL activity coefficient model consists in three contributions. The long-range contribution comes from Pitzer–Debye–Hückel model, which takes into account the electrostatic interactions of ions, especially at low concentrations. The second part of the model is the Born contribution applicable to mixed aqueous–non aqueous electrolyte solvents. The third part is the local composition NRTL contribution, which is employed for short-range forces effective at higher concentrations of ions. The model has been discussed in detail in reference [29]. Furthermore Dingman et al. (1983) [45] Austgen et al. (1991) [46], Lui et al. (1999) [47] Bishnoi and Rochelle (2000) [48], Aroua et al. (2002) [49] used electrolyte NRTL activity coefficient model with some major/ minor modifications to present CO_2 and H_2S solubility in alkanolamine aqueous solutions.

$$g^{ex} = g^{ex}_{SR} + g^{ex}_{LR} \tag{18}$$

The excess molar Gibbs energy of the short range contribution is expressed as:

$$\frac{g^{ex}_{SR}}{RT} = \sum_{m} \mathrm{E}_m \frac{\sum_j \mathrm{E}_j G_{jm}\tau_{jm}}{\sum_k \mathrm{E}_k G_{km}} + \sum_{c} \mathrm{E}_c \sum_{d'} \frac{E_{a'}}{\sum_{d''} E_{a''}} \frac{\sum_j \mathrm{E}_j G_{jc,d'c}\tau_{jc,a'c}}{\sum_k \mathrm{E}_k G_{kc,a'c}} + \sum_{a} \mathrm{E}_a \sum_{c'} \frac{E_{c'}}{\sum_{c''} E_{c''}} \frac{\sum_j \mathrm{E}_j G_{ja,c'a}\tau_{ja,c'a}}{\sum_k \mathrm{E}_k G_{ka,c'a}} \tag{19}$$

where, m= molecules, c= cations, a= anions, E= absolute charge. Mol fraction, j, k (summation over molecules+ cations + anions), τ= Binary energy interaction parameter. α= nonrandom parameter.

$$G_{jc,a'c} = e^{(-\alpha_{jc,a'c}\tau_{jc,a'c})}, \quad G_{ja,c'a} = e^{(-\alpha_{ja,c'a}\tau_{ja,c'a})}$$

$$G_{i,m} = e^{(-\alpha_{i,m}\tau_{i,m})}, \quad G_{ca,m} = e^{(-\alpha_{ca,m}\tau_{ca,m})}$$

$$\tau_{ma,ca} = \tau_{am} - \tau_{ca,m} + \tau_{m,ca}, \quad \tau_{mc,ac} = \tau_{cm} - \tau_{ca,m} + \tau_{m,ca}$$

While the long range interaction is calculated with the modified Debye–Hückel model

$$\frac{g_{DH}^{ex}}{RT} = -(\sum_k x_k)(\frac{1000}{M_m})(\frac{4A_\Phi I_x}{\theta})\ln(1+\theta I_x^{1/2}) \tag{20}$$

where θ is the closest approach parameter, I_x is the mixed solvent dielectric constant, A_Φ is a function of mixed solvent dielectric constant D_m and the mixed solvent density d_m.

10. Models based on UNIQUAC-Electrolyte equations

UNIQUAC-Electrolyte was presented by Sander et al. (1986) [50]. This model was first applied by Kaewsichan et al. (2001) [51] for calculating the activity coefficient while representing CO_2-H_2S-MEA/MDEA-H_2O systems. UNIQUAC and extended UNIQUAC models has been successfully used for representing VLE data containing mercaptan and acid gaases systems [14,73]. These models will be discussed in reference [73].

11. Models based on Solvation effects

Stokes and Robinson (1948) [52] develop a model while taking into account that ions form complexes with water. In their model they calculate chemical equilibrium together with modified Debye and Hückel model. Later on Lu and Maurer (1993) [53] and Lu et al. (1996) [54] taking into account solvation equilibrium, however for calculating physical interaction used the conventional Debye-Hückel term and UNIQUAC equation.

