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Ternary Vapor–Liquid Equilibria at 760 mmHg in the System Methanol–Acetone–Diethyl Ketone and Its Binaries

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The vapor–liquid equilibria for the ternary system methanol–acetone–diethyl ketone (DEK) and for the binary system acetone–diethyl ketone were determined at 760 mmHg by using a Dvorak and Boublik recirculation still. The data were correlated by means of the Wilson and Redlich–Kister equations. Direct correlation of the ternary data without considering binary data was found very efficient. The prediction of the binary and ternary data by the UNIFAC method was good. Boiling points of the ternary mixtures were predicted by an empirical correlation within a mean error of ±0.5%.

Introduction

The aim of the present study was to establish new vapor–liquid equilibria data at 760 mmHg for the ternary system methanol–acetone–diethyl ketone (DEK) and to check the possibility for its prediction from binary data and by the UNIFAC method (*1*). The possibility and the advantage of direct correlation of the ternary data without considering the binary data was also checked as well as various equations for correlating the data.

The following binary data were employed: for methanol–acetone the data of Marinichev and Susarev (*2*) and for methanol–DEK the data of Glukhareva et al. (*3*). The data for acetone–DEK were determined by us.

Analytical-grade reagents purchased from Merck were used. The physical properties of the pure components (refractive index and boiling point) agreed with literature data. The equilibria determinations were made in a modified all-glass Dvorak and Boublik recirculation still (*4*) and the experimental features have been described previously (*5*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Minigrator type of electronic integrator. For methanol–acetone–DEK the chromatographic column was packed with OV-17 (3%) and operated isothermally at 80 °C. The injector temperature was 150 °C and the detector operated at 150 mA and 150 °C. For acetone–DEK the column was packed with SP1200 and operated at 105 °C, the injector operated at 280 °C, and the detector at 270 °C. Concentration measurements in both cases were generally accurate to ±0.004 mole fraction.

Treatment of the Data

The correlation of ternary data by a series expansion of the Redlich–Kister type is usually based on the binary data; the ternary data are used to compute the so-called ternary constant. The magnitude of this constant gives also an indication whether it is possible to predict the ternary data from the binaries alone. When one handles multicomponent data, it is possible to avoid complex equations and a large number of adjustable variables by direct correlation of the available information, without consideration of lower order data (namely, the binary data in the case of ternary mixtures or binary and ternary data in the case of quaternary mixtures, etc.). It has been shown elsewhere (*6*) that direct correlation can be more efficient for the following arguments: (1) fewer parameters are needed in the correlated equations for the same degree of the fit of data, and (2) for an identical number of parameters, the goodness of the fit is better by means of direct correlation of the multicomponent data. The above conclusions will be demonstrated here since the binary data are available.

The following equations were used for correlating the multicomponent vapor–liquid equilibria data:

(a) One equation relates the boiling temperature of the mixture with the liquid composition solely. It has been derived (*6*) on the basis of the concept of "excess property" and it reads

$$T = \sum_{i=1}^{N} X_i T_i^\circ + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} X_i X_j [A_{ij} + B_{ij}(X_i - X_j) + C_{ij}(X_i - X_j)^2 + ...] \quad (1)$$

This equation is useful for obtaining isothermals, and to explore the azeotropic behavior and distillation paths of ternary mixtures. For binary mixtures the second summation on the right-hand side of eq 1 is exactly that suggested by Redlich and Kister (*7*). For multicomponent mixtures, we kept the binary form of the Redlich–Kister equation but the significance of the equation is different from that suggested by them in the sense that coefficients A_{ij}, B_{ij}, etc., are not binary constants; namely, they are not determined from the binary data. These coefficients are multicomponent parameters which are determined directly from the multicomponent data.

An equation for correlating boiling temperatures of multicomponent mixtures based on the complete data (binary, ternary, etc.) has been described in ref *8*. For a ternary mixture, $N = 3$, it reads

$$T = \sum_{i=1}^{N} X_i T_i^\circ + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} X_i X_j [A_{ij} + B_{ij}(X_i - X_j) + C_{ij}(X_i - X_j)^2 + ...] + X_1 X_2 X_3 [A + B(X_1 - X_2) + C(X_1 - X_3) + D(X_2 - X_3) + B'(X_1 - X_2)^2 + C'(X_1 - X_3)^2 + D'(X_2 - X_3)^2 + ...] \quad (2)$$

Here the indexed parameters are binary constants while A, B, B', etc., are ternary constants.

