Table V. Azeotropic State: 2-Propanol (1)–Toluene (2)

| | azeotropic comp X_1 | | T, K | |
p, torr	exptl	calcd	exptl	calcd
760	0.8500	0.8490	354.48	354.64
550	0.8000	0.7980	346.28	346.35

The second virial coefficients of the compounds were calculated with the Tsonopoulos correlating formula (*6*). Antoine equation was used for the determination of the pure component vapor pressure.

Estimation of Parameters. Van Laar, Margules, and Wilson's parameters have been estimated for the binary system. For Van Laar and Margules parameters least-squares technique was used. For Wilson's parameters the nonlinear least-squares technique as proposed by Hirata (*2, 7*) was used. As the vapor-phase composition Y_1 has be determined, it was possible to compare the experimentally obtained values of Y_1 with the calculated values. These results are presented in Table IV.

Prediction of Azeotropic Composition. Wilson's parameters were used to predict the azeotropic composition. Table V shows the predicted and experimental azeotropic compositions and temperatures.

Glossary

A	= estimated parameters of Margules, Van Laar, and Wilson
B	= second virial coefficient, cm^3/mol
n	= refractive index
P	= total pressure or saturated vapor pressure of pure components, torr
R	= gas constant, cm^3 torr/(mol K)
T	= temperature, K
X, Y	= liquid and vapor molar fractions, respectively

Greek Letters

γ	activity coefficients

Subscripts

1, 2	components 1 and 2, respectively
I, J	components *I* and *J*, respectively
exptl, calcd	experimental or calculated quantity, respectively

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Vapor–Liquid Equilibrium for the Acetonitrile–2-Propanol–Benzene System at 50 °C

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Isothermal vapor–liquid equilibrium for the acetonitrile–2-propanol–benzene system were measured at 50 °C by using a Boublik vapor-recirculating still. The ternary experimental VLE data were compared with calculated values derived from the UNIQUAC association theory with only binary parameters, which were obtained from VLE data for all three binary systems constituting the ternary by using the method of maximum likelihood principle. Good agreement is obtained.

This work was undertaken to report isothermal vapor–liquid equilibrium (VLE) data for ternary mixtures of acetonitrile, 2-propanol, and benzene at 50 °C, as a part of VLE measurement series for ternary mixtures containing one aliphatic alcohol and acetonitrile. Some data have already been published (*1–4*). Isothermal VLE data for three binary systems constituting the ternary system have been reported in the literature: acetonitrile-2-propanol at 50 °C (*5*); acetonitrile–benzene at 45 °C (*6*); 2-propanol–benzene at 50 °C (*7*).

Experimental Section

Materials. All reagents were purchased from Wako Chemical Industries, Ltd. Special grade acetonitrile was used without

Table I. Densities and Vapor Pressures of Compounds at 25 °C

| | density, g cm^{-3} | | vapor press., kPa | |
compd	this work	lit. (*8*)	this work	lit. (*8*)
acetonitrile	0.7766	0.77656 (9)	33.811	33.797 (9)
2-propanol	0.7813	0.78126	23.931	23.931
benzene	0.8737	0.87370	36.210	36.169

further purification. First grade 2-propanol was fractionally distilled after drying over anhydrous copper sulfate. First grade benzene was subjected to repeated recrystallization. Gas chromatography did not show any significant impurities in the reagents used. Densities were measured with an Anton Paar DMA 40 densimeter at 25 ± 0.05 °C. Densities and vapor pressures of the pure reagents are compared with the literature values in Table I.

Apparatus. The VLE determination at 50 °C was carried out using a Boublik vapor-recirculation still, and the experimental technique has been described (*10*). All vapor and liquid samples were analyzed with a Shimadzu GC 7A gas chromatograph and a Shimadzu ITG 2A digital integrator. The errors involved in the measured variables were as follows: composition, 0.002 mole fraction; pressure, 13.3 Pa; temperature, 0.05 K.

