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Phase Equilibria in the Binary and Ternary Systems Composed of Diethyl Ketone, 2-Pentanone, and 3-Pentanol at 101.3 kPa

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New vapor−liquid equilibrium data for the binary systems diethyl ketone + 2-pentanone, diethyl ketone + 3-pentanol and 2-pentanone + 3-pentanol and for the diethyl ketone + 2-pentanone + 3-pentanol ternary system are reported at 101.3 kPa. The data were found to be thermodynamically consistent according to the Van Ness−Byer−Gibbs method for the binary systems and according to the McDermott−Ellis method for the ternary one. The experimental results show that the diethyl ketone + 2-pentanone system is well represented by assuming ideal behavior. The other binary systems exhibit slight positive deviations from ideality, and no azeotrope is present. The VLE data have been correlated with the Wilson, UNIQUAC, and NRTL equations. The ternary system does not present an azeotrope and is well predicted from the binary interaction parameters.

Introduction

The experimental determinations of vapor−liquid equilibria (VLE) are indispensable for the design of separation processes such as distillation columns, extractive distillation, and selection of solvents. Although these data can be estimated from available predictive VLE models, experimental data are required to update and improve the data bank used to fit the model parameters. Among these models, group contribution methods such as UNIFAC[1−3] have been shown to be a useful tool, so they have been implemented in widely used chemical engineering simulators.

Group contribution models require a complete and updated experimental VLE data bank in order to fit the group interaction parameters. In the last few decades, a great body of experimental data for mixtures of organic compounds has been reported. However, there is still a scarcity of experimental data, that, in some cases, can lead to uncertain calculations. This is the case for the system studied herein, for which no literature data have been found. In this paper, isobaric experimental VLE data for the binary and ternary systems composed of diethyl ketone, 2-pentanone, and 3-pentanol are presented. The experimental data show slight deviations from ideality, and no azeotropes were found, while some of the commercial simulators predict three binary azeotropes, one for each binary system, and one ternary azeotrope by the UNIFAC method.

Experimental Section

Chemicals. High purity diethyl ketone, 2-pentanone, and 3-pentanol from Aldrich Chemical Co. were used without further purification. The purities of all chemicals, checked by gas chromatography (GC), were as follows: diethyl ketone (99.90 mass %), 2-pentanone (99.88 mass %), and 3-pentanol (99.91 mass %). 3-Pentanol was dehydrated by using zeolite A (4 Å). Experimental densities of the pure liquids at 298.15 K were measured with a digital precision densimeter (Anton Paar DMA55). The refractive indexes at 298.15 K were measured using a refractometer (Abbe ATAGO 3T). Temperature was controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements were ±0.01 kg·m^{-3} and ±0.0002, respectively. The boiling points were determined using the apparatus described below. The experimental values of these properties are listed in Table 1 together with the literature values.

Table 1. Density, *d*, Refractive Index, n_D, and Normal Boiling Point, T_b, of the Chemicals

	d(298.15 K)/kg·m^{-3}		n_D(298.15 K)		T_b(101.3 kPa)/K	
component	exptl	lit.	exptl	lit.	exptl	lit.
diethyl ketone	809.43	809.46[a]	1.3900	1.3900[b]	374.75	374.73[a]
2-pentanone	801.47	802.01[b]	1.3881	1.3880[b]	375.09	375.40[e]
3-pentanol	815.50	816.03[c]	1.4087	1.4085[d]	388.38	388.45[b]

[a] Reference 6. [b] Reference 16. [c] Reference 7. [d] Reference 17. [e] Reference 5.

