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Rohani Mohd Zin, Christophe Coquelet, Alain Valtz, Mohamed I Abdul Mutalib, Mohamad Khalik. A New Thermodynamic Correlation for Apparent Henry's Law Constants, Infinite Dilution Activity Coefficient and Solubility of Mercaptans in Pure Water. *Journal of Natural Gas Engineering*, 2017. hal-01700841

HAL Id: hal-01700841

<https://minesparis-psl.hal.science/hal-01700841v1>

Submitted on 5 Feb 2018

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**A New Thermodynamic Correlation for
Apparent Henry's Law Constants, Infinite Dilution Activity
Coefficient and Solubility of Mercaptans in Pure Water**

Rohani Mohd Zin^{1,2,3}, Christophe Coquelet^{1*}, Alain Valtz¹,

Mohamed I. Abdul Mutalib³, Khalik Mohamad Sabil⁴

¹Mines ParisTech PSL Research University CTP-Centre of Thermodynamics of Processes

35 Rue Saint Honorè, 77305 Fontainebleau, France

²Chemical Engineering Faculty, Universiti Teknologi MARA,

40700 Shah Alam, Selangor, Malaysia

³PETRONAS Ionic Liquids Center, Chemical Engineering Department,

Universiti Teknologi Petronas, 31750 Tronoh, Perak, Malaysia

⁴School of Energy, Geosciences, Infrastructure and Society,

Herriot-Watt University Malaysia, 62200 Putrajaya, Malaysia

Abstract

Mercaptans (RSH) or thiols are odorous substances offensive at low concentration and toxic at higher levels. The presence of mercaptans as pollutants in the environment creates a great threat on water and air safety. In this study, the solubility of mercaptans in water was studied through the use of apparent Henry's Law constant (H) and infinite dilution activity coefficients (γ_∞). These thermodynamic properties are useful for environmental impact studies and engineering

design particularly in processes where dilute aqueous systems are involved. The aim of this paper is to develop a new thermodynamic correlation for estimation of apparent Henry's Law constant (H), infinite dilution activity coefficient (γ_∞) and solubility of C1-C4 mercaptans including their isomers in pure water. This correlation was developed based on compiled literature data. New measurements of apparent Henry's Law constant and infinite dilution activity coefficients of methyl mercaptan and ethyl mercaptan in water were carried out to validate the developed correlation. Validation with new measurement data showed a good consistency with low differences (less than 5%) for majority of the data. Additionally, heat of absorption of various mercaptans in pure water was discussed based on temperature influence, Henry Law Constants and solubility.

Keywords: mercaptans, apparent Henry's Law constant, infinite dilution activity coefficient, solubility, correlation, heat of absorption

Corresponding author: Christophe.coquelet@mines-paristech.fr Tel: +33164694962 Fax: +33164695968

1. Introduction

Mercaptans (RSH) are volatile compounds that are known for causing malodorous conditions and serious environmental concerns. These compounds are introduced to the environment through anthropogenic sources such as fossil fuel burning, petrochemical industry or municipal sewage systems [1]. Among sources of these compounds are Liquefied Petroleum Gas (LPG) [2-

3], phosphate fertilizer [4-5], wastewater treatment plant [6]. According to Habibi et al. [7] mercaptans are the most important volatile organic compounds that contribute to odour problems in wastewater treatment plants.

Mercaptans have been declared to exhibit similar toxicity to hydrogen sulfide. For the past few years, several researchers have reported the effects of mercaptans towards health and the environment [1,8,9]. In the health aspect, mercaptans can affect the nervous system, paralyze the respiratory system and can trigger various health complications for example convulsion, narcosis and pulmonary edema. Due to their acidic characteristics, mercaptans can cause serious corrosion problems and environmental damage due to acid deposition and rapid acidification [1,8,9]

Thus, due to aforementioned problems, industries have to deal with these compounds and are forced to manufacture cleaner and more ecological products due to tightening demands and restriction in legislation as well as environmental concerns.

The apparent Henry's Law constant (H) has long been a question of great interest in a wide range of fields. In the environmental chemistry, atmospheric physics and environmental impact studies, the apparent Henry's Laws constant is useful as the major criterion for describing the movement and fate of the chemicals (in this study, mercaptans) in air and water. A study done by Majer et al. [10] mentioned that the apparent Henry's Law constant plays a major role in evaluating the transport of pollutants between atmosphere and aquatic systems, rain water and aerosols. Therefore, the use of an apparent Henry's Law constant is ideal in estimating the concentration of a solute near the vapor liquid interface of a dilute solution [11]. This thermodynamic quantity allows quick calculation of minute levels of chemicals resulting from their accidental spills in waterways. This is very important for mass transfer estimation. In

chemical engineering and the geochemistry industry, apparent Henry's Law constants are extensively being used for designing or describing processes where dilute aqueous systems are involved, often over a wide range of temperature and pressure [10].

For reliable process design, accurate physical properties are needed for proper sizing of the separation processes. According to Krummen et al. [12] and Hajiw et al. [13], the knowledge of infinite dilution activity coefficients (γ_∞) is important in design and optimization of separation processes because the largest separation effort is required to remove the small traces of pollutants. Similarly, Sherman et al. [14] in their studies highlighted that the thermodynamic behavior of dilute aqueous solutions governs how separation processes can be carried out successfully.

The purpose of this work lies on the development of a new thermodynamic correlation of the apparent Henry's Law constant (H) for C1-C4 mercaptans and their isomers in pure water which is essential in designing or describing processes involving dilute aqueous systems. Influence of temperature, apparent Henry Law constants and solubility on the heat of absorption of various mercaptans in pure water are also investigated in this work.

2. Theory

The concept of Henry's Law constant was first articulated by Henry [15] as an approach to estimate the gas solubility in a liquid at infinite dilution. In other words, Henry's law constant represents the proportionality factor of the concentration of dissolved gas to its partial pressure in the gas phase. This thermodynamic quantity is commonly applied in the thermodynamic description of dilute aqueous solutions and expressed as a ratio of the partial pressure of a gaseous solute to its equilibrium concentration in the liquid phase. In this work, the term

‘apparent’ is considered because the exact value of fugacity coefficients of vapor and liquid phases are unknown. In effect Henry’s law constant is defined at the solvent vapour pressure and must be corrected to take into account the effect of pressure. Therefore, the use ‘apparent Henry’s Law Constant’ is more relevant in this context.

Whitman [16] stated in his studies that the rate of absorption is controlled by the rate of diffusion through the surface films at the gas-liquid boundary. One of the concepts of diffusion is through a gas film, triggered by a difference in the partial pressure of the solute at the outside of the film (in the main body of gas) and the inside of the film (in equilibrium with the liquid). This concept is known as double layer concept as we have to consider transfer from both sides of the interface. This concept is important to visualize the transport of pollutants (in this case, mercaptans) between the atmosphere and aquatic systems. The apparent Henry’s Law constants for individual chemical solutes in water are determined from their pure component vapor pressure and water solubility data [11].

The apparent Henry’s Law constant is expressed at the solvent vapor pressure. Effect of pressure requires the knowledge of partial molar volume at infinite dilution. According to Schlauer and Kriebel [17], at higher pressure of the dissolved component (solute), Henry’s Law constant is corrected similar to the Poynting factor according to the Krichevsky–Kasarnovski equation;

$$\ln H_{i,L}(P) = \ln H_{i,L}(P_L^o) + v_i^{\infty}(P - P_L^o)/RT \quad (1)$$

where $H_{i,L}$ =Henry's Law constant of solute i in solvent L , (kPa); P = total system pressure (kPa); P_L^o = vapor pressure of the solvent (kPa); R = gas constant ($\text{J mol}^{-1} \text{K}^{-1}$); T = temperature (K) and v_i^∞ = partial molar volume at infinite dilution.

