CHAPTER 3

LITERATURE REVIEW OF THE THEORY OF SEPARATION

3.1 Introduction - Raoult's Law

Distillation is one of the corner stones of chemical engineering. A column can be envisaged as containing a number of theoretical stages, each having a liquid and vapour which are in equilibrium. In order to design a separation scheme, one must somehow be able to model this equilibrium.

One of the first attempts to describe the behaviour of a mixture involves an application of Raoult's law. Its most familiar form is:

$$P_i = x_i P_i^o \qquad\qquad (3.1)$$

where P_i is the partial pressure for component i,

x_i the liquid mole fraction and

P_i^o the vapour pressure for the component, which is usually calculated by an Antoine equation (Walas, 1985:167).

If one uses the fact that the partial pressure, P_i, is also equal to the product of the vapour mole fraction and the total pressure, P, the equation can be rewritten in the form:

$$\frac{y_i}{x_i} = \frac{P_i^o}{P} \qquad\qquad (3.2)$$

However, it is found that very few mixtures actually obey this relation. These mixtures are termed "non ideal".

3.2 Non ideal mixtures

Non ideal binary mixtures are classified into two main types, those with positive[3] and negative deviations, respectively, from Raoult's law (Hildebrand & Scott, 1950:29). Positive deviations are favoured by differences in "internal pressure" or molecular attractive force and negative deviations are favoured by a tendency to compound formation between two components or by a marked difference in size.

In short, "a positive deviation from Raoult's law corresponds to a smaller solubility for a gas and a negative deviation corresponds to a greater solubility" than would be expected from an ideal solution (p. 46).

The deviation from ideal behaviour increases by choosing components more unlike in attractive forces (p. 41). It is thus not surprising that an ideal solution between a polar and nonpolar component is impossible (p. 168).

When the vapour pressures of the components of a binary mixture are very close, it takes little positive deviation from Raoult's law to yield a minimum azeotrope. Components with a larger difference in boiling points are less likely to form an azeotrope. In any case, where the components differ considerably in internal pressure[4] or in polarity, a mixture with a minimum boiling point may be found, even when the boiling points of the pure components differ considerably (p. 221).

Except for high polymer solutions, the effect of molecular size on deviations from Raoult's law should not be significant. It is usually differences in intermolecular forces which cause large

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[3] The partial pressures of both components are *greater* than that predicted by Raoult's law and the activity coefficients are in excess of unity. The boiling point of the mixture will be lower than expected and *minimum* azeotropes may form.

[4] (intermolecular attractive forces)

heats of mixing and correspondingly large deviations from ideality which usually overshadow any small entropy corrections. For substances of not too great difference in molal volume, the entropy of mixing can almost be regarded as ideal (117).

3.3 Causes of specific interactions

There are several factors which can modify the solubility of components and so bring about the deviations from Raoult's law mentioned in the previous paragraph. A few causes deserve to be mentioned (Hildebrand & Scott, 1950: 182):

1) Polarity. Chemical combination is more frequent between molecules of high polarity than between those of low polarity. Negative deviations from Raoult's law and abnormal great solubilities occur most frequently when the components are highly polar.

(i) Forces between permanent dipoles; These are electrostatic forces caused by permanently displaced electrical charges.

(ii) Forces between a permanent dipoles and an induced dipoles[5].

2) Dispersion forces between nonpolar molecules; The thermal motion of the molecules produce an electric field and act upon the polarizability of the other molecules, leading to temporary dipoles being induced (p.50).

3) Repulsive forces.

4) Formation of hydrogen bonds. The small size of the hydrogen atom permits such a close approach that large electrostatic forces come into play.

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[5] A molecule with a permanent dipole can induce a dipole in another molecule because of the polarizability, α, of the latter.

5) Differences in positive and negative character of the components. High polarity is not in itself sufficient to cause chemical combination. It is necessary for the substances to differ in the sense implied by the contrasting terms acidic and basic, or positive and negative.

3.4 Treatment of non ideal mixtures - activity coefficients

Deviations from Raoult's law are handled by introducing a term called "fugacity". The partial fugacity of component i (f_i) at a fixed temperature is formally defined by:

$$RTd(\ln f_i) = V_i dP \qquad (3.3)$$

and

$$\lim_{P \to 0} \left(\frac{f_i}{y_i P} \right) = 1 \qquad (3.4)$$

where the term $\phi_i = f_i/x_i P$ is called the partial fugacity coefficient for component i (Walas, 1985:141). (V_i is the specific volume of component i.)

Equation 4 shows that the partial fugacity reduces to partial pressure at low pressures. In some respects fugacity can be seen as an "effective" or "corrected" pressure.

The mathematical treatment of equations 3 and 4 (which is very informative) is sadly rarely reproduced. Suffice it to state that there are two ways of integrating equation 3. One solution yields (Walas 1985:176):

$$\frac{y_i}{x_i} = \gamma_i \frac{P_i^o}{P} \left(\frac{\phi_i^{sat} (PF)_i}{\phi_i^V} \right) \qquad (3.5)$$

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where γ_i is the activity coefficient of component i,

(PF)$_i$ the Poynting Factor,

ϕ_i^V the fugacity coefficient in the vapour phase and ϕ_i^{sat} the fugacity coefficient for the pure component at saturation conditions.

At pressures of only a few atmospheres the Poynting Factor, (PF)$_i$, is little different from unity and is usually ignored (Walas, 1985:223). The same is true for the ratio of the fugacity coefficients and so equation 5 simplifies to:

$$\frac{y_i}{x_i} \approx \gamma_i \frac{P_i^o}{P}$$

(3.6)

This equation bears a great resemblance to equation 2 (which is in used in the analytical solution), and in fact equation 6 reduces to equation 2 if $\gamma_i = 1$. This leads to the following definition: In an ideal mixture $\gamma_i = 1$ for all components present and Raoult's law is obeyed.

Take a closer look at the activity coefficient. From the integration of equation 3 it can be found that it is actually the following ratio:

$$\gamma_i \equiv \frac{f_i}{x_i f_i^o}$$

(3.7)

where f_i^o is the standard partial fugacity, taken at the temperature and pressure of the system for the *pure* component. In crude non mathematical terms equation 7 is stating that:

$$\gamma_i = \frac{\text{the effective vapour pressure of}}{\text{component } i \text{ in the mixture}}$$
$$\gamma_i = \frac{\text{component } i \text{ in the mixture}}{\begin{array}{c}\text{the effective vapour pressure that}\\\text{component } i \text{ would have}\\\text{if other components were}\\\text{not present as well}\end{array}} \qquad (3.8)$$

ie, the activity coefficient contains information as to how differently component i is behaving in the mixture from the way it would in pure state.

The activity coefficient is therefore unity for a pure liquid.

3.5 Measurements of separability

The activity coefficient provides a direct quantitative indication of how easily two components in a mixture can be separated. Two terms are used in this regard.

The relative volatility, α_{ij}, is defined as:

$$\alpha_{ij} \equiv \frac{\left(\dfrac{y_i}{x_i}\right)}{\left(\dfrac{y_j}{x_j}\right)} = \left(\frac{\gamma_i}{\gamma_j}\right) \cdot \left(\frac{p_i^o}{p_j^o}\right) \qquad (3.9)$$

and it is always expressed relative to a chosen reference substance, component j in this case. The least volatile component in a mixture is often chosen for this purpose. α indicates how the ratios of the two components in the vapour phase differ from that in the liquid. A value if 1.0 indicates that there is no difference and that the two components can consequently not be separated using ordinary distillation. A value in excess of unity means that component i is more volatile than component j, ie i tends to collect in the vapour phase.

A related term, the selectivity, S_{ij}, is defined as:

$$S_{ij} \equiv \frac{\gamma_i}{\gamma_j} \qquad\qquad (3.10)$$

This term is usually reserved for infinite dilution conditions, in which case vapour pressure differences are not important.

3.6 Separation strategy

There are two cases which are of interest here:

i) Two components which have very close boiling points and as a result α is near unity.

ii) Two components which form a minimum azeotrope, ie at a certain composition $\alpha=1$ and the boiling point of the mixture is lower than that of any of the components.

