Table II. Values of the Constants A_0, A_1, and A_2 of Eq 2, and the Standard Deviations $\delta(\Delta k_s)$, for the Various Systems at 308.15 K

system	$10^{12}A_0$, Pa^{-1}	$10^{12}A_1$, Pa^{-1}	$10^{12}A_2$, Pa^{-1}	$10^{12}\delta(\Delta k_s)$, Pa^{-1}
acetone–benzene	−164.51	−5.91	32.66	1.4
acetone–toluene	−186.00	−45.93	−27.69	1.5
acetone–p-xylene	−195.44	−75.12	12.78	1.1
acetone–mesitylene	209.97	20.43	−50.91	2.1

adiabatic compressibilities for, binary mixtures of acetone with benzene, toluene, *p*-xylene, and mesitylene at 308.15 K are given in Table I, where x_1 refers to the mole fraction of acetone. The values of Δk_s, which refers to the deviations of the experimental values of k_s from the mole fraction mixture law values, are also given in Table I and have been fitted by least squares to the following equation:

$$\Delta k_s = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \quad (2)$$

The values of the constants A_0, A_1, and A_2 along with the standard deviations $\delta(\Delta k_s)$ are given in Table II.

The values of Δk_s can be discussed (*2*, *4*) from the viewpoint of the existence of specific interactions between the components of a system. The data show that the values of Δk_s are negative for acetone–benzene, acetone–toluene, and acetone–*p*-xylene and positive for acetone–mesitylene. At $x_1 = 0.5$, the values of Δk_s have the sequence

mesitylene > benzene > toluene > *p*-xylene

The above sequence along with the negative values of Δk_s for acetone–benzene, acetone–toluene, and acetone–*p*-xylene further supports earlier findings (*1*) that the dipole interaction between the components is not the only cause of the deviations, and the electron donor and acceptor properties of the components also play an important part. There is a likelihood of the formation of a weak hydrogen bond due to interaction between the H atom of the aromatic ring and the lone-pair electrons of acetone. The positive values of Δk_s for the system acetone–mesitylene can be attributed to the fact that the dispersion forces are predominant between the components of this system.

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We are extremely grateful to Professor R. P. Rastogi, Head of the Chemistry Department, Gorakhpur University, Gorakhpur, for encouragement during this investigation.

Registry No. Acetone, 67-64-1; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; mesitylene, 108-67-8.

Literature Cited

(1) Nath, J.; Dixit, A. P. *J. Chem. Eng. Data* **1983**, *28*, 190–1.
(2) Nath, J.; Dubey, S. N. *J. Phys. Chem.* **1980**, *84*, 2166–70.
(3) Nath, J.; Tripathi, A. D. *J. Chem. Eng. Data* **1983**, *28*, 263–6.
(4) Fort, R. J.; Moore, W. R. *Trans. Faraday Soc.* **1965**, *61*, 2102–11.
(5) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: Amsterdam, 1950.
(6) Nath, J.; Dixit, A. P. *J. Chem. Eng. Data*, first of two preceding articles in this issue.

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Liquid–Liquid Equilibria for the System Benzene–Water–Methanol

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Liquid–liquid equilibrium data for the system benzene–water–methanol were obtained at 293 K. Tie lines were established by correlating the refractive index of the binodal curve as a function of composition. Data were reduced by the Abrams and Prausnitz (UNIQUAC) equation. The experimental and UNIQUAC plait points were calculated by the Hand coordinates method.

Introduction

The liquid–liquid equilibrium for the system benzene–water–methanol has been previously investigated by Udovenko and Mazanko (*1*). However, equilibrium data at 293 K were not found in the literature (*2*). Most of the reported data for this system are on mutual solubility but little is known on tie-line data (*2*).

The aim of this work was to provide equilibrium data for this ternary system at 293 K.

This paper reports the results of these measurements and their correlation by the Abrams and Prausnitz equation (UNIQUAC) (*3*).

