

Vapor-Liquid Equilibria of *sec*-Butanol–Isobutanol, *sec*-Butanol–*tert*-Butanol, and Isobutanol–*tert*-Butanol Systems

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Vapor-liquid equilibrium data are determined at 760 mm Hg for the binary systems *sec*-butanol–isobutanol, *sec*-butanol–*tert*-butanol, and isobutanol–*tert*-butanol. The first system behaves like an ideal solution, and the second presents small negative deviations from the ideal solution with activity coefficients that are well represented by a one-constant Redlich-Kister equation. The third system leads to simple activity coefficients that are thermodynamically inconsistent because of homo- and heteroassociation of the different species. An explanation is provided that points to positive deviations from the ideal behavior.

Vapor-liquid equilibria information is useful for the design of separation equipment and the testing of the different theories developed to express the behavior of nonideal solutions. Data on the equilibrium of different isomers may be useful toward an understanding of the contribution of different chemical groups. Very little data are available on the vapor-liquid equilibrium of the butyl alcohols.

Quitze et al. (9) studied the behavior of the systems *n*-butanol–*sec*-butanol and *n*-butanol–*tert*-butanol at 100, 300, 500, and 700 mm Hg and found that both exhibited slight negative deviations from ideal behavior, with no azeotrope formation. Similar results were obtained by Ballard and van Winkle (7) for mixtures of propanol and butyl alcohols. The second virial coefficients for propanols and butanols have been measured by Cox (3) at atmospheric pressure and temperatures between 105° and 166°C and used to demonstrate the intermolecular hydrogen bonding present in the vapors. Murakami and Benson (5) measured the molar excess enthalpies and molar excess volumes at 25°C for binary mixtures of *n*-butanol with all its isomers and found that the excess enthalpies for mixtures of *n*-butanol and isobutanol were positive, whereas those for *n*-butanol–*sec*-butanol and *n*-butanol–*tert*-butanol were negative. The maximum excess enthalpy in the latter case was 450 J/mol. Similar thermal behavior was found for the binaries of methanol with butanol isomers (8).

Experimental

Purity of materials. Analytical grade reagents purchased from Fluka were used without further purification after gas chromatography analysis failed to show any significant impurity, particularly water. Physical properties of the compounds appear in Table I.

Apparatus and procedure. An all-glass modified Dvorak and Boublik recirculation still (2) was used in the equilibrium determinations. A vacuum system controlled by a cartesian manostat connected the vapor condenser with a Swietoslawski ebullimeter and allowed total pressure regulation. The total pressure of the system was determined from the boiling temperature of the distilled water in the ebullimeter. Temperatures were measured with a mercury thermometer that had been calibrated to 0.01°C by use of a Hewlett-Packard quartz thermometer Model 2801 A. Several 1-ml samples were

taken during each run until no significant changes in the refractive index and temperature were detected. The time required for reaching equilibrium varied between 2 hr for low-temperature determinations to 3 hr for high-temperature levels.

Analysis of the samples was made at 25°C with a Bausch & Lomb Abbe-3L precision refractometer which gave direct readings to four significant figures and estimated values reproducibly to the nearest 0.00025. The calibration data appear in Tables II and III. In every case the data may be represented by two straight lines so that the accuracy in estimating the concentration data is at least 0.02 concentration units.

The analysis of isobutanol and secondary alcohol mixtures was done by gas chromatography with a 0.2 × 100-cm column filled with Silar 10C on 100/120 Gaschrom Q, injector temperature 160°C and column temperature 40°C, in a Packard-Becker Model 417 gas chromatograph provided with an Autolab Model 6300 integrator. Calibration analyses with mixtures of known weight composition showed that the peak area ratio was equivalent to the weight percent composition of the mixture.

Results

Constant-pressure equilibria determinations were made at 760 mm Hg; the experimental results appear in Tables III–V.

