Vapor−Liquid Equilibrium Behaviors of 3-Ethoxy-4-hydroxybenzaldehyde in Alcohol

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Vapor−liquid equilibrium behaviors of the scent solid, 3-ethoxy-4-hydroxybenzaldehyde, in alcohol, ethanol, 1-propanol, 2-propanol, or 1-butanol were measured at atmospheric pressure in the dilute composition range of 3-ethoxy-4-hydroxybenzaldehyde with a recirculation still. Equilibrium compositions were determined with an ultraviolet spectrometer. The activity coefficients of 3-ethoxy-4-hydroxybenzaldehyde at infinite dilution in alcohol were less than unity.

Introduction

In the previous studies,[1−6] vapor−liquid equilibrium measurements were made for mixtures containing solid components, ferrocene,[1] 1,4-dihydroxybenzene,[2] durene,[3] tolan,[4] 5-hydroxymethylfurfural,[5] vanillin, and coumarin[6] in alcohol or water at atmospheric pressure. The authors[7] have recently reported the vapor−liquid equilibrium behaviors of vanillin in 1-butanol, 2-butanol, and 2-methyl-1-propanol at atmospheric pressure.

In the present study, the vapor−liquid equilibrium behaviors of 3-ethoxy-4-hydroxybenzaldehyde in ethanol, 1-propanol, 2-propanol, and 1-butanol were measured at atmospheric pressure in the dilute composition range of 3-ethoxy-4-hydroxybenzaldehyde. 3-Ethoxy-4-hydroxybenzaldehyde is a worthy scent component in the food industry.

Experimental

Chemicals. 3-Ethoxy-4-hydroxybenzaldehyde (ethyl vanillin, CAS Registry No. 121-32-4) was supplied by Wako Pure Chemical Industries, Ltd., with a guarantee of 98 mol % purity. 3-Ethoxy-4-hydroxybenzaldehyde is solid at room temperature. Special grade reagents of alcohol, ethanol, 1-propanol, 2-propanol, and 1-butanol were supplied by Wako Pure Chemical Industries, Ltd., and were used without further purification. The physical properties of alcohols used in this work are listed in Table 1. The purities of alcohols, ethanol, 1-propanol, 2-propanol, and 1-butanol were found to be greater than 99.9 mol % by gas chromatographic area analysis.

Apparatus and Procedures. The experimental apparatus and procedures are the same as those described previously.[1−7] The recirculation still is entirely constructed from borosilicate glass. The amount of solution required is about 45 cm^3 per determination. The boiling vapor−liquid mixture flashes to the thermometer well in the boiling still. The condensed vapor in the condensed chamber recirculates to the boiling still through the overflow tube. After attainment of steady state, equilibrium temperature was measured with a Hewlett-Packard 2804A quartz thermometer, calibrated at the triple point of water in a reference cell, with an uncertainty of ± 0.01 K. The experimental atmospheric pressure was measured with a Fortin barometer with an uncertainty of ± 0.01 kPa. Both samples of liquid and vapor phases were individually taken. The equilibrium vapor and liquid compositions were determined with a JASCO V-560DS ultraviolet spectrophotometer for 3-ethoxy-4-hydroxybenzaldehyde at 309 nm. The uncertainties of liquid and vapor compositions, respectively, seem to be (± $1 \cdot 10^{-4}$ and ± $5 \cdot 10^{-7}$) mole fraction of 3-ethoxy-4-hydroxybenzaldehyde.

Table 1. Normal Boiling Points T_b and Densities ρ of the Alcohols Used

	T_b/K		ρ(298.15 K)/(kg·m^{-3})	
material	exptl	lit.[a]	exptl	lit.[b]
ethanol	351.44	351.475	785.2	785.09
1-propanol	370.21	370.359	799.6	799.75
2-propanol	355.40	355.44	780.8	781.26
1-butanol	390.85	390.876	805.8	806.0

[a] Timmermans.[8] [b] TRC Thermodynamic Tables Non-Hydrocarbons.[9]

Results and Discussion

Table 2 gives the experimental results for the vapor−liquid equilibrium measurements at atmospheric pressure in the dilute composition range of 3-ethoxy-4-hydroxybenzaldehyde in ethanol, 1-propanol, 2-propanol, and 1-butanol. The experimental pressures were approximately 99 kPa as shown in Table 2. The volatility, K_1, is the ratio of vapor composition and liquid composition of 3-ethoxy-4-hydroxybenzaldehyde. The extrapolation of the linear relations cannot be recommended. The volatilities of 3-ethoxy-4-hydroxybenzaldehyde at infinite dilution, K_1^∞, were given in Table 2.

