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Vapor–Liquid Equilibria at 760 mmHg in the System Methanol–2-Propanol–Propyl Bromide and Its Binaries

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Vapor–liquid equilibrium at atmospheric pressure has been determined for the title ternary system and the binaries of propyl bromide with each alcohol. All systems present strong positive deviations from ideal behavior. The data were correlated by various equations, and the appropriate parameters are reported.

The present work was undertaken as part of a project devoted to the determination of UNIFAC interaction parameters for bromine derivatives.

There are only two publications in the literature on systems related to the ones reported here. Garber and Mironenko (*1*) studied the properties of azeotropes formed by propyl chloride with methanol. Lowering the pressure from 762 to 200 mmHg changed the boiling temperature of the azeotrope from 39.0 to 9.8 °C and its mole fraction composition from 0.743 to 0.813 (chloride). The system presented strong positive deviations from ideal behavior, and the data reported were found to be thermodynamically consistent according to the Herington (*2*) criterion but not consistent according to Redlich-Kister (*3*). Van Diemen et al. (*4*) measured the excess enthalpies, excess Gibbs function, and excess volumes at 298.1 K for mixtures of 2-propanol with 2-bromopropane. They also reported vapor–liquid equilibria data at 396 and 709 torr. Their results indicated that the system presented positive deviations from ideal behavior and that a minimum boiling point azeotrope was present at a mole fraction of 2-bromopropane larger than 0.8. They interpreted their results on the excess properties as an indication that the interaction of an –OH group with a –CHBr group was of less importance than the interaction with a ketone group; alcohol associated complexes remained intact to a greater extent with 2-bromopropane than in mixtures with acetone.

Both publications report that compositions were determined by refractive index measurement.

The data available on the system methanol-2-propanol have been thoroughly analyzed by Gmehling and Onken (*5*). On the basis of their analysis of the thermodynamic consistency of the different sets reported in the literature we have selected the data of Kohoutova et al. (*6*) to complete the binary picture.

Experimental Section

Purity of Materials. Analytical grade methanol and 2-propanol (99%+) were purchased from BDH. 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.

Apparatus and Procedure. An all-glass modified Dvorak and Boublikova recirculation still (*8*) was used in the equilibrium determination. The experimental features have been described in previous publications (*9*). 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 Chromosorb 101 on 80–100 mesh Supelcoport, and was operated isothermally at 150 °C. Injector and detector temperatures were 220 and 200 °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 Compounds

index	compd	refractive index at 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	2-propanol	1.3758[a] (25 °C) 1.3752[b] (25 °C)	82.30[a] 82.50[b]	99.5
3	propyl bromide	1.4316[a] 1.4317[b]	70.55[a] 70.80[b]	99.4

[a] Measured. [b] Reference 7.

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

temp, °C	x_1	y_1	γ_1	γ_3
81.70	0.045	0.074	0.897	0.991
80.30	0.120	0.191	0.910	0.992
79.40	0.160	0.264	0.924	0.989
76.10	0.343	0.503	0.969	0.963
73.50	0.489	0.653	0.968	0.961
72.90	0.525	0.685	0.967	0.961
71.00	0.630	0.784	0.973	0.937
70.50	0.668	0.807	0.975	0.931
69.40	0.737	0.855	0.975	0.925
69.00	0.765	0.871	0.971	0.0936
68.30	0.807	0.898	0.973	0.928
67.20	0.879	0.939	0.974	0.924
66.70	0.905	0.955	0.980	0.886
66.30	0.927	0.968	0.984	0.833

Results

The temperature–concentration measurements at 760 mmHg for the binaries and ternary systems are reported in Tables II–IV and Figures 1 and 2. The activity coefficients were calculated from the following equations (*10*):

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

where

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

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

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

where the constants are reported in Table V. The virial coefficients B_{ii} and the mixed coefficient B_{ij} were calculated by

