TECHNICAL NOTE

SOLUBILITY OF HYDROGEN SULFIDE AND SULFUR DIOXIDE IN TRIETHYLEN GLYCOL, TETRA-ETHYLENE GLYCOL AND DIETHANOL AMINE SOLUTION

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Abstract Natural gas sweetening is an important process which is used for treatment of sour gases. The measurement of solubility is also considered in most sweetening processes such as that of Townsend porocess. Therefore, experimental measurements would be helpful to determine the equilibrium data under actual equilibrium conditions for the gas treatment plants. In this research solubilities of hydrogen sulfide and sulfur dioxide in varous solvents were determined within a wide range of temperatures, 23 to 60°C. Solubility of hydrogen sulfide in 98 per cent tetraethylene glycol was measured at room temperature in a static pool and in an agitated vessel, were found to be 14.11 and 28. 05 mg/g of solvent, respectively. Sulfur dioxide solubility which was also measured at 23°C in a static pool and an agitated vesel, were 23.72 and 262.77 mg/g of solvent, respectively. Solubilitiy is generally reduced by increasing t emperature in most solvents, except that in diethanol amine in which it is in reverse order. The maximum solubilities of gases at 93 percent diethanol amine at 60°C, were obtained. These were 319. 31 and 549.14 mg/g of solvent, in static vessel and an agitated vessel, respectively. Based on experimental results, maximum solubilities were obtained in an agitated vessel at lower range of temperature, except for diethanol amine for which solubilities were maximized at higher range of temperature.

Key Words Diethanol Amine, Hydrogen Sulfide, Gas Sweetening, Solubility, Sulfur Dioxide, Tetra-ethylene Glycol, Townsend Process, Triethylen Glycol

چکیده   شیرین سازی گاز طبیعی و رفع آلودگی ناشی از ترکیبات گوگرددار آن از یک فرایند اساس در صنعت گاز محسوب می شود. اندازه گیری حلالیت گازها در این رابطه از نقطه نظر فنی و اقتصادی در کلیه فرآیندهای تصفیه گاز از اهمیت خاصی برخوردار است. در این کار تحقیقاتی حلالیت گازهای سولفید هیدروژن و دی اکسید گوگرد در چند حلال و در محدوده دمایی ۲۳ تا ۶۰ درجه سانتیگراد اندازه گیری شده است. اندازه گیریها در یک سیستم طراحی شده از شیشه انجام گردیده و گازهای مورد نظر نیز در یک سیستم جانبی متصل به سیستم اصلی تهیه و مورد استفاده قرار گرفته اند. محاسبات با استفاده از قانون گاز ایده آل در نرم افزار کامپیوتری کواتروپرو در انجام شده است. حلالیت گازهای فوق در حلالهای تری و تترااتیلن گلیکول ۹۳ و ۹۸ درصد و دی اتانول آمین ۳۰ و ۹۳ درصد وزنی در حالتهای ساکن و همزدن طی ۱۲۰ آزمایش اندازگیری شده و تاثیر پارامترهایی نظیر فشار، دما، درصد وزنی، نوع حلال و ... مورد ارزیابی واقع گردیده و مقایسه های نظیر نمونه ذیل صورت گرفته است. حلالیت گاز سولفیند هیدروژن در تترااتیلن گلیکول ۹۸ درصد وزنی در دمای اتاق در حالت استخر ساکن و همزدن به ترتیب ۱۴/۱۱ و ۲۸/۰۵ میلی گرم بر گرم حلال اندازه گیری شده است. همچنین حلالیت دی اکسید سولفور در ۲۳ درجه سانتیگراد در حالت استخر ساکن و همزدن به ترتیب ۲۳۵/۷۲ و ۲۶۲/۷۷ میلی گرم بر گرم حلال تعیین شد. حلالیت گازها با افزایش دما کاهش یافته، بجز در حلال دی اتانول آمین که با افزایش دما حلالیت افزایش دارد که حداکثر حلالیت آن در دمای ۶۰ درجه سانتیگراد در حالت ساکن و همزدن به ترتیب ۳۱۹/۳۱ و ۵۴۹/۱۴ میلی گرم بر گرم حلال، اندازه گیری شده است.