Table II. Vapor–Liquid Equilibrium Data for the Acetonitrile (1)–2-Propanol (2)–Benzene (3) System at 50 °C[a]

point	x_1	x_2	x_3	y_1	y_2	y_3	P, kPa	γ_1	γ_2	γ_3	ϕ_1	ϕ_2	ϕ_3
1	0.110	0.051	0.839	0.169	0.117	0.714	44.823	2.064	4.281	1.052	0.962	0.983	0.983
2	0.098	0.357	0.545	0.130	0.300	0.570	47.769	1.888	1.663	1.379	0.956	0.978	0.984
3	0.094	0.466	0.440	0.130	0.338	0.532	47.209	1.944	1.418	1.577	0.956	0.977	0.985
4	0.072	0.700	0.228	0.134	0.441	0.425	42.596	2.364	1.112	2.202	0.957	0.978	0.988
5	0.095	0.771	0.134	0.193	0.498	0.309	39.357	2.381	1.054	2.529	0.956	0.978	0.993
6	0.079	0.878	0.043	0.219	0.639	0.142	33.944	2.812	1.027	3.141	0.959	0.981	0.998
7	0.213	0.126	0.661	0.249	0.178	0.573	47.489	1.646	2.781	1.138	0.952	0.978	0.985
8	0.243	0.269	0.488	0.260	0.245	0.495	42.289	1.556	1.856	1.384	0.947	0.976	0.987
9	0.253	0.525	0.222	0.306	0.353	0.341	46.450	1.654	1.291	1.987	0.945	0.976	0.992
10	0.289	0.376	0.335	0.302	0.289	0.409	47.929	1.475	1.523	1.626	0.945	0.976	0.990
11	0.334	0.242	0.424	0.321	0.227	0.452	48.743	1.379	1.890	1.442	0.945	0.976	0.989
12	0.344	0.099	0.557	0.346	0.139	0.515	47.743	1.416	2.777	1.224	0.947	0.978	0.988
13	0.328	0.574	0.098	0.408	0.396	0.196	42.890	1.569	1.226	2.407	0.944	0.978	1.000
14	0.437	0.122	0.441	0.397	0.151	0.452	47.743	1.275	2.447	1.361	0.943	0.977	0.991
15	0.422	0.483	0.095	0.460	0.363	0.177	43.103	1.380	1.343	2.258	0.943	0.978	1.002
16	0.479	0.292	0.229	0.425	0.257	0.318	47.849	1.243	1.741	1.856	0.940	0.976	0.996
17	0.523	0.118	0.359	0.450	0.143	0.407	47.583	1.200	2.388	1.504	0.941	0.978	0.994
18	0.658	0.109	0.233	0.537	0.140	0.323	45.970	1.098	2.449	1.786	0.939	0.979	0.999
19	0.659	0.258	0.083	0.583	0.266	0.151	43.383	1.123	1.858	2.229	0.940	0.980	1.006
20	0.846	0.114	0.040	0.747	0.168	0.085	39.730	1.030	2.446	2.402	0.942	0.986	1.014
21	0.175	0.436	0.389	0.211	0.319	0.470	47.409	1.692	1.435	1.586	0.950	0.976	0.987
22	0.387	0.215	0.398	0.359	0.210	0.431	48.636	1.325	1.964	1.464	0.943	0.976	0.991
23	0.391	0.417	0.192	0.397	0.315	0.288	46.290	1.379	1.446	1.941	0.942	0.976	0.996

[a] B_{11} = -4144 cm³ mol⁻¹; B_{22} = -1619 cm³ mol⁻¹; B_{33} = -1205 cm³ mol⁻¹; B_{12} = -2268 cm³ mol⁻¹; B_{13} = -1145 cm³ mol⁻¹; B_{23} = -808 cm³ mol⁻¹; v_1^L = 54 cm³ mol⁻¹; v_2^L = 81 cm³ mol⁻¹; v_3^L = 92 cm³ mol⁻¹.

Results

The pressure–composition measurements at 50 °C are listed in Table II. Activity coefficients were calculated from the equation

$$\gamma_I = \frac{P\phi_I y_I}{x_I P_I{}^s \phi_I{}^s \exp[v_I{}^L(P - P_I{}^s)/RT]} \tag{1}$$

where P, $P_I{}^s$, x_I, and y_I are the experimental values of the total pressure, pure component vapor pressure, and liquid and vapor mole fractions. The fugacity coefficients, ϕ_I and $\phi_I{}^s$, were calculated from the volume-explicit virial equation truncated after the second term and second virial coefficients, B_{II} and B_{IJ}, estimated by the method of Hayden and O'Connell (11). The pure liquid molar volumes $v_I{}^L$ were calculated by the modified Rackett equation (12). B_{II}, B_{IJ}, and $v_I{}^L$ are given at the bottom of Table II.

