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Measurement through a Gas Stripping Technique of Henry's Law Constants and Infinite Dilution Activity Coefficients of Propyl Mercaptan, Butyl Mercaptan, and Dimethyl Sulfide in Methyldiethanolamine (1) + Water (2) with $w_1 = 0.25$ and 0.35

Christophe Coquelet, Sylvain Laurens, and Dominique Richon*

MINES ParisTech, CEP/TEP - Centre Énergétique et Procédés, CNRS FRE 2861,
35 rue St Honoré 77305 Fontainebleau Cedex, France

Reported herein are determinations of Henry's constants and limiting activity coefficients obtained by an inert gas stripping method for propyl mercaptan, butyl mercaptan, and dimethyl sulfide in the temperature range (293 to 343) K at atmospheric pressure in water and in (0.25 and 0.35) wt % methyldiethanolamine (MDEA) aqueous solutions. They are supplemented by additional data from the literature at a mass fraction of 0 and 0.5 MDEA. The influence of the solvent is discussed considering the heat of absorption for the different amine concentrations.

Introduction

This study extends the previous study concerning "Measurement of Henry's law constants and infinite dilution activity coefficients of propyl mercaptan, butyl mercaptan, and dimethyl sulfide in water and in 50 wt % methyldiethanolamine aqueous solution using a gas stripping technique" by Coquelet and Richon.[1] In the present paper, new Henry's law constants in two new aqueous amine concentrations [(25 and 35) wt %] are reported to determine the influence of the amine concentration [(0, 25, 35, and 50) wt %] on the solubility of propyl and butyl mercaptan (PM and BM) and dimethyl sulfide (DMS). We have chosen the two common aqueous amine concentrations used in the industry [(25 and 50) wt %] and the 35 wt % intermediate concentration. The comparison is done considering the determination of the heat of absorption for the different sulfur species. The stripping technique, used in this paper, has been improved several times and applied to various fields [2–7] and even at high pressures.[8] Sulfur species (mercaptans) are present in very small quantities in natural gas and are generally removed by aqueous amines. 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 like 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.

Propyl and butyl mercaptan dissociate in aqueous solution following an acid−base reaction mechanism (Iliuta and Larachi[9]).

$$\mathrm{RSH} \leftrightarrow \mathrm{RS}^- + \mathrm{H}^+ \tag{1}$$

Dimethylsulfide behaves differently as no hydrogen atom is linked to the sulfur atom ($(CH_3)_2S$). Consequently, no chemical reaction occurs, and only physical solubility is concerned.

Studies at infinite dilution are a good means to accurately 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 coefficients are directly determined from Henry's law coefficients. It provides incisive information regarding solute−solvent interactions in the absence of solute interactions.

The apparatus used is based on a dynamic method (gas stripping method). It was first proposed by Leroi et al.[10] but improved several times[2−7] to cope with various applications.

Theory. Phase equilibrium governs the distribution of molecular species between two or more phases. For a molecular solute, vapor−liquid phase equilibrium is defined by eq 2 (symmetric convention).

$$Py_i\Phi_i^{\mathrm{V}} = x_i H_i^{P_{\mathrm{solv}}^{\mathrm{sat}}} \exp\left(\int_{P_{\mathrm{solv}}^{\mathrm{sat}}}^{P} \frac{v_i^{\infty}}{RT}\mathrm{d}P\right) \tag{2}$$

where y_i and x_i are, respectively, the vapor and liquid mole fractions; P/Pa is the pressure; T/K is the temperature; 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); and $H_i^{P_{\mathrm{solv}}^{\mathrm{sat}}}$/Pa 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 at atmospheric pressure. Consequently, eq 2 can be simplified to

$$Py_i = x_i H_i^{P_{\mathrm{solv}}^{\mathrm{sat}}} \tag{3}$$

Henry's Law Coefficient Measurements

Chemicals. Methyldiethanolamine (MDEA), butyl mercaptan, and propyl mercaptan are from Aldrich with a certified GC purity > 99 %. Dimethyl sulfide is from Acros with a certified GC purity > 99 %. Water was produced with an apparatus that delivers ultrapure water (Millipore, Direct Q5). Water and amine were degassed independently, and aqueous solutions were prepared under vacuum. The respective masses of water and amine were determined by differential weighing to prepare

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* Corresponding author. E-mail: richon@mines-paristech.fr. Phone: (33) 164694965. Fax: (33) 164694968.

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MDEA of well-known concentrations in aqueous solutions (mole fraction uncertainty lower than 0.02 %).

