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Ternary Vapor–Liquid Equilibria at 760 mmHg in the Systems Methanol–Diethyl Ketone–Methyl Isobutyl Ketone and Methanol–Methyl Ethyl Ketone–Methyl Isobutyl Ketone

Abraham Tamir* and Jaime Wisniak

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

The vapor–liquid equilibria for the ternary systems methanol–diethyl ketone–methyl isobutyl ketone and methanol–methyl ethyl ketone–methyl isobutyl 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 and by an equation based on the separation factor. 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 ±1.0%.

The aim of the present study was to establish new vapor–liquid equilibria data at 760 mmHg for the ternary systems methanol–diethyl ketone (DEK)–methyl isobutyl ketone (MIBK) and methanol–methyl ethyl ketone (MEK)–MIBK and to check the possibility for their prediction from available binary data and by the UNIFAC method (*5*). 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 DEK–MIBK and MEK–MIBK the data of Wisniak and Tamir (*1*), for methanol–DEK the data of Glukhareva et al. (*3*), for methanol–MEK and for methanol–MIBK the data of Eduljee and Tiwari (*4*). It should be noted that the data of Hill and Van Winkle (*2*) for methanol–MIBK were found by Eduljee and Tiwari (*4*) incorrect because of errors in the measurements of the boiling temperature of the mixtures and vapor pressure data. In addition the conversion of mass fractions to mole fractions is in error.

Analytical grade reagents purchased from Merck were used. The physical properties of the pure components (refractive index and boiling point) appeared in ref *1*, and the properties of methanol agreed with literature data. The equilibrium determinations were made in a modified all-glass Dvorak and Boublik recirculation still (*6*), 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. For methanol–DEK–MIBK the chromatographic column was packed with Poropak Q (20%) and operated isothermally at 245 °C. The injector temperature was 340 °C, and the detector was operated at 150 mA and 340 °C. For methanol–MEK–MIBK the column was packed with Chromosorb 101 and operated at 175 °C. Other operating conditions are similar. 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 also gives an indication of whether it is possible to predict the ternary data from the binaries alone. When handling 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 (*8*) 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) An equation which relates the boiling temperature of the mixture with the liquid composition solely has been derived (*8*) on the basis of the concept of "excess property", and it reads

$$T = \sum_{i=1}^{N} x_i T_i^0 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + ...] \quad (1)$$

This equation is useful for obtaining isothermals and for exploring 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 (*11*). For multicomponent mixtures, we kept the binary form of the Redlich and 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

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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 explained in ref *9*. For a ternary mixture, $N=3$, it would read

$$T = \sum_{i=1}^{N} X_i T_i^0 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} X_i X_j [A_{ij} + B_{ij}(X_i - X_j) + C_{ij}(X_i - X_j)^2 + ...] + X_1 X_2 X_3 [A + B(X_1 - X_2) + C(X_1 - X_3) + D(X_2 - X_3) + B'(X_1 - X_2)^2 + C'(X_1 - X_3)^2 + D'(X_2 - X_3)^2 + ...] \quad (2)$$

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

(b) An additional equation used here for correlating the activity coefficient, γ_i, is the Wilson equation for multicomponent mixtures (eq 3). It should be noted that according to the original

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

concepts of Wilson, A_{ij} values 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.

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

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

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 indexes. The binary constants were calculated from the following equations (*11*):

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

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

(d) Another equation which was used relates directly vapor composition of the *i*th component, Y_i, to the composition of the liquid mixture, X_i. The equation has been suggested by Hala et al. (*16*, p 91) and is based on a series expansion of an expression for the separation factor α_{ij} defined by

$$\alpha_{ij} = \frac{Y_i}{X_i} \Big/ \frac{Y_j}{X_j} \quad (6)$$

A truncated expression for α_{ij} used here reads

$$\alpha_{ij} = \frac{1 + \sum_{r=1, r \neq i}^{N} X_r a_{ir}}{1 + \sum_{r=1, r \neq j}^{N} X_r a_{jr}} \quad (7)$$

From eq 6 and 7, Y_i results explicitly:

$$Y_i = \frac{\alpha_{iN} \frac{X_i}{X_N}}{\sum_{j=1}^{N} \alpha_{jN} \frac{X_j}{X_N}} \quad (8)$$

where $\alpha_{ii} = \alpha_{jj} = 1$ and N is the number of components. The a_{ir}'s are parameters determined directly from the multicomponent data by minimizing an appropriate objective function. Equation 8 was found sensitive to errors in measurements of Y_i and hence very useful to detect values of Y_i which deviate from the so-called normal behavior. The above fact is exhibited by a relatively large deviation between calculated and measured values.

