

CHAPTER 6

MEASUREMENT OF THE 1-OCTENE / 2-HEXANONE SYSTEM

6.1 Introduction

As noted in chapter 3, experimental vapour-liquid equilibrium (VLE) data for the 1-octene (OCT1, component 1) / methyl n-butyl ketone (MBK, component 2) system has not been found in the literature. This chapter covers the determination of data for this system.

6.2 Experimental apparatus

The modified Othmer-type still described in chapter 5 was used in the experimentation. It was operated in the same consistent manner described when comparing equipment results with DECHEMA the equipment with data from DECHEMA. A much longer time was allowed for equilibrium to be reached (typically 6 to 7 hours after circulation started). This has been found to result in much smoother data.

The equilibrium temperature was determined with a calibrated digital thermocouple accurate to 0.1 °C. The pressure was measured accurately to the nearest 1 mbar.

The compositions of the vapour and liquid phases at equilibrium were determined by gas chromatography (see the next section).

6.3 GC calibration

6.3.1 Chemicals used

Analysis with a GC indicated that the OCT1 was 99.128 % (AREA) pure and the MBK 99.154 %. The impurities involved were isomers

of the components in question, indicating that they would exert only a negligible influence on the OCT1-MBK system. The impurities appear as a number of minute peaks in the vicinity of the main peak. The use of higher purity chemicals was prohibited by the high cost of OCT1 and especially MBK. MBK is manufactured on laboratory scale and on request only.

The reagents were used without further purification. Chemicals of similar purities have been used in other studies as well (eg Wisniak, 1993:296). Calculations by this author has lead to the conclusion that there is little difference in the effect of various ways of handling impurities. Whether the two main peaks are normalized or if the isomer peaks are added to them makes little difference. This author still believes chemicals should be purified to virtually 100 % purity if such facilities are available, and that this is a must if the impurities have different properties than the main components. In this study impurities were treated by normalizing the main peak.

6.3.2 GC settings

The following GC settings were used in the analyses. The temperature program provided a complete resolution of all peaks involved.

Table 6.1: GC set points used	
Injector temperature	250 °C
Detector temperature	250 °C
Column	50 m PONA
Split	150:1
Detector	FID
Sample size	0.1 μ l
Carrier gas	N ₂ , 1 cc/min at 25 °C
Temperature program	100 °C for 8 min, +10 deg/min
ZERO	0.020
ATT^2	2
CHT SP	1.5
AR REJ	0
THRSH	0
PK WD	0.04

The retention time for MBK was 8.672 and that for OCT1 9.119.

6.3.2 Calibration

Whenever accurate work is to be done with a GC, response factors must be determined. These are usually determined by using n-heptane (with a response factor of 1) as a reference. The n-heptane used was found to be 99.734 % (AREA) pure with RT=7.290 under the above program.

Two mixtures of known composition were carefully made up. Both contained about 50 % n-heptane with the remainder either OCT1 or

MBK. The weights measured were multiplied with the purity in question, although this has almost no affect since the purities are similar and thus cancel out. Each of the samples was also analyzed three times and the average used:

Table 6.2: Sample 1: OCT1 and n-heptane		
	OCT1	n-heptane
Mass (g)	2.756	2.808
True mass %	49.541	50.459
Average GC AREA %	49.960	49.478
GC reading 1	49.9133	49.5527
GC reading 2	50.0402	49.4146
GC reading 3	49.9272	49.4679

Table 6.3: Sample 2: MBK and n-heptane		
	MBK	n-heptane
Mass (g)	2.874	2.739
True mass %	51.202	48.798
Average GC AREA %	43.990	55.528
GC reading 1	44.0243	55.5131
GC reading 2	43.9990	55.4955
GC reading 3	43.9474	55.5766

The area percentages obtained from a GC report are divided by the respective response factors (RF). The values obtained in this way are then normalized to add up to 1 or 100. If the response factors are accurate, this procedure will yield the mass composition of the sample injected. In each case the response factor for n-heptane is 1.000. Since the true compositions of the

samples were known beforehand, the response factors for OCT1 and MBK remain as the only unknowns and can be easily calculated:

Table 6.4: Response factors		
Component:	OCT1	MBK
RF:	0.99137	0.83125

These values agree roughly with those published by Dietz (1967:71). Response factors for paraffins and similar hydrocarbons are near unity while values for ketones are somewhat lower. The response factor of MBK for a TCD detector is 0.77 (an FID was used here).

