

PREDICTION OF CO₂ AND H₂S SOLUBILITY IN AQUEOUS MDEA SOLUTIONS USING AN EXTENDED KENT AND EISENBERG MODEL

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Gas sweetening, the removal of acid gases (H₂S and CO₂) by absorption in aqueous alkanolamine solutions, is an important gas treatment operation. Methyldiethanolamine (MDEA) is widely employed for gas sweetening, because of its high absorption capacity and flexibility to meet process requirements. For process simulation or design, realistic predictions of acid gas solubilities in MDEA solutions are needed. In the context of flowsheet synthesis, design and optimisation, a reliable model that is simple to use and reasonably accurate is required. This paper presents a new model for the prediction of solubilities of both H₂S and CO₂ in aqueous MDEA solutions. The model extends the Kent and Eisenberg (1976) model, which was developed for primary and secondary amines. Model predictions are validated against experimental data for both single and mixed acid gas systems. The applicability of the model is further demonstrated by comparing flowsheet simulation results and plant data for commercial units operating over a wide range of conditions.

KEYWORDS: thermodynamic model, alkanolamine, vapour–liquid equilibrium, methyldiethanolamine

INTRODUCTION

Gas sweetening is a fundamental step in gas treatment processes. In gas sweetening units, acid gases (H₂S and CO₂) are chemically absorbed from a gas using aqueous alkanolamine solutions, to product a “sweet gas”. The solvent is regenerated in a desorption column and the purified (or “lean”) solvent is recycled to the absorption column. Alkanolamines are the most commonly used solvents for gas sweetening, as they are economical for a range of gas compositions. Methyldiethanolamine (MDEA) has been increasingly applied for gas sweetening, largely because of its high capacity and excellent flexibility to meet process requirements. Vapour–liquid equilibrium (VLE) modelling of acid gas–aqueous amine systems is critical for synthesis, design and analysis of gas sweetening plants.

Existing vapour–liquid equilibrium models can be broadly divided into two main classes: empirical models based on the model of Kent and Eisenberg (1976) and activity coefficient-based models.

Kent and Eisenberg (1976) proposed a VLE model to predict the equilibrium partial pressure of H₂S and CO₂ in aqueous monoethanolamine (MEA) and diethanolamine

(DEA). The non-idealities, represented by activity coefficients, were lumped into two pseudo equilibrium constants (for the main reactions of H_2S and CO_2 with MEA or DEA) as a function of temperature. Model parameters were regressed against experimental data. The model was shown to give good predictions of the partial pressures of H_2S and CO_2 for single acid gas systems (H_2S -MEA- H_2O , CO_2 -DEA- H_2O) as well as for the mixed systems (CO_2 - H_2S -DEA- H_2O , CO_2 - H_2S -MEA- H_2O). Jou *et al.* (1982) noted that the equilibrium constants depend not only on temperature, but also on amine loading (defined as moles of acid gas per mole of amine in solution) and amine concentration. Therefore, Chakma and Meisen (1989) extended the Kent and Eisenberg approach, for the system CO_2 -DEA- H_2O . Similarly, Haji-Sulman *et al.* (1998) extended the Kent and Eisenberg model to predict the partial pressure of CO_2 in DEA, MDEA and DEA-MDEA mixtures. While the models of Chakma and Meisen (1989) and Haji-Sulman *et al.* (1998) are good for single acid gas-amine systems, mixed acid gas systems, i.e. H_2S - CO_2 -Amine- H_2O , have not been addressed.

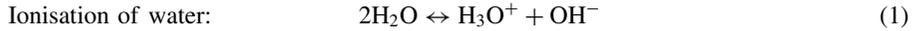
Deshmukh and Mather (1981) proposed an activity coefficient-based VLE model for H_2S and CO_2 in alkanolamine solutions. They used an extended form of the Debye-Hückel model to calculate the activity coefficients of ionic and molecular species. Other activity coefficients models include the electrolyte-NRTL model (Austegen *et al.*, 1989) and electrolyte model based on the Clegg-Pitzer equation (Li and Mather, 1997).