(b) An additional equation used here for correlating activity coefficient, γ_i, is the Wilson equation for multicomponent mixtures

$$\ln \gamma_i = 1 - \ln [\sum_{j=1}^{N} A_{ij} X_j] - \sum_{k=1}^{N} [A_{ki} X_k / \sum_{j=1}^{N} A_{kj} X_j] \quad (3)$$

It should be noted that, according to the original concepts of Wilson, A_{ij} are binary parameters. However, according to what has been previously said they should also be considered as multicomponent parameters determined directly from the multicomponent data.

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Table I. Equilibrium Data for the Binary System Acetone (1)-DEK (2) at 760 mmHg

T, °C	X_1	Y_1	T, °C	X_1	Y_1
98.81	0.025	0.085	78.90	0.315	0.635
98.28	0.030	0.105	77.38	0.350	0.665
96.32	0.050	0.160	73.85	0.435	0.750
94.00	0.075	0.200	69.29	0.535	0.835
90.56	0.120	0.335	64.48	0.695	0.910
85.38	0.195	0.485	60.48	0.835	0.970
84.55	0.215	0.520	58.35	0.920	0.980
81.40	0.275	0.590			

(c) In order to evaluate the correlation and predictive ability of the Wilson equation, the following Redlich–Kister expansion for γ_i was employed for correlating the ternary data:

$$\begin{aligned}\ln \gamma_1 = {} & X_2X_3[(B_{12} + B_{13} - B_{23}) + C_{12}(2X_1 - X_2) + \\ & C_{13}(2X_1 - X_3) + 2C_{23}(X_3 - X_2) + D_{12}(X_1 - X_2)(3X_1 - \\ & X_2) + D_{13}(X_1 - X_3)(3X_1 - X_2) - 3D_{23}(X_3 - X_2)^2 + \\ & C_1(1 - 2X_1)] + X_2^2[B_{12} + C_{12}(3X_1 - X_2) + \\ & D_{12}(X_1 - X_2)(5X_1 - X_2)] + \\ & X_3^2[B_{13} + C_{13}(3X_1 - X_3) + D_{13}(X_1 - X_3)(5X_1 - X_3)] \end{aligned} \quad (4)$$

where B_{ij}, C_{ij}, D_{ij} are binary constants and C_1 is a ternary constant. The equations for the other activity coefficients were obtained by cyclic rotation of the indices. The binary constants were calculated from the following equations (*11*):

$$\ln \gamma_i = (B_{ii} + 3C_{ij} + 5D_{ij})X_j^2 - 4(C_{ij} + 4D_{ij})X_j^3 + 12D_{ij}X_j^4 \quad (5\text{-}1)$$

$$\ln \gamma_j = (B_{ij} - 3C_{ij} + 5D_{ij})X_i^2 + 4(C_{ij} - 4D_{ij})X_i^3 + 12D_{ij}X_i^4 \quad (5\text{-}2)$$

In order to evaluate the goodness of the fit by the various correlations, the following quantities were used:

The error variance σ^2 (*9*) of an intensive property M which is defined by

$$\sigma^2 = \frac{\sum_{i=1}^{m} (M_{\text{obsd}} - M_{\text{calcd}})_i^2}{m - c - 1} \quad (6)$$

and is a measure of the spread of the error distribution; m is the number of data points and c is the number of parameters. σ^2 reaches a minimum vs. the degrees of freedom $m - c - 1$ and hence it is possible to choose the optimal number of parameters on the basis of its magnitude. By means of σ^2 it is also reasonable to compare between two expansions of a specific property because it is normalized with respect to $m - c - 1$ and thus takes into account differences between the number of parameters c and the number of data points m.

The mean overall deviation $\bar{D}$ is a more tangible element indicating the overall goodness of the fit of the data by the series expansion and its reads

$$\bar{D} = \frac{1}{m}\sum_{i=1}^{m}\left|\frac{M_{\text{obsd}} - M_{\text{calcd}}}{M_{\text{obsd}}}\right|_i \quad (7)$$

The following procedure was adopted for determining the parameters by direct correlation of multicomponent data (eq 1): First, parameters A_{12}, A_{13}, ..., A_{1N}, A_{23}, A_{24}, ..., A_{2N}, etc., were determined and then, A_{12} and B_{12}, A_{13} and B_{13}, ..., A_{1N} and B_{1N}, A_{23} and B_{23}, ..., A_{2N} and B_{2N}, etc. The optimal set of parameters was the one for which σ^2 was minimal. The correlation of multicomponent data based on the complete information (eq 2) was carried out as follows: at first parameters of all binary systems which compose the ternary system were determined. On the basis of the optimal sets of binary parameters (judged on the basis of minimal σ^2) the ternary constants were determined by considering the ternary data.

