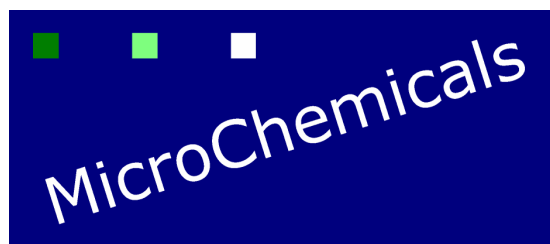


Solvents: Theory and Application



Revised: 2013-11-07 Source:

www.microchemicals.com/downloads/application_notes.html

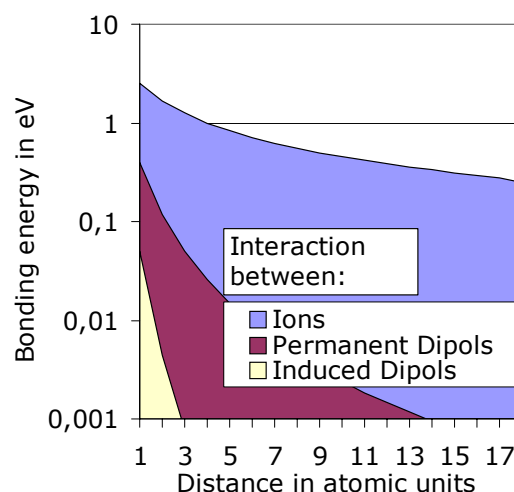
Dissolving

While etching breaks the intramolecular bonds of a solid state, solving describes the overcoming of intermolecular interactions between two solids or liquids. This chapter aims for an understanding how the chemical and physical properties of solvents can be explained, and which solvent is (un)suited for your purpose.

Interaction Between Molecules

The physical and chemical properties **vapour pressure**, **boiling point** and **solubilities** of all substances have their origin in the **Coulomb interaction** between the molecules. The various interactions itself derive from the drive to minimize the Coulomb energy of the valence electrons.

A classification of the electrostatic interaction allows an exemplification and estimation of the interaction strength as well as the predication, which kind of interaction dominates for various solids and liquids (in this document with a focus on polymers and organic solvents). Additionally, this classification detailed in the following sections allows predicting the (dis)solubility between polymers and solvents as well as between solvents.

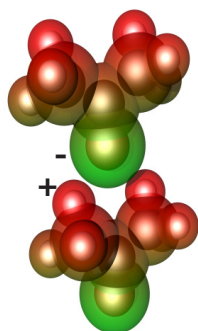


Interaction Between Ions

The appearance of ions (charged atoms or molecules) is not limited to dissolved salts: Even in pure water without any traces of impurities, at room temperature the autoprotolysis forms approx. one OH⁻ and H₃O⁺ ion pair per 1.000.000.000 H₂O molecules. In aqueous solutions of acetic (e. g. ethyl lactate) or alkaline (e. g. NMP) solvents, the ion concentration can be several orders of magnitude higher.

With a few eV, the interaction energy between ions is comparable to the chemical bonding energy within a molecule. The corresponding interaction force drops with the square of the distance between two ions and – if apparent – dominates all other interactions between molecules described in the following sections.

Interaction Between Permanent Electric Dipoles



Acetone (polar)

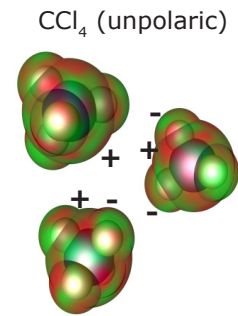
The different **electro negativity** of the atoms in polar molecules causes a spatial shift between the centre of the valence electron distribution and the centre of the nuclear charges. As a result, the molecule has an electric dipole moment. The interaction between the positive and negative poles of neighbored molecules results in an electrostatic attraction – in case of bonded H- and O-atoms also called hydrogen bonds.

The **permanent dipole moment D** of typical organic solvents is 0..3 Debye ($D_{\text{CCl}_4} = 0$ Debye, $D_{\text{methanol}} = 1.41$ Debye, $D_{\text{acetone}} = 2.88$ Debye) and results in bonding energies between neighbored molecules of some 100 meV (in case of hydrogen bonds up to 0.5 eV due to the strong difference in the electro negativities between O (3.5) and H (2.2)). The corresponding interaction force drops with the fourth power of the distance between the molecules.

Interaction Between Induced Electric Dipoles

In all polar and unpolaric atoms and molecules, the valence electron charge distribution permanently fluctuates due to interactions between the molecules with each other, with the containment and electromagnetic radiation. As a consequence, temporary electric dipoles are steadily formed.

