

Diluent effects in solvent extraction

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ABSTRACT

The fact that the choice of organic diluent is important for a solvent extraction process goes without saying. Several factors, such as e.g. price, flash point, viscosity, polarity etc. each have their place in the planning of a solvent extraction system.

This high number of variables makes the lack of compilations concerning diluent effects to an interesting topic. Often the interest for the research concerning a specific extraction system focuses on the extractant used and the complexes built up during an extraction. The diluents used are often classical ones, even if it has been shown that choice of diluent can affect extraction as well as separation in an extraction system. An attempt to point out important steps in the understanding of diluent effects in solvent extraction is here presented. This large field is, of course, not summarized in this article, but an attempt is made to present important steps in the understanding of diluents effects in solvent extraction. Trying to make the information concerning diluent effects and applications more easily accessible this review offers a selected summarizing of literature concerning diluents effects in solvent extraction.

1. INTRODUCTION

A solvent extraction process aims to extract solutes from one liquid phase to another. This can be done in order to separate two different solutes or to purify an aqueous phase from contamination. A solvent extraction system contains two immiscible liquid phases, one **aqueous phase** and one organic liquid, the **diluent**, and one or more **solute(s)**. In addition, in most extraction systems one or more **extractant(s)** is added to the diluent to increase extraction and separation. Sometimes a phase modifier is used to prevent disturbing third phase formation. The diluent, extractant(s) and phase modifiers together make up the **solvent**.

The solute often carries a charge in the aqueous phase and is surrounded by coordinated water molecules as well as **counter ions**. If there is a need for increased separation, a **suppressing agent** can be added to the aqueous phase. A suppressing agent keeps one specific solute in the aqueous phase while other metals can be extracted [1].

A solvent extraction denotes the transfer of a solute, for example a metal, from one liquid phase into another liquid phase. In the aqueous phase the solute is surrounded by water molecules, **hydrated**, while in the organic phase it is surrounded by diluent molecules, **solvated** [2]. Often in solvent extraction a solute forms extractable complexes with a chelating agent or a ligand. When trying to solvate or hydrate a complex two aspects play a role. First a cavity -a hole- needs to be created in the liquid where the complex is placed. When the complex is placed in the cavity it will interact with surrounding molecules. The result of an extraction of a complex is therefore a function of the two steps; the transfer from the aqueous phase, including collapsing the cavity in the aqueous phase and breaking the bounds between the water molecules and the complex and the dissolving of the complex in the organic phase. To solvate the species in the organic phase a cavity needs to be created. When placing the complex in the cavity interactions between the complex and the diluent molecules are introduced. This implies that the characteristics of a extracted species play an important role in an extraction. To summarize: the **size** of the solute or complex influences the cavity size and therefore

the extraction as well as **possibilities for the complex to interact** with water molecules as well as diluent molecules [3][4].

The commonly most important factors during an extraction are the **partition** of the solute between the phases and the **separation** between two, or more, different solutes. The extent of the extraction is given by the **distribution ratio** (the D value). The distribution ratio is the ratio between the total analytical concentrations of the solute in the organic phase divided by the total concentration of the solute in the aqueous phase [1]. The separation factor (SF) is given by the ratio of the D values of the different metals, and is defined to be >1. According to IUPAC nomenclature the separation factor is denoted α [1]. However, since solvent extraction chemists often works using ionizing radiation for easy detection of D value and separation factor, α is not often used to avoid misinterpretation as alpha-radiation. To our knowledge the denotation SF followed by an index telling the elements is commonly used. For example $SF_{Am/Eu}$ equals $D_{Americium}/D_{Europium}$.

