Study of Hydrogen Sulfide Absorption with Diethanolamine in Methanolic Aqueous Solutions

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The sulphur compounds are removed by various processes, among which that corresponding to the gas absorption in specific liquid solutions. This absorption is carried out by physical, chemical solvents and currently by mixing both in the so called hybrid solvents. In this work, hydrogen sulphide (H_2S) absorption in a hybrid solvent containing aqueous Di-Ethanol-Amine (DEA) dissolved in methanol have been studied extensively in a modified Lewis cell reactor. Experiments have been achieved in an extended range of temperature, 313-353 K and with two mixtures (50 % water, 30 % DEA, 20 % Methanol), (40 % water, 40 % DEA, 20 % methanol). Through these experiments, three parameters affecting the absorption of hydrogen sulfide (temperature T, loading rate α(mol H_2S/mol DEA) and mass fraction %) were studied. Absorption is accelerated by raising the temperature while it is penalized by the increase in the loading rate. The absorption rate increases as the mass fraction of DEA varies from 30 % to 40 % to achieve an optimum loading rate (α = 0.25 (1) at T = 333 K and α = 0.50 at T = 353 K) for which the absorption rate remains practically unchanged.

1. Introduction

The removal of acid gas impurities such as CO_2, H_2S, COS and CS_2 from natural and industrial gases is a frequently encountered operation in process industry. Natural gas contains varying amounts of these acid gas components. These sulphur species are toxic and corrosive to processing equipment. H_2S is the most common sulphur species in natural gas but varying amounts of COS and CS_2 are often also present. Absorption by aqueous solutions of alkanolamines is the dominant industrial process for removing acid gases, mainly carbon dioxide (CO_2), hydrogen sulphide (H_2S), carbonyl sulphide (COS) and carbon di-sulphide (CS_2) from natural gas. Such washing processes are also used in petroleum refining, coal gasification and hydrogen production. Industry would prefer to use less corrosive and more advanced solvent systems which could be formulated along with the plant design and operation, according to the feed and exit streams specifications of plants. In spite of an abundance of literature, only few works deal with absorption kinetics. The data which exist are dedicated to the study of the initial kinetics in gas unloaded solutions (Pani et al., 1997). The specifications imposed on the content of sulphur compounds in treated gas are very strict; indeed, the total content sulphur should not exceed 4 ppm. To reach this specification it is necessary to reduce the content of H_2S.

New developments are being considered in the treatment of acid gases, it is the increasing use of hybrid solvents (chemical and physical). The few studies carried out with hybrid solvents confirm the increase in solubility of acid gases such as CO_2 and H_2S as well as impurities such as COS in this solvent. There is a discrepancy about the kinetic point of view: is that absorption is physical or chemical between the acid gas and the amine according to a reaction mechanism? Santo and Rameshni (2014) discussed the design features of the units and reasons why they were selected. They discussed the options that we considered to design this unit, including the solvent evaluation and selection, the impact of H_2S/CO_2 ratio on the SRU design, and the selected optimum scheme of the Sulphur Recovery Units to meet the performance guarantees for many cases including the operating and the capital costs comparison. The challenge in their work was to deal with a wide range of feed gas compositions of H_2S and CO_2 while also dealing with a lot of impurities

such as carbonyl sulphide (COS), heavy hydrocarbons, mercaptans, and benzene, toluene, xylene where the operation of the SRU's with the lean gas and impurities are difficult. Tamajon et al. (2016) studied the CO_2 absorption into N-methyldiethanolamine hybrid (chemical and physical) solutions, using pure water, pure methanol and water + methanol mixtures as solvents. The CO_2 absorption experiments were significantly influenced by the effect of temperature, amine concentration and water/methanol ratio. The performance of CO_2 absorption into aqueous MDEA solutions was compared to that into hybrid MDEA solutions. It was concluded that MDEA aqueous solutions demonstrated lower performance than amine solutions using pure methanol or water–methanol mixtures as solvents, even at high temperatures and amine concentrations. Results showed that at high temperatures, amine concentration and chemical absorption had no relevant influence on the process. The methanol effect was noticed to improve the diffusivity and solubility in the process, by means of physical absorption.

