P^0_i	vapor pressure of component *i* pure, mmHg
rmsd	root mean square deviation $[\sum(T_{\text{exptl}} - T_{\text{calcd}})^2/n]^{1/2}$
n	number of experimental points
t, T	temperature, °C, K
T^0_i	boiling temperature of component *i* pure at pressure P, K
V^0_i	molar volume of liquid pure component
x_i, y_i	mole fraction composition of component *i* in the liquid and vapor phases
γ_i	activity coefficient of component *i*
Λ_{ij}, Λ_{ji}	Wilson constants, eq 6 and 7

Subscript

i	component *i*

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Vapor-Liquid Equilibrium in the Systems Propyl Bromide-Acetic Acid, Propyl Bromide-Propionic Acid, and Propyl Bromide-Acetic Acid-Propionic Acid

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The vapor-liquid equilibria for the title systems were determined at 760 mmHg. Activity coefficients were calculated by assuming association in the vapor phase. Boiling points of the systems were correlated by empirical expressions; none of the systems studied exhibited azeotropic behavior. Tentative UNIFAC interaction parameters are reported for the pairs COOH, Br and Br, COOH.

In previous investigations on systems containing fatty acids, we have studied the vapor-liquid equilibrium properties of the systems formic acid-acetic acid-propionic acid (*1*), water-formic acid-propionic acid (*2*), water-formic acid-acetic acid (*3*), water-acetic acid-propionic acid (*3*), propionic acid-carbon tetrachloride (*4*), propionic acid-methyl isobutyl ketone (*4*), and acetic acid-carbon tetrachloride (*5*).

Inspection of the UNIFAC parameter table has indicated that the interaction parameters for the acid group COOH and bromine are not available (*6*). The aim of the present work is to initiate the accumulation of experimental data that will allow filling the missing information. For this purpose we have selected for study the vapor-liquid equilibrium of the systems indicated in the title.

Experimental Section

Purity of Materials. Analytical-grade fatty acids (99.5% +) were purchased from Fluka; propyl bromide (99.6% +) was supplied by Bromine Compounds Ltd., Beer-Sheva. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties of the pure components appear in Table I.

Table I. Physical Properties of Pure Compounds

compd	refractive index at 20 °C	bp, °C
propyl bromide (1)	1.4316[a]	70.55[a]
	1.4317[b]	70.8[b]
acetic acid (2)	1.3717[a]	117.0[a]
	1.3716[b]	117.1[b]
propionic acid (3)	1.3860[a]	140.85[a]
	1.3865[b]	140.83[b]

[a] This work. [b] Reference *16*.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*7*) was used in the equilibrium determination. The experimental features have been described in previous publications (*3-5*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm in diameter, was packed with SP-1200 on 80-100 mesh Supelcoport, and was operated isothermally at 75 °C. Injector and detector temperatures were 200 and 210 °C, respectively. Very good separation was achieved under these conditions, and calibration analyses were carried to convert the peak ratio to the weight composition of the sample. Concentration measurements were accurate to better than ±1%. The accuracy in determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta t = \pm 0.02$ °C.

Results

The temperature-concentration measurements at 760 mmHg for the systems under consideration are presented in Tables III-V. Preliminary calculations showed that the activity coefficients calculated without taking into account the association effects were thermodynamically inconsistent. Fatty acids are known to undergo extensive association already at room temperature so that the real species present in the system are different from the nominal ones. The mathematics of associ-

Table II. Vapor Pressure Constants

compd	α_i^a	β_i^a	δ_i^a	ϵ_i	ω_i
propyl bromide	6.91065	1194.889	225.51		
acetic acid	14.39756	9399.86	698.0	-10.4205^b	3166.0^b
propionic acid	7.5476	1617.06	205.67	-10.8340^c	3316.0^c

[a] Reference *16*. [b] Reference *17*. [c] Reference *18*.

