

# 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:

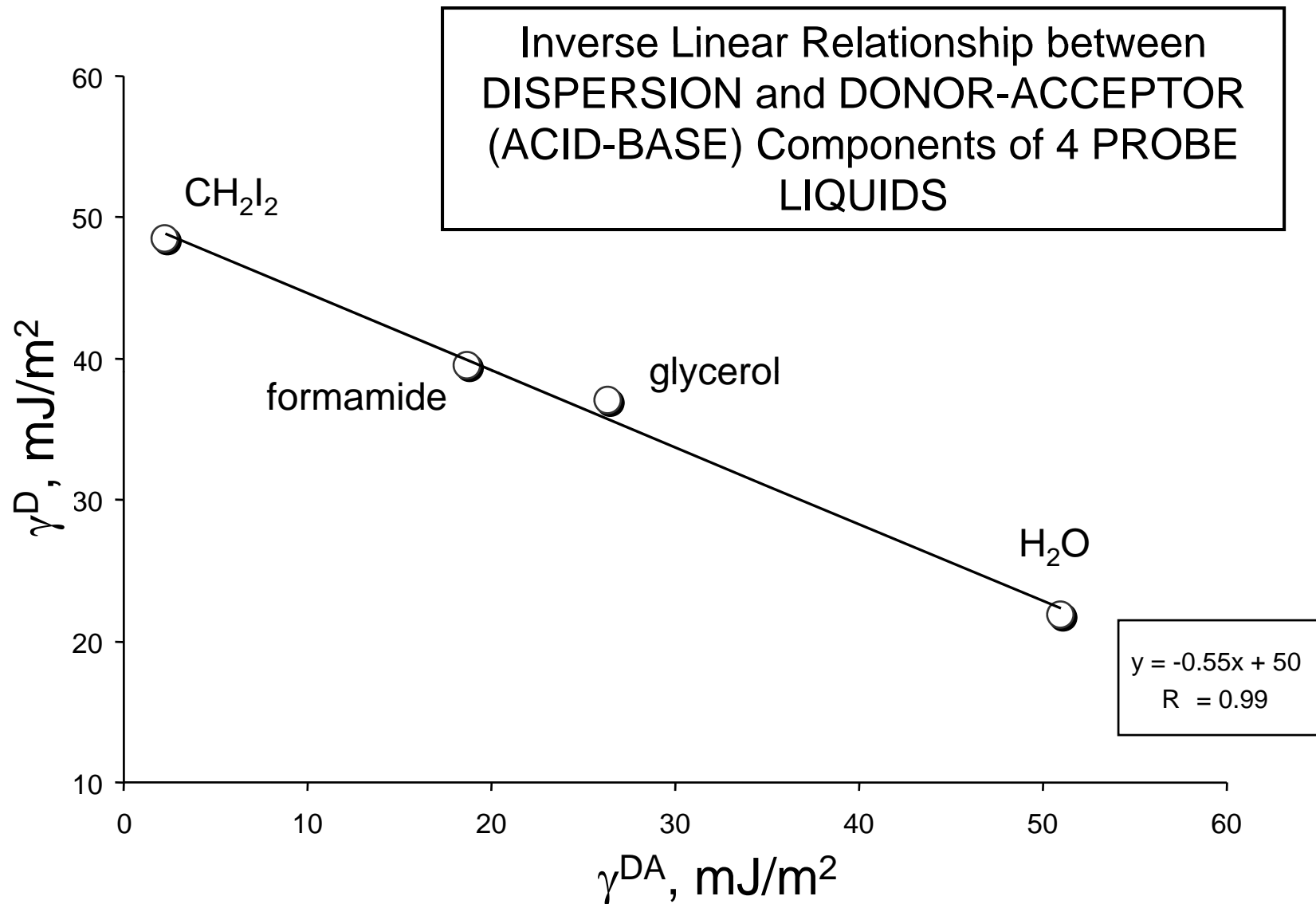
Dispersion Forces Wetting as a measure of surface phases in CH<sub>3</sub>-terminated C-18 SAMs?

