Vapor–Liquid Equilibria in the Ternary Systems Water–Formic Acid–Acetic Acid and Water–Acetic Acid–Propionic Acid

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The vapor–liquid equilibria behavior of two ternary mixtures, water–formic acid–acetic acid and water–acetic acid–propionic acid, was studied experimentally in a Dvorak and Boublik recirculation still at 760 mmHg. A ternary saddle point azeotrope exists in the first mixture which boils at 107.0 °C and contains 36.3 mole % water, 46.9 mole % formic acid, and 16.8 mole % acetic acid. No ternary azeotrope exists in the second mixture. A thermodynamic model suggested in the past, which accounts for nonideal gas behavior and association effects in a multicomponent mixture, was applied for analysis of the data.

In previous investigations on ternary systems containing fatty acids we studied experimentally the vapor–liquid equilibria properties of the systems formic acid–acetic acid–propionic acid (*16*) and water–formic acid–propionic acid (*17*). No azeotrope was found at 760 mmHg in the first case, whereas a ternary saddle point azeotrope, boiling at 107.5 °C and containing 42 mole % water, 54 mole % formic acid, and 4 mole % propionic acid, was revealed in the second system. This information is very useful in regards to the possibility of separating the acids by distillation of their mixture (which is obtained by oxidation of paraffins).

As a continuation of the above work, we studied the vapor–liquid equilibria behavior of water–formic acid–acetic acid and water–acetic acid–propionic acid. The fatty acids are known to exhibit autoassociation and heteroassociation among the species, and reliable data are available to account for these effects. Hence, the above systems are also suitable to test the thermodynamic model we suggested (*16*, *17*) for computing liquid overall activity coefficients. The values of the latter are important for checking the consistency of the measurements and testing correlations for liquid activity coefficients.

Experimental Section

Purity of Materials. Analytical grades of formic, acetic, and propionic acids purchased from Merck, Fluka, and B.D.H. were used. Gas chromatograph analysis showed some water in the acids on the order of 0.025 mole fraction. However, since the experimental systems investigated contain water, no attempt was made for further purification of the acids. Physical properties of the pure components appear in Table I where distilled water was used.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*5*) was used in the equilibrium determinations. The experimental features have been previously described (*18*). 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, packed with Chromosorb 101, and operated at 175 °C for water–acetic acid–propionic acid and at 150 °C for water–formic acid–acetic acid. Injector temperature was 240 °C and the detector operated at 150 mA and 250 °C. Concentration measurements were generally accurate to ±0.002 mole fraction units in the system water–formic acid–acetic acid, whereas in water–acetic acid–propionic acid the accuracy was ±0.0025. Boiling temperatures were measured with a Hewlett-Packard quartz thermometer, Model 2801 A, with an accuracy of ±0.0001 °C. The boiling temperatures were stable within ±0.02 °C.

Results and Discussion

The temperature–concentration measurements at 760 mmHg for the ternary systems water–formic acid–acetic acid and water–acetic acid–propionic acid are reported in Tables II and III. In the following we designate the species in a ternary system by A, B, and C, respectively, A corresponding to the most volatile component. Specie B and C undergo dimerization between their monomers, namely, $B_1 + B_1 \rightleftarrows B_2$ and $C_1 + C_1 \rightleftarrows C_2$ where by species we refer to a mixture of monomer + dimer, namely, $B = B_1 + B_2$. In addition, species B and C react according to $B_1 + C_1 \rightleftarrows BC$ to form the heterodimer BC whereas species A (water) is assumed passive. This is due to the lack of data concerning the association constants of water with the other species and consistent with the views of other publications in the area of fatty acid–water equilibria (*15*, *19*). The liquid overall activity coefficients, γ_A, γ_B, and γ_C, appearing in F_A, F_B, and F_C (eq 2) were calculated from the simultaneous solution of the following three nonlinear equations derived elsewhere (*17*)

$$F_A - y_A[P + K_{BB}\hat{\Phi}_B F_B{}^2 + K_{CC}\hat{\Phi}_C F_C{}^2 + \overline{K}_{BC}F_B F_C] = 0 \qquad (1.1)$$

$$(2 - y_B)K_{BB}\hat{\Phi}_B F_B{}^2 + F_B[1 + (1 - y_B)\overline{K}_{BC}F_C] - y_B[P + K_{CC}\hat{\Phi}_C F_C{}^2] = 0 \qquad (1.2)$$

$$(2 - y_C)K_{CC}\hat{\Phi}_C F_C{}^2 + F_C[1 + (1 - y_C)\overline{K}_{BC}F_B] - y_C[P + K_{BB}\hat{\Phi}_B F_B{}^2] = 0 \qquad (1.3)$$

where for i = A, B, C

$$F_i = \gamma_i x_i P_{i_1}{}^0/E_i \qquad (2)$$

$$E_i = \exp\left[\frac{(P - P_{i_1}{}^0)(b_i - V_i{}^L)}{RT}\right] \qquad (3)$$

$$\hat{\Phi}_i = \exp\left[\frac{b_i P}{RT}\right] \qquad (4)$$

and for i = B, C

$$P_{i_1}{}^0 = P_i{}^0\left(\frac{-1 + \left(1 + 4K_{ii}P_i{}^0 \exp\left[\frac{b_i P_i{}^0}{RT}\right]\right)^{1/2}}{2K_{ii}P_i{}^0 \exp\left[\frac{b_i P_i{}^0}{RT}\right]}\right) \qquad (5)$$

Table I. Physical Constants of Compounds at 25 °C

Compound	Density, g cm^{-3}	RI[b]
Formic acid	1.2136	1.3690
	1.2139[a]	1.3693[a]
Acetic acid	1.0435	1.3696
	1.0437[a]	1.3698[a]
Propionic acid	0.9879	1.3837
	0.9880[a]	1.3843[a]

[a] From ref 7. [b] RI = refractive index.