6.4 Results

The pressure-temperature-composition data is given in the table below. The AREA % values from the GC traces were divided by the response factors listed above and then normalized. These mass percentages were then divided by the molecular weights given in chapter 4 and normalized again to give the compositions on a mole basis:

Table 6.5: Vapour liquid equilibrium data for the OCT1 - MBK system.			
Pres mbar	Temp °C	OCT1 mole liquid fraction (X1)	OCT1 mole vapour fraction (Y1)
835	121.5	0	0
838	119.6	0.04675	0.09922
839	118.6	0.09690	0.1764
836	117.1	0.1560	0.2395
836	115.3	0.2706	0.3486
837	113.8	0.3509	0.4076
836	113.5	0.3704	0.4254
837 ³⁸	113.1	0.4176	0.4592
837	112.9	0.4800	0.5070
837	112.6	0.5179	0.5389
836	112.5	0.5692	0.5833
836	112.3	0.6627	0.6614
836	112.3	0.7621	0.7513
839	112.4	0.8241	0.8129
838	112.8	0.8811	0.8703
835	113.5	0.9464	0.9416
835	114.5	1	1

³⁸ This point has been smoothed in. If this data is to be used for compilation purposes, it may be removed.

As figure 6.1 shows, the system forms an azeotrope (at $x_1 \approx 0.654$ (mole)) with relative volatilities near unity for all values of x_1 higher than this.

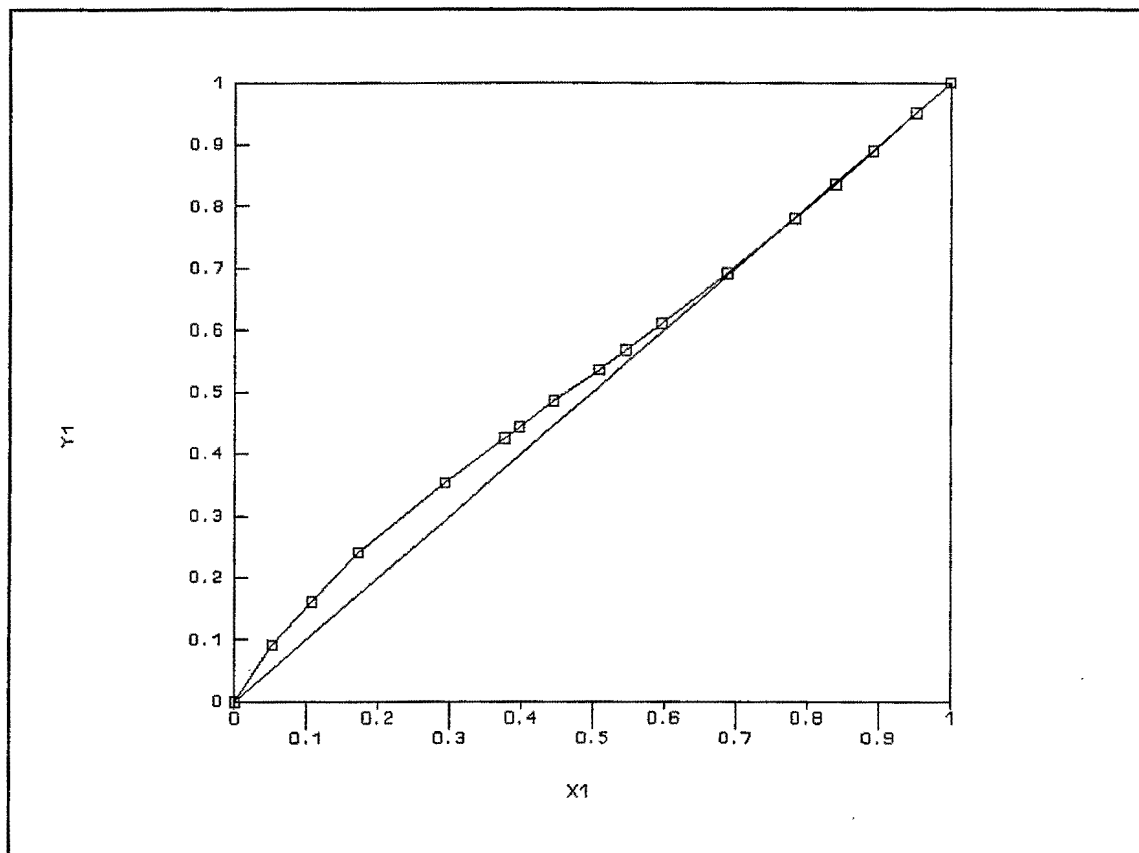


Figure 6.1: OCT1 - MBK XY diagram.

