CHAPTER 7

SCREENING OF AGENTS

7.1 Introduction

A number of potentially beneficial solvents were identified in chapter 5. Quantitative expectations of their effect on the 1-octene (OCT1) - 2-hexanone (MBK) system were also presented. The correlations used to make these predictions are all only approximate and require experimental verification (Tassios, 1969:118). This chapter describes the screening tests used to verify the theoretical predictions.

7.2 Experimental design

7.2.1 Introduction

The main reason for designing an experiment is to obtain unambiguous results at a minimum cost (Hahn, 1977:13). Before this is done, the purpose of the experiments must be clearly stated:

(i) verify predictions made earlier regarding which solvents should be effective and what type of effects can be expected,

(ii) establish whether ASEEK is successful in recommending solvents,

(iii) investigate the ability of UNIFAC to predict the effect of a solvent,

(iv) find out how effective infinite dilution selectivities can be used to identify effective solvents. The

selectivity at infinite dilution is often considered in identifying potential solvents but is effectiveness is disputed (Bastos, 1985:421),

(v) identify solvent properties which influence relative volatility,

(vi) gain a better understanding of the underlying processes to which solvent action is attributed.

In order to truly establish which solvent properties are important, one must ensure that different properties of a solvent are not varied together. For example: if all of the small solvents are nonpolar and all the larger ones polar, one would not be able to establish clearly whether molecular size or polarity is the important variable. This is the spirit of factorial design.

In this specific case it is not possible to vary a single property while maintaining the others at a constant value. A single solvent property can usually not be varied without affecting another, and the experiments must be bended to accommodate the real world. A strict traditional factorial design involving running all combinations of factors may thus not be practically possible. Keep in mind that a different *solvent* is used every time and an individual property can not be manipulated alone. The reason for this is that many solvent properties are related, for example:

The molar polarization P is defined by the Claussius-Mosotti equation:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} \qquad (7.79)$$

where ϵ=dielectric constant, M=molecular weight, and d=density. P is used to calculate the dipole moment, μ (Riddick et al,

1984:60). This shows that ϵ and μ, and μ and the molar volume (mv) can not be varied independently. The solubility parameters are also related to each other through $\delta^2=\lambda^2+\tau^2 = \delta^2_D+\delta^2_P+\delta^2_H$. Recall also that δ_P is intimately linked with ϵ and μ. It is easy to find a polar low volume solvent (such as methanol) but not possible to find a usable non polar solvent of the same volume, as the latter has lower intermolecular forces and as such it is a vapour under ambient conditions.

Solvent were thus chosen accordingly to include:

(i) Those suggested by ASEEK, which should yield good results. Solvents which were highly reactive or unstable were excluded.

(ii) Those which came up in several references and therefore also in chapter 5. These are usually known used solvents. If any of them prove effective, there is the added bonus that there are probably no unforseen barriers to using them on a larger scale in practice.

(iii) Those which can be used to demonstrate the effect of a certain parameter suspected of playing a role. For example: both highly polar and non polar as well as large and small molecules and different combinations of these factors were chosen where possible.

Examples of groups included are:

- Non polar solvents such as the large decane.
- Much smaller non polar solvents such as cyclohexane.
- Solvents with a high δ_P and low δ_H such as MIBK.
- Solvents with a low δ_P and high δ_H such as 1,4-dioxane.
- Solvents with a high dielectric constant (ϵ) such as ethanol.

- Solvent with a low dielectric constant such as tetrahydrofuran.

7.2.2 Screening test conditions

The variables of temperature, pressure and solvent concentration are known to have an effect on the selectivity of the solvent (Tassios, 1969:121). Since azeotropic and extractive distillation (and not liquid-liquid extraction) are being investigated, the temperatures are determined by the bubbling points of the mixtures. These temperatures depend in turn on the composition of the sample and the operating pressure. As the measurements are isobaric at room pressure, the composition of the initial mixture used to load the still is almost the only independent variable that may be manipulated.

In order to quantify the "effectiveness" of a solvent, two terms discussed earlier can be used: selectivity and relative volatility. The former is usually reserved for infinite dilution conditions. The relative volatility of OCT1 (component number 1) with respect to MBK (component 2) may be expressed by:

$$\alpha_{12} = \frac{K_1}{K_2} = \frac{\left(\frac{Y_1}{X_1}\right)}{\left(\frac{Y_2}{X_2}\right)} \qquad (7.80)$$

This quantity can easily be computed from a GC analysis of the liquid and vapour samples. The area % values may be substituted directly for the fractions since the response factors and molecular weights cancel out in the equation.

What solvent concentration should be used? Some studies experimentally determine infinite dilution selectivities, ie with virtually 100 % solvent, for screening purposes (see Thomas & Eckert, 1984:195). These indicators are frequently difficult to determine accurately and the correct equipment is required. Very

pure (and thus expensive) solvents are also required[41]. As stated in chapter 5, the Othmer stills used in this study have been modified to improve their ability to operate in conditions of high relative volatility or very dilute regions (see Raal, Code & Best, 1972:215). The effectiveness of the modification has however not been established. Although this author would have liked (and possibly preferred) to measure infinite dilution activity coefficients, a more practical approach has been decided on.

In reality distillation columns do not operate under infinite dilution conditions. The actual solvent concentration used is determined finally by economic considerations. As a rule of thumb 50 to 80 mol % is used in the case of extractive distillation (Berg, 1969:57).

Stephenson and Van Winkle (1962:512) also stress the fact that in industrial practise the solvent concentration is always considerably less than 100 %.

Prabhu and Van Winkle (1963:211) used solvent mole fractions of 0.33 to 0.80. Updike & Langdon (1945:717) used 67 % mole percent solvent, with other ratios also investigated in the case a promising agent, and Sceibel (1949:930) used a 70 mole % solvent concentration.

For these reasons a 67 % mole solvent ratio is selected for initial screening purposes. Each solvent will initially be tested at one solvent concentration only. The ratio of 1-octene to 2-hexanone will be maintained at the azeotropic composition, providing a convenient reference relative volatility of unity.

This solvent concentration has the advantage that it is closer to actual plant conditions than infinite dilution.

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[41] As per conversation with Prof. JD Raal, who has been involved with experimental VLE measurements for many years.

This author would prefer to have the exactly the same solvent concentration in the liquid phase for all solvents tested. Due to the fact that the relative volatilities of the various solvents differ notably and the condensed vapour forms a sizable part of the total contents of the still, a fixed solvent concentration in the feed mixture may not guarantee a constant solvent concentration in the liquid phase. Some variation should be expected. This will be dealt with later on.

In any case, "valuable information can be gained from a study of several solvents at one solvent concentration" (Stephenson & Van Winkle, 1962:513). A detailed study of particular promising systems is then advised.

7.3 Experimental

An OCT1-MBK mixture containing 0.719 mole fraction OCT1 (the azeotropic point determined earlier) was made up. For every solvent screened a mixture of ca 150 cc containing 2/3 solvent (on a mole basis) and 1/3 of OCT1-MBK mixture was carefully made up. This final mixture was loaded in the Othmer still and allowed to circulate for a minimum time of 6 hours. The vapour and liquid samples were then analyzed. From this data the relative volatilities for the alpha olefin and the solvent were then computed with reference to MBK.

All the solvents used had purities of 98% (GC assay) or higher. The nature of the impurities present were not always known, but as they manifest as a number of minute peaks near the main peak, it can be deduced that they are probably close isomers. In these calculations the area percentages of the three main peaks in every sample were used as reported. No adjustments were made for impurities.

7.4 Results

The chemical names of the solvents screened are presented in the table below. The bubble points of the mixtures and the relative volatilities are also included:

Table 7:1: Screening tests.				
Solvent chemical name	**Pressure (mbar)**	**Temp (°C)**	**α OCT1 / MBK**	**α MBK / solvent**
(No solvent) Reference	841	112.3	1.012	No solvent
methanol	829	57.2	2.721	9.419
ethanol	829	74.0	2.324	4.057
1-propanol	829	89.0	2.219	2.217
2-propanol	831	77.5	1.846	3.010
acetone	837	52.7	1.309	5.394
n-decane	841	135.7	0.741	0.273
methyl isobutyl ketone	837	107.1	1.631	1.425
dichloromethane	836	48.3	2.632	33.523
decaline	839	119.0	0.692	0.076
1-butanol	831	104.4	1.936	1.149
diethyl ether	831	39.9	1.097	25.403
cyclohexane	841	81.0	0.801	1.784
trichloroethylene	836	88.8	1.244	3.327
tetrahydrofuran	837	69.0	2.316	13.528
carbon tetrachloride	836	79.2	0.936	3.036
hexylene glycol	839	117.4	2.762	0.123
benzene	840	82.6	1.187	3.092
kerosol 200[42]	841	144.3	0.692	0.013

[42] Kerosol 200 is a paraffinic stream with an initial boiling point of 200 °C. Typically C11-C13 and heavier.

N,N-dimethyl acetamide (DIMA)	840	135.3	3.722	0.228
2-methoxyethanol (MXEA)	840	104.3	2.970	0.820
diacetone alcohol (DAA)	839	102.5	2.200	0.758
N,N-dimethylformamide (DMF)	837	115.0	3.089	0.491
n-propyl acetate	837	97.0	1.439	1.964
2-ethoxyethanol (EXEA)	842	94.8	1.730	0.788
isoamyl acetate	839	123.0	1.286	0.640
1,6-hexanediol	837	113.9	2.614	0.013
1,4-dioxane	840	97.2	1.625	2.089
1,2,4-trichlorobenzene	840	113.3	1.265	0.049
pyridine	840	105.9	1.944	1.546
1-methyl-2-pyrrolidinone	842	115.1	2.576	0.078
cyclohexanone	837	125.0	1.615	0.596

7.5 Correlation and statistical inferences

A theoretical interpretation of experimental results is essential. This is not only one of the most interesting and revealing parts of any project, but also allows for a better understanding of the fundamental underlying processes and hopefully enhances our ability to identify promising agents quickly without exhaustive experimentation. Factors which influence selectivity must be identified.

Updike et al (1945:731-735) discussed the variation of a quantity similar to the relative volatility[43] with factors such as solubility, dielectric constant, dipole moment and internal pressure. Plots of this quantity against these factors failed to show a significant correlation (see chapter 4). Tassios (1969:119) showed that the polar cohesive energy (τ) of a solvent should play an important role where molar volume differences are encountered (as is the case here). Dispersion and dipole - induced dipole forces should be expected. A plot of selectivity versus polar cohesive energy indicated a strong linear relationship.

Tables 7.2 to 7.5 list relevant numeric quantities obtained using the ASEEK program described earlier versus the measured relative volatility. The solvents are sorted in ascending order according to their affect.

The asterisks in table 7.2 next to the name indicate those solvents which appeared in the top 300 list generated by ASEEK. The Tassios, Weimer-Prausnitz, MOSCED and Helpinstill columns contain the infinite dilution selectivities for these methods as discussed in chapters 4 and 5. The UNIFAC value is also taken from the ASEEK results and is the relative volatility in the presence of 60% solvent in the liquid phase.

[43] The reference relative volatility was not unity in his case and so all values were divided by this reference.

Table 7.2: α_{12} versus Predictions						
Solvent	**α_{12}**	**Tassios**	**Weimer-P**	**MOS-CED**	**Helpin-still**	**UNI-FAC**
kerosol 200 (C12 par)	0.69	1.19	1.26	0.26	1.06	0.626
decalin	0.69	1.44	1.53	0.15	1.10	0.581
n-decane	0.74	1.24	1.27	0.24	1.03	0.589
cyclohexane	0.80	1.18	1.15	0.12	0.98	0.621
carbon tetrachloride	0.94	1.66	1.48	0.16	0.94	0.877
diethyl ether	1.10	1.26	1.11	0.88	0.88	1.068
benzene	1.19	1.20	1.34	0.25	1.11	1.358
trichloroethylene *	1.24	2.39	2.09	4.31	1.08	2.310
1,2,4-trichlorobenzene	1.27	1.12	1.16	NA	10.4	1.470
isoamyl acetate	1.29	1.12	1.10	5.63	0.99	1.261
acetone	1.31	5.23	4.12	1.32	1.48	2.519
n-propyl acetate *	1.44	1.69	1.55	0.73	0.98	1.374
cyclohexanone *	1.62	1.80	1.70	0.46	1.05	1.369
1,4-dioxane	1.63	5.28	4.5	NA	1.69	1.89
MIBK *	1.63	1.58	1.49	NA	0.99	1.611
2-ethoxyethanol *	1.73	10.9	9.58	NA	2.96	2.71
2-propanol *	1.85	24.86	19.52	16.6	4.45	2.460
1-butanol *	1.94	10.49	8.93	0.73	2.73	1.940
pyridine	1.94	5.77	4.88	NA	1.80	2.440
DAA *	2.20	3.13	2.97	NA	1.43	3.370

1-propanol *	2.22	23.55	18.48	0.97	4.38	2.390
tetrahydrofuran	2.32	3.18	2.65	0.46	1.18	1.292
ethanol *	2.32	120.2	84.14	1.63	13.04	2.790
1-methyl-2-pyrrolidinone *	2.58	6.71	5.99	NA	2.28	2.68
1,6-hexanediol *	2.61	7.10	6.78	NA	2.62	3.14
dichloromethane *	2.63	8.85	6.68	0.81	1.93	2.750
methanol *	2.72	1198.	660.8	4.06	62.42	3.480
hexylene glycol *	2.76	4.04	3.84	4.67	1.71	3.160
MXEA * (2-methoxyethanol)	2.97	10.05	8.20	10.57	2.56	2.180
DMF * (N,N-dimethylformamide)	3.09	11.14	9.21	0.78	2.89	3.040
DIMA * (N,N-dimethylacetamide)	3.72	4.07	3.59	NA	1.56	0.630

In table 7.3 the first set of λ and τ (the nonpolar and polar solubility parameters) as well as the first δ (solubility parameter) are those used in the Tassios and Weimer-Prausnitz methods. The second set is for MOSCED. These values are taken from ASEEK. The inscription NA indicates that the solvent is not supported by the MOSCED model.

Table 7:3

Name	α_{12}	λ	τ	λ	τ	δ	δ
kerosol 200 (from C12 n-par)	0.692	6.2	2.1	8.17	0	6.5	8.2
decalin	0.692	7.5	3.0	8.80	0	8.1	8.8
n-decane	0.741	6.5	2.2	8.07	0	6.9	8.1

cyclohexane	0.801	7.7	1.8	8.22	0	7.9	8.2
carbon tetrachloride	0.936	7.4	3.0	8.58	0.81	8.0	8.6
diethyl ether	1.097	7.2	1.9	NA	NA	7.4	NA
benzene	1.187	8.6	1.8	8.49	1.81	8.8	8.7
trichloroethylene	1.244	7.4	4.0	5.89	2.05	8.4	6.2
1,2,4-trichlorobenzene	1.265	7.7	1.7	NA	NA	7.9	NA
isoamyl acetate	1.286	6.8	1.6	5.52	1.59	7.0	5.7
acetone	1.309	7.4	5.3	7.49	3.91	9.1	8.4
n-propyl acetate	1.439	7.0	3.2	7.77	2.25	7.7	8.1
cyclohexanone	1.615	7.4	3.6	8.48	2.62	8.2	8.9
1,4-dioxane	1.625	7.4	5.7	NA	NA	9.3	NA
MIBK	1.631	6.9	3.1	NA	NA	7.6	NA
2-ethoxyethanol	1.730	6.9	7.1	NA	NA	9.9	NA
2-propanol	1.846	7.1	7.7	5.35	1.08	10.5	5.5
1-butanol	1.936	7.1	6.9	7.93	0.91	9.9	8.0
pyridine	1.944	7.4	6.0	NA	NA	9.5	NA
DAA	2.200	7.0	5.1	NA	NA	8.7	NA
1-propanol	2.219	7.1	7.8	7.79	1.06	10.5	7.9
tetrahydrofuran	2.316	7.4	4.5	8.02	2.17	8.7	8.3
ethanol	2.324	7.4	9.4	7.51	1.26	12.0	7.6
1-methyl-2-pyrrolidinone	2.576	7.1	6.9	NA	NA	9.9	NA
1,6-hexanediol	2.614	6.6	7.3	NA	NA	9.8	NA
dichloromethane	2.632	7.6	6.0	8.2	2.72	9.7	8.6

methanol	2.721	7.7	11.2	7.14	2.14	13.6	7.5
hexylene glycol	2.762	6.8	5.9	5.63	0.68	9.0	5.7
MXEA (2-methoxyethanol)	2.970	7.1	6.9	5.52	1.03	9.9	5.6
DMF (N,N-dimethylformamide)	3.089	7.3	7.3	8.26	3.98	10.3	9.2
DIMA (N,N-dimethylacetamide)	3.722	7.1	5.7	NA	NA	9.1	NA

Table 7.4 contains some of the standard listed physical properties of the solvents. The values were taken from DATAPREP[44] and Riddick et al (1984). 'NA' indicates that the value could not be found in any of the references (including PRO/II).

