CHAPTER 4

CHOICE OF AGENTS FOR THE 1-OCTENE / 2-HEXANONE SYSTEM

4.1 Introduction

Chapter 3 explored some of the theories regarding solvent effects in azeotropic and extractive distillation. These guidelines will now be utilized to identify potential agents for use with the 1-octene / 2-hexanone[12] system.

All possible attempts must be made to identify those agents which can reasonably be expected to produce a good separation before actual experimental work commences. Ideally one would test al known compounds, but this is practically impossible. Most studies test only a handful of agents, say three to fifteen, and if these are not carefully selected[13], one is almost sure to miss a good agent.

Unfortunately, there is no single correlation which can be used to predict the effectiveness of an arbitrary agent with high accuracy. Suggested methods and correlations will thus be used in an attempt to characterize promising agents as fully as possible.

4.2 Initial consideration of the 1-octene / 2-hexanone system

4.2.1 Physical properties of the constituents

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[12] 2-hexanone is also known as methyl n-butyl ketone, or MBK for short. It is not to be confused with the better known isomer MIBK, methyl isobutyl ketone.

[13] This may happen more frequently than one would expect. Except for the case of polar solvents with non-polar systems, few studies present a justification of the agents tested, or appear to have carefully selected them prior to testing.

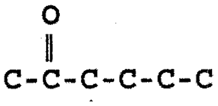
Some physical properties for the components are available from Riddick et al (1984: 171-172, 346-347) and Flick (1985: 41, 475). These are listed in the following tables.

Table 4.1: 1-Octene & 2-Hexanone		
	1-Octene	**2-Hexanone**
Abbreviation used:[14]	OCT1	MBK
CAS Registry Number	111-66-0	591-78-6
Structural formula	$CH_3(CH_2)_5CH=CH_2$	$CH_3(CH_2)_3COCH_3$
Empirical formula	C_8H_{16}	$C_6H_{12}O$

The structures of the components are:

1-octene: C=C-C-C-C-C-C-C

2-hexanone:



$$C-\overset{\overset{\displaystyle O}{\|}}{C}-C-C-C-C$$

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[14] These abbreviations will be used from now on.

Table 4.2: Physical Properties			
Property	Conditions	OCT1	MBK
Molecular weight, mw (g/mol)		112.214	100.160
Index of refraction, n_D	Sodium	1.4062	1.3987
Boiling point, bp (°C)	1 atm	121.286	127.583
Density, d (g/cm^{3})	20 °C 25 °C 120 °C(15)	0.71492 0.71085 0.63162	0.8113 0.8067 0.7193
Coefficient of density, dd/dt (g cm-^{3} °C^{-1})	25 °C	0.000834	0.00092
Molar volume(16), v (cm^{3}/mol)	25 °C 120 °C[17]	157.86 177.66	124.16 139.25
Temperature coefficient of pressure, dt/dp (K/kPa)	1 atm	0.3534	0.3479
Pressure coefficient, dp/dt (kPa/K)	1 atm	2.830	2.874
Vapour pressure (kPa)	25 °C	2.3	1.549
Freezing point, fp (°C)		-101.690	-55.8
Thermal expansion coefficient, α (/K)		N/A[18]	N/A
Isothermal compressibility, κ_T	25 °C	N/A	1.012E-6
Viscosity coefficient, ^{n} (cP)	20 °C 25 °C	0.470 0.447	N/A 0.584

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[15] Computed from the value at 25°C and dd/dt.

[16] As computed from the density and molecular weight.

[17] Computed from the density at this temperature and MW.

[18] N/A: Not available.

Surface tension, γ (N/m)	24.8 °C 25 °C	N/A 0.02128	0.02550 N/A
Heat of vaporization, ΔH_v (kJ/mol)	25 °C bp	40.55 33.95	42.9 36.0
Heat capacity, C_p ($J\ K^{-1} mol^{-1}$)	25 °C	241.0	213.4
Thermal conductivity coefficient, λ (J/(s m K))	37.8 °C	0.128	N/A
Critical pressure, atm		25.2	32.8
Critical temperature, °C		293.4	313.8
Critical density, g/cm^3		0.238	0.271[19]
Critical volume, m^3/mol		0.000472	0.000369
Acid dissociation constant in H_2SO_4 water, pKa		N/A	-8.3
Base dissociation constant in water, pKb		N/A	N/A
Dielectric constant, ϵ (Water: 80.16)	20 °C	2.084	14.56
Dipole moment, μ (Debye) (Water: 1.82)	20 °C 22 °C	0.34	2.66
Solubility parameter, δ ($cal^{1/2}\ cm^{-3/2}$) (Water: 23.53)	25 °C	7.6	8.6
Polar component of the solubility parameter, δ_P (Water: 7.8)	~ 20-25 °C	0.20	3.10
Hydrogen bonding component of the solubility parameter, δ_H (Water: 20.7)	~ 25 °C	~ 0	~ 2.0

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[19] Computed from the mw and critical volume.