The infinite dilution is the special state of liquid mixture where the concentration of one component (the solute), goes to zero, while the mole fraction of the other component or the total mole fraction of the others (the solvent mole fraction) is close to one. The activity coefficient of the infinitely dilute solute, named as the infinite dilution activity coefficient or the limiting activity coefficient, is a limiting measurement of the nonideality of the solute in this mixture [18]. Water often exhibits significant nonideal behavior as compared to the behavior of other solvents. This condition is presumably due to its unique structure and hydrogen-bonding characteristics. With water, depending of the types of solute, hydrophobic interactions (a sort of cage is created around the solute due to hydrogen-bonding) can occur. But these hydrogen-bonds disappear as the temperature increases (thermal agitation). Therefore, it is essential to study this nonideal behavior through limiting activity coefficients (γ_∞) of a solute in water as it also can be used to determine directly the phase equilibria of dilute aqueous mixtures. According to Sherman et al. [14], these coefficients provide a direct measure of the interaction between unlike molecules in solution without the complicating effects of solute-solute interactions. Hence, the magnitude of these coefficients offers insight into the types of chemical and physical forces experienced by the water and solute molecules.

Infinite dilution activity coefficients can be directly determined from the apparent Henry's Law constant and they provides incisive information regarding solute-solvent interactions in the absence of solute-solute molecular interactions [19]. Its value closely reflects solute-solvent

interactions, representing thus for aqueous organic solutes a convenient measure of their hydrophobicity [20].

3. Experimental Section

3.1 Chemicals.

Details on purities and suppliers of materials used are presented in Table 1. Ultra-pure water was used which was purified and distilled through a Millipore (Direct Q5) osmosis membrane. No further purifications of the chemicals were made.

Table 1. CAS numbers, purities and suppliers of materials.

[INSERT TABLE 1 HERE]

3.2 Apparatus and Experimental Procedure.

The measurements of the apparent Henry's Law constant and the infinite dilution activity coefficient were performed using a specially designed apparatus of dilutor and saturator cell based on the gas stripping method. The simplified flow diagram of the apparatus is shown in our previous paper [19]. Full descriptions of the principles have been thoroughly discussed by [12,21,22,23] in their studies. Experiment procedures have been fully explained in [19,24,25] and hence, only relevant points will be emphasized in the paper.

For the present work, both saturator and dilutor cells were immersed inside a liquid bath regulated to within 0.01 K. A constant stripping gas 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 (mercaptans) into the vapor phase. A platinum probe was dipped in the liquid phase of the

dilutor cell and connected to an electronic display for temperature readings. Temperature uncertainty of the probe was estimated; $u(T, k=2) = 0.2$ K. A gas chromatograph (PERICHRON model PR2100, France) equipped with a flame ionization detector (FID) connected to a data acquisition system was used for the analytical work. The composition of the gas leaving the dilutor cell was periodically sampled (using a gas sampling valve) and analyzed by the gas chromatography. The same volume of gas was injected in the gas chromatograph. A packed column was used as the analytical column and helium was used as the stripping gas in this experiment. Temperature platinum probe and total volume were calibrated. The volume uncertainty was estimated as; $U_r(V) = 2$ %. The flow meter (Analyt-MTC, Messtechnik GmbH & co, model 358) was calibrated using a bubble flow meter with the carrier gas. The uncertainty on flows was estimated to be around 2-3 %. The slope (in fact $\frac{\partial N}{\partial T}$) was determined by using the evolution of $\left(\frac{S_i}{(S_i)_{t=0}}\right)$ and utilization of FID with linear response thus, no calibration is needed.

Upon completion of the measurement, the values of apparent Henry's Law constant were calculated using equation (2) obtained from mass balance on the dilutor cell [13,19,24,25].

$$H_i = -\frac{1}{t} \ln \left(\frac{S_i}{(S_i)_{t=0}} \right) \cdot \frac{RTN}{\frac{D}{1 - \frac{P^{sat}_{solv}}{P}} + \frac{V_G}{t} \ln \left(\frac{S_i}{(S_i)_{t=0}} \right)} \quad (2)$$

where D = carrier gas flow rate ($\text{m}^3 \cdot \text{s}^{-1}$); N = total number of moles of pure water inside the dilutor cell; V_G (m^3) = volume of the vapor phase inside the dilutor cell; S_i = chromatograph solute i peak area; t (s) = time; T (K) = temperature inside the cell; P (atmospheric pressure around 101 300 Pa) = pressure inside the cell (around 1 atm); P^{sat}_{solv} (Pa) = saturation pressure of the pure water and R ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) = ideal gas constant.

According to Carroll [26], Henry's law states that the solubility of a gas in a liquid is proportional to the partial pressure of the gas. Therefore, it can be written as,

$$P_i = H_i x_i \quad (3)$$

where P_i is the partial pressure of component i in the gas; H_i is the Henry's law constant for solute i in solvent ; and x_i is the mole fraction of component i in the liquid. Hence, the solubility of the solute (x_i), can be calculated using equation (3).

By definition, equation (4) is considered to estimate the Henry's law constant.

$$H_i = \lim_{x_i \rightarrow 0} \frac{f_i^L}{x_i} \quad (4)$$

$$\text{and } f_i^L = \gamma_i x_i f_i^{0L} \quad (5)$$

where f_i^L is the liquid phase fugacity of component i ; γ_i is the activity coefficient of component i and f_i^{0L} is the standard state (or reference) fugacity.

Assuming the Poynting factor and the fugacity coefficient have a value of approximately unity [13], the symmetric convention that links the apparent Henry's law constant with the activity coefficients at infinite dilution is shown in equation (6). Therefore, the limiting activities coefficient at infinite dilution values were determined through equation (6).

$$\gamma_i^\infty = \frac{H_i(T, P_{sol}^{sat})}{P_i^{sat}} \quad (6)$$

where H_i = apparent Henry's Law constant of solute i ; P_{solv}^{sat} (Pa) = saturation pressure of the solvent and P_i^{sat} (Pa) = saturation pressure of the solute. Correlation to calculate saturation pressure is given in equation (7), with details concerning the calculation of the saturation pressure are presented Table 6 (in the Appendix)

$$P^{sat} = e^{\left(A + \frac{B}{T} + C \ln(T) + D \cdot T^E\right)} \quad (7)$$

The uncertainties of the measurements are estimated through equations (8) and (9) as shown in the Appendix.

4. Results and Discussion

4.1 Henry's Law Constant and Limiting Activity Coefficients Data of Mercaptans in Pure Water System

The apparent Henry's Law constant, infinite dilution limiting activity coefficients and solubility of mercaptans measured in this work together with extensive literature data are presented in Table 2. The literature data are subsequently used to develop the new correlation whereas the measured data in this work are used for validation purpose.

Table 2. Compilation of literature values of activity coefficient at infinite dilution and apparent Henry's Law constant and new measurements (this work) for investigated solutes (1) and water (2) in temperature range of 298K to 348 K ($u(T) = 0.2K$, $U_r(H, k=2) = 0.05$)

[INSERT TABLE 2 HERE]

As shown in Table 2, it was observed that the apparent Henry's Law constant for the various mercaptans exhibited higher values as the mercaptan alkyl groups increased in size. This indicates that the solubility of the mercaptans in pure water decreases as the alkyl groups increase in size owing to the inverse function of apparent Henry's Law constant with solubility [32].

