

Ternary Vapor–Liquid Equilibria in the System Methyl Ethyl Ketone–Diethyl Ketone–Methyl Isobutyl Ketone

Jaime Wisniak* and Abraham Tamir

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

New data of the vapor–liquid equilibria of the system methyl ethyl ketone–diethyl ketone–methyl isobutyl ketone were obtained at 760 mmHg. The system presents a small deviation from ideal solution behavior, and the activity coefficients were satisfactorily correlated according to the Redlich–Kister equation by considering only the binary data. The Wilson correlation was found to have similar ability of predicting the vapor phase composition as the Redlich–Kister equation. Boiling points of the ternary mixture were predicted by an empirical correlation within a maximum relative error of $\pm 1\%$ and a mean error of $\pm 0.3\%$.

As a continuation of our previous investigation (5) on the binaries of methyl ethyl ketone (MEK), diethyl ketone (DEK), and methyl isobutyl ketone (MIBK), the ternary system of the above components was studied and the possibility of predicting the behavior of the ternary system from the three binaries was checked. It appears also that the above ternary system has not yet been studied.

Analytical grade reagents purchased from Fluka were used without further purification after gas chromatography analysis failed to show any significant impurities. The physical properties of the pure components appeared elsewhere (5). The determinations were made in a modified all-glass Dvorak and Boublick recirculation still (7) and the experimental features have been described previously (7). 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. The column was 200 cm long and 0.32 cm in diameter and was packed with Chromosorb 101 and operated isothermally at 170 °C. Injector temperature was 210 °C and the detector operated at 150 mA and 230 °C. Calibration analyses were carried out to convert the peak area ratio to the actual weight composition of the mixture. Concentration measurements were generally accurate to ± 0.0025 mole fraction.

Results and Discussions

The temperature–concentration measurements at 760 mmHg for the ternary system MEK–DEK–MIBK are reported in Table I. The liquid activity coefficients were calculated from the equation

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ij} - V_i^0)(P - P_i^0)}{RT} + \frac{P}{2RT} \sum_{j=1}^m \sum_{k=1}^m y_j y_k (2\delta_{ji} - \delta_{jk}) \quad (1)$$

where

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \quad (2)$$

Vapor pressures P_i^0 were calculated according to Antoine's equation

$$\log P_i^0 = \alpha_i - \beta_i / (\delta_i + t) \quad (3)$$

where the constants are reported elsewhere (5).

The virial coefficients B_{ij} and the mixed virial coefficients B_{ji} were estimated by the correlation of O'Connell–Prausnitz (4) using the molecular parameters reported by the same authors.

The 64 ternary data points appearing in Table I are thermodynamically consistent and were tested by the McDermott–Ellis method (3). According to this test, two experimental points, a and b, are thermodynamically consistent if the following condition is fulfilled:

$$D < D_{\max} \quad (4)$$

The local deviation D is given by (3)

$$D = \sum_{i=1}^n (x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \quad (5)$$

According to ref 3, a fixed value is recommended for D_{\max} ; however, an equation for the local value of the maximum deviation can be derived (6) which reads

$$D_{\max} = \sum_{i=1}^n (x_{ia} + x_{ib}) \left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}} \right) \Delta x + 2 \sum_{i=1}^n |\ln \gamma_{ib} - \ln \gamma_{ia}| \Delta x + \sum_{i=1}^n (x_{ia} + x_{ib}) \frac{\Delta P}{P} + \sum_{i=1}^n (x_{ia} + x_{ib}) \beta_i \left(\frac{1}{[t_a + \delta_i]^2} + \frac{1}{[t_b + \delta_i]^2} \right) \Delta t \quad (6)$$

