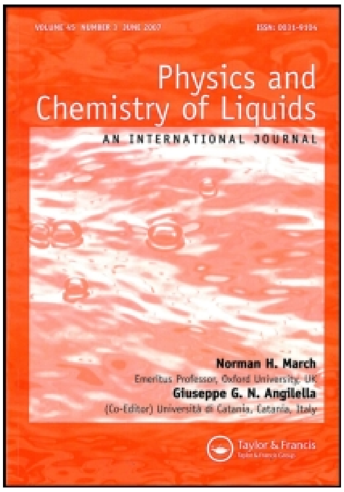

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Phase Equilibria in the Systems 4-Methyl-2-Pentanone Octane and Hexane 1,3-Dioxolane

Jaime Wisniak[a]
[a] Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

To cite this Article Wisniak, Jaime(1999) 'Phase Equilibria in the Systems 4-Methyl-2-Pentanone Octane and Hexane 1,3-Dioxolane', Physics and Chemistry of Liquids, 37: 5, 493 — 503

To link to this Article: DOI: 10.1080/00319109908035933

URL: http://dx.doi.org/10.1080/00319109908035933

Phys. Chem. Liq., 1999, Vol. 37, pp. 493–503
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

PHASE EQUILIBRIA IN THE SYSTEMS 4-METHYL-2-PENTANONE + OCTANE AND HEXANE + 1,3-DIOXOLANE

JAIME WISNIAK

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105

(Received 29 January 1998)

Vapor – liquid equilibrium at 94 kPa has been determined for the binary systems 4-methyl-2-penatanone (methyl isobutyl ketone) + octane and hexane + 1,3-dioxolane. The system 4-methyl-2-pentanone + octane behaves like a regular solution, with moderate deviations from ideal behavior, and presents an azeotrope that boils at 384.05 K and contains 70 mole % ketone. The system hexane + 1,3-dioxolane deviates strongly from ideal behavior and has an azeotrope that boils at 332.76 K and contains 55 mole % hexane. The activity coefficients and boiling points of both binary systems were well correlated with its composition by the Redlich – Kister, Wohl, Wilson, UNIQUAC, NRTL and Wisniak – Tamir equations.

Keywords: Vapor – liquid equilibrium; models

INTRODUCTION

The present work is part of our program to determine the vapor – liquid equilibria (VLE) of systems containing an oxygenate and a gasoline component. No isothermal or isobaric vapor – liquid equilibria data are available for either of the systems reported here.

EXPERIMENTAL SECTION

Purity of Materials

Hexane (99.73 mass %), octane (99.80 mass %), 1,3-dioxolane (99.94 mass %), and 4-methyl-2-pentanone (99.80 mass %) were purchased from Aldrich. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table I.

Apparatus and Procedure

An all glass vapor–liquid-equilibrium apparatus model 602, manufactured by Fischer Labor-und Verfahrenstechnik (Germany), was used in the equilibrium determinations. General details of the experimental equipment and procedure appear in another publication [1]. The equilibrium temperature was measured with an accuracy of ± 0.01 K using a Lauda thermometer, model R42/2, provided with a 4 mm diameter Pt-100 temperature sensor. The pressure was measured by a Vac Probs with an accuracy of ± 0.07 kPa. On the average the system reached equilibrium conditions after 0.5 – 1 h of operation. Samples, taken by syringing out 0.7 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a Gow-Mac

TABLE I Mole percent GLC purities (mass %), refractive index n_D at the Na D line and normal boiling points T of pure components

Component (purity/mass %)	$n_D(298.15\,K)$	T/K
hexane (99.73)	1.37281[a]	341.84[a]
	1.37226[b]	341.886[b]
octane (99.80)	1.37301[a]	341.84[a]
	1.39505[b]	398.823[b]
1,3-dioxolane (99.94)	1.3980[a]	348.60[a]
	1.3984[c]	348.55[d]
4-methyl-2-pentanone (99.80)	1.3930[a]	389.57[a]
	1.3933[e]	389.65[e]

