Molecular Interface Zone (phase?) Structures and Contact Angles on Organic Solids

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I. Molecular Structure Gradients at Liquid-Solid Interfaces:

- *"Acid-Base" + Dispersion*. Functionally-terminated C-16 SAMs + pendant-group polymers.
- Inverse adhesion work: donor-acceptor *vs* dispersion correlations.

  electronic density shifts and amphoteric structure gradients?
- SAMs as models for polymers?

II. Wetting Correlations in Controlled Coverage Alkyl Chain Monolayers:

Dispersion Forces Wetting as a measure of surface phases in CH_3-terminated C-18 SAMs?

Major points in wetting (already appreciated by many)

1. **Wetting (molecular liq/solid) interfaces are not sharp at molecular scale**

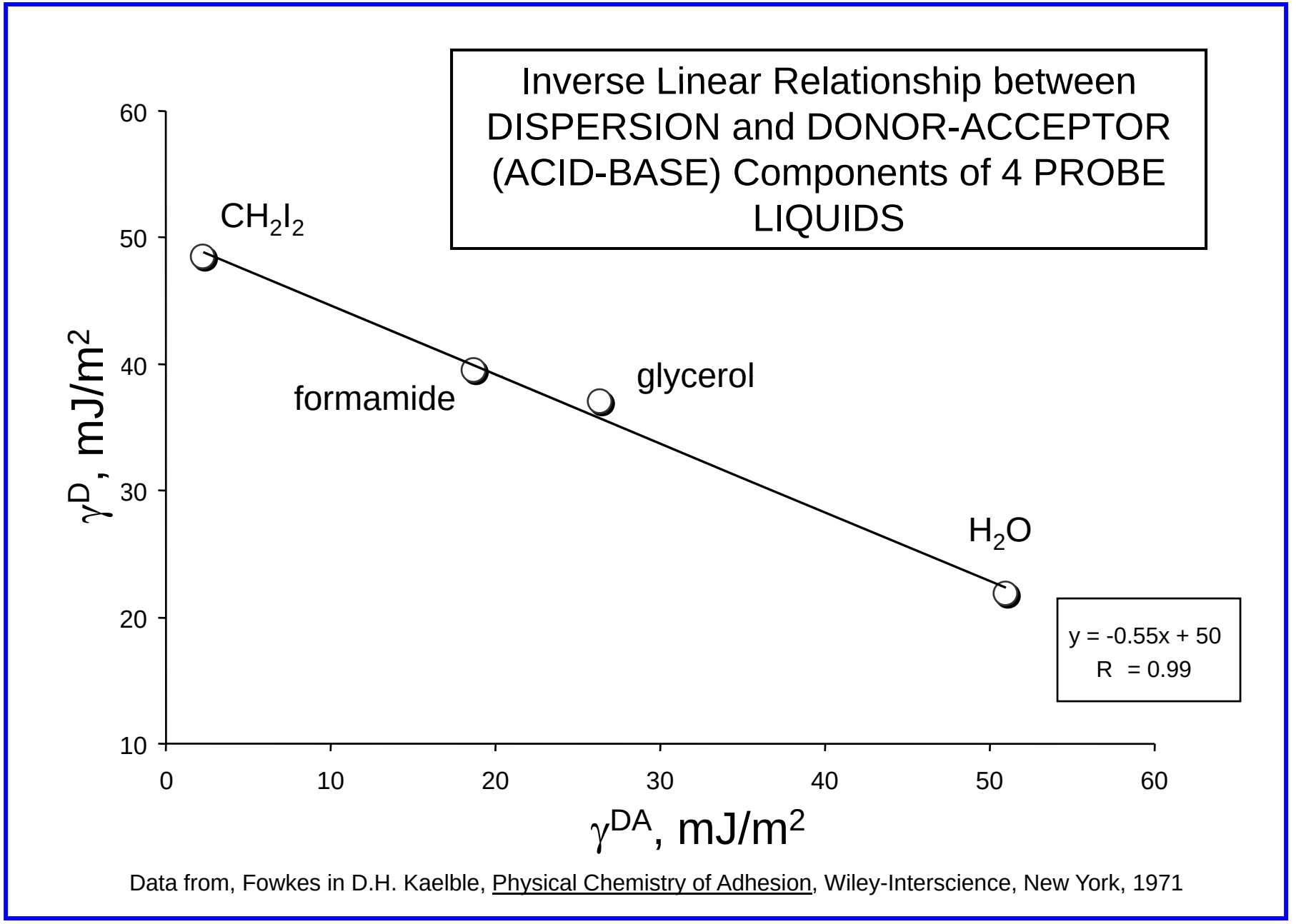
2. **Transition zones appear at interface**

