(23) Good, W. D. J. Chem. Thermodyn. 1970, 2, 237.
(24) Good, W. D. J. Chem. Thermodyn. 1972, 4, 709.
(25) Månsson, M. J. Chem. Thermodyn. 1969, 1, 141.
(26) Stern, J. H.; Dorer, F. H. J. Phys. Chem. 1962, 66, 97.
(27) Good, W. D. J. Chem. Eng. Data 1972, 17, 158.
(28) Månsson, M. J. Chem. Thermodyn. 1974, 6, 1153.
(29) Wadsö, I. Acta Chem. Scand. 1969, 23, 2061.
(30) Good, W. D.; Moore, R. T. J. Chem. Eng. Data 1970, 15, 150.
(31) Lebedeva, N. D.; Katin, Yu. A.; Akhmedova, G. Ya. Zh. Fiz. Khim. 1971, 45, 1357.
(32) Good, W. D. J. Chem. Eng. Data 1972, 17, 28.
(33) McCullough, J. P.; Good, W. D. J. Phys. Chem. 1961, 65, 1430.

(34) Sunner, S.; Svensson, C.; Zelepuga, A. S. J. Chem. Thermodyn. 1979, 11, 491.
(35) Harrop, D.; Head, A. J.; Lewis, G. B. J. Chem. Thermodyn. 1970, 2, 203.
(36) Sellers, P. J. Chem. Thermodyn. 1970, 2, 211.
(37) Sellers, P. J. Chem. Thermodyn. 1977, 9, 139.
(38) Sellers, P. Acta Chem. Scand. 1971, 25, 2099.
(39) Byström, K.; Månsson, M. J. Chem. Soc., Perkin Trans. 2 1982, 565.

Activity Coefficients and Excess Gibbs Free Energies for the Systems Isobutyl Methyl Ketone (1)–1-Pentanol (2) and Isobutyl Methyl Ketone (1)–1-Hexanol (2)

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Isobaric boiling point data for the systems isobutyl methyl ketone (1)–1-pentanol (2) and isobutyl methyl ketone (1)–1-hexanol (2) were obtained by the indirect method over the entire range of composition by using a standard Swietoslawski type ebulliometer. The measurements were made at 200 and 700 mmHg. The experimental t–x data were used to estimate Wilson parameters and then used to calculate the equilibrium vapor compositions and the theoretical points for these binary mixtures. These Wilson parameters are useful to calculate activity coefficients, and these in turn are useful to calculate excess Gibbs free energy. Excess Gibbs free energies are positive over the entire range of composition in both the binary systems.

Introduction

Evaporation has been used as an effective means of separation in chemical processing. Evidently an accurate and complete knowledge of vapor–liquid equilibrium data on the mixture under consideration is necessary for the design of distillation equipment. Generally vapor–liquid equilibrium data are obtainable under two fixed conditions, namely, isothermal and isobaric. Most distillation process are carried out at constant pressure rather than constant temperature, so that the temperature–composition curves are more practical in making engineering calculations such as the number of plates, although for theoretical considerations the pressure–composition curves are preferable. Here, an attempt has been made to calculate vapor compositions, activity coefficients, and excess Gibbs free energies for the systems isobutyl methyl ketone (1)–1-pentanol (2) and isobutyl methyl ketone (1)–1-hexanol (2) at 200 and 700 mmHg.

Experimental Section

The vapor–liquid equilibrium measurements were studied in a Swietoslawski ebulliometer (1). The ebulliometer was con-

nected to a vacuum system. The pressures were measured with a mercury manometer with an accuracy of ±1 mmHg. The temperatures were measured with a PT100 thermometer with an accuracy of ±0.1 °C. The detailed procedure was described previously (1).

Isobaric Binary Systems. The boiling points of the systems isobutyl methyl ketone (1)–1-pentanol(2) and isobutyl methyl ketone (1)–1-hexanol (2) were determined over the entire range of composition. Mixtures of different compositions were prepared by taking quantities (by weight) of the pure materials. The boiling points for the known binary compositions were measured at 200 and 700 mmHg.