Activity coefficient models are relatively rigorous but require the solution of a large number of non-linear equations. These equations require good initial estimates to guarantee convergence. In contrast, Kent and Eisenberg models require the solution of significantly fewer equations and converge more easily. A key motivation for developing activity coefficient models for acid gas-amine systems was to allow accurate extrapolation at low loadings, which is very important for process design and simulation. However, for all the activity coefficient models, the interaction parameters are regressed against experimental data, so they are to a certain extent empirical in nature. Nevertheless, it is often believed that they are superior to Kent and Eisenberg models for extrapolating beyond the range of the experimental data. While this might be true in principle, it has not been demonstrated at low loadings, nor have these models been applied successfully to model commercial absorption units. Kent and Eisenberg (1976), on the other hand, successfully validated their model beyond the range of experimental data, for commercial units using MEA.

This work extends the model of Kent and Eisenberg (1976) for the simultaneous prediction of H_2S and CO_2 solubilities in aqueous MDEA solutions. In the proposed model, the equilibrium constant is expressed as a function of temperature, amine concentration, amine loading and free acid composition. The model parameters are regressed using published experimental data over a wide range of conditions: amine loading, temperature and amine concentration, for both single and mixed acid gas systems. The model predictions are validated against experimental data of single and mixed acid gas systems. The applicability of the model is further illustrated in flowsheet simulations for commercial units with a range of capacities and operating conditions.

THERMODYNAMIC FRAMEWORK FOR VLE MODELLING

Austgen *et al.* (1989) represented the equilibrium reactions of the H₂S–CO₂–MDEA–H₂O system as:



Reactions (1)–(6) completely define the H₂S–CO₂–MDEA–H₂O system; all of them must be taken into account when considering reaction equilibrium.

Chemical equilibrium (phase and reaction equilibrium) for acid gases–amine–water system implies phase equilibrium, reaction equilibrium, electroneutrality and mass balance.

The associated stoichiometric equilibrium constants for the main reactions of H₂S–CO₂–MDEA–H₂O system can be written as:

$$K_1 = \frac{[\text{H}^+][\text{RR}'\text{NR}'']}{[\text{RR}'\text{NR}''\text{H}^+]} \quad (7)$$

$$K_3 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (8)$$

$$K_5 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (9)$$

$$K_7 = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} \quad (10)$$

$$K_4 = [\text{H}^+][\text{OH}^-] \quad (11)$$

$$K_6 = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \quad (12)$$

Phase equilibrium for acid gases is represented by Henry's Law:

$$Y_{\text{CO}_2}\text{P} = H_{\text{CO}_2}[\text{CO}_2] \quad (13)$$

$$Y_{\text{H}_2\text{S}}\text{P} = H_{\text{H}_2\text{S}}[\text{H}_2\text{S}] \quad (14)$$

The electroneutrality balance among the ionic species present in the system is given by:

$$[\text{H}^+] + [\text{RR}'\text{NH}_2^+] = [\text{OH}^-] + [\text{HCO}_3^-] + [\text{HS}^-] + 2[\text{CO}_3^{2-}] + 2[\text{S}^{2-}] \quad (15)$$

The mass balance of electrolyte in aqueous phase is given by equations (18)–(20):

$$C_{\text{amine}} = [\text{RR}'\text{NH}] \quad (16)$$

$$C_{\text{H}_2\text{S}} = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^-] \quad (17)$$

$$C_{\text{CO}_2} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{--}] \quad (18)$$

where C_i is the concentration of species in $\text{kmol} \cdot \text{m}^{-3}$.

VLE calculations involve simultaneous solution of equations (7)–(18). This work uses the Newton-Raphson method to solve these equations.

PUBLISHED EXPERIMENTAL DATA

In the Kent and Eisenberg model, as the pseudo equilibrium constants are regressed against the experimental partial pressure data, the accuracy of the model depends heavily on the quality of the data. For a model that is applicable to both absorption and desorption processes, we need data over the relevant range of temperature, amine concentrations and acid gas loadings. Few data are available at low acid gas loadings, especially at high temperatures, because of experimental difficulties. It is very difficult to distinguish confidently between the high and low quality data because of the ambiguities in both experimental measurements and the VLE models used to verify data sets. Therefore, only data which various authors (Weiland *et al.*, 1993, 1995; Li and Mather, 1997; Lemoine *et al.*, 2000; Sidi-Boumedine *et al.*, 2004a,b) have scrutinised for consistency and goodness of fit or have verified using statistical analysis are considered here.

Table 1 presents a summary of the experimental data selected in this work. The maximum loading achieved with MDEA, in commercial absorbers, is always less than one to avoid corrosion (Kohl and Reisenfeld, 1985; Hiller *et al.*, 2001). The recommended maximum loading in carbon steel equipment of MDEA is 0.7–0.8. Therefore the experimental data chosen for the VLE model is restricted to loadings of less than one.

