Ternary Vapor-Liquid Equilibria for System *n*-Butanol–*sec*-Butanol–*tert*-Butanol

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Isobaric vapor-liquid equilibrium was measured for the system *n*-butanol–*sec*-butanol–*tert*-butanol at 760 mm Hg with a Dvorak-Boublik recirculation still. Liquid activity coefficients were evaluated for the three components and correlated with a Redlich-Kister type equation. Vapor composition and boiling points were correlated from binary and ternary data and showed good agreement with the experimental information.

The butanol isomer system reported here has been studied in some detail because it represents a good example for the prediction of multicomponent vapor-liquid equilibria from binary data where the chemical species differ only in the geometrical position of the group function. In addition, the possible binaries present positive and negative excess enthalpies of mixing. The vapor-liquid equilibrium data of the three binaries have already been determined (*12*).

Quitsch et al. (*7*) studied the behavior of the binaries *n*-butanol–*sec*-butanol and *n*-butanol–*tert*-butanol at 100, 300, 500, and 700 mm Hg and found that both exhibited negative deviations from ideal behavior, with no azeotrope formation. Similar results were obtained by Wisniak and Tamir at 760 mm Hg (*12*), including the binary *sec*-butanol–tert-butanol. Wisniak and Tamir also correlated the boiling point of the mixture with its composition using a two-constant modified Swiestolawski equation. Murakami and Benson (*5*) measured the molar excess enthalpies at 25°C of binary mixtures of *n*-butanol with all its isomers and found that the excess enthalpies of mixtures *n*-butanol and isobutanol were positive, whereas those of *n*-butanol–*sec*-butanol and *n*-butanol–*tert*-butanol were negative.

Experimental

Purity of Materials. Analytical grade reagents purchased from Merck and Fluka were used without further purification after gas chromatography analysis failed to show any significant impurities, particularly water. *n*-Butanol was at least 99.5% pure. Physical 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 determinations. The experimental features have been described previously (*11*). 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 diameter and was packed with 10% Hallcomid M-18-01 on 80-100 Supelcoport and operated isothermally at 70°C. Injector temperature was 170°C, and the detector operated at 150 mA and 180°C. Calibration analyses were carried on to convert the peak area ratio to the weight composition of the mixture. Concentration measurements were generally accurate to ±0.3%.

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Results

Seventy-three constant pressure equilibria determinations were made at 760 mm Hg, and most of the experimental results appear in Table III.

Activity coefficients were calculated from the equation

$$\ln \gamma_i = \ln (Py_i/P_i^\circ x_i) + (B_i - v_i^\circ)(P - P_i^\circ)/RT + (P/RT)[(1 - y_i)(y_j\delta_{ij} + \ldots y_k\delta_{ik}) - y_jy_k\delta_{jk}] \quad (1)$$

where

$$\delta_{ij} = 2B_{ij} - B_i - B_j \quad (2)$$

Vapor pressures P_i° and second virial coefficients B_i were calculated according to the general equations (*2, 9*)

$$\log P_i^\circ = A + B/(C + t) \quad (3)$$

$$\log (-B_i) = \alpha_i - \beta_i \log T \quad (4)$$

where the coefficients appear in Table II.

The mixed virial coefficients B_{ij} were estimated by the correlation suggested by O'Connell and Prausnitz (*6*), using the molecular parameters given by the same authors. In general, the contribution of the last two terms accounted for less than 6% of the activity coefficients.

The thermodynamic consistency test can be performed with the McDermott-Ellis (*4*) point-to-point method or by an overall correlation of the data with an equation such as that of Redlich-Kister or Wilson. McDermott and Ellis (*4*) have shown that a pair of experimental points *a* and *b* are thermodynamically consistent if the deviation value D_1 defined as

$$D_1 = \frac{1}{2}\sum_{i=1}^{n}(x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \quad (5)$$

is less than 0.02 if the accuracy of measurement of vapor and liquid mole fraction is within ±0.001. The McDermott-Ellis criterion has been modified by Zandjicke (*13*) to include the heat of mixing, as follows:

Table I. Physical Properties of Pure Compounds

Index	Compound	Refractive index at 25°C	Bp, °C
1	*n*-Butanol	1.3975	117.6
		1.3973 (*9*)	117.66 (*9*)
2	*sec*-Butanol	1.3949	99.7
		1.3950 (*9*)	99.6 (*9*)
3	*tert*-Butanol	1.3850	82.5
		1.3851 (*9*)	82.4 (*9*)

