

Module 3: "Components of Surface Energy"

Lecture 14: ""

The Lecture Contains:

- ☰ Surface Energy
- ☰ Spcial Cases

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Surface Energy

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \quad (3.20)$$

On the RHS, the first term is the apolar (or nonpolar) component and the latter is the polar component.

1. Lifshitz-van der Waals (LW) interactions

The LW component has contribution from the van der Waals (or dispersion) forces. These forces are always attractive in nature.

2. Acid-Base (A-B) interactions

The A-B component has contributions from the following interactions.

(i) Hydrogen bonding

This occurs in the case of Bronsted acid and bases. A Bronsted acid (or H^+ donor) is a compound having the ability to donate a proton (H^+) e.g. $CHCl_3$. And a Bronsted base (or H^+ acceptor) is a compound having the ability to accept a proton. e.g. ketones. The proton donor and acceptor capabilities are measured by the magnitude of γ^+ and γ^- , respectively.

Both characteristics might be present within the molecule leading to H-bonding with its own molecules.

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(ii) Lewis Acid-Base

A Lewis acid (or electron acceptor) is a substance which can accept an electron. A Lewis base (or electron donor) is a substance that can donate an electron. The electron acceptor and donor capabilities are measured by the magnitude of γ^+ and γ^- , respectively.

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-}$$

$$\gamma_{ij} = \gamma_{ij}^{LW} + \gamma_{ij}^{AB} \quad (4.2)$$

$$\gamma_{ij}^{LW} = \gamma_i^{LW} + \gamma_j^{LW} - 2\sqrt{\gamma_i^{LW} \gamma_j^{LW}} = \left(\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}} \right)^2 \quad (4.3)$$

$$\gamma_{ij}^{AB} = 2 \left(\sqrt{\gamma_i^+ \gamma_i^-} + \sqrt{\gamma_j^+ \gamma_j^-} - \sqrt{\gamma_i^+ \gamma_j^-} - \sqrt{\gamma_j^+ \gamma_i^-} \right) \quad (4.4)$$

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These can be used in Young's equation.

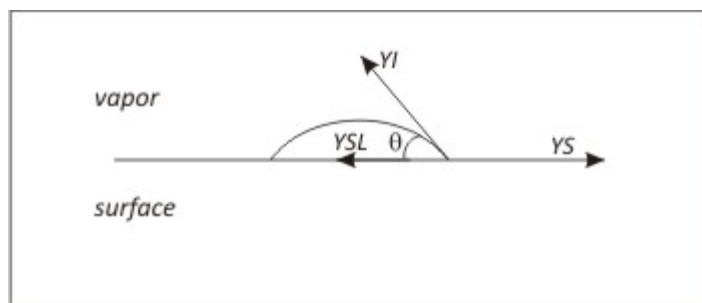


Fig. 4.1: A liquid drop on a surface

$$\gamma_l \cos \theta + \gamma_{sl} = \gamma_s$$

$$\gamma_l \cos \theta + \left(\gamma_s + \gamma_l - 2\sqrt{\gamma_s^{LW}\gamma_l^{LW}} - 2\sqrt{\gamma_s^+\gamma_l^-} - 2\sqrt{\gamma_s^-\gamma_l^+} \right) = \gamma_s$$

$$\gamma_l (\cos \theta + 1) = 2 \left(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^+\gamma_l^-} + \sqrt{\gamma_s^-\gamma_l^+} \right) \quad (4.5)$$

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$$\cos \theta \in (-1, 1)$$

If after solving the Young's equation we get $\cos \theta < -1$, it means that $\theta = 180^\circ$

If we get $\cos \theta > 1$, $\theta = 0^\circ$.

If $\theta = 0$, theoretically it would spread into a monolayer. But this is true only for van der Waals liquids.

There are six parameters for two materials, viz., γ^{LW} , γ^+ and γ^- for each of the two materials. These are to be determined. But before that, we consider the following special cases.