Table 7:4

Name	α_{12}	**V**[45]	ϵ[46]	λ[47] **Debye**	δ **(25°C)**
kerosol 200 (from C12 n-par)	0.692	283.9	2.002	0	7.24
decalin	0.692	179.3	2.154	0	8.02
n-decane	0.741	232.2	1.989	0	7.14
cyclohexane	0.801	115.9	2.040	0	7.63

[44] A part of the PRO/II simulation program.

[45] The molar volume of the solvent at its normal boiling point, cc/gmol.

[46] The dielectric constant.

[47] Dipole moment.

carbon tetrachloride	0.936	102.9	2.238	0	7.98
diethyl ether	1.097	105.3	4.335	1.15	7.02
benzene	1.187	95.2	2.270	0	8.52
trichloroethylene	1.244	97.4	3.420	0.8	8.55
1,2,4-trichlorobenzene	1.265	147.3	NA	1.26	9.38
isoamyl acetate	1.286	172.9	4.630	1.86	7.70
acetone	1.309	76.9	20.900	2.69	8.98
n-propyl acetate	1.439	127.4	6.002	1.78	8.14
cyclohexanone	1.615	119.3	16.100	3.08	9.16
1,4-dioxane	1.625	92.8	2.209	0.45	9.17
MIBK	1.631	140.3	13.110	2.29	7.93
2-ethoxyethanol	1.730	111.9	16.93	2.04	9.80
2-propanol	1.846	82.1	19.920	1.66	10.65
1-butanol	1.936	100.0	17.510	1.75	10.63
pyridine	1.944	88.5	12.91	2.37	9.92
DAA	2.200	143.0	18.200	2.86	8.65
1-propanol	2.219	81.1	20.450	3.09	11.13
tetrahydrofuran	2.316	85.4	7.580	1.75	8.66
ethanol	2.324	62.2	24.550	1.66	11.89
1-methyl-2-pyrrolidinone	2.576	112.6	32.2	4.09	11.30
1,6-hexanediol	2.614	154.9	NA	2.5	11.79
dichloromethane	2.632	65.4	8.930	1.14	9.27
methanol	2.721	42.5	32.600	2.87	13.46
hexylene glycol	2.762	149.6	25.860	2.90	11.41

MXEA (2-methoxyethanol)	2.970	89.8	18.300	2.04	10.56
DMF (N,N-dimethylformamide)	3.089	87.7	36.710	3.24	10.90
DIMA (N,N-dimethylacetamide)	3.722	107.7	37.780	3.71	10.17

Table 7:5

Name	α_{12}	x_3	δ_p	δ_H
kerosol 200 (from C12 n-par)	0.692	0.66	0	2.10
decalin	0.692	0.45	0	3.00
n-decane	0.741	0.47	0	2.20
cyclohexane	0.801	0.71	0	1.80
carbon tetrachloride	0.936	0.05	0	3.00
diethyl ether	1.097	0.52	1.50	1.16
benzene	1.187	0.76	0	1.80
trichloroethylene	1.244	0.40	1.04	3.86
1,2,4-trichlorobenzene	1.265	NA	NA	NA
isoamyl acetate	1.286	0.67	1.53	0.47
acetone	1.309	0.70	6.77	4.20
n-propyl acetate	1.439	0.58	2.16	2.36
cyclohexanone	1.615	0.63	4.98	3.43
1,4-dioxane	1.625	0.66	0.47	5.68
MIBK	1.631	0.71	3.00	0.77
2-ethoxyethanol	1.730	0.66	3.48	6.19

2-propanol	1.846	0.65	3.92	6.63
1-butanol	1.930	0.64	3.36	6.03
pyridine	1.944	0.67	5.07	3.21
DAA	2.200	0.65	4.05	3.10
1-propanol	2.210	0.66	7.41	2.45
tetrahydrofuran	2.316	0.41	3.39	2.96
ethanol	2.320	0.67	5.24	7.80
1-methyl-2-pyrrolidinone	2.576	0.59	7.55	3.06
1,6-hexanediol	2.614	0.60	NA	NA
dichloromethane	2.632	0.21	3.00	5.19
methanol	2.270	0.64	13.44	7.43
hexylene glycol	2.762	0.64	3.91	4.41
MXEA (2-methoxyethanol)	2.970	0.62	4.38	5.32
DMF (N,N-dimethylformamide)	3.089	0.63	7.65	2.29
DIMA (N,N-dimethylacetamide)	3.720	0.66	7.17	4.34

The second column in table 7.5 contains the true liquid mole fraction solvent, as estimated from the GC traces and published response factors (Dietz, 1967). The average fraction is 0.59 with a standard variation of 0.15, indicating that the solvent liquid concentration remained relatively constant.

The relationship between the factors listed above and the relative volatility is illustrated by the following figures:

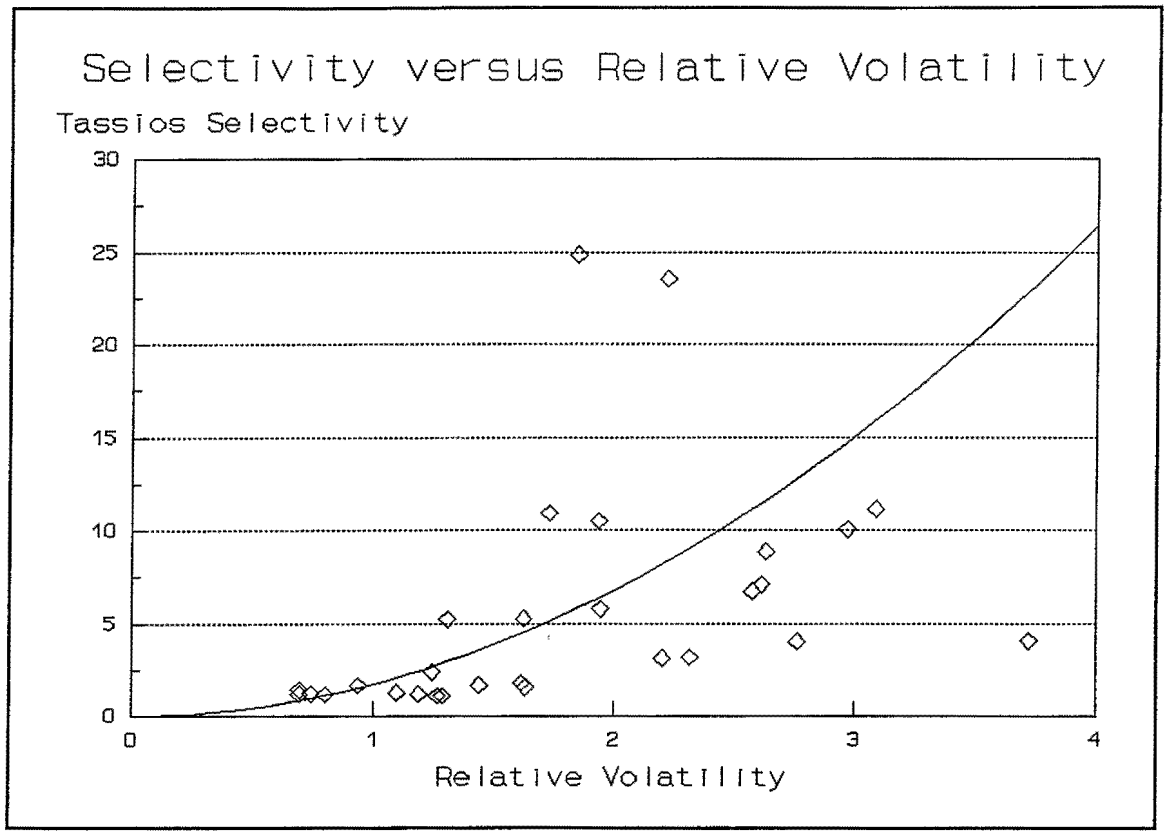

Figure 7.1: Tassios selectivity.

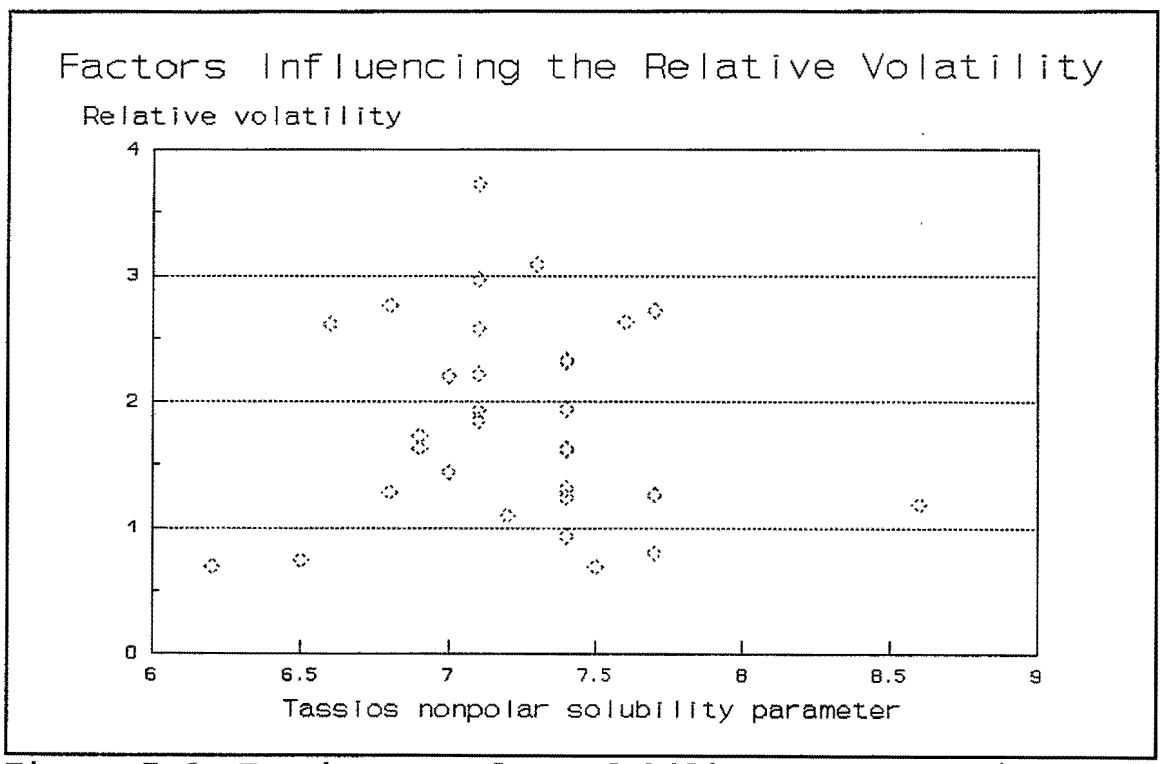

Figure 7.6: Tassios nonpolar solubility parameter, λ.

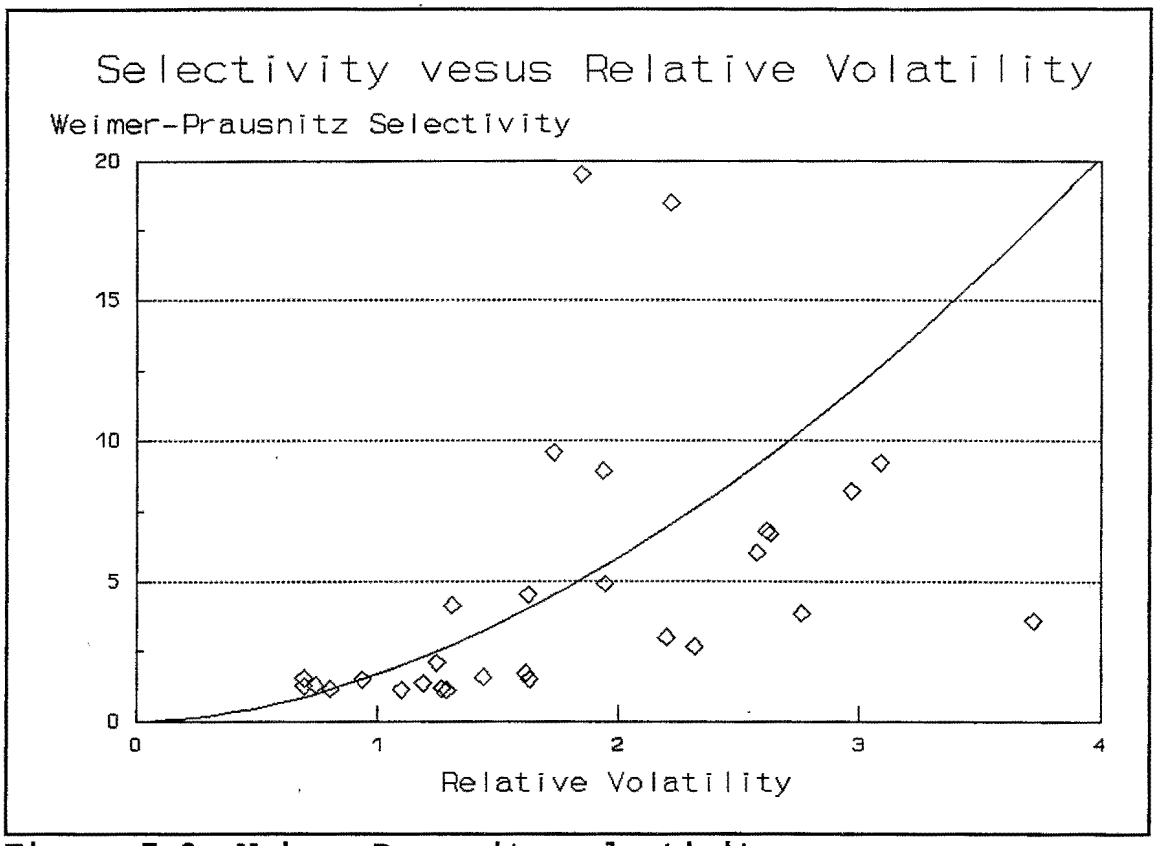

Figure 7.2: Weimer-Prausnitz selectivity.

