

Literature Cited

- (1) Ballard, L. H., van Winkle, M., *Ind. Eng. Chem.*, **44**, 2450 (1952).
- (2) Boublikova, L., Lu, B.C.Y., *J. Appl. Chem.*, **19**, 89 (1969).
- (3) Cox, J. D., *Trans. Faraday Soc.*, **57**, 1674 (1961).
- (4) Lambert, J. D., *Diss. Faraday Soc.*, **15**, 226 (1953).
- (5) Murakami, S., Benson, G. C., *Bull. Chem. Soc. Jpn.*, **46**, 74 (1973).
- (6) Nothnagel, K. H., Abrams, D. S., Prausnitz, J. M., *Ind. Eng. Chem., Process Des. Dev.*, **12**, 25 (1973).
- (7) O'Connell, J. P., Prausnitz, J. M., *ibid.*, **6**, 245 (1967).
- (8) Polack, J., Murakami, S., Lam, V. T., Pflug, H. D., Benson, G. C., *Can. J. Chem.*, **48**, 2457 (1970).
- (9) Quitzsch, von K., Kohler, S., Taubert, K., Geiseler, G., *J. Prakt. Chem.*, **311**, 429 (1969).
- (10) Redlich, O., Kister, A. T., *Ind. Eng. Chem.*, **40**, 345 (1948).
- (11) Tamir, A., Wisniak, J., *J. Chem. Sci.*, **30**, 335 (1975).
- (12) TRC Tables, "Selected Values of Properties of Chemical Compounds," Thermodynamic Research Center Data Project, College Station, Tex., 1961.

Received for review December 24, 1974. Accepted April 18, 1975.

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

Abraham Tamir¹ and Jaime Wisniak

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

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	A	B	C
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

¹ To whom correspondence should be addressed.

Table III. Experimental Vapor-Liquid Equilibrium Data for Isobutanol(1)-*n*-Butanol(2)

T_{exp}	T_{calc}	x_1	y_1	γ_1	γ_2
115.60	115.63	0.174	0.227	1.00728	1.00588
115.20	115.19	0.213	0.276	1.01254	1.00314
115.00	115.02	0.228	0.291	1.00360	1.00863
114.70	114.71	0.256	0.323	1.00128	1.01026
114.30	114.26	0.293	0.365	1.00088	1.01182
114.00	113.96	0.323	0.400	1.00422	1.00952
112.90	112.97	0.413	0.497	1.01052	1.01650
112.00	112.04	0.501	0.589	1.01264	1.01575
111.20	111.11	0.592	0.674	1.00982	1.01135
110.80	110.78	0.625	0.704	1.01241	1.01447
110.30	110.32	0.673	0.750	1.01838	1.00191
109.90	109.91	0.718	0.784	1.01128	1.01958
109.50	109.47	0.767	0.826	1.01086	1.01007
109.40	109.41	0.774	0.831	1.01122	1.01532
109.10	109.04	0.818	0.866	1.00727	1.01195
108.60	108.66	0.865	0.903	1.01037	1.00729
108.40	108.47	0.890	0.922	1.00955	1.00217

Table IV. Experimental Vapor-Liquid Data for Isopropanol(4)-*sec*-Butanol(3)

T_{exp}	T_{calc}	x_4	y_4	γ_4	γ_3
97.60	97.68	0.068	0.126	1.07406	1.00529
96.40	96.57	0.110	0.194	1.06403	1.01401
95.30	95.46	0.155	0.261	1.05412	1.01964
94.40	94.47	0.195	0.317	1.04913	1.02286
92.80	92.74	0.272	0.417	1.04508	1.02553
91.10	91.07	0.354	0.510	1.04210	1.03678
89.90	90.00	0.411	0.566	1.03945	1.05518
89.10	89.05	0.465	0.618	1.03205	1.05544
88.90	88.78	0.481	0.632	1.02761	1.05653
88.50	88.39	0.505	0.654	1.02751	1.05825
87.60	87.52	0.561	0.703	1.02714	1.06191
86.60	86.57	0.627	0.757	1.02640	1.06490
85.50	85.35	0.721	0.826	1.01418	1.06689
83.90	84.13	0.829	0.900	1.02037	1.06910
83.10	83.40	0.901	0.944	1.01497	1.06982
82.55	82.81	0.964	0.980	1.00758	1.07820

Table V. Correlation of Boiling Points

System	C_0	C_1	rmsd
Isobutanol- <i>n</i> -butanol	-2.3570	-1.0797	0.045
Isopropanol- <i>sec</i> -butanol	-10.1351	1.69414	0.147

where

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

Vapor pressures and second virial coefficients were calculated according to equations of the form (3, 8):

$$\log(-B_i) = \alpha_i - \beta_i \log T \quad (3)$$

$$\log P_i^o = A + B/(C + t) \quad (4)$$

The constants of Equations 3 and 4 appear in Table II.