Table II. Ternary Vapor-Liquid Equilibrium Data for Water (1)-Formic Acid (2)-Acetic Acid (3) at 760 mmHg

Temp, °C		Liquid compn			Vapor compn			Activity coeff		
Obsd	Calcd	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
101.09	100.68	0.957	0.030	0.013	0.975	0.016	0.009	0.982 03	0.977 89	2.614 72
102.03	101.81	0.855	0.039	0.106	0.889	0.029	0.082	0.992 05	0.987 64	1.928 00
102.19	101.68	0.900	0.076	0.024	0.943	0.040	0.017	0.976 42	0.844 88	2.159 70
103.06	102.74	0.759	0.040	0.201	0.837	0.027	0.136	1.033 29	0.787 54	1.455 52
103.10	102.81	0.827	0.099	0.074	0.873	0.068	0.059	0.971 17	0.905 54	1.870 66
103.24	104.24	0.140	0.818	0.042	0.095	0.866	0.039	0.864 95	1.006 93	1.067 97
103.25	103.34	0.777	0.089	0.134	0.792	0.081	0.127	0.960 79	1.043 23	1.886 47
103.73	102.89	0.831	0.150	0.019	0.895	0.090	0.015	0.958 83	0.851 38	1.936 51
104.00	104.85	0.175	0.761	0.064	0.125	0.816	0.059	0.870 27	1.005 87	1.062 76
104.06	104.21	0.709	0.095	0.196	0.788	0.064	0.148	1.020 90	0.742 01	1.466 56
104.14	103.04	0.822	0.161	0.017	0.894	0.093	0.013	0.954 27	0.811 86	1.851 65
104.41	104.26	0.739	0.144	0.117	0.808	0.099	0.093	0.980 55	0.800 65	1.582 72
104.61	104.50	0.726	0.159	0.115	0.800	0.108	0.092	0.983 35	0.783 89	1.564 04
104.62	104.66	0.641	0.073	0.286	0.751	0.041	0.208	1.072 91	0.572 36	1.321 70
104.87	105.32	0.210	0.691	0.099	0.164	0.745	0.091	0.903 43	0.995 26	1.068 62
105.07	105.22	0.603	0.081	0.316	0.708	0.056	0.236	1.076 25	0.676 12	1.279 57
105.12	105.30	0.658	0.149	0.193	0.741	0.108	0.151	1.011 19	0.762 41	1.392 18
105.22	104.87	0.162	0.649	0.189	0.136	0.691	0.173	0.985 65	0.966 86	1.078 59
105.45	105.63	0.236	0.637	0.127	0.186	0.697	0.117	0.884 01	0.998 23	1.078 01
105.51	105.86	0.609	0.148	0.243	0.696	0.113	0.191	1.031 41	0.761 31	1.318 17
105.53	105.42	0.578	0.075	0.347	0.689	0.054	0.257	1.083 92	0.684 77	1.231 87
105.61	104.63	0.723	0.248	0.029	0.792	0.181	0.027	0.937 42	0.863 04	1.728 16
105.61	105.09	0.692	0.226	0.082	0.757	0.170	0.073	0.951 76	0.836 84	1.584 01
106.07	106.53	0.483	0.074	0.443	0.642	0.053	0.305	1.210 86	0.649 06	1.084 31
106.07	106.02	0.524	0.073	0.403	0.642	0.053	0.305	1.116 11	0.657 95	1.191 93
106.17	105.42	0.667	0.273	0.060	0.693	0.249	0.058	0.901 96	0.970 17	1.549 20
106.19	106.15	0.606	0.238	0.156	0.659	0.203	0.138	0.964 44	0.854 74	1.395 64
106.20	106.40	0.576	0.331	0.093	0.611	0.298	0.091	0.950 56	0.903 78	1.448 93
106.32	106.22	0.599	0.262	0.139	0.648	0.225	0.127	0.957 29	0.859 36	1.417 39
106.55	106.77	0.543	0.241	0.216	0.604	0.206	0.190	0.999 35	0.812 27	1.319 60
106.66	106.82	0.534	0.264	0.202	0.583	0.236	0.181	0.983 66	0.846 26	1.314 73
106.72	107.19	0.494	0.176	0.330	0.574	0.150	0.276	1.059 03	0.768 16	1.233 17
106.87	106.76	0.454	0.065	0.481	0.583	0.047	0.370	1.169 12	0.619 21	1.138 86
106.93	107.24	0.463	0.118	0.419	0.574	0.093	0.333	1.127 13	0.687 03	1.169 27
106.95	106.59	0.551	0.344	0.105	0.577	0.320	0.103	0.926 28	0.902 08	1.393 48
106.95	106.96	0.504	0.308	0.188	0.546	0.286	0.168	0.978 10	0.869 60	1.260 80
106.97	106.40	0.579	0.367	0.054	0.609	0.337	0.054	0.912 38	0.918 31	1.436 30
106.99	106.91	0.437	0.061	0.502	0.567	0.049	0.384	1.185 15	0.680 99	1.117 80
107.00	107.41	0.473	0.199	0.328	0.546	0.175	0.279	1.053 50	0.783 92	1.222 45
107.04	106.90	0.446	0.068	0.486	0.571	0.051	0.378	1.164 88	0.637 24	1.138 46
107.10	106.97	0.442	0.455	0.103	0.429	0.464	0.107	0.906 61	0.939 53	1.319 65
107.10	107.46	0.466	0.213	0.321	0.531	0.192	0.277	1.042 30	0.801 02	1.224 58
107.10	106.91	0.493	0.362	0.145	0.513	0.346	0.141	0.943 23	0.892 70	1.323 50
107.14	106.96	0.404	0.426	0.170	0.409	0.428	0.163	0.960 20	0.908 64	1.225 16
107.20	107.11	0.445	0.359	0.196	0.469	0.343	0.188	0.975 24	0.867 51	1.280 27
107.25	106.96	0.425	0.054	0.521	0.555	0.043	0.402	1.189 18	0.665 49	1.112 65
107.28	107.15	0.495	0.482	0.023	0.473	0.503	0.024	0.859 40	0.986 72	1.315 90
107.40	107.44	0.420	0.309	0.271	0.431	0.328	0.241	0.964 55	0.937 29	1.169 67
107.40	107.29	0.376	0.362	0.262	0.396	0.362	0.242	1.005 60	0.878 55	1.191 20
107.53	106.83	0.219	0.436	0.345	0.216	0.482	0.302	1.032 04	0.942 30	1.053 99
107.61	107.93	0.414	0.195	0.391	0.487	0.181	0.332	1.081 78	0.793 62	1.166 25
107.65	107.83	0.406	0.114	0.480	0.521	0.093	0.386	1.167 05	0.681 49	1.128 33
107.79	108.08	0.382	0.229	0.389	0.443	0.221	0.336	1.080 42	0.818 52	1.153 53
108.08	107.76	0.367	0.055	0.578	0.499	0.043	0.458	1.235 93	0.626 88	1.088 06
108.13	108.43	0.361	0.167	0.472	0.451	0.154	0.395	1.152 04	0.759 35	1.120 34
108.16	108.21	0.251	0.311	0.438	0.283	0.329	0.388	1.124 34	0.872 34	1.099 20
108.34	108.56	0.347	0.149	0.504	0.440	0.137	0.423	1.169 05	0.745 64	1.114 30
108.53	108.10	0.347	0.061	0.592	0.476	0.047	0.477	1.241 15	0.608 10	1.083 87
108.61	108.70	0.330	0.172	0.498	0.414	0.163	0.423	1.159 02	0.764 79	1.108 16
108.66	108.65	0.328	0.101	0.571	0.440	0.094	0.466	1.226 88	0.737 32	1.077 60
109.15	108.95	0.305	0.104	0.591	0.421	0.094	0.485	1.253 03	0.704 79	1.064 37
109.15	109.17	0.280	0.173	0.547	0.366	0.166	0.468	1.216 08	0.755 06	1.084 74
109.27	109.29	0.278	0.142	0.580	0.376	0.137	0.487	1.248 88	0.751 97	1.067 06
109.58	109.38	0.270	0.142	0.588	0.358	0.138	0.504	1.222 94	0.749 39	1.075 89
110.00	109.57	0.254	0.086	0.660	0.367	0.078	0.555	1.312 16	0.680 99	1.050 86
110.41	110.00	0.223	0.125	0.652	0.321	0.120	0.559	1.318 05	0.717 65	1.046 96
110.80	110.26	0.208	0.104	0.688	0.300	0.111	0.589	1.319 27	0.786 25	1.031 47

