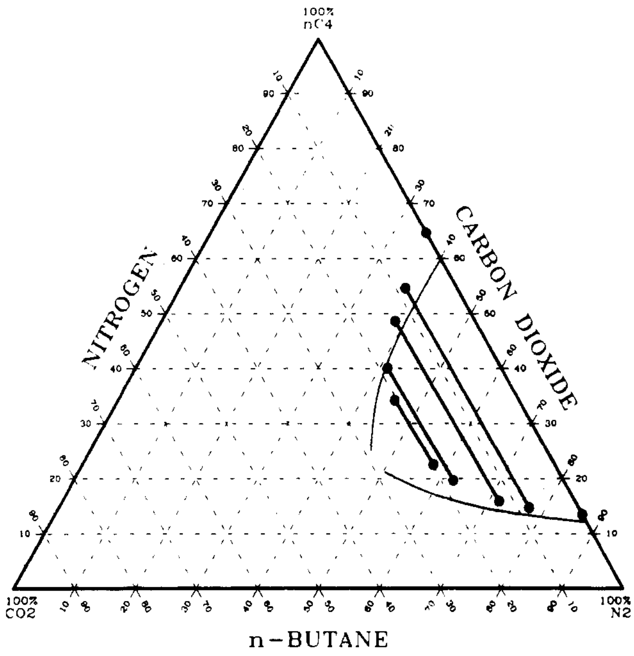

Figure 11. Phase diagram for the ternary mixture of nitrogen, carbon dioxide, and *n*-butane, at T = 310.9 K and P = 206.8 bar (3000 psia) fit with the Peng-Robinson equation of state.

Conclusions

A new, high-pressure vapor-liquid equilibrium apparatus capable of measuring the compositions and densities of the coexisting phases up to 300 °F and 5000 psia has been built, tested, and used to obtain data for the CO_2 + *n*-butane, N_2 + *n*-butane, and N_2 + CO_2 + *n*-butane systems. Data for the first of these systems are in excellent agreement with previously published data for both compositions and densities. The compositional data for the CO_2 + *n*-butane system were fit well with the Peng-Robinson equation of state with van der Waals one-fluid mixing rules, though (as is expected) the liquid density predictions were poor. Both the compositions and densities of the N_2 + *n*-butane system are poorly fit in this way, as is typical of N_2-hydrocarbon systems. Since the constituent binary systems were poorly fit with the Peng-Robinson equation of state, so was the data for the ternary N_2 + CO_2 + *n*-butane system.

Registry No. N_2, 7727-37-9; CO_2, 124-38-9; butane, 106-97-8.

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Vapor-Liquid Equilibria at 760 mmHg in the Ternary System Methyl Acetate-Propyl Bromide-Toluene

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Vapor-liquid equilibria at atmospheric pressure have been determined for the title ternary system. The data were correlated by various equations, and the appropriate parameters are reported.

The present work was undertaken to measure VLE data for the ternary system methyl acetate-propyl bromide-toluene for which no isobaric data are available. Data for the pertinent binaries have been reported previously (*1*, *2*).

Experimental Section

Purity of Materials. Methyl acetate (99.2+%) and propyl bromide (99.4+%) were purchased from Merck, and toluene (99.6+%) was purchased from Frutarom. 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 Constants of Pure Components

index	compd	refract. index at 25 °C	bp(760 mmHg), °C	purity GLC (min)
1	methyl acetate	1.3588[a] 1.3589[b]	56.94[a] 56.94[b]	99.2
2	propyl bromide	1.4320[a] 1.4317[b]	70.55[a] 70.80[b]	99.4
3	toluene	1.4926[a] 1.4941[b]	110.70[a] 110.63[b]	99.6

[a] Measured. [b] Reference *10*.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*3*) was used in the equilibrium determination. The experimental features have been described in previous publications (*4*). 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 OV-17 20%, and

