

VAPOR LIQUID EQUILIBRIUM AND PARTITION COEFFICIENTS OF *N*-PROPYLMERCAPTAN, *N*-BUTYLMERCAPTAN AND DIMETHYLSULFIDE IN MDEA AQUEOUS SOLUTION¹

*Javeed A Awan, Christophe Coquelet, Dominique Richon**

Mines Paris, Paris-Tech, CEP/TEP. CNRS FRE 2861, Fontainebleau, France.

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Extended Abstract

This investigation was carried out to determine the Vapor liquid Equilibrium and partition coefficients of *n*-Propylmercaptan, *n*-Butylmercaptan and Dimethylsulfide in Methyldiethanolamine (MDEA) 50 wt % aqueous solution while using a “static-analytic” apparatus, with pneumatic capillary samplers (Rolsi™, Armines patent) used for fluid sampling at equilibrium conditions. Measurements were made in the presence/absence of acid gases, H₂S and / or CO₂. The total pressure for most of the experiments was about 6.8-7.4 MPa, which was mentioned by methane. These experiments were carried out at 333.15 and 365.15 K. The inlet *n*-PM, *n*-BM and DMS concentration in most of the experiments was mentioned around 1000 ppm mol. The reaction between organic sulfur species and Methyldiethanolamine (MDEA) aqueous solutions has been considered while using the acid base neutralization approach.

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*: Corresponding author, Email: dominique.richon@mines-paristech.fr. Tel.: + (33) 1 64 69 49 65. Fax: + (33) 1 64 69 49 68.

Introduction

Natural gas and petroleum industries are dealing with raw materials containing variable concentrations of hydrogen sulfide, carbon dioxide and organic sulfur species like n-Propylmercaptan, n-Butylmercaptan and Dimethylsulfide (500 to 100 ppm moles approx). Treatment processes have to remove not only H₂S and CO₂ but also all these sulfur species and prohibited compounds because worldwide regulations for environmental protection are forcing the petroleum industry to decrease the sulfur content in petroleum fluids. Furthermore, any mercaptans (RSH), carbonyl sulfide (COS), and carbon disulfide (CS₂), not absorbed with from the sour gas through amine purification units complicate the process scheme for downstream liquid treatment (J.A. Awan *et al.*, 2008).

The more commonly used solvent systems for acid gases treatment from a variety of gas streams, are aqueous amines due to their capability of dissolving the acid gases through non reactive and reactive interactions. Aqueous amines in particular can also react with organic sulfur species like n-Propylmercaptan, n-Butylmercaptan and Dimethylsulfide through acid base neutralization approach to form thermally regenerate salts. However mercaptans, carbonyl sulfide (COS), and carbon disulfide (CS₂) react more slowly with amines than CO₂. If H₂S selectivity is increased by reducing the reaction rate of the solvent with CO₂ the absorption of the other sulfur-containing components is negatively effected. Since the treating target is usually a total sulfur specification, the attainable sulfur selectivity in industrial gas treating processes is limited by the presence of other sulfur-containing components like mercaptans (RSH), carbonyl sulfide (COS), and carbon disulfide (CS₂). If one hydrogen atom in H₂S is replaced by an alkyl group, we obtain a mercaptan. The simplest mercaptan is Methylmercaptan. As number of carbon atoms increases, mercaptans behave more and more like hydrocarbons in alkanolamine solutions (Seagraves, 2001). The mercaptans react with amines through acid-base properties, but CO₂ and H₂S (acid gases) have stronger acidic behavior than mercaptans thus their presence effects adversely the solubility of mercaptans in amine aqueous solutions.

Basic phase equilibrium and kinetic data of acid gases and sulfur species-hydrocarbon-amine systems are essential to design economical new amine treating plants and to improve the efficiency of existing units. Unfortunately no data are available in literature concerning the solubility of n-Propylmercaptan, n-Butylmercaptan and Dimethyl sulfide in aqueous

alkanolamine solution in the presence of acid gases. The present work was undertaken to determine the partition coefficient of n-Propylmercaptan, n-Butylmercaptan and Dimethyl sulfide in 50 wt % aqueous MDEA solution, with and without acid gases, in order to identify the effect of acid gases on the physical and chemical solubility of n-PM, n-BM and DMS.

