Solubility Study of Methane and Ethane in Promising Physical Solvents for Natural Gas Sweetening Operations

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New data are reported for the solubility of methane and ethane in six physical solvents [diethylene-, triethylene-, and tetraethylene-glycol dimethyl ethers; triethylene glycol monobutyl ether; a mixture of poly(ethylene glycol) dimethyl ethers (PEGDME 250); and *N*-formyl morpholine (NFM)]. The solubility data were measured at 25 °C, 40 °C, and 60 °C and expressed in the form of Henry's law constants.

Introduction

The removal of carbon dioxide from gas streams received increased attention with the implementation of the Kyoto Protocol in many countries and led to the development of several more economical processes for the removal of acid gases from natural gas. Contrary to chemical solvents, physical solvents require much less energy for regeneration. Physical solvents are also able to absorb mercaptans, sulfur compounds, and other impurities. Unfortunately in the process of absorbing carbon dioxide, physical solvents tend to co-absorb the hydrocarbon components of the natural gas. The amount of co-absorbed methane and ethane is an important factor in the economical viability of the process solvent. Knowledge of the solubility of methane and ethane in polar liquids is important both industrially and for the development of solution theories.

Unfortunately, solubility data for methane and ethane in polar or slightly polar solvents are scarce. In a preliminary literature study, Henni and Mather[1] concluded that ethylene glycol ethers were the solvents with the highest potential for gas sweetening. Data for the solubility of methane in 19 polar solvents and the solubility of ethane in 7 solvents were compiled from the literature. A compilation of the data for the solubility of methane[2] and ethane[3] was published in the IUPAC Solubility Data Series. Sciamanna and Lynn[4] measured the solubility of propane and *n*-butane in five glycol ethers (DEGDME, TEGDME, TTEGDME, DEGMME, and TEGMBE) with an automated gas solubility apparatus and reported the results in the form of Henry's law constants at infinite dilution at 25 °C.

In the present study, the solubility of methane and ethane was measured at 25 °C, 40 °C, and 60 °C in the five most promising solvents in terms of carbon dioxide absorption[5] (i.e., diethylene-, triethylene-, and tetraethylene-glycol dimethyl ethers, triethylene glycol monobutyl ether, and a commercial mixture of poly(ethylene glycol) dimethyl ethers (PEGDME 250)). The solubility results were compared with the solubility in *N*-formyl morpholine (NFM), a solvent recently promoted as very promising,[6] sulfolane, and NMP (*N*-methylpyrrolidinone or *N*-methyl pyrrolidone), other widely used solvents in the industry.

This is the first attempt in the open literature to compare directly the solubility of methane and ethane in the most promising poly(ethylene glycol) dimethyl ethers (that partially make up the proprietary mixture Selexol), a mixture, PEGDME 250, sulfolane, NFM, and NMP, all widely used solvents in the gas processing industry.

Experimental Procedures

The experimental apparatus consisted of an Autoclave glass reactor cell (Erie, PA). The cell was connected to a water bath (Cole Parmer, model H-08502-12) maintained at ± 0.04 °C by a temperature controller (Cole Parmer, model H-01158-65, Anjou, PQ, Canada). The temperature in the cell was measured by an Omega thermocouple. The fluid pressure in the cell was measured with a calibrated digital transducer (PX 800-010GV and an indicator DP 40 from Omega) with an estimated uncertainty of 0.1 % of the scale range (70 kPa). The liquid sample line led from the bottom of the cell to a needle valve.

Prior to the introduction of the fluid, the apparatus was brought to the desired temperature and purged with nitrogen to remove traces of oxygen (when necessary the cell was first heated under deep vacuum to remove any water present). The solvent was fed by vacuum to the equilibrium cell. The vapor pressure of the solvent was measured at equilibrium, and then methane (or ethane) was added. In general, the pressure was set at (14 to 20) kPa above the local atmospheric pressure to allow for the removal of the liquid sample. To ensure that equilibrium was reached, the mixer was started and kept in operation for 4 to 8 h until the pressure remained the same for more than 30 min. The liquid phase was analyzed by withdrawing a sample; 1 μL of this sample was injected into a 5939 series gas chromatograph (Hewlett-Packard) where a 3 m long, 6.35 mm o.d. column packed with Chromosorb 104 was used. The oven temperature was programmed to go from 120 °C to 250 °C or 280 °C, depending on the solvent, after the appearance of the gas peak. Depending on the gas and the amount absorbed, in general, (10 to 100) μL of pure methane or ethane was injected in the column. Care must be taken to avoid taking a sample when the mixer was in operation. Vigorous mixing created micro-size gas bubbles. Solubility values measured while the mixer was in operation and the micro-size gas bubbles were present led to solubility values that were (20 to 30) % higher than when the liquid was allowed to settle for a few seconds

