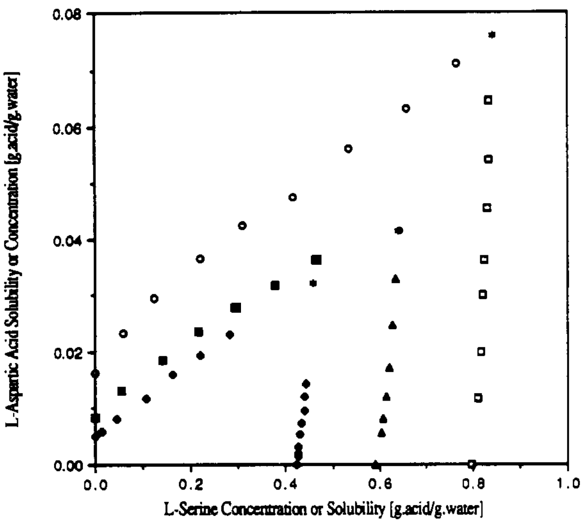

Figure 7. Solubility of L-aspartic acid and L-serine in their solutions: ◆, L-Asp solubility at 25 °C; ◇, L-Ser solubility at 25 °C; ■, L-Asp solubility at 40 °C; ▲, L-Ser solubility at 40 °C; ○, L-Asp solubility at 60 °C; □, L-Ser solubility at 60 °C.

Table VII. Total Liquid-Phase Concentration of Amino Acids at Eutectic Point

system	total solubility/ (g of acid/g of water) 25.0 °C	40.0 °C	60.0 °C
L-Glu + Gly			0.5415
L-Glu + L-Asp	0.1471	0.2500	0.5202
L-Glu + L-Ser	0.4996	0.6850	0.8934
L-Asp + L-Ser	0.4934	0.6837	0.9200

mixtures of this work has been cited in the preceding discussion in support of the existence of pure amino acid solids in preference to a solid solution. Experimentally we determine by the dry weight method the total solute concentration of the eutectic liquid solution that is saturated with both amino acids. Table VII presents the results for the four pairs of amino acids of this work.

By graphically extrapolating the experimental solubility of the two amino acids (Tables IV–VII) to intersect the measured total solubility within the uncertainty range, we determine the solubility of each amino acid in the eutectic solution and the precise total solubility reported in Table VII. The eutectic compositions indicated with an asterisk are included in Tables III–VI and Figures 4–6.

Acknowledgment

The constructive comments by Dr. William E. Acree Jr. are highly appreciated.

Registry No. L-Serine, 56-45-1; D-serine, 312-84-5; DL-proline, 609-36-9; DL-arginine, 7200-25-1; L-glutamic acid, 56-86-0; glycine, 56-40-6; L-aspartic acid, 56-84-8.

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Vapor–Liquid Equilibria of 2,3-Dimethylbutane + Methanol or Ethanol at 101.3 kPa

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Isobaric vapor–liquid equilibria were measured for 2,3-dimethylbutane + methanol or ethanol at 101.3 kPa. The experimental data were correlated with the nonrandom two-liquid (NRTL) and Wilson equations.

Introduction

In the present study, vapor–liquid equilibria (VLE) were measured for two binary systems, 2,3-dimethylbutane + methanol or + ethanol, at 101.3 kPa pressure using a vapor and liquid recirculate still. For 2,3-dimethylbutane + methanol, two sets of data are available in the literature (*1*, *2*), but those data are not consistent according to Gmehling and Onken (*3*). New reliable data seem, therefore, to be required for this system. No VLE data have been reported previously for 2,3-dimethylbutane + ethanol.

Experimental Section

Materials. 2,3-Dimethylbutane, methanol, and ethanol were special grade reagents. Methanol and ethanol were used after their minute water content was removed with molecular sieves 3A. A gas-chromatographic analysis on all three materials indicated that each had a purity of at least 99.9 mol %. Table I compares some of the measured properties with literature data.

