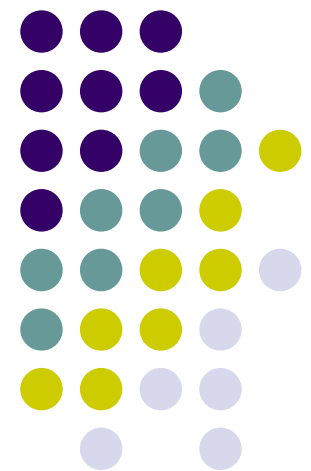
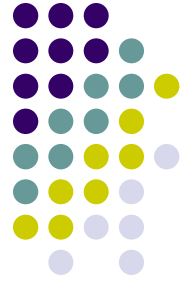


# Characterization of the aggregation of non-ionic dispersants and their adsorption on carbon black particles

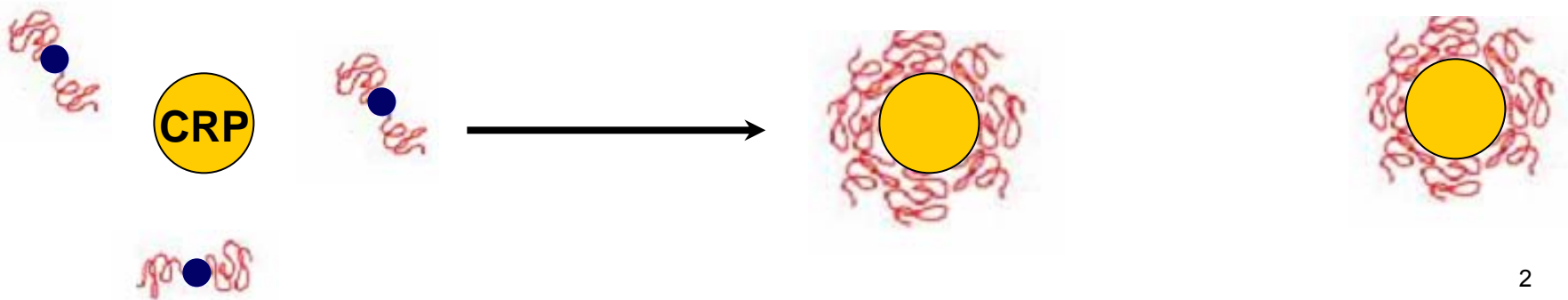
Yu Shen  
May 16, 2006



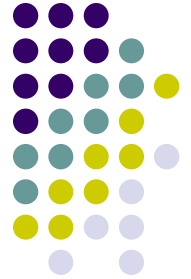
# Dispersants Used in Industry



- Industry Use
  - to stabilize carbon rich particles from aggregation
  - to prevent oil blockage
- Steric Mechanism
  - Polar core is fixed on particles' surfaces
  - Non-polar chain is well dissolved in oil



# Dispersants used as additives



Without dispersant

- Form deposits
- Cause corrosion



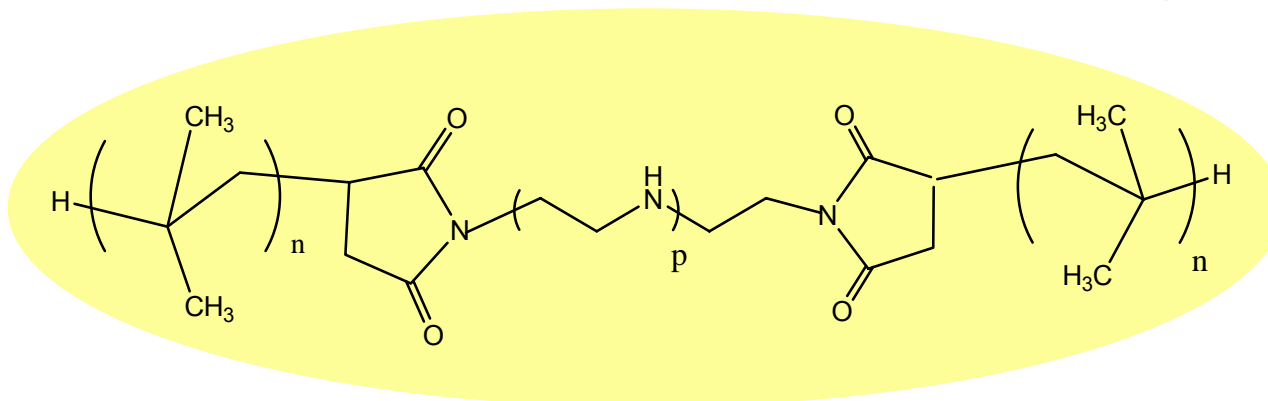
With dispersant

- No deposits
- Prevent corrosion

**Intake valve of a Mercedes Benz M102E engine after 60 test hours**

[www.basf.com/automotive-oil](http://www.basf.com/automotive-oil)

# Dispersant: BAB tri-block copolymer

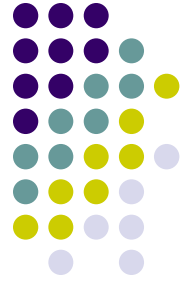


Polyisobutylene  
succinic  
anhydride  
(PIBSA)

Polyamines

Polyisobutylene  
succinic  
anhydride  
(PIBSA)

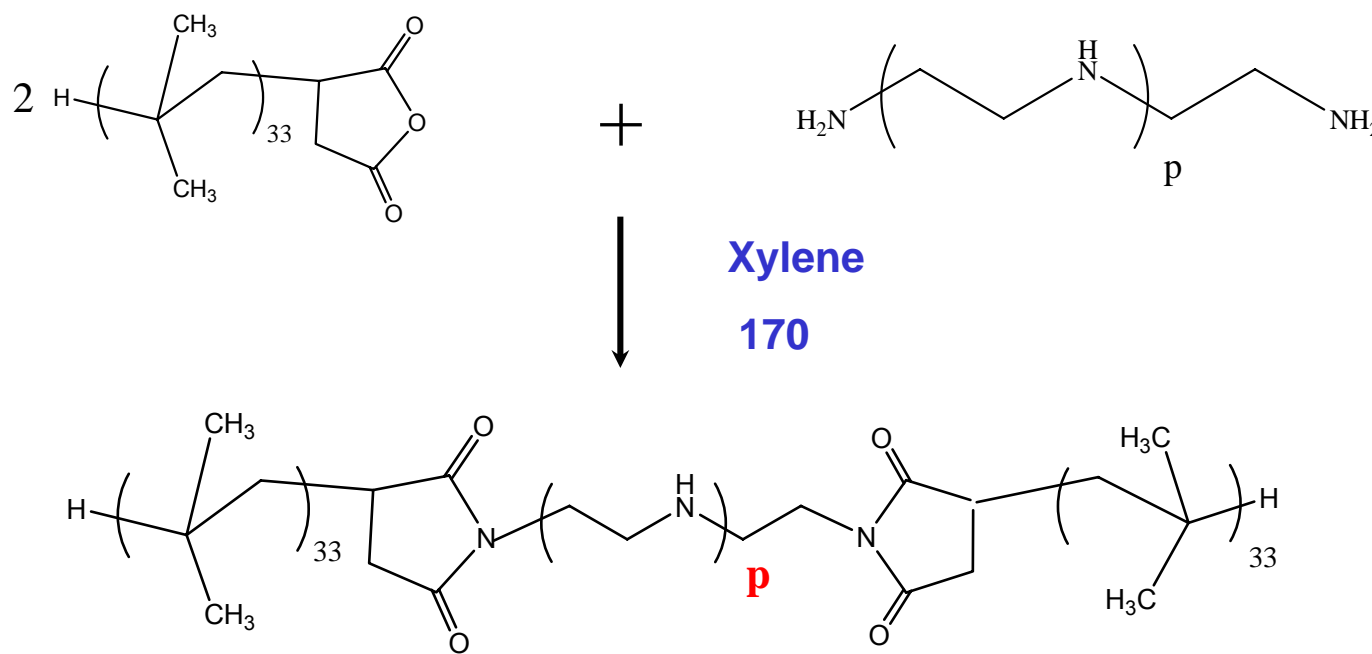
DETA (diethylene triamine)	$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_2-\text{NH}_2$
TEPA (tetraethylene pentamine)	$\text{H}_2\text{N}-(\text{CH}_2\text{CH}_2-\text{NH})_3-\text{CH}_2\text{CH}_2-\text{NH}_2$
PEHA (pentaethylene hexamine)	$\text{H}_2\text{N}-(\text{CH}_2\text{CH}_2-\text{NH})_4-\text{CH}_2\text{CH}_2-\text{NH}_2$