The boiling point of a specified composition was first measured at 200 mmHg. Then the pressure was raised to 700 mmHg and the boiling point was determined. The system was brought back to 200 mmHg, where the boiling point measurement was repeated, and finally the measurement was repeated at 700 mmHg thereby obtaining duplicate sets of boiling points at both the pressures of interest.

Purification of Materials. The alcohols were purified by the method described by Rao and Naidu (2). Isobutyl methyl ketone was purified by the method described by Reddy and Naidu (3). The purity of the samples was checked by measuring densities, refractive indices, and boiling points. The densities were measured with a standard bicapillary pycnometer which gave an accuracy of 5 parts in 10^5. Refractive indices were determined with an Abbe's refractometer which gave an accuracy of ±0.0002. The measured values are in good agreement with the literature values (4, 5).

Results and Discussion

In the present work, isobaric t–x measurements are used for the data reduction. The model for expressing the compo-

Table I. Wilson Parameters with Standard Deviation

system	P, mmHg	$(\lambda_{12} - \lambda_{11})/R$, K	$(\lambda_{12} - \lambda_{22})/R$, K	std dev σ_t, °C
isobutyl methyl ketone (1)-1-pentanol (2)	200	-289.71	1035.30	0.17
isobutyl methyl ketone (1)-1-pentanol (2)	700	-293.28	1558.51	0.54
isobutyl methyl ketone (1)-1-hexanol (2)	200	-305.93	7410.06	0.18
isobutyl methyl ketone (1)-1-hexanol (2)	700	-269.43	213.35	0.69

Table II. Antoine Constants of the Pure Compounds with Standard Deviation

compound	A	B	C	σ_P, %
isobutyl methyl ketone	15.6384	2853.03	200.83	0.4
1-pentanol	17.8107	3786.78	201.29	0.4
1-hexanol	17.9754	3982.29	206.67	0.6

Table III. Isobutyl Methyl Ketone (1)-1-Pentanol (2) t-x Data at 200 mmHg

x	t(exptl), °C	t(calcd),[a] °C	t(exptl) - t(calcd), °C
0.1471	94.6	93.9	+0.7
0.1471	94.7	93.9	0.8
0.2381	90.0	90.1	-0.1
0.2381	90.0	90.1	-0.1
0.3748	85.1	85.2	-0.1
0.3748	85.2	85.2	+0.0
0.4059	84.1	84.2	-0.1
0.4059	84.2	84.2	0.0
0.5112	81.3	81.3	0.0
0.5112	81.4	81.3	0.1
0.6653	78.1	77.9	0.2
0.6653	78.2	77.9	0.3
0.6710	78.1	77.8	0.3
0.6710	78.0	77.8	0.2
0.7725	76.3	76.3	0.0
0.7725	76.4	76.3	-0.1
0.8516	75.2	75.4	-0.1
0.9193	74.7	75.0	-0.3
0.9193	74.8	75.0	-0.2

[a] Using Wilson equation.

sition and temperature dependence is chosen to be the Wilson equation (6).

$$\ln \gamma_1 =$$

$$-\ln [x_1 + \Lambda_{12}x_2] + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right] \quad (1)$$

$$\ln \gamma_2 =$$

$$-\ln [x_2 + \Lambda_{21} x_1] + x_1 \left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} \right] \quad (2)$$

where

$$\Lambda_{12} = \frac{V_2^L}{V_1^L} \exp\left[-\frac{\lambda_{12} - \lambda_{11}}{RT} \right] \quad (3)$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L} \exp\left[-\frac{\lambda_{12} - \lambda_{22}}{RT} \right] \quad (4)$$

where V_1^L and V_2^L are liquid molal volumes and ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{12} - \lambda_{22}$) are temperature-independent (to some extent) Wilson parameters. λ's are the energies of interaction between the molecules designated in the subscripts. The optimum Wilson