Procedure. The equilibrium still used to obtain VLE data was a modified Rogalski–Malanowski (*4*) still with a provision for

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Table I. Normal Boiling Points, T_b, Densities, ρ, and Refractive Indexes, n_D, of the Materials Used

	T_b/K		ρ(298.15 K)/(g cm^{-3})		n_D(298.15 K)	
material	exptl	lit. (*16*)	exptl	lit. (*16*)	exptl	lit. (*16*)
2,3-dimethylbutane	331.16	331.138	0.661 27	0.657 02	1.3732	1.372 31
methanol	337.69	337.696	0.786 53	0.786 37	1.3288	1.326 52
ethanol	351.42	351.443	0.784 94	0.784 93	1.3594	1.359 41

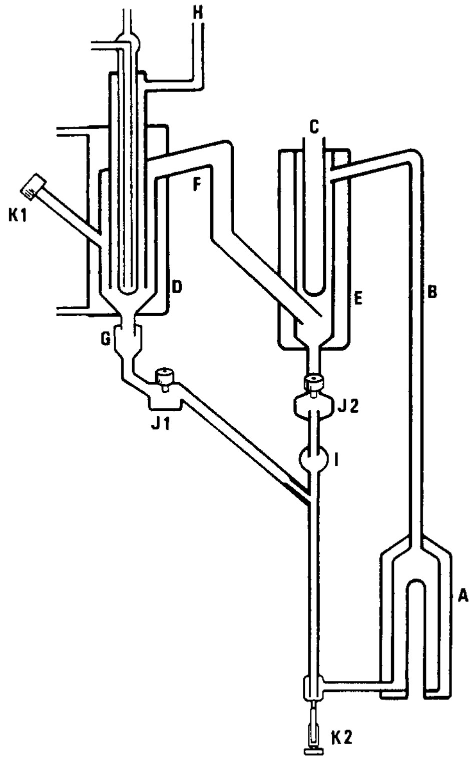

Figure 1. Schematic diagram of vapor–liquid equilibrium still: (A) boiling flask, (B) Cottrell pump, (C) thermometer well, (D) condenser, (E) equilibrium chamber, (F) heater for preventing partial condensation of vapor, (G) drop counter, (H) to atmosphere, (I) buffer for prevention of backward flow of mixing sample, (J1) and (J2) withdrawal of condensed vapor and liquid samples, (K1) valve for introducing samples, (K2) valve for removing liquid from still.

Table II. Antoine Constants of Materials Used[a] (*3*)

material	*A*	*B*	*C*
2,3-dimethylbutane	5.943 22	1131.833	−43.688
methanol	7.205 87	1582.271	−33.424
ethanol	7.237 10	1592.864	−46.966

[a] $\log (P/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) + C]$.

Table III. Isobaric Vapor–Liquid Equilibrium Data, Temperature, T, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficient, γ_i, for 2,3-Dimethylbutane (1) + Methanol (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
322.97	0.0627	0.4810	10.0603	1.0061
320.18	0.1029	0.5441	7.5557	1.0437
319.47	0.1217	0.5547	6.6619	1.0743
319.25	0.1280	0.5585	6.4218	1.0834
318.85	0.1495	0.5731	5.7116	1.0942
318.72	0.1557	0.5712	5.4898	1.1130
318.17	0.2230	0.5864	4.0036	1.1964
318.09	0.2670	0.5928	3.3879	1.2537
318.02	0.3059	0.6034	3.0147	1.2947
318.01	0.3631	0.6035	2.5411	1.4113
317.92	0.4114	0.6061	2.2587	1.5235
317.90	0.4844	0.6097	1.9305	1.7255
317.88	0.5808	0.6095	1.6108	2.1251
317.93	0.6524	0.6155	1.4404	2.5569
317.98	0.7377	0.6155	1.2758	3.3318
317.99	0.7951	0.6152	1.1828	4.2661
318.00	0.8403	0.6224	1.1313	5.3731
318.03	0.8744	0.6279	1.0954	6.7275
318.36	0.9071	0.6309	1.0492	8.8969
321.32	0.9616	0.7129	1.0109	14.8738