MODEL DEVELOPMENT AND VALIDATION

Experimental values for the equilibrium constant K_1 may be calculated for H_2S and CO_2 from the solution of the appropriate equations, (7)–(18), using data for both single and mixed acid gas systems. Equation (19) presents a model for predicting the equilibrium constants K_1 as a function of temperature, concentration of amine and amine loading. The parameters for equation (19) are obtained by minimising the sum of the squared differences between predicted and measured values for K_1 : see equation (20). The equilibrium constant K_1 is fitted for two sets of data. Set A contains only single acid gas experimental data; Set B contains both single and mixed acid gas experimental

Table 1. Summary of the experimental data selected for calculating equilibrium constants

Author	Total no. points	Points used	Amine conc. (wt%)	Temperature (°C)	Acid gas loading: mol of acid gas/mol of amine	System
Jou <i>et al.</i> (1982)	173	99	11.8,23.4,48.9	25,40,70, 100,120	0.001–1.83	H ₂ S–MDEA–H ₂ O
	120	84	23.4,48.9	25,40,70, 100,120	0.001–3.22	CO ₂ –MDEA–H ₂ O
Maddox <i>et al.</i> (1987)	27	20	11.8,20	25,37.8, 65.6,115.6	0.18–0.985	H ₂ S–MDEA–H ₂ O
	50	30	11.8,20,23.3	25,37.8,50, 65.6,115.6	0.157–1.0	CO ₂ –MDEA–H ₂ O
Jou <i>et al.</i> (1993a)	106	106	35	40,100	0.003–0.89(H ₂ S) 0.0001–0.79 (CO ₂)	H ₂ S–CO ₂ –MDEA–H ₂ O
Jou <i>et al.</i> (1993b)	50	50	35,48.9	40,100	0.0041–1.08	H ₂ S–MDEA–H ₂ O
	37	37	35	40,100	0.002–0.8	CO ₂ –MDEA–H ₂ O
Jou <i>et al.</i> (1997)	28	28	48.9	40,100	0.002–0.95(H ₂ S) 0.0004–0.97(CO ₂)	H ₂ S–CO ₂ –MDEA–H ₂ O
Austgen <i>et al.</i> (1991)	13	13	23.3,48.9	40	0.006–0.842	CO ₂ –MDEA–H ₂ O
MacGregor and Mather (1991)	37	37	23.3	40	0.13–1.725	H ₂ S–MDEA–H ₂ O
	5	4	23.3	40	0.12–0.97	CO ₂ –MDEA–H ₂ O

Table 2. Model parameters for calculating K_1 using equation (19) for experimental data sets A and B

Parameters	CO ₂		H ₂ S	
	Set A	Set B	Set A	Set B
A	-2.5722	-10.080	-8.2432	-7.3823
B	-5614.7	-2023.8	-2647.4	-3002.2
C	-1.1900	0.0307	0.4026	0.3760
D	0.1653	-0.4590	-0.6371	-0.5138
E	-0.3981	-1.2299	-1.3373	-1.1326
F	0.0000	1.1445	0.6872	1.2542
G	0.0000	-1.6730	-1.8860	-2.1542
H	0.0000	-0.5680	0.0000	-0.6564
Sum of squared errors	6.5323	9.6174	6.9678	8.5130

data. The values of parameters and sum of squared errors for each data set for CO₂ and H₂S are given in Table 2.

$$K_1 = \exp(A + B/T + C[\text{CO}_2] + D\ln(C_{\text{amine}}) + E\ln\alpha_{\text{CO}_2} + F\ln([\text{CO}_2]) + G(\alpha_{\text{CO}_2} + \alpha_{\text{H}_2\text{S}}) + H\ln([\text{CO}_2] + [\text{H}_2\text{S}])) \quad (19)$$

α_{CO_2} = moles of CO₂/mole of MDEA, $\alpha_{\text{H}_2\text{S}}$ = moles of H₂S/mole of MDEA

$$C_{\text{amine}} = \text{concentration of amine kmol/m}^3 \quad (20)$$

$$\text{Min} \sum (\ln(K_{1\text{exp}}) - \ln(K_{1\text{pre}}))^2$$

The two sets of the models developed for K_1 are used to predict the partial pressure of acid gases. The predictions of Model A for H₂S–MDEA–H₂O and CO₂–MDEA–H₂O systems at different concentrations and temperature are given in Figures 1–4. It can be seen from Figures 1–4 that the predictions of Model A for both H₂S and CO₂ are reasonably accurate over the range of experimental data. However, as shown in Figures 5 and 6, Model A fails to predict the VLE behaviour for both H₂S and CO₂ in the mixed acid gas system H₂S–CO₂–MDEA–H₂O. As the parameters for Model A are regressed using experimental data for systems with a single acid gas, the model cannot capture interactions between the acid gases.

