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Measurement and modeling of solubility of H_2S in aqueous diisopropanolamine solution

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Abstract−Modeling of solubility of acid gases in aqueous alkanolamine solutions is essential for design of an absorber for natural gas sweetening. In this work an apparatus similar to the device of Hayduk and Chen (1970), which was improved by Pahlavanzadeh and Motahhari (1997), for the measurement of gas solubility data by the synthetic method was used. The solubility of hydrogen sulfide in aqueous diisopropanolamine (DIPA) solution in mass concentration range of 30-40% for 101,325 Pa pressure and for temperature ranging from 313-343 K was reported. The obtained experimental solubility data of H_2S in aqueous solutions of DIPA was used to predict the different interaction parameters of modified UNIQUAC-NRF model for calculating the activity coefficients. For nonideality of species in liquid phase, the UNIQUAC-NRF equation with ion-pair approach was applied. For long range interaction, the Pitzer-Debye-Huckel term was used.

Key words: Diisopropanolamine, Hydrogen Sulfide, Modeling, Solubility, Data

INTRODUCTION

The removal of CO_2 and H_2S from gas stream is an important operation in the natural gas and synthetic ammonia industries, oil refinery and petrochemical plants. Design of gas treating processes with alkanolamine-based aqueous solvents requires knowledge of the vapor-liquid equilibrium (VLE) of the CO_2-H_2S-alkanolamine-water system [1]. Prior to any modeling activity, a precise knowledge of acid gas solubility in the solvent is essential. For specific formulations of solvents, which can be encountered when developing new processes, sufficient data cannot usually be found in the open literature [2], and few solubility data for Hydrogen Sulfide in DIPA solutions and modeling of it have been published [3].

Diisopropanolamine (DIPA) has been widely used in Europe for the removal of the acid gases from synthesis gas and refinery gases and liquids. It is used in the Adip process, the Sulfinol process, and the SCOT process, all licensed by Shell [4]. DIPA solution is reported to be less corrosive than MEA or DEA solution, and to have a greater selectivity for H_2S over CO_2 than either MEA or DEA.

Another advantage claimed for DIPA solutions is that they require less heat in the regeneration of the solution.

In the Sulfinol process, aqueous DIPA is in combination with the physical solvent Sulfolane (a typical Sulfinol solution contains 40% DIPA, 40% Sulfolane, 20% water) [4]. The SCOT process, a tail-gas treating process employs a DIPA solution in order to effect a selective removal of H_2S from a stream containing H_2S and CO_2. DIPA is regarded as the best compromise among the alkanolamines.

In this research, theoretical and experimental investigation for solubility of H_2S in DIPA has been done. The experimental data were used to estimate the modified UNIQUAC-NRF model parameters using an optimization method.

EXPERIMENTAL SECTION

The solubility of hydrogen sulfide in aqueous Diisopropanolamine solution within temperatures from 313.15 to 343.15 K and atmospheric pressure has been measured. To determine the solubility of gases in liquids, the solvent must first be saturated with the gas. So, the solvent and the solute are in contact in order to make the solution saturated with the solute. To estimate the solubility of gas in the solvent, the volume of solute gas is measured at experimental conditions and the molar volume of solute gas is calculated

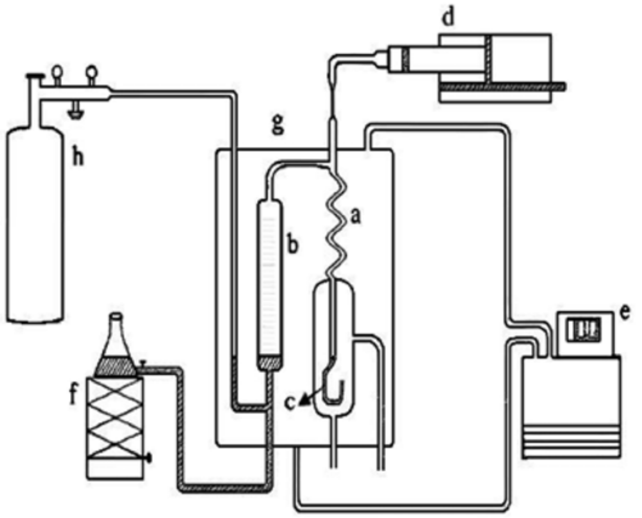

Fig. 1. The apparatus for measuring the solubility of gases in liquid.