3. **Relaxation in transition zone for soft structures**
   - **Nuclear restructuring**
     - **Position**
     - **Orientation**
   - **Electron density shifts**

4. **Inverse relationship (conjugate) between long range, polarization (dispersion) and short range (chemical / donor-acceptor) forces**

Interesting observation of literature wetting data

“inverse” dispersion – donor acceptor correlation



Data from, Fowkes in D.H. Kaelble, Physical Chemistry of Adhesion, Wiley-Interscience, New York, 1971

Using Well-Defined Terminally Functionalized Self-Assembled Monolayers (SAMS) to Test the *Inverse* Relationship

Strategy

- Correlate W_{AB} and W_D values for the range of surfaces
- Use CH_2I_2 (DIM) for dispersion work of adhesion (W_D)
- Proposed method to separate donor-acceptor and dispersion contributions using other probe measurements
- Correlate W_{AB} and W_D values for the range of surfaces

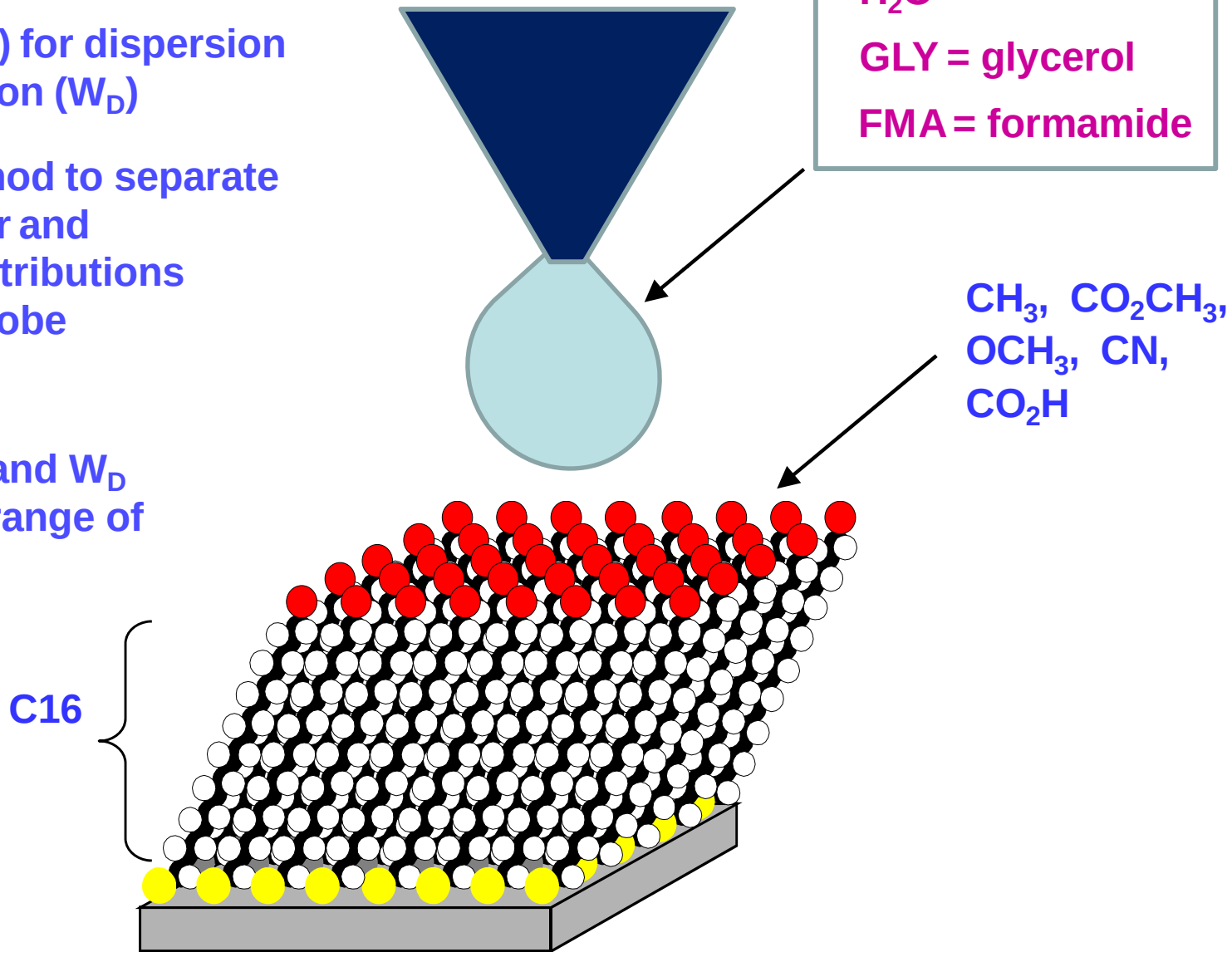
DIM = CH_2I_2

H_2O

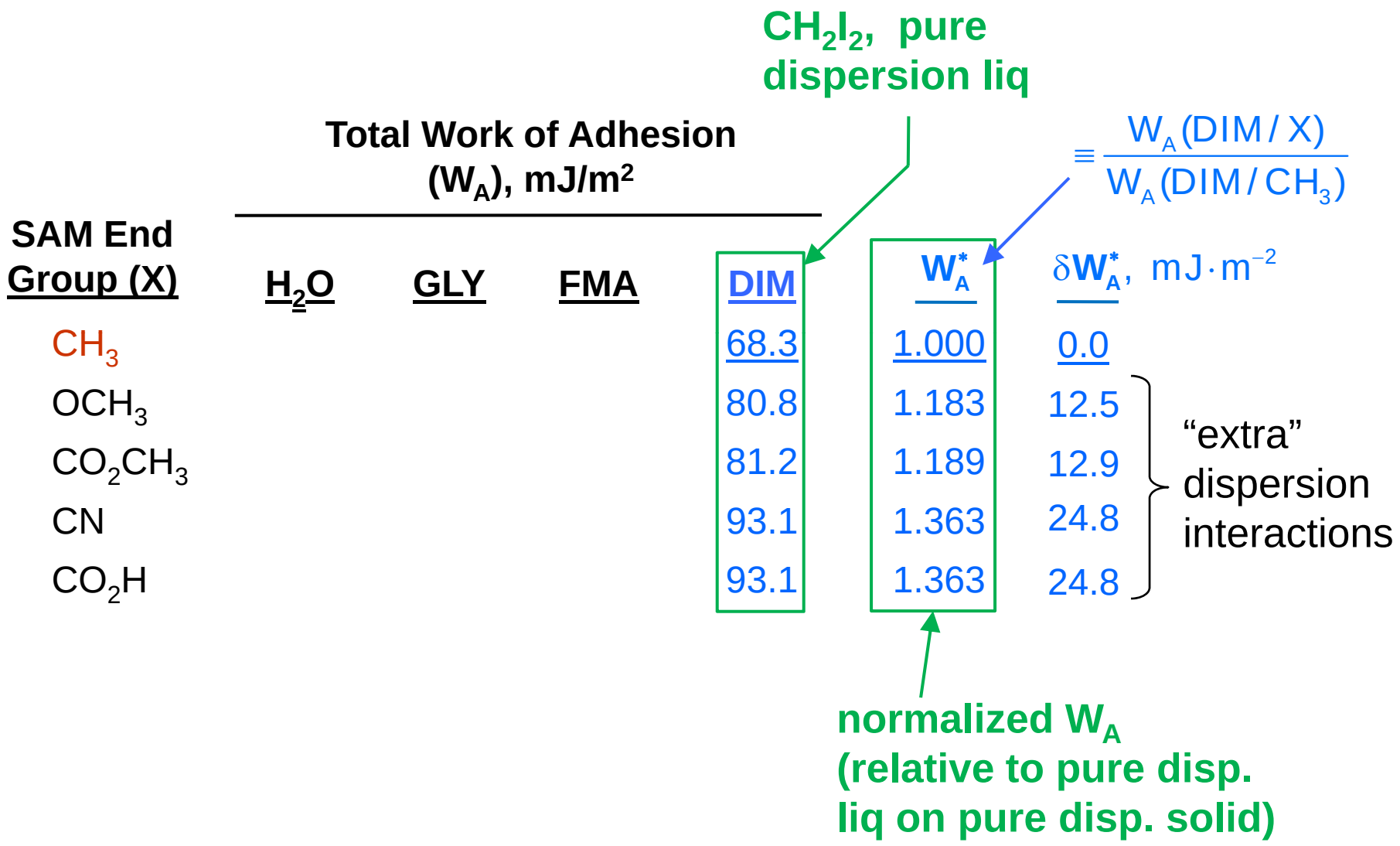
GLY = glycerol

FMA = formamide

CH_3, CO_2CH_3, OCH_3, CN, CO_2H



Data Analysis for SAMs



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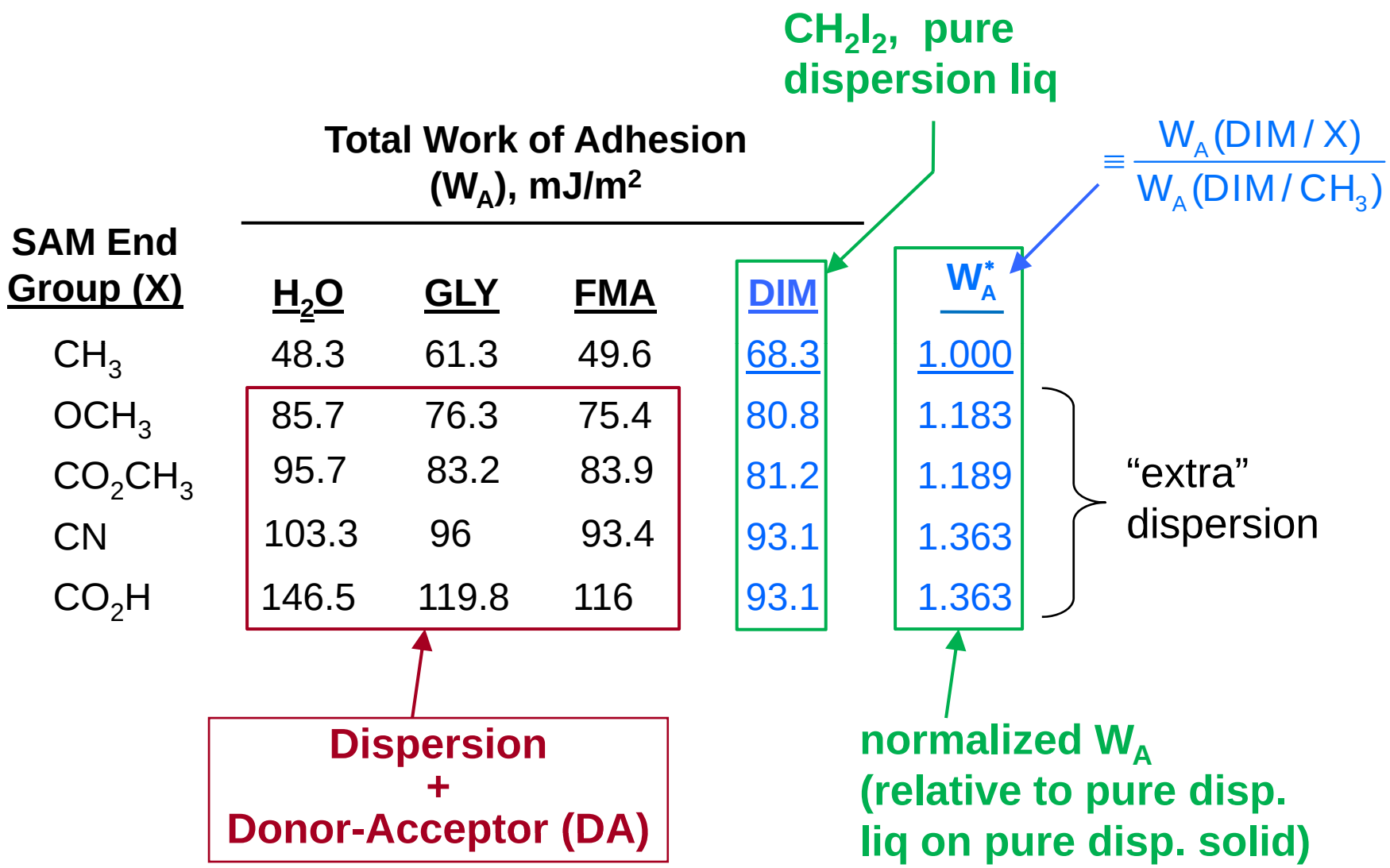


