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Vapor–Liquid Equilibria for the 2-Propanol–Toluene System at 760 and 550 torr

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Isobaric vapor–liquid equilibria have been measured for the system 2-propanol–toluene at 760 and 550 torr in a modified Yerazunis, Plowright, and Smola equilibrium still. The data have been tested for thermodynamic consistency by using the area test of Redlich–Kister and Herington and the differential test of Van Ness and Mrazek. Van Laar, Margules, and Wilson's parameters have been estimated for the binary system. Wilson's parameters were utilized to predict the azeotropic composition which was in good agreement with the experimental value.

Introduction

The present investigation deals with the study of vapor–liquid equilibria of 2-propanol–toluene system at 760 and 550 torr. The vapor–liquid equilibrium data for the system 2-propanol–toluene have been reported at 760 torr by Kireev et al. (*1*, *2*).

Experimental Section

Materials. Table I lists the chemicals used, the physical properties, and our data compared with values from the literature. All products were purified by batch distillation at atmospheric pressure in a laboratory distillation column having 22 plates. To improve the purification the reflux ratio was kept high. In a 120-s cycle time the sample was withdrawn for 5 s and for the rest of the time the column was operated under total relux. The appropriate fraction was taken as the sample.

Apparatus. The equilibrium still used in the present experimental determination of vapor–liquid equilibrium (VLE) data for the 2-propanol–toluene system is shown in Figure 1. This equilibrium still is Kay's modification (*3*) of the Yerazunis, Plowright, and Smola equilibrium still. The essential elements of the still are the Cottrell pump A, the vapor–liquid equilibrium chamber I, the condensers F and F′, the coolers E and E′, the sampling ports D and D′, the tube C filled with glass beads for mixing the vapor condensate and liquid streams before returning the mixture to the pump for the recycle operation, the ebulliometer, and a mercury manometer. The mercury heights were determined with a cathetometer whose accuracy is ±0.01 mm.

All observed pressures were corrected to give the equivalent height of a mercury column at 273.15 K. Temperatures were measured with a copper–constantan thermocouple and potentiometer (Leeds and Northrup Inc., K-3 Universal potentiometer) with a stated accuracy of 0.01 K.

Compositions of the equilibrium liquid and condensed vapor were obtained from measurement of their refractive indexes at 303.15 K with an Abbe type refractometer with an accuracy of ±0.0002, having previously established the relation between the refractive index and the composition experimentally.

Results and Discussion

Results and Consistency Criteria. The raw T-X-Y data measured for the system at two isobaric conditions along with γ_1 and γ_2 values are reported in Tables II and III. To check for the thermodynamic consistency, we used the area test of Redlich–Kister and Herington and the differential test of Van Ness and Mrazek. A detailed description of the methods was presented by Prausnitz (*4*). The required heat of mixing for the binary mixture and the heat capacities of the mixtures appear in the work of Shah and Donnelly (*5*).

Table I. Physical Properties of Pure Components

component	vendor	stated purity, %	bp, K exptl	bp, K lit.	D exptl	D lit.
2-propanol	E. Merck	99.7	355.45	355.55	1.3779	1.3776
toluene	BDH, analytical reagent	99.5	383.65	383.75	1.4957	1.4969

[a] Experimental and literature value at 293.15 K. Reference: "Lange's Handbook of Chemistry"; Dean, J. A., Ed.; McGraw-Hill: New York, 1973.

Table II. Experimental T-X-Y-γ_1-γ_2 Data for 2-Propanol (1)–Toluene (2) System at 760 torr

T, K	X_1	Y_1	γ_1	y_2
377.42	0.0241	0.1822	3.481 51	1.000 59
365.94	0.1110	0.4534	2.759 01	1.031 79
361.27	0.2124	0.5575	2.099 99	1.090 54
358.61	0.3386	0.6195	1.609 54	1.205 12
358.40	0.3730	0.6401	1.530 52	1.241 41
356.78	0.4654	0.6744	1.370 61	1.356 40
355.92	0.5600	0.7073	1.236 76	1.522 61
355.59	0.6424	0.7411	1.137 32	1.735 80
354.92	0.7381	0.7640	1.061 50	2.081 39
354.54	0.7981	0.8096	1.038 33	2.331 91
354.55	0.8691	0.8603	1.023 07	2.598 02
354.55	0.8894	0.8771	1.018 58	2.660 14
354.91	0.9358	0.9253	1.004 25	2.809 34
355.08	0.9593	0.9427	0.997 21	2.932 26
355.43	0.9848	0.9744	0.986 36	4.006 35