Activity coefficients were calculated from the equation:

$$\ln \gamma_i = \ln (P y_i / x_i P_i^\circ) + (B_i - v_i^\circ) (P - P_i^\circ) / RT + (1 - y_i)^2 P \delta / RT \quad (1)$$

where

$$\delta = 2 B_{ij} - B_{ii} - B_{jj} \quad (2)$$

Vapor pressures and second virial coefficients were calculated according to the following equations (3, 12):

sec-Butanol

$$\log P_1^\circ = 7.47431 - 1319.19 / (186.55 + t) \quad (3)$$

$$\log (-B_1) = 14.678 - 4.5 \log T \quad (4)$$

tert-Butanol

$$\log P_2^\circ = 7.31994 - 1154.48 / (177.65 + t) \quad (5)$$

$$\log (-B_2) = 15.359 - 4.8 \log T \quad (6)$$

Isobutanol

$$\log P_3^\circ = 7.22014 - 1190.38 / (166.67 + t) \quad (7)$$

$$\log (-B_3) = 14.711 - 4.5 \log T \quad (8)$$

The mixed virial coefficients B_{ij} were estimated by the correlation of O'Connell and Prausnitz (7) by use of the molecular parameters reported by the same authors. The values obtained varied between –1010 to –954 cm³/mol for the system isobutanol–*sec*-butanol, –1050 to –904 cm³/mol for the system *sec*-butanol–*tert*-butanol, and –990 to –828 cm³/mol for the binary isobutanol–*tert*-butanol. These figures are slightly smaller than the ones obtained by a simple geometric average of the virial coefficients of the pure components. In

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Table I. Physical Constants of Pure Compounds

Index	Compound	Refractive index at 25°C	Bp, °C
1	<i>sec</i> -Butanol	1.3949	99.7
		1.3950 (4)	99.6 (4)
2	<i>tert</i> -Butanol	1.3850	82.5
		1.3851 (4)	82.4 (4)
3	Isobutanol	1.3938	107.7
		1.3939 (4)	107.7 (4)

Table II. Refractive Index at 25°C of Mixtures of *sec*-Butanol and *tert*-Butanol

x_1	n	x_1	n
0.000	1.3850	0.410	1.3896
0.025	1.3853	0.456	1.3900
0.054	1.3856	0.477	1.3903
0.110	1.3864	0.509	1.3905
0.133	1.3866	0.527	1.3906
0.135	1.3867	0.572	1.3910
0.166	1.3810	0.661	1.3919
0.248	1.3879	0.681	1.3920
0.260	1.3880	0.720	1.3923
0.284	1.3885	0.802	1.3930
0.305	1.3886	0.850	1.3935
0.309	1.3887	0.919	1.3941
0.365	1.3892	1.000	1.3949

Table III. Refractive Index at 25°C of Mixtures of Isobutanol and *tert*-Butanol

x_2	n	x_2	n
0.000	1.3938	0.504	1.3900
0.035	1.3935	0.528	1.3899
0.046	1.3934	0.586	1.3895
0.064	1.3932	0.625	1.3892
0.100	1.3930	0.677	1.3887
0.149	1.3926	0.717	1.3884
0.164	1.3925	0.752	1.3880
0.229	1.3920	0.813	1.3874
0.285	1.3916	0.828	1.3873
0.374	1.3911	0.858	1.3870
0.460	1.3904	0.905	1.3865
0.492	1.3902	0.987	1.3856
		1.000	1.3850

Table IV. Experimental Vapor-Liquid Equilibrium Data for Isobutanol-*sec*-Butanol

Temp, °C	x_1	y_1	γ_1	γ_3
106.70	0.118	0.142	0.99508	1.00047
106.40	0.180	0.223	0.98877	0.99094
105.70	0.250	0.305	0.99498	0.99410
105.40	0.285	0.345	0.99642	0.99372
105.20	0.308	0.370	0.99501	0.99492
104.80	0.353	0.420	0.99793	0.99443
104.20	0.422	0.495	1.00273	0.99149
103.80	0.463	0.533	0.99701	1.00191
103.60	0.500	0.570	0.99351	0.99872
103.00	0.565	0.635	0.99895	0.99729
102.60	0.616	0.685	1.00149	0.99052
102.00	0.686	0.750	1.00460	0.98448
101.10	0.794	0.840	1.00233	0.99553
100.50	0.873	0.905	1.00268	0.98260
100.00	0.940	0.955	0.99993	1.00563

general, the contribution of the third term in Equation 1 was insignificant, and deviations from pure gas ideality accounted for less than 4% of the values of the activity coefficients.