Apparatus and Procedures. The equilibrium vessel used in this work is an all-glass, dynamic recirculating still described by Walas,[4] equipped with a Cottrell pump. The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Bonn, Germany), is capable of handling pressures from (0.25 to 400) kPa, and temperatures up to 523.15 K. In the boiler, vapor is generated by external heating. The Cottrell pump ensures intimate contact between the liquid and vapor phases and also with the temperature sensing element. The equilibrium temperature is measured with a digital Hart Scientific thermometer model 1502A and a Pt 100 probe Hart Scientific model 5622 calibrated at the Spanish Instituto Nacional de Técnica Aeroespacial. The accuracy is estimated to be ±0.02 K. For the pressure measurement, a digital manometer with an accuracy of ±0.01 kPa is used. The temperature probe was calibrated against the ice and steam points of distilled water. High purity (>99.9 mass %) hexane vapor pressures were used for the manometer calibration.

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Table 2. Antoine Coefficients, Eq 1

compound	A_i	B_i	C_i
diethyl ketone	15.2106	3681.51	−27.18
2-pentanone	15.1864	3681.15	−26.75
3-pentanol	14.8622	3045.99	−91.03

Table 3. Experimental Vapor−Liquid Equilibrium Data for Diethyl Ketone (1) + 2-Pentanone (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
375.09	0.000	0.000		
375.08	0.046	0.047	1.013	0.999
375.07	0.094	0.096	1.007	0.999
375.07	0.143	0.145	1.001	0.999
375.07	0.194	0.196	1.000	0.998
375.06	0.295	0.298	1.000	0.997
375.04	0.395	0.398	0.997	0.997
374.99	0.492	0.495	0.999	0.997
374.89	0.686	0.688	0.999	0.999
374.85	0.779	0.781	0.999	0.999
374.85	0.827	0.829	0.998	1.000
374.79	0.890	0.891	0.999	1.006
374.74	0.942	0.942	1.000	1.011
374.75	1.000	1.000		

Table 4. Experimental Vapor−Liquid Equilibrium Data for Diethyl Ketone (1) + 3-Pentanol (3) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_3
388.38	0.000	0.000		
387.94	0.019	0.031	1.101	1.003
387.34	0.048	0.078	1.119	1.004
386.40	0.095	0.146	1.088	1.011
385.58	0.137	0.211	1.119	1.008
385.16	0.167	0.249	1.097	1.009
383.85	0.237	0.336	1.080	1.020
383.01	0.292	0.401	1.073	1.022
382.23	0.343	0.455	1.060	1.031
381.34	0.404	0.519	1.054	1.035
380.70	0.448	0.570	1.063	1.024
380.07	0.494	0.615	1.062	1.021
379.51	0.536	0.652	1.054	1.028
379.02	0.583	0.690	1.040	1.038
378.50	0.629	0.725	1.030	1.054
377.83	0.674	0.766	1.035	1.048
377.40	0.721	0.799	1.024	1.064
376.91	0.765	0.832	1.019	1.079
376.48	0.811	0.867	1.015	1.077
375.99	0.857	0.900	1.011	1.097
375.48	0.900	0.929	1.009	1.128
375.11	0.942	0.959	1.008	1.123
374.85	0.974	0.981	1.005	1.146
374.75	1.000	1.000		

In each VLE experiment, the pressure was fixed and held constant by using a vacuum pump, and the heating and shaking systems of the liquid mixture were turned on. The system was kept at the boiling point at least for 30 min to ensure that the steady state was reached. Then, samples of liquid and condensed vapor were taken for analysis. The sample extractions were carried out with special syringes to withdraw small volume samples (1.0 μL). At least two analyses were made for each sample.

Analysis. All the samples of liquid and condensed vapor were analyzed by using a CE instruments GC 8000 Top gas chromatograph with a flame ionization detector. The chromatographic column was a 30 m, 0.454 mm i.d. capillary column, DB-MTBE (J&WScientific). The GC response peaks were treated with Chrom-Card for Windows, Version 1.21. Column, injector, and detector temperatures were (333, 473, and 498) K, respectively, for all the systems. The gas chromatograph was calibrated with gravimetrically prepared standard solutions. Twenty binary and sixty ternary samples covering the entire composition range were prepared to calibrate the gas chromatograph and were measured in triplicate. The standard deviation in the mole fraction was usually <0.001.