Experimental Details

Material suppliers and purities

Methane is from Messer, (99.995 vol %), Carbon dioxide is from l'Air liquide (99.995 vol %), Hydrogen sulfide is from l'Air liquide, (99.5 vol %), n-Propylmercaptan and n-Butylmercaptan are from Aldrich, (99 vol %), Dimethylsulfide is from ACROS, (99 vol %) Methyl-diethanolamine is from Aldrich, 99+ GC %). Water was purified and distilled through a Millipore direct Q osmosis membrane.

Apparatus and Method

A “static-analytic” apparatus, with pneumatic capillary samplers (ROLSI™, Armine's patent, see www.rolsi.com) has been used for fluid sampling at equilibrium conditions as shown in figure 1. The liquid and vapor samples are analyzed using a gas chromatograph (PERICHROM model PR2100, France) equipped with one thermal conductivity detector (TCD), and one flame ionization detector (FID). Water and amine were degassed separately, and aqueous solutions were prepared by gravimetric method under vacuum. The ROLSI™ samplers are fixed on top of Equilibrium cell. Thus, with this sampler we can be certain that thermodynamic equilibrium is not be disrupted in the equilibrium cell, as the size of the sample is negligible as compared to the volume of cells $> 30 \text{ cm}^3$.

Two 100 Ω platinum resistance thermometer devices (Pt 100) are used for temperature measurements inside the equilibrium cell. They are periodically calibrated against a 25 Ω reference platinum resistance thermometer (TINSLEY precision instruments). The resulting uncertainty on temperature measurements is estimated within $\pm 0.04 \text{ K}$. Pressures are measured by means of a Druck pressure transducer (0 – 10 MPa), which is maintained at constant temperature, ie 353.15 K.