ation in multicomponent systems has been described previously (*1*, *8*, *9*) and will be summarized briefly for ternary systems. Assume species A, B, C, where A is the most volatile component. Species B and C undergo homodimerization between monomers, namely, $B_1 + B_1 \rightleftarrows B_2$ and $C_1 + C_1 \rightleftarrows C_2$. In addition, species B and C react among themselves to form a heterodimer $B_1 + C_1 \rightleftarrows BC$. A more complex scenario will be one in which A also participates in the reactions. This point will be elaborated later on. Mathematical analysis of the different equilibria, coupled with a mass balance, yields the following system of three nonlinear equations (*2*):

$$F_A - y_A[P + K_{BB}\Phi_B F_B{}^2 + K_{CC}\Phi_C F_C{}^2 + \bar{K}_{BC}F_B F_C] = 0 \tag{1.1}$$

$$(2 - y_B)K_{BB}\Phi_B F_B{}^2 + F_B[1 + (1 - y_B)\bar{K}_{BC}F_C] - y_B[P + K_{CC}\Phi_C F_C{}^2] = 0 \tag{1.2}$$

$$(2 - y_C)K_{CC}\Phi_C F_C{}^2 + F_C[1 + (1 - y_C)\bar{K}_{BC}F_B] - y_C[P + K_{BB}\Phi_B F_B{}^2] = 0 \tag{1.3}$$

where for i = A, B, C

$$F_i = \gamma_i x_i P^\circ{}_{i_1}/E_i \tag{2}$$

$$E_i = \exp[(P - P^\circ{}_{i_1})(b_i - V_i{}^L)/RT] \tag{3}$$

$$\Phi_i = \exp[b_i P/RT] \tag{4}$$

for i = B, C

$$P^\circ{}_{i_1} = P^\circ{}_i\left(\frac{-1 + (1 + 4K_{ii}P^\circ{}_i \exp[b_i P^\circ{}_i/RT])^{1/2}}{2K_{ii}P^\circ{}_i \exp[b_i P^\circ{}_i/RT]}\right) \tag{5}$$

in addition

$$\bar{K}_{BC} = K_{BC}\Phi_B\Phi_C/\Phi_{BC} \tag{6}$$

$$\Phi_{BC} = \exp[(b_B{}^{1/3} + b_C{}^{1/3})^3 P/(8RT)] \tag{7}$$

For ideal gaseous mixtures and low pressures the values of E_i and the fugacity coefficients may be assumed to be unity. Equations 1–7 can be easily applied to a binary system where one or both components undergo association.

For the calculation of the vapor pressure of the pure species, $P^\circ{}_i$, and the association constants K_{ii}, the following expressions were employed:

$$\log P^\circ{}_i = \alpha_i - \beta_i/(t + \delta_i) \tag{8}$$

$$\log K_{ii} = \epsilon_i + \omega_i/T \tag{9}$$

The pertinent constants are reported in Table II, with $P^\circ{}_i$ in mmHg and K_{ii} in mmHg^{-1}.

As no reliable data were available for the heterodimerization constant, they were estimated by

$$K_{ij} = 2(K_{ii}K_{jj})^{1/2} \tag{10}$$

Table III. Vapor-Liquid Equilibrium and Activity Coefficients for the System Propyl Bromide (1)-Acetic Acid (2)

temp, °C	x_1	y_1	γ_1	γ_2
109.90	0.022	0.171	3.863	0.9996
109.50	0.025	0.185	3.684	0.9954
107.85	0.032	0.225	3.570	0.9909
104.56	0.045	0.285	3.392	1.000
103.62	0.050	0.305	3.313	1.001
101.30	0.060	0.350	3.289	1.003
99.25	0.072	0.390	3.159	1.007
96.80	0.085	0.435	3.116	1.012
96.50	0.088	0.440	3.062	1.014
95.75	0.095	0.450	2.946	1.024
92.67	0.115	0.515	2.933	1.016
91.00	0.135	0.540	2.712	1.036
89.30	0.155	0.570	2.577	1.048
88.25	0.165	0.585	2.541	1.057
85.38	0.205	0.630	2.341	1.090
84.55	0.220	0.645	2.271	1.099
84.50	0.225	0.648	2.231	1.102
84.06	0.232	0.657	2.212	1.103
83.05	0.275	0.670	1.948	1.164
82.20	0.285	0.685	1.956	1.165
80.55	0.310	0.710	1.935	1.186
79.78	0.345	0.725	1.804	1.228
78.05	0.420	0.755	1.602	1.338
75.52	0.540	0.800	1.397	1.572
74.83	0.590	0.815	1.321	1.707
73.89	0.650	0.835	1.253	1.904
72.85	0.748	0.865	1.150	2.397
72.40	0.785	0.885	1.127	2.576
71.60	0.855	0.925	1.090	3.001