Table III. Experimental T-X-Y-γ_1-γ_2 Data for 2-Propanol (1)–Toluene (2) System at 550 torr

T, K	X_1	Y_1	γ_1	γ_2
360.49	0.0504	0.3390	4.075 70	1.013 18
358.94	0.0618	0.3676	3.764 42	1.036 04
351.61	0.2222	0.5678	2.182 02	1.084 95
349.29	0.3141	0.6215	1.831 48	1.169 46
348.39	0.3930	0.6496	1.606 52	1.275 98
347.83	0.4421	0.6604	1.486 21	1.350 51
347.38	0.5196	0.6792	1.329 75	1.484 54
347.22	0.5583	0.7014	1.269 12	1.564 21
346.70	0.6488	0.7289	1.167 23	1.796 93
346.56	0.6811	0.7412	1.140 74	1.897 88
346.30	0.7655	0.7800	1.081 04	2.207 15
346.23	0.8039	0.8039	1.057 21	2.375 67
346.31	0.8349	0.8176	1.040 54	2.532 05
346.50	0.8778	0.8582	1.022 53	2.791 31
346.97	0.9475	0.9210	1.000 39	3.451 82
347.05	0.9536	0.9281	0.997 27	3.546 66

The VLE data are presented in Figures 2–5 for the 2-propanol (1)–toluene (2) system at 760 and 550 torr. The system at 760 torr forms an azeotrope with 85 mol % 2-propanol and the system at 550 torr forms an azeotrope with 80 mol % 2-propanol.

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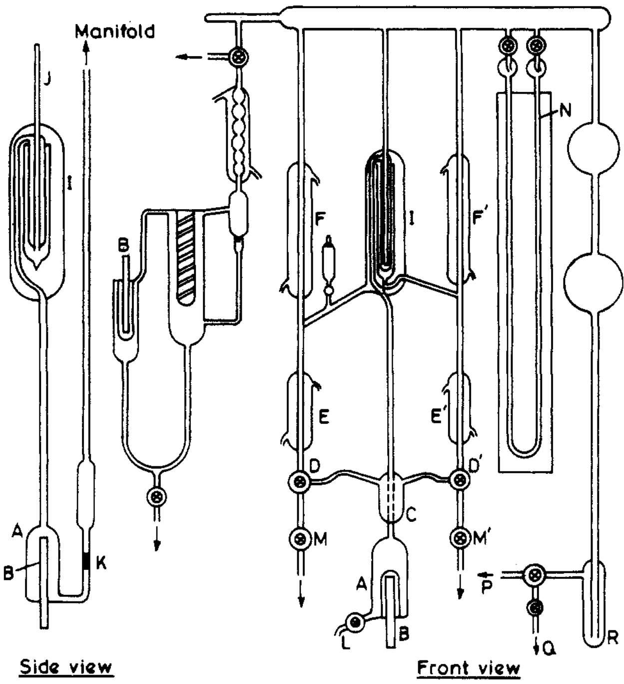

Figure 1. Modified Yerazunis-Plowright-Smola equilibrium still: A, Cottrel pump; B, electric heater; C, liquid mixing cell; D, D′, sample ports; E, E′, coolers; F, F′, condensers; I, equilibrium chamber; J, thermocouple well; K, check valve; L, drain; M, M′, liquid traps; N, mercury manometer; P, vacuum pump; O, compressed nitrogen gas tank; R, cold trap; T, surge tanks.

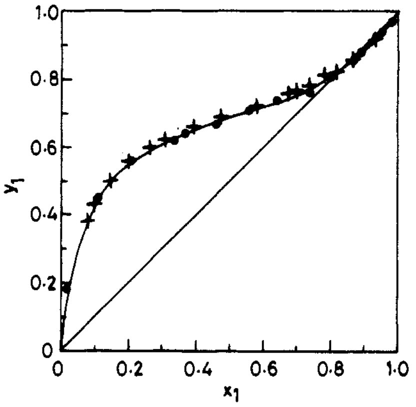

Figure 2. Vapor-liquid equilibrium data for the 2-propanol (1)-toluene (2) system at 760 torr: ●, experimental data; —; fitted curve; X_1 (azeotrope) = 0.85; +, experimental data of Kireev et al.

Table IV. Estimated Parameters and Comparison of Experimental and Calculated Vapor-Phase Composition for the System 2-Propanol (1)–Toluene (2)

	p, torr	A_{12}	A_{21}	$\Delta Y_{\text{mean}}{}^{a}$	ΔY_{max}
Margules	760	1.333 51	1.222 62	0.0161	0.0481
	550	1.662 14	1.236 67	0.0161	0.0669
Van Laar	760	1.334 01	1.218 80	0.0156	0.0464
	550	1.627 92	1.271 20	0.0118	0.0552
Wilson	760	0.385 48	0.545 75	0.0126	0.0313
	550	0.348 12	0.497 50	0.0065	0.0240

[a] $\Delta Y_{\text{mean}} = (\sum|Y_{1\text{exptl}} - Y_{1\text{calcd}}|)/N$ where N = number of data points.