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

The error variance σ^2 (*10*) of an intensive property M is defined by eq 9, and is a measure of the spread of the error

$$\sigma^2 = \frac{\sum_{i=1}^{m} (M_{\text{obsd}} - M_{\text{calcd}})_i^2}{m - c - 1} \quad (9)$$

distribution; m and c are respectively the number of data points and parameters which correspond to the mixture of the highest order. 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 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 it reads

$$\bar{D} = \frac{1}{m} \sum_{i=1}^{m} \left| \frac{M_{\text{obsd}} - M_{\text{calcd}}}{M_{\text{obsd}}} \right|_i \quad (10)$$

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.

Results and Discussions

The temperature–concentration measurements at 760 mmHg for the ternary systems methanol–DEK–MIBK and methanol–MEK–MIBK are reported on Tables I and II. The liquid activity coefficients were calculated from

$$\ln \gamma_i = \ln \frac{Y_i P}{X_i P_i^0} + \frac{(B_{ii} - V_i^l)(P - P_i^0)}{RT} + \frac{P}{2RT} \sum_{j=1}^{m} \sum_{k=1}^{m} Y_j Y_k (2\delta_{ji} - \delta_{jk}) \quad (11)$$

where

$$\delta_{ij} = 2B_{ji} - B_{jj} - B_{ii} \quad (12)$$

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

$$\log P_i^0 = A_i - B_i/(t + C_i) \quad (13)$$

Table I. Equilibrium Data for Methanol (1)-DEK (2)-MIBK at 760 mmHg

T °C	X_1	X_2	Y_1	Y_2
65.42	0.930	0.020	0.965	0.012
65.58	0.906	0.056	0.947	0.036
65.65	0.899	0.037	0.953	0.021
66.10	0.862	0.100	0.932	0.053
66.28	0.845	0.104	0.891	0.089
66.28	0.852	0.073	0.925	0.044
66.72	0.805	0.146	0.904	0.076
67.00	0.798	0.072	0.912	0.040
67.75	0.743	0.105	0.902	0.050
68.16	0.729	0.073	0.894	0.039
68.55	0.646	0.182	0.871	0.080
68.80	0.653	0.258	0.843	0.126
68.85	0.673	0.170	0.869	0.081
68.94	0.685	0.074	0.881	0.035
69.00	0.624	0.264	0.832	0.130
69.05	0.627	0.173	0.869	0.072
69.20	0.618	0.230	0.847	0.108
69.22	0.592	0.262	0.842	0.114
69.28	0.652	0.109	0.881	0.047
69.35	0.628	0.143	0.871	0.059
69.45	0.574	0.250	0.839	0.109
69.55	0.605	0.293	0.826	0.141
69.62	0.589	0.325	0.820	0.153
69.67	0.636	0.073	0.865	0.038
70.00	0.564	0.236	0.839	0.060
70.50	0.548	0.266	0.828	0.116
70.50	0.610	0.075	0.862	0.034
70.90	0.511	0.413	0.758	0.213
71.38	0.556	0.073	0.834	0.034
71.52	0.541	0.173	0.838	0.075
71.73	0.477	0.380	0.781	0.175
71.80	0.458	0.263	0.820	0.099
71.90	0.530	0.175	0.834	0.075
72.00	0.517	0.092	0.821	0.047
72.35	0.441	0.483	0.736	0.237
72.65	0.488	0.160	0.773	0.104
72.73	0.500	0.178	0.818	0.077
72.90	0.451	0.219	0.804	0.095
73.21	0.494	0.066	0.822	0.031
73.30	0.413	0.419	0.756	0.191
73.40	0.420	0.358	0.760	0.176
73.61	0.419	0.464	0.759	0.208
73.88	0.480	0.078	0.822	0.036
73.90	0.418	0.311	0.781	0.137
74.25	0.432	0.120	0.789	0.054
74.30	0.378	0.459	0.744	0.207
74.47	0.364	0.570	0.668	0.306
74.95	0.354	0.510	0.707	0.247
75.17	0.368	0.325	0.715	0.169
75.40	0.412	0.058	0.798	0.027
75.75	0.354	0.359	0.734	0.186
75.89	0.361	0.225	0.758	0.107
75.90	0.307	0.633	0.628	0.349
76.00	0.365	0.343	0.751	0.158
76.05	0.337	0.405	0.719	0.198
76.25	0.382	0.092	0.785	0.041
76.28	0.301	0.596	0.695	0.273
76.46	0.301	0.577	0.683	0.275
76.67	0.325	0.338	0.738	0.151
76.83	0.369	0.191	0.727	0.105
78.50	0.306	0.197	0.713	0.097
78.80	0.253	0.645	0.652	0.313
80.42	0.224	0.561	0.645	0.284
81.00	0.213	0.579	0.633	0.296
81.26	0.212	0.610	0.596	0.342
81.45	0.215	0.463	0.615	0.274
81.80	0.223	0.277	0.654	0.147
82.25	0.181	0.758	0.566	0.416
83.24	0.179	0.662	0.573	0.373
84.21	0.206	0.120	0.688	0.062
84.27	0.197	0.340	0.603	0.205
85.01	0.158	0.630	0.545	0.382
85.40	0.181	0.277	0.607	0.173
85.60	0.136	0.639	0.512	0.396
86.17	0.127	0.711	0.483	0.449
86.34	0.136	0.821	0.489	0.496
86.75	0.172	0.319	0.625	0.161
88.89	0.146	0.275	0.598	0.159
89.22	0.087	0.880	0.386	0.601
89.80	0.093	0.638	0.442	0.433
90.11	0.134	0.104	0.596	0.071
92.11	0.109	0.199	0.532	0.133
92.36	0.052	0.923	0.317	0.668
92.90	0.114	0.060	0.567	0.043
92.92	0.064	0.779	0.343	0.585
93.40	0.093	0.421	0.439	0.320
94.25	0.068	0.574	0.353	0.454
94.40	0.096	0.251	0.462	0.191
94.45	0.098	0.085	0.519	0.063
94.68	0.039	0.868	0.262	0.694
96.42	0.041	0.775	0.197	0.706
97.60	0.054	0.419	0.330	0.350