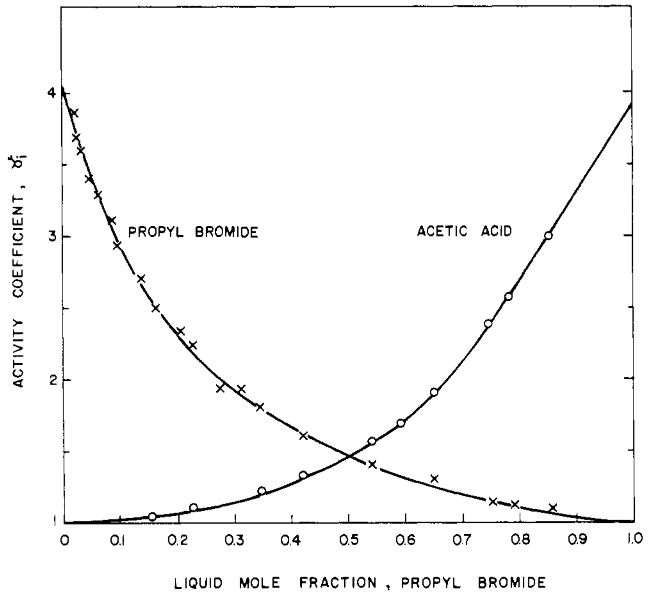

Figure 1. Propyl bromide–acetic acid boiling-point diagram.

Association of propyl bromide with itself or with the fatty acids was also investigated since dipole–dipole interactions can be expected. The pertinent constants are unknown and were estimated by the method proposed by Nothnagel, Abrams, and Prausnitz (*10*). Calculation of the pertinent activity coefficients indicated that assumption of propyl bromide participation in the different possible reactions either did not improve or affected adversely the consistency quality of the data. It was then decided to assume that propyl bromide plays a passive role in these reactions.

Activity coefficients were hence calculated by solution of the proper equations in set 1–10, and the pertinent results are reported in Tables III–V.

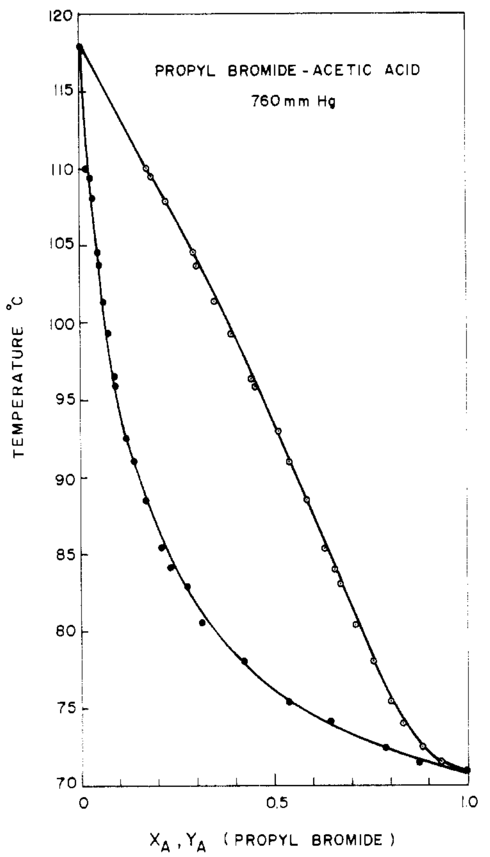

Figure 2. Propyl bromide-acetic acid activity coefficients.

We will now analyze some of the most important features.

Propyl Bromide-Acetic Acid. The vapor-liquid equilibria and the activity coefficients calculated by assuming association of the acid alone appear in Table III and Figures 1 and 2. Area tests for the individual activity coefficients, as well as their ratio, showed that the data were thermodynamically consistent.

Propyl Bromide-Propionic Acid. The pertinent vapor-liquid equilibrium data appear in Table IV. The values of the activity coefficients calculated according to eq 1-10 are also reported in Table IV; these do not satisfy the area test for thermodynamic consistency. We assume that experimental errors are not a main source of inconsistency because, in spite of rechecking the analytical procedure and duplication of experiments, we observed a normal scattering of x, y points. Further testing indicated that assuming dimerization and/or heterodimerization of propyl bromide yields activity coefficients that are even more inconsistent. We then tested the possibility that, although propyl bromide has a passive role, it may affect the association characteristics of propionic acid, similar to the behavior reported by Posch and Kohler (*11*) for acetic acid and solvents. No improvement was observed. The next examination was performed by assuming that heat effects are present in the system. In this case the usual area and slopes tests based on the Gibbs-Duhem restriction are not valid. Since no data were available, it was decided to test the data according to Herrington's criterium (*12*). Herrington has suggested for systems with heat effects that the following two quantities be compared:

$$\mathbf{D} \equiv \left| \frac{\text{area above } x \text{ axis} - \text{area below } x \text{ axis}}{\text{area above } x \text{ axis} + \text{area below } x \text{ axis}} \right| \qquad (11)$$

$$\mathbf{J} = 150 |T^\circ_1 - T^\circ_2| / T^\circ_{\min} \qquad (12)$$

where T°_1 and T°_2 are the boiling points of the pure components and $T^\circ_{\min}$ is the lowest boiling point in the full composition range. The constant 150 is empirical, based on Herrington's analysis of typical heat of mixing data. Herrington suggests that, if $|\mathbf{D} - \mathbf{J}| < 10$, the data are probably consistent. Application of the data given in Table IV yields $\mathbf{D} = 42.6$ and $\mathbf{J} = 30.44$ so that according to Herrington the data are inconsistent. An interesting feature of this system is that, if propionic acid is assumed to be fully dimerized, **D** decreases to 25.4 so that the data become consistent. Both sets of γ_i are shown in Table IV.

Table IV. Vapor-Liquid Equilibrium and Activity Coefficients for the System Propyl Bromide (1)-Propionic Acid (3)

			partly associated, eq 19		fully associated	
temp, °C	x_1	y_1	γ_1	γ_2	γ_1	γ_2
138.17	0.005	0.055	2.730	1.008	3.757	0.9916
137.10	0.007	0.076	2.737	1.012	3.718	0.9895
134.80	0.019	0.185	2.456	0.9592	3.178	0.9298
131.20	0.024	0.216	2.448	1.008	3.092	0.9593
130.80	0.027	0.230	2.323	1.004	2.919	0.9545
129.60	0.032	0.260	2.250	1.001	2.789	0.9479
128.60	0.035	0.260	2.110	1.027	2.607	0.9667
121.10	0.065	0.410	2.013	1.037	2.340	0.9570
118.40	0.080	0.455	1.903	1.052	2.176	0.9650
116.50	0.088	0.495	1.940	1.044	2.190	0.9563
112.70	0.105	0.540	1.916	1.081	2.127	0.9817
113.10	0.108	0.545	1.856	1.066	2.061	0.9709
107.75	0.140	0.620	1.811	1.096	1.965	0.9930
105.50	0.165	0.655	1.696	1.111	1.824	1.006
102.50	0.190	0.705	1.680	1.102	1.786	1.002
98.40	0.225	0.780	1.697	1.042	1.777	0.9601
96.25	0.245	0.790	1.667	1.093	1.739	1.003
93.25	0.270	0.800	1.658	1.180	1.723	1.074
91.30	0.295	0.810	1.616	1.240	1.674	1.126
91.00	0.310	0.825	1.570	1.210	1.623	1.107
90.50	0.311	0.830	1.593	1.205	1.645	1.102
90.45	0.315	0.835	1.581	1.190	1.632	1.092
90.42	0.330	0.825	1.499	1.265	1.549	1.154
89.28	0.345	0.840	1.498	1.257	1.544	1.152
88.26	0.360	0.865	1.506	1.183	1.547	1.099
85.30	0.415	0.880	1.439	1.297	1.472	1.204
85.83	0.415	0.860	1.396	1.412	1.432	1.293
85.73	0.425	0.870	1.377	1.374	1.411	1.267
84.90	0.455	0.870	1.318	1.481	1.350	1.361
82.10	0.515	0.905	1.296	1.469	1.320	1.379
80.98	0.540	0.890	1.264	1.752	1.289	1.610
79.90	0.570	0.905	1.250	1.760	1.272	1.634
79.55	0.580	0.910	1.246	1.758	1.267	1.640
77.80	0.640	0.920	1.198	1.999	1.216	1.873
76.56	0.700	0.935	1.149	2.180	1.164	2.077
75.85	0.715	0.938	1.152	2.273	1.166	2.169
76.70	0.725	0.935	1.105	2.369	1.119	2.258
75.82	0.725	0.930	1.131	2.545	1.146	2.395
74.95	0.755	0.940	1.123	2.658	1.136	2.534
74.68	0.775	0.945	1.107	2.762	1.119	2.656
73.30	0.805	0.948	1.115	3.202	1.126	3.076
72.55	0.837	0.949	1.098	3.869	1.109	3.710

Propyl Bromide-Acetic Acid-Propionic Acid. The T-x-y data are reported in Table V. On the basis of what was learned from the binary systems, the activity coefficients were cacualted by assuming a passive role for propyl bromide and dimerization constants expressed by eq 9 and 10. The results appear in Table V.

