Vapor–Liquid Equilibria in the Ternary Systems *tert*-Butyl Alcohol–Diethyl Ketone–Methyl Isobutyl Ketone and Diethyl Ketone–Methyl Isobutyl Ketone–*n*-Butyl Alcohol and Their Binaries

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New data of the vapor–liquid equilibria of the ternary systems *tert*-butyl alcohol diethyl ketone–methyl isobutyl ketone and diethyl ketone–methyl isobutyl ketone–*n*-butyl alcohol and their binaries were obtained at 760 mmHg. The activity coefficients were satisfactorily correlated according to the Redlich–Kister equation and the behavior of the ternary mixtures could be predicted from the binary data. Boiling points of the mixtures were correlated well by an empirical correlation and could be predicted within a mean error of 0.07–0.7%. The ternary systems do not exhibit azeotropic behavior. The binary system methyl isobutyl ketone–*n*-butyl alcohol forms an azeotrope that boils at 113.28 °C and contains 63.3 mol % methyl isobutyl ketone.

Introduction

The ternary systems *tert*-butyl alcohol (*t*-BuOH)–diethyl ketone (DEK)–methyl isobutyl ketone (MIBK) and diethyl ketone–methyl isobutyl ketone–*n*-butyl alcohol and their binaries were studied in order to determine the possibility of predicting their behavior of the binaries. These ternary systems have not been reported in the literature and of the possible binaries only the methyl isobutyl ketone–*n*-butyl alcohol and diethyl ketone–methyl isobutyl ketone are known (*2*).

The measurements were carried out in a modified all-glass Dvorak and Boublik recirculation still (*3*) and the experimental features have been reported previously (*4*). The accuracy in the determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta T = \pm 0.02$ °C. Analytical grade reagents, purchased from Merck, were used without further purification; their physical properties appear in Table I. All analyses were carried out by gas chromatography using a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab minigrator electronic integrator. In all cases the column dimensions were 0.32 × 200 cm, the detector temperature 290–300 °C, and injection temperature 250–260 °C. For mixtures of *t*-BuOH–DEK–MIBK, *t*-BuOH–MIBK, and *t*-BuOH–DEK the column material was OV17-20%; for the ternary system the column was operated at 65 °C and the mole fraction was determined to $\Delta X = \pm 0.001$ units. For the binary systems the column temperatures and accuracies were 95 °C, $\Delta X = \pm 0.002$, and 78 °C, $\Delta X = \pm 0.001$. Analyses of *n*-BuOH–DEK–MIBK, *n*-BuOH–DEK, and *n*-BuOH–MIBK mixtures were carried with a Poropak Q column. Column temperatures and accuracies were 55 °C, $\Delta X = \pm 0.001$; 165 °C, $\Delta X = \pm 0.001$; and 202 °C, $\Delta X = \pm 0.001$.

Table I. Physical Properties of Pure Compounds

compd	refractive index at 25 °C	bp, °C
t-BuOH	1.3850 1.3851 (*5*)	82.5 82.4 (*5*)
DEK	1.39003 1.39002 (*5*)	101.7 101.77 (*5*)
MIBK	1.3935 1.3933 (*5*)	116.30 116.50 (*5*)
n-BuOH	1.3975 1.3973 (*5*)	117.6 117.66 (*5*)

Table II. Vapor Pressure Constants (*5*)

compd	α_i	β_i	δ_i
t-BuOH	7.444 27	1220.499	184.586
DEK	6.978 40	1281.2	210.90
MIBK	6.672 72	1168.41	191.94
n-BuOH	7.476 80	1362.39	178.77

Table III. Experimental Vapor–Liquid Equilibria Data for *tert*-Butyl–Diethyl Ketone at 760 mmHg

Temp, °C	x_1	y_1	γ_1	γ_2
82.96	0.853	0.890	1.0395	1.3330
83.18	0.835	0.874	1.0342	1.3506
83.22	0.796	0.853	1.0572	1.2729
83.56	0.786	0.842	1.0434	1.2899
83.80	0.644	0.750	1.1241	1.2077
84.50	0.676	0.771	1.0725	1.1979
86.41	0.517	0.649	1.0997	1.1585
87.22	0.464	0.611	1.1198	1.1276
89.10	0.359	0.519	1.1483	1.0987
90.45	0.309	0.476	1.1659	1.0645
92.60	0.234	0.390	1.1691	1.0460
93.41	0.200	0.361	1.2309	1.0235
95.32	0.150	0.282	1.2002	1.0215
95.86	0.136	0.258	1.1889	1.0219
96.42	0.121	0.236	1.1993	1.0170

Results and Discussion

The temperature–concentration measurements at 760 mmHg for the binary and ternary systems are reported in Tables III–VIII. The liquid activity coefficients were calculated from the equation

