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Liquid-Vapor Equilibria at 760 mmHg in the Systems Methanol-Acetonitrile and Acetonitrile-Propyl Bromide

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Vapor-liquid equilibrium for the title binary systems has been determined at 760 mmHg. The systems deviate from ideal behavior. The activity coefficients and the boiling points were well correlated by appropriate equations.

The present work was undertaken to measure VLE data for the binary systems methanol-acetonitrile and acetonitrile-propyl bromide for which no isobaric VLE data are available. Such data may be used to test the possibility of predicting the behavior of a ternary mixture based on the above binaries.

Experimental Section

Purity of Materials. Analytical grade methanol (99%+) was purchased from BDH, propyl bromide (99.6%+) was supplied by Bromine Compounds Ltd., Beer-Sheva, and acetonitrile (99.5%+) was purchased from H.P.L.C. 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-Boublik recirculation still (*1*) was used in the equilibrium determinations. The experimental features have been described previously (*2*). All analyses were carried out by gas chromatography on a Packard-Becker 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 Chromosorb 101. For acetonitrile-propyl bromide the column operated at 160 °C and the detector at 270 °C, and the injector temperature was 190 °C. For methanol-acetonitrile the column operated at 125 °C and the detector at 255 °C, and the injector temperature was 250 °C. In both cases, the detector operated at 150 mA. Calibration analyses were carried out to convert the peak area ratio to the weight composition of the mixture. Concentration measurements were generally accurate to ±0.5%. 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 are presented in Tables II and III. Activity coefficients were calculated from the equation

$$\ln \gamma_i = \ln (P y_i / P_i^0 x_i) + (\beta_{ii} - V_i^L)(P - P_i^0)/RT + P(1 - y_i)^2 \delta / RT \tag{1}$$

where

$$\delta = 2B_{ij} - B_{ii} - B_{jj} \tag{2}$$

Vapor pressures at P_i^0 were calculated according to Antoine's equation

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

where the constants appear in Table IV (*3*). The virial coefficients B_{11} and B_{22} and the mixed coefficient B_{12} were estimated by the method of Tsonopoulos (*4*, *5*), using the molecular parameters suggested by the author.

Table I. Physical Properties of Pure Components

compd	refractive index	normal bp, °C
acetonitrile	1.3410[a] (25 °C)	97.40[a]
	1.3416[b] (25 °C)	97.35[b]
methanol	1.3280[a] (20 °C)	64.68[a]
	1.3284[b] (20 °C)	64.70[b]
propyl bromide	1.4300[a] (25 °C)	70.55[a]
	1.4302[b] (25 °C)	70.80[b]

[a] This work. [b] Reference *3*.

Table II. Experimental Vapor-Liquid Equilibria Data for Methanol-Acetonitrile at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
79.20	0.025	0.095	2.478	0.978
77.95	0.040	0.135	2.286	0.983
76.77	0.055	0.175	2.233	0.986
75.12	0.097	0.265	2.002	0.967
73.12	0.140	0.330	1.839	0.984
72.07	0.170	0.375	1.776	0.984
70.96	0.200	0.420	1.749	0.983
68.85	0.247	0.455	1.653	1.048
68.39	0.289	0.505	1.583	1.030
66.00	0.415	0.595	1.405	1.118
65.35	0.470	0.625	1.330	1.173
64.75	0.545	0.655	1.226	1.289
64.34	0.630	0.715	1.168	1.346
64.03	0.690	0.745	1.122	1.463
63.80	0.745	0.780	1.094	1.561
63.77	0.825	0.825	1.043	1.836
63.76	0.860	0.860	1.041	1.857
63.87	0.900	0.880	1.012	2.235
64.05	0.930	0.915	1.010	2.275
64.18	0.950	0.930	1.000	2.626
64.40	0.970	0.955	0.996	2.817

