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The Volatility of Dimethyl Sulfide in Water in Infinite Dilution Measured by Rayleigh Distillation and Dohnal Method

This work is about the volatility of dimethyl sulfide (DMS) in water in infinite dilution. DMS is an important flavour indicative for the wort quality. It is an unwanted flavour component whose reduction by vaporisation is of great interest for the brewer. Different vaporisation systems are available which perform vaporisation at different temperatures. For validating their vaporisation effectivity the temperature dependent volatility of DMS has to be known. Therefore the volatility of dimethyl sulfide is measured by Rayleigh distillation and Dohnal method in a broad temperature range. The resulted values confirm recently published data measured with flash distillation and disclose a volatility maximum at low temperatures.

Descriptors: dimethyl sulfide, DMS, volatility, wort, vaporisation, overall-evaporation

1 Introduction

The flavour dimethyl sulfide (DMS) is an unwanted flavour component in beer [1]. The threshold of DMS in beer is in a range of 30-60 µg/l [2, 3], furthermore the odour threshold value of DMS in water is 0.3 µg/l [4]. Known precursors of DMS are S-methylmethionine (SMM) and dimethyl sulfoxide (DMSO), both of which originate in malt [5]. SMM is cleaved in DMS by heating, whereas DMSO is reduced to DMS by yeast metabolism during fermentation [6, 7]. For wort production the only important precursor of DMS is SMM [7]. It is recommended that the sum of DMS and its relevant precursor at the beginning of fermentation should be below 100–120 µg/l which corresponds to technical norms of 100 µg/l [1].

Vaporisation is the common tool to reduce the content of DMS for which various systems are offered. In the process “vaporisation by boiling” the liquid phase is heated to increase the vapour pressure to atmospheric pressure. The vaporisation can be recognised by vapour bubbles. In contrast, heating the liquid phase to a temperature below the boiling point cannot produce stable vapour bubbles. For vaporising DMS a gas phase has to be brought in contact to the heated liquid. So not vapour but gas bubbles symbolise this process. It is defined as “vaporisation by vaporescence” [8].

Boiling wort under atmospheric conditions by using internal and external heaters is an established and validated method [9, 10]. The vaporization of DMS is performed at temperatures varying around 100 °C. More recently, different vaporescence systems have been developed. Their temperature range is from 76 to 98 °C. Furthermore the vaporisation of DMS out of cold wort is in discussion [11, 12, 13]. For the validation and comparison of all these systems the temperature-dependent volatility of DMS is a substantial tool.

Volatility data can be found for atmospheric boiling conditions [14]. Furthermore volatility data measured by flash distillation covering the temperature range from 30 to 98.5 °C have been recently published [15]. Flashing means a pressure drop by which DMS is vaporised. Measuring the total evaporation and the vaporisation of DMS the volatility of DMS can be determined.

For expanding these values the volatility of DMS in water has been measured by Rayleigh distillation and Dohnal method. So for creating volatility data of high quality and for the validating of the existing ones, this article provides volatility data measured by Rayleigh distillation and Dohnal method.

2 Material and Methods

The basics of Rayleigh distillation and Dohnal method are equal. It is described in the Rayleigh equation which comes from a mass balance for vaporisation processes [16]. For low concentrations it can be simplified to [14]:

$$\frac{x_{i1}}{x_{i0}} = \frac{L_1}{L_0}^{\left(K_i-1\right)} \qquad \text{(eq. 1)}$$

L_1/L_0 describes the ratio of the liquid volume at the end (*1*) of the vaporisation process to its volume at the beginning (*0*) of the vaporisation process. x_{i1}/x_{i0} describes the ratio of the flavour content *i* (in this publication DMS) at the end and at the beginning of the vaporisation process. The factor K_i is one possible expression

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for the volatility and needed for vaporisation processes. Another name for this parameter is distribution factor which is based on the definition that the ratio of the concentration in the vapour phase to he concentration in the liquid phase is described as:

$$K_i = \frac{y_i}{x_i} \quad \text{(eq. 2)}$$

For the calculation of vaporisation processes the factor K_i of DMS in wort has to be known. The content of DMS can be reduced by vaporisation. Therefore the concentration in the vapour phase has to be higher than the concentration in the liquid phase. As a consequence, the volatility for an effective reduction of DMS in wort must have a value greater than 1.

The predicting of the technological properties of the complex mixtures wort can be very difficult. But for experiments concerning the volatility of DMS in wort, two thermodynamic conventions have to be considered:

- DMS in wort is highly diluted (infinite dilution: $x_i < (10^{-3}–10^{-5})$) [14]. Molecular interactions occur only between water and DMS molecules [17, 18, 19]. Therefore, in the relevant concentration range the volatility is independent from the DMS concentration.
- Furthermore the extract in wort has no significant influence on volatility [14, 17, 20]. Therefore, the volatility of DMS in wort accords with the volatility of DMS in water [11].