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

where

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

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

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

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Table IV. Experimental Vapor-Liquid Equilibria Data for *tert*-Butyl Alcohol-Methyl Isobutyl Ketone at 760 mmHg

Temp, °C	x_1	y_1	γ_1	γ_2
83.30	0.920	0.959	1.0254	1.3951
83.80	0.896	0.943	1.0160	1.4669
83.95	0.888	0.940	1.0162	1.4265
84.60	0.840	0.920	1.0261	1.3025
86.00	0.759	0.884	1.0360	1.1963
86.05	0.759	0.880	1.0294	1.2355
86.63	0.720	0.860	1.0381	1.2169
88.10	0.637	0.819	1.0591	1.1559
90.32	0.545	0.764	1.0662	1.1183
91.73	0.489	0.724	1.0712	1.1127
94.80	0.385	0.651	1.0994	1.0604
95.80	0.350	0.628	1.1273	1.0364
96.01	0.350	0.618	1.1014	1.0573
98.15	0.293	0.560	1.1091	1.0479
100.85	0.223	0.495	1.1778	1.0080
102.22	0.193	0.453	1.1910	1.0089
103.31	0.168	0.410	1.1955	1.0218
105.10	0.137	0.361	1.2191	1.0121
106.38	0.112	0.328	1.3013	0.9965
107.10	0.099	0.311	1.3647	0.9862
108.04	0.079	0.253	1.3512	1.0181
110.87	0.040	0.168	1.6249	1.0038

Table V. Experimental Vapor-Liquid Equilibria Data for Methyl Isobutyl Ketone-*n*-Butyl Alcohol at 760 mmHg

Temp, °C	x_1	y_1	γ_1	γ_2
113.93	0.838	0.820	1.0409	1.2653
114.00	0.832	0.814	1.0387	1.2576
113.40	0.695	0.689	1.0700	1.1833
113.28	0.633	0.633	1.0829	1.1654
113.22	0.617	0.622	1.0935	1.1527
113.41	0.579	0.590	1.0995	1.1298
113.13	0.568	0.579	1.1085	1.1418
113.42	0.558	0.568	1.0980	1.1334
113.60	0.495	0.505	1.0950	1.1295
113.51	0.430	0.465	1.1636	1.0850
113.82	0.372	0.411	1.1786	1.0724
114.07	0.368	0.406	1.1689	1.0652
114.00	0.335	0.377	1.1946	1.0644
114.50	0.263	0.307	1.2222	1.0497
114.70	0.232	0.276	1.2387	1.0450
115.52	0.160	0.206	1.3109	1.0181
116.23	0.096	0.128	1.3316	1.0135
116.30	0.084	0.108	1.2816	1.0207
116.40	0.068	0.100	1.4619	1.0087
116.57	0.060	0.080	1.3194	1.0163

where the constants are reported in Table II. The virial coefficients B_{ii} and the mixed virial coefficients B_{ij} were estimated by the correlation of Tsonopoulos (*6*) using the molecular parameters reported by the same author.

The binary data appearing in Tables III–VI were tested for thermodynamic consistency by the Herrington test (*12*). The consistency test results appear in Table XI and it may be concluded that the binary data are thermodynamically consistent. The ternary data were tested by the McDermott–Ellis method (*7*) and those appearing in Tables VII and VIII are thermodynamically consistent. According to this test, two experimental points a and b are thermodynamically consistent if the following condition is fulfilled:

$$D < D_{\max} \tag{4}$$

The local deviation D is given by (*7*)

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

Table VI. Experimental Vapor-Liquid Equilibria Data for Diethyl Ketone-*n*-Butyl Alcohol at 760 mmHg

Temp, °C	x_1	y_1	γ_1	γ_2
102.60	0.826	0.865	1.0225	1.3420
102.90	0.777	0.831	1.0354	1.2958
103.50	0.707	0.788	1.0607	1.2091
104.90	0.587	0.686	1.0689	1.2048
105.53	0.536	0.654	1.0963	1.1539
106.20	0.485	0.613	1.1145	1.1340
106.85	0.446	0.592	1.1494	1.0847
107.70	0.382	0.531	1.1756	1.0830
108.02	0.362	0.510	1.1810	1.0832
109.52	0.300	0.446	1.1959	1.0564
110.34	0.262	0.406	1.2190	1.0427
110.53	0.253	0.387	1.1971	1.0558
111.95	0.183	0.314	1.2923	1.0263
112.59	0.156	0.262	1.2434	1.0446
112.70	0.156	0.276	1.3060	1.0208
113.73	0.106	0.197	1.3347	1.0304
114.37	0.075	0.151	1.4216	1.0293
115.30	0.048	0.097	1.3923	1.0296

where n is the number of components. The maximum deviation can be derived (*8*) and reads

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

The errors in the measurements Δx, ΔP, and Δt were as previously indicated.