Use W_A^* to Break W_A for Each Liquid into The "Core" Dispersion Component and the Conjugate Donor-Acceptor Component for SAM Terminal Group X

1.) Define $W_A^{CD}(liq/X)$

$$\frac{W_A^{CD}(liq/X)}{W_A(liq/X)} = \frac{W_A(DIM/CH_3)}{W_A(DIM/X)} \equiv W_A^*$$

$$W_A^{CD}(liq/X) \equiv \frac{W_A(liq/X)}{W_A^*}$$

2.) Assert: $W_A^{CD}(liq/X) \sim W_A^{D}(liq/X)$

3.) Calculate $W_A^{DA}(liq/X)$

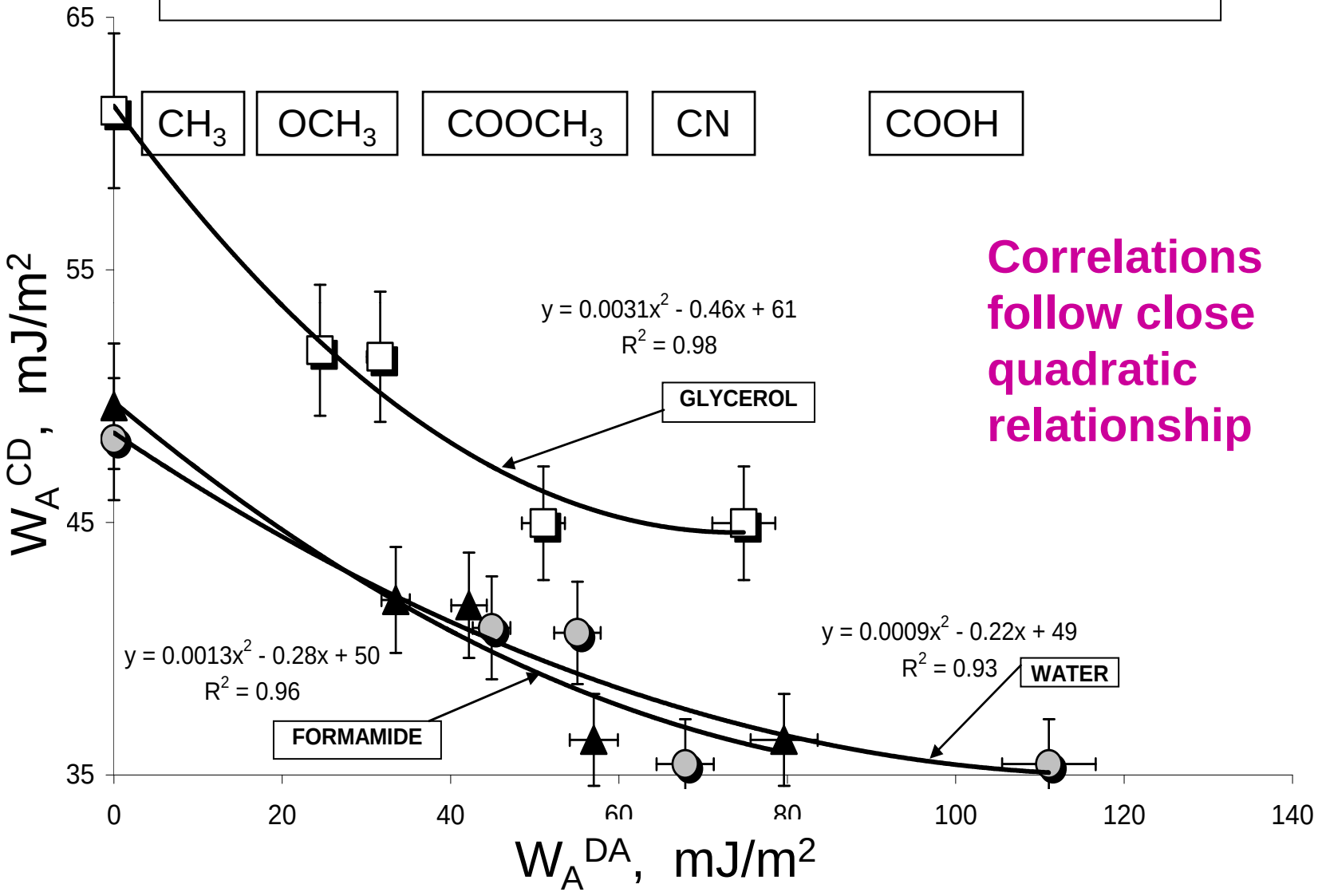
$$W_A(X) = W_A^{CD}(liq/X) + W_A^{DA}(liq/X)$$