a. Spiral tube	e. Thermometer
b. Scaling burette	f. Mercury jack
c Manometer	g. Cell
d. Syringe pump	h. H_2S capsule

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Table 1. Experimental data for H_2S solubility in aqueous DIPA solution

			First exp.	Second exp.	Third exp.	Average
DIPA mass percent	Temperature (K)	DIPA+H_2O (ml)	V_{H_2S} (ml)	V_{H_2S} (ml)	V_{H_2S} (ml)	V_{H_2S} (ml)
30%	313	0.3397	0.017	0.015	0.019	0.017
	323	0.4262	0.016	0.022	0.016	0.018
	333	0.4691	0.16	0.16	0.16	0.016
	343	0.6284	0.015	0.015	---	0.015
31.82%	313	0.6969	0.046	0.040	0.040	0.042
	323	0.3708	0.019	0.020	0.018	0.019
	333	0.5637	0.023	0.023	---	0.023
	343	0.7180	0.020	0.022	0.021	0.021
35%	313	0.2986	0.02	0.02	---	0.02
	323	0.3366	0.02	0.021	0.019	0.02
	333	0.3621	0.018	0.018	---	0.018
	343	0.5488	0.021	0.02	0.19	0.02
40%	313	0.3266	0.022	0.021	0.02	0.021
	323	0.3945	0.016	0.02	0.02	0.02
	333	0.4791	0.017	0.022	0.02	0.02
	343	0.3049	0.009	0.011	0.01	0.01

by an equation of state. The apparatus for measuring the solubility of a gas in a liquid solvent is similar to the device of Hayduk and Cheng [5] which later was improved by Pahlavanzadeh and Motahhari [6] (1997).

This apparatus, presented in Fig. 1, consists of the following parts:

1. Spiral Tube

In this tube, the number of turns is constant; the vapor and liquid phase interact in this tube. The number of turns, the slope, and the diameter of the tube depend on the solute and solvent. As the solubility of the gas increases, the number of turns must be increased and the slope of the tube decreased to assure that the solvent and solute are in equilibrium at the end of the spiral tube.

2. Scaling Burette

To estimate the volume of the solvent gas and also to maintain the gas in the apparatus, a scaling burette is needed. This burette is jointed to the spiral tube at the top, and is connected to an internal valve at the bottom. This valve is connected to a H_2S capsule and a mercury vessel. The mercury vessel is on a moving platform for adjusting the levels of the solution in the manometer.

3. Manometer

At the bottom of the spiral tube a manometer is constructed. It shows the pressure variation in the apparatus. One end of the manometer is joined to the spiral tube, and the other end is open to the atmosphere.

4. Syringe Pump

After degassing, the solvent is injected into the apparatus at a constant rate by a syringe pump. The pump is composed of two parts: a minicomputer that controls the rate of injection and a mechanical part for maintaining good accuracy. Each experiment was repeated at least 2 times, and the average results were considered.

For measurement of the gas solubility, first the solvents were put into a vacuum flask for degassing. Vacuum was then applied and the degassing process was continued for 10 min. Next, the degassing solvent was mixed to prepare a solution containing a certain percentage. The mixed solvent was subsequently injected slowly into the spiral tube of the solubility apparatus by means of the syringe pump. The flow rate of the injection was 2.24 ml/hr. The solvent became saturated with the gas while flowing down the spiral tube. After the first droplet of solution appeared in the U-tube manometer, the flow of the solute gas was shut off and the mercury level was raised by means of lifting the mercury vessel. As the gas dissolved in the solvent, the pressure inside the apparatus dropped. The gas pressure in the apparatus was adjusted by elevating the mercury vessel and with the help of the U-shaped tube at the end of the spiral tube. The volume of mercury displaced was equal to the solute gas dissolved in the solvent. The volume of mercury or the elapsed time was recorded. The solubility was then calculated by using the reduction in the gas volume and solvent flow rate.

The results of gas volume reduction recorded for each concentration and temperature of the solution are presented in Table 1.

