Vapor Pressures, Enthalpies of Vaporization, and Limiting Activity Coefficients in Water at 100 °C of 2-Furanaldehyde, Benzaldehyde, Phenylethanal, and 2-Phenylethanol

Vladimir N. Emel'yanenko, Aldona Dabrowska, and Sergey P. Verevkin

Department of Physical Chemistry, University of Rostock, Hermannstrasse 14, 18051 Rostock, Germany

Marcus O. Hertel,* Hans Scheuren, and Karl Sommer

TU München-Weihenstephan, Lehrstuhl für Maschinen- und Apparatekunde, Am Forum 2, 85350 Freising, Germany

In our previous work, limiting separation factors K_i^∞ of 2-furanaldehyde, benzaldehyde, phenylethanal, and 2-phenylethanol in water were determined using a recirculating still of the Gillespie type. Limiting activity coefficients γ_i^∞ were calculated out of the limiting separation factors K_i^∞ in the previous work, too. As it was announced in those papers, a revised calculation of the limiting activity coefficient γ^∞ data was performed in this work. For this work, vapor pressure measurements were performed with the transpiration method. The results of these measurements are given here together with the derived enthalpies of vaporization of the investigated components and their formerly calculated and recalculated limiting activity coefficients in water at 100 °C.

Introduction

In our previous work,[1,2] limiting separation factors of 2-furanaldehyde (x), benzaldehyde (x), phenylethanal (x), and 2-phenylethanol (x) in water ($1 - x$) were determined with a recirculating still of the Gillespie type.[3] These data were also used to calculate the resulting limiting activity coefficient. Christensen[4] has shown that limiting activity coefficients, calculated from experimental K^∞ data measured with a recirculating still, compared favorably with several independent determinations if high quality vapor pressure data are available. In the majority of cases, the pure component vapor pressures of our previous work[1,2] were calculated with a pure component property program[5] that is based on the contribution of the DIPPR database. In the case of the component phenylethanal, no data existed in the pure component property program.[5] Thus, the vapor pressure of this component was calculated with the Antoine equation,[6] based on data from the Dortmund Data Bank.[7] The used data sets were measured in the temperature range of (288 to 333) K.[8] Because of this fact, the calculation of the vapor pressure of phenylethanal at 373.15 K exhibited an extrapolation.

To improve and to control the calculation of the limiting activity coefficients for the investigated components, their vapor pressures were measured with the transpiration method at the Department of Physical Chemistry at the University of Rostock. With this new vapor pressure data, revised limiting activity coefficients are calculated for 2-furanaldehyde, benzaldehyde, phenylethanal, and 2-phenylethanol in water at 100 °C.

Experimental Section

Materials. Samples of the flavors were of commercial origin: 2-furanaldehyde (2-furfural) (from Merck, > 99.0 % assay, Chemical Abstracts Service Registry No. (CASRN) 98-01-1), benzaldehyde (from Merck, > 99.0 % assay, CASRN 100-52-7), phenylethanal (phenylacetaldehyde) (from Acros Organics, 98.0 % assay, CASRN 122-78-1) and 2-phenylethanol (from Merck, > 99.0 % assay, CASRN 60-12-8). Samples were purified by fractional micro-distillation. The purity was determined using a Hewlett-Packard gas chromatograph 5890 series II equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. The carrier gas (nitrogen) flow was 12.1 $cm^3 \cdot s^{-1}$. A capillary column HP-5 (stationary phase crosslinked 5 % phenyl methyl silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 mm. The standard temperature program of the GC was $T = 333$ K for 180 s followed by a heating rate of 0.167 $K \cdot s^{-1}$ to $T = 523$ K. No total impurities (greater than mass fraction 0.003) could be detected in the samples used for the vapor pressure measurements.

Vapor Pressure Measurements. Vapor pressures and enthalpies of vaporization were determined using the transpiration method in a saturated N_2 stream[9,10] and applying the Clausius−Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with diameter of 1 mm provide a surface that is large enough for vapor−liquid equilibration. At constant temperature (± 0.1 K), a nitrogen stream was passed through the U-tube, and the transported amount of gaseous material was collected in a cooling trap. The flow rate of the nitrogen stream was measured using a soap bubble flowmeter and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The flow rate of the nitrogen stream in the saturation tube should be not too slow in order to avoid the transport of the material from U-tube due to diffusion and not too fast in order to reach the saturation of the nitrogen stream with the compound. Our apparatus was tested at different flow rates of the carrier gas in order to check the lower flow rate

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* Corresponding author. Tel. +49-8161-713680. Fax: +49-8161-714242. E-mail: m.hertel@lrz.tum.de.

