Vapor−Liquid Equilibrium Behaviors of Coumarin and Vanillin in Ethanol, 1-Propanol, and 2-Propanol

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(Vapor + liquid) equilibrium of scent components, coumarin (1-benzopyran-2-one, CAS Registry No. 91-64-5) and vanillin (4-hydroxy-3-methoxybenzaldehyde, CAS Registry No. 121-33-5), in alcohols, ethanol, 1-propanol, and 2-propanol were measured at atmospheric pressure in the dilute composition range of solid components with a recirculation still. Equilibrium compositions were determined with an ultraviolet spectrometer. The activity coefficients of coumarin at infinite dilution in alcohol were almost unity. The activity coefficients at infinite dilution of vanillin in alcohol were less than unity.

Introduction

In the previous studies,[1−4] vapor−liquid equilibrium measurements were performed for mixtures containing solid components, ferrocene,[1] 1,4-dihydroxybenzene,[2] durene,[3] and tolan[4] in alcohol at atmospheric pressure. In the present study, the (vapor + liquid) equilibria of coumarin (1-benzopyran-2-one, CAS Registry No. (CASRN) 91-64-5) + ethanol, coumarin + 1-propanol, coumarin + 2-propanol, vanillin (4-hydroxy-3-methoxybenzaldehyde, CASRN 121-33-5) + ethanol, vanillin + 1-propanol, and vanillin + 2-propanol were measured at atmospheric pressure in the dilute composition range of solid components. Coumarin and vanillin are used in the food industry.

Experimental Section

Chemicals. Coumarin was supplied by Tokyo Kasei Chemical Industries, Ltd. with a stated purity of at least 99 mol %. Vanillin was supplied by Wako Pure Chemical Industries, Ltd. with a stated purity of better than 98 mol %. Coumarin and vanillin are solids at room temperature. Special grade reagents of ethanol, 1-propanol, and 2-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 ethanol, 1-propanol, and 2-propanol were found by gas chromatographic area analysis to be greater than 99.9 mol %.

Apparatus and Procedures. The experimental apparatus and procedures are almost the same as those described previously.[1−5] The experimental apparatus is shown schematically in Figure 1. The recirculation still is entirely constructed from borosilicate glass. The main parts are a boiling still (B), two condensers (C), two cocks (K), an overflow tube (O), a condensate chamber (S), and a thermometer (T). About 45 cm^3 of solution is required per measurement. At the start of the experiments, cocks K_1 and K_2 are closed. A prepared solution is charged to the boiling still (B) from the top of the condenser. The boiling vapor−liquid mixture flashes to the thermometer well in the boiling still. The vapor is condensed and introduced to the condensate chamber (S). The condensed vapor in the condensed chamber (S) recirculates to the boiling still (B) through the overflow tube (O). After attainment of steady state, equilibrium temperature was measured with an accuracy of ± 0.01 K, using a Hewlett-Packard 2804A quartz thermometer, calibrated at the triple point of water in a reference cell. Atmospheric pressure was measured with a Fortin barometer with an accuracy of ± 0.01 kPa. Samples of both the liquid and vapor phases were taken individually from cocks K_1 and K_2, respectively. The equilibrium

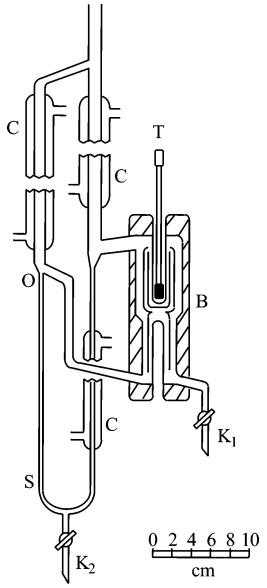

Figure 1. Experimental apparatus for measuring isobaric vapor−liquid equilibria: B, boiling still; C, condenser; K, cock; O, overflow tube; S, condensate chamber; T, quartz thermometer.

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	351.46	351.475	785.1	785.09
1-propanol	370.21	370.30	799.6	799.75
2-propanol	355.39	355.44	780.8	781.26

[a] Ref 6. [b] Ref 7.