Table IV. Isobaric Vapor–Liquid Equilibrium Data, Temperature, T, Liquid-Phase, x_1, and Vapor-Phase, y_1, Mole Fractions, and Activity Coefficient, γ_i, for 2,3-Dimethylbutane (1) + Ethanol (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
343.05	0.0211	0.2977	10.2451	1.0001
336.35	0.0501	0.4851	8.4123	1.0032
331.93	0.0896	0.5890	6.4721	1.0162
330.57	0.1105	0.6182	5.7305	1.0278
329.29	0.1361	0.6473	5.0581	1.0369
327.90	0.1850	0.6754	4.0467	1.0790
327.60	0.2113	0.6835	3.6176	1.1026
327.21	0.2333	0.6906	3.3498	1.1292
327.21	0.2404	0.6925	3.2596	1.1329
326.76	0.2834	0.6998	2.8326	1.1973
326.35	0.3367	0.7087	2.4446	1.2799
326.01	0.3853	0.7147	2.1767	1.3745
325.70	0.4569	0.7208	1.8688	1.5451
325.60	0.5263	0.7251	1.6371	1.7529
325.46	0.5328	0.7272	1.6287	1.7754
325.42	0.5583	0.7289	1.5599	1.8699
325.27	0.6175	0.7320	1.4228	2.1501
325.25	0.6773	0.7332	1.3000	2.5396
325.23	0.7022	0.7333	1.2550	2.7536
325.16	0.7536	0.7354	1.1752	3.3128
325.28	0.7832	0.7422	1.1368	3.6503
325.39	0.8286	0.7610	1.0974	4.2652
325.56	0.8468	0.7699	1.0804	4.5613
325.59	0.8765	0.7806	1.0570	5.3925
326.47	0.9273	0.8155	1.0149	7.4187
327.27	0.9455	0.8448	1.0055	8.0446
328.88	0.9777	0.9149	1.0017	10.0805

vapor and liquid circulation. The modification concerned the withdrawal of the liquid sample (Figure 1) and prevented its contamination with the vapor condensate sample. A still with a total capacity of about 100 mL was used. An electric cartridge heater was inserted into the boiling flask, and a little glass dust was put on the wall of the heat-transfer surface to stabilize the boiling. The pressure, P, in the still was measured by means of a Fortin-type mercury barometer. Since the barometric pressure changed slightly, the experimental temperatures were corrected to 101.3 kPa. The equilibrium temperature, T, was measured with a calibrated platinum resistance thermometer with an accuracy of ±0.03 K.

Analysis. The equilibrium composition of the samples was determined using a Shimazu gas chromatograph, type GC-14A, equipped with a flame ionization detector. PEG-20M was used as column packing. The relationship between peak area and composition was determined from analysis of samples of known composition. The accuracy of liquid, x_i, and vapor, y_i, composition measurements is estimated to ±0.002 in mole fraction.

Results and Discussion

The activity coefficients γ_i were calculated using the following rigorous equation:

$$\phi_i P y_i = \gamma_i P_i^s x_i \phi_i^s \exp[v_i^L(P - P_i^s)/RT] \qquad (1)$$

where ϕ_i and ϕ_i^s, the fugacity coefficients of component i in the mixture and pure vapor, respectively, were evaluated by using the second virial coefficients obtained by the Hayden–

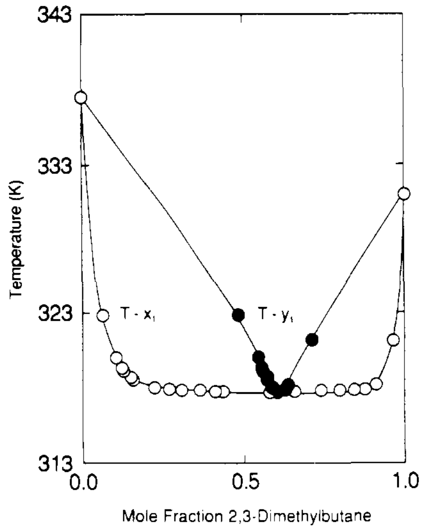

Figure 2. Temperature-composition diagram for the 2,3-dimethylbutane + methanol system: (○) and (●) this work, (—) NRTL equation.

O'Connell method (*5*). The vapor pressures of the pure component, P_i^s, were obtained using the Antoine equation constants (Table II). The liquid molar volumes, v_i^L, were calculated by the Rackett equation (*6*).

