Table II shows that the current measurements supports the relative enthalpy data reported by Yerlett and Wormald (*8*) over that of Machado and Streett (*7*), at all temperatures. However, as the temperature increases, the relative enthalpies reported here increase at a faster rate than those reported by Yerlett and Wormald, until at the highest temperature the difference is nearly 6.0%. Yerlett and Wormald report their enthalpy measurements to be accurate to 0.6%. The estimated overall error of the heat capacity measurements in the present measurements is estimated to be 0.9%. While the standard deviation of the data from eq 2 is considerably greater (1.65%), the error in the enthalpies resulting from the integration of eq 2 will be much smaller. We cannot explain the significant differences between the high-temperature enthalpies calculated from the heat capacities reported in this work and those reported by Yerlett and Wormald.

Registry No. Methanol, 67-56-1.

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Vapor–Liquid Equilibria at 760 mmHg in the Ternary System Methanol–1,1-Dichloroethane–Propyl Bromide

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Vapor–liquid equilibrium at atmospheric pressure has 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 methanol–1,1-dichloroethane–propyl bromide for which no isobaric data are available.

Experimental Section

Purity of Materials. Analytical grade methanol (99.5%+) was purchased from Frutarom; propyl bromide (99.4%) and 1,1-dichloroethane analytical grade (99.6% +) were purchased from Merck. 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 (*1*) was used in the equilibrium determination. The experimental features have been described in previous publications (*2*). 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 200 cm long and 0.2 cm in diameter, was packed with 20% OV-17, and was operated isothermally at 75 °C. Injector and detector temperatures were 220 and 230 °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.

Table I. Physical Constants of Pure Components

index	compd	refractive index (20 °C)	bp(760 mmHg), °C	purity [GLC (min)]
1	methanol	1.3280[a] 1.3284[b]	64.68[a] 64.70[b]	99.5
2	1,1-dichloroethane	1.4138[a] 1.4135[b]	57.29[a] 57.28[b]	99.6
3	propyl bromide	1.4348[a] 1.4343[b]	70.55[a] 71.0[b] 70.80[c]	99.6

[a] Measured. [b] Reference *12*. [c] Reference *13*.

Results

The temperature–concentration measurements at 760 mmHg for the ternary system are reported in Table II together with the activity coefficients which were calculated from the following equation (*3*)

$$\ln \gamma_1 = \ln (Py_1/P_1{}^0x_1) + (B_{11} - v^{L}{}_1)(P - P_1{}^0)/RT + (P/2RT)\sum\sum y_jy_k(2\delta_{ji} - \delta_{jk}) \quad (1)$$

where

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

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

$$\log P_i{}^0 = \alpha_i - \beta_i/(\delta_i + t) \quad (3)$$

0021-9568/88/1733-0429$01.50/0

Table II. Experimental Vapor–Liquid Equilibria Data for Methanol (1)–1,1-Dichloroethane (2)–Propyl Bromide (3) at 760 mmHg