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Table III. Experimental Vapor–Liquid Equilibria Data for 2-Propanol (2)–Propyl Bromide (3) at 760 mmHg

temp, °C	x_2	y_2	γ_2	γ_3
64.00	0.020	0.180	9.165	1.040
56.73	0.090	0.365	5.487	1.099
56.10	0.135	0.400	4.113	1.116
55.70	0.195	0.440	3.185	1.134
54.85	0.260	0.460	2.584	1.224
54.80	0.285	0.465	2.388	1.257
54.67	0.350	0.470	1.976	1.376
54.65	0.365	0.480	1.937	1.382
54.58	0.405	0.480	1.751	1.479
54.58	0.485	0.480	1.462	1.708
54.60	0.515	0.495	1.419	1.760
54.47	0.550	0.520	1.404	1.810
54.59	0.575	0.510	1.310	1.949
54.62	0.590	0.510	1.275	2.018
54.66	0.610	0.525	1.268	2.053
54.63	0.615	0.520	1.247	2.104
54.70	0.630	0.530	1.238	2.139
55.34	0.735	0.757	1.123	2.640
66.63	0.780	0.590	1.072	3.037
57.00	0.880	0.685	1.047	4.077
58.15	0.915	0.735	1.033	4.656
60.31	0.950	0.820	1.021	4.998
61.72	0.965	0.860	0.998	5.301
62.40	0.978	0.902	1.007	5.771
62.96	0.985	0.930	1.009	5.934
63.60	0.990	0.950	1.001	6.227

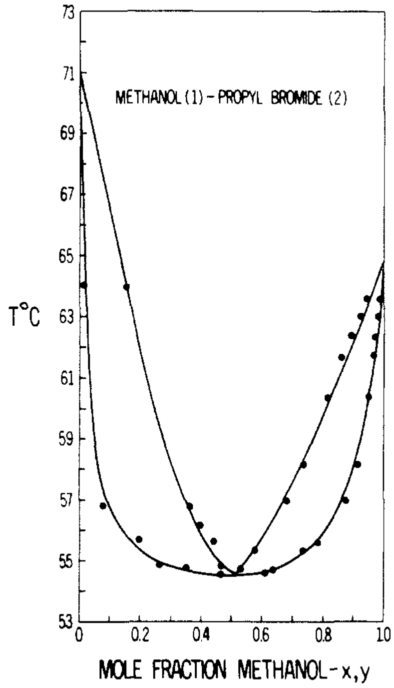

Figure 1. Boiling point curve for methanol (1)–propyl bromide (3) at 760 mmHg.

the method of Tsonopoulos (*11*), using the molecular parameters suggested by the same author. For the binary systems the last two terms in eq 1 accounted for less than 5% of the activity coefficients; their influence was important only at dilute concentrations.

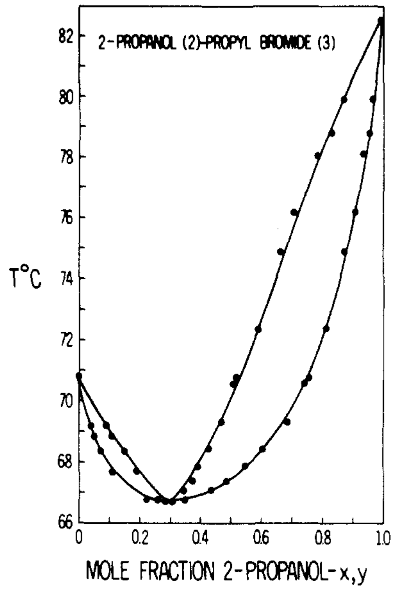

Figure 2. Boiling point curve for 2-propanol (2)–propyl bromide (3) at 760 mmHg.

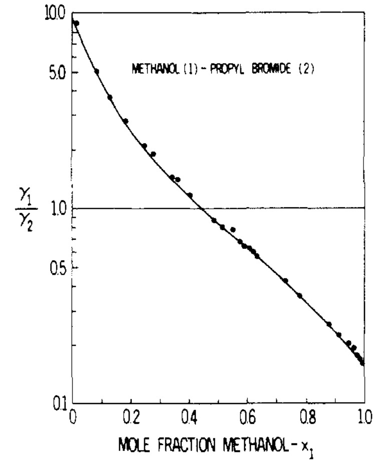

Figure 3. Activity coefficients for methanol (1)–propyl bromide (3).