## **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  $\text{CH}_2\text{I}_2$  (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 =  $\text{CH}_2\text{I}_2$

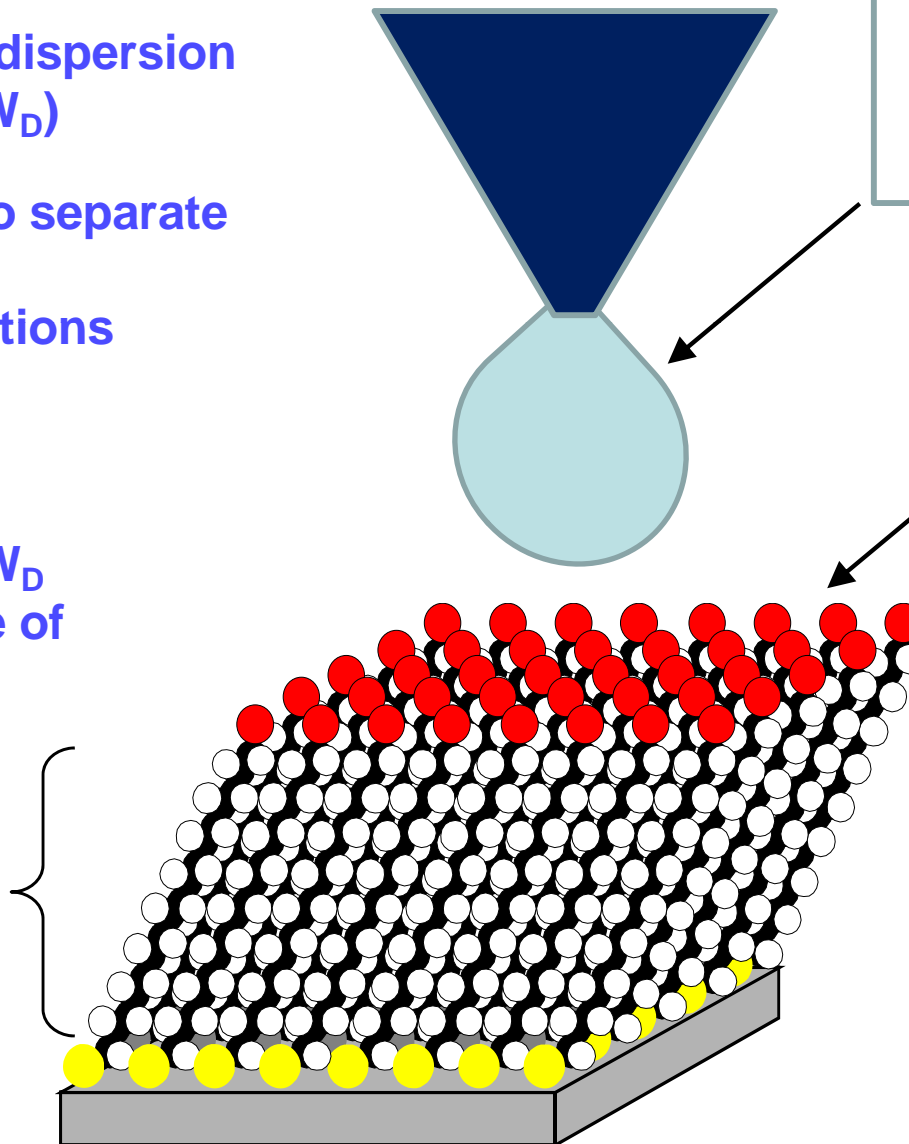
$\text{H}_2\text{O}$

GLY = glycerol

FMA = formamide

$\text{CH}_3$ ,  $\text{CO}_2\text{CH}_3$ ,  
 $\text{OCH}_3$ ,  $\text{CN}$ ,  
 $\text{CO}_2\text{H}$