In the present study, the errors in the measurements were estimated to be: $\Delta P = \pm 2$ mmHg, $\Delta t = \pm 0.02$ °C, and $\Delta x = 0.0025$ mole fraction units. It was found that the first term in eq 6 which accounts for the error in the concentration measurements was usually the dominant one. In correlating the ternary data in Table I, namely, the activity coefficients and boiling points, we used the binary data reported in ref 5. The x - y data for the latter were successfully correlated here through the relative volatility which according to Hala (2) is generally expressed by:

$$\frac{y_1 x_2}{x_1 y_2} = a_{12} \frac{1 + x_2 a_1 + x_2^2 a_2 + x_2^3 a_3 + \dots}{1 + x_1 b_1 + x_1^2 b_2 + x_1^3 b_3 + \dots} \quad (7)$$

a_{12} , a_1 , b_1 , etc., are adjustable parameters. Equation 7 is useful in case the equilibrium data are needed in the form of an analytical expression. The parameters for the three binaries were calculated by the Simplex method and are reported in Table II. The table also contains information which gives an indication of the goodness of the correlation.

The activity coefficients reported in Table I show that the ternary system presents a small deviation from the ideal solution. It would be noted that the three binaries (5) revealed similar behavior. The activity coefficients were correlated by the following Redlich–Kister expansion:

$$\ln \gamma_1 = x_2 x_3 [(B_{12} + B_{13} - B_{23}) + C_{12}(2x_1 - x_2) + C_{13}(2x_1 - x_3) + 2C_{23}(x_3 - x_2) + D_{12}(x_1 - x_2)(3x_1 - x_2) + D_{13}(x_1 - x_3)(3x_1 - x_2) - 3D_{23}(x_3 - x_2)^2 + C_1(1 - 2x_1)] + x_2^2 [B_{12} + C_{12}(3x_1 - x_2) + D_{12}(x_1 - x_2)(5x_1 - x_2)] + x_3^2 [B_{13} + C_{13}(3x_1 - x_3) + D_{13}(x_1 - x_3)(5x_1 - x_3)] \quad (8)$$

Table I. Ternary Vapor–Liquid Equilibrium Data for Methyl Ethyl Ketone–Diethyl Ketone–Methyl Isobutyl Ketone at 760 mmHg