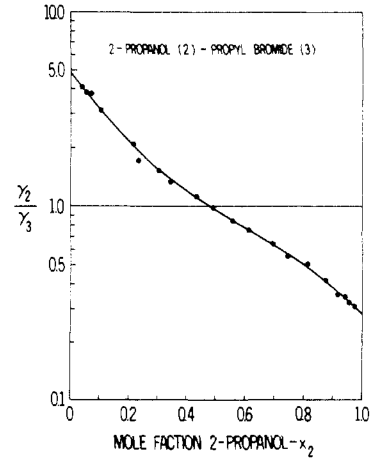

Figure 4. Activity coefficients for 2-propanol (2)–propyl bromide (3).

The activity coefficients calculated according to eq 1 are reported in Tables II–IV and Figures 3 and 4, and show that the binaries exhibit very strong positive deviations from ideal behavior and that both have a minimum boiling azeotrope. The azeotrope of the binary methanol–propyl bromide boils at 54.6 °C and contains 51.5% mole alcohol while that of 2-propanol–propyl bromide boils at 66.6 °C and cntains 29% mole alcohol. The positive deviation from ideal behavior and presence of a minimum boiling point azeotrope is in accordance with that of the other similar alkyl halide–alcohols systems reported above (*1*, *4*).

The binary data appearing in Tables II and III were tested for thermodynamic consistency by the area and slope test as well as the Herington criteria (*2*). The consistency test parameters appear in Table VI and from it, it is concluded that the data are thermodynamically consistent.

The ternary data reported in Table V were found to be thermodynamically consistent by the McDermot–Ellis method (*12*). According to this test, two experimental points a and b are 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. The maximum deviation can be derived (*13*) and reads

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

The errors in the measurements Δx, ΔP, and Δt were as previously indicated. The activity coefficients reported in Tables II and III were correlated with the Wilson equation (*14*):

$$\ln \gamma_1 = -\ln (x_1 + x_2\Lambda_{12}) + x_2\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right] \tag{7}$$

$$\ln \gamma_2 = -\ln (x_2 + x_1\Lambda_{21}) - x_1\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right] \tag{8}$$

The values of the parameters Λ_{ij} and the quality of the fit appear in Table VII.

The activity coefficients for the binary data were also correlated by the following Redlich–Kister expansion (*3*):

$$\ln \gamma_i = (B_{ij} + 3C_{ij} + 5D_{ij})x_j^2 - 4(C_{ij} + 4D_{ij})x_j^3 + 12D_{ij}x_j^4 \tag{9}$$

$$\ln \gamma_j = (B_{ij} - 3C_{ij} + 5D_{ij})x_i^2 + 4(C_{ij} - 4D_{ij})x_i^3 + 12D_{ij}X_i^4 \tag{10}$$

The corresponding coefficients appear in Table VIII. The ternary data were correlated by means of eq 11 where B_{ij}, C_{ij}, and D_{ij}

$$\begin{aligned}\ln \gamma_1 = {} & x_2x_3[(B_{12} + B_{13} - B_{23}) + C_{12}(2x_1 - x_2) + C_{13}(2x_1 - x_3) + 2C_{23}(x_3 - x_2) + D_{12}(x_1 - x_2)(3x_1 - x_2) + \\ & D_{13}(x_1 - x_3)(3x_1 - x_2) - 3D_{23}(x_3 - x_2)^2 + C_1(1 - 2x_1)] + x_2^2[B_{12} + C_{12}(3x_1 - x_2) + D_{12}(x_1 - x_2)(5x_1 - x_2)] + \\ & x_3^2[B_{13} + C_{13}(3x_1 - x_3) + D_{13}(x_1 - x_3)(5x_1 - x_3)]\end{aligned} \tag{11}$$

are the binary constants and C_1 is a ternary constant reported in Table VIII. The equations for two other activity coefficients were obtained by cyclic rotation of the indices.

