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Limiting Separation Factors and Limiting Activity Coefficients for Hexanal, 2-Methylbutanal, 3-Methylbutanal, and Dimethylsulfide in Water at (98.1 to 99.0) °C

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This work is a continuation of preceding work in which limiting separation factors of important wort flavor components in water at 100 °C were determined. In unpublished experiments, the vapor−liquid equilibrium (VLE) of the same aromatic compounds was also researched at atmospheric conditions. No significant differences between the previous published limiting separation factors at 100 °C and the unpublished ones at atmospheric conditions could be observed. Because of this fact, the results of the measurements were used to calculate residue curves during the atmospheric boiling of wort. This study was only investigated at atmospheric conditions. A recirculating Gillespie-type still was used to determine the limiting separation factor (K^{∞}) for hexanal (x), 2-methylbutanal (x), 3-methylbutanal (x), and dimethylsulfide (x) in water ($1 - x$). Since the solutions were highly dilute ($x < 10^{-6}$), infinite dilution was assumed. As the investigated components do not have large absorbances in the UV region, they could not be analyzed by UV spectroscopy. Therefore, in contrary to the preceding work, they were analyzed by gas chromatography. As the boiling point of the solution only changed slightly at the given atmospheric conditions ($\Delta T \leq 0.9$ °C), the limiting separation factors were acquired assuming a constant average temperature of 98.55 °C. Thus, limiting activity coefficients were calculated at the same average temperature. The calculated limiting activity coefficient depends highly on the reliability of the vapor pressure data of the pure components.

Introduction

An important function of the boiling of wort is the evaporation of unwanted flavors. If the total evaporation is not sufficient, off-flavor will occur in beer. Furthermore, a decrease in the flavor stability can be recognized. The aim of this work was to determine the steaming behavior of important flavors that have to be reduced during the boiling of wort. This work is the continuation of preceding works,[1,2] in which limiting separation factors of important wort flavor components in water at 100 °C were determined. In unpublished experiments, the limiting separation factors of the former investigated flavor components were also measured at atmospheric conditions. No significant differences between the previous published limiting separation factors at 100 °C and the unpublished ones at atmospheric conditions could be observed. Because of this fact and the fact that the results of the measurements are used to calculate residue curves during the atmospheric boiling of wort, this study was only investigated at atmospheric conditions.

The liquid part of wort consists mainly of water with flavor components near infinite dilution. Thus the limiting separation factors of flavors in wort can be accounted as limiting separation factors of the same flavors in pure water.[3] With the knowledge of these separation factors in pure water, residue curves for atmospheric wort boiling conditions can be calculated to predict individually for each brew the needed total evaporation. Limiting separation factors (K^{∞}) are measures of the vapor−liquid equilibrium (VLE) behavior of highly dilute solutions. One technique to determine values of K^{∞} is the measurement of vapor and liquid compositions of highly dilute mixtures sampled from a recirculating still.[4] This method provides a simple and direct experimental technique, given an accurate method for the analysis of the liquid and condensed vapor samples. Since the absorption by hexanal, 2-methylbutanal, 3-methylbutanal, and dimethylsulfide in the UV range is very low, they could not be analyzed by UV spectroscopy. In contrary to the preceding work, they had to be analyzed by gas chromatography. As the boiling point of the solution only changed slightly at atmospheric conditions ($\Delta T \leq 0.9$ °C), the limiting separation factors were acquired assuming a constant average temperature of 98.55 °C. The used method was already successfully applied at previous measurements,[1,2] showing that it is capable of determining the limiting separation factor K^{∞} for organic solutes in water. Christensen[5] has shown that limiting activity coefficients, calculated from experimental K^{∞} data for ethanol (x) or methanol (x) + water ($1 - x$) measured with a recirculating still, compared favorably well with several independent results. Since the aqueous solutions were highly dilute ($x < 10^{-6}$), infinite dilution was assumed, and limiting activity coefficients were calculated from the measured K^{∞} values at the same average temperature of 98.55 °C.