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Table 1. Vapor Pressures *p* and $\Delta_l^g H_m$ Obtained by the Transpiration Method

T	m	$V(N_2)$	flow	p	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$
K[a]	mg[b]	dm^3 [c]	$dm^3 \cdot h^{-1}$	Pa[d]	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
2-Furanaldehyde $\Delta_l^g H_m$ (298.15 K) = (50.65 ± 0.22) $kJ \cdot mol^{-1}$						
$\ln(p/Pa) = \frac{277.9}{R} - \frac{69106.8}{R(T/K)} - \frac{61.0}{R}\ln\left(\frac{T/K}{298.15}\right)$						
276.7	3.15	1.615	3.23	52.5	1.2	51.98
281.5	1.82	0.647	1.08	74.6	−0.7	51.69
285.4	2.22	0.575	1.08	101.1	−0.6	51.44
288.4	3.72	0.753	3.23	129.3	1.5	51.26
290.6	4.19	0.719	1.08	151.6	1.8	51.12
293.2	3.06	0.439	1.05	182.0	0.7	50.96
295.5	1.82	0.226	0.97	208.8	−3.8	50.82
298.2	2.63	0.263	1.05	258.9	2.6	50.65
300.5	2.62	0.226	0.97	300.2	0.6	50.51
303.1	4.95	0.351	1.05	365.2	8.9	50.35
308.2	5.00	0.263	1.05	491.1	−4.3	50.03
312.2	6.32	0.263	1.05	621.3	−14.5	49.78
315.1	6.52	0.226	0.97	741.1	−17.3	49.61
317.9	8.65	0.246	1.05	910.8	15.0	49.43
320.1	9.89	0.246	1.05	1040.4	21.9	49.30
323.4	11.50	0.236	1.09	1255.5	25.5	49.09
Benzaldehyde $\Delta_l^g H_m$ (298.15 K) = (49.04 ± 0.67) $kJ \cdot mol^{-1}$						
$\ln(p/Pa) = \frac{267.6}{R} - \frac{67021.2}{R(T/K)} - \frac{60.3}{R}\ln\left(\frac{T/K}{298.15}\right)$						
278.4	2.86	1.699	2.08	40.83	−0.60	50.24
282.3	3.20	1.387	2.08	55.24	−0.64	50.00
286.3	4.27	1.317	2.08	76.97	1.76	49.76
290.3	4.27	1.040	2.08	96.97	−3.28	49.52
294.3	5.07	0.867	2.08	137.18	4.76	49.28
298.4	5.25	0.693	2.08	177.48	2.96	49.03
303.2	5.28	0.501	2.08	245.98	7.54	48.74
308.2	4.76	0.347	2.08	319.49	−6.52	48.44
313.2	5.46	0.295	2.08	430.65	−9.82	48.14
2-Phenylethanal $\Delta_l^g H_m$ (298.15 K) = (59.83 ± 0.27) $kJ \cdot mol^{-1}$						
$\ln(p/Pa) = \frac{293.6}{R} - \frac{79565.4}{R(T/K)} - \frac{66.2}{R}\ln\left(\frac{T/K}{298.15}\right)$						
293.2	1.53	1.87	5.63	16.83	0.34	60.16
298.1	1.67	1.41	5.63	24.56	−0.16	59.83
303.1	2.41	1.33	3.33	37.24	0.47	59.50
308.2	2.20	0.833	3.33	54.36	0.06	59.17
313.7	3.03	0.778	3.33	80.10	−1.50	58.80
317.9	4.20	0.778	3.33	111.0	1.20	58.52
323.0	1.74	0.239	0.96	150.0	−5.09	58.19
328.1	2.51	0.239	0.96	216.2	−0.82	57.85
332.1	3.13	0.223	0.96	288.3	8.26	57.58
338.0	4.37	0.223	0.96	402.9	−0.87	57.19
343.0	17.71	0.662	2.84	549.8	8.62	56.86
2-Phenylethanol $\Delta_l^g H_m$ (298.15 K) = (66.74 ± 0.28) $kJ \cdot mol^{-1}$						
$\ln(p/Pa) = \frac{315.8}{R} - \frac{89488.7}{R(T/K)} - \frac{76.3}{R}\ln\left(\frac{T/K}{298.15}\right)$						
287.8	1.11	8.990	7.10	2.51	0.0	67.53
289.7	1.06	7.524	7.28	2.85	−0.1	67.39
292.7	1.13	5.670	5.58	3.99	0.0	67.16
295.1	1.11	4.531	7.35	4.82	−0.1	66.98
297.5	1.25	4.059	4.35	6.26	0.1	66.79
302.5	1.30	2.705	4.06	9.76	0.1	66.41
308.2	1.36	1.800	4.00	15.30	−0.4	65.98
312.5	1.29	1.150	4.31	22.76	0.5	65.65
316.6	3.95	2.575	3.82	30.91	0.0	65.34
317.6	2.72	1.656	3.82	32.85	−0.6	65.26
322.7	2.08	0.827	3.82	50.22	0.9	64.87
322.7	2.53	1.017	3.94	50.28	0.9	64.87
322.8	3.09	1.237	3.89	50.55	0.8	64.86
327.8	2.69	0.781	1.46	69.13	−2.7	64.48
332.8	1.46	0.295	1.14	98.39	−4.0	64.10
337.9	3.42	0.495	1.10	139.53	−5.6	63.71
342.9	2.96	0.285	1.10	209.69	7.9	63.33
348.1	4.93	0.355	1.18	279.45	−1.5	62.93
353.2	7.45	0.396	1.19	377.66	−6.6	62.54
358.3	8.59	0.337	1.19	524.33	4.5	62.15
363.3	8.80	0.255	1.18	692.15	0.0	61.77