Table I. Physical Properties of Chemicals at 293 K

	density/(g cm^{-3})		refractive index	
	exptl	lit.	exptl	lit.
benzene	0.8790	0.879 03[b]	1.5011	1.501 10[b]
methanol	0.7911	0.791 31[a]	1.3290	1.328 40[a]
water	0.9983	0.998 20[b]	1.3330	1.332 99[b]

[a] Reference *7*. [b] Reference *8*.

Experimental Section

Materials. Benzene was Merck analytical-grade reagent used without any further purification. The certified minimum purity of this chemical was 99.5%. Methanol was AnalaR; it was used after distillation in a high-efficiency packed column. Water was deionized and distilled in an all-glass distillation unit prior to use. Some physical properties of the reagents are listed in Table I together with literature values.

Binodal-Curve Determination. Depending upon the region of the binodal curve (i.e., whether benzene- or water-rich phase), homogeneous samples of known compositions were titrated in a thermostated glass-stoppered bottle. The thermo-

Table II. Binodal-Curve Data for the System Benzene (1)-Water (2)-Methanol (3) at 293 K

	x_1	x_2	x_3
1	0.0004	0.9996	0.0000
2	0.0025	0.8698	0.1277
3	0.0028	0.8016	0.1956
4	0.0029	0.7700	0.2271
5	0.0042	0.6985	0.2973
6	0.0047	0.6508	0.3445
7	0.0055	0.5890	0.4055
8	0.0105	0.5422	0.4473
9	0.0187	0.4946	0.4867
10	0.0316	0.4400	0.5284
11	0.0443	0.3913	0.5644
12	0.0632	0.3472	0.5896
13	0.0862	0.3075	0.6063
14	0.1117	0.2732	0.6151
15	0.1371	0.2448	0.6181
16	0.1977	0.1963	0.6060
17	0.2282	0.1778	0.5940
18	0.2665	0.1519	0.5816
19	0.2965	0.1440	0.5595
20	0.3386	0.1236	0.5378
21	0.3880	0.1095	0.5025
22	0.4897	0.0746	0.4357
23	0.6072	0.0536	0.3392
24	0.6698	0.0418	0.2884
25	0.7341	0.0322	0.2337
26	0.8992	0.0113	0.0895
27	0.9974	0.0026	0.0000

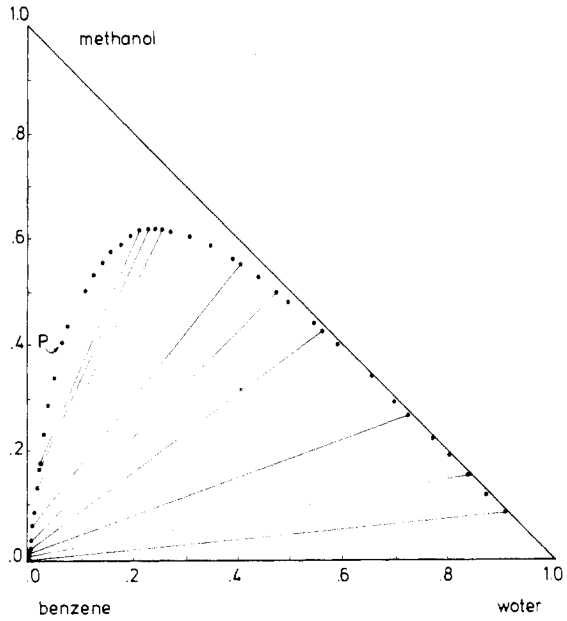

Figure 1. Liquid-liquid equilibria for the system benzene (1)-water (2)-methanol (3) at 293 K.

static bath was maintained to within ±0.1 K of the desired temperature. The addition of appropriate amounts of benzene to a miscible mixture of methanol and water, and that of water to a homogeneous mixture of benzene and methanol, rendered the system immiscible. The titrant was added in small amounts from a Kimax microburet with an accuracy of ± 0.01 cm^3. The contents of the glass-stoppered bottles were shaken vigorously for proper mixing and equilibrium. The amount of titrant thus added was calculated from its volume and density. The binodal-curve data for the ternary system benzene-water-methanol at 293 K are reported in Table II and are shown in Figure 1.