From the experimental measurement data, the volume of dissolved gas was calculated. The truncated virial equation of state was used in order to calculating of the molar volume of gas, V_g.

By using the critical data and acentric factor, ω, that are presented in Table 2, the second coefficient of the virial equation for H_2S can be calculated. The number of dissolved moles of H_2S in Diisopropanolamine solution is calculated as follows:

$$n_g = \frac{V}{V_g} \tag{1}$$

Where V is the displaced volume of mercury and V_g is the molar volume of H_2S. Also the amount of consumed solvent and the mole numbers of solution is calculated by Eq. (2):

Table 2. Critical coefficient and Acentric factor of H_2S [8]

T_c (K)	373.53
P_c (Pa)	9000000
V_c (m^3/kmol)	0.099
Acentric factor (w)	0.096

Table 3. Density of DIPA (gr/cm^3) [7,9]

Temperature (K)	Density of DIPA (gr/cm^3)
313	0.98889
323	0.9849
333	0.9773
343	0.96958

Table 4. Vapor pressure of H_2S and H_2O

	Vapor pressure (Pa)	
H_2S	-exp[85.584+((−3839.9)/T)−11.199×ln(T)+0.018848×T]	[8]
H_2O	-exp[73.649+((−7258.2)/T)−7.3037×ln(T)+(4.1653E−06)×T^2]	[8]

Table 5. Data from experiment and calculated α for H_2S in DIPA solution with mass fraction of 30%

Temperature (K)	313	323	333	343
mass%	30	30	30	30
F (ml/hr)	2.24	2.24	2.24	2.24
t (second)	546	685	754	1010
V (ml)	0.017	0.018	0.016	0.015
DIPA+H_2O (ml)	0.3397	0.4262	0.4691	0.6284
DIPA+H_2O (gr)	0.3391	0.4251	0.4671	0.6244
DIPA (gr)	0.10174	0.12754	0.14013	0.18734
n_{DIPA} (mole)	0.000764	0.000958	0.001052	0.001407
ρ_{sol} (gr/cm^3)	998.215	997.5	995.6	993.7
B^o	−0.4765	−0.4491	0.4238	−0.40035
B^1	−0.16769	−0.12308	−0.0851	−0.05262
B	−0.16999	−0.15904	−0.14904	−0.13989
V_g (ml)	29.63747	30.60046	31.56247	32.52362
n_g (mole H_2S)	0.0005736	0.0005883	0.0005069	0.0004743
a	0.750924	0.614257	0.481817	0.3372

Mass%: DIPA weight Fraction, F: Solvent flow rate (ml/hr), T: time (second), V: H_2S solved volume (ml), n_{DIPA}: number of DIPA moles, ρ_{sol}: Density of DIPA+H_2O (gr/cm^3), B: second Virial coefficient, V_g: Virial volume (ml), n_g: mole number of solved H_2S, α: mole of H_2S/mole of DIPA (calculated)

$$w=(F*t*\rho_{sol}*\text{mass\%})/(100*M) \tag{2}$$

Where F is the injection velocity of solvent into the apparatus, t is the solubility time, ρ is the density of DIPA solution and M is the molecular weight of aqueous DIPA solution. The densities of DIPA solution at different Temperatures were found from the database of Aspen Plus [7] as shown in Table 3. The value of the density of DIPA solution was correlated as a function of temperature and concentration as Eq. (3):

$$\rho_{sol}=1/\left(\left(\frac{100-\text{mass\%}}{\rho_{DIPA}*100}\right)+\frac{\text{mass\%}}{\rho_1*100}\right) \tag{3}$$

Also the loading factor of H_2S in aqueous DIPA solution is calculated as follows:

$$\alpha=\frac{\text{mole } H_2S}{\text{mole DOPA}} \tag{4}$$

Table 6. Data from experiment and calculated α for H_2S in DIPA solution with mass fraction of 31.82%