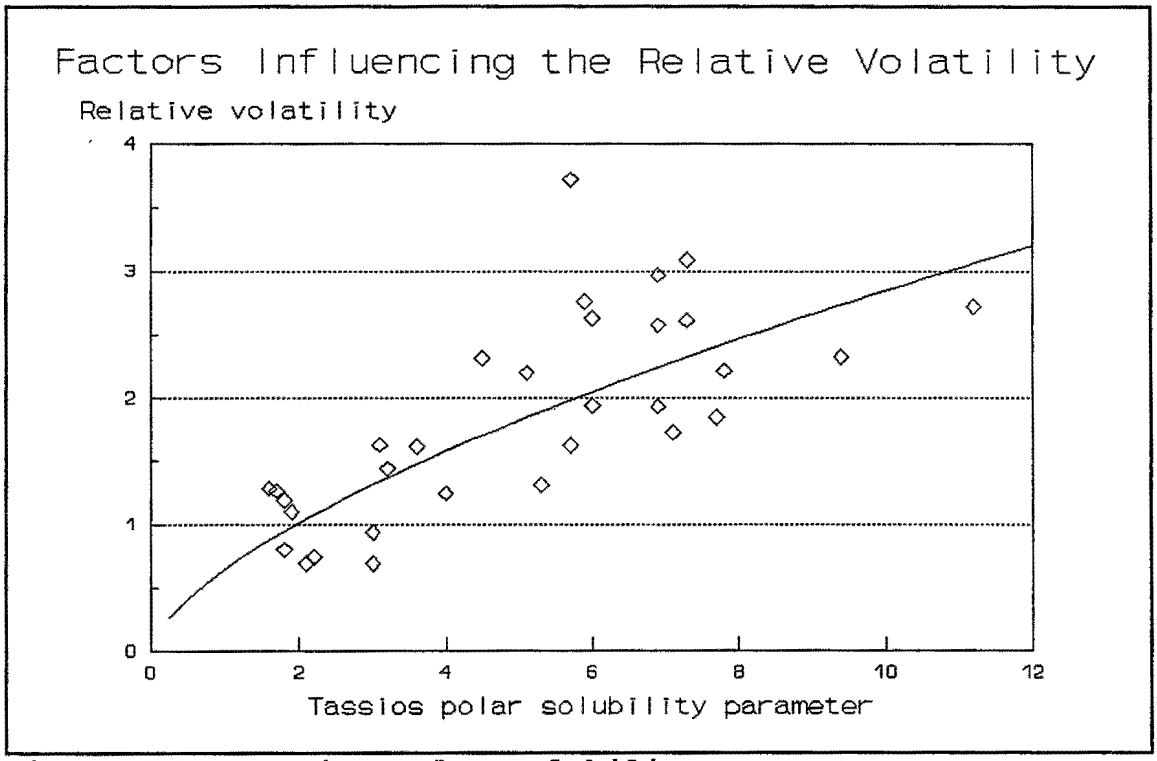

Figure 7.7: Tassios polar solubility parameter, τ.

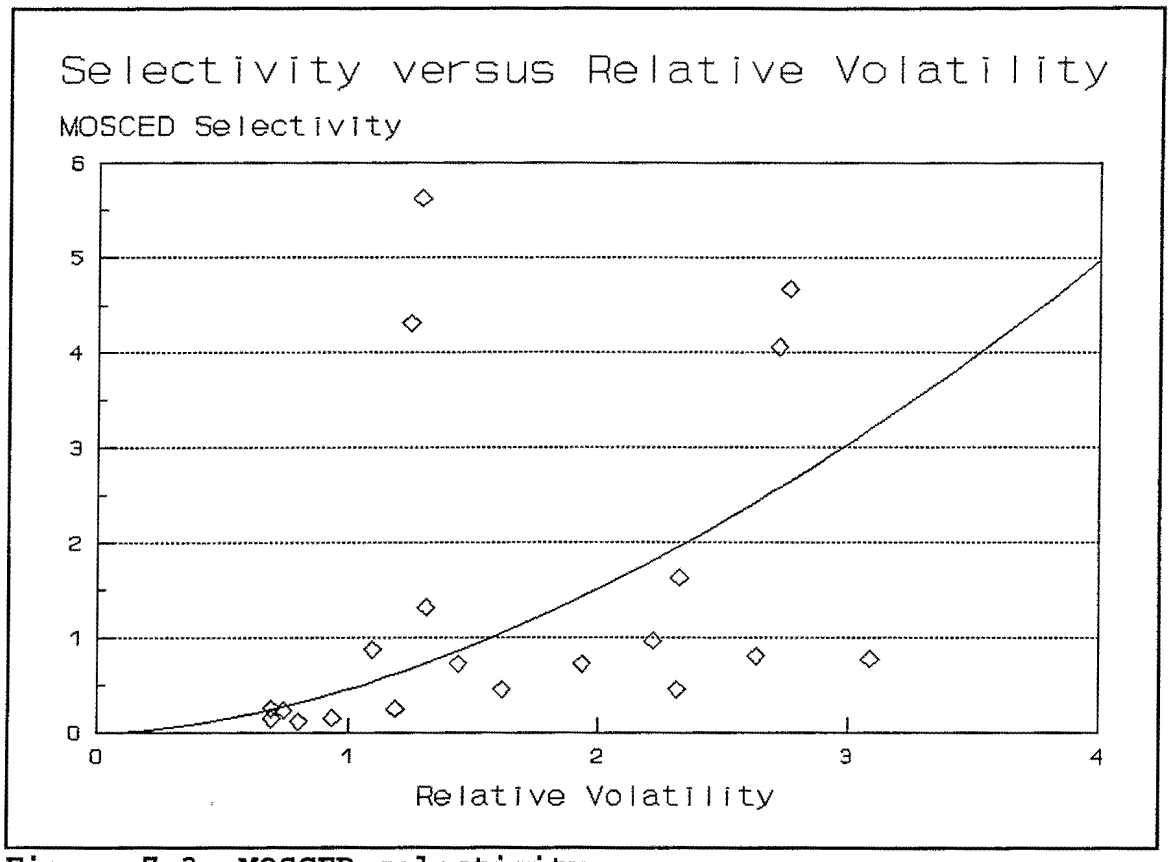

Figure 7.3: MOSCED selectivity.

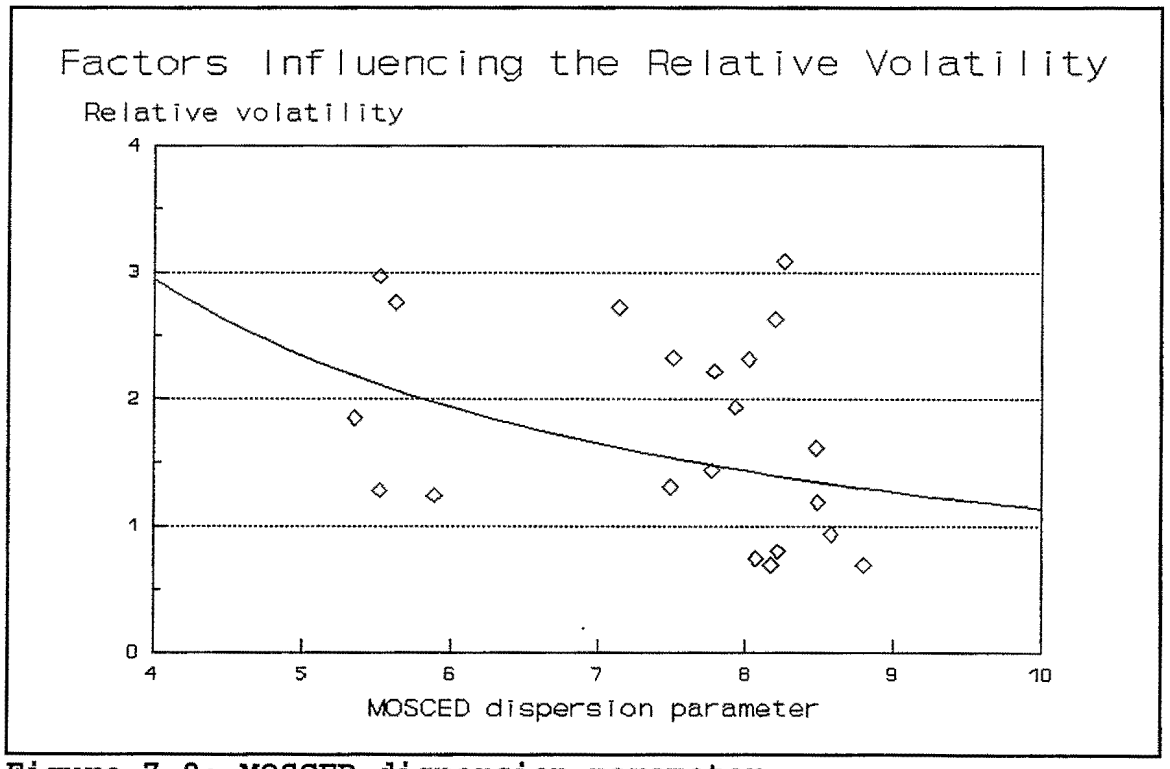

Figure 7.8: MOSCED dispersion parameter.

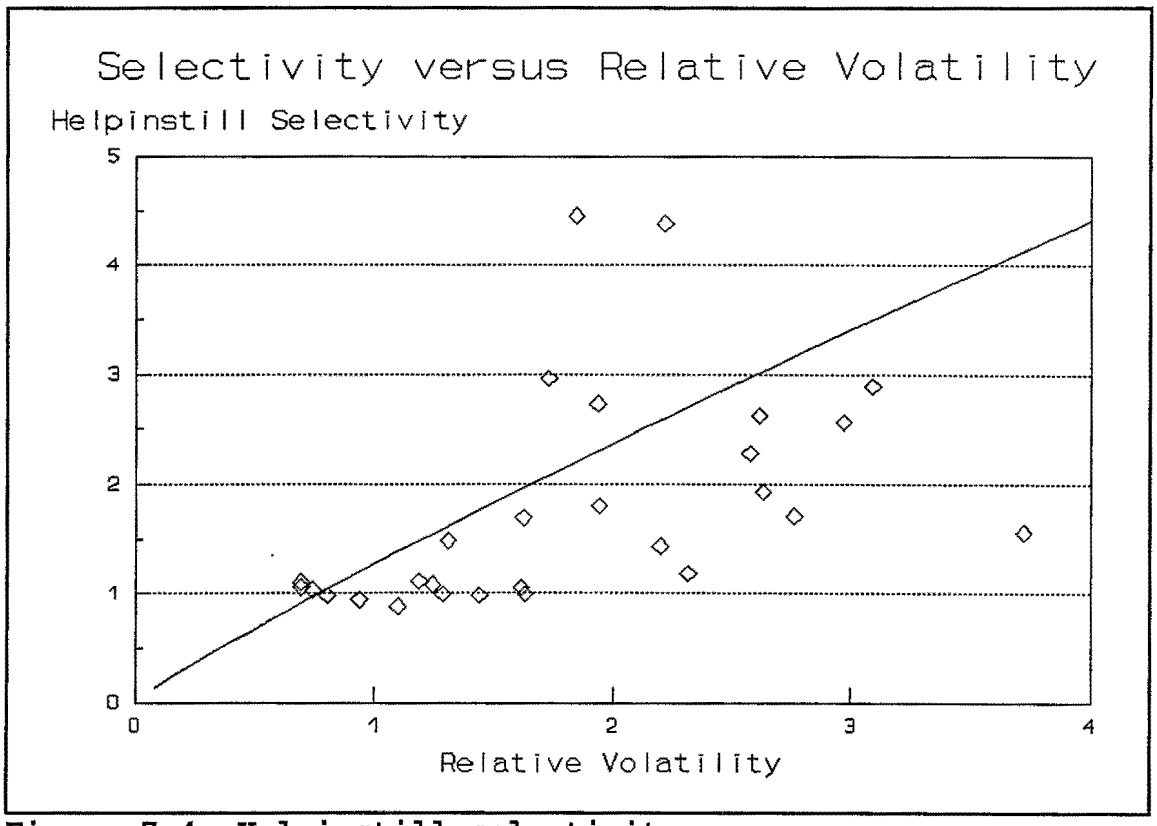

Figure 7.4: Helpinstill selectivity.

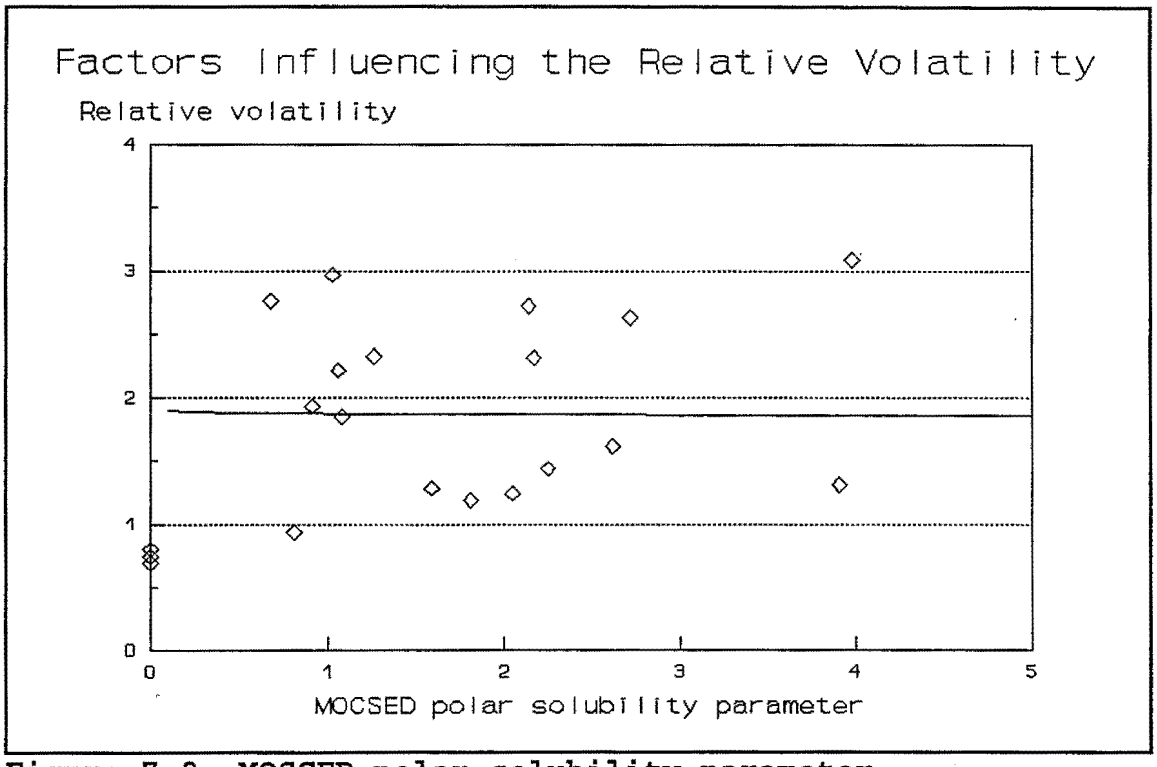

Figure 7.9: MOSCED polar solubility parameter.