Dispersion component of the solubility parameter, δ_D (Water: 7.6)	~ 20-25 °C	~ 7.60	~ 7.77
Solubility in water (weight %)	25 °C 20 °C	0.000410 N/A	N/A 1.75
Solubility of water (weight %)	20 °C	N/A	2.12
Aqueous azeotrope			
- weight % water	88.0 °C	71.3	N/A
- volume %	90.5 °C	N/A	74[20]

Published values for the components of the solubility parameter for OCT1 and MBK could not be found. However, δ_P is usually calculated from a slight modification of Böttcher's equation:

$$\delta_P^2=\left(\frac{12108}{V^2}\right)\left(\frac{\epsilon-1}{2\epsilon+n_D^2}\right)(n_D^2+2)\mu^2 \tag{4.55}$$

where V is the molar volume, ϵ is the dielectric constant, n_D is the index of refraction for D (sodium) light, and μ is the dipole moment expressed in Debye units. Values for these constants were taken from the table above and the δ_P's agree well with those of similar components (see Kirk-Othmer, 1971:891-892).

The value of δ_H for MBK is assumed to be ~2.0 since it is 2.0 for three similar ketones: methyl i-butyl ketone (MIBK), methyl i-amyl ketone and di-(i-butyl) ketone (see Kirk-Othmer, 1971:893). δ_H for OCT1 should be nearly 0, since it has negligible hydrogen bonding ability.

δ_D is computed from the relation:

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[20] About 78 weight % water.

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \qquad \textbf{(4.56)}$$

While it is also possible to estimate δ_D from homomorph considerations, it is known that if all four parameters are estimated independently they fit the above equation very well (891).

4.2.1 Interpretation

The physical properties listed in table 4.2 actually contain a wealth of useful information. For example:

- The solubility parameters of the components differ by only 1.0. This is much less than the typical 3.5 which is required for two liquid phases to form (see Doolittle, 1954:807). OCT1 and MBK should thus be fully miscible at 25°C and higher temperatures.

- The normal boiling points of OCT1 and MBK differ by only 6.3 °C. In such situations only a small positive deviation from Raoult's law is required to cause a maximum in the vapour-composition curve (see Hildebrand & Scott, 1950:221 and Horsley, 1984:615). Since the ketone is highly polar (compare μ), a minimum azeotrope can be expected. This is significant because the binary can then no longer be separated using ordinary distillation. UNIFAC also predicts a minimum boiling azeotrope.

- The solubility parameters, δ, of components are far removed from that of water. At 25 °C (as also shown at the end of the table), a mixture of OCT1 and MBK will be virtually immiscible with water.

4.2.2 Azeotropic data

Horsley (1973) lists a number of known azeotropes involving OCT1 or MBK. His extensive compilation does not contain any data for the OCT1-MBK interaction. A DIALOG computer search also failed to find any studies on this binary. The simulation packages

PRO/II and HYSIM, both of which contain extensive libraries of parameters for virtually all systems studied, also do not have any interaction parameters for this system. As far as could be established, this is the first study on the OCT1-MBK system.

(Unless otherwise stated, all azeotropes are minimum boiling.)

Table 4.3: Azeotropic data for OCT1

Other component	Weight %	Azeo Bp (°C)
Water	28.7	88.0
Nitromethane	52.3	91.2
Acetonitrile	60 vol. %	78.0
Ethyl benzene	Non-azeotrope	
Water & Nitromethane	Ternary azeotrope	
Carbon tetrachloride	Non-azeotrope	

Table 4.4: Azeotropic data for MBK

Other component	Weight %	Azeo Bp (°C)
Water	26 % vol.	90.5
Methyl trichloromethyl ether	Non-azeotrope	
2-Chloroethanol (maximum azeotrope)	75	129.0
Propionic acid	Non-azeotrope	
2-Methoxyethanol	< 56	< 121.5
Methyl pyruvate	Non-azeotrope	
Ethyl chloroacetate	Non-azeotrope	
Butyl alcohol[21]	81.8	116.5
Isobutyl alcohol	Non-azeotrope	
Ethyl carbonate	65	125.7
2-Pentanol	Non-azeotrope	
Allyl sulfide	Non-azeotrope	
Water & Propyl alcohol	Ternary azeotrope	
Butyl acetate	68	125.4
Isoamyl formate	Non-azeotrope	
Propyl isobutyrate	Non-azeotrope	

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[21] Another source indicated a non-azeotrope.

4.3 Selection criteria

Two closely related parameters are usually associated with the "effectiveness" of an agent, namely selectivity and relative volatility which are defined as follows:

$$S_{ij}=\frac{\gamma_i}{\gamma_j} \tag{4.57}$$

$$\alpha_{ij}=\frac{K_i}{K_j}=S_{ij}\frac{p_i^o}{p_j^o}=\frac{\left(\frac{y_i}{x_i}\right)}{\left(\frac{y_j}{x_j}\right)} \tag{4.58}$$

For two close boiling components such as OCT1 and MBK the two are numerically similar since the vapour pressures of the components are nearly equal. (The ratio of the nbp's is 0.951.)

Many predictions operate under infinite dilution conditions. As stated in paragraph 3.3, actual solvent concentrations are much lower. Due also to the known possible inability of the specific Othmer stills used here to measure data at very dilute concentrations, a 67 % mole solvent ratio is chosen for those models which are not derived from infinite dilution considerations or where experiments are involved.

4.4 Qualitative identification of potential agents

Since all separation processes exploit some difference in behaviour or characteristics demonstrated by the components to be separated, differences in the physical properties of OCT1 and MBK may provide indications of potential solvents.

