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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

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Henry's law constants of propyl mercaptan, butyl mercaptan, and dimethyl sulfide in the temperature range (293 to 343) K at atmospheric pressure in methyldiethanolamine (1) + water (2) with $w_1 = 0.50$ have been measured using a gas stripping method. The influence of the solvent is discussed, and experimental results are compared to literature data when available.

Introduction

Removal of acid gas components such as H_2S, CO_2, and other sulfur species (COS, CS_2, and mercaptan) from natural gas, refinery gas, or natural gas liquids by aqueous amines is a frequently encountered operation. MDEA (methyldiethanolamine) is one of the most widely employed gas-treating alkanolamine solvents. This solvent is very attractive for selective removal of H_2S from process streams containing CO_2 and hydrocarbons. As sulfur species such as mercaptans are found in very small quantities, the Henry's law approach is generally used. By definition, the Henry's law coefficient is defined at infinite dilution. The approach to infinite dilution is an important state of liquid mixtures mainly for testing models in drastic conditions. For a binary mixture, the concentration of solute approach infinite dilution, and then close neighbors of solute molecules are only solvent molecules that have a mole fraction that can be considered to one. Study at infinite dilution is a good mean to evaluate nonideality of solute−solvent mixtures. The Henry's law constant is directly related to the residual chemical potential of the solute at infinite dilution, which is evaluated from the intermolecular potential between one solute molecule and one solvent molecule. Limiting activity coefficient is directly determined from Henry's law coefficient. It provides incisive information regarding solute solvent interactions in the absence of solute solute interactions. The apparatus used is based on a dynamic method. It was first proposed by Leroi et al.[1] and concerns a gas stripping method.

Theory

Phase equilibrium governs the distribution of molecular species between two or more phases. For a molecular solute, vapor−liquid-phase equilibrium is given by eq 1 (symmetric convention):

$$Py_i\Phi_i^V = x_i H_i^{P_{solv}^{sat}} \exp\left(\int_{P_{solv}^{sat}}^{P} \frac{v_i^{\infty}}{RT} \mathrm{d}P\right) \quad (1)$$

where y_i and x_i are respectively the vapor and liquid compositions, P is the pressure, Φ_i^V is the fugacity coefficient (equal to one as we consider that, at atmospheric pressure, the vapor phase is considered as an ideal gas), $H_i^{P_{solv}^{sat}}$ is the Henry's law coefficient at the solvent vapor pressure, and the exponential term is the Poynting factor. This last quantity can be considered equal to unity. Consequently, eq 1 can be written as

$$Py_i = x_i H_i^{P_{solv}^{sat}} \quad (2)$$

Henry's Law Coefficient Measurements

Materials. Methyldiethanolamine (MDEA), butyl mercaptan, and propyl mercaptan were provided by Aldrich with a certified GC purity >99 %. Dimethyl sulfide is from Acros with a certified GC purity >99 %. Water is produced with an apparatus that delivers ultrapure water (Millipore, Direct Q5). Water and amine were degassed independently, and aqueous solutions were prepared under a vacuum. The respective masses of water and amine were determined by differential weighing to prepare a mass fraction (w) of 50 % MDEA aqueous solution (mass fraction uncertainty lower than 0.02 %).

Equipment. The principles and equipment have been fully described previously by Richon et al.[2] and then by Krummen et al.[3] A simplified flow diagram of the apparatus appears in Figure 1. The carrier gas (helium) was initially brought to the required temperature with the help of the heat exchanger coil (E1). On this figure, two 60 cm^3 cells are displayed, one upstream (saturator S) permits saturation of the gas with the solvent (it guaranties a constant amount of solvent in the measurement cell) while the second (dilutor D) contains the highly diluted solute to be stripped from the solvent by the solvent saturated stripping gas. The two cells are inside a liquid bath regulated to within 0.01 K. A platinum probe, in contact with the liquid phase of the "dilutor cell", was connected to an electronic display. Temperature uncertainty after careful calibration of the probe was below 0.1 K. Analytical work was carried out using a gas chromatograph (PERICHROM model PR2100, France) equipped with a flame ionization detector (FID) connected to a data acquisition