# Outline

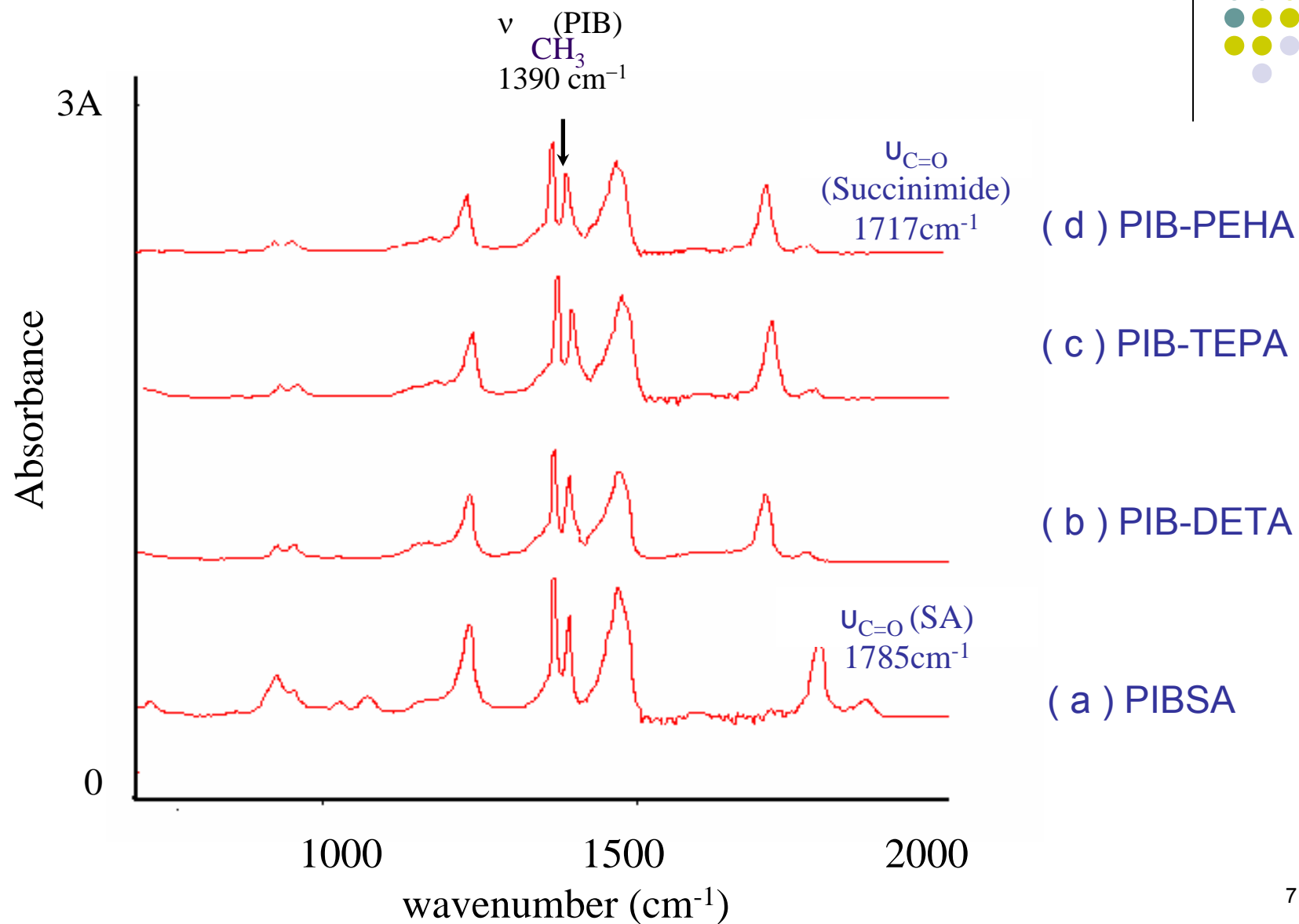
- Synthesis of dispersants
- Characterization of dispersants
- Measurement of associative strength of dispersants
- Adsorption of dispersants on carbon black particles
- Conclusions

# Synthesis of Dispersants



<b>p</b>	<b>Dispersant</b>
1	PIB-DETA
3	PIB-TEPA
4	PIB-PEHA

# Characterization of Dispersants (FT-IR)

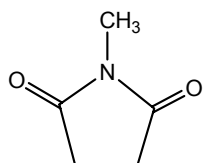




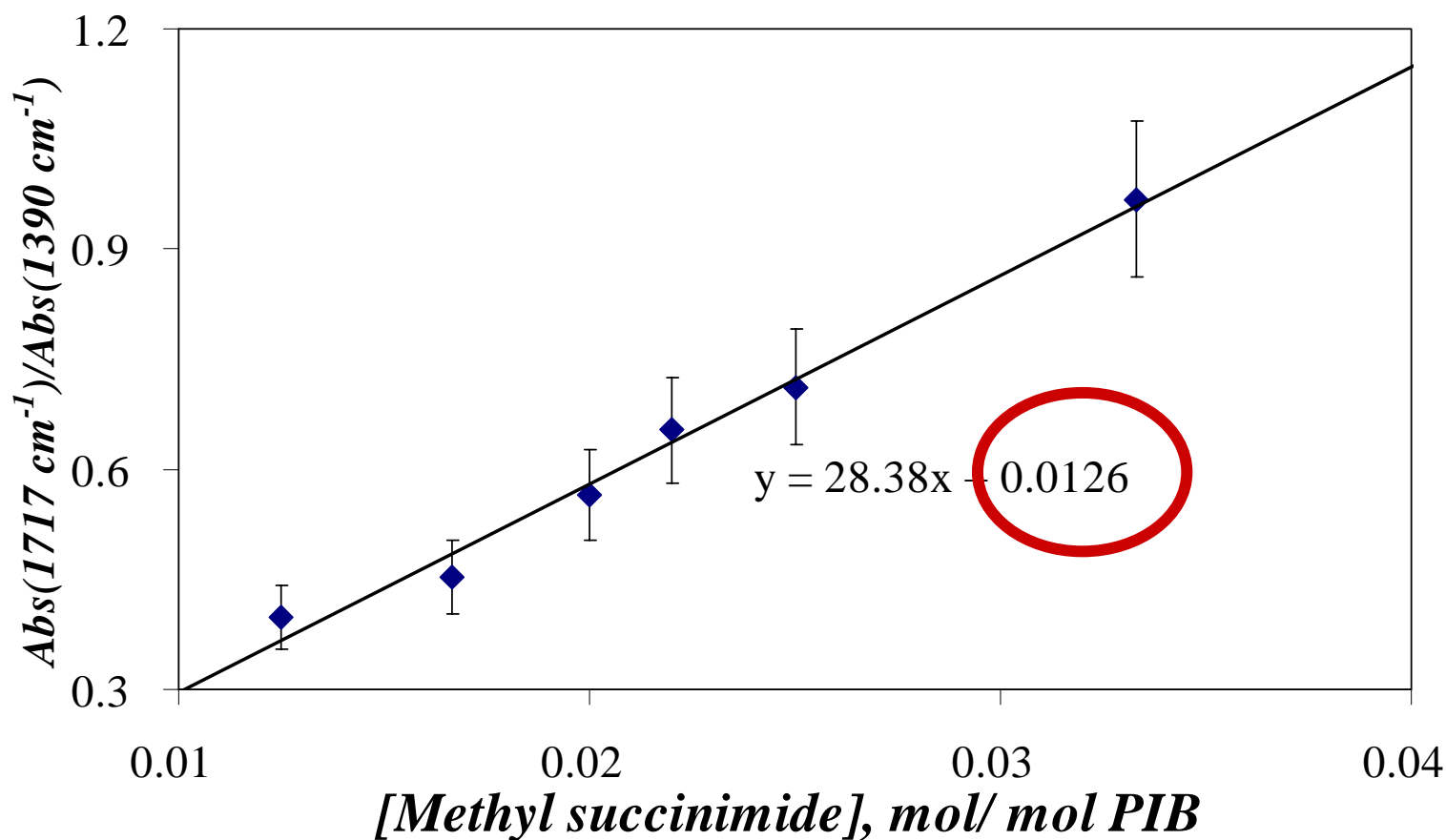
# Succinimide Content of Dispersant



Calibration by FT-IR:



+ polyisobutylene (model compound)



# Characterization of Dispersant



Building Block	Absorption Ratio $\text{Abs}(1785 \text{ cm}^{-1})/\text{Abs}(1390 \text{ cm}^{-1})$	$N_{SA}/N_{IB}$
PIBSA	0.79	1:(33)
Dispersant	Absorption Ratio $\text{Abs}(1717 \text{ cm}^{-1})/\text{Abs}(1390 \text{ cm}^{-1})$	$N_{succinimide}/N_{IB}$
PIB-DETA	0.87	1:(33.3 $\pm$ 3.8)
PIB-TEPA	0.89	1:(32.3 $\pm$ 4.1)
PIB-PEHA	0.89	1:(32.5 $\pm$ 3.1)