4.4.1 Difference in polarity

As can be seen from the dipole moment, μ, MBK is significantly more polar than OCT1. In such cases water should always be considered first (see Gerster, 1969:44). Table 4.2 shows that miscibility with water is limited[22] (at 25 °C). When heated, both components also form aqueous azeotropes with water[23] with insufficient differences between the water concentrations and boiling points for a meaningful separation.

When water is not applicable, a heavy hydrocarbon or low-boiling glycol is suggested. However, limited miscibility is also encountered with most of these solvents.[24]

4.4.2 Difference in hydrogen bond forming ability

Consider the classification developed by Berg (1969:52) (chapter 3). MBK is a class III liquid - it contains donor atoms but no active hydrogen atoms (as in an acid). OCT1 is a class V liquid - it has no hydrogen bond forming capabilities. Mixtures of classes III and V liquids may exhibit positive deviations from Raoult's law, again indicating a likely minimum boiling azeotrope for OCT1-MBK.

The main use of this classification is that it may identify solvents which interact differently with the two classes of liquids involved. An agent which forms an azeotrope with either MBK or OCT1 has separation potential.

OCT1 may show positive deviations (and thus potentially minimum azeotropes) with liquids of the following classes:

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[22] In which case Gerster advises that it not be used.

[23] All immiscible systems form minimum azeotropes no matter how small their range of immiscibility or how great their difference in boiling points (Berg, 1969:54).

[24] Based on personal experience and tests performed using liquid-liquid extraction.

II: Liquids composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen and fluorine) - e.g.: alcohols, acids, phenols, primary and secondary amines, oximes, nitro compounds with alpha-hydrogen atoms, nitriles with alpha-hydrogen atoms, hydrazine, hydrogen chloride, hydrogen cyanide, etc.

Classes II and V <u>always</u> form + deviations, indicating a likelihood for minimum azeotropes.

III: Liquids composed of molecules containing donor atoms but no active hydrogen atoms - e.g.: ethers, ketones, aldehydes, esters, tertiary amines (including pyridine type), nitro compounds and nitriles without alpha-hydrogen atoms, etc.

IV: Liquids composed of molecules containing active hydrogen atoms but no donor atoms. These are molecules having two or three chlorine atoms on the same carbon atom as a hydrogen atom, or one chlorine on the same carbon atom and one or more chlorine atoms on adjacent carbon atoms - e.g.; $CHCl_3$, CH_2Cl_2, $CH_2Cl\text{-}CH_2Cl$, etc.

On the other hand, MBK will have positive deviations with the following:

I: Liquids capable of forming three dimensional networks of strong hydrogen bonds - e.g.: water, glycol, glycerol, amino alcohols, hydroxylamine, hydroxy acids, polyphenols, amides, etc.

(Class I can be excluded on account of miscibility limitations.)

II: See the description above.

III: See the description above.

V: Liquids having no hydrogen bond forming capabilities. (Usually quasi-ideal, always + deviations or ideal.)

MBK will always show negative deviations from ideality with class IV liquids (H and Cl containing). This can lead to rare high boiling azeotropes.

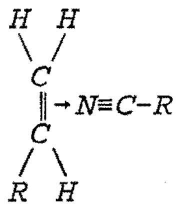
Liquids from class II are thus strongly indicated and should be included in experimental tests. Classes III, IV and I can also be considered.

4.4.3 Differences in molar volume and complex forming ability

For non-polar components it is known that in most cases the volume difference is large enough (> 5%) to make the effect of polar cohesive energy significant (Tassios, 1969:119). The larger hydrocarbon molecule has a higher probability of interacting with the polar solvent than the smaller hydrocarbon. Hence the effect of the polar contribution is to cause larger positive deviations from Raoult's law for larger hydrocarbons. The hydrocarbon with the larger molecule will have the higher activity coefficient (Prausnitz & Anderson, 1961:99).

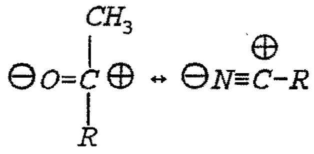
In the OCT1 / MBK system OCT1 has a much larger molar volume than MBK (see table 4.2) and the difference amounts to over 20 %. If both were non-polar then a polar solvent would enhance the volatility of OCT1. However, there are additional chemical effects which must be considered. OCT1 can act as a base (electron donor) to form an acid-base type complex with a polar solvent, which will reduce its volatility:

MBK, having a highly polar carbonyl group, should also be able to form a complex. This complex will be a dipole-dipole



(4.59)

interaction type:



$$\ominus O{=}\overset{CH_3}{\underset{R}{C}}\oplus \leftrightarrow \ominus N{\equiv}\overset{\oplus}{C}{-}R$$

(4.60)

The more polar MBK, can, however, be expected to form a much more stable complex than OCT1. Complex formation will therefore reduce the volatility of MBK, and so also favour a higher relative volatility for the larger OCT1.

According to Prausnitz and Anderson (1961:96) effective solvents of this type are highly polar and have small molecular sizes.

4.4.4 Differences in solubility parameter components

Figure 4.1 shows a plot of the hydrogen bonding component and the polar component of the solubility parameter for OCT1 and MBK as well as for several common solvents (Kirk-Othmer, 1971:899). The dividing line for OCT1-MBK is also drawn in. As can be expected, it shows that most of the components will increase the volatility of OCT1 over that of MBK due to interaction with MBK. It must be remembered that MBK has partial hydrogen bonding ability while OCT1 has almost none. Although there are dispersion forces between OCT1 and solvents such as hexane, these forces are much weaker than hydrogen bonding forces (see Yeh and Berg).

