

2010/2011 SECOND SEMESTER CHM 332 – NON AQUEOUS SOLVENTS NOTES

TOPIC

CLASSIFICATION AND GENERAL CHARACTERISTICS OF SOLVENTS

There are three types of liquid substances that can serve as solvents. They include

1. molecular liquids: aside from water, they include many organic and some inorganic solvents such as HF, liquid ammonia, SO₂
2. ionic liquids: these are molten salts. They are used at high temperatures
3. atomic liquids: very few exist at room temperature, metallic mercury is a typical example

Solvents other than water are generally called non aqueous solvents. Non aqueous solvents are often mixed with water or other non aqueous solvents in order to obtain desirable solvent properties.

PROPERTIES OF SOLVENTS

Physical Properties

- Boiling point and Melting point determine the liquid range of solvents.
- Vapour pressure is a vaporization property and it is useful in determination of the toxicity and hazards of solvents. The heat of vaporization determines the cohesive energy density.

The cohesive energy density C is a measure of the stickiness of a solvent and is related to the work necessary to create cavities to accommodate solute particles in the solvent. It is defined by the equation

$$C = (\Delta_v H - RT) / V_m \quad (1)$$

Where $\Delta_v H$ is the heat of vaporization and V_m is the molar volume.

The solubility parameter $\delta = C^{1/2} = [(\Delta_v H - RT) / V_m]^{1/2}$ (2)

is useful in predicting the solubilities of non-electrolyte solutes in low polarity solvents. Two liquid substances with similar δ values are miscible while those with dissimilar δ values are immiscible.

$\Delta_v H(T_b)$ determines the Trouton's constant $[\Delta_v S(T_b) / R] = \Delta_v H(T_b) / R$. (3)

Solvents with $\Delta_v S(T_b) / R \geq 12$ are structured and those with $\Delta_v S(T_b) / R \leq 11.6$ are non structured.

- The viscosity η is the resistance of a liquid to flow. It influences the rate of mass transfer and the conductivity of electrolyte solutions.
- The relative permittivity ϵ_r influences the electrostatic interactions between the electric charges q_1 and q_2 placed in a vacuum and separated by a distance r . the electrostatic force F_{vac} between them is expressed as

$$F_{vac} = q_1 q_2 / 4\pi\epsilon_0 r^2 \quad (4)$$

If the two charges are placed in a solvent of relative permittivity at a distance r , the electrostatic force F_{solv} between the charges is expressed as

$$F_{\text{solv}} = q_1 q_2 / 4\pi\epsilon_0 \epsilon_r r^2 = F_{\text{vac}} / \epsilon_r \quad (5)$$

If q_1 and q_2 are of the same sign F_{vac} is a repulsive force. If they are oppositely charged F_{vac} is attractive force.

Absolute permittivity of a material is given as $\epsilon_0 \epsilon_r$.

Electrostatic interaction is weakened by solvents. The relative permittivity of a solvent influences the electrostatic solute – solute and solute – solvent interactions as well as on the dissolution and dissociation of electrolytes. It is used in classifying solvent polarity or solvating capability. Solvents of low permittivity are classified as apolar or non polar solvents while those of high permittivity are classified as polar solvents.

- The refractive index n_D is defined as the ratio of light speed at the sodium D- line in a vacuum to that of the medium. It is used in obtaining the polarizability, a , of the solvent molecules. Polarizability and refractive index are related by the equation

$$a = (3V_m / 4\pi N_A) (n^2_D - 1) / (n^2_D + 2) \quad (6)$$

Where N_A is the Avogadro constant, V_m is the molar volume. Solvents with High values of 'a' tend to interact easily with one another or with other polarizable solute particles by dispersion forces.

- The dipole moment μ is used to assess solvent polarity. Solvents with high dipole moments are called dipolar solvents. Those with low dipole moments are called apolar or non polar solvents. The dipole moments tend to underestimate the polarity of small solvent molecules because it depends on the distance between the positive and negative charge centers in the molecule.

