T	temperature, K
$\bar{V}_1^\circ$	partial molar volume of the solvent, $cm^3\ mol^{-1}$
$\bar{V}_2^\circ$	partial molar volume of the solute, $cm^3\ mol^{-1}$
ρ	density, $g\ cm^{-3}$
η	absolute viscosity of solution, cP
η_0	absolute viscosity of pure solvent, cP
$\Delta\mu_1^{\circ\ddagger}$	free energy of activation per mole of the pure solvent, $kJ\ mol^{-1}$
$\Delta\mu_2^{\circ\ddagger}$	contribution per mole of the solute to the free energy of activation for viscous flow of the solution, $kJ\ mol^{-1}$

Registry No. NFM, 4394-85-8; KI, 7681-11-0.

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Vapor–Liquid Equilibria at 1 atm for Binary and Ternary Systems Composed of Benzene, Toluene, and *m*-Xylene

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The vapor–liquid equilibrium data for the binary and ternary systems composed of benzene, toluene, and *m*-xylene at the isobaric condition of 1 atm are presented. The experimental data of the binary systems were used to calculate the binary parameters of the Wilson equation. The calculated vapor-phase compositions and boiling points of the three binary and of the ternary systems agree well with the experimental data.

Introduction

In continuation of our previous paper (*1*), we report now vapor–liquid equilibrium data at 1 atm of binary and ternary systems containing benzene, toluene, and *m*-xylene.

Benzene + toluene had been investigated previously by several authors (see ref 2). Isothermal data have been reported for benzene + *m*-xylene (see ref 2) or toluene + *m*-xylene (*3*). No data are available for the ternary system benzene + toluene + *m*-xylene.

Experimental Section

Materials. The compounds used in this study were pure-grade materials obtained from E. Merck AG, Darmstadt, FRG. Their physical constants appear in Table I.

***Apparatus and* Procedure.** The apparatus has been described previously (*1*). The samples of vapor and liquid phases were analyzed by using a Perkin-Elmer Model 154-C gas chromatograph equipped with a Supelcowax 10 column (column temperature, 50–150 °C at 4 °C/min; flow rate, 5 mL/min of He (flow controlled)). The chromatograph was calibrated with gravimetrically prepared samples. The vapor-liquid equilibrium compositions were determined from the calibration curve with a linear interpolation technique (*4*) applied to related peak area composition data.

Table I. Pure Component Normal Boiling Points, T_b, and Refractive Indexes, n

	T_b (1 atm)/K		n_D (293.15 K)	
component	ref 16	measured	ref 16	measured
benzene	353.244	353.23	1.501 12	1.5008
toluene	383.780	383.73	1.496 78	1.4963
m-xylene	412.270	412.29	1.497 22	1.4978

Table II. Constants, C_i, of Modified Riedel's Equation (*5*, *6*) for the Pure Compounds Vapor Pressure, P_i, as Function of Temperature, T [a]

compound	C_1	C_2	C_3	C_4
benzene	978.622 633	−32 050.796 227	0.244 124	−166.030 37
toluene	85.415 932	−7 153.257 436	0.011 228	−11.946 659
m-xylene	72.700 426	−7 949.796 502	0.005 357	−9.421 028

[a] $\ln (P_i/\mathrm{atm}) = C_1 + C_2/(T/\mathrm{K}) + C_3(T/\mathrm{K}) + C_4 \ln (T/\mathrm{K})$.

The accuracies of x, y, P, and T are respectively 0.002, 0.002, 0.001 atm, and 0.1 K.

Experimental Results and Correlations

Vapor Pressure. The vapor pressures of the three components have been calculated by using the modified Riedel equation (*5*). The constants of this equation were determined previously by Gültekin (*6*) for more than 1000 substances. These constants are shown in Table II.

Binary Systems. The binary parameters λ_{ij} of the Wilson equation (*7*) were calculated from the related pure component data and the experimental results of the binary systems under consideration by using a simplex search method (*8*). Then, the vapor-phase compositions y_1 and boiling points T of the mixtures were calculated by using these parameters. The standard and mean deviations between experimental and calculated boiling points and vapor-phase compositions and the calculated activity coefficients γ_i for each binary system are given in Tables III–V. Vapor-phase nonideality has been taken into

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Table III. Experimental Boiling Points, T, and Vapor-Phase Mole Fractions, y_1, at 1 atm of Benzene (1) + Toluene (2) and Calculated Activity Coefficients, γ_1 and γ_2, as a Function of Liquid Mole Fraction, x_1[a]

x_1	y_1	T/K	γ_1	γ_2
0.008	0.018	383.90	1.098	1.000
0.022	0.051	383.17	1.076	1.000
0.077	0.170	380.45	1.069	1.001
0.088	0.191	379.95	1.068	1.001
0.230	0.424	373.94	1.049	1.004
0.352	0.573	369.53	1.035	1.010
0.449	0.668	366.44	1.025	1.017
0.519	0.727	364.37	1.019	1.022
0.599	0.786	362.20	1.014	1.030

[a] Wilson equation parameters: $(\lambda_{12} - \gamma_{11})$/cal mol^{-1} = 145.65; $(\lambda_{21} - \gamma_{22})$/cal mol^{-1} = −85.12. Mean deviations: MD(T) = 0.06 K; MD(y_1) = 0.001. Standard deviations: SD(T) = 0.07 K; SD(y_1) = 0.002.