Tie-Line-Data Determination. Liquid-liquid equilibrium data were measured in the thermostated cell of 250-cm^3 capacity. The mixture was stirred by a magnetic stirrer and the cell was equipped with baffles. Tie lines were obtained by mixing pure components to give a 1:1 volume ratio approximately.

Table III. Liquid-Liquid Equilibrium Data for the System Benzene (1)-Water (2)-Methanol (3) at 293 K

	benzenic phase			aqueous phase		
	x_1	x_2	x_3	x_1	x_2	x_3
1	0.9967	0.0026	0.0007	0.0020	0.9066	0.0914
2	0.9915	0.0030	0.0055	0.0026	0.8371	0.1603
3	0.9852	0.0034	0.0114	0.0036	0.7230	0.2734
4	0.9760	0.0041	0.0199	0.0073	0.5605	0.4322
5	0.9574	0.0055	0.0371	0.0245	0.4722	0.5033
6	0.9249	0.0084	0.0667	0.0400	0.4053	0.5547
7	0.8500	0.0161	0.1339	0.1279	0.2539	0.6182
8	0.8080	0.0212	0.1708	0.1496	0.2317	0.6187
9	0.7986	0.0225	0.1789	0.1698	0.2141	0.6161

Table IV. Uniquac Parameters for the System Benzene (1)-Water (2)-Methanol (3)

i-j	$[(u_{ij} - u_{jj})/R]/\mathrm{K}$	$[(u_{ji} - u_{ii})/R]/\mathrm{K}$	rmsd	ref
		$T = 293$ K		
1-2	504.76	932.79		
1-3	362.14	-86.130		
2-3	-421.30	-626.87	0.49	this work
		$T = 303$ K		
1-2	753.90	315.18		
1-3	428.62	-51.480		
2-3	-284.24	266.87	1.38	*1*
		$T = 318$ K		
1-2	583.44	331.19		
1-3	495.96	-56.442		
2-3	-140.47	144.84	0.88	*1*
		$T = 333$ K		
1-2	633.85	283.21		
1-3	364.15	-85.755		
2-3	-334.07	240.38	1.21	*1*

After equilibrium was reached, the mixture were settled, and samples of each phase were taken, the upper phase with a syringe, the lower phase through the sampling stopcock. Samples were analyzed by measuring the refractive indexes at 293 K. The refractive indexes of mixtures on the binodal curve were also measured by using a Baush and Lomb Abbe-3L refractometer.

The mole fraction of each component on the binodal curve was correlated as a function of the refractive index. The spline-fit technique extended by Klaus and Van Ness (*4*) was used for this correlation. Then, the refractive index of both phases at equilibrium gives the tie-line compositions. The accuracy of composition measurements was estimated to be within ±0.0005 mole fraction. Liquid-liquid equilibrium data for the ternary system benzene-water-methanol at 293 K are reported in Table III and shown in Figure 1.

Results and Discussion

The liquid-liquid equilibrium data were reduced by the Abrams and Prausnitz (UNIQUAC) equation (*3*). The generalized UNIQUAC equation has the following form for the excess Gibbs energy:

$$g^{\mathrm{E}} = g^{\mathrm{E}}(\text{combinatorial}) + g^{\mathrm{E}}(\text{residual}) \tag{1}$$

$$\frac{g^{\mathrm{E}}}{RT}(\text{combinatorial}) = \sum_i^N x_i \ln \frac{\Phi_i}{x_i} + \frac{Z}{2}\sum_i^N q_i x_i \ln \frac{\theta_i}{\Phi_i} \tag{2}$$

$$\frac{g^{\mathrm{E}}}{RT}(\text{residual}) = -\sum_i^N q_i x_i \ln \sum_j^N \theta_i \tau_{ji} \tag{3}$$