temp, °C	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
49.05	0.163	0.777	0.060	0.329	0.628	0.043	4.0351	1.0626	1.4913
49.51	0.376	0.563	0.061	0.329	0.624	0.047	1.7126	1.4344	1.5771
49.51	0.216	0.745	0.039	0.299	0.678	0.023	2.7109	1.1776	1.2053
49.52	0.344	0.599	0.057	0.329	0.329	0.042	1.8707	1.3587	1.5078
49.54	0.248	0.714	0.038	0.316	0.660	0.024	2.4901	1.1952	1.2908
49.55	0.321	0.627	0.052	0.336	0.628	0.036	2.0436	1.2949	1.4160
49.57	0.283	0.670	0.047	0.326	0.642	0.032	2.2476	1.2378	1.3907
49.58	0.363	0.575	0.062	0.336	0.617	0.047	1.8052	1.3856	1.5485
49.68	0.254	0.675	0.071	0.321	0.637	0.042	2.4547	1.2143	1.2030
49.86	0.158	0.808	0.034	0.285	0.696	0.019	3.4689	1.0990	1.1247
50.07	0.381	0.519	0.100	0.365	0.555	0.080	1.8261	1.3583	1.6080
50.26	0.335	0.502	0.163	0.340	0.544	0.116	1.9221	1.3662	1.4175
50.27	0.114	0.861	0.025	0.266	0.720	0.014	4.4176	1.0542	1.1120
50.34	0.542	0.394	0.064	0.439	0.495	0.066	1.5197	1.5843	2.0641
50.40	0.491	0.406	0.103	0.386	0.524	0.090	1.4751	1.6216	1.7380
50.41	0.450	0.435	0.115	0.370	0.529	0.101	1.5436	1.5266	1.7440
50.43	0.469	0.407	0.124	0.385	0.495	0.120	1.5396	1.5257	1.9214
50.59	0.265	0.560	0.175	0.341	0.543	0.116	2.4002	1.2090	1.3051
50.60	0.270	0.555	0.175	0.320	0.527	0.153	2.2144	1.1826	1.7175
50.60	0.289	0.517	0.194	0.335	0.517	0.148	2.1639	1.2457	1.5001
50.89	0.538	0.344	0.118	0.406	0.483	0.111	1.3842	1.7353	1.8405
51.00	0.650	0.300	0.050	0.435	0.500	0.065	1.2185	2.0554	2.5413
51.10	0.611	0.310	0.079	0.512	0.404	0.084	1.5153	1.6044	2.0816
51.15	0.207	0.555	0.238	0.335	0.522	0.143	2.9455	1.1593	1.1590
51.17	0.315	0.431	0.254	0.377	0.446	0.177	2.1742	1.2649	1.3457
51.25	0.398	0.363	0.239	0.400	0.405	0.195	1.8181	1.3603	1.5728
51.31	0.461	0.309	0.230	0.424	0.376	0.200	1.6577	1.4811	1.6750
51.32	0.184	0.584	0.232	0.327	0.532	0.141	3.2106	1.1078	1.1648
51.35	0.573	0.291	0.136	0.432	0.422	0.146	1.3540	1.7647	2.0685
51.39	0.153	0.619	0.228	0.312	0.561	0.127	3.6733	1.0995	1.0643
51.45	0.708	0.282	0.010	0.450	0.536	0.014	1.1317	2.3122	2.6998
51.50	0.606	0.301	0.093	0.640	0.276	0.084	1.8682	1.1183	1.7605
51.60	0.075	0.790	0.135	0.268	0.656	0.076	6.3784	1.0005	1.0660
51.70	0.371	0.335	0.294	0.406	0.366	0.228	1.9408	1.3116	1.4710
51.75	0.183	0.516	0.301	0.347	0.470	0.183	3.3602	1.0915	1.1483
51.91	0.267	0.387	0.346	0.385	0.385	0.230	2.5356	1.1856	1.2501
51.94	0.529	0.255	0.216	0.441	0.343	0.216	1.4597	1.6032	1.8855
52.18	0.464	0.284	0.252	0.438	0.296	0.266	1.6373	1.2312	1.9710
52.26	0.625	0.201	0.174	0.468	0.317	0.215	1.2908	1.8608	2.3077
52.43	0.527	0.188	0.285	0.458	0.261	0.281	1.4897	1.6265	1.8266
52.45	0.301	0.295	0.404	0.405	0.310	0.285	2.3102	1.2293	1.3020
52.51	0.581	0.181	0.238	0.466	0.265	0.269	1.3690	1.7113	2.0897
52.55	0.648	0.188	0.164	0.476	0.306	0.218	1.2495	1.9022	2.4587
52.66	0.485	0.186	0.329	0.431	0.248	0.321	1.5109	1.5486	1.7888
52.73	0.410	0.210	0.380	0.438	0.244	0.318	1.8099	1.3465	1.5313
52.75	0.645	0.190	0.165	0.456	0.319	0.225	1.1929	1.9483	2.5013
52.78	0.211	0.389	0.400	0.370	0.365	0.265	2.9696	1.0857	1.2070
52.80	0.555	0.153	0.292	0.468	0.212	0.320	1.4222	1.6027	2.0037
52.84	0.348	0.172	0.480	0.441	0.198	0.361	2.1384	1.3283	1.3699
52.96	0.605	0.138	0.257	0.473	0.212	0.315	1.3087	1.7678	2.2295
52.97	0.263	0.279	0.458	0.397	0.286	0.317	2.5348	1.1781	1.2532
53.05	0.543	0.125	0.332	0.485	0.167	0.348	1.4895	1.5321	1.9005
53.13	0.500	0.126	0.374	0.465	0.163	0.372	1.5476	1.4786	1.7955
53.22	0.335	0.173	0.492	0.423	0.199	0.378	2.0973	1.3102	1.3793
53.36	0.600	0.110	0.290	0.471	0.167	0.362	1.2922	1.7226	2.2367
53.44	0.660	0.094	0.246	0.500	0.155	0.345	1.2405	1.8674	2.5110
53.53	0.760	0.160	0.080	0.505	0.349	0.146	1.0787	2.4732	3.2743
53.57	0.067	0.683	0.250	0.249	0.607	0.144	6.0877	1.0023	1.0168
53.57	0.735	0.137	0.128	0.512	0.271	0.217	1.1303	2.2369	3.0334
53.58	0.557	0.086	0.357	0.453	0.154	0.393	1.3278	2.0157	1.9544
53.58	0.411	0.099	0.490	0.453	0.118	0.429	1.8011	1.3409	1.5531
53.60	0.761	0.164	0.075	0.637	0.260	0.103	1.3482	1.8018	2.4838
53.64	0.320	0.127	0.553	0.429	0.151	0.420	2.1869	1.3349	1.3431
53.65	0.708	0.075	0.217	0.519	0.131	0.350	1.1883	1.9649	2.8698
53.74	0.232	0.174	0.594	0.374	0.187	0.439	2.6269	1.2020	1.2987
53.80	0.593	0.047	0.360	0.476	0.078	0.446	1.2979	1.8534	2.1829
53.81	0.365	0.090	0.545	0.435	0.110	0.455	1.9305	1.3639	1.4673
53.97	0.239	0.086	0.675	0.416	0.094	0.490	2.8048	1.2126	1.2668
54.00	0.421	0.054	0.525	0.451	0.064	0.485	1.7205	1.3138	1.6133
54.13	0.302	0.065	0.633	0.438	0.074	0.488	2.3176	1.2566	1.3394
54.13	0.816	0.170	0.014	0.552	0.416	0.032	1.0653	2.7306	4.0414
54.30	0.759	0.108	0.133	0.534	0.226	0.240	1.1047	2.3104	3.1509
54.43	0.176	0.154	0.670	0.375	0.165	0.460	3.3683	1.1713	1.1780
54.45	0.242	0.076	0.682	0.429	0.084	0.487	2.7938	1.2073	1.2266
55.00	0.126	0.197	0.677	0.377	0.191	0.432	4.6074	1.0409	1.0744
55.26	0.122	0.117	0.761	0.390	0.120	0.490	4.8704	1.0911	1.0741