The constants A_i, B_i, and C_i were taken from ref *1* and those for methanol from Hirata et al. (*12*). For the convenience of the reader the constants are reported here for P_i^0 in mmHg:

	A_i	B_i	C_i
methanol	7.8970	1474.0	229.1
DEK	6.9748	1281.2	210.9
MIBK	6.6727	1168.4	191.9
MEK	7.2086	1368.2	236.5

The virial coefficients B_{ii} and the mixed virial coefficients B_{ij} were estimated by the correlation of Tsonopoulos (*13*). It should be noted that the γ_i values calculated according to $Y_iP/X_iP_i^0$ and according to eq 11 differ in extreme cases by not more than 5%.

The ternary data appearing in Tables I and II are thermodynamically consistent and were tested by the McDermott–Ellis method (*14*). According to this test, two experimental points, *a* and *b*, are thermodynamically consistent if

$$D < D_{\max} \qquad (14)$$

The local deviation D is given by

$$D = \sum_{i=1}^{N} (X_{ib} + X_{ia})(\ln \gamma_{ib} - \ln \gamma_{ia}) \qquad (15)$$

According to ref *14* a fixed value for $D_{\max}$ is recommended; however, an equation can be derived (*15*) which reads

$$D_{\max} = \sum_{i=1}^{N} (X_{Ia} + X_{ib}) \left(\frac{1}{X_{ia}} + \frac{1}{Y_{ia}} + \frac{1}{X_{ib}} + \frac{1}{Y_{ib}} \right) \Delta X + 2 \sum_{i=1}^{N} |\ln \gamma_{ib} - \ln \gamma_{ia}| \Delta X + 2 \sum_{i=1}^{N} (X_{ia} + X_{ib}) \frac{\Delta P}{P} + \log e \sum_{i=1}^{N} (X_{ia} + X_{ib}) B_i \left(\frac{1}{[t_a + C_i]^2} + \frac{1}{[t_b + C_i]^2} \right) \Delta t \qquad (16)$$

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 units. Usually the first term on the right-hand side of eq 16 was the dominant one.