The results for the system isobutanol-*sec*-butanol appear in Table IV. This mixture behaves like an ideal one that can be described by Raoult's law.

Table V reports the equilibrium data for the system *sec*-butanol-*tert*-butanol and shows that both components exhibit small negative deviations from ideal solution behavior. The area test showed that the activity coefficients calculated with Equation 1 were thermodynamically consistent.

Several analytical models were tested to represent the experimental data for *sec*-butanol-*tert*-butanol. The following one-constant Redlich-Kister (10) equations provided a fit with less than 4% average error.

$$\ln \gamma_1 = -0.1597 x_2^2 \quad (9)$$

$$\ln \gamma_2 = -0.1597 x_1^2 \quad (10)$$

Calculation of the activity coefficients for the system isobutanol-*tert*-butanol with Equation 1 provided data that were thermodynamically inconsistent; in the full concentration range, the deviations from ideal behavior were negative for *tert*-butanol, whereas for isobutanol they were positive (Figure 1). A possible explanation to this behavior is strong heat

Table V. Experimental Vapor-Liquid Equilibrium Data for *sec*-Butanol-*tert*-Butanol

Temp, °C	x_1	y_1	γ_1	γ_2
83.00	0.066	0.031	0.89678	1.01524
83.40	0.105	0.050	0.89370	1.02342
84.65	0.185	0.093	0.89534	1.02475
85.75	0.235	0.122	0.88385	1.01528
86.90	0.290	0.160	0.89624	1.00408
87.90	0.357	0.216	0.94317	0.99873
89.50	0.433	0.294	0.99239	0.96430
90.50	0.484	0.348	1.00989	0.94537
91.30	0.528	0.395	1.01809	0.93319
92.20	0.587	0.451	1.00943	0.93886
93.10	0.648	0.510	0.99862	0.95415
93.80	0.690	0.565	1.01133	0.94003
94.80	0.740	0.630	1.01245	0.92267
95.40	0.780	0.682	1.01655	0.91944
96.30	0.830	0.745	1.00929	0.92706
97.50	0.892	0.830	1.00135	0.93664
98.50	0.935	0.900	0.99917	0.88728
99.00	0.970	0.952	1.00070	0.90908

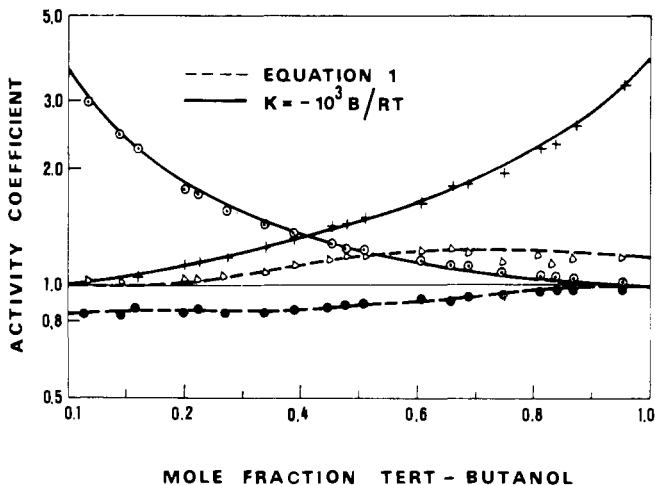


Figure 1. Activity coefficients for isobutanol-*tert*-butanol

Table VI. Experimental Vapor-Liquid Equilibrium Data for *tert*-Butanol–Isobutanol