In addition, it is observed that isopropyl mercaptan exhibits a higher apparent Henry's Law constant as compared to the n-propyl mercaptan in pure water system. The same trend was observed in between isobutyl and n-butyl mercaptans systems. Similar findings were observed in the literature [25,33]. As pointed by Zin et al. [25], this trend could be explained by comparing the densities of the mercaptans compounds involved. The higher density of n-propyl and n-butyl mercaptan compounds allows more compact molecular arrangement thus leading to smaller molecular size which could fit more easily in the solvent cavity. Moreover, Fenclová et al. [34] also stated that the structure compactness of isomeric molecules is an important factor affecting various pure component properties of isomer.

The temperature dependence of the limiting activity coefficient for methyl mercaptan, ethyl mercaptan, n-propyl mercaptan, isopropyl mercaptan, n-butyl mercaptan and isobutyl mercaptan in pure water are depicted in Figure 1-4 respectively.

[INSERT FIGURE 1 HERE]

Figure 1. Logarithm of limiting activity coefficient of methyl mercaptan, in pure water as a function of inverse temperature (o water-MM (this work); Δ water-MM [Przyjazny et al. (1983)]; \square water-MM [Gillespie and Wilson (1984)])

[INSERT FIGURE 2 HERE]

Figure 2. Logarithm of limiting activity coefficient of ethyl mercaptan, in pure water as a function of inverse temperature (o water-EM (this work); Δ water-EM [Przyjazny et al. (1983)]; \blacksquare water-EM [Hwang et al. (1992)]; \square water-EM [Gillespie and Wilson (1984)])

As depicted by Figure 1, at 298K, our measured values of limiting activity coefficient of methyl mercaptan are in good agreement with measurements made by Przyjazny et al. [28]. Agreement is also fairly good between our measurement at 308K and the value reported by Gillespie and Wilson [29] at 310K. The percentage deviation (actual values) of limiting activity coefficient gives about 21.5 % and the relative deviation gives about 12.4%.

Figure 2 shows the values limiting activity coefficient of ethyl mercaptan from works by Przyjazny et al. [28], Hwang et al. [30] and Gillespie and Wilson [29]. In these measurements Przyjazny et al. [28] used the headspace chromatography, Hwang et al. [30] used the steam stripping technique and Gillespie and Wilson [29] utilized the rocked cell method. Discrepancies of about 21.1-34.9 % (based on actual values of limiting activity coefficient) are found between the values plotted at 298K. For the same temperature, these values give a relative deviation of about 15.7%. Uncertainty or precision of the measurements, type of experimental method applied, instrumentation and procedure used, approximations adopted, properties of the system and conditions or purities of chemicals are the possible factors contributing to these discrepancies.

It is noticed from Figures 1 and 2, the shape of the graph for our measurement data is not similar with the shape plotted with Gillespie and Wilson [29] data. This could be caused by the

temperature variations of apparent Henry Law's Constants which are primarily a consequence of the variation in vapor pressure (P_i^{sat}) as the temperature dependence of limiting activity coefficient is modest near the ambient temperature. Smith and Harvey [35] explained that at higher temperature limiting activity coefficient varies more rapidly thus temperature variation of apparent Henry Law's Constants becomes more strongly dependent on the combined variations of both.

Another interesting point that can be observed from Table 2 is that although the branched isomers (iso-propyl and iso-butyl mercaptans) have higher apparent Henry's Law constant values than n-propyl and n butyl mercaptan but the trend is opposite to that on limiting activity coefficient. This reversal trend is due to the fact that the branching increases the mercaptans vapor pressure to a greater extent than it decreases its limiting activity coefficient. This reversal trend finding is consistent with previous works observed by Fenclová et al. [34].

[INSERT FIGURE 3 HERE]

Figure 3. Logarithm of limiting activity coefficient of n-propyl mercaptan and iso-propyl mercaptan, in pure water as a function of inverse temperature (● water-nPM [Coquelet et al. (2008)] ; ◇ water-nPM [Haimi et al. (2006)]; Δ water-nPM [Przyjazny et al. (1983)]; o water-iPM [Zin et al. (2016)]; ◆ water-iPM [Haimi et al. (2006)]).

[INSERT FIGURE 4 HERE]

Figure 4. Logarithm of limiting activity coefficient of n-butyl mercaptan and iso-butyl mercaptan, in pure water as a function of inverse temperature (● water-nBM [Coquelet et al.

(2008)]; \diamond water-nBM [Haimi et al. (2006)]; \blacksquare water-nBM [Hwang et al. (1992)]; \blacktriangle water-nBM [Yaws et al. (1992)]; \circ water-iBM [Zin et al. (2016)]

Figure 3 compares the values of limiting activity coefficient of n-propyl mercaptan and isopropyl mercaptan in pure water. Haimi et al. [31] investigated the measurement of n-propyl mercaptan and isopropyl mercaptan using similar technique as used in our works [19,24,25] but they used nitrogen as the inert stripping gas. For both components, the authors' data showed fair agreement with our measurement values from previous works in [24] and [25]. Meanwhile, comparison at the 298K for n-propyl mercaptan between measurement data published by Przyjazny et al. [28] and Haimi et al. [31] showed a slight difference where the limiting activity coefficient for the latter was found to be higher. It is probable that the type of experimental method, instrumentation and procedure used contributed to the difference.

Hwang et al. [30], Haimi et al. [31] and Yaws et al. [27] published measurement of limiting activity coefficient for n-butyl mercaptan in pure water at 298K. Values published by Haimi et al. [31] and Hwang et al. [30] showed a reasonable agreement with our previous work in Coquelet et al. [24] as shown in Figure 4. However, the experimental value by Yaws et al. [27] differs substantially from the values measured by Hwang et al. [30], Haimi et al. [31] and our previous work in Coquelet et al. [24].

4.2 Development of Apparent Henry's Law Constant Correlation

Gillespie and Wilson [29] in GPA Research Report RR 78 reported Henry's Law constant data on methyl mercaptan and ethyl mercaptan in order to provide a good basis for evaluating the

behaviour of these components in water at higher temperatures up to 588.7 K. Figures 5 and 6 combine the apparent Henry's Law constant data from Przyjazny et al. [28], Hwang et al. [30] and Yaws et al. [27] and with the data reported by Gillespie and Wilson [29] for both components respectively.

[INSERT FIGURE 5 HERE]

Figure 5. Apparent Henry's Law Constant of methyl mercaptan in water as a function of temperature (o water-MM [Gillespie and Wilson (1984)]; Δ water-MM [Przyjazny et al. (1983)]; \square water-MM [Yaws (1999)]).

[INSERT FIGURE 6 HERE]

Figure 6. Apparent Henry's Law Constant of ethyl mercaptan in water as a function of temperature (o water-EM [Gillespie and Wilson (1984)]; Δ water-EM [Przyjazny et al. (1983)]; \square water-EM [Yaws (1999)]; X water-EM [Hwang et al. (1992)]).

