

CHAPTER 8

BINARY VLE DATA FOR SOLVENTS

8.1 Introduction

Screening tests were used in chapter 7 in order to identify potentially effective solvents. As is often done in the literature, these tests are performed at one selected point only. However, for an identified solvent to be of any real value it must actually be able to economically effect a high degree of separation.

In order to establish the true virtues of a solvent, its interaction with the components to be separated must be known. Can the solvent be easily recovered and recycled, or are new azeotropes formed?

Four solvents were therefore chosen for a more complete study. The solvents chosen were not only chosen on the basis of their influence, but demonstrate variations of enhanced distillation. As will be seen, one is a heavy extractive solvent, one a standard azeotropic solvent and the other two are special cases of azeotropic solvents.

In order to develop processes for the separation of 1-octene and 2-hexanone, accurate VLE correlations must be available. Parameters for such correlations must be regressed from experimental work.

8.2 Experimental planning

The question to be answered is: What measurements must be made in order to facilitate accurate simulations of the effect of a

solvent on the OCT1-MBK system? Should binary or ternary data be measured?

From the literature it appears that multi component systems can be represented quite well by using binary interaction data. A few references will illustrate this:

"With the existence of equations representing multi component liquid mixtures with binary parameters only, the amount of experimental work required to describe multi component systems has been reduced considerably" (DECHEMA, 1977:III).

"Present thermodynamic theory allows for the accurate prediction of multi-component vapour-liquid equilibrium (VLE) data for completely miscible systems from binary data only." (Thomas & Eckert, 1984:194) (References to this effect are given in the article).

As far as modelling is concerned, DECHEMA (1977:XXII) suggests that the Wilson, NRTL or UNIQUAC models should be used because they can represent multi component equilibria with binary parameters only.

While there are known limitations to predicting ternary (or higher) data from binary data only, "these limitations are rarely serious for engineering work. As a practical matter, it is common that experimental uncertainties in binary data are as large as the errors which result when multi component equilibria are calculated with some model for g^E by using only parameters obtained from binary data. ... Experience has shown that multi component vapour-liquid equilibria can usually be calculated with satisfactory engineering accuracy by using the Wilson equation, the NRTL equation, or the UNIQUAC equation..." (Reid, Prausnitz & Anderson, 1987:281)

While the appropriate measurements are not too difficult in either case, they can be very time consuming, especially for multi component systems. Binary data has the added advantages of being more easily measured and renders itself more readily to thermodynamic consistency tests.

The measurement of a binary data set requires about 150 cc of each of the chemicals involved. In the case of ternary data much more chemicals are required since it is no longer so easy to use an existing mixture and just modify its composition by adding a small amount of one chemical. This is important if the chemicals are expensive, as is the case here.

Accurate experimental studies on ternary systems are therefore understandably scarce. Most compilations (such as DECHEMA) contain binary interaction data. Such parameters can then generally be used whenever the two components appear together in a multi component mixture.

It thus appears that little can be gained by measuring ternary data in stead of binary data.

8.3 Measured systems and tables

In all the cases below the first component whose name appears in the heading will be referred to as component number 1. In all cases the first component will be either 1-octene (OCT1) or 2-hexanone (MBK), and given composition data is then for this component. The sections contain the following tables and diagrams:

- i) PTXY data for component 1, ie the equilibrium pressure and temperature with the corresponding liquid mole fraction of component 1 in the vapour versus its fraction in the liquid.
- ii) Results from regressions with model parameters.

iii) The values of $\ln \gamma_1$, $\ln \gamma_2$ and $\ln(\gamma_1/\gamma_2)$ versus the liquid mole fraction of component 1.

In all cases the model which fits the data best is also used to predict infinite dilution activity coefficients. These are contained in brackets in the tables ($\ln \gamma^\infty$)⁵⁴.

The data was treated in exactly the same way as for the OCT1-MBK system in chapter 4. This includes the consistency tests. For this reason the results are summarized in a series of tables.

A set of data should at least pass the area test if it is to be accepted. Ideally it should also perfectly pass a well developed point test as well. The examination of $\ln \gamma_1$ data is probably the acid test and will clearly reveal small errors not easily detectable from TXY and $\ln(\gamma_1/\gamma_2)$ data. Sadly it is not uncommon for data to fail some part of the point test, as the DECHEMA collection testifies. While such data is still useful and collected, it means that it is not absolutely consistent. Graphs⁵⁵ from the consistency tests are included here to give to reader a better indication of the reliability of the different data sets. For convenience the tables with the activity coefficients are also reproduced here because they belong with the PTXY data.

The GC response factors used are as follows:

⁵⁴ Note: \ln is the natural logarithm (base $e=2.718\dots$), or \log_e and NOT \log_{10} .

⁵⁵ Due to the fact that Lotus is unable to represent the γ symbol in graphs, the titles of some of the vertical axes appear with the number of the figure.

Table 8.1: Solvents with FID Response Factors			
Component	Chemical Name	NBP °C	RF
n-heptane	(reference)	98.4	1 (exactly)
MEOH	methanol	64.7	0.4188
DMF	N,N-dimethylformamide	153.0	0.2709
MXEA	2-methoxyethanol	124.4	0.3753
kerosol 200	Iso paraffinic stream (IBP≈200°C)	200 - 260	1 (assumed)

Due to its paraffinic nature the response factor for kerosol 200 was assumed to be near unity.

8.3.1 1-Octene (OCT1) and Methanol

The PRO/II simulation package already has binary interaction parameters for this system. While the source of the data used is not available from PRO/II, a literature search revealed that this system was studied by Gmehling and Meents (1992:156). The enthalpy of mixing was evaluated at a constant pressure of 5 atm and temperatures of 298.15 and 328.18 °K. The binary interaction parameters for the NRTL and UNIQUAC methods are as follows (as reported by PRO/II):

Table 8.2: PRO/II Parameters for OCT1 (1) / Methanol (2)	
NRTL (3 parameter)	b_{12} : 577.599 b_{21} : 732.867 α_{12} : 0.4396
UNIQUAC	$(u_{12}-u_{11})$: 702.648 $(u_{21}-u_{22})$: -16.232

Wilson parameters are not available, probably because two liquid phases are expected and Wilson is unable to handle this (Reid, Prausnitz & Anderson, 1987:255). While the Wilson equation is unable to represent phase splitting into two liquids, it yields a good fit for even highly non ideal systems such as alcohol-hydrocarbon mixtures (DECHEMA, 1977:XXII)

The fact that 1-octene has almost no hydrogen bond forming ability while that of methanol is considerable leads one to expect a highly non ideal azeotropic system.

During the study of this system two liquid phases were not encountered inside the stills. The liquid in the condenser did not have any typical "milky" appearance of an emulsion. The condenser liquid did form two phases when cooled down to room temperature (and given several hours). The X-Y diagram shows a region which appears horizontal at first glance. This would indicate two liquid phases. If one examines the values, a slight angle is noted. It is thus concluded that, at its boiling point, the system is very near the point of immiscibility but not quite there yet. During the tests the compositions were found to be reproducible in this area. Raal et al (1992:256) reported that when two liquid phases are encountered in the equipment used here, an unstable emulsion forms and the compositions are not reproducible.

In any case, although there are no maxima or minima in the activity coefficients data, it is interesting to note that the

Wilson equation correlates the data slightly less well than the other models.

The curve of $\ln \gamma_1$ shows one bad point for $x_1 \approx 0.97$. The gradient of the XY curve in this region understandably makes it difficult to measure a good point in this region.

Table 8.3: VLE data			
Pressure (mbar)	Temperature (°C)	Liquid mole fraction	Vapour mole fraction
835	114.4	1	1
838	68.9	0.9670	0.3600
839	58.6	0.8042	0.1413
838	57.0	0.6962	0.1404
839	56.9	0.5806	0.1389
839	56.9	0.4739	0.1388
836	56.8	0.2671	0.1351
836	56.8	0.1751	0.1272
835	56.8	0.1495	0.1233
833	56.6	0.1105	0.1157
833	56.7	0.0798	0.1042
835	56.8	0.0563	0.0959
833	57.5	0.0208	0.0518
833	57.5	0.0091	0.0292
835	59.7	0	0

Table 8.4: Regression Models and Results		
Model	Average absolute deviation in vapour composition.	Interaction Parameters
Wilson	0.016	$(\lambda_{12}-\lambda_{11})$: 354.360 $(\lambda_{21}-\lambda_{22})$: 1279.432
Van Laar	0.013	A_{12} : 2.6093 A_{21} : 2.2295
NRTL	0.012	b_{12} : 337.6995 b_{21} : 646.4594 α_{12} : 0.23721
UNIQUAC	0.010	$(u_{12}-u_{11})$: 637.841 $(u_{21}-u_{22})$: 5.490

Table 8.5: Activity Coefficient Data.			
Liquid mole fraction	$\ln \gamma_1$	$\ln \gamma_2$	$\ln (\gamma_1/\gamma_2)$
1	0.0008	(1.857)	
0.9670	0.5545	2.6022	-2.0477
0.8042	0.2230	1.5263	-1.3033
0.6962	0.4304	1.1525	-0.7221
0.5806	0.6060	0.8371	-0.2311
0.4739	0.8086	0.6106	0.1979
0.2671	1.3561	0.2838	1.0723
0.1751	1.7174	0.1748	1.5426
0.1495	1.8433	0.1475	1.6958

0.1105	2.0873	0.1172	1.9701
0.0798	2.3048	0.0921	2.2127
0.0563	2.5689	0.0743	2.4947
0.0208	2.9145	0.0535	2.8609
0.0091	3.1716	0.0652	3.1064
0	(2.926)	-0.0020	

Table 8.6: Consistency Test Block	
AREA TEST	
Area A:	0.163
Area B:	0.249
$D=100 \left \frac{A-B}{A+B} \right $	20.9
ΔT_{\max}	57.8
T_{\min}	56.6
$J=150 \left \frac{\Delta T_{\max}}{T_{\min}} \right $	26.6
$ D-J $	5.7 (want $\leq 10\%$)

Table 8.7: Lu Consistency Test	
Condition	Value
$\ln \gamma_1 (x_1=0.5) \approx$	0.809
$0.25 * \ln \gamma_2 \text{ (at } x_1=1)$	0.732

$\ln \gamma_2 (x_2=0.5) \approx$ $0.25 * \ln \gamma_1 (\text{at } x_2=1)$	0.611 0.464
$\ln \gamma_1 (x_1=0.25) \approx$ $\ln \gamma_2 (\text{at } x_1=0.75)$	1.356 1.215
$\ln \gamma_1 < \ln \gamma_2 (x=0.5)$	0.809 vs 0.611 FAIL
$\ln \gamma$ approaches its zero with horizontal tangence.	True
With no maximum or minimum, $\ln \gamma_1$ and $\ln \gamma_2$ should be on the same side of zero.	True

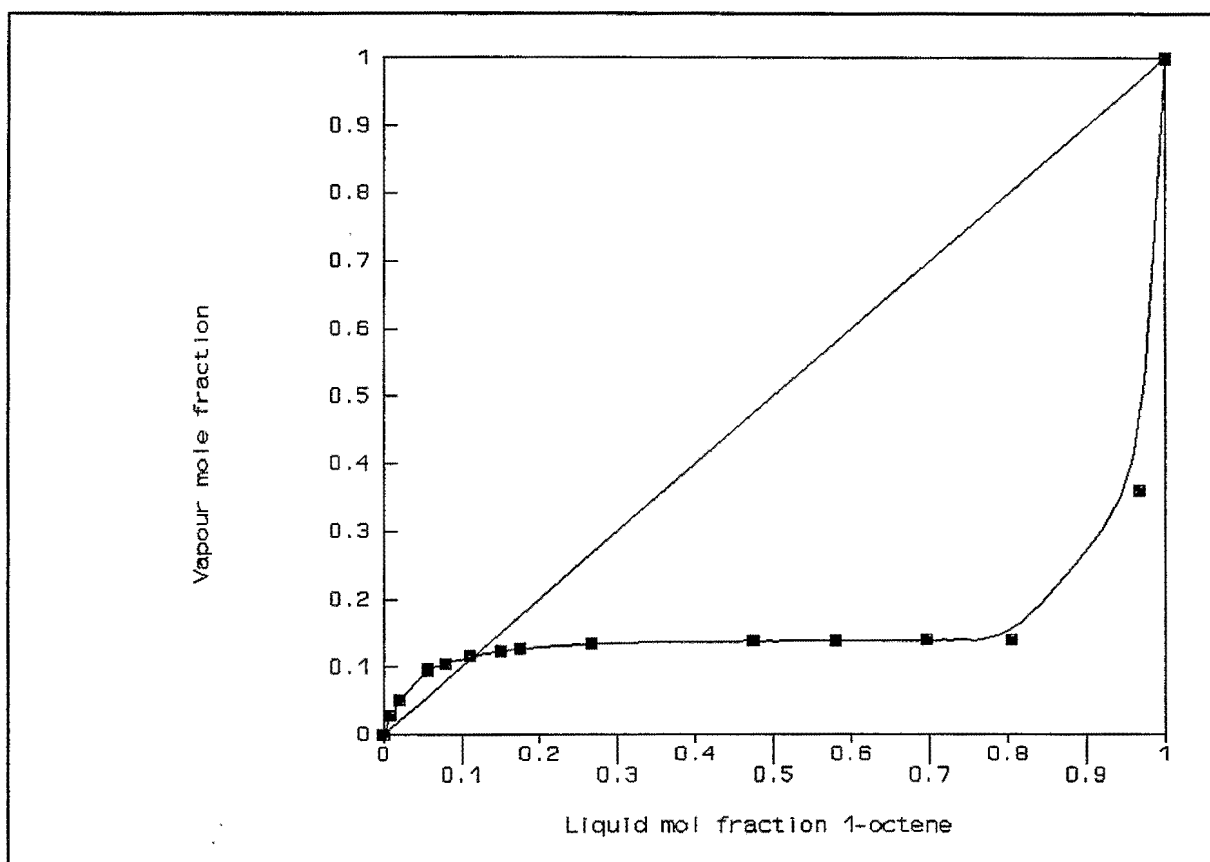


Figure 8.1: OCT1 - Methanol XY.

