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Nomenclature

α, β, δ = constants, Equation 2
$a(i), b(i), c(i)$ = constants, Equations 3 and 4
C_k = constant, Equation 7
I = number of terms in the series expansion of $(x_1 - x_2)$
P = overall pressure, mm Hg
P_i° = vapor pressure of component i pure, mm Hg
rmsd = root-mean-square deviation, $\sqrt{\Sigma(T_{exp} - T_{calc})^2/n}$
n = number of experimental points
t, T = temperature, °C, K
T_i° = boiling temperature of component i pure at pressure P, K
x_i, y_i = mole fraction composition of component i in the liquid and vapor phases
γ_i = activity coefficient of component i
$\Lambda_{ij}, \Lambda_{ji}$ = Wilson constants, Equations 5 and 6

Subscripts

exp = experimental
calc = calculated
i = component i

Literature Cited

(1) Boublikova, L., Lu, B.C.Y., J. Appl. Chem., **19**, 89 (1969).
(2) Brusset, H., Duboc, U., Coppel, A. M., Bull. Soc. Chim., 1203 (1966).
(3) Hafslund, E. R., Lovell, C. L., Ind. Eng. Chem., **38**, 556 (1947).
(4) Hudson, J. W., Van Winkle, M., Ind. Eng. Chem. Process Des. Dev., **9**, 446 (1970).
(5) Ivanov, A. B., Gershanovsky, V. C., Zelviensky, Y., Zelinsky, V. G., Khim. Farm. Zh., **8**, 2 (1974).
(6) Ocon, J., Espantoso, J., Mato, F., An. Fis. Quim., **52B**, 657 (1956).
(7) Ocon, J., Mato, F., ibid., **53B**, 461 (1957).
(8) Redlich, O., Kister, A. T., Ind. Eng. Chem., **40**, 345 (1948).
(9) TRC Tables, "Selected Values of Properties of Chemical Compounds," Thermodynamic Research Center Data Project, College Station, Tex., 1961.
(10) Wilson, G. M., J. Am. Chem. Soc., **86**, 127 (1964).
(11) Wisniak, J., Tamir, A., J. Chem. Eng. Data, **20**, 168 (1975).
(12) Wisniak, J., Tamir, A., Chem. Eng. Sci., in press.

Vapor-Liquid Equilibria of Methyl Ethyl Ketone–Diethyl Ketone, Methyl Ethyl Ketone–Methyl Isobutyl Ketone, and Diethyl Ketone–Methyl Isobutyl Ketone Systems

Jaime Wisniak* and Abraham Tamir

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

Vapor-liquid equilibrium data were determined at 760 mm Hg for the binary systems methyl ethyl ketone–diethyl ketone, methyl ethyl ketone–methyl isobutyl ketone, and diethyl ketone–methyl isobutyl ketone. The three systems presented small deviations from ideal solution behavior. The activity coefficients were correlated by the Redlich-Kister correlation. Boiling points were predicted by an empirical expression to within a maximum error of ±0.25 °C and a mean error of ±0.05 °C.

The present work was undertaken as part of a project devoted to the prediction of thermodynamic properties for chemically similar compounds. The ketone compounds investigated here differ in chain length and in spatial symmetry.

Experimental

Purity of materials. Analytical grade reagents purchased from Fluka were used without further purification after gas chromatography analysis failed to show any significant impurities. 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 (6). 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 internal diameter and packed with Chromosorb 101 and operated isothermally at 155 °C. Injector temperature was 210 °C, and the detector operated at 150 mA and 210 °C. Calibration analyses were carried out to convert the peak area ratio to the actual weight composition of the mixture. Concentration measurements were generally accurate to ±0.2%.