$$\Phi_i = r_i x_i / \sum_j (r_j x_j) \tag{4}$$

$$\theta_i = q_i x_i / \sum_j (q_j x_j) \tag{5}$$

Table V. Deviation between Calculated and Experimental Concentrations

	water		methanol		benzene		calcd − exptl rms
	aqueous	organic	aqueous	organic	aqueous	organic	
exptl tie line	90.6600	0.2600	9.1400	0.0700	0.2000	99.6700	
calcd tie line	90.7328	0.7726	9.2491	0.0058	0.0181	99.2216	
calcd − exptl	0.0728	0.5126	0.1091	−0.0642	−0.1819	−0.4484	0.2939
exptl tie line	83.7100	0.3000	16.0300	0.5500	0.2600	99.1500	
calcd tie line	83.8009	0.5509	16.1329	0.0551	0.0662	99.3939	
calcd − exptl	0.0909	0.2509	0.1029	−0.4949	−0.1938	0.2439	0.2658
exptl tie line	72.3000	0.3400	27.3400	1.1400	0.3600	98.5200	
calcd tie line	72.2885	0.3594	27.4077	0.4543	0.3039	99.1863	
calcd − exptl	−0.0115	0.0194	0.0677	−0.6857	−0.0561	0.6663	0.3921
exptl tie line	56.0500	0.4100	43.2200	1.9900	0.7300	97.6000	
calcd tie line	55.8279	0.3179	42.7204	2.4131	1.4516	97.2690	
calcd − exptl	−0.2221	−0.0921	−0.4996	0.4231	0.7216	−0.3310	0.4314
exptl tie line	47.2200	0.5500	50.3300	3.7100	2.4500	95.7400	
calcd tie line	47.3073	0.3653	49.8638	4.4139	2.8289	95.2208	
calcd − exptl	0.0873	−0.1847	−0.4662	0.7039	0.3789	−0.5192	0.4411
exptl tie line	40.5300	0.8400	55.4700	6.6700	4.0000	92.4900	
calcd tie line	40.3295	0.4435	54.9794	6.7589	4.6912	92.7976	
calcd − exptl	−0.2005	−0.3965	−0.4906	0.0889	0.6912	0.3076	0.4120
exptl tie line	25.3900	1.6100	61.3200	13.3900	12.7900	85.0000	
calcd tie line	25.9819	0.8168	61.6840	14.4900	12.3341	84.6932	
calcd − exptl	0.5919	−0.7932	−0.1360	1.1000	−0.4559	−0.3068	0.6468
exptl tie line	23.1700	2.1200	61.8700	17.0800	14.9600	80.8000	
calcd tie line	22.6125	0.9914	62.0067	17.1497	15.3808	81.8589	
calcd − exptl	−0.5575	−1.1286	0.1367	0.0697	0.4208	1.0589	0.6960
exptl tie line	21.4100	2.2500	61.6100	17.8900	16.9800	79.8600	
calcd tie line	21.1317	1.0863	61.9415	18.4527	16.9268	80.4610	
calcd − exptl	−0.2783	−1.1637	0.3315	0.5627	−0.0532	0.6010	0.6086
calcd − exptl rms	0.3072	0.6483	0.3130	0.5709	0.4221	0.5533	0.4870

where the coordination number z is set equal to 10; and r and q are pure-component molecular-structure constants

$$\tau_{ij} = \exp\{-(u_{ij} - u_{jj})/RT\} \tag{6}$$

where u_{ij} is the physical parameter for the i–j pair interaction.

The parameter estimation method used in this work has been already described by Sørensen et al. (*5*). An objective function stated in terms of concentration is used to represent as accurately as possible the experimental tie lines.

$$F = \sum_{i}^{M} \min \sum_{k}^{2} \sum_{j}^{3} \{x_{jk}(i) - x_{jk}{}^{*}(i)\}^2 \tag{7}$$

where $x_{jk}(i)$ stands for the mole fraction of component j in phase k; and i is the serial number of a given experimental tie line (i = 1, 2, ..., M). $x_{jk}{}^{*}(i)$ is the $x_{jk}(i)$ calculated from the UNIQUAC equation; and min denotes the minimum values.