It appears that these curves exhibit the similar behaviour where the apparent Henry's Law constant increases with temperature. However, findings in Gillespie and Wilson [29] revealed that the apparent Henry's Law constant increases with temperature to a maximum and then decreases to a value that is identical to critical pressure at the critical temperature of water. Since apparent Henry's Law constants are defined at infinite dilution of the component in the water, hence the critical point of the mixture become the critical point of pure water. In addition, it appears that if Henry's Law Constant presents a maximum value at certain temperature thus it exists a temperature of minimum of solubility.

Based on Figure 5 and 6, a new correlation is developed for the mercaptan components. The correlation curves on the fitted data (as illustrated by Figure 5 and 6) are obtained based on parameters that covered the temperature range between 288.2K and 588.7K. For the correlation development, an exponential expression (equation 10) is considered. It is inspired from the expression used by Yaws et al. [36] or Design Institute for Physical Properties (DIPPR) equation n°101 which was obtained from Daubert et al. [37].

$$\ln(H_i^{cor} / MPa) = A + \frac{B}{T} + C \ln(T) \quad (10)$$

The objective function is inspired from least square objective function for parameter optimization. Equation (11) reminds the expression of the objective function.

$$F = \frac{1}{N_{data} - N_{parameter}} \sum_{N_{data}} (H_i^{lit} - H_i^{cor})^2 \quad (11)$$

The purpose of this correlation is to illustrate the effect of temperature to apparent Henry's Law constant of the component in infinite dilution. This correlation can be used to obtain an estimate of apparent Henry's Law constant of mercaptans at certain temperature. Table 3 presents the values of the parameters of equation (10), obtained for the all the mercaptan components and their respective uncertainties.

Table 3. Values of parameters for mercaptans apparent Henry's Law constant correlation (equation 10).

[INSERT TABLE 3 HERE]

4.3 Correlation Validation for Methyl and Ethyl Mercaptans in Pure Water Systems

The validity of the correlation developed has been verified through the comparison between new measured values of apparent Henry's Law constant (for methyl and ethyl mercaptan) with the values obtained through the new correlation. Figure 7 and 8 show the comparison between the new measured values and values obtained from newly-developed correlation (equation 10).

[INSERT FIGURE 7 HERE]

Figure 7. Validation of correlation of Apparent Henry's Law constant of methyl mercaptan in water. (o validation-new measurement; ◆ new correlation (this work); ◇ correlation by Lange et al [38]).

[INSERT FIGURE 8 HERE]

Figure 8. Validation of correlation of Apparent Henry's Law constant of ethyl mercaptan in water. (o validation-new measurement; ◆ new correlation (this work); ◇ correlation by Lange et al [38]).

From Figure 7, it can be observed that for methyl mercaptan, there are small differences of about 1.1-3.6% between new measured values and values calculated from new correlation using regression coefficient parameters shown in Table 3. However, slightly higher differences are found for ethyl mercaptan of about 2.0-9.6% as illustrated by Figure 8. It is noted that, the higher

percentage differences are discovered at 298K and 308K with percentage difference of about 9.6% and 5.1% respectively. However, for the rest of the temperature points, the error differences are less than 5%. Therefore, due to the low error differences the newly-developed correlation can be used as good estimation for apparent Henry Laws constant of mercaptans in water.

Comparisons are also being made with the correlation developed by Lange et al [38]. In their work, the correlation (equation 12) was developed only based on the data from Gillespie and Wilson [27] in GPA Research Report RR 78.

$$\ln(H_{i,S}(T, P_s^0(T)) [\text{bar}]) = \Phi 1_i + \frac{\Phi 2_i}{T[\text{K}]} + \Phi 3_i \ln(T[\text{K}]) + \Phi 4_i T[\text{K}] \quad (12)$$

where Φ is the parameter of the Henry's Law constant.

It can be seen from Figure 7 and 8, our new correlation (where the parameters are adjusted based on all available literature data) gives similar results and our new measurements confirm the predictive capabilities of our new correlation.

4.4 Effect of Temperature, Apparent Henry's Law Constant and Solubility on Heat of Absorption of Mercaptans in Pure Water

Data on heat of absorption of mercaptans in water are scarce. To the best of our knowledge, no heat of absorption data are available for mercaptans in the open literature. In this work, heat of absorption are determined from the newly-developed apparent Henry's Law correlation and the Gibbs-Helmholtz equation. Heat of absorption values for methyl mercaptan and ethyl mercaptan

in pure water at different temperatures are presented in Table 4. The heat of absorption values for C3–C4 mercaptans and their isomers in pure water are presented in Table 5.

Table 4. Values of heat of absorption for methyl mercaptan and ethyl mercaptan in pure water for different temperature according to equation 14.

[INSERT TABLE 4 HERE]

Table 5. Values of heat of absorption for C3-C4 mercaptans and their isomers in pure water

[INSERT TABLE 5 HERE]

For evaluation on the effect of various mercaptans (solute) in pure water, heat of absorption is determined through equation (13) derived from the Gibbs-Helmholtz equation using excess thermodynamic properties [24,39];

$$\left(\frac{\partial \ln H_i}{\partial 1/T}\right)_P = \frac{\Delta H_i^{abs}}{R} \quad (13)$$

For methyl mercaptan and ethyl mercaptan, the heat of absorption (ΔH_i^{abs} (kJ.mol⁻¹)) can be determined by differentiating equation (10) as a function of 1/T and subsequently the heat of absorption of the respective compounds can be calculated by equation (14):

$$\Delta H_i^{abs} = R(B - CT) \quad (14)$$

Whereas for propyl mercaptan, isopropyl mercaptan, butyl mercaptan and isobutyl mercaptan, it can be seen (from equation 10 and coefficients in Table 3) that their respective Henry's Law constant can be expressed as per written in equation (15).

$$\ln H_i = A + \frac{B}{T} \quad (15)$$

Hence, by differentiating equation (15) as a function of $1/T$, heat of absorption for those compounds can be obtained from equation (16). For both equations (11) and (13), R is the ideal gas constant ($8.314 \text{ J. mol}^{-1} \cdot \text{K}^{-1}$).

$$\Delta H_i^{abs} = RB \quad (16)$$

Heat of absorption of methyl mercaptan and ethyl mercaptan is considered to be temperature dependent as indicated by equation (14). Results from Table 4 reveals that the heat of absorption for both components in the given temperature range shows a steady decrease with respect to temperature. This steady decrease pattern could be possibly due to the higher Henry's Law constant values as the temperature increases i.e., the solubility decreases thus less energy absorbed.

It is important to note that there is a proportional relationship between the heat of absorption and number of carbon in mercaptans as indicated in Table 5. In other words, the heat of absorption exhibited higher values as the mercaptans alkyl group increase in size. Concerning this finding, the difference between the heats of absorption values is certainly due to size effect. A closer inspection on Table 5 also discovered that the heat of absorption for n-compounds are found to

be higher than the iso-compounds. Presumably, this is due to higher values of apparent Henry's Law constant of iso-propyl and iso-butyl mercaptan, indicating that the solutes are less soluble in the water hence less energy required to be absorbed. It also can be assumed that, mercaptans probably behave like hydrocarbons thus it is difficult to consider if there is a chemical reaction occurs when in contact with water.