Thermodynamic consistency was tested by the McDermott-Ellis (*13*) method, by which two experimental points a and b are consistent if the following condition is fulfilled:

$$D < D_{\max} \qquad (13)$$

The local deviation D is given by

$$D = \sum_{i=1}^{n} (x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \qquad (14)$$

Table V. Vapor-Liquid Equilibrium and Activity Coefficients for the Ternary System Propyl Bromide (1)-Acetic Acid (2)-Propionic Acid (3)

temp, °C	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
133.40	0.020	0.075	0.250	0.088	3.163	0.8731	0.8789
128.20	0.035	0.157	0.255	0.185	2.100	0.9813	0.9347
126.82	0.045	0.085	0.315	0.095	2.025	0.9715	0.9540
125.25	0.060	0.065	0.400	0.065	1.925	0.9212	0.9123
121.40	0.045	0.470	0.178	0.502	1.427	1.012	1.020
120.85	0.065	0.150	0.415	0.150	2.048	1.016	0.9165
120.20	0.055	0.095	0.435	0.110	2.554	1.202	0.9049
119.30	0.045	0.290	0.352	0.295	2.700	1.045	0.8905
118.80	0.080	0.250	0.423	0.235	1.782	0.9996	0.8859
118.05	0.035	0.497	0.243	0.497	2.635	1.027	0.9339
117.83	0.035	0.517	0.232	0.510	2.547	1.015	0.9708
117.80	0.050	0.300	0.366	0.298	2.608	1.058	0.9002
117.50	0.025	0.492	0.243	0.482	3.743	1.017	0.9687
116.50	0.085	0.440	0.312	0.426	1.395	1.042	0.9737
115.10	0.030	0.554	0.281	0.499	3.763	0.9900	0.9558
114.90	0.085	0.500	0.315	0.425	1.467	0.9461	1.147
114.80	0.105	0.148	0.540	0.130	1.816	1.072	0.8844
113.95	0.055	0.591	0.274	0.528	2.073	1.003	1.035
113.73	0.079	0.438	0.366	0.392	1.839	1.036	0.9548
113.35	0.095	0.070	0.588	0.058	2.219	1.074	0.9031
112.96	0.040	0.598	0.286	0.525	3.034	1.009	0.9902
112.85	0.060	0.617	0.296	0.520	2.088	0.9731	1.086
111.20	0.095	0.265	0.510	0.205	2.113	1.001	0.9522
110.05	0.060	0.645	0.325	0.528	2.432	1.008	1.018
109.75	0.074	0.719	0.304	0.588	1.883	1.007	1.067
108.60	0.083	0.730	0.302	0.522	1.722	0.9007	1.973
108.25	0.079	0.739	0.322	0.588	1.926	1.015	1.050
107.05	0.126	0.187	0.696	0.110	2.226	0.9504	0.7587
106.80	0.095	0.433	0.505	0.315	2.360	1.027	0.8984
106.26	0.157	0.238	0.605	0.175	1.652	1.118	0.9223
106.12	0.090	0.370	0.525	0.285	2.611	1.115	0.8510
106.00	0.135	0.145	0.690	0.085	2.122	0.9632	0.8562
105.30	0.060	0.880	0.364	0.608	3.034	0.9465	1.072
104.85	0.162	0.062	0.724	0.038	1.885	1.070	0.8950
104.19	0.120	0.800	0.391	0.550	1.654	0.9721	1.753
103.55	0.080	0.885	0.374	0.608	2.440	0.9777	1.232
103.50	0.126	0.197	0.670	0.130	2.381	1.121	0.8426
103.40	0.135	0.465	0.528	0.320	1.882	1.054	0.9795
102.45	0.070	0.845	0.423	0.543	3.160	0.9525	1.001
100.70	0.196	0.103	0.750	0.066	1.784	1.261	0.8732
100.35	0.210	0.223	0.675	0.152	1.564	1.242	0.9420
100.20	0.090	0.850	0.473	0.505	2.846	0.9420	0.9872
99.90	0.110	0.850	0.460	0.517	2.300	0.9640	1.550
99.45	0.157	0.520	0.590	0.310	1.953	1.030	0.9094
99.15	0.118	0.772	0.495	0.467	2.311	0.9905	0.9634
99.00	0.125	0.535	0.603	0.309	2.522	1.017	0.7756
98.60	0.185	0.310	0.700	0.170	1.910	1.063	0.8495
97.15	0.223	0.114	0.770	0.065	1.757	1.243	0.9278
96.65	0.152	0.570	0.589	0.324	2.178	1.038	0.9805
96.60	0.125	0.545	0.617	0.298	2.740	1.021	0.8254
95.88	0.209	0.393	0.657	0.228	1.745	1.139	0.9748
95.70	0.194	0.311	0.709	0.165	1.989	1.102	0.9095
94.90	0.155	0.745	0.562	0.415	2.172	1.033	0.7364
94.60	0.152	0.590	0.640	0.307	2.444	1.032	0.7034
94.40	0.179	0.561	0.645	0.287	2.098	1.023	0.9038
94.00	0.120	0.850	0.537	0.431	2.787	0.9420	3.431
92.85	0.215	0.520	0.657	0.265	1.848	1.063	1.067
92.06	0.303	0.324	0.750	0.175	1.465	1.273	0.8255
90.80	0.405	0.290	0.745	0.165	1.131	1.367	1.241
90.76	0.303	0.141	0.819	0.070	1.609	1.346	0.9469
90.70	0.280	0.435	0.705	0.225	1.581	1.185	0.9854
88.85	0.265	0.383	0.755	0.175	1.843	1.159	0.8898
87.87	0.355	0.162	0.835	0.075	1.510	1.379	0.9830
84.82	0.410	0.285	0.797	0.135	1.387	1.396	1.180
84.70	0.345	0.510	0.770	0.205	1.618	1.135	0.8745
84.42	0.574	0.217	0.824	0.120	1.024	1.731	1.508
83.50	0.432	0.173	0.855	0.078	1.430	1.546	1.050
82.75	0.497	0.306	0.830	0.125	1.247	1.342	1.360
82.70	0.506	0.202	0.855	0.090	1.250	1.554	1.191
79.05	0.600	0.165	0.905	0.035	1.219	0.9368	2.082
78.11	0.583	0.214	0.873	0.086	1.261	1.624	1.515
77.60	0.607	0.264	0.847	0.128	1.208	1.845	1.372
77.50	0.593	0.355	0.840	0.150	1.233	1.584	1.342
75.70	0.676	0.172	0.902	0.070	1.195	1.912	1.628
75.25	0.728	0.144	0.914	0.065	1.134	2.251	1.543
75.02	0.685	0.230	0.885	0.102	1.190	1.989	1.295
74.70	0.755	0.165	0.910	0.075	1.109	2.256	1.760
74.30	0.725	0.205	0.905	0.085	1.165	2.033	1.328
73.60	0.775	0.165	0.915	0.075	1.122	2.362	1.649