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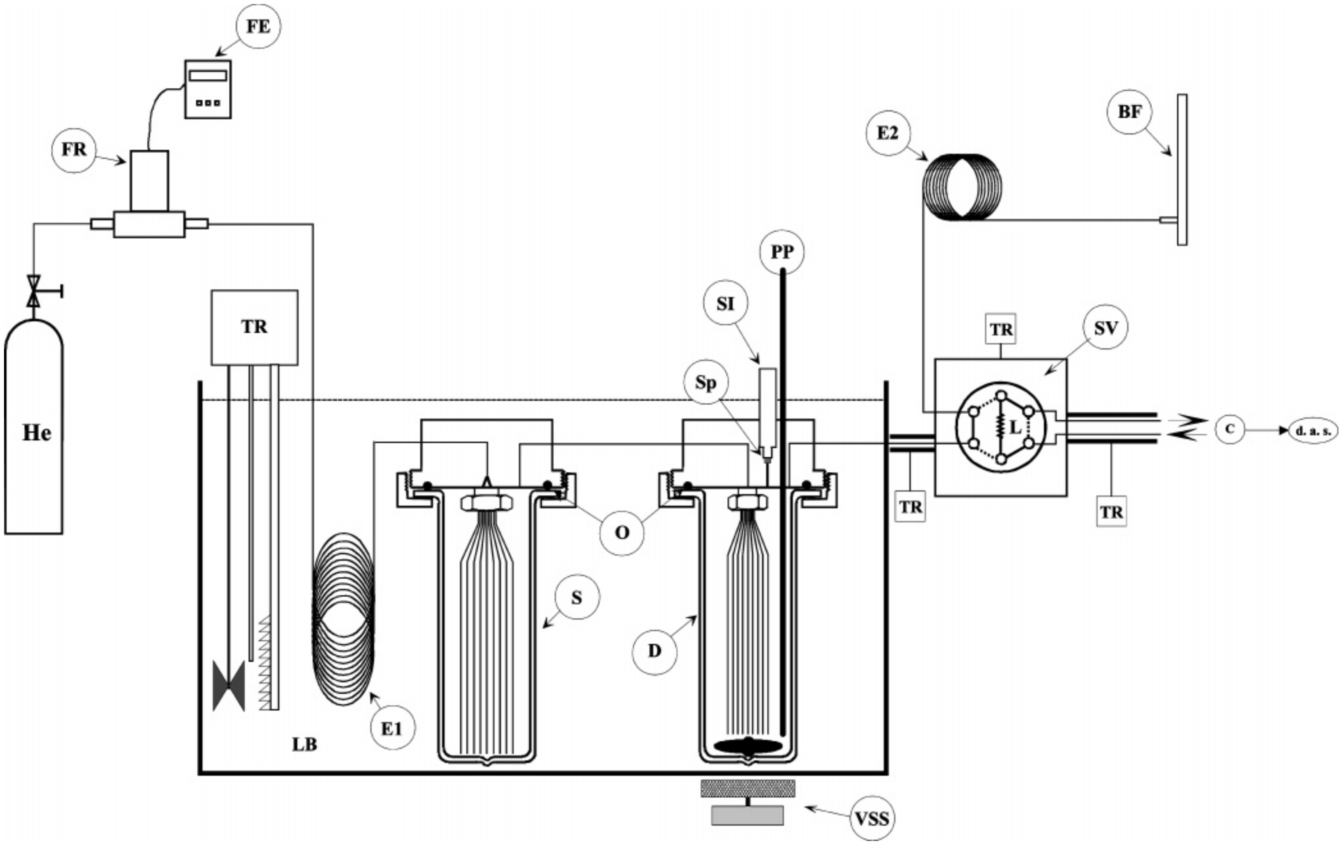

