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Solubilities of Hexanal, Benzaldehyde, 2-Furfural, 2-Phenylethanol, Phenylethanal, and γ-Nonalactone in Water at Temperatures between (50 and 100) °C

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Data of the solubility x_S of wort flavor compounds in water is useful to understand the behavior of these components during the production of wort. Because of this fact, the maximum solubility x_S of hexanal, benzaldehyde, 2-furfural, 2-phenylethanol, phenylethanal, and γ-nonalactone in water has been measured at different temperatures. The method used was the analysis of the mole fraction of a component in water after liquid−liquid-equilibrium has been reached in a thermostat. As the investigated components show a large absorption of UV light, the mole fractions were analyzed with a spectrophotometer. Furthermore, a literature review of already reported solubility data at temperatures between (50 and 100) °C, including a comparison to the measured values, is given in this article.

1. Introduction

Accurate liquid−liquid solubility data are needed to check theoretical solubility relationships and to determine solubility parameters for liquid−liquid mixtures. Also, the brewing industry has a strong interest in the solubility of wort flavor components, especially at the temperatures of wort production (50 to 100) °C. Such information is necessary to understand the behavior of flavor components during the brewing process. The knowledge of the solubility of wort flavor components is important for the basics of possible aroma recovery out of steam leaving a kettle during the boiling of wort. As some flavors can be desirable in beer, recovery of these components out of initial wort is the only possibility to produce aroma extracts in accordance with the German purity law. As this could be a completely new approach in the production of aromatic beers, the results of this work will be used for a first insight.

In the case of wort flavor components, only limited data is given in the literature, especially at the atmospheric boiling temperature of wort. Thus, the maximum solubility x_S of important flavor components in water was measured in this work. For this, the equilibrium mole fractions of wort flavor components in water were analyzed with a spectrophotometer after liquid−liquid equilibrium (LLE) was reached in a thermostat. This analysis method was used, because of the large absorbance of UV light of the investigated components. The results of our measurement are compared to previously reported data.

2. Experiments

2.1. 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), benzaldehyde (from Merck, > 99.0 % assay, CAS Registry No. 100−52-7), 2-furfural (from Merck, > 99.0 % assay, CAS Registry No. 98−01-1), 2-phenylethanol (from Merck, > 99.0 % assay, CAS Registry No. 60−12-8), phenylethanal (from Acros Organics, > 98.0 % assay, CAS Registry No. 122−78-1), and γ-nonalactone (from TCI Europe, ≥ 98.0 % assay, CAS Registry No. 104−61-0) were used as received.

2.2. Procedure. An overspill amount of a flavor component and purest water were placed into tubes, agitated, and brought into LLE at a given temperature in a thermostat (Heraeus, BT 5042 E). The uncertainty of the thermostat was checked with a digital thermometer (model ama-digit ad 15 th, from Labotech LTS AG, Biel, Switzerland) and was found to be 0.1 K.

As there existed a small insulated hole in the catch of the tubes, samples could be taken directly with a syringe without prior opening. Because of the fact that the tubes were closed and because of the low mutual solubility of the flavor components and water, the resulting system pressure was approximately given by an addition of the pure components vapor pressure and the vapor pressure of pure water at the investigated temperatures. As the effect of low pressures on LLE can in general be disregarded[1] and as the resulting pressure in the tubes was small at the investigated temperatures, the influence of the system pressure on the solubility of the researched components in water was neglected. To minimize the losses during sampling, the samples were taken directly with a gastight syringe (Hamilton Gastight #1750) after equilibrium has been reached.

After the samples were taken, they were immediately diluted with purest water. One purpose for this dilution was the fact that the solubility of a flavor compound in water could also decline with declining temperature.[2] Thus a miscibility gap that would make a measurement impossible could occur. Another purpose for the dilution is to reside in the recommended ideal absorbance range of 0.1 to 1 (Kortüm[3]).

The resulting uncertainty of the dilution was estimated to be 3 %. This uncertainty is clearly lower than the one that would result of a measurement in an obvious higher absorption range.

The mole fraction of a flavor component diluted in water x_S was measured with a spectrophotometer (Milton Roy, Spectronic 1201) in the differential mode against pure water at predetermined absorption maxima.

The cuvettes used were silica glass cuvettes from Hellma (type 115-QS) with an optical length of 10 mm. The spectrophotometer was calibrated for each flavor component with

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Table 1. Maximum Absorbance Wavelength (λ) of the Investigated Wort Flavor Components

flavor component	λ/nm
hexanal	285.5
benzaldehyde	251.0[6]
2-furfural	277.5[6]
2-phenylethanol	217.0[7]
phenylethanal	209.5[7]
γ-nonalactone	190.0[6]

Table 2. Measured and Literature Solubilities x_S of Hexanal in Water

T/°C	x_S	ref
100	$(11.9 \pm 0.2)\cdot10^{-4}$	this work
90	$(6.82 \pm 0.28)\cdot10^{-4}$	this work
90	$(7.22 \pm 0.18)\cdot10^{-4}$	5
80	$(5.91 \pm 0.32)\cdot10^{-4}$	this work
80	$(6.13 \pm 0.18)\cdot10^{-4}$	5
70	$(5.59 \pm 0.18)\cdot10^{-4}$	5
60	$(5.05 \pm 0.18)\cdot10^{-4}$	5
50	$(6.32 \pm 0.18)\cdot10^{-4}$	5