The activity coefficients for the binary data were correlated by the following Redlich–Kister expansion (eq 8).

$$\ln \gamma_i = (B_{ij} + 3C_{ij} + 5D_{ij})x_j^2 - 4(C_{ij} + 4D_{ij})x_j^3 + 12D_{ij}x_j^4 \tag{7}$$

$$\ln \gamma_j = (B_{ij} - 3C_{ij} + 5D_{ij})x_i^2 + 4(C_{ij} - 4D_{ij})x_i^3 + 12D_{ij}x_i^4 \tag{8}$$

The corresponding coefficients appear in Table VIII. The ternary data were correlated by means of eq 9 where B_{ij}, C_{ij}, and D_{ij}

$$\ln \gamma_1 = x_2x_3[(B_{12} + B_{13} - B_{23}) + C_{12}(2x_1 - x_2) + C_{13}(2x_1 - x_3) + 2C_{23}(x_3 - x_2) + D_{12}(x_1 - x_2)(3x_1 - x_2) + D_{13}(x_1 - x_3)(3x_1 - x_2) - 3D_{23}(x_3 - x_2)^2 + C_1(1 - 2x_1)] + x_2^2[B_{12} + C_{12}(3x_1 - x_2) + D_{12}(x_1 - x_2)(5x_1 - x_2)] + x_3^2[B_{13} + C_{13}(3x_1 - x_3) + D_{13}(x_1 - x_3)(5x_1 - x_3)] \tag{9}$$

are the binary constants and C_1 is a ternary constant reported in Table IX. The equations for the two other activity coefficients were obtained by cyclic rotation of the indices.

The boiling points of the binary and ternary systems were correlated by the following equations.

$$T = \sum_{i=1}^{2} T_i^\circ x_i + x_1x_2\sum_{k=0}^{l} C_k(x_i - x_j)^k \tag{10}$$

$$T = \sum_{i=1}^{3} T_i^\circ x_i + \sum_{i,j=1}^{3} [x_ix_j \sum_{k=0}^{l} C_k(x_i - x_j)^k] + x_1x_2x_3[A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + \ldots] \tag{11}$$

T° 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 where A, B, C, and D are ternary