C16



# Data Analysis for SAMs

**CH<sub>2</sub>I<sub>2</sub>, pure dispersion liq**

**Total Work of Adhesion (W<sub>A</sub>), mJ/m<sup>2</sup>**

SAM End Group (X)	<b>Total Work of Adhesion (W<sub>A</sub>), mJ/m<sup>2</sup></b>			<b>DIM</b>	<b>W<sub>A</sub><sup>*</sup></b>	<b>ΔW<sub>A</sub><sup>*</sup>, mJ·m<sup>-2</sup></b>	
	<b>H<sub>2</sub>O</b>	<b>GLY</b>	<b>FMA</b>				
<b>CH<sub>3</sub></b>				<u>68.3</u>	<u>1.000</u>	<u>0.0</u>	} "extra" dispersion interactions
OCH <sub>3</sub>				80.8	1.183	12.5	
CO <sub>2</sub> CH <sub>3</sub>				81.2	1.189	12.9	
CN				93.1	1.363	24.8	
CO <sub>2</sub> H				93.1	1.363	24.8	

$$\equiv \frac{W_A(\text{DIM}/X)}{W_A(\text{DIM}/\text{CH}_3)}$$

**normalized W<sub>A</sub> (relative to pure disp. liq on pure disp. solid)**

# Data Analysis for SAMs

**Total Work of Adhesion ( $W_A$ ), mJ/m<sup>2</sup>**

<b>SAM End Group (X)</b>	<b>Total Work of Adhesion (<math>W_A</math>), mJ/m<sup>2</sup></b>			<b>DIM</b>	<b><math>W_A^*</math></b>
	<b>H<sub>2</sub>O</b>	<b>GLY</b>	<b>FMA</b>		
CH <sub>3</sub>	48.3	61.3	49.6	68.3	1.000
OCH <sub>3</sub>	85.7	76.3	75.4	80.8	1.183
CO <sub>2</sub> CH <sub>3</sub>	95.7	83.2	83.9	81.2	1.189
CN	103.3	96	93.4	93.1	1.363
CO <sub>2</sub> H	146.5	119.8	116	93.1	1.363

**CH<sub>2</sub>I<sub>2</sub>, pure dispersion liq**

$$\equiv \frac{W_A(\text{DIM}/X)}{W_A(\text{DIM}/\text{CH}_3)}$$

**“extra” dispersion**

**Dispersion + Donor-Acceptor (DA)**

**normalized  $W_A$  (relative to pure disp. liq on pure disp. solid)**

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  $W_A^{CD}(\text{liq}/X)$

$$\frac{W_A^{CD}(\text{liq}/X)}{W_A(\text{liq}/X)} = \frac{W_A(\text{DIM}/\text{CH}_3)}{W_A(\text{DIM}/X)} \equiv W_A^*$$