Conjugate DA component

Results

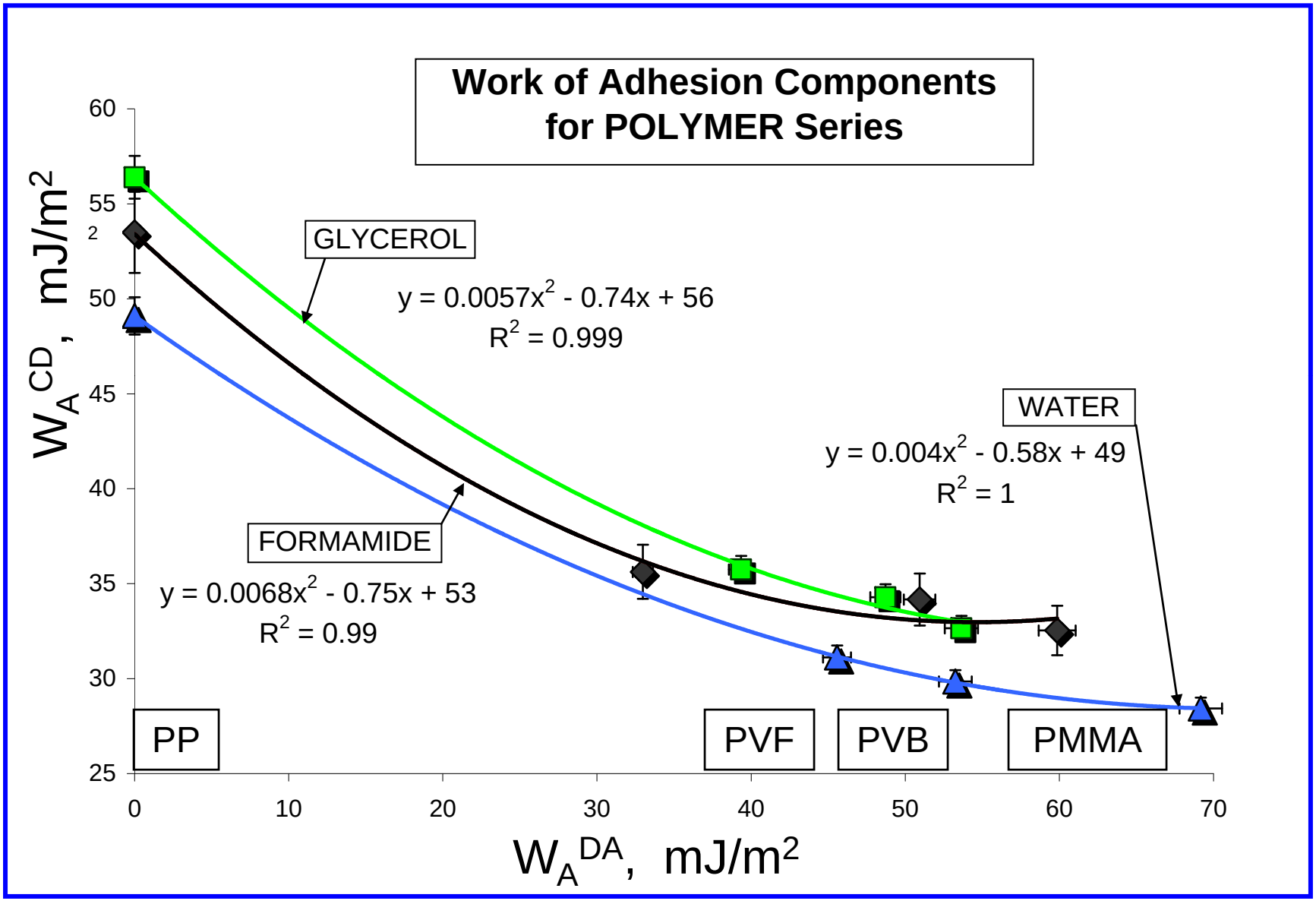
X	"Core" Dispersion Component $\left[W_A^{CD}(liq/X)\right]$ (mJ/m^2)			Component due to X capable of Donor-Acceptor Components $\left[W_A^{DA}(liq/X)\right]$ (mJ/m^2)		
	H_20	GLY	FMA	H_20	GLY	FMA
CH_3	48.3	61.3	49.6	0.0	0.0	0.0
OCH_3	40.8	51.8	41.9	44.9	24.5	33.5
CO_2CH_3	40.6	51.6	41.7	55.1	31.6	42.2
CN	35.4	45.0	36.4	67.9	51.0	57.0
CO_2H	35.4	45.0	36.4	111.1	74.8	79.6