Table IV. Isobutyl Methyl Ketone (1)-1-Pentanol (2) t-x Data at 700 mmHg

x	t(exptl), °C	t(calcd),[a] °C	t(exptl) - t(calcd), °C
0.1471	128.1	128.2	-0.1
0.1471	128.2	128.2	0.0
0.2381	123.7	124.6	-0.9
0.2381	123.8	124.6	-0.8
0.3748	119.6	119.9	-0.3
0.3748	119.8	119.9	-0.1
0.4059	118.9	119.0	-0.1
0.4059	119.0	119.0	0.0
0.5112	116.8	116.2	0.6
0.5112	116.8	116.2	0.6
0.6653	113.8	113.2	0.6
0.6653	113.7	113.2	0.5
0.6710	113.8	113.1	0.7
0.6710	113.7	113.1	0.6
0.7725	111.8	111.8	0.0
0.7725	111.8	111.8	0.0
0.8516	110.8	111.2	-0.4
0.8516	110.8	111.2	-0.4
0.8516	110.8	111.2	-0.4
0.9193	110.2	111.0	-0.8
0.9193	110.3	111.0	-0.7

[a] Using Wilson equation.
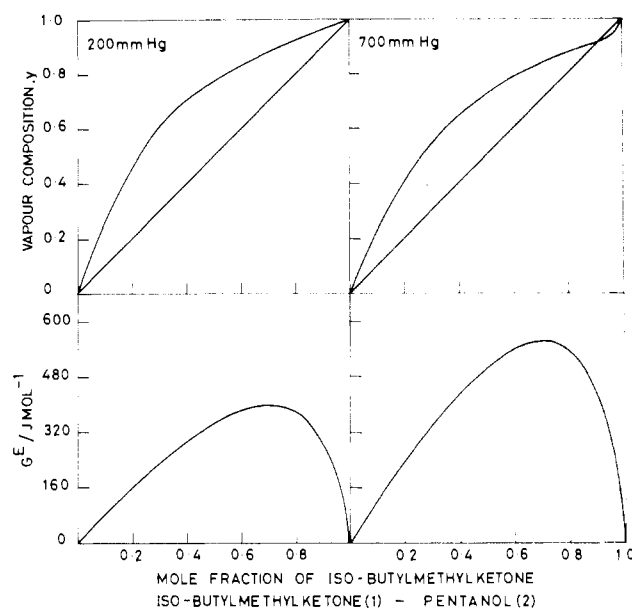
Figure 1. Vapor compositions and excess Gibbs free energies for the system isobutyl methyl ketone (1)-1-pentanol (2) at 200 and 700 mmHg.

parameters ($\lambda_{12} - \lambda_{11}$)/$R$ and ($\lambda_{12} - \lambda_{22}$)/$R$ are obtained by minimizing the objective function ϕ as defined by eq 5 using

$$\phi = \sum (P_{calcd}/P_{exptl} - 1.0)^2 \quad (5)$$

Neldar-Mead optimization technique. Wilson parameters so obtained are presented in Table I along with the standard deviation of the fit.

Since the prediction of vapor-liquid equilibrium data involves the vapor pressure data of pure compounds, the same has been determined for isobutyl methyl ketone, 1-pentanol, and 1-hexanol. The Antoine constants for the pure components were obtained by nonlinear regression analysis of the experimental data. The Antoine constants are presented in Table II. The measured boiling points, calculated boiling points from the Wilson equation, and ideal boiling points are presented in Tables III-VI. The excess Gibb free energies were calculated by using activity coefficients.

$$G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (6)$$

Table V. Isobutyl Methyl Ketone (1)-1-Hexanol (2) t-x Data at 200 mmHg

x	t(exptl), °C	t(calcd),[a] °C	t(exptl) − t(calcd), °C
0.1263	108.0	108.0	0.0
0.1263	108.1	108.0	0.1
0.2090[b]	102.8	101.7	1.1
0.2090[b]	102.8	101.7	1.1
0.3381	93.5	93.6	−0.1
0.3381	93.5	93.6	−0.1
0.4705	87.2	87.1	0.1
0.4705	87.1	87.1	0.0
0.5371	84.5	84.4	0.1
0.5371	84.6	84.4	0.2
0.6374	81.1	80.9	0.3
0.6374	81.2	80.9	−0.2
0.7512	77.6	77.8	−0.2
0.7512	77.6	77.8	−0.1
0.8041	76.6	76.7	−0.1
0.8041	76.7	76.7	0.0
0.8614	75.6	75.8	−0.2
0.8614	75.6	75.8	−0.2
0.9043	74.9	75.2	−0.3
0.9043	74.8	75.2	−0.4

[a] Using Wilson equation. [b] Points rejected from analysis.