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

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

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

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

↑  
Conjugate DA component

## Results

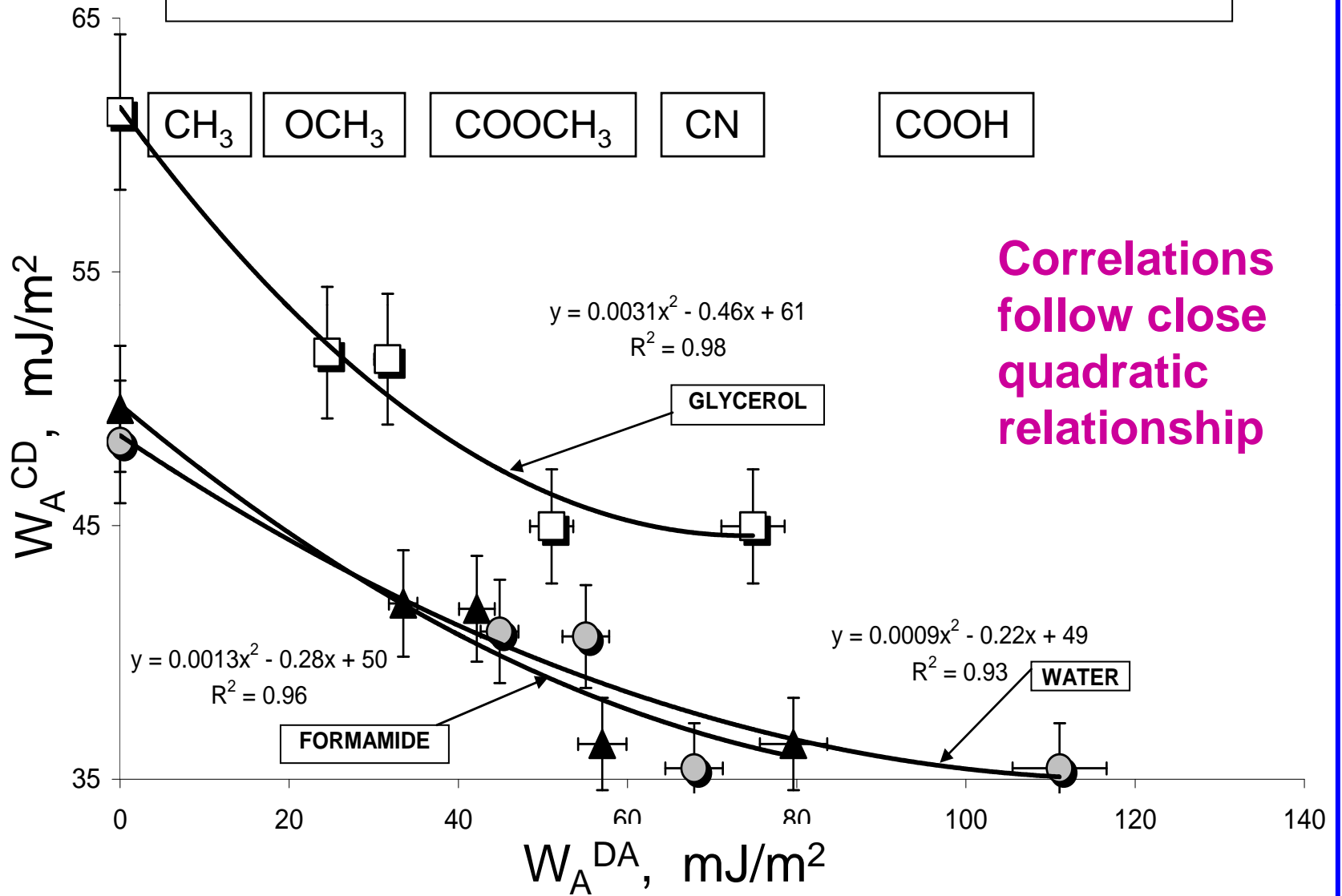
“Core” Dispersion Component  
 $[W_A^{CD} (\text{liq}/X)]$  (mJ/m<sup>2</sup>)

<u>X</u>	<u>H<sub>2</sub>O</u>	<u>GLY</u>	<u>FMA</u>
CH <sub>3</sub>	48.3	61.3	49.6
OCH <sub>3</sub>	40.8	51.8	41.9
CO <sub>2</sub> CH <sub>3</sub>	40.6	51.6	41.7
CN	35.4	45.0	36.4
CO <sub>2</sub> H	35.4	45.0	36.4