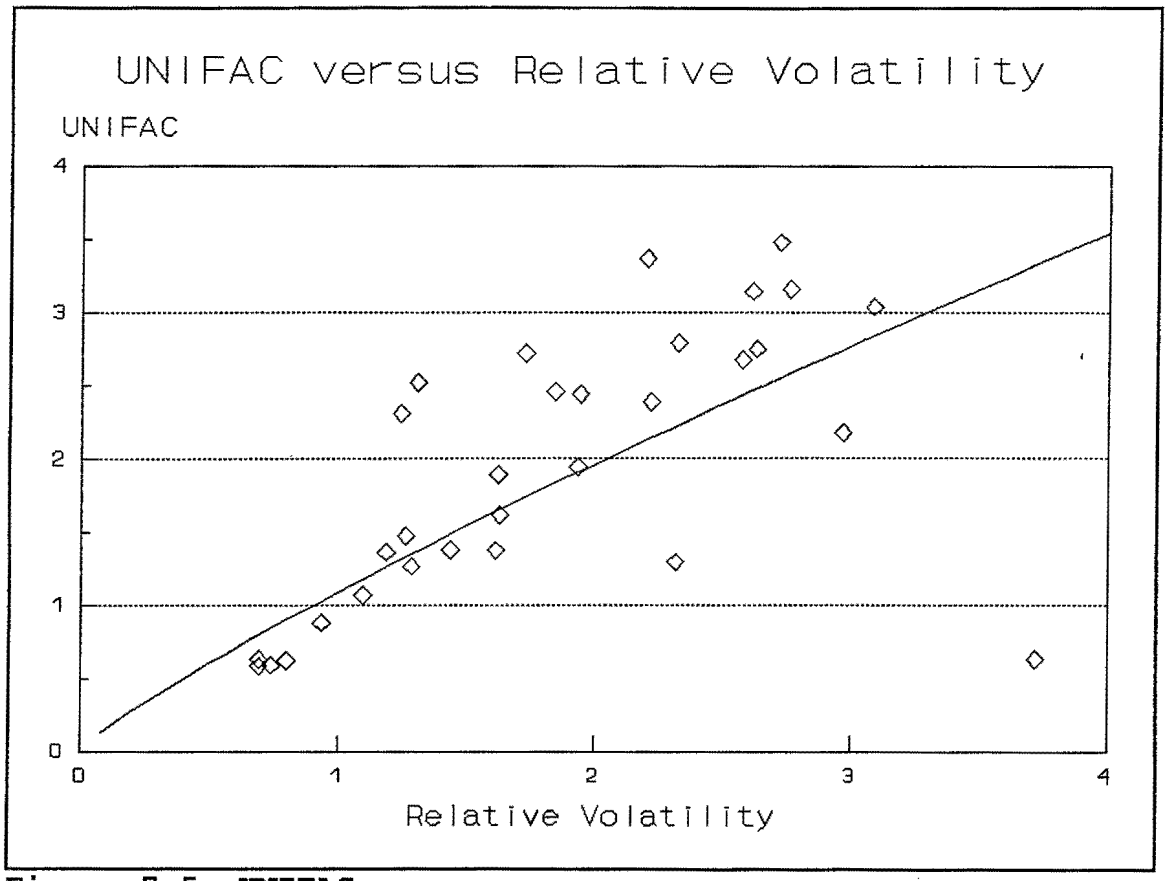

Figure 7.5: UNIFAC.

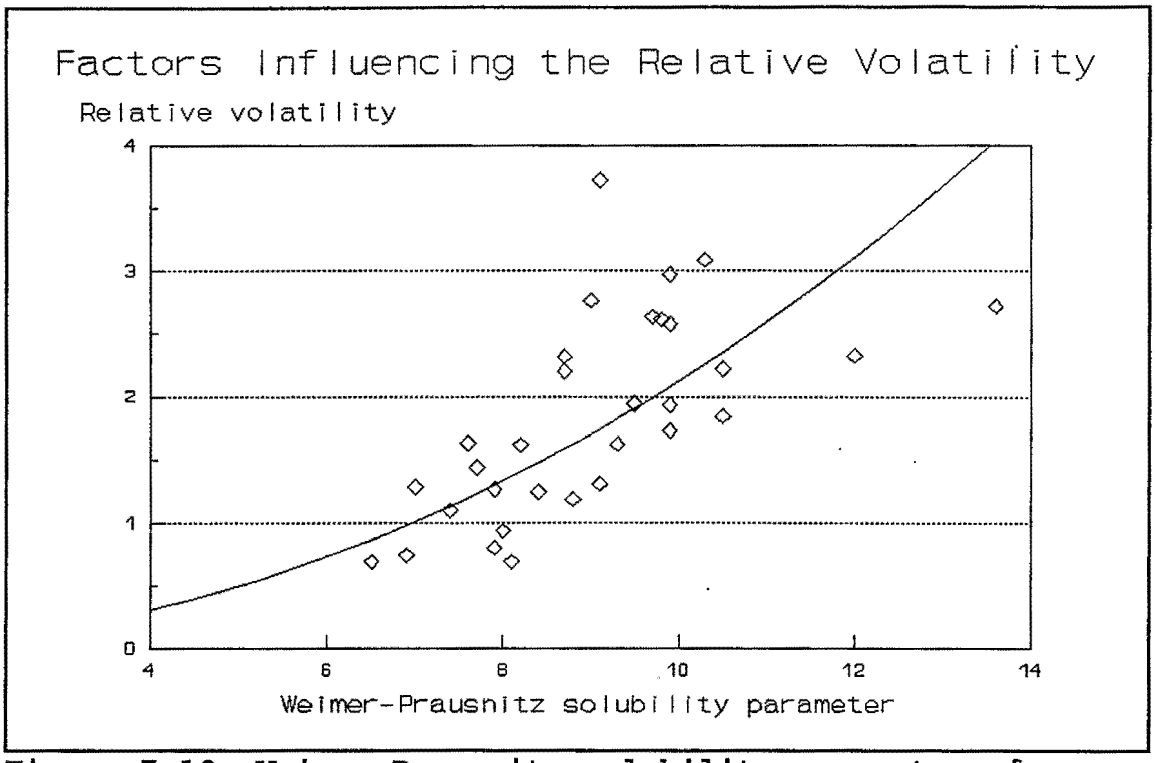

Figure 7.10: Weimer-Prausnitz solubility parameter, δ.

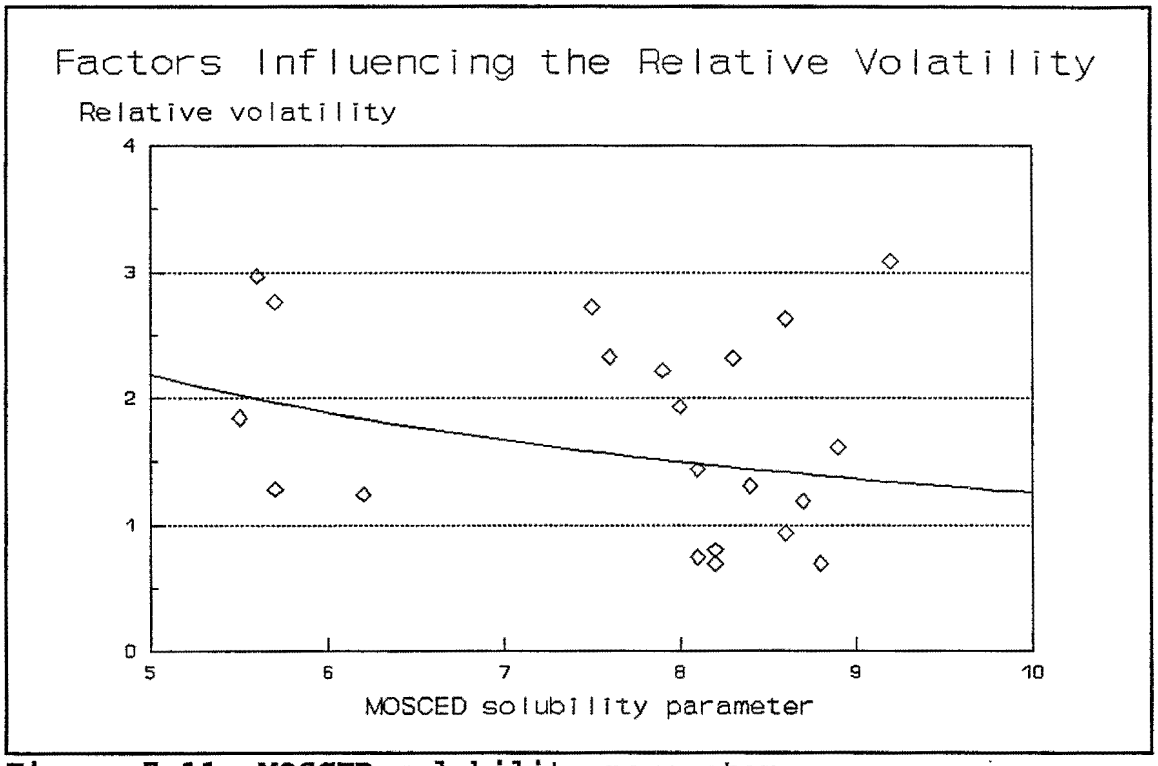

Figure 7.11: MOSCED solubility parameter.

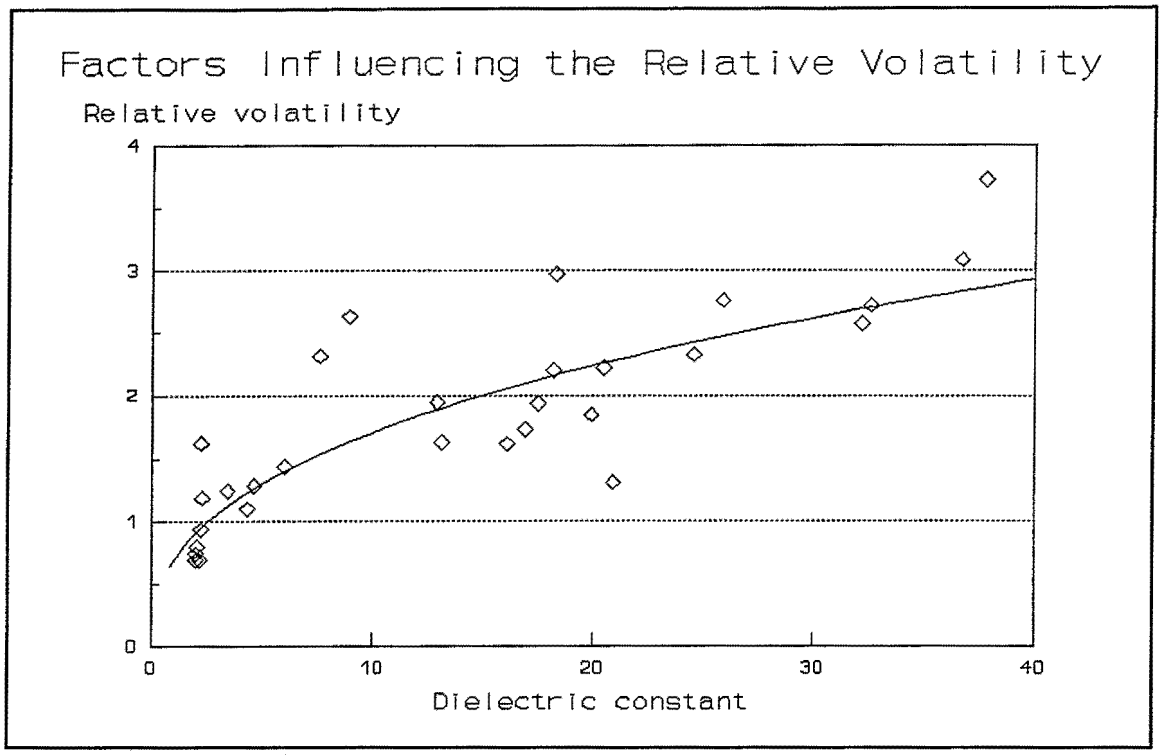

Figure 7.12: Dielectric constant, ϵ.

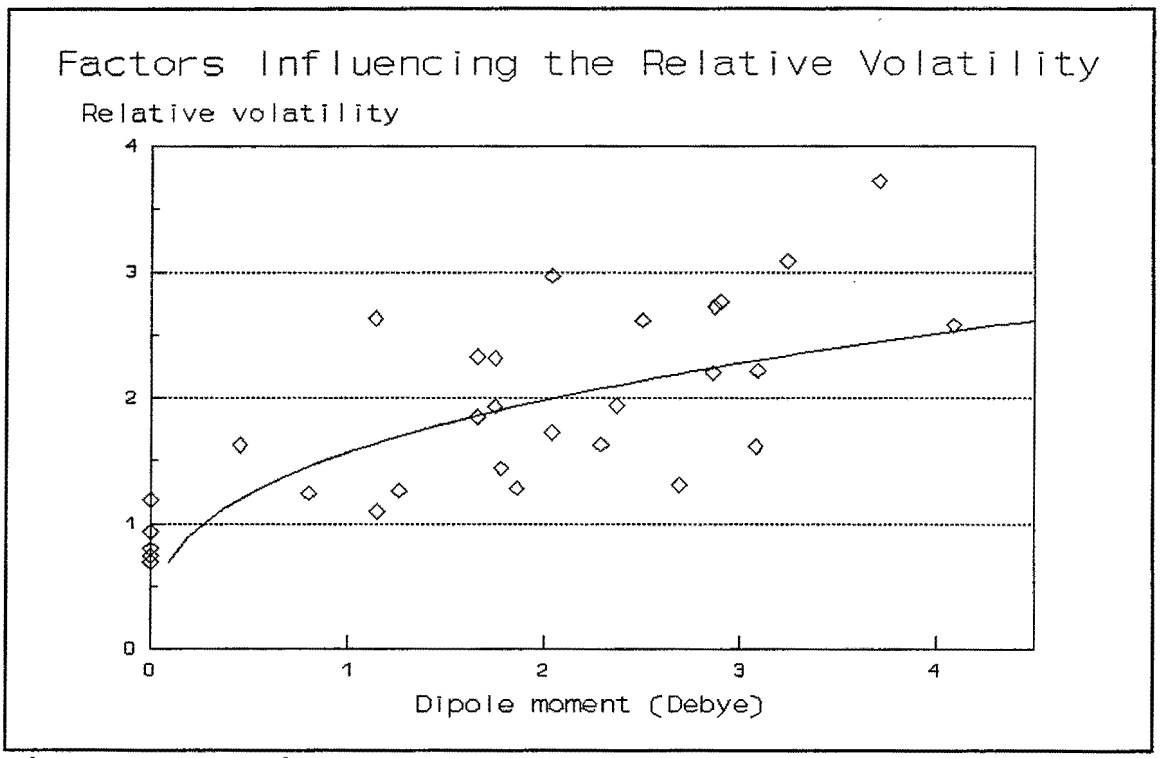

Figure 7.13: Dipole moment, μ.