Table 5. Experimental Vapor−Liquid Equilibrium Data for 2-Pentanone (2) + 3-Pentanol (3) at 101.3 kPa

T/K	x_2	y_2	γ_2	γ_3
388.38	0.000	0.000		
387.96	0.017	0.029	1.142	1.003
387.31	0.048	0.079	1.159	1.004
386.47	0.097	0.152	1.125	1.009
385.59	0.149	0.227	1.155	1.006
384.77	0.201	0.289	1.134	1.010
383.98	0.246	0.346	1.110	1.016
383.28	0.296	0.402	1.104	1.020
382.17	0.348	0.465	1.089	1.029
381.45	0.404	0.519	1.080	1.032
380.82	0.451	0.566	1.080	1.031
380.20	0.501	0.612	1.086	1.017
379.48	0.552	0.660	1.083	1.013
378.95	0.598	0.698	1.073	1.018
378.31	0.646	0.743	1.058	1.028
377.75	0.697	0.782	1.046	1.044
377.25	0.752	0.822	1.050	1.037
376.85	0.800	0.859	1.038	1.054
376.35	0.847	0.896	1.032	1.068
375.75	0.894	0.929	1.027	1.066
375.35	0.943	0.962	1.023	1.086
375.15	0.973	0.982	1.020	1.117
375.09	1.000	1.000		

Results and Discussion

Vapor pressures, $P_i°$, of pure components were determined experimentally using the same equipment as that for obtaining the VLE data, and they were correlated using the Antoine equation

$$ln(P_i°/\mathrm{kPa}) = A - \frac{B}{(C + T/\mathrm{K})} \qquad (1)$$

The constants in eq 1 (Table 2) were fitted by a nonlinear optimization method to minimize the mean relative deviation in $P_i°$. Experimental data were compared with literature values. For diethyl ketone, the mean relative deviations were 1.14% and 1.67% for the data in refs 5 and 6, respectively. For 2-pentanone,[5] the mean relative deviation was 1.10%. For 3-pentanol,[7] the mean relative deviation was 3.26%.

Binary Systems. The experimental VLE data for the binary systems are reported in Tables 3−5. VLE data for the systems diethyl ketone (1) + 3-pentanol (3) and 2-pentanone (2) + 3-pentanol (3) are plotted in Figures 1 and 2, respectively. The activity coefficients γ_i were calculated from the equation[8]

$$\gamma_i = \frac{y_i P}{x_i P_i°} \qquad (2)$$

where P is the total pressure and $P_i°$ is the vapor pressure. In eq 2, also known *as the modified Raoult's law*, the vapor phase is assumed to be an ideal gas and the pressure dependence of the liquid phase fugacity is neglected. Equation 2 was selected to calculate activity coefficients because the low pressures observed in the VLE data make these simplifications reasonable. In addition, in such almost ideal mixtures the activity coefficients become very sensitive to the vapor phase corrections, and the estimation methods of vapor phase corrections can introduce uncertainties in the calculated activity coefficients.[9] As can be observed from the activity coefficients, the systems show slight positive deviations from ideality and that no azeotrope is present.

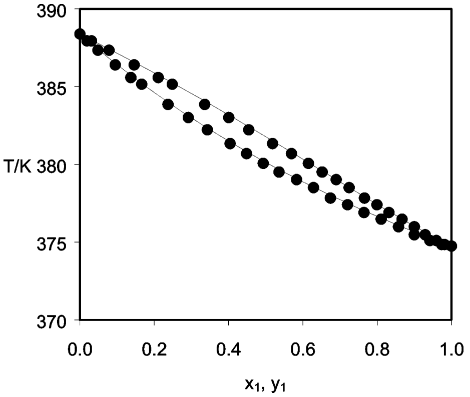

Figure 1. Temperature versus composition (x_1, y_1) for the diethyl ketone (1) + 3-pentanol (3) system at 101.3 kPa: ●, experimental; —, Wilson model.