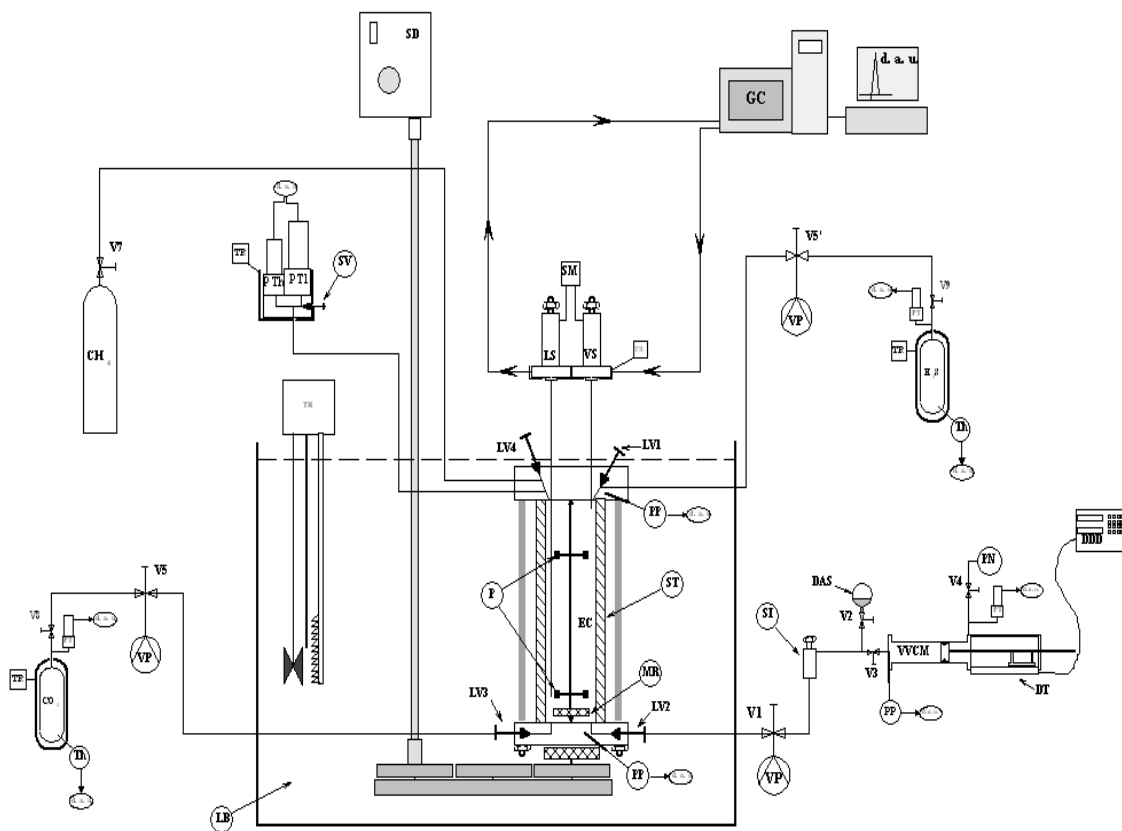


Figure 1: Schematic diagram of apparatus.

d. a. u. : Data Acquisition Unit ; DDD : Digital Displacement Display ; DM : Degassed Mixture ; DT : Displacement Transducer ; EC : Equilibrium Cell ; GC : Gas Chromatograph ; LB: Liquid Bath; LS: Liquid Sampler; LV_i: Loading Valve; MR; Magnetic Rod; P: Propeller; PP : Platinum Probe ; PTh: Pressure transducer for high pressure values; PTL: Pressure transducer for low pressure values; SD : Stirring Device ; SM: Sample Monitoring; ST : Sapphire Tube ; TR: Thermal Regulator; V_i: Valve; VP: Vacuum Pump; VS: Vapor Sampler; VVCVM: Variable Volume Cell for Mixture.

The pressure transducers are calibrated against a dead-weight pressure balance (Desgranges & Huot 5202S, CP 0.3-40 MPa, Aubervilliers, France). Correlatively, uncertainty on pressure measurements is estimated to be within ± 0.0003 MPa. The uncertainties on n-PM / n-BM / DMS inlet concentrations are ± 0.06 %, and on MDEA concentrations, they are ± 0.01 %. For each equilibrium conditions, samples were withdrawn using the pneumatic ROLSITM samplers and analyzed by gas chromatography. Gas chromatograph detectors are calibrated using chromatographic syringes with maximum uncertainties of 2 % on TCD and 1.5 % on FID. Quantities of MDEA and water are negligible in vapor phase. Consequently samples of liquid phase are determined considering the $\frac{n_{H_2O}}{n_{MDEA}}$ ratio constant at equilibrium.

A known amount of amine-water mixture is loaded into the equilibrium cell from the variable volume cell, it carries organic sulfur species which is injected along the path of the solution, through a special septum arrangement. H₂S and CO₂ are then loaded respectively, their mole numbers are being calculated by using the reservoir volume, temperature as well as pressure drop observed inside the reservoir. Finally, methane is added to the system to reach desired pressure. The required temperature is obtained by putting the cell into a thermo-regulated oil bath.

Liquid Loading

CO₂ and H₂S partial pressures are function of their loadings. The liquid loading is defined as the ratio of acid gas moles to the moles of amines in liquid phase at equilibrium and shown as follows (L_{CO_2} and L_{H_2S}). The amount of acid gas introduced into the equilibrium cell (*i.e* molar density) can be determined from temperature and pressure conditions from the storage press, as explained in experimental procedure section.

To calculate the liquid loading, we have to estimate the number of moles of each species present in the vapor phase. The following equations are used.

$$V = V^L + V^V \quad (1)$$

V is the total volume of the cell, V^L and V^V are volume of liquid phase and vapor phase respectively

For CO₂ the molar balance is as follows

$$n_{CO_2} = n_{CO_2}^L + n_{CO_2}^V \quad (2)$$

In the vapor phase, the mole number of CO₂ is calculated considering the vapor phase composition.