[a] Measured.
[b] TRC *a*-1010, 1995 [11].
[c] Castellari *et al.* [12].
[d] Wu and Sandler [13].
[e] TRC *a*-5920, 1994 [14].

series 550 P apparatus equipped with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter, packed with SE-30 for the analysis of the system 4-methyl-2-pentanone + Octane and OV-17 for the analysis of the hexane + 1,3-dioxolane system. Injector and detector temperatures for both binaries were 493.15 and 543.15 K respectively, and column temperatures were 383.15 K for the system 4-methyl-2-pentanone + octane and 313.15 K for the system hexane + 1,3-dioxolane. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fits had a correlation coefficient R^2 better than 0.99. Concentration measurements were accurate to better than ±0.005 mole fraction.

RESULTS

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at $P = 94\,\mathrm{kPa}$ are reported in Tables II and III and Figures 1–4, together with the activity coefficients γ_i which were calculated from the following equation [2]

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + y_j^2 \frac{d_{ij} P}{RT} \tag{1}$$

where T and P are the boiling point and the total pressure, V_i^L is the molar liquid volume of component i, P_i^0 is the pure component vapor pressure, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} the cross second virial coefficient and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \tag{2}$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Eq. (1) is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range

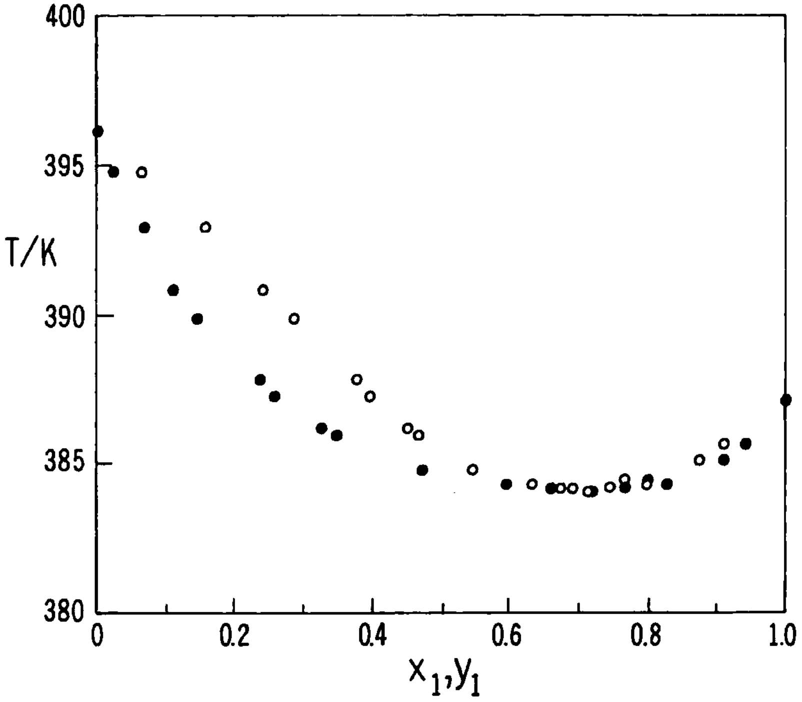

FIGURE 1 Boiling temperature diagram for the system 4-methyl-2-pentanone (1) + octane (2) at 94 kPa (●, ○).

under consideration. The pure component vapor pressures P_i^0 were calculated according to the Antoine equation:

$$\log(P_i^0/kPa) = A_i - \frac{B_i}{(T/K) - C_i} \tag{3}$$

where the Antoine constants A_i, B_i and C_i are reported in Table IV. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of O'Connell and Prausnitz [3] using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. The last two terms in Eq. (1), particularly the second one that expresses the correction due to the non-ideal behavior of the vapor phase, contributed less than 2% to the activity coefficients of both binary systems; in general, their influence was important only at

