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The Volatility of Dimethyl Sulfide Measured by Flash Distillation

Vaporisation of dimethyl sulfide (DMS) out of wort is expensive because much more water has to be vaporised. To reduce the needed overall-evaporation the vaporisation behaviour of DMS has to be known. Therefor the temperature-dependent volatility of dimethyl sulfide in water can be measured by flash distillation. In order to determine the temperature-dependent volatility of dimethyl sulphide (DMS), binary mixtures of DMS and water in infinite dilution are overheated and flashed at a specific temperature. The temperature-dependent volatility of dimethyl sulfide in water is calculated by determining the changes in the concentration of DMS and by measuring the overall-evaporation. These results can be applied for the calculation of DMS development in wort production and for the prediction of flash vaporisation processes.

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

1 Introduction

A major goal of wort production is the vaporisation of unrequested flavours. Hereby, the main flavour is dimethyl sulfide (DMS). Its reduction is of great interest for the brewer and, as a consequence, different vaporisation systems are available. Interestingly, different systems use different vaporisation temperatures. For validating theses systems the temperature-dependent vaporisation of DMS in wort has to be known. Because of the lack of brewing relevant data the aim of this work is to determine the vaporisation behaviour of DMS in a broad temperature range from 30 to 90 °C. Therefore, the volatility of DMS in water is measured by using a flash distillation method.

Flashing is defined as a spontaneous reduction of pressure, which results in a vaporisation process at a defined temperature [2]. In a first step, a liquid is heated 1 °C above a defined boiling temperature. For measuring the volatility of DMS in water at 70 °C, the liquid is heated to 71 °C. In a second step the pressure is reduced from atmospheric pressure to the pressure of the defined boiling temperature. The resulting energy difference between the overheated temperature and the boiling temperature is free vaporisation energy. This causes a flash evaporation and the temperature-dependent volatility can be determined by measuring the overall-evaporation and changes in flavour concentration.

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2 Basics

The liquid part of wort mainly consists of water. Due to the fact that flavour components are highly diluted, molecular interactions only occur between water and DMS molecules [6, 8, 4]. Therefore, the volatility is independent from the DMS concentration in this relevant concentration range. In addition, the extract in wort has no significant influence on the volatility [2, 6, 1]. Thus, the volatility of DMS in wort can be assumed as the volatility of DMS in water. Collectively, the volatility of DMS in water is only dependent on the temperature [6, 7, 8].

In order to measure the temperature-dependent volatility of DMS in water, a flash distillation method is used which is described by the following equation based on mass balance [6]:

$$\frac{x_1}{x_0} = \frac{L_0}{L_1 + K \cdot \left(L_0 - L_1\right)} \qquad \text{eq. 1}$$

The volume L_1 is the liquid volume at the beginning of the vaporisation process and L_0 is the volume of the end of the vaporisation process. The parameter x_{i1}/x_{i0} defines the ratio of the aromatic content i (in this publication DMS) from the beginning of the vaporisation process to the end of the vaporisation process. The factor K_i is the volatility to be determined. Another name for this parameter is distribution factor, which is based on the fact that the ratio of the concentration in the vapour phase to the concentration in the liquid phase is described as:

$$K_i = \frac{y_i}{x_i} \qquad \text{eq. 2}$$

For an effective vaporisation of a component i the vaporous concentration must be of a higher value than the concentration in the liquid phase. A volatility of one causes no change in the liquid concentration whereas a volatility smaller one results in an increased liquid concentration.

Flashing a water-DMS-mixture allows the calculation of the volatility. Therefore, equation 1 has to be written as follows:

$$K_i = \frac{L_0 \cdot x_0 - L_1 \cdot x_1}{(L_0 - L_1) \cdot x_1} \qquad \text{eq. 3}$$

In the field of thermodynamics of mixtures a more common parameter named activity coefficient is used instead of volatility. For binary mixtures in infinite dilution the activity coefficient γ_i can be calculated using following equation:

$$\gamma_i = \cdot K_i \frac{p_j^S}{p_i^S} \qquad \text{eq. 4}$$

The ratio p^S_j/p^S_i contains the vapour pressures of the component *i* (in this publication DMS) and the component *j* (in this publication water). One advantage of the activity coefficient is given by the elimination of the ratio of the vapour pressures. These vapour pressures reflect properties of the pure components and contrary to that the activity coefficient exclusively describes the mixture properties. Like volatility, the activity coefficient of mixtures in infinite dilution is only dependent on the temperature.

In summary, the flash vaporisation method is based on the overheating of a liquid, followed by a subsequent pressure reduction that results in the vaporisation of water and DMS. By measuring the overall-evaporation and the change in DMS concentration, this method can be applied to determine the temperature-dependent volatility of DMS in water.

