Vapor−Liquid Equilibrium of Ferrocene in Methanol or Ethanol

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The vapor−liquid equilibrium behavior of ferrocene in methanol or ethanol was measured at atmospheric pressure in the dilute composition range of ferrocene with a recirculation still. Equilibrium compositions were determined with an ultraviolet spectrometer having an accuracy of ±0.000 001 mole fraction of ferrocene. The accuracies of temperature and pressure are ±0.01 K and ±0.01 kPa, respectively. The volatilities of ferrocene at infinite dilution were determined to be 0.032 and 0.036 in methanol and ethanol, respectively.

Introduction

The chemical properties of complexes are now attractive as catalysts in chemical industries. For the development of chemical processes which involve complexes, vapor−liquid equilibrium behavior of solutions containing complexes is required. However, phase equilibrium data of complexes are not available. Ferrocene is a typical complex. In the present study, the vapor−liquid equilibrium behavior of ferrocene in methanol or ethanol was measured at atmospheric pressure in the dilute composition range of ferrocene.

Experimental Section

Chemicals. Ferrocene was supplied by Wako Pure Chemical Co., Ltd., with a guaranteed 98% purity at least. Special grade reagents of methanol and ethanol were supplied by Wako Pure Chemical Co., Ltd., and were used without further purification. The physical properties of the methanol and ethanol used are listed in Table 1.

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

	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 (1950). [b] *TRC Thermodynamic Tables-Non-Hydrocarbons* (1996).

Apparatus and Procedures. The experimental apparatus and procedures are almost the same as those described previously by Tanaka et al. (1992). 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 2804A 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 Shimazu UV265FS ultraviolet spectrophotometer at 440 nm with an accuracy of ±0.000 001 mole fraction of ferrocene. Linear relations were experimentally observed between the absorbance and composition in the dilute range of ferrocene.

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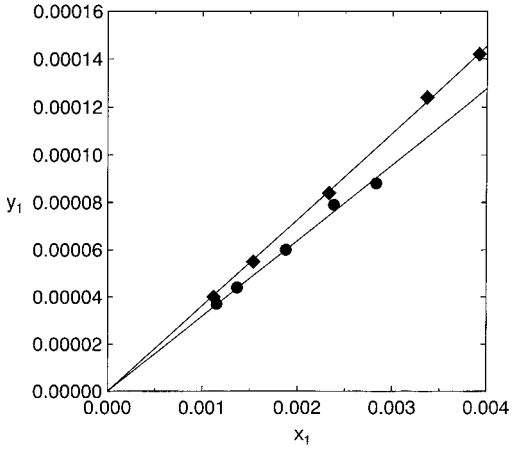

Figure 1. Experimental vapor−liquid equilibrium composition diagram at atmospheric pressure: (●) ferrocene (1) + methanol (2); (◆) ferrocene (1) + ethanol (2).

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
Ferrocene (1) + Methanol (2)				
0.001 154	0.000 037	0.032	337.00	98.91
0.001 370	0.000 044	0.032	336.98	98.82
0.001 880	0.000 060	0.032	336.99	98.78
0.002 385	0.000 079	0.033	336.98	98.70
0.002 833	0.000 088	0.031	336.98	98.68
Ferrocene (1) + Ethanol (2)				
0.001 121	0.000 040	0.036	350.50	97.99
0.001 539	0.000 055	0.036	350.49	97.92
0.002 333	0.000 084	0.036	350.50	97.86
0.003 363	0.000 124	0.037	350.73	98.69
0.003 917	0.000 142	0.036	350.56	97.92

Results

Table 2 gives the experimental vapor−liquid equilibrium data obtained at atmospheric pressure in the dilute com-

10.1021/je990050n CCC: $18.00
Published on Web 10/01/1999

position range of ferrocene in methanol or ethanol. The volatility K_1 of ferrocene is the ratio of the vapor composition and the liquid composition of ferrocene. Figure 1 shows the equilibrium vapor and liquid composition diagram at atmospheric pressure in the dilute composition range of ferrocene, 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 ferrocene at infinite dilution were determined to be 0.032 and 0.036 in methanol and ethanol, respectively.

Conclusion

The vapor−liquid equilibrium behavior of ferrocene in methanol or ethanol was measured at atmospheric pressure in the dilute composition range of ferrocene with the recirculation still. Significantly, large values of the volatilities of ferrocene were observed in methanol or ethanol.

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Received for review February 12, 1999. Accepted July 15, 1999. A research grant of the College of Engineering, Nihon University, was given to D.K.

JE990050N