$$n_{CO_2}^V = \frac{V^V}{v_T^V} y_{CO_2} \quad (3)$$

The molar volumes (v_i^V) of pure gases were used at T, and P to calculate molar volumes (v_T^V)

$$v_T^V \approx \sum_i y_i v_i^V \quad (4)$$

Finally, liquid loadings for CO₂ and H₂S can be defined as

$$L_{CO_2} = \frac{n_{CO_2} - n_{CO_2}^V}{nMDEA} \quad (5)$$

and

$$L_{H_2S} = \frac{n_{H_2S} - n_{H_2S}^V}{nMDEA} \quad (6)$$

3.4 Partition coefficient

Partition coefficient of organic sulfur species is the ratio of mole fraction in vapor phase to its mole fraction in liquid phase at equilibrium. Gas liquid partition coefficients and Henry's constant are often calculated to get the differential solubility between two phases

$$i.e. \quad K_i = \frac{y_i}{x_i}, \quad \text{where } i = \text{n-PM or n-BM or DMS}$$

Results and Discussions

Most of the experimental data were obtained at about 6.8-7.4 MPa and at 332 and 365 K. The partition coefficients of n-Propylmercaptan, n-Butylmercaptan and Dimethyl sulfide in the presence of CO₂ and or H₂S are plotted in figures 3, 4 and 5. It is observed that gas-liquid partition coefficients of n-Propylmercaptan, n-Butylmercaptan and Dimethyl sulfide increase when increasing CO₂ and H₂S loadings. It is difficult to make direct comparison for the system containing acid gases and organic sulfur species in amine aqueous solution as too few literature are available. Furthermore no information is available concerning the chemical reaction between MDEA and mercaptans in the presence of acid gases. Only (Bedell and Miller, 2007) described the solubility of mercaptans in aqueous amine solutions on the basis of acid-base neutralization approach. Henry's constant of Methylmercaptan is increasing function of acid gas loading (Jou *et al.*, 1999).

The thiols are much weaker acids than H₂S and they do not react with alkanolamines also that H₂S and CO₂ have the same effect on the solubility of mercaptans (Jou *et al.*, 2000), More experimental data are required for better understanding of H₂S and CO₂ effect on the reaction phenomenon between amine and mercaptans. The presence of acid gases modifies instantaneously the pH of the solution and Mercaptans (RSH) reactions are pH dependent.

It is our hypothesis that neutralization of MDEA with CO_2 and H_2S results in decreases of mercaptans solubility and cause one reason for increase the partition coefficient of mercaptans. Although mercaptans are much weaker acids than H_2S and CO_2 they can react with amines to form mercaptide salts. The effect of acid gas is to transfer mercaptide salts in to molecular form due to common ion effect, consequently their partition coefficient increases.

The solubility of n-PM in water is lower than solubility in MDEA aqueous solution. The absorption rate increases with the increase of amine concentration in the solution (Seagraves, 2001). We performed experiments to study the partition coefficient of n-PM, n-BM and DMS with mixed and single acid gas loadings. The partition coefficients of n-PM, n-BM and DMS as a function of liquid CO_2 loading and liquid H_2S loadings have been plotted in Figures 2 and 3, and 4 respectively.