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Table II. Experimental Vapor-Liquid Equilibria Data for Methyl Acetate (1)-Propyl Bromide (2)-Toluene (3) at 760 mmHg

t, °C	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
58.51	0.885	0.062	0.053	0.942	0.051	0.007	1.0099	1.2319	0.6810
59.14	0.856	0.079	0.907	0.930	0.067	0.003	1.0104	1.2480	0.2130
59.72	0.658	0.274	0.068	0.776	0.223	0.001	1.0761	1.1600	0.0774
61.59	0.625	0.209	0.166	0.786	0.188	0.026	1.0797	1.2053	0.7589
61.93	0.378	0.596	0.026	0.510	0.480	0.010	1.1454	1.0695	1.8389
62.08	0.626	0.187	0.186	0.803	0.162	0.035	1.0830	1.1451	0.8989
63.01	0.472	0.369	0.160	0.655	0.316	0.029	1.1400	1.0973	0.8406
63.31	0.306	0.659	0.035	0.440	0.550	0.010	1.1688	1.0593	1.3147
63.31	0.404	0.473	0.123	0.572	0.409	0.020	1.1489	1.0980	0.7304
63.71	0.636	0.104	0.260	0.842	0.095	0.062	1.0623	1.1475	1.0867
63.80	0.355	0.515	0.130	0.532	0.447	0.021	1.1983	1.0848	0.7441
63.99	0.600	0.112	0.289	0.842	0.097	0.061	1.1159	1.0840	0.9392
64.10	0.587	0.114	0.299	0.841	0.097	0.062	1.1358	1.0566	0.9180
64.80	0.283	0.616	0.101	0.439	0.542	0.019	1.2036	1.0656	0.8173
64.95	0.502	0.212	0.286	0.742	0.193	0.065	1.1404	1.0970	0.9808
65.01	0.554	0.129	0.317	0.812	0.115	0.073	1.1292	0.0721	0.9888
65.04	0.446	0.206	0.349	0.748	0.184	0.068	1.2918	1.0748	0.8354
65.26	0.193	0.793	0.014	0.310	0.688	0.002	1.2248	1.0358	0.6179
65.41	0.477	0.234	0.289	0.715	0.216	0.068	1.1395	1.0970	1.0070
65.6	0.309	0.513	0.178	0.489	0.470	0.041	1.1974	1.0802	0.9627
65.66	0.230	0.686	0.085	0.372	0.612	0.016	1.2200	1.0527	0.7945
66.45	0.406	0.295	0.299	0.649	0.275	0.076	1.1767	1.0717	1.0360
66.53	0.572	0.038	0.391	0.868	0.026	0.106	1.1150	0.7886	1.1036
66.92	0.295	0.481	0.224	0.494	0.452	0.054	1.2158	1.0655	0.9652
67.12	0.158	0.785	0.058	0.272	0.717	0.012	1.2434	1.0282	0.8138
67.36	0.224	0.591	0.185	0.395	0.558	0.047	1.2560	1.0567	1.0010
67.62	0.160	0.748	0.092	0.279	0.701	0.020	1.2396	1.0386	0.8611
67.65	0.332	0.377	0.291	0.559	0.363	0.078	1.1939	1.0677	1.0480
67.75	0.193	0.661	0.146	0.333	0.629	0.038	1.2187	1.0511	1.0135
67.93	0.399	0.254	0.347	0.670	0.238	0.092	1.18032	1.0309	1.0216
68.16	0.225	0.580	0.195	0.400	0.553	0.048	1.2391	1.0386	0.9407
68.30	0.131	0.785	0.084	0.238	0.742	0.020	1.2632	1.0264	0.9187
68.45	0.141	0.758	0.101	0.256	0.720	0.024	1.2560	1.0272	0.8876
68.85	0.278	0.424	0.298	0.494	0.425	0.082	1.2128	1.0685	1.0272