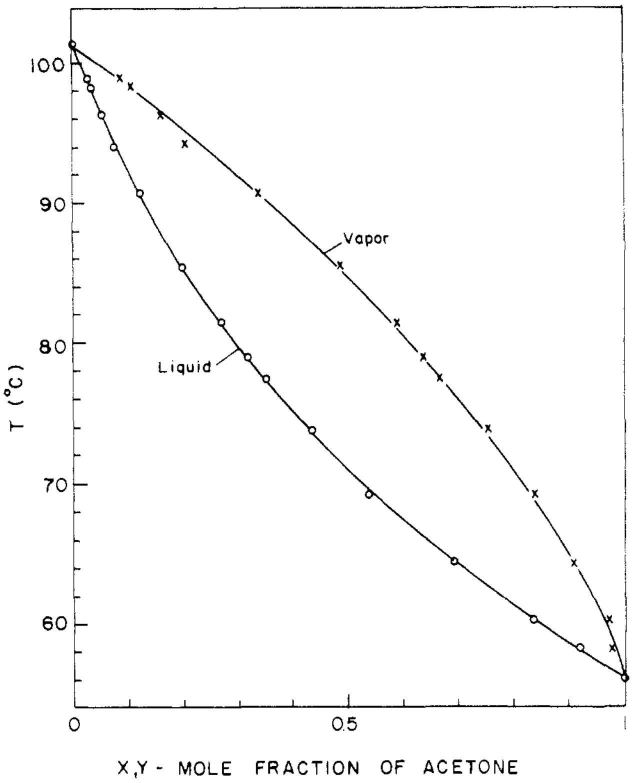

Figure 1. Boiling point-composition diagram at 760 mmHg for acetone-DEK.

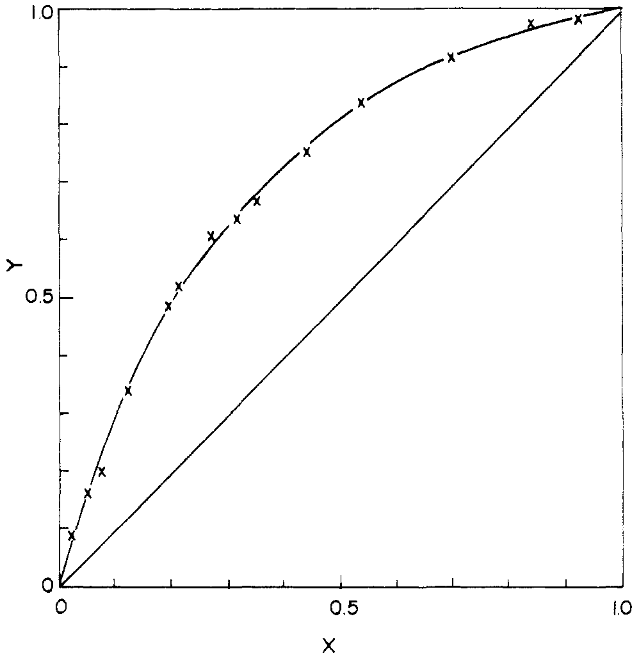

Figure 2. Vapor composition vs. liquid composition at 760 mmHg for acetone-DEK.

Results and Discussion

The temperature-concentration measurements at 760 mmHg for the binary system acetone-DEK and for the ternary system methanol-acetone-DEK are reported in Tables I and II and in

Table II. Equilibrium Data for the Ternary System Methanol (1)-Acetone (2)-DEK at 760 mmHg