4.4.5 Differences in solubility

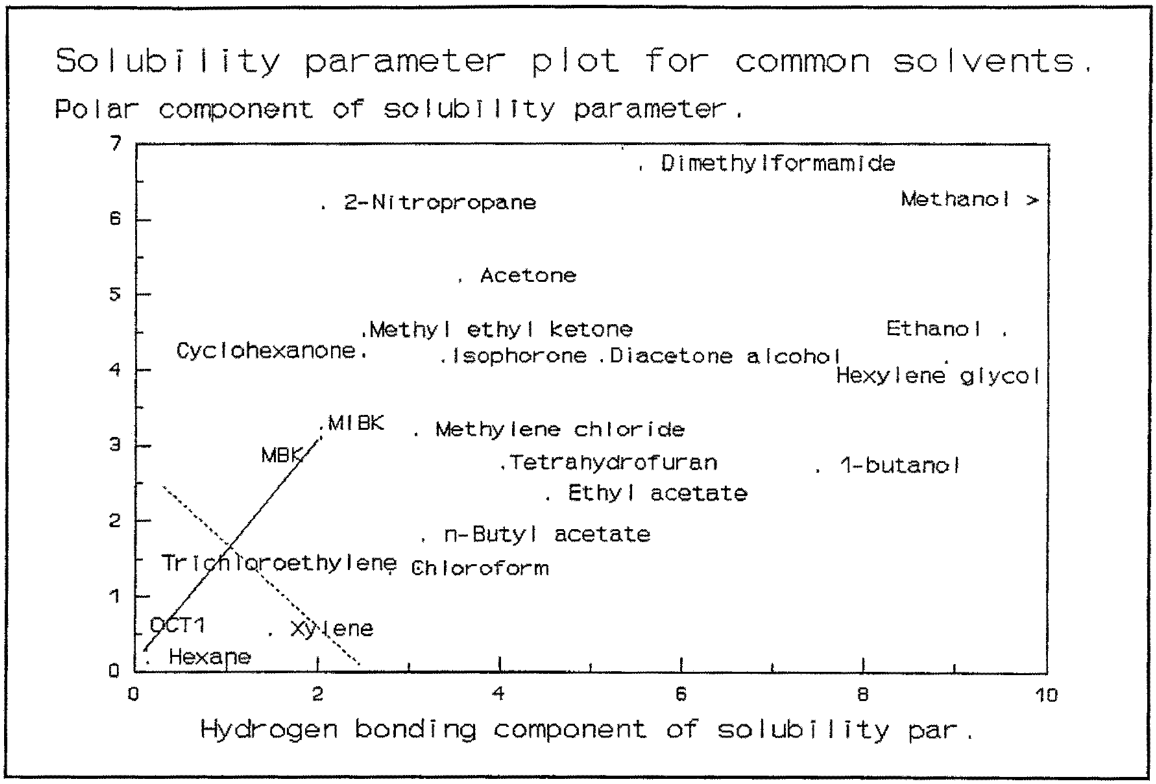


Figure 4.1: Polarity diagram for OCT1-MBK.

It is known that solubility is largely a hydrogen bond forming phenomenon and has little to do with dipole moment (which explains why MBK is immiscible with water despite being highly polar). Where hydrogen bonds are not involved, solubility is determined by internal pressures (related to the solubility parameter) which has a minor effect on solubility when hydrogen bonding is the dominant factor (Berg, 1969:53).

If one associates this with the fact that non-ideal behaviour is enhanced when the mixture is near the point of (but not yet) forming two liquid phases (see Hildebrand & Scott, 1950:168, Prabhu & Van Winkle, 1963:19 and Updike & Landon, 1945:731), it is a clear indication that strong hydrogen bond forming liquids should be tested[25]. Remember that OCT1 has no hydrogen bond forming ability while MBK has only donor abilities. Class I liquids (which may be excluded because two liquid phases could

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[25] This is especially relevant if one considers that the SLO is highly non-polar because it contains significantly more olefins than oxygenates.

form on account of their strong bonding ability) and especially II liquids (of which alcohols is the best known constituent), as mentioned above, can therefore be considered.

4.4.6 Boiling points

A suitable entrainer (azeotropic distillation) boils within a limited range (0 to 30 °C) of the hydrocarbon to be separated and forms a minimum azeotrope with one of the hydrocarbons (Berg, 1969:56).

In the case of extractive distillation the solvent must have a boiling point high enough to ensure that new azeotropes are not formed.

4.5 Quantitative identification of agents

A number of quantitative models have been proposed for the prediction of selectivities. These are discussed in section 3.11. To exploit these theories to their fullest it was decided to write a program to calculate the selectivity for a binary in the presence of a specific solvent. This program would do so for over 1100 solvents and then sort the results to present a list of solvents which should theoretically be effective.

In all cases values are expressed relative to MBK, so that the subscript i (or 1) refers to OCT1 and j (or 2) to MBK. Selectivities and relative volatilities in excess of 1 thus indicate an increase in the volatility of OCT1 relative to MBK.