MODEL APPLICATION FOR FLOWSHEET SIMULATION

As discussed earlier, it is important that the VLE model is valid in the region of low acid gas loadings, even though few experimental data are available in this range. This work validates the model by applying it for the simulation of a commercial

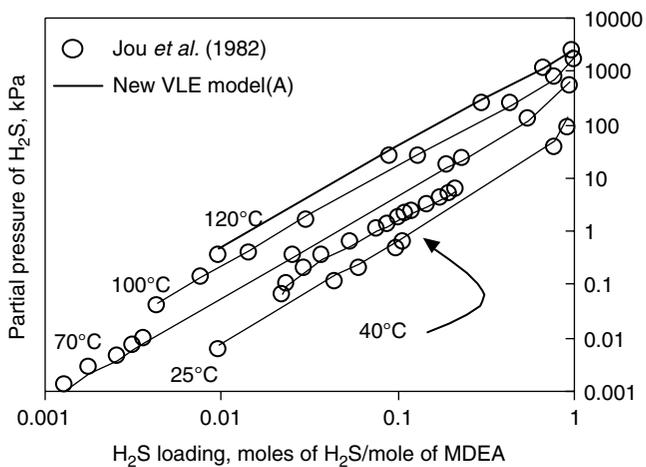


Figure 1. Partial pressure of H_2S in 48.9 wt% aqueous MDEA solution at 25, 40, 70, 100 and 120°C by Model(A)

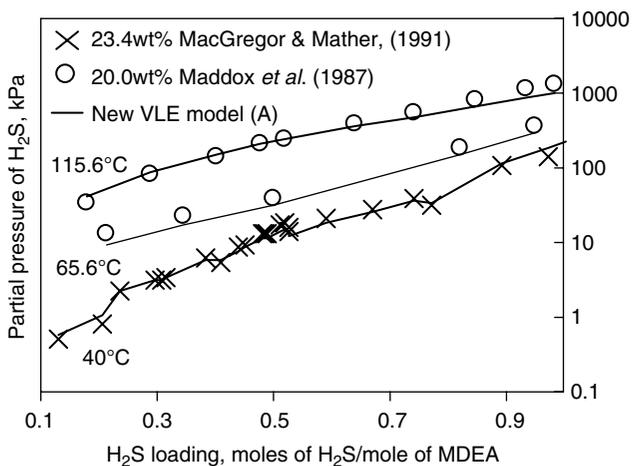


Figure 2. Partial pressure of H_2S in 20.0 wt% and 23.4 wt% MDEA aqueous solution at 40, 65.6 and 115.6°C by model(A)

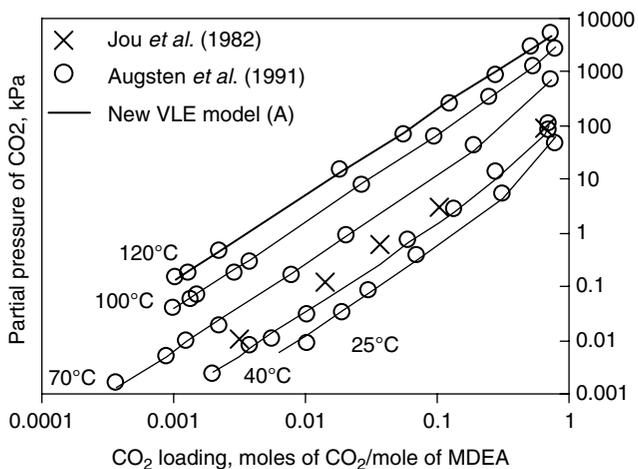


Figure 3. Partial pressure of CO₂ in 48.9 wt% aqueous MDEA solution at 25, 40, 70, 100 and 120°C by Model(A)