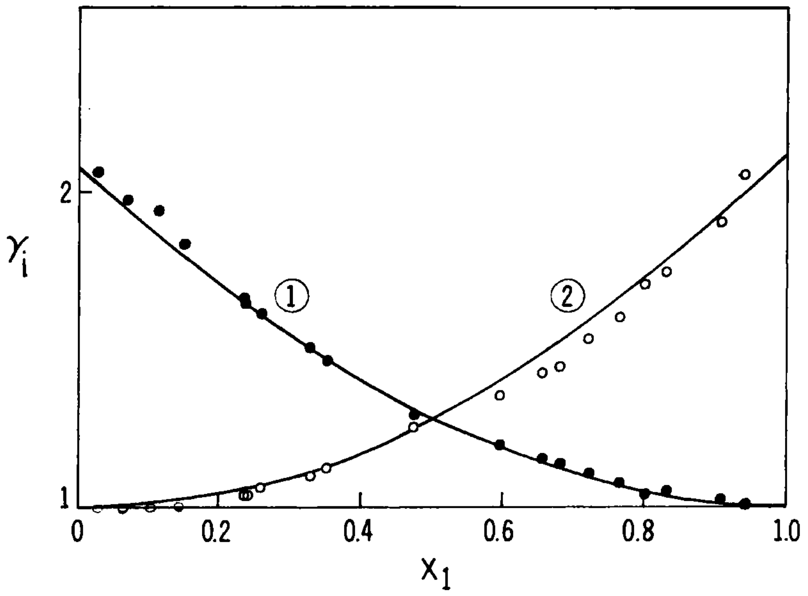

FIGURE 2 Activity coefficients for the system 4-methyl-2-pentanone (1) + octane (2) at 94 kPa. Experimental data (●, ○), predicted by the UNIQUAC model (———).

very dilute concentrations. The calculated activity coefficients are reported in Tables II and III and are estimated accurate to within ± 3%. Tables II and III contain also the activity coefficients at infinite dilution, calculated by the procedure suggested by Wisniak *et al.* [4]. The results reported in these tables indicate that the binary system 4-methyl-2-pentanone + octane deviates moderately from ideal behavior and presents an azeotrope that boils at 384.05 K and contains 70 mole % ketone. The results for the system hexane (3) + 1,3-dioxolane (4) indicate that it deviates strongly from ideal behavior and has an azeotrope that boils at 332.76 K and contains 55 mole % hexane. In both cases the azeotropic conditions were determined by double interpolation of the variables. The vapor-liquid equilibria data reported in Tables II and III were found to be thermodynamically consistent by the L-W point-to-point and area method of Wisniak [5], and the point-to-point method of Van Ness *et al.* [6], as modified by Fredenslund *et al.* [7]. For both binaries, the residuals of the Fredenslund test were randomly distributed, as measured by the

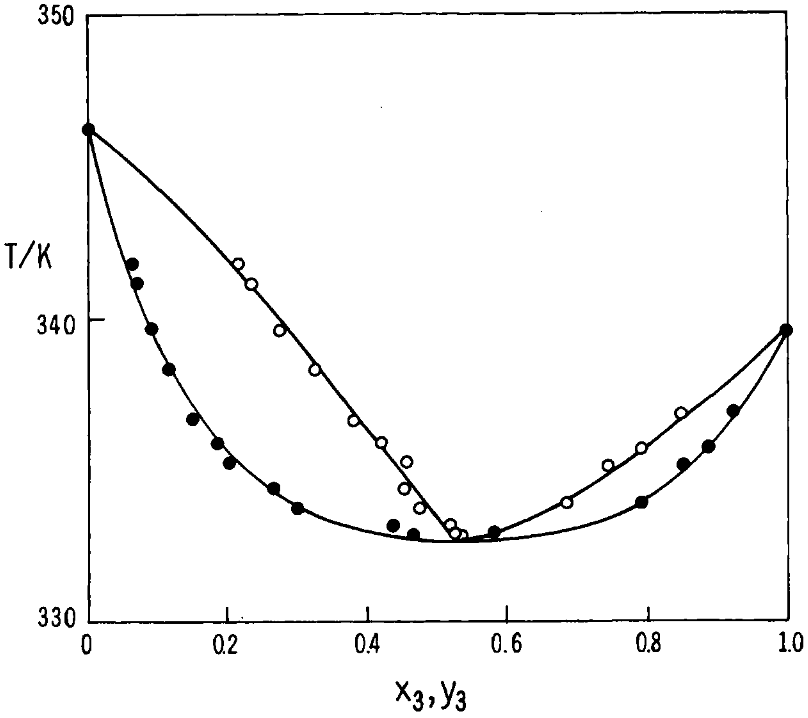

FIGURE 3 Boiling temperature diagram for the system hexane (3) + 1,3-dioxolane (4) at 94 kPa (●, ○ ———).