In our work, hydrogen sulphide (H_2S) absorption in a hybrid solvent containing aqueous Di-Ethanol-Amine (DEA) dissolved in methanol have been studied extensively in a modified Lewis cell reactor. We used the same type of apparatus as described by Molina and Bouallou (2013). Experiments have been achieved in an extended range of temperature, 313-353 K and with two mixtures (50 % water, 30 % DEA, 20 % Methanol), (40 % water, 40 % DEA, 20 % methanol).
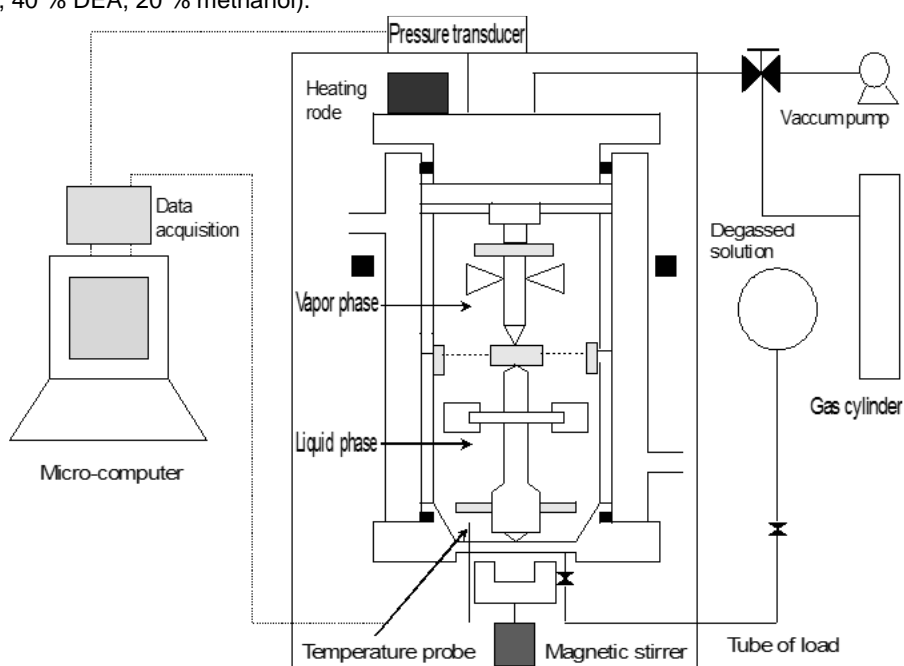

Figure 1: Experimental apparatus

2. Experimental section

The Distilled water grade is used. DEA is from Aldrich, with a certified minimum purity of 99 % (mass). MDEA is from Fluka, with a certified minimum purity of 98 % (mass). The experimental apparatus (Figure 1) is a thermostated Lewis type reactor with flat horizontal gas-liquid interface (15.34 ± 0.05) 10^{-4} m^2. The total volume available for gas and liquid is (0.3653 ± 0.0003) 10^{-3} m^3. The temperature is controlled by circulating a thermostatic fluid through the glass double jacket. Experimental set up and procedure have been described in more detail by Amararene and Bouallou (2004). The originality here is the use of non-rotating stem valve; the loading time is thus considerably reduced. Kinetics of gas absorption are measured by recording the absolute pressure drop through a DRUCK pressure transducer, working in the range (0 to 250) kPa. This transducer is thermostated at a temperature higher than the experiment temperature to avoid liquid condensation in its measuring chamber. For each temperature investigated, it is calibrated within ±80 Pa against a pressure calibration device. A microcomputer fitted with a data acquisition card is used to convert the pressure transducer signal directly into pressure units (Pa), using calibration constants previously determined, and record it as a function of time. Water and amine are degassed independently and aqueous solutions are prepared under a vacuum. The mass of water and amine are known by differential weightings. The flask containing the solution is connected to the reactor to allow the solution to transfer by gravity under vacuum. Accurate weightings of the flask before and after transfer yield the mass of solution actually present in the cell,

and the liquid phase volume was calculated using the density. At a given temperature, and under solution vapour pressure P_l, pure H_2S is introduced during a very short time in the upper part of the cell, the volume of which is noted as V_g. Then stirring is started, and the pressure drop resulting from absorption is recorded. The estimated maximum experimental error in the H_2S absorption rate is 8 %.

3. Results

We conducted two types of measures: absorption measurements from fresh solutions and from H_2S loaded solutions. In the first case, the cell Lewis is directly connected to the gas reserve, the amount of absorbed gas (assuming an ideal gas) is given by:

$$n_{g,a} = \frac{(P_{g,0} - P_{g,eq}) \times V_g}{RT}$$
(1)

where R is the gas constant (8.3143 J.K^{-1}.mol^{-1}), T is the absolute temperature (K). V_g is the volume of gas (m^3). In the second type of tests, the gas contained in a press at constant volume, provided with a sensor and a probe for measurement of its temperature, is introduced into the cell through the liquid phase. The gas number of moles introduced is known thanks to the pressure difference in the press loading, which allows the determination of the density of the gas. This is calculated by ALLPROPS® software. The circuit volume (reserve + tube) connecting the press load to the cell is estimated at (149.31 ± 0.18) cm^3.