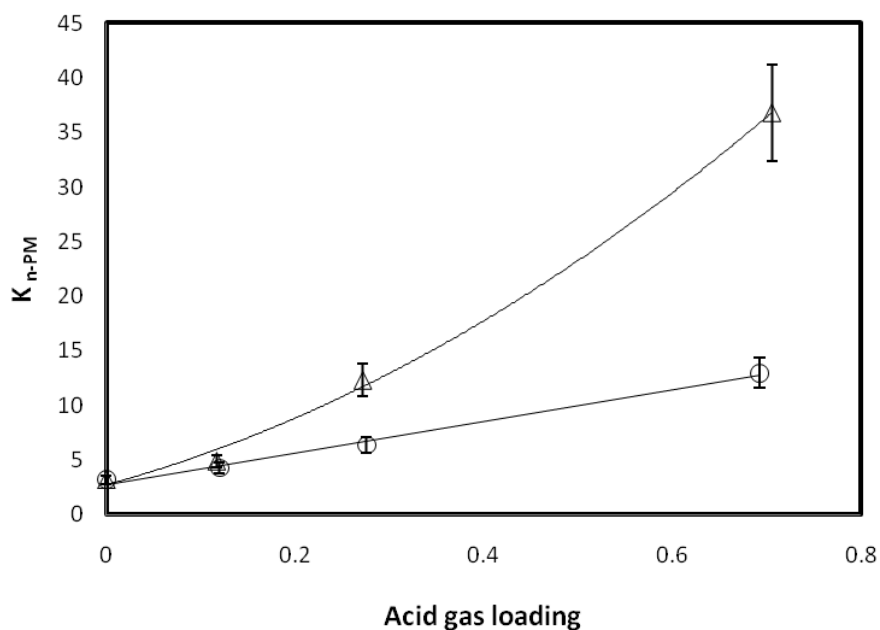


Figure 2: n-PM partition coefficient as a function of CO_2 loading (O) (no H_2S), at 356 K and 6.9 MPa, with 1000 ppm of n-PM introduced, solid line: tendency curve, Error bar: 11 %. And n-PM partition coefficient as a function of H_2S loading (Δ) (no CO_2), at 356 K and 6.9 MPa, with 1000 ppm of n-PM introduced, solid line: tendency curve, Error bar: 12 %.

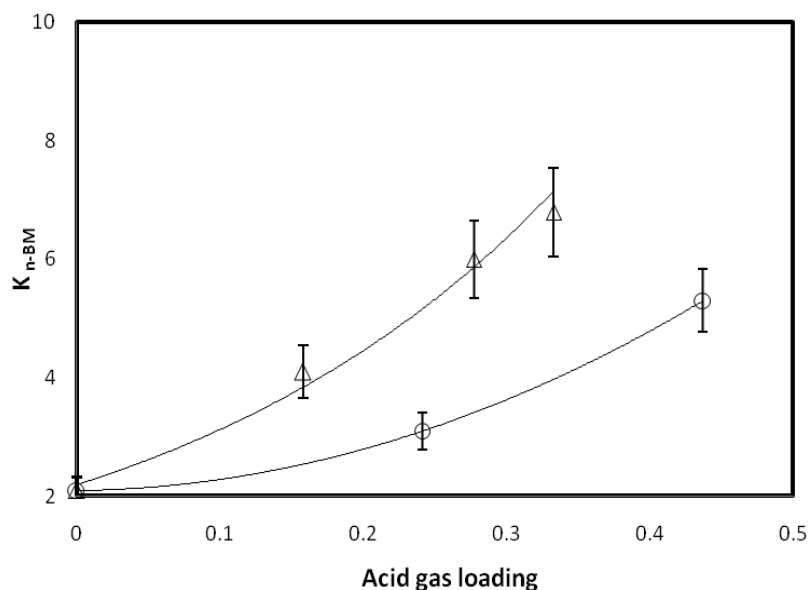


Figure 3: n-BM partition coefficient as a function of CO₂ loading (O) (no H₂S), at 356 K and 6.9 MPa, with 1000 ppm of n-BM introduced, solid line: tendency curve, Error bar: 10 %, and n-PM partition coefficient as a function of H₂S loading (Δ) (no CO₂), at 356 K and 6.9 MPa, with 1000 ppm of n-BM introduced, solid line: tendency curve, Error bar: 11 %.

The partition coefficient of Dimethyl sulfide and n-BM increases in the presence of acid gases at 365.15 K, but not as much as observed in the case of n-PM. Further DMS carries only physical solubility in MDEA aqueous solution (*i.e.* there is no chemical reaction between DMS and MDEA aqueous solution). The partial pressure of acid gases modifies the partial pressure of organic sulfur species; unfortunately no information is available concerning the kinetics of reaction of mercaptans with amine in the presence of acid gases, therefore it is difficult to make a direct comparison of partition coefficients of different organic sulfur species. However in our experimental studies it is observed the effect of CO₂ on partition coefficient of mercaptans and DMS are more pronounced than that of H₂S. This is in agreement with literature studies, the presence of acid gases affect the solubility of the thiols, any increase in acid gas loadings results in increase of Henry's constants of thiols, and this effect is more pronounced in the presence of CO₂. (Jou *et al.*, 2000). It is important to consider, that as the alkyl group attached to the -SH becomes heavier, it starts behaving like hydrocarbons. Primary and secondary amines may provide good removal of mercaptans as they have more affinity for hydrocarbon part of RSH group (Seagraves, 2001). The limiting activity coefficient increases with the number of carbon atoms of sulfur species and as a consequence with molecular size (Coquelet *et al.*, 2005).