There are five types of extraction mechanisms [5]. The first type, Class A, is the **extraction of simple inorganic compounds**. This extraction mechanism takes place when a non charged solute itself or together with a non electrolytic extractant forms an adduct which distributes between the phases. Class B is **chelation extraction**. Chelation extraction occurs when a metal ion forms a neutral complex with one or more organic anions, chelation agents. A chelating agent is bidentate and occupies several coordinating sites of the metal creating a hydrophobic extractable complex. The hydrophobicity is increased since the chelation agent replaces coordinated water molecules as well as neutralises the charge of the metal. Class C is denoted **solvent extraction** and this extraction mechanism also includes the formation of an extractable complex. The metal charge is neutralized by an anion of a salt in the aqueous phase. Some or all of the remaining coordinating water molecules are replaced by coordination with an organic solvating agent. This agent may either be in the aqueous, organic or distributed between both phases. This replacement increases the hydrophobicity of the complex and increases the extraction. Class D denotes the **extraction of ion pairs**. A common example of ion pair extraction is when a metal, M^{v+} is exchanged towards v hydrogens from a hydrophobic complex soluble in the organic phase. The metal extracts as a part of the complex. Class E includes **all other extraction mechanisms**, for example, crown ethers. Crown ethers have a ring structure that fits an atom with a certain ionic radius, forming a hydrophobic complex. Notice that many extractants also combine several of the mechanisms mentioned above [5][6].

2. THEORY

2.1. History

Solvent extraction has a long tradition and references exist for example in the works by Raimundus Lullus in the 15th century. However, the more systematic investigations date back to the beginning of the 19th century. One of the first scientific references concerning solvent extraction was presented by Bucholz in 1805. Bucholz extracted uranium from a nitric acid solution into ether and back-extracted it into pure water [7]. The possibility to purify and separate chemical elements from each other made the solvent extraction an interesting field for curious researchers. Between the time from Bucholz first publication and the beginning of the twentieth century some basic scientific steps were taken. For example Jungfleisch and Berthelot described the distribution factor for several organic and inorganic compounds between ether or carbon disulphide and water [8]. In 1891 Nernst proposed that if a species has the same molecular formula in the organic phase as in the aqueous phase (for example I_2^{org} and I_2^{aq} but not I_2^{org} and I_2^{-aq}) the final distribution is independent of total solute concentration. This law is called the Nernst distribution law [9]. In 1902 Morse presented the extraction constants for extractable complexes (i.e. $HgCl_2$) [10]. The need for molecules which were able to increase extraction of specific ions and thereby increase separation factors made solvent extraction an expanding research field in the 20th century. Selective extractants for analytical purpose of several elements became available during the first decades of the century. Before the 1940'ties the solvent extraction technique was primary used for analytical purposes [6].

In the 1940s and 1950s the possibilities to produce pure uranium by reprocessing irradiated nuclear materials expanded the solvent extraction technique. The first large scale industrial solvent extraction plant for uranium recovery was built in 1942 by the Mallinckrodt Chemical Co in St Louis. It used the

same method as was presented by Bucholz more than 140 years earlier. High purities were achieved and ether was used and then ether was replaced by dibutyl methanol and methylisobutylketone [11]. At the same time increased understanding and rigorous research about extractant behavior made the extractants more effective. The development of selective extractants and solvation agents made it possible to use solvent extraction in a number of chemical and metallurgical processes in the 1950s and early 1960s [11]. One important milestone in the understanding of the solvent extraction process was the discovery of the synergistic effect in a solvent extraction system. A synergistic system is a system where two different extractants cooperate and the final D value is higher than the sum of the D value for the extractants. Notice that this definition only is valid for comparable conditions [1]. The synergistic effect is obtained when using solubilising organic ligands that replace coordinated water in an extractable complex [12]. By doing so, the hydrophobicity of the complex is increased and therefore the D value increases – as in the case of chelation extraction.

2.2. Demands on Diluents and Extractants

The choice of extractant(s) and diluent are two important aspects of a successful solvent extraction operation. In many cases the aqueous phase is acidic, basic or in other ways aggressive to the diluent and the extractant. This may affect both the long term behaviour of the extraction system as well as following chemical treatment such as scrubbing or stripping. Also a radioactive or otherwise ionizing environment can destroy the diluent or the extractant. Preferably the diluent as well as the extractant(s) should be completely incinerable in order to reduce waste production. Following demands are summarised by Retegan [13]

- It should contain only carbon, hydrogen, nitrogen and oxygen to be totally incinerable This is important for nuclear systems where the waste shall be reduced [14].
- It should have a high flash point and preferably a high boiling point.
- It should have a low freezing point as well as low water solubility and a low chemical transformation rate with water, extractants and solute.
- The formation of a third phase should be avoided, thus diluents should not form third phases during loading conditions.
- A diluent used in ionizing environments should be resistant towards irradiation and, if not, be regenerable.

