# Fundamentals of Distribution Separations (III)

**(01/16/15)**

$$K = \exp\left(\frac{-\Delta\mu_i^0 - \Delta\mu_i^{ext}}{RT}\right)$$ *distribution coefficient*

$$C_i = \exp\left(\frac{-\Delta\mu^0}{RT}\right)$$ *solubility*

$$\Delta\mu_i^0 = \Delta\bar{H}_i^0 - T\Delta\bar{S}_i^0$$

$$\mathbf{A{-}{-}{-}B \xrightarrow{q} A + B}$$

$$\Delta H_i^0 = \Delta H_{i,\beta}^0 - \Delta H_{i,\alpha}^0$$

$$\boxed{\Delta H^0 = E_L + E_I + E_D + E_{AB}}$$

# Quantitative Approach for the Strength of Molecular Interactions (II)

A more quantitative approach in estimating the strength of molecular interactions is to use various scales that describe molecular polarity.

(a) Polarizability
(b) Dipole Moments
(c) Solubility parameters

**(b) Dipole Moments**

(1) The dipole moment (μ) is a measure of the electron distribution in a compounds
(2) The dipole moment of a compound is determined by
    - The electronegativity of all atoms in the compound
    - The way in which these atoms are connected and the 3-D structure

(3) Examples of electronegativities for some elements

| Element | Electronegativity (Pauling Scale) |
|---|---|
| Hydrogen | 2.1 |
| Carbon | 2.5 |
| Sulfur | 2.5 |
| Nitrogen | 3.0 |
| Oxygen | 3.5 |
| Fluorine | 4.0 |
| Chlorine | 3.0 |
| Bromine | 2.8 |
| Iodine | 2.5 |

(4) For a non-symmetrical molecule made up of neighboring atoms with different electronegativities, a partial separation of positive and negative charge is produced (i.e., a dipole).

(5) The magnitude of the dipole moment in a compound is given by

$$\boxed{\mu = e\,d}$$

Where: $\mu$ = dipole moment (Debye units)
$e$ = Magnitude of the charge (electrostatic units)
$d$ = Distance (cm)

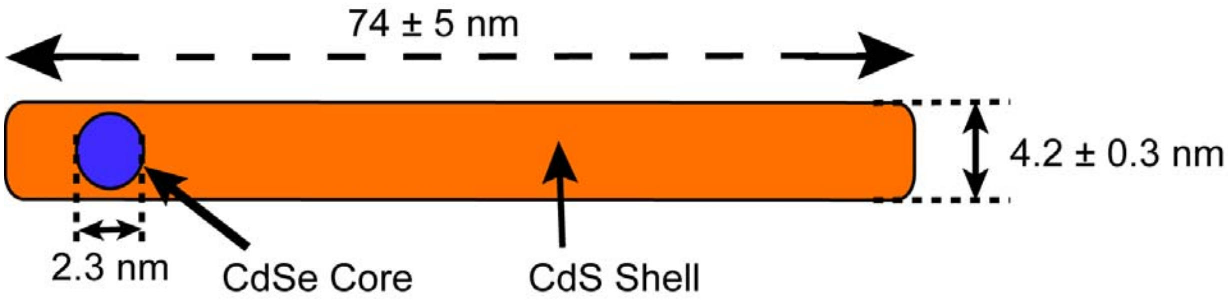
(6) Dipole moments for some common compounds are given:

| Compound | Dipole Moment (Debye units) |
|---|---|
| $CO_2$ | 0 |
| $CH_4$ | 0 |
| $CCl_4$ | 0 |
| $CH_3Cl$ | 1.87 |
| $NH_3$ | 1.47 |
| HF | 1.82 |
| $H_2O$ | 1.87 |

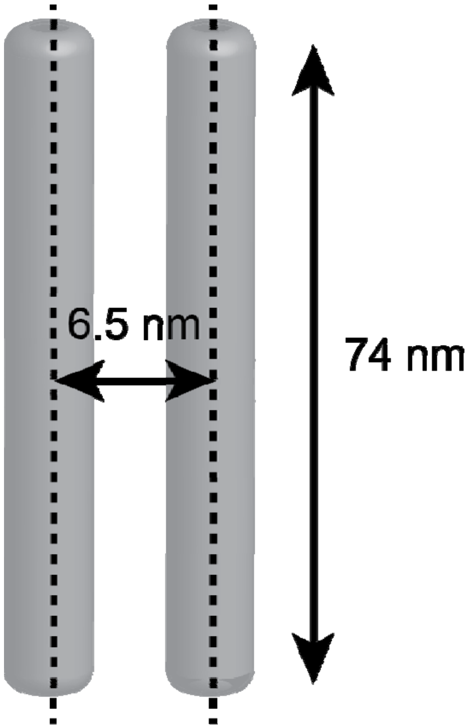
(7) advantages:

Dipole moments are easy to measure
Useful in predicting interactions due to dipole-dipole interaction

# Dipole-Dipole Interactions Between Two Nanorods



**Dipole moments of the CdSe/CdS nanorods = $(1.0\pm0.2) \times 10^3$ D**



$$E_{dipole} = \frac{-\mu^2}{4\pi\varepsilon_0\varepsilon r^3}$$

| | **toluene** | **1-dodecanethiol** |
|---|---|---|
| **Dipole-dipole interaction (meV)** | 977±306 | 832±259 |
| **Dipole-dipole interaction (kT)** | 38.2±11.8 | 32.5±10.1 |

## (C) Solubility parameters

(1) Because of the limitation in using polarizability and dipole moments, a number of alternative scales have been developed to assess how polar a compound is, or to determine how well it will interact with another molecules.

(2) The most famous such scale is that based on the Hildebrand solubility parameter ($\delta$).

(3) The value of $\delta$ for given compound is defined as follow:

$$\boldsymbol{\delta = (\Delta E_v/V)^{1/2}}$$

Where: $\Delta E_v/V$ = energy per unit volume, required to completely vaporize a solution of pure compound

(4) $\Delta E_v/V$ is also known as the cohesive energy density of the compound. In other words, it is a measure of the total interaction energy between two Molecules or atoms of the same solute.

*Note: $\delta$ is a measure of the total interactions a compound has with itself.*

(4) Values of $\delta$ for common solvents at 25 °C

| Solvent | $\delta$ $(cal/cm^3)^{1/2}$ |
|---|---|
| Water | 23.4 |
| Ammonia | 16.3 |
| Methanol | 14.5 |
| Ethanol | 12.7 |
| Benzene | 9.2 |
| Carbon tetrachloride | 8.6 |
| Cyclohexane | 8.2 |
| n-Octane | 7.5 |
| n-Heptane | 7.4 |
| n-Hexane | 7.3 |
| n-Pentane | 7.1 |

(5) By knowing the value of $\delta$ for two compounds, the solubility of one in the other may be predicted. Solubility is predicted by using the following equation for the change in total free energy due to mixing of the two compounds ($\Delta G_m$).

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

Where: $\Delta H_m$ = Changes in enthalpy due to mixing
$\Delta S_m$ = Change in entropy due to mixing

(6) For the preparation of a relatively dilute solution of solute i of solvent j, the change in energy due to mixing ($-T\,\Delta S_m$) is approximately given by:

$$-T\,\Delta S_m = RT\ln(X_i)$$

where: $X_i$ =mole fraction of compound i in the final solution

(7) The value of $\Delta H_m$ for mixing a solution of i in j may be determined from the values of $\delta$ for the two compounds*:

$$\mathbf{\Delta H_m = \bar{V}_i\,(\delta_i - \delta_j)^2}$$

Where: $\bar{V}_i$ = molar volume of pure solute i ($MW_i$/$density_i$)

* J. H. Hildebrand and R. L. Scott, The solubility of noneletrolytes, 3rd ed.,Dover, New York, 1973

# Quantitative Approach for the Strength of Molecular Interactions (II)

A more quantitative approach in estimating the strength of molecular interactions is to use vrious scales that decribe molecular polarity.

(a) Polarizability
(b) Dipole Moments
(c) Solubility parameters (Hidebrand)

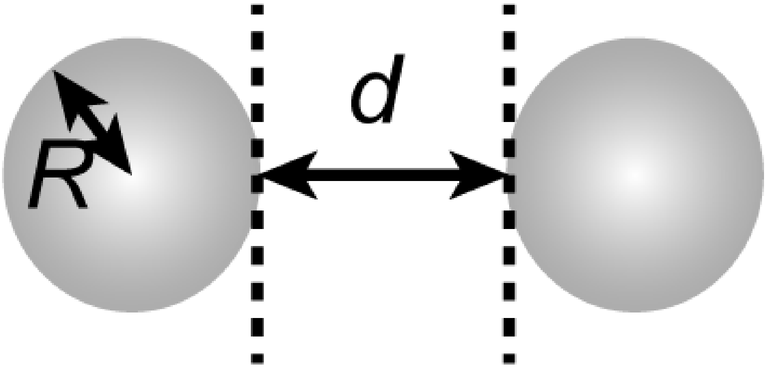
(d) Kamlet-Taft parameters (solvatochromic parameter)
Abraham's paramters: (solute descriptors and system constant)
"empirical model"