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Table 1. Comparison of the Solubility Data (*H*/MPa) in This Work with Other References (115 kPa)

methane (*T*/°C)	this work	ref 9	ref 7
TEGDMEC (25)	37.3	41.4	
TTEGDME(25)	38.1	39.6	
NFM (25)	164.5		167.4
NFM (40)	162.2		165.5

ethane (*T*/°C)	this work	ref 9	ref 8
TEGDME (25)	4.4	7.1	
TTEGDME (25)	5.9	7.0	
NFM (25)	30.3		32.7
NFM (40)	31.9		36.9

after the agitator was turned off. At least three equilibrium measurements were done, and each sample was analyzed at least three times. The Henry's law constants reported were the average of three equilibrium data points. Jou et al.[7,8] measured the solubility of methane and ethane in NFM at high pressures, used the Peng−Robinson equation of state to calculate the fugacities of the gases, and used the Krichevsky-Illinskaya equation to extract Henry's law constants. de la Iglesia et al.[9] recently published the solubility of methane and ethane in TEGDME and TTEGDME at 25 °C. They used a pressure decay method and an iteration technique to find the moles of gas absorbed in the liquid. Solubility data interpolated/extrapolated from the literature to 115 kPa are presented in Table 1. The deviations are plotted in Figure 1. The average uncertainties were estimated to be 5 % for methane and 10 % for ethane when compared with values in the literature, except for an explained large deviation for one data point at 25 °C (TEGDME−ethane) with the value obtained by de la Iglesia et al.[9] The value we got is close to the other values we obtained at 40 °C and 60 °C for TEGDME and to solubility values of ethane in DEGDME and TTEGDME.

Materials

Diethylene glycol dimethyl ether (DEGDME) was > 99 % pure. Triethylene glycol dimethyl ether (TEGDME) was > 98 % pure. Tetraethylene glycol dimethyl ether (TTEGDME) was > 99 % pure. Triethylene glycol monobutyl ether (TEGMBE) was > 70 % pure (the rest was mainly tetraethylene glycol monobutyl ether and pentaethylene glycol monobutyl ether); *N*-formyl morpholine (NFM) was > 98 % pure. TTEGDME was purchased from Lancaster (Pelham, NH). All other solvents were purchased from Fluka. The glycol ether solvents are hygroscopic and must be dried before use. The solvent samples were degassed under vacuum while being stirred and heated in a fractionator (Büchi, Switzerland). The degassing was completed when gas bubbles stopped evolving from the solvent or when the solvent itself appeared to be boiling. The solvents were kept under vacuum on molecular sieves.

Table 2. Henry's Law Constant of Methane in Glycol Ethers and Other Solvents

	(*H*/MPa) at		
solvents	25 °C	40 °C	60 °C
DEGDME	40.5	41.4	43.1
TEGDME	37.3	38.2	39.4
TTEGDME	38.1	39.7	41.2
TEGMBE	38.7	41.3	45.1
PEGDME 250	36.4	38.7	40.4
NFM	164.5	162.2	161.7
sulfolane[18]	216.2	218.3	219.0
NMP[14]	103.9	106.8	110.0

Results and Discussion

The definition of the Henry's law constant used in this work was

$$H_1 = (P_1/x_1) \tag{1}$$

Henry's law constant relates the equilibrium mole fraction of substance in the liquid phase (x_1) to its partial pressure (P_1) in the gas phase. The solubilities of methane in the most promising ethylene glycol solvents (and NFM) were measured at temperatures of 25 °C, 40 °C, and 60 °C. The results are presented in Table 2 and Figure 2. The figure shows that sulfolane was, by far, the solvent that absorbed methane the least, followed by NFM and NMP. All the other solvents followed with approximately the same high capacity for methane absorption.