Durbin-Watson statistic. The activity coefficients of both binary systems were correlated well with the Redlich–Kister, Wohl, Wilson, NRTL, and UNIQUAC equations [8]. The UNIQUAC parameters of the different components appear in Table V. The following expression was used for the Redlich–Kister [9] expansion

$$\log(\gamma_1/\gamma_2) = B(x_2 - x_1) + C(6x_1x_2 - 1) + D(x_2 - x_1)(8x_1x_2 - 1) \tag{4}$$

The values of the constants B, C and D were determined by multilinear regression and appear in Table VI together with the pertinent statistics. It is seen that the Redlich–Kister model gives a good representation of the data for both systems and that the system

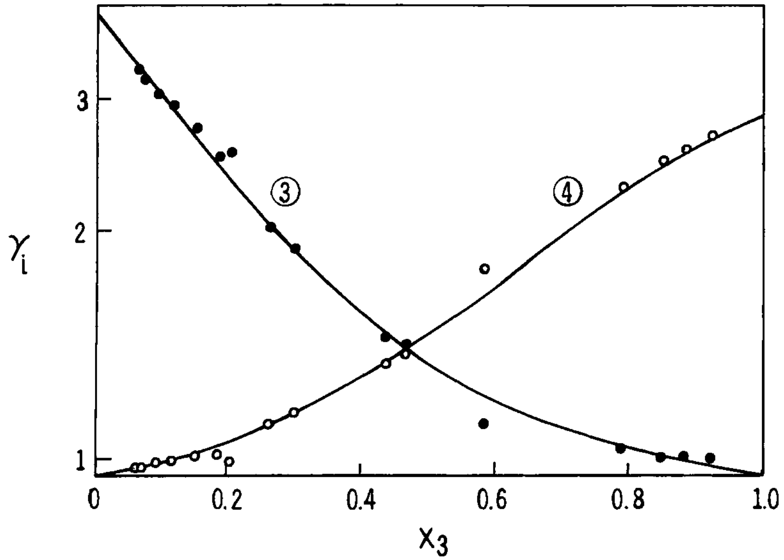

FIGURE 4 Activity coefficients for the system hexane (3) + 1,3-dioxolane (4) at 94 kPa. Experimental data (●, ○), predicted by the Wohl model (———).

TABLE II Experimental vapor–liquid equilibrium data for octane (1) + 4-methyl-2-pentanone (2) at 94 kPa

T/K	x_1	y_1	γ_1	γ_3	$-B_{11}/$ $(cm^3\ mol^{-1})$	$-B_{33}/$ $(cm^3\ mol^{-1})$	$-B_{13}/$ $(cm^3\ mol^{-1})$	$\Delta G^E/RT$
396.17	0	0						0
394.80	0.026	0.066	2.0838	0.9942	1386	1784	1578	0.013
392.93	0.068	0.156	1.9603	0.9877	1404	1806	1598	0.034
390.86	0.113	0.239	1.9113	0.9902	1424	1832	1620	0.064
389.84	0.148	0.284	1.7801	0.9982	1434	1844	1631	0.084
387.78	0.234	0.377	1.5781	1.0236	1454	1871	1655	0.125
387.78	0.238	0.379	1.5615	1.0252	1454	1871	1655	0.125
387.2	0.259	0.396	1.5241	1.0425	1460	1878	1661	0.140
386.19	0.328	0.454	1.4165	1.0698	1470	1891	1673	0.160
385.91	0.350	0.467	1.3758	1.0886	1473	1895	1676	0.167
384.75	0.474	0.543	1.2209	1.1913	1485	1910	1690	0.187
384.22	0.595	0.629	1.1431	1.2758	1490	1917	1696	0.178
384.09	0.657	0.672	1.1088	1.3395	1492	1919	1698	0.168
384.10	0.680	0.689	1.0991	1.3585	1492	1919	1697	0.162
384.00	0.721	0.713	1.0754	1.4431	1493	1920	1699	0.155
384.17	0.765	0.745	1.0544	1.5133	1491	1918	1697	0.138
384.40	0.802	0.767	1.029	1.6294	1489	1915	1694	0.120
384.24	0.831	0.798	1.0363	1.6732	1490	1917	1696	0.116
385.05	0.909	0.875	1.0169	1.8685	1482	1906	1686	0.072
385.65	0.942	0.910	1.0037	2.0748	1476	898	1679	0.046
387.04	1	1						0
γ_i^∞ [4]	2.28	2.26						