Temperature (K)	313	323	333	343
mass%	31.82	31.82	31.82	31.82
F (ml/hr)	2.24	2.24	2.24	2.24
t (second)	426	596	906	1154
V (ml)	0.042	0.019	0.023	0.021
DIPA+H_2O (ml)	0.696983	0.370844	0.563733	0.718044
DIPA+H_2O (gr)	0.695569	0.369791	0.561	0.71305
DIPA (gr)	0.22132992	0.1176675	0.178510077	0.226892365
n_{DIPA} (mole)	0.001662	0.000883	0.00134	0.001704
ρ_{sol} (gr/cm^3)	997.97	997.159	995.151	993.044
B^o	−0.47654	−0.44909	−0.42377	−0.40035
B^1	−0.16769	−0.12308	−0.0851	−0.05262
B	−0.16999	−0.15904	−0.14904	−0.13989
V_g (ml)	29.63747	30.60046	31.56247	32.52362
n_g (mole H_2S)	0.0014171	0.0006209	0.0007237	0.0006473
a	0.852785	0.702814	0.54	0.38

Mass%: DIPA weight Fraction, F: Solvent flow rate (ml/hr), T: time (second), V: H_2S solved volume (ml), n_{DIPA}: number of DIPA moles, ρ_{sol}: Density of DIPA+H_2O (gr/cm^3), B: second Virial coefficient, V_g: Virial volume (ml), n_g: mole number of solved H_2S, α: mole of H_2S/mole of DIPA (calculated)

Table 7. Data from experiment and calculated α for H_2S in DIPA solution with mass fraction of 35%

Temperature (K)	313	323	333	343
mass%	35	35	35	35
F (ml/hr)	2.24	2.24	2.24	2.24
t (second)	480	541	582	882
V (ml)	0.02	0.02	0.018	0.02
DIPA+H_2O (ml)	0.298667	0.336622	0.362133	0.5488
DIPA+H_2O (gr)	0.297933	0.335471	0.36007	0.544366
DIPA (gr)	0.1042765	0.117415	0.126025	0.19053
n_{DIPA} (mole)	0.000783	0.000882	0.000946	0.00143
ρ_{sol} (gr/cm^3)	997.543	996.581	994.304	991.9202
B^o	−0.47654	−0.44909	-0.42377	−0.40035
B^1	−0.16769	−0.12308	−0.0851	−0.05262
B	−0.16999	−0.15904	−0.14904	−0.13989
V_g (ml)	29.63747	30.60046	31.56247	32.52362
n_g (mole H_2S)	0.0006748	0.0006535	0.0005772	0.0006149
a	0.861934	0.741396	0.61	0.429877

Mass%: DIPA weight Fraction, F: Solvent flow rate (ml/hr), T: time (second), V: H_2S solved volume (ml), n_{DIPA}: number of DIPA moles, ρ_{sol}: Density of DIPA+H_2O (gr/cm^3), B: second Virial coefficient, V_g: Virial volume (ml), n_g: mole number of solved H_2S, α: mole of H_2S/mole of DIPA (calculated)

Experimental data such as DIPA weight fraction, solvent flow rate, volume of dissolved gas and calculated for H_2S in DIPA solution for different concentrations and different Temperatures are reported in Tables 5 to 8.

The dissociation constants of DIPA were obtained from the data-

Table 8. Data from experiment and calculated α for H_2S in DIPA solution with mass fraction of 40%

Temperature (K)	313	323	333	343
mass%	40	40	40	40
F (ml/hr)	2.24	2.24	2.24	2.24
t (second)	525	634	770	490
V (ml)	0.021159	0.022	0.021195	0.01
DIPA+H_2O (ml)	0.326667	0.394489	0.479111	0.304889
DIPA+H_2O (gr)	0.325645	0.392782	0.475745	0.301888
DIPA (gr)	0.1302579	0.1571127	0.1902981	0.1207554
n_{DIPA} (mole)	0.000978	0.00118	0.001429	0.000907
ρ_{sol} (gr/cm^3)	996.872	995.6725	992.975	990.1589
B^o	−0.47654	−0.44909	−0.42377	−0.40035
B^1	−0.16769	−0.12308	−0.0851	−0.05262
B	−0.16999	−0.15904	−0.14904	−0.13989
V_g (ml)	29.63747	30.60046	31.56247	32.52362
n_g (mole H_2S)	0.00039108	0.0007189	0.0006715	0.00029919
a	0.73	0.609474	0.47	0.33