# Hamaker Theory of Van der Waals Interactions (London forces)

**1. Van der Waals interactions between two neighboring spherical nanoparticles**

$$U_{spherical-spherical} = \frac{A}{12}\left\{ \frac{R}{d(1+d/4R)} + \frac{1}{1+d/R+d^2/4R^2} + 2\ln\left( \frac{d(1+d/4R)}{R(1+d/R+d^2/4R^2)} \right) \right\}$$

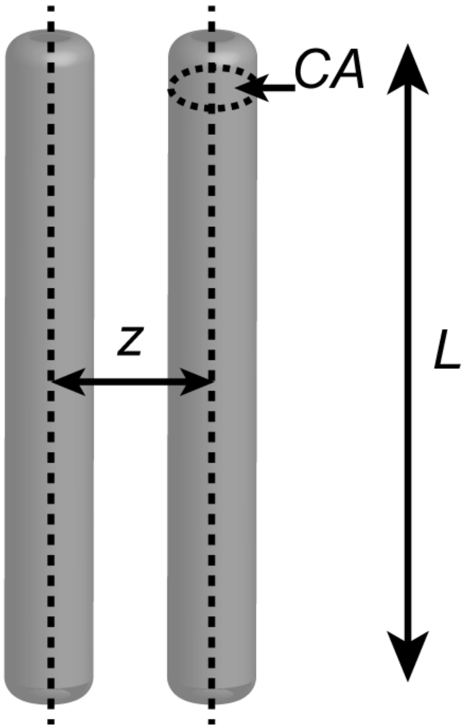
**where *R* is the nanoparticle radius and *d* is the distance of the closest approach**



# Van der Waals interactions between two neighboring nanorods

$$U_{rod-rod} = -\frac{3A_{rod-rod}}{8\pi}\frac{CA_{rod}{}^{2}}{z^{5}} \times L_{rod}$$

**where *z* is the center-to-center distance between two crystals, $CA_{rod}$ is the cross-sectional area of the rods, and *L* is the length of the crystals.**



# Van der Waals interactions between a nanorod and a spherical nanoparticle

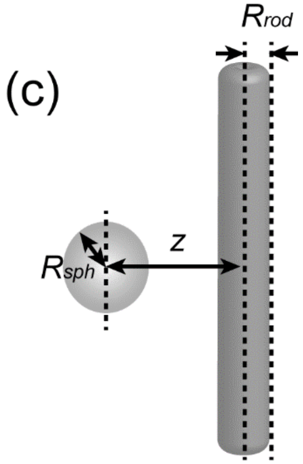
$$U_{rod-sph} = -\frac{A\pi}{8}\{\}$$

$$\{\} = \frac{R_{sph}{}^2 - (z+R_{rod})^2}{2(z+R_{rod}+R_{sph})^2} + \frac{-R_{sph}{}^2 + (z-R_{rod})^2}{2(z-R_{rod}+R_{sph})^2} - \frac{-R_{sph}{}^2 + (z-R_{rod})^2}{2(z-R_{rod}-R_{sph})^2} + \frac{-R_{sph}{}^2 + (z+R_{rod})^2}{2(z+R_{rod}-R_{sph})^2}$$

$$+ \frac{2z+2R_{rod}}{z+R_{rod}+R_{sph}} - \frac{2z+2R_{rod}}{z+R_{rod}-R_{sph}} + \frac{-2z+2R_{rod}}{z-R_{rod}+R_{sph}} + \frac{2z+2R_{rod}}{z+R_{rod}+R_{sph}}$$