TABLE III Experimental vapor – liquid equilibrium data for hexane (3) + 1,3-dioxolane (4) at 94 kPa

T/K	x_3	y_3	γ_3	γ_4	$-B_{33}/$ $(cm^3\ mol^{-1})$	$-B_{34}/$ $(cm^3\ mol^{-1})$	$-B_{44}/$ $(cm^3\ mol^{-1})$	$\Delta G^E/RT$
346.30	0	0						0
341.18	0.061	0.215	3.290	0.969	1332	1332	1332	0.043
339.63	0.070	0.235	3.190	0.974	1338	1338	1338	0.056
338.25	0.091	0.278	3.046	0.990	1354	1354	1354	0.092
336.62	0.115	0.326	2.949	0.995	1368	1368	1368	0.120
335.88	0.151	0.379	2.747	1.011	1385	1385	1385	0.161
335.21	0.185	0.416	2.521	1.015	1392	1392	1392	0.183
334.31	0.204	0.455	2.550	0.994	1400	1400	1400	0.186
333.67	0.263	0.454	2.028	1.110	1409	1409	1409	0.263
333.15	0.301	0.475	1.897	1.149	1416	1416	1416	0.29
332.83	0.436	0.518	1.447	1.335	1422	1422	1422	0.324
332.93	0.466	0.536	1.416	1.373	1425	1425	1425	0.331
333.87	0.583	0.528	1.111	1.781	1424	1424	1424	0.302
335.05	0.790	0.684	1.032	2.287	1414	1414	1414	0.199
335.65	0.850	0.744	1.005	2.485	1401	1401	1401	0.141
336.82	0.884	0.791	1.008	2.572	1395	1395	1395	0.117
273.15	0.924	0.851	1.001	2.684	1383	1383	1383	0.076
339.56	1	1						0
γ_i^∞ [4]	4.10	3.55						

TABLE IV Antoine coefficients, Eq. (3)

Compound	A_i	B_i	C_i
hexane[a]	6.000 139	1170.875	48.833
octane[b]	6.050 75	1356.36	63.515
1,3-dioxolane[c]	6.231 82	1236.7	55.91
4-methyl-2-pentanone[d]	5.822 203	1190.69	77.70

[a] TRC *k*-1440, 1994 [11].
[b] TRC *k*-1490, 1990 [11].
[c] Wu and Sandler [13].
[d] TRC *k*-5981, 1981 [14].

TABLE V UNIQUAC parameters

Component	*R*	*Q*
hexane	4.998	3.856
octane	5.8486	4.936
1,3-dioxolane	2.5110	2.100
4-methyl-2-pentanone	4.5959	3.912

4-methy-2-pentanone + octane behaves like a regular solution. The parameters of the Wohl, Wilson, NRTL and UNIQUAC equations were obtained by minimizing the following objective function (OF)

$$\mathrm{OF}=\sum_{i=1}^{N}\left(\frac{\gamma_{1,i}^{\mathrm{exptl}}-\gamma_{1,i}^{\mathrm{calc}}}{\gamma_{1,i}^{\mathrm{exptl}}}\right)^{2}+\left(\frac{\gamma_{2,i}^{\mathrm{exptl}}-\gamma_{2,i}^{\mathrm{calc}}}{\gamma_{2,i}^{\mathrm{exptl}}}\right)^{2} \tag{5}$$