6.4 Thermodynamic consistency test

The tests described and used here are utilized by DECHEMA (1977: XXII) and several other authors such as Zhonggxiu C, Wangming H. et al (1991:227):

Thermodynamic consistency tests are all based on the Gibbs-Duhem equation, for which the directly useful form is:

$$\frac{\Delta H}{RT^2} dT - \frac{\Delta V}{RT} dP + \sum_i x_i d(\ln \gamma_i) = 0 \quad (6.67)$$

with ΔH the molar enthalpy of mixing, and ΔV the molar excess volume of mixing. Equilibrium data are usually given either as isothermal or as isobaric. For binary isobaric systems the equation thus becomes:

$$\frac{\Delta H}{RT^2} dT + x_1 d(\ln \gamma_1) + x_2 d(\ln \gamma_2) = 0 \quad (6.68)$$

Integration yields:

$$\int_0^1 \left(\ln \frac{\gamma_1}{\gamma_2} \right) dx = \int_{x=0}^{x=1} \left(\frac{\Delta H}{RT^2} \right) dT \quad (6.69)$$

For real data this requirement will not be exactly fulfilled because of experimental error and also of assumptions made in calculations (ideal vapour phase) and in the derivation of the equation. Therefore it is reasonable to define a deviation which should not be exceeded, if a set of data is to be considered thermodynamically consistent. This deviation is given by:

$$D = 100 \left| \frac{A-B}{A+B} \right| \quad [\%] \quad (6.70)$$

where A is the area above $x=0$ and B the area below.

In many cases the second integral,

$$\int_{x=0}^{x=1} \left(\frac{\Delta H}{RT^2} \right) dT \quad (6.71)$$

may be neglected, e.g. for systems consisting of chemically similar components (with low ΔH), or if the boiling temperatures

in the system are close together. This integral can be estimated by:

$$J=150 \frac{|\Delta T_{\max}|}{T_{\min}} \quad [\%] \quad (6.72)$$

For the OCT1-MBK system this gives:

$$J=150 \frac{(121.5-112.3)}{(112.3+273.15)} = 3.6\% \quad (6.73)$$

Table 6.6: Data for consistency test. ³⁹			
X1 (mole)	γ_1	γ_2	$\ln (\gamma_1/\gamma_2)$
0	(2.478)	0.9986	
0.0468	1.8370	1.0030	0.6051
0.0969	1.6230	0.9991	0.4852
0.156	1.4235	1.0301	0.3235
0.271	1.2573	1.0798	0.1522
0.351	1.1857	1.1582	0.02349
0.370	1.1817	1.1675	0.01204
0.418	1.1459	1.2045	-0.04983
0.480	1.1070	1.2379	-0.1118
0.518	1.1001	1.2608	-0.1364
0.569	1.0854	1.2777	-0.1631
0.663	1.0714	1.3147	-0.2046
0.762	1.0616	1.3447	-0.2364
0.824	1.0608	1.3614	-0.2495
0.881	1.0491	1.3430	-0.2471
0.946	1.0265	1.2981	-0.2347
1	0.9979	(1.5132)	

Accord to the trapezium rule with values taken at 0.1 intervals:

³⁹ The two values in brackets are the infinite dilution activity coefficients as predicted by UNIQUAC model fitted to the data.