[a] Temperature of saturation. [b] Mass of transferred sample, condensed at T = 243 K. [c] Volume of nitrogen, used to transfer mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at T = 243 K.

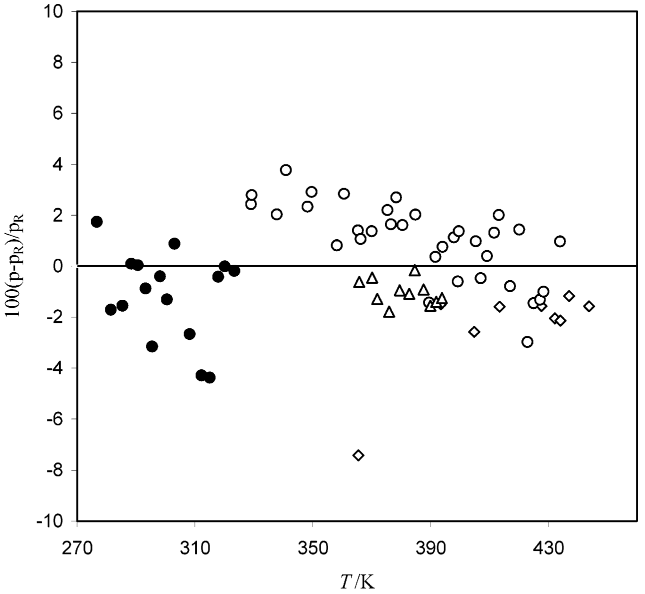

Figure 1. Comparison of vapor pressures of 2-furanaldehyde obtained in this work with literature data. ●, this work; ○, ref 15; ◇, ref 13; △, ref 22. p_R is the reference pressure calculated according to the equation for 2-furanaldehyde (see Table 3).

Table 2. Compilation of Data on Enthalpies of Vaporization $\Delta_l^g H_m$ (298.15 K)

technique	temperature range K	$\Delta_l^g H_m$(298 K)[a] $kJ \cdot mol^{-1}$	ref
2-Furanaldehyde			
ebulliometry	365.5−443.8	51.41 ± 0.48	13
ebulliometry	329.0−433.9	50.63 ± 0.42	14
ebulliometry	329.0−433.9	50.49 ± 0.19	15
ebulliometry	365.8−393.8	50.72 ± 0.21	22
transpiration	276.7−323.4	50.65 ± 0.22	this work
Benzaldehyde			
ebulliometry	299.3−452.0	52.8	16
static	273.1−322.1	46.2	17
calorimetry	298	49.80 ± 0.80	18
ebulliometry	311.6−481.4	50.87 ± 0.16	19
transpiration	278.4−313.2	49.04 ± 0.67	this work
2-Phenylethanol			
ebulliometry	331.3−492.6	68.0	16
gas chromatography	304.2−363.2	73.4 ± 1.5	20
ebulliometry	406.2−492.0	64.90 ± 0.28	21
effusion	283.5−287.2	69.7 ± 1.6	23
effusion	288.2−333.2	69.1 ± 0.2	24
transpiration	287.8−363.3	66.74 ± 0.28	this work