Hence, the parameter K_i is constant for a given process temperature and depends only on temperature. Furthermore, an experimental matrix of DMS in water in infinite dilution prevents an influence from DMS recreation. By boiling this mixture, measuring the DMS liquid concentration and the over-all-evaporation the volatility can be calculated. Therefore equation 2 has to be transferred into following expression [21]:

$$K_i = \frac{\ln\left(\frac{x_{i1}}{x_{i0}}\right)}{\ln\left(\frac{L_1}{L_0}\right)} + 1 \quad \text{(eq. 3)}$$

The Rayleigh method is based on the pressure-dependent boiling of water. So a classical batch boiling process on laboratory scale is used. The pressure range varies from atmospheric pressure about 1 bar (the resulting measured boiling temperature is 98.5 °C) to a low pressure of 0.044 bar (the resulting measured boiling temperature is 30.0 °C). In this setup, the vaporization of DMS depends on the temperature and the over-all-evaporation. To access DMS vaporisation, the initial and final concentrations of DMS in water were measured. At the end of each experiment, the over-all-evaporation was gravimetrically measured. Using equation 3 the temperature-dependent volatility of DMS in water was calculated.

The Dohnal method is based on the saturation of gas bubbles going through sample liquid [21]. Therefore a volume flow of gas is brought in contact to the DMS-water-mixture. Between bubbles and the ambient liquid a heat and mass transfer occur which is given by the thermodynamic equilibrium. Contrary to the Rayleigh distillation the process pressure is the ambient one and it is constant. Comparable with Rayleigh distillation the vaporization of DMS depends on the temperature and the over-all-evaporation. The procedure of taking samples, measuring the overall evaporation and calculating the temperature-dependent volatility of DMS in water is the same, too.

Both experiments were performed at 30, 40, 50, 60, 70, 80 and 90 °C. Additionally the Rayleigh distillation was performed at 98.5 °C.

The experimental setup of Rayleigh distillation consists of a rotation evaporator which has a rotating glass flask in a water bath for heating and vaporisation of the boiling DMS-water-mixture. The resulting vapour was collected in a water-cooled glass flask. A self-adjusting vacuum pump was installed in order to control and maintain different pressures. The accuracy of the pressure maintenance is 1 mbar. For the experiments performed under atmospheric pressure at a temperature of 98.5 °C the pressure maintenance was switched off and the system was open.

The experimental setup of Dohnal method consists of specialised form of a gas washing bottle. This bottle variant is higher and smaller to provide an optimal process time for bringing the bubbles in thermodynamic equilibrium with the liquid and effecting homogenous desorption of the complete mixture. The bottle was positioned in a self-adjusting water bath for heating and vaporisation of the boiling water-DMS-mixture.

For preparation water (purest water made with “Milli Q Plus” from Millipore, Boston, MA) was mixed with DMS (from Merck, > 99 %, CAS Registry No. 75-18-3) and serially diluted in order to obtain dilution in the molar concentration range of 10^{-7} to 10^{-6}. 500 ml of this mixture were filled into the different experimental setups. Next the heating process to boiling temperature was initiated.

Close to the boiling temperature, in both experiments a reference sample was taken and the mass was gravimetrically measured, reflecting the starting point of the experiment. The Rayleigh distillation started by initiating a defined pressure, the Dohnal method started by flowing gas into the bottle. After a defined process time each experiment stopped.

The overall-evaporation was measured by a second weighing, followed by a redilution of the mixture. The mixture was cooled down and a second sample was taken. The samples were analyzed with a gas chromatograph [22]. The temperature-dependent volatility was calculated using equation 3.

3 Results and Discussion

The measured temperature-dependent volatilities and their confidence intervals (95 %) for both methods are summarised in figure 1.

In figure 2 the measured values are compared with published data using different measurement methods (flash distillation and distillation in a recirculating still).

The data indicate an increase in volatility of DMS with decreasing temperatures. Therefore, maxima were observed at 30 and 40 °C. Over the whole temperature range there is a crossover of the