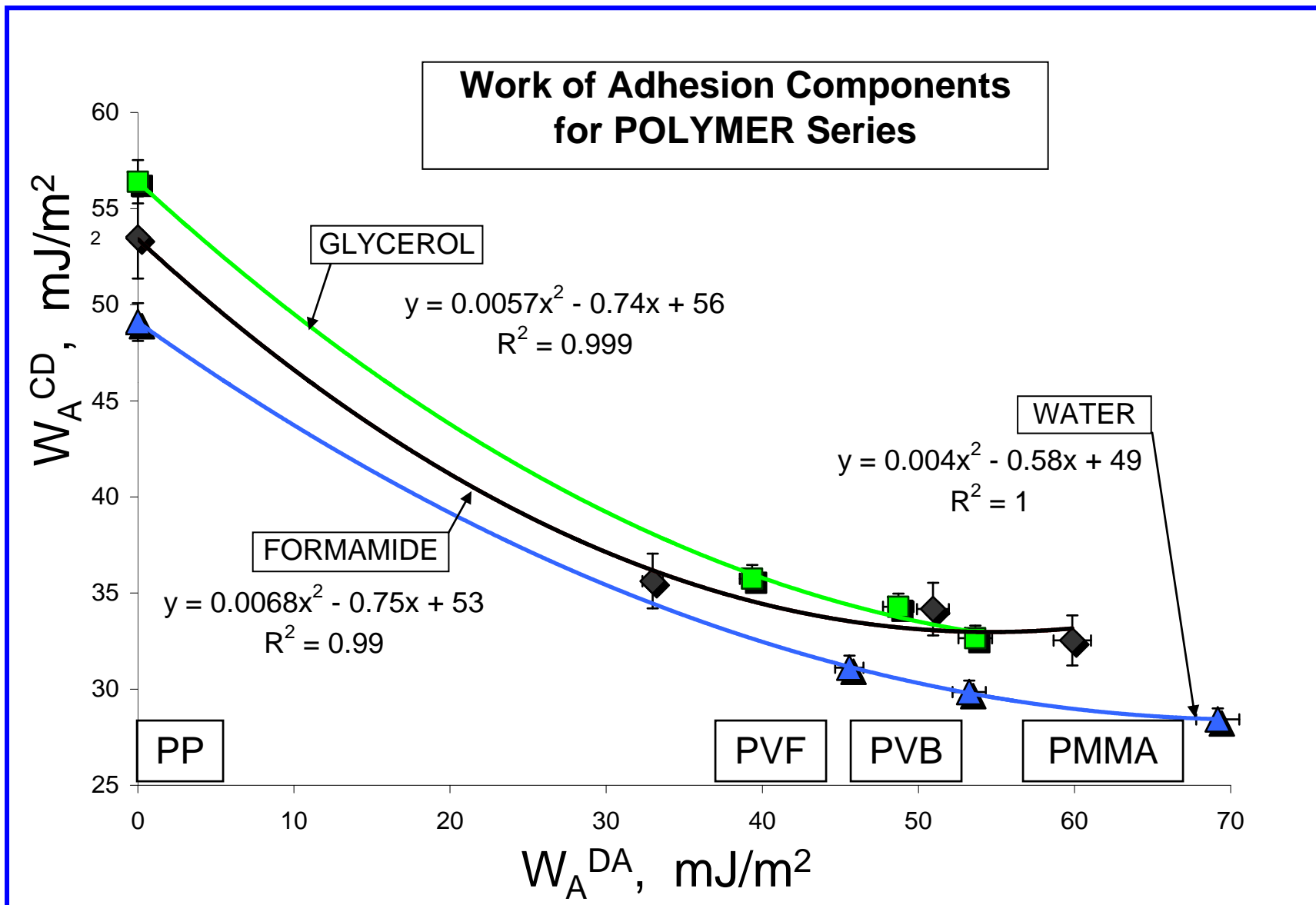
Component due to X capable of  
Donor-Acceptor Components  
 $[W_A^{DA} (\text{liq}/X)]$  (mJ/m<sup>2</sup>)

<u>H<sub>2</sub>O</u>	<u>GLY</u>	<u>FMA</u>
0.0	0.0	0.0
44.9	24.5	33.5
55.1	31.6	42.2
67.9	51.0	57.0
111.1	74.8	79.6