Table III. Ternary Vapor-Liquid Equilibrium Data for Water (1)-Acetic Acid (2)-Propionic Acid (3) at 760 mmHg

Temp, °C		Liquid compn			Vapor compn			Activity coeff		
Obsd	Calcd	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
100.81	100.85	0.858	0.060	0.082	0.921	0.034	0.045	1.060 92	1.564 97	2.592 74
100.60	100.58	0.877	0.040	0.083	0.928	0.024	0.048	1.051 47	1.710 95	2.822 03
100.85	100.87	0.859	0.063	0.078	0.924	0.034	0.042	1.060 65	1.505 32	2.568 60
101.03	100.90	0.827	0.045	0.128	0.920	0.022	0.058	1.091 13	1.338 70	2.121 16
101.04	100.99	0.849	0.070	0.081	0.902	0.063	0.035	1.047 82	2.318 60	1.904 71
101.08	101.09	0.832	0.067	0.101	0.916	0.035	0.049	1.079 31	1.407 94	2.235 48
101.15	101.04	0.814	0.048	0.138	0.906	0.027	0.067	1.091 80	1.465 27	2.162 76
101.48	101.33	0.806	0.070	0.124	0.855	0.053	0.092	1.046 57	1.713 59	2.873 93
101.50	101.25	0.834	0.136	0.030	0.907	0.076	0.017	1.053 39	1.444 63	2.502 17
101.56	101.22	0.832	0.151	0.017	0.008	.083	0.009	1.054 51	1.422 85	2.340 22
101.62	101.28	0.784	0.046	0.170	0.907	0.022	0.071	1.115 49	1.235 64	1.842 29
101.68	101.68	0.789	0.096	0.115	0.874	0.060	0.066	1.077 78	1.470 23	2.307 73
101.76	i01.72	0.785	0.095	0.120	0.896	0.050	0.054	1.099 10	1.309 77	1.912 09
101.95	101.73	0.789	0.166	0.045	0.880	0.096	0.024	1.072 67	1.370 33	2.157 89
102.08	102.00	0.772	0.137	0.091	0.877	0.077	0.046	1.088 50	1.318 64	2.024 43
102.13	101.85	0.762	0.076	0.162	0.882	0.040	0.078	1.105 02	1.250 49	1.952 01
102.16	102.05	0.743	0.071	0.186	0.892	0.033	0.075	1.141 03	1.133 50	1.677 12
102.18	102.08	0.766	0.157	0.077	0.869	0.090	0.041	1.086 20	1.315 78	2.086 16
102.19	101.60	0.791	0.187	0.022	0.838	0.146	0.016	1.025 63	1.675 63	2.666 79
102.65	102.16	0.712	0.044	0.244	0.887	0.021	0.092	1.165 36	1.135 43	1.527 70
102.67	102.59	0.731	0.167	0.102	0.849	0.097	0.054	1.100 50	1.261 66	1.961 09
102.70	102.31	0.707	0.049	0.244	0.885	0.022	0.093	1.169 66	1.061 23	1.534 21
102.72	102.78	0.701	0.081	0.218	0.870	0.040	0.090	1.164 88	1.123 59	1.600 49
102.80	102.62	0.724	0.197	0.079	0.848	0.113	0.039	1.105 16	1.239 19	1.818 09
102.89	102.86	0.713	0.183	0.104	0.849	0.102	0.049	1.119 46	1.204 43	1.735 05
103.07	102.39	0.717	0.252	0.031	0.827	0.156	0.017	1.086 42	1.275 78	1.926 15
103.18	102.78	0.704	0.232	0.064	0.828	0.138	0.034	1.102 96	1.225 52	1.864 72
103.20	102.55	0.709	0.251	0.040	0.824	0.154	0.022	1.090 82	1.254 10	1.915 39
103.32	103.37	0.687	0.157	0.156	0.845	0.085	0.070	1.140 27	1.149 67	1.621 82
103.50	103.53	0.661	0.086	0.253	0.858	0.043	0.099	1.189 89	1.087 40	1.447 00
103.51	103.57	0.676	0.147	0.177	0.835	0.083	0.082	1.141 51	1.171 09	1.634 98
103.70	103.76	0.666	0.148	0.186	0.841	0.077	0.082	1.156 53	1.086 94	1.565 96
103.98	103.16	0.654	0.308	0.038	0.783	0.198	0.019	1.110 41	1.209 27	1.600 17
104.09	103.65	0.643	0.282	0.075	0.786	0.174	0.040	1.127 81	1.163 37	1.710 11
104.25	103.89	0.636	0.273	0.091	0.779	0.173	0.048	1.126 73	1.178 86	1.668 17
104.60	104.72	0.614	0.224	0.162	0.795	0.128	0.077	1.168 69	1.080 57	1.525 79
104.61	104.41	0.616	0.265	0.119	0.770	0.168	0.062	1.139 21	1.155 89	1.613 48
104.80	105.11	0.603	0.157	0.240	0.807	0.086	0.107	1.193 66	1.051 53	1.451 51
105.20	104.87	0.592	0.079	0.329	0.827	0.040	0.133	1.219 03	0.997 31	1.347 99
105.45	104.91	0.559	0.359	0.082	0.723	0.233	0.044	1.166 48	1.096 81	1.537 71
105.50	105.71	0.558	0.283	0.159	0.750	0.170	0.072	1.205 15	1.057 67	1.350 89
105.85	106.01	0.553	0.261	0.186	0.748	0.161	0.091	1.189 89	1.064 87	1.429 76
106.10	106.43	0.535	0.268	0.197	0.745	0.160	0.095	1.215 62	1.021 43	1.395 74
106.14	106.07	0.530	0.324	0.146	0.722	0.204	0.074	1.199 07	1.047 84	1.427 43
106.85	106.03	0.476	0.452	0.072	0.647	0.315	0.038	1.285 62	1.063 18	1.361 39
107.26	107.73	0.495	0.154	0.351	0.764	0.087	0.149	1.282 93	0.966 31	1.223 49
107.45	107.13	0.455	0.417	0.128	0.647	0.284	0.069	1.234 35	0.026 52	1.371 38
107.67	108.33	0.468	0.263	0.269	0.717	0.156	0.127	1.279 63	0.951 19	1.275 46
108.10	108.78	0.455	0.249	0.296	0.709	0.153	0.138	1.286 13	0.968 42	1.236 48
108.90	108.48	0.386	0.477	0.137	0.581	0.348	0.071	1.279 26	1.016 68	1.215 01
109.41	109.81	0.380	0.395	0.225	0.619	0.266	0.115	1.335 50	0.954 17	1.215 89
111.15	111.66	0.311	0.437	0.252	0.552	0.319	0.129	1.411 76	0.955 05	1.119 96
112.62	113.23	0.306	0.235	0.459	0.632	0.145	0.223	1.503 38	0.827 59	1.083 69
113.68	112.60	0.163	0.753	0.084	0.310	0.642	0.048	1.571 36	0.960 85	1.072 42
113.75	114.35	0.253	0.391	0.356	0.520	0.282	0.198	1.514 51	0.880 24	1.127 31
114.00	114.83	0.241	0.389	0.370	0.511	0.291	0.198	1.555 55	0.904 22	1.073 60
114.78	115.42	0.224	0.398	0.378	0.495	0.305	0.200	1.589 94	0.904 78	1.034 83
114.78	115.35	0.208	0.464	0.328	0.462	0.363	0.175	1.624 71	0.909 61	1.028 11
115.75	115.12	0.136	0.689	0.175	0.288	0.608	0.104	1.645 28	0.950 30	1.060 07
116.80	116.32	0.216	0.207	0.577	0.567	0.137	0.296	1.701 67	0.780 77	0.995 66
117.61	117.56	0.180	0.368	0.452	0.455	0.283	0.262	1.680 37	0.843 40	1.045 45
117.60	116.96	0.120	0.635	0.245	0.280	0.568	0.152	1.705 06	0.927 77	1.060 70
118.50	117.05	0.188	0.133	0.679	0.563	0.090	0.347	1.834 46	0.769 91	0.952 09
120.35	118.90	0.160	0.186	0.654	0.489	0.139	0.372	1.817 92	0.788 54	0.979 04
123.65	122.28	0.084	0.420	0.496	0.240	0.409	0.351	1.725 84	0.891 57	1.051 48