Data Analysis

The UNIQUAC associated solution theory (4, 13–15) was used to analyze the ternary VLE data. According to the theory 2-propanol self-associates ($B_i + B = B_{i+1}$) and forms chemical complexes with acetonitrile and benzene ($B_i + A = B_iA$; $B_i + C = B_iC$). The activity coefficients of acetonitrile (A), 2-propanol (B), and benzene (C) are given by

$$\ln \gamma_A = \ln\left(\frac{\Phi_{OA}}{x_A}\right) + 1 - \frac{r_A}{V} - \left(\frac{Z}{2}\right)q_A\left[\ln\left(\frac{\Phi_A}{\theta_A}\right) + 1 - \frac{\Phi_A}{\theta_A}\right] + q_A\left[1 - \ln\left(\sum_J \theta_J\tau_{JA}\right) - \sum_J \frac{\theta_J\tau_{AJ}}{\sum_K \theta_K\tau_{KJ}}\right] \tag{2}$$

$$\ln \gamma_B = \ln\left(\frac{\Phi_{B_1}}{\Phi_{B_1}^{\circ}x_B}\right) + \frac{r_B}{V^{\circ}} - \frac{r_B}{V} - \left(\frac{Z}{2}\right)q_B\left[\ln\left(\frac{\Phi_B}{\theta_B}\right) + 1 - \frac{\Phi_B}{\theta_B}\right] + q_B\left[1 - \ln\left(\sum_J \theta_J\tau_{JB}\right) - \sum_J \frac{\theta_J\tau_{BJ}}{\sum_K \theta_K\tau_{KJ}}\right] \tag{3}$$

In γ_C is derived by changing the subindex A to C in eq 2.

The coordination number Z is equal to 10 and segment fraction Φ, surface fraction θ, and binary parameter τ are expressed by

$$\Phi_I = x_I r_I / \sum_J x_J r_J \tag{4}$$

$$\theta_I = x_I q_I / \sum_J x_J q_J \tag{5}$$

$$\tau_{IJ} = \exp(-a_{IJ}/T) \tag{6}$$

The nominal segment fractions are related to the monomer segment fractions.

$$\Phi_A = \Phi_{OA}\left[1 + \frac{r_A K_{BA}\Phi_{B_1}}{(1 - K_B\Phi_{B_1})}\right] \tag{7}$$

$$\Phi_B = \frac{\Phi_{B_1}}{(1 - K_B\Phi_{B_1})^2}[1 + r_B(K_{BA}\Phi_{OA} + K_{BC}\Phi_{OC})] \tag{8}$$

$$\Phi_C = \Phi_{OC}\left[1 + \frac{r_C K_{BC}\Phi_{B_1}}{(1 - K_B\Phi_{B_1})}\right] \tag{9}$$

Equations 7–9 are solved by iteration for Φ_{OA}, Φ_{B_1}, and Φ_{OC} with subroutine NOLBR built in a FACOM M-170F computer. Then $\Phi^{\circ}_{B_1}$, V, and V° are given by

$$\Phi^{\circ}_{B_1} = [(2K_B + 1) - (4K_B + 1)^{1/2}]/2K_B{}^2 \tag{10}$$

$$\frac{1}{V} = \frac{\Phi_{OA}}{r_A}\left[1 + \frac{K_{BA}r_A\Phi_{B_1}}{(1 - K_B\Phi_{B_1})}\right] + \frac{\Phi_{B_1}}{r_B(1 - K_B\Phi_{B_1})} + \frac{\Phi_{OC}}{r_C}\left[1 + \frac{K_{BC}r_C\Phi_{B_1}}{(1 - K_B\Phi_{B_1})}\right] \tag{11}$$

$$\frac{1}{V^{\circ}} = (1 - K_B\Phi^{\circ}_{B_1})/r_B \tag{12}$$

The value of K_B for 2-propanol was taken from Brandani (16): K_B = 49.1 at 50 °C. The pure component structural parameters were calculated by the method of Vera et al. (17): for acetonitrile, r = 1.50, q = 1.40; for 2-propanol, r = 2.23, q = 1.98; for benzene, r = 2.56, q = 2.05.

Table III. Binary Parameters and Root Mean Square (RMS) Deviations

	temp, °C	no. of data points	RMS deviations						
			ΔP, kPa	ΔT, K	comp, mol %		parameters, K		$K_{AB}{}^a$
					Δx	Δy	a_{AB}	a_{BA}	
2-propanol (A)–acetonitrile (B)	50	15	0.0696	0.01	0.05	0.37	538.50	84.11	23
acetonitrile (A)–benzene (B)	45	12	0.1040	0.02	0.05	0.36	−10.54	258.38	
2-propanol (A)–benzene (B)	50	15	0.1040	0.02	0.06	0.41	129.75	12.72	2.5

^{a} At 50 °C.