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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
Coumarin (1) + Ethanol (2)				
0.0202	0.000038	0.0019	351.54	98.25
0.0321	0.000063	0.0020	351.66	97.09
0.0391	0.000076	0.0020	351.89	98.15
0.0503	0.000100	0.0020	351.84	97.13
$K_1^\infty = 0.0020$, $\gamma_1^\infty = 1.17$				
Coumarin (1) + 1-Propanol (2)				
0.0108	0.000045	0.0042	370.30	99.06
0.0166	0.000068	0.0041	370.49	99.21
0.0218	0.000091	0.0042	370.65	99.39
0.0257	0.000108	0.0042	370.63	98.65
$K_1^\infty = 0.0042$, $\gamma_1^\infty = 1.07$				
Coumarin (1) + 2-Propanol (2)				
0.0171	0.000039	0.0023	355.72	99.40
0.0226	0.000057	0.0025	355.70	98.80
0.0281	0.000065	0.0023	355.85	98.91
0.0324	0.000077	0.0024	356.14	99.60
$K_1^\infty = 0.0024$, $\gamma_1^\infty = 1.21$				
Vanillin (1) + Ethanol (2)				
0.0097	0.000013	0.0013	351.21	99.13
0.0179	0.000022	0.0013	351.62	99.46
0.0265	0.000033	0.0012	352.16	99.73
0.0357	0.000046	0.0013	352.25	98.98
$K_1^\infty = 0.0013$, $\gamma_1^\infty = 0.52$				
Vanillin (1) + 1-Propanol (2)				
0.0109	0.000025	0.0023	369.79	97.15
0.0199	0.000048	0.0024	370.38	98.47
0.0262	0.000068	0.0026	370.48	98.14
0.0298	0.000075	0.0025	370.09	96.61
$K_1^\infty = 0.0025$, $\gamma_1^\infty = 0.44$				
Vanillin (1) + 2-Propanol (2)				
0.0062	0.000009	0.0015	355.44	99.61
0.0102	0.000016	0.0015	354.92	98.10
0.0171	0.000028	0.0016	355.90	99.34
0.0196	0.000031	0.0016	356.22	98.84
$K_1^\infty = 0.0016$, $\gamma_1^\infty = 0.54$				

vapor and liquid compositions were determined with a JASCO V-560DS ultraviolet spectrophotometer for coumarin at wavelength of 274 nm and for vanillin at a wavelength 309 nm. The uncertainty with which the solid component was determined in the liquid and vapor compositions were $\pm 1 \times 10^{-4}$ and $\pm 1 \times 10^{-6}$ mole fraction, respectively.

Results

Table 2 lists the results obtained for the (vapor + liquid) equilibrium measurements at atmospheric pressure in the dilute composition range of coumarin and vanillin in ethanol, 1-propanol, and 2-propanol. 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 solid components, coumarin and vanillin. Figures 2 and 3, respectively, show the equilibrium vapor and liquid composition diagrams at atmospheric pressure in the dilute composition range of coumarin and vanillin, giving linear relations for the six systems. The extrapolation of the linear relations cannot be recommended. Volatilities of coumarin and vanillin at infinite dilution in ethanol, 1-propanpl, and 2-propanpl are listed in Table 2.

The activity coefficients of solid component γ_1 were evaluated as follows:

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

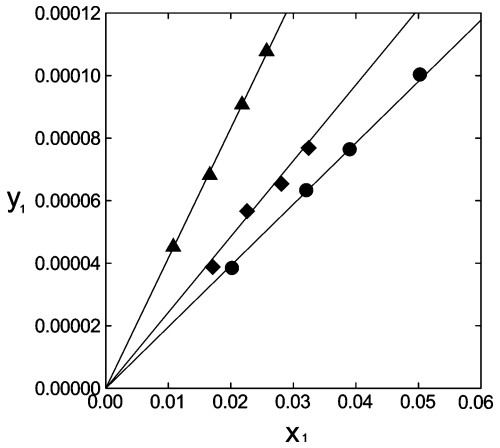

Figure 2. Vapor−liquid equilibrium behavior of coumarin in alcohol at atmospheric pressure: ●, coumarin (1) + ethanol (2); ▲, coumarin (1) + 1-propanol (2); ◆, coumarin (1) + 2-propanol (2).

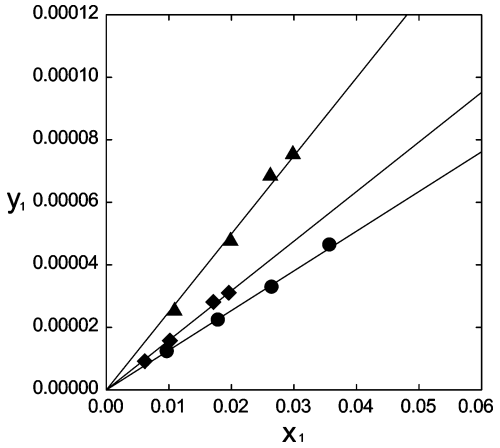

Figure 3. Vapor−liquid equilibrium behavior of vanillin in alcohol at atmospheric pressure: ●, vanillin (1) + ethanol (2); ▲, vanillin (1) + 1-propanol (2); ◆, vanillin (1) + 2-propanol (2).

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

The vapor pressures of solid component P_1 were calculated by applying the following Clausius−Clapeyron equation and the Trouton's rule:

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

where $P^0 = 1.01325 \times 10^5$ Pa is the reference pressure; $\Delta H_1 = T_1^0 \Delta S^0$ is the enthalpy of vaporization for which $\Delta S^0 = 85$ J·K^{-1}·mol^{-1}, the entropy of evaporation; the gas constant $R = 8.314472$ J·K^{-1}·mol^{-1}; and T is the temperature. The superscript 0 indicates the reference condition of 1 atm.

The normal boiling point T_1^0 of coumarin and vanillin were obtained from the literature[8] as $T_1^0 = 571$ K for coumarin and $T_1^0 = 558$ K for vanillin. The activity coefficients at infinite dilution of coumarin and vanillin in ethanol, 1-propanol, and 2-propanol were consequently evaluated as shown in Table 2, giving almost unity for coumarin and less than unity for vanillin.

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