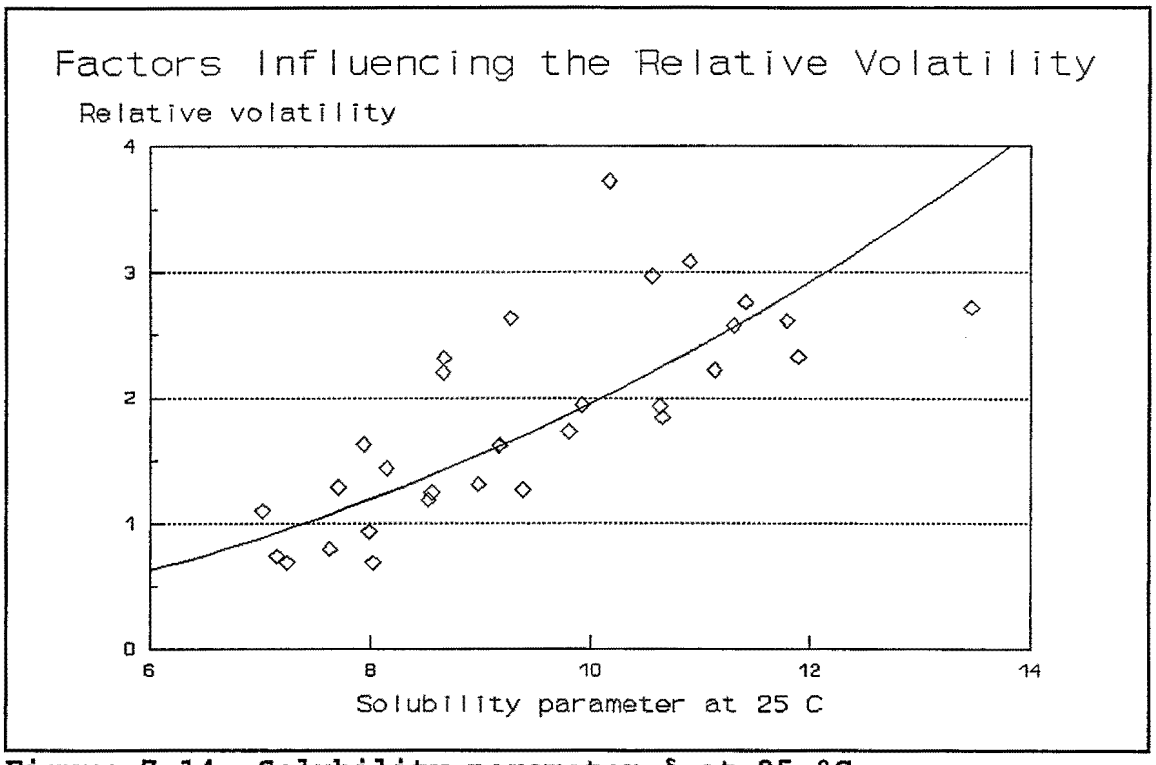

Figure 7.14: Solubility parameter δ at 25 °C.

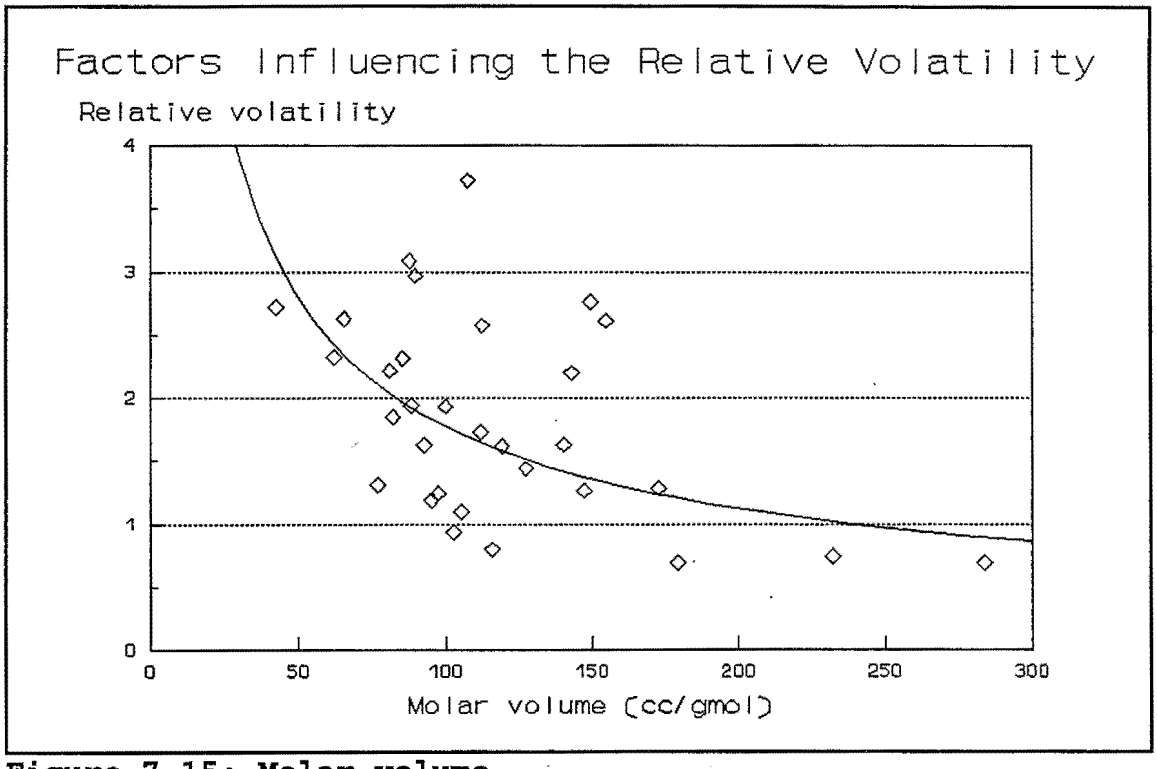

Figure 7.15: Molar volume.

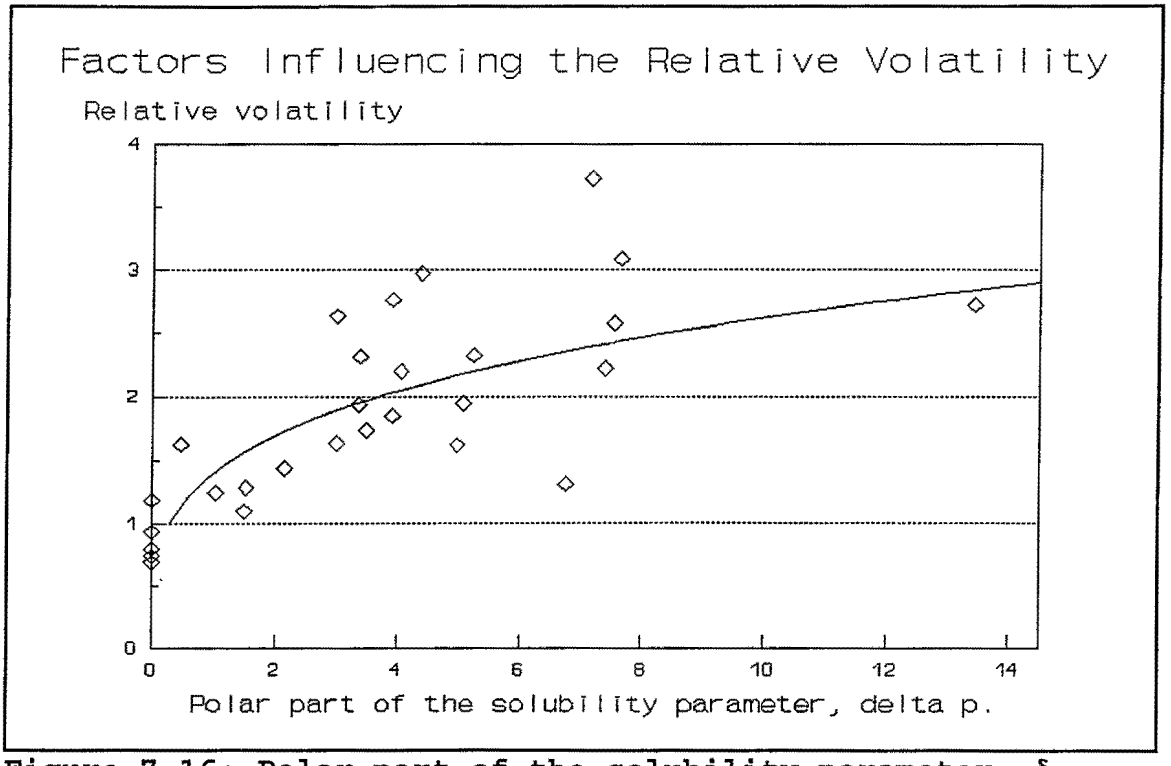

Figure 7.16: Polar part of the solubility parameter, δ_P.

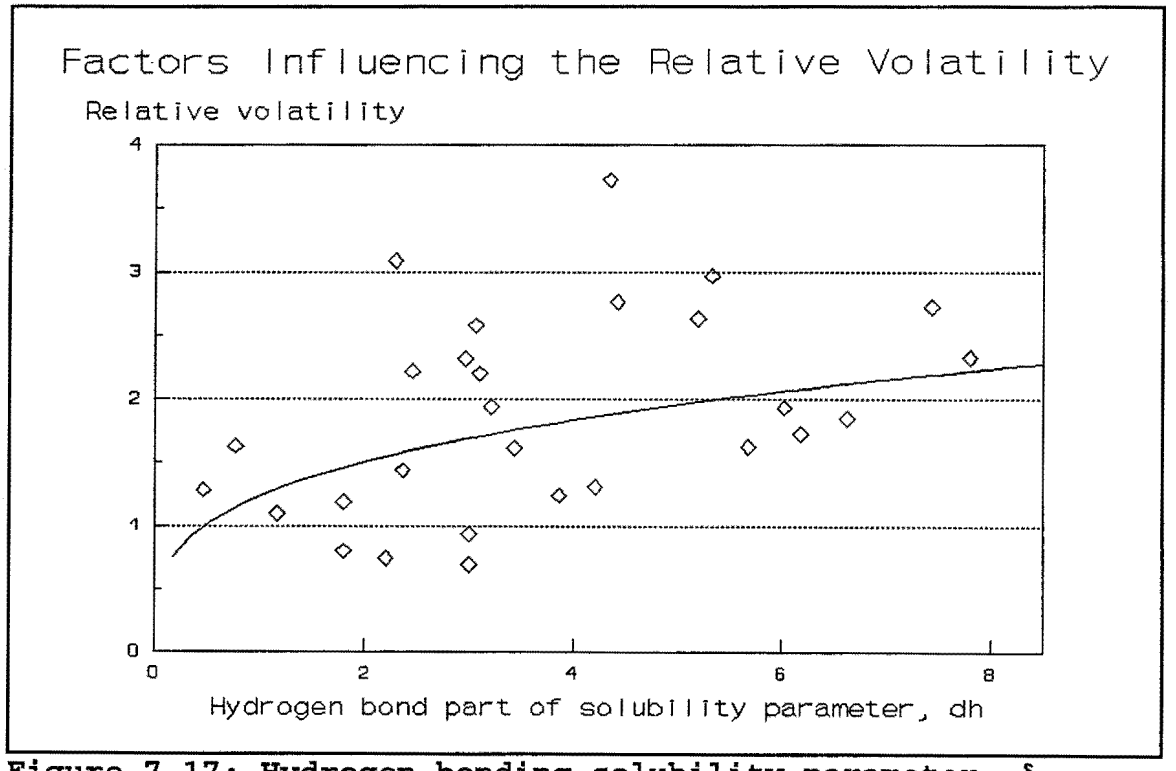

Figure 7.17: Hydrogen bonding solubility parameter, δ_H.

Both the power function

$$y = a \cdot x^b \qquad (7.81)$$

and a straight line was used to fit the selectivity and UNIFAC data the correlation factors are as follows:

Table 7.6: Correlation factor, r^2		
Factor involved	**Linear**	**Power function**
Tassios selectivity	0.23	0.362
Weimer-Prausnitz selectivity	0.23	0.358
MOSCED selectivity	0.31	0.365
Helpinstill selectivity	0.24	0.20
UNIFAC	0.60	0.50

Correlation coefficients provide a normalized and scale-free measure of the linear association between two variables. The values fall between -1 and +1. A positive correlation indicates that the variables vary in the same direction while a negative correlation indicates that the variables vary in the opposite direction. Statistically independent variables have an expected correlation of zero (Statgraphics manual version 5, 1991:C-201). The second important factor is the significance level, which indicates the probability that of a relationship occurring by chance. Levels less than 0.05 indicate significant non zero correlations.

Values for correlation with the relative volatility are given in table 7.7.

Table 7.7: Correlation with the relative volatility	
Factor involved	**Correlation factor, r^2 (significance level)**
Molar volume	-0.47 (0.007)
Tassios nonpolar solubility parameter λ	-0.05 (0.81)
Tassios polar solubility parameter τ	**0.73 (≈0)**
MOSCED dispersion parameter λ	-0.32 (0.15)
MOSCED polar solubility parameter τ	0.44 (0.048)
Weimer-Prausnitz solubility parameter δ	**0.65 (≈0)**
MOSCED solubility parameter δ	-0.24 (0.29)
Dielectric constant ϵ	**0.84 (≈0)**
Dipole moment μ	**0.76 (≈0)**
Polar part of the solubility parameter, δ_P	**0.71 (≈0)**
Hydrogen bond part of the solubility parameter, δ_H	0.46 (0.010)
Standard solubility parameter at 25 °C, δ	**0.76 (≈0)**

The best linear correlation of α with the properties listed in table 7.7 was found by using piecewise linear regression with a

breakpoint. The correlation (in terms of ϵ[48], τ[49], δ[50] and μ[51]) is:

$$\alpha = -0.6025 - 0.0371 * \epsilon - 0.0652 * \tau + 0.1805 * \delta + 0.3679 * \mu \quad (7.82)$$

but when $\alpha > 1.863$ then rather:

$$\alpha = 1.577 + 0.06869 * \epsilon - 0.3657 * \tau + 0.2777 * \delta - 0.3175 * \mu \quad (7.83)$$

This correlation accounts for a fraction of 0.92 of the variance in the relative volatility. This is considered good for 30 valid cases with 10 constants.

Important correlations (significance level: α=0.05) between the different parameters are shown in table 7.9:

Table 7.8: Significant correlations

Factors involved.	Correlation factor	Significance level
mv[52] & λ(Tassios)	-0.62	0.0002
mv & τ(Tassios)	-0.58	0.0006
mv & δ(Tassios)	-0.71	0.0000
mv & δ(25°C)	-0.52	0.0028

[48] Solvent dielectric constant.

[49] Tassios polar solubility parameter.

[50] Tassios solubility parameter.

[51] Dipole moment, Debye

[52] Molar volume.

mv & μ	-0.50	0.03
mv & δ_P	-0.53	0.0028
τ(Tassios) & δ(Tassios)	0.94	0.0000
δ(Tassios) & δ (25°C)	0.91	0.0000
τ(Tassios) & ϵ	0.76	0.0000
τ(Tassios) & μ	0.57	0.0007
τ(Tassios) & δ_P	0.78	0.0000
τ(Tassios) & δ_H	0.81	0.0000
λ & δ (MOSCED)	0.97	0.0000
τ(MOSCED) & μ	0.60	0.0043
δ(Tassios) & ϵ	0.69	0..0000
δ(Tassios) & δ_P	0.77	0.0000
δ(Tassios) & δ_H	0.77	0.0000
δ(Tassios) & δ(25°C)	0.91	0.0000
δ(25°C) & μ	0.63	0.0001
ϵ & δ(25 °C)	0.82	0.0000
ϵ & μ	0.86	0.0000
ϵ & δ_P	0.87	0.0000
μ & δ_P	0.82	0.0000
δ (25°C) & δ_P	0.78	0.0000
δ (25°C) & δ_H	0.73	0.0000

Note that these correlations are not surprising (as stated earlier on):

- δ_H and δ_P should correlate well with τ (Tassios) because $\tau^2 = \delta_H^2 + \delta_P^2$.
- τ and λ should correlate well with δ because $\delta^2 = \tau^2 + \lambda^2$.
- ϵ, μ and the molar volume should also show some correlation as indicated earlier on, and
- δ_P is a function of ϵ and μ.

The significance levels near 0 indicate that the correlations are by no means due to chance.