These **temporary dipoles** interact with the valence electron orbitals of neighbored atoms/molecules and hereby induce anti-parallelly orientated electric dipoles resulting in a weak (< 100 meV) interaction. Since both, the dipole **induction** and the resulting **interaction** depend on the distance between two molecules, the interaction force drops with the 7th power of the distance, and therefore is very short-range.

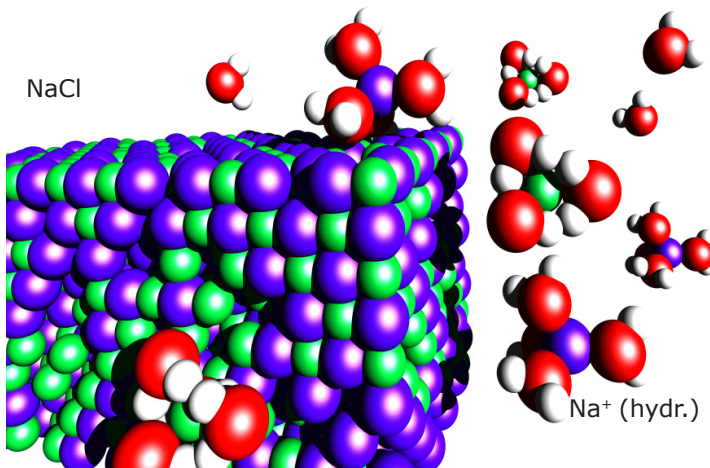


Mixed Interactions

Mixed interactions (e. g. between ions and dipoles in dissolved salts) or between permanent and induced dipoles also have to be considered.

Solubility: Energy and Entropy

The average bonding energy of atoms or molecules in a liquid or solid state is negative (otherwise, at the given temperature and pressure, the substance would be in the gaseous state). Therefore, dissolving the substance requires energy in order to overcome this bonding energy.



Since not only within a substance, but also between a substance and a solvent interactions occur, dissolving can further reduce the average bonding energy of all molecules involved (**exothermic** process = positive heat of mixing). A good example for exothermic mixing is a solution/dilution of KOH or sulphuric acid with water.

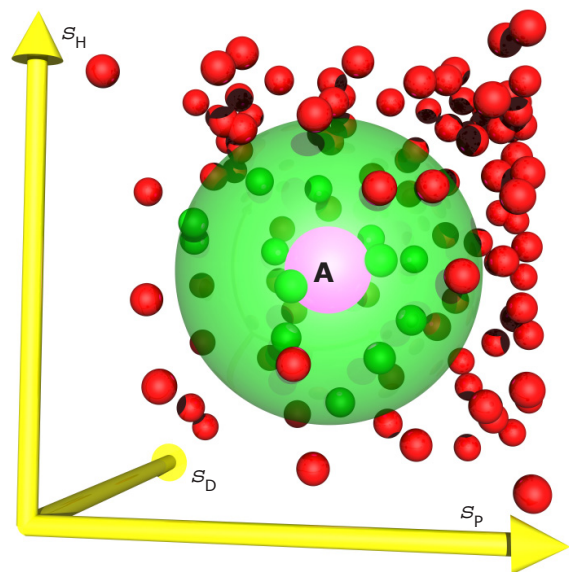
On the other hand, when e. g. NaCl is solved in water, the solution cools below the temperature of the educts → the mixing is **endothermic** and requires additional energy. In this example, removing the Na⁺ and Cl⁻ ions from the crystal consumes more energy than the hydration by the water molecules (dipole/ion interaction) provides (scheme above).

The reason why e. g. NaCl is nevertheless soluble in water despite additional energy ΔU required lies in the increasing **entropy** by ΔS of the system: Dissolved ions have more degrees of freedom in space and velocity, and hereby a higher entropy than ions fixed in the crystal. Following a fundamental equation of thermodynamics, at a given volume and pressure, each system tries to minimize its **free enthalpy** $F = U - T \cdot S$ at given temperature T . Therefore, solubility depends on the condition $\Delta U - T \cdot \Delta S < 0$.