These cases are of great practical importance because pure products can no longer be obtained through ordinary distillation.

How can this situation be remedied?

The definition of the activity coefficient implies that a certain component may behave differently in a mixture than it would in pure form. It follows logically that we may be able to modify the mixture in some way so as to have a beneficial influence on γ. An easy way of doing this is by adding a third component, known as a solvent or an agent.

A suitable solvent should be chosen, ie one which discriminates between the solutes and so interacts differently with the different solutes. If it consequently influences their relative volatilities (through γ) accordingly, it may so enable separation.

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This principle is applied in the industry and it is found in two important forms: azeotropic and extractive distillation. Gerster (1969:43) provides the following definitions:

Azeotropic distillation: An agent[6] is added which has about the same vapour pressure as the feed components, and is removed with the overheads product, with which it usually (but not always) forms an azeotrope.

Extractive distillation: An agent which has a low vapour pressure is added near the top of the column and removed with the bottoms product. It usually does not form an azeotrope with components in the mixture.

3.7 Extractive and azeotropic distillation

The well known Kirk-Othmer Encyclopedia (Supplement Volume, 1984:821-824) describes enhanced distillation as follows:

3.7.1 Extractive distillation

In extractive distillation a solvent is introduced near the top of a column to increase the relative volatility of the materials being separated. The solvent is less volatile than the materials being separated and flows down to the bottom of the column, where it is removed with the less volatile material. The solvent and extract mixture in the bottoms product is separated in a separate column. The solvent is then cooled and returned to the first column (Fig 3.1).

A large solvent flow is usually required: from one to ten times the molar rate of feed to the column. The improvement in relative volatility results entirely from changes in activity coefficients in the liquid phase, because the solvent is concentrated there and the vapour phase usually deviates little from ideal. The

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[6] The term 'solvent' is often used in place of 'agent', but the two terms have the same meaning.
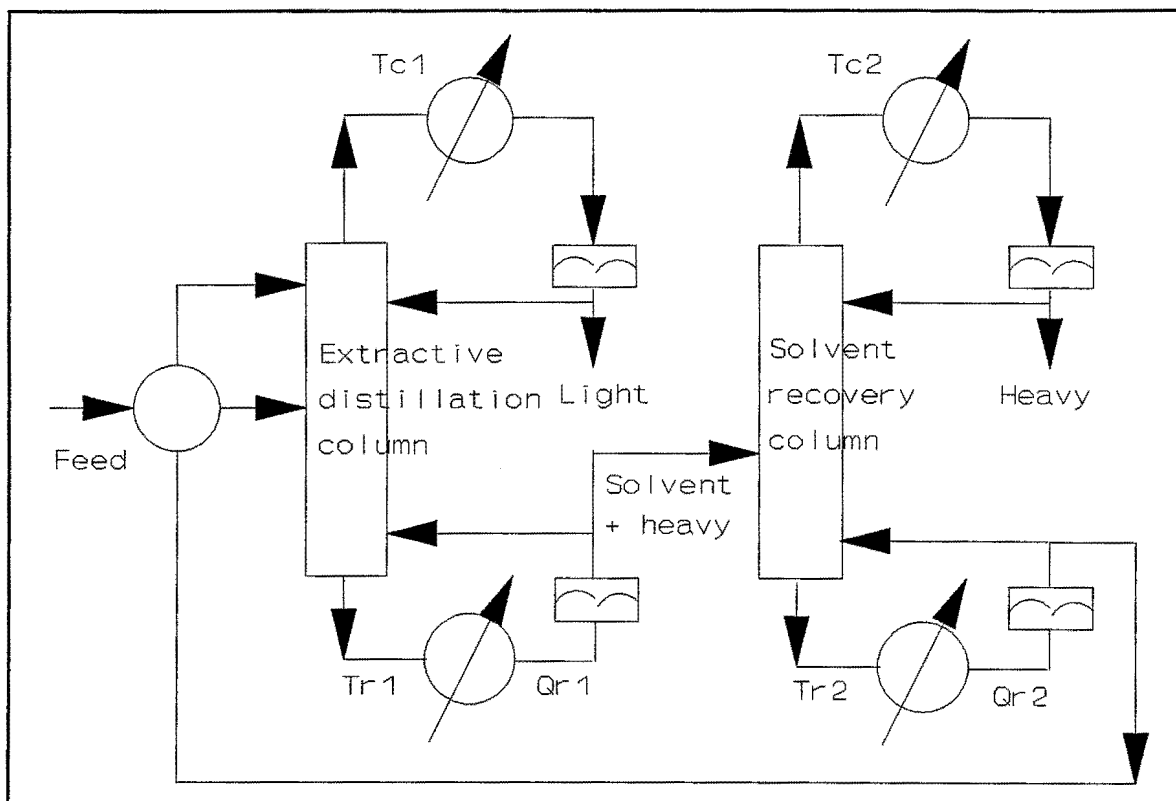
Figure 3.1: Typical extractive distillation process scheme.

solvent and its concentration are usually chosen so as to ensure that only one liquid phase exists within the column.

Since extractive distillation depends for its effectiveness on selective enhancement of the non ideal behaviour of one of the components to be separated, the materials to be separated must not form an ideal solution and must differ in chemical type for this enhancement to be feasible. It is well-suited for separating materials that differ in polarity or hydrogen bonding tendency. The solvents used in extractive distillation usually are polar or hydrogen-bonding and selectively decrease the volatility of the more polar or hydrogen-bonding-potential material relative to the less-polar or lower hydrogen-bonding-potential material.

Desired solvent properties include high selectivity. This should result more from a decrease in the activity coefficient of the extracted material, for which the solvent has a high affinity, than from an increase in the activity coefficient of the material which goes overhead. A high activity coefficient for the more

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volatile material, when it is dissolved in the solvent, is apt to increase tower height requirements. High solubility of the feed material in the solvent is also desirable. The critical factor is usually the solubility of the less-polar material. The solvent should not be very volatile to minimize the number of trays above the solvent feed point and to simplify solvent recovery. The volatility must also not be too low as to make the recycle solvent stream too hot.

An extractive distillation agent should boil considerably higher than the components being separated, ensuring that no new azeotropes are formed with the components (Berg, 1969:57).

Much of the energy lost in solvent recirculation may be economically recovered by using the solvent to vaporize the feed or to reboil the contents of the first column.

3.7.2 Azeotropic distillation

In azeotropic distillation (Fig. 3.2) a solvent is added, generally at the feed or occasionally with the reflux, to increase the relative volatility of the materials to be separated. The solvent volatility is similar to that of the materials being separated. It passes overhead with the distillate product, normally forming a minimum-boiling, frequently homogeneous azeotrope.

Although the added solvent should be miscible with the column liquid at the temperature and concentration in the column, two liquid phases frequently form in the distillate. One is solvent-rich and the other product-rich, which simplifies recovery. In such a case usually only a small concentration of agent is needed.