T, °C	X_1	X_2	Y_1	Y_2
56.07	0.126	0.854	0.130	0.864
56.20	0.161	0.819	0.167	0.826
56.20	0.310	0.672	0.296	0.694
56.32	0.352	0.624	0.328	0.661
56.31	0.190	0.790	0.191	0.800
56.60	0.125	0.845	0.138	0.850
56.73	0.104	0.857	0.116	0.860
57.05	0.276	0.591	0.284	0.698
57.46	0.113	0.795	0.132	0.853
57.85	0.380	0.562	0.356	0.620
58.16	0.535	0.428	0.462	0.516
58.17	0.270	0.625	0.334	0.632
59.00	0.190	0.756	0.142	0.823
59.11	0.487	0.430	0.446	0.520
59.10	0.485	0.422	0.449	0.518
60.50	0.342	0.448	0.385	0.555
60.65	0.600	0.345	0.632	0.238
60.85	0.449	0.385	0.446	0.493
60.90	0.480	0.353	0.485	0.470
60.92	0.822	0.148	0.690	0.300
61.00	0.385	0.390	0.418	0.520
61.20	0.690	0.200	0.640	0.290
61.22	0.700	0.276	0.700	0.276
61.31	0.583	0.282	0.556	0.393
61.30	0.101	0.673	0.133	0.805
61.75	0.410	0.340	0.445	0.475
61.90	0.680	0.203	0.645	0.305
61.93	0.385	0.360	0.440	0.482
62.00	0.735	0.167	0.700	0.225
62.15	0.492	0.305	0.512	0.416
62.99	0.455	0.300	0.456	0.451
63.20	0.526	0.246	0.562	0.340
62.26	0.182	0.545	0.238	0.680
62.66	0.665	0.200	0.690	0.305
63.30	0.362	0.342	0.436	0.468
63.08	0.755	0.115	0.745	0.195
64.15	0.845	0.058	0.845	0.100
64.15	0.092	0.572	0.133	0.775
64.28	0.660	0.116	0.700	0.202
64.30	0.878	0.044	0.873	0.058
64.31	0.772	0.072	0.784	0.133
64.42	0.135	0.500	0.215	0.680
64.52	0.820	0.063	0.817	0.105
63.15	0.240	0.437	0.330	0.582
65.38	0.280	0.310	0.400	0.470
64.55	0.878	0.034	0.870	0.063
65.53	0.397	0.216	0.509	0.330
65.53	0.781	0.039	0.829	0.063
65.51	0.435	0.265	0.525	0.365
65.55	0.729	0.053	0.792	0.091
65.67	0.318	0.287	0.437	0.418
65.80	0.525	0.130	0.624	0.217
66.00	0.505	0.147	0.612	0.233
66.15	0.568	0.079	0.725	0.125
66.95	0.162	0.389	0.255	0.585
67.01	0.420	0.170	0.553	0.286
67.15	0.175	0.357	0.278	0.557
67.31	0.473	0.094	0.637	0.166
67.71	0.285	0.238	0.445	0.370
68.65	0.263	0.227	0.430	0.367
68.85	0.390	0.105	0.592	0.191
69.04	0.320	0.140	0.555	0.260
69.60	0.310	0.137	0.512	0.239
70.75	0.060	0.400	0.106	0.654
70.80	0.185	0.220	0.377	0.387
71.52	0.305	0.080	0.560	0.157
72.50	0.204	0.172	0.510	0.213
72.55	0.218	0.140	0.443	0.271
72.80	0.277	0.070	0.525	0.138
73.60	0.050	0.339	0.112	0.623
74.89	0.050	0.306	0.132	0.585
75.25	0.182	0.113	0.412	0.246
76.80	0.192	0.100	0.500	0.110
77.58	0.152	0.099	0.392	0.221
81.30	0.018	0.182	0.072	0.485
81.60	0.108	0.072	0.332	0.181
81.80	0.117	0.066	0.343	0.167
82.62	0.135	0.020	0.413	0.060
84.39	0.087	0.056	0.297	0.154
89.50	0.056	0.036	0.200	0.097

Figures 1 and 2. The liquid activity coefficients were calculated from

$$\ln \gamma_i = \ln \frac{Y_iP}{X_iP_i^\circ} + \frac{(B_{ii} - V_i^l)(P - P_i^\circ)}{RT} + \frac{P}{2RT} \sum_{j=1}^{m} \sum_{k=1}^{m} Y_jY_k(2\delta_{ji} - \delta_{jk}) \qquad (8)$$

where

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \qquad (9)$$

Vapor pressures P_i° were calculated according to Antoine's equation

$$\log P_i^\circ = A_i - B_i/(t + C_i) \qquad (10)$$

For the convenience of the reader, the constants A_i, B_i, C_i are reported here for P_i° in mmHg and t in (°C)

	A_i	B_i	C_i
methanol	7.89150	1474.08	229.13
acetone	7.23157	1277.03	237.33
DEK	7.30218	1481.17	233.07

The virial coefficients B_{ii} and the mixed virial coefficients B_{ij} were estimated by the correlation of Tsonopoulos (*10*). It should be noted that the γ_i's calculated according to YP/XP_i° and according to eq 8 differ in extreme cases by not more than 5%.