The binary data reported elsewhere (*1*, *3*, and *4*) 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 of Wilson's equation. In the case of Redlich–Kister's equation (eq 4), the binary parameters were used, and the ternary constants C_1 were 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

Table II. Equilibrium Data for Methanol(1)-MEK(2)-MIBK

T, °C	X_1	X_2	Y_1	Y_2	T, °C	X_1	X_2	Y_1	Y_2
64.35	0.869	0.107	0.880	0.108	70.05	0.608	0.092	0.824	0.069
64.47	0.826	0.136	0.842	0.143	70.10	0.565	0.082	0.820	0.075
64.52	0.872	0.104	0.878	0.108	70.15	0.516	0.157	0.760	0.146
64.54	0.855	0.125	0.862	0.126	70.35	0.419	0.293	0.687	0.234
64.55	0.902	0.079	0.906	0.083	71.18	0.475	0.194	0.779	0.145
64.60	0.818	0.147	0.875	0.109	71.60	0.312	0.435	0.580	0.345
64.75	0.917	0.040	0.919	0.061	71.60	0.370	0.469	0.596	0.361
64.70	0.889	0.071	0.899	0.084	72.22	0.161	0.746	0.355	0.615
64.78	0.925	0.037	0.940	0.041	72.25	0.499	0.054	0.810	0.047
64.92	0.797	0.183	0.811	0.178	72.30	0.301	0.434	0.547	0.367
65.08	0.798	0.135	0.836	0.139	72.72	0.296	0.575	0.482	0.476
65.35	0.751	0.212	0.781	0.199	73.27	0.268	0.627	0.469	0.502
65.83	0.758	0.133	0.836	0.123	73.35	0.123	0.772	0.300	0.672
65.87	0.588	0.364	0.706	0.278	73.35	0.420	0.173	0.760	0.135
65.92	0.712	0.205	0.788	0.190	73.67	0.291	0.552	0.512	0.434
66.08	0.716	0.214	0.778	0.191	73.72	0.078	0.897	0.258	0.732
66.10	0.570	0.383	0.677	0.308	74.12	0.404	0.235	0.720	0.191
66.16	0.560	0.384	0.694	0.291	74.75	0.267	0.552	0.469	0.474
66.43	0.685	0.237	0.743	0.221	75.18	0.365	0.094	0.759	0.078
66.50	0.821	0.049	0.900	0.047	75.20	0.287	0.248	0.646	0.216
66.62	0.503	0.436	0.639	0.341	75.40	0.393	0.048	0.787	0.041
66.68	0.777	0.074	0.882	0.066	75.50	0.248	0.603	0.440	0.516
66.70	0.709	0.133	0.834	0.113	75.50	0.275	0.285	0.621	0.244
66.83	0.683	0.164	0.813	0.138	75.51	0.310	0.167	0.697	0.152
66.99	0.612	0.231	0.679	0.257	75.62	0.242	0.327	0.583	0.289
67.23	0.569	0.352	0.609	0.297	75.68	0.129	0.764	0.238	0.724
67.35	0.455	0.480	0.629	0.351	76.75	0.232	0.580	0.436	0.506
67.52	0.536	0.334	0.701	0.259	76.91	0.159	0.736	0.283	0.684
67.65	0.496	0.380	0.665	0.299	77.23	0.128	0.797	0.227	0.738
67.82	0.620	0.182	0.752	0.161	77.50	0.149	0.738	0.291	0.672
68.15	0.513	0.303	0.722	0.224	77.74	0.193	0.643	0.360	0.585
68.25	0.523	0.240	0.748	0.184	78.30	0.036	0.749	0.201	0.725
68.37	0.344	0.530	0.553	0.423	79.00	0.115	0.507	0.319	0.521
68.48	0.366	0.608	0.531	0.425	82.95	0.117	0.312	0.406	0.356
68.50	0.589	0.178	0.786	0.146	83.70	0.062	0.598	0.147	0.711
68.53	0.397	0.497	0.584	0.380	85.82	0.211	0.286	0.481	0.300
68.55	0.598	0.154	0.800	0.126	87.60	0.112	0.262	0.342	0.369
68.65	0.447	0.392	0.636	0.317	89.25	0.039	0.498	0.106	0.682
68.75	0.686	0.076	0.758	0.104	91.45	0.185	0.088	0.504	0.124
68.78	0.329	0.596	0.524	0.455	92.05	0.123	0.167	0.382	0.201
68.88	0.375	0.483	0.593	0.371	93.95	0.061	0.256	0.228	0.418
68.90	0.535	0.254	0.736	0.200	95.15	0.163	0.099	0.352	0.157
68.93	0.658	0.067	0.847	0.058	99.14	0.079	0.061	0.373	0.114
69.25	0.398	0.429	0.607	0.340	101.13	0.035	0.141	0.127	0.355
69.39	0.541	0.184	0.778	0.142	101.92	0.044	0.099	0.229	0.197
69.55	0.320	0.564	0.548	0.415	105.35	0.024	0.136	0.093	0.309