INTRODUCTION

Natural gas seewtening process is an important process in petroleum industries, for obtaining clean fuel as energy. Treatment of sour gas in the Townsend Process is a method of sulfur recovery. In this process two moles of hydrogen sulfide are reacted with one mole of sulfur dioxide, as in the Claus sulfur Process, in an aqueous phase solution of a solvent such as Ethylene glycol. The reaction yields elemental sulfur in presence of potassium benzoate, bauxite or kaiser S-201 catalysts [1]. The solubility of hydrogen sulfide and sulfur dioxide, the diffusivities of hydrogen sulfide and sulfur dioxide in the liquid phase were theorically extrapolated in the rate equation for the reactor design. Determination and evaluation of solubility data were important for this research to investigate detail conditions and actual status of gases present in the above process.

Clever and Battino [2] have suggested that the solubility of gases in liquids could be measured by mole fraction of disolved gases in liquids. Therefore, for comparison studies it was decided to calculate mole fraction of gases in liquid solvents. The equilibrium data for most systems, solid liquid gas system was conducted by Gibbs free energies of solvation of solute in a solution [3]. The influence of pressure and temperature on the solubility of gases was reported by several investigator [4-9]. The solubility data depend absoultly upon temperature and pressure of gas liquid system. In addition , solubility of sulfur dioxide and chlorofluromethane in polar organic solvents was studied by Albright and his coworkers at Purdue University [10,11]. They defined optimum solvent at specific conditions. It was reported [11], that the pressure of the system should be related to the solubility of gases. The chemical structure of solvents and the hydrogen bound between the solute and solvent would play major role in the solubility data. Recently Jou et al. [12] conducted solubility study on acid gas in glycol for the design of dehydration process. The goal of the present exprimental research is to present solubility data for equilibrium studies of sulfur gases specially applied in Townsend process [1].

MATERIAL AND METHOD

An experimental system in laboratory scale was constructed by glasses. A vacuum pump was connected to the system to evacuate the whole system. An external gas generator was installed in order to stablize the pressure of the gas at atmospheric load. Solvents were gradually introduced into the system to dissolve gases, based on equilibrium values which were usually obtained with a limited time. The pressure drop vs time was recorded in a spread sheet (Quattro pro.), for further calculations. The amount of soluble gases in solvents was calculated by ideal gas law. After addition of several mililiters of a solvent, a complete run of experiment was over within one day.

The apparatus used in this research is shown in Figure 1. It consisted of 1000 mL distilling flask (Pyrex-Exelo) fitted with 24/29 standard taper middle neck and two 14/23 standard taper side necks. A 25 mL buret was fitted into a rubber stopper into the midle neck. A thermometer was inserted into a rubber stopper into the side neck. A connecting tube was attached to evacuate the system. The whole system was placed on oil bath with a heating element and a thermo-sensor into the oil bath for temperature control. The sensor was attached to a controller model Electro-thermal (Southend SS2 5PH). The temperature was quite regulated to ±0.5°C. A hot plat with magnetic stirrer manufactured by Janke & Kunkel (GMBHS, Co. KG) was used for the mixing system. Gas trapes

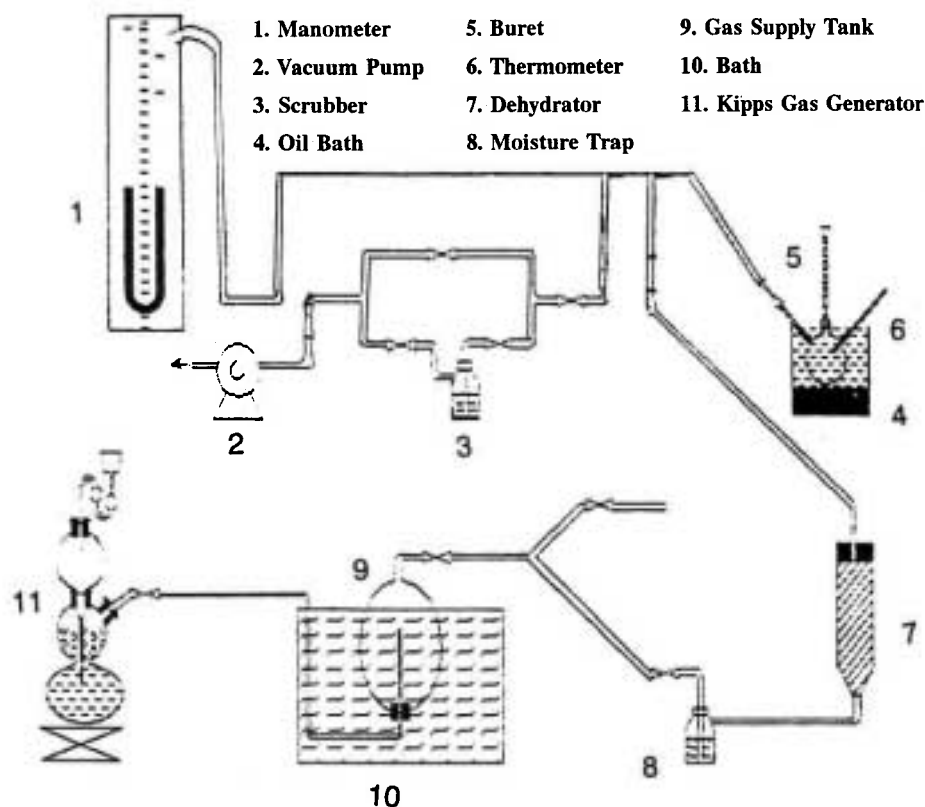| 1. Manometer | 5. Buret | 9. Gas Supply Tank |
2. Vacuum Pump	6. Thermometer	10. Bath
3. Scrubber	7. Dehydrator	11. Kipps Gas Generator
4. Oil Bath	8. Moisture Trap	