T (°C)	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
81.93	0.872	0.068	0.060	0.935	0.040	0.025	1.0017	1.0886	1.2036
83.00	0.824	0.093	0.083	0.904	0.057	0.039	0.9933	1.0947	1.3074
83.58	0.785	0.159	0.056	0.881	0.094	0.025	0.9990	1.0360	1.2180
84.00	0.778	0.118	0.104	0.883	0.072	0.045	0.9980	1.0545	1.1631
84.35	0.781	0.064	0.155	0.890	0.042	0.068	0.9920	1.1211	1.1646
85.30	0.745	0.073	0.182	0.876	0.046	0.078	0.9959	1.0437	1.1013
85.33	0.716	0.148	0.136	0.839	0.099	0.062	0.9916	1.1070	1.1705
86.02	0.715	0.051	0.234	0.863	0.034	0.103	1.0014	1.0787	1.1032
86.89	0.700	0.048	0.252	0.859	0.031	0.110	0.9931	1.0161	1.0625
86.95	0.659	0.181	0.160	0.808	0.120	0.072	0.9905	1.0412	1.0938
87.65	0.522	0.457	0.021	0.681	0.310	0.009	1.0330	1.0421	1.0186
87.99	0.622	0.191	0.187	0.792	0.126	0.082	0.9988	1.0022	1.0294
88.25	0.606	0.210	0.184	0.777	0.141	0.082	0.9984	1.0116	1.0371
88.68	0.603	0.174	0.223	0.780	0.119	0.101	0.9951	1.0164	1.0387
90.65	0.517	0.259	0.224	0.711	0.185	0.104	1.0013	0.9977	0.9980
90.75	0.576	0.067	0.357	0.773	0.052	0.175	0.9747	1.0805	1.0490
91.62	0.407	0.446	0.147	0.580	0.344	0.076	1.0100	1.0455	1.0769
91.89	0.510	0.161	0.329	0.719	0.118	0.163	0.9921	0.9849	1.0219
91.96	0.486	0.227	0.287	0.687	0.169	0.144	0.9928	0.9983	1.0329
92.00	0.343	0.598	0.059	0.506	0.461	0.033	1.0345	1.0328	1.1516
93.30	0.426	0.305	0.269	0.624	0.238	0.138	0.9916	1.0041	1.0116
93.36	0.294	0.659	0.047	0.443	0.529	0.028	1.0179	1.0314	1.1741
94.18	0.353	0.394	0.253	0.530	0.325	0.145	0.9925	1.0333	1.0984
94.55	0.415	0.233	0.352	0.628	0.186	0.186	0.9904	0.9887	1.0006
94.78	0.302	0.570	0.128	0.468	0.455	0.077	1.0075	0.9820	1.1325
95.10	0.380	0.269	0.351	0.591	0.221	0.188	1.0030	1.0007	0.9967
95.61	0.209	0.749	0.042	0.334	0.645	0.021	0.0157	1.0332	0.9175
95.82	0.320	0.413	0.267	0.501	0.347	0.152	0.9901	1.0015	1.0360
96.15	0.189	0.780	0.031	0.304	0.674	0.022	1.0076	1.0200	1.2803
96.41	0.369	0.138	0.493	0.584	0.121	0.295	0.9861	1.0267	1.0667
96.95	0.269	0.492	0.239	0.435	0.424	0.141	0.9922	0.9930	1.0365
97.24	0.284	0.322	0.394	0.464	0.290	0.246	0.9954	1.0288	1.0852
97.55	0.309	0.246	0.445	0.506	0.228	0.266	0.9896	1.0490	1.0289
97.65	0.151	0.765	0.084	0.250	0.695	0.055	0.9967	1.0253	1.1265
97.75	0.220	0.579	0.201	0.367	0.511	0.122	0.0019	0.9930	1.0404
98.00	0.339	0.195	0.466	0.541	0.173	0.286	0.9531	0.9907	1.0418
98.40	0.193	0.625	0.182	0.321	0.565	0.114	0.9819	0.9977	1.0524
98.50	0.258	0.363	0.379	0.436	0.331	0.233	0.9957	1.0034	1.0281
98.60	0.101	0.836	0.063	0.169	0.784	0.047	0.9822	1.0290	1.2463
98.74	0.247	0.410	0.343	0.419	0.374	0.207	0.9930	0.9966	1.0023
99.00	0.160	0.675	0.165	0.272	0.622	0.106	0.9878	0.9991	1.0597
99.28	0.147	0.695	0.158	0.252	0.655	0.093	0.9887	1.0135	0.9628
99.30	0.076	0.873	0.051	0.129	0.838	0.033	0.9781	1.0317	1.0582
99.35	0.205	0.482	0.313	0.352	0.450	0.198	0.9892	1.0019	1.0311
99.70	0.246	0.331	0.423	0.427	0.311	0.262	0.9912	0.9980	0.9982
100.00	0.161	0.587	0.252	0.281	0.563	0.156	0.9882	1.0098	0.9897
100.40	0.125	0.675	0.200	0.221	0.650	0.129	0.9905	1.0021	1.0190
100.65	0.234	0.269	0.497	0.406	0.263	0.331	0.9671	1.0103	1.0417
101.20	0.246	0.210	0.544	0.442	0.202	0.356	0.9875	0.9782	1.0066
101.50	0.099	0.652	0.249	0.174	0.661	0.165	0.9572	1.0219	1.0120
102.13	0.180	0.295	0.525	0.327	0.300	0.373	0.9751	1.0070	1.0622
102.90	0.208	0.175	0.617	0.373	0.182	0.445	0.9443	1.0075	1.0532
103.01	0.231	0.125	0.644	0.431	0.127	0.442	0.9796	0.9810	0.9992
103.31	0.129	0.428	0.443	0.243	0.448	0.309	0.9804	1.0017	1.0076
103.85	0.225	0.073	0.702	0.431	0.074	0.495	0.9849	0.9558	1.0008
106.25	0.159	0.133	0.708	0.314	0.150	0.536	0.9563	0.9941	1.0013
106.30	0.173	0.057	0.770	0.353	0.064	0.583	0.9873	0.9885	0.9996
107.25	0.143	0.124	0.733	0.287	0.141	0.572	0.9483	0.9750	1.0024
107.85	0.058	0.364	0.578	0.112	0.429	0.459	0.8979	0.9934	1.0033
108.05	0.144	0.047	0.809	0.296	0.054	0.650	0.9531	0.9640	1.0081
108.95	0.111	0.096	0.793	0.235	0.116	0.649	0.9602	0.9891	1.0009
109.32	0.073	0.205	0.722	0.147	0.253	0.600	0.9046	0.9998	1.0059
110.58	0.087	0.074	0.839	0.182	0.096	0.722	0.9127	1.0164	1.0046
110.60	0.099	0.034	0.867	0.207	0.041	0.752	0.9121	0.9445	1.0119