The properties of a usable extractant have been summarized by the following, similar, sentences by Andersson [15]

- It should contain only carbon, hydrogen, nitrogen and oxygen to be totally incinerable. This important for nuclear systems were the waste shall be reduced [14].
- An extractant used in ionizing environments should preferably be stable towards irradiation,
- It should not form third phases,
- It should not be soluble in the aqueous phase, but of course in the organic phase.
- It should form extractable complexes with the solute to be separated, preferably selectively, and this extracted complex should be possible to strip in reasonable manner.

These demands make screenings of every system used in a process an important evaluation step. If the solvent (remember: solvent=diluents+extractant+modifier...) is not resistant towards the aqueous phase it is of highly interest to improve this stability. If the solvent is not resistant towards irradiation it can be an alternative to use a scavenging molecule. Examples of such molecules are nitrobenzene [16] or sulphur hexafluoride [17].

2.3. Diluent categories

Since numerous of organic diluents are used in different liquid-liquid extraction systems, several attempts to categorize them have been made. One classification scheme of liquids, including hydrocarbons as well as highly polar molecules such as water, has been described by Marcus [2]. He uses the molecules capability of forming hydrogen bonding and from this creates five classes of liquids. Class one include liquids capable of forming three-dimensional networks of strong hydrogen bonds (Water, polyamino alcohols, hydroxi acids etc.). Class two includes other liquids that have both active hydrogen atoms and acceptor atoms, but rather than three dimensional networks they prefer forming chainlike oligomers (primary alcohols, carboxylic acids, primary and secondary amines etc.). Class three includes dipolar aprotic substances. They are solvents containing molecules with acceptor atoms but no active hydrogen atoms (ethers, ketones, aldehydes etc.). Class four covers liquids composed of molecules containing active hydrogen atoms but no acceptor atoms (e.g. chloroform). Finally, class five includes liquids without hydrogen bonding capability and without donor atoms, such as hydrocarbons, carbon disulfide and carbon tetrachloride. This classification results in different outcomes relevant to solvent extraction. For example; The diluents in class 1 are highly soluble in water and could not be used as organic phase, while diluents from class 3, ketones and aldehydes, react directly with inorganic compounds, forming extractable organic complexes. One example on such extraction in absence of extractant is given by Aneheim et al [18], where cyclohexanone by itself extracts metals. Ketones and aldehydes are aprotic dipolar molecules and since they only consist of donor atoms they tend not to dimerize or self associate.

Classes of diluents used for solvent extraction purposes are aliphatic molecules e.g. hexane, aromatic ones, e.g. benzene, ketones eg. cyclohexanone and alcohols e.g. octanol. During a screening, the aliphatic diluents are often considered in order to obtain high distribution ratios, easy handling and easy manufacturing. The type of molecules is typically included in class five according to the Marcus classification. They form no hydrogen bonds. Aliphatic diluents have a low polarizability and a low dipole moment, which makes the cohesive forces in such solvents dependent on the dispersion interactions between the molecules. These interactions are weak, which means that separation of this kind of molecules is relatively easy. The energetic cost for cavity formation -formation of the hole in the liquid where a species can be placed- is proportional to the energy needed for separating the liquid molecules. This means that liquids exclusively interacting through dispersion interactions, weak attractive interactions, contain a low energy cost for cavity formation. On the other hand, there is no permanent dipole moment in aliphatic diluents which can increase attractive interactions between the complex and the diluent. Several authors have reported that aliphatic hydrocarbons are giving the most efficient extraction systems [19][20]. Healy et al. described high water solubility in the organic phase as a decreasing factor for extraction [21]. Water solubility is low in aliphatic molecules and higher in polar molecules and in diluents having a high dielectric constant. This theory therefore correlates with the one proposed where aliphatic ones, which have a low cavity cost, increase extraction. Among the aliphatic hydrocarbons the extraction seems to decrease with increasing number of carbon atoms in the chain. Siekierski et al. explained this with the solubility of the extractant in the diluents used [20].