The calculation method of the H_2S absorption flux in unloaded hybrid solvent solutions is similar to that used in the work of Bouallou Rivera-Tinoco (2007). In the case of H_2S loaded solvents, the mass balance is determined by:

$$k_l Ea_i (C_{H2S,int} - C_{H2S,eq}) = \frac{-V_g}{RT} \frac{dP_{H2S}}{dt}$$
(2)

where k_L is the liquid-side mass transfer coefficient (m s^{-1}), E the enhancement factor, a_i the interface area (m^2), t the time (s) and $C_{H2S,eq}$ represents the gas concentration at equilibrium:

$$C_{H2S,eq} = \frac{P_{H2S,eq}}{H_{H2S}}$$
(3)

Integration of equation (2) yields:

$$\ln\left(\frac{P_T - P_{T,eq}}{P_{T,0} - P_{T,eq}}\right) = -\beta(t - t_0)$$
(4)

$P_{T,eq}$ represents the total pressure in equilibrium with the loaded solution. The experimental absorption flux is calculated by the following equation:

$$\phi = \frac{\beta V_g}{RTa_i}(P_{T,0} - P_{T,eq})$$
(5)

For each experiment, the enhancement factor E is obtained from β using Eq 5 and estimates of data for the Henry's law constant H_{H2S} and the liquid-side mass-transfer coefficient k_L. Given the absence of data on the solubility, we considered the following equation to calculate the constant of Henry's Law of H_2S in the hybrid solvent:

$$\ln H_{H2S,hyb} = \varphi_{water} \ln H_{H2S,water} + \phi_{methanol} \ln H_{H2S,methanol}$$
(6)

This equation is similar to that given in the model of Wang et al. (1992), we have neglected in this case the excess term and the participation of the amine. The actual composition of water and methanol in the hybrid solvent is considered in the term corresponding to the volume fraction (φ_{water}, $\varphi_{methanol}$).

We used the Kuranov et al. (1996) correlation to estimate the constant of H_2S Henry's Law in water, this correlation covers a wide temperature range from 273.15 to 473.15 K, it is given by the following equation:

$$H_{H2S}(Pa\ m^3 mol^{-1}) = \frac{10^{-6} \times \exp(340.305 - \frac{132368}{T} + 0.059565T - 55.0551\ln T)}{\rho}$$
(7)

The H_2S Henry's Law constants in methanol $H_{H2S,methanol}$ (bar) at 313, 333 and 353 K are respectively 53.65; 73.92 and 96.64. They were obtained using the model PSRK (DDB database).

Knowing the density of the hybrid solvent is necessary to calculate the volume of liquid phase that permits to derive therefrom the gas phase during the operation data from the absorption tests. Indeed, the latter in the

computation of the absorption rate or in the calculation of flow rates imposed for the designing of a column. Measuring the density of the mixtures is carried out by a vibrating tube densimeter (Anton Paar, DMA5000 model). The measuring cell is a U-shaped glass tube, located inside the apparatus. This cell can be observed from the outside through a transparent window. The densimeter is first calibrated at 293 K by measuring the density of air and the degassed water. The temperature range covered is from 278 K to 353 K. All blends were prepared at room temperature in volumetric flasks of 20 mL previously evacuated; the amine is then introduced and then degassed. We introduce later water and finally methanol. The composition of the solvent is determined by weighing. The solvent of a known composition is transferred into a syringe and then introduced into the densimeter (Amararene et al., 2003). Note that at high temperature, the density measurement is difficult because for this temperature range, the methanol begins to evaporate and lowering the density, this phenomenon is more pronounced for solvents with high concentration of methanol. The density of the studied hybrid mixtures is a function of temperature and composition of the mixture. For a given composition, the density decreases with increasing temperature. The mixture density for the high MeOH mass fraction is lowest. Methanol is the lightest compound and its presence in large quantity required to the mixture a low density (the density of pure MeOH at 298.15 K is 0.78958 g cm^{-3}).