Figure 1. Schematic diagram of experimental apparatus.

and a U tube glass Mercury Manometer with 42 cm height of each arm were used. The manometer was filled with mercury (Cox Chemicals LTD) to indicate at most 760 mmHg vacuum pressure. The system was also connected by a branch line to a high vacuum pump Model Eb 3A (Edward, U.K.) for absolute evacuation. The system was leak proved . It was checked often with liquid soap solution.

An off-side gas generator Kipps (Glass work) was attached to a supply tank with five litters capacity. The tank was immersed in a bath for regulating gas transfer into the system by exerting liquid level in the supply tank. the generated gas was dried by sulfuric Acid moisture trap and a calcium choloride column as a gas dehydrator. The purity of the generated gas was analyzed by a perkin-Elemer gas chromatograph Sigma 300. Hydrogen sulfide and sulfur dioxide were

supplied by the gas generator with purity of 99 percent. A by pass of gas absorber was installed in between the flask and the vacuum pump. A concentrated sodium hydroxide solution was used in the gas absorber. Pure solvents were purchased from Fluka, saturated with water. Triethylenglycol, Tetra-ethyleneglycol and Diethanol amine were used as solvents in this research. For each run, the system was absoultely clean, dried and evacuated. The system was very stable and reliable during an experimental run. The gas in the supply tank was conducted to the system by balancing mercury in manometer arms as atmospheric peressure. Temperature of the system, barometeric pressure and the pressure drop vs time with adition of each 2 mL of solvent were recoreded into a Quattro pro spreadsheet for the calculation of solubility data in a particular solvents.

TABLE 1: Solubility of SO_2 in Tetraethylene Glycol 98% at 23°C.

Experimental Conditions:

Run. No.	58			Evacuated Press:	715	mm,Hg
Atm. Press.:	752.5	mm,Hg		Vol. of Container:	1230	ml L
Solv. Dens:	1.115067	gm/ml		State of Solvent:	Mixing	

Time Min	Pres mmHg	Solvent ml	SO_2 mg	Solvent gm	Sol. mg/gm	Sol. mg/l	SO_2 x
0	715	2	0				
2	599	2	541.91497	2.230134	242.997	270,957	0.381248
5	594	2	565.27338	2.230134	253.471	282,637	0.391251
15	590	2	583.9601	2.230134	261.850	291,980	0.399024
30	584	2	611.99019	2.230134	274.419	305,995	0.410318
45	582	2	621.33355	2.230134	278.608	310,667	0.413989
60	580	2	630.67691	2.230134	282.798	315,338	0.417615
90	579	2	635.34859	2.230134	284.893	317,674	0.419411
120	579	2	635.34859	2.230134	284.893	317,674	0.419411
0	579	4					
2	501	4	999.73969	4.460268	224.143	249,935	0.362387
5	500	4	1004.4114	4.460268	225.191	251,103	0.363465
15	498	4	1013.7547	4.460268	227.286	253,439	0.36561
30	498	4	1013.7547	4.460268	227.286	253,439	0.36561
45	497	4	1018.4264	4.460268	228.333	254,607	0.366677
60	496	4	1023.0981	4.460268	229.380	255,775	0.367741
90	496	4	1023.0981	4.460268	229.380	255,775	0.367741
120	496	4	1023.0981	4.460268	229.380	255,775	0.367741
0	496	6					
2	449	6	1242.6671	6.690402	185.739	207,111	0.320176
5	448	6	1247.3388	6.690402	186.437	207,890	0.320993
15	445	6	1261.3538	6.690402	188.532	210,226	0.323434
30	445	6	1261.3538	6.690402	188.532	210,226	0.323434
45	445	6	1261.3538	6.690402	188.532	210,226	0.323434
60	445	6	1261.3538	6.690402	188.532	210,226	0.323434
90	445	6	1261.3538	6.690402	188.532	210,226	0.323434
120	445	6	1261.3538	6.690402	188.532	210,226	0.323434
1205	445	6	1261.3538	6.690402	188.532	210.226	0.323434