The aromatic molecule benzene has no dipole moment. Therefore it is not supposed to extract charged species. On the other hand benzene has a slightly enhanced dielectric constant [2]. This implies the existence of some polarisable part of the molecule. This theory has been strengthened when benzene was described as a π -electron-donor that strongly interacts with polar complexes and thereby extracts them [22].

Long chained primary alcohols are included in class two and their interaction energy as well as their solubility in water decreases with longer aliphatic chains. Several diluent screenings have been performed using alcohols, for example by Nilsson et al [23]. Nilssons results showed surprisingly that shorter aliphatic chain in the alcohol increased extraction. Nilsson et al. explained this with the higher solubility of the extractant in the diluents containing a higher concentration of OH-groups. These diluents are the alcohols having a shorter aliphatic chain [16].

The consensus was for a long time that non polar diluents were the most effective for extraction efficiency explained by the small cost for cavity forming. However, when trying different combinations of extractants and diluents the opposite of this behaviour was observed. For example, Jaber et al. [24] tried surface active agents, such as polyethylene glycol (PEG), in combination with picrate acid for extraction. Surprisingly, this test indicated that diluents having a high dielectric constant, including high dipolarity and high water solubility [25][26], enhanced the extraction. This effect were explained by stabilizing of the helix formed complex by high dielectric medium as well as high solubility of the picrate anions in such diluent. Also the BTBP molecules show higher extraction into polar diluents [16]. The mentioned studies i.e. [24][16] are examples where the energetic cost for cavity formation is less important, since interactions with the diluent makes the extraction more favourable into medium having a higher dielectric constant. This shows that the nature of the diluent plays an important role in an extraction and that possibility to interact with the diluent is sometimes more important for enhanced extraction of a species than low energetic cost for cavity formation

2.4. Attempts to describe diluent interactions

The understanding of energy cost for cavity formation as an important aspect in the outcome of an extraction was early understood -as described by Taube et al and Marcus-. Therefore Hildebrandt and Scott developed a way of predicting the cohesive energies in a solution using the heat of vaporisation and summarized it in 1970 [27]. The cohesive energy density, c , is related to the heat of vaporisation of a liquid and valid for organic as well as aqueous phases in solvent extraction:

$$c = \frac{\Delta H_{vap} - RT}{V_m} \quad (2.1)$$

where ΔH_{vap} is the heat of vaporisation per mole, R is the gas constant, T is the temperature and V_m is the molar volume. The heat of vaporisation of a liquid is the energy required to separate the molecules in a liquid from each other, turning the liquid into a vapour. This energy can be translated as the amount of energy that holds the molecules together. Thus the Hildebrand solubility parameter is based on the assumption that the same intermolecular attractive forces have to be overcome to vaporise a liquid as to dissolve a solute in it:

$$\delta = \left[\frac{\Delta H_{vap} - RT}{V_m} \right]^{1/2} \quad (2.2)$$

the energy for cavity formation is given by

$$\Delta G_{Cav} = A_{Cav} V_B \delta_A^2 \quad (2.3)$$

where A_{cav} is the proportionality coefficient, V_B is the molar volume of the solute B and δ is the Hildebrandt solubility parameter for the diluent A. From this formula it is easily understood that the size of the complex influences the solvation.

With the basis in the theory concerning solubility parameters and by proposing the solubility parameters being a vector, composed of hydrogen bonding, polar interactions and dispersion interactions, Hansen et al. developed the Hansen solubility parameter. The result was successfully used for predicting the solubility of polymers and resins in solvents and plasticizers [28]. The Hansen parameter divides the Hildebrandt parameter in three parts, which corresponds to hydrogen interactions, dipole-induced dipole interactions and dispersion interactions.

$$\delta^2 = \delta_{Hydrogen}^2 + \delta_{Dipole}^2 + \delta_{Dispersion}^2 \quad (2.4)$$

