Vapor–Liquid Equilibria of Acetonitrile–*sec*-Butyl Alcohol and Acetonitrile–*tert*-Butyl Alcohol

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Isobaric vapor–liquid equilibrium data for the systems acetonitrile–*sec*-butyl alcohol and acetonitrile–*tert*-butyl alcohol are measured and reported at 760 mmHg. Both the systems show positive deviations from Raoult's law and form minimum boiling azeotropes. Margules three suffix equations fit the data well and thermodyamic consistency is tested by the Herington method.

Vapor–liquid equilibrium data are useful for the design of distillation columns and other allied separation equipment and to understand the behavior of nonideal solutions. As no data are available on vapor–liquid equilibria of acetonitrile and butyl alcohols, isobaric vapor–liquid equilibrium data on acetonitrile with *sec*-butyl alcohol and *tert*-butyl alcohol are obtained at 760 mmHg pressure.

Experimental Section

Purity of Materials. Analytical grade reagents are used after further purification in a laboratory distillation column. Physical properties of the compounds are presented in Table I along with the literature values (*6*).

Apparatus and Procedure. A vapor recirculatory equilibrium still of Ward (*5*) is used in the equilibrium determinations. Temperatures are measured with a standard mercury-in-glass thermometer having an accuracy of 0.1 °C. Refractive index measurements are adopted to analyze vapor and liquid samples with the aid of a standard refractive index vs. composition plot, prepared earlier. An Abbé refractometer controlled at 30 ± 0.1 °C is used. The measurements are reproducible to within ±0.0005.

Results and Thermodynamic Analysis

The experimental results are given in Tables II and III. The liquid-phase activity coefficients are calculated by the expression

$$\ln y_i/x_i = \ln \frac{\gamma_i P_i^0}{\pi} - \frac{(V_i - \beta_i)(P_i^0 - \pi)}{RT} \qquad (1)$$

The second virial coefficients are estimated by the following Wohl's generalized relation (*7*)

$$\beta_i = \frac{RT_c}{P_c}\left(0.197 - 0.012\,T_r - \frac{0.4}{T_r} - \frac{0.146}{T_r^{3.27}}\right) \qquad (2)$$

The vapor pressure data are obtained from the Antoine equations given by Weissberger et al. (*6*) and Hala et al. (*1*). The molal liquid volumes are determined at the desired temperatures by the expansion factor method presented by Hala et al. (*2*).

Figures 1 and 2 represent the boiling point diagrams for both the systems.

Table II. Experimental Vapor–Liquid Equilibrium Data (System: Acetonitrile–*sec*-Butyl Alcohol)

				Exptl		Calcd	
No.	Temp, °C	x_1	y_1	γ_1	γ_2	γ_1	γ_2
(1)	81.2	0.960	0.950	1.00	2.60	1.00	2.37
(2)	81.1	0.925	0.920	1.01	2.23	1.01	2.21
(3)	81.2	0.899	0.898	1.01	2.10	1.01	2.10
(4)	81.3	0.818	0.848	1.05	1.73	1.04	1.83
(5)	81.7	0.773	0.818	1.06	1.66	1.05	1.70
(6)	81.8	0.745	0.797	1.06	1.62	1.07	1.64
(7)	82.0	0.705	0.782	1.10	1.63	1.09	1.55
(8)	82.9	0.581	0.723	1.20	1.28	1.18	1.33
(9)	84.1	0.478	0.668	1.29	1.17	1.30	1.21
(10)	85.9	0.288	0.552	1.68	1.07	1.57	1.07
(11)	87.3	0.240	0.478	1.67	1.11	1.67	1.05
(12)	91.2	0.132	0.374	2.11	1.03	1.91	1.01

Table III. Experimental Vapor–Liquid Equilibrium Data (System: Acetonitrile–*tert*-Butyl Alcohol)

				Exptl		Calcd	
No.	Temp, °C	x_1	y_1	γ_1	γ_2	γ_1	γ_2
(1)	81.1	0.986	0.975	1.00	1.88	1.00	1.98
(2)	80.7	0.966	0.936	1.00	2.01	1.00	1.96
(3)	77.5	0.870	0.804	1.05	1.84	1.01	1.84
(4)	76.7	0.788	0.722	1.07	1.65	1.02	1.68
(5)	75.7	0.564	0.550	1.17	1.35	1.13	1.41
(6)	75.8	0.474	0.506	1.25	1.23	1.22	1.20
(7)	76.1	0.418	0.460	1.31	1.20	1.30	1.23
(8)	76.3	0.350	0.411	1.39	1.16	1.32	1.17
(9)	76.7	0.266	0.358	1.57	1.10	1.62	1.10
(10)	77.2	0.180	0.310	1.98	1.04	1.92	1.05

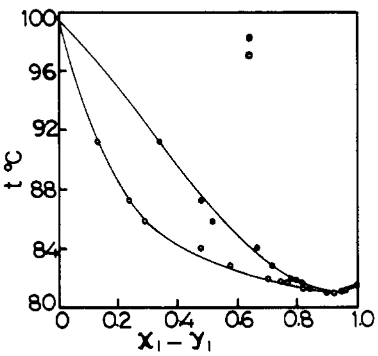

Figure 1. Boiling point diagram for the system acetonitrile–*sec*-butyl alcohol: ●, dew.point; O, bubble point.

