University of Waterloo

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

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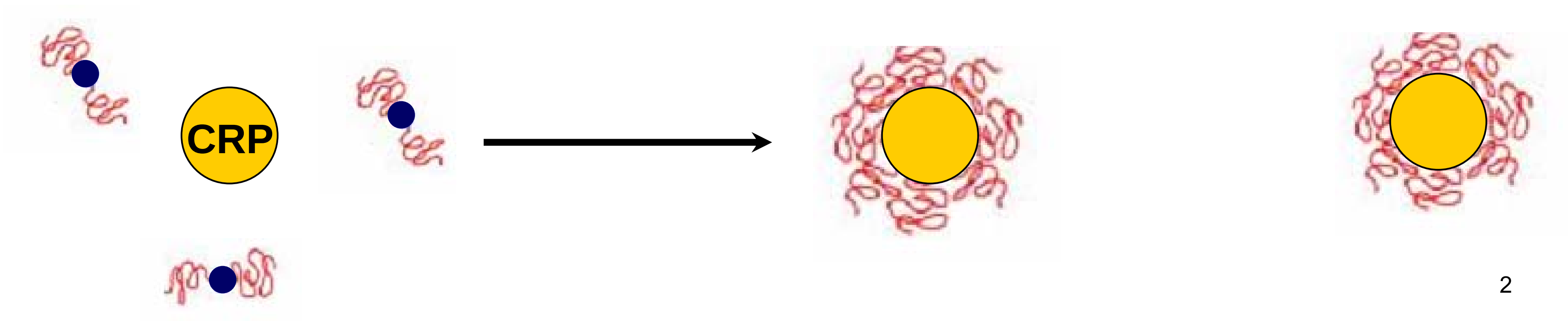
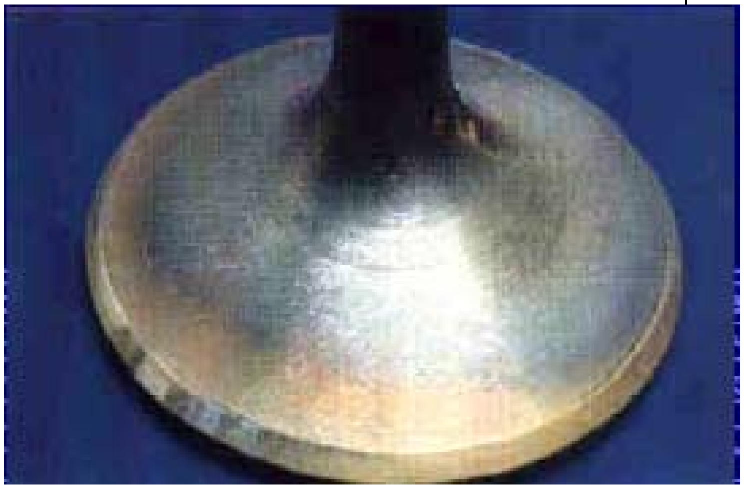
Dispersants Used in Industry

- 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



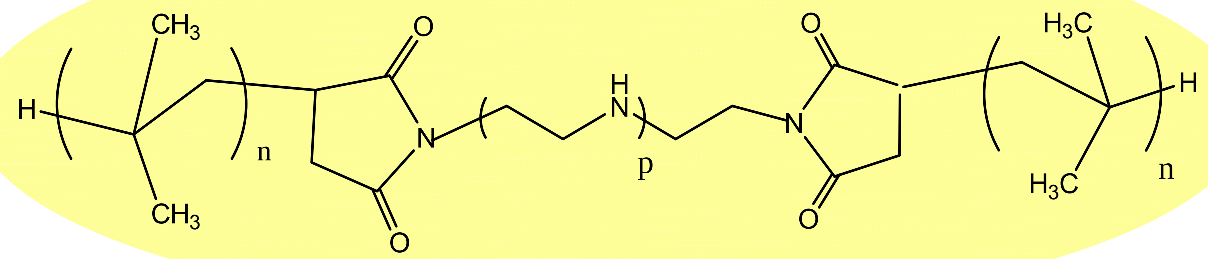
Without dispersant
- Form deposits
- Cause corrosion

With dispersant
- No deposits
- Prevent corrosion

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

www.basf.com/automotive-oil

Dispersant: BAB tri-block copolymer



Polyisobutylene succinic anhydride (PIBSA)

Polyamines

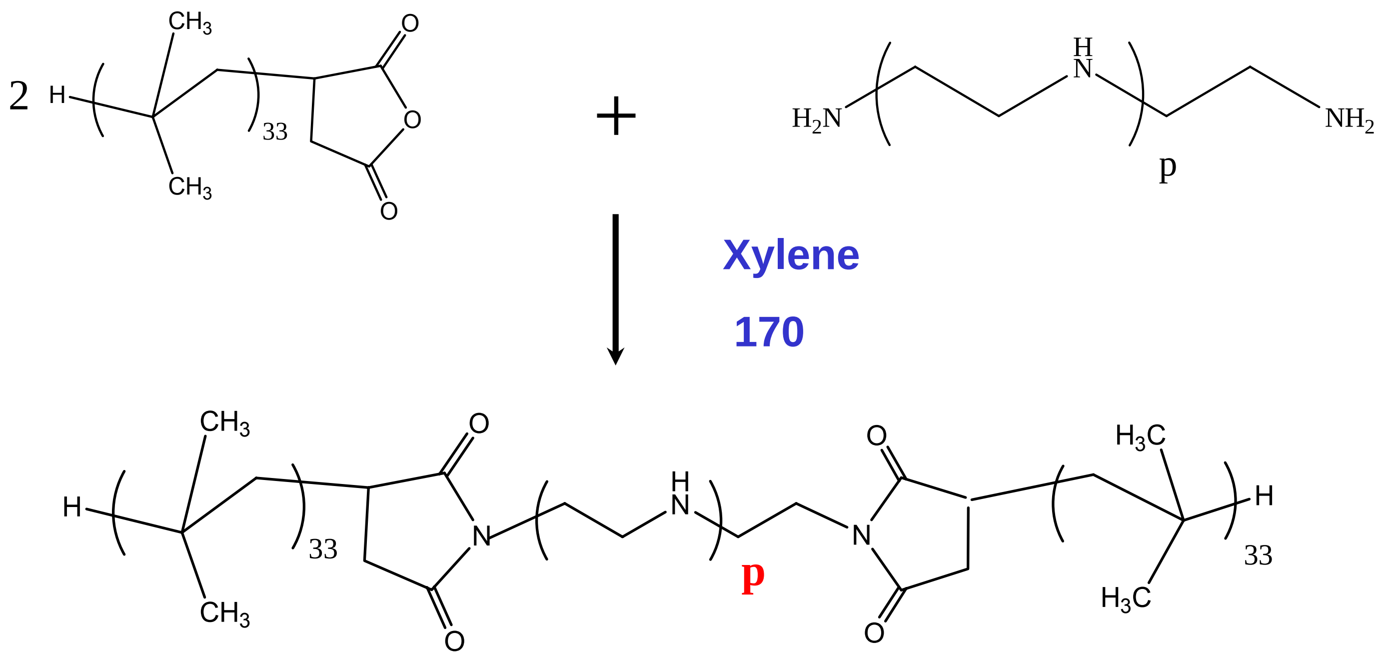
Polyisobutylene succinic anhydride (PIBSA)

DETA (diethylene triamine)	$H_2N{-}CH_2CH_2{-}NH{-}CH_2CH_2{-}NH_2$
TEPA (tetraethylene pentamine)	$H_2N{-}(CH_2CH_2{-}NH)_3{-}CH_2CH_2{-}NH_2$
PEHA (pentaethylene hexamine)	$H_2N{-}(CH_2CH_2{-}NH)_4{-}CH_2CH_2{-}NH_2$