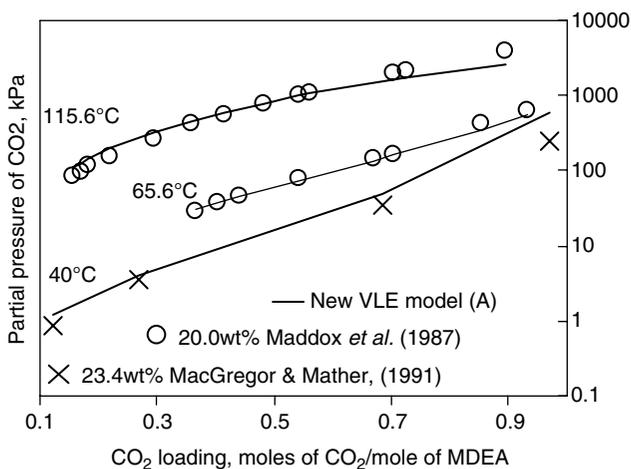


Figure 4. Partial pressure of CO₂ in 20.0 wt% and 23.4 wt% MDEA aqueous solution at 40, 65.6 and 115.6°C by Model(A)

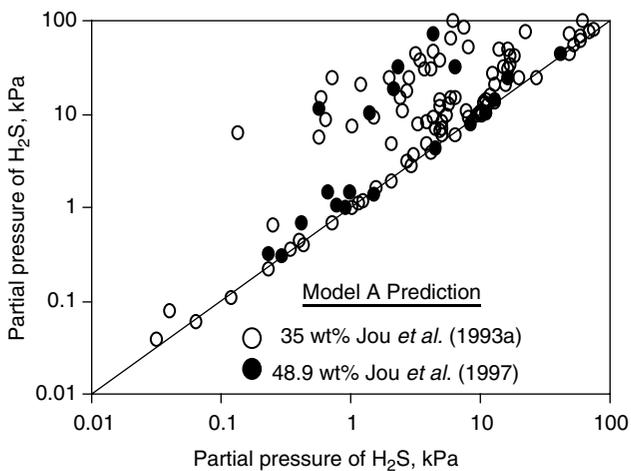


Figure 5. Comparison of predicted and experimental partial pressure of H_2S in $\text{H}_2\text{S}-\text{CO}_2$ -MDEA- H_2O by Model(A)

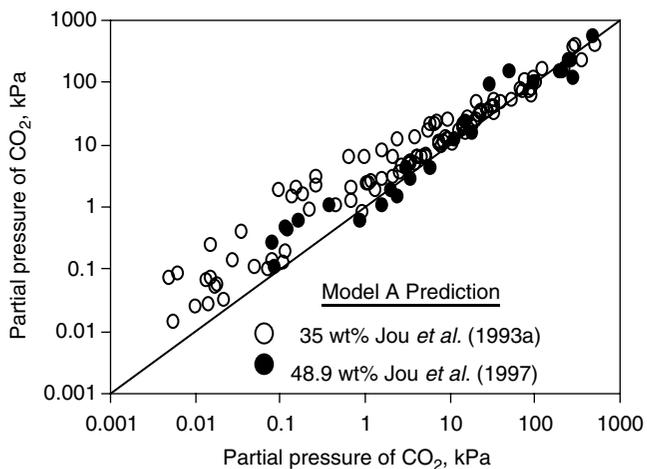


Figure 6. Comparison of predicted and experimental partial pressure of CO_2 in $\text{H}_2\text{S}-\text{CO}_2$ -MDEA- H_2O by Model(A)

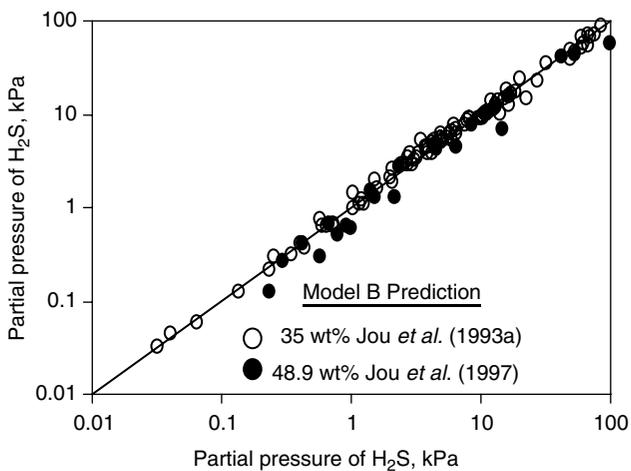


Figure 7. Comparison of predicted and experimental partial pressure of H₂S in H₂S–CO₂–MDEA–H₂O Model(B)