12. Models based on equations of state

Models based on different equations of state have been used for the last 40 years to represent the solubility of acid gases in alkanolamine aqueous solutions. There are some models which do not use Debye and Hückel theory to describe electrolyte part of the solution, but rather use theory of statistical mechanics. For example one theory to represent long range interactions, is the mean spherical approximation (MSA), which is expressed in a simplified form by Fürst and Renon (1993) [55]. More considerable work has been done by Vallée et al. (1999) [56] , Chunxi and Fürst (2000) [57], Liu et al.(1999) [13]. In these equations of state (EoS), chemical equilibrium reactions in the liquid phase, have been used to describe both phases. The model developed by Vallée et al. (1999) [56] and Chunxi and Fürst (2000) [57] are based on the electrolyte EoS by Fürst and Renon (1993) [55]. Kuranov et al. (1997) [58] developed a model based on the quasi-chemical hole model by Smirnova and Victorov (1997) [59].

Button and Gubbins (1999) [60] use the statistical association fluid theory (SAFT) EoS to model the VLE of a ternary mixture containing CO_2-H_2O- MEA/ DEA. In this approach, no specific chemical reactions of absorption are included in the model. It seems like the chemical reactions are accounted for by assigning association sites to the molecules.

The common problem in most of the models is the large number of adjustable parameters that have to be fitted to experimental data. The complexity is due to the fact that both chemical and phase equilibrium are described simultaneously; furthermore, the liquid phase is a solution containing electrolytes but probably with a substantial ionic strength. Gabrielsen et al. (2005) [61] presented simple correlations for the calculation of the partial pressure and enthalpy of absorption of CO_2 solubility in different alkanolamines aqueous solutions. They use comparatively more simplified approach for the VLE calculations, substantially only one chemical equilibrium reaction is taken into account to describe the chemical absorption/desorption of CO_2.

13. Model Proposed by Renon and Fürst (1993)

The model of Fürst and Renon (1993) [55], Vallée et al. (1999) [56] and Chunxi and Fürst (2000) [57] are based on the expression of molar Helmholz energy. In this approach both the liquid and the vapor phase are represented with an equation of state. Additional electrolyte terms for the forces resulting from the presence of ions are added to the molecular equation of state. The Helmholtz energy is given by the equation below and is defined as the sum of four contributions:

$$(\frac{a-a^{o}}{RT}) = (\frac{a-a^{o}}{RT})_{RF} + (\frac{a-a^{o}}{RT})_{SR_1} + (\frac{a-a^{o}}{RT})_{SR_2} + (\frac{a-a^{o}}{RT})_{LR} \qquad (21)$$

Where RF represent repulsive forces, SR_1 stands for dissipation forces due to neutral molecules, SR_2 for dissipative forces due to ions and LR for long range forces between species. The long range interaction force is developed from mean spherical model for asymmetric electrolytes by introducing short range interactions between neutral molecules. Blum and Høye (1997) [63] provide mean spherical approximation expression. Planche and Fürst 1997 [62] further extend the expression by adding a short range interactions for charged and neutral hard spheres. Planche and Renon (1981) [64] extend the MSA with a non primitive model for electrolyte solutions. They provide a simple analytical expression for the Helmholtz energy of the mixture which can be used to represent osmotic coefficients of fully dissociated salt solution in water. Ball et al. (1985) [65] use the model proposed by Planche and Renon (1981) [64] and calculate the osmotic coefficients of strong aqueous electrolytes. Later on Fürst and Renon (1993) [55] modified their model while separating the short range interactions of neutral molecules and ionic species. Schwartzentruber and Renon (1989) [66] use SRK-EoS to calculate the interaction between neutral molecules, which was further modified by Vallée et al. (1999) [56] with Wong-Sandler mixing rule. Detailed information about SRK-EoS and Wong-Sandler mixing rule are available in following references [67, 68]. Thus at present the model consists of long range MSA term taken from Blum and Høye (1997), short range interaction term for ions taken from Fürst and Renon (1993) and short range terms for neutral molecules from SRK-EoS with Wong-Sandler mixing rule.

14. Model Proposed by Liu and coworkers (1999)

Based on perturbation theory Liu et al. (1999) [13] try to develop a real non primitive model for electrolyte aqueous fluids, which is composed of ion–ion, ion–dipole, dipole–dipole, Lennard–Jones dispersion, hydrogen bonding association and hard sphere repulsion terms. In this model they use MSA equation from Blum and Høye (1997) [63] and association term from SAFT equation of Huang and Radosz (1990) [68] .They could not successfully develop an entirely non-primitive electrolyte model, because they use water dielectric constant in their equation which violates the spirit of non-primitive ionic solutions and decreases the theoretical meaning of EoS. Although on the basis of perturbation theory, Anderko and Pitzer [69] and Jiang and Pitzer [70] developed the non-primitive EoS to correlate VLE data for NaCl and $CaCl_2$ aqueous solutions at high temperatures, respectively. But all of them ignored the ionic species in their systems.

