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Limiting Separation Factors and Limiting Activity Coefficients for 2-Phenylethanol and 2-Phenylethanal in Water at 100 °C

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A recirculating Gillespie-type still was used to determine the limiting separation factor (K^∞) for 2-phenylethanol (x) or 2-phenylethanal (x) + water ($1 - x$). Since the solutions are highly dilute ($x < 10^{-5}$), infinite dilution is assumed. The condensed vapor and liquid samples were analyzed using UV spectroscopy. The confidence intervals are very small, and thus the method has a good reproducibility. The calculated limiting activity coefficient depends highly on the reliability of the pure components vapor pressure data.

Introduction

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 diluted mixtures sampled from a recirculated still.[1] 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-phenylethanol and 2-phenylethanal (phenylacetaldehyde) is very strong, UV spectroscopy provides such an accurate method.

To prove that this method of measuring limiting separation factors (including UV spectroscopy) is capable for aromatic compounds, a self-conducted test trial with phenol (x) + water ($1 - x$) was done before the main measurements started. The measured value for the limiting separation factor for phenol in water at 100 °C is 1.94 with an uncertainty of 0.03. This shows excellent agreement with literature data where the value of the limiting separation factor for phenol in water at 100 °C is given between 1.84 (Dohnal and Fenclova[2]) and 2.0 (Langen et al.[3]).

Christensen[4] 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 too. Since the aqueus solutions were highly dilute ($x < 10^{-5}$), infinite dilution is assumed, and limiting activity coefficients are calculated from the measured K^∞ values.

Experimental Section

Materials. Water (purest water made with Milli Q Plus from Millipore, Bedford, MA), 2-phenylethanol (from Merck, > 99.0 % assay, CAS Registry No. 60-12-8), and 2-phenylethanal (phenylacetaldehyde) (from Acros Organics, 98.0 % assay, CAS Registry No. 122-78-1) 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.[5] The used equilibrium apparatus was an all-glass, dynamic recirculating still (Labodest VLE 602 D, "Fischer Techology", Bonn, Germany), equipped with a Cottrel pump.[6] 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 at 100 °C of ± 0.08 °C. The pressure in the still is measured and controlled with an uncertainty of ± 1 mbar, according to the manufacturer. The still is able to work in a broad range of pressure and temperature and is described in detail elsewhere.[7]

Procedure. Volumetrically prepared solutions from 10 μL/L to 20 μL/L of 2-phenylethanol or 2-phenylethanal in water were placed into the boiler. The electrical heater was turned on, and the pressure was set to 1013 mbar by injecting 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 are 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^∞. Since there is a strong absorption of UV light exhibited by aromatic compounds, the compositions of the liquid and the condensed vapor phase were analyzed using a Milton Roy spectrophotometer (Spectronic 1201). The absorbances were measured at the 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 are situated in the recommended absorption range of 0.1 to 1.0 (Kortüm[8]). 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 the 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 gives the limiting separation factor (K^∞). Dohnal and Fenclova[2] showed that since proportionality relationships between the absorbances and concentrations of highly

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Table 1. Maximum absorbance wavelength (λ) for 2-Phenylethanol and 2-Phenylethanal

component	λ/nm
2-phenylethanol	217.0
2-phenylethanal	209.5

Table 2. Measured Absorbances (Abs_y and Abs_x) for 2-Phenylethanol and 2-Phenylethanal in Water

2-phenylethanol		2-phenylethanal	
Abs_y	Abs_x	Abs_y[a]	Abs_x
0.981	0.447	0.491	0.482
1.003	0.435	0.678	0.629
0.986	0.429	0.692	0.653
0.453	0.198	0.679	0.628
0.204	0.475	0.678	0.629

[a] Dilution 1:5.

diluted solutions are known to exist, there is no need to calibrate the analytical response and the limiting separation factor (K^∞) is directly obtained as a ratio of absorbances of the equilibrium vapor- and liquid-phase samples:

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

Calculation of Activity Coefficients. Since the system pressure (P) was only 1013 bar and the difference to the vapor pressure of the pure component (p^0) at the same temperature is small, the Poynting correction and the nonideality of the gas were neclected in the calculation of the activity coefficient in this work. This assumption and the assumption that the activity coefficient in such high dilutions is equal to the limiting activity coefficient (γ^∞) leads to

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

Results

Measurements of the liquid- and condensed vapor-phase samples were made for dilute binary mixtures of water ($1 - x$) + 2-phenylethanol (x) or 2-phenylethanal (x) at 100 °C. The maximum absorbance wavelength (λ) for 2-phenylethanol and 2-phenylethanal are shown in Table 1.

The measured absorbances of the liquid (Abs_x) and the condensed vapor phase (Abs_y) are shown in Table 2. The absorbances of the condensed vapor phase of 2-phenylethanal were diluted 1:5. This dilution factor has to be considered at the determination of K^∞.

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 was measured. The absorbances of the liquid phases from the still all lie well below the absorption determined for the prepared test solutions. Thus, all the measured absorbances from the equilibrium cell belong to a concentration 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^∞) and the resulting limiting activity coefficients (γ^∞) for 2-phenylethanol and 2-phenylethanal are shown in Table 3 together with their uncertainties. The uncertainty in the pure solute vapor pressure value is not involved in the calculation of the limiting activity coefficient as this uncertainty depends highly on the way the vapor pressure curve is acquired. As we do not know how the vapor pressure data in the pure component property programs were acquired and in which temperature range, this uncertainty is not considered in this work. We estimate a general uncertainty in vapor pressure data calculated from fitted vapor pressure curves of at least 3% that could be considered by others in the calculation of the limiting activity coefficients.

Table 3. Pure Components Vapor Pressures (p^0), Limiting Separation Factors (K^∞), and Limiting Activity Coefficients (γ^∞) for 2-Phenylethanol and 2-Phenylethanal

component	t/°C	p^0/mbar	K^∞	γ^∞
2-phenylethanol	100	13.857[a]	2.28 ± 0.05	167 ± 4
2-phenylethanal	100	23[b]	5.32 ± 0.13	234 ± 6

[a] Calculated with Component Plus[9]. [b] Calculated with the Antoine equation at the Dortmund Data Bank.[10]

No data of limiting separation factors or activity coefficients at infinite dilution for both of the components in water could be found to the best of the authors knowledge. Thus, the results cannot be compared to other data.

Conclusion

The results of the measurements show that the limiting separation factor (K^∞) for 2-phenylethanal in water is approximately twice the amount for 2-phenylethanol in water. 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 pure components vapor pressure.

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