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# Limiting Separation Factors and Limiting Activity Coefficients for 2-Furfural, $\gamma$-Nonalactone, Benzaldehyde, and Linalool in Water at 100 °C

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In combination with previous work in which limiting separation factors of important wort flavor components in water at 100 °C were determined, this work deals with the limiting separation factor ($K^\infty$) for 2-furfural ($x$), $\gamma$-nonalactone ($x$), benzaldehyde ($x$), and linalool ($x$) in water ($1 - x$). As the solutions are highly dilute ($x < 10^{-5}$), infinite dilution is assumed. The condensed vapor and liquid samples were analyzed using UV spectroscopy. As the confidence intervals are very small, the method showed a good reproducibility. The calculated limiting activity coefficient depends highly on the reliability of the vapor pressure data of the pure components. The measurements of the limiting separation factors of wort aroma compounds in water were investigated to figure out the steaming behavior of these components during the atmospheric boiling of wort. With this knowledge, residue curves can be calculated to predict a needed total evaporation individually for every brew.

## Introduction

In wort boiling, the evaporation of unrequested flavors is an important factor. 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 is to get cognition of the steaming behavior of important flavors that have to be reduced during the boiling of wort. The liquid part of wort consists mainly of water with flavor components in infinite dilution. For this, the limiting separation factors can be obtained for wort flavor components in water. With the knowledge of these separation factors, residue curves for atmospheric boiling conditions can be calculated to predict a needed total evaporation individually for every brew. Limiting separation factors ($K^\infty$) are measures of the vapor−liquid equilibrium behavior of highly dilute solutions.[1] One technique to determine values of $K^\infty$ is the measurement of vapor and liquid compositions of highly diluted mixtures sampled from a recirculating still.[2] This method provides a simple, direct experimental technique given an accurate method for the analysis of the liquid and condensed vapor samples. Since the absorption of UV light by 2-furfural, $\gamma$-nonalactone, benzaldehyde, and linalool is very strong, UV spectroscopy gives such an accurate method.

The used method was already successfully applied at previous measurements,[1] showing that it is capable of determining the limiting separation factor ($K^\infty$) for organic solutes in water. Christensen[3] has shown that limiting activity coefficients, calculated from experimental $K^\infty$ data for ethanol ($x$) or methanol ($x$) + water ($1 - x$) measured with a recirculating still, compared favorably well with several independent results. Since the aqueus solutions were highly dilute ($x < 10^{-5}$), infinite dilution is assumed, and limiting activity coefficients are calculated from the measured $K^\infty$ values.

## Experimental Section

***Materials.*** Water (purest water made with Milli Q Plus from Millipore, Boston, MA), 2-furfural (from Merck, > 99.0 % assay, CAS Registry No. 98-01-1), $\gamma$-nonalactone (from TCI Europe, ≥ 98.0 % assay, CAS Registry No. 104-61-0), benzaldehyde (from Merck, > 99.0 % assay, CAS Registry No. 100-52-7), and linalool (from Merck, > 97.0 % assay, CAS Registry No. 78-70-6) were used as received.

***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.[4] The used equilibrium apparatus was an all-glass, dynamic recirculating still (Labodest VLE 602 D, Fischer Techology, Bonn, Germany), equipped with a Cottrel pump.[5] 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 with an uncertainty of ± 0.08 °C at 100 °C. The pressure in the still is measured and controlled with an uncertainty of ± 0.1 kPa, according to the manufacturer. The still enables us to work in a broad range of pressure and temperature and is described in detail elsewhere.[6]

***Procedure.*** Volumetrically prepared solutions from (10 to 40) $\mu\text{L}\cdot\text{L}^{-1}$ of 2-furfural, $\gamma$-nonalactone, benzaldehyde, or linalool + water were placed into the boiler. The solutions were heated to their boiling point and set under pressure (101.3 kPa) by inert gas ($N_2$). Although less than 4 h is generally sufficient to establish steady state, due to the expected strong deviation from ideal behavior, boiling was continued for (7 to 8) h. The measurements were repeated five times with different solutions. Since the aqueus solutions were highly dilute, their boiling temperature was practically indistinguishable from that of pure water.