# Measurement of the Associative Strength of Dispersants

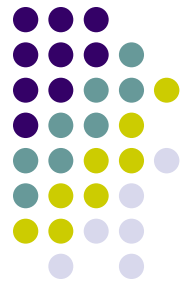


## Associative Strength

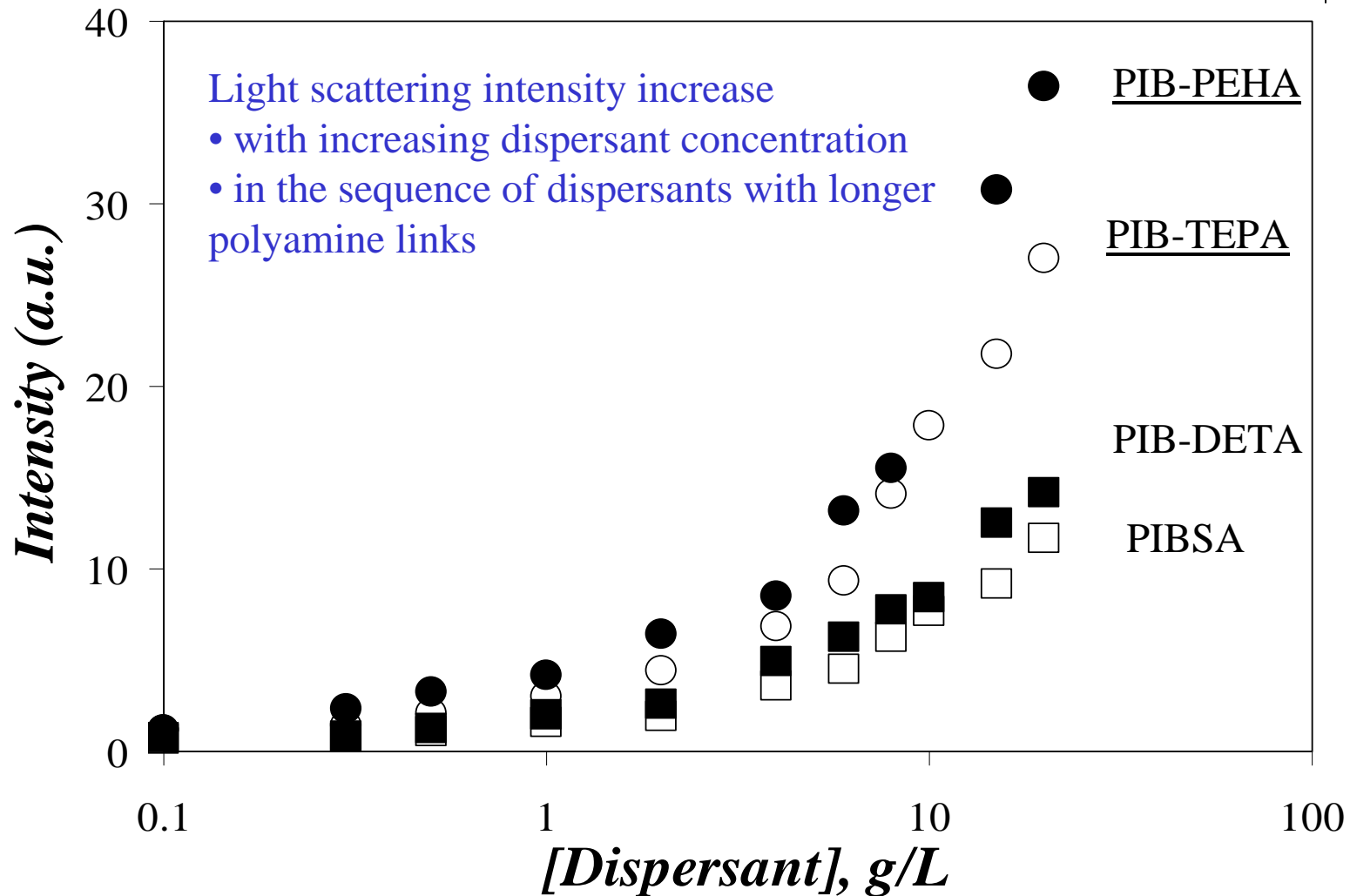
- Ability of dispersants to self-associate in solution into reverse micelles
- Characterized by the CMC
  - CMC: critical micelle concentration

## Measurements of the Associative Strength of Dispersants

- Light scattering
- Fluorescence techniques



# Measurement of the Associative Strength of Dispersants by Light Scattering

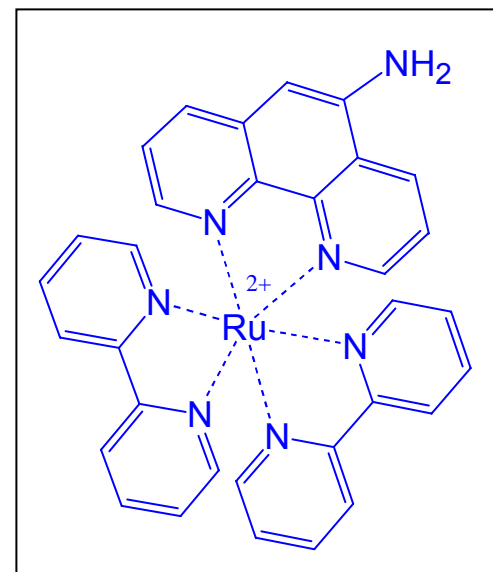


# Measurement of the Associative Strength of Dispersants by Fluorescence

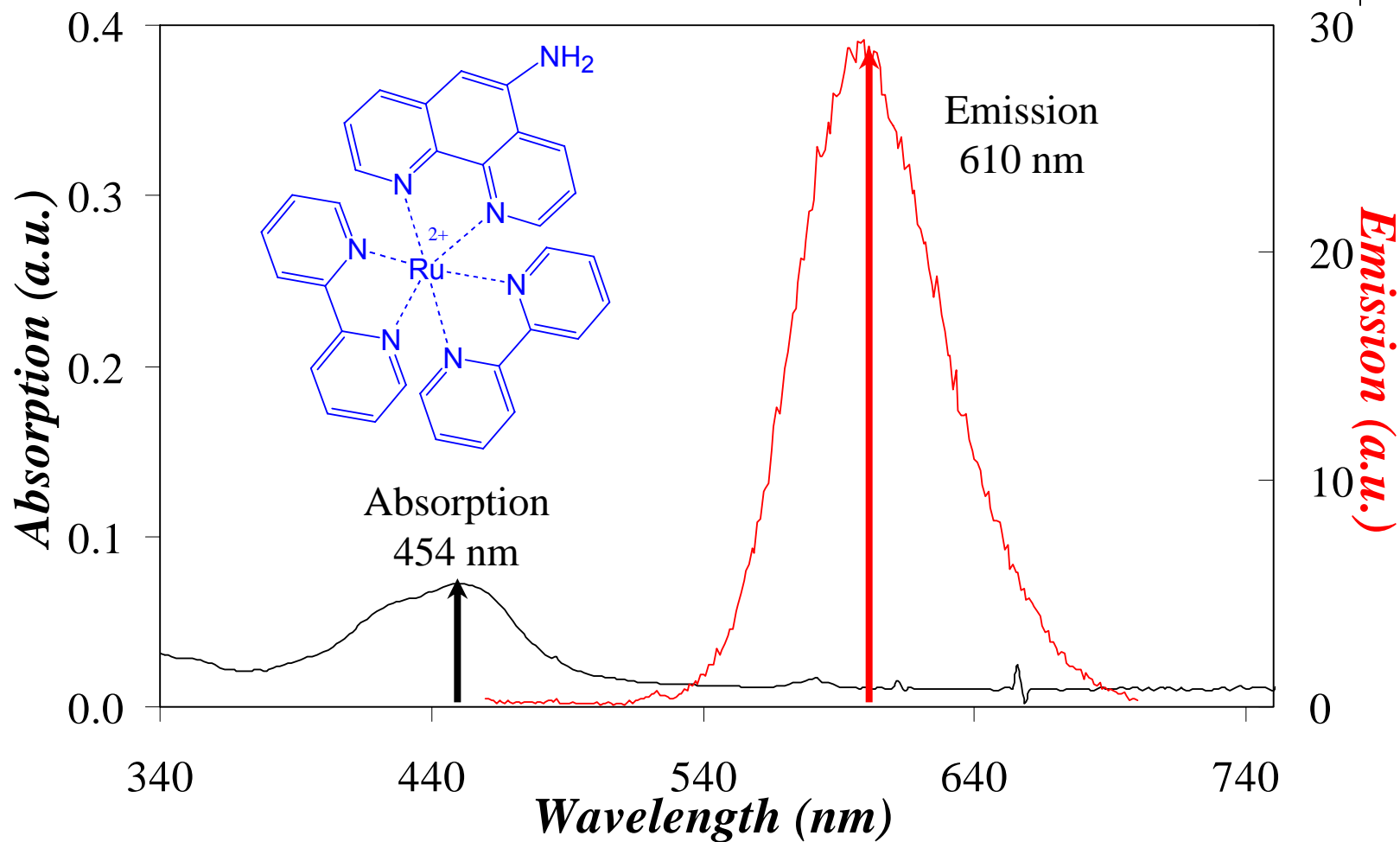


The advantages of chromophore Ruthenium bisbipyridine 5-aminophenanthroline hexafluorophosphate (Ru-bpy):