Equipment and Experimental Procedure. The apparatus and the experimental procedure are fully described in our previous paper (Coquelet and Richon[1]). The two cells are immersed inside a liquid bath regulated to within 0.01 K. A platinum probe, in contact with the liquid phase of the "dilutor cell" connected to an electronic display, is used for temperature readings. Temperature uncertainty after careful calibration of the probe is less than 0.2 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 system (BORWIN ver 1.5, from JMBS, Le Fontanil, France). The reference of the analytical column is: PORAPAK R 80/100 Mesh (Silcosteel, length: 2 m, diameter: 2 mm) from RESTEK France. The carrier gas used was helium.

The mass flow meter and regulator (Analyt-MTC, Messtechnik GmbH & Co, model 358) was calibrated against a bubble flow meter using the carrier gas. The uncertainty on flow was estimated to be around 1.5 %. The Henry's law coefficient, H_i (Pa), of solute i was calculated by means of eq 4 assuming equilibrium is reached between the gas leaving the cell and the liquid phase inside the cell. Equation 4 is obtained considering mass balance around the equilibrium cell concerning the solute. The composition of the gas leaving the cell is periodically sampled and analyzed by use of a gas sampling valve.

$$H_i = -\frac{1}{t}\ln\left(\frac{S_i}{(S_i)_{t=0}}\right)\cdot\frac{RTN}{D\left(1+\frac{P^{\mathrm{sat}}_{\mathrm{solv}}}{P}\right)+\frac{V_{\mathrm{G}}}{t}\ln\left(\frac{S_i}{(S_i)_{t=0}}\right)} \qquad (4)$$

where D is the carrier gas flow rate ($\mathrm{m^3 \cdot s^{-1}}$); N is the total number of moles of solvent inside the dilutor cell; V_{G} ($\mathrm{m^3}$) is the volume of the vapor phase inside the dilutor cell; S_i is the chromatograph solute i peak area; t (s) is the time; T (K) is the temperature inside the cell; P (101 300 Pa) is the pressure inside the cell (around 1 atm); $P^{\mathrm{sat}}_{\mathrm{solv}}$ (Pa) is the saturation pressure of the solvent; and R ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$) is the ideal gas constant. Uncertainty concerning the Henry's law coefficient is estimated to be 5 %. This estimation comes from propagation of errors taking into account the uncertainty on the flow, the solute i peak area determination, and uncertainties related to temperature and number of moles of solvent.

Experimental Results and Discussion

The values of Henry's law constants in pure water and in 50 wt % MDEA aqueous solution are taken from our previous paper (Coquelet and Richon[1]). They are reported in Tables 1 to 3. Table 1 concerns the propyl mercaptan, Table 2 the butyl mercaptan, and Table 3 the dimethyl sulfide. New results concerning the values of Henry's law constants in (25 and 35) wt % MDEA aqueous solutions are also reported in Tables 1 to 3. Considering the symmetric convention and the fact that $T < T_{\mathrm{C}}$ (T_{C} (K) is the critical temperature of solute i), the limiting activity coefficients are calculated through eq 5. Details concerning the calculation of the saturation pressure are presented in the Appendix.

$$\gamma_i^{\infty} = \frac{H_i^{P^{\mathrm{sat}}_{\mathrm{solv}}}}{P_i^{\mathrm{sat}}} \qquad (5)$$

Table 1. Temperature Dependence of Henry's Law Constant for Propyl Mercaptan in Water and in (25, 35, and 50) wt % MDEA Aqueous Solutions

T/K	H/MPa	γ^{∞}
	Water[a]	
293.2	$23._9$	1455
303.1	$46._8$	1844
333.1	$93._9$	1191
	Aqueous MDEA solution	
	25 wt %	
298.1	$4._3$	209
303.1	$5._4$	211
313.1	$6._9$	181
323.1	$10._4$	187
333.1	$15._0$	189
343.1	$17._1$	157
	35 wt %	
303.1	$4._5$	176
323.1	$6._7$	120
343.1	$12._1$	111
	50 wt %[a]	
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

[a] Results from Coquelet and Richon.[1]

Table 2. Temperature Dependence of Henry's Law Constant for Butyl Mercaptan in Water and in (25, 35, and 50) wt % MDEA Aqueous Solutions[a]

T/K	H/MPa	γ^{∞}
	Water[a]	
292.8	$29._3$	6223
312.8	$70._1$	5717
332.8	$125._7$	4504
	Aqueous MDEA Solution	
	25 wt %	
293.1	$3._4$	708
303.1	$4._9$	622
313.1	$7._8$	623
318.1	$10._0$	644
	35 wt %	
293.1	$2._7$	552
303.1	$4._6$	577
313.1	$6._1$	487
323.1	$8._6$	451
333.1	$12._6$	446
343.1	$16._9$	413
	50 wt %[a]	
292.8	1.8_0	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

[a] Results from Coquelet and Richon.[1]

Figures 1 to 3 shows the temperature dependence of the logarithm of the limiting activity coefficient as a function of ($1/T$) concerning the three sulfur species in pure water and (25, 35, and 50) wt % MDEA aqueous solutions, respectively. These figures show clearly the effect of the amine: the values of limiting activity coefficients in MDEA aqueous solutions are smaller than those in pure water and are a decreasing function of the amine concentration. Addition of MDEA to water changes its alkalinity. With propyl and butyl mercaptans, there are two different absorption types: physical and chemical, whereas with dimethyl sulfide, there is only physical absorption.

