Vapor–Liquid Equilibria at 760 mmHg in the Ternary System Methanol–Acetonitrile–Propyl Bromide

Abraham Tamir* and Jaime Wisniak

Department of Chemical Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel 84105

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 methanol–acetonitrile–propyl bromide for which no isobaric data are available.

Experimental Section

Purity of Materials. Analytical grade methanol (99%+) was purchased from Frutarom, propyl bromide (99.0%) from Merck, and acetonitrile (99.5%+) from H.P.L.C. Bio-Lab. 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 an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm in diameter and was packed with Poropak Q. Injector and detector temperatures were 210 and 220 °C, respectively. Operating conditions of the column were programed between 125 and 140 °C and were changed at the rate of 2 °C/min. 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 ΔP = ±2 mmHg and Δt = ±0.02 °C.

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 equations (*3*)

$$\ln \gamma_i = \ln\frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^0)(P - P_i^0)}{RT} + \frac{P}{2RT}\sum_{j=1}^{N}\sum_{k=1}^{N} y_j y_k (2\delta_{ji} - \delta_{jk}) \quad (1)$$

where

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

Vapor pressure P_i^0 was calculated acording to Antoine's equation

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

where the constants are reported in Table III. The 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.

Table I. Physical Constants of Pure Components

index	compd	refractive index at 20 °C	bp(760 mmHg), °C	purity GLC(min)
1	methanol	1.3280[a]	64.68[a]	99.5
		1.3284[b]	64.70[b]	
2	acetonitrile	1.3410[a] (25 °C)	81.1	99.5
		1.3416[b] (25 °C)	81.3	
3	propyl bromide	1.4316[a]	70.55[a]	99.0
		1.4317[b]	70.80[b]	

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

The ternary data reported in Table II were found to be thermodynamically consistent by the McDermot–Ellis method (*5*). According to this test, two experimental points a and b are thermodynamically consistent if the following condition is fulfilled:

$$D < D_{max} \quad (4)$$

The local deviation D is given by

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

where N is the number of components. The maximum deviation can be derived (*6*) and reads

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

The errors in the measurements Δx, ΔP, and Δt were as previously indicated. The activity coefficients were correlated by the following equation:

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

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 (*7*, *8*).

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*):

$$T = \sum_{i=1}^{N} x_i T_i^0 + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + ...] \quad (8)$$

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Table II. Ternary Vapor–Liquid Equilibrium Data for Methanol (1)–Acetonitrile (2)–Propyl Bromide (3) at 760 mmHg