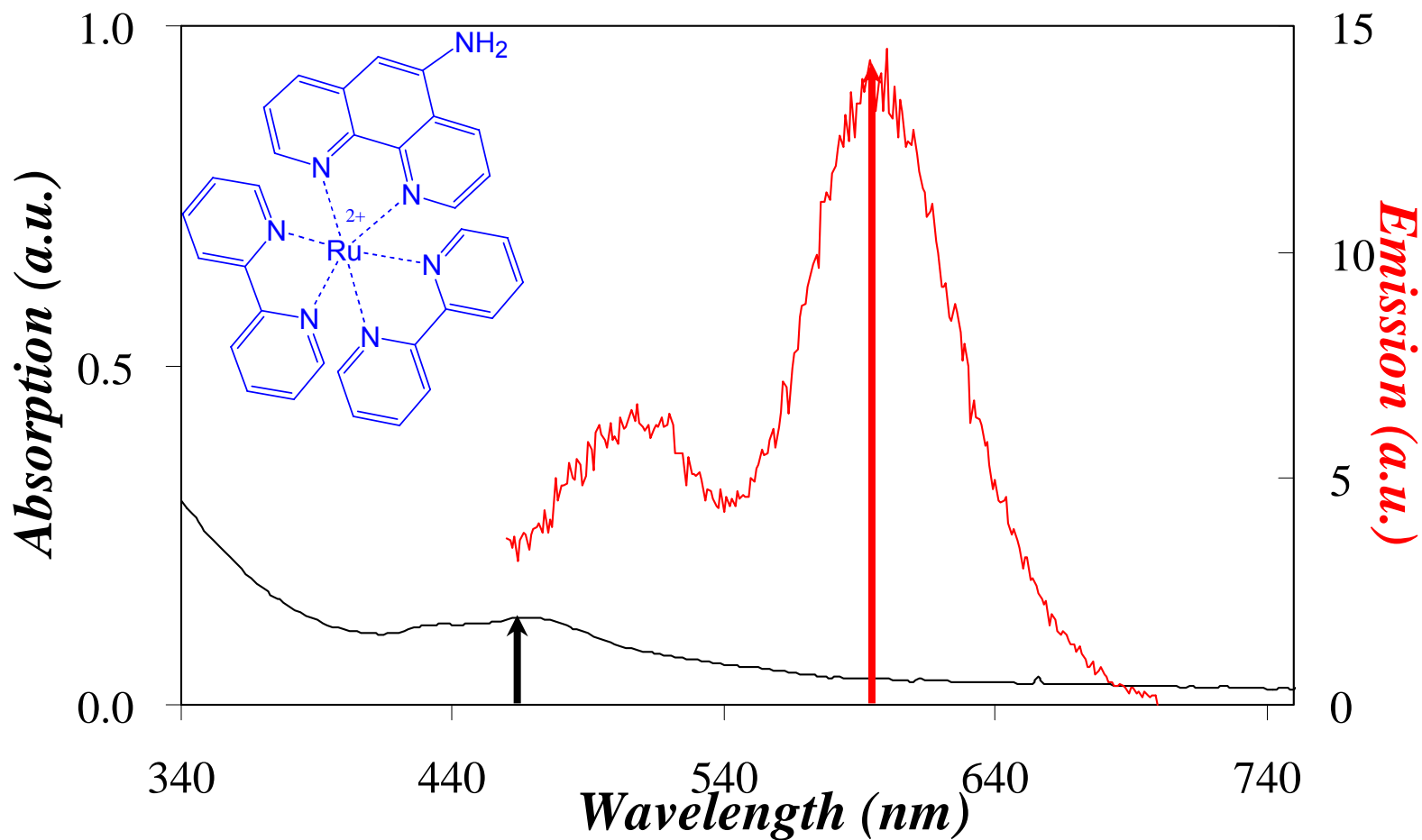
- confirm existence of dispersant aggregates
- probe the polar core of dispersant micelles
- not soluble in apolar solvents
- ideal to study the CMC of dispersants in hexane



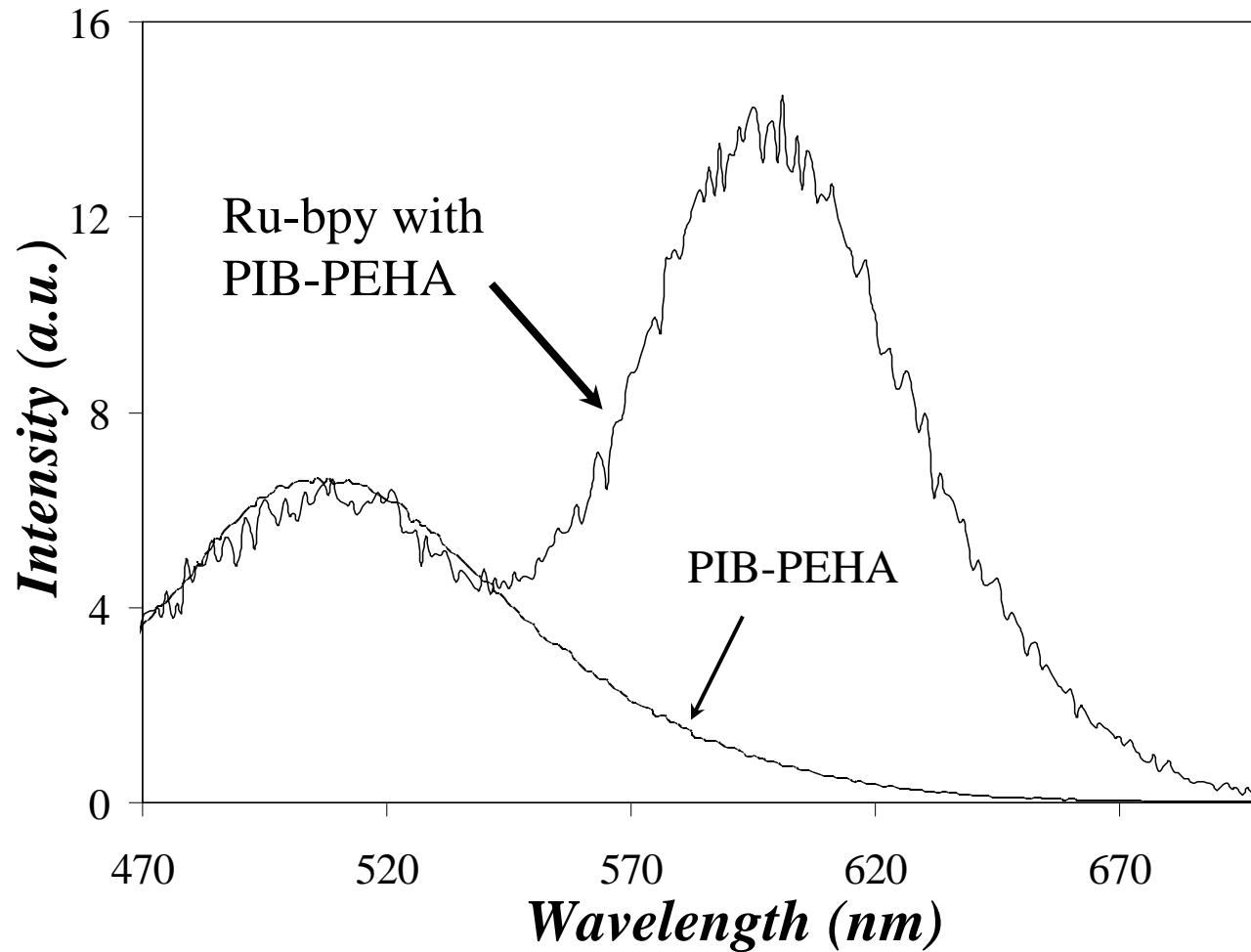
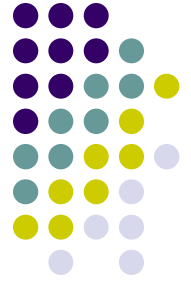
# Absorption/Emission Spectra of Ru-bpy in methanol