and are reported in Table VI, together with the relative deviation of the vapor composition. Inspection of the results given in Table VI shows that the four models give a good fit of the experimental data. For the system 4-methyl-2-pentanone + octane the UNIQUAC model gave the best fit while for the binary hexane + 1,3-dioxolane the best fit was that of the Wohl model. The simultaneous capability of predicting the vapor phase composition and the bubble-point temperature was used as the ranking factor. An interesting feature is that when fitting the NRTL model to the system hexane + 1,3-dioxolane with the commonly used value of $\alpha(=0.2)$ gives poorer results than the one obtained by optimization, not only that, the optimal value of parameter α is negative. Figure 5 describes the

TABLE VI Parameters and deviations between experimental and calculated values for G^E-different models

A. Redlich-Kister, Eq. (4)

System	*B*	*C*	*D*	*max dev* %[a]	*avg dev* %[b]	*rmsd*[c]
4-methyl-2-pentanone (1)	0.3367			6.5	2.8	0.009
+ octane (2)	0.3373	0.0052	6.3	2.9	0.009	
hexane (3) + 1,3-dioxolane (4)	0.5893	−0.0953	−0.0933	8.8	3.4	0.02

B. Other models[d]

Model	*System*	A_{12}	A_{21}	q_1/q_2	α	$\delta(y)$[e]
Wohl	1 + 2	0.7553	0.7776	0.9713		0.004
	3 + 4	1.3661	0.8799	0.5853		0.009
Wilson	1 + 2	2147.44[f]	617.059[f]			0.004
	3 + 4	26.547[f]	4404.1[f]			0.023
NRTL	1 + 2	1284.35[f]	1286.01[f]	0.200	0.004	
	3 + 4	3286.2[f]	0.42832[f]	−0.181	0.010	
	3 + 4	4155.7[f]	0.40398[f]	0.200	0.032	
UNIQUAC	1 + 2	2071.34[f]	−906.56[f]			0.004
	3 + 4	1086.32[f]	568.10[f]			0.011

[a] maximum deviation %.

[b] average deviation %.

[c] root mean square deviation.

[d] All equations in ln γ_i form.

[e] $\delta(y)=\Sigma\,|y_{\mathrm{exptl}}-y_{\mathrm{calcd}}|/N$ (N = number of data points).

[f] J/mol.

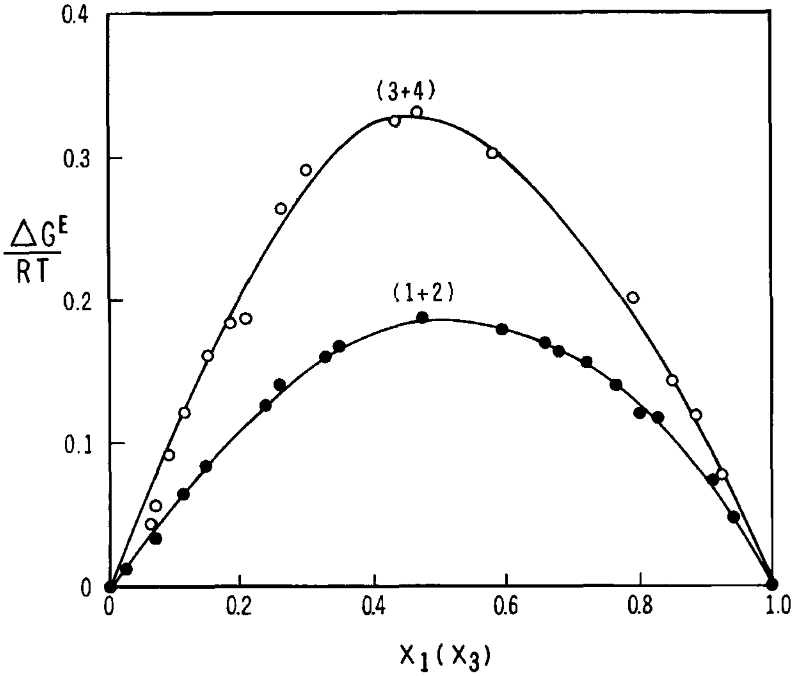

FIGURE 5 Variation of the Gibbs number $\Delta G^E/RT$ with concentration of the nonhydrocarbon component.