Outline

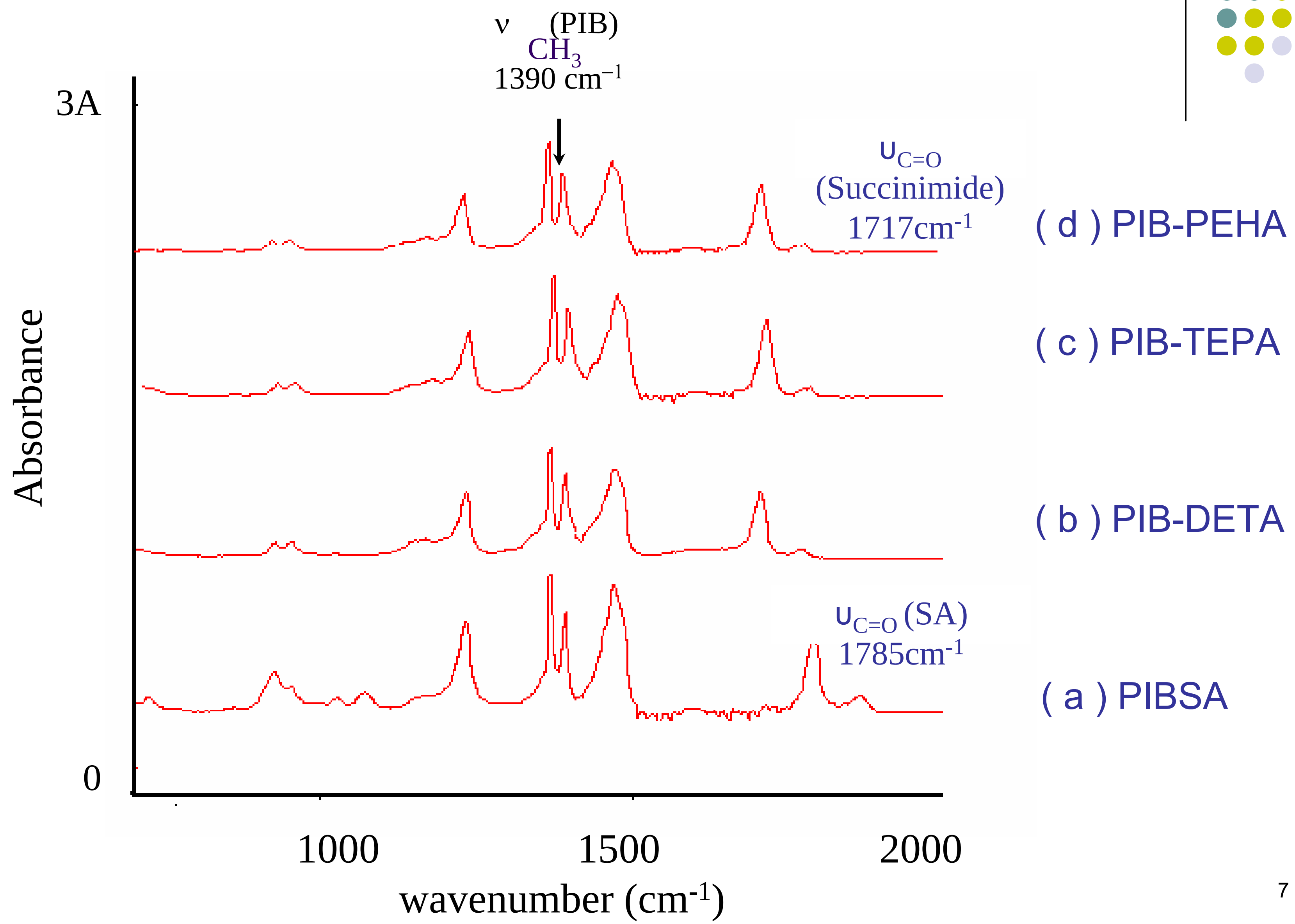
- Synthesis of dispersants
- Characterization of dispersants
- Measurement of associative strength of dispersants
- Adsorption of dispersants on carbon black particles
- Conclusions

Synthesis of Dispersants

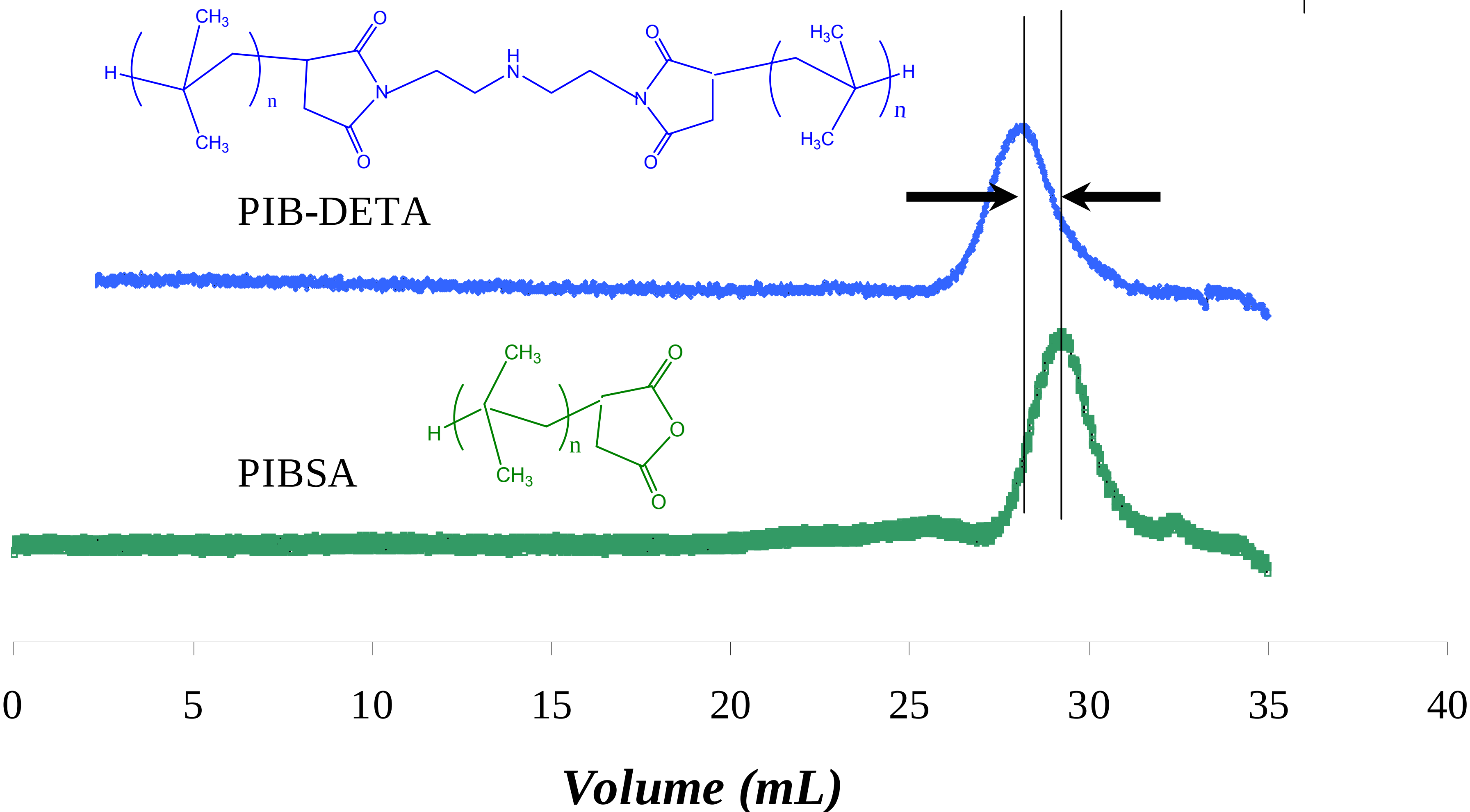


p	Dispersant
1	PIB-DETA
3	PIB-TEPA
4	PIB-PEHA

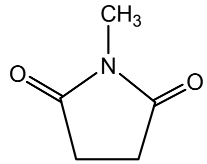
Characterization of Dispersants (FT-IR)