Table II. Virial and Vapor-Pressure Constants

Compound	α_i	β_i	A	B	C
n-Butanol	14.711	4.5	7.47680	−1362.39	178.77
sec-Butanol	14.678	4.5	7.47431	−1314.19	186.55
tert-Butanol	15.359	4.8	7.31994	−1154.48	177.65

Table III. Ternary Vapor-Liquid Equilibrium Data for *n*-Butanol(1)–*sec*-Butanol(2)–*tert*-Butanol(3)

Temp, °C		Liquid compn			Obs vapor compn			Calc vapor compn			Obs activity coeff			Calc activity coeff		
Obs	Calc	x_1	x_2	x_3	y_1	y_2	y_3	y_1	y_2	y_3	γ_1	γ_2	γ_3	γ_1	γ_2	γ_3
84.6	84.8	0.076	0.067	0.857	0.019	0.037	0.944	0.020	0.037	0.931	0.94377	0.98937	1.01176	1.00899	0.98736	0.99726
87.3	87.5	0.099	0.212	0.689	0.029	0.144	0.827	0.030	0.125	0.827	0.97993	1.09011	0.99428	1.02127	0.94867	0.99468
88.2	88.5	0.197	0.133	0.670	0.065	0.091	0.844	0.061	0.085	0.821	1.06076	1.05905	1.00865	1.00008	0.98439	0.98140
88.8	88.9	0.232	0.105	0.663	0.075	0.072	0.853	0.074	0.069	0.827	1.01228	1.03620	1.00723	0.99458	0.99859	0.97683
89.1	89.8	0.044	0.403	0.553	0.016	0.271	0.713	0.015	0.258	0.702	1.12381	1.00409	0.99813	1.05845	0.95758	0.98298
90.4	89.8	0.138	0.291	0.571	0.058	0.217	0.725	0.048	0.198	0.759	1.22747	1.05754	0.93655	1.02397	0.96263	0.98090
90.4	90.2	0.242	0.165	0.593	0.080	0.121	0.799	0.083	0.115	0.783	0.96546	1.03999	0.99386	0.99702	0.98449	0.97353
91.0	91.9	0.035	0.526	0.439	0.014	0.384	0.602	0.013	0.374	0.581	1.13832	1.01115	0.98934	1.06186	0.98539	0.95473
92.3	92.3	0.179	0.368	0.453	0.063	0.283	0.654	0.068	0.274	0.633	0.94727	1.01236	0.99311	1.01851	0.98077	0.96188
92.3	92.1	0.272	0.219	0.509	0.107	0.152	0.741	0.101	0.164	0.715	1.05877	0.91368	1.00142	0.99709	0.98350	0.96594
93.8	94.1	0.115	0.550	0.335	0.068	0.443	0.489	0.047	0.443	0.481	1.49327	1.00051	0.95093	1.02505	1.00031	0.93488
94.5	95.2	0.211	0.468	0.321	0.070	0.421	0.509	0.087	0.386	0.475	0.81346	1.08778	1.00730	1.00605	0.99771	0.94088
94.7	94.6	0.210	0.436	0.354	0.083	0.355	0.562	0.087	0.361	0.531	0.96103	0.97706	1.00130	1.00890	0.99385	0.94603
94.8	95.4	0.247	0.419	0.334	0.111	0.365	0.524	0.102	0.349	0.502	1.08813	1.04135	0.98596	1.00236	0.99474	0.94534
94.8	94.6	0.341	0.237	0.422	0.143	0.200	0.657	0.140	0.196	0.642	1.01540	1.00879	0.97843	0.99076	0.98961	0.95625
95.6	95.7	0.281	0.385	0.334	0.124	0.338	0.538	0.120	0.330	0.518	1.03336	1.01796	0.98380	0.99841	0.99353	0.94720
95.7	95.3	0.465	0.069	0.466	0.206	0.060	0.734	0.195	0.061	0.728	1.03309	1.01367	0.95751	0.97581	1.02272	0.95044