The mixed virial coefficients B_{ij} were estimated by the correlation of O'Connell and Prausnitz (6) using the molecular parameters reported by the same authors. The values ob-

tained varied between -874 to -930 cm³/mol for the system isobutanol-*n*-butanol and -887 to -1025 cm³/mol for the system isopropanol-*sec*-butanol. In general, the contribution of the third term in Equation 1 was insignificant, and the deviations from pure gas ideality accounted for less than 4% of the value of the activity coefficients.

From the activity coefficients reported in Tables III and IV, both binaries exhibit slight positive deviations from ideal solution behavior. The coefficients were correlated with the following two-constant Redlich-Kister equation (7) with a relative error of less than 3%:

Isobutanol-*n*-butanol

$$\ln \gamma_1 = 0.00002550 x_2^2 - 0.00215 x_2^3 \quad (5)$$

$$\ln \gamma_2 = -0.003200 x_1^2 - 0.00215 x_1^3 \quad (6)$$

sec-Butanol-isopropanol

$$\ln \gamma_3 = -0.01923 x_4^2 + 0.1130 x_4^3 \quad (7)$$

$$\ln \gamma_4 = 0.15026 x_3^2 - 0.1130 x_3^3 \quad (8)$$

The boiling points were correlated using the general equation suggested by Wisniak and Tamir (10):

$$T = x_1 T_1^o + x_2 T_2^o + w + x_1 x_2 [C_0 + C_1(x_1 - x_2) + C_2(x_1 - x_2)^2 + \dots] \quad (9)$$

$$w = x_1 \ln(y_1/x_1) + x_2 \ln(y_2/x_2) \quad (10)$$

The predicted values of the boiling points appear in Tables III and IV, and the constants in Table V. From the values of the rmsd, a two-constant fit gives excellent results.

Acknowledgment

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

Nomenclature

α, β, A, B, C = constants

B_i = second virial coefficient, cm³/mol

P = overall pressure, mm Hg

P_i^o = vapor pressure of component i pure, mm Hg

R = gas constant

rmsd = root-mean-square deviation, $\sqrt{\sum (T_{exp} - T_{calc})^2 / n}$

t, T = temperature, °C, K

T_i^o = boiling temperature of component i pure at pressure P , K

v_i^o = specific molar volume of pure liquid i , cm³/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

Literature Cited

- (1) Ballard, L. H., van Winkle, M., *Ind. Eng. Chem.*, **44**, 2450 (1952).
- (2) Boublikova, L., Lu, B.C.Y., *J. Appl. Chem.*, **19**, 89 (1969).
- (3) Cox, J. D., *Trans. Faraday Soc.*, **57**, 1674 (1961).
- (4) Kay, W. B., Donham, W. E., *Chem. Eng. Sci.*, **4**, 1 (1955).
- (5) Murakami, S., Benson, G. C., *Bull. Chem. Soc. Jpn.*, **46**, 74 (1973).
- (6) O'Connell, J. P., Prausnitz, J. M., *Ind. Eng. Chem., Process Des. Dev.*, **6**, 245 (1967).
- (7) Redlich, O., Kister, A. T., *Ind. Eng. Chem.*, **40**, 345 (1948).
- (8) TRC Tables, "Selected Values of Properties of Chemical Compounds," Thermodynamics Research Center Data Project, College Station, Tex., 1961.
- (9) Wisniak, J., Tamir, A., *J. Chem. Eng. Data*, **20** (2), 168 (1975).
- (10) Wisniak, J., Tamir, A., *Chem. Eng. Sci.*, submitted for publication.

Received for review January 23, 1975. Accepted May 27, 1975.