Table VII. Ternary Vapor-Liquid Equilibrium Data for *tert*-Butyl Alcohol-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
84.86	0.901	0.042	0.057	0.942	0.031	0.027	0.9666	1.2680	1.2667
85.25	0.786	0.038	0.176	0.885	0.028	0.087	1.0257	1.2455	1.2991
85.30	0.874	0.055	0.071	0.925	0.040	0.035	0.9619	1.2303	1.2969
85.38	0.608	0.286	0.106	0.815	0.149	0.036	1.2156	0.8745	0.8856
85.50	0.685	0.266	0.049	0.789	0.189	0.022	1.0399	1.1868	1.1645
85.60	0.803	0.085	0.112	0.902	0.054	0.044	1.0093	1.0629	1.0215
85.70	0.722	0.108	0.170	0.838	0.080	0.082	1.0394	1.2312	1.2451
86.15	0.781	0.100	0.119	0.875	0.070	0.055	0.9856	1.1487	1.1774
86.24	0.792	0.094	0.114	0.878	0.068	0.054	0.9719	1.1838	1.2032
86.27	0.606	0.178	0.216	0.761	0.131	0.108	1.1010	1.1967	1.2605
86.33	0.645	0.211	0.144	0.776	0.153	0.071	1.0521	1.1778	1.2418
86.40	0.761	0.108	0.131	0.860	0.078	0.062	0.9848	1.1747	1.1944
86.40	0.513	0.407	0.080	0.743	0.221	0.036	1.2636	0.8791	1.1291
86.42	0.595	0.181	0.224	0.757	0.131	0.112	1.1091	1.1710	1.2538
86.60	0.613	0.235	0.152	0.751	0.172	0.077	1.0607	1.1773	1.2626
87.80	0.535	0.157	0.308	0.724	0.121	0.155	1.1196	1.1909	1.2023
88.40	0.516	0.353	0.131	0.659	0.269	0.072	1.0337	1.1532	1.2841
89.20	0.474	0.140	0.386	0.678	0.116	0.206	1.1233	1.2222	1.2140
89.60	0.443	0.133	0.424	0.651	0.108	0.241	1.1374	1.1816	1.2743
89.70	0.415	0.496	0.089	0.585	0.369	0.046	1.0877	1.0781	1.1534
89.85	0.412	0.499	0.089	0.586	0.371	0.043	1.0913	1.0724	1.0729
91.90	0.380	0.462	0.158	0.569	0.351	0.080	1.0650	1.0272	1.0506
92.00	0.350	0.303	0.347	0.558	0.252	0.190	1.1305	1.1201	1.1314
92.28	0.278	0.678	0.044	0.433	0.543	0.024	1.0957	1.0671	1.1135
92.40	0.357	0.516	0.127	0.547	0.391	0.062	1.0704	1.0083	0.9960
92.78	0.304	0.443	0.253	0.523	0.297	0.180	1.1863	0.8808	1.4320
93.00	0.337	0.419	0.244	0.539	0.332	0.129	1.0935	1.0345	1.0574
93.00	0.342	0.372	0.286	0.546	0.298	0.156	1.0914	1.0460	1.0910
93.14	0.321	0.561	0.118	0.502	0.439	0.059	1.0643	1.0167	0.9947
93.47	0.323	0.427	0.250	0.520	0.346	0.134	1.0824	1.0423	1.0553
93.69	0.307	0.422	0.271	0.509	0.344	0.147	1.1061	1.0412	1.0601
94.10	0.255	0.526	0.179	0.479	0.423	0.098	1.0678	1.0140	1.0553
94.10	0.229	0.653	0.118	0.376	0.556	0.068	1.0825	1.0717	1.1080
94.15	0.265	0.452	0.283	0.465	0.389	0.146	1.1525	1.0830	0.9923
94.15	0.284	0.455	0.261	0.482	0.376	0.142	1.1142	1.0402	1.0470
94.40	0.414	0.033	0.553	0.658	0.026	0.316	1.0309	0.9876	1.0960
94.72	0.193	0.760	0.047	0.332	0.639	0.029	1.1101	1.0379	1.1622
94.75	0.210	0.692	0.098	0.356	0.586	0.058	1.0922	1.0447	1.1142
94.80	0.375	0.051	0.574	0.635	0.042	0.323	1.0831	1.0191	1.0648
95.50	0.247	0.615	0.138	0.420	0.503	0.077	1.0646	0.9873	1.0273
95.96	0.277	0.354	0.369	0.491	0.303	0.206	1.0904	1.0199	1.0145
96.05	0.149	0.804	0.047	0.273	0.698	0.029	1.1292	1.0288	1.1132
96.41	0.246	0.412	0.342	0.447	0.355	0.198	1.1011	1.0121	1.0362
96.60	0.206	0.500	0.294	0.383	0.444	0.173	1.1208	1.0362	1.0454
96.70	0.337	0.026	0.637	0.594	0.024	0.382	1.0544	1.0773	1.0670
97.48	0.114	0.803	0.083	0.215	0.731	0.054	1.1068	1.0330	1.1214
97.62	0.213	0.458	0.329	0.398	0.405	0.197	1.0861	1.0011	1.0308
98.07	0.180	0.525	0.295	0.313	0.491	0.196	0.9972	1.0436	1.1261
98.20	0.093	0.831	0.076	0.183	0.767	0.050	1.1270	1.0250	1.1085
98.60	0.264	0.075	0.661	0.521	0.066	0.413	1.1060	0.9690	1.0458
98.82	0.273	0.101	0.626	0.516	0.096	0.388	1.0512	1.0399	1.0304
99.13	0.067	0.872	0.061	0.142	0.820	0.038	1.1764	1.0158	1.0196
99.28	0.181	0.411	0.408	0.359	0.388	0.253	1.0891	1.0169	1.0133
99.35	0.236	0.185	0.579	0.460	0.176	0.364	1.0655	1.0238	1.0270
99.68	0.202	0.285	0.513	0.408	0.270	0.322	1.0927	1.0090	1.0140
99.75	0.052	0.894	0.054	0.115	0.851	0.034	1.2023	1.0096	1.0109
99.93	0.157	0.557	0.286	0.316	0.509	0.175	1.0814	0.9655	0.9797
99.97	0.094	0.690	0.216	0.203	0.658	0.139	1.1624	1.0054	1.0273
100.10	0.097	0.687	0.216	0.211	0.650	0.139	1.1653	0.9938	1.0233
100.24	0.233	0.063	0.704	0.478	0.062	0.460	1.0873	1.0318	1.0388
100.40	0.066	0.774	0.160	0.148	0.746	0.106	1.1911	1.0032	1.0432
100.80	0.130	0.619	0.251	0.270	0.571	0.159	1.0842	0.9498	0.9870
100.80	0.057	0.803	0.140	0.133	0.769	0.098	1.2229	0.9852	1.0888
101.00	0.180	0.252	0.568	0.369	0.250	0.381	1.0610	1.0161	1.0401
101.20	0.110	0.658	0.232	0.233	0.619	0.148	1.0918	0.9571	0.9815
101.55	0.158	0.232	0.610	0.346	0.235	0.419	1.1131	1.0207	1.0470
102.34	0.129	0.340	0.531	0.293	0.344	0.363	1.1252	0.9962	1.0168
102.65	0.118	0.449	0.433	0.262	0.451	0.287	1.0890	0.9801	0.9765
106.36	0.115	0.122	0.763	0.284	0.136	0.580	1.0709	0.9790	1.0037
107.94	0.087	0.085	0.828	0.243	0.098	0.659	1.1519	0.9687	1.0034
109.28	0.072	0.077	0.851	0.197	0.094	0.709	1.0822	0.9884	1.0104
110.68	0.054	0.058	0.888	0.158	0.074	0.768	1.1082	0.9942	1.0077
111.17	0.048	0.141	0.811	0.095	0.168	0.737	0.7393	0.9162	1.0441

constants. The various constants are reported in Table X, which also contains information indicating the degree of goodness of the correlation. By means of eq 11 it was possible to draw the isothermals given in Figures 1 and 2. The latter might be used