96.4	96.3	0.426	0.179	0.395	0.226	0.149	0.625	0.185	0.159	0.633	1.20170	0.93635	0.93933	0.98287	0.99730	0.95160
97.7	97.0	0.300	0.413	0.287	0.141	0.386	0.473	0.139	0.384	0.477	1.00906	1.00115	0.93460	0.99436	0.99692	0.94329
98.0	97.7	0.228	0.559	0.213	0.101	0.526	0.373	0.107	0.531	0.354	0.93943	0.99670	0.98268	0.99184	1.00570	0.93142
98.2	98.2	0.331	0.416	0.253	0.163	0.433	0.404	0.156	0.395	0.428	1.03581	1.09431	0.88983	0.99071	0.99797	0.94274
98.4	98.4	0.106	0.783	0.111	0.054	0.760	0.186	0.050	0.756	0.187	1.06282	1.01288	0.92727	0.99265	1.00718	0.93133
98.9	99.2	0.349	0.435	0.216	0.184	0.441	0.375	0.169	0.424	0.374	1.07774	1.03843	0.94413	0.98817	0.99928	0.94249
99.7	99.4	0.296	0.530	0.174	0.147	0.534	0.319	0.147	0.535	0.309	0.98277	0.00190	0.96974	0.98540	0.00419	0.93835
99.8	99.4	0.442	0.287	0.271	0.217	0.323	0.460	0.221	0.288	0.487	0.96762	0.11501	0.89475	0.98679	0.99382	0.94727
99.8	99.6	0.527	0.155	0.318	0.264	0.160	0.576	0.262	0.157	0.571	0.98733	1.02269	0.95479	0.98076	1.00224	0.94608
100.1	100.6	0.364	0.469	0.167	0.188	0.493	0.319	0.184	0.479	0.302	1.00569	1.02998	0.99653	0.98545	1.00071	0.94415
100.2	99.9	0.413	0.360	0.227	0.217	0.373	0.410	0.210	0.367	0.413	1.01898	1.01149	0.93903	0.98773	0.99558	0.94590
100.3	100.7	0.618	0.049	0.333	0.317	0.053	0.630	0.313	0.052	0.605	0.99078	1.05205	0.98022	0.97661	1.02905	0.94188
100.4	100.1	0.204	0.707	0.089	0.117	0.729	0.154	0.104	0.735	0.163	1.10335	0.99924	0.89344	0.97968	1.00722	0.94332
100.4	100.3	0.277	0.600	0.123	0.138	0.626	0.236	0.141	0.623	0.224	0.95842	1.01108	0.99069	0.98084	1.00618	0.94126
100.4	100.2	0.412	0.374	0.214	0.208	0.382	0.410	0.212	0.384	0.392	0.97124	0.98981	0.98924	0.98754	0.99613	0.94578
101.4	101.8	0.455	0.368	0.177	0.278	0.394	0.328	0.243	0.392	0.336	1.12921	1.00024	0.92460	0.98743	0.99527	0.94783
101.6	101.3	0.465	0.328	0.207	0.252	0.352	0.396	0.250	0.352	0.396	0.99362	0.99531	0.94801	0.98734	0.99430	0.94714
102.0	101.6	0.275	0.655	0.070	0.149	0.715	0.136	0.149	0.721	0.137	0.97769	0.99777	0.94977	0.97773	1.00613	0.95385
102.4	102.2	0.540	0.238	0.222	0.300	0.258	0.442	0.300	0.263	0.436	0.98667	0.97657	0.96017	0.98622	0.99456	0.94632
102.8	102.7	0.510	0.309	0.181	0.296	0.347	0.357	0.288	0.346	0.361	1.01457	0.99711	0.93840	0.98805	0.99329	0.94808
104.4	105.1	0.680	0.109	0.211	0.454	0.133	0.413	0.408	0.131	0.440	1.09590	1.02287	0.88250	0.98527	1.01026	0.94072
104.5	104.2	0.415	0.531	0.054	0.267	0.624	0.109	0.250	0.636	0.116	1.05193	0.98160	0.90705	0.98480	1.00008	0.96464