The activity coefficients of 3-ethoxy-4-hydroxybenzaldehyde at infinite dilution γ_1^∞ were evaluated as follows

$$\gamma_1^\infty = \frac{P^0}{P_1}\cdot\frac{y_1}{x_1} = \frac{P^0}{P_1}K_1^\infty \qquad (1)$$

where, P^0, P_1, y, x, and K, respectively, denote the reference total pressure, vapor pressure, vapor mole fraction, liquid mole fraction, and volatility. The subscript 1 means 3-ethoxy-4-hydroxybenzaldehyde. The superscript ∞ denotes the infinite dilution. The infinite volatility of 3-ethoxy-4-hydroxybenzaldehyde at one atmospheric pressure was approximated as the one at the experimental atmospheric pressure.

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Table 2. Experimental Vapor−Liquid Equilibrium Data, Liquid-Phase (x_1) and Vapor-Phase (y_1) Mole Fraction, Volatility K_1, Equilibrium Temperature T, and Atmospheric Pressure P

x_1	y_1	$K_1(=y_1/x_1)$	T/K	P/kPa
3-Ethoxy-4-hydroxybenzaldehyde (1) + Ethanol (2)				
0.0053	0.0000085	0.0016	351.02	98.52
0.0123	0.0000190	0.0015	351.23	98.58
0.0194	0.0000292	0.0015	351.51	98.73
0.0274	0.0000424	0.0015	351.91	99.31
$K_1^\infty = 0.0015$	$\gamma_1^\infty = 0.63$			
3-Ethoxy-4-hydroxybenzaldehyde (1) + 1-Propanol (2)				
0.0087	0.0000185	0.0021	369.90	98.75
0.0105	0.0000225	0.0021	370.18	99.60
0.0147	0.0000310	0.0021	370.15	98.97
0.0194	0.0000420	0.0022	370.24	98.78
$K_1^\infty = 0.0021$	$\gamma_1^\infty = 0.38$			
3-Ethoxy-4-hydroxybenzaldehyde (1) + 2-Propanol (2)				
0.0056	0.0000096	0.0017	354.99	98.83
0.0112	0.0000175	0.0016	355.59	100.50
0.0165	0.0000269	0.0016	355.50	99.53
0.0220	0.0000356	0.0016	355.82	100.25
$K_1^\infty = 0.0016$	$\gamma_1^\infty = 0.56$			
3-Ethoxy-4-hydroxybenzaldehyde (1) + 1-Butanol (2)				
0.0047	0.0000203	0.0043	390.51	99.55
0.0088	0.0000398	0.0045	390.36	98.52
0.0129	0.0000615	0.0048	390.60	98.82
0.0178	0.0000801	0.0045	390.78	99.04
$K_1^\infty = 0.0045$	$\gamma_1^\infty = 0.36$			

The vapor pressures of 3-ethoxy-4-hydroxybenzaldehyde, P_1, were calculated by applying the following Clausius−Clapeyron equation and the Trouton rule.

$$\ln P_1 = \ln P^0 - \frac{\Delta H_1}{R}\left(\frac{1}{T} - \frac{1}{T_1^0}\right) \tag{2}$$

$$\Delta H_1 = T_1^0 \Delta S^0 \qquad \Delta S^0 = 85\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} \tag{3}$$

$$P^0 = 1.01325{\cdot}10^5\ \mathrm{Pa} \qquad R = 8.314472\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} \tag{4}$$

where, P^0, ΔH, ΔS, R, and T, respectively, denote the reference total pressure, heat of vaporization, entropy of vaporization, gas constant, and temperature. The superscript 0 means the reference condition of one atmosphere. The normal boiling point, T_1^0, of 3-ethoxy-4-hydroxybenzaldehyde was obtained from the literature[10] as follows

$$T_1^0 = 558\ \mathrm{K} \tag{5}$$

The activity coefficients of 3-ethoxy-4-hydroxybenzaldehyde at infinite dilution, γ_1^∞, were evaluated as shown in Table 2, giving less than unity.

Conclusions

The vapor−liquid equilibrium behaviors of 3-ethoxy-4-hydroxybenzaldehyde in ethanol, 1-propanol, 2-propanol, and 1-butanol were measured at atmospheric pressure in the dilute composition range of 3-ethoxy-4-hydroxybenzaldehyde. It seems that the alcohols and 3-ethoxy-4-hydroxybenzaldehyde molecules were associated with each other because the activity coefficients of 3-ethoxy-4-hydroxybenzaldehyde at infinite dilution were less than unity.

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