69.13	0.109	0.821	0.070	0.199	0.783	0.018	1.2330	1.0102	0.9715
69.30	0.401	0.170	0.429	0.715	0.164	0.121	1.2026	1.0167	1.0385
69.37	0.085	0.864	0.051	0.151	0.836	0.013	1.1909	1.0170	0.9360
69.95	0.302	0.324	0.374	0.571	0.327	0.102	1.2489	1.0413	0.9791
70.05	0.317	0.289	0.394	0.596	0.290	0.114	1.2394	1.0343	1.0317
70.34	0.321	0.280	0.399	0.608	0.279	0.112	1.2381	1.0170	0.9975
71.25	0.367	0.141	0.492	0.710	0.144	0.146	1.2294	1.0175	1.0177
71.46	0.218	0.426	0.357	0.428	0.457	0.115	1.2414	1.0588	1.0971
71.72	0.267	0.313	0.420	0.528	0.339	0.133	1.2418	1.0601	1.0636
71.94	0.157	0.563	0.281	0.312	0.599	0.089	1.2421	1.0335	1.0630
72.08	0.144	0.592	0.264	0.290	0.627	0.083	1.2465	1.0250	1.0482
72.71	0.382	0.064	0.554	0.755	0.068	0.018	1.2040	1.0116	1.0372
74.36	0.051	0.757	0.192	0.095	0.840	0.065	1.0776	1.0045	1.0383
75.84	0.347	0.030	0.623	0.735	0.020	0.245	1.1763	0.5809	1.1470
76.41	0.176	0.343	0.481	0.413	0.416	0.172	1.2803	1.0317	1.0211
76.47	0.182	0.328	0.489	0.429	0.398	0.173	1.2840	1.0294	1.0101
76.71	0.223	0.215	0.562	0.525	0.256	0.219	1.2766	1.0043	1.1014
77.01	0.170	0.344	0.486	0.405	0.423	0.173	1.2780	1.0274	0.9975
78.31	0.075	0.552	0.373	0.159	0.690	0.151	1.1031	1.0074	1.0859
79.11	0.107	0.437	0.456	0.260	0.561	0.179	1.2304	1.0118	1.0210
79.80	0.252	0.060	0.688	0.647	0.063	0.289	1.2775	0.8135	1.0705
79.95	0.230	0.102	0.669	0.605	0.124	0.271	1.3013	0.9382	1.0278
80.52	0.143	0.295	0.562	0.358	0.397	0.246	1.2195	1.0167	1.0874
81.80	0.133	0.284	0.582	0.342	0.395	0.263	1.2038	1.0135	1.0776
82.60	0.148	0.219	0.633	0.399	0.313	0.288	1.2368	1.0203	1.0556
82.85	0.163	0.205	0.632	0.428	0.283	0.289	1.2006	0.9788	1.0519
84.34	0.094	0.312	0.594	0.247	0.460	0.293	1.1489	1.0040	1.0797
84.65	0.211	0.122	0.666	0.510	0.154	0.337	1.0475	0.8479	1.0963
84.93	0.164	0.127	0.709	0.450	0.187	0.363	1.1821	0.9843	1.1013
85.10	0.168	0.113	0.719	0.480	0.151	0.369	1.2245	0.8949	1.0966
87.39	0.101	0.218	0.681	0.284	0.342	0.374	1.1355	0.9818	1.0900
92.55	0.107	0.043	0.850	0.408	0.083	0.509	2.0283	1.0292	1.0318
94.13	0.084	0.067	0.849	0.325	0.130	0.545	1.2411	0.9996	1.0510
94.46	0.074	0.150	0.776	0.229	0.262	0.509	0.9783	0.8839	1.0634
95.60	0.048	0.109	0.844	0.210	0.226	0.565	1.3509	1.0186	1.0470
103.84	0.032	0.022	0.946	0.1[illegible]3	0.047	0.801	1.1865	0.8265	1.0306
103.90	0.029	0.020	0.951	0.149	0.047	0.804	1.2568	0.9480	1.0273