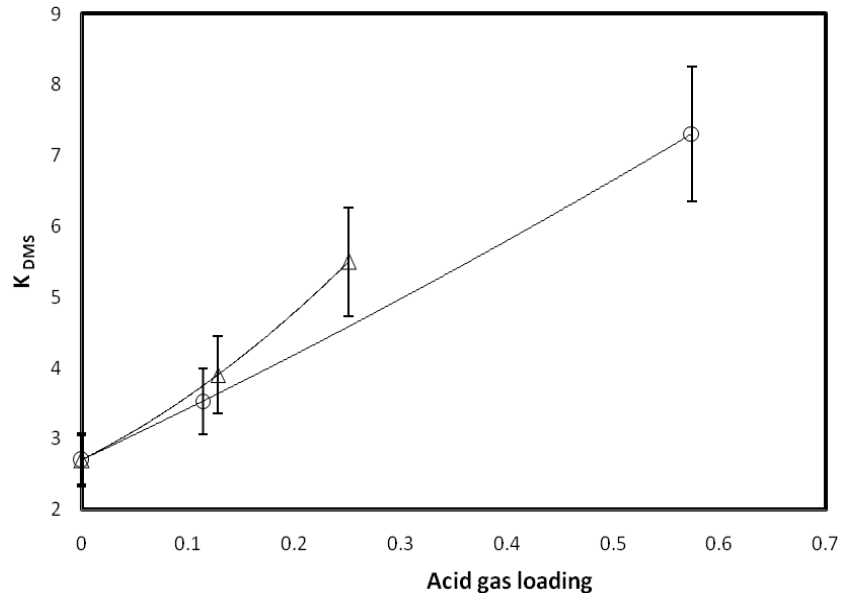


Figure 4: DMS partition coefficient as a function of CO₂ loading (O) (no H₂S), at 356 K and 6.9 MPa, with 1000 ppm of n-PM introduced, solid line: tendency curve, Error bar: 13 %. And n-PM partition coefficient as a function of H₂S loading (Δ) (no CO₂), at 356 K and 6.9 MPa, with 1000 ppm of n-PM introduced, solid line: tendency curve, Error bar: 14 %.