Figure 1. Flow diagram of the equipment: BF, bubble flow meter; C, chromatograph; D, dilutor; d.a.s., data acquisition system; He, helium cylinder; E1, E2, heat exchangers; FE, flow meter electronic; FR, flow regulator; L, sampling loop; LB, liquid bath; O, O-ring; PP, platinum resistance thermometer probe; S, saturator; SI, solute injector; Sp, septum; SV, sampling valve; TR, temperature regulator; VSS, variable speed stirrer.

system (BORWIN ver 1.5, from JMBS, Le Fontanil, France). The analytical column was PORAPAK R 80/100 MESH (Silcosteel, length: 2 m, diameter: 2 mm).

The flow meter (Analyt-MTC, Messtechnik GmbH model 358) was calibrated using bubble flow meter with the carrier gas. The uncertainty on flows was estimated to be around 1.5 %.

Experimental Procedure

About 40 cm^3 of pure solvent was introduced into the "saturator cell", while about 25 cm^3 of the solute−solvent mixture was introduced into the "dilutor cell". A constant stripping gas "helium" flow adjusted to a given value by means of a mass flow regulator was bubbled through the stirred liquid phase and stripped the volatile solute into the vapor phase. The composition of the gas leaving the dilutor cell was periodically sampled and analyzed by gas chromatography using a gas sampling valve. Equilibrium must be reached between the gas leaving the cell and the liquid phase in the cell. This can be checked by verifying the measured activity coefficient value does not depend on the eluting gas flow-rate. The peak area, S_i, of solute i decreased exponentially with time if the analysis was made in the linearity range of the detector. In these conditions, the Henry's law coefficient, H (Pa), of solute i can be calculated with

$$H_i = -\frac{1}{t}\ln\left(\frac{S_i}{(S_i)_{t=0}}\right) \times \frac{RTN}{D\left(1 + \frac{P_{solv}^{sat}}{P}\right) + \frac{V_G}{t}\ln\left(\frac{S_i}{(S_i)_{t=0}}\right)} \qquad (3)$$

where D is the carrier gas flow rate ($m^3 \cdot s^{-1}$), N is the total number of moles of solvent inside the dilutor cell, V_G (m^3) is the volume of vapor phase in the dilutor cell, S_i is the chromatograph solute i peak area, t (s) the time, T (K) the temperature in the cell, P (101 300 Pa) the pressure inside the cell, P_{solv}^{sat} (Pa) the saturation pressure of the solvent, and R ($J \cdot mol^{-1} \cdot K^{-1}$) is the ideal gas constant. Uncertainty concerning the Henry's law coefficient is estimated to be 5 %. This estimation comes from taking into account the uncertainty on the flow, the solute i peak area determination, the uncertainty in temperature, and the number of moles of solvent. This uncertainty is a consequence of the difficulty determining accurately the slope of the solute i peak area as a function of time. The slope is determined by linear regression of area logarithms. A typical representation of peak areas as a function of time is provided in Figure 2 for dimethyl sulfide.

The conversion of the gas stream determined with the flow meter (D_{FM}) to the cell condition was carried out as follows:

$$D = D_{FM}\frac{T}{T_{FM}}\frac{P_{FM}}{P} \qquad (4)$$

T_{FM} and P_{FM} are respectively the temperature and the pressure inside the flow meter.

Results and Discussion

The values of Henry's law constants in pure water and in a mass fraction of 50 % MDEA aqueous solution were given in Tables 1 to 3. Table 1 concerns the propyl mercaptan, Table 2 concerns the butyl mercaptan, and Table 3 concerns the dimethyl sulfide. Figures 3 to 5 show the temperature dependence of the logarithm of the Henry's