Table III. Wilson, Redlich-Kister, and Eq 8 Parameters

		Wilson (eq 3 or 7 and 8)		Redlich-Kister (eq 4)		
system	ij	A_{ij} or a_{ir}	A_{ji} or a_{ri}	B_{ij}	C_{ij}	D_{ij}
methanol-DEK (*3*)	12	0.6724	0.4809	0.6515	0.05929	0.3149
methanol-MIBK (*4*)	13	0.2511	1.3516	1.0752	0.03328	−0.06386
DEK-MIBK (*1*)	23	0.9211	1.1881	−0.02624	0.02068	−0.04297
methanol-MEK (*4*)	12	0.3601	1.0869	0.7907	0.04484	0.1199
MEK-MIBK (*1*)	23	0.5876	1.5716	0.03391	0.1011	0.07521
methanol	12	0.7490[a]	0.5792[a]			
		4.3637[b]	0.3567[b]			
DEK	13	0.4491[a]	0.9439[a]	$C_1 = -2.7488$		
		9.1700[b]	0.0004[b]			
MIBK	23	0.0690[a]	3.0182[a]			
		0.3062[b]	−0.5924[b]			
methanol	12	1.2734[a]	0.2773[a]			
		1.9221[b]	0.4017[b]			
MEK	13	2.3685[a]	0.1289[a]	$C_1 = 0.7932$		
		6.5035[b]	−0.3282[b]			
MIBK	23	1.6801[a]	0.7403[a]			
		2.0932[b]	−0.6661[b]			

[a] A_{ij} or A_{ji} parameters obtained by direct correlation of ternary data by Wilson's equation. [b] a_{ir} or a_{ri} parameters obtained by direct correlation of ternary data by eq 7 and 8.

methods. The following general conclusions could be drawn on the basis of considering $Y = (Y_{obsd} - Y_{calcd})/Y_{obsd}$ and its mean values.

Binary Data. (1) Wilson's equation best correlates the data, and the maximum mean deviation of predicting the vapor composition is ~2%. (2) UNIFAC method predicts the vapor

Table IV. Capability of Predicting the Vapor Composition for Methanol-MEK-MIBK and Methanol-DEK-MIBK at 760 mmHg by Wilson, UNIFAC, Eq 8, and the Redlich-Kister Methods

	Wilson (eq 3), Y, %			UNIFAC and (eq 8), Y, %			Redlich-Kister (eq 4), Y, %		
system	max	min	mean	max	min	mean	max	min	mean
methanol-DEK (*3*)	1.17	0.02	0.36	6.30	0.09	2.04	18.09	0.11	3.94
methanol-MIBK (*4*)	3.39	0.09	1.89	9.05	0.60	3.88	30.6	0.65	7.90
DEK-MIBK (*1*)	4.09	0.04	0.78	11.3	0.67	2.71	8.22	0.41	2.62
methanol-MEK (*4*)	4.52	0.18	1.89	24.2	0.80	5.07	8.77	0.05	3.42
MEK-MIBK (*1*)	2.59	0.14	1.87	4.61	0.81	8.06	7.02	1.93	4.19
methanol	26.6	0.00	2.72	15.3	0.06	4.64	45.2	0.13	9.31
	46.9[a]	0.05[a]	6.26[a]	30.0[b]	0.04[b]	3.70[b]	30.7[a]	0.00[a]	6.71[a]
DEK	39.1	0.00	6.81	89.9	0.00	9.42	62.2	0.04	7.48
	89.4[a]	0.18[a]	9.26[a]	48.3[b]	0.23[b]	11.3[b]	54.7[a]	0.02[a]	9.28[a]
MIBK									
methanol	49.7	0.22	6.95	121	0.04	14.3	147	0.08	14.3
	159[a]	0.12[a]	18.5[a]	48.7[b]	0.01[b]	6.17[b]	167[a]	0.19[a]	22.8[a]
MEK	37.3	0.00	8.02	32.9	0.06	6.30	39.9	0.12	11.0
	33.9[a]	0.46[a]	9.50[a]	39.9[b]	0.01	6.68[b]	38.0[a]	0.04[a]	7.87[a]
MIBK									