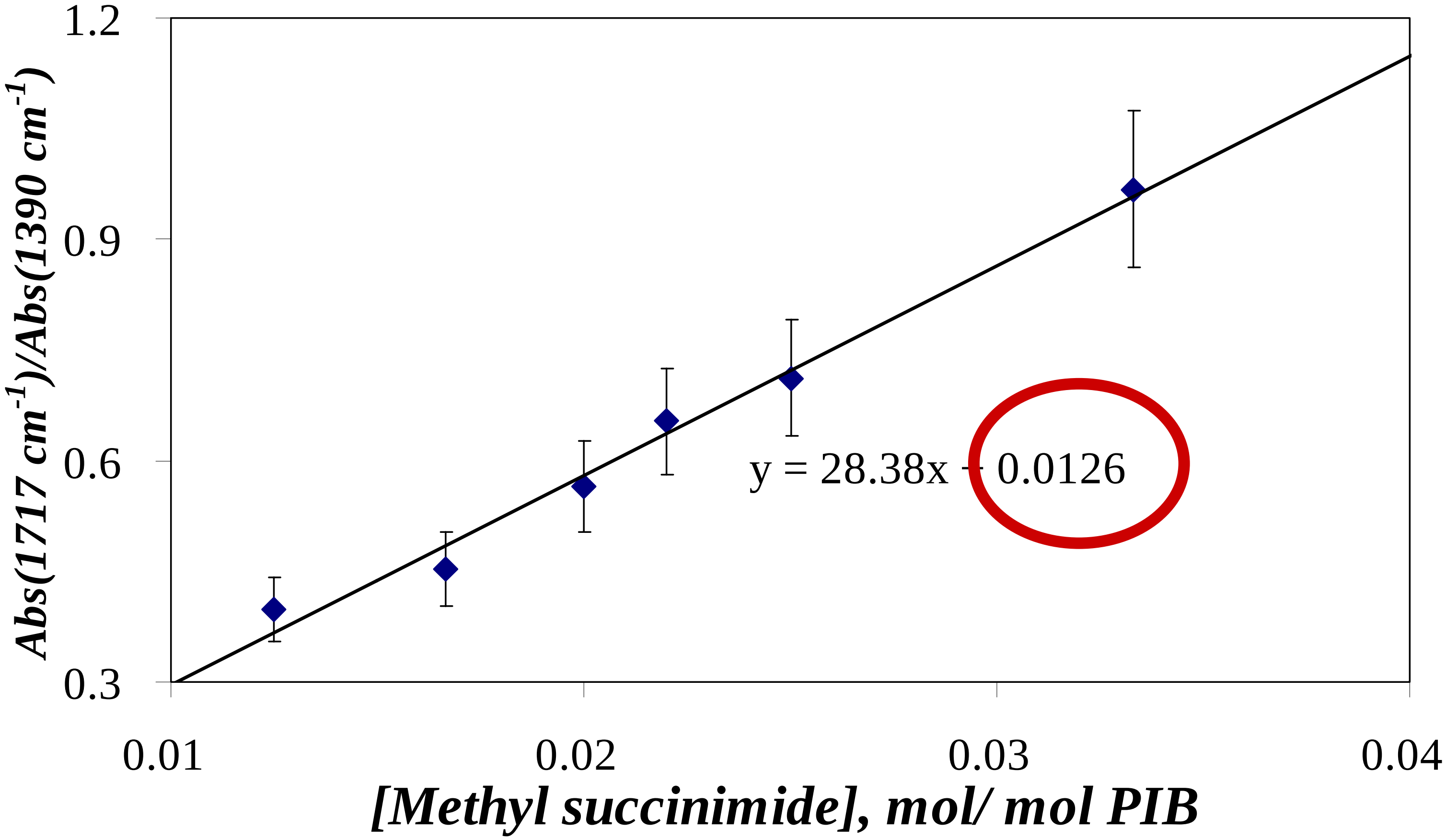
Characterization of Dispersants (GPC)



Succinimide Content of Dispersant

Calibration by FT-IR: 

+ polyisobutylene (model compound)



Characterization of Dispersant

Building Block	Absorption Ratio Abs(1785 cm^{-1})/Abs(1390 cm^{-1})	N_{SA}/N_{IB}
PIBSA	0.79	1:(33)

Dispersant	Absorption Ratio Abs(1717 cm^{-1})/Abs(1390 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

