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Isobaric Vapor−Liquid Equilibria for the Binary System 2-Propanol + Methyl Ethyl Ketone and for the Ternary System 1-Butanol + 2-Propanol + Methyl Ethyl Ketone at 101.3 kPa

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Isobaric vapor−liquid equilibrium data have been measured for the 2-propanol + methyl ethyl ketone binary system and for the 1-butanol + 2-propanol + methyl ethyl ketone ternary system at 101.3 kPa in a temperature range from 351 to 382 K. The data were found to be thermodynamically consistent according to the point to point L−W method of Wisniak. The equilibrium data were correlated using Wilson, NRTL, and UNIQUAC models for which the parameters are reported.

Introduction

Vapor−liquid equilibrium (VLE) data are indispensable in the design of separation processes such as distillation. These data can be obtained experimentally or by using generalized methods that allow the calculation of the properties of the mixtures. Experimental measurements of vapor−liquid equilibria for ternary or higher mixtures are quite scarce because of the experimental effort necessary to obtain a complete description of the system.

This paper reports the results of measurements of vapor−liquid equilibria for the system 1-butanol + 2-propanol + methyl ethyl ketone at 101.3 kPa. For this system no VLE data have been previously reported, as far as we know. For the three binary systems included in this ternary system, VLE data at 101.3 kPa can be found in the literature: 1-butanol + 2-propanol, ref 1; 1-butanol + methyl ethyl ketone, ref 2; 2-propanol + methyl ethyl ketone, ref 3.

But for one of them, the 2-propanol + methyl ethyl ketone binary system, only a few tie lines were reported. Hence, we decided to include this binary system in our experimental study.

Experimental Section

Chemicals. Ethanol (Panreac), 1-butanol (Merck), 2-propanol (Merck), and methyl ethyl ketone (Merck) had nominal purities >99.5, >99.9, >99.7, and >99.5 mass %, respectively. The first one was used as internal standard for chromatography. All of them were used as supplied after chromatography failed to show any significant organic impurities. The Karl Fischer method determined that the water content in the chemicals was negligible.

Apparatus and Procedure. The vessel used in this work was an all glass, dynamic recirculating still described elsewhere,[4] equipped with a Cottrell pump. The still (Labodest model) manufactured by Fischer Labor und Verfahrenstechnik (Germany) is capable of handling pressures from 0.25 to 400 kPa and temperatures up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in close contact between themselves and with the sensor element. The equilibrium temperatures were measured by means of a Pt-100 thermometer connected to an ERTCO-Hart (model 5614) with an uncertainty of 0.006 °C according to the certificate of calibration (scale ITS 90[5]). A Fischer M101 phase equilibrium control system was used to measure and control the pressure and the heating power. The measured pressure in the still was 101.3 ± 0.1 kPa.

Table 1. Experimental Vapor−Liquid Equilibrium Data for the Binary System Methyl Ethyl Ketone (3) + 2-Propanol (2) at 101.3 kPa

T/K	x_3	y_3	T/K	x_3	y_3
355.71	0.000	0.000	350.82	0.450	0.493
354.40	0.038	0.071	350.58	0.550	0.569
353.74	0.082	0.133	350.54	0.720	0.700
353.00	0.139	0.205	350.87	0.846	0.815
352.00	0.239	0.312	351.86	0.955	0.937
351.33	0.338	0.402	352.74	1.000	1.000

In each experiment, after the pressure was fixed, heating and shaking of the liquid mixture was started. The still was operated until equilibrium was reached. Equilibrium conditions were assumed when temperature and pressure remained constant for at least 30 min. After this time, 0.5 mL samples of liquid and condensed vapor phases were taken with syringes without disruption of the operation. An internal standard was added to each sample for the analytical determination. The standard compound used for this purpose was ethanol.

All the samples were analyzed by gas chromatography (Shimadzu chromatograph GC-14A, equipped with an electronic integrator Shimadzu C-R6A Chromatopac and an automatic injector Shimadzu AOC-14). Good separation of the four components (including the internal standard) was obtained on a 2 m by 3.175 mm column packed with Porapack Q-S 80/100. The column temperature was 160 °C, and detection was carried out using FID for all the samples. The helium flow rate was adjusted to 30 mL·min^{-1}. The standard deviation in the mole fraction was <0.002 for all the samples.

