Vapor–Liquid Equilibrium Behaviors of 5-Methyl-2-(1-methylethyl)phenol in Alcohol

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Vapor–liquid equilibrium behaviors of scent solid, 5-methyl-2-(1-methylethyl)phenol, in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, or 2-methyl-1-propanol were measured at atmospheric pressure in the dilute composition range of 5-methyl-2-(1-methylethyl)phenol with a recirculation still. Equilibrium compositions were determined with an ultraviolet spectrometer. The activity coefficients of 5-methyl-2-(1-methylethyl)phenol at infinite dilution in alcohol were less than unity.

Introduction

In the previous studies,[1–7] 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] and vanillin[7] in alcohol or water at atmospheric pressure. The authors[8] have recently reported the vapor–liquid equilibrium behaviors of 3-ethoxy-4-hydroxybenzene in ethanol, 1-propanol, 2-propanol, and 1-butanol at atmospheric pressure.

In the present study, the vapor–liquid equilibrium behaviors of 5-methyl-2-(1-methylethyl)phenol in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol were measured at atmospheric pressure in the dilute composition range of 5-methyl-2-(1-methylethyl)phenol. 5-Methyl-2-(1-methylethyl)phenol is a preservative and disinfectant with aromatic and stimulation which is widely used as drug raw materials, dental medicine, gargle, and tooth powder.

Experimental

Chemicals. 5-Methyl-2-(1-methylethyl)phenol (thymol, CAS Registry No. 89-83-8) was supplied by Wako Pure Chemical Industries, Ltd., with a guarantee of 98 mol % purity. 5-Methyl-2-(1-methylethyl)phenol is solid at room temperature. Special grade reagents of alcohol, methanol, ethanol, 1-propanol, 2-propanol, 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 alcohols, methanol, ethanol, 1-propanol, 2-propanol, 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.[1–8] 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 5-methyl-2-(1-methylethyl)phenol at 276 nm. The uncertainties of liquid and vapor compositions, respectively, seem to be ($\pm 1 \cdot 10^{-4}$ and $\pm 5 \cdot 10^{-7}$) mole fraction of 5-methyl-2-(1-methylethyl)phenol.

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]
methanol	337.64	337.651	786.6	786.64
ethanol	351.46	351.475	785.2	785.09
1-propanol	370.21	370.35	799.6	799.75
2-propanol	355.40	355.410	780.8	781.26
1-butanol	390.81	390.85	805.7	806.0
2-butanol	372.63	372.65	802.3	802.3
2-methyl-1-propanol	380.92	381.040	797.8	797.8

[a] Timmermans.[9] [b] TRC Thermodynamic Tables Non-Hydrocarbons.[10]

Results and Discussion

Table 2 gives the experimental results for the vapor–liquid equilibrium measurements at atmospheric pressure in the dilute composition range of 5-methyl-2-(1-methylethyl)phenol in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-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 5-methyl-2-(1-methylethyl)phenol. The volatilities of 5-methyl-2-(1-methylethyl)phenol at infinite dilution, K_1^∞, were given in Table 2.

The activity coefficients of 5-methyl-2-(1-methylethyl)phenol at infinite dilution γ_1^∞ were evaluated as follows

$$\gamma_1^\infty = \frac{P^0}{P_1}\left(\frac{y_1}{x_1}\right)_{x_1 \to 0} = \frac{P^0}{P_1}K_1^\infty \quad (1)$$

where P^0, P_1, y, x, and K, respectively, denote the reference total pressure, vapor pressure, vapor mole fraction, liquid mole

