Vapor−Liquid Equilibrium of 1,4-Dihydroxybenzene in Methanol or Ethanol

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The vapor−liquid equilibrium behavior of 1,4-dihydroxybenzene in methanol or ethanol was measured at atmospheric pressure in the dilute composition range of 1,4-dihydroxybenzene with a recirculation still. Equilibrium compositions were determined with an ultraviolet spectrometer. The reliabilities of liquid and vapor compositions were $\pm 1 \times 10^{-6}$ and $\pm 1 \times 10^{-7}$ mole fraction of 1,4-dihydroxybenzene, respectively. The accuracies of temperature and pressure are ±0.01 K and ±0.01 kPa, respectively. The volatilities of 1,4-dihydroxybenzene at infinite dilution were determined to be 0.0013 and 0.0007 in methanol and ethanol, respectively.

Introduction

In the previous study of Kodama et al.,[1] vapor−liquid equilibrium measurements were made for mixtures including ferrocene + methanol and ferrocene + ethanol at atmospheric pressure.

In the present study, the vapor−liquid equilibrium behavior of 1,4-dihydroxybenzene in methanol or ethanol was measured at atmospheric pressure in the dilute composition range of 1,4-dihydroxybenzene. 1,4-Dihydroxybenzene (hydroquinone) is practically used as a polymerization inhibitor and assistant developer.

Experimental Section

Chemicals. 1,4-Dihydroxybenzene was supplied by Tokyo Chemical Industry Co., Ltd. with a guaranteed 99% purity or better. Special grade reagents of methanol and ethanol were supplied by Wako Pure Chemical Industries, Ltd. and were used without further purification. The physical properties of methanol and ethanol used in this work are listed in Table 1.

Apparatus and Procedures. The experimental apparatus and procedures are almost the same as those described previously.[1,4] The recirculation still is entirely constructed from borosilicate glass. The amount of solution required is about 45 cm^3 per determination. The experimental atmospheric pressure was measured with a Fortin barometer with an accuracy of ±0.01 kPa. The equilibrium temperature was measured with a Hewlett-Packard 2804 A quartz thermometer, calibrated at the triple point of water in a reference cell, with an accuracy of ±0.01 K. The equilibrium vapor and liquid compositions were determined with a Shimadzu UV265FS ultraviolet spectrophotometer at 295 nm. The reliabilities of liquid and vapor compositions seem to be $\pm 1 \times 10^{-6}$ and $\pm 1 \times 10^{-7}$ mole fraction of 1,4-dihydroxybenzene, respectively. Linear relations were experimentally observed between the absorbance and composition in the dilute range of 1,4-dihydroxybenzene.

Results

Table 2 gives the vapor−liquid equilibrium measurements obtained at atmospheric pressure in the dilute composition range of 1,4-dihydroxybenzene in methanol or ethanol. The volatility K_1 of 1,4-dihydroxybenzene is the ratio of vapor composition and liquid composition of 1,4-dihydroxybenzene. Figure 1 shows the equilibrium vapor and liquid composition diagram at atmospheric pressure in the dilute composition range of 1,4-dihydroxybenzene, giving linear relations for both systems. The linearity is only true within the range of the present experimental values. The extrapolation of the linear relations cannot be recommended. The volatilities of 1,4-dihydroxybenzene at infinite dilution were determined to be 0.0013 and 0.0007 in methanol and ethanol, respectively.

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

	T_b/K		ρ(298.15 K)/(kg·m^{-3})		n_D(298.15 K)	
material	exptl	lit.[a]	exptl	lit.[b]	exptl	lit.[b]
methanol	337.67	337.651	786.6	786.64	1.3266	1.326 52
ethanol	351.48	351.475	785.2	785.09	1.3596	1.359 41

[a] Timmermans.[2] [b] *TRC Thermodynamic Tables—Non-Hydrocarbons.*[3]

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
1,4-Dihydroxybenzene (1) + Methanol (2)				
0.001 379	0.000 001 8	0.0013	336.74	98.38
0.002 039	0.000 002 8	0.0014	337.11	99.66
0.002 345	0.000 003 1	0.0013	336.76	98.28
0.002 901	0.000 003 9	0.0013	336.63	97.58
0.004 349	0.000 006 0	0.0014	336.99	98.92
1,4-Dihydroxybenzene (1) + Ethanol (2)				
0.001 334	0.000 001 0	0.0007	350.53	98.85
0.001 926	0.000 001 4	0.0007	350.53	98.86
0.002 334	0.000 001 6	0.0007	350.54	98.85
0.002 648	0.000 001 7	0.0007	350.56	98.90
0.004 233	0.000 002 8	0.0007	350.59	98.78

Conclusion

The vapor−liquid equilibrium behavior of 1,4-dihydroxybenzene in methanol or ethanol was measured at atmo-

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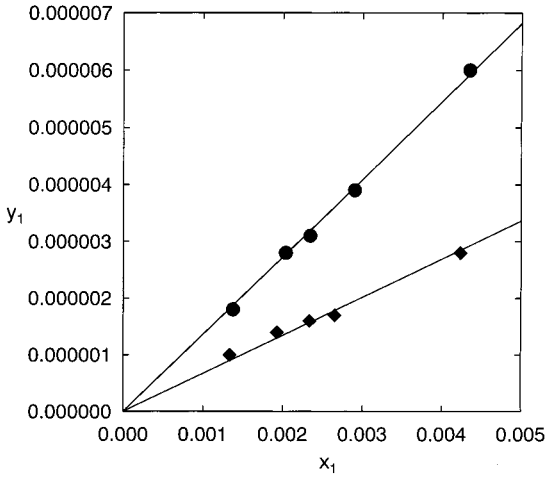

Figure 1. Experimental vapor−liquid equilibrium composition diagram at atmospheric pressure: ●, 1,4-dihydroxybenzene (1) + methanol (2); ◆, 1,4-dihydroxybenzene (1) + ethanol (2).

spheric pressure in the dilute composition range of 1,4-dihydroxybenzene with a recirculation still. The boiling point of methanol is lower than that of ethanol. The vapor pressure of 1,4-dihydroxybenzene in methanol is therefore lower than that in ethanol. A higher volatility was however observed in methanol than in ethanol. The reason is that the infinite dilution activity coefficient of 1,4-dihydroxybenzene in methanol is much higher than that in ethanol. The actual values of the activity coefficients at infinite dilution, however, could not be calculated because the vapor pressure of 1,4-dihydroxybenzene was not available in the literature.

Acknowledgment

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