The VLE data for 2,3-dimethylbutane (1) + methanol (2) and 2,3-dimethylbutane (1) + ethanol (2) are reported in Tables III and IV along with the activity coefficients calculated using eq 1. Both binary systems form a minimum boiling azeotrope. The azeotropic points were determined on the basis of the experimental VLE data, and are x_1(AZ) = 0.612 and T(AZ) = 317.87 K for 2,3-dimethylbutane (1) + methanol (2), and x_1(AZ) = 0.733 and T(AZ) = 325.15 K for 2,3-dimethylbutane (1) + ethanol (2).

The experimental data were tested for thermodynamic consistency by using the point test of Fredenslund et al. (*7*) and of Van Ness et al. (*8*) and the area test of Herington (*9*) and of Redlich and Kister (*10*) as described by Gmehling and Onken (*3*). The results indicate that the experimental data for both systems are thermodynamically consistent.

The activity coefficients were correlated with the Wilson (*11*), modified Wilson (*12*), nonrandom two-liquid (NRTL) (*13*), and UNIQUAC (*14*) equations (see ref 3, Vol. I, Part 1). The parameters in each of these equations were obtained by using the Marquardt method (*15*). The sum of the squares of relative deviations in temperature and vapor composition was minimized during optimization of the parameters.

For 2,3-dimethylbutane (1) + methanol (2), the NRTL equation yielded the lowest mean deviations between the experimental and calculated temperatures, 0.08 K and vapor compositions, 0.004. The NRTL parameters for this system are found to be

$$g_{12} - g_{11} = 1492.715 \text{ J mol}^{-1}$$

$$g_{12} - g_{22} = 1325.630 \text{ J mol}^{-1} \qquad \alpha = 0.4427$$

The data for the system 2,3-dimethylbutane (1) + ethanol (2) were best correlated using the Wilson equation with parameters

$$\lambda_{12} - \lambda_{11} = 619.630 \text{ J mol}^{-1}$$

$$\lambda_{12} - \lambda_{22} = 1648.854 \text{ J mol}^{-1}$$

and an absolute average deviation of 0.006 in mole fraction and of 0.09 K in temperature. The calculated results using each of the activity coefficient equations are shown by solid lines in Figures 2–5.

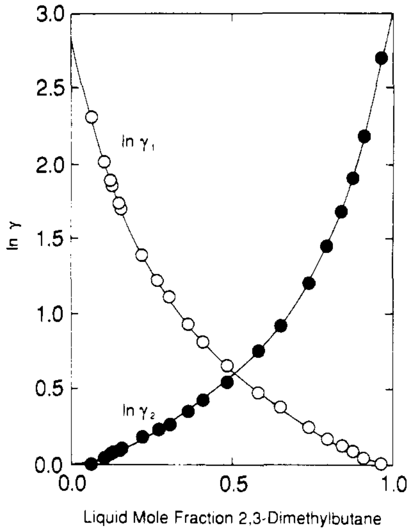

Figure 3. Activity coefficient–liquid composition diagram for the 2,3-dimethylbutane + methanol system: (○) and (●) this work, (—) NRTL equation.

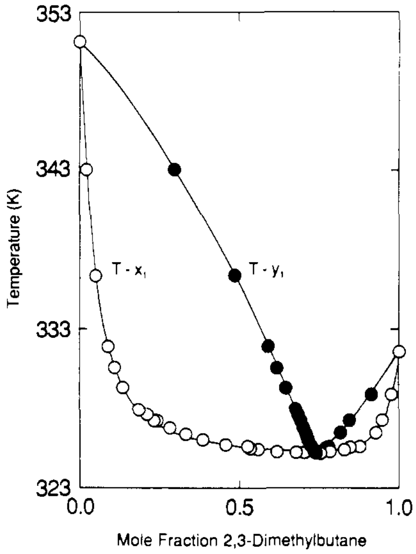

Figure 4. Temperature-composition diagram for the 2,3-dimethylbutane + ethanol system: (○) and (●) this work, (—) Wilson equation.