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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
5-methyl-2-(1-methylethyl)phenol (1) + methanol (2)				
0.0118	0.0000161	0.0014	337.07	98.24
0.0242	0.0000313	0.0013	337.50	98.14
0.0392	0.0000555	0.0014	337.71	98.29
0.0491	0.0000698	0.0014	338.03	98.69
0.0626	0.0000834	0.0013	338.44	98.91
$K_1^\infty = 0.0014$, $\gamma_1^\infty = 0.28$				
5-methyl-2-(1-methylethyl)phenol (1) + ethanol (2)				
0.0054	0.0000169	0.0031	350.90	99.20
0.0125	0.0000324	0.0026	350.76	98.02
0.0178	0.0000449	0.0025	351.24	99.26
0.0247	0.0000652	0.0026	351.20	98.46
0.0337	0.0000874	0.0026	351.77	99.51
$K_1^\infty = 0.0027$, $\gamma_1^\infty = 0.29$				
5-methyl-2-(1-methylethyl)phenol (1) + 1-propanol (2)				
0.0058	0.0000270	0.0047	369.49	98.96
0.0120	0.0000568	0.0047	369.46	98.17
0.0259	0.0001147	0.0044	369.88	98.11
0.0329	0.0001364	0.0041	370.49	99.65
0.0453	0.0002005	0.0044	370.42	97.98
$K_1^\infty = 0.0045$, $\gamma_1^\infty = 0.22$				
5-methyl-2-(1-methylethyl)phenol (1) + 2-propanol (2)				
0.0058	0.0000134	0.0023	354.61	98.28
0.0125	0.0000310	0.0025	354.83	98.32
0.0174	0.0000411	0.0024	354.97	98.44
0.0223	0.0000523	0.0023	355.14	98.48
0.0293	0.0000724	0.0025	355.33	98.28
$K_1^\infty = 0.0024$, $\gamma_1^\infty = 0.22$				
5-methyl-2-(1-methylethyl)phenol (1) + 1-butanol (2)				
0.0058	0.0000479	0.0082	389.98	99.11
0.0114	0.0000981	0.0086	389.95	98.72
0.0223	0.0001929	0.0087	390.52	99.24
0.0326	0.0003200	0.0098	390.68	98.60
0.0438	0.0004108	0.0094	391.26	99.30
$K_1^\infty = 0.0089$, $\gamma_1^\infty = 0.21$				
5-methyl-2-(1-methylethyl)phenol (1) + 2-butanol (2)				
0.0065	0.0000264	0.0041	371.59	97.52
0.0114	0.0000448	0.0039	371.76	97.77
0.0219	0.0000864	0.0040	372.07	97.66
0.0320	0.0001303	0.0041	372.52	97.93
0.0409	0.0001684	0.0041	372.92	98.43
$K_1^\infty = 0.0040$, $\gamma_1^\infty = 0.18$				
5-methyl-2-(1-methylethyl)phenol (1) + 2-methyl-1-propanol (2)				
0.0058	0.0000389	0.0067	380.16	98.75
0.0114	0.0000844	0.0074	380.25	98.33
0.0171	0.0001173	0.0069	380.47	97.85
0.0227	0.0001588	0.0070	380.35	97.52
0.0348	0.0002478	0.0071	380.96	98.42
$K_1^\infty = 0.0070$, $\gamma_1^\infty = 0.23$				

fraction, and volatility. The subscript 1 means 5-methyl-2-(1-methylethyl)phenol. The superscript ∞ denotes the infinite dilution. The infinite volatility of 5-methyl-2-(1-methylethyl)phenol at one atmospheric pressure was approximated as the one at the experimental atmospheric pressure.

The vapor pressures of 5-methyl-2-(1-methylethyl)phenol, P_1, were calculated by applying the following Clausius−Clapeyron equation and Kistiakowski's rule.[11]

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

$$\Delta H_1 = T_1^0 \Delta S^0,\ \Delta S^0 = 4.4R + R \ln T_1^0 = 88.4\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \quad (3)$$

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

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 5-methyl-2-(1-methylethyl)phenol was obtained from the literature[12] as follows

$$T_1^0 = 506\ \mathrm{K} \quad (5)$$

The activity coefficients of 5-methyl-2-(1-methylethyl)phenol at infinite dilution, γ_1^∞, were evaluated as shown in Table 2, giving less than unity.

Conclusions

The vapor–liquid equilibrium behaviors of 5-methyl-2-(1-methylethyl)phenol in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol were measured at atmospheric pressure in the dilute composition range of 5-methyl-2-(1-methylethyl)phenol. It seems that the alcohols and 5-methyl-2-(1-methylethyl)phenol molecules were associated with each other because the activity coefficients of 5-methyl-2-(1-methylethyl)phenol at infinite dilution were less than unity.

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