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" (*15*):

$$T = \sum_{i=1}^{N} x_iT_i^0 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_ix_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + ...] \tag{12}$$

This equation is useful for obtaining isothermals and for exploring the azeotropic behavior and distillation paths of ternary mixtures. For binary mixtures ($N = 2$) the second summation on the right-hand side of eq 12 is exactly that suggested by Redlich–Kister (*3*). For multicomponent mixtures, the binary form of the Redlich and Kister equation was kept, but the significance of the equation is different in that coefficients A_{ij}, B_{ij}, etc., are not binary constants, namely, they are not determined from the binary data. These coefficients are multicomponent parameters which are determined directly from the multicomponent data. An equation for correlating boiling temperatures of multicomponent mixtures based on the complete data (binary, ternary, etc.) has been reported (*16*). For a ternary mixture ($N = 3$), it reads

$$T = \sum_{i=1}^{3} x_iT_i^0 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + ...] + x_1x_2x_3[\mathrm{A} + \mathrm{B}(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + B'(x_1 - x_2)^2 + C'(x_1 - x_3)^2 + D'(x_2 - x_3)^2 + ...] \tag{13}$$

Here the indexed parameters are binary constants while A, B, B′, etc. are ternary constants.

When handling multicomponent data it is possible to perform direct correlation of the available information without knowledge of lower order data (i.e., binary data in the case of ternary mixtures or binary and ternary data in the case of quaternary mixtures, etc.). It has been shown before (*15*) that this direct correlation can be more efficient for the following arguments: (*1*) fewer parameters are needed in the correlated equations for the same degree of the fit of the data, and (*2*) for an identical number of adjustable parameters, the goodness of the fit is better. The above conclusions can be demonstrated here since the binary and ternary data are available for the systems dealt here. The following procedure was adopted for determining the parameters in eq 12 by direct correlation of the multicomponent data.

First, parameters A_{12}, A_{13}, ... A_{1N}, A_{23}, A_{24}, ... A_{2N}, were determined and then A_{12} and B_{12}, A_{13} and B_{13}, A_{1N} and B_{1N}, A_{23} and B_{23}, ... A_{2N} and B_{2N}, etc. The optimal set of parameters was the one for which the error variance, σ^2, was minimal:

$$\sigma^2 = \frac{\sum_{i=1}^{m} (T_{\mathrm{obsd}} - T_{\mathrm{calcd}})_i^2}{m - c - 1} \tag{14}$$

The pertinent results, summarized in Table IX, are as follows: three sets of parameters are reported, (A_{ij} to B_{ij}, A_{ij} to C_{ij} and A_{ij} to E_{ij}) corresponding to eq 12 ($N = 3$) for the ternary system under consideration. The parameters were obtained by direct correlation. For each set, deviations from experimental data as well as the magnitude of σ^2 are given, as a measure of goodness of the fit. The parameters for the binary systems as well as the ternary constants corresponding to eq 13 are not given, but the appropriate parameters indicating the goodness of fit are reported in Table IX. The following conclusions may be drawn. (1) Direct correlation with nine parameters gives a value of $\sigma^2 < 2.5$. On the other hand, a correlation based on binary and ternary data requires 19 parameters ($c' + c$) in order to obtain the minimal value of $\sigma^2 = 3.9$. (2) To obtain the minimal value of $\sigma^2 = 2.1$ by direct correlation, 15 parameters are needed, which is still less than the above 19 parameters.

The parameters obtained by direct correlation (eq 12) were used to explore the azeotropic behavior of the ternary system as explained in ref 15 (Figure 5 and 6). Analysis of the isotherms indicates the possible presence of a saddle-point type azeotrope and that each of the binary systems has two azeotropes, an unrealistic prediction. The existence of the ternary