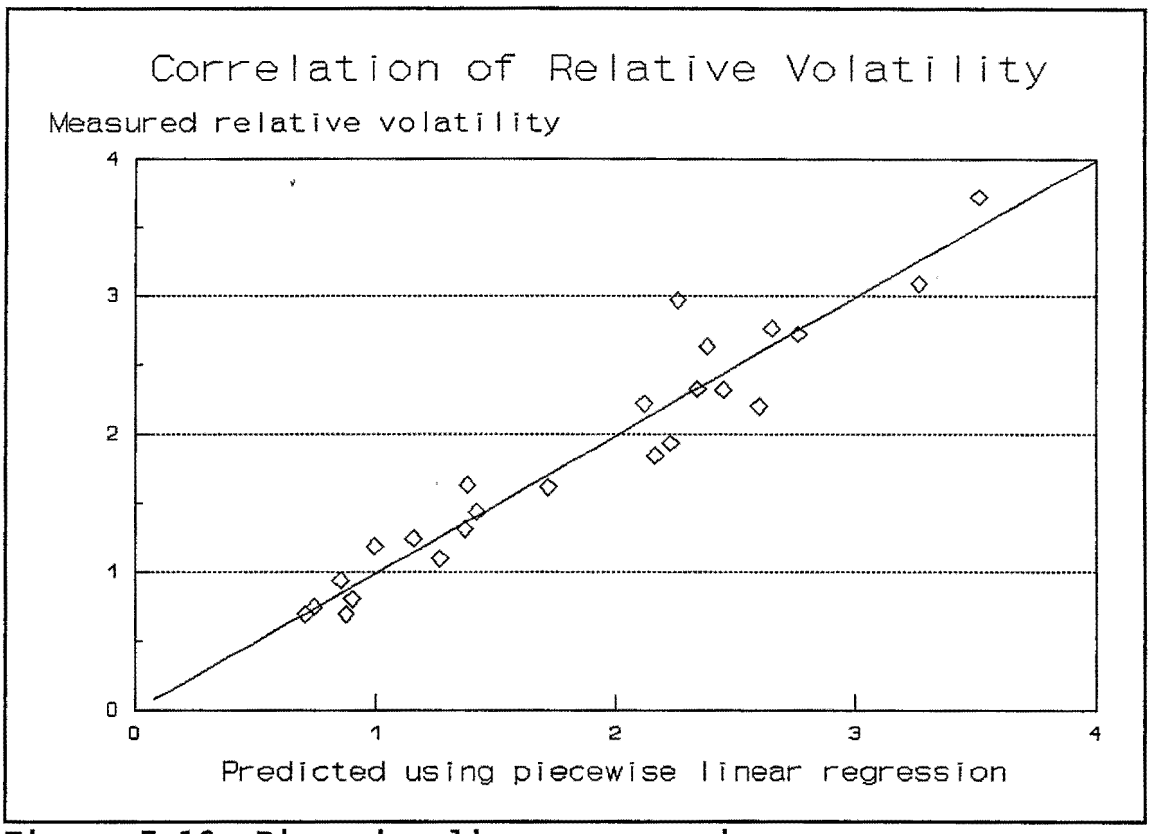

Figure 7.18: Piecewise linear regression.

The Draftsman plot in figure 7.19 shows all possible binary combinations of the variables and can be used to obtain a cursory overview of the relationships. The symbols in this plot are as follows:

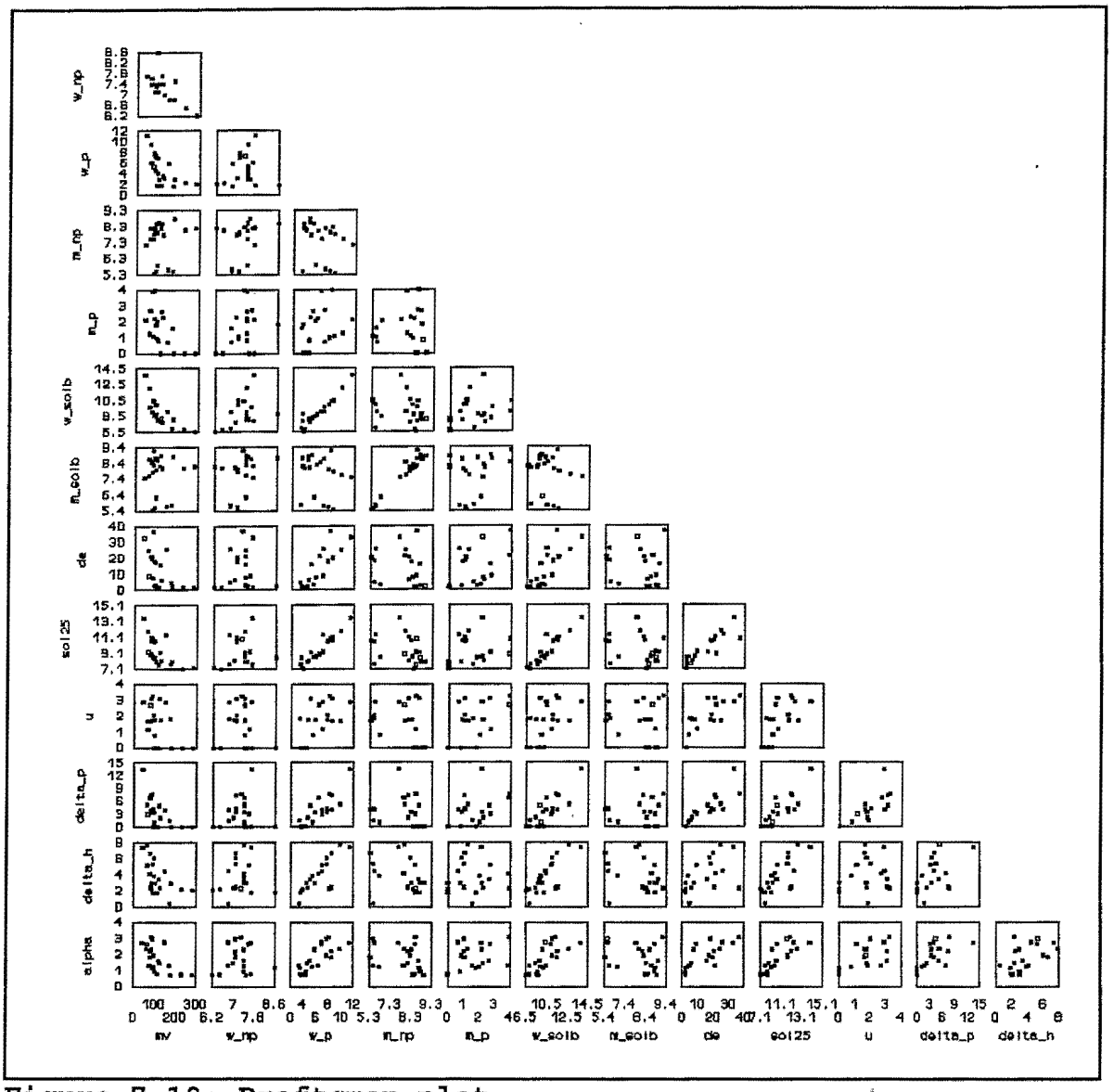

Figure 7.19: Draftsman plot.

Table 7.9: Symbols for the Draftsman Plot	
Symbol	**Meaning**
alpha	α, the relative volatility
delta_h	δ_H
delta_p	δ_P
u	μ (dipole moment)

sol25	δ, (solubility parameter) as usually tabulated.
de	ϵ (dielectric constant).
m_solb	δ, according to the MOSCED model.
w_solb	δ, according to the Weimer Prausnitz method.
m_p	τ, according to MOSCED.
m_np	λ, according to MOSCED.
w_p	τ, according to Weimer Prausnitz.
w_np	λ, according to Weimer Prausnitz.

Principle component analyses of the non standardized data shows that the number of properties listed in the tables above can be reduced to two basic linear sets of combinations of variables that explain most of the variability. The first group accounts for about 95.1% of variance and consists of the various solubility parameters and electrical properties. The second group accounts for another 4.5% of the variation and is composed of the molar volumes of the solvents. The diagram of the two component weights (figure 7.20) illustrate this point, with the point towards the far right being the molar volumes and the top left one being the dielectric constant. The scatter plot (figure 7.21) shows how the data is distributed around the two principle components. The biplot (figure 7.22) is probably the best illustration of this. The nearly horizontal line is the molar volume while the longest nearly vertical line is the dielectric constant. The length of these lines are related to the variances of the variables involved. Since the two mentioned variables have the largest variances, they should be very useful in modelling.

Note how most of the other variables tend in the same direction as the dielectric constant.

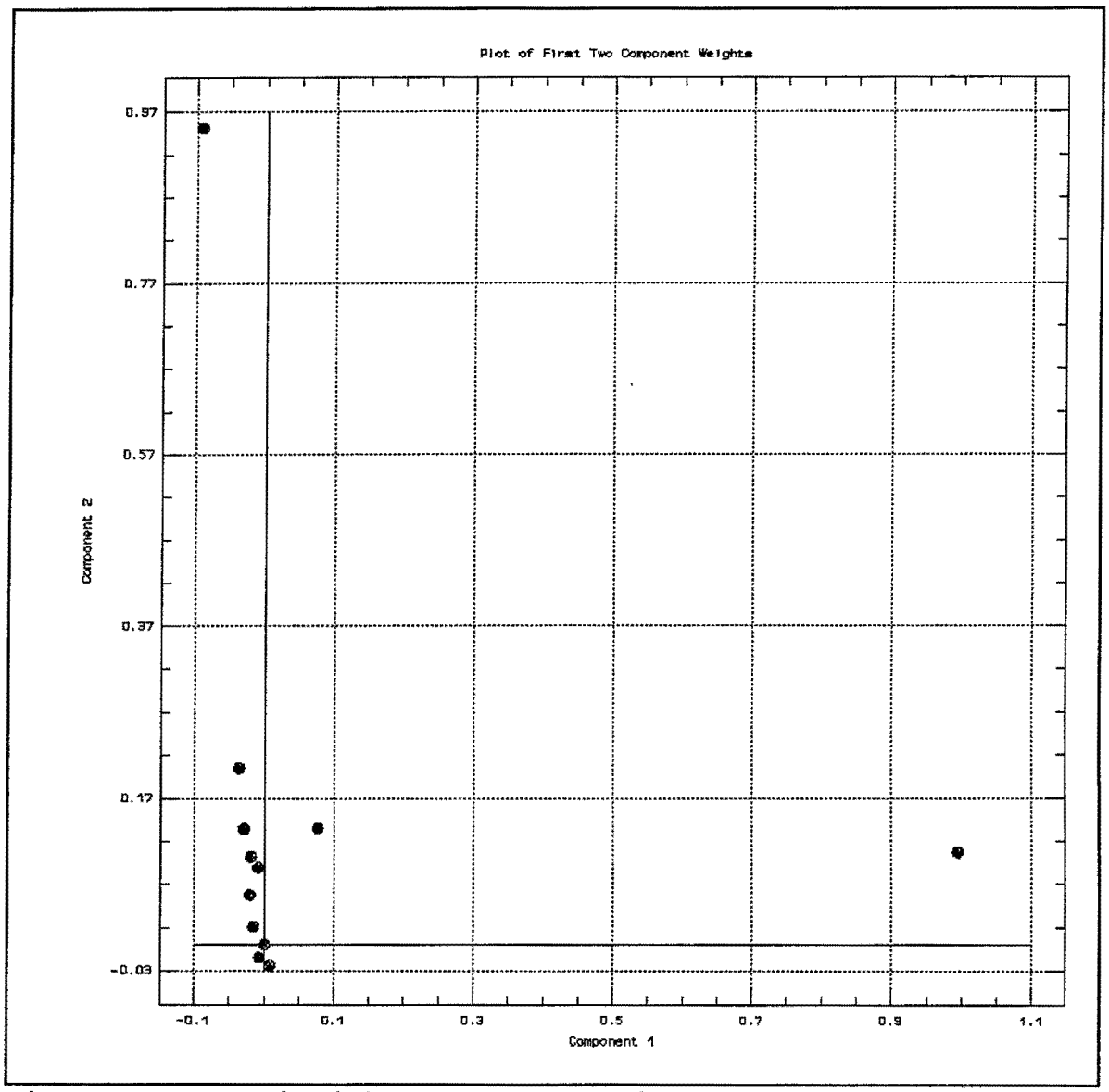

Figure 7.20: Principle component weights plot.

This shows that the earlier piecewise correlation is not acceptable because of the good correlations between the different parameters used. The values of the constants are therefore not very significant. A sound correlation must be developed with due consideration of the parameters to be added.

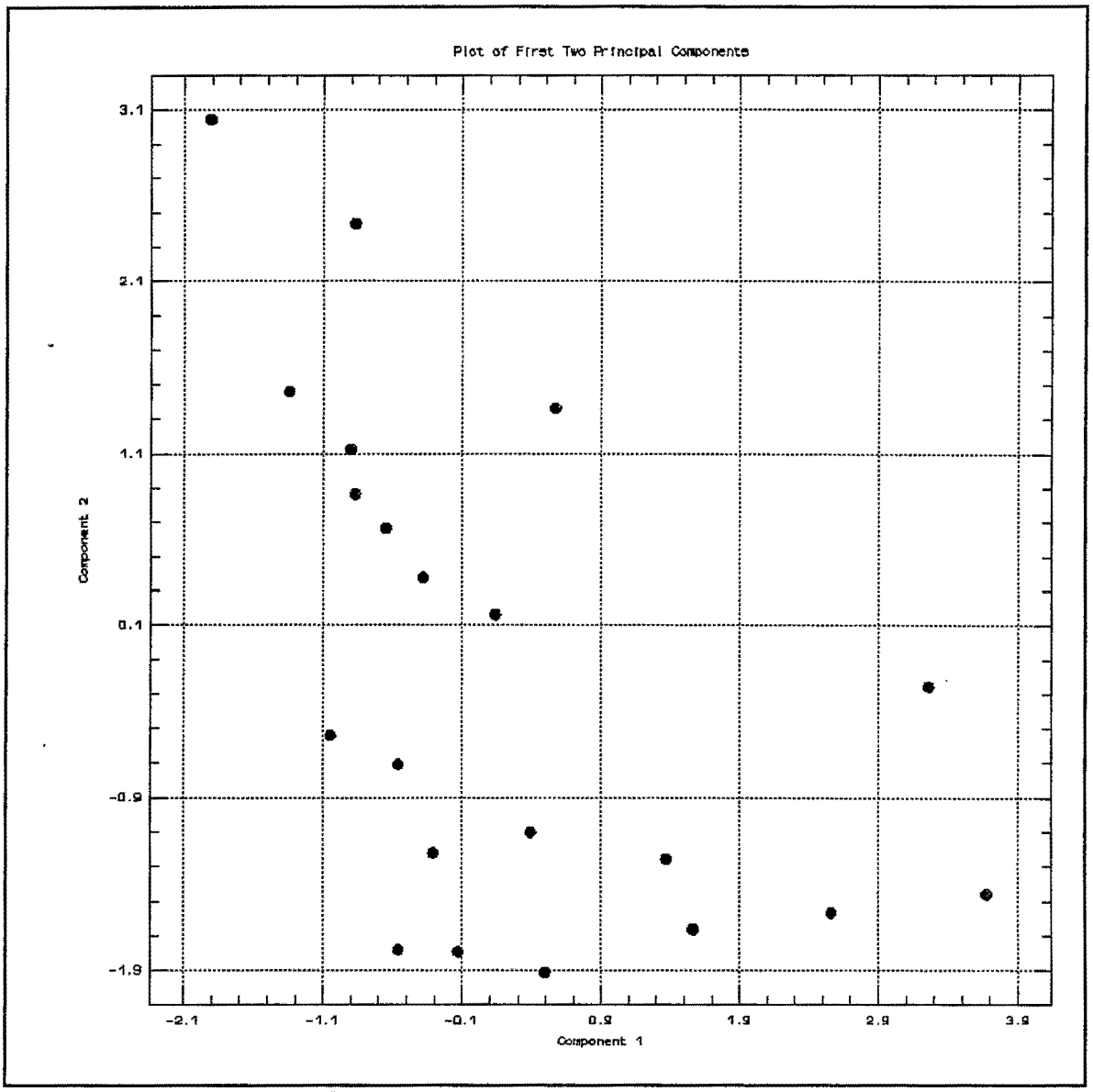

Figure 7.21: Principle component scatter plot.