A general observation leads to the conclusion that the limiting activity coefficient is an increasing function of the solute

Table 3. Temperature Dependence of Henry's Law Constant for Dimethylsulfide in Water and in (25, 35, and 50) wt % MDEA Aqueous Solutions[a]

T/K	H/MPa	γ^{∞}
	Water[a]	
292.6	$8._{4}$	161
302.7	$13._{0}$	170
312.5	$18._{8}$	174
332.8	$37._{1}$	183
	Aqueous MDEA solution	
	25 wt %	
293.1	$6._{4}$	121
303.1	$8._{4}$	107
313.1	$11._{2}$	100
323.1	$14._{4}$	93
333.1	$19._{3}$	92
343.1	$28._{2}$	101
	35 wt %	
294.1	$5._{7}$	103
303.1	$7._{0}$	89
313.1	$10._{1}$	91
323.1	$11._{8}$	77
333.1	$14._{9}$	71
343.1	$17._{9}$	64
	50 wt %[a]	
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

[a] Results from Coquelet and Richon.[1]

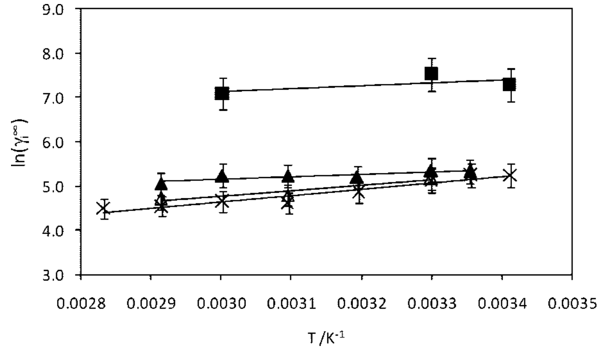

Figure 1. Logarithm of limiting activity coefficient of propyl mercaptan in ■, water and in various MDEA weight fractions: ▲, 25 %; △, 35 %; and ×, 50 % as a function of inverse temperature.

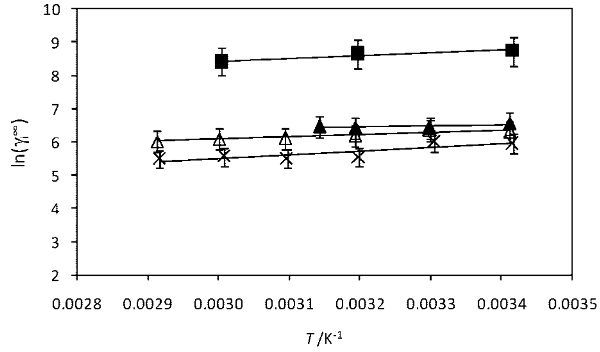

Figure 2. Logarithm of limiting activity coefficient of butyl mercaptan in ■, water and various MDEA weight fractions: ▲, 25 %; △, 35 %; and ×, 50 % MDEA aqueous solutions as a function of inverse temperature.

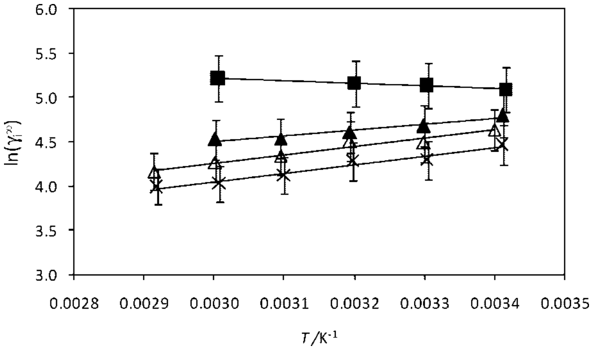

Figure 3. Logarithm of limiting activity coefficient of dimethyl sulfide in ■, water and in various MDEA weight fractions: ▲, 25 %; △, 35 %; and ×, 50 % MDEA aqueous solutions as a function of inverse temperature.

Table 4. Values of Heat of Solution Corresponding to Equation 5 for the Three Sulfur Species and Different MDEA Molar Concentrations

	heat of solution/J·mol⁻¹		
aqueous MDEA solution /wt %	DMS	BM	PM
0	−2468	6469	5753
25	5600	2968	4490
35	7782	5487	10160
50	8033	8954	11956

molecular size at constant MDEA concentration. The physical absorption is the predominant mechanism.