Conclusion

A new thermodynamic correlation for estimation of apparent Henry's Law constant (H) of C1-C4 mercaptans including their isomers in pure water has been developed based on compiled literature data. New measurements have been performed to validate the newly-developed correlations. The new data are well predicted by the new correlation (for methyl mercaptan and ethyl mercaptan). The newly developed correlation is found to be reliable for good estimation as the validation with new measurement data showed a good consistency with low differences (less than 5% for majority of data). Comparisons with the correlation developed by Lange et al [38] (based on data by Gillespie and Wilson [27]) shows that the newly-developed correlation (where the parameters are adjusted based on all available literature data) gives similar results with an average deviation of 1.94%. The new measurements confirm the predictive capabilities of the new correlation. Effects of temperature, apparent Henry's Law constant and solubility on heat of absorption of mercaptans in pure water system were discussed. Heat of absorption of the methyl mercaptan and ethyl mercaptan are considered to be temperature dependent. Steady decrease in the heat of absorption of mercaptans in water were found (as the temperature increases) due to the higher apparent Henry's Law constant values which implying decrease in solubility thus less

energy is being absorbed. A proportional relationship is also found between the heat of absorption and number of carbon in mercaptans.

Appendix

Table 6. Vapor pressure correlation (equation 7) parameters.

[INSERT TABLE 6 HERE]

Equations (8) and (9) demonstrate how the uncertainties of the measurements are estimated. Uncertainties on repeatability (u_{rep}) are calculated considering the measurements of apparent Henry's Law constant with at least three different flow values and are about 2 - 3%.

$$u(H_i) = \sqrt{(u_{rep}(H_i))^2 + u_{cal}(H_i)^2} \quad (8)$$

$$u_{cal}(H_i) = \sqrt{\left\{ \begin{aligned} &\left(\frac{\partial H_i}{\partial \alpha}\right)_{P,D,T,N,V_G}^2 u(\alpha)^2 + \left(\frac{\partial H_i}{\partial P}\right)_{\alpha,D,T,N,V_G}^2 u(P)^2 + \left(\frac{\partial H_i}{\partial D}\right)_{\alpha,P,T,N,V_G}^2 u(D)^2 + \left(\frac{\partial H_i}{\partial T}\right)_{\alpha,D,P,N,V_G}^2 u(T)^2 \\ &+ \left(\frac{\partial H_i}{\partial N}\right)_{\alpha,D,T,P,V_G}^2 u(N)^2 + \left(\frac{\partial H_i}{\partial V_G}\right)_{\alpha,D,T,N,P}^2 u(V_G)^2 \end{aligned} \right\}} \quad (9)$$

$$\alpha \text{ the slope of the curve } -\frac{1}{t} \ln \left(\frac{S_i}{(S_i)_{t=0}} \right).$$

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Table 1. CAS numbers, purities and suppliers of materials.

| Chemical Name | Cas No. | Mass Fraction Purity | Supplier |
|--------------------------------|-----------|----------------------|---------------------|
| Methyl Mercaptan /Methanethiol | 74-93-1 | 99 + / GC | Aldrich |
| Ethyl Mercaptan /Ethanethiol | 75-08-1 | 99 + / GC | Acros |
| Water | 7732-18-5 | Ultra pure | Millipore/ Direct Q |

Table 2. Compilation of literature values of activity coefficient at infinite dilution and apparent Henry's Law constant and new measurement (this work) for investigated solutes (1) and water (2) in temperature range of 298K to 348 K ($u(T) = 0.2K$, $U_r(H, k=2) = 0.05$).

| Solute | T(K) | γ^∞ (measured) | γ^∞ (literature) | H(MPa) (measured) | u(H)/ MPa | H(MPa) (literature) | x_i ($\times 10^{-4}$) (measured) | x_i ($\times 10^{-4}$) (literature) |
|--|--|-------------------------------|---------------------------------|----------------------|--------------|------------------------|--|--|
| Methyl Mercaptan (MM)/ Methanethiol | 288.2 | | 76.5[27] | | | 10.9[27] | | 92.9[27] |
| | 298.6 | 78 | 69.0[28] | 15.9 | 0.8 | 14.1[28] | 63.7 | 7.2[28] |
| | 308.6 | 80 | | 22.5 | 1.1 | | 45.0 | |
| | 310.9 | | 101.9[29] | | | 30.7[29] | | 3.3[29] |
| | 323.5 | 77 | | 33.5 | 1.7 | | 30.2 | |
| | 333.4 | 75 | | 42.5 | 2.1 | | 23.8 | |
| | 348.4 | 74 | | 60.4 | 3.0 | | 16.8 | |
| | 366.5 | | 76.1[29] | | | 92.4[29] | | 11.0[29] |
| | 422.0 | | 38.5[29] | | | 130.0[29] | | 7.8[29] |
| | 469.9 | | 22.1[29] | | | 160.0[29] | | 6.3[29] |
| | 533.2 | | 7.3[29] | | | 149.0[29] | | 6.8[29] |
| | 588.7 | | 1.6[29] | | | 102.0[29] | | 9.9[29] |
| | Ethyl Mercaptan (EM)/ Ethanethiol | 298.2 | | 231.4[27] | | | 16.3[27] | |
| 298.4 | | 355 | 280 [28] | 25.2 | 1.3 | 19.9 [28] | 40.2 | 50.9[28] |
| | | | 231 [30] | | | 16.4[30] | | 61.830] |
| 308.3 | | 329 | | 33.5 | 1.7 | | 30.2 | |
| 310.9 | | | 276.4[29] | | | 30.8[29] | | 32.9[29] |
| 318.4 | | 338 | | 48.5 | 2.4 | | 20.9 | |
| 323.4 | | 322 | | 54.1 | 2.7 | | 18.7 | |
| 333.3 | | 321 | | 72.9 | 3.7 | | 13.9 | |
| 348.2 | | 295 | | 102.0 | 5.1 | | 9.9 | |
| 350.6 | | | 266.5[29] | | | 98.0[29] | | 10.3[29] |
| 394.3 | | | 184.3[29] | | | 186.0[29] | | 5.4[29] |
| 435.9 | | | 111.2[29] | | | 241.0[29] | | 4.2[29] |
| 498.7 | | | 39.2[29] | | | 214.0[29] | | 4.7[29] |
| 588.7 | | 6.6[29] | | | 103.0[29] | | 9.8[29] | |

| | | | | |
|--|---|-----------|-----------|----------|
| n-Propyl mercaptan (nPM)/ Propane-1-thiol | 288.2 | 1423[31] | 18.5[31] | 54.8[31] |
| | 293.2 | 1455 [24] | 23.9[24] | 42.4[24] |
| | 298.2 | 1495[31] | 30.7[31] | 33.0[31] |
| | | 1100[28] | 23.1[28] | 43.9[28] |
| | 303.1 | 1844 [24] | 46.8[24] | 21.7[24] |
| | 308.2 | 1455[31] | 45.5[31] | 22.3[31] |
| | 318.2 | 1448[31] | 66.9[31] | 15.2[31] |
| | 333.1 | 1309[31] | 103.0[31] | 9.8[31] |
| | | 1191[24] | 93.9[24] | 10.8[24] |
| isopropyl mercaptan (iPM)/ Propane-2-thiol | 288.2 | 1116[31] | 27.0[31] | 37.5[31] |
| | 298.5 | 916[25] | 34.9[25] | 29.0[25] |
| | | 1135[31] | 42.0[31] | 24.1[31] |
| | 308.3 | 1005[25] | 54.3[25] | 18.7[25] |
| | | 1188[31] | 65.0[31] | 15.6[31] |
| | 318.3 | 999[25] | 75.8[25] | 13.4[25] |
| | | 1127[31] | 88.5[31] | 11.5[31] |
| | 323.3 | 988[25] | 88.3[25] | 11.5[25] |
| | 333.3 | 840[25] | 103.3[25] | 9.8[25] |
| | 348.2 | 730[25] | 142.9[25] | 7.1[25] |
| n-Butyl Mercaptan (nBM)/ butane-1-thiol | 288.2 | 6027[31] | 21.2[31] | 47.8[31] |
| | 292.8 | 6223[24] | 29.3[24] | 34.6[24] |
| | | 298.2 | 6042[31] | 36.7[31] |
| | 6600[30] | | 41.4[30] | 24.5[30] |
| | 8830[27] | 55.0[27] | 18.4[27] | |
| | 312.8 | 5717[24] | 70.1[24] | 14.5[24] |
| | 318.2 | 4504[24] | 125.7[24] | 8.1[24] |
| | | 5338[31] | 81.4[31] | 12.4[31] |
| | 333.2 | 4140[31] | 115.6[31] | 8.8[31] |
| | isobutyl Mercaptan (iBM)/ 2-methylpropane-1-thiol | 298.3 | 5803[25] | 54.2[25] |
| 308.3 | | 5461[25] | 80.4[25] | 12.6[25] |
| 323.4 | | 5046[25] | 138.4[25] | 7.3[25] |
| 333.2 | | 5145[25] | 204.1[25] | 5.0[25] |
| 348.1 | | 4674[25] | 310.4[25] | 3.3[25] |