The UNIQUAC parameters obtained for the ternary system benzene–water–methanol at 293 K are reported in Table IV.

This table also includes numerical values of the root-mean-square deviation defined as

$$\text{rmsd} = 100\{\sum_{i}^{M} \sum_{k}^{2} \sum_{j}^{3} [x_{jk}(i) - x_{jk}{}^{*}(i)]^2/6M\}^{1/2} \tag{8}$$

The final residual compares well with those obtained by Sørensen and Arlt (*2*) for the data reported by Udovenko and Mazanko (*1*).

The calculated UNIQUAC tie lines are reported in Table V along with the experimental values and its deviations.

Finally, the experimental plait point was calculated by using the Hand (*6*) method. Also, the UNIQUAC plait point was calculated by the same procedure. The plait points are reported on Table VI.

Table VI. Plait Point for the System Benzene (1)–Water (2)–Methanol (3) at 293 K

	exptl	UNIQUAC
x_1	0.523	0.567
x_2	0.071	0.061
x_3	0.406	0.372

Acknowledgment

J. C. Gómez performed the experimental measurements.

Glossary

F	objective function defined by eq 7
g^E	excess Gibbs energy function, J mol^{-1}
M	number of experimental tie lines
N	number of components
q_i	molecular-geometric area parameter for the pure component i
r_i	molecular volume parameter for the pure component i
R	gas constant, J mol^{-1} K^{-1}
rmsd	root-mean-square deviation defined by eq 8
T	absolute temperature, K
u_{ij}	UNIQUAC binary interaction parameter, J mol^{-1}
x_i	mole fraction of component i in liquid phase
$x_{jk}(i)$	mole fraction of component j in phase k for the ith tie line
$x_{jk}{}^{*}(i)$	$x_{jk}(i)$ calculated by the UNIQUAC model
z	lattice coordination number, a constant set equal to 10

Greek Letters

Φ_i	volume fraction defined by eq 4
θ_i	area fraction defined by eq 5
τ_{ij}	UNIQUAC binary parameter defined by eq 6

Registry No. Benzene, 71-43-2; methanol, 67-56-1.

Literature Cited

(1) Udovenko, V. V.; Mazanko, T. F. *Zh. Fiz. Khim.* **1963**, *37*, 2324.

(2) Sørensen, J. M.; Arlt, W. "Liquid–Liquid Equilibrium Data Collection", 1st ed.; DECHEMA: Frankfurt, 1979; vol. V, Parts 1–3.

(3) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(4) Klaus, R. L.; Van Ness, H. C. *AIChE J.* **1967**, *13*, 1132.
(5) Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib* **1979**, *3*, 47.
(6) Hand, D. B. *J. Phys. Chem.* **1930**, *34*, 1961.
(7) Wilhoit, R. C.; Zwolinski, B. J. "Physical and Thermodynamic Properties of Aliphatic Alcohols"; American Chemical Society: Washington, DC, 1973; *J. Phys. Chem. Ref. Data, Suppl. 1*, Vol. 2.
(8) Dreisbach, R. R. "Physical Properties of Chemical Substances"; Dow Chemical Co.: Midland, MI, 1952.

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Fluid Phase Equilibria for the System Dimethyl Ether/Water from 50 to 220 °C and Pressures to 50.9 MPa

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Experimental studies of vapor-liquid, vapor-liquid-liquid, and liquid-liquid equilibria in the system dimethyl ether/water (DME/H_2O) have been carried out at 14 temperatures in the range 50-220 °C and pressures up to 50.9 MPa. The data have been obtained by using a vapor-recirculating apparatus operating at isothermal conditions. The phase diagram for this system exhibits a three-phase region of vapor-liquid-liquid equilibrium, ending at an upper critical end point where the vapor phase and the DME-rich liquid phase become identical. The mixture critical line consists of two branches. One begins at the critical point of pure dimethyl ether (126.9 °C and 5.27 MPa) and ends at the upper critical end point (157.0 °C and 6.72 MPa). The other branch begins at the critical point of pure water (374.2 °C and 22.09 MPa) as a liquid-vapor critical line and merges into a liquid-liquid critical line that rises sharply in pressure as the temperature drops below that of the upper critical end point.