Results and Discussion

The experimental VLE data for the binary system 2-propanol + methyl ethyl ketone are given in Table 1 and Figure 1, where published results for this system[3] were also included. Only five binary equilibrium data points were

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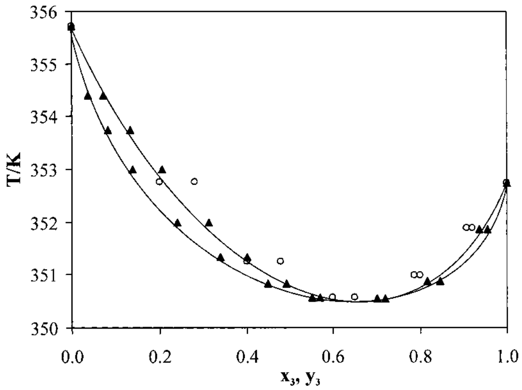

Figure 1. Temperature versus composition for the binary system 2-propanol (2) + methyl ethyl ketone (3) at 101.3 kPa: experimental (▲); literature (○).

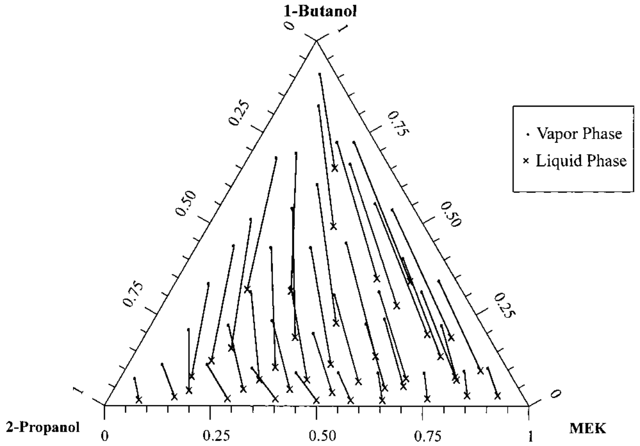

Figure 2. Vapor–liquid equilibrium tie lines for the ternary system 1-butanol (1) + 2-propanol (2) + methyl ethyl ketone (3) at 101.3 kPa.

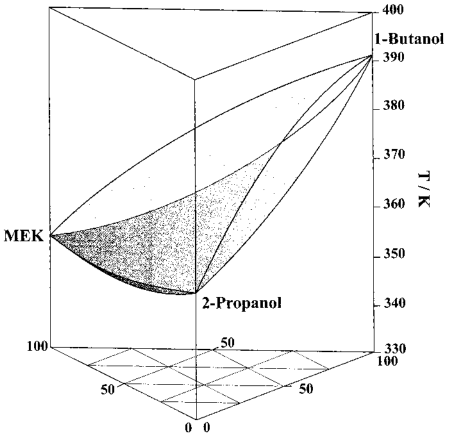

Figure 3. Experimental liquid and vapor equilibrium surfaces' temperature–composition plots for the ternary system 1-butanol (1) + 2-propanol (2) + methyl ethyl ketone (3) at 101.3 kPa.

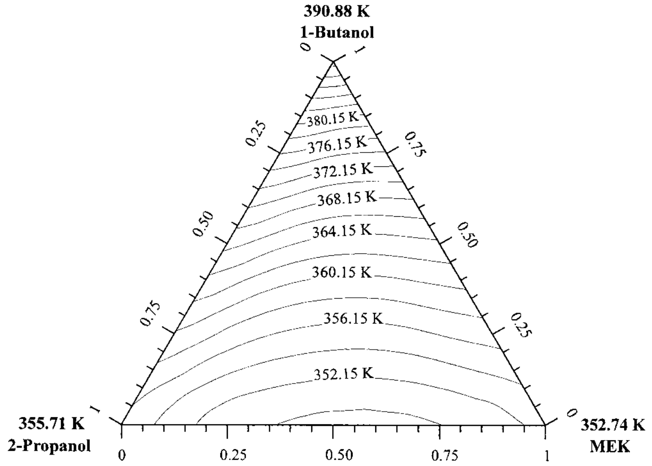

Figure 4. Liquid–vapor isotherms for the ternary system 1-butanol (1) + 2-propanol (2) + methyl ethyl ketone (3) at 101.3 kPa, calculated with the UNIQUAC equation as a function of the liquid mole fraction.