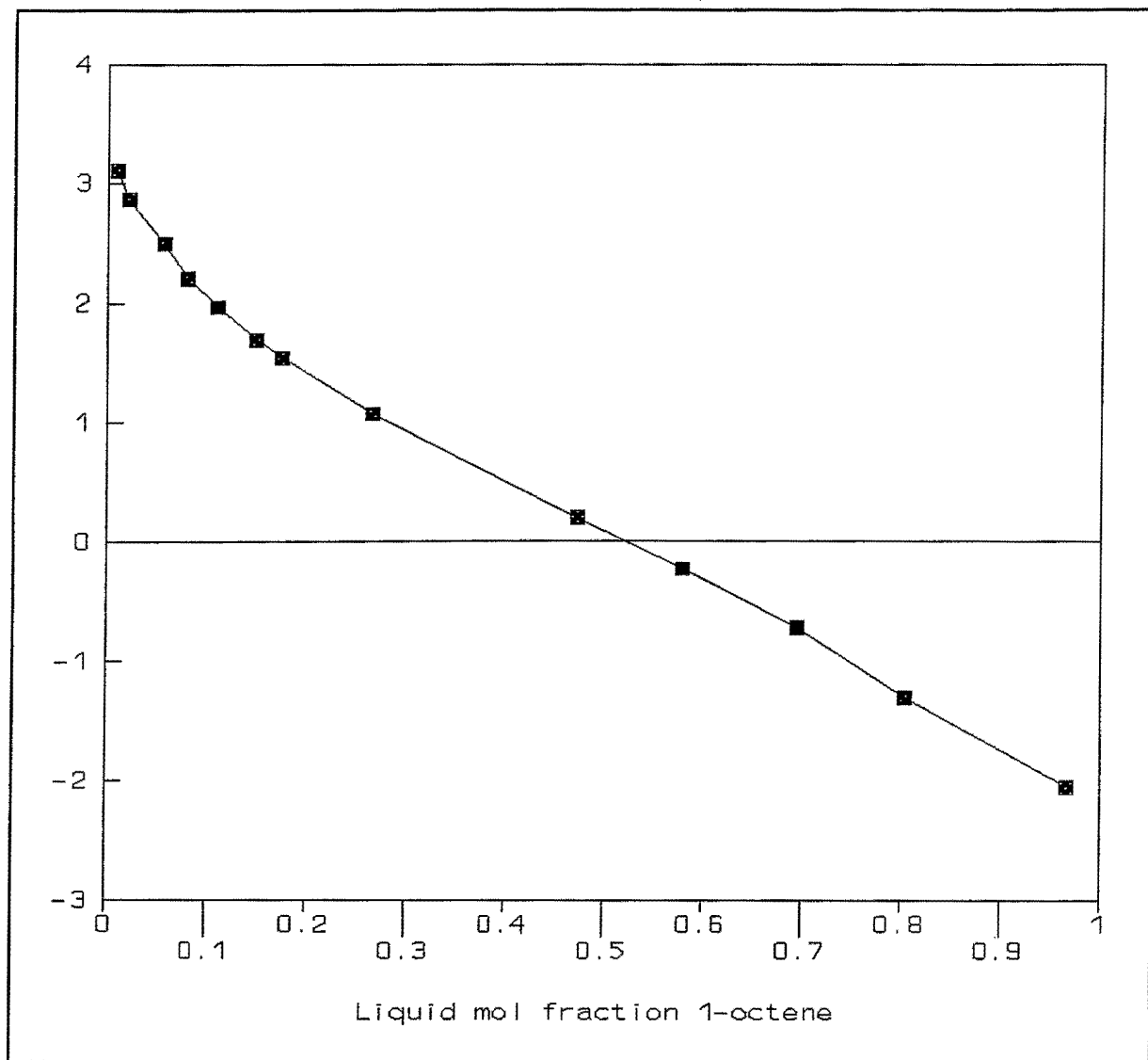


Figure 8.2: OCT1 - Methanol $\ln(\gamma_1/\gamma_2)$.

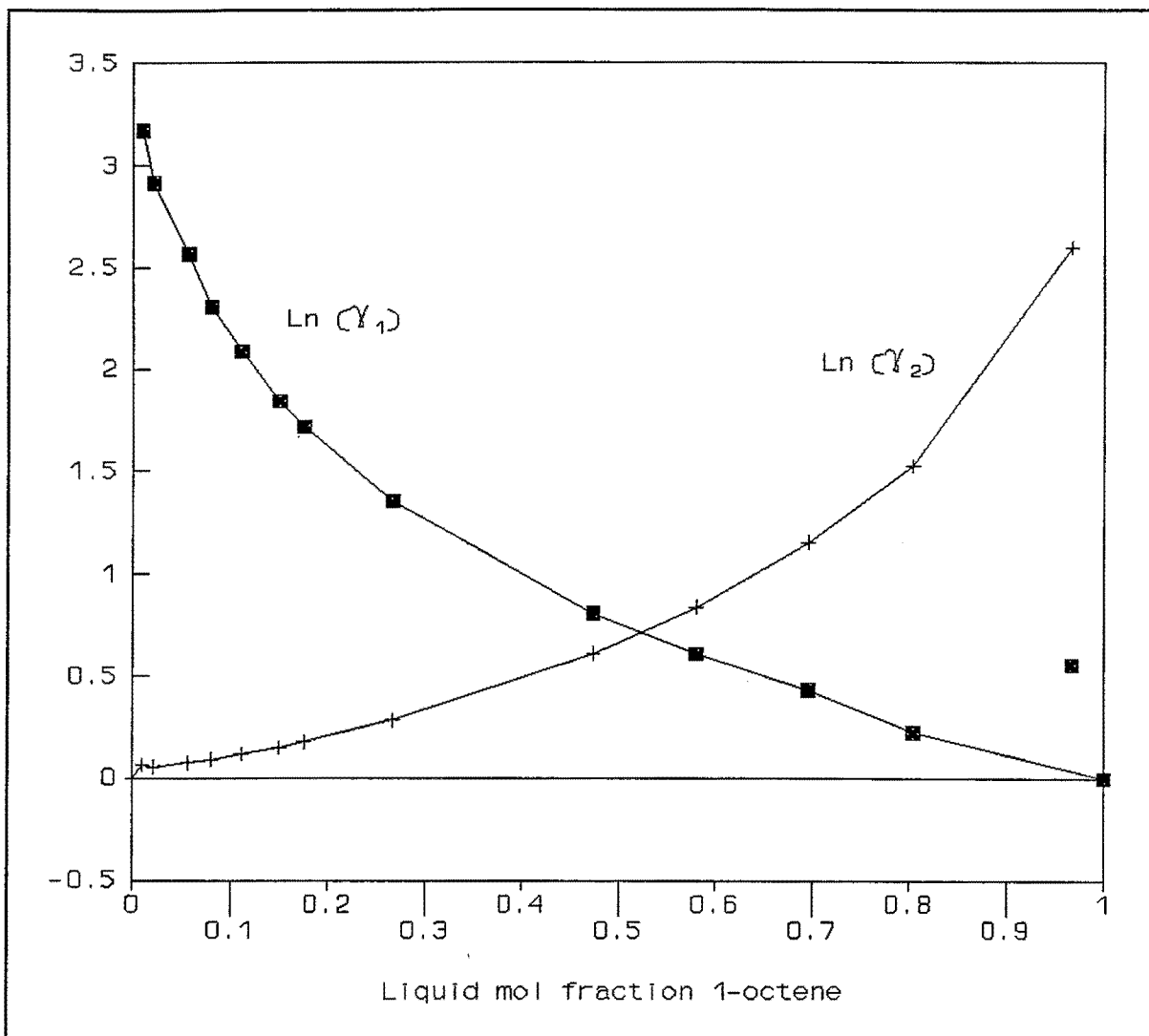


Figure 8.3: OCT1 - Methanol $\ln(\gamma_1)$ and $\ln(\gamma_2)$.

8.3.2 2-Hexanone (MBK) and Methanol

Simulations with UNIFAC indicate that the system should be a typical non ideal non azeotrope. This is also to be expected from the characteristics of the system: The presence of hydrogen bonding abilities lead to non ideality, but since the components both have similar bonding properties, the system should not be so non ideal as to form an azeotrope.

The consistency tests reveal that the data could very well be inconsistent.

The $\ln \gamma_1$ versus x_1 curve shows that, as for the previous system, measuring good points for x_1 high is a challenge.

Table 8.8: VLE Data			
Pressure (mbar)	Temperature (°C)	Liquid mole fraction	Vapour mole fraction
835	121.6	1	1
839	107.7	0.9605	0.4300
838	85.8	0.8925	0.2730
838	76.6	0.7877	0.2280
839	71.7	0.6908	0.1917
836	67.6	0.5913	0.1501
836	65.0	0.4757	0.1148
835	64.5	0.4012	0.0923
833	63.0	0.3061	0.0728
833	62.5	0.2302	0.0554
835	62.3	0.1772	0.0451
833	60.8	0.0389	0.0138
833	60.5	0.0275	0.0098
835	59.7	0	0

Table 8.9: Regression Models and Results		
Model	Average absolute deviation in vapour composition.	Interaction Parameters
Wilson	0.029	$(\lambda_{12}-\lambda_{11})$: -292.354 $(\lambda_{21}-\lambda_{22})$: 960.438
Van Laar	0.029	A_{12} : 0.9873 A_{21} : 1.6739
NRTL	0.028	b_{12} : 501.787 b_{21} : 232.454 α_{12} : 0.74363
UNIQUAC	0.022	$(u_{12}-u_{11})$: 581.608 $(u_{21}-u_{22})$: -127.926

Table 8.10: Activity Coefficient Data.			
Liquid mole fraction	$\ln \gamma_1$	$\ln \gamma_2$	$\ln (\gamma_1/\gamma_2)$
1	-0.0044	(1.1609)	
0.9605	-0.3669	0.9940	-1.3608
0.8925	0.0222	0.9384	-0.9162
0.7877	0.3257	0.6428	-0.3170
0.6908	0.4855	0.4947	-0.0092
0.5913	0.5661	0.4183	0.1478
0.4757	0.6281	0.3110	0.3171
0.4012	0.5999	0.2219	0.3780
0.3061	0.6974	0.1526	0.5448

0.2302	0.7318	0.0872	0.6445
0.1772	0.7977	0.0421	0.7557
0.0389	1.1983	-0.0233	1.2217
0.0275	1.2144	-0.0190	1.2334
0	(0.9376)	-0.0020	

Table 8.11: Consistency Test Block	
AREA TEST	
Area A:	0.147
Area B:	0.202
$D=100 \left \frac{A-B}{A+B} \right $	15.8
ΔT_{\max}	61.9
T_{\min}	59.7
$J=150 \left \frac{\Delta T_{\max}}{T_{\min}} \right $	27.9
$ D-J $	12.1 FAIL (want $\leq 10\%$)

Table 8.12: Lu Consistency Test	
Condition	Value
$\ln \gamma_1 (x_1=0.5) \approx$	0.628
$0.25 * \ln \gamma_2 \text{ (at } x_1=1)$	0.290 FAIL
$\ln \gamma_2 (x_2=0.5) \approx$	0.311
$0.25 * \ln \gamma_1 \text{ (at } x_2=1)$	0.234

$\ln \gamma_1 (x_1=0.25) \approx$	0.732
$\ln \gamma_2 (\text{at } x_1=0.75)$	0.643
$\ln \gamma_1 > \ln \gamma_2 (x=0.5)$	0.629 0.311
$\ln \gamma$ approaches its zero with horizontal tangence.	FAIL
With no maximum or minimum, $\ln \gamma_1$ and $\ln \gamma_2$ should be on the same side of zero.	FAIL

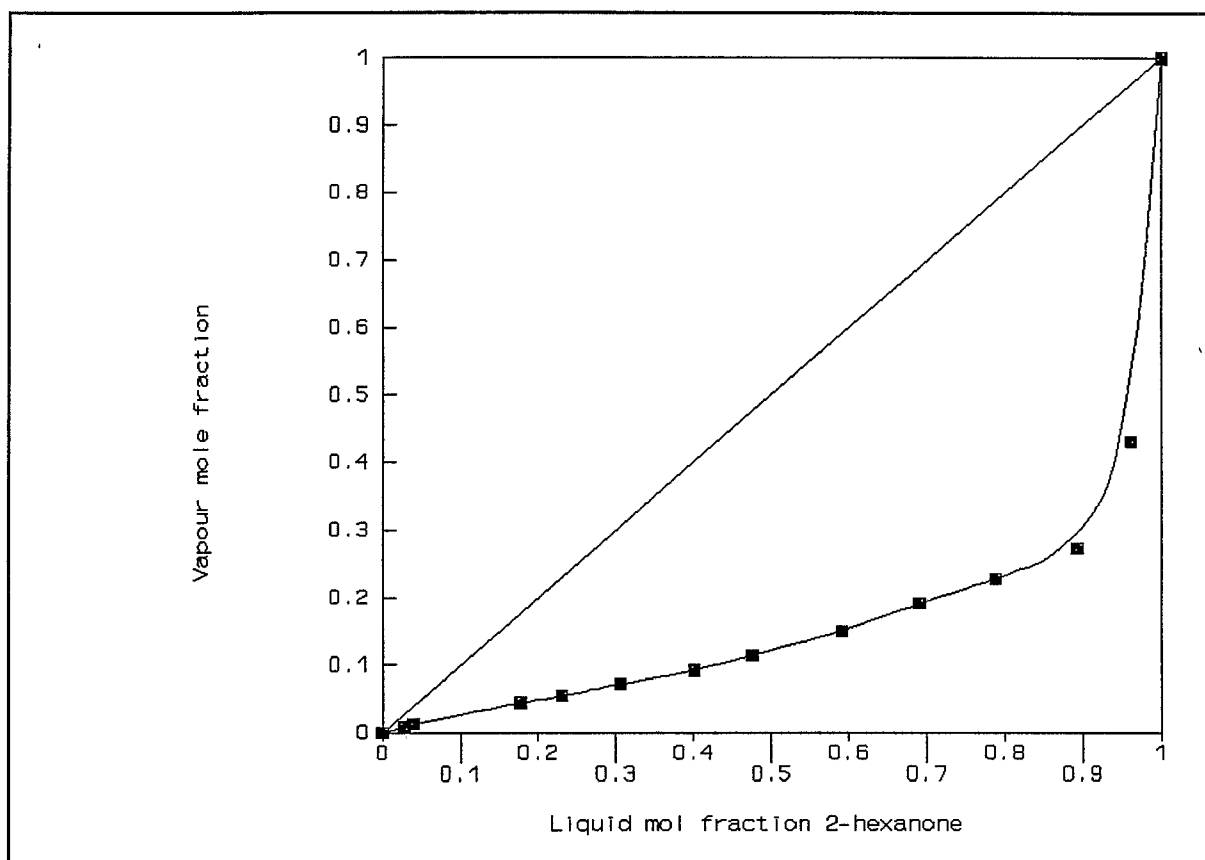


Figure 8.4: MBK - Methanol XY.

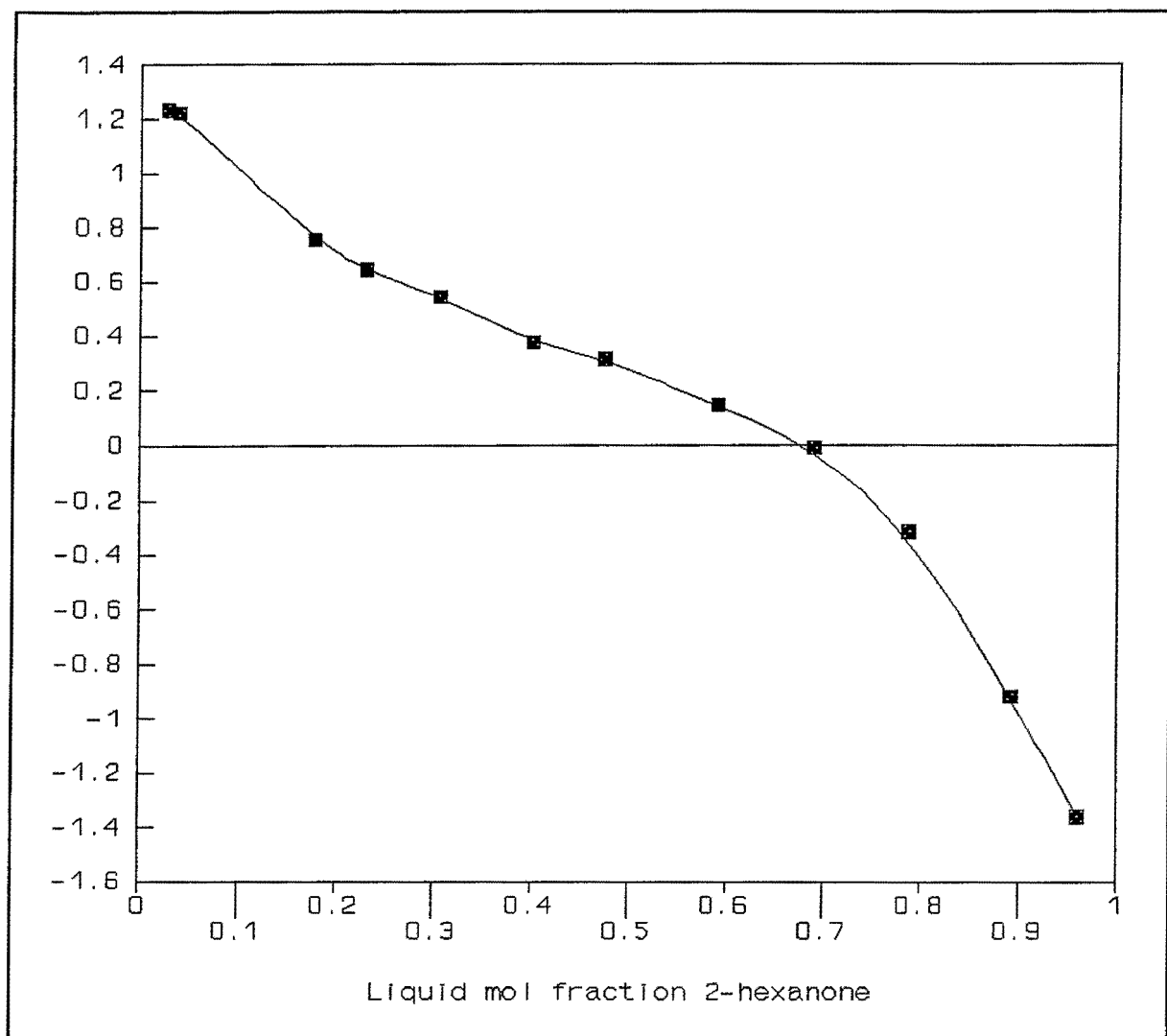


Figure 8.5: MBK - Methanol $\ln(\gamma_1/\gamma_2)$.