Table IV. Ternary Vapor–Liquid Equilibrium Data for Methanol (1)–2-Propanol (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
55.2	0.371	0.040	0.589	0.422	0.020	0.558	1.717	1.691	1.586
55.3	0.406	0.046	0.548	0.442	0.020	0.538	1.637	1.465	1.640
55.5	0.535	0.061	0.404	0.467	0.020	0.513	1.301	1.095	2.111
55.6	0.540	0.060	0.400	0.497	0.021	0.482	1.360	1.158	1.994
56.6	0.571	0.105	0.324	0.470	0.030	0.500	1.165	0.899	2.464
56.9	0.684	0.080	0.236	0.540	0.025	0.435	1.104	0.972	2.928
57.1	0.583	0.126	0.291	0.482	0.036	0.482	1.144	0.877	2.602
57.2	0.289	0.093	0.618	0.350	0.036	0.614	1.687	1.186	1.550
57.3	0.648	0.111	0.241	0.518	0.035	0.447	1.099	0.962	2.905
57.4	0.523	0.166	0.311	0.452	0.056	0.492	1.183	1.022	2.461
57.4	0.194	0.041	0.765	0.369	0.030	0.601	2.610	2.218	1.218
57.7	0.726	0.090	0.184	0.579	0.030	0.391	1.076	0.997	3.292
57.8	0.543	0.176	0.281	0.465	0.055	0.480	1.153	0.930	2.627
57.8	0.128	0.036	0.836	0.348	0.030	0.622	3.675	2.482	1.138
57.9	0.790	0.060	0.150	0.616	0.020	0.364	1.043	0.988	3.739
58.2	0.580	0.180	0.240	0.495	0.060	0.445	1.129	0.973	2.816
58.8	0.650	0.172	0.178	0.553	0.056	0.391	1.095	0.923	3.278
58.8	0.351	0.199	0.450	0.523	0.061	0.416	1.919	0.869	1.378
58.9	0.555	0.220	0.225	0.487	0.066	0.447	1.125	0.845	2.944
58.9	0.698	0.129	0.173	0.571	0.045	0.384	1.047	0.982	3.298
59.0	0.650	0.182	0.168	0.551	0.056	0.393	1.080	0.862	3.462
59.1	0.072	0.020	0.908	0.282	0.030	0.688	5.013	4.191	1.107
59.3	0.630	0.207	0.163	0.579	0.066	0.355	1.156	0.881	3.197
59.4	0.418	0.211	0.371	0.413	0.092	0.495	1.244	1.202	1.944
59.6	0.814	0.070	0.116	0.596	0.066	0.338	0.908	2.566	4.236
59.6	0.107	0.107	0.786	0.268	0.072	0.660	3.138	1.836	1.208
59.8	0.261	0.191	0.548	0.309	0.103	0.588	1.468	1.457	1.536
59.9	0.326	0.247	0.427	0.372	0.097	0.531	1.409	1.058	1.780
60.0	0.492	0.271	0.237	0.437	0.096	0.467	1.088	0.946	2.812
60.1	0.136	0.120	0.744	0.289	0.082	0.629	2.606	1.821	1.198
60.2	0.368	0.285	0.347	0.378	0.102	0.520	1.249	0.948	2.121
60.5	0.836	0.084	0.080	0.712	0.030	0.258	1.016	0.932	4.571
60.8	0.405	0.313	0.282	0.379	0.123	0.498	1.111	1.013	2.455
60.9	0.920	0.035	0.045	0.772	0.016	0.212	0.982	1.168	6.594
61.1	0.074	0.074	0.852	0.282	0.074	0.644	4.486	2.544	1.037
61.3	0.655	0.228	0.117	0.618	0.080	0.302	1.091	0.882	3.557
61.6	0.411	0.340	0.249	0.410	0.138	0.452	1.144	1.007	2.461