Table VIII. Ternary Vapor-Liquid Equilibrium Data for Diethyl Ketone-Methyl Isobutyl Ketone-*n*-Butyl Alcohol at 760 mmHg

T, °C	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
102.46	0.897	0.074	0.029	0.920	0.057	0.023	1.0055	1.1387	1.4230
102.47	0.868	0.064	0.068	0.908	0.047	0.045	1.0252	1.0855	1.1865
102.72	0.860	0.094	0.046	0.891	0.069	0.040	1.0081	1.0769	1.5437
102.92	0.807	0.107	0.086	0.873	0.081	0.046	1.0466	1.1040	0.9419
103.00	0.835	0.108	0.057	0.850	0.085	0.065	0.9826	1.1453	2.0015
103.54	0.785	0.133	0.082	0.842	0.095	0.063	1.0195	1.0229	1.3196
103.79	0.789	0.060	0.151	0.762	0.042	0.196	0.9116	0.9961	2.2041
103.84	0.757	0.156	0.087	0.774	0.109	0.117	0.9636	0.9921	2.2813
104.29	0.671	0.179	0.150	0.749	0.137	0.114	1.0386	1.0723	1.2665
104.46	0.698	0.110	0.192	0.777	0.076	0.147	1.0309	0.9635	1.2664
104.60	0.612	0.268	0.120	0.676	0.206	0.118	1.0187	1.0671	1.6192
105.13	0.363	0.049	0.588	0.678	0.038	0.284	1.6977	1.0617	0.7770
105.17	0.595	0.125	0.280	0.707	0.101	0.192	1.0785	1.1039	1.1024
105.27	0.622	0.227	0.151	0.697	0.174	0.129	1.0141	1.0435	1.3693
105.29	0.520	0.319	0.161	0.609	0.258	0.133	1.0592	1.1003	1.3237
105.60	0.548	0.337	0.115	0.633	0.265	0.102	1.0357	1.0600	1.4043
105.75	0.572	0.260	0.168	0.667	0.199	0.134	1.0412	1.0275	1.2545
106.13	0.482	0.103	0.415	0.595	0.082	0.323	1.0909	1.0588	1.2035
106.23	0.480	0.124	0.396	0.628	0.112	0.260	1.1528	1.1970	1.0118
106.50	0.338	0.433	0.229	0.425	0.371	0.204	1.0991	1.1256	1.3609
106.93	0.432	0.110	0.458	0.559	0.099	0.342	1.1183	1.1696	1.1190
107.00	0.478	0.309	0.213	0.570	0.255	0.175	1.0281	1.0686	1.2303
107.09	0.511	0.356	0.133	0.602	0.284	0.114	1.0132	1.0298	1.2799
107.20	0.400	0.250	0.350	0.508	0.211	0.281	1.0890	1.0875	1.1916
107.80	0.410	0.348	0.242	0.504	0.291	0.205	1.0365	1.0582	1.2294
107.97	0.234	0.493	0.273	0.290	0.451	0.259	1.0398	1.1521	1.3684
108.07	0.456	0.428	0.116	0.547	0.353	0.100	1.0040	1.0349	1.2397
108.09	0.342	0.200	0.458	0.456	0.177	0.367	1.1156	1.1123	1.1480
108.43	0.354	0.375	0.271	0.446	0.318	0.236	1.0440	1.0541	1.2333
108.52	0.413	0.482	0.105	0.499	0.397	0.104	0.9988	1.0203	1.4000
108.82	0.298	0.175	0.527	0.405	0.161	0.434	1.1147	1.1330	1.1465
108.90	0.389	0.518	0.093	0.470	0.432	0.098	0.9884	1.0219	1.4682
109.35	0.330	0.487	0.183	0.398	0.438	0.164	0.9744	1.0883	1.2264
109.45	0.270	0.158	0.572	0.364	0.152	0.484	1.0870	1.1642	1.1495
109.55	0.309	0.572	0.119	0.391	0.498	0.111	1.0168	1.0472	1.2678
109.57	0.310	0.571	0.119	0.391	0.491	0.118	1.0129	1.0338	1.3466
109.79	0.319	0.406	0.275	0.243	0.463	0.294	0.6079	1.3637	1.4372
109.95	0.244	0.437	0.319	0.318	0.398	0.284	1.0357	1.0842	1.1892
110.23	0.206	0.287	0.507	0.278	0.364	0.358	1.0644	1.4988	0.9325
110.37	0.211	0.181	0.608	0.304	0.203	0.493	1.1327	1.3222	1.0636
110.40	0.131	0.559	0.310	0.178	0.531	0.291	1.0664	1.1163	1.2332
110.52	0.153	0.513	0.334	0.206	0.467	0.327	1.0534	1.0665	1.2796
110.53	0.183	0.350	0.467	0.253	0.337	0.410	1.0816	1.1287	1.1457
110.80	0.126	0.594	0.280	0.204	0.559	0.237	1.2570	1.0932	1.0959
110.92	0.220	0.685	0.095	0.282	0.611	0.107	0.9922	1.0320	1.4539
111.05	0.167	0.229	0.604	0.241	0.227	0.532	1.1138	1.1466	1.1258
111.15	0.201	0.703	0.096	0.265	0.634	0.101	1.0142	1.0367	1.3465
111.18	0.163	0.144	0.693	0.250	0.153	0.597	1.1801	1.2256	1.0951
111.20	0.142	0.224	0.634	0.210	0.230	0.560	1.1369	1.1830	1.1224
111.25	0.187	0.062	0.751	0.296	0.075	0.629	1.2161	1.3936	1.0616
111.37	0.147	0.222	0.631	0.218	0.229	0.553	1.1348	1.1827	1.1065
111.26	0.148	0.596	0.256	0.187	0.536	0.277	0.9688	1.0315	1.3760
111.50	0.128	0.626	0.246	0.170	0.586	0.244	1.0118	1.0662	1.2506
111.60	0.178	0.745	0.077	0.241	0.670	0.089	1.0290	1.0208	1.4548
111.80	0.112	0.677	0.211	0.148	0.643	0.209	0.9986	1.0725	1.2356
111.84	0.185	0.769	0.046	0.238	0.704	0.058	0.9716	1.0321	1.5735
111.93	0.132	0.200	0.668	0.200	0.213	0.587	1.1422	1.2025	1.0861
112.00	0.106	0.602	0.292	0.154	0.530	0.316	1.0919	0.9893	1.3378
112.30	0.093	0.735	0.172	0.123	0.692	0.185	0.9861	1.0482	1.3173
112.60	0.083	0.766	0.151	0.110	0.733	0.157	0.9803	1.0564	1.2598
112.66	0.124	0.824	0.052	0.173	0.762	0.065	1.0307	1.0190	1.5129
113.10	0.073	0.811	0.116	0.091	0.751	0.158	0.9098	1.0082	1.6199
113.20	0.114	0.069	0.817	0.173	0.086	0.741	1.1069	1.3611	1.0682
113.28	0.037	0.673	0.290	0.043	0.659	0.298	0.8439	1.0614	1.2117
113.30	0.062	0.847	0.091	0.084	0.806	0.110	0.9837	1.0302	1.4281
113.50	0.073	0.127	0.800	0.121	0.166	0.713	1.1988	1.4147	1.0382
113.63	0.056	0.865	0.079	0.067	0.841	0.092	0.8611	1.0429	1.3595
114.65	0.045	0.088	0.867	0.072	0.113	0.815	1.1231	1.3481	1.0491
115.10	0.044	0.077	0.879	0.063	0.104	0.833	0.9933	1.4008	1.0402