Table VI. Isobutyl Methyl Ketone (1)-1-Hexanol (2) t-x Data at 700 mmHg

x	t(exptl), °C	t(calcd),[a] °C	t(exptl) − t(calcd), °C
0.1263[b]	141.1	143.3	−2.2
0.1263[b]	141.2	143.3	−2.1
0.2090	136.7	137.3	−0.6
0.2090	136.8	137.3	−0.5
0.2370	134.4	135.5	−1.1
0.2370	134.5	135.5	−1.0
0.3381	129.7	129.7	0.2
0.3381	129.7	129.7	0.2
0.3414	129.4	129.4	0.0
0.3414	129.6	129.4	0.2
0.4705	124.0	123.2	0.8
0.4705	124.2	123.2	1.0
0.6374	118.1	117.3	0.8
0.6374	118.2	117.3	0.9
0.7512	114.9	114.5	0.2
0.7512	114.8	114.5	0.3
0.8041	113.5	113.6	−0.1
0.8041	113.5	113.6	−0.1
0.8614	111.8	112.8	−1.0
0.8614	111.9	112.8	−0.9

[a] Using Wilson equation. [b] Points rejected from analysis.

Table VII. Vapor Compositions, Activity Coefficients, and Excess Gibbs Free Energies for the System Isobutyl Methyl Ketone (1)-1-Pentanol (2) at 200 mmHg

x	y(calcd)	t(calcd), °C	γ_1	γ_2	G^E, J mol^{-1}
0.05	0.1513	98.6	1.3420	1.0001	44
0.10	0.2772	96.1	1.3320	1.0004	86
0.15	0.3824	93.8	1.3220	1.0010	125
0.20	0.4708	91.6	1.3118	1.0020	163
0.25	0.5457	89.6	1.3013	1.0035	199
0.30	0.6093	87.7	1.2902	1.0058	232
0.35	0.6636	86.0	1.2785	1.0091	264
0.40	0.7102	84.4	1.2660	1.0140	294
0.45	0.7503	82.9	1.2523	1.0208	321
0.50	0.7850	81.6	1.2375	1.0306	345
0.55	0.8151	80.4	1.2211	1.0445	366
0.60	0.8412	79.2	1.2031	1.0644	383
0.65	0.8641	78.2	1.1831	1.0931	395
0.70	0.8840	77.4	1.1610	1.1356	400
0.75	0.9016	76.6	1.1365	1.2002	396
0.80	0.9171	76.0	1.1096	1.3031	380
0.85	0.9312	75.5	1.0804	1.4799	347
0.90	0.9446	75.1	1.0493	1.8199	288
0.95	0.9600	74.9	1.0188	2.6540	185

Table VIII. Vapor Compositions, Activity Coefficients, and Excess Gibbs Free Energies for the System Isobutyl Methyl Ketone (1)-1-Pentanol (2) at 700 mmHg

x	y(calcd)	t(calcd), °C	γ_1	γ_2	G^E, J mol^{-1}
0.05	0.1260	132.5	1.4840	1.0002	65
0.10	0.2348	130.2	1.4682	1.0008	126
0.15	0.3290	128.1	1.4522	1.0019	185
0.20	0.4110	126.0	1.4358	1.0037	240
0.25	0.4824	124.1	1.4190	1.0064	293
0.30	0.5450	122.4	1.4015	1.0102	343
0.35	0.5998	120.7	1.3832	1.0156	389
0.40	0.6481	119.2	1.3639	1.0231	433
0.45	0.6906	117.8	1.3434	1.0333	472
0.50	0.7282	116.5	1.3216	1.0475	507
0.55	0.7614	115.4	1.2983	1.0670	537
0.60	0.7908	114.3	1.2732	1.0942	561
0.65	0.8169	113.4	1.2461	1.1329	577
0.70	0.8401	112.6	1.2169	1.1890	584
0.75	0.8607	112.0	1.1853	1.2737	579
0.80	0.8790	115.5	1.1511	1.4088	557
0.85	0.8954	111.2	1.1142	1.6448	512
0.90	0.9103	111.0	1.0746	2.1287	431
0.95	0.9295	111.1	1.0331	3.5384	289