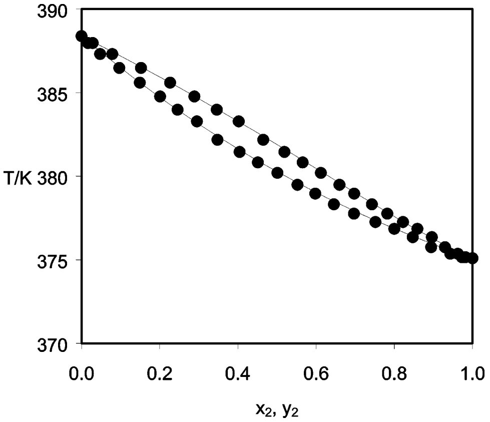

Figure 2. Temperature versus composition (x_2, y_2) for the 2-pentanone (2) + 3-pentanol (3) system at 101.3 kPa: ●, experimental; —, Wilson model.

Table 6. Consistency Test for the Binary Subsystems Diethyl Ketone (1) + 2-Pentanone (2), Diethyl Ketone (1) + 3-Pentanol (3), and 2-Pentanone (2) + 3-Pentanol (3)

system	100 × MAD(y)[a]	MAD(P)[b]/kPa
(1) + (2)	0.11	0.03
(1) + (3)	0.40	0.14
(2) + (3)	0.48	0.25

[a] Mean absolute deviation in vapor phase composition. [b] Mean absolute deviation in pressure.

Table 7. Correlation Parameters for Activity Coefficients, and Mean Absolute Deviations MAD(*y*) and MAD(*T*) for the Binaries Diethyl Ketone (1) + 3-Pentanol (3) and 2-Pentanone (2) + 3-Pentanol (3) at 101.3 kPa

model	ij	A_{ij} J·mol^{-1}	A_{ji} J·mol^{-1}	α_{ij}	100 × MAD(y)	MAD(T) K
Wilson	(1) + (3)	−368.74	947.20		0.37	0.11
	(2) + (3)	−838.25	1602.60		0.36	0.11
NRTL	(1) + (3)	2164.39	−1247.95	0.47	0.26	0.14
	(2) + (3)	1795.67	−986.25	0.47	0.37	0.11
UNIQUAC	(1) + (3)	74.89	47.11		0.29	0.23
	(2) + (3)	58.63	81.43		0.37	0.18

The thermodynamic consistency of the three binary VLE experimental data was checked by the point-to-point test of Van Ness−Byer−Gibbs[10] using a two-parameter Legendre polynomial for the excess Gibbs free energy. The objective function selected to minimize was the sum of the squared relative deviations in the total pressure. The consistency criterion in this test is that the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase, MAD(y), is less than 0.01. Table 6 presents the pertinent consistency statistics.