[a] Based on prediction from binary parameters. The results without footnote *a* for ternary mixtures are based either on direct correlation of ternary data (by Wilson equation) or on the binary plus ternary data (by Redlich-Kister equation). [b] Equation 8. $Y = (Y_{\text{obsd}} - Y_{\text{calcd}})/Y_{\text{obsd}}$. Mean $= 1/m \sum_{i=1}^{m} |Y_i|$.

Table V. Parameters[c] in Correlation of Binary T-X Data (Eq 5-1 and 5-2)

							D,[a] %		
system	A_{ij}	B_{ij}	C_{ij}	D_{ij}	E_{ij}	F_{ij}	max	min	mean[b]
methanol-DEK (*3*)	−47.674	31.217	−27.026	61.089	−53.660		0.229	0.0039	0.058
methanol-MIBK (*4*)	−76.120	65.909	−58.669	27.745			0.232	0.0098	0.128
DEK-MIBK (*1*)	−1.475	−0.557					0.385	0.0025	0.098
methanol-MEK (*4*)	−30.057	14.437	3.169	−28.388	−36.043	59.072	0.472	0.082	0.201
MEK-MIBK (*1*)	−17.796	3.769	−4.672	4.014			0.017	0.0005	0.008

[a] $D = |(T_{\text{obsd}} - T_{\text{calcd}})/T_{\text{obsd}}|$. [b] Mean $= (1/m)\Sigma D_i$. [c] Corresponding to minimal σ^2 (eq 9).

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

		direct correlation of ternary data								correlation based on binary and ternary data (eq 2)					
						D, %									
system	ij	A_{ij}	B_{ij}	C_{ij}	D_{ij}	max	min	mean	$\sigma^2_{\min}$	c'	c	max	min	mean	$\sigma^2_{\min}$
methanol-	12	−22.729	1.466							6					
MEK-	13	−67.344	36.187							4					
MIBK	23	−31.238	8.685			6.21	0.01	1.39	2.49	4	4	7.05	0.03	1.68	4.05
methanol-	12	−53.307	34.969	−25.538	28.587					5					
DEK-	13	−72.869	63.919	−58.541	24.605					4					
MIBK	23	−27.343	−6.528	0.543	22.529	1.76	0.00	0.52	0.33	2	4	3.12	0.00	0.68	0.62

[a] Corresponding to minimal σ^2 (eq 9). $T_1{}^0 = 64.7$ °C; $T_2{}^0 = 79.56$ (MEK) and 101.7 °C (DEK); $T_3{}^0 = 116.3$ °C.

composition values within a mean deviation of 2.04–8.06% of measured values.

Ternary Data. (1) Direct correlation of ternary data by Wilson's equation is superior (maximum mean deviation of 8%) to prediction of the ternary data from the binary parameters (maximum mean deviation from experimental data is 18.5%). (2) Equation 8 predicts the vapor composition satisfactorily with a maximum mean deviation of 6.17%. (3) UNIFAC method predicts the vapor composition in comparison to measured values with a mean deviation of 3.7–11.3%.