The ternary data appearing in Table II were tested by the McDermott-Ellis method (*11*) and found to be thermodynamically consistent. According to this test, two experimental points, a and b, are thermodynamically consistent if

$$\mathrm{D} < \mathrm{D}_{\max} \qquad (11)$$

The local deviation D is given by

$$\mathrm{D} = \sum_{i=1}^{N} (X_{i\mathrm{b}} + X_{i\mathrm{a}})(\ln\gamma_{i\mathrm{b}} - \ln \gamma_{i\mathrm{a}}) \qquad (12)$$

According to ref *11* a fixed value for $\mathrm{D}_{\max}$ is recommended; however, an equation can be derived (*12*) which reads

$$\mathrm{D}_{\max} = \sum_{i=1}^{N} (X_{i\mathrm{a}} + X_{i\mathrm{b}})\left(\frac{1}{X_{i\mathrm{a}}} + \frac{1}{Y_{i\mathrm{a}}} + \frac{1}{X_{i\mathrm{b}}} + \frac{1}{Y_{i\mathrm{b}}}\right)\Delta X + 2\sum_{i=1}^{N} |\ln \gamma_{i\mathrm{b}} - \ln \gamma_{i\mathrm{a}}|\Delta X + 2\sum_{i=1}^{N} (X_{i\mathrm{a}} + X_{i\mathrm{b}})\frac{\Delta P}{P} + \log e \sum_{i=1}^{N} (X_{i\mathrm{a}} + X_{i\mathrm{b}})B_i\left(\frac{1}{[t_\mathrm{a} + C_i]^2} + \frac{1}{[t_\mathrm{b} + C_i]^2}\right)\Delta t \qquad (13)$$

In this study the errors in the measurements were estimated to be $\Delta P = \pm 2$ mmHg, $\Delta t = \pm 0.02$ °C, and $\Delta X = 0.004$ mole fraction unit. Usually the first term on the right-hand side of eq 13 was the dominant one.

The binary data reported elsewhere (*2*, *3*) were correlated by Wilson and Redlich-Kister equations (eq 3 and 4, respectively) and the binary parameters are reported in Table III. For ternary mixtures, the data were correlated directly by means

Table III. Wilson and Redlich-Kister Parameters[a]

system	ij	Wilson (eq 3) A_{ij}	Wilson (eq 3) A_{ji}	Redlich-Kister (eq 5) B_{ij}	Redlich-Kister (eq 5) C_{ij}	Redlich-Kister (eq 5) D_{ij}
methanol-acetone	12	0.3475	1.3638	0.6272	0.1213	0.04708
methanol-DEK	13	0.8788	0.4103	0.6424	0.03056	0.6335
acetone-DEK	23	0.6808	1.4746	0.1296	−0.4391	0.1243
methanol-acetone-DEK	12	0.8399	0.7476			
	13	1.0338	0.3304	$C_1 = 0$ (eq 4)		
	23	2.0985	0.2391			

[a] The parameters A_{ij} and A_{ji} were obtained by direct correlation of the ternary data. These parameters, as well as the binary ones, were obtained by minimizing the objective function $\Sigma_{k=1}{}^{m}[\{(P_{\rm obsd} - P_{\rm calcd})/P_{\rm obsd}\}_k{}^2 + \{(Y_{1,\rm obsd} - Y_{1,\rm calcd})/Y_{1,\rm obsd}\}_k{}^2 + \{Y_{2,\rm obsd} - Y_{2,\rm calcd})/Y_{2,\rm obsd}\}_k{}^2]$.