Table 8. Experimental Vapor−Liquid Equilibrium Data for Diethyl Ketone (1) + 2-Pentanone (2) + 3-Pentanol (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
375.12	0.8688	0.0785	0.8846	0.0795	1.006	1.011	1.099
375.43	0.0602	0.8829	0.0619	0.9012	1.007	1.010	1.033
375.51	0.4201	0.5009	0.4345	0.5122	1.010	1.009	1.073
375.52	0.6059	0.3068	0.6262	0.3137	1.009	1.009	1.092
375.59	0.2219	0.7055	0.2298	0.7209	1.009	1.006	1.075
375.65	0.5127	0.3984	0.5343	0.3982	1.013	0.982	1.201
375.71	0.3143	0.5989	0.3264	0.6130	1.008	1.004	1.102
375.75	0.7653	0.1029	0.8036	0.1063	1.018	1.012	1.076
375.85	0.1186	0.7864	0.1239	0.8116	1.010	1.008	1.065
375.88	0.6787	0.1834	0.7146	0.1898	1.017	1.010	1.086
376.55	0.4198	0.3964	0.4524	0.4197	1.020	1.013	1.063
376.78	0.6745	0.0949	0.7351	0.1021	1.024	1.022	1.070
376.88	0.2855	0.5034	0.3123	0.5432	1.025	1.022	1.034
376.91	0.6983	0.0635	0.7659	0.0686	1.027	1.022	1.048
376.95	0.2066	0.5825	0.2266	0.6276	1.026	1.018	1.041
377.05	0.0973	0.6858	0.1073	0.7456	1.028	1.024	1.018
377.06	0.4438	0.3163	0.4900	0.3437	1.029	1.023	1.040
377.44	0.5212	0.1994	0.5820	0.2181	1.029	1.019	1.057
377.71	0.5786	0.0990	0.6571	0.1113	1.038	1.039	1.052
377.73	0.3206	0.3917	0.3630	0.4346	1.034	1.024	1.029
377.85	0.3819	0.3028	0.4362	0.3394	1.040	1.031	1.036
377.97	0.1855	0.5024	0.2135	0.5637	1.043	1.028	1.035
378.31	0.0730	0.6006	0.0848	0.6820	1.043	1.030	1.023
378.53	0.4253	0.2024	0.4993	0.2323	1.047	1.034	1.024
378.85	0.4735	0.1013	0.5672	0.1185	1.058	1.044	1.038
378.86	0.2238	0.4029	0.2640	0.4636	1.042	1.027	1.024
378.95	0.5260	0.0529	0.6300	0.0625	1.055	1.050	1.021
378.95	0.2843	0.2940	0.3419	0.3569	1.059	1.081	0.999
379.18	0.0962	0.4865	0.1189	0.5781	1.081	1.051	1.007
379.79	0.3272	0.1972	0.4048	0.2376	1.063	1.046	1.020
380.11	0.3729	0.1021	0.4787	0.1276	1.092	1.075	1.005
380.23	0.1870	0.3049	0.2380	0.3757	1.079	1.056	1.014
380.75	0.0854	0.3900	0.1106	0.4868	1.082	1.054	1.005
381.47	0.3353	0.0554	0.4502	0.0726	1.098	1.083	0.999
381.55	0.1085	0.2849	0.1489	0.3749	1.119	1.085	0.999
381.72	0.1835	0.2062	0.2482	0.2688	1.098	1.069	1.000
381.74	0.2756	0.1018	0.3699	0.1322	1.089	1.065	1.010
383.16	0.1837	0.1021	0.2621	0.1404	1.110	1.081	1.005
383.49	0.0813	0.1983	0.1159	0.2757	1.099	1.083	1.002
384.56	0.1058	0.0980	0.1599	0.1421	1.130	1.095	1.001
385.38	0.0951	0.0536	0.1550	0.0824	1.189	1.135	0.994

For diethyl ketone + 3-pentanol and 2-pentanone + 3-pentanol, the activity coefficients were correlated with the Wilson,[11] NRTL,[12] and UNIQUAC models.[13] The binary parameters were obtained by minimizing the objective function (OF)

$$\mathrm{OF} = \sum_{i=1}^{N} \left(\left| \frac{T_i^{\mathrm{exp}} - T_i^{\mathrm{cal}}}{T_i^{\mathrm{exp}}} \right| + |y_i^{\mathrm{exp}} - y_i^{\mathrm{cal}}| \right) \tag{3}$$

where N is the number of data points. The parameters A_{12}, A_{21}, and α_{12} for the correlation equations, and mean absolute deviations are given in Table 7. Inspection of these results shows that all the considered models are adequate to predict the binary data.

For the diethyl ketone + 2-pentanone binary system, ideal behavior was assumed to represent experimental data. The mean absolute deviations between experimental and calculated vapor phase mole fractions and temperatures were MAD(y) = 0.0004 and MAD(T) = 0.04 K.

