Vapor−Liquid Equilibrium Behavior of Tolan in Alcohol

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The vapor−liquid equilibrium behavior of tolan in alcohol was measured at atmospheric pressure in the dilute composition range of tolan with a recirculation still. Equilibrium compositions were determined with an ultraviolet spectrometer. The reliabilities of the compositions in the liquid and vapor seem to be $\pm 2 \times 10^{-5}$ and $\pm 2 \times 10^{-7}$ mole fraction of tolan, respectively. The accuracies of temperature and pressure are ±0.01 K and ±0.01 kPa, respectively. The volatilities $K_i = y_i/x_i$ of tolan at infinite dilution were determined to be 0.0033, 0.0029, 0.0031, and 0.0054 in methanol, ethanol, 2-propanol, and 1-propanol, respectively.

Introduction

In the previous studies,[1−3] vapor−liquid equilibrium measurements were made for mixtures containing solid components (ferrocene,[1] 1,4-dihydroxybenzene,[2] and durene[3]) in methanol or ethanol at atmospheric pressure.

In the present study, the vapor−liquid equilibrium behavior of diphenylacetylene (tolan) in methanol, ethanol, 2-propanol, and 1-propanol was measured at atmospheric pressure in the dilute composition range of tolan. Liquid-crystalline tolans are now attractive in information technology (e.g., supertwisted nematic liquid-crystal displays for computers[4]).

Experimental Section

Chemicals. Tolan was supplied by Tokyo Kasei Chemical Industries, Ltd. with a guarantee of 99 mol % purity. Tolan is a solid at room temperature. Special-grade reagents of alcohols, including methanol, ethanol, 2-propanol, and 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 the alcohols (methanol, ethanol, 2-propanol, and 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 almost the same as those described previously.[1−3,5] 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 Jasco V-560DS ultraviolet spectrophotometer at 278 nm. The reliabilities of the liquid and vapor compositions seem to be $\pm 2 \times 10^{-5}$ and $\pm 2 \times 10^{-7}$ mole fraction of tolan, respectively.

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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	337.67	337.651	786.5	786.64
ethanol	351.46	351.475	785.1	785.09
2-propanol	355.41	355.44	780.8	781.26
1-propanol	370.19	370.30	799.5	799.75

[a] Timmermans.[6] [b] *TRC Thermodynamic Tables. Non-Hydrocarbons*.[7]

Table 2. Experimental Vapor−Liquid Equilibrium Data, Liquid-Phase (x_1) and Vapor-Phase (y_1) Mole Fractions, Volatility K_1, Equilibrium Temperature T, and Atmospheric Pressure P

x_1	y_1	$K_1(=y_1/x_1)$	T/K	P/kPa
Tolan (1) + Methanol (2)				
0.00044	0.0000016	0.0036	336.86	98.53
0.00109	0.0000033	0.0030	336.76	98.05
Tolan (1) + Ethanol (2)				
0.00056	0.0000015	0.0027	350.28	97.20
0.00094	0.0000029	0.0031	350.47	97.85
Tolan (1) + 2-Propanol (2)				
0.00113	0.0000034	0.0030	354.50	98.25
0.00169	0.0000054	0.0032	354.59	98.59
Tolan (1) + 1-Propanol (2)				
0.00054	0.0000031	0.0057	369.37	98.83
0.00118	0.0000060	0.0051	369.41	98.79

Results

Table 2 gives the experimental results for the vapor−liquid equilibrium measurements at atmospheric pressure in the dilute composition range of tolan in methanol, ethanol, 2-propanol, and 1-propanol. The experimental pressures were approximately 98 kPa as shown in Table 2. The volatility K_1 of tolan is the ratio of the vapor composition to the liquid composition of tolan. Figure 1 shows the equilibrium vapor and liquid composition diagram at atmospheric pressure in the dilute composition range of tolan, giving linear relations for the four systems. The extrapolation of the linear relations cannot be recommended. The volatilities of tolan at infinite dilution were determined to be 0.0033, 0.0029, 0.0031, and 0.0054 in

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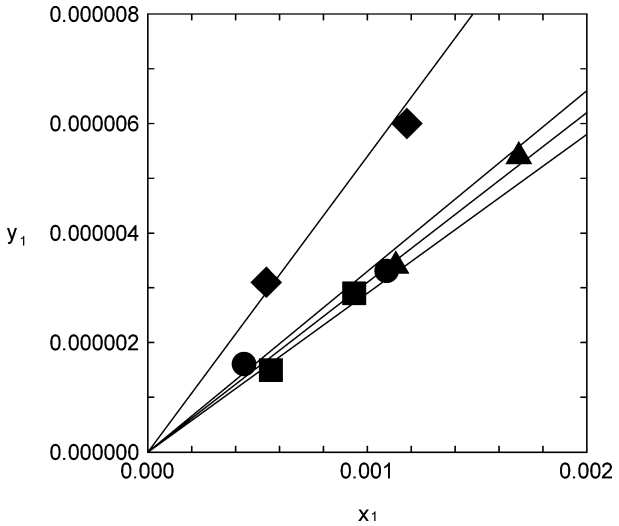

Figure 1. Experimental vapor−liquid equilibrium composition diagram at atmospheric pressure: −●−, tolan (1) + methanol (2); −■−, tolan (1) + ethanol (2); −▲−, tolan (1) + 2-propamol (2); and −◆−, tolan (1) + 1-propanol (2).

methanol, ethanol, 2-propanol, and 1-propanol, respectively.

The infinite activity coefficients of tolan γ_1^∞ were evaluated as follows:

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

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

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

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

$$\Delta H_1 = T_1^0 \Delta S^0 \qquad \Delta S^0 = 85 \text{ J/K mol} \qquad T_1^0 = 573 \text{ K} \quad (3)$$

$$P^0 = 1.01325 \times 10^5 \text{ Pa} \qquad R = 8.314472 \text{ J/K mol} \quad (4)$$

where P^0, ΔH, ΔS, R, and T denote the reference pressure, heat of vaporization, entropy of vaporization, gas constant, and temperature, respectively. The superscript 0 means the reference condition of 1 atm. The normal boiling point of tolan T_1^0 was obtained from the literature.[8]

The activity coefficients of tolan were consequently evaluated to be 4.2, 1.9, 1.6, and 1.5 in methanol, ethanol, 2-propanol, and 1-propanol, respectively.

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