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

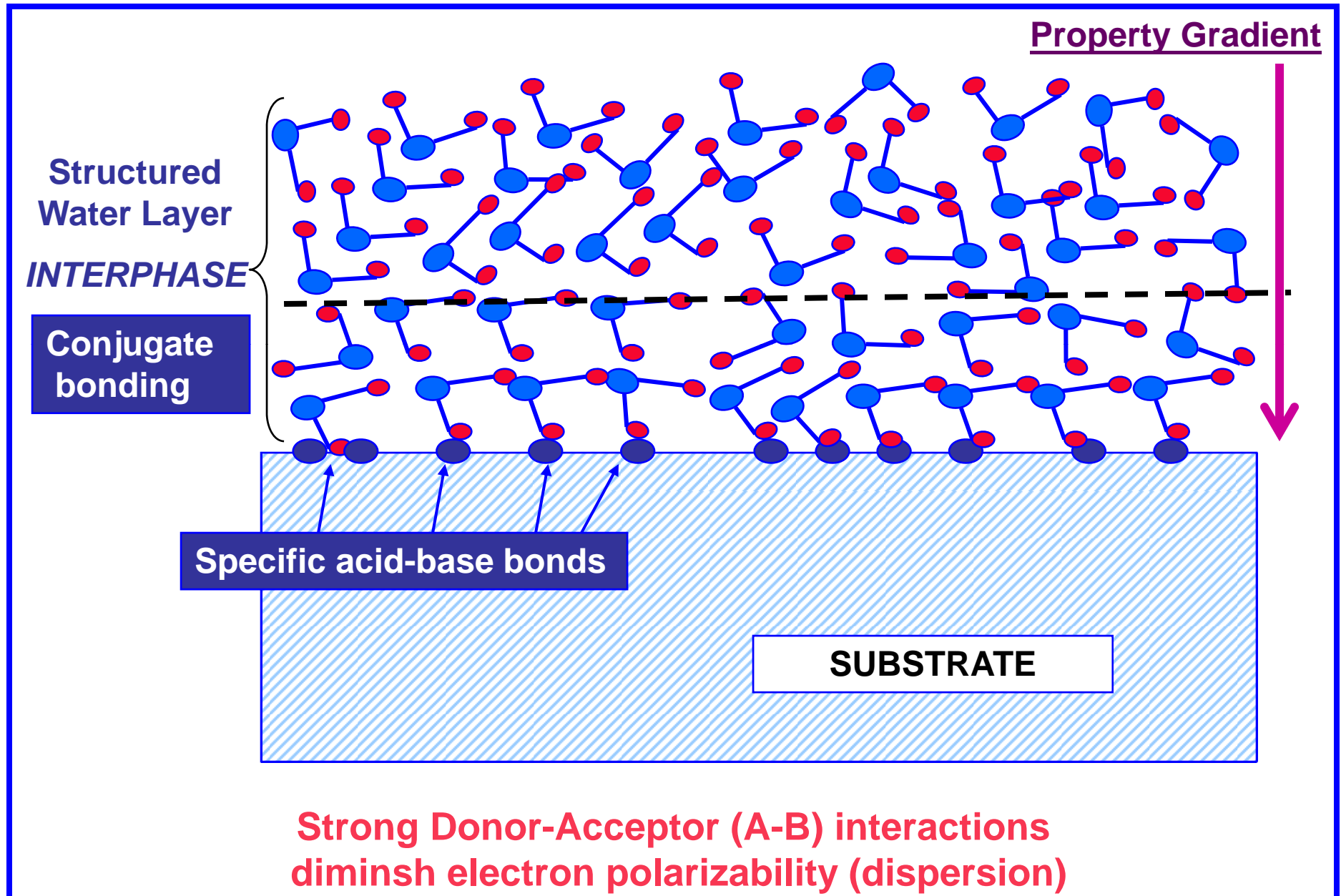


## Using literature values for polymers



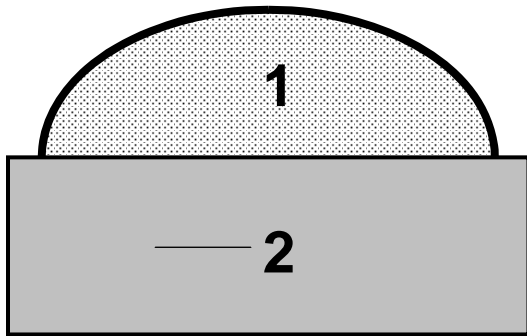
Data taken from: C. Della Volpe, et al., *J. Adhesion Sci. Technol.* **17**, 1425 (2003), and reanalyzed.

# Interface Zone Nuclear and Electronic Gradients



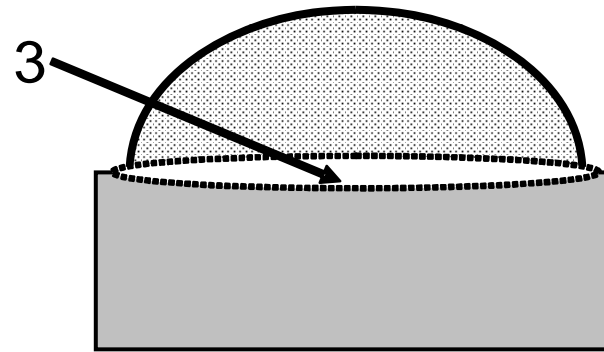
# HAMAKER CONSTANTS

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