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

$$T = X_1T_1{}^0 + X_2T_2{}^0 + X_1X_2[A_{12} + B_{12}(X_1 - X_2) + C_{12}(X_1 - X_2)^2 + ...] \quad (17)$$

The parameters are reported in Table V, and their number corresponds to minimal σ^2 (eq 9). In Table VI we report the parameters obtained for direct correlation of the ternary data according to the ternary form of eq 1 which reads

$$T = \sum_{i=1}^{3} X_iT_i{}^0 + X_1X_2[A_{12} + B_{12}(X_1 - X_2) + C_{12}(X_1 - X_2)^2 ...] + X_1X_3[A_{13} + B_{13}(X_1 - X_3) + C_{13}(X_1 - X_3)^2 + ...] + X_2X_3[A_{23} + B_{23}(X_2 - X_3) + C_{23}(X_2 - X_3)^2 + ...] \quad (18)$$

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

(1) From the values of the mean overall deviation, eq 1 may be considered as very useful in correlating directly T vs. X. Note that, with six adjustable parameters, T may be correlated directly vs. X with a mean deviation of 1.39% (Table VI) for methanol-MEK-MIBK and with a deviation of 0.52% for methanol-DEK-MIBK with 12 parameters.

(2) Direct correlation of T vs. X for the ternary mixtures is very efficient, and for relatively a similar mean deviation (1.68 and 1.39% for methanol-MEK-MIBK), 6 parameters are re-

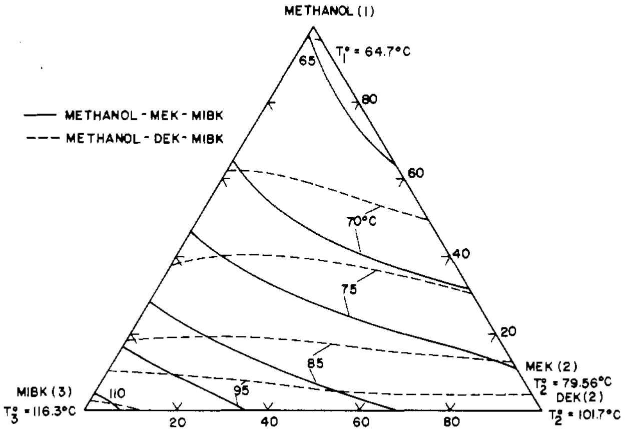

Figure 1. Isotherms for methanol–MEK–MIBK and methanol–DEK–MIBK at 760 mmHg.

quired in direct correlation and 18 parameters are required when all binary parameters are taken into account. Alternatively, with 12 parameters (for methanol–DEK–MIBK) the mean deviation for direct correlation is 0.52%, whereas with 15 parameters the mean deviation is 0.68% taking into account the binary information.

Isotherms (Figure 1) were calculated on the basis of eq 18, 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
a_{ir}, a_{jr}	adjustable parameters in eq 7
C_1	ternary constant
c'	total number of parameters per binary system
c	total number of parameters which correspond to the mixture of the highest order (ternary) system
$\bar{D}$	mean overall deviation from observed values; eq 10
DEK	diethyl ketone
M	intensive property; $M = T$ or Y
MEK	methyl ethyl ketone
MIBK	methyl isobutyl ketone
m	total number of data points which correspond to the system of the highest order
N	number of components in a mixture
P	total pressure
P_i^0	vapor pressure of pure component i
V_i^l	liquid molar volume of component i
T	absolute temperature
T_i^0	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; $Y = (Y_{\text{obsd}} - Y_{\text{calcd}})/Y_{\text{obsd}}$
α_{ij}	separator factor; eq 6
γ_i	activity coefficient of component i
σ^2	error variance; eq 9
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

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Transference Numbers for KCl in Ethanol–Water Mixtures at 25 °C

Miguel A. Esteso* and Domingo M. Grandoso

Departamento de Química Física, Universidad de La Laguna, Tenerife, Canary Islands, Spain

Cation and anion transference numbers for KCl at different ionic concentrations in 5, 10, 20, and 30 wt % ethanol–water mixtures at 25 °C are determined by the direct moving boundary method. Limiting cation transference numbers, T_+^0, are obtained by using the various Fuoss–Onsager and Pitts' equations and verify the earlier data of Fratiello and Kay. The variation of these T_+^0 values with the ethanol content in the mixture was analyzed as a function of a selective solvation effect on both K^+ and Cl^- ions in these media.

Introduction

In a previous paper by this laboratory (*1*) cation and anion transference numbers for KCl in 10 wt % ethanol–water mixture were obtained to establish which of the two sets of existing data (*2*, *3*) was correct. Because the biggest differences between them are from the 15 wt % ethanol–water mixture, we realized the necessity of obtaining some other points which would help us in this purpose.

Experimental Section

The quality of the chemicals and solvents used, their purifi-