Temp, °C	x_2	y_2	Equation 1		$K = -B/RT$		$K = -10^3B/RT$	
			γ_2	γ_3	γ_2	γ_3	γ_2	γ_3
105.7	0.055	0.105	0.87380	1.0127	0.87895	1.01482	3.02027	1.01912
104.8	0.090	0.165	0.86298	1.01519	0.87365	1.01837	2.47682	1.03545
103.8	0.120	0.220	0.88930	1.01681	0.88985	1.02120	2.24446	1.05114
101.4	0.200	0.330	0.86177	1.04947	0.85439	1.05706	1.78196	1.11724
100.6	0.225	0.375	0.89231	1.04143	0.89479	1.05007	1.72966	1.12894
99.3	0.275	0.425	0.86226	1.07572	0.86633	1.08638	1.55800	1.18595
99.1	0.280	0.430	0.86096	1.07990	0.87518	1.09080	1.54486	1.19243
97.4	0.340	0.495	0.86357	1.11627	0.87915	1.12999	1.42552	1.26568
95.9	0.390	0.550	0.87856	1.14113	0.88519	1.15734	1.35855	1.33004
94.1	0.455	0.615	0.89391	1.17372	0.90194	1.19312	1.28572	1.42445
93.3	0.480	0.640	0.90588	1.18777	0.90453	1.20860	1.26689	1.46603
92.6	0.510	0.670	0.91387	1.18895	0.91307	1.21094	1.24114	1.50745
90.3	0.605	0.755	0.93934	1.20415	0.94058	1.23012	1.17404	1.67441
89.5	0.660	0.790	0.92635	1.24041	0.92853	1.26858	1.12306	1.81880
88.7	0.690	0.820	0.94589	1.20640	0.94876	1.23512	1.11620	1.86418
87.2	0.750	0.870	0.97204	1.14972	0.98635	1.17930	1.09630	1.98727
86.0	0.815	0.905	0.97331	1.19836	0.98907	1.23108	1.06106	2.30466
85.3	0.840	0.925	0.99006	1.12787	0.99658	1.15966	1.05925	2.35318
85.1	0.875	0.940	0.97291	1.16575	0.98971	1.19906	1.03152	2.63884
83.2	0.955	0.980	0.99673	1.17343	0.99778	1.20953	1.01279	3.73765

effects. Equation 1 assumes that the enthalpy of mixing is negligible, but for the mixtures of isobutanol and *tert*-butanol, there is strong experimental evidence that suggests a large heat of mixing effect. Polack et al. (8) measured the heats of mixing of methanol and the butanol isomers at 25°C and found that the mixture with isobutanol was endothermic with a maximum excess energy of mixing of 157 J/mol. With *tert*-butanol the mixture was exothermic with a maximum excess energy of mixing of -665 J/mol. This behavior is similar to that of *n*-butanol with its isomers (5). Again, solutions with isobutanol are endothermic with a maximum excess energy of mixing of 11.4 J/mol. With *tert*-butanol they are strongly exothermic with a maximum excess energy of mixing of -451 J/mol.

According to Polack et al. (8), the observed differences in the excess properties must reflect differences in the shapes of the component molecules and in the interaction between them. On one hand, the association of alcohols is thought to decrease with increasing molecular weight and in the sequence primary > secondary > tertiary. On the other hand, formation of heterodimers increases in the order *n*-butanol < isobutanol < *sec*-butanol < *tert*-butanol. The Stockmayer potential functions obtained by Cox (3) in his estimation of the second virial coefficients of the butanols points to the large intermolecular hydrogen bonding in their vapor phase.

To try to improve the calculation of the activity coefficients, the association constants were estimated by the method of Lambert (4). According to Lambert, the second virial coefficient may be considered formed by two contributions, one due to the normal intermolecular forces and the other to the chemical association forces. In the case of small degrees of association, $B_{\text{polar}} = -RTK$, where K is the dimerization constant. The method of O'Connell and Prausnitz (7) for calculation of the second virial coefficients allows separation of the polar contribution to B and thus calculation of K . The method of Lambert is restricted to very low degrees of association and for the binaries studied here yields dimerization constants in the order of 10^{-5} mm^{-1} , which were too low to improve the results obtained with Equation 1.

Better results were obtained by the method of Nothnagel et al. (6). These authors applied the chemical theory of vapor imperfections to derive empirical equations for the dimeriza-

tion constants of the pure components and the heteroassociation constant of the vapor mixture. The suggested equations are adaptable to nonpolar as well as polar mixtures, and they can be applied to any degree of association. Application of this method to the present work gave values of the association constants one order of magnitude larger than those obtained by Lambert's method. The coefficients of activity were recalculated by using the model for binary solutions developed by Tamir and Wisniak (11) for associating mixtures, based on a material balance of the monomeric and dimeric species present in both phases, and appear in Table VI. There is an improvement, but it is far from being enough.