Table 3. Measured and Literature Solubilities x_S of Benzaldehyde in Water

T/°C	x_S	ref
100	$(3.60 \pm 0.22)\cdot10^{-3}$	this work
90	$(2.61 \pm 0.18)\cdot10^{-3}$	this work
90	$(2.41 \pm 0.05)\cdot10^{-3}$	5
80	$(2.36 \pm 0.29)\cdot10^{-3}$	this work
80	$(2.13 \pm 0.05)\cdot10^{-3}$	5
70	$(1.75 \pm 0.05)\cdot10^{-3}$	5
60	$(1.59 \pm 0.05)\cdot10^{-3}$	5
50	$(1.40 \pm 0.05)\cdot10^{-3}$	5

Table 4. Measured and Literature Solubilities x_S of 2-Furfural in Water

T/°C	x_S	ref
100	$(3.40 \pm 0.08)\cdot10^{-2}$	this work
90	$(3.14 \pm 0.11)\cdot10^{-2}$	this work
90	$(3.100 \pm 0.002)\cdot10^{-2}$	5
88	$3.19\cdot10^{-2}$	2
85.8	$3.21\cdot10^{-2}$	8
80.4	$2.69\cdot10^{-2}$	2
80	$(2.80 \pm 0.09)\cdot10^{-2}$	this work
80	$(2.600 \pm 0.002)\cdot10^{-2}$	5
70	$(2.30 \pm 0.002)\cdot10^{-2}$	5
60	$(2.100 \pm 0.002)\cdot10^{-2}$	5
53.1	$2.00\cdot10^{-2}$	8
50	$(1.900 \pm 0.002)\cdot10^{-2}$	5

Table 5. Measured and Literature Solubilities x_S of 2-Phenylethanol in Water

T/°C	x_S	ref
100	$(6.50 \pm 0.34)\cdot10^{-3}$	this work
90	$(6.50 \pm 0.09)\cdot10^{-3}$	this work
80	$(5.50 \pm 0.09)\cdot10^{-3}$	this work
70	$(5.60 \pm 0.10)\cdot10^{-3}$	this work
60.3	$(4.03 \pm 0.03)\cdot10^{-3}$	9
60	$(5.10 \pm 0.15)\cdot10^{-3}$	this work
55	$2.99\cdot10^{-3}$	10
50	$(3.85 \pm 0.03)\cdot10^{-3}$	9
50	$2.92\cdot10^{-3}$	10

Table 6. Measured and Literature Solubilities x_S of Phenylethanal in Water

T/°C	x_S	ref
100	$(4.00 \pm 0.09)\cdot10^{-3}$	this work
90	$(3.00 \pm 0.08)\cdot10^{-3}$	this work
80	$(2.60 \pm 0.08)\cdot10^{-3}$	this work
70	$(2.30 \pm 0.06)\cdot10^{-3}$	this work
60	$(1.90 \pm 0.07)\cdot10^{-3}$	this work
50	$(1.80 \pm 0.02)\cdot10^{-3}$	this work

Table 7. Measured and Literature Solubilities x_S of γ-Nonalactone in Water

T/°C	x_S	ref
100	$(1.28 \pm 0.02)\cdot10^{-3}$	this work
90	$(1.18 \pm 0.04)\cdot10^{-3}$	this work
80	$(0.99 \pm 0.07)\cdot10^{-3}$	this work
70	$(1.09 \pm 0.04)\cdot10^{-3}$	this work
60	$(0.87 \pm 0.07)\cdot10^{-3}$	this work
50	$(0.72 \pm 0.09)\cdot10^{-3}$	this work

different volumetrically prepared solutions at least five times. The coefficient of determination of the calibration was high ($r^2 \geq 0.98$). In general, it can be said that this method has a major accuracy benefit in comparison to a single comparison measurement.[4] The amount of a flavor compound in the water layer x_S was acquired out of a multiplication of the measured value in the diluted solution and the individual dilution factor.

The entire determination of solubility including the equilibration and sampling was performed for every component at each temperature at least 10 times.

To ensure that no byproducts were significantly generated out of the flavor components at high temperatures, test trials were performed with the pure components at infinite dilution in pure water. A possible generation of by products could have an influence on the absorption of the resulting solution. For these trials, the pure components were clearly considerably more diluted than their maximum solubility in water and placed in the thermostat at 100 °C. After specified time intervals, the absorption of the solution was measured and compared to the absorption of the start solution. As the absorption did not change significantly, a generation of byproducts out of the flavor components was assumed to be negligible.

3. Results and Discussion

The wavelengths of the determined absorption maxima of the investigated components are shown in Table 1.

The experimental results of the solubility measurements are given together with their uncertainties and literature values in Tables 2 to 7.

As shown, the measured values of this work of hexanal, benzaldehyde, and 2-furfural compare favorably well to the ones previously reported by Stephenson[5] at the same temperatures. Because of this fact, it was assumed that the method used in this work is applicable for the measurement of the solubility of wort flavor components in water at the investigated temperatures and no measurements at temperatures already reported in the literature were performed further on. It can also be seen that the uncertainty in the measured values of this work is higher compared to the literature[5] values. This can be due to the dilution of the samples, which is needed for this analysis method. The solubility x_S of hexanal in water reaches a minimum at 60 °C first and increases at higher temperatures. The solubility of 2-furfural, benzaldehyde, and phenylethanal in water monotonically increases with increasing temperature. This is also valid for 2-phenylethanol and γ-nonalactone. Because of the fact that the solubility of all components is increasing from (60 to 100) °C, solubility equations that assume an increasing solubility with temperature can be used for further data treatment in this limited temperature range.

The solubility limit of all investigated flavor components is clearly higher than their normal concentrations in wort or in its steam condensate. Thus, a possible aroma recovery according to the German purity law could only be performed by a downstream fractional distillation.

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