RESULTS AND DISCUSSION

The results of solubility studies of hydrogen sulfide and sulfur dioxide in three different solvents are presented in Figures 2 through 7 and Table 1.

Table 1 shows the rate of solubility of sulfur dioxide in 98 percent Tetra ethylene glycol solution in agitated vessel at room temperature (23°C). Equilibrium solubility data were obtained within 120 minutes. The rate of solubility of sulfur dioxide was 262.77 mg/g of solvent at equilibriun condition.

Table is shows the data entery in the spreadsheet and a sample calculation for each experimental run.

Figures 2 and 3 show that the solubility of sulfur dioxide varies as it was influenced by temperature variation in 98 percent Triethylen glycol, Tetra-ethylene glycol and 93 percent Diethanol amine in the static pool. Higher solubilities of sulfur dioxide were achieved at room temperature (23°C). The maximum solubility of sulfur dioxide in 98 percent Tetra ethylene glycol at 600 mmHg was 0.24 g of gas/g solvent.
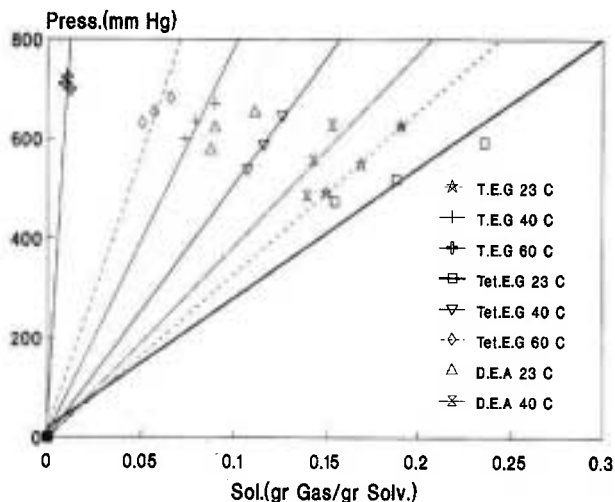
Figure 2. Solubility of sulfur dioxide in 98 percent Tetra ethylene glycol and 93 percent Diethanol amine in static pool.
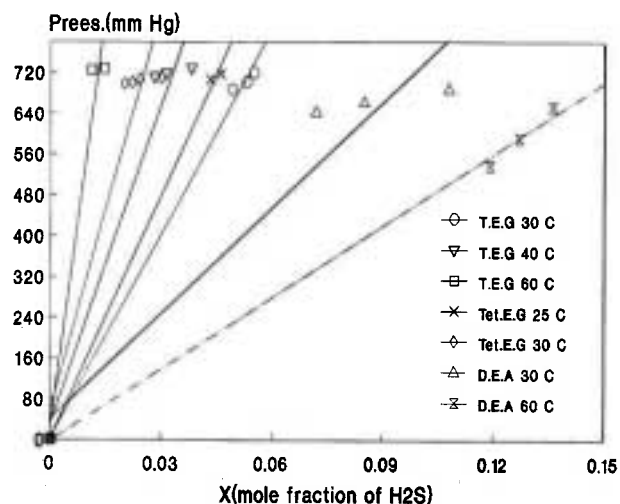

Figure 4. Solubility of hydrogen sulfide in 98 percent Tetra ethylene glycol and 93 percent Diethanol amine in static pool.
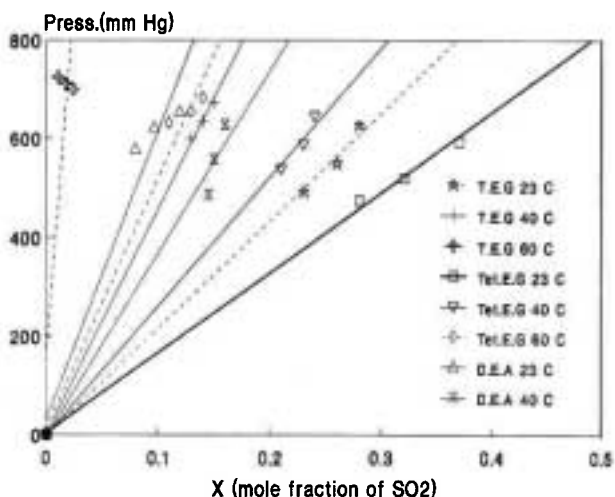