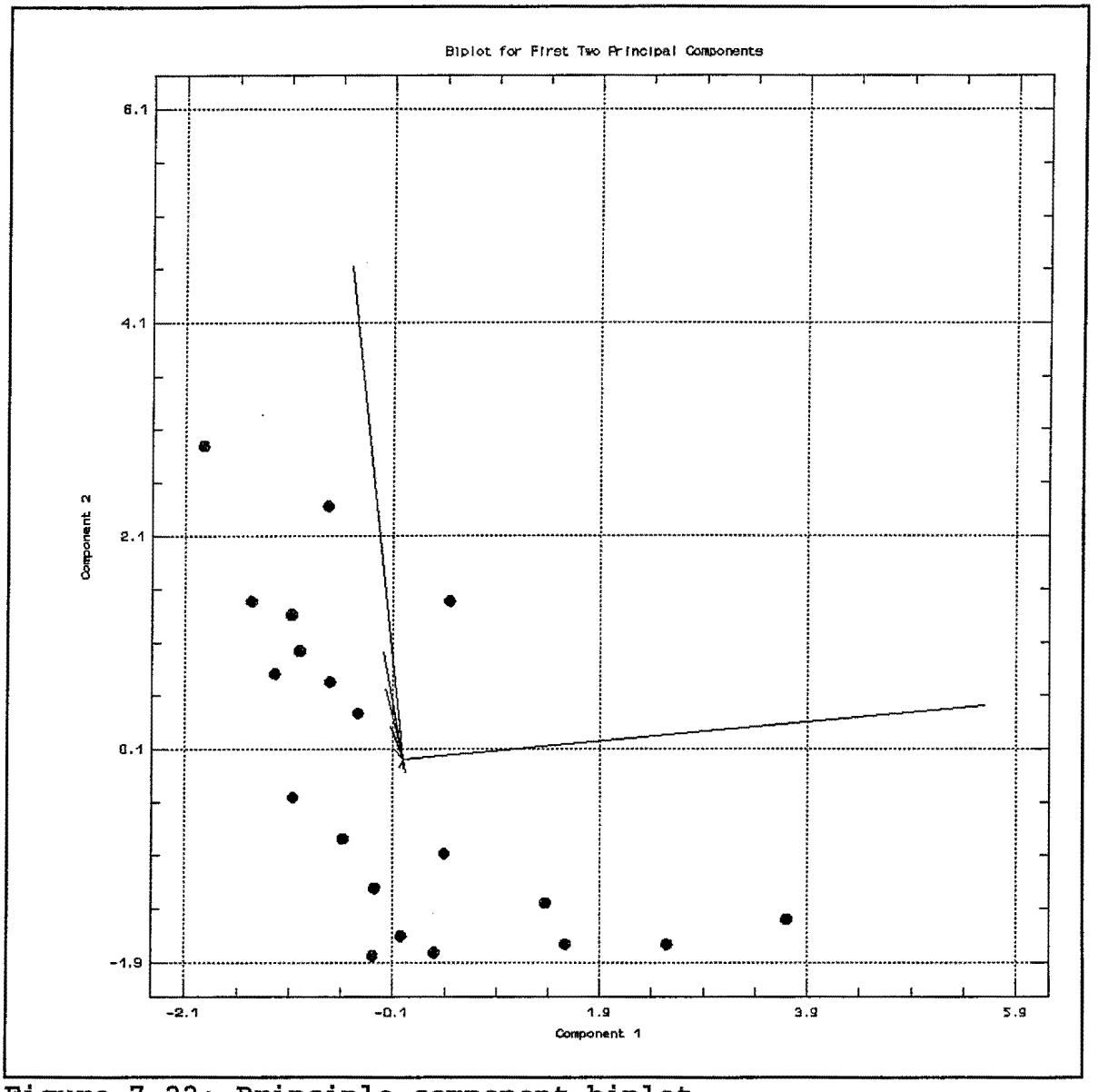

Figure 7.22: Principle component biplot.

If a single linear model is developed using non standardized data, it is therefore easy to understand that the properties ϵ (dielectric constant) and the molar volumes (mv) make a good choice. The correlation:

$$\alpha \approx 1.38396 - 0.002738 * mv + 0.05488 * \epsilon \qquad (7.84)$$

has an adjusted r^2 of 0.71 and the regression results are:

Table 7.10: Model fitting results

Variable	coefficient	std. error	t-value	significance level
constant	1.383957	0.275846	5.02	0.0000
mv	-0.002738	0.001721	-1.59	0.1234
ϵ	0.05488	0.007661	7.16	0.0000

The graph of the predicted values versus the residuals (figure 7.24) show that the residuals appear to reasonably well distributed about 0 and that no clear trend is visible.

The significance levels in table 7.10 represent the probability that a larger absolute t-value would occur if there was no marginal contribution from that variable. The high level for the molar volume suggests that it is not a good estimator while the low value for ϵ indicates that it is a good indicator.

Non linear combinations of the variables failed to produce any better correlations.

Table 7.11 contains the predicted versus actual values for this correlation.

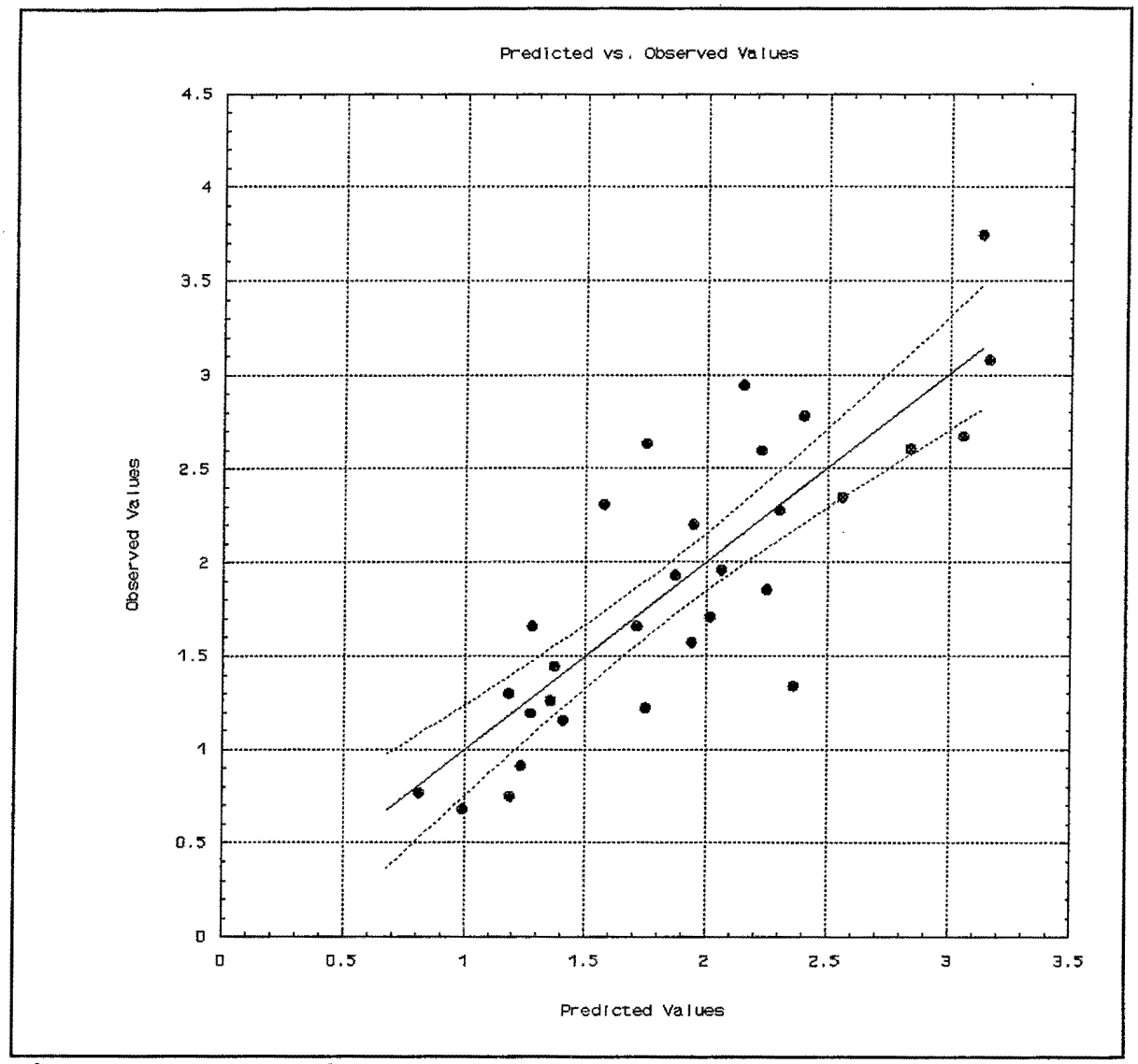

Figure 7.23: Predicted versus observed relative volatilities.

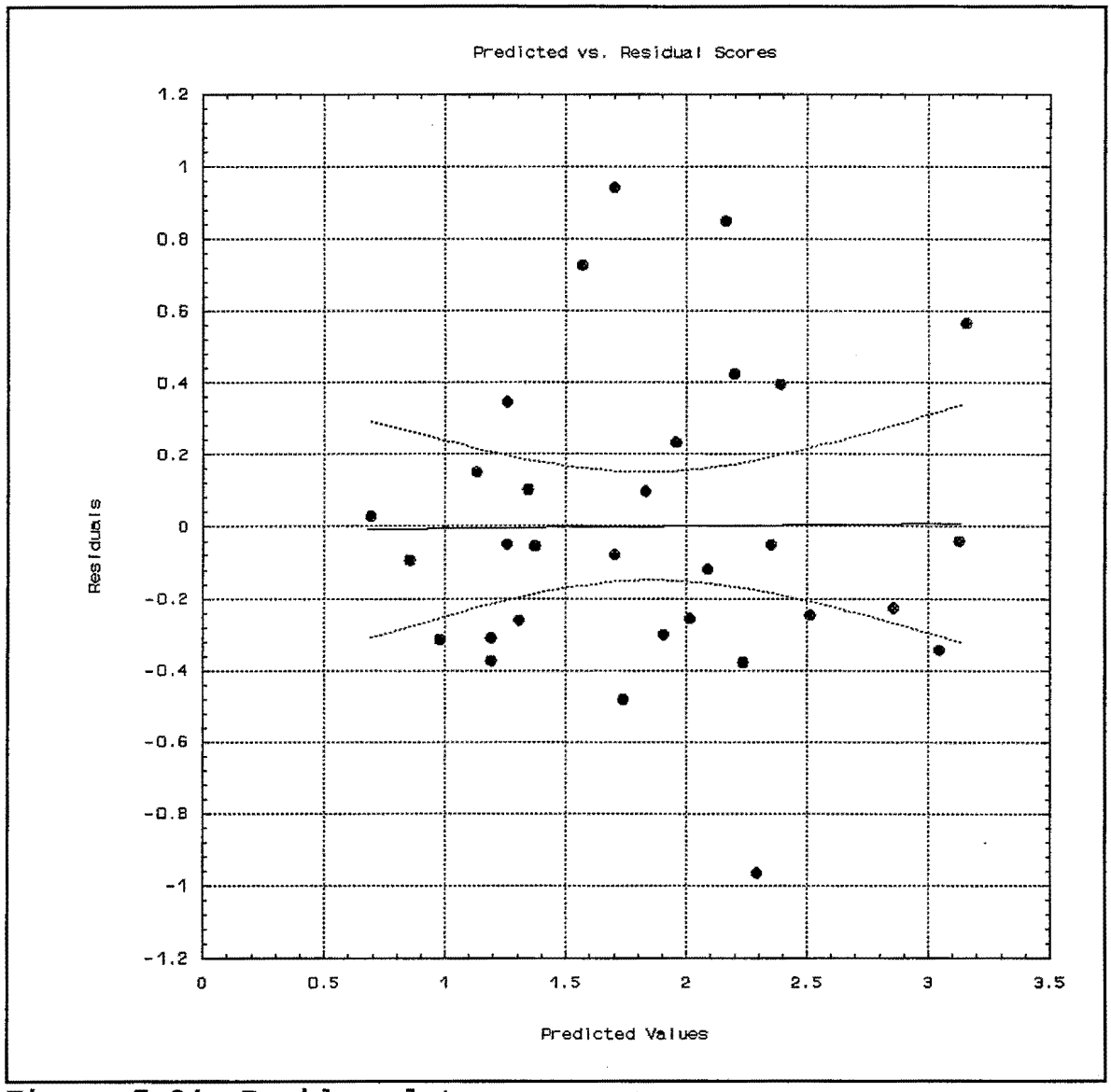

Figure 7.24: Residue plot.

Table 7:11: Measured versus correlated α		
Name	α_{12}	**Pred**
kerosol 200 (from C12 n-par)	0.692	0.682
decalin	0.692	0.993
n-decane	0.741	0.831
cyclohexane	0.801	1.17
carbon tetrachloride	0.936	1.22
diethyl ether	1.097	1.33
benzene	1.187	1.24
trichloroethylene	1.244	1.30
1,2,4-trichlorobenzene	1.265	1.76
isoamyl acetate	1.286	1.15
acetone	1.309	2.31
n-propyl acetate	1.439	1.35
cyclohexanone	1.615	1.92
1,4-dioxane	1.625	1.25
MIBK	1.631	1.70
2-ethoxyethanol	1.730	1.989
2-propanol	1.846	2.24
1-butanol	1.930	2.06
pyridine	1.944	1.84
DAA	2.200	1.97
1-propanol	2.210	2.27
tetrahydrofuran	2.316	1.56

ethanol	2.320	2.55
1-methyl-2-pyrrolidinone	2.576	2.82
1,6-hexanediol	2.614	2.19
dichloromethane	2.632	1.69
methanol	2.720	3.04
hexylene glycol	2.762	2.36
MXEA (2-methoxyethanol)	2.970	2.13
DMF (N,N-dimethylformamide)	3.089	3.13
DIMA (N,N-dimethylacetamide)	3.720	3.13

Since the variables are measured on scales that have different ranges, they should be standardized for better analysis. Principle component analyses of the standardized data reveals that there are actually about 7 significant groups of variables. The percentages for the groups are: 47.5, 18.8, 11.6, 8.8, 7.4, 2.9 and 1.4 respectively.

The biplot (figure 7.25) for the variables with respect to the first two principle components shows the different variables with the experimental points distributed about them. Note how the molar volume leans towards the top right while the other variables are more similar.

7.6 Discussion

The ASEEK program succeeded to some extend in discerning good solvents from less effective ones. The asterisks in table 7.2 show that good solvents were indeed picked out by ASEEK.