An azeotropic agent should preferably form a minimum-boiling azeotrope with one of the components to be separated; this allows for ready separation of the azeotropic agent. As in extractive
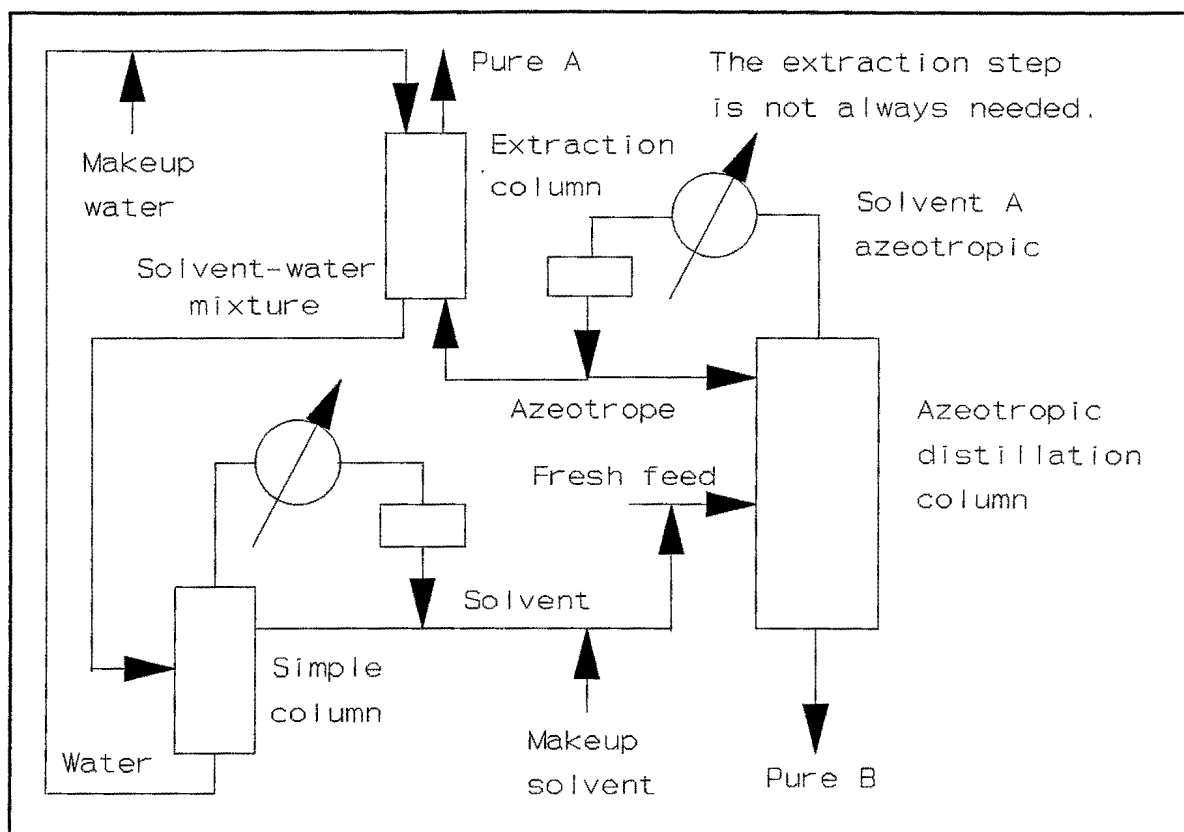
Figure 3.2: Typical scheme for azeotropic distillation.

distillation the agent increases the relative volatilities of the components most dissimilar to it. The agent should be of high enough volatility to pass overhead, but low enough to have a sufficient liquid-phase concentration to exert the desired influence on the liquid-phase activity coefficients. The agent should be minimally soluble with the compound being driven overhead. However, it should be soluble enough in the column liquid to ensure complete miscibility and solution throughout the column so as influence the material being driven overhead and to avoid the downcomer and flooding problems characteristic of two liquid phases.

The agent should be easily recoverable from the overhead product as, for example, in systems where the agent forms a second phase or in systems where the agent or the distillate product is preferentially water-soluble and can be separated by water washing. The agent should have a low heat of vaporization, resulting in minimum vaporization energy requirements.

Pressure rectification can also be used to recover the solvent provided that the vapour pressure-temperature relation is such that the azeotrope composition varies considerably with pressure.

"Azeotropic distillation is particularly useful when the feed component selected to come overhead as an azeotrope with the agent is present in the feed in small amounts. In such an instance the amount of agent needed to be circulated is small, resulting in only small additional steam costs because of the presence of the agent, and in a low agent recovery cost." (Gerster, 1969:44)

There are many variations of azeotropic distillation. Apart from the entrainer forming a binary minimum azeotrope with one component which is sufficiently lower than the original minimum azeotrope, it can also form a ternary minimum azeotrope which is sufficiently lower than any binary minimum azeotrope and in which the ratio of the original components is different from their ratio in the binary minimum azeotrope (Berg (1969:56).

A given entrainer may form azeotropes with each type of hydrocarbon in a specific range, but the azeotropes will not all have the same boiling points. Such an entrainer is termed nonselective. A selective entrainer forms azeotropes with only certain types of hydrocarbons. For example: All olefinic and paraffinic hydrocarbons which boil in the range 100-110°C form minimum azeotropes with methanol while only some form azeotropes with methyl ethyl ketone.

The proximity of the entrainer and hydrocarbons boiling point is important in entrainer selection. Both lower and high boiling entrainers have their advantages:

> When the entrainer boils considerably below a hydrocarbon mixture, first the azeotrope boils a few degrees below the pure entrainer to give a large spread between the undesired hydrocarbon azeotrope and the desired hydrocarbon, and

second, the composition of the azeotrope is low in removed hydrocarbon.

When the entrainer boiling point is considerably above that of the mixture, the azeotrope boils a few degrees below the hydrocarbon mixture resulting in a small temperature spread. Here the azeotrope is low in the removed hydrocarbon.

A commercially suitable entrainer invariably has a boiling point below that of the hydrocarbon mixture along with the following properties:

1. Boil within a limited range (0-30°C) of the hydrocarbon to be separated.
2. Form, on mixing with the hydrocarbon, a large positive deviation from Raoult's law to give a minimum azeotrope with one or more of the hydrocarbon types in the mixture.
3. Be soluble in the hydrocarbon at the distillation temperature and for some degrees below it.
4. Be easily separated from the hydrocarbons with which it forms an azeotrope.
5. Be inexpensive and readily obtainable.
6. Be stable at the distillation temperature.
7. Be nonreactive with the hydrocarbons or the column material.

3.8 Solubility parameters

Non ideal behaviour is encountered when the intermolecular forces between molecules from different species differ from the forces between molecules from the same species. Some quantitative measure of these forces is therefore useful.

The "cohesive energy" of a mole of liquid mixture is essentially the negative of its potential energy E, but taken with the opposite sign (Hildebrand & Scott, 1950:124). For pure components

we have the "cohesive energy density" ($\Delta E^V/V$), which can be taken as measure of "internal pressure". This assumes an important role in the theory of solutions and values of $(\Delta E^V/V)^{1/2}$ are often referred to as the solubility parameter, and designated by the symbol δ.

Internal pressure is *not* a measure of solvent polarity. Polarity represents the ability of a solvent to interact with a solute. Internal pressure is a structural parameter. When derived from latent heats of vaporization, it is a measure of the energy required to create a hole in a particular solvent to accommodate a solute (see also Dack, 1976:146).

As the name suggests, the solubility of liquids in other liquids is related to the difference in solubility parameters ($\delta_1 - \delta_2$).

Since both the energy of vaporization and the molal liquid volume are temperature dependant, the solubility parameter is also temperature dependant. At low vapour pressures, the vapour in equilibrium with the liquid is essentially ideal, and we may replace -E by ΔE^V the energy of vaporization and that in turn by ΔH^V-RT, where ΔH^V is the heat of vaporization.

The solubility parameter can thus be evaluated from:

$$\delta \approx \sqrt{\left(\frac{\Delta H^V - RT}{V^l}\right)} \qquad (3.11)$$

(When data is really scarce it may be approximated from:

$$\delta \approx 1.25 \sqrt{P_c} \qquad (3.12)$$

with P_c in atmospheres.)

Internal pressure is a measure of intermolecular forces which is less specific than the electrical properties. Qualitatively, it is the cohesive force which accounts for the distinctive properties of the liquid phase; quantitatively, it is given by the second term in the thermodynamic equation of state:

$$P + (\frac{\partial E}{\partial V})_T = T(\frac{\partial P}{\partial T})_V \qquad (3.13)$$

The term

$$(\frac{\partial E}{\partial V})_T \qquad (3.14)$$

is the internal pressure, π. The liquid's external pressure, P, is negligible in comparison with this internal pressure. This allows for the internal pressure to be calculated from the coefficient of thermal expansion α, and the compressibility, ß:

$$\alpha = \frac{1}{V}(\frac{\partial V}{\partial T})_P \qquad (3.15)$$

$$\beta = \frac{-1}{V}(\frac{\partial V}{\partial P})_T \qquad (3.16)$$

$$\pi = (\frac{\partial E}{\partial V})_T \approx T(\frac{\partial P}{\partial T})_V \qquad (3.17)$$

A different source of internal pressure is the van der Waals' equation of state, in which the term a/v^2 represents the internal pressure, at least to the extend to which the Van der Waals's equation expresses liquid behaviour. As shown elsewhere, another expression for internal pressure is:

$$\pi \propto \frac{\Delta E_v}{V} \tag{3.18}$$

where ΔE_v and V are the change of internal energy during vaporization and the volume, respectively. ΔE_v is difficult to evaluate.