Table IX. Vapor Compositions, Activity Coefficients, and Excess Gibbs Free Energies for the System Isobutyl Methyl Ketone (1)-1-Hexanol (2) at 200 mmHg

x	y(calcd)	t(calcd), °C	γ_1	γ_2	G^E, J mol^{-1}
0.00	0.0000				
0.05	0.2311	114.9	1.2562	0.9999	35
0.10	0.4015	110.2	1.2482	0.9996	67
0.15	0.5289	106.1	1.2420	0.9991	96
0.20	0.6257	102.3	1.2367	0.9983	124
0.25	0.7001	98.9	1.2322	0.9973	149
0.30	0.7582	95.8	1.2281	0.9962	174
0.35	0.8040	93.0	1.2202	0.9950	198
0.40	0.8406	90.4	1.2157	0.9941	221
0.45	0.8700	88.0	1.2105	0.9935	244
0.50	0.8939	85.9	1.2041	0.9940	266
0.55	0.9134	83.9	1.1962	0.9961	287
0.60	0.9295	82.2	1.1862	1.0012	307
0.65	0.9427	80.6	1.1737	1.0113	325
0.70	0.9536	79.1	1.1579	1.0299	341
0.75	0.9627	77.9	1.1384	1.0634	352
0.80	0.9702	76.8	1.1381	1.1247	356
0.85	0.9764	75.9	1.1134	1.2445	347
0.90	0.9816	75.3	1.0830	1.5141	316
0.95	0.9857	94.9	1.0455	2.3911	239
1.00	1.0000				

Table X. Vapor Compositions, Activity Coefficients, and Excess Gibbs Free Energies for the System Isobutyl Methyl Ketone (1)-1-Hexanol (2) at 700 mmHg

x	y(calcd)	t(calcd), °C	γ_1	γ_2	G^E, J mol^{-1}
0.00					0
0.05	0.1874	149.8	1.4505	1.0001	63
0.10	0.3379	145.5	1.4340	1.0005	122
0.15	0.4521	141.5	1.4182	1.0012	177
0.20	0.5459	137.9	1.4030	1.0023	229
0.25	0.6217	134.7	1.3880	1.0040	277
0.30	0.6834	131.6	1.3729	1.0065	323
0.35	0.7340	128.9	1.3576	1.0101	365
0.40	0.7759	126.4	1.3417	1.0152	405
0.45	0.8108	124.1	1.3250	1.0224	441
0.50	0.8400	122.0	1.3072	1.0327	474
0.55	0.8645	120.2	1.2879	1.0473	504
0.60	0.8853	118.5	1.2670	1.0682	528
0.65	0.9029	117.0	1.2441	1.0987	546
0.70	0.9179	115.7	1.2187	1.1441	556
0.75	0.9307	114.6	1.1907	1.2143	557
0.80	0.9416	113.6	1.1595	1.3286	542
0.85	0.9509	112.9	1.1249	1.5329	507
0.90	0.9589	112.5	1.0864	1.9636	438
0.95	0.9658	112.2	1.0437	3.3005	309
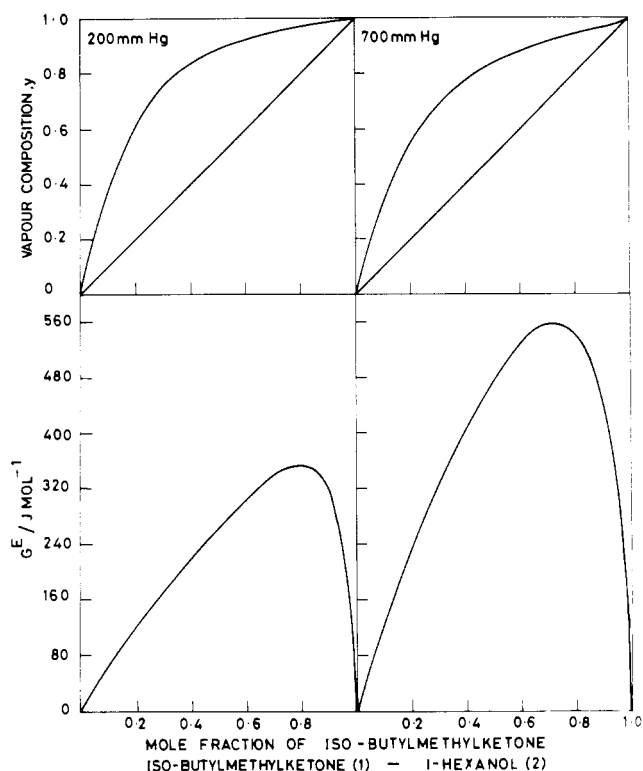
Figure 2. Vapor compositions and excess Gibbs free energies for the system isobutyl methyl ketone (1)-1-hexanol (2) at 200 and 700 mmHg.