Table IV. Constants in Equations 8 and 9

	Constants				
Species	$\alpha_i{}^a$	$\beta_i{}^a$	$\delta_i{}^a$	ϵ_i	ω_i
Water	7.966 81	1668.21	228.0		
Formic acid	7.377 9	1563.28	247.06	−10.743[b]	3083.0
Acetic acid	14.397 56	9399.86	698.0	−10.4205[c]	3166.0
Propionic acid	7.547 6	1617.06	205.67	−10.8340[b]	3316.0
Formic acid–propionic acid				−10.3558[d]	3193.

[a] Reference 20. [b] Reference 19. [c] Reference 10. [d] Reference 3.

in addition

$$\bar{K}_{BC} = K_{BC}\hat{\Phi}_B\hat{\Phi}_C/\hat{\Phi}_{BC} \qquad (6)$$

$$\hat{\Phi}_{BC} = \exp\left[\frac{(b_B{}^{1/3} + b_C{}^{1/3})^3 P}{8RT}\right] \qquad (7)$$

For ideal gaseous mixtures and low pressures, the values of E_i and the fugacity coefficients $\hat{\Phi}$ approach unity. For the calculation of the vapor pressure of the pure species, $P_i{}^0$, and association constants, K_{ii}, the following equations were employed

$$\log P_i{}^0 = \alpha_i - \beta_i/(t + \delta_i) \qquad i = \text{A, B, C} \qquad (8)$$

$$\log K_{ii} = \epsilon_i + \omega_i/T \qquad i = \text{B, C} \qquad (9)$$

The constants α_i, β_i, δ_i, ϵ_i, and ω_i appear in Table IV where $P_i{}^0$ is in mmHg and K_{ii} is in mmHg^{-1}. The heterodimerization constant K_{BC} for formic acid–propionic acid was calculated by an equation similar to eq 9 where the constants are given in Table IV. For the other heterodimers of the acids, the heterodimerization constant was calculated as twice the geometrical mean of the association constant for the pure species (*3*). The data required for computing the fugacity coefficients were taken from ref 4 and 12.

The data appearing in Tables II and III were tested by the McDermott–Ellis method (*8*) to reject those points that were clearly thermodynamically inconsistent.

According to this test, two experimental points *a* and *b* are thermodynamically consistent if the following condition is fulfilled:

$$D < D_{\max} \qquad (10)$$

The local deviation *D* is given by (*14*)

$$D = \sum_{i=1}^{n} (x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \qquad (11)$$

McDermott (*8*) recommended the use of a fixed value of 0.01 for $D_{\max}$ if the accuracy in the measurement of the vapor and the liquid mole fraction is within ±0.001. However, the value of 0.01 is in error and should be 0.001 (*9*). In principle, the local maximum deviation, $D_{\max}$, due to experimental errors, is not constant and can be derived by noting from eq 11 that

$$D = D(x_{ia}, x_{ib}, \gamma_{ia}, \gamma_{ib}) \qquad (12)$$

and analyzing the total differential d*D*. The effect of temperature and pressure is introduced by considering eq 12 for γ_i in the work of Chang and Lu (*6*) which yields that

$$\mathrm{d} \ln \gamma_i = \mathrm{d} \ln P - \mathrm{d} \ln P_i{}^0 + \mathrm{d} \ln y_i - \mathrm{d} \ln x_i \qquad (13)$$