The different ways of calculating it agree in order of magnitude, but there is no consistency in the results.

Since forces measured are not limited to dipole interactions, the use of internal pressures as a measure of polarity implies an extension of the term "polarity". The very nonspecific nature of internal pressure, however, may qualify it as a more adequate basis than simpler criteria for predicting solution behaviour (Updike & Langdon, 1945:719).

It has been suggested (Weimer & Prausnitz, 1965:238) that polar interactions can be taken care of by the assumption that the solubility parameter can be considered as being made up of various components, ie:

$$\delta^2 = \lambda^2 + \tau^2 \tag{3.19}$$

where λ is the dispersion parameter and τ the polar cohesive energy. A later expansion is:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{3.20}$$

where δ_d is the contribution due to dispersion forces, δ_p is the contribution due to dipole-dipole interactions, and δ_h is the contribution due to hydrogen bonding (see Shinoda, 1974: 70).

3.9 Qualitative indications of a solvent

When considering the separation of components, one must first study any differences between them. A solvent must then be selected whose interactions with the solutes depend on the properties in which they differ. The solvent can then be expected to interact to a different degree with the different solutes. The relevant activity coefficients will then also change and a separation may be possible. This section of the chapter will deal with a few such differences which may be exploited.

3.9.1 Difference in molar volume

If the molar volumes of solutes differ by 5% or more, the polar cohesive energy (τ) of the solvent is an important factor (Tassios, 1969:118). The physical interaction between the solvent and a hydrocarbon is essentially that of a polar-nonpolar system, where the forces to be expected are dispersion forces and dipole-induced dipole forces. High selectivity is achieved when

(a) The difference in molar volume between the hydrocarbons is large, and

(b) The solvent has a high polar cohesive energy.

The selectivities (as defined by equation 3.10) of various solvents for the system n-pentane and 1-pentene (studied by Gerster & Gorton, 1960:423) illustrate this (Table 3.1):

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Table 3.1: Selectivities vs Polar cohesive energies.		
Solvent	Selectivity, S*	Polar cohesive energy, τ
Tetra ethyl furan	1.41	3.71
Di-ethyl ketone	1.43	4.44
Di-ethyl carbonate	1.52	4.49
Pyridine	1.60	3.71
Methyl ethyl ketone	1.62	5.33
Butyronitrile	1.62	6.28
Cyclopentanone	1.65	5.37
Acetophenone	1.65	3.69
Acetone	1.67	6.14
2-4 Pentanedione	1.72	5.69
Di-ethyl oxalate	1.75	5.94
Propionitrile	1.85	7.69
Di-methyl acetamide	1.85	7.69
Furfural	1.87	7.62
Di-methyl formamide	1.96	8.07
Ethylenediamine	2.11	9.40
Acetonitrile	2.16	8.98
γ-Butyrolactone	2.17	8.01
Nitromethane	2.19	9.44

The effects of molar volume and polar cohesive energy may be expressed mathematically as:

$$\ln S_{ij} \sim (\tau_s)^2 \cdot (V_j - V_i) \qquad (3.21)$$

If the molar volumes of the two hydrocarbons are equal, separation is not effected by the solvent according to physical effects alone. Fortunately, separation of components of identical size is very rare; and in most cases the volume difference is large enough to make the effect of polar cohesive energy significant. For example, the relatively small difference in molar volume between isobutane (105 ml/mole) and normal butane (101 ml/mole) is enough to cause their relative volatility in the presence of furfural to be as large as 1.3 (Tassios, 1969:119).

Prausnitz and Anderson (1961:99) argue that the solvent should also have a small molar volume. On a molecular level the larger hydrocarbon molecule is seen as having a higher probability of interacting with the polar solvent than the smaller hydrocarbon. This causes larger positive deviations from Raoult's law for larger hydrocarbons and thus also higher activity coefficients (The larger hydrocarbon will therefore be more volatile)[7].

3.9.2 Complex formation

Another important factor is the formation of complexes of loosely bound aggregates. This phenomenon, called solvation, is considered to be the result of a Lewis acid-base interaction, in which an acid is a substance acting as an electron acceptor, and a base is an electron donor (Tassios, 1969:119).

The stability of a complex depends primarily on the ionization potential of the hydrocarbon and on the electron affinity of the electron acceptor. A stable complex is formed between a base having a low ionization potential and an acid having a large

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[7] The principles given here are valid for both azeotropic and extractive distillation processes. The only fundamental difference between these two processes is that higher boiling solvents are used in extractive distillation. This inhibits azeotrope formation.

electron affinity. The hydrocarbon forming the most stable complex will have the lowest volatility (Prausnitz & Anderson, 1961:100).

Good selectivities are obtained when:

1) The difference between the hydrocarbon ionization potentials is large, and

2) The solvent electron affinity is high.

Usually differences in molar volume is more important than any chemical effect, but the different effects frequently complement one another (Tassios, 1969:119). Complex formation becomes increasingly important when the hydrocarbons are of nearly the same size.

Complex formation may also account for the ability of a solvent to separate olefins from paraffins. It is known that the π electron in unsaturated hydrocarbons is strongly polarizable and so aromatics and olefins have basic properties whereas paraffins do not (Prausnitz & Anderson, 1961:100).

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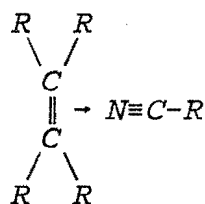
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3.9.3 Hydrogen bonding

Many researchers (eg Eduljee & Tiwari, 1976) emphasize the importance of hydrogen bonding, and in fact: "the most important single cause of deviation from ideal behaviour in liquid mixtures is hydrogen bonding."

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Berg (1969:52) presents a system of classification of liquids into groups which can be used to obtain qualitative predictions of the deviations from Raoult's law. The five classes are as follows:

I: Liquids capable of forming strong three dimensional networks of strong hydrogen bonds, e.g. water, glycol, etc.

II: Other liquids composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen and fluorine), e.g. alcohols and acids.

III: Liquids composed of molecules containing donor atoms but no active hydrogen atoms, e.g. ethers, ketones, aldehydes and esters.

IV: Liquids composed of molecules containing active hydrogen atoms but no donor atoms.

V: All other liquids, ie liquids having no hydrogen bond forming capabilities.

Combinations of components from the different classes can be expected to show the following deviations:

Table 3.2: Deviations from Raoult's Law:	
Classes	Deviations
I+V II+V	Always + deviations. I+V frequently limited solubility.
III+IV	Always - deviations.
I+IV II+IV	Always + deviations. I+IV frequently limited solubility.
I+I I+II I+III II+II II+III	Usually + deviations. Very complicated situation. Some combinations give maximum azeotropes.
III+III III+V IV+IV IV+V V+V	Quasi-ideal systems, always + deviations or ideal; azeotropes, if any, will be minimum.

Consider the case where a ketone (class III) and an olefin (class V) are separated using a class II solvent. The system shows that the solvent and the ketone may behave in a quasi-ideal way while the solvent and class V liquids will always have positive deviations, possibly form an azeotrope, and may even exhibit limited solubility.