***Sample Analysis and Resulting Limiting Separation factor ($K^\infty$).*** As the investigated compounds exhibit a strong absorption of UV light, the compositions of the liquid and the condensed vapor phase were analyzed using a Milton Roy spectrophotometer, Spectronic 1201. The absorbances were measured at predetermined absorption maxima.

While the equilibrium liquid phase samples were used directly for the measurements, most samples of the vapor-phase condensate were measured after appropriate dilution so that the absorbances took place in the recommended absorption range

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**Table 1. Maximum Absorbance Wavelength $\lambda$ for 2-Furfural, $\gamma$-Nonalactone, Benzaldehyde, and Linalool**

| component | $\lambda$/nm | component | $\lambda$/nm |
|---|---|---|---|
| 2-furfural | 277.5 | benzaldehyde | 251.0 |
| $\gamma$-nonalactone | 190.0 | linalool | 190.0 |

**Table 2. Measured Absorbances Abs$_y$ and Abs$_x$ for 2-Furfural and $\gamma$-Nonalactone in Water**

| 2-furfural | | $\gamma$-nonalactone | |
|---|---|---|---|
| Abs$_y$[a] | Abs$_x$ | Abs$_y$ | Abs$_x$ |
| 0.732 | 0.984 | 0.661 | 0.210 |
| 0.559 | 0.743 | 0.644 | 0.205 |
| 0.606 | 0.774 | 0.690 | 0.224 |
| 0.704 | 0.964 | 0.875 | 0.291 |
| 0.666 | 0.877 | 0.884 | 0.281 |

[a] Dilution 1:10.

between 0.1 and 1.0 (Kortüm[7]). The used cuvettes were silica glass cuvettes from Hellma (type 117.104-QS) with an optical length of 10 mm. The measurements were done in differential mode against pure water. In the limit of this high dilution, the ratio of the vapor $y_x$ and the liquid $x_x$ equilibrium mole fractions gave the limiting separation factor ($K^\infty$).

Dohnal and Fenclova[8] showed that proportionality relationships between the absorbances and the concentrations of highly diluted solutions exist. Because of this, there is no need to calibrate the analytical response, and the limiting separation factor ($K^\infty$) is directly obtained as a ratio of absorbances of the equilibrium vapor- and liquid-phase samples:

$$K^\infty = \lim_{x_x \to 0} \frac{y_x}{x_x} = \lim_{x_x \to 0} \frac{\mathrm{Abs}_{y_x}}{\mathrm{Abs}_{x_x}} \qquad (1)$$

***Calculation of Activity Coefficients.*** As the pressure in the system ($P$) was only 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 non-ideality 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 ($\gamma^\infty$) lead to the following equation:

$$\gamma^\infty = \frac{P \cdot y_x}{p^0 \cdot x_x} \qquad (2)$$

## Results

Measurements of the liquid- and condensed vapor-phase samples were made for dilute binary mixtures of water $(1 - x)$ + 2-furfural ($x$), + $\gamma$-nonalactone ($x$), + benzaldehyde ($x$), or + linalool ($x$) at 100 °C. The maximum absorbance wavelength $\lambda$ for 2-furfural, $\gamma$-nonalactone, benzaldehyde, and linalool are shown in Table 1.

The measured absorbances of the liquid (Abs$_x$) and the condensed vapor phase (Abs$_y$) for 2-furfural and $\gamma$-nonalactone are shown in Table 2. The absorbances of the condensed vapor phase of 2-furfural were diluted (1:10). This dilution factor had to be considered for the determination of $K^\infty$.