Mass%: DIPA weight Fraction, F: Solvent flow rate (ml/hr), T: time (second), V: H_2S solved volume (ml), n_{DIPA}: number of DIPA moles, ρ_{sol}: Density of DIPA+H_2O (gr/cm^3), B: second Virial coefficient, V_g: Virial volume (ml), n_g: mole number of solved H_2S, α: mole of H_2S/mole of DIPA (calculated)

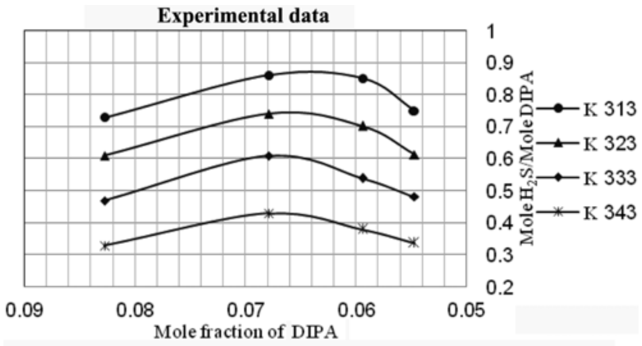

Fig. 2. Loading factor whit respect to mole fraction of DIPA for various temperature base on experimental data.

base of ref. [7]. The vapor pressure of H_2S and H_2O base on ref. [8] was used as shown in Table 4.

The densities and dielectric constants of DIPA obtained from Ref. [9] and Ref. [10] are presented in Tables 3 and 4.

Fig. 2 this figure shows that in the entire range of DIPA concentrations, an increase in temperature led to increasing H_2S solubility in DIPA+H_2S solution.

Also, increasing the concentration of DIPA until special point caused an increase in solubility but after that the solubility is decreased. Maximum solubility of H_2S takes place in 35 mass percent of DIPA solutions.

THERMODYNAMIC FRAMEWORK

1. Standard State

In this work, both water and alkanolamine are treated as a solvent. The standard state associated with each solvent is pure liquid at temperature and pressure of system. The adopted standard state for ionic (ion pair) solute is ideal infinity dilute aqueous solution (infinity dilute in solute and alkanolamine) at the system temperature and pressure. Finally, the reference state chosen for molecular solute (H_2S) is also ideal, infinity dilute aqueous solution at the system temperature and pressure. This leads to following unsymmetrical convention for normalization of activity coefficient.

Solvent:
$\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$

Pair ions and molecular solutes:
$\gamma_i^* \rightarrow 1$ as $x_i \rightarrow 0$ & $x_{s \neq w} = 0$

Where the subscript s refers to any nonaqueous solvent, i refers to ionic or neutral solutes and w refers to water. The activity coefficients of all species are assumed to be independent of pressure.

2. Chemical Equilibria

In aqueous solution H_2S react with DIPA to produce a number of ionic complex species as the following equilibrium reactions:

$$DIPAH^+ + H_2O \overset{k_1}{\Leftrightarrow} H_3O^+ + DIPA \tag{5}$$

$$H_2S + H_2O \overset{k_2}{\Leftrightarrow} H_3O^+ + HS^- \tag{6}$$

The equation governing chemical equilibria may be written as follows:

$$K_j = \Pi_i(\gamma_i x_i)^{\upsilon_{ij}} \qquad j=1, \ldots, 5 \tag{7}$$

Where x_i and γ_i are the mole fraction and activity coefficient of species i, υ_{ij} is the stoichiometric coefficient for component i in reaction j.

For simplicity, the molecular species of H_2S and the ionic species of S^{-2} in aqueous phase are neglected, because of their low concentrations in comparison with the other species dissolved in mixed alkanolamine+water system.