The Hansen Parameters

This solubility condition $\Delta U - T \cdot \Delta S < 0$ for substances such as resist and solvent can be derived from the appearance and size of the different molecule interactions (as detailed in the first sections of this document) using the Hansen model (scheme previous page):

The solubility of a polymer **A** (e. g. a photoresist), and a solvent **B** (or, respectively, between the two

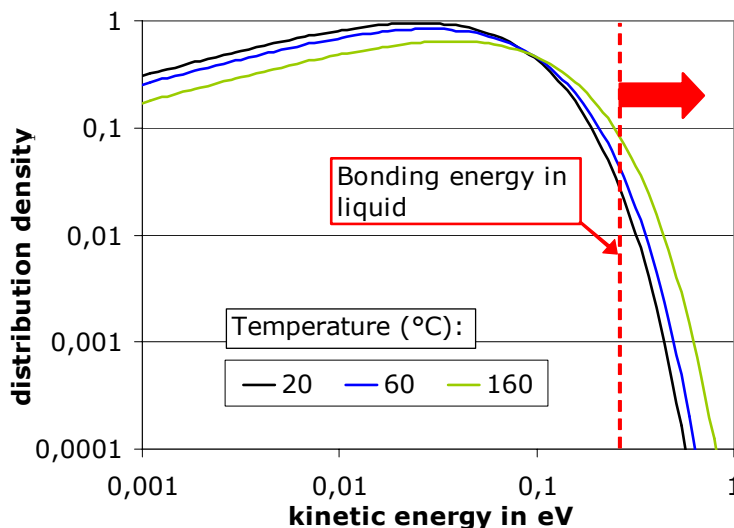


solvents **A** and **B**) is maximum if the different interactions **A-A**, **B-B**, and **A-B** are **individually coincident**.

If substance **A** and all substances **B** taken into account for dissolving **A** are plotted against its polar, dispersion (e. g. van-der-Waals-), and H-bonding interaction (expressed by the Hansen parameter s_p , s_D , s_H), **suited solvents** (green dots in the plot) appear near to **A** (in between the green sphere), and less suited solvents (red dots) far away from **A**.

Physical Properties: Vapour Pressure, Evaporation, Boiling Point

In order to pass from the liquid into the gaseous phase, an atom or molecule has to overcome its **bonding energy** E_{bonding} to neighbored molecules with its **kinetic energy** E_{kin} . In order to fulfil this condition for all molecules of water or many organic solvent at the same time, a temperature of several 1000°C would be required. At lower temperatures (such as the boiling point!), only a very small fraction of the molecules fulfils the condition $E_{\text{kin}} > E_{\text{bonding}}$ via the Maxwell-Boltzmann energy distribution (plot right-hand). An exact calculation would also have to consider the energy gain caused by the interaction between the evaporated molecules which is very small compared to the former interaction in the liquid state.



Without external energy addition, the molecules remaining in the liquid after the high-energy molecules passed to the gaseous phase have a lowered average E_{kin} corresponding to a lower temperature (\rightarrow **evaporative cooling**).

The evaporated atoms or molecules in the gaseous phase also have a Maxwell-Boltzmann energy distribution, so molecules with $E_{\text{kin}} < E_{\text{bonding}}$ return into the liquid phase. The equilibrium condition between the two transitions defines the temperature dependant **vapor pressure** of the individual liquid. If the vapor pressure surpasses the atmospheric pressure at the so defined **boiling point**, the liquid starts boiling. Below the boiling point, the liquid **evaporates**.

Since polarisability and (in case of polar molecules) dipole strength increase with the molecular size, liquids with 'large' molecules such as NMP bear a low vapor pressure and high boiling point, while liquids with 'small' molecules such as acetone have a high vapor pressure and, respectively, low boiling point.

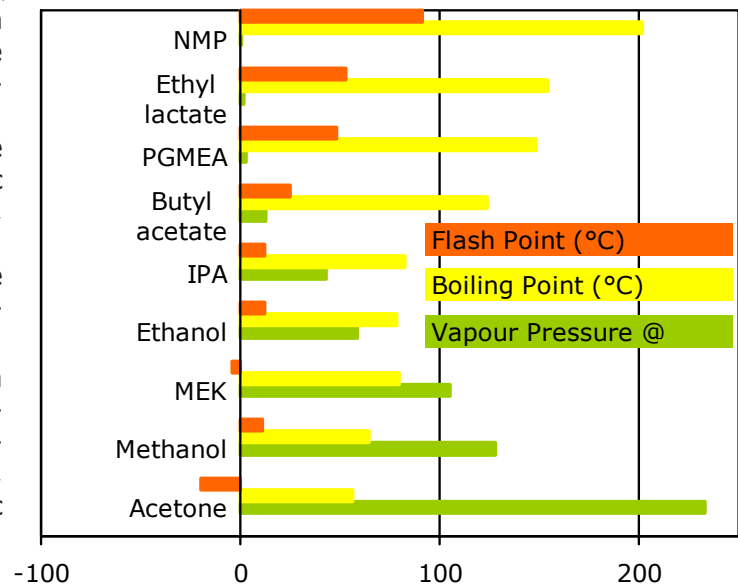
Safety Properties: TWA, Explosive Range, Flash Point, and Ignition Temperature

TWA (Time Weighted Average): This term is used in the specification of Occupational Exposure Limits (OELs) to define the average concentration of a chemical to which it is permissible to expose a worker over a period of time, typically 8 hours.