15. Statistical Association Fluid Theory (SAFT)

SAFT equation is a model with basis in statistical mechanics. Unlike many other equations of state, it is able to account for non-spherical shaped molecules, attraction and repulsion between molecules and site-site interactions. But while it has been able to successfully model a wide range of fluid systems where other models have failed, the SAFT equation is also mathematically complicated. The successful predictive capabilities of the SAFT equation of state have been discussed in detail by Huang and Radosz (1990) [68] and Chapman et al (1990) [71]. Button and Gubbins (1999) [60] use the SAFT equation of state to model the vapor-liquid equilibrium of CO_2 in MDEA aqueous solution. They express the equation interms of Helmholz energy. Their equation contain four terms: repulsive, dispersive, chain formation and association. In this work no electrolyte term is actually included . A detailed review work has been done by Müller and Gubbins (2001) [72], where they discuss in detail SAFT theory and related approches for associating fluids

16. Conclusions

In this work the comparative study of the thermodynamic models which has been used for describing the phase behavior of acid gases and sulfur species in alkanolamine aqueous solutions, is discussed in detail. It is highlighted that most of the thermodynamic models are structured with terms representing long range interactions or intermediate/short range interactions only. Thus for the proper thermodynamic presentation of electrolyte systems, all different types of interactions: ion-ion, ion-dipole, dipole-dipole, molecule-molecule should be taken into account.

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References

[1] Anderko A., Wang P., Rafal M.,Electrolyte solutions: from thermodynamic and transport property models to the simulation of industrial processes, Fluid Phase Equilibr., 2002, 123-142.

[2] Pitzer K. S. Activity Coefficient in Electrolyte Solutions, 2nd Edition, CRC Press, Boca Raton, 1991.

[3] Reson H., Electrolyte solutions, Fluid phase Equilibr, 1986, 181-195.

[4] Zematis J. F., Clark D. M., Rafal M., Scrivner N. C., Handbook of Aqueous Electrolyte Thermodynamics, AIChE-USA,1986.

[5] Loehe J. R., Donohue M. D., Recent advances in modeling thermodynamic properties of aqueous strong electrolyte system, AIChE J., 43, 1997,180-195.

[6] Friedman H. L., A., Electrolyte Solutions at Equilibrium, Annu Rev. Phys. Chem., 32, 1981, 179-204.

[7] Conway B. E., Bockris J. M., Yeager E., Comprehensive Treatise of Electrochemistry, Plenum Press, New York-USA, 1983.

[8] Falkenhagen H., Theorie der Elektrolyte. S. Hirzel Verlag Leipzing, 1971.

[9] Debye P., Hückel E., Zur Theorie der Elektrolyte I, Gefrierpunktserniedrigung und verwandte Erscheinungen, Physikalische Zeitschrift, 1923, 24, 185-206.

[10] Kaatze U., The Dielectric Properties of Water in Its Different States of Interaction, J. Solution Chem., 1997, 26,1049-1112.

[11] Thomsen K., Electrolyte Solutions Thermodynamics,Crystallization, Separation methods, http://www.phasediagram.dk/

[12] Thomsen K., Aqueous Electrolytes: Model parameters and process simulation. PhD. Thesis, Denmark Technical University, 1997.

[13] Liu W., Li Y., Lu J., A new equation of state for real aqueous ionic fluids based on electrolyte perturbation theory, mean spherical approximation and statistical association fluid theory, Fluid phase Equilibr.,1999, 595-606.

[14] Addicks J., Solubility of Carbon Dioxide and Methane in Aqueous N-methyldiethanol Solutions at Pressures between 100 and 200 bar, PhD thesis, Norwegian University of Science and Technology, 2002.

[15] Kontogeorgis G. M., Voutsas E. C., Yakoumis I.V., and Tassios D. P., An Equation of State for Associating Fluids, Ind. Eng. Chem. Res., 1996, 35, 4310-4318.

[16] Mason J.W., Dodge B. F., Equilibrium Absorption of carbon dioxide by solutions of the Ethanolmaines. Trans., Am. Inst. Chem. Engr., 1936, 32, 27-47.