[a] Vapor pressure available in the literature were treated using eqs 2 and 3 in order to evaluate enthalpy of vaporization at 298.15 K in the same way as our own results in Table 1.

below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus the contribution due to diffusion was negligible at a flow rate up to 0.45 $dm^3 \cdot h^{-1}$. The upper limit for our apparatus where the nitrogen flow rate could already disturb the equilibration was at a flow rate of 9.0 $dm^3 \cdot h^{-1}$. Thus, we performed the experiments at the flow rate of (0.9 to 7.4) $dm^3 \cdot h^{-1}$, which ensured that the transporting gas was in the saturated equilibrium with the coexisting liquid phase in the saturation tube. The amount of condensed substance was determined by GC analysis using an external standard (hydrocarbon n-C_nH_{2n+2}). The saturated vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of product collected within a definite period of time. Assuming that

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

component	t/°C	p^0/kPa[a]	K^∞	γ^∞(this work)	γ^∞(previous work)[1,2]
2-furanaldehyde	100	13.08	7.54 ± 0.20	58.4 ± 2.0	56.5 ± 1.5
benzaldehyde	100	7.75	20.76 ± 0.96	271.3 ± 13.9	251.0 ± 12.0
2-phenylethanol	100	1.19	2.28 ± 0.05	194.6 ± 6.1	167.0 ± 4.0
phenylethanal	100	2.64	5.32 ± 0.13	203.8 ± 6.8	234.0 ± 6.0

[a] The vapor pressures of flavors (see Table 2 and Figures 1−3) have been reported in refs 13−24. We have treated the available results together with our results using eq 2. The following equations could be recommended in the broad temperature range for calculation of the vapor pressure. For 2-furanaldehyde:

$$\ln(p/\text{Pa}) = \frac{278.98}{R} - \frac{69370.0}{R(T/\text{K})} - \frac{61.9}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$$

valid in temperature range of (276.7 to 443.8) K. For benzaldehyde:

$$\ln(p/\text{Pa}) = \frac{272.0}{R} - \frac{68360.6}{R(T/\text{K})} - \frac{60.0}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$$

valid in temperature range of (273.0 to 481.0) K. For 2-phenylethanol:

$$\ln(p/\text{Pa}) = \frac{317.2}{R} - \frac{89904.2}{R(T/\text{K})} - \frac{76.3}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$$

valid in temperature range of (283.5 to 492.6) K.

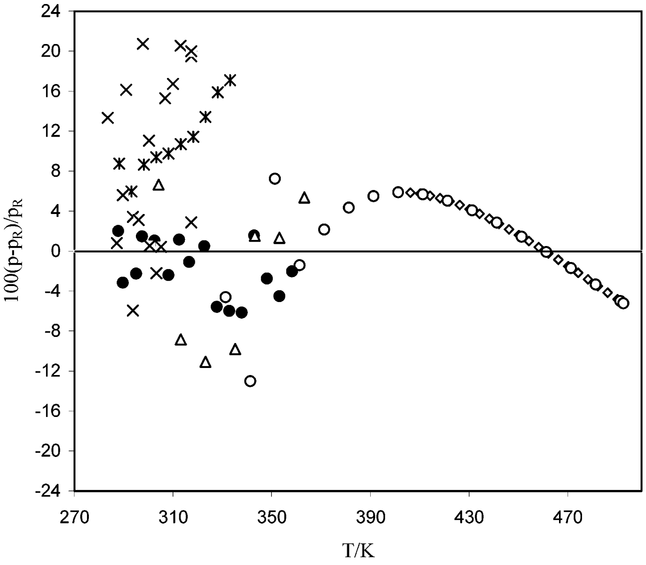

Figure 2. Comparison of vapor pressures of 2-phenylethanol obtained in this work with literature data. ●, this work; ○, ref 16; ◇, ref 21; △, ref 20; ×, ref 23; ∗, ref 24. p_R is the reference pressure calculated according to the equation for 2-phenylethanol (see Table 3).