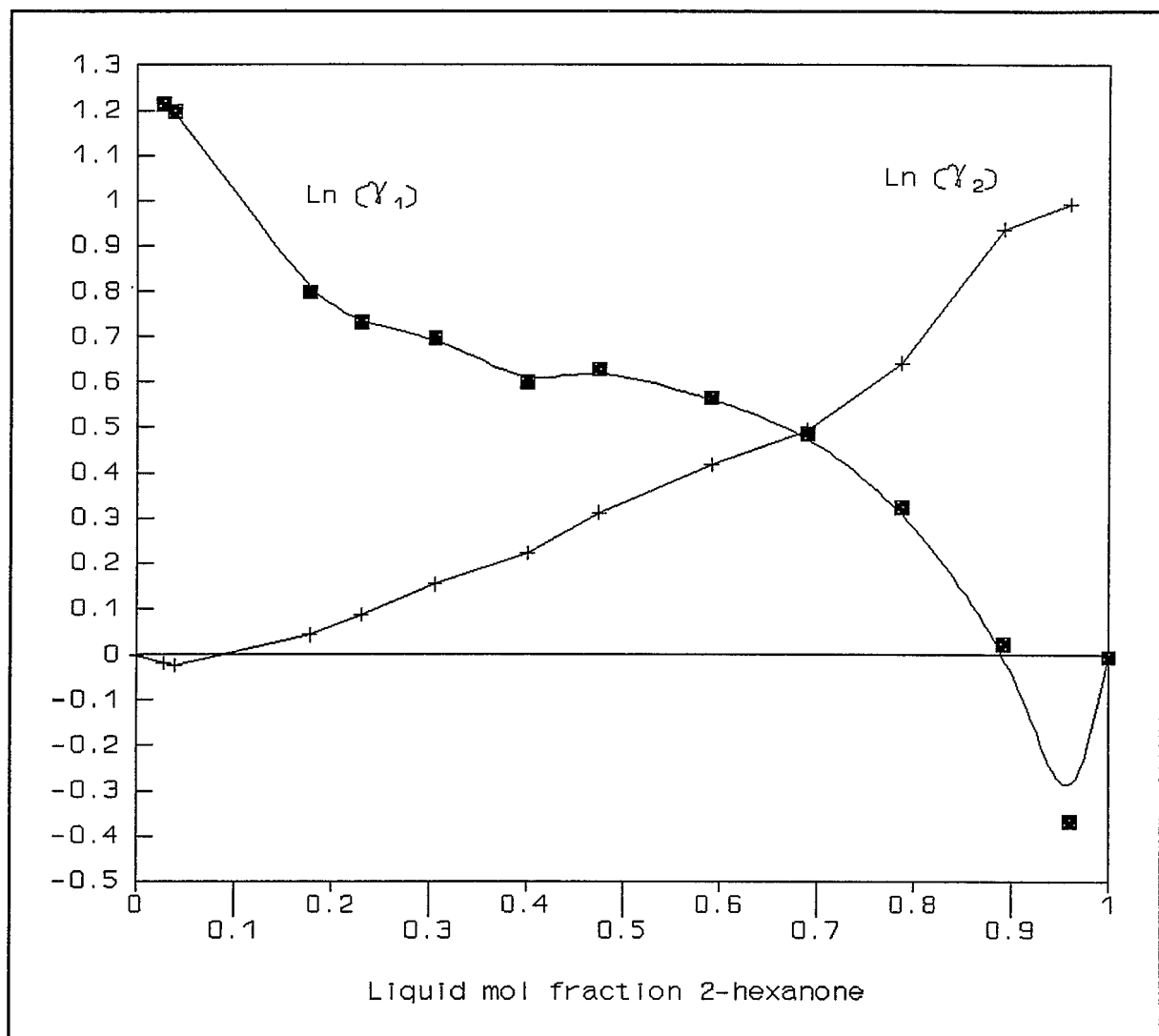


Figure 8.6: MBK - Methanol $\ln(\gamma_1)$ and $\ln(\gamma_2)$.

8.3.3 1-Octene (OCT1) and DMF

As can be expected from the difference in the hydrogen bonding ability of the two components involved, this system also forms an azeotrope.

Table 8.13: VLE Data			
Pressure (mbar)	Temperature (°C)	Liquid mole fraction	Vapour mole fraction

835	114.4	1.0000	1.0000
843	113.1	0.9184	0.8623
843	111.8	0.7541	0.7241
845	111.5	0.6311	0.6757
840	111.4	0.5721	0.6524
844	111.9	0.4283	0.6123
847	112.4	0.3435	0.5845
846	112.9	0.2366	0.5403
846	113.6	0.2143	0.5133
843	119.8	0.0937	0.3800
838	120.8	0.0880	0.3622
842	131.2	0.0190	0.2085
836	132.3	0.0179	0.1993
839	140.7	0.0052	0.0655

Table 8.14: Regression Models and Results		
Model	Average absolute deviation in vapour composition.	Interaction Parameters
Wilson	0.055	NO CONVERGENCE
Van Laar	0.072	NO CONVERGENCE
NRTL	0.052	NO CONVERGENCE
UNIQUAC	0.058	($u_{12}-u_{11}$): 105.238 ($u_{21}-u_{22}$): 104.229

Table 8.15: Activity Coefficient Data.			
Liquid mole fraction	$\ln \gamma_1$	$\ln \gamma_2$	$\ln (\gamma_1/\gamma_2)$
1.0000	0.0008	(1.2381)	
0.9184	-0.0148	1.4692	-1.4840
0.7541	0.0459	1.1038	-1.0579
0.6311	0.1660	0.8720	-0.7060
0.5721	0.2262	0.7902	-0.5640
0.4283	0.4421	0.5982	-0.1561
0.3435	0.6051	0.5163	0.0888
0.2366	0.8832	0.4492	0.4340
0.2143	0.9108	0.4546	0.4562
0.0937	1.2555	0.3540	0.9015
0.0880	1.2371	0.3391	0.8981
0.0190	1.9382	0.1789	1.7593
0.0179	1.9195	0.1507	1.7687
0.0052	1.8400	0.0646	1.7755
0	(2.625)		

Table 8.16: Consistency Test Block	
AREA TEST	
Area A:	0.162
Area B:	0.219
$D=100 \left \frac{A-B}{A+B} \right $	14.96

ΔT_{\max}	29.3
T_{\min}	112.4
$J=150 \left \frac{\Delta T_{\max}}{T_{\min}} \right $	11.39
$ D-J $	3.57

Table 8.17: Lu Consistency Test	
Condition	Value
$\ln \gamma_1 (x_1=0.5) \approx$ $0.25 * \ln \gamma_2 \text{ (at } x_1=1)$	0.332 0.310
$\ln \gamma_2 (x_2=0.5) \approx$ $0.25 * \ln \gamma_1 \text{ (at } x_2=1)$	0.711 0.656
$\ln \gamma_1 (x_1=0.25) \approx$ $\ln \gamma_2 \text{ (at } x_1=0.75)$	0.883 1.104
$\ln \gamma_1 < \ln \gamma_2 \text{ (} x=0.5)$	0.331 0.711
$\ln \gamma$ approaches its zero with horizontal tangence.	FAIL
With no maximum or minimum, $\ln \gamma_1$ and $\ln \gamma_2$ should be on the same side of zero.	OK

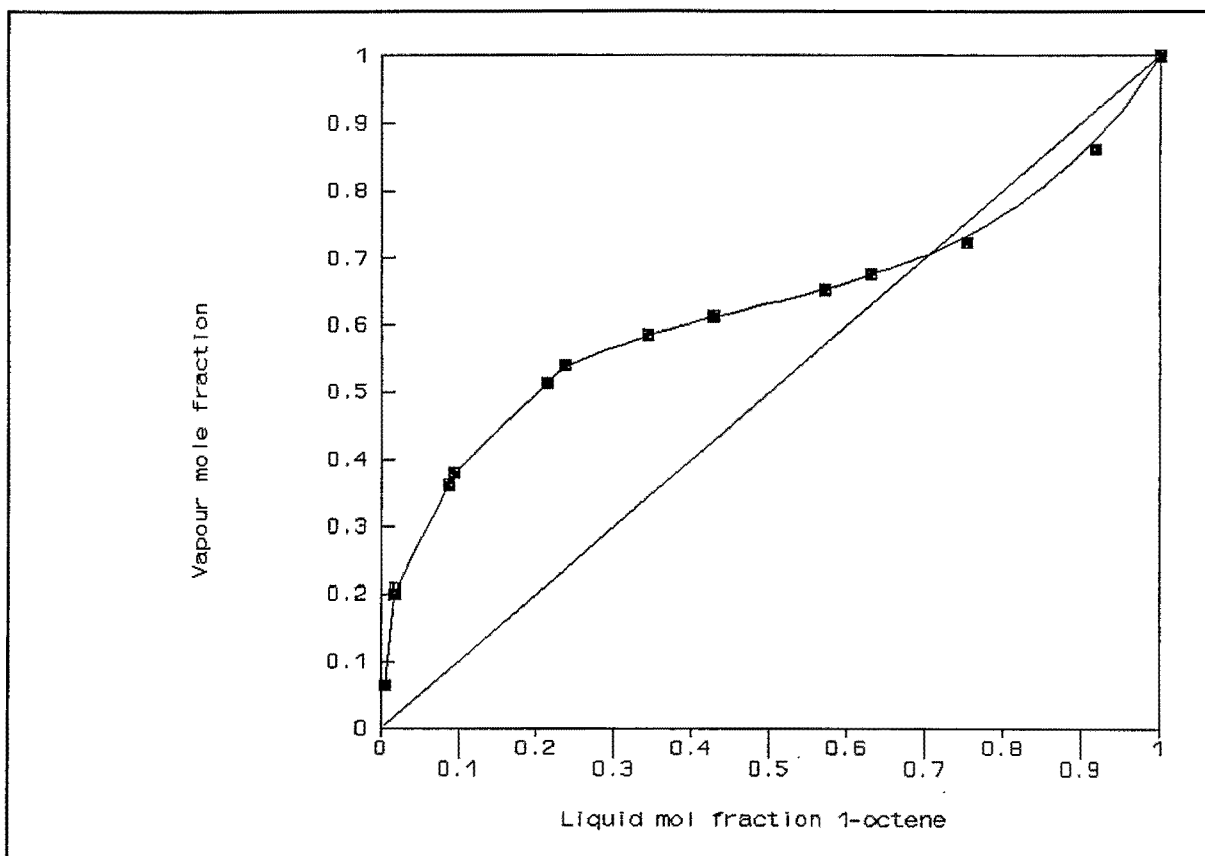


Figure 8.7: OCT1 - DMF XY.

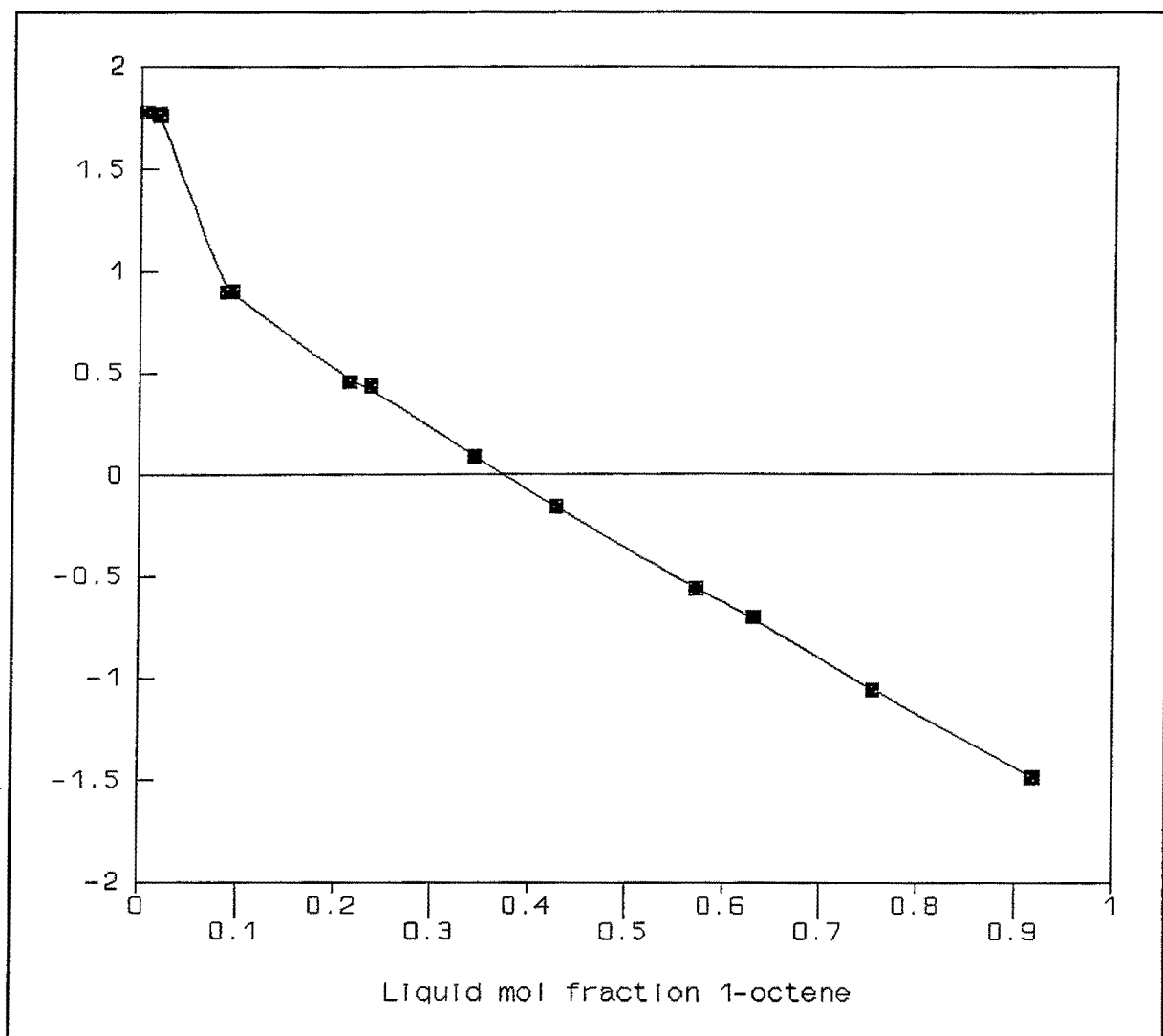


Figure 8.8: OCT1 - DMF $\ln(\gamma_1/\gamma_2)$.