Table IV. Capability of Predicting the Vapor Composition by Various Equations[a] and the Total Pressure by the Wilson Equation

system	Y,[b] % max	Y,[b] % min	Y,[b] % mean	P, % max	P, % min	P, % mean	Y,[b] % UNIFAC max	Y,[b] % UNIFAC min	Y,[b] % UNIFAC mean	Y,[b] % Redlich-Kister (eq 5) max	Y,[b] % Redlich-Kister (eq 5) min	Y,[b] % Redlich-Kister (eq 5) mean
methanol-acetone	31.8	0.48	8.09	6.34	0.16	3.23	5.06	2.40	2.64	1.90	0.41	1.45
methanol-DEK	6.61	0.0	1.33	11.9	0.61	2.74	8.36	0.01	1.94	4.19	0.0	0.90
acetone-DEK	16.2	0.38	3.07	6.94	0.0	4.00	17.7	1.20	11.2	8.07	0.50	4.65
methanol-acetone-DEK	27.0	0.04	6.06				34.9	0.21	6.54	52.0	0.01	6.37
	27.8[c]	0.12[c]	4.93[c]									
	88.7	0.12	7.44	11.5	0.55	2.87	107.9	0.49	9.37	106.5	0.03	10.0
	97.3[c]	0.04[c]	14.9[c]									

[a] Parameters are given in Table III. [b] $Y = (Y_{\rm obsd} - Y_{\rm calcd})/Y_{\rm obsd}$; for binary mixtures the Y's correspond to the first component mean $= (1/m)\Sigma_{i=1}{}^{m}|Y_i|$. [c] Based on prediction from binary parameters.

Table V. Parameters[a] in Correlation of Binary T-X Data (Eq 14) and of Ternary T-X Data Based on Binary + Ternary Data (Eq 2)

system	ij	A_{ij}	B_{ij}	C_{ij}	D_{ij}	E_{ij}	F_{ij}	D,[b] % max	D,[b] % min	D,[b] % mean
methanol-acetone	12	−16.238	−4.221	−7.143	−1.912	4.275		0.095	0.005	0.040
methanol-DEK	13	−49.388	51.703	14.497	−104.37	−136.17	225.79	1.533	0.011	0.596
acetone-DEK	23	−31.828	11.682	−5.675	17.805	−7.739		0.424	0.013	0.169
methanol-acetone-DEK		$A = -234.49$; $B = 2930.8$; $C = -2338.8$; $D = 2655.4$						12.7	0.020	6.04

[a] Corresponding to minimal σ^2 (eq 6). [b] $D = |(T_{\rm obsd} - T_{\rm calcd})/T_{\rm obsd}|$; mean $= (1/m)\Sigma_{i=1}{}^{m}|D_i|$.

Table VI. Parameters[a] in Direct Correlation of T-X Data (Eq 15) for Methanol (1)-Acetone (2)-DEK (3) at 760 mmHg and the Efficiency of Direct Correlation

system	ij	direct correlation of ternary data A_{ij}	B_{ij}	C_{ij}	D_{ij}	D, % max	D, % min	D, % mean	$\sigma^2_{\rm min}$	correlation based on binary and ternary data c	$\mathcal{T}$	D, % max	D, % min	D, % mean	$\sigma^2_{\rm min}$
methanol-	12	−10.927	12.200	−12.003	−40.747					5					
acetone-	13	−49.922	30.824	−18.876	29.971					6					
DEK	23	−31.093	18.237	−35.402	30.034	2.58	0.02	0.52	0.263	5	20	12.7	0.02	2.14	6.04

[a] Corresponding to minimal σ^2 (eq 6). $T_1^\circ = 64.5$ °C; $T_2^\circ = 56.1$ °C; $T_3^\circ = 101.7$ °C. $\mathcal{T}$ = total number of parameters: binary + ternary. c = number of binary parameters for the pairs ij which appear in Table V.

of Wilson's equation. In the case of Redlich–Kister's equation (eq 4), the binary parameters were used, and the ternary constant C_1 was determined from ternary data. This information appears in Table III. Table IV summarizes the predictive capability for the binary and ternary data of the various methods. The following general conclusions could be drawn on the basis of considering $Y = (Y_{\rm obsd} - Y_{\rm calcd})/Y_{\rm obsd}$ and its mean values:

Binary Data. (1) The binary system acetone–DEK behaves like an ideal liquid solution. (2) Wilson and Redlich–Kister equations have practically a similar ability in predicting the vapor composition. (3) The UNIFAC method predicts the vapor composition values within a mean deviation of 1.94–11.2% of measured values.

Ternary Data. (1) The ternary behavior can be predicted by the Redlich–Kister equation (eq 4) from only the binary parameters; namely, C_1 is practically zero. (2) The UNIFAC method predicts the vapor composition in comparison to measured values with a mean deviation of 6.5–9.4%. (3) Direct correlation of ternary data by Wilson's equation is better (maximum mean deviation of 7.4%) than prediction of the ternary data from the binary parameters (maximum mean deviation from experimental data is 14.9%).