Table II. Parameters in y - x Correlation, Eq 7

System	a_{12}	a_1	RMSD ^a	Y	
				Max.	Mean
MEK-DEK	1.8212	0.072 58	0.0024	0.44	0.19
MEK-MIBK	2.6462	0.088 39	0.0027	0.55	0.22
DEK-MIBK	1.7813	-0.027 52	0.0062	1.72	0.45

^a RMSD = $\sqrt{\sum(\gamma_{\text{obsd}} - \gamma_{\text{calcd}})^2/m}$. ^b Y = $((y_{\text{obsd}} - y_{\text{calcd}})/y_{\text{obsd}})100$. y_{calcd} is calculated from eq 7. Mean = $\sum^m |Y|/m$.

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 detailed equations through which the binary constants were computed and their magnitudes are reported in ref 5. Table III contains information concerning the ternary system as well as parameters which indicate the ability of correlating the data by the Redlich-Kister equations. Only for the convenience of the reader the nine binary constants are reported here again. Considering the values of the root mean squared deviation and the value of C_1 indicates that

Table III. Redlich-Kister Correlation

System	B_{ij}	C_{ij}	D_{ij}	RMSD ^a			
				γ_i	γ_j		
MEK-DEK	0.049 12	0.055 14	0.054 00	0.0177	0.0159		
MEK-MIBK	0.051 51	0.103 31	0.068 82	0.0359	0.0535		
DEK-MIBK	-0.035 58	-0.003 85	-0.079 74	0.0218	0.0484		
Overall RMSD							
				γ	y		
				$C_1 = 0.050 25$	0.0709	0.0223	
				$C_1 = 0$	0.0719	0.0219	
(($y_{\text{obsd}} - y_{\text{calcd}}$)/ y_{obsd})100 = Y ^b							
Maximum							
		MEK	DEK	MIBK	MEK	DEK	MIBK
		14.1	10.3	26.5	8.6	2.5	6.9

^a RMSD = $\sqrt{\sum(\gamma_{\text{obsd}} - \gamma_{\text{calcd}})^2/m}$. ^b y_{calcd} is based on computed values of the activity coefficients. Mean = $\sum^m |Y|/m$.