The orientational polarization and the induced polarization that occurs for solvent molecules placed in between two plates of capacitor as a vapour is given as equation (7)

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{4\pi N_A}{3V_m} \left[a + \frac{\mu^2}{3k_B T} \right]$$

k_B is the Boltzmann's constant. ' μ ' and ' a ' can be obtained from a plot of $V_m (\epsilon_r - 1) / (\epsilon_r + 2)$ and $1/T$.

Chemical Properties

Acidity and basicity of solvents

Acidity of a solvent is the ability to accept an electron, an electron pair, as well as the ability to donate a proton and a hydrogen bond.

Basicity of a solvent refers to the ability to donate an electron, an electron pair, and the ability to accept a proton and a hydrogen bond.

Conventionally acidity and basicity are defined by the proton donating and accepting capabilities by the Bronsted acid – base concept and the electron pair accepting and donating capabilities of the Lewis acid – base concept.

A solvent with a strong proton donating ability has strong hydrogen bond donating, electron pair- accepting and electron accepting abilities. A solvent that has a strong proton accepting ability has a strong hydrogen bond accepting, electron pair donating and electron donating abilities.

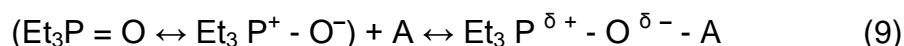
Solvent acidity and basicity have significant influence on the reactions and equilibria in solutions. Differences in reactions or equilibria among the solvents of higher permittivities are often caused by differences in solvent acidity / or basicity.

Acidity and basicity parameters include Gutmann's donor number (DN) measures solvent basicity, Mayer, Gutmann, Gerger's acceptor number (AN) - acidity scale.

The DN of solvent D - a Lewis base is determined calorimetrically as the negative value of the standard enthalpy change, for the adduct formation between solvent D and antimony pentachloride (SbCl_5), both being dilute, in 1,2 – dichloroethane at 25°C . Solvent basicity increases with increase in the DN.



The AN of a solvent A – a Lewis acid is obtained by measuring the ^{31}P – NMR chemical shift ($\Delta\delta$, ppm) of triethylphosphine oxide in a solvent A.



AN of the solvent is obtained from the equation

$$\text{AN} = 100 \times \Delta\delta (\text{A}) - \Delta\delta (\text{hexane}) / \Delta\delta (\text{SbCl}_5 \text{ in DCE}) - \Delta\delta (\text{hexane}) \quad (10)$$

$$\text{AN} = 2.348 [\Delta\delta (\text{A}) - \Delta\delta (\text{hexane})].$$

Solvent acidity increases with the increase in the AN value.

According to the Hard and Soft Acids and Bases concept (HSAB),

Lewis bases are electron pair donors and are classified as hard and soft bases. Lewis acids are electron pair acceptors and are classified as hard and soft acids. Hard acids interact strongly with hard bases. Soft acids interact strongly with strong bases.

The HSAB affects solute – solvent interactions. In general, hydrogen bond donor solvents are add hard acids and solvate strongly to hard base anions – OH^- , F^- , Cl^- and anions with a negative charge localized on a small oxygen atom – CH_3O^- , CH_3COO^- . Solvents with electron donor pair atoms like O, N, S, are soft, the softness increases in the order $\text{O} < \text{N} < \text{S}$.

Hard base solvents easily solvate strongly to hard acid cations like Na^+ , K^+ , while soft base solvents easily solvate to soft base cations like Ag^+ , Cu^+ .

CLASSIFICATION OF SOLVENTS

Solvent are classified according to their physical and chemical properties.