Explosive range: The ignition of a combustible vapor mixed with air in the proper proportions will produce an explosion. This proper proportion is called the explosive range, and includes all concentrations of a mixture of flammable vapor or gas in air, in which a flash will occur or a flame will travel if the mixture is ignited. The lowest percentage at which this occurs is the lower explosive limit, and the highest percentage is the upper explosive limit. Explosive limits are expressed in percent by volume of vapor in air and, unless otherwise specified, under normal conditions of temperature and pressure. The lower explosive limit can be below 1 % (in case of (gasoline)), the upper explosive limit of many organic solvents is typically some 10 %.

Flash point: The temperature at which a liquid will yield enough flammable vapor to ignite. There are various recognized industrial testing methods; therefore the method used must be stated. The flash point of many organic solvents such as methanol, ethanol, isopropyl alcohol and acetone is $< 20^{\circ}\text{C}$, and therefore form flammable or explosive vapor at room temperature and even below.

Ignition temperature: The minimum temperature necessary to initiate combustion (oxidation) and have self-sustained combustion of the solid, liquid, gas or vapor of interest. Most organic solvents have ignition temperatures $> 200^{\circ}\text{C}$.



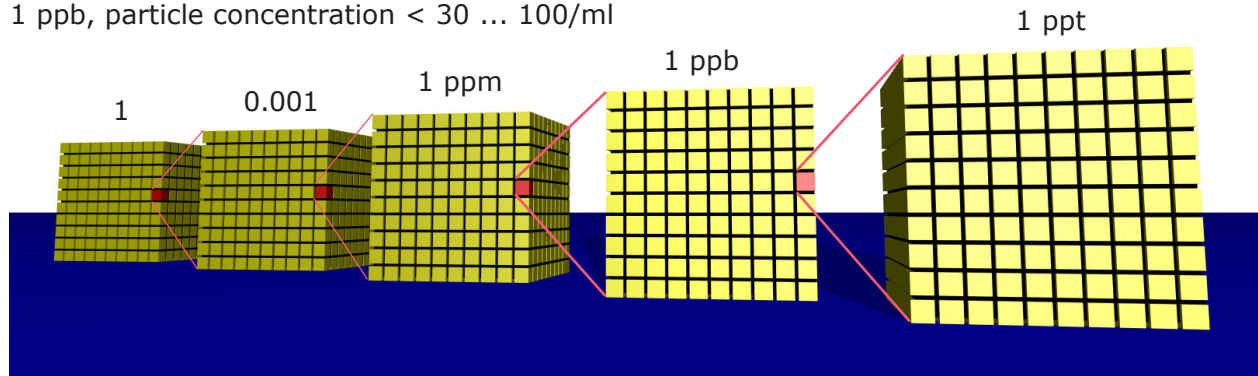
Purification Grades

MOS (metal oxide semiconductor): Impurity metal ion concentration (per element) approx. 100 ppb, particle concentration $< 1.000/\text{ml}$

VLSI (very large scale integration): Impurity metal ion concentration (per element) approx. 10-50 ppb, particle concentration $< 250/\text{ml}$

ULSI (ultra large scale integration): Impurity metal ion concentration (per element) approx. 10 ppb, particle concentration $< 30 \dots 100/\text{ml}$

SLSI (super large scale integration): Impurity metal ion concentration (per element) approx. 1 ppb, particle concentration $< 30 \dots 100/\text{ml}$



1 ppm (parts per million, 10^{-6}) approximately corresponds to a drop (approx. $30 \mu\text{l}$) in a rather big bucket.

1 ppb (parts per billion, 10^{-9}) corresponds to a drop in a comparable small swimming-pool.

1 ppt (parts per trillion, 10^{-12}) would be a drop in a small lake, or a $5 \mu\text{m}$ particle solved in a cup of coffee, or anyhow approx. 100.000 atoms in a drop!