Remember that the correlation factors in table 7.7 is the key to understanding which factors have an effect on the relative

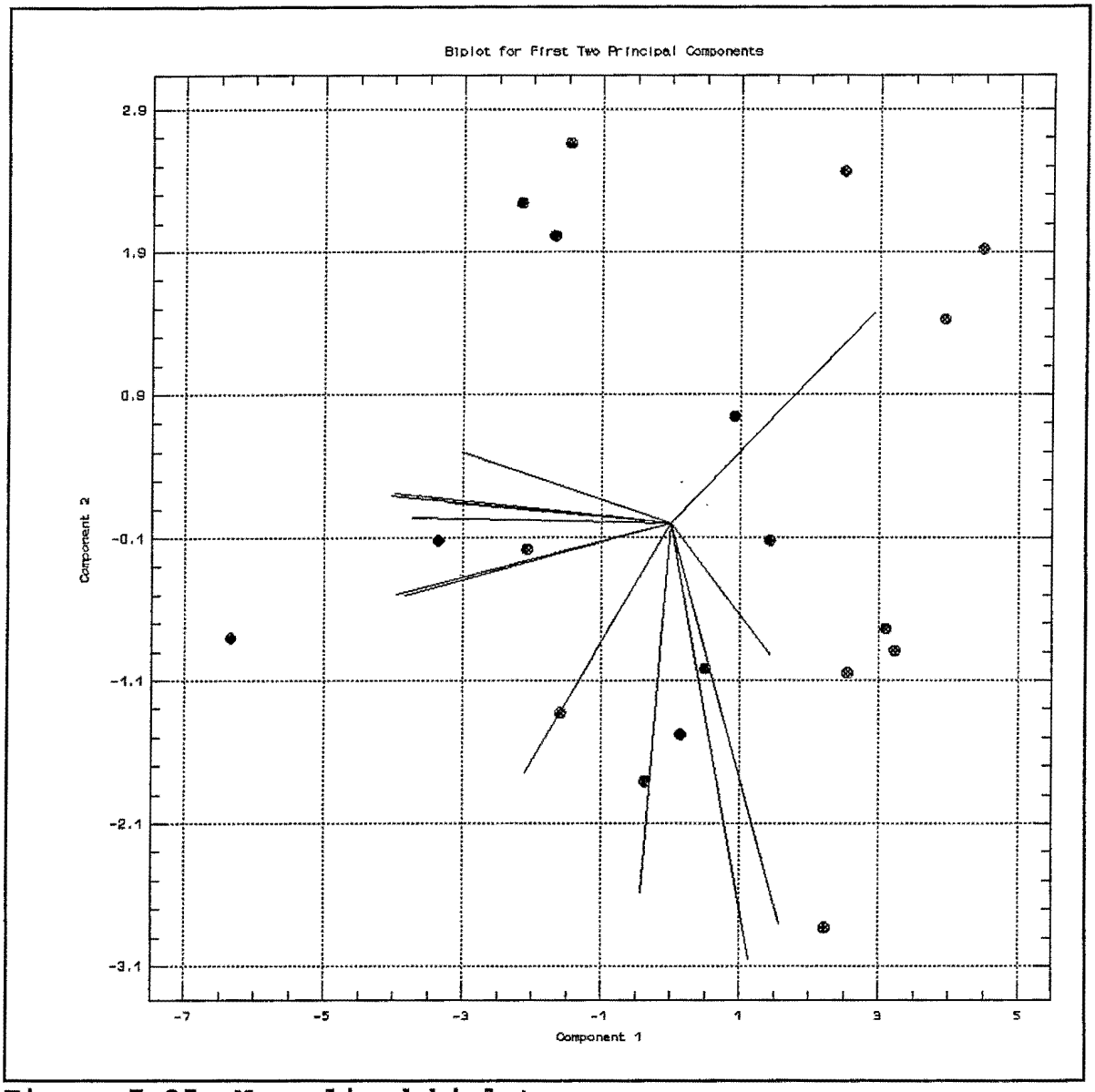

Figure 7.25: Normalized biplot.

volatility. Strong definite correlations are indicated between relative volatility and ϵ (the dielectric constant), τ (Tassios polar solubility parameter), δ (Tassios solubility parameter), μ (dipole moment), δ_P, δ_H and the molar volume.

As far as the infinite dilution selectivity models go (table 7.6), the Tassios and Weimer-Prausnitz models are similar and superior to the Helpinstill & Van Winkle model. The MOSCED model is more successful. The positive correlations, especially in the case of MOSCED, indicate that infinite dilution selectivities can be successfully used to identify effective solvents for use at

typical operating concentrations, although a strong linear quantitative relation is not evident. While these models may be effective at infinite dilution, it must be remembered that "no method is currently available for describing the vapour-liquid equilibrium behaviour for the whole concentration range, when based on such activity coefficients" (Tassios, 1969:121).

Some of these models can predict infinite dilution activity coefficients and not just selectivities. This can be used to regress interaction parameters and from these relative volatilities at typical concentrations may be estimated. This was not done because the aim was to see if these selectivities give a good indication of actual solvent performance.

The Tassios model considers effects due to the difference in molar volume between the solutes and the polar cohesive energy densities (polar solubility parameters) of the solvent. The Weimer-Prausnitz model considers contributions of dipole-dipole and dipole - induced dipole interactions. The positive correlations therefore show that these factors do come into play, but indicate clearly that separation based on the difference in molar volume between OCT1 and MBK is not the overriding factor.

Better results would be expected from the Helpinstill & Van Winkle model, which is basically an improvement over the previous two models. One could speculate as to the reason for this, but it is not clear.

Chapter 4 created the expectation that the MOSCED model is superior to the three previous models and this is confirmed by the experimental findings. Remember that MOSCED is more complex than the other models, utilizing more correlations and parameters.

One would expect UNIFAC to have fared even better since it was developed for intermediate concentrations. Although it is better

than MOSCED, many other solvent properties give a better indication of performance than does UNIFAC.

There is a strong linear correlation between the relative volatility and the values predicted by UNIFAC. In the case of the selectivity models the relationship is almost quadratic. This is probably due to the type of concentration dependence of the activity coefficients.

Now consider the values in table 7.7:

It is evident that the nonpolar solubility parameter has negligible influence on relative volatility. Dispersion forces appear to play no role. This is to be expected since it is well known that dispersion forces are negligible compared to polar cohesive energy effects, which are clearly present here. OCT1 and MBK also have similar dispersion cohesive energies (δ_D).

The polar solubility parameter[53], τ, (as calculated by the Weimer-Prausnitz method) of the solvent is shown to play an important role. This is in line with the theories expounded by Prausnitz & Anderson which suggest that the effective solvent should have a large polarity and a small molecular size. Tassios (1969:119) also suggests solvents having high polar cohesive energies when the components to be separated have different molar volumes. Recall from chapter 3 that, on a molecular level, the larger hydrocarbon (OCT1) has a higher probability of interacting with the polar solvent than the smaller hydrocarbon (Prausnitz & Anderson, 1961:98-99). The strength of this attractive interaction depends on the ability of the solvent to induce a dipole in the solutes which is related its polar cohesive energy. This inductive energy also depends on the size of the polar component.

---

[53] Remember that the solubility parameter (δ) may be subdivided into a nonpolar (λ, dispersion) and a polar solubility (τ, polar cohesive energy) parameter. The latter parameter can again be subdivided into a part due the hydrogen (δ_h) bonding and a part due to polar interaction (δ_p).

The effect of the polar cohesive energy density also manifests in the solubility parameter as computed by the Tassios method. The effect is even noticeable in the standard solubility parameter (25 °C) which is frequently tabulated. The parameter at the solvent's boiling point correlates slightly better to the relative volatility than the one computed at standard temperature.

The Weimer-Prausnitz polar solubility parameter, τ, may be subdivided into a polar (δ_P) and hydrogen bond (δ_H) component as explained in an earlier chapter. δ_P in table 7.5 is computed in the same way as was done earlier for MBK while δ_H is then taken from:

$$\delta_H = \sqrt{\tau^2 - \delta_P} \qquad (7.85)$$

The results (graphs of relative volatility versus δ_P and δ_H and correlation factors) show that a solvent with a high hydrogen bond part of the solubility parameter increases the relative volatility in favour of the olefin (which has the lower hydrogen bond part of the solubility parameter of OCT1 and MBK). A solvent with a low parameter causes a decrease in favour of MBK. The same is true of the polar part of the solubility parameter. This is of course the prediction made by Yeh and Berg (see chapter 4 and figure 4.1). As stated by the theory the molecule with more attractive (similar) forces with the solvent experience the decrease in volatility (174). This is illustrated in figure 7.26, where the experimental relative volatilities are shown along with the corresponding solubility parameters.

A decrease in molar volume is also seen to accompany an improvement in relative volatility. This is because the polarizing ability of a solvent is also related to its size (Prausnitz & Anderson, 1961:98). The correlation with molar volume is not so significant which may indicate that size is not

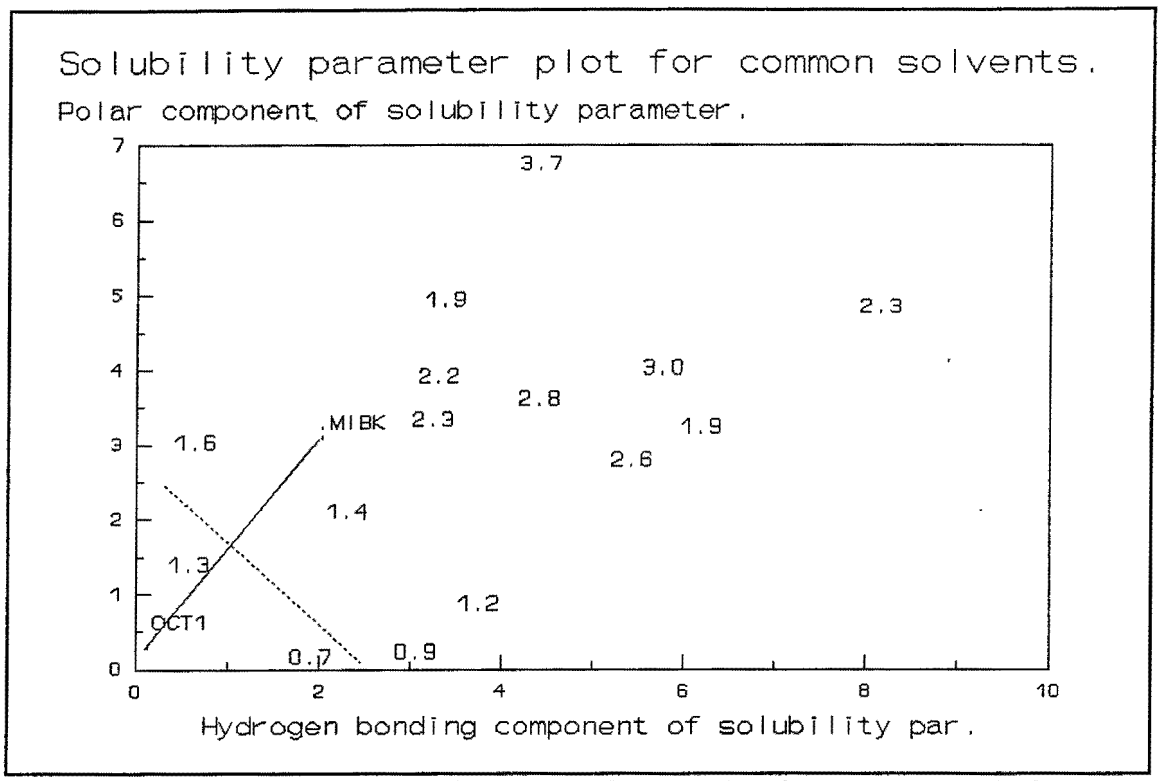

Figure 7.26: Polarity diagram with relative volatilities.

a major influence.

The correlation factor for the polar solubility parameter τ is 0.73. For the polar subpart (δ_P) it is 0.71 and for the hydrogen bond part (δ_H) 0.46. This indicates that while both dipole - induced dipole, dipole - dipole and hydrogen bond forming play important roles, the first two are much more significant. The polar part of the solubility parameter of the solvent is consequently very important and should be high. Polar interaction of some kind is clearly a major factor. From chapter 3 this can be attributed to two factors: (i) Polar solvents have stronger interactions with the more polar MBK and so reduce its volatility, and (ii) the polarity of a solvent is an indication of its ability to effect a separation based on the difference in size between MBK and OCT1. The importance of δ_H can be attributed to the fact that MBK has hydrogen bonding potential while OCT1 has almost none. This results in a decrease in the relative volatility of MBK as δ_H for the solvent increases.

The dipole moment is shown to play an important role as well. It should, since μ is related to δ_p by Böttcher's equation (Kirk-Othmer, 1971:(S)891). The inductive energy (dipole - induced dipole interaction) of a solvent is known to depend strongly on its polarity (μ) and its size (Prausnitz & Anderson, 1961:98).

Table 7.5 shows that the single most important factor is the dielectric constant of the solvent which correlates well with the relative volatility. This can be explained in terms of the theories presented by Prausnitz & Anderson (1961:98): The energy required to separate a dipole (typically a solute) from a dielectric (such as a solvent) is related to the dielectric constant of the solvent. Since the dipole moments of OCT1 and MBK (table 4.2) differ to a considerable extent, it is not surprising that a solvent with a high dielectric constant should be effective. The dipole moment of MBK (which experiences a decrease in relative volatility) is much higher than that of OCT1 (which is small) and even water. The dielectric constant is also an indication of polarity, which has already been identified as important.

The dielectric constant is also involved in the formation of two liquid phases. The greater the deviations from ideality short of partial miscibility (ie higher dielectric constant), the more likely the solvent is to affect the hydrocarbon types differently and hence increase their relative volatility (Updike et al, 1945:731). In the nonpolar separation cases studied by Updike et al the dielectric constant did not correlate well with the improvement factor.

This finding seems to agree with the general guideline given by Gerster (1969:44) which states that water and low boiling glycols should be effective for the separation of components with different polarities. Water and glycols (which typically have relatively high dielectric constants) are expected to improve the volatility of the less polar component. Note that the less polar olefin does indeed experience an increase in volatility for such

solvents. This study therefore suggests a possible explanation for Gerster's guideline.

Obviously the latter effect is not encountered in the typical separation of non polar hydrocarbons, which is the case usually discussed in the literature. The results here are therefore even more interesting.

It is interesting to note that the correlation is much better if two different linear regressions lines are used. The breakpoint remains almost constant at 1.8, irrespective of which parameters are used. This could suggest that two different effects are present in two regions. Solvents which give low relative volatilities are typically nonpolar, have low dielectric constants and low polar solubility parameters. The separation in these cases is probably due only to interaction between the solvent and the non polar 1-octene, as proposed by Yeh and Berg, 1986:174. The value of 1.8 should not be taken to mean that the effects change at this point - the spread of data may also innocently cause the apparent point of change to move.

It must be remembered that the solvent concentration in the liquid phase varied slightly during the screening runs. This should have some affect on volatilities (Berg, 1969:57). However, the containment of the fixed feed in the still will limit the concentration effect to a high degree. Table 7.5 shows that the liquid solvent concentration stayed near the 2/3 for most solvents. The average concentration is 0.59 with an STD of 0.14. It varies considerably for only the most volatile solvents. Over this small range the concentration affect should be very limited. According to figures given by Gerster (1969:43) a change in relative volatility in the order of 0.1 can maximally be expected. Despite this the factors considered here correlate much better than a similar study by Updike et al (1945:735). Statistics confirm that the slight concentration change has little influence on the relative volatility (r^2=0.01) or any other factors.

In conclusion the most important properties associated with a positive change in relative volatility are shown to be the following (in order of decreasing importance):

- dielectric constant ϵ which should be high,
- polar cohesive energy density τ, which should be high,
- polar part of the solubility parameter δ_p which should be high,
- dipole moment μ which should be high,
- hydrogen part of the solubility parameter δ_H which should be high.
- molar volume which should be low.

These guidelines should be valid whenever a larger molecule is to be separated from a smaller more polar one. Combinations of these two types of molecules are typical because the enhanced polarity of a smaller molecules increases its boiling point so that it may be found in mixtures with large non polar molecules.