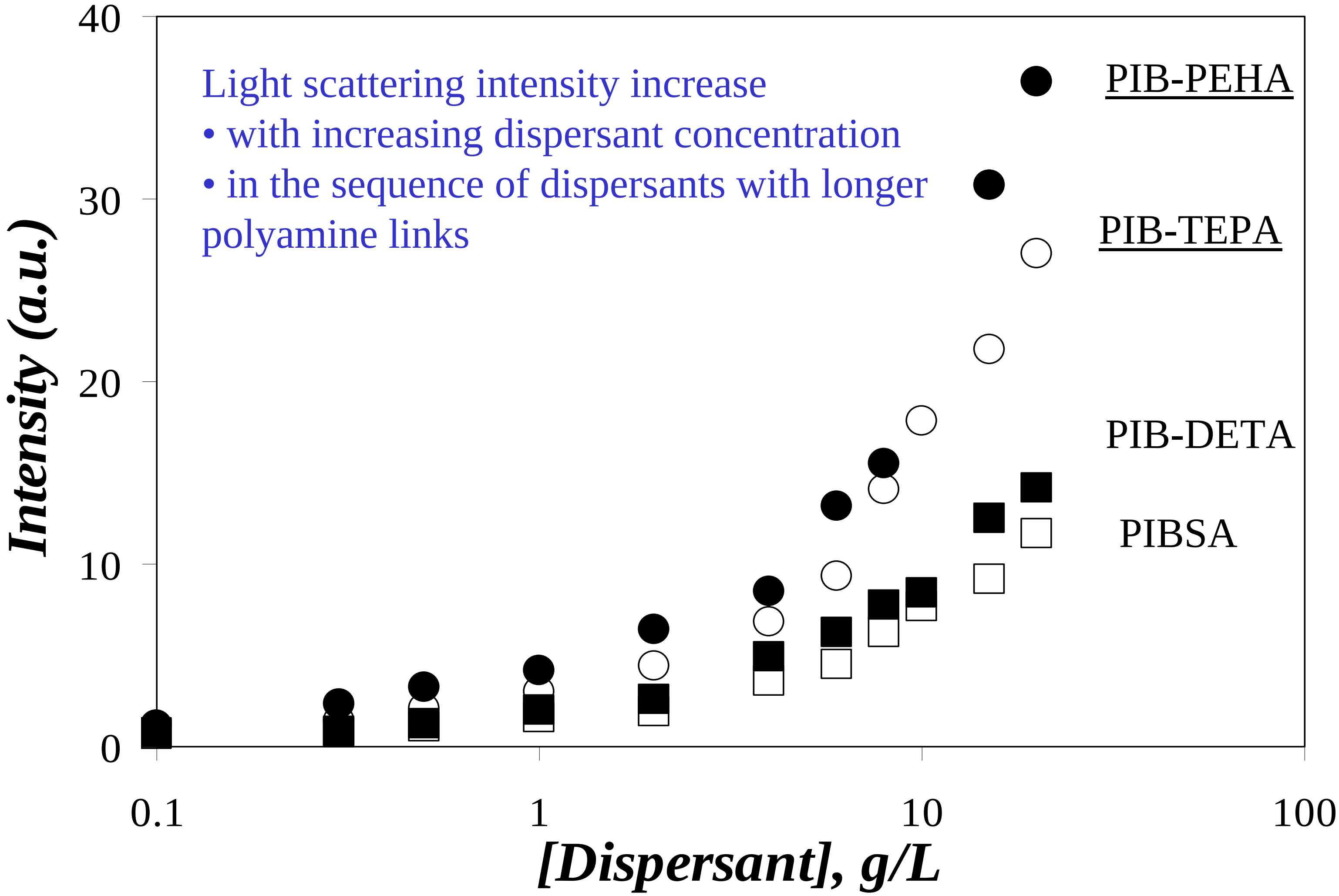
Associative Strength

- 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

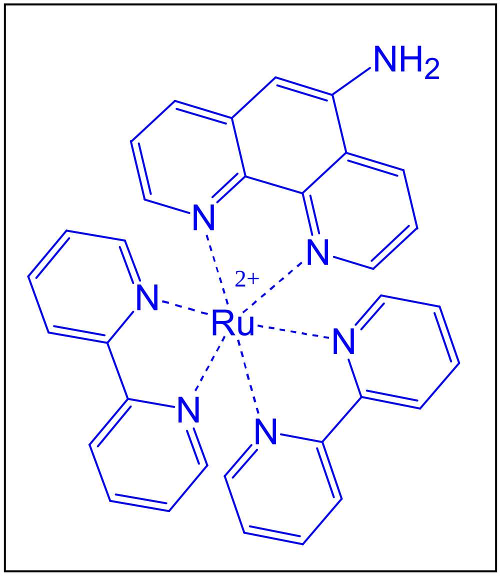
Measurement of the Associative Strength of Dispersants by Light Scattering



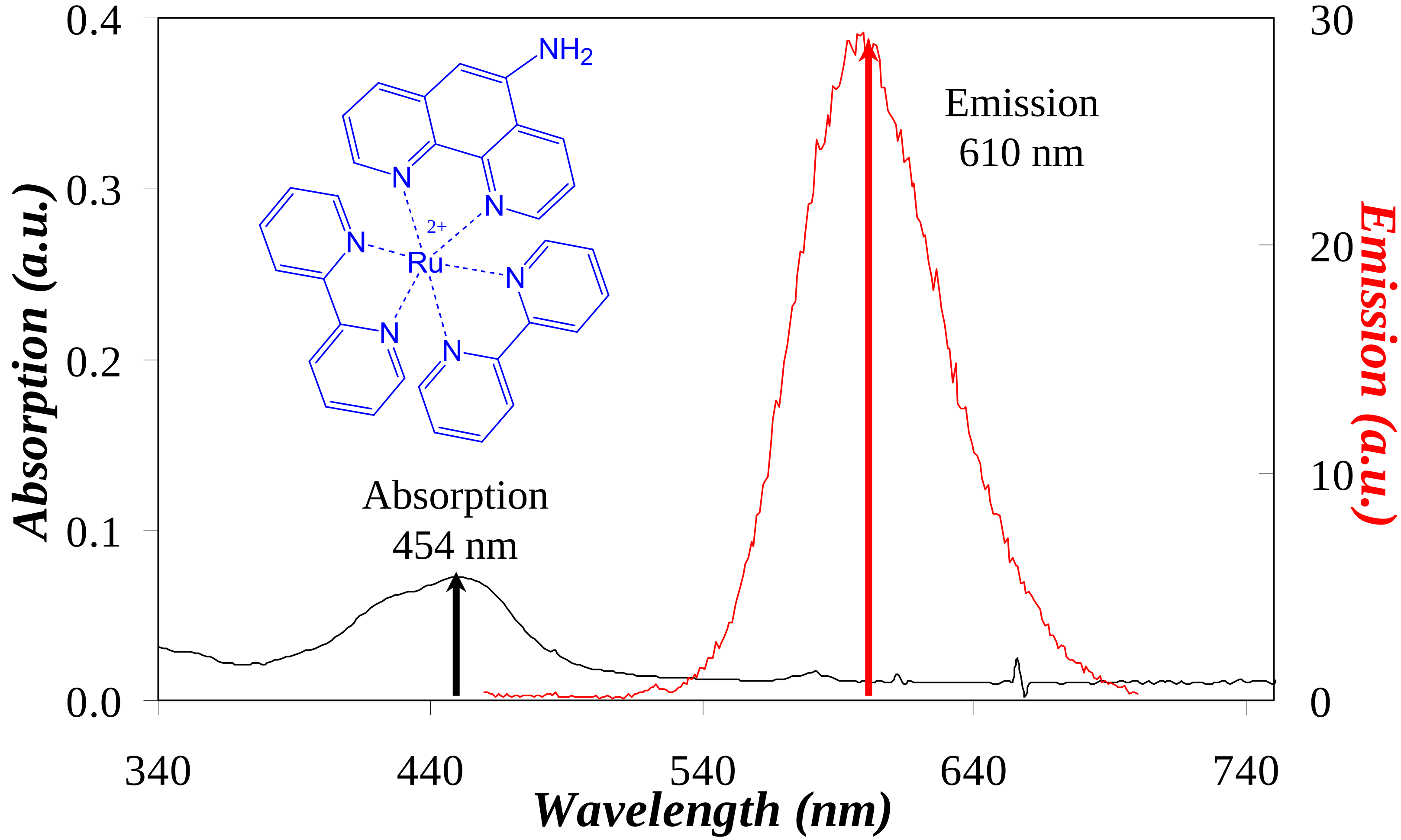
Measurement of the Associative Strength of Dispersants by Fluorescence