# Absorption/Emission Spectra of Ru-bpy in hexane with dispersant

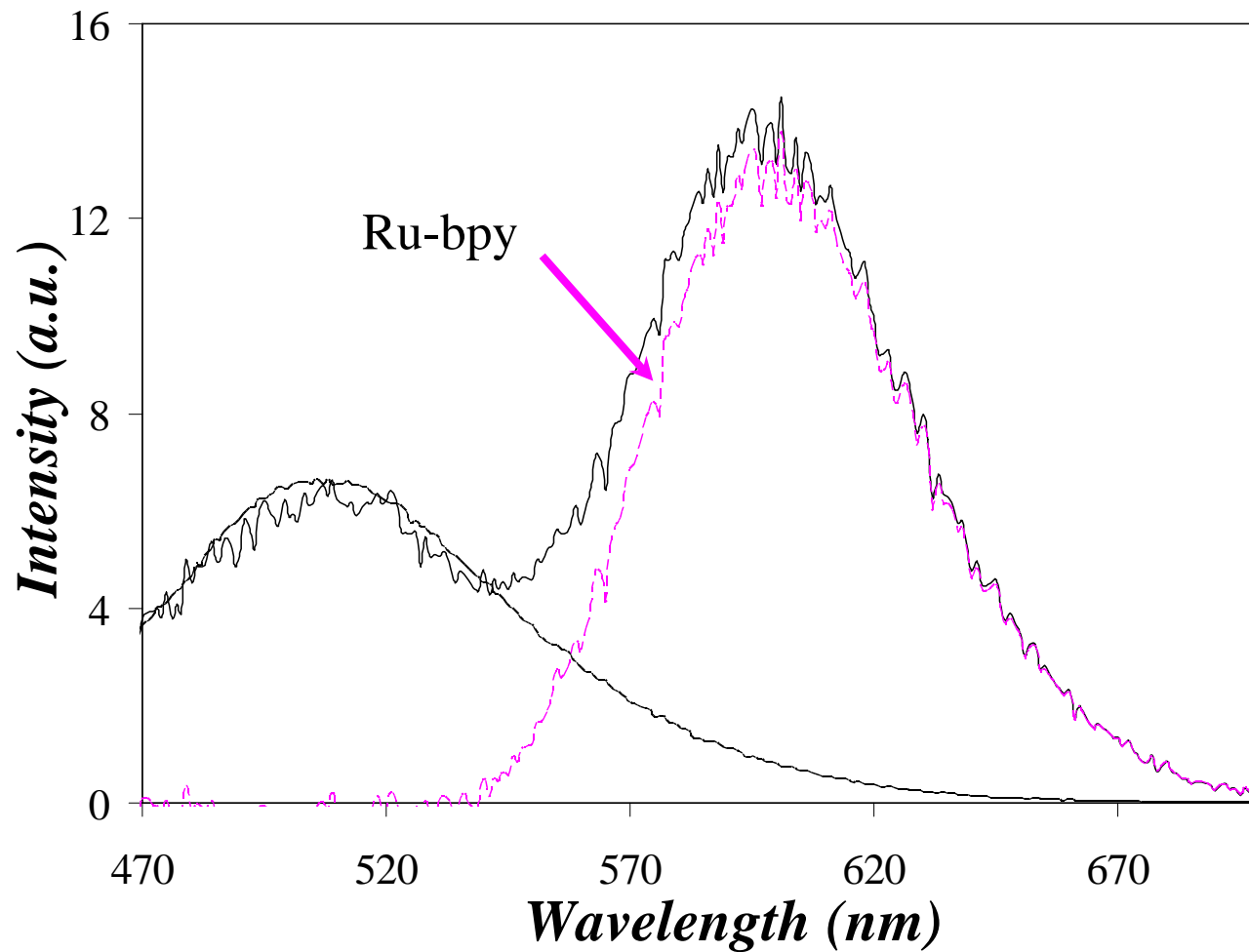
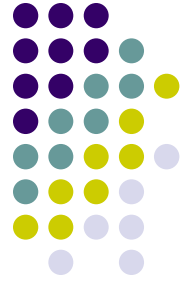


# Fluorescence Measurement with Ru-bpy



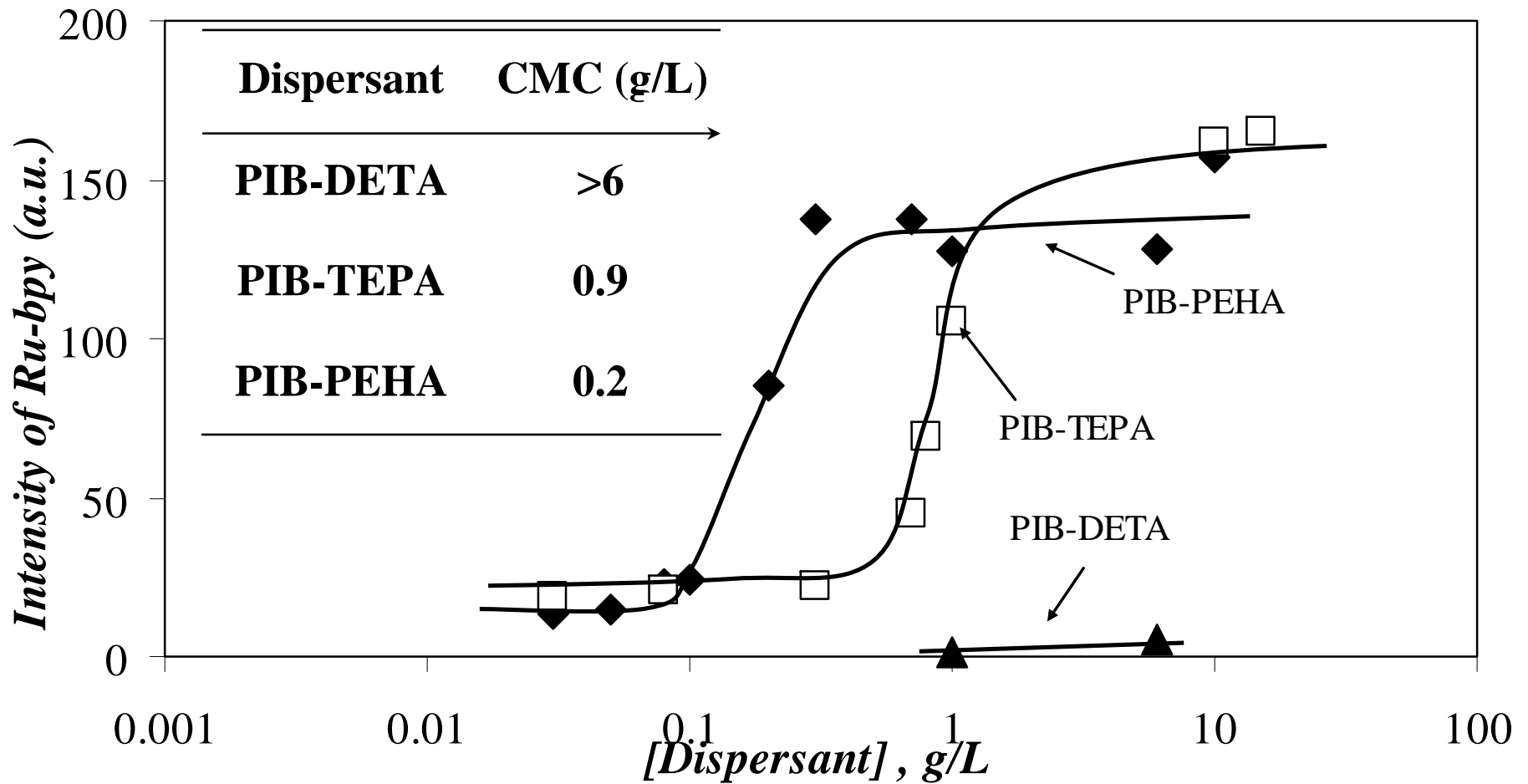
Ru-bpy in PIB-PEHA normalized by pure PIB-PEHA 0.3g/L in the emission spectrum<sup>16</sup>

# Fluorescence Measurement with Ru-bpy

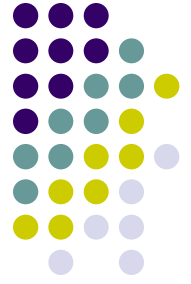


Ru-bpy in PIB-PEHA normalized by pure PIB-PEHA 0.3g/L in the emission spectrum<sup>17</sup>

# Fluorescence Measurement with Ru-bpy



# Adsorption Measurements

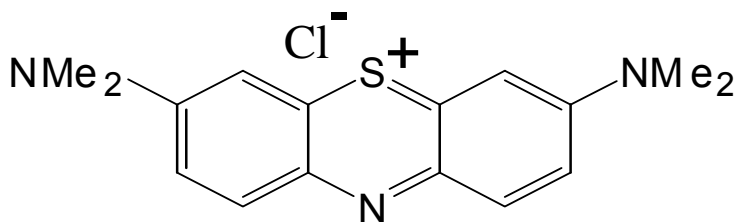


- Determination of the specific area of carbon black
- Measurement of the amount of adsorbed dispersants on carbon black
- Analysis with di-Langmuir Model