The solubilities of ethane in the most promising ethylene glycol solvents and NFM were also measured at temperatures of 25 °C, 40 °C, and 60 °C. The results are presented in Table 3 and Figure 3. The figure shows that sulfolane was the solvent that absorbed ethane the least followed by NFM and NMP. All the other solvents followed with a relatively high capacity for ethane absorption. The solubilities of methane and ethane in the solvents were of the same order of magnitude, but ethane was much more absorbed than methane.

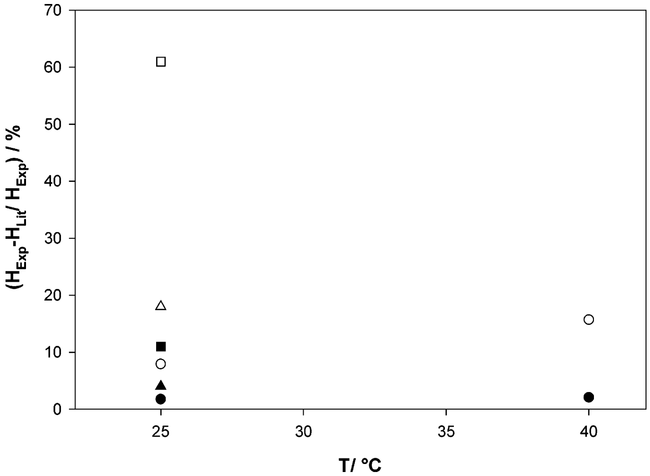

Figure 1. Comparison between literature data and this work for methane: ■, TEGDME; ▲, TTEGDME; ●, NFM; and ethane: □, TEGDME; △, TTEGDME; ○, NFM.

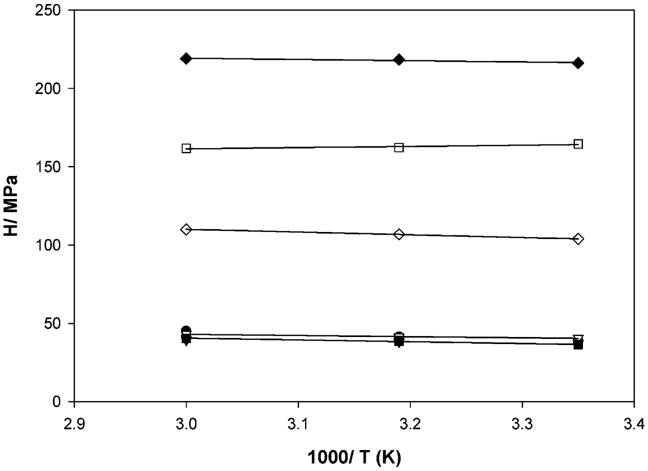

Figure 2. Henry's law constant (*H*) for methane as a function of temperature (*T*) for ◆, sulfolane; □, NFM; ◇, NMP; ●, TEGMBE; ▽, DEGDME; ○, TTEGDME; ■, PEGDME 250; ▼, TEGDME.

Table 3. Henry's Law Constants of Ethane in Glycol Ethers and Other Solvents

	H/MPa at		
solvents	25 °C	40 °C	60 °C
DEGDME	8.2	8.5	9.9
TEGDME	4.4	5.1	6.6
TTEGDME	5.9	7.1	8.4
TEGMBE	8.0	8.4	10.0
PEGDME 250	11.1	11.9	12.7
NFM	30.3	31.9	36.2
sulfolane[15,18]	50.18	55.32	58.3
NMP[16]	21.4	23.9	29.1

If the different solvents were ranked according to minimizing the function $\{H_{CO_2}/(H_{CH_4} \times H_{C_2H_6})\}$, the best solvents for carbon dioxide removal from natural gas[5] while absorbing methane and ethane the least would be sulfolane followed closely by NFM, NMP, then PEGDME 250. and TTEGDME (Figure 4). It is important to know that the viscosity of NMP (1.66 mPa•s at 25 °C)[17] was lower than that of TTEGDME (3.38 mPa•s at 25 °C),[10] Selexol (5.80 mPa•s at 20 °C−25 °C),[11] NFM (7.87 mPa•s at 25 °C),[12] and sulfolane (10.29 mPa•s at 30 °C).[13] Unfortunately, NFM was solid at ambient temperature. In a commercial process (Morphysorb, Krupp Uhde), it would be mixed with *N*-acetyl morpholine (NAM) in order to reduce its freezing point.