Table IV. Wilson Correlation

System	Λ_{ij}	Λ_{ji}	RMSD				
			γ	y			
MEK-DEK	0.659 4	1.3211	0.0205	0.0119			
MEK-MIBK	0.391 01	1.7149	0.0395	0.0244			
DEK-MIBK	1.703 1	0.5872	0.0285	0.0104			
Overall RMSD							
			γ	y			
			0.0954	0.0249			
(($y_{\text{obsd}} - y_{\text{calcd}}$)/ y_{obsd})100 = Y ^a							
Maximum							
		MEK	DEK	MIBK	MEK	DEK	MIBK
		32.0	14.0	27.1	9.9	5.7	8.9

^a Mean = $\sum^m |Y|/m$. RMSD = $\sqrt{\sum_{i=1}^n \sum_{j=1}^m (\gamma_{ij,\text{obsd}} - \gamma_{ij,\text{calcd}})^2/nm}$; similarly for y .

the ternary data can be reasonably predicted from the behavior of the different binaries that compose it without the need for interaction terms like C_1 . The ternary system was also correlated, using the multicomponent Wilson equation

$$\ln \gamma_k = 1 - \ln \left[\sum_{j=1}^n x_j \Lambda_{kj} \right] - \frac{\sum_{i=1}^n x_i \Lambda_{ik}}{\sum_{j=1}^m x_j \Lambda_{ij}} \quad (9)$$

where $\Lambda_{ij} = 1$. Equation 9 contains only parameters which can be obtained from binary data. These were calculated from the binary form of eq 9 using the data reported in ref 5. The constants for the different binaries are reported in Table IV. Application of eq 9 to the ternary system yields an overall RMSD = 0.0249 for predicting y , which is quite similar to the value of 0.0223 for predicting y according to the Redlich-Kister equation. Hence both equations can be considered as having a similar ability for predicting the vapor composition.

Table V. Correlation of Boiling Points, Eq 10

System	C_0	C_1	C_2	C_3	RMSD ^a	Y ^b	
						Maximum	Mean
MEK-DEK							
With ω	-6.8756	1.2701	-3.0310	-1.5061	0.0480	0.10	0.043
Without ω	-7.0713	1.1617	-3.1110	-1.1037	0.0481		
MEK-MIBK							
With ω	-17.137	3.5637	-4.5130	2.8715	0.1128	0.21	0.089
Without ω	-17.641	3.6966	-4.5490	3.0685	0.1125		
DEK-MIBK							
With ω	-1.5616	-1.0647	1.0056	-0.8919	0.1434	0.43	0.061
Without ω	-1.6398	-1.0730	0.9527	-1.0030	0.1435		
		A	B	C	D		
MEK-DEK-MIBK							
With ω	-4.7846	30.753	-19.151	-1.4983	0.3810	1.05	0.314
Without ω	-4.7471	30.822	-19.546	-1.6119	0.3803		
Without ternary constants						0.4260	

^a RMSD = $\sqrt{\sum(T_{\text{obsd}} - T_{\text{calcd}})^2/m}$. ^b Y = $((T_{\text{obsd}} - T_{\text{calcd}})/T_{\text{obsd}})100$. Mean = $\sum^m |Y|/m$.

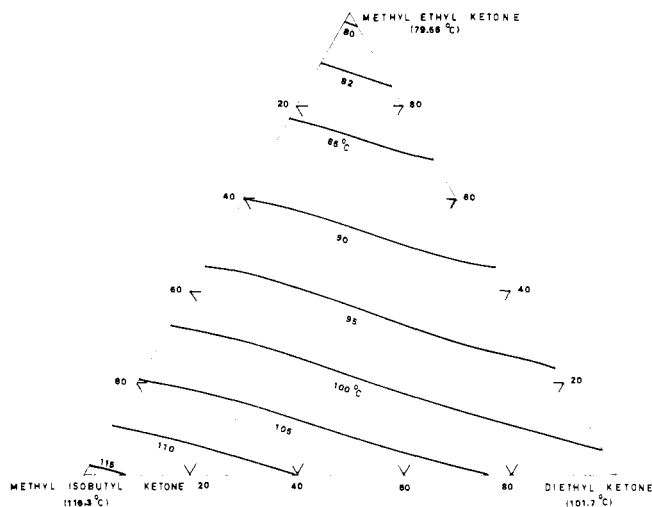


Figure 1. Isothermals at 760 mmHg for the system methyl ethyl ketone–diethyl ketone–methyl isobutyl ketone calculated by eq 10 for $\omega = 0$.