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

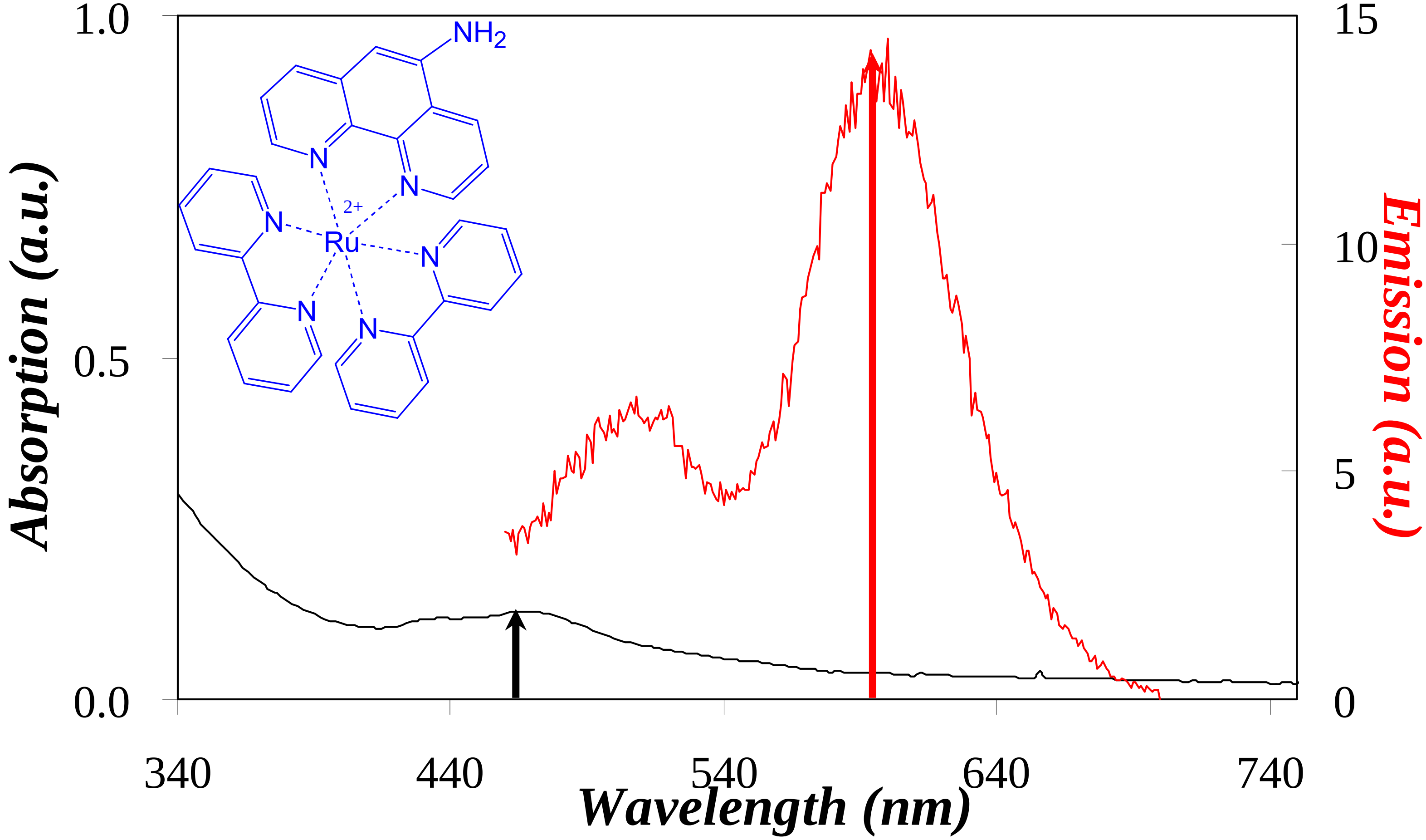
- confirm existence of dispersant aggregates
- probe the polar core of dispersant micelles
- not soluble in apolar solvents
- ideal to study the CMC of dispersants in hexane



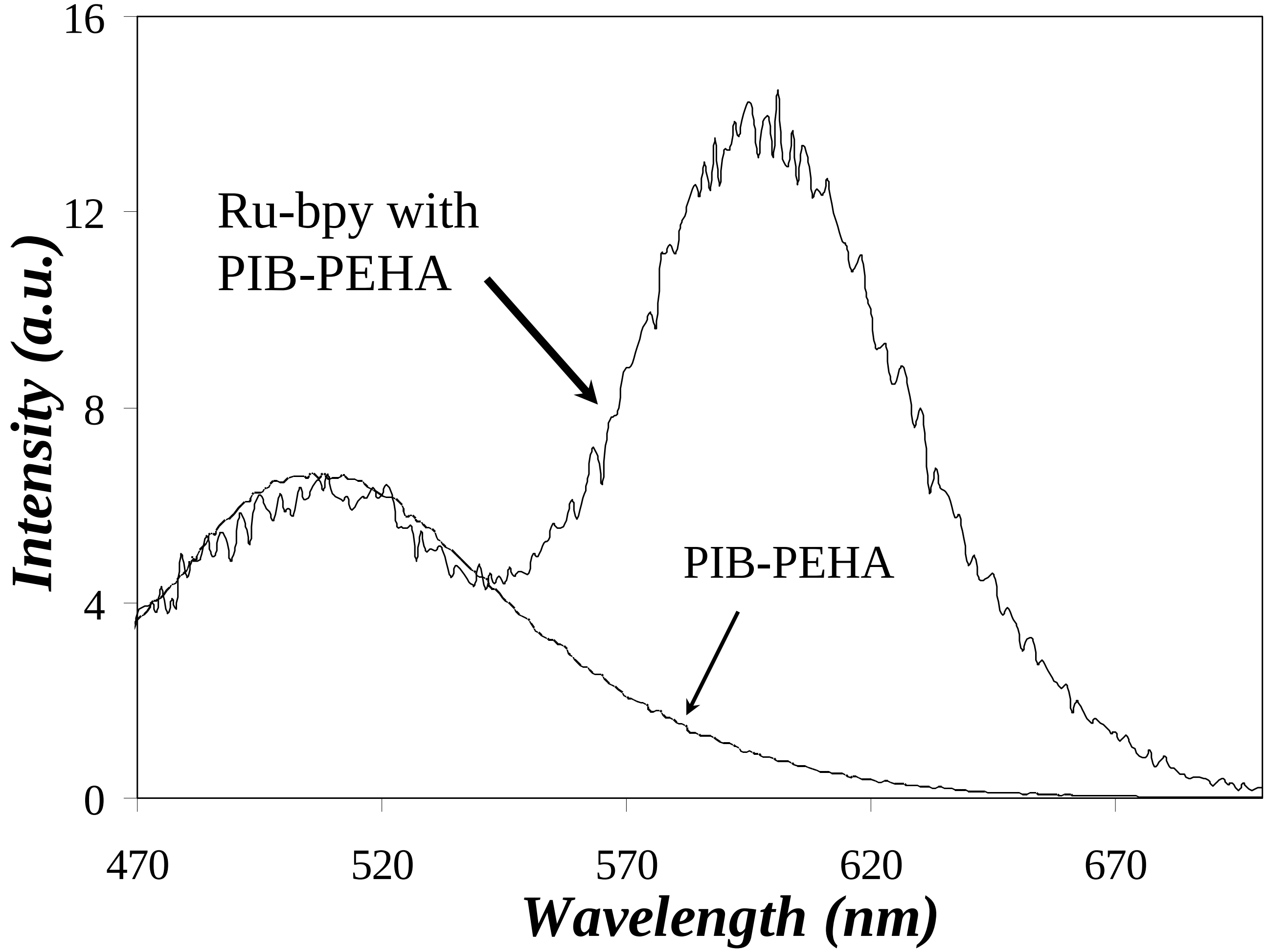
Absorption/Emission Spectra of Ru-bpy in methanol



