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Short Articles

Vapor−Liquid Equilibrium Behaviors of Vanillin in 1-Butanol, 2-Butanol, and 2-Methyl-1-propanol

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Vapor−liquid equilibrium behaviors of vanillin in 1-butanol, 2-butanol, and 2-methyl-1-propanol were measured at atmospheric pressure in the dilute composition range of vanillin with a recirculation still. Equilibrium compositions were determined with an ultraviolet spectrometer. The activity coefficients of vanillin at infinite dilution were less than unity.

Introduction

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

In the present study, the vapor−liquid equilibrium behaviors of vanillin in 1-butanol, 2-butanol, and 2-methyl-1-propanol were measured at atmospheric pressure in the dilute composition range of vanillin. Vanillin is the typical scent component in the food industry.

Experimental Section

Chemicals. Vanillin was supplied by Wako Pure Chemical Industries, Ltd. with a guarantee of 98 mol % purity. Vanillin is solid at room temperature. Special grade reagents of 1-butanol, 2-butanol, and 2-methyl-1-propanol 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 1-butanol, 2-butanol, and 2-methyl-1-propanol 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.[1−6] 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 the 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 vanillin at 309 nm. The uncertainties of liquid and vapor compositions, respectively, seem to be $\pm\ 1 \cdot 10^{-4}$ and $\pm\ 1 \cdot 10^{-6}$ mole fraction of vanillin.

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

material	T_b/K exptl	T_b/K lit.[a]	ρ(298.15 K)/(kg·m^{-3}) exptl	ρ(298.15 K)/(kg·m^{-3}) lit.[b]
1-butanol	390.846	390.876	805.8	806.0
2-butanol	372.614	372.650	802.4	802.3
2-methyl-1-propanol	380.922	381.040	797.8	797.8

[a] Timmermans.[7] [b] TRC Thermodynamic Tables Non-Hydrocarbons.[8]

Table 2. Experimental Vapor−Liquid Equilibrium Data for 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
Vanillin (1) + 1-Butanol (2)				
0.0055	0.000033	0.0060	390.10	98.47
0.0106	0.000059	0.0056	390.55	99.21
0.0174	0.000085	0.0049	390.45	98.39
0.0198	0.000100	0.0051	390.53	98.32
$K_1^\infty = 0.0054$, $\gamma_1^\infty = 0.43$				
Vanillin (1) + 2-Butanol (2)				
0.0057	0.000020	0.0035	372.30	99.28
0.0084	0.000029	0.0035	372.39	99.30
0.0117	0.000039	0.0033	372.41	99.06
0.0169	0.000056	0.0033	372.27	97.97
$K_1^\infty = 0.0034$, $\gamma_1^\infty = 0.55$				
Vanillin (1) + 2-Methyl-1-propanol (2)				
0.0078	0.000029	0.0037	380.31	97.91
0.0105	0.000041	0.0039	380.36	97.88
0.0162	0.000063	0.0039	380.70	98.27
0.0218	0.000087	0.0040	380.75	97.97
$K_1^\infty = 0.0039$, $\gamma_1^\infty = 0.45$				

Results and Discussion

Table 2 gives the experimental results for the vapor−liquid equilibrium measurements at atmospheric pressure in the dilute composition range of vanillin in 1-butanol, 2-butanol, and 2-methyl-1-propanol. The experimental pressures were ap-

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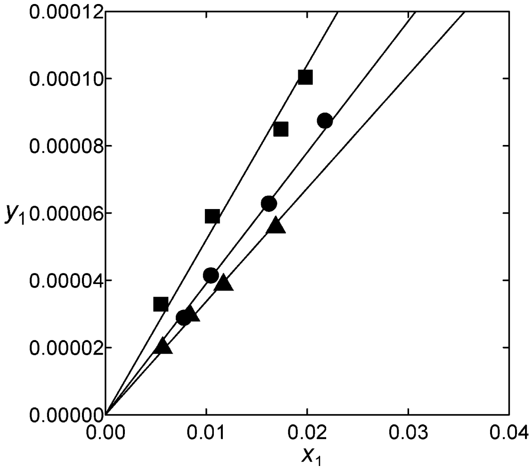

Figure 1. Vapor−liquid equilibrium behaviors of vanillin in 1-butanol, 2-butanol, and 2-methyl-1-propanol at atmospheric pressure: ■, vanillin (1) + 1-butanol (2); ▲, vanillin (1) + 2-butanol (2); ●, vanillin (1) + 2-methyl-1-propanol (2).

proximately 99 kPa as shown in Table 2. The volatility, K_1, is the ratio of vapor composition and liquid composition of the solid component, vanillin. Figure 1 shows the equilibrium vapor and liquid composition diagram at atmospheric pressure in the dilute composition range of vanillin, giving linear relations for the three systems. The extrapolation of the linear relations cannot be recommended. Volatilities of vanillin at infinite dilution in alcohols were given in Table 2.

The activity coefficients of solid component γ_1 were evaluated as follows

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

where π, P, y, x, and K, respectively, denote the total pressure, vapor pressure, vapor mole fraction, liquid mole fraction, and volatility. The subscript 1 means solid component. The superscript ∞ denotes the infinite dilution. The infinite volatility of the solid component at one atmospheric pressure, K_1^{∞}, was approximated as the one at the experimental atmospheric pressure.

The vapor pressure of the solid component, P_1, was calculated by applying the following Clausius−Clapeyron equation and the Trouton rule.

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

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

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

where P^0, ΔH, ΔS, R, and T, respectively, denote the reference 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 vanillin was obtained from the literature[9] as follows

$$T_1^{\,0} = 558\ \mathrm{K} \qquad (5)$$

The activity coefficients at infinite dilution of vanillin in 1-butanol, 2-butanol, and 2-methyl-1-propanol were consequently evaluated as shown in Table 2, giving almost less than unity similarly to the previous study.[6]

Conclusions

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

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