THE EFFECTS OF DILUENTS IN SOLVENT EXTRACTION
-a literature study

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Summary

• 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)

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

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

* (SF is named $\alpha$ if followed IUPAC recommendations and always chosen >1)

Method
* Extractant development
* Diluent screenings
* Supressing 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)]
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

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


Neat solvents
Chelating extractants
Synergism
Crown ethers
Lariat ethers
Ionic liquids

Analytical purposes

Bucholz
Jungfleisch and Berthelot
Morse, Nernst

Mallinckrodt
Nuclear applications
Industrial application
Research explosion

[Marcus, Ion exchange and solvent extraction (1969)]
[Nernst, *Z, phys. Chem.,* 8, 110 (1891)]
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).]
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
Interactions complex-diluent

• 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
Attempts to describe diluent effects

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]
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]
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

<table>
<thead>
<tr>
<th></th>
<th>Hildebrant solubility parameter (J/mL)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>47.9</td>
</tr>
<tr>
<td>Oktanol</td>
<td>20.9</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>19.7</td>
</tr>
<tr>
<td>Chloroform</td>
<td>19.5</td>
</tr>
<tr>
<td>Class five*</td>
<td>15-17</td>
</tr>
</tbody>
</table>

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

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

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

\[ \delta^2 = \delta_{\text{Hydrogen}}^2 + \delta_{\text{v.d Waals}}^2 + \delta_{\text{Dipole}}^2 \]

Cavity formation

\[ \delta^2 = \delta^2_{\text{Hydrogen}} + \delta^2_{\text{v.d Waals.}} + \delta^2_{\text{Dipole}} \]

\[ \delta_H^2 = \frac{20900N}{V_m} \]

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

\[ \delta^2 = \delta_{\text{Hydrogen}}^2 + \delta_{\text{v.d Waals}}^2 + \delta_{\text{Dipole}}^2 \]

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

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.
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, \( \mu \) is the dipole moment of a single molecule and \( V_m \) is the molar volume.
Cavity formation

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.

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 Szymanowskib, Analytica Chimica Acta, 374, 137-147 (1998)]
Cavity formation + Interactions

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

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

Where A is properties of the solute, and \( \alpha \) is the hydrogen bonding donation, \( \beta \) is the hydrogen bonding acceptance and \( \pi \) 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)]
• 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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