Another correlation used here relates the boiling temperatures of the mixture with the liquid composition only according to eq 1. The binary form of this equation reads

$$T = X_1T_1^\circ + X_2T_2^\circ + X_1X_2[A_{12} + B_{12}(X_1 - X_2) + C_{12}(X_1 - X_2)^2 + \ldots] \quad (14)$$

The parameters are reported in Table V and their number corresponds to minimal σ^2 (eq 6). In Table VI we report the

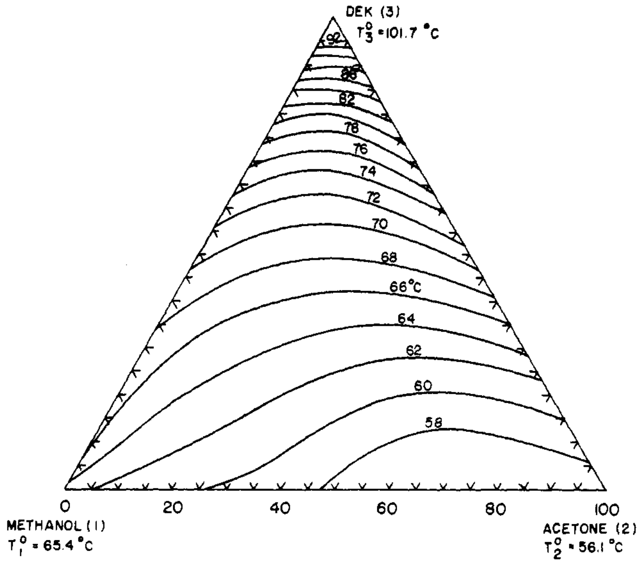

Figure 3. Isothermals for methanol–acetone–DEK at 760 mmHg.

parameters obtained for direct correlation of the ternary data according to the ternary form of eq 1 which reads

$$T = \sum_{i=1}^{3} X_i T_i^\circ + x_1 X_2[A_{12} + B_{12}(X_1 - X_2) + C_{12}(X_1 - X_2)^2 \ldots] + X_1 X_3[A_{13} + B_{13}(X_1 - X_3) + C_{13}(X_1 - X_3)^2 + \ldots] + X_2 X_3[A_{23} + B_{23}(X_2 - X_3) + C_{23}(X_2 - X_3)^2 + \ldots] \tag{15}$$

The following conclusions may be drawn on the basis of Tables V and VI

(1) For methanol–acetone–DEK, T may be correlated directly vs. X by means of eq 15 with a mean deviation of 0.52% (Table VI).

(2) Direct correlation of T vs. X for the ternary mixtures is very efficient. This is reflected by the fact that, for 12 parameters (Table VI) needed in direct correlation, the mean deviation in predicting T vs. X is 0.52%. On the other hand, for 20 parameters needed in the T–X representation by taking into account binary + ternary data (eq 2), the mean deviation is 2.14%.

Isothermals (Figure 3) were calculated on the basis of eq 15, and the parameters reported in Table VI. The shape of the curves indicates that that system does not exhibit azeotropic behavior.

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Glossary

A_{ij}, B_{ij}, etc.	multicomponent adjustable parameters in Redlich–Kister or Wilson expansions
A_i, B_i, C_i	parameters in Antoine's equation; eq 13
C_1	ternary constant in eq 4
$\bar{D}$	mean overall deviation from observed values; eq 7
DEK	diethyl ketone
M	intensive property; $M = T$ or Y
m	total number of data points
N	number of components in a mixture
P	total pressure
P_i°	vapor pressure of pure component i
V_i^l	liquid molar volume of component i
T	absolute temperature
T_i°	boiling temperature of pure component i
t	temperature in °C
x_i, y_i	mole fraction of component i in the liquid and vapor phases
Y	local deviation from observed values; $Y = (Y_{\text{obsd}} - Y_{\text{calcd}})/Y_{\text{obsd}}$
γ_i	activity coefficient of component i
σ^2	error variance; eq 6
ΔX, ΔP, Δt	errors in measurements of concentration, pressure, and temperature

Subscripts and Superscripts

calcd	calculated
obsd	observed
l	liquid phase
i	component i
max	maximum
min	minimum

Registry No. Methanol, 67-56-1; acetone, 67-64-1; diethyl ketone, 96-22-0.

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