Many studies deal with the effect of solvents on class V mixtures. Given the fact that the solvent effect depend on its non ideal interaction with solutes, it is not surprising that many reported potentially effective solvents fall into the first classes. For example: Berg et al. (1966) studied the effects of various entrainers on the separation of binary groups such as: naphthenes from paraffins, olefins from paraffins and ethyl benzene from xylenes. While no correlation could be made between the nature of the entrainer (boiling point difference, chemical

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structure, vapour pressure, etc.) and its performance as an entrainer, the best entrainers were generally found to be among the hydrogen-bond-forming liquids. In several separations the best entrainers belonged to a group that included n-propylamine, acetone, ethanol, 1,4-dioxane, methylene chloride, ethyl formate, chloroform, isopropyl acetate, 2-methylbutanol and formic acid.

3.9.4 Lowered solubility

Prabhu and Van Winkle (1963:19) suggest that solubility at the boiling point is another criterion which is related to solvent performance: "... the optimum solution abnormality (which is related to the effectiveness of a solvent) is found just short if the point where two liquid phases persist at the boiling point." Consequently, "for maximum change in relative volatility, an agent should be added which differs as much as possible in polarity from the components in the binary mixture."

For example: On the selection of solvents for the separation of the normal octane - ethylcyclohexane system (1963), it can be argued that "butyl Cellosolve has higher dielectric constant and dipole moment than 2-propanol and therefore should be a better solvent...".

However, this generalization on the selection of solvents does not always hold true and did not in the specific case considered by Prabhu & Van Winkle.

However, this idea should not be taken too far, for as Gerster (1969:45) states: "The solvents chosen can not be too polar[8] or considerable immiscibility will result. Azeotropic and extractive columns do not usually operate in immiscible regions because of difficulty in insuring uniform downflow rates of the two liquid phases. The solvent polarity is usually great enough, however,

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[8] This statement is made for nonpolar mixtures. A more general indication of low solubility is a large difference in the solubility parameter.

for it to be miscible with water, which allows solvent recovery by water washing."

Updike & Langdon (1945:731) also stated: "Solubility at the boiling point is the most obvious qualitative basis with which the effectiveness of an agent may be related. If the mutual solubility of hydrocarbons and agent is low, as in the case where two liquid phases are present at the boiling point, the concentration of agent in the hydrocarbon layer can not be great enough to affect the relative volatility greatly. Evidence shows this to be true, and also that systems near the two-phase region, but still single phase at the boiling point, had uniformly high improvement factors. This is to be expected, since the greater the deviations from ideal solution laws short of miscibility, the more likely the agent is to increase their relative volatility. The optimum is just short of the point where two liquid phases persist."

3.9.5 Solubility parameters

Yeh and Berg (1986) use several examples to illustrate that, in the case of extractive distillation, proper selection of the agent can be used to bring either component of the azeotrope overhead. This can be generalized as follows:

"In extractive distillation, if the effect of the agent is mainly dependent upon the attractive intermolecular forces occurring between the agent and key component, the molecule with more attractive intermolecular forces with the agent will be the bottoms product. Thus the potentiality of the key component to interact with the agent can be an indication of the effect of the agent. Solubility parameters, which include dispersion force, polar interaction and hydrogen bonding can be used to explain the intermolecular forces occurring between molecules. However, the interaction forces should be attractive. This indicates that the molecules must have some similar characteristics." (p. 174).

The authors categorize molecules accordingly and show a way to select an effective agent by using solubility parameters:

"The difference in the three solubility parameters between key components in each system is mainly polar interaction, δ_p, and hydrogen bonding, δ_h."

Consider the acetone-methanol system. Figure 3.3 shows a plot of δ_p versus δ_h. The location of methanol is referred to as point A and the location of acetone as point B. A segment AB is used to connect these two points. There is one point C which makes the ratio of AC to CB equal to the ratio of the specific volume of acetone to that of methanol. A vertical line is drawn through C to divide the plot into two parts. Agents on the methanol side have a greater affinity for methanol than for acetone. Those agents bring methanol down to the still pot and acetone will be the overhead product (this is confirmed by data). Similarly, agents on the acetone side have a greater affinity for acetone than for methanol. Therefore acetone will be the bottoms product. This is found to happen with the exception of DFMA. It has been shown that this agent can induce the acidity of alcohols, so that there is a strong molecular interaction with methanol.

This method can be used to obtain an initial estimate of the effect of an agent.

This idea agrees with earlier observations made by Scheibel regarding the use of some well-known properties of mixtures to select a solvent (1949:930): "First, members of a homologous series show little or no deviations from Raoult's law, Secondly, when two components show deviations from Raoult's law, one of these components shows the same type of deviation from any member of the homologous series of the other component." Thus any member of the homologous series of either component of an azeotrope might be used to separate the azeotrope. For example, for the separation of the acetone-methanol azeotrope, a number of ketones or alcohols should have the desired effect. An alcohol solvent
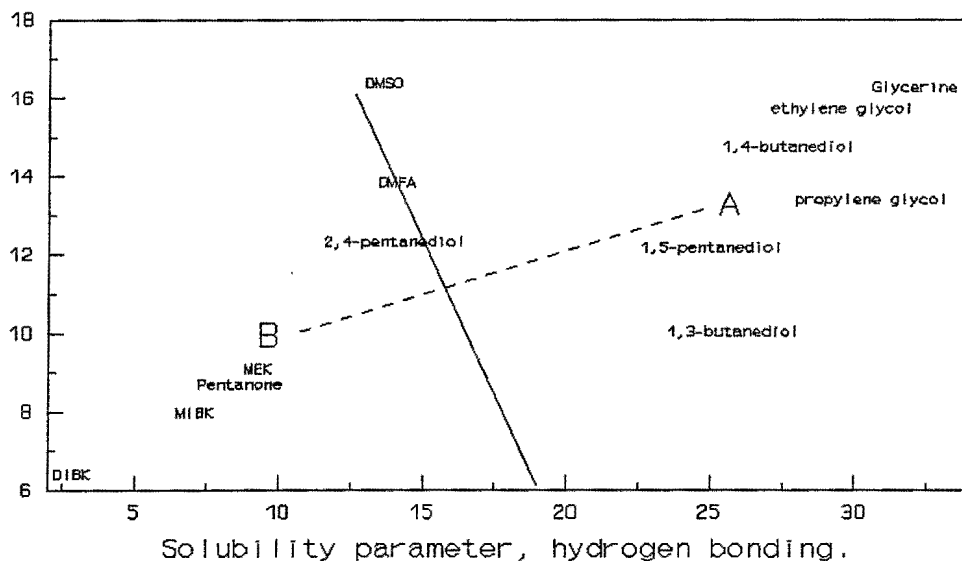
Figure 3.3: Polarity diagram.

would serve well to take acetone overhead.

Except for aromatic[9] and aqueous systems, the MOSCED model, developed by Thomas and Eckert, showed results which compare favourably with experimental measurements of Berg and Yeh. This model is discussed later on.

3.9.6 Differences in polarity and solvent polarity

Certain mixtures of polar organic compounds which are difficult to separate, respond to solvent distillation when the feed components are of different polarity. The common substances, listed in order of increasing polarity are:

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[9] This could be due to the electron withdrawal of the functional group on the benzene ring in addition to other characteristics of the molecule.

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1. <u>Hydrocarbons</u>[10]
2. Ethers
3. Aldehydes
4. <u>Ketones</u>
5. Esters
6. Alcohols
7. Glycols
8. Water

"In such cases extractive distillation with water as agent improves the volatility of the less polar compound. In cases with limited miscibility, a heavy hydrocarbon or low-boiling glycol would be possible substitutes. Glycol as an extractive agent would act to improve volatilities in the same manner and almost to the same degree as water. For these mixtures the use of higher-boiling homologues are suitable as extractive agents. For example, butanol would be an effective agent for the ethyl acetate - ethanol separation by promoting the volatility of the ester. The two alcohols would be the bottoms product." (Gerster, 1969:45)

Updike & Langdon (1945:717) studied the effects of solvents on the separation of relatively nonpolar components[11]. Almost all polar components were found to be effective and they made the following conclusions:

"'Polarity' strictly refers to the effect of interacting permanent electric dipoles in "polar" molecules. Since such effects are not always well defined, the term is usually extended to properties conferred by permanent or temporary dipoles and even by other molecular interactions. Measurements of polarity are therefore not always quantitatively consistent.