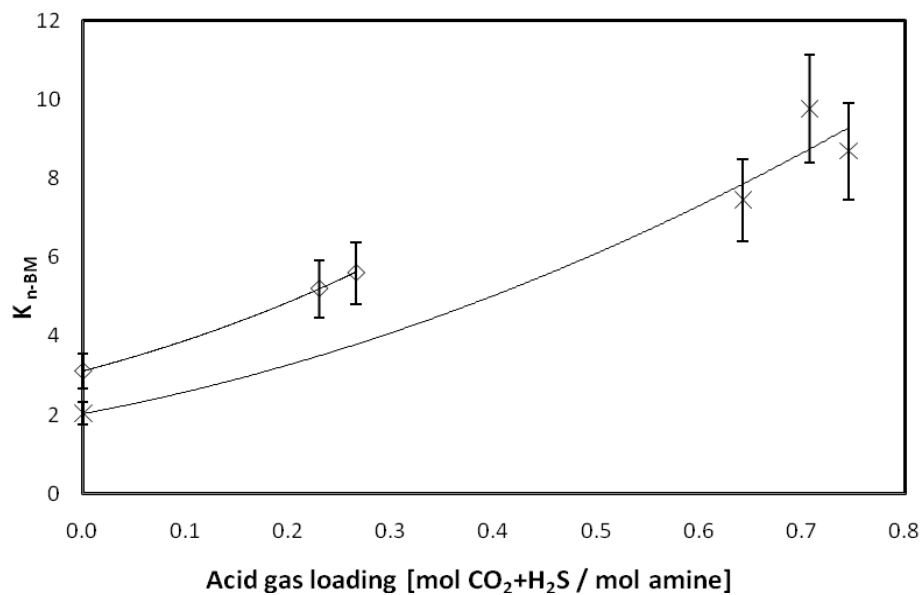


Figure 5: n-BM partition coefficient as a function of acid gas loading (CO₂ + H₂S), (◇) 500 ppm mol of n-BM, (×) 1000 ppm mol of n-BM, at a temperature of 365.15 K and 6.9 MPa system pressure. Solid line: tendency curve, Error bar: 14 %

The partition coefficient of n-BM with different injected quantities of n-BM (1000 ppm mol and 500 ppm mol) as a function of total liquid loading ($\text{CO}_2 + \text{H}_2\text{S}$ loadings) has been plotted in Figures 5. It is observed that higher will be the n-BM partition coefficient if initial concentration of n-BM is small. Similar type of results has been obtained by (Jou *et al.*, 2000) while studying the solubility of ethylmercaptan in MDEA 50 wt % aqueous solution at 70°C . Thus n-BM partition coefficient is sensitive to initial n-BM concentration at 365.15 K.

Conclusion

Vapor liquid Equilibrium of natural gas containing organic sulfur species, like n-Propylmercaptan, n-Butylmercaptan and Dimethyl sulfide has been investigated in MDEA aqueous solution at 323.15 K and 365.15 K and pressure range of 6.9-7.4 MPa, in the presence of acid gases. The partition coefficients of n-PM, n-BM and DMS are affected by the presence of CO_2 and H_2S , especially that of CO_2 . Furthermore solubility of CO_2 and H_2S are not affected by the presence of n-PM, n-BM or DMS for a concentration of 1000 ppm mol, repeatable solubility values and partial pressures of CO_2 and H_2S are observed with different mercaptans.

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Acronyms

MDEA: Methyldiethanolamine, n-PM: n-Propylmercaptan, n-BM: n-Butylmercaptan, DMS: Dimethyl sulfide, COS: Carbonyl sulfide, CS_2 : Carbon disulfide, RSH: Thiols, mercaptans, GC: Gas chromatography

Literature Cited

1. Awan J.A, Coquelet C., Richon D., 2008, Effect of acid gases on the solubility of n-propylmercaptan in 50 wt% methyldiethanolamine aqueous solution, *Chemical Engg. Research & design*, 86, 6, 600-605.
2. Bedell S.A., Miller M., 2007, Aqueous Amines as Reactive Solvents for Mercaptan Removal, *Ind. Eng. Chem. Res.*, 46,11, 3729 -3733.
3. Butwell K. F., Kubek D. J., and Sigmund P.W, 1982, Alkanolamine treating, *Hydrocarbon processing*, 4, 108-116.
4. Coquelet, C., and Richon, D., 2005, Measurement of Henry's Law Constants and Infinite Dilution Activity Coefficients of Propyl Mercaptan, Butyl Mercaptan, and Dimethyl Sulfide in Methyldiethanolamine (1) + Water (2) with $w_1 = 0.50$ Using a Gas Stripping Technique, *J. Chem. Eng. Data* , 50: 2053-2057.
5. Jou F.-Y, Mather A. E., and Ng H.-J., 2000, Solubility of Methanethiol and Ethanethiol in a Diethanolamine Solution in the Presence of Acid Gases., *J. Chem. Eng. Data*, 45: 1096-1099.
6. Jou F.-Y., Mather, A. E., Ng H.-J., 1999, Effect of CO₂ and H₂S on the solubility of methanethiol in an aqueous methyldiethanolamine solution, *Fluid Phase Equilib.* 158-160, 933-938.
7. Jou F.-Y, Mather A. E.,1999b, Vapor-liquid equilibra in the system ethanethiol + methyldiethanolamine + water in the presence of acid gases, *J. Chem. Eng. Data*, 44:1096-1099.
8. Seagraves J., 2001, Sulfur removal in amine plants, *Hydrocarbon Engineering*.