Table IV. Experimental Boiling Points, T, and Vapor-Phase Mole Fractions, y_1, at 1 atm of Benzene (1) + *m*-Xylene (2) and Calculated Activity Coefficients, γ_1 and γ_2, as a Function of Liquid Mole Fraction, x_1[a]

x_1	y_1	T/K	γ_1	γ_2
0.102	0.447	397.95	1.246	1.003
0.175	0.598	392.09	1.203	1.010
0.214	0.655	388.55	1.182	1.015
0.284	0.732	385.45	1.147	1.026
0.340	0.780	379.50	1.123	1.037
0.427	0.833	375.23	1.088	1.058
0.494	0.865	372.30	1.067	1.077
0.595	0.903	369.85	1.041	1.111
0.681	0.930	364.04	1.025	1.144

[a] Wilson equation parameters: $(\lambda_{12} - \lambda_{11})$/cal mol^{-1} = 344.76; $(\lambda_{21} - \lambda_{22})$/cal mol^{-1} = −117.63. Mean deviations: MD(T) = 0.13 K; MD(y_1) = 0.001. Standard deviations: SD(T) = 0.16 K; SD(y_1) = 0.002.

Table V. Experimental Boiling Points, T, and Vapor-Phase Mole Fractions, y_1, at 1 atm of Toluene (1) + *m*-Xylene (2) and Calculated Activity Coefficients, γ_1 and γ_2, as a Function of Liquid Mole Fraction, x_1[a]

x_1	y_1	T/K	γ_1	γ_2
0.111	0.358	406.35	1.728	1.014
0.186	0.462	403.02	1.533	1.036
0.523	0.718	392.83	1.116	1.228
0.561	0.741	391.71	1.094	1.258
0.593	0.760	391.06	1.079	1.283
0.625	0.779	390.52	1.065	1.309
0.677	0.802	389.47	1.046	1.355
0.688	0.816	389.51	1.042	1.365
0.698	0.822	389.12	1.039	1.374
0.736	0.844	388.45	1.029	1.409

[a] Wilson equation parameters: $(\lambda_{12} - \lambda_{11})$/cal mol^{-1} = 666.63; $(\lambda_{21} - \lambda_{22})$/cal mol^{-1} = −21.34. Mean deviations: MD(T) = 0.13 K; MD(y_1) = 0.004. Standard deviations: SD(T) = 0.14 K; SD(y_1) = 0.005.

account in terms of the fugacity coefficients given by the virial equation of state truncated after the second term for low or moderate pressure (*9*).

The molar second virial coefficients B_{ii} have been estimated by the method of Pitzer and Curl (*10*). The cross-coefficients B_{ij} were calculated by using suitable mixing rules (*9*) and the data of pure compounds from the literature (*11*, *12*).

The molar volumes of the pure substances have been expressed as a cubic function of temperature with coefficients determined by using literature data (*11*, *12*).

The area consistency tests of Herington (*13*) and Redlich and Kister (*14*) were applied. In general, the conditions proposed by Ellis and Bourne (*15*) for consistent data are satisfied (area ratio between 0.95 and 1.05).

Ternary System. The experimental vapor–liquid equilibrium data obtained for several different compositions are shown in Table VI. The vapor–liquid equilibrium data were calculated with the related binary Wilson parameters. The standard deviations between experimental and calculated results are shown in Table VI. The comparison indicates that the calculations show good agreement with the experimental data for the ternary benzene + toluene + *m*-xylene system. The vapor-phase composition and boiling points at atmospheric pressure can be predicted for any liquid-phase composition by using the binary parameters determined in this study.

Conclusion

The Wilson equation was found to be applicable to the binary systems investigated. The ternary system can be well represented with use of the binary parameters.