104.8	104.9	0.567	0.300	0.133	0.370	0.361	0.269	0.348	0.360	0.284	1.05452	0.99445	0.89981	0.99089	0.99129	0.95022
104.9	105.1	0.725	0.034	0.241	0.455	0.044	0.501	0.443	0.043	0.510	1.01022	1.06567	0.92178	0.98278	1.03449	0.93840
105.2	105.1	0.609	0.235	0.156	0.359	0.293	0.348	0.379	0.286	0.336	0.93788	1.01581	0.97932	0.99003	0.99289	0.94674
107.4	107.6	0.666	0.233	0.101	0.463	0.308	0.229	0.453	0.306	0.234	1.01600	0.99654	0.92573	0.99474	0.99007	0.94769
107.6	107.6	0.681	0.206	0.113	0.470	0.272	0.258	0.467	0.273	0.263	1.00095	0.98846	0.92673	0.99382	0.99240	0.94541
107.9	107.0	0.726	0.100	0.174	0.510	0.124	0.366	0.500	0.137	0.407	1.00720	0.91860	0.84491	0.98832	1.01172	0.93915
107.9	108.2	0.795	0.026	0.179	0.556	0.036	0.408	0.548	0.036	0.417	1.00274	1.02574	0.91556	0.98839	1.03773	0.93581
108.0	108.0	0.711	0.166	0.123	0.501	0.220	0.279	0.494	0.224	0.290	1.00645	0.97838	0.90816	0.99297	0.99711	0.94232
108.9	108.1	0.604	0.360	0.036	0.424	0.492	0.840	0.437	0.497	0.089	0.96892	0.97783	0.90729	0.99827	0.98669	0.96312
109.1	109.1	0.745	0.148	0.107	0.544	0.203	0.253	0.541	0.208	0.261	1.00026	0.97460	0.91347	0.99440	0.99897	0.94045
109.3	109.5	0.732	0.188	0.080	0.555	0.261	0.184	0.537	0.264	0.197	1.03078	0.97964	0.88284	0.99698	0.99179	0.94368
109.8	110.0	0.689	0.286	0.025	0.517	0.416	0.067	0.518	0.405	0.063	1.00106	1.00883	1.01225	1.00204	1.98271	0.95628
110.3	110.5	0.786	0.129	0.085	0.602	0.183	0.215	0.598	0.189	0.215	1.00276	0.96713	0.94016	0.99631	1.00121	0.93782
111.2	111.2	0.790	0.149	0.061	0.635	0.216	0.149	0.623	0.224	0.159	1.01752	0.95831	0.88216	0.99856	0.99564	0.93881
111.5	111.2	0.742	0.235	0.023	0.588	0.352	0.060	0.594	0.353	0.061	0.99200	0.98010	0.93318	1.00269	0.98311	0.94935
112.4	112.4	0.831	0.120	0.049	0.695	0.182	0.123	0.686	0.189	0.132	1.01255	0.96253	0.87269	0.99924	1.00054	0.93461
113.8	113.8	0.878	0.086	0.036	0.767	0.140	0.093	0.763	0.143	0.101	1.00449	0.98551	0.85944	0.99968	1.00888	0.92929
114.6	114.7	0.908	0.065	0.027	0.819	0.108	0.073	0.813	0.112	0.770	1.00726	0.98384	0.87129	0.99987	1.01553	0.92572
90.5	91.5	0.283	0.175	0.542	0.096	0.134	0.770	0.097	0.122	0.713	0.98643	1.08164	1.04404	0.99307	0.98812	0.96718
92.2	90.3	0.301	0.076	0.623	0.099	0.056	0.846	0.110	0.059	0.873	0.88452	0.97378	0.93697	0.98660	1.01648	0.96785
101.5	103.3	0.632	0.125	0.632	0.363	0.140	0.497	0.338	0.135	0.461	1.05729	1.04253	1.01700	0.98315	1.00725	0.94233