Table 2. Experimental Vapor–Liquid Equilibrium Data for the Ternary System 1-Butanol (1) + 2-Propanol (2) + Methyl Ethyl Ketone (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2
353.56	0.099	0.046	0.024	0.062
358.51	0.337	0.045	0.097	0.067
364.43	0.535	0.052	0.186	0.090
370.58	0.722	0.049	0.339	0.110
382.28	0.906	0.040	0.653	0.133
377.61	0.818	0.087	0.491	0.216
371.70	0.723	0.090	0.346	0.186
370.06	0.660	0.091	0.274	0.173
363.82	0.550	0.087	0.194	0.144
360.50	0.399	0.097	0.133	0.142
355.88	0.307	0.099	0.079	0.135
355.35	0.215	0.099	0.069	0.135
352.69	0.091	0.106	0.024	0.136
352.13	0.087	0.202	0.016	0.232
354.29	0.234	0.224	0.050	0.272
357.02	0.310	0.198	0.073	0.255
361.03	0.442	0.210	0.133	0.295
368.41	0.603	0.198	0.224	0.342
372.47	0.689	0.204	0.311	0.405
372.79	0.675	0.256	0.317	0.504
366.17	0.538	0.290	0.188	0.456
361.22	0.428	0.300	0.115	0.411
356.26	0.299	0.308	0.066	0.370
354.07	0.221	0.273	0.047	0.317
351.29	0.085	0.312	0.015	0.338
351.31	0.086	0.406	0.013	0.415
353.14	0.195	0.409	0.035	0.446
356.95	0.320	0.401	0.069	0.489
360.46	0.430	0.393	0.104	0.546
365.00	0.507	0.402	0.157	0.623
360.80	0.435	0.476	0.120	0.688
356.12	0.307	0.499	0.071	0.599
354.56	0.229	0.490	0.045	0.542
351.53	0.086	0.505	0.013	0.494
352.03	0.101	0.602	0.017	0.589
354.39	0.217	0.598	0.042	0.653
359.28	0.329	0.588	0.077	0.754
356.96	0.205	0.699	0.040	0.781
353.49	0.108	0.702	0.018	0.700
354.74	0.108	0.809	0.020	0.826
355.00	0.068	0.893	0.011	0.912

presented in the previous paper. We have obtained nine VLE data points. Discrepancies are evident between the two series of results. However, the actual scale of the plot, where the *y*-axis has been magnified to show the equilibrium data clearly, should be considered to avoid misinterpretations. For example, with a maximum difference in the equilibrium temperature of 0.5 °C, discrepancies between the present study and the literature can be explained.

The binary equilibrium data were found to be thermodynamically consistent as tested by two point-to-point methods, the Van Ness[6] (modified by Fredenslund[7]) and Wisniak[8] consistency tests. The 2-propanol + methyl ethyl ketone binary system shows a minimum boiling azeotrope that has been previously determined by other authors.[9] The azeotrope contains 0.665 mol fraction of methyl ethyl ketone and boils at 350.65 K.

Table 3. Correlation Results of the Experimental Binary and Ternary Data and Prediction Using Interaction Parameters from Binary Data for the System 1-Butanol (1) + 2-Propanol (2) + Methyl Ethyl Ketone (3) Using Wilson, NRTL, and UNIQUAC Equations

model	ij	A_{ij}[a]	A_{ji}	α_{ij}	MAD(T)[b]/K	MAD(y_1)	MAD(y_2)	MAD(y_3)
Prediction Using Interaction Parameters from Binary Data in the Literature[11]								
Wilson					0.82	0.0122	0.0074	0.0074
NRTL					0.81	0.0125	0.0085	0.0085
UNIQUAC					1.11	0.0141	0.0116	0.0116
Correlation of the Experimental Binary and Ternary Data								
Wilson	1-2	147.03	−82.49		0.67	0.010	0.008	0.009
	1-3	124.32	48.67					
	2-3	62.35	233.41					
NRTL	1-2	−337.72	502.66	0.3	0.68	0.010	0.008	0.008
	1-3	−73.01	262.55	0.3				
	2-3	242.20	24.31	0.3				
UNIQUAC	1-2	−86.70	108.76		0.67	0.010	0.009	0.009
	1-3	−6.04	63.12					
	2-3	122.55	−18.00					

[a] $A_{ij} = (g_{ij} - g_{jj})/R$ (K). [b] MAD = mean absolute deviation.

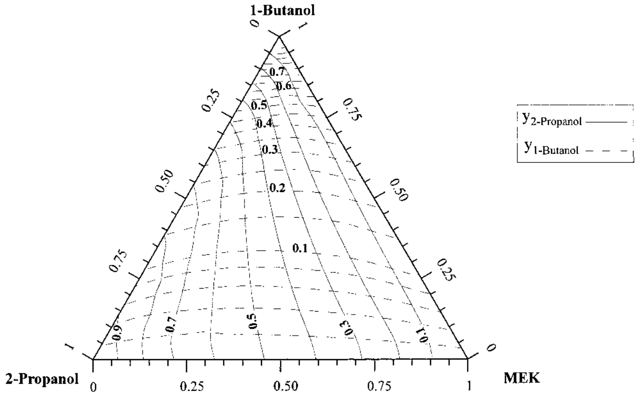

Figure 5. Vapor phase composition for the ternary system 1-butanol (1) + 2-propanol (2) + methyl ethyl ketone (3) at 101.3 kPa calculated with the UNIQUAC equation as a function of the liquid mole fraction; the basic grid represents the liquid composition (x_i); the parametric curves indicate equilibrium vapor mole fractions of 1-butanol (- - -) and 2-propanol (—).