Table I. Physical Properties of Pure Compounds

Index	Compound	Refractive index at 25 °C	Bp, °C
1	Methyl ethyl ketone	1.3764	79.56
		1.3764 (5)	79.64 (5)
2	Diethyl ketone	1.39003	101.7
		1.39002 (5)	101.77 (5)
3	Methyl isobutyl ketone	1.3935	116.30
		1.3933 (5)	116.50 (5)

Table II. Vapor-Pressure Constants

Compound	α_i	β_i	δ_i
Methyl ethyl ketone	7.20867	1368.21	236.50
Diethyl ketone	6.97840	1281.2	210.9
Methyl isobutyl ketone	6.67272	1168.41	191.94

Table III. Experimental Vapor-Liquid Equilibrium Data for System Methyl Ethyl Ketone(1)–Diethyl Ketone(2)

t_{exp}	t_{calc}	x_1	y_1	γ_1	γ_2
99.40	99.39	0.078	0.143	1.0535	0.9961
97.15	97.18	0.155	0.263	1.0348	0.9992
96.75	96.77	0.170	0.286	1.0370	0.9974
95.50	95.45	0.220	0.352	1.0199	1.0001
94.40	94.34	0.264	0.406	1.0098	1.0046
93.45	93.51	0.298	0.444	1.0040	1.0149
90.95	90.97	0.407	0.562	0.9967	1.0225
89.37	89.38	0.479	0.631	0.9937	1.0303
87.50	87.44	0.570	0.712	0.9933	1.0339
83.85	83.90	0.743	0.846	1.0056	1.0410
81.26	81.34	0.881	0.933	1.0091	1.0657
81.10	81.06	0.898	0.942	1.0043	1.0820
81.02	80.94	0.905	0.946	1.0032	1.0845
80.31	80.31	0.946	0.969	1.0040	1.1217

Table IV. Experimental Vapor-Liquid Equilibrium Data for System Methyl Ethyl Ketone(1)–Methyl Isobutyl Ketone(3)

t_{exp}	t_{calc}	x_1	y_1	γ_1	γ_3
110.73	110.88	0.089	0.222	1.0851	0.9926
106.85	106.64	0.172	0.369	1.0245	0.9899
105.99	105.89	0.188	0.394	1.0222	0.9940
102.51	102.72	0.259	0.492	1.0108	1.0123
100.11	100.07	0.323	0.572	1.0018	1.0043
99.22	99.36	0.341	0.588	0.9983	1.0206
97.11	96.98	0.403	0.654	0.9927	1.0105
93.96	93.94	0.487	0.727	0.9933	1.0254
92.00	91.98	0.544	0.766	0.9882	1.0534
88.41	88.44	0.654	0.843	0.9994	1.0489
85.82	85.84	0.743	0.887	0.9962	1.1093
83.73	83.77	0.820	0.923	0.9977	1.1598
83.27	83.21	0.842	0.934	0.9964	1.1509

Table V. Experimental Vapor-Liquid Equilibrium Data for System Diethyl Ketone(2)–Methyl Isobutyl Ketone(3)

t_{exp}	t_{calc}	x_2	y_2	γ_2	γ_3
102.52	102.39	0.951	0.972	1.0002	0.8478
103.67	103.68	0.849	0.911	1.0160	0.8443
104.00	104.03	0.823	0.891	1.0155	0.8734
104.60	104.63	0.778	0.857	1.0159	0.8971
105.45	105.50	0.715	0.798	1.0050	0.9622
105.70	105.69	0.701	0.789	1.0064	0.9509
106.50	106.65	0.633	0.717	0.9906	1.0144
107.60	107.56	0.570	0.663	0.9867	0.9982
108.50	108.04	0.537	0.637	0.9816	0.9730
109.34	109.45	0.443	0.544	0.9935	0.9912
109.50	109.68	0.428	0.528	0.9938	0.9945
110.00	110.25	0.391	0.489	0.9941	0.9967
111.20	111.17	0.332	0.420	0.9737	0.9968
111.35	111.25	0.327	0.413	0.9682	0.9971
111.83	111.74	0.296	0.378	0.9667	0.9965
112.32	112.30	0.260	0.339	0.9744	0.9936
113.66	113.61	0.177	0.236	0.9623	0.9948
114.28	114.35	0.129	0.171	0.9417	1.0026
114.40	114.40	0.126	0.161	0.9050	1.0078