The vapor composition (Y), activity coefficients, and excess Gibbs free energies are presented in Tables VII–X and represented in Figures 1 and 2. The excess Gibbs free energies are positive over the entire range of composition. The G^E values for the two binary systems fall in the order 1-pentanol,

1-hexanol. The positive G^E values over the entire range of composition indicated that there is a strong attraction between unlike molecules through hydrogen bonding.

Glossary

A, B, C	Antoine constants
P	pressure, mmHg
t	temperature, °C
x	mole fraction in liquid phase
y	vapor composition

Greek Letters

γ	activity coefficient
Λ	Wilson parameter

Subscripts

1	isobutyl methyl ketone
2	normal alcohols

Registry No. Isobutyl methyl ketone, 108-10-1; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3.

Literature Cited

(1) Hala, E.; Pick, J.; Fried, V.; Vilim, O. "Vapor-Liquid Equilibrium"; Pergamon Press: Oxford, 1967.
(2) Rao, M. V. P.; Naidu, P. R. Can. J. Chem. **1974**, 52, 788.
(3) Reddy, K. S.; Naidu, P. R. Aust. J. Chem. **1979**, 32, 687.
(4) Timmermans, J. "Physico Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1965.
(5) Dean, J. A. "Langes Handbook of Chemistry"; McGraw-Hill: New York, 1973.
(6) Wilson, G. M. J. Am. Chem. Soc. **1964**, 86, 127.

Activity Coefficients and Excess Gibbs Free Energies of 1,2-Dichloroethane with 1-Pentanol and 1-Hexanol

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Vapor–liquid equilibrium data for the systems 1,2-dichloroethane (1)-1-pentanol (2) and 1,2-dichloroethane-1-hexanol (2) were measured by the indirect method from the composition vs. boiling point (x–t) measurements made in a standard Swietoslawski type ebulliometer. The measurements were made at 200 and 700 mmHg. The experimental t-x data were used to estimate Wilson parameters; these in turn are useful to calculate vapor compositions, boiling points, and activity coefficients. These activity coefficients are useful to calculate excess Gibbs free energy G^E.

Introduction

Evaporation has been used as an effective means of separation in chemical processing. Evidently an accurate and complete knowledge of vapor–liquid equilibrium on the mixture

under consideration is necessary for the design of distillation equipment. Generally vapor–liquid equilibrium data are obtainable under two fixed conditions, namely, isothermal and isobaric. Most distillation processes are carried out at constant pressure rather than constant temperature. Temperature–composition curves are more practical in making engineering calculations such as the number of plates, although for theoretical consideration the pressure–composition curves are preferable. As part of a continuing study of alcohol–chloroethane systems, vapor–liquid equilibrium data on 1,2-dichloroethane-1-pentanol and 1,2-dichloroethane-1-hexanol systems are determined at 200 and 700 mmHg, because the data on these systems have not been reported in literature.

Experimental Section

The vapor–liquid equilibrium measurements were studied in a standard Swietoslawski type ebulliometer (1). The ebulliom-