For mixtures having the same MeOH mass fraction, the denser mixture is that corresponding to the highest mass fraction of DEA, which is the highest density of compound (the density of pure DEA at 298.15 K is 1.09627 g cm^{-3}).
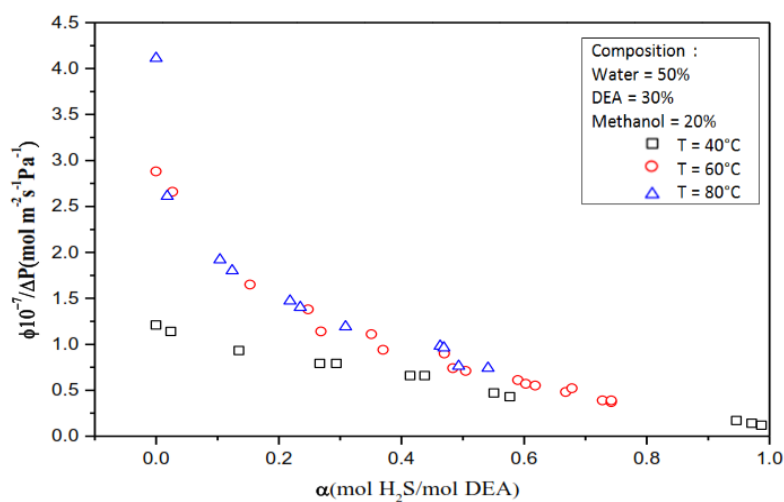

Figure 2: Influence of temperature and the loading rate on the H2S absorption
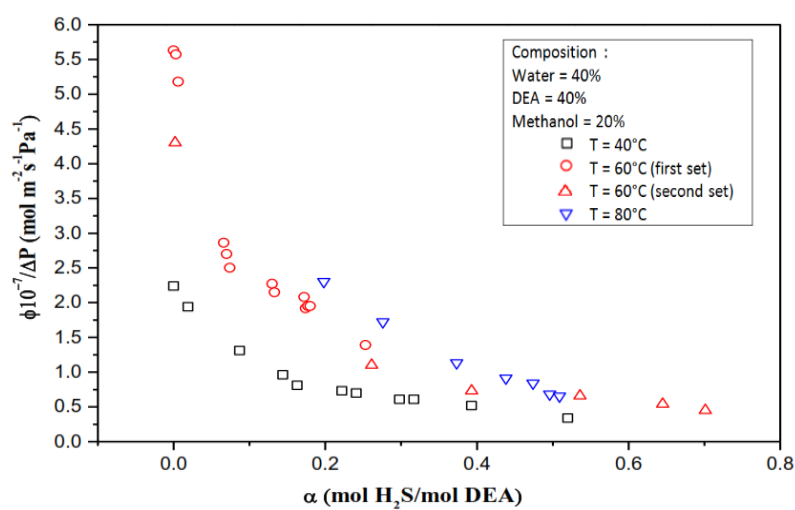

Figure 3: Influence of temperature and the loading rate on the H$_2$S absorption

Following the experimental procedure described above, we conducted absorption tests at three temperatures 40 ° C (293 K), 60 ° C (333 K) and 80 ° C (353 K), in two mixtures with 50 % water, 30 % DEA and 20 % methanol and 40 % water, 20 % methanol for various loading rate (α) values. The latter is defined as the ratio of the gas absorbed moles number on the amine moles number; it depends on the temperature and amine mass fraction. To observe the influence of various parameters, we consider the ratio between the experimental absorption rate calculated by the Eq.5 and the driving force $\Delta P = P_{T,0} - P_I$. Figures 2 and 3 specify the influence of the temperature and the loading rate on absorption.

Figure 2 (50 % Water 30 % DEA, 20 % methanol), show that for fresh solutions, the absorption rate increases with increasing temperature. In the case of the loaded solutions, the absorption rate increases as the temperature rises from 40 °C to 60 °C, elevating the temperature to 80 °C does not seem to have a significant influence on the absorption rate for loaded solutions. For the second composition Figure 3 (40 % water, 40 % DEA, 20 % methanol), the absorption rate increases with increasing temperature regardless of the solution used (fresh or loaded). The same Figures also show the influence of the loading rate on the H_2S absorption. For a given composition and temperature, increasing the loading rate leads to the decrease of the absorption rate.