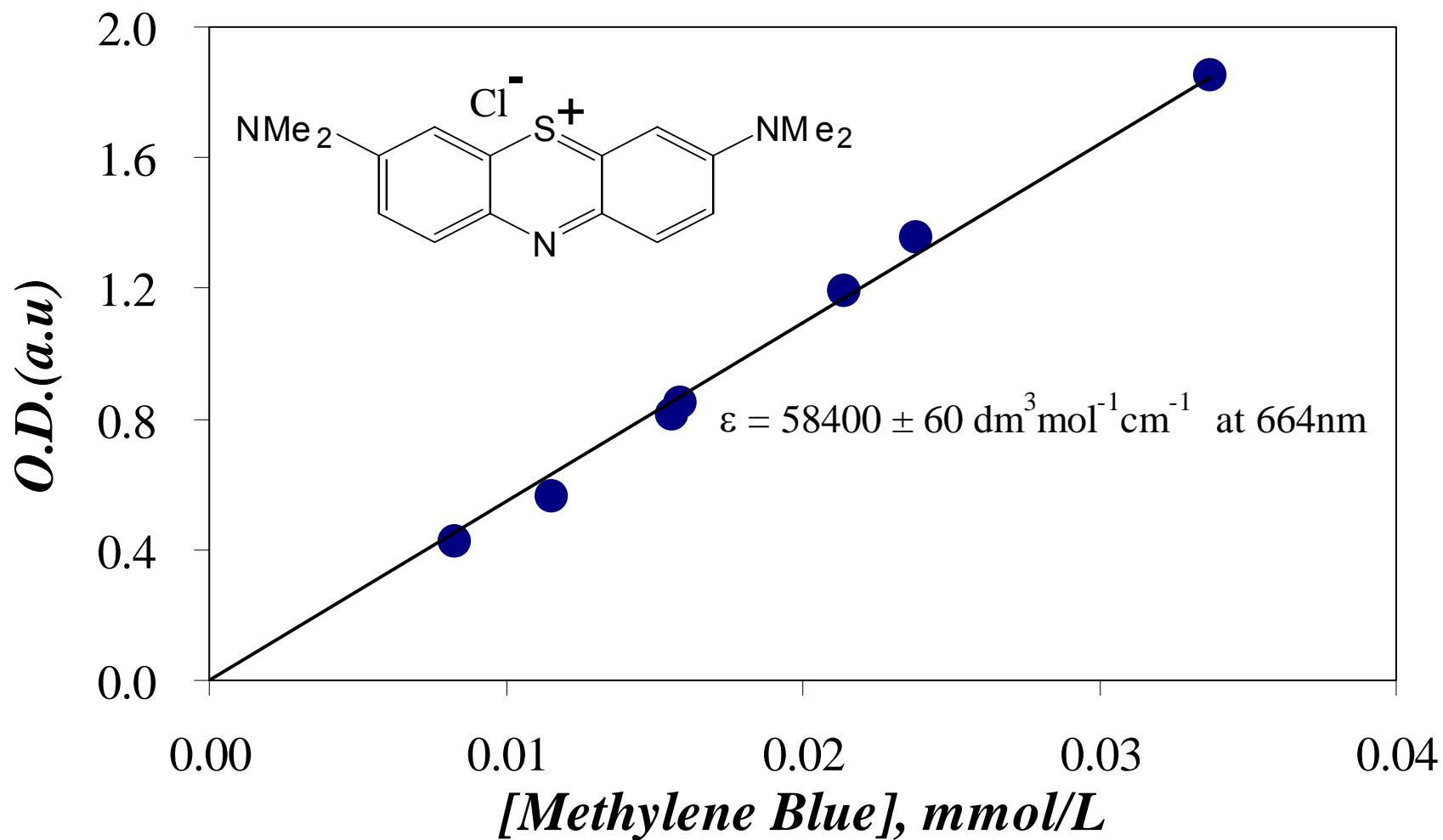
# Determination of the Specific Area of Carbon Black (CB) Particles

- Constant volume of aqueous MB solutions with different amount of CB are prepared
- The concentration of MB in supernatant is measured
- The specific area of CB is determined from the absorbed amount of MB

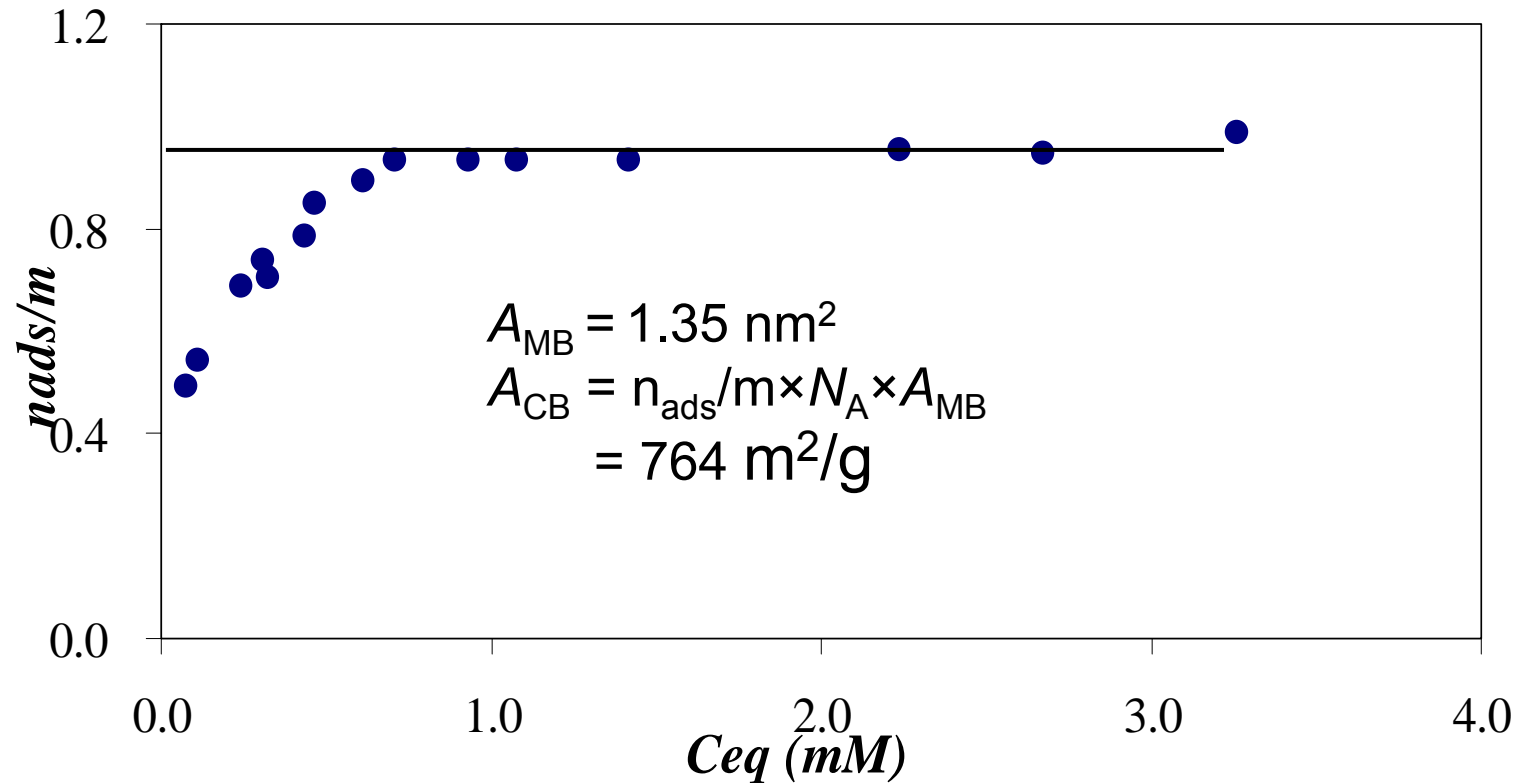


Methylene Blue  
(MB)

# Determination of the Extinction Coefficient of Methylene Blue

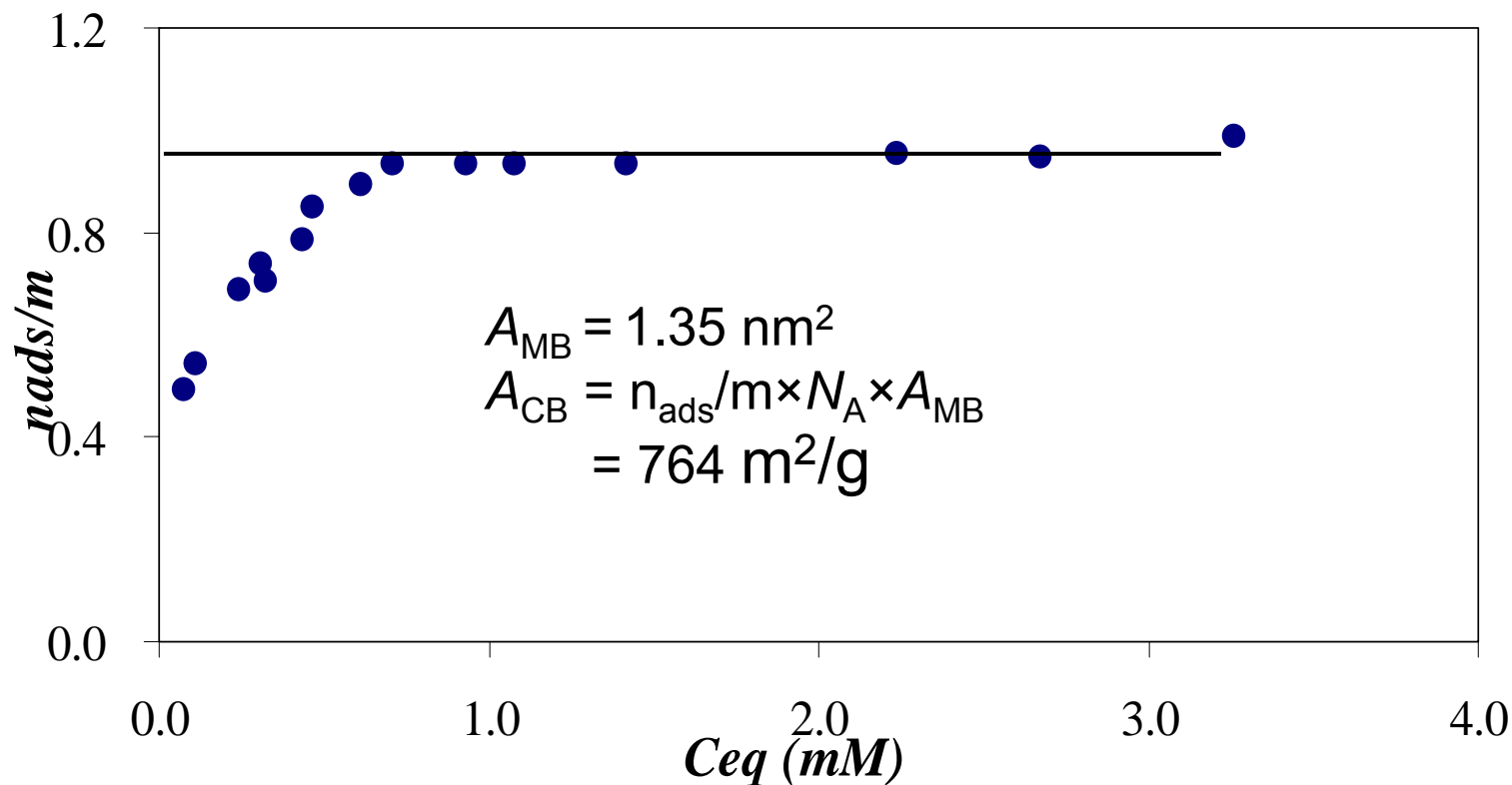


# Determination of the Specific Area of Carbon Black (CB) Particles



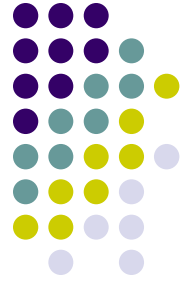
$C_{eq}$ : concentration of MB at equilibrium in supernatant  
 $n_{ads}/m$ : mmol of adsorbed MB per gram of carbon black