for considering possible distillation paths in ternary systems as well as to conclude whether a ternary system exhibits azeotropic behavior.

On the basis of the data gathered in this work the following may be concluded. (1) The ternary systems do not exhibit azeotropic behavior. The binary system MIBK–*n*-BuOH forms an azeotrope which has a composition of 63.3 mol % MIBK with a boiling point of 113.28 °C at 760 mmHg. Dakshinamurty (*1*) has reported a similar composition but the boiling point was 111.2 °C, whereas Lecat (*1*) has reported that the boiling point

Table IX. Redlich-Kister Constants

system	B_{ij}	C_{ij}	D_{ij}	RMSD[a] γ_i	RMSD[a] γ_j
t-BuOH-DEK	0.4834	5.573×10^{-4}	1.007×10^{-5}	0.1255	0.0421
t-BuOH-MIBK	0.3479	3.342×10^{-4}	2.469×10^{-4}	0.0662	0.0427
DEK-MIBK	−0.05082	8.016×10^{-5}	5.412×10^{-6}	0.0178	0.0489
DEK-*n*-BuOH	0.47017	3.470×10^{-4}	3.154×10^{-5}	0.0744	0.0256
MIBK-*n*-BuOH	0.45427	3.526×10^{-4}	2.936×10^{-5}	0.0742	0.0366

		overall RMSD[b] γ	overall RMSD[b] y
t-BuOH-DEK-MIBK	$C_1 = -1.6176$	0.1462	0.0270
	$C_1 = 0$	0.1464	0.0387
DEK-MIBK-*n*-BuOH	$C_1 = -0.21417$	0.1426	0.0301
	$C_1 = 0$	0.1426	0.0302