variation of the Gibbs number $\Delta G^E/RT$ for both binaries. It is seen that the value of $\Delta G^E/RT$ at $x = 0.5$ for the system hexane (3) + 1,3-dioxolane is almost double that of the system 4-methyl-2-pentanone (1) + octane (2) probably due to the fact that hexane molecules are packed more closely than those of octane and more energy is provided by the second component to breack the packing.

The boiling points of the two binaries were correlated by the equation proposed by Wisniak and Tamir [10]:

$$T/K = x_1 T_1^0 + x_2 T_2^0 + x_1 x_2 \sum_{k=1}^{m} C_k (x_1 - x_2)^k \tag{6}$$

In this equation T_i^0/K is the boiling point of the pure component i at the operating pressure and m is the number of terms in the series expansion of $(x_1 - x_2)$. The various constants of Eq. (6) are reported in

TABLE VII Coefficients in correlation of boiling points, Eq. (6), average % deviation and root mean square deviations in temperature, rmsd (T/K)

System	C_0	C_1	C_2	C_3	*max dev %*[a]	*avg dev %*[b]	*rmsd*[c]
4-methyl-2-pentanone (1) + octane (3)	−27.5831	7.67192	−15.1101	−3.93526	0.2	0.07	0.02
hexane (3) + 1,3-dioxolane (4)	−40.6217	15.2925	−26.9815		0.6	0.27	0.05

[a] maximum deviation %/K.
[b] average deviation %/K.
[c] root mean square deviation/K.

Table VII, which also contains information indicating the degree of goodness of the correlation.

Acknowledgements

Yehudit Reizner helped in the experimental part.

References

[1] Wisniak, J., Embon, G., Shafir, R., Reich, R. and Segura, H. (1997). *J. Chem. Eng. Data*, **42**, 1191.
[2] Van Ness, H. C. and Abbott, M. M., Classical Thermodynamics of Nonelectrolyte Solutions (McGraw-Hill Book Co.: New York, 1982), pp. 306–310.
[3] O'Connell, J. P. and Prausnitz, J. M. (1967). *Ind. Eng. Chem. Process Des. Develop.*, **6**, 245.
[4] Wisniak, J., Segura, H. and Reich, R. (1996). *Phys. Chem. Liq.*, **32**, 1.
[5] Wisniak, J. (1993). *Ind. Eng. Chem. Res.*, **32**, 1531.
[6] Fredenslund, A., Gmehling, J. and Rasmussen, P., Vapor-liquid Equilibria Using UNIFAC (Elsevier: Amsterdam, 1977), pp. 68–74.
[7] Van Ness, H. C., Byer, S. M. and Gibbs, R. E. (1973). *AIChE J.*, **19**, 238.
[8] Walas, S. M., Phase Equilibria in Chemical Engineering (Butterworth Publishers: Boston, 1985), pp. 192–207.
[9] Redlich, O. and Kister, A. T. (1948). *Ind. Eng. Chem.*, **40**, 345.
[10] Wisniak, J. and Tamir, A. (1976). *Chem. Eng. Sci.*, **31**, 631.
[11] TRC-Thermodynamic Tables-Hydrocarbons; *a*-1010, 1995, *k*-1440, 1994; *k*-1490, 1990: Thermodynamics Research Center: Texas A&M University System, College Station, TX, extant 1996.
[12] Castellari, C., Francesconi, R., Comelli, F. and Ottani, S. (1984). *J. Chem. Eng. Data*, **29**, 283.
[13] Wu, H. S. and Sandler, S. I. (1989). *J. Chem. Eng. Data*, **34**, 209.
[14] TRC-Thermodynamic Tables-Non-Hydrocarbons; *a*-5920, 1994; *k*-5921, 1981; Thermodynamics Research Center: Texas A&M University System, College Station, TX, extant 1996.