Table VI. Wilson Parameters

system	Λ_{ij}	Λ_{ji}	$\bar{D}_{y_1}$ (eqn 24), %	$\bar{D}_{\gamma_1}$, %
propyl bromide (1)–	0.3115[a]	1.2064[a]	1.88	
acetic acid (2)	0.2522[b]	0.9743[b]		
propyl bromide (1)-	0.4790[a]	1.1730[a]	4.43	
propionic acid (3)	0.2801[b]	1.4793[b]		
acetic acid (2)–	2.7500[a]	0.4374[a]	3.92	
propionic acid (3)	3.3487[b]	0.0155[b]		
	0.5494[c]	1.8766[c]		5.22

[a] Based on eq 18 and 19. [b] Based on the ternary system data only and eq 20, with $\bar{D}_{y_1} = 7.79\%$ and $\bar{D}_{y_2} = 10.5\%$. [c] Based on Min $(G^E_{\text{exptl}} - G^E_{\text{calcd}})^2$.

According to ref *13* a fixed value for $D_{\max}$ is recommended; however, a better criterium is to use the following expression (*3*):

$$D_{\max} = \sum_{i=1}^{N} (x_{ia} + x_{ib})\left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}}\right)\Delta x + 2\sum_{i=1}^{N} |\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + 2\sum_{i=1}^{N} (x_{ia} + x_{ib})\frac{\Delta P}{P} + \log e \sum_{i=1}^{N} (x_{ia} + x_{ib})B_i(\frac{1}{[t_a + C_i]^2} + \frac{1}{[t_b + C_i]^2}\Delta t \quad (15)$$

In this work, the errors in the measurements were estimated to be $\Delta P = \pm 2$ mmHg, $\Delta t = \pm 0.02$ °C, and $\Delta x = \pm 0.004$ mole fraction units.