Kolthoff () has classified solvents into two groups,

1. Amphiprotic solvents: these solvents have both basic and acidic properties in terms of the Bronsted acid – base concept. Using water as reference, an amphiprotic solvent having acidity and a basicity comparable to that of water is a neutral solvent, while one with a stronger acidity and weaker basicity than water is called a protogenic solvent. A solvent with weaker basicity and stronger acidity than water is called a protophilic solvent. Solvents with relatively strong acidity have in its molecule a hydrogen atom bonded to an electronegative atom that has electron donor capacity like oxygen, nitrogen, or halogen.
2. Aprotic solvents do not have hydrogen joined to an electronegative atom, they have proton donor abilities. Aprotic solvents whose basicity is lower than water are protophobic, those with basicity higher than water are protophilic e.g. includes solvents that have oxygen or nitrogen on which negative charge is located.
3. Dipolar aprotic solvents are those with relatively high permittivities ($15 \geq 20$) or large dipole moments and very weak ($\mu \geq 2.5$ D). Solvents like THF, Py, diethyl ether are classified as dipolar solvents because they possess acidic or basic properties that make them behave as dipolar solvents.
4. Inert solvents have low permittivities or dipole moments and are have very weak acidic and basic properties.

In summary, solvents are classified as follows,

Protic Solvents

- i) amphiprotic hydroxylic solvents e.g. methanol, glycol,
- ii) amphiprotic protogenic solvents e.g. methanoic acid, ethanoic acid, hydrogen fluoride, H_2SO_4
- iii) protophilic H- bond donor solvents e.g. liquid ammonia, NMF.
- iv) dipolar aprotic solvents
 - a) aprotic protophilic solvents, DMF, DMSO, Pyridine
 - b) aprotic protophobic solvents, AN, Ac, NM, PC
- v) low permittivity electron donor solvents, diethyl ether, dioxane, THF
- vi) low polarity and inert solvents
 - a) low polarity solvents of high polarizability, CH_2Cl_2 , $CHCl_3$, benzene
 - b) inert solvents, n- hexane, cyclohexane.

EFFECT OF SOLVENTS ON CHEMICAL REACTIONS

Two important properties of solvents used to correlate solvent effects on various chemical processes are solvent permittivity and solvent acidity and basicity. If the permittivity of one solvent is higher than that of another, the difference in a chemical process in the two solvents is attributed to the permittivity of the solvents. (Explain). The difference in a chemical process in two solvents of high permittivities is attributed to the influence of the acidity or basicity of the two solvents.

Acid – Base Properties of Solvents and the Characteristic of Reactions

Solvents with weak (strong) acidity	Solvents with weak (strong) basicity
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A solvent with weak acidity is a weak hydrogen donor and solvates only very weakly to small anions (F ⁻ , Cl ⁻ , OH ⁻ ;) small anions are very reactive in it. Solvents with strong acidity solvates small anions easily by hydrogen bonding that weaken their reactivity.	Solvation to small cations is difficult with solvents that have weak basicity and small cations are reactive in solvents that are weak bases and unreactive in solvents that are strong bases.
The pH region for a solvent with weak acidity falls within the basic range, the solvent molecule cannot release a proton easily. Strong bases are differentiated (leveled).	Solvents with weak basicity do not accept protons with ease, their pH tends to acidic. Those that are strongly basic accept protons with ease.
Solvents with weak acidity are weak electron acceptor; the potential is more negative than water. Strong reducing agent is stable in the solvent. A solvent that is strongly acidic is an electron acceptor and the potential is less negative. Strong reducing agents are unstable in the solvent.	Oxidation of solvents with weak basicity is difficult, potential is widely positive. Those with strong basicity have narrowly positive potentials and are easily oxidized. Strong oxidizing agent is stable in weakly basic solvents and substances difficult to oxidize can be oxidized in them. But unstable in strongly basic solvents.

Water has high permittivity and moderate acidity and basicity. Many cations and anions are easily solvated and many electrolytes are highly soluble and dissociates into ions. Water has a fairly high pH and potential ranges and a suitable liquid temperature range. It is adjudged as an excellent and the most popular solvent. However its anomalous behaviour arising from its hydrogen bonding ability to form three dimensional networks makes water unsuitable for large hydrophobic molecules that do not possess hydrophilic sites to dissolve in it.