The dependence of $P_i{}^0$ on temperature is taken according to eq 8. Errors in measurements of vapor and liquid concentrations are of the same magnitude. The final expression for the local maximum deviation reads

$$D_{\max} = \sum_{i=1}^{n} (x_{ia} + x_{ib}) \left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}}\right) \Delta x + 2 \sum_{i=1}^{n} \left|\ln \gamma_{ib} - \ln \gamma_{ia}\right| \Delta x + \sum_{i=1}^{n} (x_{ia} + x_{ib}) \frac{\Delta P}{P} + \sum_{i=1}^{n} (x_{ia} + x_{ib})\beta_i \left(\frac{1}{[t_a + \delta_i]^2} + \frac{1}{[t_b + \delta_i]^2}\right) \Delta t \qquad (14)$$

It can be shown that eq 14 is equivalent to eq 22 in ref 6. The last term in eq 22 in ref 6 which is spelled out must be zero. It should be emphasized that, for the associating species, y_i in eq 14 should be replaced by η_{i_1}, which is a mole fraction of the monomer of species *i* in the vapor phase. This arises from vapor–liquid equilibria considerations detailed in ref 16 and 17. In the present study, the errors in the measurements were estimated to be $\Delta P = \pm 2$ mmHg and $\Delta t = \pm 0.02$ °C, where $\Delta x = 0.002$ mole fraction units. It was found that the first term in eq 14 which accounts for the error in the concentration measurements was usually the dominant one.

The correlation of the overall activity coefficients in the liquid, which were computed by eq 1 and reported in Tables II and III, was made according to the following Redlich–Kister equation (*14*):

$$\ln \gamma_1 = x_2x_3[(B_{12} + B_{13} - B_{23}) + C_{12}(2x_1 - x_2) + C_{13}(2x_1 - x_3) + 2C_{23}(x_3 - x_2) + D_{12}(x_1 - x_2)(3x_1 - x_2) + D_{13}(x_1 - x_3)(3x_1 - x_3) - 3D_{23}(x_3 - x_2)^2 + C_1(1 - 2x_1)] + x_2{}^2[B_{12} + C_{12}(3x_1 - x_2) + D_{12}(x_1 - x_2)(5x_1 - x_2)] + x_3{}^2[B_{13} + C_{13}(3x_1 - x_3) + D_{13}(x_1 - x_3)(5x_1 - x_3)] \qquad (15)$$

The equations for γ_2 and γ_3 are obtained by cyclic rotation of the indices. C_1 is a ternary constant computed from the ternary data reported in Tables II and III. The binary constants B_{ij}, C_{ij} and D_{ij} are obtained by fitting the binary activity coefficients according to

Table V. Redlich–Kister Correlation of Binary and Ternary Data, Equations 15 and 16

				RMSD	
	B_{ij}	C_{ij}	D_{ij}	γ_i	γ_j
Water–formic acid	−0.345 22	0.112 01	0.054 85	0.0433	0.0148
Water–acetic acid	0.767 73	0.194 63	0.119 60	0.1639	0.0462
Water–propionic acid	1.355 8	0.510 97	0.082 17	0.1729	0.6530
Formic acid–acetic acid	−0.199 06	−0.069 325	−0.083 90	0.0153	0.0266
Acetic acid–propionic acid	0.072 12	−0.190 13	0.191 93	0.2013	0.0918
				Overall RMSD	
				γ	*y* (eq 17)
Water–formic acid–acetic acid	$C_1 = 0.5089$			0.1132	0.03237
	$C_1 = 0$			0.1079	0.03178
Water–acetic acid–propionic acids	$C_1 = -2.2337$			0.2566	0.03483
	$C_1 = 0$			0.2168	0.04237

Table VI. Correlation of Boiling Points, Equation 18

System	C_0	C_1	C_2	C_3	RMSD (eq 20)
		Water–Formic Acid			
With ω	28.088	−12.145	−5.3119	7.6118	0.0661
Without ω	28.073	−12.291	−5.6276	7.7589	0.0669
		Water–Acetic Acid			
With ω	−15.881	6.1843	−7.7400	7.9182	0.1118
Without ω	−16.010	6.1894	−7.8485	8.1860	0.1131
		Water–Propionic Acid			
With ω	−59.645	39.865	−58.845	38.657	0.3248
Without ω	−60.397	41.015	−60.139	39.839	0.3306
		Formic Acid–Acetic Acid			
With ω	−5.5167	−1.3462	6.7512	5.5044	0.1057
Without ω	−5.5679	−1.3184	6.7661	5.4946	0.1050
		Water–Formic Acid–Acetic Acid			
With ω	23.565	172.53	−49.803	2.9791	0.3893
Without ω	23.021	173.31	−49.664	3.6168	0.3910
		Water–Acetic Acid–Propionic Acid			
	A	B	C	D	
With ω	49.896	87.154	−43.481	−3.4788	0.5128
Without ω	48.331	83.104	−39.466	−5.4946	0.5109

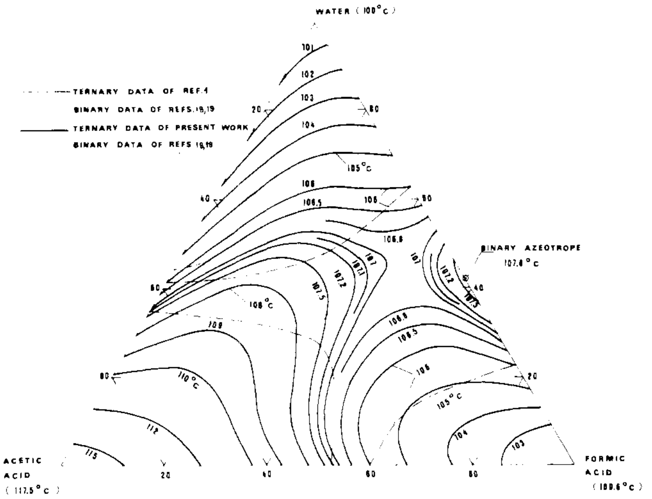

Figure 1. Isothermals at 760 mmHg for the water–formic acid–acetic acid systems calculated by eq 18 for $\omega = 0$.

$$\ln \gamma_i = (B_{ij} + 3C_{ij} + 5D_{ij})x_j^2 - 4(C_{ij} + 4D_{ij})x_j^3 + 12D_{ij}x_j^4 \quad (16)$$

$$\ln \gamma_j = (B_{ij} - 3C_{ij} + 5D_{ij})x_i^2 + 4(C_{ij} - 4D_{ij})\, x_i^3 + 12D_{ij}x_i^4 \quad (16\text{-}1)$$