Figure 3. Solubility of sulfur dioxide in 98 percent Tetra ethylene glycol and 93 percent Diethanol amine in static pool.
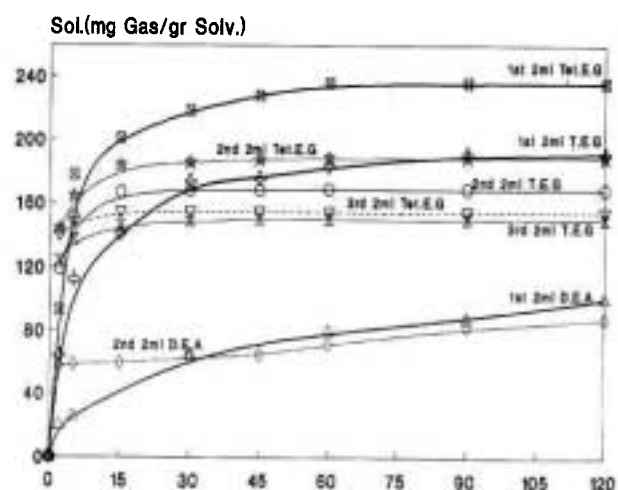

Figure 5. Rate of solubility of sulfur dioxide in 98 percent Tetra ethylene glycol, Triethylen glycol and 93 percent Diethanol amine in static pool at room temperature.

Generally the solubility data depends on gas pressure, as high gas partial pressure resulted in higher gas solubility. As Figure 4 shows, the solubility of hydrogen sulfide was influenced by the temperature in 98 percent Triethylen glycol, Tetra ethylene glycol and 93 percent Diethanol amine at static pool. As temperature was increased, the amount of disolved gas was decreased except for Diethanol amine for which the solubility of gases was increased

as the temperature increased. The temperature dependency of Diethanol amine may refer to the chemical sturcture and the chemical bound of the solvent with gases in liquid phase. The effectiveness of the last solvent might be related to the energy supply caused by effective and strong solubility acheived at higher temperature.

Figure 5 shows the solubility data vs time for reaching equilibrium at 1st, 2nd and 3rd, 2mL of 98
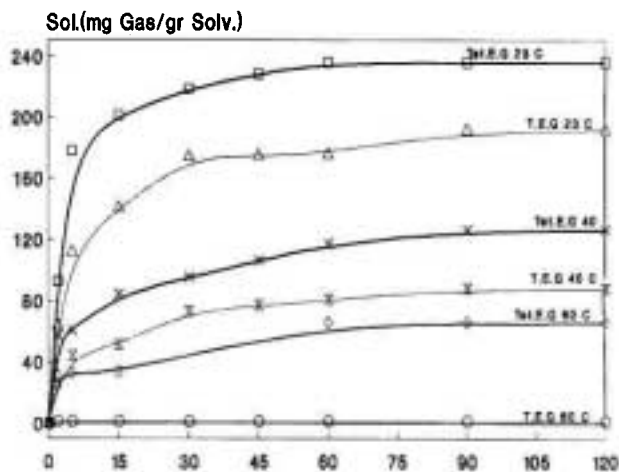
Figure 6. Rate of solubility of sulfur dioxide in 98 percent Tetra ethylene glycol and Triethylen glycol in equilibrium, static pool.
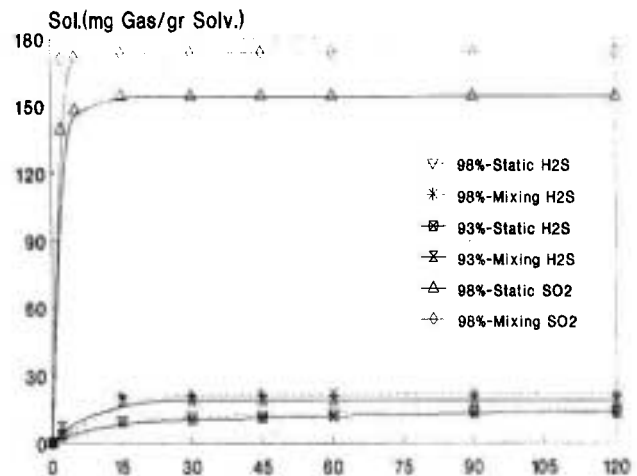