$((y_{\text{obsd}} - y_{\text{calcd}})/y_{\text{obsd}})100 = Y$

Maximum			Mean $= \Sigma^m \lvert Y \rvert / m$		
t-BuOH	DEK	MIBK	*t*-BuOH	DEK	MIBK
64.0	30.9	35.5	8.7	7.7	14.5
DEK	MIBK	*n*-Bu	DEK	MIBK	*n*-BuOH
68.7	26.8	57.2	6.4	6.7	8.6

[a] RMSD $= (\Sigma(\gamma_{\text{obsd}} - \gamma_{\text{calcd}})^2/\text{m})^{1/2}$. [b] Overall RMSD $= (\Sigma_{i=1}{}^{m}\Sigma_{j=1}{}^{n}(\gamma_{ij,\text{obsd}} - \gamma_{ij,\text{calcd}})^2/\text{mn})^{1/2}$; similarly for Y.

Table X. Correlation of Boiling Points, Eq 10 and 11

System	C_0	C_1	C_2	C_3	RMSD[b]	Y[a] Max	Y[a] Mean
t-BuOH-DEK	−22.465	5.0445	−0.2248	4.3529	0.229	0.79	0.188
t-BuOH-MIBK	−30.802	11.933	−18.609	23.956	0.349	1.03	0.262
DEK-MIBK	−1.6501	−0.8143	1.0206	0.2269	0.147	0.17	0.092
DEK-*n*-BuOH	−14.626	0.3890	−3.0144	11.816	0.182	0.30	0.134
MIBK-*n*-BuOH	−14.019	−2.1143	−5.7872	−1.3947	0.0972	0.17	0.073

System	A	B	C	D	RMSD	Y[a] Max	Y[a] Mean
t-BuOH-DEK-MIBK	−9.0079	−54.414	46.782	1.3285	0.827	2.30	0.729
DEK-MIBK-*n*-BuOH	−12.585	28.835	−24.815	−3.0806	0.625	2.88	0.382

[a] $Y = ((T_{\text{obsd}} - T_{\text{calcd}})/T_{\text{obsd}})100$. Mean $= \Sigma^m \lvert Y \rvert / m$. [b] RMSD $= (\Sigma(T_{\text{obsd}} - T_{\text{calcd}})^2/m)^{1/2}$.

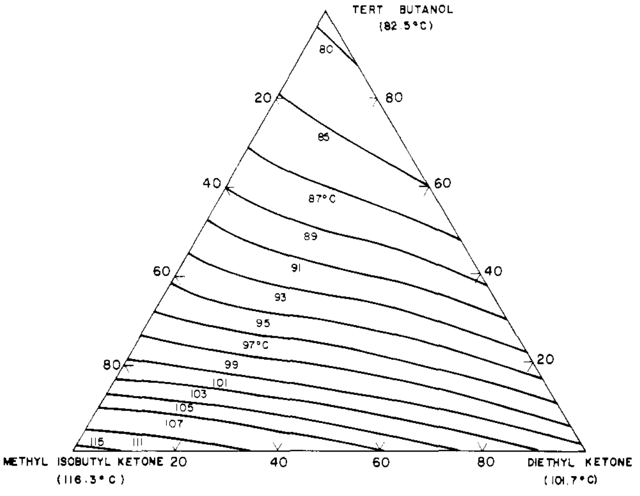

Figure 1. Isothermals at 760 mmHg for the system *tert*-butyl alcohol–diethyl ketone–methyl isobutyl ketone calculated by eq 11.

was 114.35 °C. (*2*) The ternary behavior may be predicted from the binary data (see Table IX). (*3*) The boiling point of the mixtures can be predicted within a mean error of ±0.07 to ±0.7%. (*4*) Comparison of the activity coefficients of the different systems in Tables VII and VIII shows that in spite of the substantial difference in the spacial configuration of the species involved, the activity coefficients are essentially the same.