[17] Van Krevelen D. W., Hoftijzer P. J., Huntjens F. J., Composition and vapor pressures of aqueous solutions of Ammonia, Carbon dioxide and Hydrogen sulfide. Recueil, 1949, 68, 191-216.

[18] Atwood K., Arnold M. R., Kindrick R. C., Equilibria for the systems, ethanolamines-Hydrogen sulfide-water., Ind. Eng. Chem.,1957, 49, 1439-1444.

[19] Kent R. L., Eisenberg B., Better data for amines treating. Hydro. Proces., 1976, 55-87.

[20] Posey M. L., Tapperson K. G., Rochelle G. T., A simple model for prediction of acis gas solubilities in alkanolamines, Gas. Sep. purif., 1996, 10, 181-186.

[21] Danckwerts P. V., Mcneil K. M., The absorption of Carbon dioxide into aqueous amine solutions and the effects of catalysis., Trans. Instn. Chem. Engrs., 1967, 45, 32-49.

[22] Klyamer S. D., Kolesnikova T. L., Rodin Y., Equilibrium in Aqueous Solutions of Ethanolamines during the Simultaneous Absorption of Hydrogen Sulfide and Carbon Dioxide from Gases, Gazov. Promst., 1973, 18, 44-48.

[23] Lee J. I., Otto F. D., Mather A. E., The measurement and prediction of the solubility of mixtures of carbon dioxide and hydrogen sulfide in a 2.5 N Monoethanolamine solution, Can. J. Chem. Eng., 1976, 54, 214-219.

[24] Hu W., Chakma A., Modeling of Equilibrium solubility of CO2 and H2S in aqueous Amino methyl Propanol (AMP) Solutions, Chem. Eng. Comm., 1990, 94, 53-61.

[25] Hu W., Chakma A., Modeling of Equilibrium solubility of CO2 and H2S in aqueous Diglycolamine (DGA) Solutions. Chem. Eng. Comm., 1990, 68, 523-526.

[26] Li M. –H., Shen K. –P., Calculation of equilibrium solubility of carbon dioxide in aqueous mixture of monoethanolamine with methyldiethanolamine, Fluid phase Equilib., 1993, 85, 129-140.

[27] Haji-Suliman M. Z., Aroua M. K., Benamor A., Analysis of Equilibrium data of CO2 in aqueous solutions of diethanolamine (DEA), methyldiethanolamine (MDEA) and their mixtures using the modified Kent Eisenbeg model, Trans IChemE., 1998, 76, 961-968.

[28] Abu-Arabi M. K., Al-Muhtaseb S.A., modeling and prediction of the solubility of acid gases in diethanolamine solutions, High temp. High press., 2000, 32, 216-270.

[29] Boumedine R. S., Etude des systèmes Gaz Acide/Alcanolamine/Eau, PhD thesis, Mines-ParisTech, France, 2003.

[30] Park S. H., Lee K. B., Hyun J. C., Kim S. H., Correlation and prediction of the solubility of carbon dioxide in aqueous Alkanolamine and Mixed alkanolamine solutions, Ind. Eng. Chem. Eng., 2002, 41, 1658-1665.

[31] Debye P., Hückel E., Zur Theorie der Elektrolyte I, Gefrierpunktserniedrigung und verwandte Erscheinungen, Physikalische Zeitschrift, 1923, 24, 185-206.

[32] Edwards T. J., Newman J., Prausnitz J. M., Vapor-liquid Equilibria in Multicomponent aqueous solutions of volatile weak electrolytes, AIChE J., 1978, 24, 966-976.

[33] Deshmukh R. D., Mather A. E., A mathematical model for equilibrium solubility of hydrogen sulfide and carbon doixide in aqueous alkanolamine solutions, Chem. Eng. Sci., 1981, 26, 355-362.

[34] Guggenheim E. A., Turgeon J.C., specific interaction of ions, Trans. Fraday soc., 1955, 51, 747-761.

[35] Chakravarty T., Phukan U. K., Weiland R. H., Reaction of acid gases with mixtures of amines, Chem. Eng. Prog., 1985, 81, 32-36.

[36] Weiland R. H., Chakravarty T., Mather A.E., Solubility of CO2 and H2S in aqueous alkanolamines, Ind. Eng. Chem. Res., 1993, 34, 3173.