61.7	0.047	0.052	0.901	0.227	0.066	0.707	5.553	3.139	1.053
61.8	0.755	0.176	0.069	0.672	0.061	0.267	1.007	0.851	5.255
61.8	0.675	0.223	0.102	0.568	0.082	0.350	0.952	0.901	4.635
62.3	0.621	0.277	0.102	0.576	0.106	0.318	1.027	0.915	4.144
63.0	0.162	0.335	0.503	0.223	0.176	0.601	1.493	1.218	1.538
63.2	0.198	0.346	0.456	0.231	0.172	0.597	1.259	1.146	1.679
63.2	0.130	0.290	0.580	0.190	0.165	0.645	1.579	1.312	1.425
63.2	0.215	0.381	0.404	0.465	0.484	0.051	2.303	2.915	0.164
63.3	0.691	0.246	0.063	0.670	0.115	0.215	1.030	1.069	4.416
63.4	0.604	0.304	0.092	0.578	0.126	0.296	1.015	0.944	4.138
63.4	0.384	0.409	0.207	0.276	0.175	0.449	1.040	0.973	2.770
63.5	0.556	0.338	0.106	0.580	0.125	0.295	1.099	0.837	3.562
63.5	0.243	0.411	0.346	0.259	0.190	0.551	1.132	1.048	2.021
63.5	0.209	0.406	0.385	0.246	0.193	0.561	1.252	1.078	1.850
63.6	0.465	0.386	0.149	0.446	0.164	0.390	1.008	0.955	3.323
63.8	0.752	0.204	0.044	0.740	0.085	0.175	1.022	0.929	5.069
64.1	0.800	0.171	0.029	0.791	0.090	0.119	1.015	1.160	5.198
64.3	0.857	0.123	0.020	0.835	0.065	0.100	0.991	1.153	6.297
64.5	0.292	0.464	0.244	0.287	0.218	0.495	1.000	1.015	2.495
65.4	0.247	0.506	0.247	0.277	0.244	0.479	1.099	1.000	2.319
65.6	0.347	0.487	0.166	0.354	0.234	0.412	0.989	0.986	2.953
65.6	0.311	0.500	0.189	0.305	0.253	0.442	0.951	1.037	2.778
65.8	0.558	0.381	0.061	0.460	0.151	0.389	0.793	0.807	7.562
65.8	0.623	0.330	0.047	0.642	0.165	0.193	0.987	1.017	4.898
66.3	0.082	0.512	0.406	0.108	0.290	0.602	1.252	1.131	1.720
66.3	0.432	0.466	0.102	0.464	0.235	0.301	1.010	1.001	3.446
66.8	0.512	0.426	0.062	0.540	0.230	0.230	0.971	1.048	4.277
66.9	0.442	0.476	0.082	0.490	0.252	0.258	1.019	1.025	3.616
67.4	0.640	0.336	0.024	0.701	0.181	0.118	0.986	1.021	5.599
67.7	0.069	0.590	0.341	0.081	0.349	0.570	1.055	1.108	1.857
67.9	0.361	0.546	0.093	0.410	0.282	0.308	1.004	0.955	3.680
68.2	0.368	0.567	0.065	0.354	0.381	0.265	0.840	1.226	4.487
70.0	0.353	0.555	0.092	0.447	0.327	0.226	1.029	0.991	2.560
70.2	0.123	0.706	0.171	0.147	0.425	0.428	0.968	1.005	2.576
70.6	0.357	0.586	0.057	0.414	0.369	0.217	0.922	1.033	3.900
71.6	0.135	0.741	0.124	0.162	0.486	0.352	0.921	1.031	2.807
72.0	0.272	0.665	0.063	0.325	0.443	0.232	0.898	1.026	3.604
73.1	0.307	0.656	0.037	0.396	0.446	0.158	0.930	0.999	4.055
73.2	0.160	0.765	0.075	0.195	0.540	0.265	0.875	1.030	3.325
73.6	0.391	0.586	0.023	0.431	0.456	0.113	0.779	1.119	4.602