3. Phase Equilibria

The nonideality of gas phase was neglected and the fugacity of molecular species (H_2S) in liquid phase is written as:

$$f_i = X_i H_i \gamma_i \qquad (i=H_2S) \tag{8}$$

Where Henry's law was used as a reference state and "H" refers to Henry's constant. We assume that the solubility of molecular species in liquid phase is ideal so the activity coefficient, γ_i, is unity and the partial pressure of hydrogen sulfide is expressed as:

Table 9. Required data (Density (Kg/m^3), Dielectric constant, Henry's constant)

		Expression	
Density (Kg/m^3)	H_2O	$d=0.999382+0.00007208t-7.28491*10^{-2}t^{-2}+2.65177*10^{-2}t^{-2}$	[8]
Henry's constant	H_2S	$\ln(H_{H_2S})=358.138-(13236.8/T)-55.0551\ln(T)+0.059565T$	[8]
Dielectric constant	DOPA	$D=28.8247-0.07191T+0.000074526T$	[10]
Dielectric constant	H_2O	$D=78.54[1-4.579*10^{-2}*(t-25)+1.19*10^{-2}(t-25)^2-2.8*10^{-2}(t-25)^2]$	[11]

$$P_i=x_iH_i \tag{9}$$

The unit of Henry's constant, H_i, is in Pascal and its temperature dependence is expressed by the same function form as Eq. (10).

$$\ln H_i=C_1+C_2/T+C_3\ln T+C_4T \tag{10}$$

Where the coefficients C1-C4 of Eq. (10) have been taken from databases of Aspen and are shown in Table 9.

4. Activity Coefficient

The molar excess Gibbs energy of an electrolyte system was assumed to consist of short-range (g^{SR}) and long-range (g^{LR}) terms:

$$g^E=g^{LR}+g^{SR} \tag{11}$$

For short-range interaction with ion pair assumption the UNIQUAC-NRF equation as a nonelectrolyte model with both combinatorial and residual terms is expressed as:

$$\frac{g^{SR}}{RT}=\left(\frac{g^E}{RT}\right)_C+\left(\frac{g^E}{RT}\right)_R \tag{12}$$

The combinatorial and residual parts of activity coefficient from UNIQUAC-NRF equation were used for calculation of activity coefficient of both ion-pair and molecular species.

In modeling of the electrolyte system, we assumed that the cations and anions to form the ion pairs; for instance, the $DIPAH^+$ and HS^- ions form an ion-pair as $DIPAH^+$+HS^-. For an electrolyte solution containing n cations and m anions then "m*n" ion-pairs can be formed. So the probability of formation of an ion-pair, $c_{Z_a}a_{Z_c}$, was calculated as:

$$r_{c_{Z_a}a_{Z_c}}=\frac{z_c[c_{z_c}]}{\Sigma_i z_i[c_{z_i}]}*\frac{z_a[a_{z_a}]}{\Sigma_j z_j[a_{z_j}]} \tag{13}$$

Where the values in the brackets show the concentration of both cation and anion species. Thus, using the electroneutrality of the system, $\Sigma_i z_i[c_{z_i}]=\Sigma_j z_j[a_{z_j}]$, the concentration of the ion-pair can be obtained:

$$[c_{z_a}a_{z_c}]=r_{c_{z_a}a_{z_c}}*\frac{1}{2}[\Sigma_i z_i[c_{z_i}]+\Sigma_j z_j[a_{z_j}]] \tag{14}$$

The volume (r) and surface (q) parameters of an ion-pair are calculated as follows:

$$q_{c_{z_a}a_{z_c}}=z_aq_c+z_cq_a \text{ and } r_{c_{z_a}a_{z_c}}=z_ar_c+z_cr_a \tag{15}$$

The values of r and q for molecules are presented in Table 10. On the other hand, the residual activity coefficient of an ion-pair is expressed as:

$$\ln\gamma^R_{c_{z_a}a_{z_c}}=\frac{z_a}{z_c+z_a}\ln\gamma^R_c+\frac{z_c}{z_c+z_a}\ln\gamma^R_a \tag{16}$$

Where γ_c and γ_a are the activity coefficient of cation and anion, respectively.