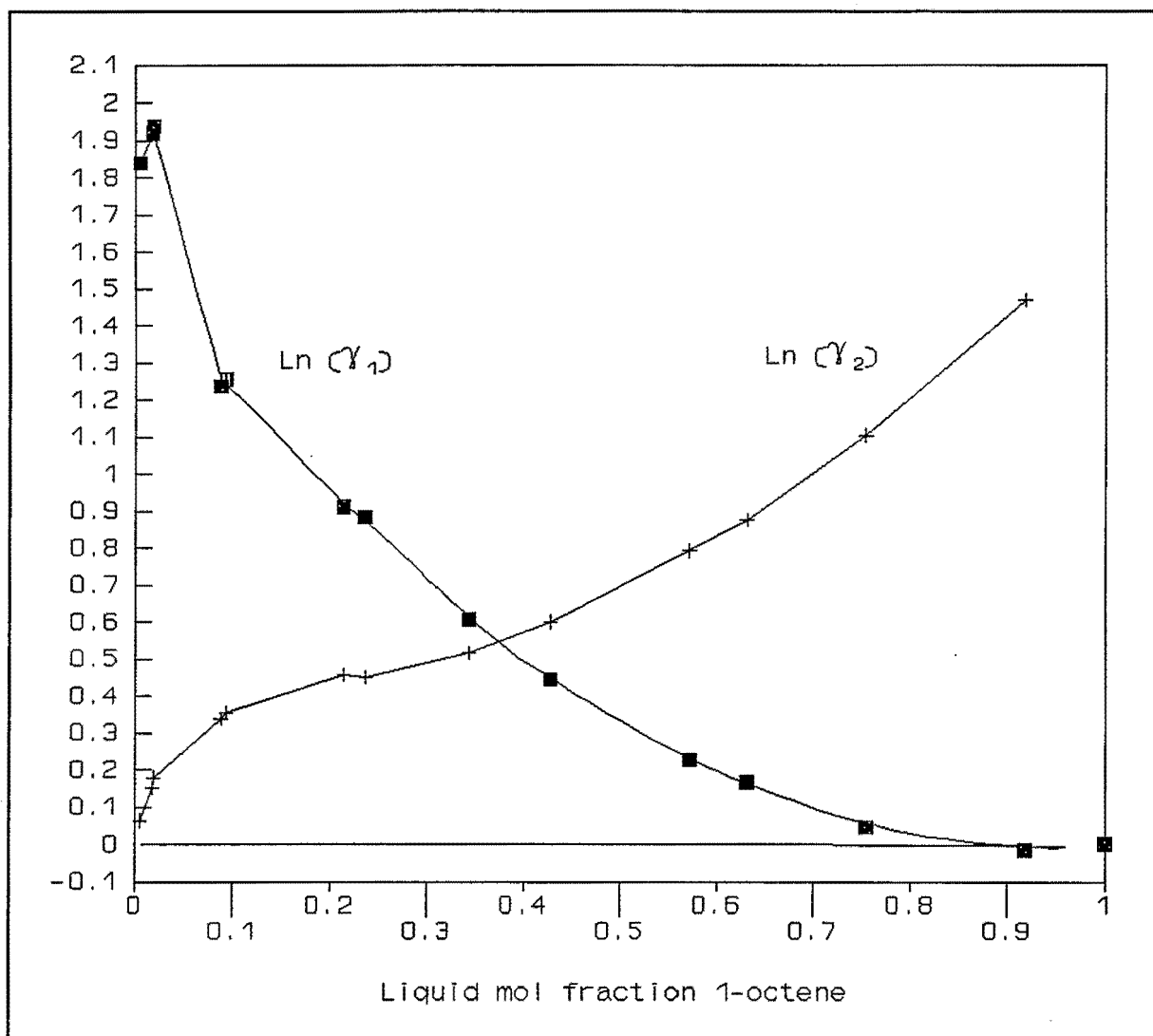


Figure 8.9: OCT1 - DMF $\ln(\gamma_1)$ and $\ln(\gamma_2)$.

8.3.4 2-Hexanone (MBK) and DMF

The system is especially interesting. The diagram of $\ln(\gamma_1/\gamma_2)$ is a straight line which alone would indicate a simple mixture. However, the diagram of $\ln \gamma_1$ shows a maximum and while $\ln \gamma_2$ shows the corresponding minimum (Prausnitz et al, 1986:202). This latter diagram is particularly interesting because it shows how $\ln \gamma_1$ varies with $\ln \gamma_2$ according to the Gibbs Duhem equation. Note how the changes in $\ln \gamma_1$ are larger than those in $\ln \gamma_2$, but

that this difference is neatly cancelled out by the fact that x_1 is smaller than x_2 .

Table 8.18: VLE Data			
Pressure (mbar)	Temperature (°C)	Liquid mole fraction	Vapour mole fraction
835	121.6	1	1
843	122.4	0.9123	0.9400
843	123.6	0.8187	0.8740
845	125.8	0.6732	0.7777
840	127.5	0.5484	0.6813
844	128.1	0.4987	0.6289
847	129.8	0.4006	0.5471
846	132.1	0.3142	0.4832
846	134.4	0.2277	0.4329
843	137.1	0.1292	0.3365
838	138.5	0.0921	0.2772
842	141.4	0.0542	0.1625
836	142.2	0.0481	0.1300
839	144.7	0.0188	0.0501

Table 8.19: Regression Models and Results		
Model	Average absolute deviation in vapour composition.	Interaction Parameters
Wilson	0.014	$(\lambda_{12}-\lambda_{11})$: 209.329 $(\lambda_{21}-\lambda_{22})$: 71.320
Van Laar	0.014	A_{12} : 0.7807 A_{21} : 0.3295
NRTL	0.017	b_{12} : 77.9461 b_{21} : 154.660 α_{12} : 1.000
UNIQUAC	0.015	$(u_{12}-u_{11})$: -15.397 $(u_{21}-u_{22})$: 84.614

Table 8.20: Activity Coefficient Data.			
Liquid mole fraction	$\ln \gamma_1$	$\ln \gamma_2$	$\ln (\gamma_1/\gamma_2)$
1	-0.0044	(0.3412)	
0.9123	0.0109	0.2751	-0.2641
0.8187	0.0107	0.2537	-0.2431
0.6732	0.0271	0.1686	-0.1415
0.5484	0.0443	0.1495	-0.1052
0.4987	0.0466	0.1846	-0.1380
0.4006	0.0811	0.1591	-0.0780
0.3142	0.1334	0.0895	0.0439
0.2277	0.2812	-0.0012	0.2825

0.1292	0.5173	-0.0424	0.5598
0.0921	0.6182	-0.0427	0.6609
0.0542	0.5404	-0.0096	0.5500
0.0481	0.4084	-0.0063	0.4147
0.0188	0.3301	-0.0108	0.3409
0	(0.6129)		

Table 8.21: Consistency Test Block	
AREA TEST	
Area A:	0.071
Area B:	0.061
$D=100 \left \frac{A-B}{A+B} \right $	7.6
ΔT_{\max}	23.1
T_{\min}	121.6
$J=150 \left \frac{\Delta T_{\max}}{T_{\min}} \right $	8.78
$ D-J $	1.2

Table 8.22: Lu Consistency Test	
Condition	Value
$\ln \gamma_1 (x_1=0.5) \approx$	0.047
$0.25 * \ln \gamma_2 \text{ (at } x_1=1)$	0.085

$\ln \gamma_2 (x_2=0.5) \approx$	0.185
$0.25 * \ln \gamma_1 (\text{at } x_2=1)$	0.153
$\ln \gamma_1 (x_1=0.25) \approx$	0.292
$\ln \gamma_2 (\text{at } x_1=0.75)$	0.214
$\ln \gamma_1 < \ln \gamma_2 (x=0.5)$	0.047 0.185
$\ln \gamma$ approaches its zero with horizontal tangence.	OK
With no maximum or minimum, $\ln \gamma_1$ and $\ln \gamma_2$ should be on the same side of zero.	OK

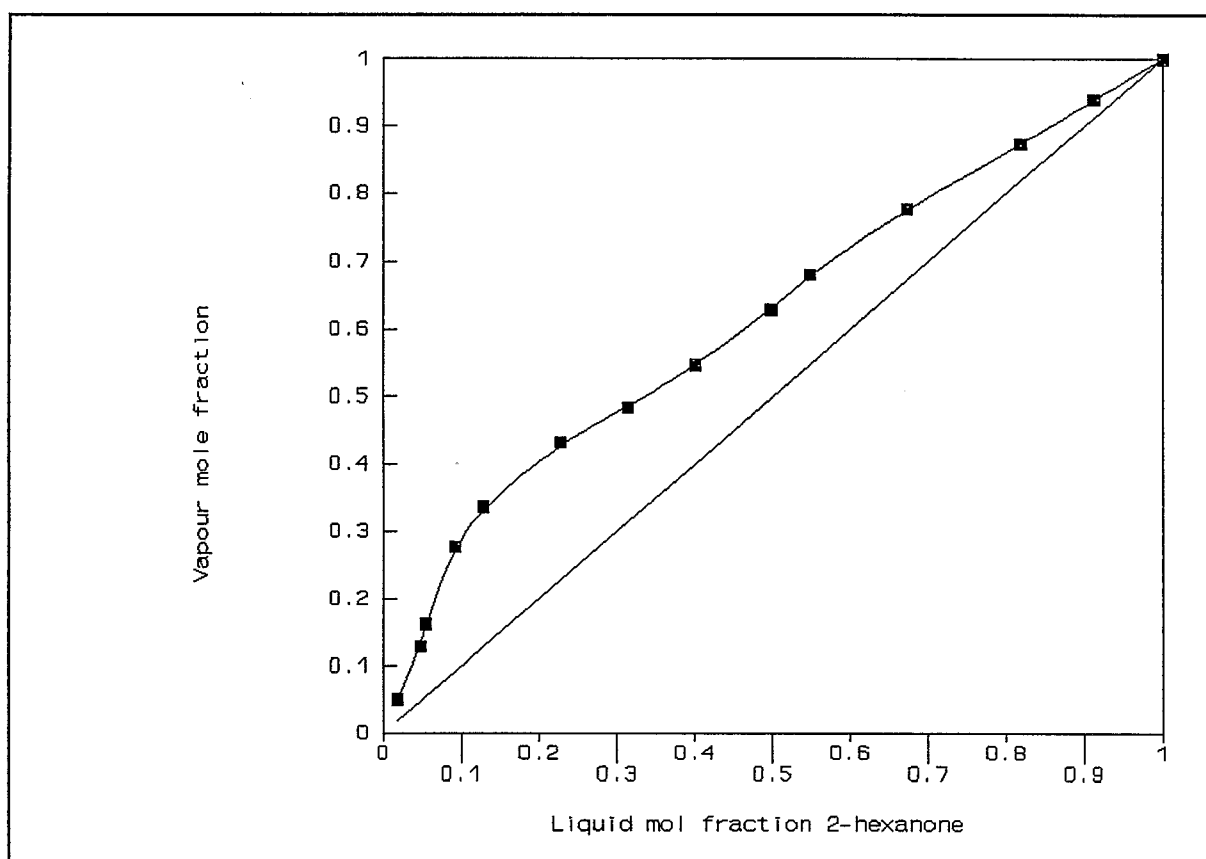


Figure 8.10: MBK - DMF XY.

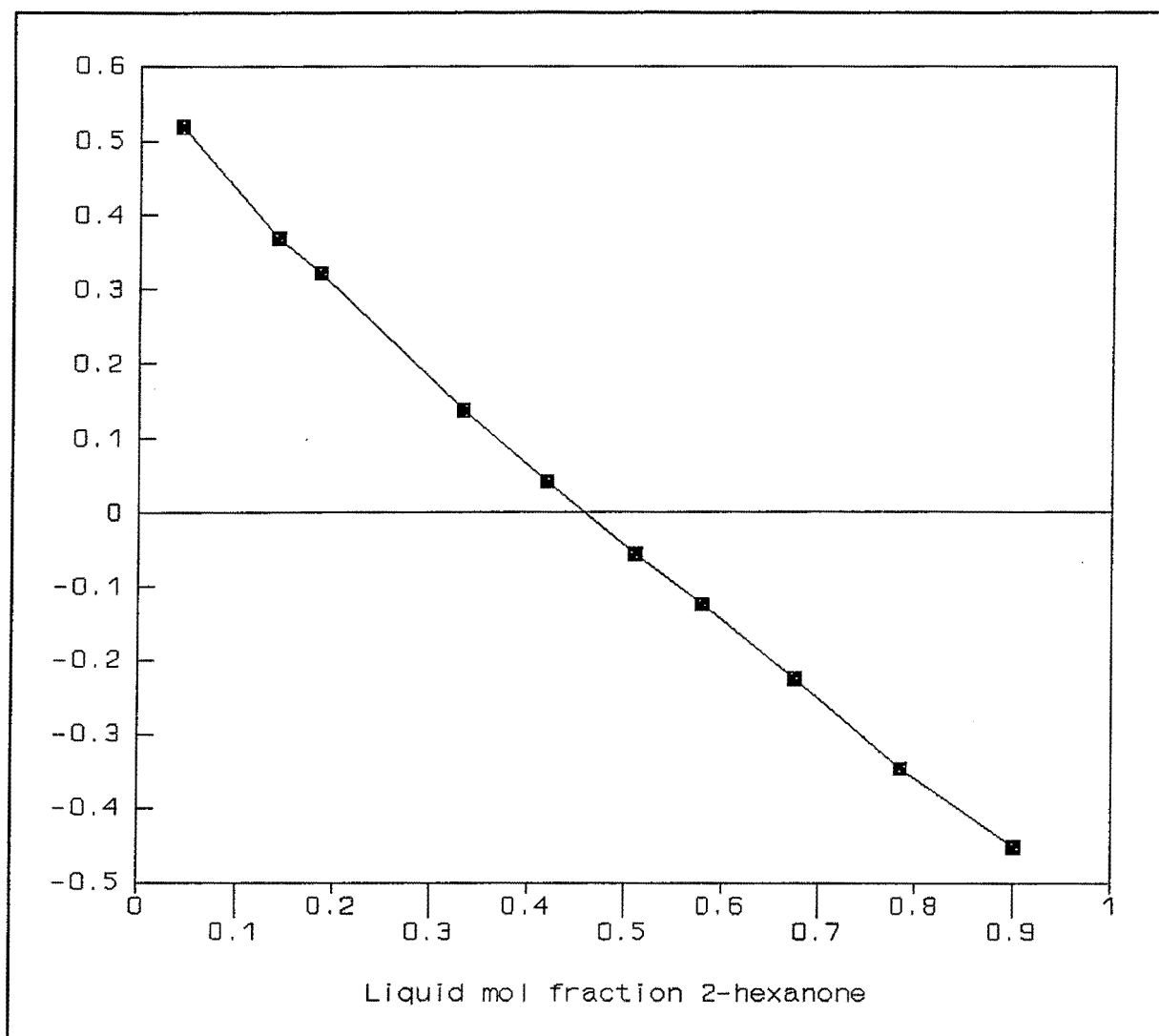


Figure 8.11: MBK - DMF $\ln(\gamma_1/\gamma_2)$.