Table IV (Continued)

T, °C	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
74.4	0.227	0.729	0.044	0.276	0.551	0.173	0.834	1.049	3.582
76.3	0.095	0.860	0.045	0.133	0.691	0.176	0.896	1.029	3.365
77.2	0.150	0.825	0.025	0.212	0.677	0.111	0.873	1.011	3.725

Table V. Vapor Pressure Constants (7)

compd	α_i	β_i	δ_i
methanol	7.897 50	1474.08	229.13
2-propanol	8.117 78	1580.92	219.61
propyl bromide	6.910 65	1194.889	225.51

Table VI. Consistency according to Herrington

system	D	τ	J	$\|D - J\|$[a]
methanol (1)–propyl bromide (3)	2.33	15.6	6.9	4.6
2-propanol (2)–propyl bromide (3)	6.02	16.4	7.51	1.5

[a] Data are consistent if $|D - J| < 10$.

Table VII. Wilson Parameters for Binary Systems

binary system	Λ_{ij}	Λ_{ji}	% diff[a]
methanol (1)–propyl bromide (3)	0.1538	0.3593	2
2-propanol (2)–propyl bromide (3)	0.2375	0.8956	4.3

[a] $(\sum|y_i - y_{i\,\mathrm{calcd}}|/n)\ 100$.

azeotrope was explored experimentally; however, no azeotrope was detected. Figure 6 reports the isothermals obtained on the basis of the six parameters reported in Table IX. In this case the predicted behavior agrees with the experimental one, namely, that two binary azeotropes exist and that there is no ternary azeotrope. The abnormal behavior in Figure 5 can be explained by the well-known fact (*15*) that an increase in the number of adjustable parameters generates unwarranted inflection points due to mathematical reasons that do not necessarily reflect physical reasons.

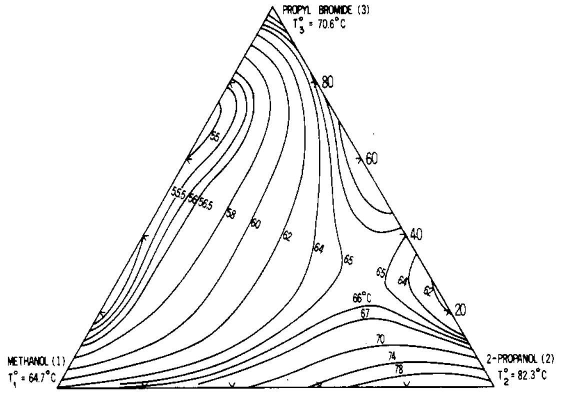

Figure 5. Isothermals for methanol (1)–2-propanol (2)–propyl bromide (3) (with nine constants in eq 12).

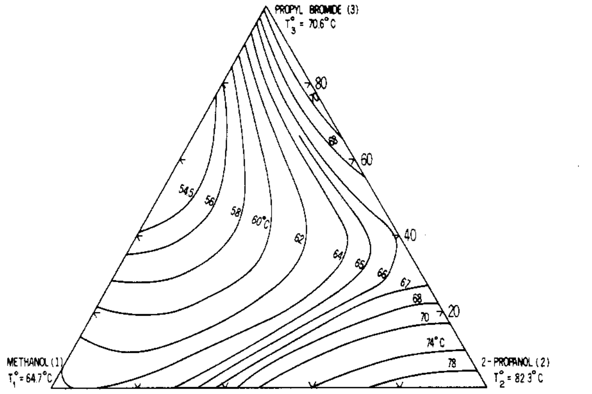

Figure 6. Isothermals for methanol (1)–2-propanol (2)–propyl bromide (3) (with six constants in eq 12).

Conclusion

Vapor–liquid equilibrium at atmospheric pressure has been determined for the ternary system methanol–2-propanol–propyl bromide and the binaries of propyl bromide with each alcohol. All systems present strong positive deviations from ideal behavior. The data were correlated by various equations and the appropriate parameters are reported.

Table VIII. Redlich–Kister Constants for Eq 9–11

system	B_{ij}	C_{ij}	D_{ij}	C_i
methanol (1)–2-propanol (2)	–0.18270	$-0.381\,69 \times 10^{-4}$	$0.340\,45 \times 10^{-5}$	
methanol (1)–propyl bromide (3)	1.8794	$0.116\,65 \times 10^{-2}$	$0.917\,01 \times 10^{-4}$	
2-propanol (2)–propyl bromide (3)	1.2944	–0.131 87	–0.060 59	
methanol (1)–2-propanol (2)–propyl bromide (3)				–0.84812