T, °C	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
54.55	0.583	0.025	0.392	0.520	0.019	0.461	1.392	1.845	2.022
55.04	0.238	0.035	0.727	0.463	0.030	0.507	2.984	2.037	1.174
55.09	0.714	0.020	0.266	0.558	0.020	0.422	1.188	2.388	2.686
55.36	0.438	0.170	0.392	0.418	0.117	0.465	1.448	1.613	1.971
55.45	0.559	0.138	0.303	0.541	0.097	0.362	1.450	1.655	1.995
55.56	0.577	0.138	0.285	0.487	0.108	0.405	1.263	1.829	2.355
55.82	0.469	0.196	0.335	0.462	0.128	0.410	1.460	1.510	2.007
55.84	0.347	0.291	0.362	0.369	0.185	0.446	1.586	1.461	2.008
55.85	0.706	0.102	0.192	0.553	0.086	0.361	1.152	1.959	3.101
56.00	0.535	0.232	0.233	0.503	0.152	0.345	1.378	1.509	2.420
56.15	0.719	0.122	0.159	0.553	0.107	0.340	1.116	2.016	3.491
56.17	0.276	0.235	0.489	0.361	0.160	0.479	1.924	1.546	1.578
56.28	0.199	0.224	0.577	0.338	0.159	0.503	2.492	1.604	1.398
56.32	0.148	0.179	0.673	0.328	0.138	0.534	3.249	1.738	1.270
56.32	0.401	0.305	0.294	0.390	0.190	0.420	1.418	1.409	2.294
56.35	0.282	0.241	0.477	0.363	0.161	0.476	1.878	1.507	1.598
56.45	0.159	0.159	0.682	0.314	0.134	0.552	2.882	1.890	1.289
56.56	0.299	0.294	0.407	0.433	0.175	0.392	2.082	1.228	1.538
56.56	0.758	0.090	0.152	0.602	0.075	0.323	1.129	1.894	3.434
56.64	0.387	0.322	0.291	0.392	0.186	0.422	1.456	1.292	2.304
56.75	0.470	0.283	0.247	0.437	0.223	0.340	1.325	1.760	2.184
56.82	0.208	0.259	0.533	0.361	0.185	0.454	2.481	1.585	1.343
56.88	0.545	0.258	0.197	0.485	0.202	0.313	1.257	1.746	2.518
56.95	0.362	0.327	0.311	0.421	0.200	0.379	1.845	1.355	1.919
57.14	0.704	0.080	0.216	0.628	0.070	0.302	1.235	1.952	2.220
57.43	0.204	0.398	0.398	0.316	0.245	0.439	2.165	1.334	1.701
57.55	0.098	0.148	0.754	0.287	0.133	0.580	4.083	1.936	1.180
57.70	0.337	0.352	0.311	0.395	0.221	0.384	1.608	1.353	1.894
57.95	0.157	0.188	0.655	0.350	0.155	0.495	3.037	1.756	1.147
57.98	0.317	0.401	0.282	0.368	0.244	0.388	1.577	1.297	2.088
58.43	0.353	0.428	0.219	0.431	0.239	0.330	1.618	1.175	2.260
58.83	0.365	0.433	0.202	0.427	0.266	0.307	1.524	1.274	2.249
58.97	0.517	0.389	0.094	0.485	0.337	0.178	1.210	1.795	2.799
59.00	0.316	0.408	0.276	0.372	0.274	0.354	1.529	1.381	1.882
59.15	0.371	0.459	0.170	0.422	0.281	0.297	1.462	1.255	2.558
59.19	0.420	0.420	0.160	0.449	0.258	0.293	1.369	1.260	2.682
59.60	0.212	0.458	0.330	0.301	0.307	0.392	1.808	1.346	1.704
59.65	0.746	0.200	0.054	0.667	0.162	0.171	1.109	1.659	4.639
59.77	0.070	0.141	0.789	0.230	0.149	0.621	4.183	2.103	1.120
59.80	0.189	0.463	0.348	0.305	0.310	0.385	2.037	1.335	1.577
60.07	0.917	0.039	0.044	0.797	0.035	0.168	1.055	1.831	5.583
60.41	0.403	0.488	0.109	0.440	0.315	0.245	1.328	1.268	3.161
60.48	0.608	0.346	0.046	0.620	0.268	0.112	1.224	1.536	3.457
60.54	0.352	0.533	0.115	0.396	0.376	0.228	1.365	1.377	2.770
60.61	0.455	0.464	0.081	0.485	0.309	0.206	1.282	1.303	3.562
60.70	0.743	0.194	0.063	0.641	0.167	0.192	1.025	1.696	4.303
60.97	0.764	0.192	0.044	0.680	0.180	0.140	1.044	1.835	4.467
61.02	0.558	0.377	0.065	0.555	0.275	0.170	1.171	1.413	3.631
61.09	0.922	0.039	0.039	0.800	0.045	0.155	1.009	2.272	5.619
61.10	0.438	0.484	0.078	0.507	0.318	0.175	1.362	1.265	3.097
61.16	0.404	0.498	0.098	0.450	0.330	0.220	1.312	1.269	3.082
61.20	0.343	0.548	0.109	0.425	0.335	0.240	1.459	1.168	3.015
61.65	0.555	0.405	0.040	0.596	0.308	0.096	1.229	1.445	3.274
62.10	0.578	0.390	0.032	0.611	0.308	0.081	1.186	1.479	3.406
62.20	0.362	0.541	0.097	0.478	0.328	0.194	1.486	1.122	2.659
62.72	0.209	0.618	0.173	0.318	0.393	0.289	1.694	1.148	2.168
62.75	0.912	0.063	0.025	0.831	0.074	0.095	0.988	2.189	5.102
63.00	0.856	0.124	0.020	0.813	0.118	0.069	1.020	1.755	4.586
63.47	0.043	0.425	0.532	0.124	0.326	0.550	3.168	1.343	1.303
63.78	0.270	0.670	0.060	0.337	0.534	0.129	1.327	1.390	2.699
64.05	0.029	0.389	0.582	0.118	0.330	0.552	4.365	1.456	1.174
64.08	0.348	0.611	0.041	0.389	0.542	0.069	1.170	1.534	2.097
64.31	0.088	0.492	0.420	0.144	0.373	0.483	1.732	1.291	1.412
64.46	0.247	0.693	0.060	0.356	0.529	0.115	1.488	1.302	2.356
64.60	0.394	0.580	0.026	0.519	0.401	0.080	1.339	1.182	3.798
64.68	0.304	0.636	0.060	0.365	0.535	0.100	1.228	1.424	2.036
65.01	0.019	0.289	0.695	0.069	0.296	0.636	3.761	1.720	1.097
65.28	0.184	0.700	0.116	0.338	0.451	0.211	1.837	1.068	2.178
65.42	0.030	0.069	0.901	0.131	0.100	0.769	4.420	2.375	1.012
65.96	0.181	0.743	0.076	0.324	0.504	0.172	1.742	1.098	2.652
66.00	0.020	0.049	0.931	0.110	0.075	0.815	5.447	2.459	1.020
66.22	0.221	0.723	0.056	0.284	0.621	0.095	1.241	1.378	1.968
66.25	0.150	0.597	0.253	0.234	0.418	0.348	1.511	1.120	1.593
66.50	0.200	0.753	0.047	0.346	0.529	0.125	1.645	1.118	3.067
66.58	0.273	0.667	0.060	0.395	0.454	0.151	1.367	1.082	2.901
67.50	0.048	0.667	0.285	0.103	0.480	0.417	1.998	1.102	1.626
67.51	0.034	0.659	0.307	0.078	0.473	0.449	2.141	1.098	1.625