The energy for a hydrogen interaction can be calculated from the typical energy value for a hydrogen bond. The dispersion interaction can be interpreted by using a homomorph of the molecule. A homomorph is a molecule as similar as possible to the interesting one, but in total absence of permanent dipole moments. By measuring the interactions for the homomorph solution the dispersion part of the Hansen parameter can be estimated. The value of a hydrogen bonding can be estimated from data given from IR spectroscopy

$$\delta_{Hydrogen}^2 = \frac{20900N}{V_m} \quad (2.5)$$

where V_m is the molar volume and N is the number of hydrogen bonds. Böttcher et al. [29] have described a way of estimating dipole-dipole interactions. This estimation is given by

$$\delta_{Dipole}^2 = \frac{12108}{V_m^2} \cdot \frac{\epsilon_0 \epsilon - 1}{2\epsilon_0 \epsilon + n_D^2} \cdot (n_D^2 + 2) \mu^2 \quad (2.6)$$

where ϵ is the dielectric constant of the medium, ϵ_0 is the dielectric constant for vacuum, n_D is the index of refraction for the sodium–D line, μ is the dipole moment of a single molecule and finally V_m is the molar volume. In order to increase the applicability of the Hansen parameter it has been further developed. One example is given by Wingefors et al [30].

The interactions between a species and a surrounding diluent are commonly coupled to the Gibbs free energy of solvation. In order to summarize the cavity cost and the gaining in interaction energy between the solute/complex and surrounding molecules, aqueous as well as diluent molecules, Kamlet and Taft developed the solvatochromic parameters for a number of elements. Such constants concerning numbers of diluents can be found in tables, diagrams etc. For example Kamlet and Taft, 1983 and Marcus, 2004 [31][2]. The free energy change for solvation of a solute is given by [2]

$$\Delta_{Solv} G_B^o = A_0 + A_\pi \pi^* + A_\alpha \alpha + A_\beta \beta + A_\delta \delta^2 \quad (2.7)$$

where α is the hydrogen bonding donation parameter for the diluent, β is the hydrogen bonding acceptance parameter for the diluent and π is the polarity or polarizability parameter for the diluent. A is the characterized parameters for the solute. The first two terms shows the dispersion interactions, while the second two shows hydrogen interaction and the last term show the cavity cost. By comparing the free energy for solvation in the organic phase with the free energy for solvation in the aqueous phase the extraction can be predicted. The common problem using this calculation is the lack of information concerning the nature of the complex and therefore the lack of parameters concerning the complex. Quantifying parameters for several complexes are highly time consuming, hence this equation is not commonly used for predicting extraction outcome. A regular diluent screening is often less time consuming and less expensive.

CONCLUSIONS

The summarized parameters affecting the outcome of an extraction can be summarized in the free energy for solvation in the aqueous and organic phases. In a solvation process the energy cost for cavity formation in the liquid and the energetic gain in interactions between the species and the surrounding molecules plays a role. The aqueous phase is often invariable during a solvent extraction process because of certain properties for dissolving metals or other solutes. Hence the interactions in the aqueous phase and the energy for cavity formation in the aqueous phase are not easily varied, while the diluent often can be adjusted. Therefore one important aspect to consider when designing a solvent extraction system is the nature of the diluent. The nature of the diluent influences the attractive energies between the extracted species and the organic phase as well as the energy needed for cavity formation.

Another important aspect is the nature of the extracted species which can enhance or decrease interactions with surrounding diluent. These parameters, the nature of diluent as well as nature of the extracted species, should preferably be taken into account when drawing conclusions concerning general extraction behaviour. By comparing the solvation in the aqueous phase and the organic phase the distribution of a complex can be predicted. The problem is the lack of information such as solvatochromic parameters concerning complexes and diluents.

The research today focuses on optimizing extraction system and in the absence of parameters concerning extracted complex the most reasonable thing to do so is to perform a diluent screening for novel extraction systems.