[37] Pitzer K. S., Thermodynamics of Electrolytes-I, Theoretical Basis and General Equations, J. Phys. Chem., 1973, 77(2), 268-277.

[38] Kuranov G., Rumpf B., Smirnova N.A., Maurer G., Solubility of single acid gases carbon dioxide and hydrogen sulfide in aqueous solutions of N-methyldiethanolamine in the temperature range 313-413 K at pressures up to 5 MPa, Ind. & Eng. Chem. Res., 1996, 35, 1959-1966.

[39] Pérez-Salado Kamps P., Balaban A., Jodecke M., Kuranov G., Smirnova N.A., Maurer G., Solubility of single acid gases carbon dioxide and hydrogen sulfide in aqueous solutions of N-methyldiethanolamine in the temperature range 313-393 K at pressure up to 7.5 MPa: new experimental data and model extension. Ind. Eng. Chem. Res., 2001, 40, 696-706.

[40] Silkenbaumer D., Rumpf B., Lichtenthaler R. N., Solubility of carbon dioxide in aqueous solutions of 2-amino,2-methyl, 1-propanol and N-methyldiethanolamine and their mixtures in the temperautre range from 313 to 353 K and pressures up to 2.7 MPa, Ind. Eng. Chem. Res., 1998, 37, 3133-3141.

[41] Clegg S. L., Pitzer K. S., Thermodynamics of multicomponent, miscible, ionic solutions: generalized equation for symetrical electrolytes, J. phys. Chem., 1992, 96, 3513-3520.

[42] Li Y. –G., Mather A. E., Correlation and Prediction of the solubility of CO2 in a mixed alkanolamine solution, Ind. Eng. Chem. Res., 1996, 35, 4804-4809.

[43] Chen C. -C, Britt H. I., Boston J.F., Evans L.B., Local composition model for excess Gibbs energy of electrolyte systems. Part I: Single solvent, single completely dissociated electrolyte systems, 1982, 28, 529-703.

[44] Renon H., Prausnitz J.M., Local compositions in thermodynamic excess functions for liquid mixtures, AIChE J., 1968, 14, 135-144.

[45] Dingman J. C., Jackson J. L., Moore T.F., Branson J.A., Equilibrium data for the H2S-CO2-Diglycolamine-water system, 62th Annual Gas Process Asso., San Francisco 1983.

[46] Austgen D. M., Rochelle G. T., Peng X., Chen C. -C., Model for vapor-liquid equilibria for aqueous acid gas-alkanolamine systems, Ind. Eng. Chem. Res., 1991, 30, 543-555.

[47] Lui Y., Zhang L., Watanasiri S., Representing vapor-liquid equilibrium for an aqueous MEA-CO2 system using the electrolyte nonrandom-two-liquid model, Ind. Eng. Chem. Res., 1999, 38, 2080-2090.

[48] Bishnoi S., Rochelle G.T., Physical and chemical solubility of CO2 in aqueous Methyldiethanolamine, Fluid Phase equilibr., 2000, 168, 241-258.

[49] Aroua M. K., Haji-sulaiman M. Z., Ramasamy K., Modeling of CO2 absorption in aqueous solutions of AMP and MDEA and their blend using Aspenplus. Sepra. & Puri. Tech., 2002, 29, 153-163.

[50] Sander B., Fredenslund A., Rasmussen P., Calculation of Vapor-Liquid Equilibria in Mixed Solvent /salt Systems using an extended UNIQUAC Equation, Chem. Eng. Sci., 1986, 41, 1171-1183.

[51] Kaewsichan L., Al-Boferson O., Yesavage V.F., Selim M.S., Predictions of the solubility of acid gases in Monoethanolamine (MEA) and methyldiethanolamine (MDEA) solutions using the electrolyte-UNIQUAC model, Fluid phase Equilib., 2001, 183, 159-171.

[52] Stokes R. H., Robinson R. A., Ionic hydration and activity in electrolyte solution. J. Am. Chem. Soc., 1948, 70, 1870-1874.

[53] Lu X., Maurer G., Model for describing activity coefficients in mixed electrolyte aqueous solutions. AIChE J., 1993, 39, 1527-1538.

[54] Lu X., Zhang L., Wang Y., Shi J., Maurer G., Prediction of activity coefficients of electrolytes in aqueous solutions at high temperatures, Ind. Eng. Chem. Res., 1996, 35, 1777-1784.