operated at 95 °C. Injector and detector temperatures were 210 and 220 °C, respectively. Very good separation was achieved under these conditions, and calibration analyses were carried out 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 $\Delta P = \pm 1$ mmHg and $\Delta t = \pm 0.02$ °C.

Table III. Vapor-Pressure Constants (*10*)

compound	α_i	β_i	δ_i
methyl acetate	7.061 31	1156.43	219.69
propyl bromide	6.910 65	1194.889	225.51
toluene	6.954 64	1344.800	219.482

Results

The temperature-concentration measurements at 760 mmHg for the ternary system are reported in Table II as well as the activity coefficients which were calculated from the following equation (*5*):

$$\ln \gamma_i = \ln (y_iP/x_iP_i^\circ) + (B_{ii} - V^L_i)(P - P_i^\circ)/RT + (P/RT)\sum_{j=1}^{n}\sum_{k=1}^{n} y_j y_k (\delta_{ji} - \delta_{jk}) \quad (1)$$

where

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

Vapor pressure P_i° was calculated according to the Antoine equation:

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

where the constants are reported in Table III. The molar virial coefficients B_{ii} and the mixed molar coefficient B_{ij} were calculated by the method of Tsonopoulos (*6*) using the molecular parameters suggested by the same author.

The ternary data reported in Table II were found to be thermodynamically consistent by the McDermott-Ellis method (*7*), modified by Wisniak and Tamir (*8*).

The activity coefficients were correlated by the following equation reported by Redlich and Kister (*5*):

$$\begin{aligned}\ln \gamma_1 = {} & x_2x_3[(B_{12} + B_{13} - B_{23}) + C_{12}(2x_1 - x_2) + \\ & C_{13}(2x_1 - x_3) + 2C_{23}(x_3 - x_2) + \\ & D_{12}(x_1 - x_2)(3x_1 - x_2) + D_{13}(x_1 - x_3)(3x_1 - x_2) - \\ & 3D_{23}(x_3 - x_2)^2 + C_1(1 - 2x_1)] + \\ & x_2^2[B_{12} + C_{12}(3x_1 - x_2) + D_{12}(x_1 - x_2)(5x_1 - x_2)] + \\ & x_3^2[B_{13} + C_{13}(3x_1 - x_3) + D_{13}(x_1 - x_3)(5x_1 - x_3)] \quad (4)\end{aligned}$$

B_{ij}, C_{ij}, and D_{ij} are the binary constants and C_1 is a ternary constant in Table IV. The equations for two other activity coefficients were obtained by cyclic rotation of the indices. The binary data used for calculating the binary constants were reported elsewhere (*1*, *2*).

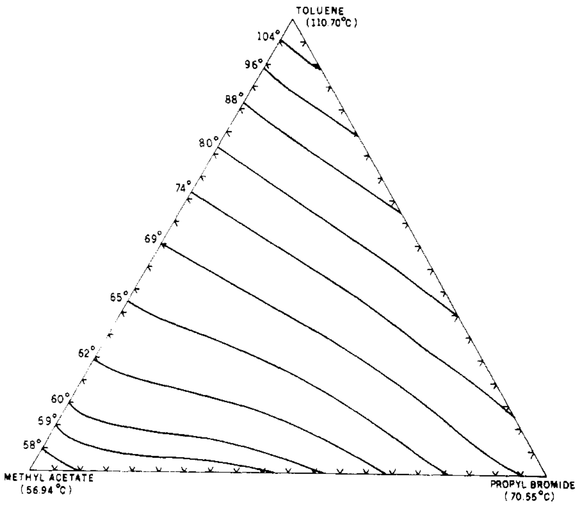

Figure 1. Isothermals for the ternary system (760 mmHg).

The binary and ternary Redlich-Kister coefficients were obtained by the Simplex optimization algorithm and are reported in Table IV. Comparison of the relative values of the root mean square deviation for the cases with and without ternary constant C_1 suggest that the predictor with a ternary constant is only slightly better.

The boiling temperature of the mixture was correlated solely with the liquid composition by the following equation, which has been derived on the basis of the concept of "excess property" (*9*):

$$T = \sum_{i=1}^{n} x_iT_i^\circ + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} x_ix_j[A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 ...] \quad (5)$$

This equation is useful for obtaining isothermals and for exploring the azeotropic behavior and distillation paths of ternary mixtures (*9*). The coefficients A_{ij}, B_{ij}, and C_{ij} are multicomponent parameters which are determined directly from the multicomponent data. Figure 1 reports the isothermals obtained on the basis of the parameters A_{ij} and B_{ij} reported in Table V by applying eq 5 for $n = 3$.

Table IV. Redlich-Kister Correlation of Binary and Ternary Data

system	B_{ij}	C_{ij}	D_{ij}	rmsd γ_1	rmsd γ_2	rmsd γ_3
methyl acetate (1)-propyl bromide (2)	0.578 96	0.006 55	0.000 164	0.193	0.0830	
methyl acetate (1)-toluene (3)	0.399 79	-0.054 66	0.126 19	0.0172		0.0349
propyl bromide (2)-toluene (3)	-0.024 29	0.9014×10^{-4}	0.8092×10^{-6}		0.0788	0.0643

system	C_1	overall rmsd[a] γ	overall rmsd[a] y
methyl acetate (1)-propyl bromide (2)-toluene (3)	0	0.209	0.033
	-1.9399	0.170	0.023

[a] Lumped ternary data.