Table IV. Ternary Calculated Results for the System Acetonitrile (1)-2-Propanol (2)-Benzene (3) at 50 °C

	$\Delta y_1{}^a$	$\Delta y_2{}^a$	$\Delta y_3{}^a$	ΔP, KPa	$\Delta P/P$, %
mean deviation	0.23	0.26	0.29	0.4627	1.00
RMS deviation	0.27	0.32	0.40	0.5660	1.20

^{a} In mol %.

The thermodynamic consistency of the binary data was confirmed by the area test (*18*). Binary and ternary VLE and liquid–liquid equilibrium (LLE) data for many alcohol mixtures have been reduced with the UNIQUAC association theory (*15*). Binary parameter estimation was performed by using a computer program similar to that described by Prausnitz et al. (*19*), which is based on the maximum likelihood principle. Standard deviations in the measured variables were the same as those used by Prausnitz et al.: for pressure, σ_P = 133.3 Pa; for temperature, σ_T = 0.05 K; for liquid mole fraction, σ_x = 0.001; for vapor mole fraction, σ_y = 0.003. The results of the parameter estimation for the three binary systems were taken from the previous paper (*15*) and are shown in Table III. Table IV presents ternary predicted results, indicating that a good agreement is obtained between the experimental values and calculated results. Figure 1 shows the experimental and calculated tie lines and suggests that the system may include a ternary azeotrope. It is to be noted that the values of the solvation constant and energy parameters for the acetonitrile–2-propanol system were used successfully to predict ternary LLE for the acetonitrile–2-propanol–cyclohexane system at 50 °C (*15, 20*).

Glossary

A, B, C	acetonitrile, 2-propanol, and benzene
a_{IJ}	binary interaction energy parameter
B_{II}, B_{IJ}	pure and cross second virial coefficients
I, J	components
i	alcohol i-mer
K_B	association constant, $(\Phi_{B_{i+1}}/\Phi_{B_i}\Phi_{B_1})[i/(i + 1)]$
K_{BA}	solvation constant, $(\Phi_{B_iA}/\Phi_{B_i}\Phi_{OA})[i/(ir_B + r_A)]$
K_{BC}	solvation constant, $(\Phi_{B_iC}/\Phi_{B_i}\Phi_{OC})[i/(ir_B + r_C)]$
P	total pressure
$P_I{}^s$	saturated vapor pressure of pure component I
q	pure component area parameter
R	universal gas constant
r	pure component volume parameter
T	absolute temperature
V	true molar volume of alcohol mixture
$V°$	true molar volume of pure alcohol solution
$v_I{}^L$	molar volume of pure liquid I
x_I	liquid-phase mole fraction of component I
y_I	vapor-phase mole fraction of component I
Z	coordination number equal to 10

Greek Letters

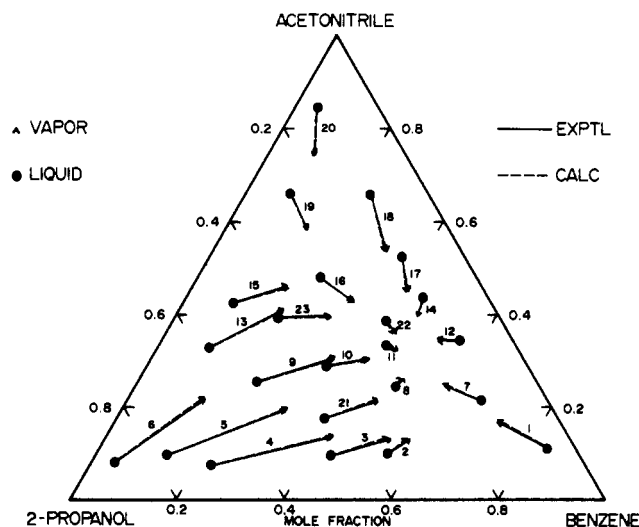| | |
γ_I	liquid-phase activity coefficient of component I
θ_I	area fraction of component I
σ_P, σ_T	standard deviations in pressure and temperature
σ_x, σ_y	standard deviations in liquid and vapor mole fractions
τ_{IJ}	$\exp(-a_{IJ}/T)$

Figure 1. Equilibrium tie lines.

Φ_I	segment fraction of component I
Φ_{OA}	segment fraction of acetonitrile monomer in mixture
Φ_{B_1}	segment fraction of alcohol monomer in mixture
$\Phi°_{B_1}$	segment fraction of alcohol monomer in pure alcohol solution
Φ_{OC}	segment fraction of benzene monomer in mixture
ϕ_I	vapor-phase fugacity coefficient of component I
$\phi_I{}^s$	vapor-phase fugacity coefficient of pure component I at its saturation pressure $P_I{}^s$ and system temperature T

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