The binary constants were computed from the binary data reported in ref 6 and 9 and the various constants are reported in Table V. The overall values of the RMSD (root mean square deviation) were computed by

$$\text{RMSD} = \left[\left(\sum_{j=1}^{m}\sum_{i=1}^{n}(y_{ji,\text{obsd}} - y_{ji,\text{calcd}})^2\right)\bigg/ mn\right]^{1/2} \quad (17)$$

and reported in Table V. A similar equation was used for γ. These values give a general indication of the goodness of the correlation to predict compositions in the vapor phase. Additional information is as follows. For the system water–formic acid–acetic acid, the mean value of $(y_{1,\text{obsd}} - y_{1,\text{calcd}})/y_{1,\text{obsd}}$ based on 67 data points is 9.1%, for y_2 and y_3 7.7 and 7.9%. The worst values are 14, 20, and 20%, respectively, where similar values were obtained for the activity coefficients. For the system water–acetic acid–propionic acid, the mean values of $(y_{1,\text{obsd}} - y_{1,\text{calcd}})/y_{1,\text{obsd}}$ based on 65 data points are 6.0%, for y_2 and y_3 8.4 and 16.3%. The worst values are 16.6, 58, and 48%, respectively.

The following equation suggested by the authors (*21*) was employed to correlate the boiling points vs. concentrations of the ternary mixtures:

$$T = x_1T_1^0 + x_2T_2^0 + x_3T_3^0 + \omega + \sum_{i,j=1}^{3}\left[x_ix_j\sum_{k=0}^{l}C_k(x_i - x_j)^k\right] + x_1x_2x_3[A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + \ldots] \quad (18)$$

where T^0 is the boiling point of the pure components in °C and

$$\omega = \sum_{i=1}^{3} x_i \ln (y_i/x_i) \quad (19)$$

l is the number of terms in the series expansion of $(x_i - x_j)$, and C_k are the binary constants computed from the binary data of ref 18 and 19. A, B, C, and D are ternary constants computed from the ternary data in Tables II and III. The various constants are reported in Table VI as well as the values of the overall root mean square deviation,

$$\text{RMSD} = \left(\sum^{m}(T_{\text{obsd}} - T_{\text{calcd}})^2\bigg/ m\right)^{1/2} \quad (20)$$

where m is the number of data points. An empirical analysis based on the values of the RMSD indicate that the term ω in eq 18 may be neglected. 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.

By using eq 18, isothermals for both ternary systems were obtained as shown in Figures 1 and 3. The prominent fact which may be concluded from the behavior of the isothermals in Figure 1 is the existence of a ternary saddle point azeotrope in the water–formic acid–acetic acid system. On the other hand, it may be concluded from Figure 3 that the system water–acetic acid–propionic acid does not exhibit a ternary azeotrope. The difference between our ternary data and those measured by Aristovich (*1*) can be appreciated by considering the identical isothermals (106, 107.2 °C) reported in Figure 1. They were based on identical binary data and as seen there is a difference

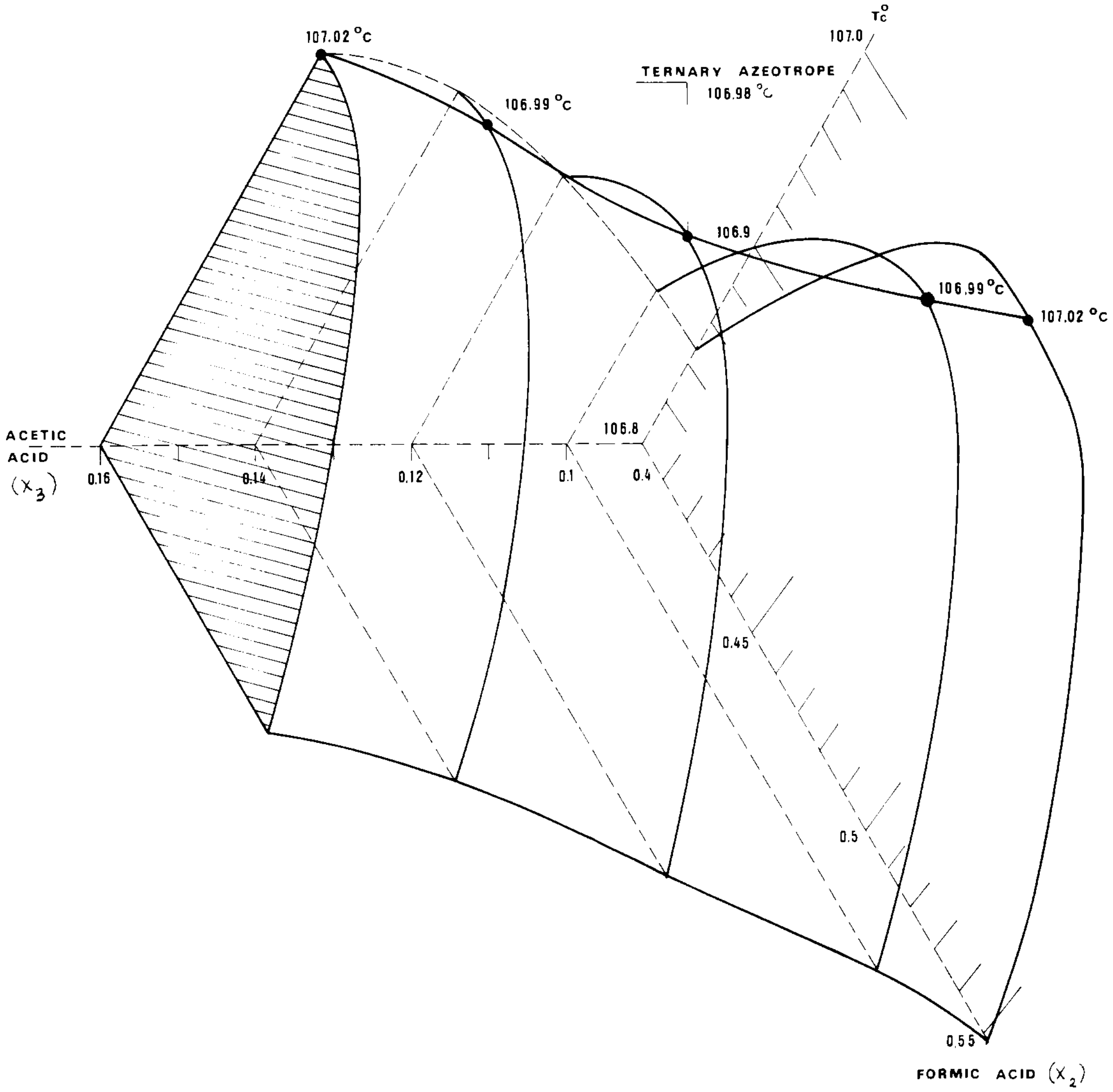

Figure 2. Determination of the ternary saddle point azeotrope for the water-formic acid-acetic acid system at 760 mmHg.

