Determination of Solubility Parameters using Inverse Gas Chromatography

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Overview

• Introduction
• Inverse Gas Chromatography
• Solubility Parameter
• Hansen Solubility Parameter
• Q&A
Spectroscopic techniques will normally yield analytical information on solid state materials such as what is present, where is it present and how much is present. This data contain little, if any, thermodynamic information.

The best techniques for determining surface thermodynamic and related physicochemical information about solid surfaces use vapour phase molecules as molecular probes for studying, in detail, gas-solid interactions – sorption techniques.
Advantages

Techniques that use vapour-phase probes offer a number of significant advantages over traditional analytical or spectroscopic approaches including:

• samples can be studied under real world conditions – ambient temperature and pressure;

• probe molecules can be chosen with chemical properties that are appropriate or relevant to the information required or problem to be addressed and may be site specific

• both bulk and surface properties can be elucidated as molecular probes can diffuse into materials giving an insight into internal molecular structure;

• vapour-phase molecular probes are extremely sensitive probes for determining the surface chemistry at sub-monolayer coverages for particulate materials;

• typically, both kinetic and equilibrium thermodynamic data can be obtained using molecular probe techniques.
The two main characterization techniques in current usage that use molecular vapour sorption approaches for characterizing solid state materials are dynamic vapour sorption (DVS) and inverse gas chromatography (iGC).

Surface Measurement Systems (SMS) is the World Leader Company in Sorption Science. SMS produces the first commercial iGC system and it is the lead company in dynamic sorption technique.
Inverse Gas Chromatography
Inverse Gas Chromatography (IGC) principles*: 1st developed in 1960’s.

The iGC-SEA system is the first commercial inverse Gas Chromatography technique. It is specially designed to determine the surface energy heterogeneity but nevertheless suitable to measure different surface and bulk properties of solid materials such as Adsorption isotherms, Heat of sorption, Glass Transition Temperature, Solubility Parameters and so on.
Analytical Gas Chromatography

INVERSE Gas Chromatography

Animation by L. Teng, Surface Measurement Systems
**iGC-SEA Introduction**

- **Gas phase injection** (like Headspace) - 12 vapor reservoirs (50 ml)

- **Carrier gas** is helium

- 2 column position oven design: **20 to 150 °C**

- **Background Humidity Controller**

- **Flame Ionization Detector (FID)**

- **User Friendly** Control and Analysis **Software**

**Safety Features:**

Hydrogen Leak & Organic Vapor Leak Detectors

- Carbon fiber
- Cotton
- Hair
- Granules
- Powder
- Medical metal implants
Unique Analysis Software (Cirrus Plus) for the quick sample analysis, which contains all the methods and theories.

The surface energy calculation based on surface coverage.
The IGC-SEA provides unique access to the following physico-chemical properties of a wide range of solid materials in a controlled humidity environment:

- Dispersive and Polar **Surface Energies**
- Heats and Entropies of Adsorption
- **Acid/Base** Interactions
- **BET** Specific Surface Area
- Phase Transitions
- Sorption **Isotherms**
- Permeability, Solubility and Diffusion
- Competitive (Multicomponent) Adsorption
- Thermodynamic Work of **Cohesion** and **Adhesion**
- Surface Energy **heterogeneity mapping**
- **Constantly extend the applications** – future applications e.g. Chemisorption
iGC Principle

Pack a column with the sample of interest

Select probes
- Non-polar solvent for the dispersive interaction
- Polar solvents for the specific interactions

Inject them at infinite and/or finite dilution

From the retention time the different physico-chemical properties can be determined
Benefits of iGC-SEA

- **2 column position** oven design - two sample can be prepared and can be run sequentially, automatically

- **No need** for outgassing facilities, since this will be achieved by conditioning the sample inside the column and flashing it with inert gas

- **Easier column packing** procedure due to the column is straight

- Precise and wide range of injectable amounts – **vapour phase injection** not liquid