Table 10. The volume (r) and surface (q) parameters of solvents [7]

Solvent	MW	r	q
H_2O	18.02	0.92	1.3997
DIPA	133.19	7.35107	6.13904
H_2S	34	1.2338	1.07

Table 11. The values of the coefficient of binary interaction parameters obtained by using the NRTL [18] binary interaction parameters for DIPA+H_2O system

	$\tau_{nn'}$	$x_{nn'}$	$y_{nn'}$
H_2O-DIPA	τ_{22}	−3.6019	1831.198
DIPA-H_2O	τ_{22}	1.94125	0.986899

Due to presence of the common ions in the system, one may define the average activity coefficient of the common ion in terms of the activity coefficient of ion-pairs as:

$$\ln\bar{\gamma}^R_c=\Sigma_a\left(\frac{[c_{z_a}a_{z_c}]}{\Sigma_a[c_{z_a}a_{z_c}]}\right)*\ln\gamma^R_{c_{z_a}a_{z_c}} \tag{17}$$

$$\ln\bar{\gamma}^R_a=\Sigma_c\left(\frac{[c_{z_a}a_{z_c}]}{\Sigma_c[c_{z_a}a_{z_c}]}\right)*\ln\gamma^R_{c_{z_a}a_{z_c}} \tag{18}$$

For long-range term, the Pitzer-Debye-Huckel equations for molecular and ionic species were used [14-17].

5. Determining the Interaction Parameters

For DIPA+H_2O binary systems, the binary parameters of UNIQUAC-NRF equation, τ_{ij}, were obtained by using the NRTL [18] binary interaction parameters. In fact, due to inaccessibility of the binary activity coefficient data for the binary system, the values of activity coefficient were reproduced from the NRTL energy parameters. So the binary interaction parameters were assumed to be dependent on temperature and correlated by the following relation:

$$\tau_{nn'}=x_{nn'}+\frac{y_{nn'}}{T} \tag{19}$$

Table 11 shows the binary parameters and the fitted coefficients for aqueous system of DIPA.

To determine the interaction parameters of the UNIQUAC-NRF equation, we used the solubility data of the gas-amine in the concentration range of 30-40 mass percent and temperature range of 313-343 K. The interaction parameters were assumed as a function of temperature as Eq. (20) [11]:

$$a_{ij}=x_{ij}+\frac{y_{ij}}{T}+z_{ij}\left[\frac{T-T^w}{T}+\ln\frac{T}{T^0}\right] \tag{20}$$

Where x, y and z are the coefficients of the interaction parameters.

By combining chemical reactions (5) and (6), for DIPA-H_2S-H_2O system one can obtain:

$$H_2S+DIPA\xleftrightarrow{K_1/K_2}DIPA^++HS^- \tag{21}$$

Only four true species, two neutral solvents and two ionic species, exist in this ternary system and we may assume that all the dissolved H_2S is converted into HS^- ions. The concentration of each species can be obtained by electroneutrality condition and mass balance equations as follows:

$$C_{DIPAH^+}=C_{HS^-}=C^0_{DIPA}\alpha \tag{22}$$

$$C^0_{DIPA}=C_{DIPA}+C_{DIPAH^+} \tag{23}$$

$$C^0_{H_2O}=C_{H_2O}+C_{DIPAH^+}-C_{HS^-} \tag{24}$$

Table 12. The coefficients of the interaction parameters for ternary system DIPA-H_2S-H_2O. 1=H_2O, 2=DIPA, 3=DIPAH$^+$HS$^-$ parameter (a_{ij})

Parameter	Temperatures (K)			
	313	323	333	343
a_{13}	−554.662217	−585.63493	−648.63389	−760.12646
a_{31}	−195.367393	−149.59604	−95.899873	−61.90655
a_{23}	−256.374657	−253.96883	−243.94156	−224.90026
a_{32}	209.784812	210.649300	213.391664	209.72510

Table 13. The coefficients of the interaction parameters for ternary system DIPA-H_2S-H_2O. 1=H_2O, 2=DIPA, 3=DIPAH$^+$HS$^-$

Coefficients	Parameter (a_{ij})			
	a_{13}	a_{31}	a_{23}	a_{32}
x_{ij}	−599.8961205	−283.2059267	−273.889592	206.2936492665
y_{ij}	−0.59474688	13.79293584	2.531196101	3.586141867995
z_{ij}	−69.45433729	870.7323325	166.1308638	37.076594812

Where the superscript “o” represents the initial concentration and the variable α is the H_2S loading in equilibrated liquid phase, expressed in mole of H_2S/mole of amine. All experiments were performed at low pressure, therefore $\varphi_1=1$ and $y_1P=P_1$.