The measured absorbances of the liquid (Abs$_x$) and the condensed vapor phase (Abs$_y$) for benzaldehyde and linalool are shown in Table 3. The absorbances of the condensed vapor phase of benzaldehyde and linalool were also diluted (1:10). This dilution factor had to be considered at the determination of $K^\infty$.

**Table 3. Measured Absorbances Abs$_y$ and Abs$_x$ for Benzaldehyde and Linalool in Water**

| benzaldehyde | | linalool | |
|---|---|---|---|
| Abs$_y$[a] | Abs$_x$ | Abs$_y$[a] | Abs$_x$ |
| 0.346 | 0.170 | 0.670 | 0.195 |
| 0.382 | 0.170 | 0.642 | 0.288 |
| 0.330 | 0.162 | 0.750 | 0.210 |
| 0.306 | 0.150 | 0.780 | 0.209 |
| 0.206 | 0.102 | 0.837 | 0.234 |

[a] Dilution 1:10.

**Table 4. Pure Components Vapor Pressures ($p^0$ ), Limiting Separation Factors ($K^\infty$), and Limiting Activity Coefficients ($\gamma^\infty$) for 2-Furfural, $\gamma$-Nonalactone, Benzaldehyde, and Linalool**

| component | $t$/°C | $p^0$/kPa | $K^\infty$ | $\gamma^\infty$ |
|---|---|---|---|---|
| 2-furfural | 100 | 13.51[a] | 7.54 ± 0.2 | 56.5 ± 1.5 |
| $\gamma$-nonalactone | 100 | 55.8[b] | 3.10 ± 0.06 | 5.6 ± 0.1 |
| benzaldehyde | 100 | 8.38[a] | 20.76 ± 0.96 | 251 ± 12 |
| linalool | 100 | 3.49[c] | 35.46 ± 1.28 | 1029 ± 37 |

[a] Calculated with Component Plus.[10] [b] Estimated with the method of Mackay et al.[9] [c] Calculated with the Antoine equation at the Dortmund Data Bank,[11]

To demonstrate that the mole fractions of the liquid phases were $< 10^{-5}$, a test solution of each component in water with $x = 10^{-5}$ was volumetrically prepared and its absorption measured. The absorbances of the liquid phases from the still lie all well below the absorption determined for the prepared test solutions. Thus, all the measured absorbances from the equilibrium cell relate to a concentration of clearly less than $x = 10^{-5}$ and, thus, lie in the limit of infinite dilution under the made assumptions.

The calculated pure components vapor pressures and the measured values for the limiting separation factors ($K^\infty$) and the resulting limiting activity coefficients ($\gamma^\infty$) for 2-furfural, $\gamma$-nonalactone, benzaldehyde, and linalool are shown in Table 4 together with their uncertainties. The uncertainty in the pure solute vapor pressure value is not considered in the calculation of the limiting activity coefficient as it depends highly on the way the vapor pressure curve is 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 is 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 $\gamma$-nonalactone, no vapor pressure data could be found. Thus, the vapor pressure was estimated using the method according to Mackay et al.[9] Due to the faults of an estimation method, the uncertainty in the calculation of this activity coeficient 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.

## Conclusions

The results show that the measured limiting separation factors ($K^\infty$) of wort flavor components differ strongly in their magnitude. Linalool has the highest limiting separation factor in water, followed by benzaldehyde, 2-furfural, and $\gamma$-nonalactone. As the confidence intervals are small, the reproducibility of the used method is very good.

The accuracy 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 low. As no vapor pressure data could be found for $\gamma$-nonalactone, the vapor pressure was estimated with a correlation method for low-volatility environmental chemicals. Therefore, the resulting uncertainty in the calculation of the limiting activity coefficient for this component is higher. To minimize the uncertainty in the calculation and to get more accurate values of the resulting limiting activity coefficients, it is planned to make exact vapor-pressure measurements for the investigated compounds at given temperatures, which will be the subject of a following work.

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