Table III. Experimental Vapor-Liquid Equilibria Data for Acetonitrile-Propyl Bromide at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
67.31	0.170	0.230	2.109	1.040
67.18	0.190	0.250	2.060	1.041
66.98	0.205	0.255	1.961	1.061
66.68	0.255	0.290	1.810	1.089
66.74	0.280	0.310	1.759	1.094
66.64	0.355	0.350	1.571	1.154
66.82	0.400	0.370	1.465	1.195
66.77	0.425	0.385	1.437	1.220
67.17	0.460	0.405	1.378	1.241
66.90	0.460	0.405	1.390	1.251
67.20	0.525	0.435	1.295	1.338
67.18	0.540	0.435	1.260	1.383
69.19	0.695	0.535	1.125	1.613
69.39	0.710	0.540	1.104	1.668
69.03	0.715	0.545	1.120	1.698
69.60	0.725	0.555	1.104	1.691
70.00	0.735	0.555	1.075	1.734
70.17	0.760	0.575	1.071	1.819
70.85	0.785	0.595	1.049	1.895
70.99	0.790	0.605	1.055	1.885
72.54	0.825	0.650	1.032	1.913
73.00	0.855	0.670	1.011	2.147
73.73	0.875	0.715	1.029	2.105
77.19	0.935	0.820	1.000	2.309
78.74	0.950	0.885	1.000	1.835

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Table IV. Vapor-Pressure Constants (*3*)

compd	α_1	β_1	δ_1
acetonitrile	7.073 52	1279.2	224.0
methanol	7.897 50	1474.0	229.13
propyl bromide	6.910 65	1194.889	225.51

Table V. Redlich-Kister and Wilson Parameters

system	B_{ij}	C_{ij}	D_{ij}	Λ_{12}	Λ_{21}
methanol–acetonitrile	0.8466	0.848×10^{-3}	0.241×10^{-4}	0.8368	0.4322
acetonitrile–propyl bromide	1.082	0.105×10^{-2}	0.282×10^{-4}	0.5811	0.4970

The activity coefficients reported Tables II and III show that the systems present a significant deviation from ideal solution behavior. These coefficients, which were found thermodynamically consistent according to the Herington criteria (*6*), were well correlated by the following Redlich–Kister equation (*7*)

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

$$\ln \gamma_j = (B_{ij} - 3C_{ij} + 5D_{ij})x_i^2 + 4(C_{ij} - 4D_{ij})x_i^3 + 12D_{ij}x_i^4 \qquad (5)$$

and a Wilson (*8*) correlation

$$\ln \gamma_1 = -\ln (x_1 + x_2\Lambda_{12}) + x_2\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right] \qquad (6)$$

$$\ln \gamma_2 = -\ln (x_2 + x_1\Lambda_{21}) - x_1\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right] \qquad (7)$$

The corresponding coefficients appear in Table V. For the system methanol–acetonitrile it was also possible to predict the activity coefficients by means of the UNIFAC method. It was found that the vapor-phase composition could be predicted with a mean deviation from experimental values of 1.9%, where the maximum deviation was 3.4%.

Boiling points of the binary were correlated by the equations suggested by Wisniak and Tamir (*9*) and Tamir (*10*).

$$T = x_1T_1^0 + x_2T_2^0 + x_1x_2[C_0 + C_1(x_1 - x_2) + C_2(x_1 - x_2)^2 + ...] \qquad (8)$$

An optimization routine yielded the following values for the constants $C_0 = -36.36$, $C_1 = -11.29$, and $C_2 = -20.24$, with an rmsd of 0.216 for acetonitrile–propyl bromide, and $C_0 = -30.95$, $C_1 = -15.05$, and $C_2 = -12.84$ with an rmsd of 0.210 for methanol–acetonitrile. With the above correlation, boiling points can be predicted within 0.2% deviation from experimental values.

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Glossary

α, β, A, B, C	constants
B_{ii}, B_{ij}	virial coefficients
n	number of experimental points
P	overall pressure, mmHg
P_i^0	vapor pressure of pure component i, mmHg
R	gas constant
rmsd	root-mean-square deviation $\sum(T_{\text{exptl}} - T_{\text{calcd}})^2/n$
t, T	temperature, °C, K
v_i^l	molar volume, pure liquid i, cm^3/mol
x_i, y_i	mole fraction composition of component i in the liquid and vapor phases
γ_i	activity coefficients
Λ_{12}, Λ_{21}	Wilson constants

Subscripts

exptl	experimental
calcd	calculated
i	component i

Registry No. MeCN, 75-05-8; PrBr, 106-94-5; MeOH, 67-56-1.

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