3 Experimental

This article uses a flash vaporisation process in laboratory scale for the measurement of the volatility of DMS in water. As the volatility is dependent on the temperature, the flash temperature is varied from low pressure to atmospheric conditions. Therefore, the experiments were performed at temperatures of 30, 40, 50, 60, 70, 80 and 90 °C.

The experimental setup consists of a rotation evaporator. The evaporator has a rotating glass flask in a water bath for heating and vaporisation of the boiling water-DMS-mixture. In the closed system, a water-cooled glass flask was used for collecting the condensation of the resulting vapour. For maintaining and controlling the different low pressures a self-adjusting vacuum pump was installed. The accuracy of the pressure maintenance is 1 mbar.

4 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) in a two-step dilution in order to obtain a molar concentration in the range of 10^{-7} to 10^{-6}. A volume of 500 ml of this mixture was filled in an experimental glass flask and the heating process to a temperature above 1 °C over the planed boiling temperature was initiated. Close to the boiling temperature, a blank sample was taken and the mass was gravimetrically measured, reflecting the starting point of the experiment. After finishing the heating process the system was closed. Vaporisation is initiated by starting the vacuum pump. The vaporisation, caused by pressure reduction, is quite spontaneous and has to be seen as flash vaporisation from the overheated temperature to the defined temperature. 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 analysed gaschromatographly [5].

For the calculation of the temperature-dependent volatility equation 3 was used. The activity coefficient was calculated using equation 4.

5 Results and discussion

The measured temperature-dependent volatilities and their confidence intervals (95 %) are summarised in table 1. Furthermore figure 1 (see page 71) shows and clarifies the temperature dependence of the volatility.

Table 1

Temperature [K]	Volatility [–]	Confidence (95 %) [–]
303.0	3852	564
313.0	2455	388
323.0	1910	250
333.0	657	144
343.0	367	55
353.0	136	77
363.0	190	94

Using these results as well as published data of vapour pressures of DMS [3], the ratio p^S_j/p^S_i and the activity coefficient γ_i were calculated. These results are shown in table 2.

Table 2

Temperature [K]	Pressure ratio [–]	Gamma [–]	Confidence (95 %) [–]
303.0	18.6	207	30
313.0	15	164	26
323.0	12.4	154	20
333.0	10.5	63	14
343.0	8.9	41	6
353.0	7.7	18	10
363.0	6.7	28	14

These data suggest that the volatility of DMS in water in infinite dilution increases with decreasing temperature. The maximum of volatility can be found at the lowest temperature of 30 °C. This behaviour corresponds to the ratio of the vapour pressures of DMS and water (Table 2). For temperatures below 30 °C the vapour pressures ratio increases, so it has to be guessed that the volatility increases too.

Interestingly, the slope of volatility is steeper than the slope of the pressure ratio. Of note, the molecular interactions in this process have to be considered. In this context, the activity coefficient serves as a describing parameter and it increases with decreasing temperatures.

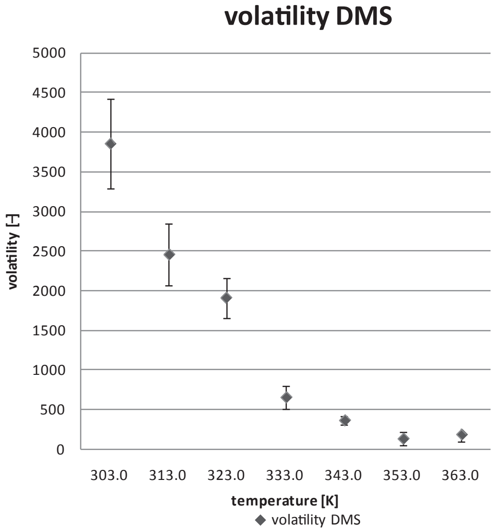

Fig. 1

Taken together, these results suggest the use of low temperatures for the vaporisation of DMS.

6 Summary and Perspectives

The volatility of DMS was measured over a broad temperature range from 30 to 90 °C. These findings show a maximum of the volatility at a low temperature of 30 °C. Since the confidence intervals are small, the presented flash distillation is a useful method for the determination of volatilities of flavours in water in infinite dilution. Especially the short test time of about 10 min is a great advantage of the method, when compared to experiments using a recirculating still of the Gillespie-type [3] that need 9 hours to obtain one value.

An interesting application for the above-described method consists in the calculation of flash vaporisation for wort treatment. Using equation 1 all flash systems can be calculated and thereby validated. Furthermore, the different systems can be compared in regard to their DMS vaporisation.

The results presented here will be validated and completed using additional measurement techniques. In this line, results won by different methods (Rayleigh distillation and Dohnal method) will be presented.

7 Literature

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