DISPERSION *versus* DONOR-ACCEPTOR COMPONENTS
of ***SAM*** WORK of ADHESION



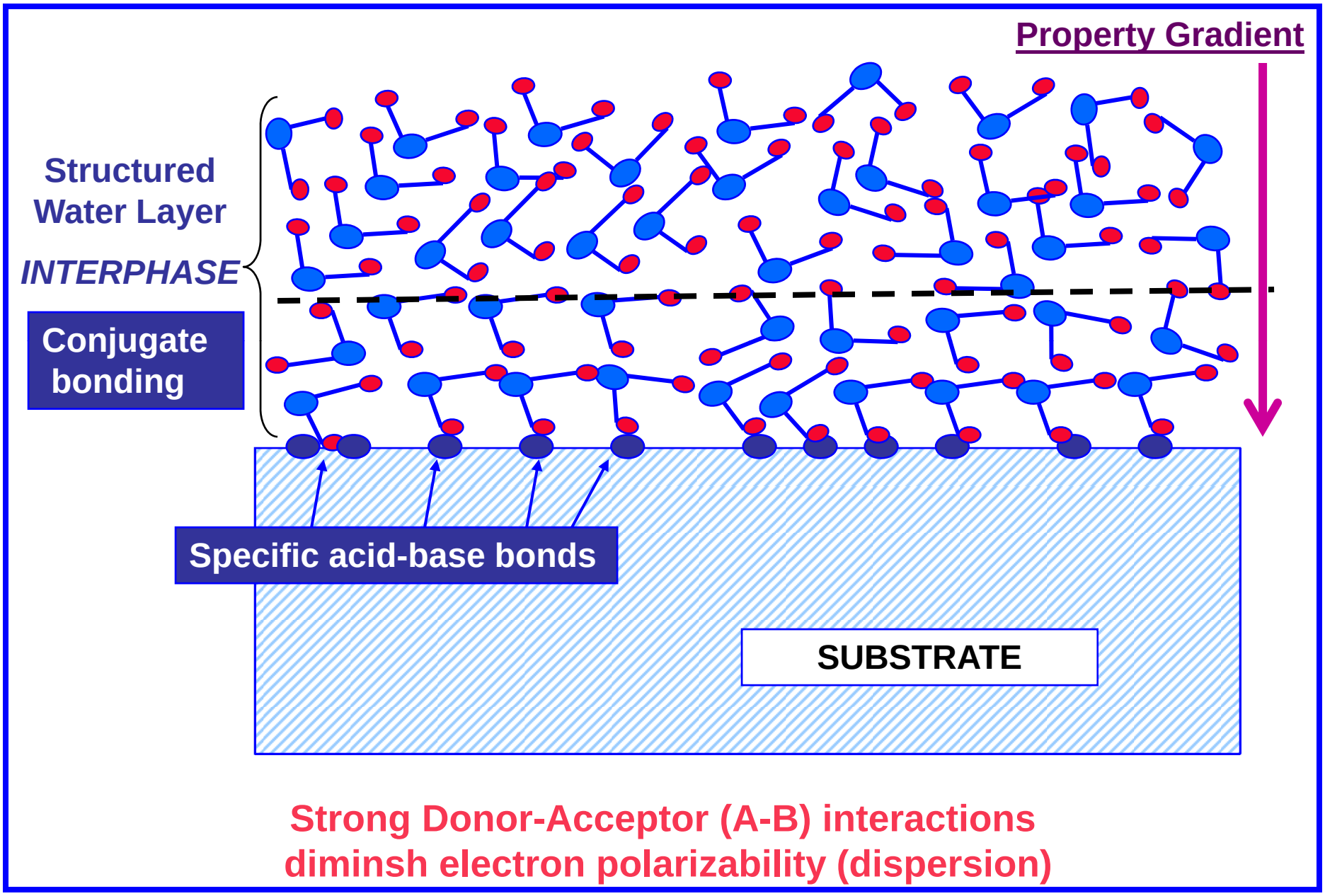
Correlations follow close quadratic relationship