$$D_2 = \frac{1}{2}\left(\frac{Q_a}{T_a} + \frac{Q_b}{T}\right)(T_b - T_a) \tag{6}$$

where

$$Q_j = \sum_{j=1}^{n} x_j \ln \gamma_j \tag{7}$$

According to Zandjicke, the data are consistent if the following criterion is met:

$$|D_1 - 3\,D_2| \leq 0.02 \tag{8}$$

Ma et al. (*3*) concluded that if a set of data can be shown to be well correlated by a multicomponent thermodynamic equation such as that of Redlich-Kister or Wilson, then the assumption that the data are inconsistent according to the point-to-point test is not justified. They set an upper arbitrary limit for the rmsd of 1.5% in the vapor phase to indicate a good correlation.

Susuki et al. (*9*), in their prediction model for quaternary systems of alcohols, obtained rmsd in the vapor-phase compositions of between 1.17 and 4.15 mol % and concluded that a good correlation had been obtained.

The data obtained in this work were first tested by the McDermott-Ellis method to reject those points that were clearly inconsistent. Table III reports the points that passed the test. The consistent points were then correlated using the following Redlich-Kister equation (*8*):

$$\begin{aligned}\ln \gamma_1 = x_2x_3\,[&(B_{12} + B_{13} - B_{23}) + C_{12}(2\,x_1 - x_2) + \\ &C_{13}(2\,x_1 - x_3) + 2\,C_{23}(x_3 - x_2) + \\ &D_{12}(x_1 - x_2)(3\,x_1 - x_2) + D_{13}(x_1 - x_3)(3\,x_1 - x_3) - \\ &3\,D_{23}(x_3 - x_2)^2 + C_1(1 - 2\,x_1)] + \\ x_2^2\,[&B_{12} + C_{12}(3\,x_1 - x_2) + D_{12}(x_1 - x_2)(5\,x_1 - x_2)] + \\ x_3^2\,[&B_{13} + C_{13}(3\,x_1 - x_3) + \\ &D_{13}(x_1 - x_3)(5\,x_1 - x_3)]\end{aligned} \tag{9}$$

where B_{ij}, C_{ij}, D_{ij} are the binary constants, and C_1 is a ternary constant. The equations for the two other activity coefficients were obtained by cyclic rotation of the indices. Equation 9 was used with and without the ternary constant to predict the values of the experimental activity coefficients and vapor-phase composition. For the latter, the rmsd's were 1.44% and 1.50%, respectively, values that indicate that the overall correlation is good and that they are not statistically different. In other words, the ternary vapor-liquid equilibria of *n*-butanol–*sec*-butanol–*tert*-butanol can be predicted from the behavior of the different binaries that compose it without the need for interaction terms like C_1. Table III reports the predicted values of the activity coefficients and vapor-phase composition and Table IV the correlating constants for the three binaries.

The boiling points of the ternary system were then correlated using the equation suggested by Wisniak and Tamir (*12*)

$$\begin{aligned}T = x_1T_1^\circ + x_2T_1^\circ + x_3T_3^\circ + \\ \omega + \sum^{n}\,[x_ix_j\sum_{0}^{k} C_k\,(x_i - x_j)^k] + \\ x_1x_2x_3\,[A + B(x_1 - x_2) + C(x_1 - x_3) + \ldots]\end{aligned} \tag{10}$$

where

$$\omega = x \ln (y_1/x_1) + x_2 \ln (y_2/x_2) + x_3 \ln y_3/x_3) \tag{11}$$

The constants of Equation 10 appear in Table V. From the value of rmsd, the correlation is very good, considering particularly that the last three points in Table III contribute 0.15 to the rmsd.

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Table IV. Correlation of Binary Vapor-Liquid Data, Equation 9

System	B_{ij}	C_{ij}	D_{ij}
n-Butanol–*sec*-butanol	$-2.05600 \cdot 10^{-2}$	$-2.82625 \cdot 10^{-3}$	$6.24375 \cdot 10^{-2}$
n-Butanol–*tert*-butanol	$-1.26499 \cdot 10^{-1}$	$-8.67847 \cdot 10^{-2}$	$-4.96390 \cdot 10^{-2}$
sec-Butanol–*tert*-butanol	$-1.24924 \cdot 10^{-1}$	$6.80822 \cdot 10^{-3}$	$1.59776 \cdot 10^{-1}$
n-Butanol–*sec*-butanol–*tert*-butanol			
	$C_1 = 2.74276 \cdot 10^{-1}$		

Table V. Correlation of Boiling Points, Equation 10

System	C_0	C_1	C_2	Rmsd
n-Butanol–*sec*-butanol	−5.73859	−0.51795		0.111
n-Butanol–*tert*-butanol	−19.3248	−0.41736	6.6263	0.287
sec-Butanol–*tert*-butanol	−1.13340	2.39065	−8.03177	0.102
n-Butanol–*sec*-butanol–*tert*-butanol				
	$A = -12.94441$	$B = 21.7434$		0.515

Nomenclature

α, β, A, B, C = constants
B_i = second virial coefficient, cm^3/mol
n = number of components
P = overall pressure, mm Hg
P_i° = vapor pressure of component i pure, mm Hg
R = gas constant
rmsd = root-mean-square deviation

$$\sqrt{\sum_j \sum_i (y_{ji,exp} - y_{ji,calc})^2 / 3n}$$

t, T = temperature, °C, K
T_i° = boiling temperature of component i pure at pressure P, K
v_i° = molar liquid volume of component i pure, cm^3/mol
x_i, y_i = mole fraction composition of component i in the liquid and vapor phases
γ_i = activity coefficient of component i

Subscripts

exp = experimental
calc = calculated
i = component i

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