Introduction

This is the third in a series of reports of vapor-liquid equilibrium (VLE) studies of binary mixtures containing dimethyl ether ($(CH_3)_2O$, DME), carbon dioxide (CO_2), methanol (CH_3OH), and water (H_2O). VLE data for the systems CO_2/DME, DME/CH_3OH have been reported (*1*, *2*).

Phase equilibrium data for these systems are needed to support the development of the Mobil process for converting methanol to gasoline (*3*, *4*). These studies will also provide data to be used for testing and refining data prediction methods based on statistical mechanics and intermolecular potential theory (*5*).

This report presents the tabulated experimental data and describes the principal quantitative and qualitative features of the *P-T-X-Y* phase diagram. A brief qualitative description of the phase diagram has been published separately (*6*).

Experimental Section

The essential features of the apparatus and method were similar to those used in earlier studies of CO_2/DME (*1*) and DME/methanol (*2*). A vapor-recirculating equilibrium system was used, and measurements of the compositions of coexisting liquid and vapor phases were made as functions of pressure at selected fixed temperatures. The earlier papers (*1*, *2*) should be consulted for general details of the method.

To facilitate the DME/H_2O experiments described here, several changes were made in the apparatus. The most important of these were the following: (1) the use of windowed cells at low to moderate pressures (up to 29 MPa) to provide visual observation of the mixture in the three-phase region and along the critical line; and (2) the use of a separately heated sampling chamber to ensure the complete vaporization of samples withdrawn from the liquid phase.

To facilitate observation of the mixtures the heated oil bath previously used for temperature control was replaced by a commercial windowed oven (Blue M Co. Blue Island, IL) suitable for use at temperatures up to 250 °C. The oven uses forced convection and horizontal air flow and is capable of maintaining temperatures constant to within ±0.02 °C, with no significant gradients in the region of the equilibrium system.

A diagram of the modified apparatus is shown in Figure 1. The heart of the system is the equilibrium cell A, coupled to the magnetically operated pump C, by $^1/_8$ in. o.d. stainless steel tubing to form a closed loop (shown by the dark lines). The action of the pump withdraws the least dense phase from the top of the cell and recirculates it around the closed loop, so that it bubbles through the remaining phase (or phases) in the lower part of the cell. This bubbling action provides intimate contact between phases and promotes a rapid approach to equilibrium, which is usually reached in 10-15 min. The recirculating system works equally well for studies of liquid-vapor, liquid-liquid-vapor, or liquid-liquid phase equilibrium. In the latter case the less dense liquid phase (the DME-rich phase) is bubbled through the more dense, H_2O-rich liquid phase.

At low pressures, up to about 8 MPa, we used an equilibrium cell made of extra heavy wall Pyrex tubing, confined between stainless steel flanges and sealed by Teflon O rings. This provided complete visibility of the mixture and was especially useful as an aid to sampling in the three-phase region. It also provided interesting views of critical opalescence at the DME-rich end of the vapor-liquid critical line. At intermediate pressures (up to about 29 MPa) we used a windowed cell of experimental design, fitted with several small windows of synthetic sapphire. The window seals developed leaks at high pressures and temperatures, so we switched finally to an all stainless steel cell for the remaining studies of the liquid-liquid region at high pressures.

In previous experiments on CO_2/DME and DME/methanol, samples were withdrawn through heated capillary sampling lines and passed directly into the gas sampling valve of a gas chromatograph. In this work we found that cooling effects, resulting from throttling the liquid samples to low pressure through the sampling valves, caused partial condensation of the