Before discussing the program, the essence and applicabilities of the five different models incorporated are summarized:

4.5.1 Tassios

Tassios (1969:119) showed that in cases where the molar volumes of the close-boiling hydrocarbons differ by more than 5 %, a high selectivity can be achieved by using a solvent of high polar cohesive energy. The selectivity can be related by:

$$\ln S^{*}_{ij} \sim (\tau_s)^2 (V_j - V_i) \tag{4.61}$$

with τ_s the polar cohesive energy (or polar solubility parameter) of the solvent and V the molar volume.

The equation is accurate for relatively non-polar components in the presence of a polar solvent. In many other cases the author has found it to give selectivities in excess of actual values.

4.5.2 Weimer-Prausnitz

This correlation (1965:237) is valid for paraffins, naphthenes, pentene and benzene in a large variety of polar solvents. The correlation appears to be applicable primarily to the separation of non-polar binary components using a polar solvent. The equation is:

$$\begin{aligned} RT\ln S^{*}_{12} = {} & V_2 (\lambda_f - \lambda_2)^2 - V_1 (\lambda_f - \lambda_1)^2 + RT\left[\ln\left(\frac{V_2}{V_1}\right) + \frac{(V_1 - V_2)}{V_f}\right] \\ & + 2 (V_1 \Psi_{f1} - V_2 \Psi_{f2}) + \tau^2 (V_2 - V_1) \end{aligned} \tag{4.62}$$

It should be more accurate than the one presented by Tassios, but the author has found it prone to give slightly conservative estimates. (This also happens in the example given by Tassios.)

4.5.3 Helpinstill & Van Winkle

This method (1968:213) is an improvement over the Weimer-Prausnitz model and the equations are very similar. It can be applied to saturated, unsaturated, and aromatic hydrocarbons. Infinite dilution activity coefficients for all three basic binary systems - nonpolar-nonpolar, nonpolar-polar and polar-polar - may be predicted

The correlation is valid over a wide temperature range, 0 °C to 125 °C.

4.5.4 Thomas & Eckert (MOSCED)

(1984: 194)

The MOSCED model is superior to UNIFAC in predicting infinite dilution activity coefficients. The data used in this correlation includes both protic and aprotic (but nonaqueous) systems over wide temperature ranges.

The predictions are poorest where steric considerations predominate and it is not applicable to aqueous systems. In general very few unsatisfactory predictions were found.

The distinctions in forces allow for more accurate calculation of temperature effects than models such as UNIFAC which do not.

According to Reid, Prausnitz & Pauling (1987:304) MOSCED also has the advantage that the parameters have some physical significance which give a "feel" for the relative magnitudes of the types of forces in a solution. The model is also widely applicable. However, it works only for systems with activity coefficients below 100.

4.5.5 UNIFAC

(see Fredenslund, Jones and Prausnitz, 1975:1086)

UNIFAC is currently a popular technique for predicting activity coefficients. Hunek et al (1989) used it with success to model the separation of higher (C2-C5) alcohols using methanol as a "reverse extractive" agent. They justify their choice as follows:

"To describe phase equilibrium in multi component mixtures, the most successful methods currently used for the prediction of activity coefficients in the liquid phase are group contribution methods. The best known of those proposed so far is the UNIFAC model, Fredenslund et al. It has already been used successfully in many area. We chose it because of the reliable results produced for VLE as well as for its wide area of application."

In cases where polar components are present and no experimental data is available, Wilcox and White (1986:143) also recommend the UNIFAC method.

UNIFAC is not applicable to molecules with functional groups in secondary or tertiary positions and gives unsatisfactory predictions for the first member of a homologous series. It is also ineffective at predicting data for systems with molecules of greatly differing sizes, incapable of handling polar molecules with cyclic backbones and it is not appropriate for polar aromatic molecules.

Despite these limitations it gives satisfactory predictions for most systems.

4.6 Calculation details: ASEEK

The computer program (ASEEK) calculates the selectivities according to the qualitative methods described. It can do so for a single selected solvent and binary system as well as test all the solvents listed in its database to identify potentially effective solvents. The sorting of solvents can be tailored by providing weights for the different models as mandated by their respective applicabilities.

4.6.1 Introduction

All of the models listed above require specific information about the components involved. The constants used in many of the correlations depend on the component category. To provide in this need, the program has its own data-bank named AGENTS.INF. This data-bank contains data for over 1100 components. It was drawn up by first obtaining a list of names from PRO/II with normal boiling points added. Other required information was then added where it could be found. The data-bank contains the following:

- A code, 0 to 9, which classifies the component as a chloride, ester, alcohol etc (for MOSCED).

- A code to indicate if the homomorph of the component is a paraffin, cycloparaffin or aromatic.

- The q parameter as calculated from the number of carbon atoms and carbon-carbon double bonds (for MOSCED).

- The PRO/II library name and normal boiling point (°C) as provided by the PRO/II data-bank.

- The refractive index for the component (MOSCED).

- The assigned number of carbon atoms (MOSCED).

- The full chemical name.

Complete information is available for all the components, except for the MOSCED model in which case data is available for about a third of the components only. ASEEK also contains special regressed MOSCED parameters for 112 components (including OCT1), some of which do not fit into the general classification.