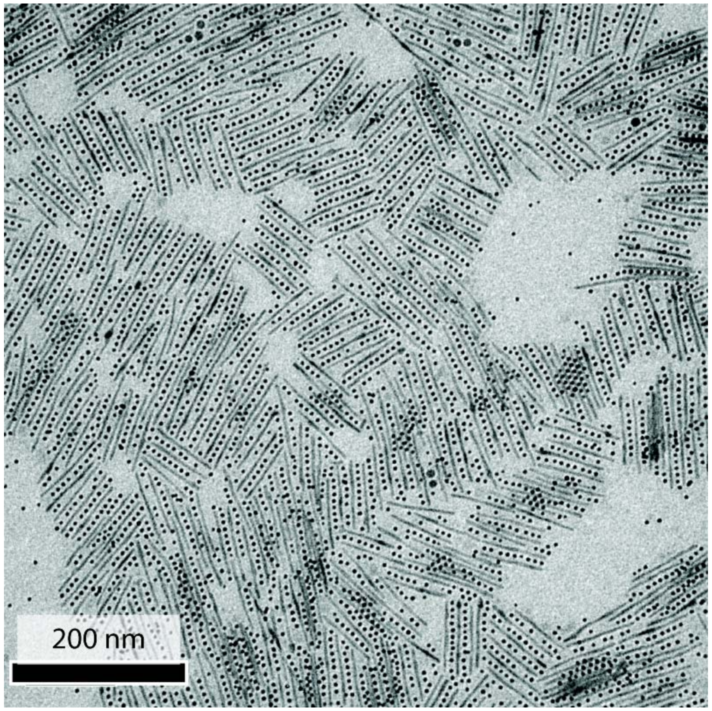
$$+ \ln\left(\frac{z+R_{rod}+R_{sph}}{z+R_{rod}-R_{sph}}\right) + \ln\left(\frac{z-R_{rod}-R_{sph}}{z-R_{rod}-R_{sph}}\right)$$

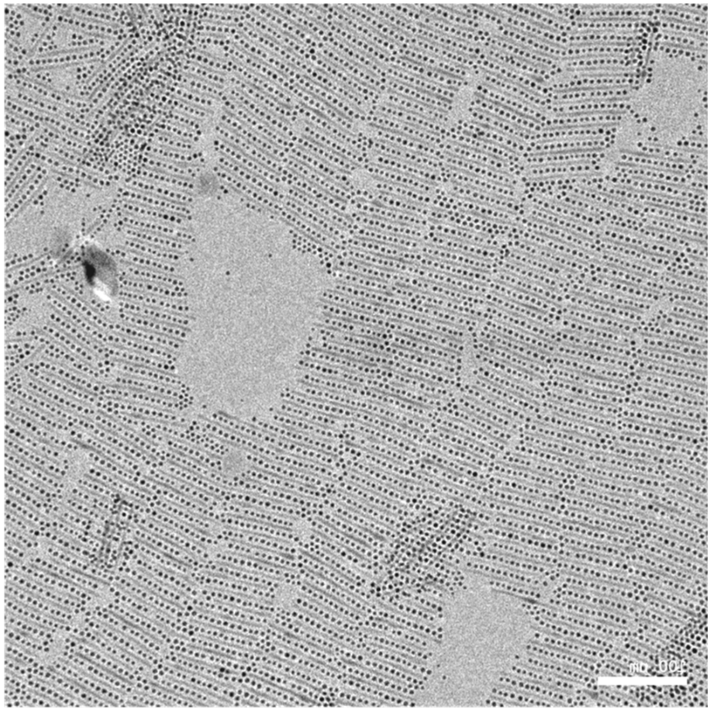
**where $L_{rod}$ is the length of the nanorods, $R_{rod}$ is the radius of the nanorods, $R_{sph}$ is the radius of the spherical crystals, and $z$ is the center-to-center distance.**



# Formation of Dot/Rod Assemblies

| | Gold-gold in toluene | Gold-gold in DDT | CdS-CdS in toluene | CdS-CdS in DDT | Gold-CdS in toluene | Gold-CdS in DDT |
|---|---|---|---|---|---|---|
| vdW (meV) | -10.7 | -11.6 | -3.95 | -6.43 | -23.1 | -30.4 |
| vdW (kT) | -0.416 | -0.452 | -0.153 | -0.249 | -0.895 | -1.18 |





# HOMEWORK DISCUSSION

8. Explain the mathematical physical basis for each of the following statement. Be as specific as possible in your answers, using equations where appropriate.

(a) Acetic acid ($CH_3COOH$) has much a higher boiling point and melting point than ethane ($CH_3CH_3$). (b) “like” dissolves “like”.

**10. Rank the following solvents in terms of their solubility for dimethyl sulfoxides ($\delta$ = 12.0 (cal/cm$^3$)$^{1/2}$): Water, Methanol, Cyclohexane, Carbon tetrachlotide. Use calculations to prove your answers.**

**11. Which solvent (water or benzene) has a higher solubility of trichloromethane ($\delta$ = 9.3) at 25 $^0$C? How do those results compare? Explain the results obtained.**

13. A solute with a value of $\delta = 14.3$ is to be extracted from water with carbon tetrachloride. The extraction is to be performed at 25 $^{o}$C. The molecular weight and density of the compound are 165 g/mol and 1.25 g/ml, respectively. Calculate the distribution coefficient for this compound.