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Special Cases

1. Apolar liquids $\gamma_l^+ = \gamma_l^- = 0$

Examples of apolar liquids are low molecular weight oils like hexane, decane, and octane.

$$\Rightarrow \gamma_l = \gamma_l^{LW}$$

$$\Rightarrow \gamma_l^{LW}(1 + \cos \theta) = 2\sqrt{\gamma_s^{LW}\gamma_l^{LW}}$$

$$\Rightarrow \cos \theta = 2\sqrt{\gamma_s^{LW}/\gamma_l^{LW}} - 1$$

2. Polar liquids (e.g. water) on apolar surface (e.g. Teflon)

$$\cos \theta = 2\sqrt{\gamma_s^{LW}/\gamma_l^{LW}} \left(\gamma_l^{LW}/\gamma_l^{LW} \right) - 1$$

Teflon is a low surface tension material and so is polyethylene (though it sometimes has a small residual polarity).

If $\gamma_l > \gamma_l^{LW}$ the contact angle would increase. This would mean that the surface is a hydrophobic surface.

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3. Mono-polar surface (γ^-) and monopolar liquid (γ_s^-, γ_l^-), i.e. ($\gamma_s^+ \approx 0, \gamma_l^+ \approx 0$)

Usually only electron donor polarity is observed.

$$\gamma_l^{LW}(1 + \cos \theta) = 2 \sqrt{\gamma_s^{LW} \gamma_l^{LW}}$$

This is similar to the case where there was an apolar liquid on a surface. This is because for AB interactions to have any significance, both the conjugate interactions should be present.

Some numbers have been presented below for better understanding.

1. Monopolar surfaces ($\gamma^+ \approx 0$)

Table 4.1:

Substance	γ^-	γ^{LW}
DMSO	35	41
Benzene	1.9	28.9
Toluene	1.6	28.5

Gelatin, PMMA, PVA, dextran, PEG, serum, albumin, and agarose are some other examples of important monopolar liquids.

2. Apolar and liquids having both electron donor and acceptor capabilities

Table 4.2:

Substance	γ^{LW}	γ^-	γ^+	γ^{total}
Water	21.8	25.5	25.5	72.8
glycerol	34	57.4	3.92	64
Formamide	39	39.6	2.28	58
Diiodomethane	50.8	-	-	50.8
α -bromonaphthalene	44.4	-	-	44.4

Note: It might appear that glycerol is monopolar with electron donor capability as γ^-/γ^+ is quite high for it. But it is not so, because the product $\gamma^- \gamma^+$ is comparable to γ^{LW} in magnitude.

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We can make use of these known values to measure the values of γ^{LW} , γ^+ and γ^- for unknown surfaces.

To do this, we take 3 liquids, with at least two of them polar, and put a drop of each of these liquids on the surface. These liquids are called probe liquids. We measure the contact angle of these drops with the surface and then use Young's equation. The device used to measure the contact angle is called a goniometer.

We now have 3 unknowns and 3 equations which can be solved to obtain γ^{LW} , γ^+ and γ^- for the surface. But there is a problem with this procedure.

It has been found that it is the advancing rather than receding equilibrium contact angle that should be measured. This is because when receding equilibrium contact angle is measured, the surface has already been contaminated by the probing liquid.


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But even if we measure the receding contact angle, the parameter estimates would still be inaccurate. This is because the surface properties get modified as soon as a liquid drop is put on it. And by measuring the contact angles it is the property of modified surface we are estimating instead of that of the native surface. Further, the surrounding vapor also has a significant effect. Some surfaces might even chemically react with the probe liquid. For example, bio-surfaces are extremely fragile and might even solubilize when brought in contact with a liquid.

Having measured the three surface properties, the total interfacial tension for that surface can be computed. Further the contact angle a liquid makes with the surface can also be computed from the Young's equation.

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