Figure 7. Rate of solubility of hydrogen sulfide and sulfure dioxide in 98 percent Tetra ethylene glycol and 93 percent Diethanol amine in static pool and mixing vessel at room temperature.

percent Triethylen glycol, Tetra ethylene glycol and 93 percent Diethanol amine in the static pool at room temperature. As the gas pressure droped, the amount of soluble gas was also droped in 2nd and 3rd additional 2 mL of solvent. The rate of solubility of sulfur dioxide in Tetra ethylene glycol was also higher than that Diethanol amine solution.

Figure 6 shows a comparison of the rate of solubility data in 98 percent Triethylen glycol, Tetra ethylene glycol solution at various temperatures in static pool. The results are compatible with previous figures, where the temperature dependency was discussed. As the temperature was increased the rate of solubility was decreased. The equilibrium was reached with in two hours.

The comparison study of static pool and agitated vessel for hydrogen sulfide and sulfur dioxide at room temperature for 98 percent Triethylen glycol, Tetra ethylene glycol and 93 perecent Diethanol amine is demonstrated in Figure 7. The agitation may solubilize more sulfur gases in liquid phase. A 20 percent improvement was achieved for agitated solvent. Since more surface area of gas exposure was created by agitation, uniform mixing in liquid phase

caused reduction of the liquid film resistance. Therefore greater mass transfer coefficient were obtained in liquid phase. The effects of temperature and agitation were examined independently. The results of temperature and agitation studies were compatible with those of static pool, i.e., the rate of solubility was decreased as the temperature increased. The rates of solubility of hydrogen sulfide and sulfur dioxide were also compared in Figure 6. The rate of solubility of sulfur dioxide was about five times faster than hydrogen sulfide in static pool and in agitated vessel. The purity of the solvent was effective on the rate of solubility . The 98 percent Tetra ethylene glycol showed higher rate of solubility of hydrogen sulfide than the 93 percent Tetra ethylene glycol solution.

Comparison study was conducted to find the best solvent. The results depended on the conditions of the process. As Figure 7 shows, agitation may improve the solubility of sulfur dioxide in Tetra ethylene glycol about 29 percent. Also the rate of solubility in Diethanol amine would be more considerable at higher temperature in the agitated vessel.
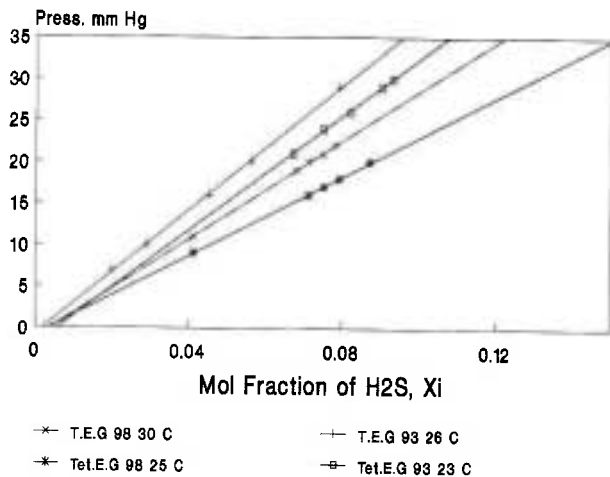
Figure 8. Solubility of hydrogen sulfide in different solvent.

Figure 8 is a plot of the solubility of hydrogen sulfide in different solvents. The pressure of hydrogen sulfide versus mole fraction of hydrogen sulfide in the liquid phase is absolutely related to each other. The experimental data are perfectly fitted as straight lines.

CONCLUSIONS

The solubility of hydrogen sulfide and sulfur dioxide in three different solvents, Triethylen glycol and Tetra ethylene glycol and Diethanol amine with different weight percent (93 and 98%) have been determined at atmospheric pressure and below at temperatures ranging from 20°C to 60°C.

The solubilites obtained in different solvents were compared with each set of data. The rate of solubility for sulfur dioxide was about five times higher than that of hydrogen sulfide. The rates were decreased with increasing temerature except for Diethanol amin in which the rate was increased with increase in temerature for both gases. The rate of solubility of both gases were also increased by agitation or any system with higher mass transfer coefficient. The interfacial area of gas and liquid phase would be directly proportional with mass flux in aqueous phase.

Therefore, the rate of solubility of both gases were more effective for the agitated vessel than for static pool.

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