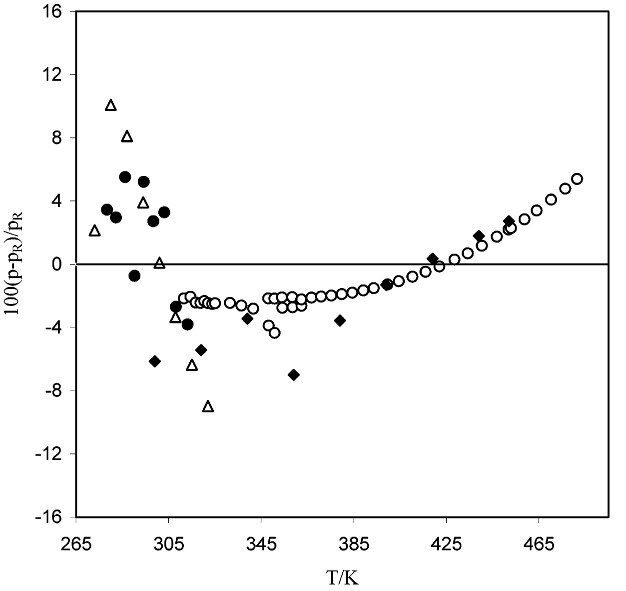

Figure 3. Comparison of vapor pressures of benzaldehyde obtained in this work with literature data. ●, this work; ○, ref 19; ◆, ref 16; △, ref 17. p_R is the reference pressure calculated according to the equation for benzaldehyde(see Table 3).

Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated:

$$p_i^{\text{sat}} = m_i R T_a / V M_i; \quad V = V_{N_2} + V_i; \quad (V_{N_2} \gg V_i) \tag{1}$$

where $R = 8.31447\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; m_i is the mass of transported compound; M_i is the molar mass of the compound; and V_i is its volume contribution to the gaseous phase. V_{N_2} is the volume of transporting gas and T_a is the temperature of the soap bubble meter. V_{N_2} was determined from the flow rate and time measurements. Data of p_i^{sat} were obtained as a function of temperature and were fitted using following equation:

$$R\ln(p_i^{\text{sat}}/\text{Pa}) = a + \frac{b}{(T/\text{K})} + \Delta_l^g C_p \ln\left(\frac{T}{T_0}\right) \tag{2}$$

where a and b are adjustable parameters and $\Delta_l^g C_p$ is the difference of the molar heat capacities of the gaseous and the liquid phases, respectively. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from eq 2 the expression for the vaporization enthalpy at temperature T is derived:

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p T \tag{3}$$

The values of $\Delta_l^g C_p$ have been calculated from the isobaric molar heat capacities of liquid sample (from ref 11), C_p^l, according to a procedure developed by Chickos and Acree.[12] The experimental results, parameters a and b, are listed in Table 1.

Calculation of the Resulting Limiting Activity Coefficients. Since the system pressure (P) at the previous measurements was only 101.3 kPa and the difference to the vapor pressure of the pure component (p_i^{sat}) at the same temperature is 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 leads to

$$\gamma_i^\infty = \frac{P K_i^\infty}{p_i^{\text{sat}}} \tag{4}$$

The pure components vapor pressure p_i^{sat} was determined for each component i with eq 2, and the constants are given in Table 1. The uncertainty of the pure components vapor pressure calculated with eq 2 is about 2 % for the investigated compounds. This uncertainty and the uncertainty in the measured system pressure of ± 1 mbar are considered in the calculation of the limiting activity coefficient for each component.

Results

Enthalpies of vaporization could be found in the literature for the components 2-furanaldehyde, benzaldehyde, and 2-phenylethanol. No enthalpy of vaporization could be found for phenylethanal to the best of our knowledge. A compilation of data of enthalpies of vaporization is given in Table 2.

The agreement of the results of this work for the vapor pressures at different temperatures with literature data is presented in Figures 1 to 3.

The calculated vapor pressures, limiting separation factors, and resulting limiting activity coefficients in water at 100 °C of 2-furanaldehyde, benzaldehyde, phenylethanal, and 2-phenylethanol are given in Table 3 together with the values of our previous work.[1,2]

Conclusion

The results of the new limiting activity coefficient calculations show that the revised activity coefficients at infinite dilution (γ^∞) of phenylethanal and 2-phenylethanol in water differ significantly from the formerly determined ones. The limiting activity coefficients (γ^∞) for these components given in our previous paper[2] were thus more inaccurate and should be replaced by the ones of this work. In the case of 2-furanaldehyde and benzaldehyde, no significant differences in the limiting activity coefficients (γ^∞) could be recognized.

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