Experimental Section

Materials. Water (purest water made with Milli Q Plus from Millipore, Boston, MA), hexanal (from Merck, >98.0 % assay, CAS Registry No. 66-25-1), 2-methylbutanal (from Fluka,

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>90 % assay, CAS Registry No. 96-17-3), 3-methylbutanal (from Merck, >98 %, CAS Registry No. 590-86-3), and dimethylsulfide (from Merck, >99 %, CAS Registry No. 75-18-3) were used as received. This is due to the fact that the samples were highly diluted and that they were analyzed by gas chromatography.

Apparatus. The liquid and vapor compositions and the values for pressure and temperature were obtained from measurements made with a recirculating still of the Gillespie-type.[6] The used equilibrium apparatus was an all-glass, dynamic recirculating still (Labodest VLE 602 D, Fischer Techology, Bonn, Germany), equipped with a Cottrel pump.[7] The producer gives an uncertainty in the measurement of the temperature of ± 0.1 °C. The apparatus is equipped with a glass temperature probe PT 100, having an uncertainty of ± 0.08 °C at 100 °C. The pressure in the still is measured with an uncertainty of ± 1 mbar according to the manufacturer. The still enables us to work in a broad range of pressure and temperature and is described in detail elsewhere.[8]

Procedure. Volumetrically prepared, highly diluted solutions of hexanal, 2-methylbutanal, 3-methylbutanal, and dimethylsulfide in water were placed into the boiler and heated to their boiling point. Although less than 4 h generally sufficed to establish a steady state due to the expected strong deviation from ideal behavior, boiling was continued for (7 to 8) h. The measurements were repeated at least four times. Since the aqueous solutions were highly dilute, their boiling temperature was practically indistinguishable from that of pure water.

Sample Analysis and Resulting Limiting Separation Factors (K^∞). The compositions of the liquid and condensed vapor phases taken from the recirculating still were analyzed by gas chromatography at an external laboratory.[9] The carbonyl components hexanal, 2-methylbutanal, and 3-methylbutanal were enriched by steam distillation and extracted with dichloromethane. Afterward, the solvent phase was analyzed by gas chromatography using a flame ionization detector. The verification of the detector's linearity and the determination of the concentration occurred via several concentration levels within the relevant area, under evaluation of the relative peak areas. The gas chromatograph was a Perkin-Elmer Autosystem XL equipped with a M&N optima 5 ms column (column length, 60 m; i.d., 0.25 mm; film thickness, 0.25 μm).

The sulfur component dimethylsulfide was analyzed by gas chromatography using a headspace technique with a flame photometer detector. The concentration was determined via several concentration levels within the relevant area by evaluation of the relative peak heights. The gas chromatograph was the same as used before but with another column (column length, 30 m; i.d., 0.53 mm; film thickness, 3.0 μm). A closer examination of the parameters of both gas chromatographic analyzes can be found in the literature.[10] The uncertainties in the composition determinations of the gas chromatographic analyzing methods were evaluated at 1 %.

By this way, the concentrations of the different components in the condensed vapor and in the liquid phases from the recirculating still were attained. In the limit of this high dilution, the ratio of the vapor (y) and the liquid (x) equilibrium mole fractions calculates the limiting separation factor K^∞:

$$K^\infty = \lim_{x_x \to 0} \frac{y_x}{x_x} \tag{1}$$

Table 1. Measured Equilibrium Compositions of Hexanal (x) and 2-Methylbutanal (x) in Water ($1 - x$)

hexanal		2-methylbutanal	
x	y	x	y
6.66×10^{-7}	3.51×10^{-5}	3.77×10^{-7}	2.36×10^{-5}
8.10×10^{-7}	3.96×10^{-5}	1.15×10^{-7}	7.48×10^{-6}
6.66×10^{-7}	2.88×10^{-5}	4.77×10^{-7}	2.11×10^{-5}
5.58×10^{-7}	2.70×10^{-5}	8.37×10^{-7}	4.76×10^{-5}
		9.20×10^{-7}	5.30×10^{-5}
		4.18×10^{-7}	2.43×10^{-5}
		6.28×10^{-7}	3.66×10^{-5}

Table 2. Measured Equilibrium Compositions of 3-Methylbutanal (x) and Dimethylsulfide (x) in Water ($1 - x$)