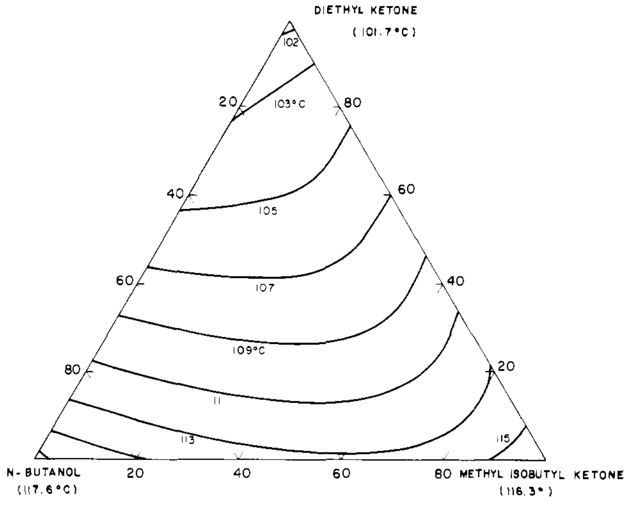

Figure 2. Isothermals at 760 mmHg for the system diethyl ketone–methyl isobutyl ketone–*n*-butyl alcohol calculated by eq 11.

Table XI. Consistency Test Data for Binary Systems[a]

binary systems	D	J	$\lvert D - J \rvert$
t-BuOH-DEK	16.2	8.2	8
t-BuOH-MIBK	6.5	14.3	7.8
MIBK-*n*-BuOH	5.3	5.8	0.3
DEK-*n*-BuOH	10.8	6.3	4.5

[a] According to Herrington (*12*) if $\lvert D - J \rvert < 10$ the data are probably thermodynamically consistent.

Acknowledgment

Thanks are due to Mrs. Yehudit Reizner for helping with the experimental work.

Glossary

α, β, δ, A, B, C, D	constants
B_{ii}, B_{ij}	second virial coefficient for pure component and the mixed virial coefficient, respectively
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°	vapor pressure component i, mmHg
P	total pressure
R	gas constant
t, T	temperature, °C, K
V_i°	molar volume of the pure component
x_i, y_i	mole fraction composition of component i in the liquid and vapor phases
γ_i	activity coefficient
Δx, Δp, Δt	errors in measurements of concentration, pressure, and temperature

Subscripts

calcd	calculated	max	maximum
obsd	observed	i	component i

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Surface Tension and Density of Liquid Tin–Lead Solder Alloys

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As part of the Bureau of Mines program to either conserve scarce domestic mineral resources or substitute for them, development of new soldering systems was undertaken. To support and facilitate this study, the properties of tin–lead solders were investigated. Surface tensions and densities of tin–lead solder alloys have been determined by use of an improved maximum-bubble-pressure system that includes provisions for density measurements. Results show general agreement with accepted theories for simple solutions. Comparisons with other reported measurements on these alloys are made.

Introduction

Over the years many measurements of the surface tensions of tin, lead, and tin-lead alloys have been reported. The results of most of these may be divided into two groups. Some report straight-line temperature–surface tension relationships and show, for binary alloys at constant temperatures, that the relationshsip between the surface tension and composition is represented by concave-upward smooth curves (*5*, *9*, *10*, *23*), in agreement with the accepted theories for simple solutions. Others present curves that deviate from these theories (*1*, *2*, *6*, *7*, *12*, *14*). It is rather interesting that White (*23*), although reporting isotherms that follow accepted theory (*8*, *13*, *19*), shows variable-temperature coefficients for the surface tensions of the binary alloys along with straight-line relationships for the two unalloyed metals. This paper presents data to add to the evidence for normal, simple-solution behavior for surface tension and density of the tin–lead alloys. These data are important becase the general theories of spontaneous wetting and spreading do not agree with the surface tension data for tin-lead solders. Because tin and lead form a simple eutectic system, minimum surface tension, maximum wetting and spreading, and deviations in other properties may be expected to occur at the approximately 63 wt % tin–37 wt % lead eutectic alloy. In actual soldering tests a 50–50 wt % tin–lead alloy spontaneously wets and spreads best (*11*), while the surface tension is lowest for 100% lead and rises according to theories for ideal or simple solutions to a maximum at 100% tin.

The problems of measuring the surface tensions of molten metals are extensive and complicated. The data obtained by others that deviate from simple solution theory may be correct—we cannot judge this —but theory and data should be consistent. This in not true for some of the reported observations. That complete miscibility exists above the liquidus of simple binary eutectic systems, such as tin and lead, cannot be denied, so we prefer to stay with the theory. The data obtained from the improved maximum-bubble-pressure (MBP) system (*17*) have been consistent and reproducible. Several of the researchers who have reported curves that deviate from solution theory relied on sessile-drop or contact-angle systems for determining the surface tension. It is felt that, in light of the anomalous wetting and spreading properties of tin–lead solders, the method of surface tension measurement may enter into the deviations shown. Some of these problems have been reiterated by White in his two reviews on this subject (*21*, *22*) and were illustrated rather vividly by Wilkinson in his review of the surface properties of mercury (*24*).

Experimental Procedure

All measurements were made with an improved maximum-bubble-pressure system which has been described in detail (*17*). This system used a modified form of the Sugden twin-capillary method (*18*), where two capillaries of different radii are placed side by side at exactly the same depth in the liquid.