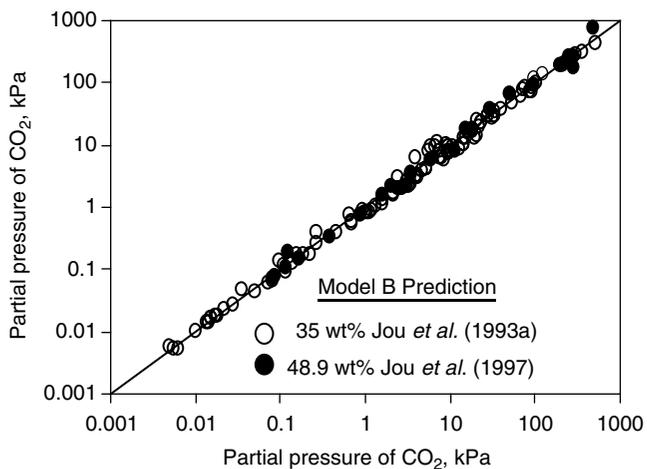


Figure 8. Comparison of predicted and experimental by partial pressure of CO₂ in H₂S–CO₂–MDEA–H₂O by Model(B)

absorption–regeneration process and comparing model predictions to plant operating data. A number of case studies of gas sweetening processes are simulated; modelling results are compared with actual operating conditions and with HYSYS (v 3.2) simulation results. HYSYS, in the Amines property package, uses non-equilibrium stage models for the simulation of the absorption and regeneration units, employing a proprietary Kent and Eisenberg VLE model. The new VLE model is applied to a simplified process simulation model developed by Patil (2005) for the purposes of chemical absorption process design and optimisation. The model uses a modified Kremser group method in which key component efficiencies incorporate non-equilibrium effects. Patil (2005) demonstrated the validity of the simplified model for various simple and complex gas sweetening flowsheets; modelling results were compared to plant data and to HYSYS simulation results.

The model predictions using the new VLE model within the simplified model of Patil (2005) are presented in Table 3. It can be seen that model predictions for the sweet gas composition are in good agreement with the operating data, and in most cases they are better than those predicted by HYSYS. It can be seen from the results that the H₂S prediction for Plant 1 in Case C (MacKenzie *et al.*, 1987) is not very accurate. However, MacKenzie *et al.* (1987) mentioned some discrepancies in H₂S measurements, and therefore discarded both high and low readings of H₂S and reported the average of the rest. It is our belief that some measurement errors are responsible for the under-predictions of the model for this case.

Table 3. Comparison of model results for commercial absorber–regenerator loop simulation

Amine concentration (wt%)	Absorption column pressure (bar)	Sweet gas concentration		Plant	Model	HYSYS	
36.2	29.8	Plant 1	H ₂ S	ppm	2.8	3.14	Nil
		Case A	CO ₂	%	2.05	2.16	2.03
32.4	27.1	Plant 1	H ₂ S	ppm	0.6–1.5	0.77	Nil
		Case B	CO ₂	%	1.95	2.18	2.06
32.25	27.1	Plant 1	H ₂ S	ppm	3.2–3.7	6.91	Nil
		Case C	CO ₂	%	2.13	2.32	2.07
36	55.0	Plant 2	H ₂ S	ppm	2–3 [#]	0.5	57
		Case A	CO ₂	%	2.8	3.08	2.8
36	55.0	Plant 2	H ₂ S	ppm	2–3 [#]	0.34	13
		Case B	CO ₂	%	>2.0	1.97	1.8
45	90.6	Plant 3	H ₂ S	ppm	0.13	0.99	Nil
			CO ₂	%	2.7	3.25	2.7

[#]Calculated by mass balance.

Plant 1: MacKenzie *et al.* (1987); Plant 2 and Plant 3: Pakistan Petroleum Limited.

CONCLUSIONS

This work presents an extended Kent and Eisenberg model for the prediction of the vapour–liquid equilibrium of acid gases and the ternary amine, MDEA. The model parameters are regressed using both single and mixed experimental data. The pseudo equilibrium constants in the Kent and Eisenberg model are expressed in terms of temperature, free acid concentration, acid gas loading and amine concentration. The new model predictions are validated against published experimental data for both H₂S and CO₂ in H₂S–CO₂–MDEA–H₂O systems. The model predictions are shown to be in very good agreement for both acid gases. The model is validated against commercial absorption–regeneration plant operating data by performing flowsheet simulations. The new model is simple and computationally efficient and therefore can be applied for synthesis, design and optimisation of gas sweetening flowsheets.

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