Figures 4 and 5 show the influence of DEA mass fraction on the given temperature absorption kinetics. The increase in the DEA mass fraction causes an increase of the absorption rate, upon reaching a loading rate of 0.25 moles of H_2S / mole of DEA at T = 60 °C; absorption rates are then comparable (see Figure 4). At T = 80 °C, there is also an increase in the rate with the composition, in this case the loading rate at which the rates are substantially identical is 0.50 moles H_2S / mole of DEA (see Figure 5).
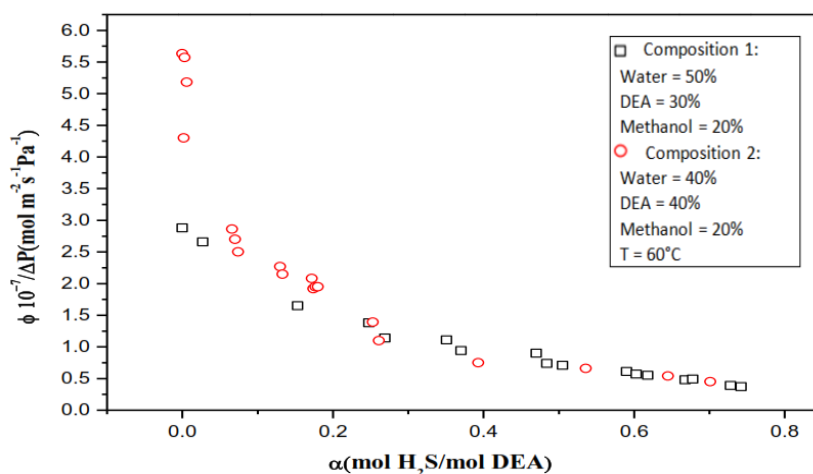

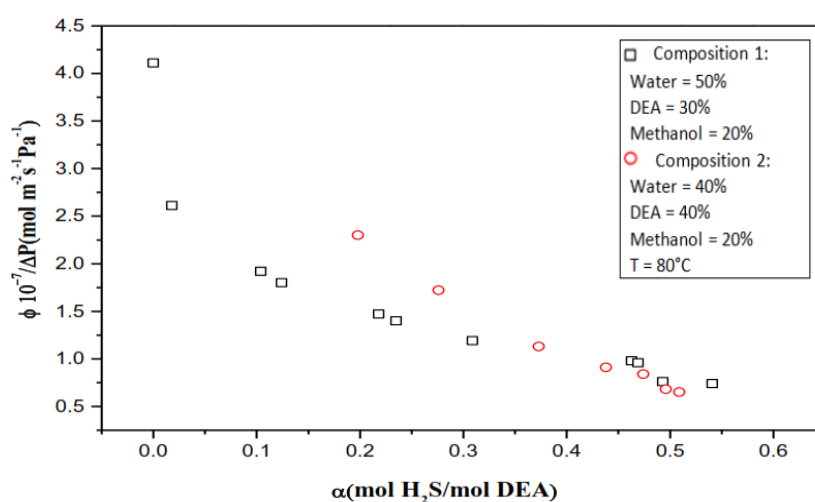Figure 4: Influence of DEA mass fraction on the H_2S absorption

Figure 5: Influence of DEA mass fraction on the H_2S absorption

4. Conclusions

The H_2S absorption in hybrid mixtures has been studied. We have conducted tests comprising reproducibility tests with two blends: 50 % Water 30 % DEA and 20 % Methanol, 50 % Water, 30 % DEA and 20 % methanol. Through these experiments, three parameters affecting the absorption of hydrogen sulphide (temperature T, loading rate α and mass fraction %) were studied. Absorption is accelerated by raising the temperature while it is penalized by the increase in the loading rate. The absorption rate increases as the mass fraction of DEA varies from 30 % to 40 % to achieve an optimum loading rate ($\alpha = 0.25$ at T = 333 K and $\alpha = 0.50$ T = 353 K) for which the absorption rate remains practically unchanged.

In terms of absorption capacity, two different behaviors of hybrid solvent following operating conditions are observed:

- At low H_2S partial pressure and for a loading rate up to 0.78 mol / mol, absorption capacity of aqueous amine solution is highest;
- At high partial pressure and for a loading rate higher than 0.78 mol / mol, the hybrid solvent has the highest absorption capacity. The use of a hybrid solvent is more favourable in high pressure conditions and high loading rate.

On the basis of comparisons carried out in this work, it appears that the new hybrid solvent is the better solvent for the absorption of H_2S compared to a conventional chemical solvent particularly at high loading rate. At high partial pressure and for a loading rate higher than 0.78 mol / mol, the hybrid solvent has the highest absorption capacity. The use of a hybrid solvent is more favourable in high pressure conditions and high loading.

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