Most dipolar aprotic solvents are non – structured or weakly structured so they are capable of dissolving many large molecules and ions.

REFERENCES/ TEXT

ELECTROCHEMISTRY IN AQUEOUS SOLUTIONS BY KOSUKE IZUTSU
SECOND SEMESTER 2010/2011 ACADEMIC SESSION
CHM 104 LECTURE NOTES PART B

1. HYBRIDISATION OF SHAPES OF SIMPLE MOLECULES INCLUDING CARBON COMPOUNDS.
2. EXTRACTION OF METALS.

PLEASE NOTE:

This note is a guide, explanations, diagrams and other important notations will be discussed in class.

HYBRIDISATION OF SHAPES OF SIMPLE MOLECULES INCLUDING CARBON COMPOUNDS.

DEFINITIONS:

Hybridisation is the process of mixing atomic orbitals. The new orbitals formed from this process are called hybrid orbitals.

The number of hybrid orbitals on an atom equals the number of atomic orbitals that are mixed.

Hybridization is also defined as the arrangement of extra nuclear electrons in atoms such as carbon.

COMMON TYPES OF HYBRIDISATION

1. Hybridisation in Beryllium in BeF_2 : sp hybridisation

The valence shell electron pair repulsion (VSEPR) model predicts BeF_2 is linear with two identical Be – F bonds



The electronic configuration of F, $1s^2 2s^2 2p^5$ indicates there is unpaired electron in the 2p orbital. The 2p electron in F can be paired with an unpaired electron from Be atom to form a polar covalent bond.

Be electronic configuration is $1s^2 2s^2$ (this shows that there are no unpaired electrons). In this state Be is not capable of forming covalent bonds with the F atom. Be can form two bonds by extra nuclear rearrangement of the 2s electrons by promoting an electron from the 2s orbital to an empty an orbital. Configuration of Be before bonding with F becomes $1s^2 2s^1 2p^1$. With this two unpaired electrons Be can form polar bonds with F atoms.

Sp hybrid orbitals on Be overlaps with a 2p orbital on F to form a bond. The two bonds are equivalent to each other and form an angle of 180° . The arrangement of the orbitals is linear. Thus BeF_2 is a linear molecule. This type of hybridization is called sp because it involves one s and one p orbitals.

Sp² Hybridisation

Example is BF_3

Boron electronic configuration is $1s^2 2s^2 2p^1$

Fluorine electronic configuration is $1s^2 2s^2 2p^5$

Electronic configuration of hybridized B is $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$, this sp² hybrid orbital of boron overlap to form 3 covalent bonds with F. The 3 sp² hybrid orbitals are equivalent and arranged in the same plane 120° apart from one another forming a trigonal planar shape.

Hybridisation: involves hybridization of one s, three p and two d orbitals

Examples: SF_6 , SF_4 , BrF_3 . Shape of molecule formed is octahedral

Two of these examples will be explained in class.

Sp³d (d Sp³) Hybridisation: involves hybridization of one s, three p and one d orbitals

Examples: PF_5 , ClF_5 , XeF_4 , PF_6 . : Shape of molecule formed is trigonal bipyramidal

Two of these examples will be explained in class.

d^3s (sd^3) Hybridisation: involves hybridization of one s, and three d orbitals
Example MnO_4^- . Shape of molecule formed is tetrahedral

To be explained in class.

sp^3 Hybridisation: involves hybridization of one s and three p orbitals. Each sp^3 hybrid orbital has a large lobe that points toward a vertex of a tetrahedron at an angle of 109.5° . Example CH_4, NH_4^+ .