Concluding Remarks

Screening studies are expensive and require a long time. This study reports on the solubility of methane and ethane in ethylene glycol ethers. Its importance consists of the fact that it compares the whole family of commercially available glycol ethers and NFM using the same experimental procedure and calculation technique with sulfolane and NMP. The solubility measurements were done using the same procedure and equipment at low pressure and thus allowed a direct comparison based on the same conditions.

Sulfolane had the lowest capacity for methane absorption. NFM and then NMP had a somewhat lower capacity for methane than ethylene glycol ethers. All ethylene glycol ethers (including the mixture PEGDME 250, NMP, and sulfolane) were liquid at ambient temperature. NFM was solid at ambient temperature.

In terms of ethane absorption, once again, sulfolane had a much lower absorption capacity for ethane than NFM and NMP. All the remaining solvents have approximately the same relatively high capacity for ethane absorption.

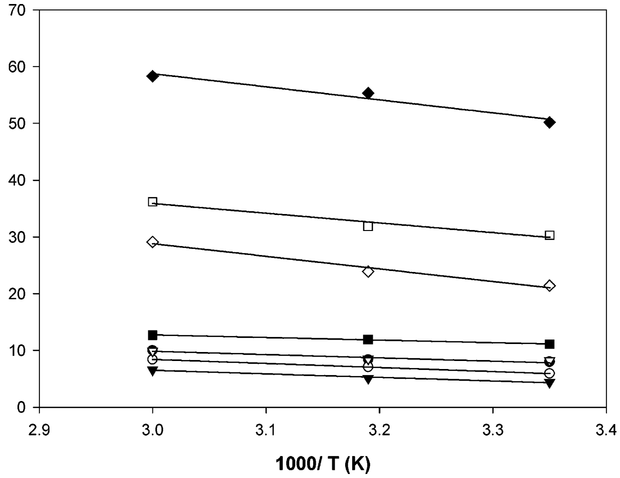

Figure 3. Henry's law constant (*H*) for ethane as a function of temperature (*T*) for ◆, sulfolane; □, NFM; ◇, NMP; ■, PEGDME 250; ●, TEGMBE; ▽, DEGDME; ○, TTEGDME; ▼, TEGDME.

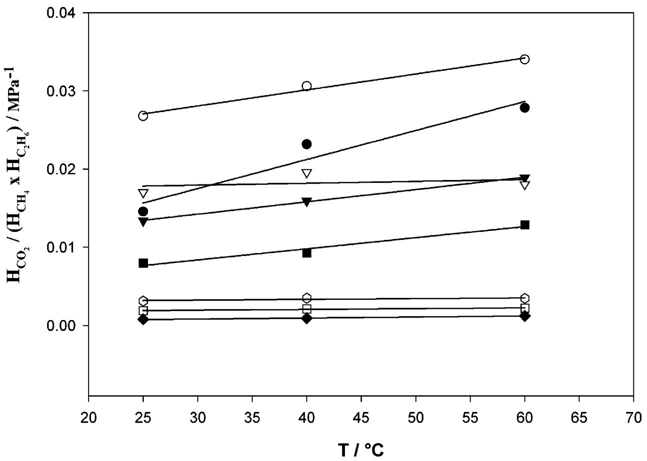

Figure 4. Comparison of the capacity for CO_2 absorption and methane and ethane co-absorption as a function of temperature (*T*) for ○, TEGDME; ●, DEGDME; ▽, TEGMBE; ▼, TTEGDME; ■, PEGDME 250; ○, NMP; □, NFM; ◆, sulfolane.

The absorption of ethane was much higher than that of methane for all solvents. As presented in Figure 4, the study confirmed why some of these solvents (i.e., sulfolane, NMP, and NFM) were so popular in gas sweetening in terms of carbon dioxide absorption and hydrocarbon co-absorption. The study presents a direct comparison between the most widely used solvents in the gas industry. Process engineering and economic studies must always be undertaken for several combinations of process schemes and solvents to determine the optimum combination.

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