Table 3. Values of parameters for mercaptans apparent Henry's Law constant correlation (equation 10).

| Component | A | u(x) | B | u(x) | C | u(x) | No of Parameters |
|----------------------|----------|---------|-------------|----------|----------|--------|------------------|
| Methyl Mercaptan | 131.3248 | 13.1791 | -8347.5246 | 841.8811 | -17.6339 | 1.8490 | 3 |
| Ethyl Mercaptan | 190.0012 | 2.9498 | -11715.9368 | 182.8741 | -25.9405 | 0.4160 | 3 |
| n-Propyl Mercaptan | 14.0662 | 0.7353 | -3153.3048 | 237.1916 | - | - | 2 |
| iso Propyl Mercaptan | 12.1139 | 0.5374 | -2482.0454 | 176.0167 | - | - | 2 |
| n-Butyl Mercaptan | 13.6710 | 0.7972 | -2963.4190 | 253.4547 | - | - | 2 |
| isoButyl Mercaptan | 16.1145 | 0.3146 | -3609.3721 | 106.4450 | - | - | 2 |

u(x) : standard deviation of the parameters

Table 4. Values of heat of absorption for methyl mercaptan and ethyl mercaptan in pure water for different temperature according to equation 14.

| Temperature(K) | Heat of Absorption /kJ.mol ⁻¹ | | | | | |
|----------------|--|-------|-------|-------|-------|-------|
| | 298 | 308 | 318 | 328 | 338 | 348 |
| MM | -25.7 | -24.2 | -22.8 | -21.3 | -19.8 | -18.4 |
| EM | -33.1 | -31.0 | -28.8 | -26.7 | -24.5 | -22.4 |

MM : Methyl Mercaptan

EM : Ethyl Mercaptan

Table 5. Values of heat of absorption for C3-C4 mercaptans and their isomers in pure water.

| Component | Heat of Absorption /kJ.mol ⁻¹ | | | |
|-----------|--|-------|-------|-------|
| | nPM | iPM | nBM | iBM |
| | -17.9 | -20.6 | -24.6 | -30.0 |

nPM : n-Propyl Mercaptan

iPM : isoPropyl Mercaptan

nBM : n-Butyl Mercaptan

iBM : isoButyl Mercaptan

Table 6. Vapor pressure correlation (equation 7) parameters.

| Parameter[39] | MM | EM | nPM | iPM | nBM | iBM | Water |
|---------------|------------------------|-----------------------|------------------------|------------------------|------------------------|------------------------|-----------------------|
| A | 54.15 | 65.551 | 61.813 | 74.676 | 64.649 | 61.213 | 73.649 |
| B | -4337.7 | -5027.4 | -5623 | -5272 | -6262 | -5909 | -7258.2 |
| C | -4.8127 | -6.6853 | -5.7934 | -8.1974 | -6.1280 | -5.6431 | -7.3037 |
| D | 4.50×10^{-17} | 6.32×10^{-6} | 6.51×10^{-18} | 3.42×10^{-16} | 6.84×10^{-18} | 1.48×10^{-17} | 4.17×10^{-6} |
| E | 6 | 2 | 6 | 6 | 6 | 2 | 2 |

* Temperature ranges for vapor pressure data underlying the correlation T(K) for mercaptan compounds ;

MM; 253.2-498.6 iPM; 283.8 -358.9

EM; 221.9-469.9 nBM: 323.1-408.8

nPM; 284.6-383.2 iBM: 310.5-394.6

*Parameters were obtained after adjustment on literature data from ThermoDataEngine version 3.0 from NIST) [40] by minimising the objective function, $F = \sum (P_{\text{exp}} - P_{\text{cal}})^2$

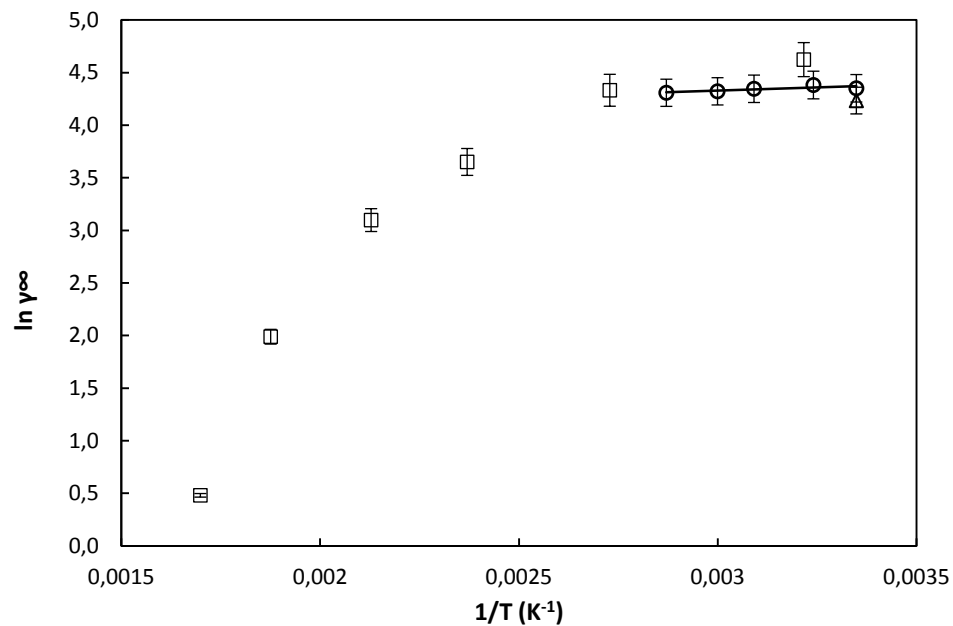


Figure 1. Logarithm of limiting activity coefficient of methyl mercaptan, in pure water as a function of inverse temperature (o water-MM (this work); Δ water-MM [Przyjazny et al. (1983)]; □ water-MM [Gillespie and Wilson (1984)])