All of the data reported in Table V satisfy the McDermott–Ellis test.

Correlation of Activity Coefficients. UNIFAC (6). The data for the binary system propyl bromide (1)–acetic acid (2) were used to determine the following interaction parameters:

$$a(\text{COOH, Br}) = 280.6 \quad (16)$$

$$a(\text{Br, COOH}) = 279.0 \quad (17)$$

With these parameters the activity coefficients can be reproduced with a mean percent deviation of 5%. When they were used for prediction of the activity coefficients of the binary propyl bromide (1)–propionic acid (3), it was found that calculated values in the range $0.04 < x < 0.55$ were within 8% of the experimental ones, but outside the range the error grew to 10–20%, particularly in the $x_i < 0.01$ range. For this reason the values given in eq 16 and 17 should be considered only provisional, until additional experimental data be collected.

Wilson (14). The experimental data for the two new binaries were correlated by the Wilson equation

$$\ln \gamma_i = -\ln (x_i + \Lambda_{ij}x_j) + x_j\left[\frac{\Lambda_{ij}}{x_i + \Lambda_{ij}x_j} - \frac{\Lambda_{ji}}{\Lambda_{ji}x_i + x_j}\right] \quad (18)$$

$$\ln \gamma_j = -\ln (x_j + \Lambda_{ji}x_i) - x_i\left[\frac{\Lambda_{ij}}{x_i + \Lambda_{ij}x_j} - \frac{\Lambda_{ji}}{\Lambda_{ji}x_i + x_j}\right] \quad (19)$$

If one uses as an objective funciton (OF) one that will minimize the error in the prediction of the vapor composition (*15*)

$$\text{OF} = \sum_{k=1}^{m}\left(\frac{y_{1,\text{exptl}} - y_{1,\text{calcd}}}{y_{1,\text{exptl}}}\right)_k^2 + \sum_{k=1}^{m}\left(\frac{y_{2,\text{exptl}} - y_{2,\text{calcd}}}{y_{2,\text{exptl}}}\right)_k^2 \quad (20)$$

The pertinent parameters Λ_{ij} and Λ_{ji}, together with the mean percentage deviation of y_1 predicted, are reported in Table VI. The table also contains for the sake of comparison the values of the parameters for the system acetic acid (2)–propionic (3) as calculated by eq 20 or an objective function based on minimizing $|G^E_{\text{exptl}} - G^E_{\text{calcd}}|^2$ (*9*), and the Wilson parameters obtained directly from only the data of the ternary system. For the latter parameters, Λ_{ij} and Λ_{ji} (in the general Wilson's equation for $\ln \gamma_i$ for multicomponent mixtures) are not binary constants but multicomponent parameters determined directly from the data of the mixture of the highest order.

Boiling Points. The boiling points of the binary and ternary systems have been correlated by using two different expressions: (a) The first is an equation for correlating the boiling points of multicomponent mixtures based on the complete data (binary, ternary, etc.), as developed in ref *9*. For a ternary mixture ($N = 3$) it reads

$$T = \sum_{i=1}^{N} x_iT^\circ_i + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_ix_j[A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + ...] + x_1x_2x_3\,[A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + ... + B'(x_1 - x_2)^2 + C'(x_1 - x_3)^2 + D'(x_2 - x_3)^2 + ...] \quad (21)$$

The pertinent coefficients appear in Table VII. (b) The second is an equation which relates the boiling point of the multicomponent mixture directly from the data without recourse to lower-order systems (see ref *15*):

$$T = \sum_{i=1}^{N} x_iT^\circ_i + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_ix_j[A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + ...] \quad (22)$$

Coefficients A_{ij}, B_{ij}, etc., are not binary constants; they are multicomponent parameters determined directly from the data. The pertinent parameters appear in Table VIII.

It should be noted that the approach of direct correlation suggested by Tamir (*15*) is more efficient than a correlation based on the complete data in two respects: (a) The number of parameters needed for representing T vs. x_i is smaller—for example, 9 instead of 16 parameters, as seen in Tables VII and VIII. (b) The goodness of fit is better as observed from the values of the error variance, σ_T^2, and the mean percentage deviation, $\bar{D}_T$, which are equal to 6.86 and 1.83% for 9 parameters and 7.57 and 2.01% for 16 parameters, respectively.