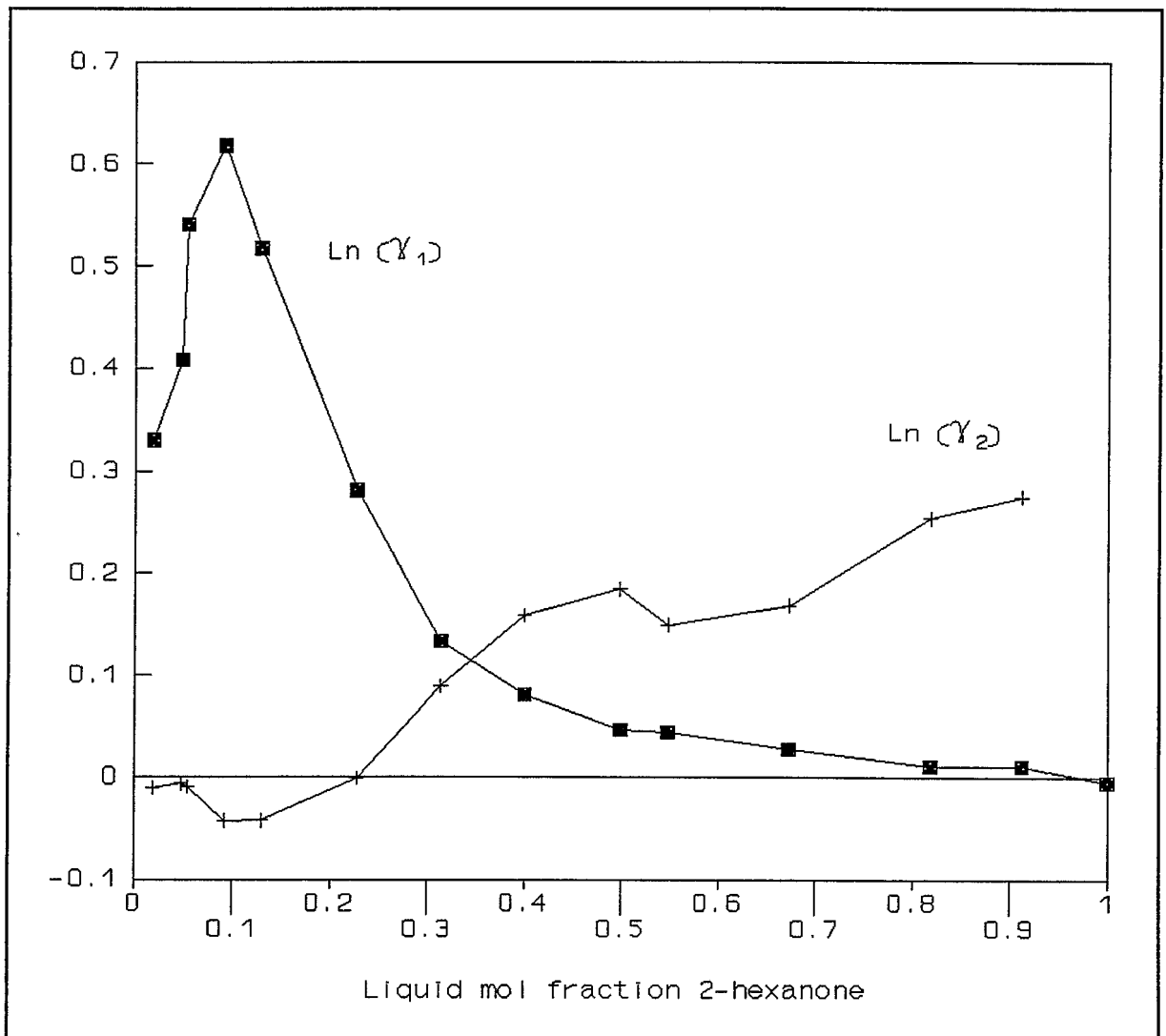


Figure 8.12: MBK - DMF $\ln(\gamma_1)$ and $\ln(\gamma_2)$.

8.3.5 1-Octene (OCT1) and MXEA

Table 8.23: VLE Data			
Pressure (mbar)	Temperature (°C)	Liquid mole fraction	Vapour mole fraction
835	114.4	1	1
842	104.6	0.8960	0.6982
847	102.5	0.7643	0.5806

841	101.8	0.6094	0.5245
839	101.7	0.5042	0.4974
839	101.6	0.4200	0.4655
839	101.7	0.4215	0.4674
833	101.6	0.3243	0.4447
837	102.5	0.1589	0.4101
839	103.1	0.1153	0.3975
842	105.1	0.0756	0.3263
842	118.7	0	0

Table 8.24: Regression Models and Results		
Model	Average absolute deviation in vapour composition.	Interaction Parameters
Wilson	0.017	$(\lambda_{12}-\lambda_{11})$: 631.184 $(\lambda_{21}-\lambda_{22})$: 524.229
Van Laar	0.021	A_{12} : 2.4263 A_{21} : 1.4041
NRTL	0.020	b_{12} : 220.2377 b_{21} : 801.2740 α_{12} : 0.3979
UNIQUAC	0.022	$(u_{12}-u_{11})$: 125.182 $(u_{21}-u_{22})$: 100.937

Table 8.25: Activity Coefficient Data.			
Liquid mole fraction	$\ln \gamma_1$	$\ln \gamma_2$	$\ln (\gamma_1/\gamma_2)$
1	0.0008	(1.5647)	
0.8960	0.0536	1.5314	-1.4778
0.7643	0.0992	1.1220	-1.0228
0.6094	0.2390	0.7602	-0.5212
0.5042	0.3763	0.5782	-0.2019
0.4200	0.4960	0.4862	0.0098
0.4215	0.4934	0.4817	0.0117
0.3243	0.7014	0.3647	0.3367
0.1589	1.3106	0.1791	1.1316
0.1153	1.5837	0.1309	1.4529
0.0756	1.7494	0.1322	1.6171
0	(2.777)	-0.0060	

Table 8.26: Consistency Test Block	
AREA TEST	
Area A:	0.174
Area B:	0.195
$D=100 \left \frac{A-B}{A+B} \right $	5.69
ΔT_{\max}	17.1
T_{\min}	101.6

$J=150 \left \frac{\Delta T_{\max}}{T_{\min}} \right $	6.84
$ D-J $	1.15

Table 8.27: Lu Consistency Test	
Condition	Value
$\ln \gamma_1 (x_1=0.5) \approx$ $0.25 * \ln \gamma_2 \text{ (at } x_1=1)$	0.376 0.391
$\ln \gamma_2 (x_2=0.5) \approx$ $0.25 * \ln \gamma_1 \text{ (at } x_2=1)$	0.578 0.694
$\ln \gamma_1 (x_1=0.25) \approx$ $\ln \gamma_2 \text{ (at } x_1=0.75)$	1.001 1.122
$\ln \gamma_1 < \ln \gamma_2 \text{ (x=0.5)}$	0.376 0.578
$\ln \gamma$ approaches its zero with horizontal tangence.	OK
With no maximum or minimum, $\ln \gamma_1$ and $\ln \gamma_2$ should be on the same side of zero.	OK

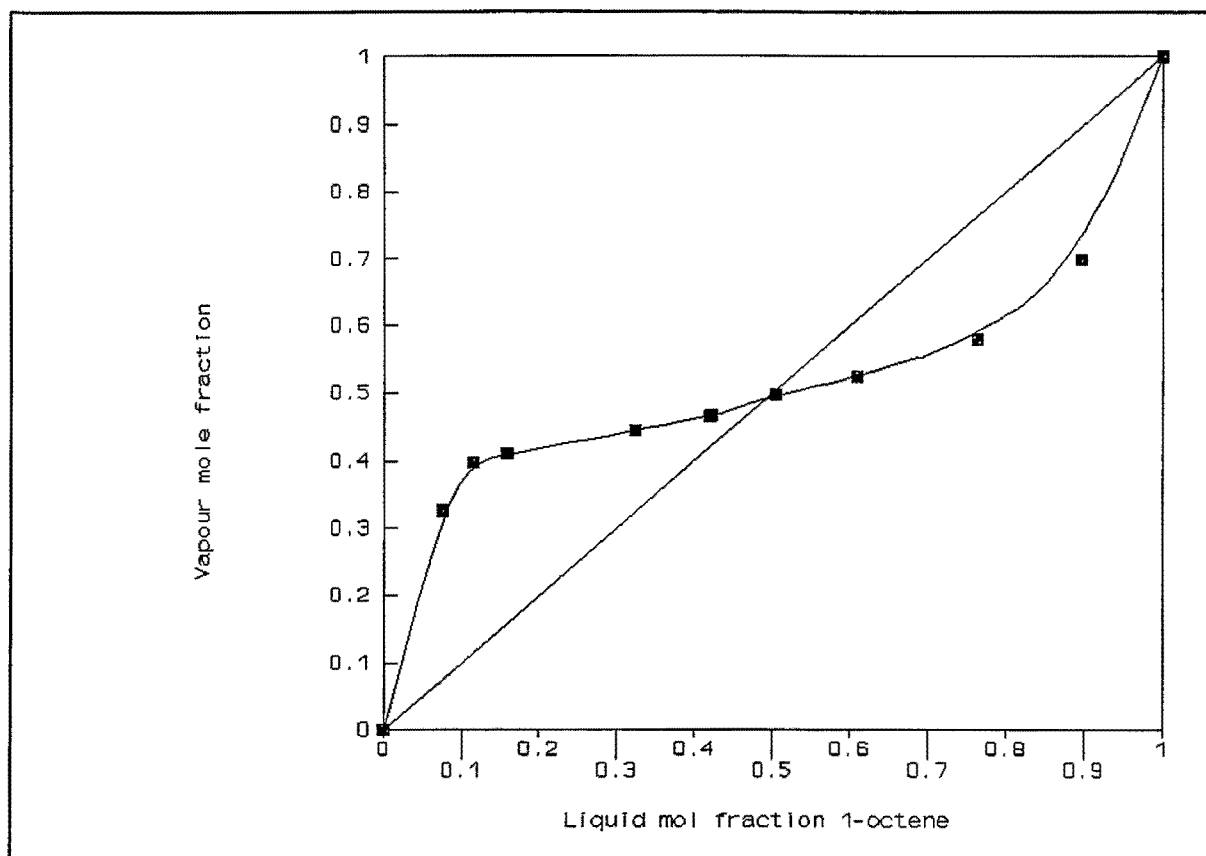


Figure 8.13: OCT1 - EXEA XY.

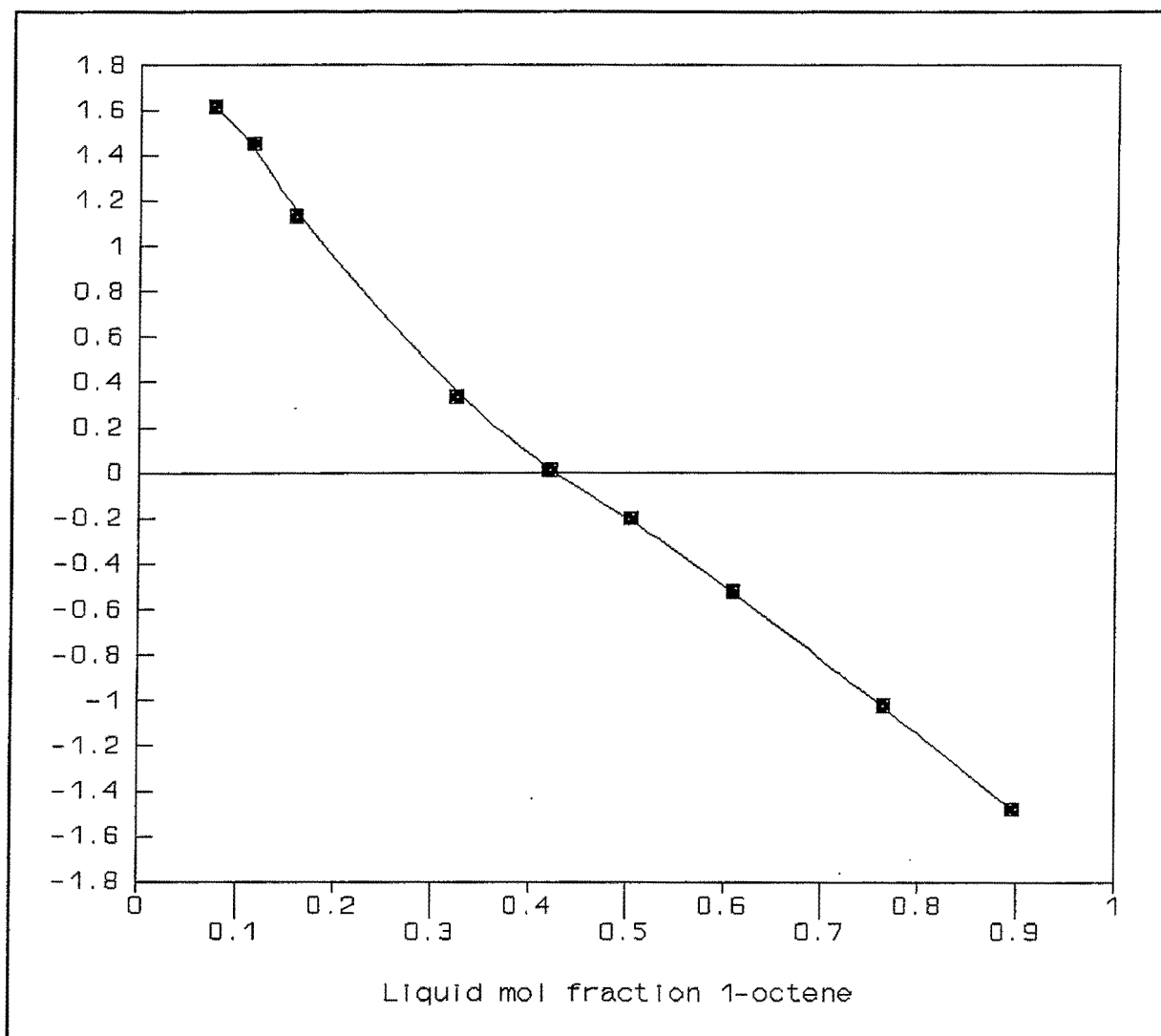


Figure 8.14: OCT1 - EXEA $\ln(\gamma_1/\gamma_2)$.

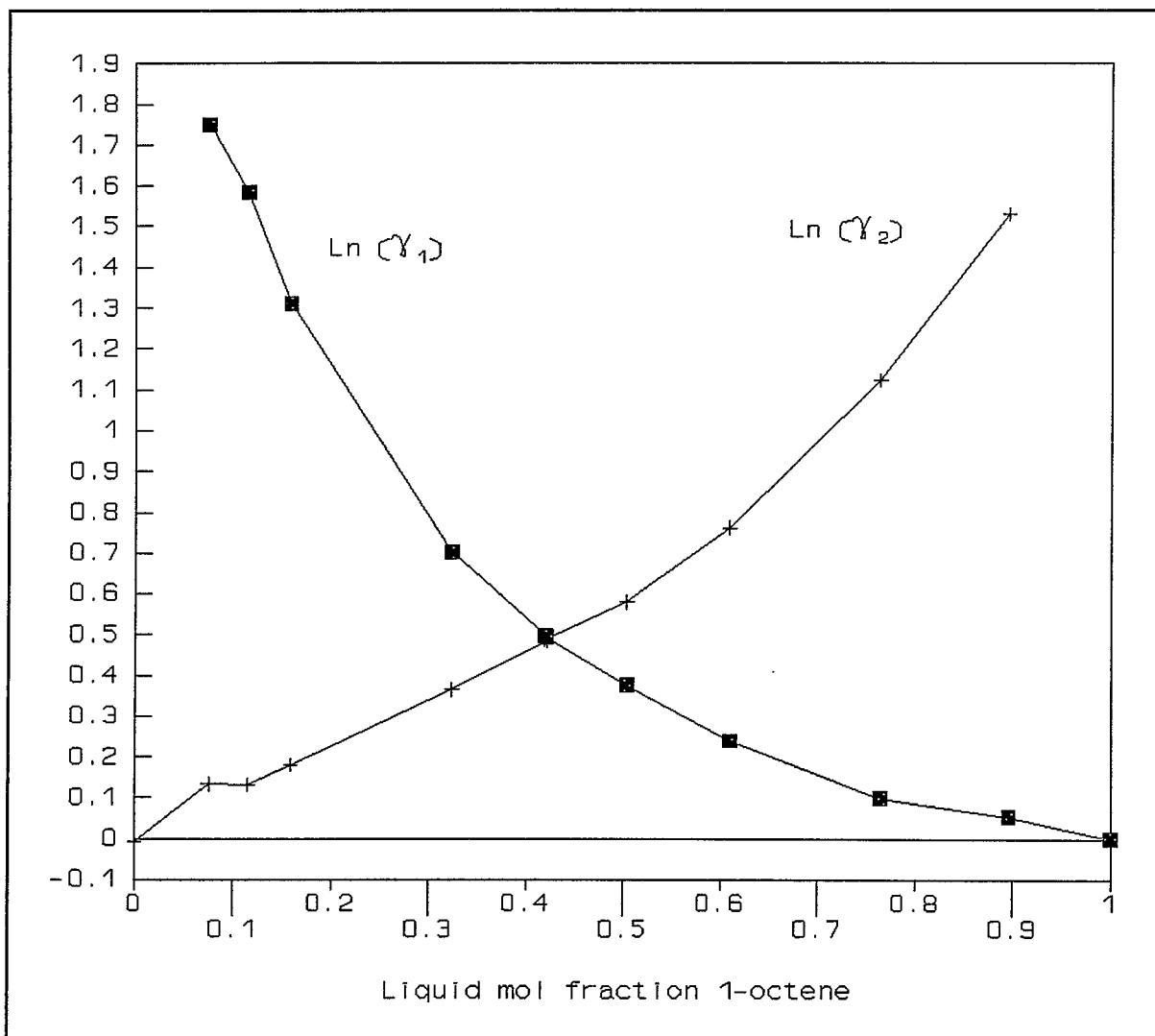


Figure 8.15: OCT1 - EXEA $\ln(\gamma_1)$ and $\ln(\gamma_2)$.