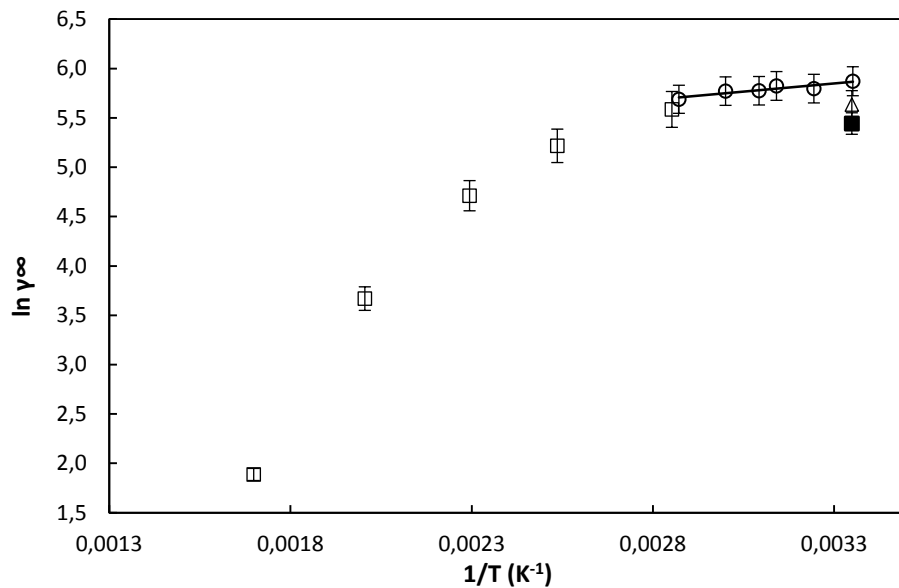


Figure 2. Logarithm of limiting activity coefficient of ethyl mercaptan, in pure water as a function of inverse temperature (o water-EM (this work); Δ water-EM [Przyjazny et al. (1983)]; \blacksquare water-EM [Hwang et al. (1992)]; \square water-EM [Gillespie and Wilson (1984)])

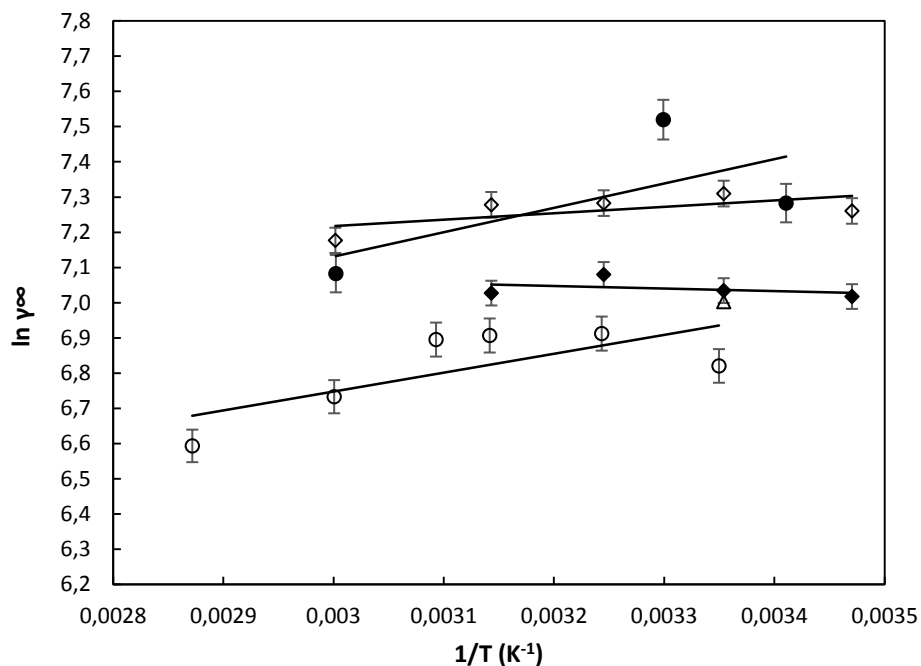


Figure 3. Logarithm of limiting activity coefficient of n-propyl mercaptan and iso-propyl mercaptan, in pure water as a function of inverse temperature (● water-nPM [Coquelet et al. (2008)] ; ◇ water-nPM [Haimi et al. (2006)]; △ water-nPM [Przyjazny et al. (1983)]; ○ water-iPM [Zin et al. (2016)]; ◆ water-iPM [Haimi et al. (2006)]).

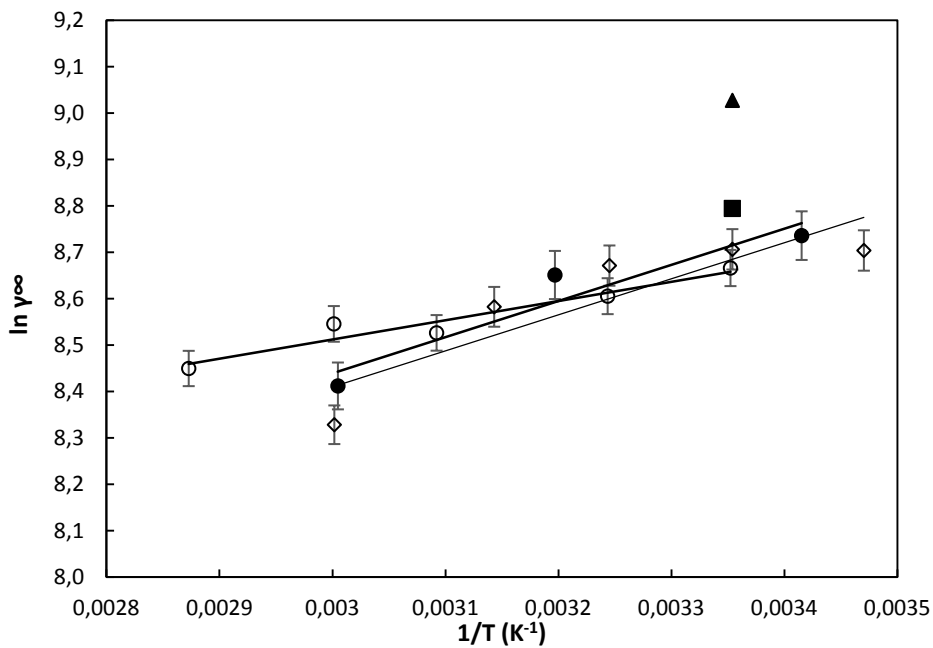


Figure 4. Logarithm of limiting activity coefficient of n-butyl mercaptan and iso-butyl mercaptan, in pure water as a function of inverse temperature (● water-nBM [Coquelet et al. (2008)] ; ◇ water-nBM [Haimi et al. (2006)]; ■ water-nBM [Hwang et al. (1992)]; ▲ water-nBM [Yaws et al. (1992); ○ water-iBM [Zin et al. (2016)])