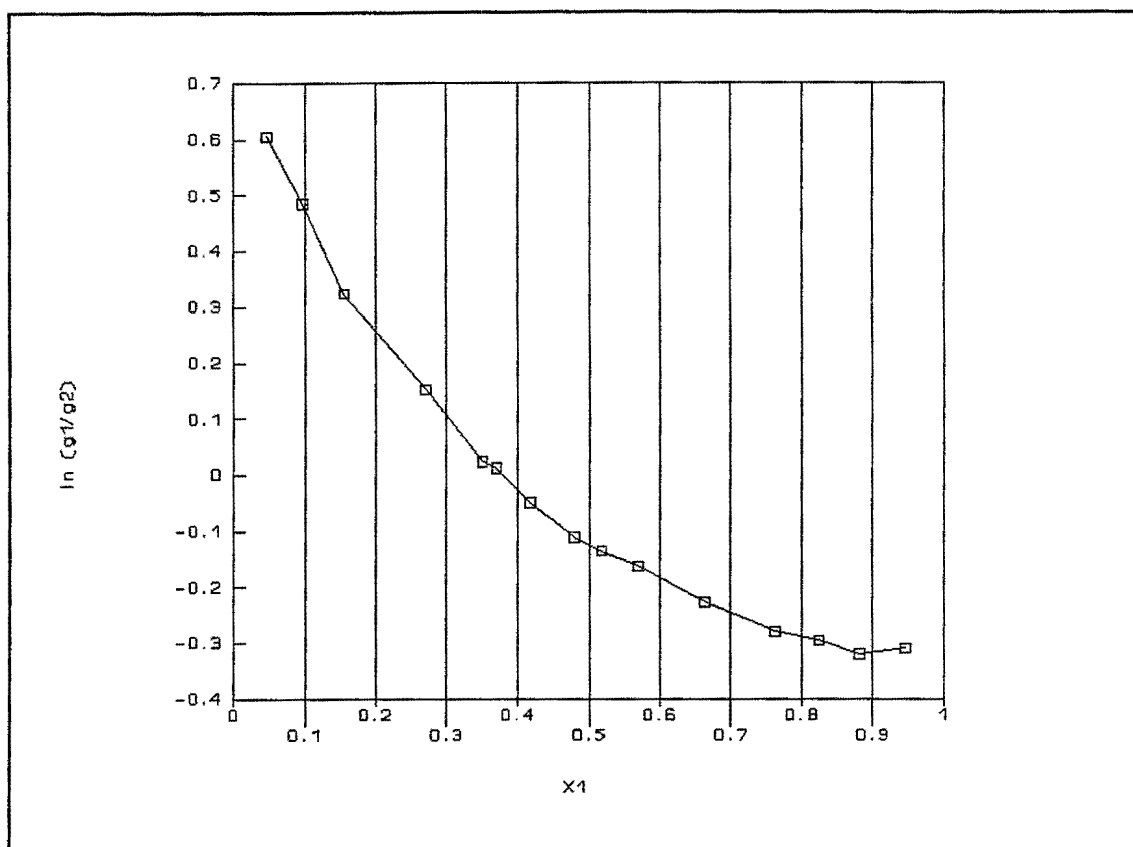


Figure 6.3: Area test with $\ln(\gamma_1/\gamma_2)$

$$A = \int_0^{0.4} \left(\ln \frac{\gamma_1}{\gamma_2} \right) dx \approx 0.145 \quad (6.74)$$

$$B = \int_{0.4}^1 \left(\ln \frac{\gamma_1}{\gamma_2} \right) dx \approx -0.142 \quad (6.75)$$

This gives:

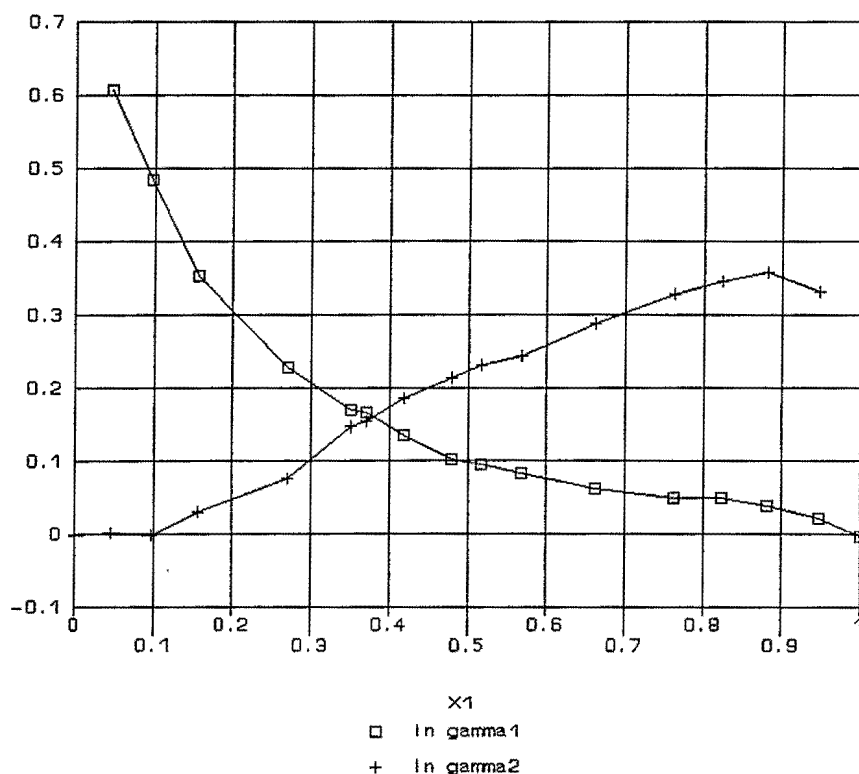


Figure 6.3: $\ln (\gamma_i)$

$$D=100 \left| \frac{(0.145-0.142)}{(0.145+0.142)} \right| = 1.05\% \quad (6.76)$$