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[10] Keep in mind that this project deals with the separation of an olefin and a ketone.

[11] Specifically: benzene & cyclohexane and toluene & methyl cyclohexane.

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A high dielectric constant is one indication of the presence of molecular dipoles. Dielectric constant is defined as the ratio of electric flux density to electric field intensity in a dielectric. In polar liquids, the orientation of the dipoles permits high flux densities and high dielectric constants. Since interaction between the dipoles causes secondary effects, the actual electric dipole moment of the molecule is a better indication than the measured dielectric constant. Dipole moment is still an incomplete criterion, since more than one dipole present in the same molecule will add vectorially, giving a net moment not indicative of the effect of dipole forces on a molecular scale" (1945:718).

"In certain ranges, an increase in the dielectric constant is accompanied by an increase in the improvement factor. For other values no correlation could be found. Components with too high dielectric constants were beyond optimum polarity, forming mixtures with two liquid phases and thus giving low improvement factors. Compounds with a large value in of molecular dipole moment show large improvement factors, as could be expected from the dielectric results. The improvement in relative volatility appears to be *roughly* related to dipole moment in a linear fashion" (Updike & Langdon, 1945:733).

It must be stressed that Updike and Langdon decided that solvent polarity and dielectric constants do not define the behaviour of the solvent well.

3.10 Factors influencing the performance of a specific solvent

Once a specific solvent has been chosen, a number of other factors can also influence its selectivity:

3.10.1 Solvent concentration

"Although infinite-dilution activity coefficients for different hydrocarbons in a variety of solvents can be predicted, no method

is currently available for describing the whole concentration range, when based on such activity coefficients." However, the dependence of selectivity on solvent concentration may take three forms:

1) A continuous and almost linear increase in selectivity with solvent concentration. This is the main pattern.

2) A rapid increase of selectivity with concentration, usually encountered when immiscibility occurs at high solvent concentrations.

3) An unusual pattern with maximum selectivity at an intermediate concentration.

"The relative concentration of key components also affects the selectivity. If j refers to that key forming the more non ideal system with the solvent, and i refers to the key forming the less non ideal system, then (at constant x_x) the rate of increase of γ with decreasing x is much larger for component j than for component i. Consequently the value of selectivity, S_{ij}, should increase with decreasing amounts of the more non ideal component. Experimental evidence corroborates this." (Tassios, 1969:121).

In azeotropic distillation, solvent concentration is generally not a variable, but instead is fixed by the composition of the azeotrope. In extractive distillation, the quantity of agent relative to the components is a variable which has a marked degree in its effectiveness and a number of different amounts must be looked at for each potential agent. Equi-molar to four moles of agent can be used a rule of thumb (Berg, 1969:57).

3.10.2 Temperature

Over moderate temperature ranges there appears to be a linear relationship between $\ln S^*_{ji}$ and $(1/T)$ (Tassios, 1969:122). However, this is more significant for liquid-liquid extraction

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than for azeotropic and extractive distillation since the temperature can really only be manipulated in the former case.

3.10.3 Mixed solvents

The use of mixed solvents for improved selectivity is not unusual. Small amounts of water may be added to improve the selectivity of a solvent. Mixed solvent-selectivity lies between the selectivity exhibited by pure solvents and the selectivity of the main solvent may be lowered by the addition of a second. Occasionally the addition of a second solvent may be necessary to improve solubility (Tassios, 1969:122).

3.11 Correlations and Interpretations

There are two general approaches as far as mathematical models are concerned. On the one hand researchers like Pierotti et al use simple relations to correlate selectivities for specific situations. On the other hand, most models have a sound general theoretical basis and are extensions of the "regular solution" theories developed by Hildebrand and Scott. Virtually all of these models predict selectivities under conditions of infinite dilution. Advantages to this approach are (Thomas, 1984:195):

   - Binary azeotropes can be predicted from infinite dilution activity coefficients,

   - Reasonable estimates of mutual solubilities may be obtained, and

   - Incisive information for statistical thermodynamics is provided.

At infinite dilution a modeller can safely neglect solute-solute interactions. This simplifies the situation and allows for easier modelling. It is thus not surprising that so many models are developed for infinite dilution conditions.

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). In azeotropic distillation the composition is generally not a variable but fixed by the composition of the azeotrope (Berg, 1969:57).

Stephenson and Van Winkle (1962:512) also stress the fact that in industrial practice 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.

3.11.1 The Pierotti-Deal-Derr method (1959:95)

This method correlates activity coefficients at infinite dilution of structurally related systems to the number of carbon atoms of the solute and solvent. The relation employed depends on whether the solute and solvent are straight-chain or cyclic compounds. The constants in relations, however, depend only on the structural groups of solute and solvent, i.e. methyl, hydroxyl, etc.

For example, infinite-dilution activity coefficients for members of a homologous series of alkylated compounds in a common solvent are given by an expression of the form:

$$\log (\gamma^*) = A_{1,2} + B_2 \cdot \frac{n_1}{n_2} + C_1 \cdot \frac{1}{n_1} + D \cdot (n_1 - n_2)^2 + F_2 \cdot \frac{1}{n_2} \qquad (3.23)$$

where the constants vary according to the solvent and the homologous series.

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A few interesting remarks are also made in the article:

i) As paraffin solvents have no functional group, certain possible associations do not occur and the equation simplifies.

ii) Ketones in paraffin solvents represent a situation parallel to alcohols in paraffins. (The two groups are thus similar.)

iii) Polar groups are 'diluted' by methylene groups.

iv) Moderate branching of alkyl groups of the solutes has generally only secondary effects on $\gamma°$.

vi) In spite of inherent type selectivity, diethylene or ethylene glycols have relatively low $\Delta n°$'s and are not useful for extracting broad range fractions. These solvents are good for narrow molecular weight range fractions.

For cases in which constants are available, the PDD method can provide quite good estimates. As is often the situation, this is unfortunately rare.

3.11.2 The regular solution theory of Hildebrand & Scott

3.11.2.1 Introduction

Although relatively old (1950), this valued work can be seen as one of corner stones regarding the subject of solvents. It was one of the first to investigate the nature of non ideal mixtures.

3.11.2.2 Regular solutions

Hildebrand and Scott defined the so-called "regular solutions" as follows:

"Many non ideal solutions have sufficient thermal energy virtually to overcome the tendency to segregation due to

different molecular fields, and therefore posses nearly ideal entropy of mixing due to maximum randomness, just as in an ideal solution. In other words, there would be no change in randomness and therefore in entropy in transferring one component from the solution to an ideal solution of the same composition. Such solutions are designated as "regular"." (Hildebrand & Scott, 1950:46). The entropy is thus the same as in an ideal solution of the same composition but where the heat content increases on mixing.

Assuming that the component molecules do not differ markedly in size, there is no volume change on mixing, and no specific attractive forces, the heat of mixing can be written as:

$$\Delta H = (x_1 V_1 + x_2 V_2) \left[\left(\frac{\Delta E_1^v}{V_1} \right)^{\frac{1}{2}} - \left(\frac{\Delta E_2^v}{V_2} \right)^{\frac{1}{2}} \right] \Phi_1 \Phi_2 \qquad (3.24)$$

This leads to the definition of "solubility parameter", δ, or $(\Delta E^v/V)^{1/2}$. Positive deviations from Raoult's law depend primarily on the quantities of δ_1 and δ_2 which are the energies of vaporization per cubic centimetre. The quantity $\Delta E^v/V$ (δ^2) is a measure of the internal pressure of liquids and is also called the cohesive-energy density since it is a measure of the cohesive forces between molecules in a liquid. The more dissimilar these forces, the greater are the positive deviations. When the cohesive forces are sufficiently different, phase separation and limited solubility occur. At 25°C, $|\delta_1 - \delta_2| \geq 3.5$ can be taken as a limit (Doolittle, 1954:807).