4.6.2 Program steps

For every solvent involved, a PRO/II input file is generated and submitted to the simulation program. This file performs three sets of six flashes each. The first six contains 2/3 mole fraction solvent with varying ratios of the two components to be separated. The second set of flashes uses varying ratios of the first component and the potential solvent only while the third set similarly establishes the relationship between the second component and the solvent.

In the case of infinite selectivities, the temperature used is the boiling point of the solvent in question. (Some of the examples given by authors are at different selected temperatures, as many of the models can also be used for extraction studies.)

The enthalpy of evaporation for the solvent is calculated by modelling a pure solvent stream at its bubbling point and dew point respectively. The reduced temperature as well as the molar volume of the component are also computed from data given by PRO/II. This allows the solubility parameter to be estimated from the preferred formula:

$$\delta^2 = \frac{\Delta U}{V} \propto \frac{\Delta H - RT}{V} \qquad \textbf{(4.63)}$$

Using the molar volume and the reduced temperature, the nonpolar solubility parameter, λ^2, can be read from the appropriate homomorph diagram (see Weimer & Prausnitz, 1965:238-239). ASEEK mimics this by using double linear interpolation on sets of data provided.

The polar solubility parameter is then found from:

$$\tau = \sqrt{(\delta^2 - \lambda^2)} \qquad \textbf{(4.64)}$$

The rest of the calculations are straight forward and carried out exactly as illustrated in the relevant articles. The various MOSCED parameters are calculated as described in chapter 3.

Before any agent is tested, ASEEK first calculates all the parameters for the two binary components involved.

With all these parameters available the selectivities can finally be calculated.

ASEEK is able to detect errors in PRO/II output files and rejects any components which cause them[26]. It also replaces estimated MOSCED parameters with actual regressed ones where available.

4.6.3 Integrity

Care was taken during the development of ASEEK to ensure that, for every model, the parameters are estimated in the exact same way it was done by the developers of the correlation. This is critical because different estimation techniques are known to give different numeric values.

The program was tested by submitting examples provided by the developers themselves and then tracing through the calculations to ensure that the correct values are being produced all the way.

Tassios (1969:121) uses the cyclohexane-benzene system with furfural as an example[27]. ASEEK gives the exact numerical values for the Tassios and Weimer-Prausnitz equations that were calculated by Tassios.

Helpinstill & Van Winkle (1968:219) provide two partial examples (which are reproduced quite well by ASEEK) but only one example with a final selectivity[28]. The value calculated by ASEEK is 4 % lower.

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[26] These errors are very rare and usually caused by lack of physical properties or operating under exceptional pressures or temperatures.

[27] The PRO/II name for cyclohexane is CH. For benzene it is BNZN and for furfuraldehyde FALD.

[28] The example features the solvent Cellosolve. It is recorded in the data bank as 2-ethoxyethanol with the PRO/II name EXEA. n-Hexane is HEXANE and 1-Hexene is identified by HXE1.

Thomas & Eckert (1984:204) give a table of predicted and actual selectivity values which may be used to test the implementation of MOSCED. The values agree well with those given by ASEEK.

ASEEK is generally able to reproduce examples quite accurately. Small deviations are present, but these have been traced to differences in the physical data (mostly molar volume and enthalpy of vaporization) used. This is not serious since all of these methods are only approximate.

4.7 Quantitative evaluations

ASEEK is useful in the sense that it can be used to obtain an indication of the potential of a selected solvent as well as to search through the database for potential solvents.

4.7.1 Selected solvents

The qualitative guidelines described in this chapter have identified certain classes or types of components which may act as suitable solvents. Much more specific information can be obtained by using the ASEEK program to examine specific members these groups. Trends within groups can also be identified.

Since this the heart of the selection procedure for the solvents used for screening, numerous examples are provided. The reader will note (chapter 7) that many of the solvents cited here were tested.

(Keep in mind that the Tassios model can be expected to give too high selectivities. It describes the effect of differences in molar volume and solvent cohesive energy only.)

Strong hydrogen bond forming / Class II liquids:

Results from ASEEK run	
Solvent PRO/II name:	METHANOL
Solvent chemical name:	Methanol
NBP (°C):	64.7
Selectivities	
Tassios	1198
Weimer & Prausnitz	661
Helpinstill & Van Winkle	62
MOSCED	4.1
UNIFAC	
Good separation with α's of 2.6 to 5.3 in the presence of 2/3 methanol. Methanol forms an azeotrope with OCT1 but not MBK.	
Comments	
Typical azeotropic entrainer behaviour. Miscible with C8 but can be easily separated again with water. The selectivities are promising.	

Results from ASEEK run	
Solvent PRO/II name:	ETHANOL
Solvent chemical name:	Ethanol
NBP (°C):	78.3
Selectivities	
Tassios	120
Weimer & Prausnitz	84
Helpinstill & Van Winkle	13
MOSCED	1.6
UNIFAC	

<table>
<tr><td>α's of 2.1 to 4. Azeotrope with OCT1 only.</td></tr>
<tr><th>Comments</th></tr>
<tr><td>Typical entrainer behaviour.</td></tr>
</table>

<table>
<tr><th colspan="2">Results from ASEEK run</th></tr>
<tr><td>**Solvent PRO/II name:**</td><td>PROPANOL</td></tr>
<tr><td>**Solvent chemical name:**</td><td>n-Propanol</td></tr>
<tr><td>**NBP (°C):**</td><td>97.2</td></tr>
<tr><th colspan="2">Selectivities</th></tr>
<tr><td>**Tassios**</td><td>23</td></tr>
<tr><td>**Weimer & Prausnitz**</td><td>18</td></tr>
<tr><td>**Helpinstill & Van Winkle**</td><td>4.4</td></tr>
<tr><td>**MOSCED**</td><td>0.97</td></tr>
<tr><th colspan="2">UNIFAC</th></tr>
<tr><td colspan="2">α's of 1.9 to 3.2. Azeotrope with OCT1 only.</td></tr>
<tr><th colspan="2">Comments</th></tr>
<tr><td colspan="2">Entrainer behaviour.</td></tr>
</table>

Notice how the selectivities decrease as the alcohol chain length increases. The alcohol is gaining nonpolar character and the effect of the polar group is "diluted".