To compare the effect of amine concentration, we have calculated the heat of solution using eq 6 (this equation is obtained from the Gibbs−Helmholtz equation using excess thermodynamic properties).

$$\left(\frac{\partial \ln \gamma_i^{\infty}}{\partial T}\right)_P \cong \frac{-\Delta H_i}{RT^2} \tag{6}$$

The heat of solution (Δh_i (J·mol^{-1})) is also considered to be the partial molar excess enthalpy of component i in the solution.

If we consider that the heat of solution is a constant, we can write

$$\ln \gamma_i^{\infty} = A + \frac{B}{T} \tag{7}$$

with $\Delta h_i = RB$.

Table 4 reports the values of heats of solution determined through our measurements. The resulting uncertainty is around 10 %.

In pure water, DMS produces negative values of the heat of solution, while propyl and butyl mercaptan lead to positive values. Moreover, the heat of solution of butyl mercaptan is higher than that of propyl mercaptan. Three effects contribute to the heat of solution: a positive heat of cavitation, a negative heat of hydrophobic interactions, and the heat of reaction.

With DMS, no chemical reaction occurs. Figure 4 shows the evolution of the heat of solution as a function of MDEA mole fraction. It is a second-order polynomial behavior, and two effects are present: heat of cavitations and heat of hydrophobic interactions.

Concerning propyl and butyl mercaptan, in pure water, the difference is certainly due to a size effect (physical solubility): butyl mercaptan has one alkyl group more compared to propyl mercaptan, and consequently its partial molar excess enthalpy is slightly higher. When we add MDEA into the aqueous solution, we probably increase the contribution of the chemical reaction: the shape of the curve is completely different with respect to the curve obtained for DMS (see Figure 5).

The heats of solution of propyl and butyl mercaptan have the same order of magnitude and the same shape.

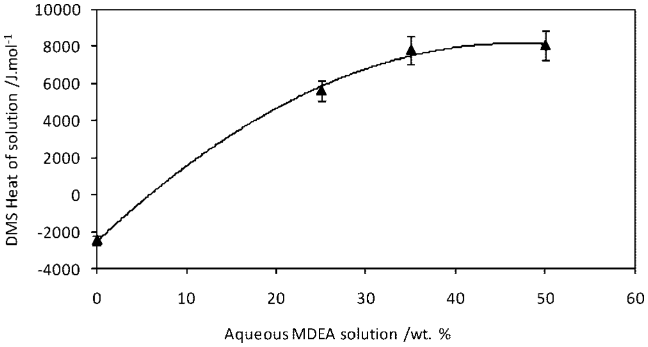

Figure 4. Dimethyl sulfide heat of solution as a function of MDEA molar concentration. Solid line: tendency curve.

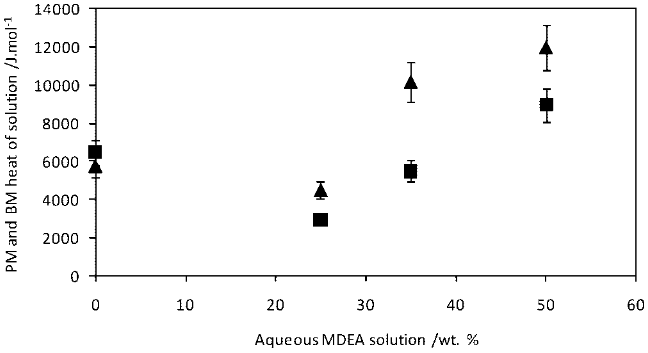

Figure 5. Butyl and propyl mercaptan heats of solution as a function of MDEA molar concentration. ▲, propyl mercaptan; ■, butyl mercaptan.

Conclusion

New values for Henry's law constant and infinite dilution activity coefficients of three sulfur species in (25 and 35) wt % MDEA aqueous solutions between (293 and 343) K have been obtained from gas stripping measurements. These measurements extend those published in one of our previous papers.[1]

The amine solvent power on sulfur species has been discussed by comparison to solubility values in water. In all cases, the Henry's law constant depends on the solute molecular size. Finally, the experimental technique has provided information about heats of solution that could be confirmed by direct calorimetric measurements or by measurements of solubility for improvement of their reliability.

Appendix

Correlation used to calculate the vapor pressure is

$$P^{\text{sat}} = e^{\left(A+\frac{B}{T}+C\ \ln(T)+D\cdot T^{E}\right)}$$

with the following parameters[11]

parameter	PM	BP	DMS
A	62.165	65.382	83.485
B	−5624	−6262.4	−5711.7
C	−5.8595	−6.2585	−9.4999
D	$2.06\cdot10^{-17}$	$1.49\cdot10^{-17}$	$9.84\cdot10^{-06}$
E	6	6	2

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