Table II (Continued)

temp, °C	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
55.31	0.824	0.124	0.052	0.660	0.247	0.093	1.1954	2.1426	3.0544
55.55	0.133	0.129	0.738	0.365	0.140	0.495	4.1334	1.1437	1.1067
55.56	0.763	0.019	0.218	0.588	0.038	0.374	1.1453	2.1156	2.8684
55.96	0.833	0.072	0.095	0.604	0.175	0.221	1.0555	2.5476	3.8562
56.07	0.800	0.014	0.186	0.584	0.033	0.383	1.0612	2.4520	3.3819
56.14	0.847	0.105	0.048	0.732	0.188	0.080	1.2419	1.8799	2.7822
56.40	0.075	0.249	0.676	0.314	0.247	0.439	6.0819	1.0179	1.0401
57.61	0.884	0.082	0.034	0.742	0.178	0.080	1.1317	2.1743	3.7379
58.47	0.902	0.039	0.059	0.701	0.112	0.187	1.0119	2.7869	4.8607
58.98	0.068	0.042	0.890	0.327	0.045	0.628	6.2716	1.0111	1.0351
61.23	0.950	0.025	0.025	0.823	0.086	0.091	1.0009	3.0800	5.1489
62.32	0.965	0.010	0.025	0.912	0.046	0.042	1.0425	4.0003	2.3106

Table III. Vapor Pressure Constants (*12*)

compound	α_i	β_i	δ_i
methanol	7.897 50	1474.08	229.13
1,1-dichloroethane	6.985 30	1171.42	228.12
propyl bromide	6.910 65	1194.889	225.51