Glossary

B_{ij}	molar second virial coefficients
C_i	constants of vapor pressure equation, Table II
MD	mean deviation, MD = $(1/N)\sum(Q_{\mathrm{exp}} - Q_{\mathrm{cal}})$ ($Q = P$ or y_1)
N	number of experimental points
P	pressure
SD	standard deviation, SD = $[\sum(Q_{\mathrm{exp}} - Q_{\mathrm{cal}})^2/(N - 1)]^{0.5}$
T	temperature
x_i	liquid-phase mole fraction
y_i	vapor-phase mole fraction

Greek Letters

γ_i	activity coefficient
λ_{ij}	Wilson parameter

Table VI. Experimental Boiling Points, T, and Vapor Phase Mole Fractions, y_1 and y_2, at 1 atm of Benzene (1) + Toluene (2) + *m*-Xylene (3) and Calculated Activity Coefficients, γ_1, γ_2, and γ_3, as a Function of Liquid Mole Fractions, x_1 and x_2[a]

x_1	x_2	y_1	y_2	T/K	γ_1	γ_2	γ_3
0.136	0.252	0.360	0.359	388.13	1.032	1.298	1.103
0.153	0.147	0.463	0.247	389.36	1.079	1.449	1.055
0.217	0.198	0.513	0.253	383.35	1.040	1.310	1.099
0.298	0.201	0.611	0.213	378.32	1.026	1.250	1.128
0.375	0.224	0.675	0.197	371.81	1.012	1.184	1.172
0.413	0.262	0.694	0.205	371.37	1.004	1.137	1.215
0.462	0.293	0.722	0.205	368.92	1.000	1.101	1.264
0.506	0.333	0.743	0.211	366.62	1.001	1.069	1.322
0.525	0.315	0.758	0.197	366.02	1.001	1.072	1.315
0.565	0.346	0.776	0.200	364.13	1.004	1.051	1.367

[a] Mean deviations: MD(T) = 0.16 K; MD(y_1) = 0.004; MD(y_2) = 0.004. Standard deviations: SD(T) = 0.18 K; SD(y_1) = 0.004; SD(y_2) = 0.003.

Subscripts

i,j component numbers

Registry No. C_6H_6, 71-43-2; PhMe, 108-88-3; *m*-xylene, 108-38-3.

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Vapor–Liquid Equilibria at 1 atm for Ternary and Quarternary Systems Composed of Acetone, Methanol, 2-Propanol, and 1-Propanol

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The vapor–liquid equilibrium data for each system composed of acetone, methanol, 2-propanol, and 1-propanol at the isobaric condition of 1 atm are presented. The experimental data of the binary systems were used to calculate the binary parameters of the Wilson equation. These binary parameters have been used to calculate vapor-phase compositions and boiling points of related ternary and quarternary systems. Calculated vapor-phase compositions and boiling points have been obtained very close to the experimental data for each system investigated.

Introduction

The usual technique for obtaining vapor–liquid equilibrium data for binary systems is by direct measurement; i.e., equilibrium is established, and phases are sampled and analyzed. However, experimental measurements of vapor–liquid equilibria are quite scarce for multicomponent mixtures. Further, good experimental data are not easily obtained but require considerable experimental skill, experience, and patience. It is, therefore, an economic necessity to consider techniques for calculating vapor–liquid equilibria for multicomponent mixtures. Such techniques must require only a limited amount of experimental information and should be based on a theoretical foundation in order to be reliable for interpolation and extrapolation with respect to temperature, pressure, and composition.

The equation required to calculate vapor–liquid equilibria in multicomponent systems are, in principle, the same as those required for binary systems. In a system containing N components, we must solve simultaneously N nonlinear equations, applying tedious trial-and-error calculation that can be effectively carried out by an electronic computer (*1*) for each of the N components (eq 1).

$$\phi_i y_i P = \gamma_i x_i f_i \qquad (1)$$

For accurate calculation of vapor–liquid equilibria, it is usually necessary to take vapor-phase nonideality into account. This may be done through the use of an equation of state as discussed in numerous references (*2*, *3*). The fugacity coefficient ϕ_i can be calculated by using the equation-of-state rigorous thermodynamic relation (*4*). For pure polar gases, a correlation based on an extended corresponding state theory had been developed by O'Connell and Prausnitz (*5*).

The activity coefficient plays a key role in the calculation of vapor–liquid equilibria. The variation of activity coefficients with composition is best expressed through an auxiliary function g^E, the Gibbs energy defined by

$$G^E = RT\sum_{i=1}^{N} n_i \ln \gamma_i$$

Individual activity coefficients can be obtained from g^E upon introducing the Gibbs–Duhem equation for a multicomponent system at constant temperature and pressure.

$$\sum_{i=1}^{N} n_i \,\mathrm{d} \ln \gamma_i = 0$$

$$RT \ln \gamma_i = (\partial_G{}^E/\partial n_i)_{T,P,n_j} \; (j \neq i)$$

The key problem in calculating a multicomponent vapor–liquid equilibrium is to find an expression for g^E that provides a good approximation for the properties of the mixture. There are different types of expressions for g^E for binary systems can be extended to multicomponent systems (*6*, *7*, *8*). The Wilson equation (*6*) for a multicomponent muxture requires only parameters that can be obtained from related binary mixtures data. This feature provides an important economic advantage since the amount of experimental work required to characterize a multicomponent mixtures is thereby very much reduced. The extension of the Wilson's equation from the binary to the multicomponent case requires no additional assumptions. For a mixture composed of components i and j, the two parameters

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