[55] Fürst W., Renon H., Representation of excess properities of electrolyte solutions using a new equation of state, AIChE J., 1993, 39, 335-343.

[56] Vallée G., Mougin P., Jullian S., Fürst W., Representation of CO2 and H2S absorption by aqueous solutions of Diethanolamine using an electrolyte equation of state. Ind. Eng. Chem. Res., 1999, 38, 3473-3480.

[57] Chunxi L., Fürst W., Representation of CO2 and H2S absorption by aqueous solutions in aqueous MDEA solutions using an electrolyte equation of state, Chem. Eng. Sci, 2000, 55, 2975-2988.

[58] Kuranov G., Rumpf B., Maurer G., Smirnova N. A., VLE modelling for aqueous systems containing methyldiethanolamine, carbon dioxide and hydrogen sulphide, Fluid Phase Equilibr., 1997, 136, 147.

[59] Smirnova N. A, Victorov A. I., Thermodynamic properties of pure fluids and solutions from the hole group-contribution model, Fluid Phase Equilibr., 1987, 34, 235.

[60] Button J. K., Gubbins K. E., SAFT prediction of vapor-liquid equilibria of mixtures containing carbon dioxide and aqueous monoethanolamine or diethanolamine, Fluid Phase Equilibr., 1999, 158−160, 175.

[61] Gabrielsen J., Michelsen M. L., Stenby E.H., Kontogeorgis G. M., A Model for Estimating CO2 Solubility in Aqueous Alkanolamines, Ind. Eng. Chem. Res., 2005, 44, 3348–3354.

[62] Planche H., Fürst W., Modélisation de la thermodynamique de l'extraction des Gaz acides par les Amines, Entropie., 1997, 202, 31–35.

[63] Blum L., Høye J. S., The Mean spherical model for asymmetric electrolytes: thermodynamic properties and the pair correlation function, J. Phys. Chem., 1997, 1311-1316.

[64] Planche H., Renon H., Mean spherical approximation applied to a simple but non-primitive model of interaction for electrolyte solutions and polar substances, J. Phys. Chem., 1981, 85, 3924-3929.

[65] Ball F. X., Planche H., Fürst W., Renon H., Representation of deviation from ideality in concentrated aqueous solutions of electrolyte using a mean spherical approximation molecular model, AIChE J., 1985, 31, 1233-1240.

[66] Schwartzentruber J., Renon H., Extension of UNIFAC to high pressures and temperatures by the use of a cubic equation of states, Ind. Eng. Chem. Res., 1989, 28, 1049-1055.

[67] Wong D. S. H., Sandler S. I., A theoretical correct mixing rule for cubic equations of state, AIChE J., 192, 38, 671-680.

[68] Huang S. H., Radosz M., Equation of state for small, large and associating molecules. Ind. Eng. Chem. Res., 1990, 29, 2284-2294.

[69] Anderko A., and Pitzer K. S., Equation of state representation of phase-equilibria and volumetric properties of the system NaCl–H2O above 573 K, Geochim. Cosmochim. Acta, 1993, 57, 1657–1680.

[70] Jiang S., Pitzer K.S., Thermodynamics Phase equilibria and volumetric properties of aqueous CaCl2 by an equation of state, AIChE J., 1994, 42(2), 585-594.

[71] Chapman W.G., Gubbins K.E., Jackson G., Radosz M., New Reference Equation of State for Associating Liquids. Ind. Eng. Chem. Res., 1990, 29, 1709-1721.

[72] Müller E. A, Gubbins K. E, Molecular-based equation of state for associating fluids: a review of SAFT and related approaches, Ind. Eng. Chem. Res., 2001, 40, 2193-2211.

[73] Awan J. A., Thomsen K., Coquelet C., Fosbøl P. L., Richon D., VLE Measurements and Modeling of the n-Propyl Mercaptan-Methane-Water System, J. Chem. & Eng. Data, 2010, 55,842–846.

[74] Awan J. A., Tsivintzelis I., Breil M.P., Coquelet C., Richon D., Kontogeorgis G. M., Phase Equilibria of Mixtures Containing Organic Sulfur Species (OSS) and Water/ Hydrocarbons: VLE Measurements and Modeling Using the Cubic-Plus-Association Equation of State, Ind. Eng. Chem. Res.,2011, 1076-1082.