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

				rmsd	
system	B_{ij}	C_{ij}	D_{ij}	γ_1	γ_2
methanol (1)–1,1-dichloroethane (2)	1.6315	−0.38290	0.22779	0.220	0.104
methanol (1)–propyl bromide (3)	1.7884	−0.33412	0.51777	0.478	0.247
1,1-dichloroethane (2)–propyl bromide (3)	0.11295			0.039	0.056

		overall rmsd	
system	C_1	γ	y
methanol (1)–acetonitrile (2)	0	0.829	0.0458
propyl bromide (3)	−0.47348	0.815	0.0465

where the constants are reported in Table III. The molar virial coefficients B_{ii} and the mixed coefficient B_{ij} were calculated by the method of Tsonopoulos (*4*) using the molecular parameters suggested by the same author.

The ternary data reported in Table II were found to be thermodynamically consistent as tested by the McDermot–Ellis method (*5*) modified by Wisniak and Tamir (*6*). Two experimental points a and b are considered thermodynamically consistent if the following condition is fulfilled:

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

The local deviation D is given by

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

where N is the number of components and

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

The errors in the measurements Δx, ΔP, and Δt were as previously indicated. The first term in eq 6 was the dominant one. The activity coefficients were correlated by the following Redlich–Kister expansion (*7*)

$$\begin{aligned}\ln \gamma_1 = {} & x_2x_3[(B_{12} + B_{13} - B_{23}) + C_{12}(2x_1 - x_2) + C_{13}(2x_1 - x_3) + 2C_{23}(x_3 - x_2) + \\ & D_{12}(x_1 - x_2)(3x_1 - x_2) + D_{13}(x_1 - x_3)(3x_1 - x_2) - 3D_{23}(x_3 - x_2)^2 + C_1(1 - 2x_1)] + \\ & x_2^2[B_{12} + C_{12}(3x_1 - x_2) + D_{12}(x_1 - x_2)(5x_1 - x_2)] + \\ & x_3^2[B_{13} + C_{13}(3x_1 - x_3) + D_{13}(x_1 - x_3)(5x_1 - x_3)]\end{aligned} \tag{7}$$

where B_{ij}, C_{ij}, and D_{ij} are the binary constants and C_1 is a ternary constant. The equations for two other activity coefficients were obtained by cyclic rotation of the indexes. The binary data used for calculating the binary constants were reported elsewhere (*8*, *9*).

The binary and ternary Redlich–Kister coefficients were obtained by a Simplex optimization technique and are reported in Table IV. The relative values of the root mean square deviation and the ternary constant C_1 suggest that ternary data can be predicted directly from the binary systems.

Boiling points of the binary and ternary systems were correlated by the equation suggested by Wisniak and Tamir (*10*):

$$T = \sum_{i=1}^{2}x_1T_1^0 + x_1x_2\sum_{k=0}^{l}C_k(x_1 - x_j)^k + ...] \tag{8}$$

$$T = \sum_{i=1}^{3}x_1T_1^0 + \sum_{i,j=1}\{x_ix_j\sum_{k=0}^{l}C_k(x_1 - x_j)^k\} + x_1x_2x_3\{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + ...\} \tag{9}$$

T_i^0 is the boiling point of the pure component in K 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, D are ternary constants. The various constants are reported in Table V, which also contains information indicating the degree of goodness of the correlation.

The boiling temperature of the mixture was correlated solely with the liquid composition by the following equation which has

Table V. Correlation of Boiling Points, Eq 8 and 9

system	C_0	C_1	C_2	C_3	rmsd	diff %[a]
methanol (1)–1,1-dichloroethane (2)	−45.370	−14.962	−62.648	27.211	0.67	1.0
methanol (1)–propyl bromide (3)	−49.552	6.9473	−87.823	45.215	0.97	1.1
1,1-dichloroethane (2)–propyl bromide (3)	−5.7398	−4.9563	0.0	−1.8268	0.14	0.2

system	A	B	C	rmsd	diff %
methanol (1)–acetonitrile (2)–propyl bromide	−32.203	114.00	218.25	0.607	0.91

[a] Diff % = $(100/n)\sum_{i=1}^{n}(|T_{\text{exptl}} - T_{\text{calcd}}/T_{\text{exptl}})$.