Accordingly, $|D-J| = |1.5-3.06| = 1.56 \%$

It is assumed that with $|D-J| \leq 10 \%$ a given data set is probably consistent.

The activity coefficients were calculated from the relation:

$$\gamma_i = \left(\frac{y_i}{x_i} \right) * \left(\frac{P}{P^o} \right) \quad (6.77)$$

While this area test is necessary, it is not a sufficient condition for consistency as errors might cancel out. For this reason the data must be examined more closely.

Lu (1960:105) also presents a number of tests for data consistency. These are considered below:

$$1. \ln \gamma_1 \text{ (at } x_1=0.5) \approx 0.25 * \ln \gamma_2 \text{ (at } x_1=1):$$

$$0.09 \approx 0.25 * 0.41 = 0.1 \quad \text{True}$$

$$2. \ln \gamma_2 \text{ (at } x_2=0.5) \approx 0.25 * \ln \gamma_1 \text{ (at } x_2=1):$$

$$0.23 \approx 0.25 * 0.88 = 0.22 \quad \text{True}$$

$$3. \text{ At } x_1=0.25, \ln \gamma_1 \approx (\ln \gamma_2 \text{ at } x_1=0.75):$$

$$0.25 \approx 0.32 \quad \text{True(?)}$$

$$4. \text{ Since } \ln \gamma_1 \text{ (at } x_1=0) > \ln \gamma_2 \text{ (at } x_2=0), \text{ then}$$

$$(\ln \gamma_1 \text{ at } x_1=0.5) < (\ln \gamma_2 \text{ at } x_1=0.5):$$

$$0.10 < 0.23 \quad \text{True}$$

$$5. \text{ Both } \ln \gamma_1 \text{ and } \ln \gamma_2 \text{ should approach their zero values}$$

$$\text{with a horizontal tangence.} \quad \text{True}$$

$$6. \text{ With no minimum or maximum involved, both } \ln \gamma_1 \text{ and } \ln \gamma_2$$

$$\text{should be on the same side of 0.} \quad \text{True}$$

(Note that γ_1 and γ_2 are always greater than unity, so that $\ln \gamma > 0$ in all cases.)

The Gibbs-Duhem test does not show the data to be inconsistent. The values calculated lie within the limits specified. The data is therefore probably consistent, although plots of $\ln \gamma_1$ and $\ln \gamma_2$ show that while the lines are smooth, experimental errors are visible.

6.5 Data Correlation

The experimental data was used in a REGRESS⁴⁰ input file (refer to appendix B1). The Wilson, Van Laar, 3-parameter NRTL, and UNIQUAC models were used in the regression. The output file, which contains measured versus calculated values for all the models, is in appendix B2. In short, the results are:

Table 6.7: Regression Models and Results		
Model	Average absolute deviation in vapour composition.	Interaction Parameters
Wilson	0.006	$(\lambda_{12}-\lambda_{11})$: 405.435 $(\lambda_{21}-\lambda_{22})$: -26.497
Van Laar	0.007	A_{12} : 0.82879 A_{21} : 0.42200
NRTL	0.007	b_{12} : -4.728832 b_{21} : 345.7976 α_{12} : 0.819200
UNIQUAC	0.008	$(u_{12}-u_{11})$: -119.016 $(u_{21}-u_{22})$: 209.751

Note that the Wilson, NRTL and UNIQUAC parameters are in K only, not in KCAL. This is important because different simulation programs have different default units.

The objective function used is:

$$S = \sum_{i=1}^N \left(\sum_{j=1}^{NOC} \left(1.0 - \frac{Y_{ijcalc}}{Y_{ijexpt}} \right)^2 + \left(1.0 - \frac{P_{icalc}}{P_{iexpt}} \right)^2 \right) \quad (6.78)$$

⁴⁰ REGRESS is part of the PRO/II simulation program.

This function is recommended in the REGRESS manual for isobaric binary VLE data.

The Wilson equation gives slightly better results than the other models.