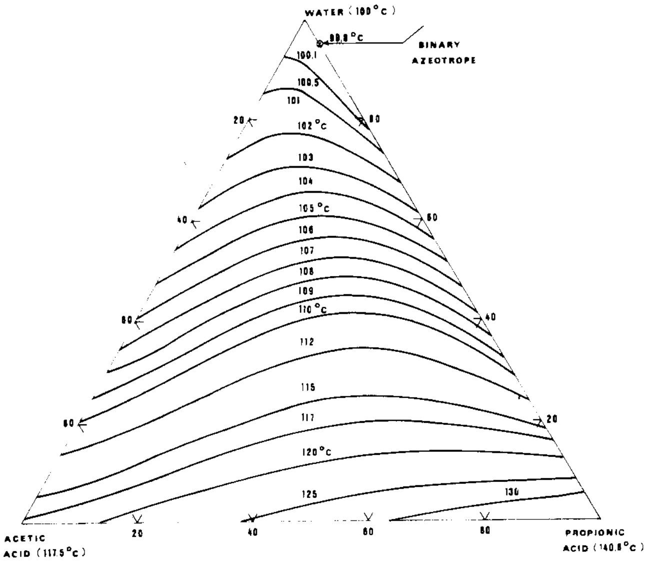

Figure 3. Isothermals at 760 mmHg for the water–acetic acid–propionic acid system calculated by eq 18 for $\omega = 0$.

between the isothermals. The second system, water–acetic acid–propionic acid was also studied by Aristovich (*2*); however, no comparison could be made with his data as they were not accessible.

In order to determine the coordinates of the ternary azeotrope, Figure 2 was drawn. It is a spatial plot of the region where the azeotropic point might be located. According to the general theorem of Gibbs-Konovalov (*11*), a ternary system exhibits azeotropic behavior at constant pressure if

$$\frac{\partial T}{\partial x_2} = \frac{\partial T}{\partial x_3} = 0$$

This condition is fulfilled in the present case as shown in Figure 2. The temperatures were computed with eq 18 and the constants were directly determined from the present ternary data and the binaries of ref 18 and 19. Similar calculations were made on the basis of the ternary data of Aristovich (*1*) with the same binary data. A summary of the computations is given in Table VII and a comparison is made between the computed results and the experimental data for the azeotropic point of Aristovich (*1*). The following experiment was performed in order to check the validity of the predicted values: Ternary solutions with the calculated compositions were prepared and introduced in the vapor and liquid collectors of the Dvorak and Boublik recirculating still. The system was boiled until equilibrium was achieved. A gas chromatography analysis yielded the equilibrium compositions of the vapor and the liquid reported in Table VII and designated by +. It is seen that the liquid compositions x_i deviate from y_i; namely, the computed values do not correspond to true azeotropes. On the other hand, it is observed that the azeotropic boiling temperature is very accurately predicted. We checked

Table VII. Comparison between Observed and Calculated Values of the Azeotropic Point for the Ternary System Water–Formic Acid–Acetic Acid

Ref of data	x_1			x_2			x_3			T, °C		
	Obsd	Calcd	D,[a] %	Obsd	Calcd	D, %	Obsd	Calcd	D, %	Obsd	Calcd	D, %
(*1*)	0.355 $x_1 = 0.363^b$ $y_1 = 0.366$			0.491 $x_2 = 0.469^b$ $y_2 = 0.465$			0.154 $x_3 = 0.168^b$ $y_3 = 0.168$			107.05 107.00^b		
(1) ternary		0.292	17.7		0.457	6.9		0.250	38.4		106.99	0.056
(*18, 19*) binary	$x_1 = 0.330^b$ $y_1 = 0.314$			$x_2 = 0.423^b$ $y_2 = 0.438$			$x_3 = 0.247^b$ $y_3 = 0.248$			107.25^b		
(Present) ternary		0.442	24.5		0.434	11.6		0.124	19.5		106.98	0.065
(*18, 19*) binary	$x_1 = 0.419^b$ $y_1 = 0.388$			$x_2 = 0.440^b$ $y_2 = 0.473$			$x_3 = 0.141^b$ $y_3 = 0.140$			107.07^b		

[a] $D = |x_{i,\mathrm{obsd}} - x_{i,\mathrm{calcd}}|/x_{i,\mathrm{obsd}}$ and similary for T. [b] Our experimental check.

also the azeotropic coordinates of Aristovich (*1*) by charging the still with the reported compositions. As seen in Table VII our results are slightly different from those of Aristovich (*1*) and within the experimental error they obey the condition for azeotropic behavior that $x_i = y_i$.

We believe that our results are more accurate than those reported by Aristovich et al. Aristovich used a set of chemical analyses to determine the composition of the phases in equilibrium and reported that error did not exceed 0.5% for formic acid, 0.8% for acetic acid, and 0.5% for water. On the other hand, we have indicated in the Experimental Section that our gas chromatography analyses were accurate within 0.2%.

Diagrams, such as Figure 1, may be an aid in demonstrating distillation paths. For example, in an ideal differential distillation, a material balance on each species in a multicomponent mixture yields that

$$\frac{dL}{L} = \frac{dx_i}{y_i - x_i} \tag{21}$$

where L is the number of moles of liquid left in the still. A numerical integration of the above equation from a prescribed feedstock composition, and with the aid of the y_i–x_i data, provides the distillation path for a ternary system defined by

$$\frac{dx_2}{dx_1} = \frac{y_2 - x_2}{y_1 - x_1} \tag{22}$$

which may be conveniently drawn on Figure 1. Such paths, and their proximity to the azeotropic point, might reflect the possibility of separating the acids by distillation. For more detailed information regarding to the aspects of rectification in ternary systems containing binary and ternary azeotropes, the attention of the reader is addressed to ref 7.

Acknowledgments

Thanks are due to Yehudit Reizner and Moshe Golden for their contribution in the experimental and numerical work, and also to Professor J. Zabicky for the useful discussions concerning some distillation aspects of azeotropic mixtures.