Acknowledgements

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THE EFFECTS OF DILUENTS IN SOLVENT EXTRACTION

-a literature study

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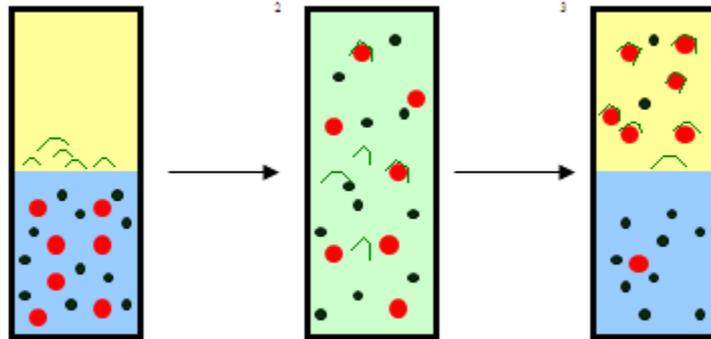
- Extraction is a function of the solvatisation energy in the aqueous phase as well as the solvatisation energy in the organic phase
- The important facts are the physical properties of the complex and the diluent. Such as dielectric constant, dipole moment and solubility parameters.
- The solubility parameters can describe the energetic cost for cavity formation, while measured values for polarity, hydrogen bonding etc. can describe the gain in energy for solvation.

Terminology solvent extraction

Diluent+Extractant+
(modifier) = Solvent :



“Pregnant” feed
= aqueous
phase+solute(s)



Extract
→

Raffinate
→

Goal

- * Increase extraction (D) $D = [Y]_{\text{org}} / [Y]_{\text{aq}}$
- ** Increase separation factor ($SF_{x/y}$) $SF_{x/y} = D_x / D_y$

* (SF is named α if followed IUPAC recommendations and always chosen > 1)

Method

- * Extractant development
- * Diluent screenings
- * Suppressing agents during extraction/Stripping
- * Control conditions of the aqueous phase
- * Control physical properties

[Cox Solvent extraction, Principles and Practice, Chapter one (2004).]

*[N. M. RICE, IUPAC Recommendations (1993)]



EURATOM



Diluent

The liquid or homogeneous mixture of liquids in which **extractant(s) and possible modifier(s) may be dissolved to form the solvent phase.**

***"Solvent" should not be used as it has a much wider meaning in the context of liquid-liquid extraction**

***The diluent by itself does not extract the main (extractable) solute appreciably**



EURATOM

[N. M. RICE, IUPAC Recommendations (1993)]

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Historical outlook

1805 // 1940 1950 1960 1970 1980 1990 2000 2010

Neat solvents

Analytical purposes

Bucholz

Jungfleisch
and
Berthelot
Morse,
Nernst

Chelating extractants **Synergism**

Mallinckrodt
Nuclear
applications

Industrial application

Crown ethers

Research
explosion

Lariat ethers

Ionic liquids

[BUCHOLZ, C.F., 1805, *Neues allgem. J. der Chemie*, 4, 157]

[BERTHELOT, M., JUNGFLAISCH, 1872, *J. Ann. Chim. Phys.*, 26, 396]

[Marcus, Ion exchange and solvent extraction (1969)]

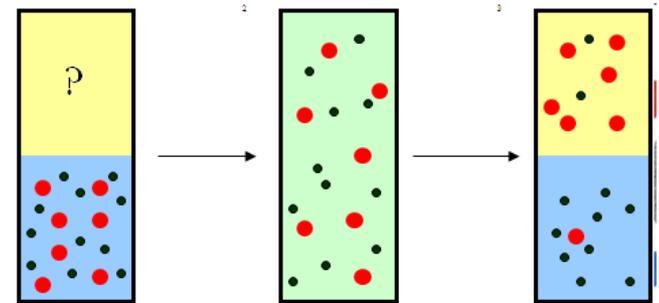
[MORSE, H., *Z. Phys. Chemie*, 41, 709 (1902)]

[Nernst, *Z. phys. Chem.*, **8**, 110 (1891)]

[M. Taube, *Journal of Inorganic and Nuclear Chemistry*, Vol. 15, 171-176 (1959)]

Several attempts have been made trying to systemize the diluents' role in an extraction system, and a number of parameters have been used to find the perfect way to predict an extraction.

For example the polarity, the dielectric constant, connectivity and solubility parameters. No general way has been found.