8.3.6 2-Hexanone (MBK) and MXEA

Table 8.28: VLE Data			
Pressure (mbar)	Temperature (°C)	Liquid mole fraction	Vapour mole fraction
835	121.6	1	1
842	118.9	0.9007	0.8395

847	117.5	0.7849	0.7009
841	116.4	0.6753	0.6017
839	115.7	0.5803	0.5265
839	115.4	0.5104	0.4730
839	115.2	0.4192	0.4067
833	115.0	0.3327	0.3428
839	115.7	0.1853	0.2223
842	116.1	0.1417	0.1784
837	117.6	0.0428	0.0638
842	118.7	0	0

Table 8.29: Regression Models and Results		
Model	Average absolute deviation in vapour composition.	Interaction Parameters
Wilson	0.004	$(\lambda_{12}-\lambda_{11})$: 21.413 $(\lambda_{21}-\lambda_{22})$: 227.205
Van Laar	0.003	A_{12} : 0.66386 A_{21} : 0.4795
NRTL	0.005	b_{12} : 303.6959 b_{21} : -93.2835 α_{12} : -0.04487
UNIQUAC	0.003	$(u_{12}-u_{11})$: 50.634 $(u_{21}-u_{22})$: 25.320

Table 8.30: Activity Coefficient Data.
--

Liquid mole fraction	$\ln \gamma_1$	$\ln \gamma_2$	$\ln (\gamma_1/\gamma_2)$
1	-0.0044	(0.4683)	
0.9007	0.0154	0.4673	-0.4518
0.7849	0.0215	0.3680	-0.3464
0.6753	0.0461	0.2714	-0.2254
0.5803	0.0837	0.2081	-0.1244
0.5104	0.1143	0.1708	-0.0565
0.4192	0.1663	0.1252	0.0411
0.3327	0.2254	0.0880	0.1374
0.1853	0.3630	0.0410	0.3220
0.1417	0.4025	0.0343	0.3682
0.0428	0.5197	0.0012	0.5185
0	(0.6653)	-0.0060	

Table 8.31: Consistency Test Block	
AREA TEST	
Area A:	0.065
Area B:	0.063
$D=100 \left \frac{A-B}{A+B} \right $	1.56
ΔT_{\max} T_{\min}	6.6 115.0

$J=150 \left \frac{\Delta T_{\max}}{T_{\min}} \right $	2.55
$ D-J $	0.99

Table 8.32: Lu Consistency Test	
Condition	Value
$\ln \gamma_1 (x_1=0.5) \approx$	0.114
$0.25 * \ln \gamma_2 \text{ (at } x_1=1)$	0.117
$\ln \gamma_2 (x_2=0.5) \approx$	0.171
$0.25 * \ln \gamma_1 \text{ (at } x_2=1)$	0.166
$\ln \gamma_1 (x_1=0.25) \approx$	0.321
$\ln \gamma_2 \text{ (at } x_1=0.75)$	0.357
$\ln \gamma_1 < \ln \gamma_2 \text{ (x=0.5)}$	0.114 0.171
$\ln \gamma$ approaches its zero with horizontal tangence.	OK
With no maximum or minimum, $\ln \gamma_1$ and $\ln \gamma_2$ should be on the same side of zero.	OK

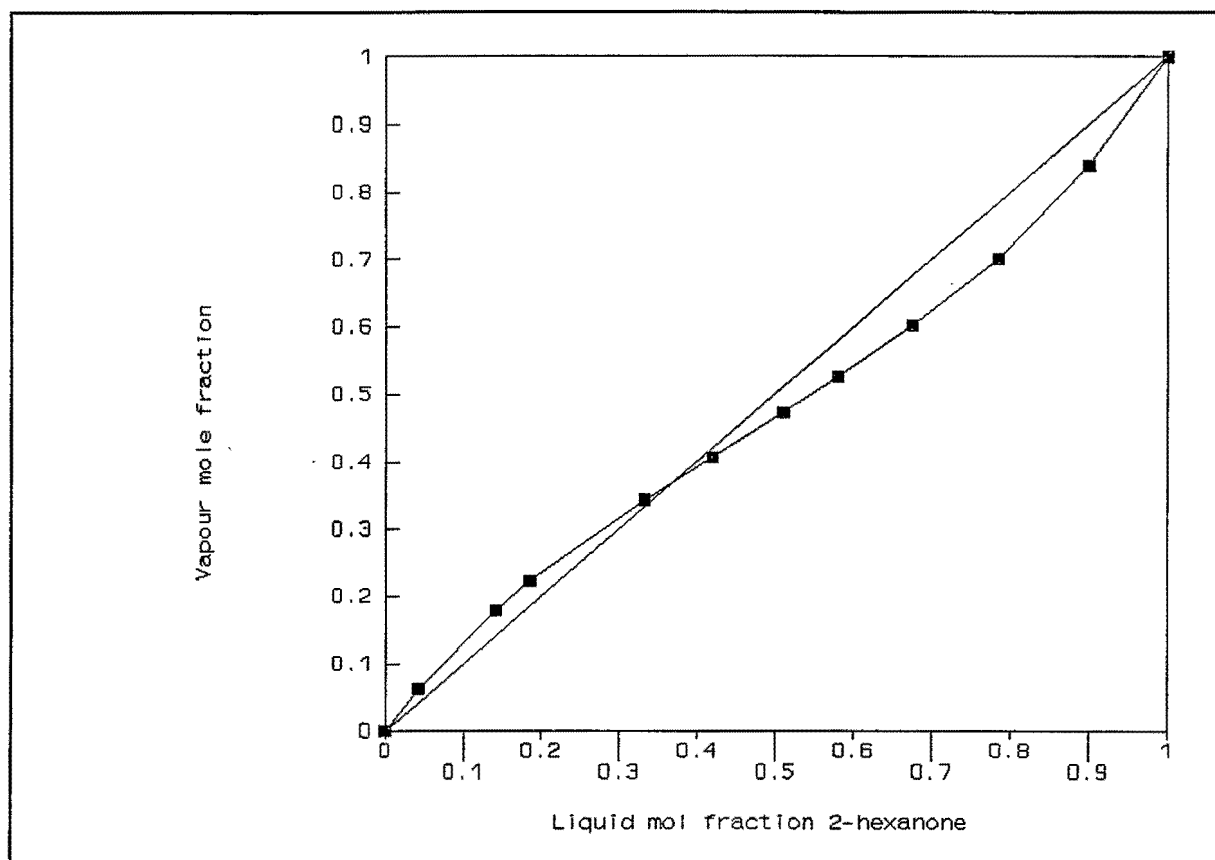


Figure 8.16: MBK - EXEA XY.

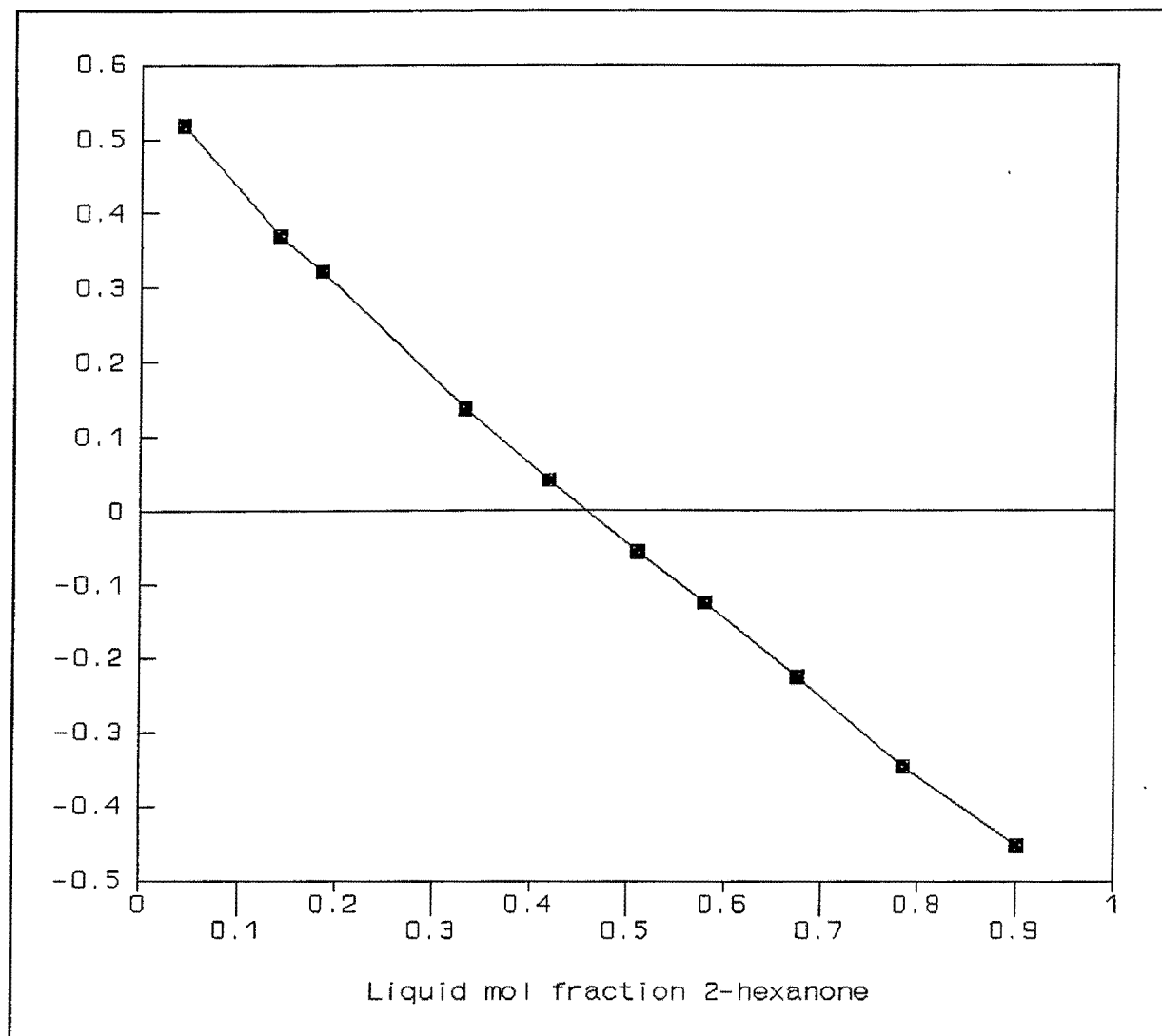


Figure 8.17: MBK - EXEA $\ln(\gamma_1/\gamma_2)$.

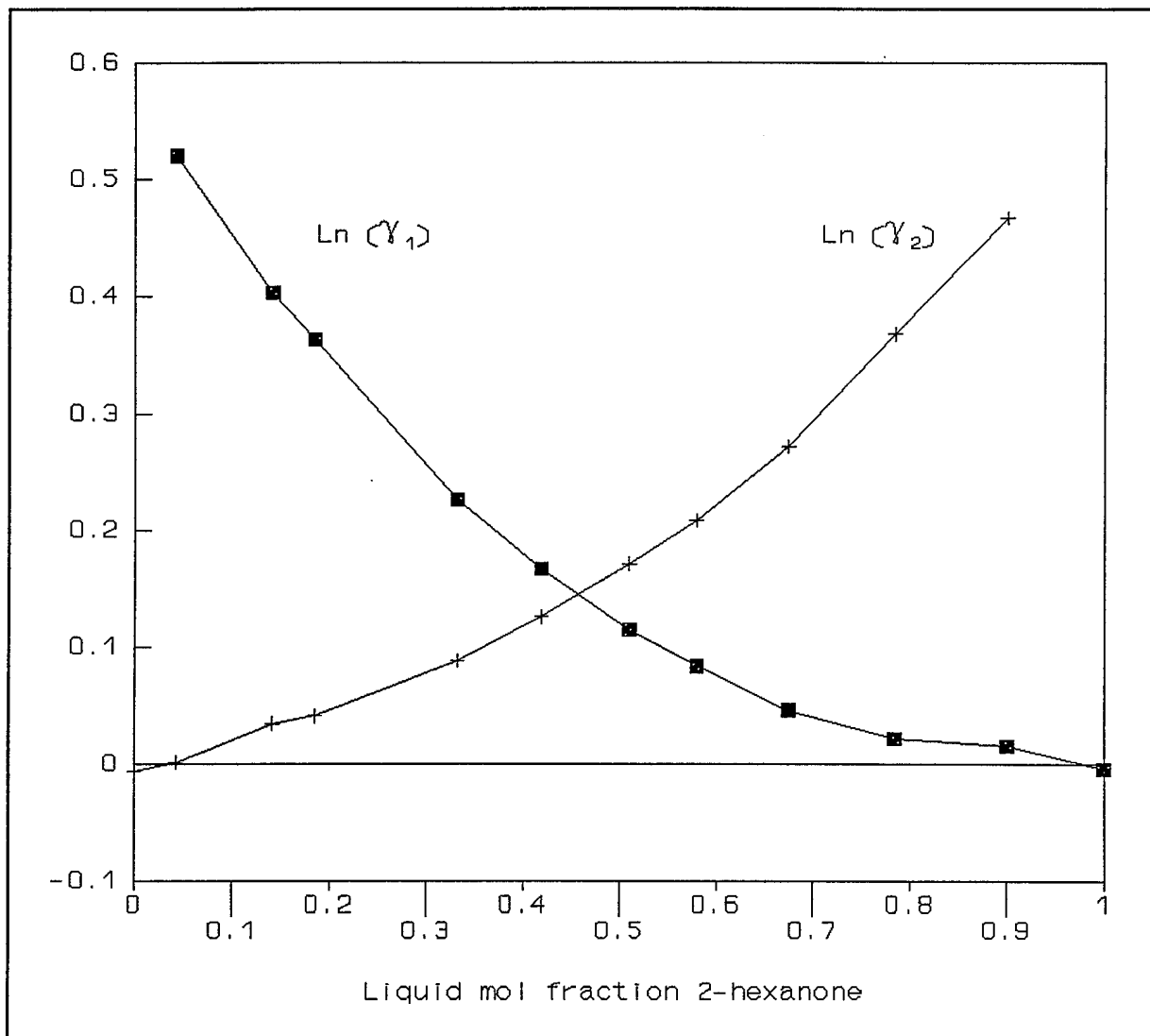


Figure 8.18: MBK - EXEA $\ln(\gamma_1)$ and $\ln(\gamma_2)$.

8.3.7 1-Octene (OCT1) and kerosol 200

Diagrams of the activity coefficients clearly indicate serious consistency problems. For kerosol 200 it must be remembered that a mixture with a wide boiling range and dozens of components was used. The regression was done by modelling the stream as a single normal paraffin. Kerosol 200 was specifically included in order to have an industrial solvent as well. In this case the consistency tests were only done for interest, but the data was not expected to be consistent. This solvent was included more for practical reasons than for theoretical considerations.

It need not be stated that the data for kerosol 200 is not suited to be taken up in any sort of compilation, especially as the solvent is a mixture.