HYBRIDISATION IN CARBON

Electronic configuration of C is $1s^2 2s^2 2p^2$ which indicates that carbon has only two unpaired electrons and should be divalent. The quadrivalency (tetravalency) of carbon is accounted for by assuming that the arrangement of electrons in carbon is changed in such a way as to provide unpaired 4 electrons prior to reaction i.e. an electron is promoted into an empty 2p orbital from 2s orbital.

Electronic configuration of hybridized C is $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$.

If the four unpaired electrons took part in the formation of 4 covalent bonds with hydrogen for example, the one 2s and three 2p orbitals combine into four different hybrid orbitals to form bonds which are tetrahedrally arranged. This type of hybridization is sp^3 .

sp^2 Hybridisation In Carbon.

This leads to the formation of double bond between 2 carbon atoms.

One 2s and two 2p orbitals are hybridized to form a coplanar structure at 120° . One of the 2p orbitals remain unchanged, each carbon atom is linked by bond has three equivalent sp^2 orbitals. Two of the orbitals from each carbon forms a sigma bond with hydrogen atoms, the remaining sp^2 orbitals of each carbon atoms forms a sigma bond between the 2 carbon atoms. The 2 carbon atoms and four hydrogen atoms are all in the same plane. At right angles to this plane there remain the unchanged 2p orbitals of each carbon atom and these two 2p orbitals interact to form a pi-bond between the 2 carbon atoms. A double bond in carbon consists of one sigma bond and one pi bond.

A sigma bond is stronger than a pi-bond. Two atoms linked by a sigma bond can rotate freely about the bond unless there is steric interference. Free rotation is prevented when two atoms are linked by a pi-bond.

sp Hybridization in Carbon. Formation of carbon – carbon triple bond.

One 2s and one 2p orbitals are hybridized to form two equivalent orbitals which are collinear. The two 2p orbitals which are unchanged on each carbon atom interact to form two pi-bonds between the carbon atoms, the two bonds being placed at right angles to each other. In ethyne, one of the sp orbital from each carbon forms a sigma bond with hydrogen atoms and the remaining sp orbital of each carbon atoms forms a sigma bond between the 2 carbon atoms two. A triple bond in carbon consists of one sigma bond and two pi bonds.

EXTRACTION OF METALS

There are four ways in which metals are extracted from their ores.

1. Mining of the pure metals, e.g. noble metals like gold, silver, platinum
2. Reduction of the oxide ore, e.g. some transition metals, most especially, Iron.
3. Roasting the sulphide ore and the reduction of the oxide, e.g. Pb, Ni, Zn, Hg, Cu
4. Electrolysis of the molten solid, e.g. reactive elements of group I, II and III – Na, Mg, Al.

REDUCTION OF THE OXIDE

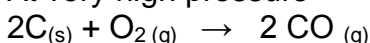
Extraction of Iron from its ore, Haematite – Fe_2O_3 and magnetite – Fe_3O_4 Reduction of the ore is carried out in a blast furnace. [Picture of a blast furnace to be shown in class]. The furnace is charged with a mixture of limestone, coke, and iron ore. Air is passed through the bottom of furnace. At the bottom of the furnace, coke combines with oxygen to form carbonmonoxide. This reaction releases energy that keeps the furnace going. The reduction of the ore takes place at the top of the furnace and the carbonmonoxide generated is employed in the reduction of the ores.

Limestone is decomposed to give calcium oxide which reacts with part of the ore that contains silica to give calcium silicate. The silicate is the chief component of the molten slag that is tapped off near the bottom of the furnace. The liquid iron is run off at the bottom and this can be cast into pigs {pig iron}. The bulk of the molten iron can be turned into steel by blasting oxygen through the impure iron. This oxidizes impurities like carbon, phosphorus. There are different grades and qualities of steel, each having a different set of characteristics. The amount of carbon mixed with iron determines the nature of the steel like tensile strength, malleability. Small amounts of magnesium can be added to give desirable qualities.