Table V. Parameters of *T-x* Correlation (Eq 5, *n* = 3) for Methyl Acetate (1)-Propyl Bromide (2)-Toluene (3) at 760 mmHg[a]

ij	A_{ij}	B_{ij}	C_{ij}	D_{ij}	E_{ij}	F_{ij}	G_{ij}	mean *D*%	rmsd
12	-19.341	5.4133	-1.583					0.148	0.0298
13	-53.956	32.975	-32.688	16.095	33.602	25.318	-65.404	1.79	0.196
23	-20.759	5.5655	12.836	-6.485				0.213	0.0507
				Ternary Parameters					
12	-17.833	9.0536	12.453						
13	-59.527	34.028	-6.9215					0.440	0.0694
23	-21.279	3.9775	5.7545						

[a] T_1° = 330.09 K; T_2° = 383.85 K; T_3° = 343.70 K. $D = |(T_{obsd} - T_{calcd})|/T_{obsd}$. Mean $D\% = (100/n)\sum D_i$.

None of the three possible binaries exhibit azeotropic behavior, and as shown by Figure 1, neither does the ternary system. Table V contains also the group of parameters A_{ij}, B_{ij}, and C_{ij} for the T–x correlation (eq 5) which yield the smaller mean deviation between the calculated and observed values of T.

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental work and numerical calculations.

Glossary

A_{ij}, B_{ij}, etc.	multicomponent adjustable parameters in eq 5
B_{ii}, B_{ij}	virial coefficients, eq 2
B_{ii}, C_{ij}, D_{ii}	Redlich–Kister constants, eq 4
V^L_i	molar volume, component i
n	number of components
P	total pressure, mmHg
P_i°	vapor pressure of pure component i, mmHg
T	boiling temperature of a mixture, K
T_i°	boiling temperature of pure component i, K
t	temperature, °C
x_i, y_i	mole fraction of component i in the liquid and vapor phases
α_i	coefficient, Antoine equation
β_i	coefficient, Antoine equation
γ_i	activity coefficient of component i
δ_i	coefficient, Antoine equation
δ_{ij}	virial coefficient parameter, eq 2

Subscripts

calcd	calculated
obsd	observed

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The Systems Vinyl Acetate–Toluene and Vinyl Acetate–Propyl Bromide–Toluene

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Vapor–liquid equilibrium at 760 mmHg has been determined for the title systems. The binary vinyl acetate–toluene deviates positively from ideal behavior and does not have an azeotrope. The binary and ternary data were correlated by various equations, and the appropriate parameters are reported.

The present work was undertaken to measure VLE data for the title systems for which no isobaric data are available. Data for the two other binaries have already been measured (*1*, *2*).

Experimental Section

Purity of Materials. Vinyl acetate analytical grade (99%+) was purchased from Fluka, propyl bromide (99.4%) from Merck, and analytical grade toluene (99.6%+) from Frutarom. 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.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*3*) was used in the equilibrium determination. A vacuum system connected the vapor condenser with a Swietoslawski ebulliometer and allowed total pressure regulation. The total pressure of the system was determined from the boiling temperature of the distilled water in the ebulliometer. The experimental features have been described in a previous publication (*4*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter. Column packing, operating temperature, and injector and detector temperatures were as follows: 20% O.V. 17, 120 °C, 210 °C, 220 °C for the binary system; GP 20% SP-2100/0.1% Carbowax 1500 on 100/120 Supelcoport, 100 °C, 230 °C, 230 °C, for the ternary system. Very good separation was achieved under these conditions, and calibration analyses were carried out 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 $\Delta P = \pm 1$ mmHg and $\Delta t = \pm 0.02$ °C.

Table I. Physical Constants of Pure Components

index	compd	refractive index (25 °C)	bp (760 mmHg), °C	purity, GLC (min)
1	vinyl acetate	1.3932[a]	72.56[a]	99
		1.3934[c]	72.49[c]	
2	propyl bromide	1.4320[a]	70.55[a]	99.4
		1.4317[b]	70.80[b]	
3	toluene	1.4926[a]	110.7[a]	99.6
		1.4940[b]	110.63[b]	

[a] Measured. [b] Reference *15*. [c] Reference *16*.

Results

The temperature–concentration measurements at 760 mmHg for the binary and ternary systems are reported in Figures 1 and