Table IX. Parameters in Direct Correlation of T-x Data for Methanol (1)-2-Propanol (2)-Propyl Bromide (3) at 760 mmHg

		direct correlation of ternary data (eq 12)									correlation based on binary and ternary data (eq 13)				
							D,[a] %				D, %				
ternary system	ij	A_{ij}	B_{ij}	C_{ij}	D_{ij}	E_{ij}	max	min	mean	σ^2	c'	c	max	min	mean
methanol	12	–10.59	–27.63												
2-propanol	13	–60.56	43.69												
propyl bromide	23	–38.16	–54.28				21.4	0.2	2.6	6.1					
methanol	12	–7.03	–26.19	32.06											
2-propanol	13	–49.83	12.08	–80.69											
propyl bromide	23	–34.97	–55.93	–130.07			10.0	0.03	1.47	2.5					
methanol	12	–8.36	–17.77	29.59	–71.52	84.63									
2-propanol	13	–51.75	8.56	–46.59	27.10	–76.81									
propyl bromide	23	–39.54	–29.50	26.91	–179.9	–353.7	6.77	0.01	1.22	2.1[b]	15	4	26.1	0.05	1.53

[a] $D = |(T_{\mathrm{obsd}} - T_{\mathrm{calcd}})/T_{\mathrm{obsd}}|$; mean $= (1/m)\sum D_i$. [b] Corresponding to minimal σ^2 (eq 14).

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Yehudit Reizner and Moshe Golden helped in the experimental and numerical determinations.

Glossary

A_{ij}, B_{ij}, etc	multicomponent adjustable parameters in eq 12 and 13
B_{ii}, B_{ij}	virial coefficients, eq 2
c'	total number of adjustable parameters corresponding to the binary mixtures in eq 13
c	total number of ternary parameters in eq 13
m	total number of data points which correspond to the system of the high order (ternary system in the present work)
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
σ^2	error variance, eq 14
Λ_{ij}	constant, Wilson equation

Subscripts and Superscripts

calcd	calculated
obsd	observed
max	maximum
min	minimum

Registry No. Methanol, 67-56-1; 2-propanol, 67-63-0; propyl bromide, 106-94-5.

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Osmotic and Activity Coefficients of Some Cobaltammine Salts

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Osmotic coefficients of aqueous solutions of chloropentaaminecobalt(III) chloride, hexaamminecobalt(III) chloride, hexaamminecobalt(III) bromide, hexaamminecobalt(III) iodide, hexaamminecobalt(III) nitrate, hexaamminecobalt(III) perchlorate, aquopentaamminecobalt(III) chloride, and aquopentaamminecobalt(III) bromide have been measured from 0.00 to 0.04 mol kg^{-1}. The freezing point method was used for the determination of the osmotic coefficients. These results were fitted to semiempirical least-squares equations, and these equations were used to calculate the mean molal activity coefficients.

Introduction

The osmotic and activity coefficients of single and mixed electrolytes have been available in the literature for many years. A considerable number of aqueous solutions containing salts were investigated by Scatchard and his collaborators (*1-8*) who developed the freezing point method for the determination of the osmotic coefficients to a high degree of precision. The same method was used by Lange (*9*, *10*) to investigate other systems at low solute concentrations, and more recently by Prue et al. (*11*, *12*) and Lilley and Scott (*13*). From the freezing point temperatures the osmotic and activity coefficients can be determined, and plots of data of this type result in families of curves which are useful in estimating the properties of the solutions.

The object of this work is to extend the above-mentioned studies and present experimental results on aqueous cobaltammine salts solutions in the molality range 0-0.04 mol kg^{-1}.

Experimental Section

Apparatus. The freezing point lowering determinations were carried out in an apparatus similar to that used by Prue (*11*), with the exception that the thermocouple was replaced by a HP 2801A quartz crystal thermometer with a resolution of 0.0001 °C coupled to a digital clock recorder. A diagram of the equipment is shown on Figure 1.

The thermometer probes were calibrated in the range of operating temperatures by determining the freezing point temperatures of KCl solutions and comparing with the existing literature values (*2-10*, *14-17*).

The probes were connected to an oscillator and its outputs were scanned and measured by the quartz thermometer.

The calibration process was done taking care to eliminate hysteresis effects. In this way two independent temperature runs were made: the first determining the freezing point temperatures of KCl solutions beginning with a high concentration and then diluting; the second beginning from a low molality and then increasing it to cover the experimental temperature range.