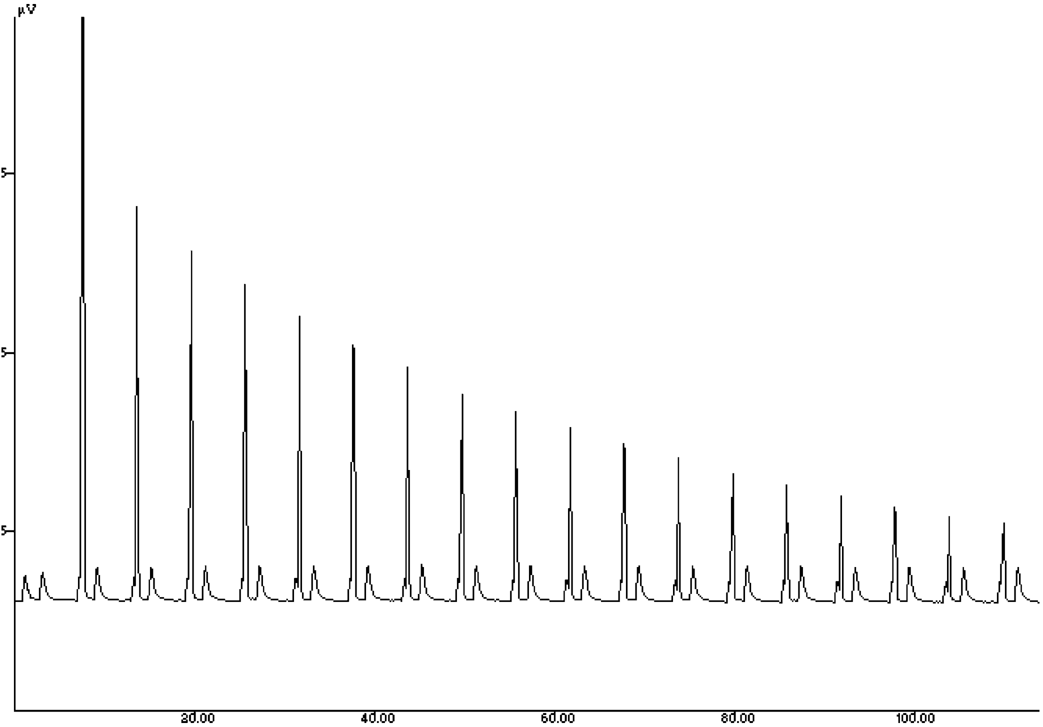

Figure 2. Chromatographic peak area as a function of time for dimethyl sulfide in methyldiethanolamine (1) + water (2) with $w_1 = 0.50$ aqueous solution. $T = 313$ K and $D = 0.167$ cm^3·s^{-1}.

Table 1. Temperature Dependence of Henry's Law Constant for Propyl Mercpatan in Methyldiethanolamine (1) + Water (2) with $w_1 = 0.50$ Aqueous Solution

T/K	H/MPa	γ^{∞}
	Water	
293.2	23.9	1455
303.1	46.8	1844
333.1	93.9	1191
	Methyldiethanolamine (1) + Water (2) with $w_1 = 0.50$	
293.1	3.1	188
298.0	3.9	190
303.1	4.3	168
312.9	4.9	129
323.1	5.6	101
333.1	8.3	105
343.1	10.2	93
353.1	13.1	89

Table 2. Temperature Dependence of Henry's Law Constant for Butyl Mercaptan in Methyldiethanolamine (1) + Water (2) with $w_1 = 0.50$ Aqueous Solution

T/K	H/MPa	γ^{∞}
	Water	
292.8	29.3	6223
312.8	70.1	5717
332.8	125.7	4504
	Methyldiethanolamine (1) + Water (2) with $w_1 = 0.50$	
292.8	1.80	383
302.6	3.2	411
312.7	3.1	253
322.9	4.7	246
332.4	7.2	262
342.8	9.3	241

law constants of the three sulfur species in methyldiethanolamine (1) + water (2) with $w_1 = 0.50$ aqueous solution, respectively. These figures show clearly the effect of the amine: the Henry's law constants in MDEA aqueous solution are smaller than those in pure water. This behavior highlights the two different absorption types: physical with water and chemical with amine. The Henry's law constant value increases with the solute molecular size.