In general, it is found that binary liquid systems that are expected to behave as regular solutions do not behave in said manner. Another requirement of a regular solution is that the interaction of unlike molecules be approximately the geometric mean of that of like molecules. This condition is satisfied as long as the molecules are nonpolar so that their interaction is largely due to London forces. Regular solution behaviour can not

be expected when forces arising from polarity, hydrogen bonding, or localization of the attraction and repulsion due to the positive and negative charges in the molecules are operative.

In the case of polar molecules, dipole-dipole and dipole-induced-dipole forces exist in addition to London forces. The effect of such forces is to increase positive deviations from Raoult's law beyond that anticipated from δ values. This increase is usually rather small.

Although deviations were frequently viewed as being caused by compounds formation, it is more consistent with other information to view this as a physical situation involving greater probabilities of the two unlike molecules being near each other than two like molecules.

It should be stressed that the regular solution theory can not handle systems with hydrogen bonding, which has the effect of linking molecules together into networks (810).

Deviations from Raoult's law due to relative molecular size can be neglected in all but the most precise investigations of binary systems of small molecules (811).

3.11.3 Weimer and Prausnitz

3.11.3.1 Introduction

This correlation (1965:237-242) was developed to predict infinite dilution activity coefficients of nonpolar hydrocarbons in polar solvents. The method is based on a semi-empirical correlation employing polar and nonpolar solubility parameters.

The activity coefficient of a hydrocarbon is assumed to depend on its size as given by its molar liquid volume and also on its induction energy with the polar solvent. The latter is given by

the product of the polar energy density and a constant which depends on the hydrocarbon class.

"The correlation shows that the ability of a polar solvent to distinguish between a saturated and an unsaturated hydrocarbon depends primarily on the solvent's polar cohesive energy and on its molecular size; if the former is large and the latter is small, the polar solubility parameter is high and solvent selectivity is good. The affinity of a polar solvent for a hydrocarbon depends on the degree of unsaturation of the hydrocarbon; the larger the unsaturation the larger is the affinity tending to lower the activity coefficient of the hydrocarbon. However, solvent selectivity is also affected by the molecular sizes of the hydrocarbons to be separated; for a given class of hydrocarbons the activity coefficient of the hydrocarbon rises with its size. Selectivity therefore tends to be high when the unsaturated hydrocarbon is smaller than the saturated hydrocarbon. When the unsaturated hydrocarbon has a larger molecular size than the saturated hydrocarbon there is a certain amount of cancellation between the effect of solvent affinity and the effect of hydrocarbon size resulting in low selectivity." (242).

3.11.3.2 The model

In its most general form the Scatchard-Hildebrand equation for g^E, the excess Gibbs energy of a binary solution, is:

$$g^E = \Phi_1 \Phi_2 (x_1 V_1 + x_2 V_2) (C_{11} + C_{22} - 2C_{12}) \qquad (3.25)$$

where Φ stands for volume fraction, x for mole fraction and V for molar liquid volume. C_{11} and C_{22} are the cohesive energy densities in the pure components and C_{12} is a corresponding energy density for the interaction between unlike species. If both species are nonpolar, then $C_{11} \equiv \lambda_1^2$ and $C_{22} \equiv \lambda_2^2$, in which case $C_{12} = \lambda_1 \lambda_2$.

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However, if species 1 is polar, its energy of vaporization must be split into two parts, one resulting from nonpolar (dispersion) interactions and the other including dipole-dipole and induction effects, i.e. $C_{11} \equiv \lambda_1^2 + \tau_1^2$ where λ is the nonpolar and τ the polar solubility parameter. For the interaction between a polar and a nonpolar substance, an energy term, ψ_{12}, corresponding to the induction energy between the polar and nonpolar species, must be added to give:

$$G^E = \Phi_s \Phi_j (x_s V_s + x_j V_j) \left[(\lambda_s - \lambda_j)^2 + \tau_s^2 - 2\psi_{sj} \right] + RT \left[\left(\frac{x_s \ln\Phi_s}{x_s} + \frac{x_j \ln\Phi_j}{x_j} \right) \right]$$

(3.26)

where

$$d_{sj} = \left(\frac{x_s \ln\Phi_s}{x_2} + \frac{x_j \ln\Phi_j}{x_j} \right)$$

(3.27)

is the Flory-Huggins expression for the entropy of mixing for liquids having greatly different molar volumes.

λ_j, the solubility parameter of the nonpolar component j is equal to $(\Delta U_j / V_j)^{1/2}$ where ΔU can be estimated from

$$\frac{\Delta U}{V} = \frac{\Delta H - RT}{V}$$

(3.28)

λ_s and τ_s, the nonpolar and polar solubility parameters for the polar compound, are related through:

$$\lambda_s^2 + \tau_s^2 = \frac{\Delta U_s}{V_s} = \frac{\Delta U(nonpolar)}{V_s} + \frac{\Delta U(polar)}{V_s}$$

(3.29)

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The required λ_s can be obtained by using several figures. Three graphs are available, depending on whether the homomorph of the solvent is a paraffin, a cycloparaffin, or an aromatic hydrocarbon. The homomorph of a non-hydrocarbon solvent is that hydrocarbon which has the same number and bonding arrangement of atoms other than hydrogen. For example, the homomorph of ethanol is propane.

The induction energy between the polar and nonpolar components, ψ_{sj}, is $k\tau_s$, where k is a constant whose value depends on the particular hydrocarbon series: 0.396 for paraffins, 0.415 for olefins, and 0.450 for benzenes, all at 0 - 100 °C.

The final activity coefficient of the nonpolar component, j, at infinite dilution in the polar component, s, is obtained by differentiation:

$$RT\ln\gamma_i^* = V_j\left[(\lambda_s - \lambda_j)^2 + \tau_s^2 - 2\psi_{sj}\right] + RT\left[\ln\left(\frac{V_j}{V_s}\right) + 1 - \frac{V_j}{V_s}\right] \qquad (3.30)$$

3.11.4 Helpinstill and Van Winkle

A correlation is given for predicting infinite dilution activity coefficients for saturated, unsaturated and aromatic hydrocarbons from which the selectivity of solvents can be calculated for solvent-hydrocarbon systems. This correlation is also an extension of the Scatchard and Hildebrand activity coefficient equations as applied to polar-nonpolar and polar-polar binary hydrocarbon systems. The energy density of the Scatchard-Hildebrand equations for polar substances is divided into a polar and nonpolar part composed of polar and nonpolar solubility parameters (1968:213).

Data from 83 binary hydrocarbon-polar solvents were used to develop the correlation. Errors reported are within experimental

limitations and the correlations are claimed to be valid for a temperature range of 0 to 125 °C.

The correlation presented is very similar to and in fact an improvement of Weimer and Prausnitz equation. It is deduced in exactly the same manner. The only difference is that one more species is assumed to be polar. This improves the Weimer-Prausnitz equation by replacing τ_1^2 with $(\tau_1 - \tau_2)^2$, yielding:

$$RT\ln\gamma_i^* = V_j\left[(\lambda_s - \lambda_j)^2 + (\tau_s - \tau_j)^2 - 2\psi_{sj}\right] + RT\left[\ln\left(\frac{V_j}{V_s}\right) + 1 - \frac{V_j}{V_s}\right] \quad (3.31)$$

3.11.5 MOSCED - Thomas & Eckert (1984)

A modified separation of cohesive energy density (MOSCED) model was developed to predict limiting activity coefficients using only pure component parameters (1984:194). This model is also an extension of the regular solution theory to polar and associating systems. Data included both aprotic and protic systems over wide temperature ranges.

3.11.5.1 The model

The MOSCED model calculates the infinite activity coefficients by a modified separation of cohesive energy density model and UNIFAC:

$$\ln\gamma_2^\infty = v_2\frac{\left[(\lambda_1 - \lambda_2)^2 + \dfrac{q_1^2 q_2^2 (\tau_1 - \tau_2)^2}{\psi_1} + \dfrac{(\alpha_1 - \alpha_2)(\beta_1 - \beta_2)}{\xi}\right]}{RT} + d_{12} \quad (3.32)$$

In this equation subscript 2 refers to the solute present in infinitesimal amounts in solvent 1. The values of the liquid molar volume, v, and the dispersion parameter, λ, were assumed to be temperature independent. The polar parameter, τ, acidity

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parameter, α, and basicity parameter, ß, were temperature dependent. Thomas and Eckert present a detailed discussion of the parameter estimation. ψ is the polar asymmetry parameter and ζ the hydrogen asymmetry factor.