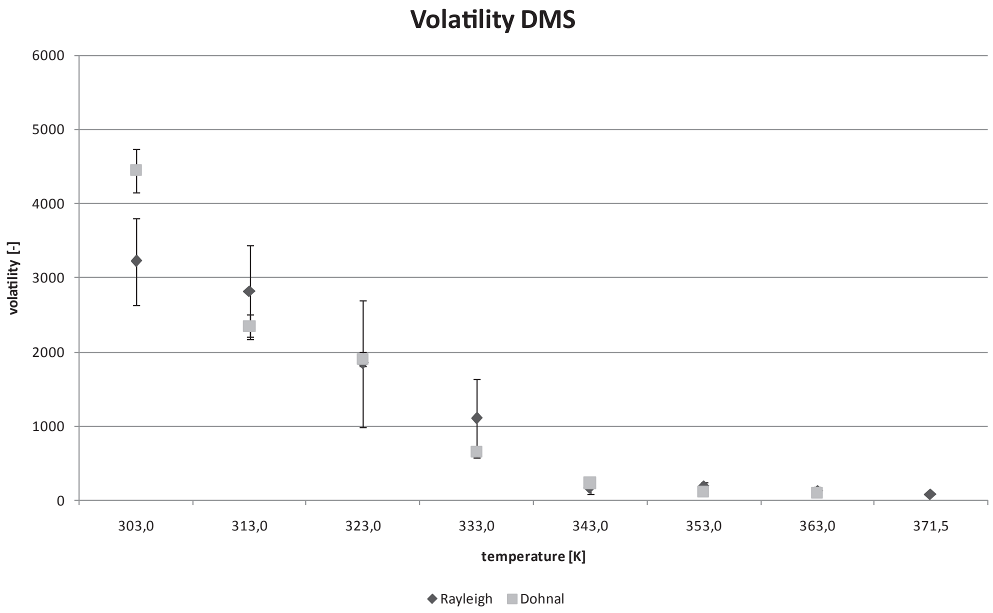

Fig. 1 The Temperature dependent Volatility of DMS measured with Rayleigh (grey Rhombuses) and Dohnal (bright Quadrate)

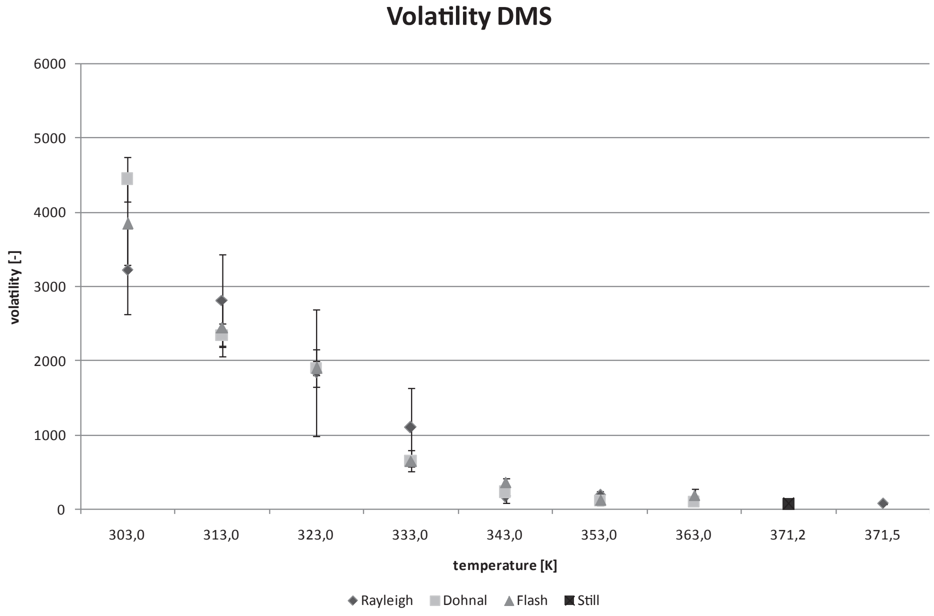

Fig. 2 Comparison of Temperature dependent Volatility of DMS measured by Rayleigh (grey Rhombuses), Dohnal (bright Quadrate), Flash (grey Triangle) and Still (grey Cross)

values due to the range of the calculated confidences. The flash values are validated and the Rayleigh measured value at 98.5 °C is in accordance with a literature value at 98.2 °C published by Hertel et al. which was measured using a recirculating still [23].

Taken together, these results recommend low temperatures for the vaporisation of DMS. This is contrast with the traditional and the most actual technique which perform the boiling processes at temperatures at 100 °C.

The volatility of DMS was measured over a broad temperature range from 30 to 98.5 °C. The use of equation 1 together with the measured volatilities suggest that the needed vaporisation energies are minimised at low temperatures. DMS volatility measurements should be used to predict the effectiveness of new processes and apparatus. For example, this approach reflects an interesting tool for the development of "cold wort vaporisation systems" [11, 12].

Notably, another possible application of the data consists in their combination with SMM cleavage data. Formulating differential equation systems including vaporisation and recreation of DMS inable to predict the development of DMS and SMM concentrations during the wort production process. Thus, the wort production can be precisely controlled and optimised in terms of the required vaporisation energy.

Abbreviations and Nomenclature

SMM: S-methylmethionine

DMSO: dimethyl sulfoxide

DMS: Dimethyl sulfide

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