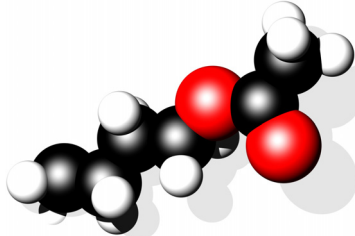
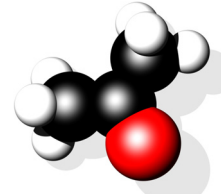
The **reasonable purity degree** of process chemicals depends – among many other parameters – on the minimum feature size to be realized, the required yield, the cleanroom class, and subsequent process steps.

It is almost impossible to definitely correlate suboptimum process results with a purity degree of the chemicals applied being too low. Therefore, one cannot give a certain statement on the required purity grade.

With VLSI and ULSI quality, we fulfil almost all requirements in research and development as well as in production.

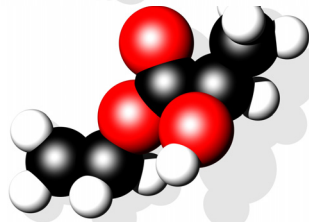
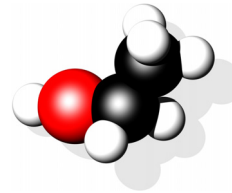
Our Solvents and Their Fields of Application

Acetone removes organic impurities from substrates and is well-suited for greasy/oily contaminations. Its high evaporation rate, however, requires a subsequent cleaning step in e. g. isopropyl alcohol in order to avoid striations on the substrate. Acetone is not well-suited as lift-off medium due to the high fire danger when heated and the trend of particles to be lifted to resorb onto the substrate.



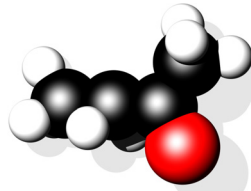
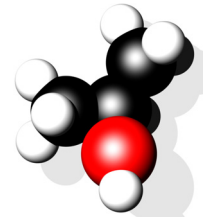
Butyl Acetate is – besides PGMEA – a suited thinner for AZ[®] and TI photoresists due to its high boiling point.

Ethanol is used for cleaning, and as an additive for HF-based anodic porous silicon etching.



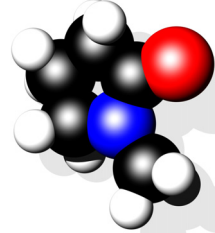
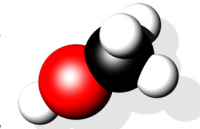
Ethyl lactate is – besides PGMEA – a suited thinner for AZ[®] and TI photoresists due to its high boiling point.

Isopropyl alcohol is well-suited for rinsing contaminated acetone off as well as removing particles from surfaces. Therefore, this solvent is often used in the second substrate cleaning step after acetone. Additionally, isopropyl alcohol is used as additive for anisotropic Si-etching.



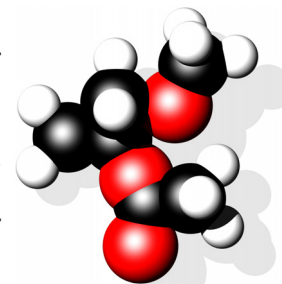
MEK (methyl ethyl ketone) with its low boiling point can be used as additional thinner for spray coating resists, which require a fast resist film drying on the substrate.

Methanol can be used as a powerful solvent for contaminated acetone in a three-step (substrate) cleaning process (acetone → methanol → isopropyl alcohol). However, due to its toxicity, its application should be carefully considered.



NMP (1-methyl-2-pyrrolidone) is a powerful lift-off medium due to its physical properties: NMP yields a low vapour pressure (no striation formation), strongly solves organic impurities as well as resists, keeps solved particles in solution, and can be heated due to its high boiling point. For the same reasons, NMP (pure or diluted in H₂O) gives a very well-suited stripper for photoresists processed under harsh conditions.

PGMEA (1-methoxy-2-propyl-acetate) is the solvent/thinner of almost all AZ[®] and TI photoresists due to its low vapour pressure and its suppression of particle formation in the (further diluted) resist. Additionally, PGMEA is often used for edge bead removal, since its low vapor pressure prevents further thinning of the coated resist film. The trade name of PGMEA is AZ[®] EBR Solvent.



Quality Grade, Specifications, Sales Volumes, and Shipping

Beside Butyl acetate and ethanol, we supply all solvents listed above in VLSI quality in 2.5 L sales units. Acetone, isopropyl alcohol, and NMP are additionally available in ULSI grade. Other sales units or purification grades on request!

Contact us!

Interested? Please send your request to:

e-mail: sales@microchemicals.eu
phone: +49 (0)731 36080 409
fax: +49 (0)731 36080 908