Table I. Physical Properties of Chemicals

	Bp, °C		Refractive index at 25 °C		
	Exptl	Lit.	Exptl	Lit.	Vapor pressure eq
(1) Acetonitrile	81.6	81.6	1.3420	1.3416	$\log P = 7.24299 - 1397.929/(t + 238.899)$
(2) *sec*-Butyl alcohol	99.5	99.53	1.3952	1.3978 (20 °C)	$\log P = 46.42483 - (4261.0/T) - 12.4877 \log T$
(3) *tert*-Butyl alcohol	82.4	82.41	1.3825	1.3823	$\log P = 8.24380 - 1675.4/(t + 230)$

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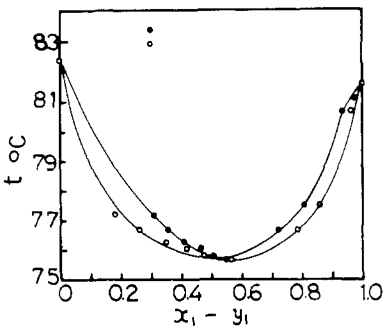

Figure 2. Boiling point diagram of the system acetonitrile–*tert*-butyl alcohol; ●, dew point; O, bubble point.

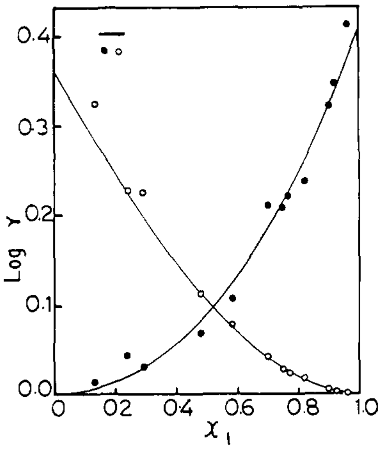

Figure 3. Activity coefficient–liquid-phase composition plot for the system acetonitrile–*sec*-butyl alcohol: O, γ_1 (exptl); ●, γ_2 (exptl); —, theoretical model.

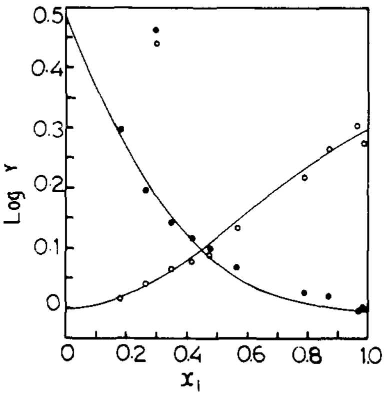

Figure 4. Activity coefficient–liquid-phase composition plot for the system acetonitrile–*tert*-butyl alcohol: ●, γ_1 (exptl); O, γ_2 (exptl); —, theoretical model.

The two systems studied form minimum boiling azeotropes. It is observed from Table II that the binary mixture of acetonitrile and *sec*-butyl alcohol constantly boils at 81.20 °C with a composition of approximately 0.899 mole fraction acetonitrile and it is further confirmed that the temperature and azeotropic composition for the system are to be 81.20 °C and 0.90 mole fraction, respectively, by distilling a binary mixture of similar composition in a laboratory packed distillation column. In a similar way the azeotropic composition and temperature of the system acetonitrile–*tert*-butyl alcohol are found to be 0.54 mole fraction acetonitrile and 75.7 °C, respectively.

The activity coefficient–composition data for both the systems are correlated by the Margules three-suffix equations

system: acetonitrile–*sec*-butyl alcohol

$$\log \gamma_1 = 0.46x_2^2 - 0.1x_2^3 \tag{3}$$

$$\log \gamma_2 = 0.31x_1^2 + 0.1x_1^3 \tag{4}$$

system: acetonitrile–*tert*-butyl alcohol

$$\log \gamma_1 = 0.11x_2^2 + 0.38x_2^3 \tag{5}$$

$$\log \gamma_2 = 0.68x_1^2 - 0.38x_1^3 \tag{6}$$

The average and maximum deviations between the experimental and calculated values of activity coefficient data are as follows

	Av dev in %		Max dev in %	
System	γ_1	γ_2	γ_1	γ_2
Acetonitrile–*sec*-butyl alcohol	1.86	3.45	9.5	11.5
Acetonitrile–*tert*-butyl alcohol	2.63	2.08	5.03	5.32

The maximum deviation in γ values for the system acetonitrile–*sec*-butyl alcohol is found to be at the end values.

The data for both the systems are found to be thermodynamically consistent by applying the Herington test (*3*).

From the activity coefficient composition diagrams, Figures 3 and 4, it is evident that the systems show positive deviations from Raoult's law and it appears that the association of alcohols is negligible. It is in accordance with the view that the association of alcohols in the presence of acetonitrile decrease in the sequence primary → secondary → tertiary as is observed by Srinivasa Rao (*4*).

Glossary

P_c	critical pressure, atm
P^0	vapor pressure of pure component, mmHg
P_r	reduced pressure
R	gas constant
t, T	temperature, °C, K
T_c	critical temperature
T_r	reduced temperature
V	specific molar volume of liquid, cm^3/mol
x	mole fraction in liquid phase
y	mole fraction in vapor phase
β	second virial coefficient
γ	activity coefficient
π	total pressure, mmHg

Subscripts

1	more volatile component
i	any component

Literature Cited

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