The boiling points vs. concentration of the ternary system were correlated by the following equation suggested by the writers (8)

$$T = x_1 T_1^0 + x_2 T_2^0 + x_3 T_3^0 + \omega + \sum_{i,j=1}^3 \left[x_i x_j \sum_{k=0}^l C_k (x_i - x_j)^k \right] + x_1 x_2 x_3 [A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + \dots] \quad (10)$$

where

$$\omega = \sum_{i=1}^3 x_i \ln (y_i/x_i) \quad (11)$$

T^0 is the boiling point of the pure components in °C and l is the number of terms in the series expansion of $(x_i - x_j)$. C_k are the binary constants computed on the basis of the data in ref 5 where A , B , C , and D are ternary constants computed from the ternary data in Table I. The various constants are reported in Table V which also contains information indicating the degree of goodness of the correlation.

The values of RMSD show that the ω in eq 10 may be neglected. The contribution of ω to the boiling point was usually in the order of 0.01 °C. Hence the boiling point of the mixture becomes solely a function of the liquid composition which introduces a considerable simplification in vapor–liquid equilibria computations. Based on eq 10 without ω , isothermals were obtained which are given in Figure 1. The shape of the curves indicates that the system does not exhibit an azeotropic behavior.

Acknowledgment

Thanks are due to Yehudit Reizner and Moshe Golden for their contribution in the experimental and numerical work.

Glossary

$\alpha, \beta, \delta, B, C, D$	constants
B_{ii}, B_{ij}	second virial coefficient of pure component, and the mixed virial coefficient respectively in eq 1 and 2, $\text{cm}^3 \text{mol}^{-1}$
C_1	ternary constant
DEK	diethyl ketone
D, D_{\max}	local deviation and maximum local deviation defined by eq 5 and 6, respectively
m	total number of experimental points
MEK	methyl ethyl ketone
MIBK	methyl isobutyl ketone
n	number of components
P_i^0	vapor pressure of pure component i , mmHg
P	total pressure
R	gas constant

RMSD	$\sqrt{\sum_{j=1}^m \sum_{i=1}^n (y_{ji, \text{obsd}} - y_{ji, \text{calcd}})^2 / mn}$; similarly for γ
t, T	temperature, °C, °K
V_i^0	molar volume of pure component i , $\text{cm}^3 \text{mol}^{-1}$
x_i, y_i	mole fraction composition of component i in the liquid and vapor phases
γ_i	activity coefficients.
$\Delta x, \Delta p, \Delta t$	errors in measurements of concentration, pressure, and temperature
$\dot{\Lambda}_{ij}$	constants, Wilson equation

Subscripts

calcd	calculated
obsd	observed
max	maximum
i	component i

Literature Cited

- (1) Boublikova, L., Lu, B. C. Y., *J. Appl. Chem.*, **19**, 89 (1969).
- (2) E. Hala, et al., "Vapor-Liquid Equilibrium", Pergamon Press, New York, N.Y., 1967.
- (3) McDermott, C., Ellis, S. R. M., *Chem. Eng. Sci.*, **20**, 293 (1965).
- (4) O'Connell, J. P., Prausnitz, J. M., *Ind. Eng. Chem., Process Des. Dev.*, **6**, 245 (1967).
- (5) Wisniak, J., Tamir, A., *J. Chem. Eng. Data*, **21**, 185 (1976).
- (6) Wisniak, J., Tamir, A., submitted for publication in *J. Chem. Eng. Data*.
- (7) Wisniak, J., Tamir, A., *J. Chem. Eng. Data*, **20**, 168 (1975).
- (8) Wisniak, J., Tamir, A., *Chem. Eng. Sci.*, in press.

Received for review February 23, 1976. Accepted June 4, 1976.