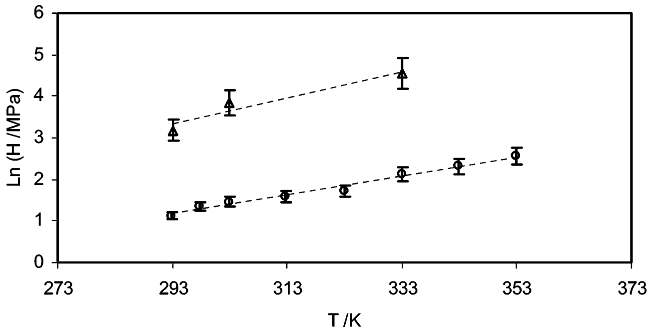

Figure 3. Logarithm of Henry's law constant of propyl mercaptan in water (△) and in methyldiethanolamine (1) + water (2) with $w_1 = 0.50$ aqueous solution (○) as a function of T.

Figure 6 presents limiting activity coefficient values as a function of T for sulfur species in water. The limiting activity coefficient is calculated through eq 5. Details concerning the calculation of the saturation pressure are presented in the table shown in the Appendix:

$$\gamma_i^{\infty} = \frac{H_i^{P_{solv}^{sat}}}{P_i^{sat}} \tag{5}$$

We have found no literature data about propyl mercaptan, butyl mercaptan, and dimethyl sulfide either in water or mixtures but limiting activity coefficient of other sulfur species (i.e., methyl mercaptan,[5] hydrogen sulfide,[6] and carbonyl sulfide[7]) in water. From all data collected, it is obvious that the value of limiting activity coefficient increases with the number of carbon atoms of sulfur species and as a consequence with molecular size. Moreover, carbonyl sulfide is the most soluble certainly due to his particular molecular form.

Figure 7 presents the limiting activity coefficient as a function of T for the sulfur species in methyldiethanolamine (1) + water (2) with $w_1 = 0.50$ aqueous solution. The measurements are compared with those for the methyl

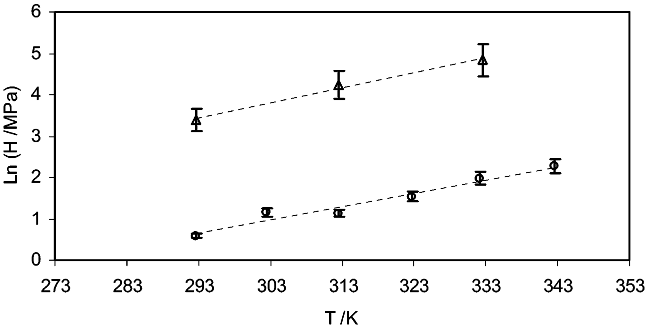

Figure 4. Logarithm of Henry's law constant of butyl mercaptan in water (△) and in methyldiethanolamine (1) + Water (2) with $w_1 = 0.50$ aqueous solution (○) as a function of T.

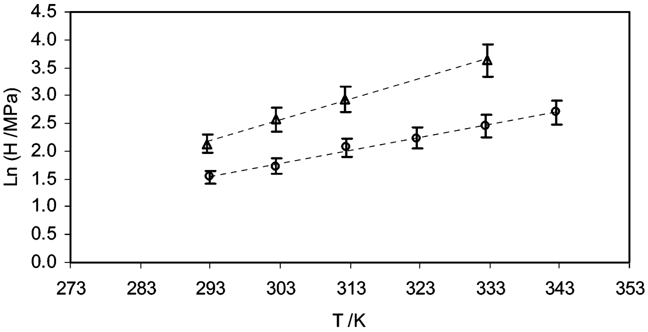

Figure 5. Logarithm of Henry's law constant of dimethyl sulfide in water (△) and in methyldiethanolamine (1) + water (2) with $w_1 = 0.50$ aqueous solution (○) as a function of T.