Table 8.33: VLE Data			
Pressure (mbar)	Temperature (°C)	Liquid mole fraction	Vapour mole fraction
835	114.4	1	1
840	115.3	0.9762	0.9982
841	117.1	0.9150	0.9924
841	119.9	0.8337	0.9880
840	122.5	0.7709	0.9811
842	126.1	0.6887	0.9582
837	132.2	0.5507	0.9302
836	134.9	0.5160	0.9038
840	144.6	0.3765	0.8312
839	153.8	0.2584	0.7312
837	164.2	0.1360	0.5416

Table 8.34: Regression Models and Results		
Model	Average absolute deviation in vapour composition.	Interaction Parameters
Wilson	0.010	$(\lambda_{12}-\lambda_{11})$: 556.826 $(\lambda_{21}-\lambda_{22})$: -437.267

Van Laar	0.008	A_{12} : -1.6245 A_{21} : -0.1008
NRTL	0.010	b_{12} : 94.5333 b_{21} : -160.473 α_{12} : -0.47087
UNIQUAC	0.015	$(u_{12}-u_{11})$: -9.240 $(u_{21}-u_{22})$: -9.240

Table 8.35: Activity Coefficient Data.			
Liquid mole fraction	$\ln \gamma_1$	$\ln \gamma_2$	$\ln (\gamma_1/\gamma_2)$
1	0.0008	(-0.1526)	
0.9762	0.0030	-0.2778	0.2807
0.9150	0.0113	-0.1643	0.1756
0.8337	0.0206	-0.4920	0.5126
0.7709	0.0181	-0.4549	0.4730
0.6887	0.0109	-0.0985	0.1095
0.5507	0.0366	-0.1771	0.2137
0.5160	0.0018	-0.0273	0.0291
0.3765	-0.0051	-0.0400	0.0349
0.2584	0.0235	-0.0420	0.0655
0.1360	0.1277	0.0247	0.1030

Table 8.36: Consistency Test Block	
AREA TEST	
Area A:	0.077
Area B:	≈ 0

$D=100 \left \frac{A-B}{A+B} \right $	100
ΔT_{\max} T_{\min}	58.6 114.4
$J=150 \left \frac{\Delta T_{\max}}{T_{\min}} \right $	22.7
$ D-J $	77.3

Table 8.37: Lu Consistency Test	
Condition	Value
$\ln \gamma_1 (x_1=0.5) \approx$ $0.25 * \ln \gamma_2 (at x_1=1)$	0.002 -0.038
$\ln \gamma_2 (x_2=0.5) \approx$ $0.25 * \ln \gamma_1 (at x_2=1)$	-0.027 0.14
$\ln \gamma_1 (x_1=0.25) \approx$ $\ln \gamma_2 (at x_1=0.75)$	0.024 -0.455 FAIL
$\ln \gamma_1 < \ln \gamma_2 (x=0.5)$	0.002 -0.03 FAIL
$\ln \gamma$ approaches its zero with horizontal tangence.	OK
With no maximum or minimum, $\ln \gamma_1$ and $\ln \gamma_2$ should be on the same side of zero.	OK

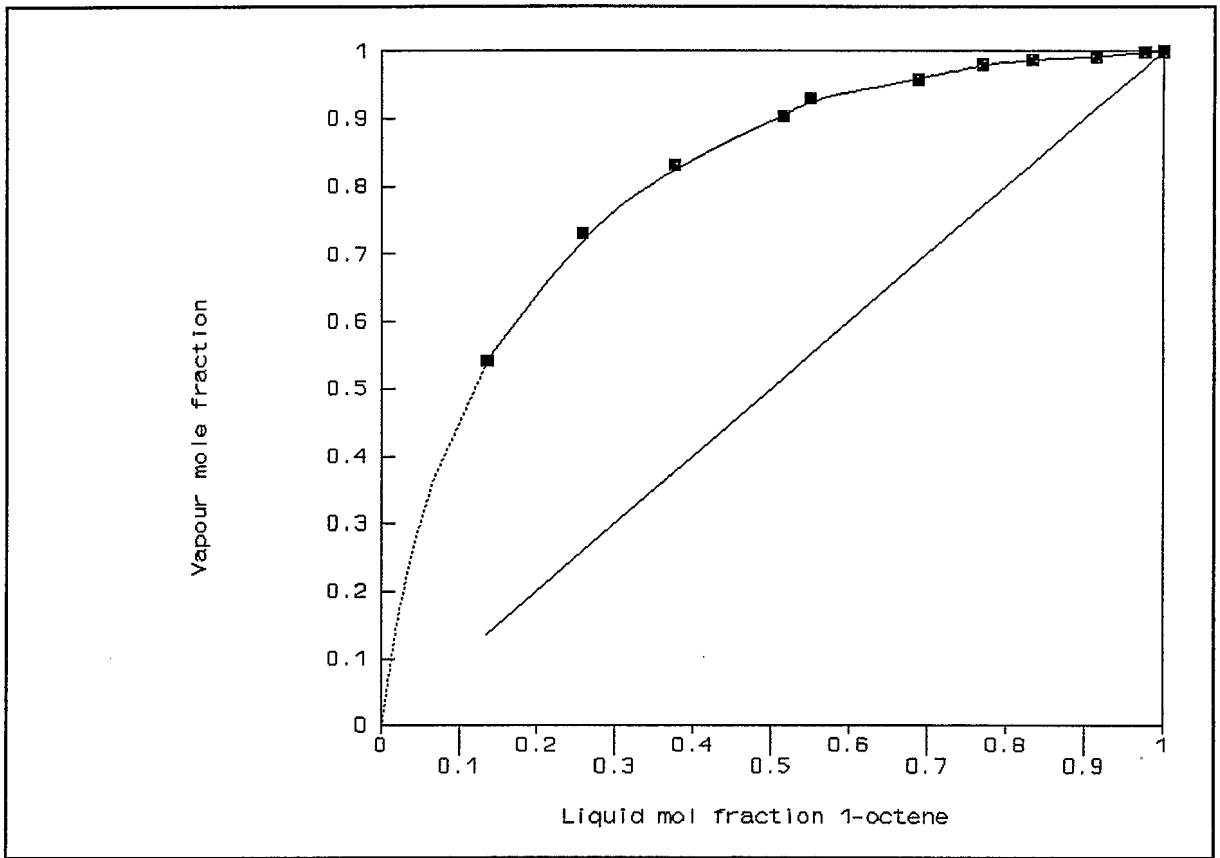


Figure 8.19: OCT1 - kerosol XY.

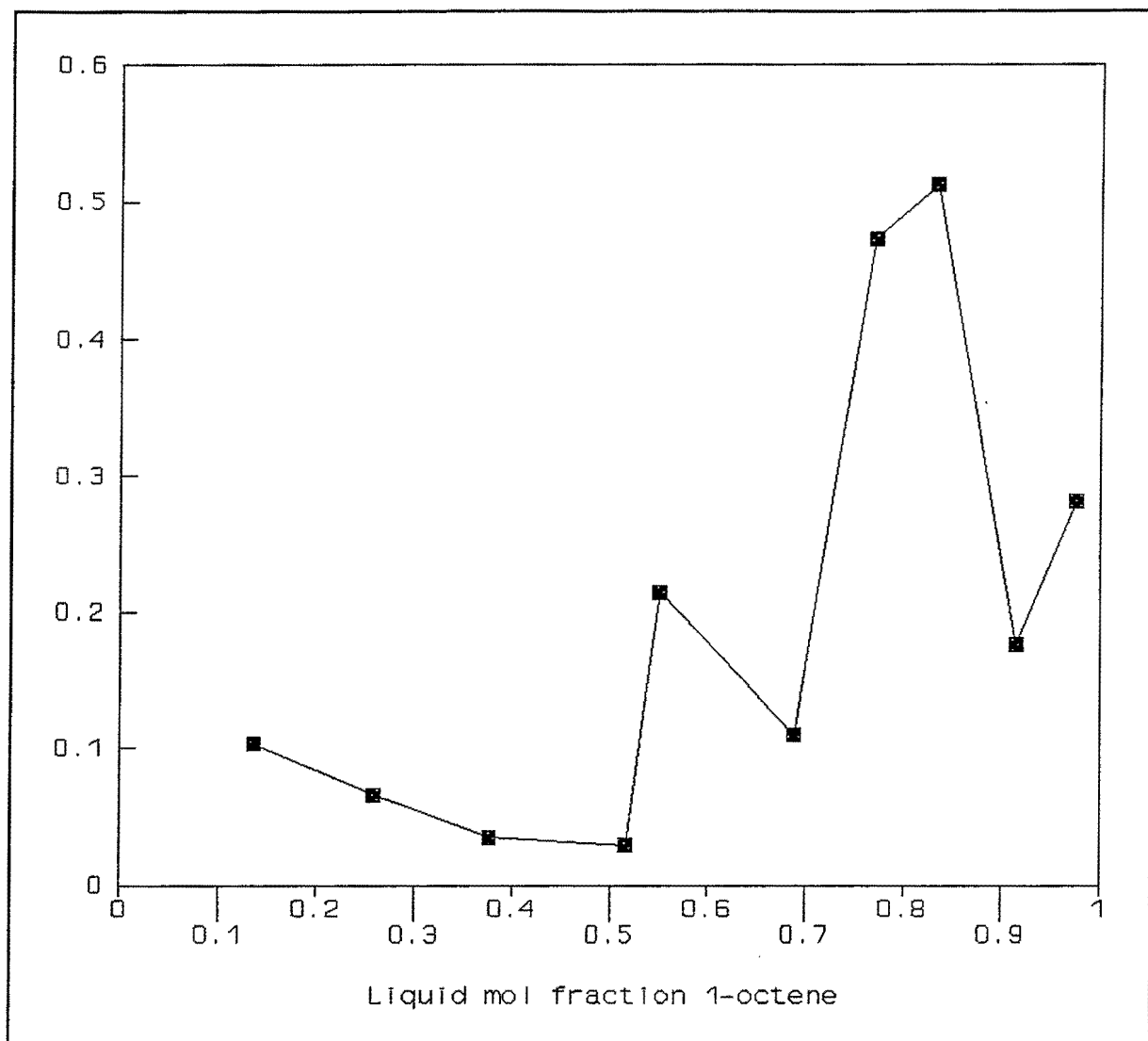


Figure 8.20: OCT1 - kerosol $\ln(\gamma_1/\gamma_2)$.

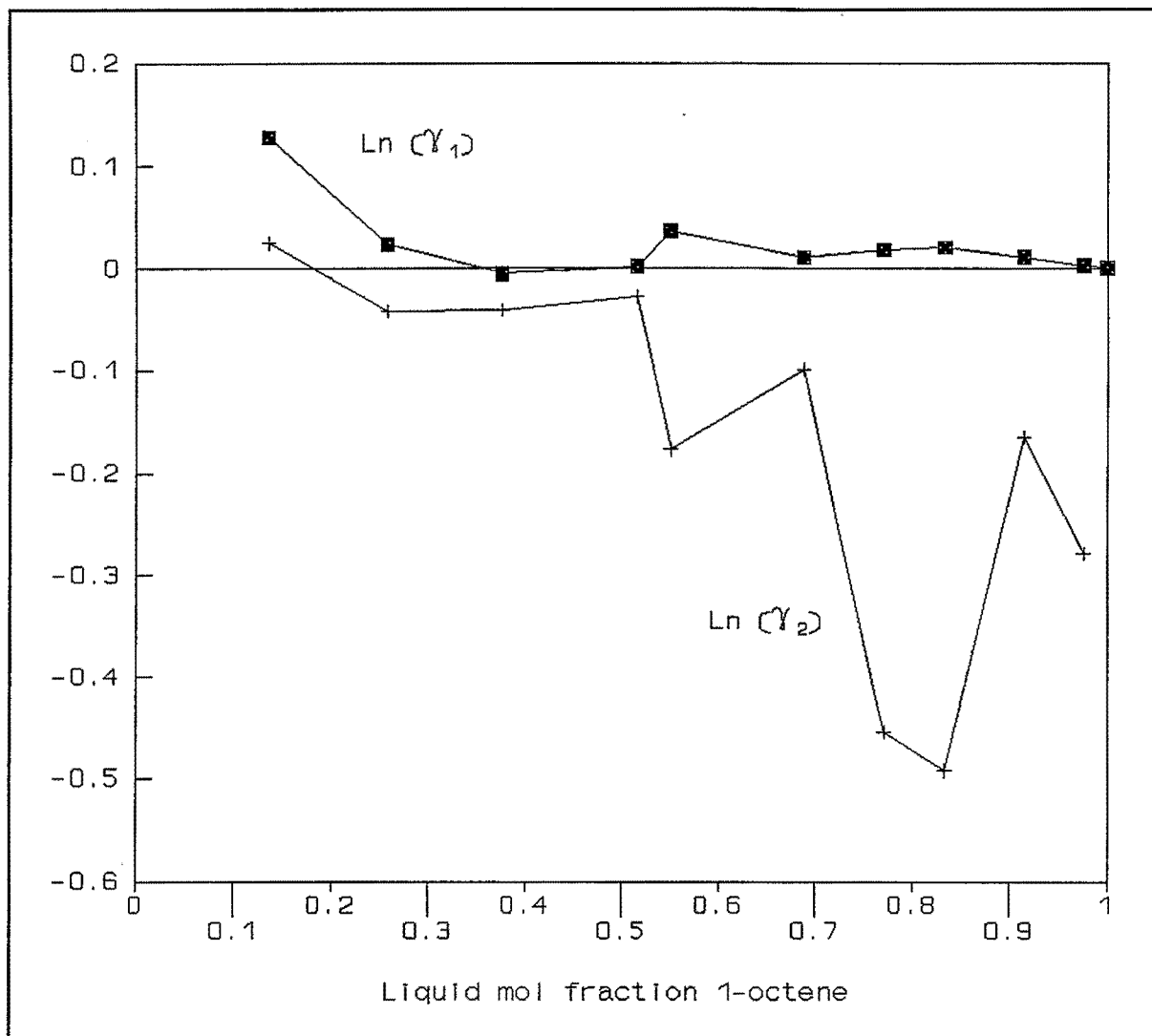


Figure 8.21: OCT1 - kerosol $\ln(\gamma_1)$ and $\ln(\gamma_2)$.

8.3.8 2-Hexanone (MBK) and kerosol 200

While the same can be said for this system than the previous one, the consistency tests show the data to have somewhat more integrity.