# Determination of the Specific Area of Carbon Black (CB) Particles



$A_{CB}$  measured by MB <  $A_{CB}$  measured by  $N_2$  adsorption (1600  $M^2/g$ )

- limited accessible surface area
- reduced ability of MB molecules to follow the surface contours



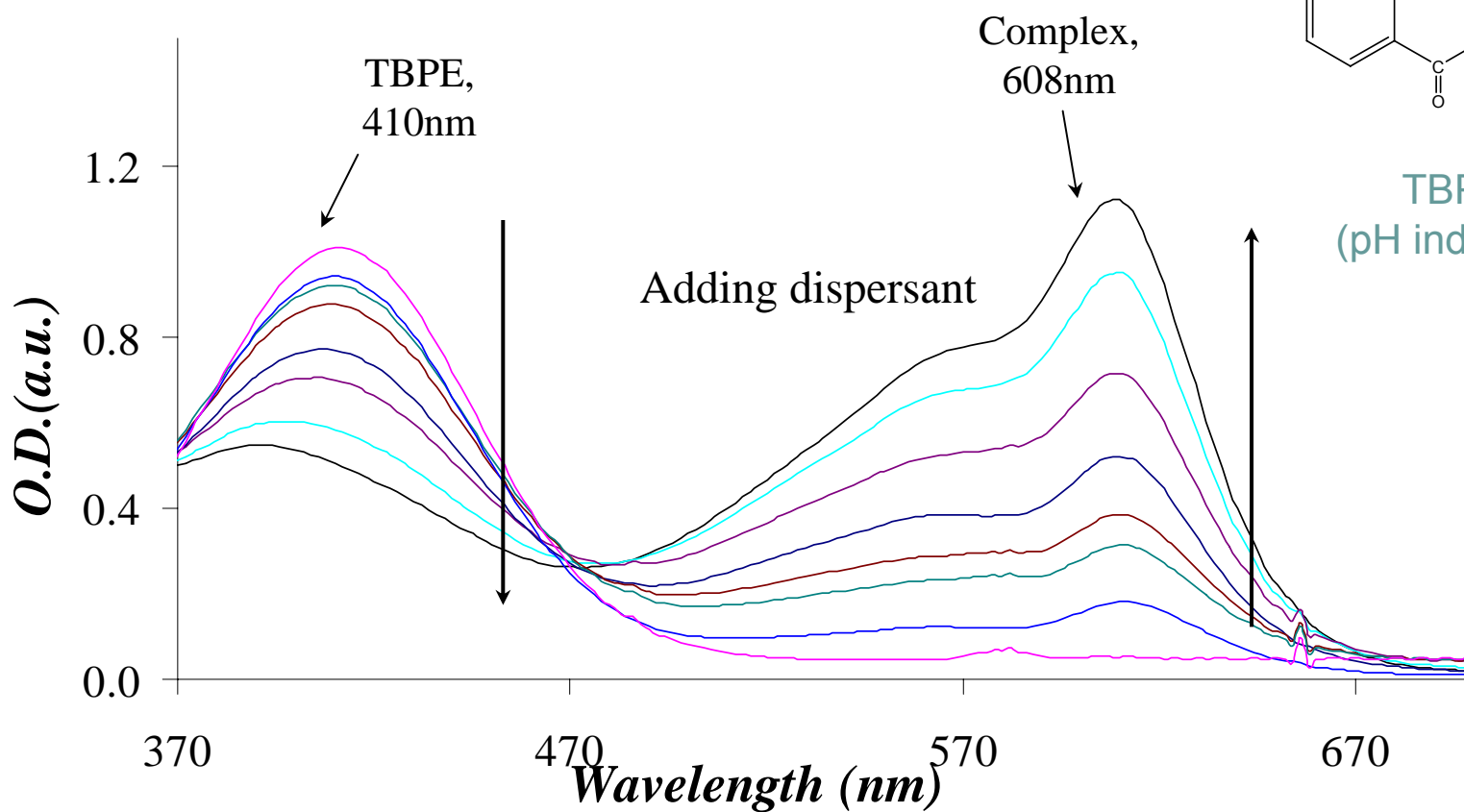
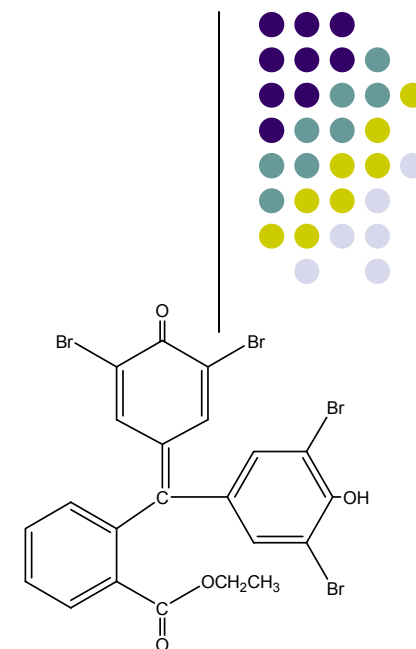
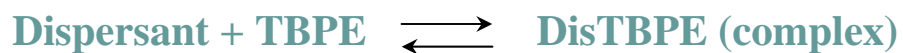
# Adsorption Measurements

- ✓ Determination of the specific area of carbon black

Measurement of the amount of adsorbed dispersants on carbon black

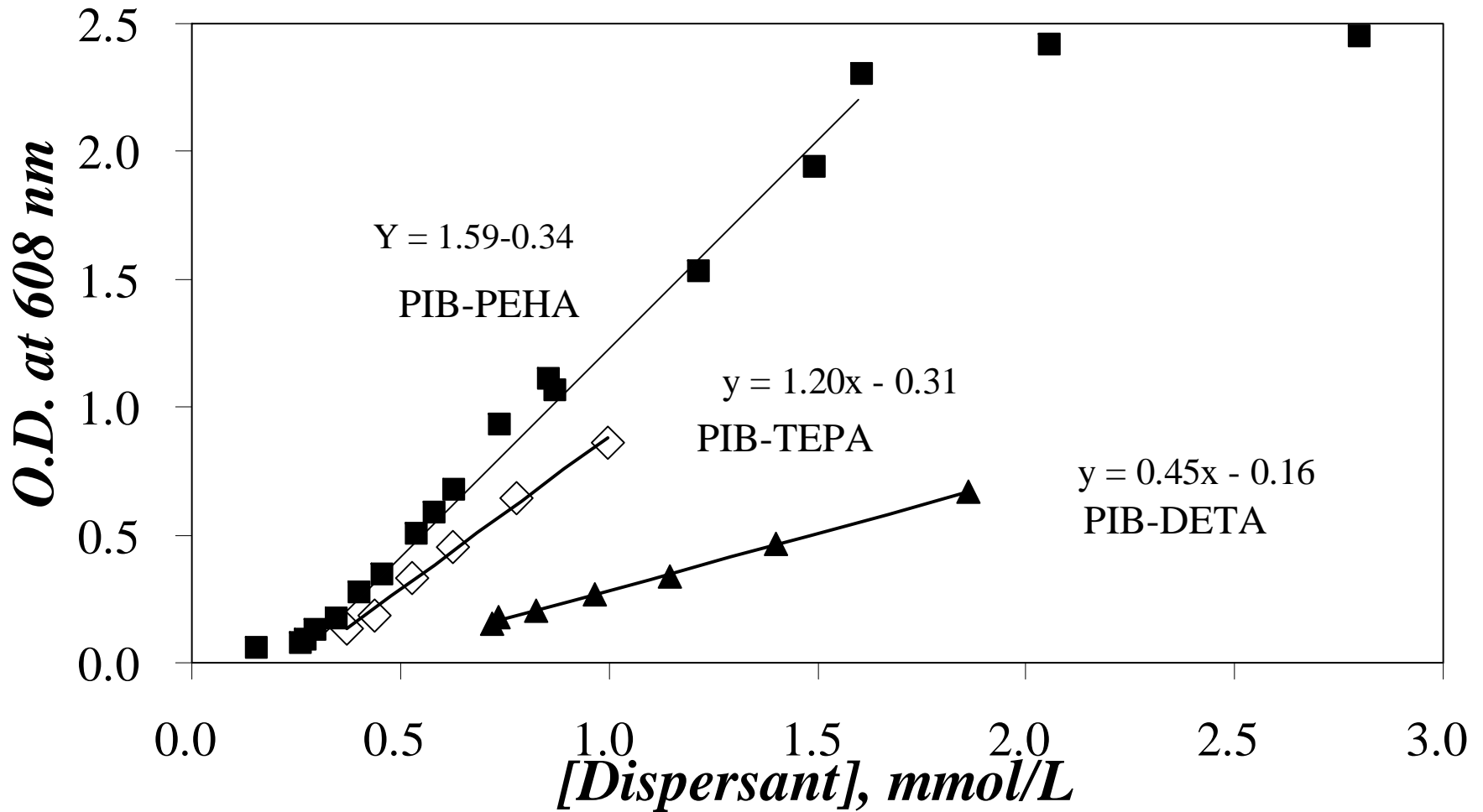
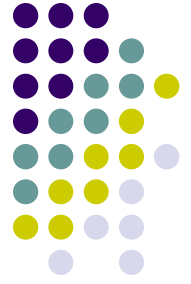
Analysis with di-Langmuir Model