Glossary

A, A_1	species A, monomer of A
b	size parameter
B, B_1, B_2	species B formed by $B_1 + B_2$, monomer of B, dimer of B
C, C_1, C_2	species C formed by $C_1 + C_2$, monomer of C, dimer of C
BC	heterodimer formed by $B_1 + C_1$
D	parameters in eq 15, 16, and 18. Local deviation defined in by the eq 11
E_i	defined by eq 3
F_i	defined by eq 2
K_{AA}, K_{BB}, K_{CC}, K_{BC}	vapor-phase equilibrium constant for the formation of A_2, B_2, C_2, BC, respectively, mmHg^{-1}
m	total number of experimental runs
n	number of species
p	total pressure, mmHg
P_i^0	vapor pressure of the pure species i (i = A, B, C), mmHg
$P_{i_1}^0$	vapor pressure of the pure monomer of species i (i = B, C), mmHg
R	universal gas constant
t, T	temperature °C, °K
V	molar volume
x_i, y_i	stoichiometric mole fraction of species i in the liquid phase, in the vapor phase (i = A, B, C)
$y_{ji,\mathrm{calcd}}$	the calculated vapor composition of the ith component in the jth experimental run based on values of liquid activity coefficients which were computed from their multicomponent thermodynamic correlation
γ_A, γ_B, γ_C	overall liquid activity coefficients of a species
$\hat{\Phi}$	fugacity coefficient for a component in a mixture
α_i, β_i, δ_i, ϵ_i, ω_i	constants in eq 8 and 9 and Table IV
Δx, Δp, Δt	errors in measurements of concentrations, pressure, and temperature, respectively
RMSD	root mean square deviation

Subscripts and Superscripts

A, B, C	water–formic acid–acetic acid or water–acetic acid–propionic acid, respectively
i	species
L	in the liquid phase
calcd	calculated
obsd	observed
max	maximum
0	pure species
1, 2	monomer, dimer
1, 2, 3	water, formic acid, and acetic acid or water, acetic acid, and propionic acid in eq 15 and 16 and in Tables V and VI.

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A Crude Oil–Natural Gas System Vapor–Liquid Equilibrium Ratios (Data at 250 °F and System Containing 20% C_{7+})

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Vapor–liquid equilibrium ratios (*K* values) have been determined experimentally on a Devonian crude oil–natural gas system containing 20% of the C_{7+} or heavy fraction. The data were obtained at 250 °F and five pressures.

Some of the new and improved oil recovery methods require use of vapor–liquid equilibrium ratios to estimate the total oil recovery. Woertz provided a recent correlation, and his paper cites sources of vapor–liquid equilibrium ratio data (*2*). The need for additional experimental data is clearly evident. This paper presents the vapor–liquid equilibrium constants (*K* values) between a crude oil and natural gas system.

A Devonian crude oil of 40° API gravity from New Mexico free of hydrogen sulfide, nitrogen, or carbon dioxide and forming no precipitates when mixed with gas at high pressures was used as the base crude. Hexane–*n*-pentane, *n*-butane, propane, ethane gas, and a Texas natural gas were added to form the desired mixture. The mixture was prepared so that it contained 20.06% C_{7+} in the total system. The C_{7+} fraction of each system was characterized by measurement of its specific gravity and molecular weight. Sufficient volume of the C_{7+} fraction was not available for ASTM distillation.

The basic apparatus consisted of a Ruska high pressure equilibrium cell in a constant temperature oil bath. Podbielniak low temperature fractional distillation apparatus with an external kettle was used for the analyses. A Hart pressure balance was used for pressure measurements. A high pressure storage cell was used to store the total mixture. See Figure 1. A Ruska mercury pump was used for fluid displacement. The benzene freezing point depression apparatus was equipped with a Beckmann thermometer.

The desired materials were charged into an evacuated rocking mixing cell using displacement with mercury into a fluid storage cell. This formed the total mixture. The mixed sample was displaced into the equilibrium cell located in the oil bath. The sample was expanded to a two-phase condition and rocked until constant pressure achieved. A constant pressure was maintained on the equilibrium sample during displacement of either a gas or liquid phase sample into the Podbielniak low temperature fractional distillation apparatus. An external kettle on the Podbielniak column was used to collect the heptanes–plus residue. The density was determined by weight and volume using a 2.0-mL pycnometer. The molecular weight of the C_{7+} was determined by the freezing point depression of benzene measured with a Beckmann thermometer.

Table I. Total Composition of Mixture and Equilibrium Values at 1795 psia, Temperature 250 °F

Component	Total composition mol fraction	1795 psia Gas frac	Liquid frac	*K*-Value Y_i/X_i
Methane	0.4747	0.7771	0.2885	2.6937
Ethane	0.0651	0.0737	0.0570	1.2938
Propane	0.0489	0.0446	0.0532	0.8386
n-Butane	0.0661	0.0385	0.0833	0.4623
n-Pentane	0.0687	0.0283	0.0919	0.3079
Hexane	0.0759	0.0211	0.1087	0.1940
Heptanes–plus	0.2006	0.0167	0.3174	0.0526
	1.0000	1.0000	1.0000	
Heptanes-plus:				
Mol wt	181.0	105.9	182.3	
Sp gr 60/60	0.8259	0.7314	0.8266	

The pressure is considered to within ±0.08% using the Hart pressure balance. The average mole fraction deviation in composition analysis on duplicate samples was 0.0036.

The total composition of the mixture is shown in Table I as well as equilibrium constants at 1795 psia. The equilibrium constant (*K* value) is the mole fraction of a component in the vapor divided by the mole fraction of the component in the liquid.

The bubble point of this mixture at 250 °F was found to be 3190 psia. Tables II and III show the equilibrium constants at pressures of 2095, 2295, 2545, and 2845 psia and a temperature of 250 °F.

Figure 2 shows a plot of the experimental *K*-value data as a function of pressure. The NGAA correlations for each component are shown as the solid lines (*1*). The NGAA *K* values for the C_{7+} shown plotted were assumed to be the average of heptane and octane *K* values. The NGAA method was used to calculate the convergence pressure. The critical temperature of the heptanes–plus fraction in the overall system was obtained from the plot of the critical temperatures of straight chain paraffin hydrocarbons against molecular weight.

A comparison of these experimental *K* values with the charts published by Woertz shows the experimental data for methane and ethane to be lower and the experimental data of the heavier components to be higher than the Woertz charts *K* values. The

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[†] Deceased.