- **Automatic** injection system and automatic calculation

- **Excellent reproducibility** (RSD 1% for surface energy)
The Solubility Parameter is directly related to the cohesion energy density and therefore stability of a material:

$$\delta = \left( \frac{\Delta E_{vap}}{V_m} \right)^{1/2} = \left( \frac{\Delta H_{vap} - RT}{V_m} \right)^{1/2} = CED^{1/2}$$

Applications:
- Drug delivery
- Formulation
- Storage stability
- Coatings
- Polymer compatibility
- Optimising solvent selection for nanoparticle preparation

Application of the Hildebrandt theory in combination with Flory-Huggins concept

• Determination of the Activity Coefficient $\Omega$ from the ret.-volume $V_N$

$$\ln \Omega = \ln \left[ \frac{273.15 \cdot R}{P_0 \cdot MW \cdot V_N} \cdot 10^6 \right] - \frac{P_0 \cdot (B_{11} - V_m)}{R \cdot T \cdot 10^6}$$

• Calculation of the Flory-Huggins interaction parameter $\chi$

$$\chi = \ln \Omega + \ln \left[ \frac{D_1}{D_2} \right] - \left[ 1 - \left( \frac{V_{m1}}{V_{m2}} \right) \right]$$
Solubility Parameter

Variation of probe molecule or temperature

- **Guilett Approach:**
  \[
  \frac{\delta_1^2}{RT} - \frac{\chi}{V_1} = \left(\frac{2\delta_2}{RT}\right) \cdot \delta_1 - \left(\frac{\delta_2^2}{RT} - \frac{\chi_S}{V_1}\right)
  \]

- **Benczedi Approach:**
  \[
  \delta_2 = \delta_1 - \left[R \cdot \frac{\partial (\chi^\infty / V_1)}{\partial (1/T)}\right]^{1/2}
  \]

**Solubility Parameter for Starch:**

22.6 MPa^{1/2}

(measured between 373 K and 433 K)
**“Hildebrandt” Sol. Parameter for PMMA:**

19.08 MPa$^{1/2}$

(measured at 363 K with Undecane, Decane, Nonane, Octane, Heptane, Dichloromethane, 1-Butanol, Ethyl Acetate, 1,4-Dioxane)

**Literature value:** 17.4 – 21.3 MPa$^{1/2}$
Hansen Solubility Parameters

Dispersive component:
Solvents: Alkanes

\[ \delta_d = \frac{\text{slope}_{\text{alkanes}} \cdot R \cdot T}{2} \]

Polar component:
Solvents: Aromatic hydrocarbons, Ketones, Nitropropane

\[ \delta_p = \frac{(\text{slope}_{\text{polar}} - \text{slope}_{\text{alkanes}}) \cdot R \cdot T}{2} \]

Hydrogen Bonding component:
Solvents: Alcohols, Pyridine

\[ \delta_h = \frac{(\text{slope}_{\text{alcohols}} - \text{slope}_{\text{alkanes}}) \cdot R \cdot T}{2} \]
Hansen Solubility Parameters

\[ \delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \]

“Hansen” Total Sol. Parameter for Polymer X:

22.13 MPa\(^{1/2}\)

Literature: 19.30 MPa\(^{1/2}\)

(measured at 343 K with 32 solvents)
Relationship between oral absorption in humans and solubility parameters

‘Solubility parameter and oral absorption’


Correlation between release rate of chlorohexidine from ethylcellulose films and solubility parameters

‘Casting solvent controlled release of chlorhexidine from ethylcellulose films prepared by solvent evaporation’


**SMS Ref.:** Application Note 205 IGC Solubility Starch

**SMS User’s Publication:** Journal of Chromatography A, 1216 (2009) 1551–1566, A. Voelkel, Inverse gas chromatography as a source of physiochemical data

Thank you for your attention!
Any questions or thoughts?