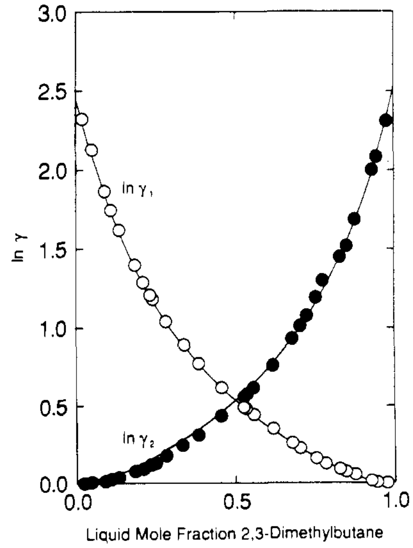

Figure 5. Activity coefficient–liquid composition diagram for the 2,3-dimethylbutane + ethanol system: (○) and (●) this work, (—) Wilson equation.

Glossary

P	total pressure
R	molar gas constant, $R = 8.3144$ J mol^{-1} K^{-1}
T	equilibrium temperature
x	mole fraction in liquid phase
y	mole fraction in vapor phase
Greek Letters	
γ	activity coefficient
Subscripts	
$i,j,1,2$	components

Registry No. 2,3-Dimethylbutane, 79-29-8; ethanol, 64-17-5; methanol, 67-56-1.

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Excess Molar Volumes of Tetrachloroethene + 1,4-Dioxane + Tetrahydrofuran at 298.15 and 308.15 K[†]

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Densities were determined for the tetrachloroethene (1) + 1,4-dioxane (2) + tetrahydrofuran (3) system at 298.15 and 308.15 K as a function of composition. From the experimental results, molar excess volumes were calculated. Different expressions exist in the literature to predict these excess properties from the binary mixtures. The empirical correlation of Jacob and Fitzner is the best for this system.

Introduction

A number of researchers (*1–6*) have proposed equations to predict ternary excess volume data from binary excess volume data. In this work we have tested these equations using data from the binary sets and ternary system generated from the following compounds: tetrachloroethene (1), 1,4-dioxane (2), and tetrahydrofuran (3). No data could be found for the excess volume of such mixtures. However, the main reason for the present investigation has to be found in our interest in ternary liquid mixtures having a tetrachloroethene as one component and cyclic ethers as the others.

Experimental Section

Materials. The chemicals used in the present study were tetrachloroethene and tetrahydrofuran supplied by Merk and 1,4-dioxane supplied by J. T. Baker. All solvents were used from freshly opened bottles without further purification. According to the specification of the suppliers, the purities were better than 99.5 mass % for tetrachloroethene, 99.8 mass % for tetrahydrofuran, and 99.5 mass % for 1,4-dioxane. All liquids were stored over molecular sieves (Union Carbide Type 4 A, from Fluka). The purity of the compounds was checked by determing their refractive indices and densities, which agreed well with the literature values.

Table I. Densities of Pure Substances

	$\rho \times 10^{-3}/(\mathrm{kg\ m^{-3}})$			
	298.15 K		308.15 K	
substance	exptl	lit.	exptl	lit.
tetrachloroethene (1)	1.6148	1.614 32[a]	1.5980	
1,4-dioxane (2)	1.0282	1.027 97[a]	1.0167	1.016 35[b]
tetrahydrofuran (3)	0.8823		0.8702	

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

Air and bidistilled water were used for densimeter calibration.

Mixture Preparation. All the solutions were prepared by using a Mettler H 315 balance (precision of 1×10^{-4} g) and air-tight stoppered bottles. The more volatile component was poured directly into the bottle. The charged bottle was closed and weighed. The second component (and the third component for ternary mixtures) was injected into the bottle through the stopper by means of a syringe. This procedure hindered any vapor loss and contamination. Hence, the possible error in the mole fraction is estimated to be lower than $\pm 2 \times 10^{-4}$.

Density Measurements. A digital densimeter (Anton Paar Model DMA 45) was employed for the determination of the densities of the pure components, the binary mixtures, and ternary mixtures. Water and air were chosen as calibrating fluids since they span a wide range and their densities are known at a high precision level. All measurements were carried out at atmospheric pressure. Pressure was measured by means of a mercury barometer. A Haake constant-temperature bath circulator was used with a temperature control interval of ±0.01 K. Temperature was detected with a digital thermometer (Digitec) calibrated and checked at the water triple

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