Table 8.38: VLE Data			
Pressure (mbar)	Temperature (°C)	Liquid mole fraction	Vapour mole fraction
835	121.6	1	1

840	122.5	0.9733	0.9950
841	123.9	0.9163	0.9810
841	124.2	0.8886	0.9758
840	126.1	0.8162	0.9617
842	127.1	0.7439	0.9487
837	128.5	0.6671	0.9395
835	130.3	0.6134	0.9309
836	131.3	0.5699	0.8988
840	132.4	0.5306	0.8941
839	138.1	0.4044	0.8741
837	154.4	0.1714	0.7067

Table 8.39: Regression Models and Results		
Model	Average absolute deviation in vapour composition.	Interaction Parameters
Wilson	0.011	$(\lambda_{12}-\lambda_{11})$: 279.110 $(\lambda_{21}-\lambda_{22})$: -9.062
Van Laar	0.011	A_{12} : 0.3586 A_{21} : 0.9495
NRTL	0.010	b_{12} : 336.015 b_{21} : 63.9000 α_{12} : 1.000
UNIQUAC	0.010	$(u_{12}-u_{11})$: -20.360 $(u_{21}-u_{22})$: 87.449

Table 8.40: Activity Coefficient Data.			
Liquid mole fraction	$\ln \gamma_1$	$\ln \gamma_2$	$\ln (\gamma_1/\gamma_2)$
1	-0.0044	(0.8079)	
0.9733	-0.0035	0.3668	-0.3703
0.9163	0.0023	0.5066	-0.5043
0.8886	0.0189	0.4510	-0.4321
0.8162	0.0321	0.3398	-0.3077
0.7439	0.0845	0.2655	-0.1810
0.6671	0.1373	0.1106	0.0267
0.6134	0.1580	0.0270	0.1310
0.5699	0.1693	0.2676	-0.0983
0.5306	0.2091	0.1918	0.0173
0.4044	0.2990	-0.0715	0.3705
0.1714	0.5190	-0.0864	0.6054

Table 8.41: Consistency Test Block	
AREA TEST	
Area A:	0.097
Area B:	0.043
$D=100 \left \frac{A-B}{A+B} \right $	38.6
ΔT_{\max}	47.4
T_{\min}	121.6

$J=150 \left \frac{\Delta T_{\max}}{T_{\min}} \right $	18.0
$ D-J $	20.6

Table 8.42: Lu Consistency Test	
Condition	Value
$\ln \gamma_1 (x_1=0.5) \approx$	0.211
$0.25 * \ln \gamma_2 \text{ (at } x_1=1)$	0.220
$\ln \gamma_2 (x_2=0.5) \approx$	0.171
$0.25 * \ln \gamma_1 \text{ (at } x_2=1)$	0.155
$\ln \gamma_1 (x_1=0.25) \approx$	0.42
$\ln \gamma_2 \text{ (at } x_1=0.75)$	0.266
$\ln \gamma_1 < \ln \gamma_2 \text{ (x=0.5)}$	0.211 0.171 FAIL
$\ln \gamma$ approaches its zero with horizontal tangence.	FAIL
With no maximum or minimum, $\ln \gamma_1$ and $\ln \gamma_2$ should be on the same side of zero.	FAIL

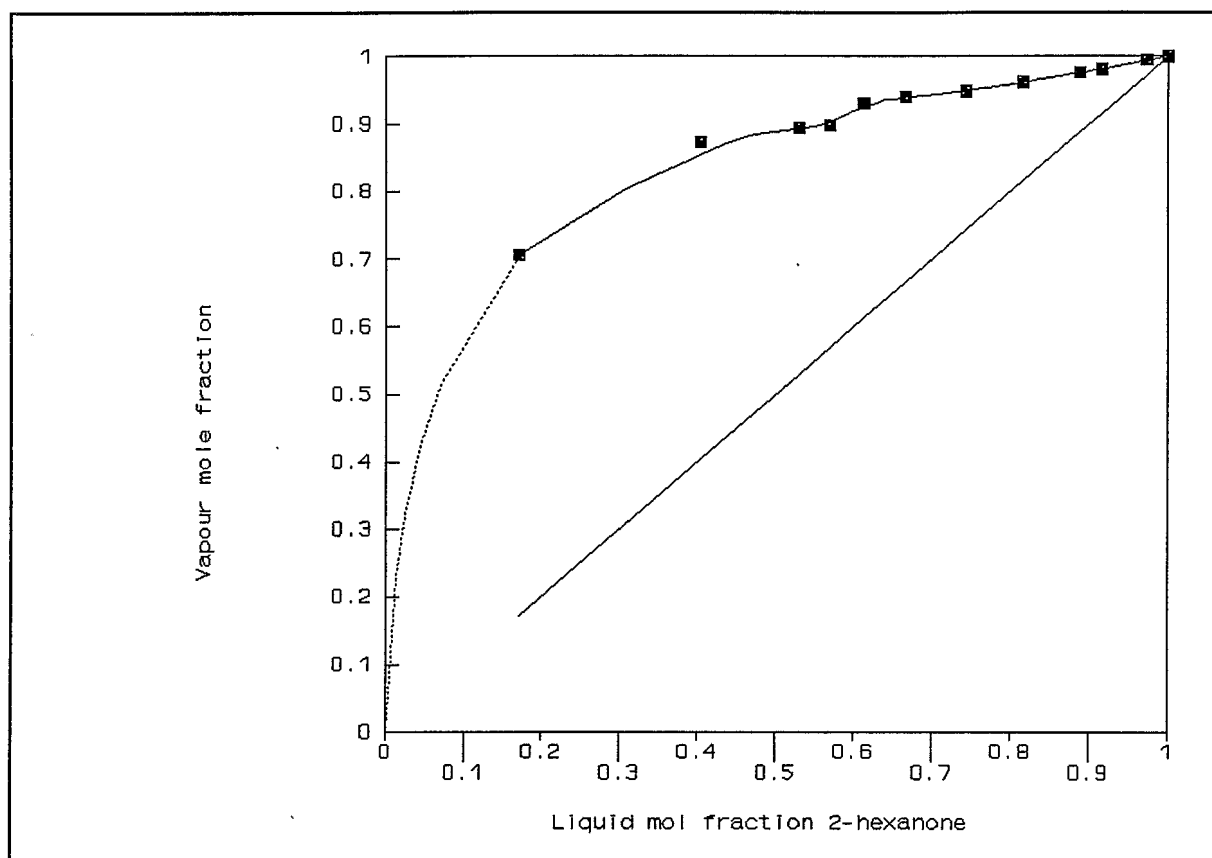


Figure 8.22: MBK - kerosol XY.

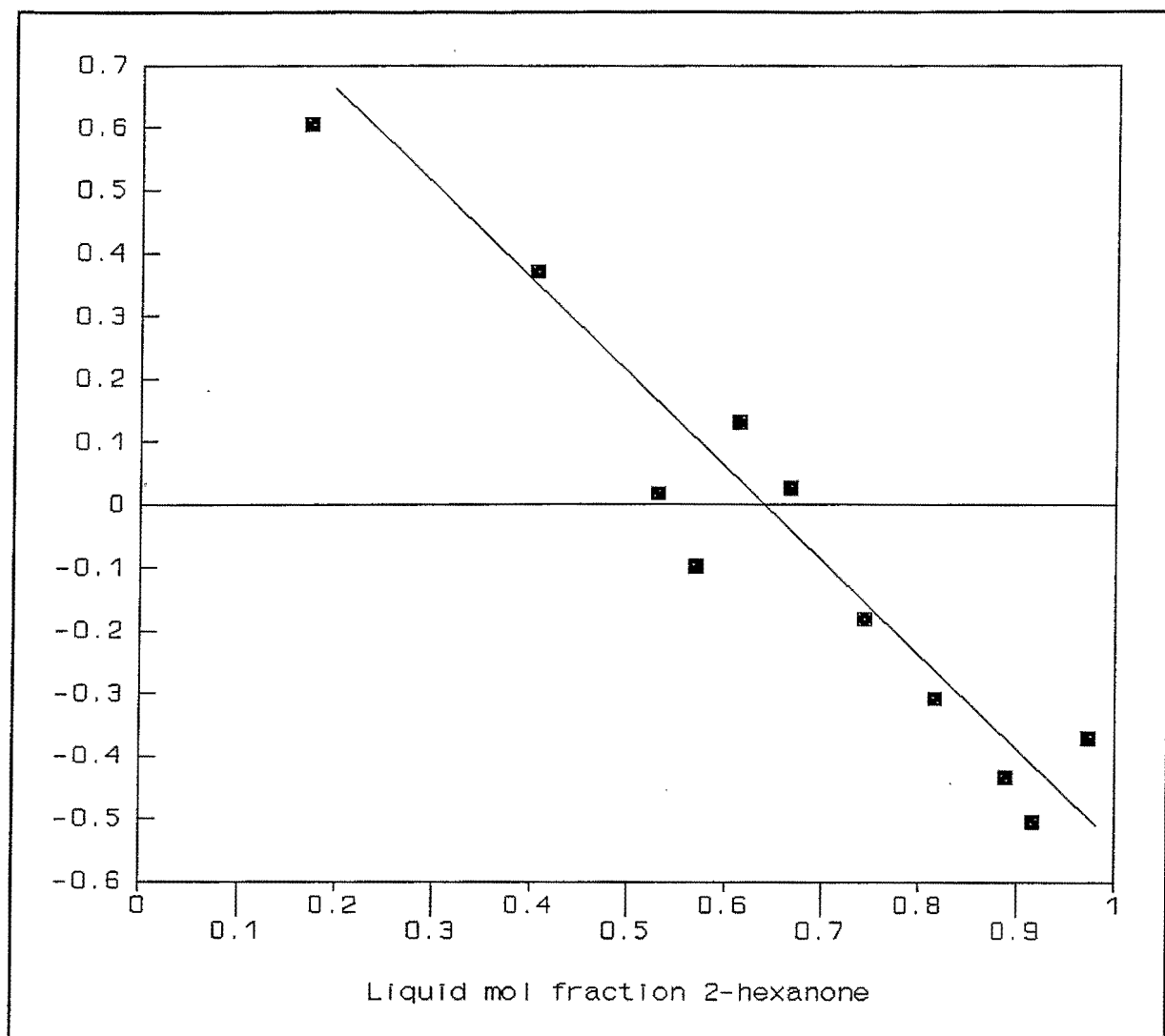


Figure 8.23: MBK - kerosol $\ln(\gamma_1/\gamma_2)$.

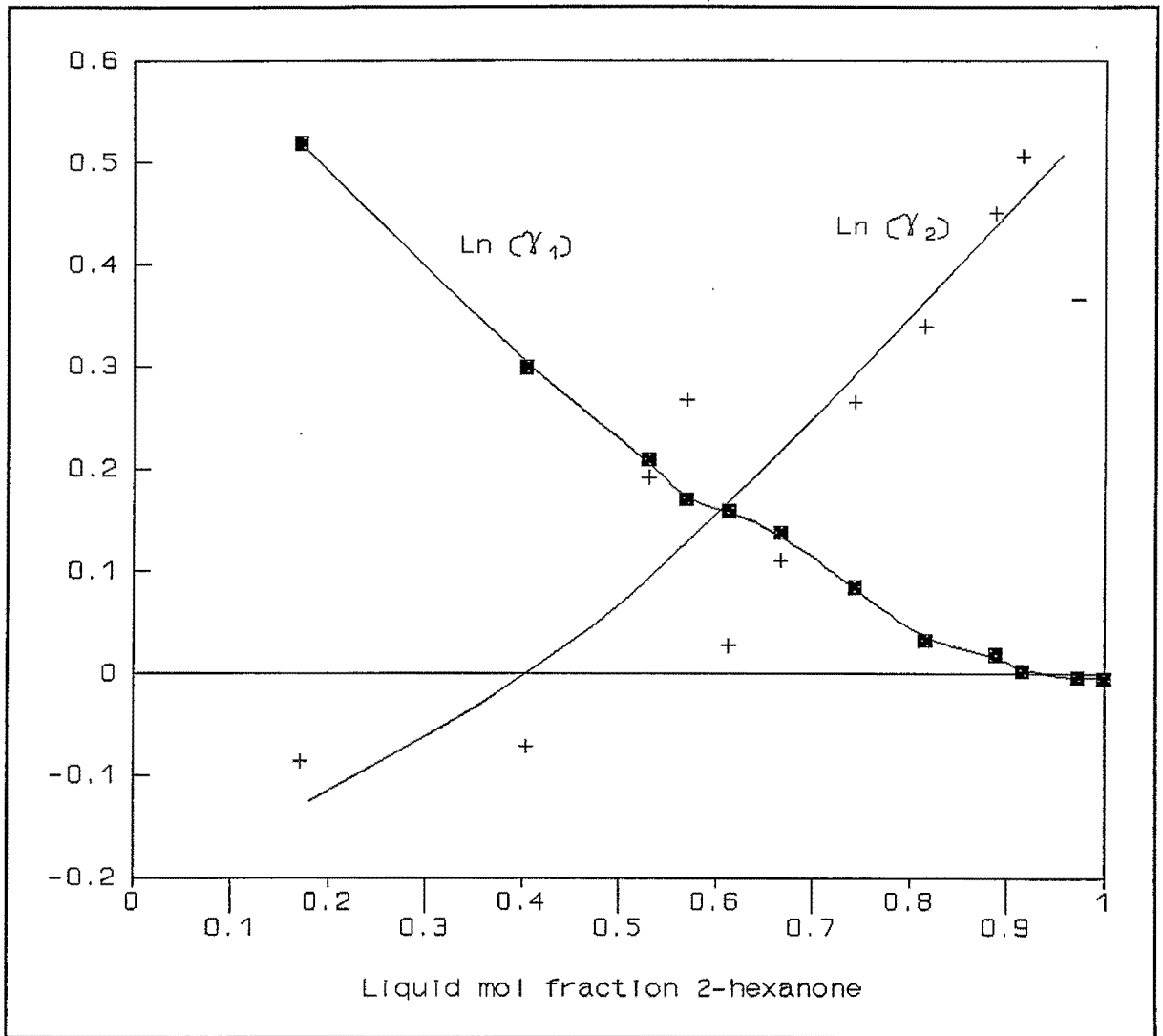


Figure 8.24: MBK - kerosol $\ln(\gamma_1)$ and $\ln(\gamma_2)$.

8.4 Conclusions

The tables with the regression results indicate that UNIQUAC is usually able to present many of the systems as well or slightly better than the other models tested. For this reason it is chosen for further modelling work.

Although UNIQUAC is mathematically more complex than simpler equations (such as Wilson) with equal correlation merits, in a computer age the ability to represent data is the main criterium.

The binary VLE data sets do not pass all the consistency tests. Except for the kerosol solvent and one other marginal case all sets pass the area test. As far as the point tests are concerned, more failures are present. In this respect it must be remembered that in broad general most systems pass the area test, but it is not at all uncommon for systems not to pass a points test. This fact can easily be verified by looking at the DECHEMA collection.

Figure 8.25 illustrates the effect of two thirds solvent on the vapour liquid mole fraction curve of 1-octene and 2-hexanone. The values are on a solvent free basis. Compare this figure with figure 6.1. Note how kerosol decreases the relative volatility of 1-octene and the other three solvents increase it.

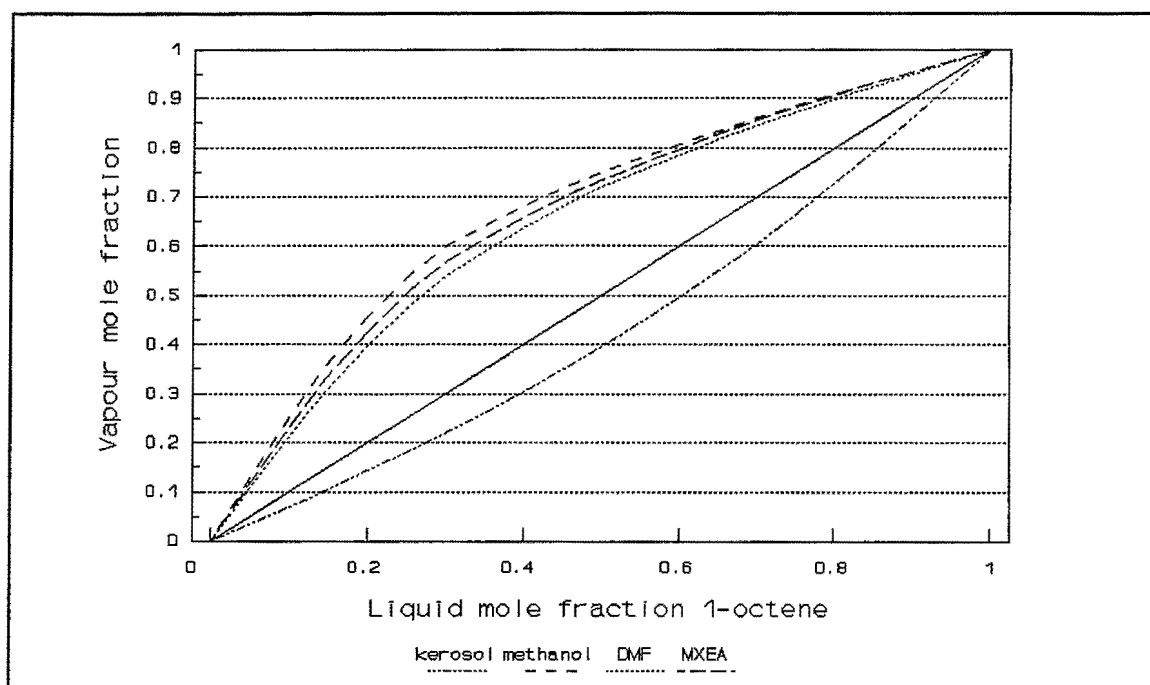


Figure 8.25: Effects of 2/3 solvent on the 1-octene / 2-hexanone system.