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

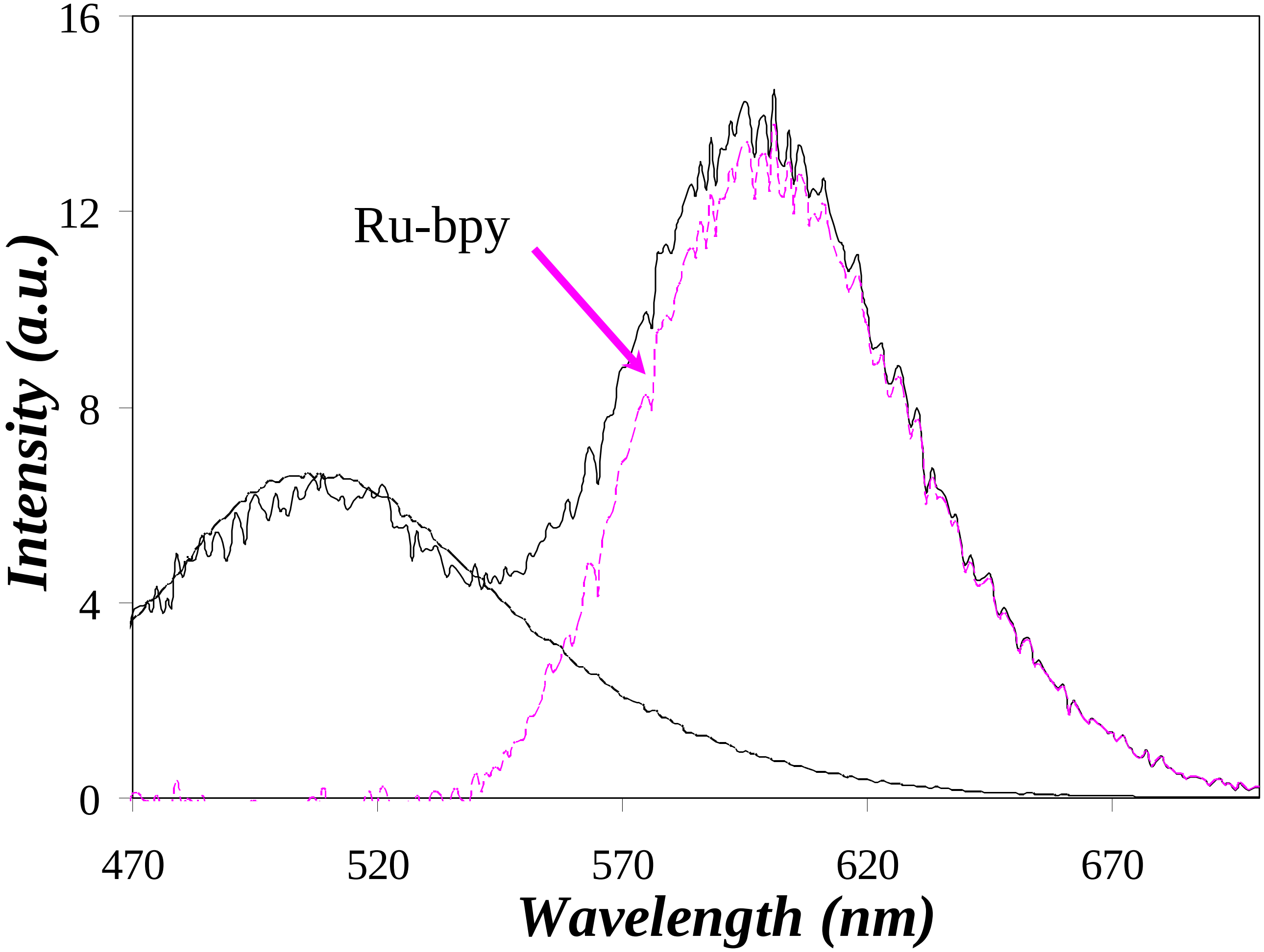


Fluorescence Measurement with Ru-bpy



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

Fluorescence Measurement with Ru-bpy



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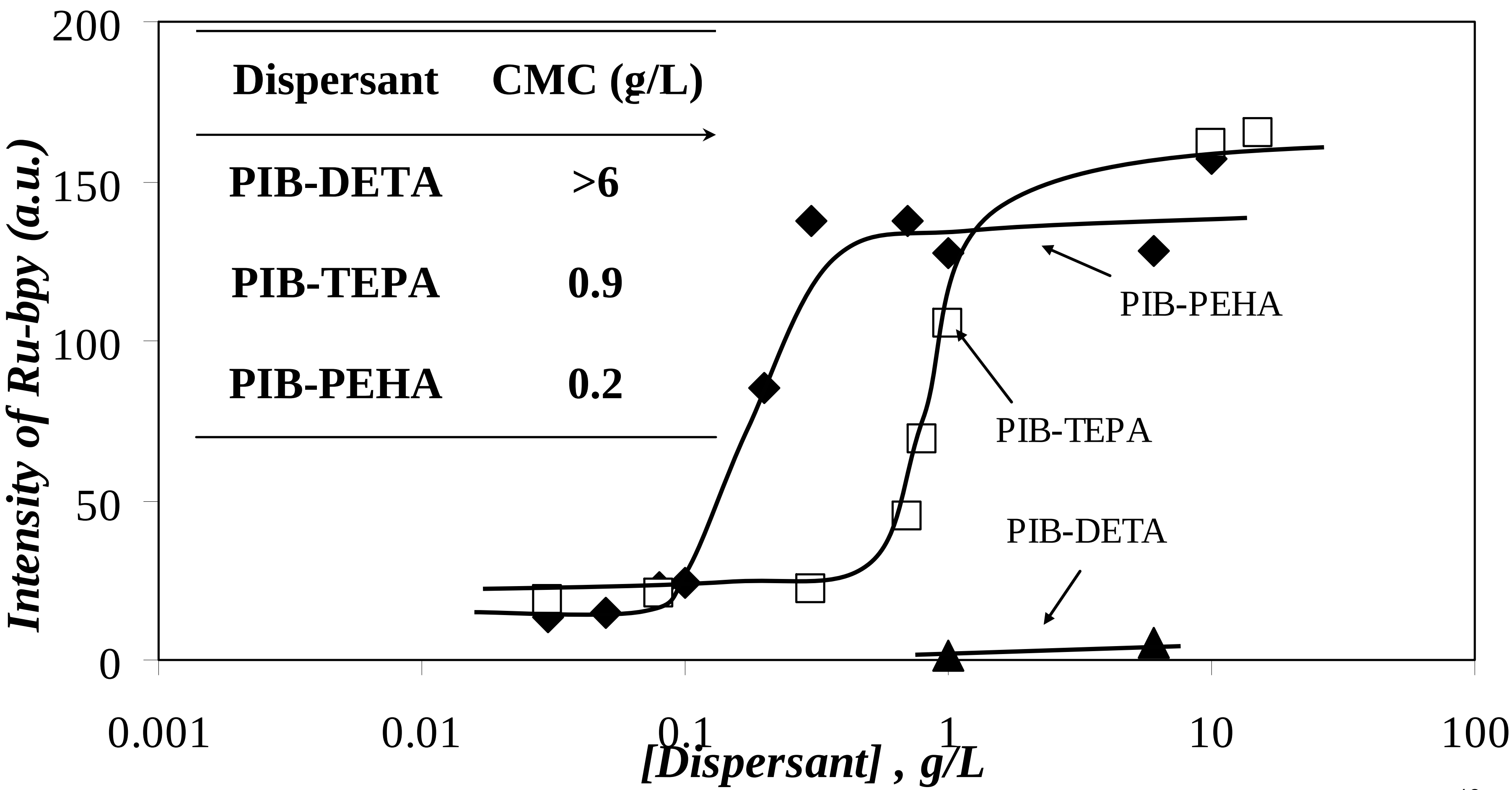
Fluorescence Measurement with Ru-bpy