Using literature values for polymers



Data taken from: C. Della Volpe, et al., *J. Adhesion Sci. Technol*. **17**, 1425 (2003), **and reanalyzed**.

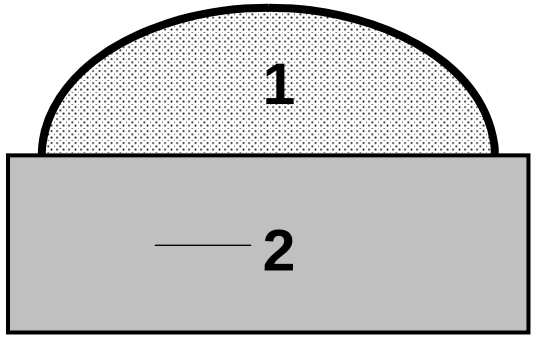
Interface Zone Nuclear and Electronic Gradients



Strong Donor-Acceptor (A-B) interactions diminsh electron polarizability (dispersion)

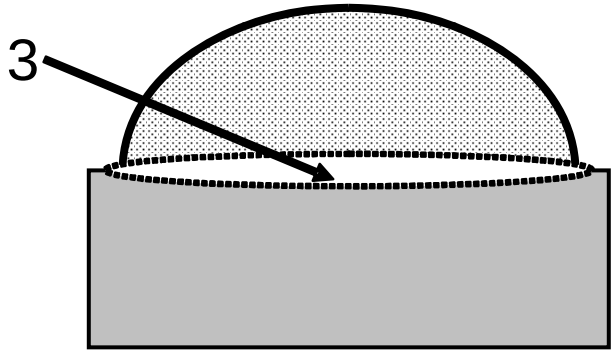
HAMAKER CONSTANTS

Interface line



$$A_{12} = (A_{11} \times A_{22})^{1/2}$$

Molecular Interface Zone



$$A_{123} = (A_{11}^{1/2} - A_{33}^{1/2})(A_{22}^{1/2} - A_{33}^{1/2})$$

CONCLUSIONS

- Interfacial ZONE exists in L/S & L/L cases
- unique structure, electron density and nuclear properties from spectroscopy (literature --- SFG, SFG, etc.)
- Often an average between bulk phases
- Hamaker relations w/A_{33} are 1/quadratic
- W^{D} shows 1/quadratic relationship to W^{DA} for both SAMs and Polymers