As for the other "regular solution" models the excess Gibbs energy can be expressed as:

$$g^E = \Phi_1 \Phi_2 (x_1 V_1 + x_2 V_2) (c_{11} + c_{22} - 2[c_{11} c_{22}]^{1/2}) \tag{3.33}$$

where Φ is the component volume fraction, x the liquid mole fraction, v the molar volume and the cc's are energy densities.

This yields for the infinite dilution activity coefficients of component 2 in a binary mixture:

$$\gamma^\infty = \exp\left[\frac{V_2}{RT}(c_{11} + c_{22} - 2[c_{11}c_{22}]^{1/2}\right] \tag{3.34}$$

If the solubility parameter δ is defined as the square root of the cohesive energy density this gives:

$$\gamma_2^\infty = \exp\left[\frac{V_2}{RT}(\delta_1 - \delta_2)^2\right] \tag{3.35}$$

While this regular solution equation gives good semi-quantitative representations of nonpolar and moderately polar solutions, it is not applicable to mixtures containing highly polar or protic components. Later researchers thus assumed the forces contributing to c act independently and are additive. The MOSCED form is:

$$C_{11} = \lambda_1^2 + \tau_1^2 + \sigma_1 \tau_1 + \alpha_1 \beta_1 \qquad (3.36)$$

leading to:

$$C_{12} = \lambda_1 \lambda_2 + \tau_1 \tau_2 + \frac{1}{2} (\sigma_1 \tau_2 + \sigma_2 \tau_1 + \alpha_1 \beta_2 + \alpha_2 \beta_1) \qquad (3.37)$$

where the $\lambda_i \lambda_j$, $\tau_i \tau_j$, $\sigma_i \tau_j$ and $\alpha_i \beta_j$ terms represent the dispersion, orientation, induction, and hydrogen bonding forces, respectively. λ is a measure of the molecule's polarizability, τ represents its polarity, σ reflects the ability of the nonpolar part of a molecule to interact with a dipole, and α and β are acidity and basicity parameters, respectively. Using the above expression for cohesive energy densities, the activity coefficient for component 2 infinitely dilute in solvent 1 becomes:

$$\ln \gamma_2^\infty = \frac{V_2}{RT} ((\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 + (\sigma_1 - \sigma_2) * (\tau_1 - \tau_2) + (\alpha_1 - \alpha_2)(\beta_1 - \beta_2)) \qquad (3.38)$$

To account for differences in molecular size, the Flory-Huggins term d_{12} was added. It is defined as:

$$d_{12} = \ln\left(\frac{V_2}{V_1}\right)^{aa} + 1 - \left(\frac{V_2}{V_1}\right)^{aa} \qquad (3.39)$$

with aa a term to correct for overprediction

The final expression becomes:

$$\ln\gamma_2^{\infty} = \frac{V_2}{RT}\left((\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 + (\sigma_1 - \sigma_2) * (\tau_1 - \tau_2) + (\alpha_1 - \alpha_2)(\beta_1 - \beta_2)\right) + d_{12} \qquad (3.40)$$

The equation can be simplified to:

$$\ln\gamma_2^{\infty} = \frac{V_2}{RT}\left[(\lambda_1 - \lambda_2)^2 + q_1^2 q_2^2 (\tau_1 - \tau_2)^2 + (\alpha_1 - \alpha_2)(\beta_1 - \beta_2)\right] + d_{12} \qquad (3.41)$$

where q is assumed to be a function only of the class of compound of the solute and is a measure of the dipole-induced energy. To account for asymmetry, the terms ψ and ζ are added: The equation thus becomes:

$$\ln\gamma_2^{\infty} = \frac{V_2}{RT}\left[(\lambda_1 - \lambda_2)^2 + \frac{q_1^2 q_2^2 (\tau_1 - \tau_2)^2}{\psi_1} + \frac{(\alpha_1 - \alpha_2)(\beta_1 - \beta_2)}{\xi_1}\right] + d_{12} \qquad (3.42)$$

3.11.5.2 Parameter estimation

The parameters have been correlated as follows:

For non aromatics:

$$\lambda = 10.3 \left[\frac{(n_D^2 - 1)}{(n_D^2 + 2)} \right] + 3.02 \qquad (3.43)$$

but for aromatics:

$$\lambda = 19.5 \left[\frac{(n_D^2 - 1)}{(n_D^2 + 2)} \right] + 2.79 \qquad (3.44)$$

And:

$$\tau, \alpha, \beta = C_{(\tau, \alpha, \beta)} \left[\frac{4.5}{3.5 + no.C} \right] \left[1 + \frac{(no.C - 1)}{100} \right] \qquad (3.45)$$

with C_τ, C_α and C_β constants according to the compound type (ie. chloride, ester, ketone etc.).

The temperature dependence is given by:

$$\tau_T = \tau_{293} \left[\frac{293}{T} \right]^{0.4} \qquad (3.46)$$

$$\alpha, \beta_T = \alpha, \beta_{293} \left[\frac{293}{T} \right]^{0.8} \qquad (3.47)$$

Also q=1 for saturated compounds, 0.9 for aromatics and otherwise:

$$q = 1.0 - 0.5 \left(\frac{no.\ C = C\ bonds}{no.\ C\ atoms} \right) \qquad (3.48)$$

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For ψ and ζ:

$$POL = q^4 (1.15 - 1.15 \exp(-0.020 \tau_T^3)) + 1 \qquad \text{(3.49)}$$

$$t = \frac{293}{T} \qquad \text{(3.50)}$$

$$\psi = POL + 0.011 \alpha_T \beta_T \qquad \text{(3.51)}$$

$$\xi = 0.68(POL-1) + (3.4 - 2.4 \exp((\alpha_0 \beta_0)^{1.5}(-0.023)))t^2 \qquad \text{(3.52)}$$

For

$$d_{12} = \ln\left(\frac{V_2}{V_1}\right)^{aa} + 1 - \left(\frac{V_2}{V_1}\right)^{aa} \qquad \text{(3.53)}$$

aa is computed as:

$$aa = 0.953 - 0.00968(\tau_2^2 + \alpha_2 \beta_2) \qquad \text{(3.54)}$$

For 3357 γ's, an average error of 9.1 % was achieved with very few errors greater than 30 %. The average error with UNIFAC was 20.5 %

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.

The MOSCED model is superior to UNIFAC in predicting infinite dilution activity coefficients.

UNIFAC and MOSCED compare as follows:

Table 3.3: Comparison of MOSCED and UNIFAC		
	MOSCED	UNIFAC
Average error	9.1 %	20.5 %
Data with error > 30 %	2.0 %	23.0 %
Temperature dependence	very good	fair
Molecules of greatly different sizes	very good	fair
Nonpolar-nonpolar	excellent	excellent
Polar aromatics	good	poor
Associated-associated	good	good
Associated-solvated	good	good
Polar-nonpolar	very good	fair
Polar-polar	very good	very good
Aqueous systems	poor	fair

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.

3.12 Conclusions

Hildebrand and Scott made a very interesting observation:

Different methods of formulating the specific interactions which produce abnormal deviations from Raoult's law lead in many cases to equations which, while mathematically different, are hardly

distinguishable when applied to experimental data (1950:194). This lead the authors to the suspicion that "the differences between physical and chemical approaches may be largely a matter of viewpoint, and that when properly formulated, they might prove to be identical."

Although this statement is somewhat simplistic, it definitely has merit. At said time (1950) treatments of the subject left a lot to be desired. More recent and more refined models such as MOSCED, do however employ parameters which also provide a "feel" for the situation.

In any case, irrespective of the true intermolecular situation, the main practical value of the models and guidelines in this chapter is that they provide a perception of solvent action which can frequently be applied to new cases in order to predict the effect of untested solvents.