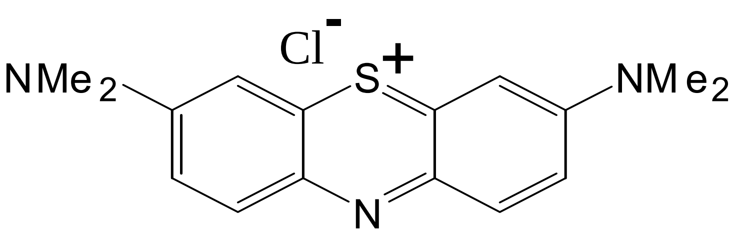


Adsorption Measurements

- 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

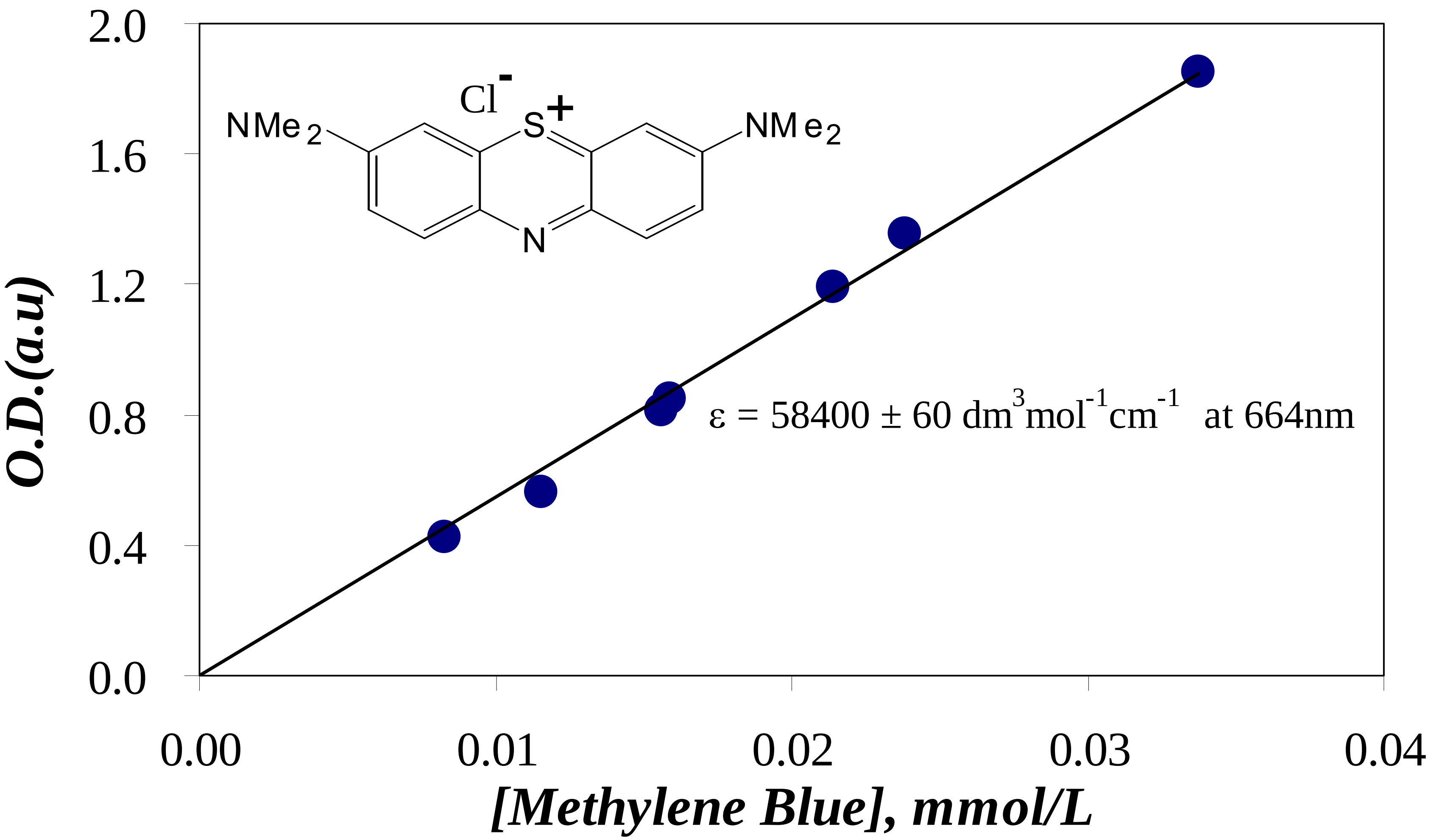


Methylene Blue

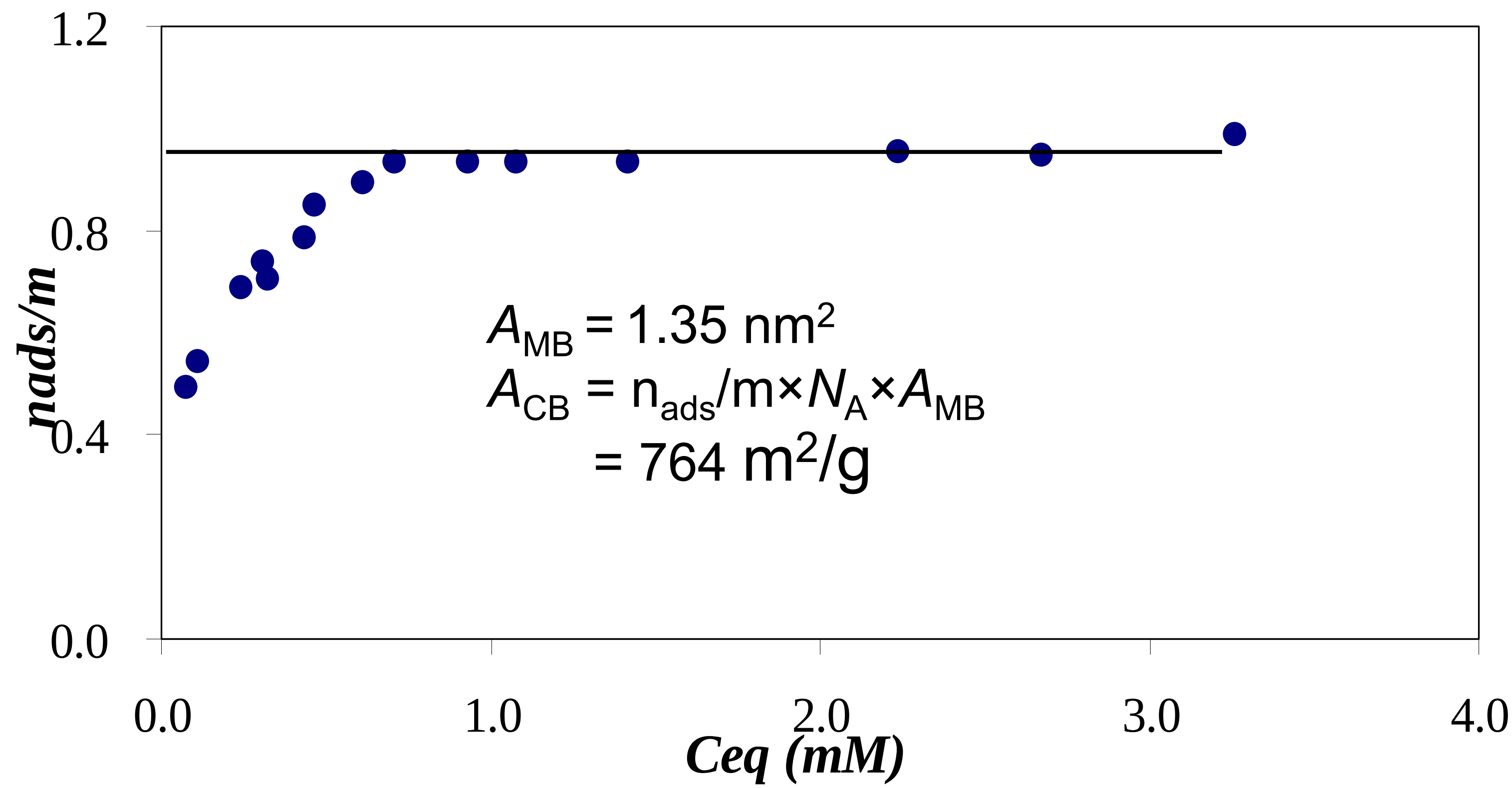
(MB)

Tomlinson, A. ; Danks, T. N. ; Heyes, D. M.; Taylor, S. E.; Moreton, D. J. *Carbon* **2000**, *38*, 13-28