Ternary VLE measurements (compositions of the liquid and vapor phases and the corresponding equilibrium temperatures) are listed in Table 2 and shown in Figure 2, where liquid and vapor equilibrium compositions are represented in a triangle and connected with straight lines. In Figure 3, liquid and vapor surfaces, including experimental equilibrium points obtained in this paper, are quantitatively shown.

The ternary VLE experimental data were found to be thermodynamically consistent as tested by the point-to-point L−W method of Wisniak.[8] All the values of $D = 100(L-W)/(L+W)$ were less than 3. Vapor pressures were calculated with the Antoine equation, whose parameters A_i, B_i, and C_i for 1-butanol, 2-propanol, and methyl ethyl ketone were taken from the literature.[10]

The Wilson, NRTL, and UNIQUAC equations have been used to predict the ternary data using interaction parameters obtained from binary data.[11] Mean absolute deviations (MAD(T) and MAD(y_i)) between calculated and experimental data are included in Table 3.

Experimental binary and ternary data have been correlated simultaneously using also Wilson, NRTL, and UNIQUAC models. Equilibrium data for 1-butanol + 2-propanol and 1-butanol + methyl ethyl ketone have been taken from the literature.[1,2] The pure component molecular structure constants for the UNIQUAC equation were those included in the databank of ChemCad 5.[11] An ideal vapor phase was assumed. The objective function for the optimization was

$$\mathrm{OF} = \sum_n \sum_i (y_{i,n(\exp)} - y_{i,n(\mathrm{cal})})^2$$

where $y_{i,n}$ is the mole fraction in the vapor phase for the i-component at equilibrium point number n, and exp and cal represent the experimental and the calculated data.

The interaction parameters obtained and the mean absolute deviations are reported in Table 3. A very satisfactory correlation of the experimental temperature−composition results was obtained with the three models.

Figure 4 shows the isotherms of the ternary system as a function of liquid mole fraction. In Figure 5, the mole fraction of component i in the liquid, x_i, is represented by the basic grid, and the vapor mole fraction, y_i, in equilibrium with the liquid is shown as parametric curves.

Literature Cited

Morozov, A. V.; Sarkisov, A. G.; Turovsky, V. B. *Zh. Fiz. Khim.* **1978**, *52*, 1822 (in Russian) (Found at: Gmehling, J., Onken, U., Weidlich, U., Eds. *Vapor-Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Franckfurt/Main, 1982; Supplement 2, Vol. I, Part 2d, p 55).

Park, W. K.; Chung, B. Y.; Shim, H. S. *Hwahak Konghak* **1972**, *10*, 281 (in Russian) (Found at: Gmehling, J., Onken, U., Weidlich, U., Eds. *Vapor-Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Franckfurt/Main, 1982; Supplement 2, Vol. I, Part 2d, p 165).

Zharov, V. T.; Malegina, N. D.; Morchevsky, A. G. *Zh. Prikl. Khim.* **1965**, *38*, 2132 (in Russian) (Found at: Gmehling, J., Onken, U., Artl, W., Eds. *Vapor-Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Franckfurt/Main, 1978; Vol. I, Part 2b, p 54).

Walas, S. M. *Phase Equilibria in Chemical Engineering*; Butterworth: London, 1985.

Mangum, B. W.; Furukawa, G. T. *Guidelines for realizing the International Temperature Scale*; Technical Note 1265; U.S. Department of Commerce National Technical Information Service: Springfield, 1990.

Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor-Liquid Equilibrium: I. Appraisal of data reduction method. *AIChE J.* **1973**, *19*, 238−244.

Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.

Wisniak, J. A New Test for the Thermodynamic Consistency of Vapor-Liquid Equilibrium. *Ind. Eng. Chem. Res.* **1993**, *32*, 1531−1533.

Nagata, I. Isobaric Vapor-Liquid Equilibrium Data for Binary Systems. *Can. J. Chem. Eng.* **1963**, *41*, 21−23.

Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

CHEMCAD V; Process Flowsheet Simulator, version 5.1; Chemstations Inc.: Houston, TX, 1993.

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