[Aly et al. journal of radioanalytical chemistry, 49, 213-224 (1979)]

[Nilsson M. Thesis for the degree of licentiate, Chalmers university of technology, Sweden (2003)]

[Taube et al, journal of inorganic chemistry, 15, 171-176, (1959)]

Diluent effects in solvent extraction have been described as a function of:

- * Cavity forming in the organic phase

(A function of the cohesive interactions between the diluent molecules, solubility parameters)

- * Complex-Diluent interactions

(A function of the cohesive interactions between the diluent molecules and the extracted complex; dipole-dipole interactions, dipole-induced dipole and induced dipole-induced dipole interactions)

[Taube, journal of inorganic chemistry, 15, 171-176, (1959)
[Y. Marcus, Solvent extraction and ion exchange, chapter 11 (1969).]



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Interactions between diluent and complex depends of the art of the diluent molecule as well as the nature of the complex

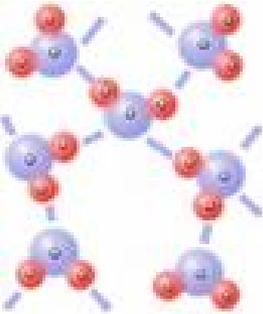
Hydrogen bonding > dipole-dipole >
dipole-induced dipole > induced dipole-induced dipole

- There is an energetic cost for cavity formation
- There is an energetic gain in placing the complex in the cavity. The gain is a function of the interactions between the diluent and the complex.

Remember...

Hydrogen bonding > dipole-dipole > dipole-induced dipole > induced dipole-induced dipole

Diluents can be classified according to their physical properties and preferable according to their ability to form ordered networks



Class 1: Liquids capable of forming three dimensional networks of strong hydrogen bonds.

e.g. water, poly- and amino-alcohols, hydroxyl-acids.



Class 2: Liquids that have the capacity to form hydrogen bonds, but forms chainlike oligomers.

e.g. primary alcohols, carboxylic acids etc.

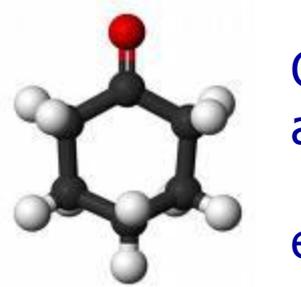
[Yizhak Marcus, Principles of solubility and solutions,
Chapter 2 Solvent extraction principles and Practice, 04]



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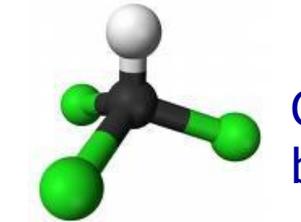


Attempts to describe diluent effects

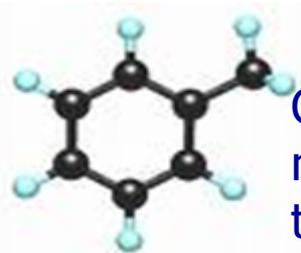


Class 3: Liquids composed of molecules containing donor atoms, but no active hydrogen atoms.

e.g. ethers, ketones, aldehydes, ester



Class 4: Liquids composed of molecules containing active hydrogen atoms but no donor atoms, e.g. chloroform and aliphatic halides.



Class 5: Liquids with no hydrogen bond forming capability and no donor atoms e.g. hydrocarbons, carbon disulfide, carbon tetrachloride etc.

[Yizhak Marcus, Principles of solubility and solutions,
Chapter 2 Solvent extraction principles and Practice, 04]

Cavity formation

The energy for cavity forming can be translated as the amount of energy that keeps the molecules together. That is a function of how the molecules interact. The Hildebrandt solubility parameter describes the interactions between molecules in the diluent and the energy needed for cavity formation using the heat of vaporisation.

$$\delta_t^2 = \frac{\Delta_v H - RT}{V}$$

The heat of vaporisation is the energy required to separate the molecules in a liquid from each other, turning the liquid into a gas (vapour). V is the molar volume.

Cavity formation

	Hildebrandt solubility parameter (J/mL) ^{1/2}
Water	47.9
Oktanol	20.9
Cyclohexanone	19.7
Chloroform	19.5
Class five*	15-17

$$\Delta G_{Cav} = A_{Cav} V_B \delta_A^2$$

[Yizhak Marcus, Principles of solubility and solutions,
Chapter 2 Solvent extraction principles and Practice, 04]



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The Hildebrandt solubility parameter can be divided in three parts
The Hansen parameter.