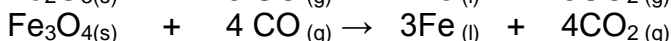
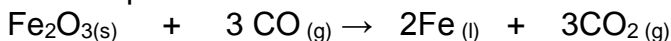
Equation of the major reactions at the furnace:

Bottom of the furnace,

At very high pressure

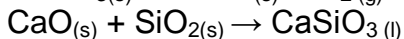


At the top of the furnace



Temperature at the furnace = 1500 – 2000 °C

Formation of slag



REDUCTION OF SULPHIDE ORES

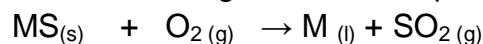
The sulphide ores are treated by

- Crushing to fine particles

Froth flotation – This technique takes advantage of the fact that metal sulphides are relatively non polar and are attracted to oil. Water, light weight oil and some chemicals are added to the crushed ore. The mixture is shaken vigorously. Froths are formed by bubbling air through the mixture. The chemicals added to the water act as an interface between the mineral particles, water and air (surfactants)

Roasting in air converts the sulphide into oxide

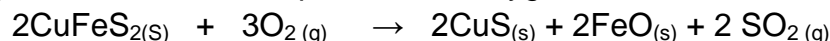
General equation for roasting of metal sulphides is written as



Examples

The isolation of copper from its most common ore Chalcopyrite requires several additional steps:

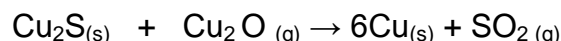
The chalcopyrite is roasted in the presence of oxygen



Copper sulphide and iron oxide from the reaction above are mixed with limestone and sand in a blast furnace, CuS is converted to Cu₂S. The limestone and sand form the molten slag CaSiO₃ in which the Fe dissolves. The copper sulphide melts and sinks to the bottom of the furnace. The less dense iron containing slag floats above the molten copper sulphide and is drained off.

The isolated copper sulphide is roasted in air to give the copper metal. The copper obtained is known as blister copper and is purified by electrolysis using the blister copper as the anode and copper sulphate solution as the electrolyte.

Equation of reaction:



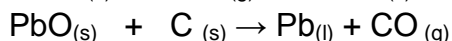
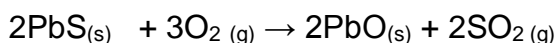
Lead from impure galena PbS is obtained by

Mixing the ore with limestone and roasting in air to produce lead (II) oxide – PbO.

PbO lumps are mixed with more limestone and reduced with coke at about 900°C in a blast furnace.

The molten lead run off at the bottom of the furnace can be further purified.

Equations of reaction:



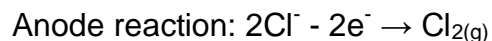
ELECTROLYTIC METHODS

This method is useful in recovering reactive metals from their ores.

The Downs process for the extraction of sodium from sodium chloride.

Electrolysis of molten sodium chloride is carried out in a Downs cell. Calcium chloride is added to lower the melting point of the molten sodium chloride (ratio 2 to 3) from the normal melting point of 804°C to about 600°C. Sodium is discharged at the cathode which is made of steel and Chlorine is released at the anode is made of graphite. The sodium collects in inverted troughs above the cathode ring.

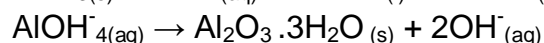
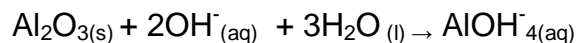
Equations at the electrodes:



Extraction of Aluminium from Bauxite - Bayer process:

Bauxite contains 60% alumina (Al_2O_3)

The ore is concentrated by dissolving in sodium hydroxide solution at 250°C and 40 atmospheres to form aluminium hydroxide



The hydrated aluminium oxide produced in equation ii is dried at approximately 1000°C to obtain the anhydrous aluminium oxide.

The electrolytic process for aluminium is known as the Hall – Heroult process (smelting).