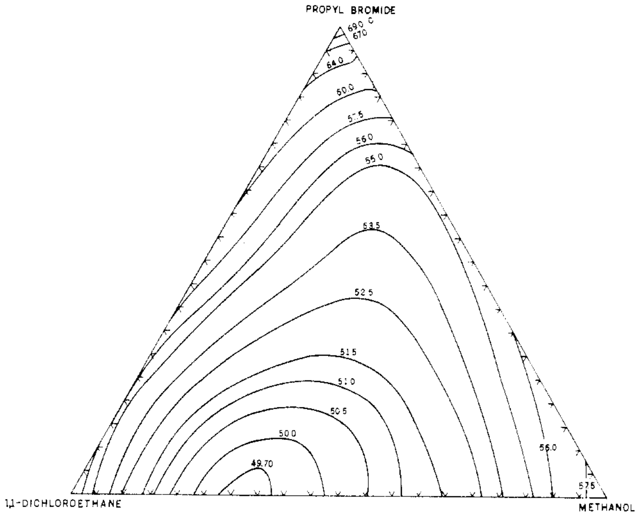

Figure 1. Isothermals for the ternary system at 760 mmHg.

Table VI. Parameters of T–x Correlation (eq 10, $N = 3$) for Methanol (1)–1,1-Dichloroethane (2)–Propyl Bromide (*3*) at 760 mmHg[a]

ij	A_{ij}	B_{ij}	C_{ij}	D_{ij}	mean D, %	rmsd
12	−46.33	5.278				
13	−51.377	3.803			2.03	0.154
23	−28.01	25.82				
12	−41.44	1.869	−35.44	6.058		
13	−46.88	16.42	−82.66	38.13	0.397	0.0238
23	−21.46	6.750	−25.67	−26.67		

[a] $t_1^0 = 64.68$ °C; $t_2^0 = 81.1$ °C; $t_3^0 = 70.55$ °C. $D = |(T_{\mathrm{exptl}} - T_{\mathrm{calcd}})/T_{\mathrm{exptl}}|$; mean D, % $= (100/m)\sum D_i$.

been derived on the basis of the concept of "excess property" (*11*):

$$T = \sum_{i=1}^{N} x_i T_i^0 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + ...] \qquad (10)$$

This equation is useful for obtaining isothermals and for exploring the azeotropic behavior and distillation paths of ternary mixtures as explained in ref *11*. The coefficients A_{ij}, B_{ij}, 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}, B_{ij} reported in Table VI by applying eq 10 for $N = 3$. These isothermals might be used for considering possible distillation paths in ternary systems as well as to conclude whether a ternary system exhibits azeotropic behavior.

As observed, whereas all binary systems have azeotropes, the ternary system does not exhibit a clear azeotropic behavior. It is possible that there is a ternary azeotrope very close in composition to that of the binary azeotrope between 1,1-dichloroethane and methanol. Table VI also contains the group of parameters A_{ij}, B_{ij}, C_{ij} for the T–x correlation (eq 10) which yield the smaller mean deviation between the calculated and observed values of T.

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Glossary

A_{ij}, B_{ij}, etc.	multicomponent adjustable parameters in eq 8
B_{ii}, B_{ij}	virial coefficients, eq 2
N	number of components
P	total pressure, mmHg
P_i^0	vapor pressure of pure component i, mmHg
T	boiling temperature of a mixture, K
T_i^0	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

Registry No. Methanol, 67-56-1; 1,1-dichloroethane, 75-34-3; propyl bromide, 106-94-5.

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Association Effects in the Methanol–1-Pentanol System

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New vapor–liquid equilibria for the title system have been determined at 760 mmHg. The methanol–1-pentanol system shows strong positive deviations from ideal behavior, and thermodynamic consistency can only be explained on the basis of thermal effects and that methanol associates in the vapor phase. The boiling points were well correlated with the composition of the liquid phase.

The only literature reference to the title system is that of Hill and Van Winkle (*1*) who reported data on the vapor–liquid in different methanol–alcohol binary systems.

Inspection of the activity coefficients reported by Hill and Van Winkle indicates that they are not thermodynamically consistent and also that there are substantial numerical errors in the conversion of weight composition to molar composition. The *Dechema Data Series* (*2*) are also in error since they report the original data in molar terms, without correcting the mistakes.

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