The Hansen parameter was developed in order to predict the possibility to dissolve polymers in solvents in paint systems

$$\delta^2 = \delta_{Hydrogen}^2 + \delta_{v.d\ Waals.}^2 + \delta_{Dipole}^2$$

Hansen C.M., The Three Dimensional Solubility Parameter – Key to Paint Component Affinities: I. Solvents, Plasticizers, Polymers and Resins, *Journal of Paint Technology*, vol 39, 505, 104-117, (1967).

Cavity formation

$$\delta^2 = \delta_{Hydrogen}^2 + \delta_{v.d\ Waals.}^2 + \delta_{Dipole}^2$$

$$\delta_H^2 = \frac{20900N}{V_m}$$

Where the hydrogen part can be estimated from knowing that the energy of a hydrogen bonding is approximately 20.9kJ/mol

Cavity formation

$$\delta^2 = \delta_{Hydrogen}^2 + \delta_{v.d. Waals.}^2 + \delta_{Dipole}^2$$

$$\delta_t^2 - \delta_{v.d. Waals.}^2 = \delta_{Hydrogen}^2 + \delta_{Dipole}^2$$

Where the dispersion part can be estimated from using the heat of vaporisation for the homomorph of the substance. The homomorph is a nonpolar molecule as similar to the one used as possible, but that only interacts according to dispersion interactions. The dispersion value is then subtracted from the Hildebrandt value.

Cavity formation

$$\delta^2 = \delta_{Hydrogen}^2 + \delta_{v.d\ Waals.}^2 + \delta_{Dipole}^2$$

$$\delta_{Dipole}^2 = \frac{12108}{V_m^2} \cdot \frac{\epsilon_0 \epsilon - 1}{2\epsilon_0 \epsilon + n_D^2} \cdot (n_D^2 + 2) \mu^2$$

Böttcher has developed a method to estimate the cohesive energy between permanent dipoles. where epsilon is the **dielectric constant** of the medium, n_D is the index of refraction for the sodium-D line, **μ is the dipole moment** of a single molecule and V_m is the molar volume.



One great drawback in Hansen's solubility parameter is that it does not take the asymmetry of molecular interactions into consideration.

Hence further developments have been made. See reference for more information.

[Wingefors S., Liljenzin J-O., Saalman E., Proc ISEC'80, Liege, Belgium, (1980), paper 3-15A-80-116.]



A suggestion for predicting the partition for a solute/complex is the Kamlet and Taft solvatochromic parameter.

This parameter takes into account the polarity or polarizability of the diluent and the solute, the ability to accept/donate hydrogen bonds and the solubility parameter for the diluent.

By using the difference in Free energy for solvation for the two phases (water/organic) the partition can be predicted.

[Kamlet J. M. J. org. chem (1983)]

[Wiesław Apostoluka and Jan Szymanowski, *Analytica Chimica Acta*, 374, 137-147 (1998)]

Cavity formation+Interactions

A generalized equation for the free energy for solvation can be calculated using

$$\Delta_{Solv}G_B^0 = A_0 + A_\pi \pi^* + A_\alpha \alpha + A_\beta \beta + A_\delta \delta^2$$

Where A is properties of the solute, and α is the hydrogen bonding donation, β is the hydrogen bonding acceptance and π is the polarity or polarizability.

The first two terms shows the dispersion interactions, while the second two shows hydrogen interaction and the last term show the cavity cost.

By comparing the solvation energy for the aqueous phase v.s. the diluent phase the partition can be predicted

This is valid for diluted solutions

[Marcus, Solvent extraction, principles and practice, chapter 2 (2004)]

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- Extraction is a function of the solvatisation energy in the aqueous phase as well as the solvatisation energy in the organic phase
- The important facts are the physical properties of the complex and the diluent. Such as dielectric constant, dipole moment and solubility parameters.
- The solubility parameters can describe the energetic cost for cavity formation, while measured values for polarity, hydrogen bonding e.t.c. can describe the gain in energy for solvation.

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