Table II (Continued)

T, °C	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
67.96	0.276	0.697	0.027	0.439	0.481	0.080	1.417	1.051	3.278
68.00	0.230	0.737	0.033	0.378	0.548	0.074	1.467	1.128	2.471
71.52	0.049	0.824	0.127	0.118	0.598	0.284	1.906	0.976	2.201
72.55	0.171	0.816	0.013	0.344	0.629	0.027	1.504	1.008	1.992
73.35	0.101	0.865	0.034	0.229	0.661	0.110	1.656	0.971	3.021
74.28	0.072	0.865	0.063	0.166	0.668	0.166	1.632	0.952	2.391
74.70	0.135	0.855	0.010	0.300	0.643	0.057	1.534	0.918	5.125

Table III. Vapor Pressure Constants[a]

compound	α_i	β_i	δ_i
methanol	7.89750	1474.08	229.13
acetonitrile	7.07352	1279.2	224.00
propyl bromide	6.91065	1194.889	225.51

[a] Reference *10*.

Table IV. Redlich-Kister Constants for Eq 7

system	B_{ij}	C_{ij}	D_{ij}	C_1
methanol (1)–acetonitrile (2)	0.9654	−0.1605	−0.07595	
methanol (1)–propyl bromide (3)	1.7917	−0.6799	−0.1024	
acetonitrile (2)–propyl bromide (3)	1.0708	−0.06928	−0.09350	
methanol (1)–acetonitrile (2)–propyl bromide (3)				−1.1757

Table V. Parameters of T–x Correlation (Eq 8, N = 3) for Methanol (1)–Acetonitrile (2)–Propyl Bromide (3) at 760 mmHg[a]

ij	A_{ij}	B_{ij}	C_{ij}	mean D,[b] %	rmsd[c]
12	−40.38	16.82			
13	−60.51	16.25		1.79	0.196
23	−41.70	8.96			
12	−38.45	10.50	2.18		
13	−57.48	16.25	−43.07	1.4	0.171
23	−36.00	−4.79	−61.89		

[a] T_1^0 = 64.68 °C; T_2^0 = 81.1 °C; T_3^0 = 70.55 °C. [b] Mean $D = (1/m)\sum D_i$. [c] $D = |(T_{obsd} - T_{calcd})/T_{obsd}|$.

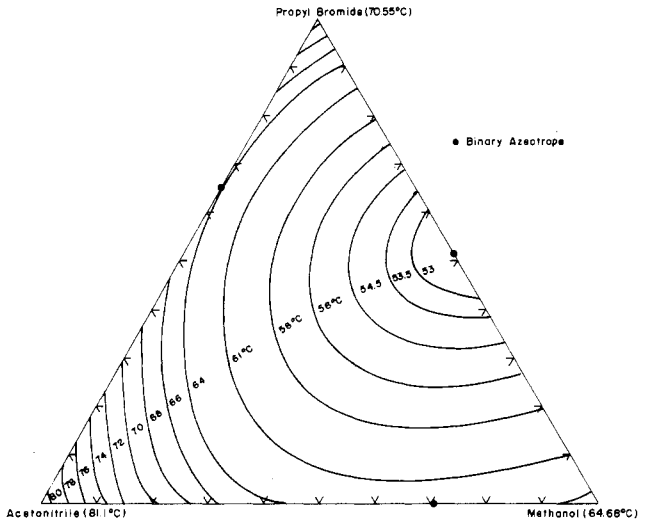

Figure 1. Isothermals for methanol–acetonitrile–propyl bromide at 760 mmHg (with disc adjustable parameters).

This equation is useful for obtaining isothermals and for exploring the azeotropic behavior and distillation paths of ternary mixtures as explained in ref *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 8 for N = 3.

As observed, the ternary system does not exhibit azeotropic behavior whereas all binary systems have azeotropes. Table V contains also the group of parameters A_{ij}, B_{ij}, and C_{ij} for the T–x correlation (eq 8) which yield a 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
T_i^0	boiling temperature of pure component i
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; acetonitrile, 75-05-8; propyl bromide, 106-94-5.

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