# Measurement of Adsorbed Dispersants on CB Particles



TBPE  
(pH indicator)

# Calibration of Dispersants Concentration



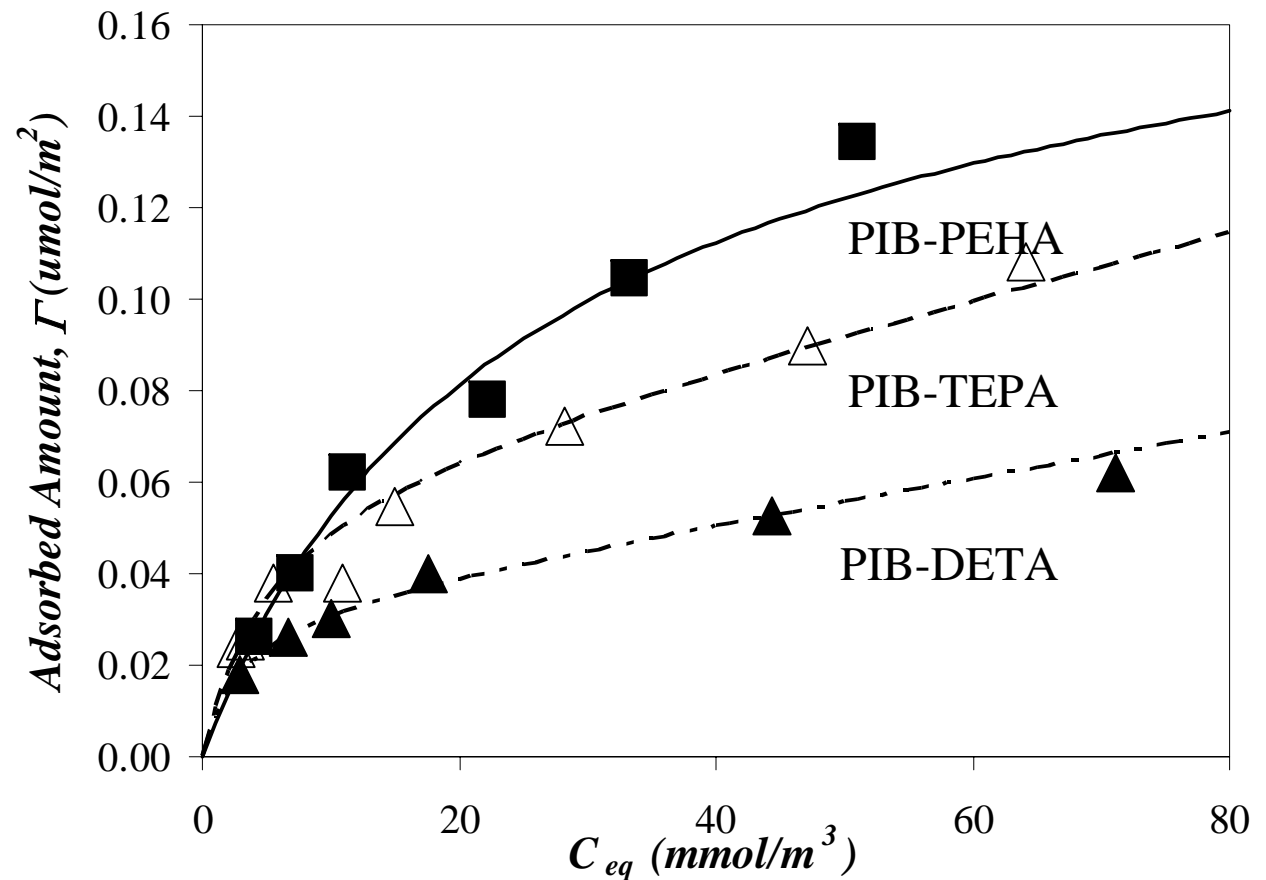
# Adsorption Isotherm

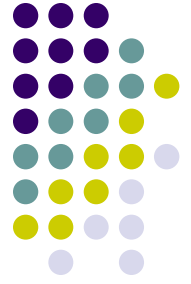


$$\Gamma = \frac{(C_0 - C_{eq})V}{mA} \quad (\mu\text{mol} / \text{m}^2)$$

$\Gamma$ : adsorbed amount of dispersant per unit area  
 $C_{eq}$ : concentration of dispersant in supernatant at equilibrium  
 $m$ : CB weight

$V$ : volume of solution  
 $C_0$ : initial concentration of the dispersant  
 $A$ : specific area of CB



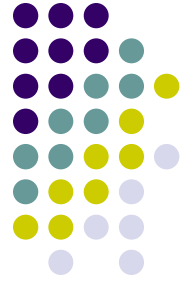


# Adsorption Measurements

- ✓ Determination of the specific area of carbon black
- ✓ Measurement of the amount of adsorbed dispersants on carbon black

Analysis with di-Langmuir Model

# Analyzing the Adsorption Isotherm with di-Langmuir Model



$$\Gamma = \frac{\Gamma_1 K_1 C_{eq}}{1 + K_1 C_{eq}} + \frac{\Gamma_2 K_2 C_{eq}}{1 + K_2 C_{eq}} \approx \frac{\Gamma_1 K_1 C_{eq}}{1 + K_1 C_{eq}} + \Gamma_2 K_2 C_{eq}$$

**$\Gamma_1, \Gamma_2$  : maximum amount of dispersant adsorbed at saturation**  
 **$K_1, K_2$  : equilibrium constants of the two sites**

---

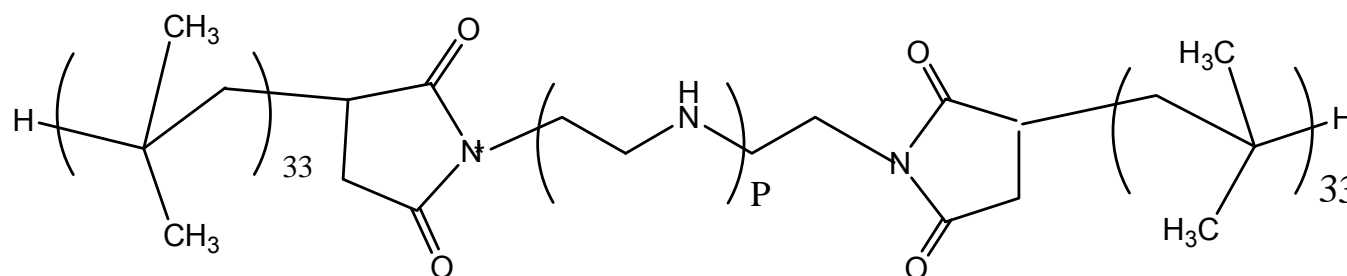
	$\Gamma_1$ (mol.m <sup>-2</sup> )	$K_1$ (m <sup>3</sup> .mol <sup>-1</sup> )	$\Gamma_2 K_2$ (m)
<b>PIB-DETA</b>	1.70×10 <sup>-7</sup>	43	1.13×10 <sup>-7</sup>
<b>PIB-TEPA</b>	6.31×10 <sup>-8</sup>	193	6.91×10 <sup>-7</sup>
<b>PIB-PEHA</b>	3.35×10 <sup>-8</sup>	336	4.82×10 <sup>-7</sup>

---

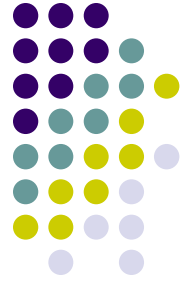


# Conclusions

- A series of oil-soluble dispersants were synthesized.



- The CMC of the dispersants was determined by using the fluorescence of Ru-bpy. The CMC decreases with increasing p values.
- The adsorption of the dispersants onto carbon black particles was investigated. Dispersants adsorbed on carbon black particles more strongly for larger p values.



# Acknowledgements

- Dr. Jean Duhamel
- Dr. Mario Gauthier
- Colleagues from both labs
- Special thanks to Cristina Quinn
- Imperial Oil and NSERC for funding