Table VI. Redlich-Kister Constants

System	B_{ij}	C_{ij}	D_{ij}	rmsd γ_i	rmsd γ_j
Methyl ethyl ketone–diethyl ketone	0.04912	0.05514	0.05400	0.0177	0.0159
Methyl ethyl ketone–methyl isobutyl ketone	0.05151	0.10331	0.06882	0.0359	0.0535
Diethyl ketone–methyl isobutyl ketone	−0.03558	−0.00385	−0.07974	0.0218	0.0484

Table VII. Correlation of Boiling Points

System	C_0	C_1	C_2	C_3	rmsd
Methyl ethyl ketone–diethyl ketone	−6.8756	1.2701	−3.0310	−1.5061	0.048
Methyl ethyl ketone–methyl isobutyl ketone	−17.137	3.5637	−4.5130	2.8715	0.1128
Diethyl ketone–methyl isobutyl ketone	−1.5616	−1.0647	1.0056	−0.8919	0.1434

Results

Constant pressure determinations were made at 760 mm Hg, and the experimental results appear in Tables III, IV, and VI. Activity coefficients were calculated from the equation

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

where

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

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

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

The constants α_i, β_i, and δ_i are reported iTable II (2, 5). The data constants for methyl isobutyl ketone were taken from ref. 2 because those reported in ref. 5 are grossly in error.

The mixed virial coefficients B_{ij} were estimated by the correlation of O'Connell-Prausnitz (3) using the molecular parameters reported by the same authors.

The activity coefficients reported in Tables III–V show that the three binaries present small deviations from ideal solution behavior. These coefficients were well correlated by the following Redlich-Kister expansion (4)

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

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

with a rmsd for any particular activity coefficient of less than 5.4%. The corresponding coefficients appear in Table VI.

Boiling points of the binary systems were correlated with the equation suggested by Wisniak and Tamir (7):

$$T = x_1 T_1^{\circ} + x_2 T_2^{\circ} + w + x_1 x_2 [C_0 +$$
$$C_1(x_1 - x_2) + C_2(x_1 - x_2)^2 + \ldots] \quad (6)$$

where

$$w = x_1 \ln (y_1/x_1) + x_2 \ln (y_2/x_2) \quad (7)$$

The corresponding constants of Equation 6 appear in Table VII together with the root-mean-square deviation. Equation 6 is capable of predicting the boiling points to within a maximum error of ±0.25 °C and a mean value of ±0.05 °C.

Acknowledgment

Nomenclature

α, β, A, B, C = constants
B_i = second virial coefficient, cm^3/mol
n = number of experimental points
P = overall pressure, mm Hg
P_i° = vapor pressure of pure component i, mm Hg
R = gas constant
rmsd = root-mean-square deviation $\sqrt{\Sigma(T_{exp} - T_{calc})^2/n}$, $\sqrt{\Sigma(\gamma_{exp} - \gamma_{calc})^2/n}$
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

Subscripts

exp = experimental
calc = calculated
i = component i

Literature Cited

(1) Boublikova, L., Lu, B.C.Y., J. Appl. Chem., **19**, 89 (1969).
(2) Fuge, E.T.J., Bowden, S. T., Jones, W. J., J. Phys. Chem., **56**, 1013 (1952).
(3) O'Connell, J. P., Prausnitz, J. M., Ind. Eng. Chem. Process Des. Dev., **6**, 245 (1967).
(4) Redlich, O., Kister, A. T., Ind. Eng. Chem., **40**, 345 (1948).
(5) TRC Tables, "Selected Values of Properties of Chemical Compounds," Thermodynamics Research Center Data Project, College Station, Tex., 1974.
(6) Wisniak, J., Tamir, A., J. Chem. Eng. Data, **20**, 168 (1975).
(7) Wisniak, J., Tamir, A., Chem. Eng. Sci., in press.