<table>
<tr><th colspan="2">Results from ASEEK run</th></tr>
<tr><td>**Solvent PRO/II name:**</td><td>ENDM</td></tr>
<tr><td>**Solvent chemical name:**</td><td>Ethylene diamine</td></tr>
<tr><td>**NBP (°C):**</td><td>117.3</td></tr>
<tr><th colspan="2">Selectivities</th></tr>
<tr><td>**Tassios**</td><td>27</td></tr>
<tr><td>**Weimer & Prausnitz**</td><td>21</td></tr>
</table>

Helpinstill & Van Winkle	4.9
MOSCED	Not applicable
UNIFAC	
α's of 3.2 to 4.8. Azeotropes with OCT1 and MBK.	
Comments	
Not typical entrainer behaviour. Unfriendly to work with. Forms two liquid phases even at elevated temperatures.	

Results from ASEEK run	
Solvent PRO/II name:	NTRETH
Solvent chemical name:	Nitroethane
NBP (°C):	114.1
Selectivities	
Tassios	9.6
Weimer & Prausnitz	7.7
Helpinstill & Van Winkle	2.4
MOSCED	1.01
UNIFAC	
α's of 2.6 to 4. Azeotrope with OCT1 only.	
Comments	
Some safety concerns. (Nitromethane is considered by some sources to be an explosive[29].)	

Results from ASEEK run	
Solvent PRO/II name:	PRNT

---

[29] Many sources of safety data thus treats nitroethane the same way, although it is significantly less dangerous.

Solvent chemical name:	Propionitrile
NBP (°C):	97.4
Selectivities	
Tassios	9.8
Weimer & Prausnitz	7.7
Helpinstill & Van Winkle	2.3
MOSCED	1.4
UNIFAC	
α's of 2.3 to 3.6. Azeotrope with OCT1 only.	
Comments	
Typical entrainer behaviour. (The lighter acetonitrile has miscibility limitations and can not be tested an Othmer still. It should clearly be effective.)	

Class III liquids:

Results from ASEEK run	
Solvent PRO/II name:	DEK
Solvent chemical name:	Diethyl ketone
NBP (°C):	102.0
Selectivities	
Tassios	1.9
Weimer & Prausnitz	1.7
Helpinstill & Van Winkle	1.02
MOSCED	0.72
UNIFAC	
α's of 1.4 to 2. Almost an azeotrope with OCT1.	
Comments	
Possible azeotropic solvent. Selectivity is low.	

Results from ASEEK run	
Solvent PRO/II name:	IPAC
Solvent chemical name:	isopropyl acetate
NBP (°C):	88.5
Selectivities	
Tassios	1.6
Weimer & Prausnitz	1.5
Helpinstill & Van Winkle	0.96
MOSCED	10.45
UNIFAC	
α's of 1.3 to 2.1. No azeotropes with volatile solvent.	
Comments	
May be too volatile too use.	

Results from ASEEK run	
Solvent PRO/II name:	ACH
Solvent chemical name:	Acetaldehyde
NBP (°C):	20.5
Selectivities	
Tassios	22
Weimer & Prausnitz	15
Helpinstill & Van Winkle	3.1
MOSCED	Not applicable.
UNIFAC	
No azeotropes.	
Comments	
Too volatile to use.	

The higher boiling valeraldehyde (103 °C) gives similar results but has lower selectivities.

Class IV liquids:

Members of this group (such as chloroform (CLFR) and cis-1,2-dichloroethylene (CE12)) have promising selectivities (around 3), but they are much more volatile than OCT1 and MBK and form no new azeotropes. This limits their practical usefulness.

Other small polar solvents and diverse groups:

Many solvents in this group (such as n-propyl amine and ethyl formate) have promising selectivities, but also form no new azeotropes and are too volatile.

Other heavier solvents (such as 2-methyl-1-butanol, 2-ethoxyethanol (EXEA) and 2-methoxyethanol (MXEA)) are also promising but form azeotropes themselves with both OCT1 and MBK.

Results from ASEEK run	
Solvent PRO/II name:	DOXN
Solvent chemical name:	1,4-Dioxane
NBP (°C):	101.3
Selectivities	
Tassios	5.3
Weimer & Prausnitz	4.5
Helpinstill & Van Winkle	1.7
MOSCED	0.6
UNIFAC	
α's of 1.5 to 2.6. Azeotrope with OCT1 only.	
Comments	
Typical entrainer behaviour is indicated.	