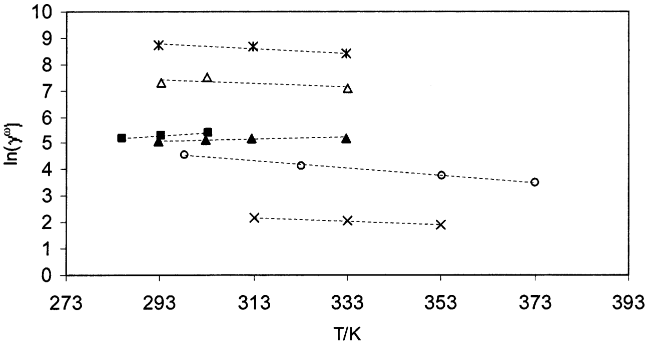

Figure 6. Logarithm of limiting activity coefficient in water as a function of T. ○, methyl mercaptan;[5] △, propyl mercaptan; *, butyl mercaptan; ×, hydrogen sulfide;[6] ▲, dimethyl sulfide; ■, carbonyl sulfide.[7]

Table 3. Temperature Dependence of Henry's Law Constant for Dimethyl Sulfide in Methyldiethanolamine (1) + Water (2) with w_1 = 0.50 Aqueous Solution

T/K	H/MPa	γ^∞
	Water	
292.6	8.4	161
302.7	13.0	170
312.5	18.8	174
332.8	37.1	183
Methyldiethanolamine (1) + Water (2) with $w_1 = 0.50$		
293.2	4.6	87
302.7	5.6	74
312.7	7.1	72
322.7	9.4	62
332.6	11.6	56
342.7	14.8	54

mercaptan[5] and ethyl mercaptan.[8] The limiting activity coefficients of ethyl mercaptan and dimethyl sulfide are very close. This is due to their similar molecular formula (C_2H_6S) and their similar physical properties.

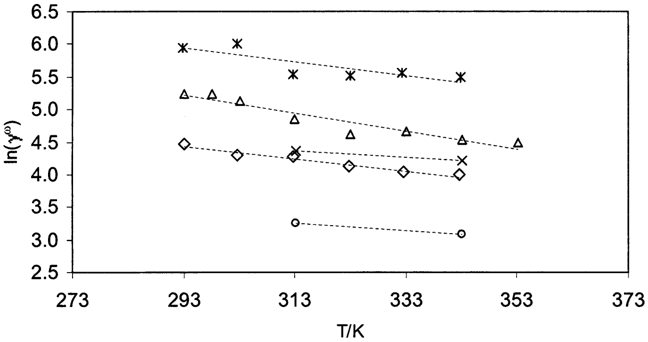

Figure 7. Logarithm of limiting activity coefficient in methyldiethanolamine (1) + water (2) with $w_1 = 0.50$ aqueous solution as a function of T. ○, methyl mercaptan;[5] △, propyl mercaptan; *, butyl mercaptan; ×, ethyl mercaptan;[8] ▲, dimethyl sulfide.

Conclusion

Henry's law constant and infinite dilution activity coefficients of three sulfur species in methyldiethanolamine (1) + water (2) with $w_1 = 0.50$ aqueous solution in the temperature range (293 and 343) K have been obtained from gas stripping measurements. The amine solvent power on sulfur species has been stressed by regarding the solubility of these species in water. In all cases, the Henry's law constant depends on the solute molecular size.

Appendix

Correlation used to calculate the vapor pressure has the following form:

$$P^{sat} = e^{(A+(B/T)+C\ln(T)+D\times T^{E})}$$

with the following parameters:[4]

parameter	propyl mercaptan	butyl mercaptan	dimethyl sulfide
A	62.165	65.382	83.485
B	−5624	−6262.4	−5711.7
C	−5.8595	−6.2585	−9.4999
D	2.06×10^{-17}	1.49×10^{-17}	9.84×10^{-06}
E	6	6	2

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