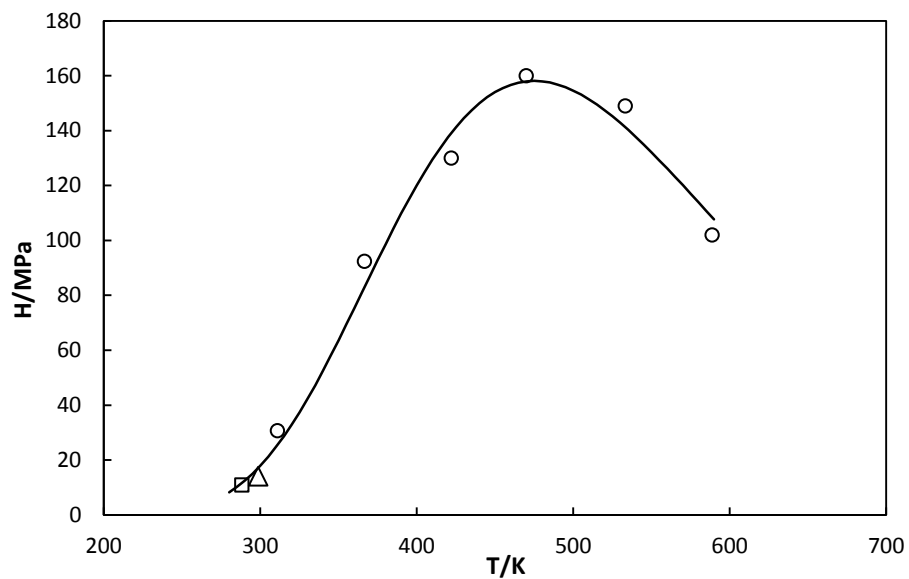


Figure 5. Apparent Henry's Law Constant of methyl mercaptan in water as a function of temperature (o water-MM [Gillespie and Wilson (1984)]; Δ water-MM [Przyjazny et al. (1983)]; \square water-MM [Yaws (1999)]).

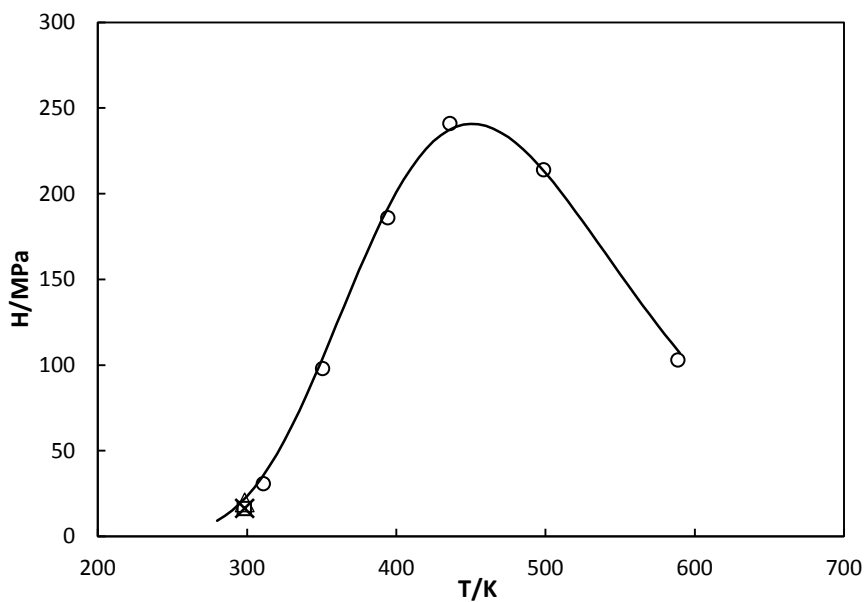


Figure 6. Apparent Henry's Law Constant of ethyl mercaptan in water as a function of temperature (o water-EM [Gillespie and Wilson (1984)]; Δ water-EM [Przyjazny et al. (1983)]; \square water-EM [Yaws (1999)]; X water-EM [Hwang et al. (1992)]).

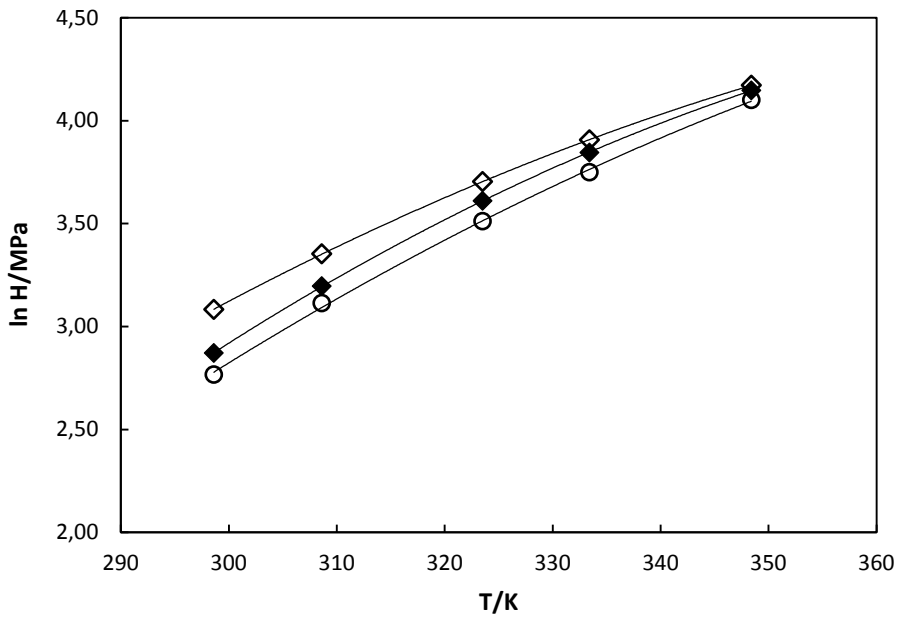


Figure 7. Validation of correlation of Apparent Henry's Law constant of methyl mercaptan in water. (o validation-new measurement; ♦ new correlation (this work); ◇ correlation by Lange et al [38]).

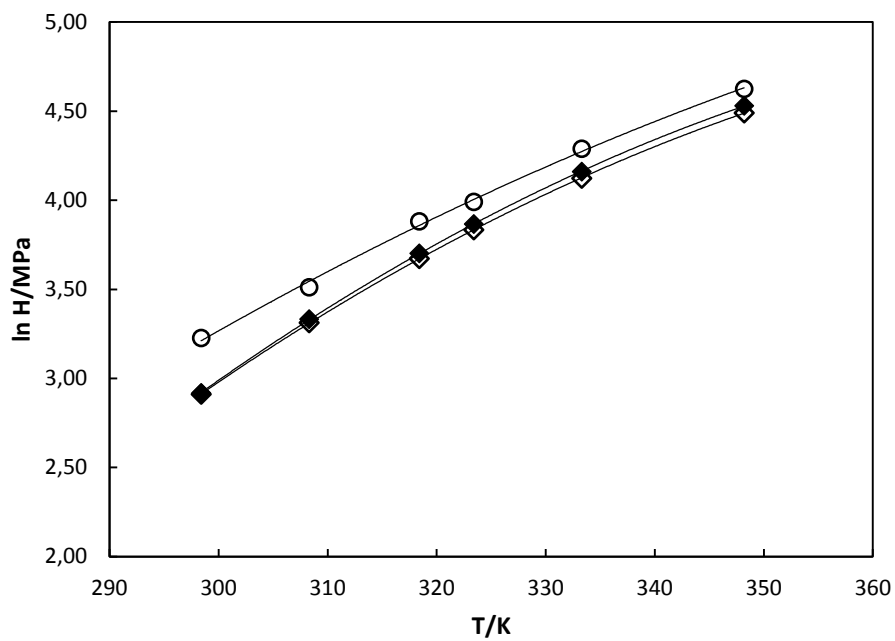


Figure 8. Validation of correlation of Apparent Henry's Law constant of ethyl mercaptan in water. (o validation-new measurement; \blacklozenge new correlation (this work); \diamond correlation by Lange et al [38]).