3-methylbutanal		dimethylsulfide	
x	y	x	y
2.34×10^{-6}	1.12×10^{-4}	1.45×10^{-7}	1.09×10^{-5}
2.77×10^{-6}	1.61×10^{-4}	1.21×10^{-7}	8.45×10^{-6}
2.77×10^{-6}	1.57×10^{-4}	1.29×10^{-7}	9.22×10^{-6}
2.62×10^{-6}	1.58×10^{-4}	1.18×10^{-7}	9.46×10^{-6}
2.77×10^{-6}	1.51×10^{-4}	1.24×10^{-7}	1.01×10^{-5}

Table 3. Pure Components Vapor Pressures p^0, Limiting Separation Factors K^∞, and Limiting Activity Coefficients γ^∞ of Hexanal, 2-Methylbutanal, 3-Methylbutanal, and Dimethylsulfide

	T/°C	p^s/kPa	K^∞	γ^∞
hexanal	98.55	40.40[a]	48.3 ± 3.9	121.1 ± 9.7
2-methylbutanal	98.55	128.4[b]	57.5 ± 6.6	45.4 ± 5.2
3-methylbutanal	98.55	121.1[c]	55.5 ± 4.8	46.4 ± 4.0
dimethylsulfide	98.55	572.4[a]	75.6 ± 5.1	13.4 ± 0.9

[a] Calculated with Component Plus.[12] [b] Estimated with the method of Marrero and Gani.[11] [c] Calculated with the Antoine equation at the Dortmund Data Bank.[13]

Calculation of Activity Coefficients. As the pressure P in the system was less than 101.3 kPa and as the difference to the vapor pressure of the pure component p^0 at the same temperature was small, the Poynting correction and the nonideality of the gas were neglected in the calculation of the activity coefficient in this work. This assumption and the one that the activity coefficient in such high dilutions is equal to the limiting activity coefficient γ^∞ lead to the following equation:

$$\gamma^\infty = \frac{P}{p^0} \frac{y_x}{x_x} \tag{2}$$

Results

Measurements of the liquid and condensed vapor-phase samples were made for dilute binary mixtures of water ($1 - x$) + hexanal (x), + 2-methylbutanal (x), + 3-methylbutanal (x), and + dimethylsulfide (x) at atmospheric conditions. The measured concentrations of the liquid (x) and the condensed vapor (y) equilibrium mole fractions of hexanal and 2-methylbutanal are shown in Table 1. For 3-methylbutanal and dimethylsulfide, these results are shown in Table 2.

The calculated pure components vapor pressures, the measured values for the limiting separation factors K^∞, and the resulting limiting activity coefficients γ^∞ for the compounds hexanal, 2-methylbutanal, 3-methylbutanal, and dimethylsulfide are shown in Table 3 together with their uncertainties. The uncertainty in the pure solute vapor pressure value was not considered in the calculation of the limiting activity coefficient as it depends highly on the way the vapor pressure curve was determined. As we do not know how the vapor pressure data in the pure component property programs were acquired and in what temperature range, this uncertainty was not considered in this work. However, we estimate a general uncertainty in vapor pressure data calculated from fitted vapor pressure curves of at least 3 %, which could be considered by others in the calculation of the limiting activity coefficients. In the case of 2-methylbutanal, no vapor pressure data could be found in the literature. Thus, the vapor pressure was estimated using a method according to Marrero and Gani.[11] Due to the faults of an estimation method, the uncertainty in the calculation of this activity coefficient at infinite dilution is even higher than 3 %. No data of limiting separation factors or activity coefficients at infinite dilution for all of the components in water could be found. Hence, the results cannot be compared to other data.

Conclusion

As expected, the results of the measurements show that the limiting separation factors (K^{∞}) for 2-methylbutanal and 3-methylbutanal are equal within their uncertainties. Hexanal has the lowest limiting separation factor of all investigated wort flavor compounds, and dimethylsulfide has the highest one. As all the limiting separation factors of the investigated compounds are quite high (> 40), those compounds can be easily evaporated during the atmospheric boiling of wort. Since the confidence intervals are small, the reproducibility of the used method is good. The uncertainty of the calculated limiting activity coefficients depends highly on the quality of the calculated vapor pressure of the pure components and is even for fitted vapor pressure curves quite high. As no vapor pressure data could be found for 2-methylbutanal, its vapor pressure was calculated with an estimation method based on group contribution. Therefore, the resulting uncertainty in the calculation of the limiting activity coefficient for this component is higher.

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