The liquid-phase activity coefficients were obtained from the following equation which takes into account the vapor-phase imperfections.

$$\ln \gamma_i = \ln \frac{YP}{XP_i^{\text{sat}}} + \frac{B_{ii}(P - P_i^{\text{sat}}) + P\delta_{ij}Y_j^2}{RT} \tag{1}$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \tag{2}$$

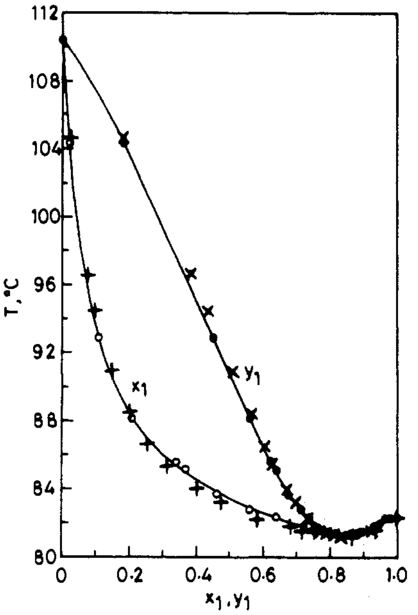

Figure 3. T-X-Y diagram at constant pressure for 2-propanol (1)-toluene (2) system: p = 760 torr; ○, ●, experimental data; —, fitted curve; +, ×, experimental data of Kireev et al.

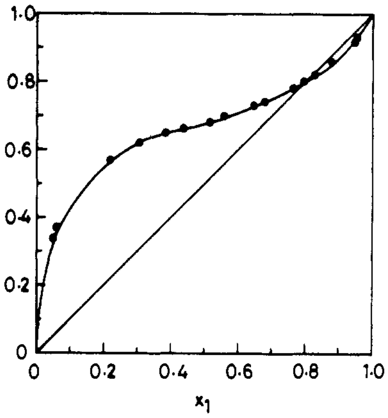

Figure 4. Vapor-liquid equilibrium data for the 2-propanol (1)-toluene (2) system at 550 torr: ●, experimental data; —, fitted curve; X_1 (azeotrope) = 0.80.

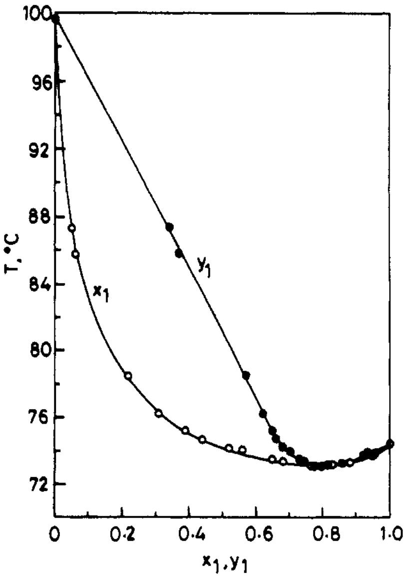

Figure 5. T-X-Y diagram at constant pressure for 2-propanol (1)-toluene (2) system: p = 550 torr; ○, ●, experimental data; —, fitted curve.

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

Registry No. 2-Propanol, 67-63-0; toluene, 108-88-3.

Literature Cited

(1) Kireev V. A.; Sheinker, Y. N.; Peresleni, E. M. *Zh. Fiz. Khim.* **1952**, *26*, 352. Gmehling, J.; Onken, V. "Vapor Liquid Equilibrium Data Collection"; Dechema Chemistry Data Series, 1977; Vol. I.
(2) Hirata, M.; Ohe, S.; Nagahama, K. "Computer Aided Data Book of Vapor Liquid Equilibrium"; Elsevier: Amserdam, 1975.
(3) Kay, W. B. *AIChE J.* **1979**, *25*, 179.
(4) Prausnitz, J. M. "Molecular Thermodynamics of Fluid Phase Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1969.
(5) Shah, V. D.; Donnelly, H. G. *Chem. Eng. Prog. Symp. Ser.* **1967**, *63*, 105.
(6) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(7) Nagahama, K.; Suzuki, I.; Hirata, M. *J. Chem. Eng.* (*Jpn*) **1971**, *4*, 1.

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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 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.

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

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.

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