By trial and error, the appropriate association constants, particularly for heteroassociation, should be of the order of 10^{-2} mm^{-1} ; the corresponding results are reported in Table VI and Figure 1. The data are thermodynamically better, and both components show a positive deviation from ideal behavior.

Analysis of the results for the three systems reported here shows that the addition of *tert*-butanol causes deviation from ideal behavior and that this deviation increases significantly with increasing spatial symmetry of the components.

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Nomenclature

- B_i = second virial coefficient, cm^3/mol
- K = dimerization constant, mm^{-1}
- P = total pressure, mm Hg
- P_i° = vapor pressure of pure component, mm Hg
- R = gas constant
- t = temperature, °C
- T = temperature, K
- v_i° = specific volume of pure liquid, cm^3/mol
- x_i = equilibrium composition, liquid phase
- y_i = equilibrium composition, vapor phase
- γ_i = activity coefficient
- i = component, 1 for *sec*-butanol, 2 for *tert*-butanol, 3 for isobutanol

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Vapor-Liquid Equilibria of Isobutanol-*n*-Butanol and Isopropanol-*sec*-Butanol Systems

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Vapor-liquid equilibria data are measured at 760 mm Hg for the systems isobutanol-*n*-butanol and isopropanol-*sec*-butanol. Both systems exhibit slight positive deviations from ideal solution behavior, and their activity coefficients can be correlated by a two-constant Redlich-Kister equation. Boiling points of the mixtures are adequately described by a two-constant equation.

Data on the vapor-liquid equilibrium of isomeric species are useful for an understanding of the contribution of the different chemical groups to mixture properties such as boiling points and activity coefficients. Very little data are available on the vapor-liquid equilibrium of the butyl isomers and their mixtures with isopropanol.

Kay and Donham (4) determined the liquid-vapor phase boundaries of isobutanol-*n*-butanol at pressures between 260 and 623 psig, without calculation of the activity coefficients. Ballard and van Winkle (7) measured the vapor-liquid equilibrium at 760 mm Hg of isopropanol with methanol ethanol, propanol, and isobutanol and found that the first binary exhibited negative deviations from ideal solution behavior and the other three binaries behaved ideally. Activity coefficients were calculated assuming ideal gas behavior. Murakami and Benson (5) measured the heat of mixing at 25°C of *n*-butanol-isobutanol and found that the excess enthalpy of mixing was always positive, with a maximum value of about 11.4 J/mol at equimolar composition.

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 wt % pure. Physical properties of the pure components appear in Table I.

Apparatus and procedure. An all-glass modified Dvorak and Boublik recirculation still (2) was used in the equilibrium determinations. The experimental features have been described previously (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 diameter and was packed with 10% Hallcomid M-18-OL 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%.

Results

Constant-pressure equilibria determinations were made at 760 mm Hg; the experimental results appear in Tables III and IV.

Activity coefficients were calculated from the equation:

$$\ln \gamma_i = \ln (P y_i / P_i^\circ x_i) + (B_i - v_i^\circ)(P - P_i^\circ) / RT + (1 - y_i)^2 P \delta_i / RT \quad (1)$$

Table I. Physical Constants of Pure Compounds

Index	Compound	Refractive index at 25°C	Bp, °C
1	Isobutanol	1.3938 ^a 1.3939 (8)	107.7 ^a 107.7 (8)
2	<i>n</i> -Butanol	1.3975 ^a 1.3973 (8)	117.6 ^a 117.66 (8)
3	<i>sec</i> -Butanol	1.3949 ^a 1.3950 (8)	99.7 ^a 99.6 (8)
4	Isopropanol	1.3754 ^a 1.3752 (8)	82.5 ^a 82.5 (8)

^a Measured.

Table II. Virial and Vapor-Pressure Constants

Compounds	α_i	β_i	<i>A</i>	<i>B</i>	<i>C</i>
Isobutanol	14.711	4.5	7.22014	-1190.38	166.67
<i>n</i> -Butanol	14.711	4.5	7.47680	-1362.39	178.77
<i>sec</i> -Butanol	14.678	4.5	7.47431	-1314.19	186.55
Isopropanol	14.012	4.3	8.11778	-1580.92	219.61

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