The above quantities are defined for an intensive or molar property M by

$$\sigma_M^2 = \frac{\sum_{i=1}^{m} (M_{\text{exptl}} - M_{\text{calcd}})_i^2}{m - c - 1} \quad (23)$$

$$\bar{D}_M = \frac{1}{m}\sum_{i=1}^{m} |(M_{\text{exptl}} - M_{\text{calcd}})/M_{\text{calcd}}|_i \quad (24)$$

Table VII. Boiling-Points Correlation for Eq 21[a]

system	A_{ij}	B_{ij}	C_{ij}	D_{ij}	E_{ij}
propyl bromide (1)–acetic acid (2)	−70.0342	53.1477	−35.1955	57.4628	−67.6993
propyl bromide (1)–propionic acid (3)	−94.2171	72.6357	−30.8799	20.7126	−89.9754
acetic acid (2)–propionic acid (3)	−5.6928	10.4722			

system	A	B	C	D
propyl bromide (1)–acetic acid (2)–propionic acid (3)	−69.9746	75.3070	247.176	−54.3069

[a] rmsd = 0.301. $\sigma_T^2 = 7.57$. $\bar{D}_T = 2.01\%$.

Table VIII. Parameters in Direct Correlation of T-x Data for Eq 22[a]

system	ij	A_{ij}	B_{ij}	C_{ij}
propyl bromide-acetic acid	12	−71.5368	79.5414	−50.1714
acetic acid-propionic acid	13	−94.4513	104.4467	−86.8320
propionic acid-propyl bromide	23	−22.1129	3.1855	47.1385

[a] rmsd = 0.277. $\sigma_T^2 = 6.86$ and $\bar{D}_T = 1.83\%$.

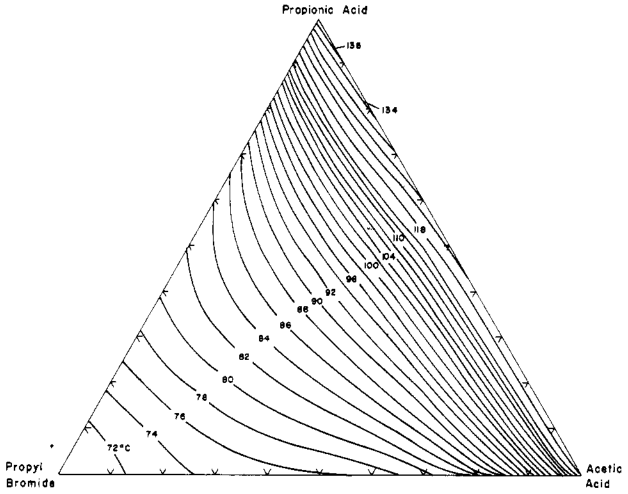

Figure 3. Ternary isotherms.

where $M = T$, γ_i, or γ_i; m and c are the number of data points and the number of parameters, respectively, corresponding to the mixture of the highest order. In other words, if binary plus ternary data are available, either in direct correlation which considers only the ternary data or in indirect correlation which takes into account the complete information (binary plus ternary), σ_M^2 and $\bar{D}_M$ are computed from m and c which correspond to the ternary system. The procedure of determining the number of parameters is detailed in ref (*15*); however, it should be noted that the parameters reported in Tables VII and VIII correspond to the minimal value of σ_M^2. The latter quantity, which is the measure of the spread of the error distribution, attains a minimum vs. the degrees of freedom $m - c - 1$ and is used as a criterium for choosing the optimal number of parameters.

Ternary isotherms were calculated on the basis of eq 22 and appear in Figure 3.

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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	parameter in eq 21
D	local deviation defined by eq 14
E_i	defined by eq 3
$\bar{D}_M$	mean deviation of an intensive property M, defined by eq 24
F_i	defined by eq 1
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}
P	total pressure, mmHg
P°_i	vapor pressure of the pure species i, mmHg
$P^\circ_{i_1}$	vapor pressure of the pure monomer of species i, mmHg
R	universal gas constant
rmsd	root mean square deviation
t, T	temperature, °C, K
V	molar volume
x_i, y_i	stoichiometric mole fraction of species i in the liquid phase and in the vapor phase, respectively
Φ	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 II
Λ_{ij}, Λ_{ji}	Wilson parameters
Δx, ΔP, Δt	errors in measurements of concentrations, pressure, and temperature, respectively
σ_M^2	error variance of an intensive property M, defined by eq 23
γ_i	overall liquid activity coefficient

Subscripts

calcd	calculated
exptl	experimental

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