So the modified Raoult’s law has been simplified to:

$$\gamma_1=\frac{P_1}{x_1P_1^{sat.}} \tag{25}$$

If species 1 is H_2O, for species H_2S we have:

$$\gamma_2=\frac{P_2}{x_2P_2^{sat.}} \tag{26}$$

Total pressure is equal to:

$$P=y_1P+y_2P=x_1\gamma_1P_1^{sat.}+x_2\gamma_2P_2^{sat.} \tag{27}$$

And according to UNIQUAC-NRF activity coefficient:

$$\ln\gamma_n=\ln\gamma_n^R+\ln\gamma_n^C+\ln\gamma_n^{PDH} \tag{28}$$

Directly we can have $\ln\gamma_n^C+\ln\gamma_n^{PDH}$ because of independence of inter activity parameters and $\ln\gamma_n$ has been obtained from Raoult’s low equation. Only $\ln\gamma_n^R$ is involving with interaction model.

After replacing 4 experimental data in set finally we reach a set of 4 equations with 4 unknown (a_{23}, a_{32}, a_{13}, a_{31}) and by solving this set of equations by try and error we approach answers. So the objective functions for optimization of the interaction parameters is:

$$\delta\%=100\times(1/n)*\Sigma_{i=1}^{n}|[(\ln\gamma_n^R)_{Cal.}-(\ln\gamma_n^R)_{Exp.}]/(\ln\gamma_n^R)_{Exp.}| \tag{29}$$

By global optimization of experimental VLE data [19], the interaction parameters for ternary system of DIPA-H_2S-H_2O were calculated and shown in Tables 12 and 13.

Fig. 2 shows the loading factor of H_2S versus the mole fraction of DIPA for the aqueous ternary system of DIPA+H_2S+H_2O. Agreement between experimental data and the calculated values is very good.

Calculations were carried out for the DIPA-H_2S-H_2O system, and using general relation (29), globally all six interaction parameters were optimized and shown in Tables 11 and 13.

CONCLUSION

In the entire range of DIPA concentrations, an increase in temperature led to an increase in H_2S solubility in DIPA+H_2S solution. But for any temperature, the loading factor (α) has a maximum point.

In this work, using ion-pair assumption the UNIQUAC-NRF activity coefficient equation was applied to model the solubility of H_2S in aqueous solution of DIPA. The model with an average deviation of 8.6% for solubility correlation of H_2S in DIPA solution successfully correlated the experimental data at the whole range of temperatures and concentrations. The model can be used for prediction of solubility of acid gases in the alkanolamines and also may be used in equilibrium stage design calculation of the absorption columns for gas sweetening processes.

NOMENCLATURE

$A\varphi$: Debye-Huckel parameter for osmotic coefficient
A_x : Debye-Huckel parameter on mole fraction basis
a : interaction parameter of UNIQUAC-NRF
F : flow
C : molar concentration
D : dielectric constant
d : density, g/ml
f : fugacity
gE : excess Gibbs free energy
H : Henry’s constant [Pa]
K : thermodynamic chemical equilibrium constant
P : pressure
T : absolute temperature [K]
t : temperature [°C]
v : molar volume
w : weight fraction
x : liquid-phase mole fraction based on true molecular and ionic species.
z : valence of anion

Greek Letters

α : H_2S loading in liquid phase, mol of gas/mol of amine, loading factor
τ : interaction parameter between and among neutral species
φ : volume fraction

γ : activity coefficient
ω : acentric factor
s : objective function

Superscripts

^{o} : initial concentration
* : unsymmetrical convention
PDH : Pitzer-Debye-Huckel
LR : long- range
SR : short-range
C : combinatorial
R : residual

Subscripts

a, X : anion
c, M : cation
c : critical
i, j : any species
mix : mixed solvent system
sol : solution
n, s : neutral solvent species
sat. : saturated
w, 1 : water
1 : H_2O
2 : DIPA
3 : $DIPAH^+HS^-$
M : $DIPAH^+$
X : H_2S^-
Exp. : experimental value

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