Results from ASEEK run	
Solvent PRO/II name:	IPA
Solvent chemical name:	Isopropanol
NBP (°C):	82.3
Selectivities	
Tassios	25
Weimer & Prausnitz	20
Helpinstill & Van Winkle	4.5
MOSCED	16.6
UNIFAC	
α's of 2 to 3.4. Forms an azeotrope with OCT1 and not MBK.	
Comments	
Typical azeotropic solvent.	

Very low boiling (volatile) solvents can not be used in practice because they tend to concentrate in the vapour phase (which is usually almost ideal) and have little effect on the activities in the liquid phase.

Higher boiling solvents:

Phenol is excluded because of its high melting point. It is a solid at room temperature.

Cyclooctane (COCT, 151.2 °C) gives selectivities of 1.2, 1.2, 0.96 and 0.14. UNIFAC predicts values of 0.54 to 0.83. Separation from OCT1 and MBK should be easy although an MBK-COCT azeotrope may form at high MBK concentrations. If one keeps in mind that the first model (and possibly the second as well) can not handle a nonpolar solvent, there is reason to believe that COCT may be of some use. Similar values are predicted for n-nonane, but the selectivities are slightly lower.

Results from ASEEK run	
Solvent PRO/II name:	HXG
Solvent chemical name:	Hexylene glycol
NBP (°C):	197.5
Selectivities	
Tassios	4.0
Weimer & Prausnitz	3.8
Helpinstill & Van Winkle	1.7
MOSCED	4.7
UNIFAC	
α's of 2.7 to 3.7. Small possibility of high OCT1/MBK - low HXG azeotropes.	
Comments	
HXG is miscible with C8 and can be removed with water.	

4.7.2 Search for solvents

ASEEK also has the ability to search through the entire database and calculate the selectivities for every possible solvent. This can be used to generate a list of the best potential solvents. Given the merits of the various models and the fact that this is a polar-nonpolar separation the following weights were assigned to the various models.

Weights used	
Tassios	1
Weimer & Prausnitz	1
Helpinstill & Van Winkle	1
MOSCED	3
UNIFAC	2

The parameters generated for OCT1 and MBK by ASEEK are as follows:

Parameters generated and used by ASEEK		
Parameter	OCT1	MBK
Molar volume, V (cc/gmol)	178.3	140.2
Nonpolar solubility parameter[30], λ	6.76	6.94
Polar solubility parameter, τ	2.05	2.44
MOSCED dispersion parameter, λ	8.04	5.52
Polar parameter, τ	0.20	1.72
Acidity parameter, α	0.00	0.00
Basicity parameter, ß	0.166	1.89
Induction parameter, q	0.94	1.00
Polar asymmetry factor, ψ	1.00	1.11
Hydrogen bonding asymmetry factor, ζ	1.00	1.08

This list contains 300 agents which affect the selectivity. The list is reproduced in appendix C1 and the program in appendix C2. Due to the large variety of components in the data bank, a number of the unacceptable potential solvents must be manually removed. Keep in mind that the ideal solvent must not only affect the selectivity but also be non-reactive, non-explosive, non-toxic etc. The amount of solvent (capacity) required is also a factor which must be considered.

Obvious unacceptable groups such as acids (eg perchloroacid and nitric acid), highly reactive substances (such as diketene) and highly unsaturates (such as dibutene) were thus removed from the list. Other groups (such as expensive and highly toxic substances) can also be removed, but this was not done because they serve to characterize the kinds of solvents to be used and make for interesting reading.

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[30] The units of all solubility parameters are (cal/cc)^0.5 by default.

4.9 Agreement between quantitative and qualitative results

Numerous guidelines are employed in this chapter. On the hand one are a number of qualitative guidelines for choosing solvents (discussed in paragraph 4.4) while on the other a number of quantitative indications (paragraph 4.5).

Two clear examples can be used to illustrate that these two sets are in general agreement:

> In section 4.7.1 the selectivities and UNIFAC relative volatilities show that methanol will significantly enhance the relative volatility of OCT1 with respect to MBK. On the qualitative side, figure 4.1 shows that methanol lies on the side of MBK and will consequently interact to a greater extend with it, resulting in the same volatility change.
>
> Similarly, numerical values for components such as hexane and cyclo octane show that they decrease the relative volatility of OCT1. Again, according to figure 4.1, OCT1 lies close to these components. The resulting stronger interaction will thus decrease the relative volatility of OCT1.

The agreement also extends to other qualitative guidelines. Recall that polar solvents are expected to favourably enhance the relative volatility of the larger OCT1. This is confirmed by the values in section 4.7. Also note that the class II liquids do have the effect predicted in paragraph 4.4.2.

This agreement will become more obvious in chapter 7.

4.9 Conclusion

It is comforting to note that there is good agreement between the agents identified through qualitative means and the list of top agents generated through selectivity estimations. The results in this chapter showers promise on finding not only one but several solvents capable of acting in an azeotropic / extractive manner.

It appears that especially low boiling alcohol-like components such as methanol can be expected to be effective. Strong hydrogen bond formers should yield good selectivities. These should typically function as azeotropic agents.

Higher boiling hydrocarbons such as nonane for extractive distillation might also prove usable, but lower selectivities should be expected.

Some of the components which appear in the top list form two liquid mixtures (eg ethylene glycol), confirming the known fact that liquid-liquid extraction methods can be used to effect a separation.

More detail on the specific solvents chosen for screening can be found in chapter 7.