Ternary System. The VLE data for the ternary system are shown in Table 8 and Figure 3. In this figure, each tie line corresponds to one Txy VLE datum. The ternary system does not present an azeotrope. The activity coefficients γ_i were calculated from eq 2. The ternary data were found to be thermodynamically consistent, as tested by the

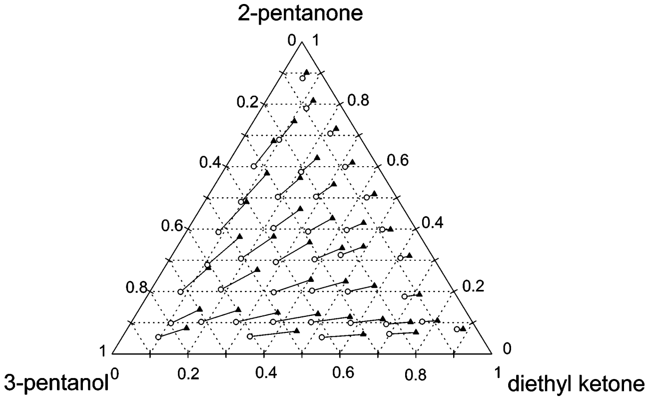

Figure 3. Vapor−liquid equilibrium tie lines for the diethyl ketone (1) + 2-pentanone (2) + 3-pentanol (3) system at 101.3 kPa: ○, liquid-phase mole fraction; ▲, vapor phase mole fraction.

Table 9. Correlation of Experimental Ternary Data with Wilson, NRTL, and UNIQUAC Equations Using Binary Interaction Parameters for Diethyl Ketone (1) + 2-Pentanone (2) + 3-Pentanol (3) at 101.3 kPa

model[a]	100 × MAD(y_1)	100 × MAD(y_2)	100 × MAD(y_3)	MAD(T)/K
Wilson	0.56	0.25	0.77	0.12
NRTL	0.51	0.24	0.66	0.12
UNIQUAC	0.67	0.28	0.87	0.13

[a] Model parameters for the binary subsystems (1) + (3) and (2) + (3) from Table 7. Ideal behavior for the binary (1) + (2) subsystem.

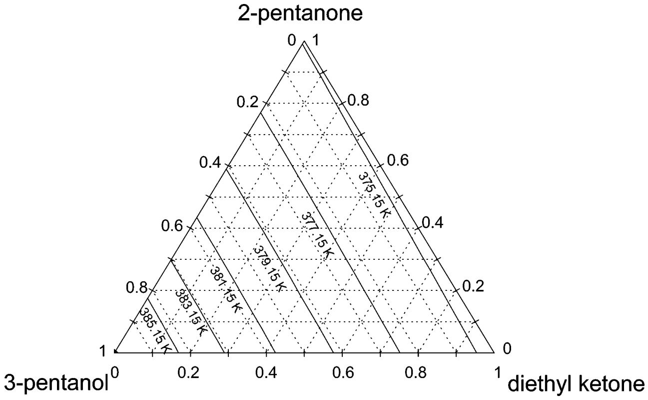

Figure 4. Boiling isotherms for the diethyl ketone (1) + 2-pentanone (2) + 3-pentanol (3) system at 101.3 kPa calculated with the Wilson model as a function of the liquid mole fraction.

McDermott−Ellis[14] method modified by Wisniak and Tamir.[15] The test requires that $D_i < D_{\max}$ for every experimental point. The values calculated of $D_{\max}$ were at least 0.038, while a value of $D = 0.024$ was not exceeded.

Vapor−liquid equilibrium for the ternary system has been predicted by using the Wilson, NRTL, and UNIQUAC models for the activity coefficients of the components with the binary interaction parameters obtained from the regression of binary data. Table 9 lists the mean absolute deviations between experimental and calculated temperatures and vapor phase mole fractions of the components. The three models yield similar deviations, representing the data successfully. Thus, the models can be used to predict the vapor phase compositions and boiling points from liquid phase compositions at the system pressure. As an example, boiling isotherms calculated with the Wilson model are presented in Figure 4.

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