Determination of the Extinction Coefficient of Methylene Blue

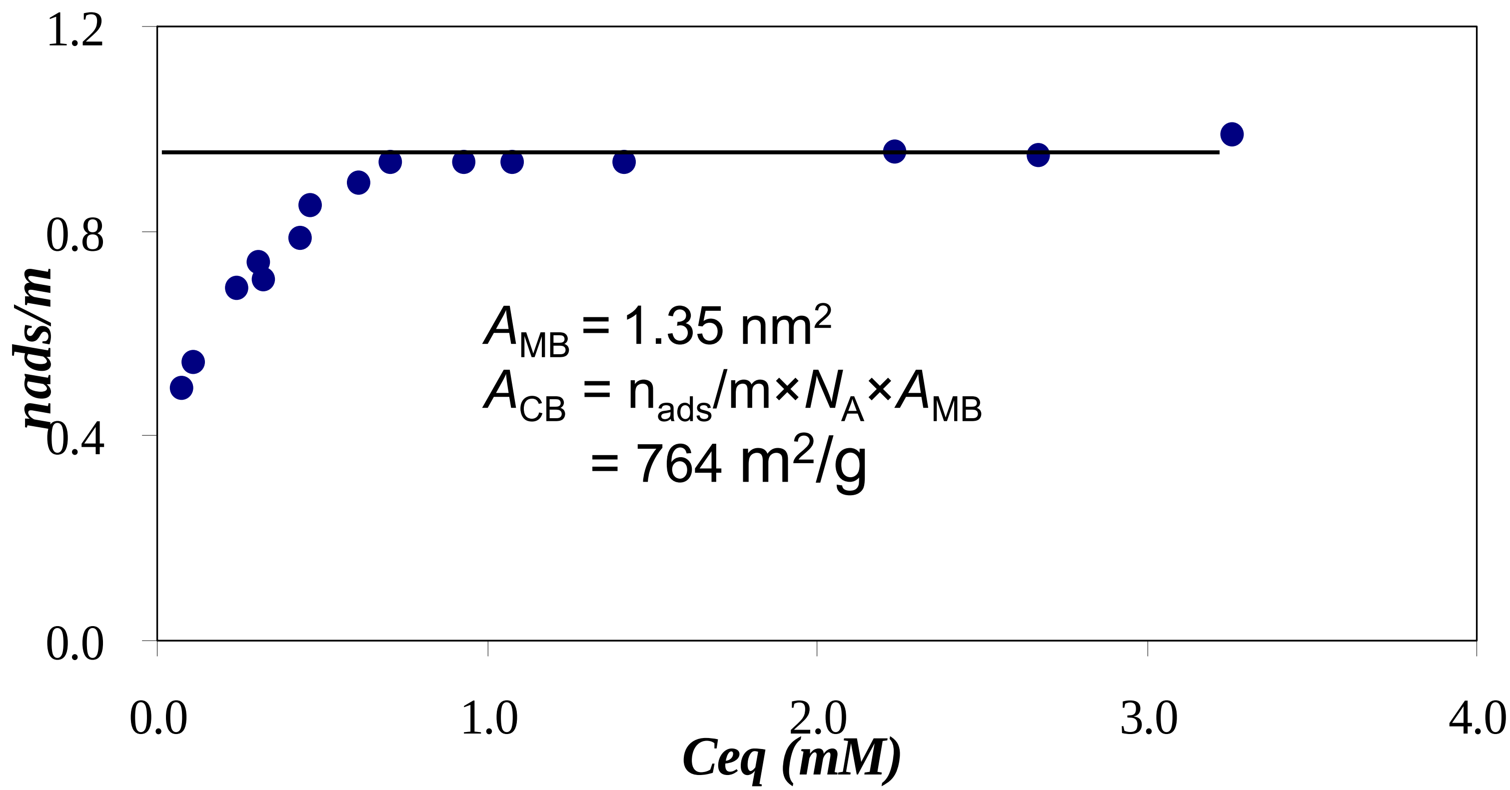


Determination of the Specific Area of Carbon Black (CB) Particles



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

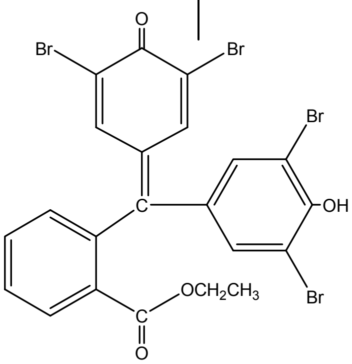
- ✓ Determination of the specific area of carbon black

  Measurement of the amount of adsorbed dispersants on carbon black

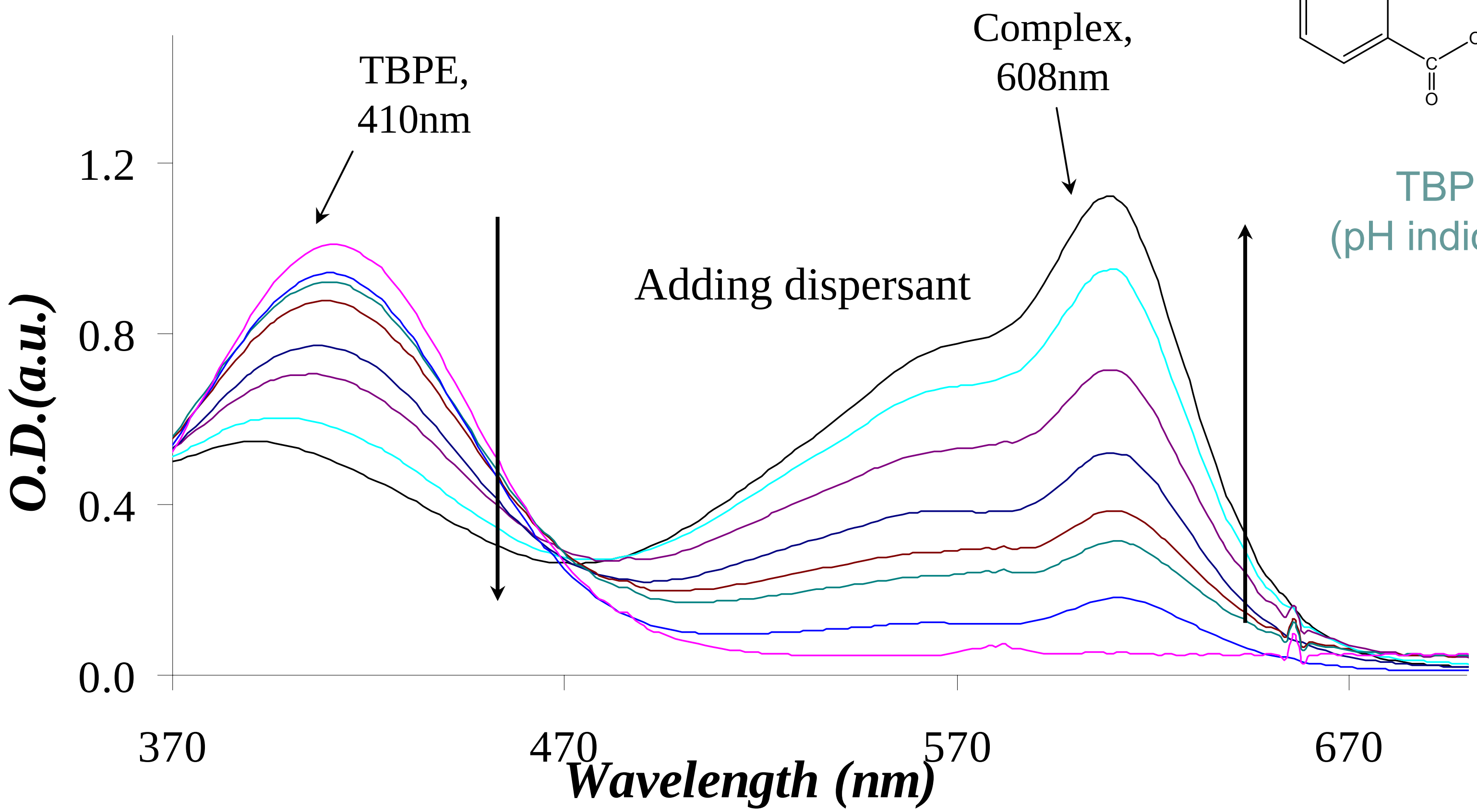
  Analysis with di-Langmuir Model

Measurement of Adsorbed Dispersants on CB Particles

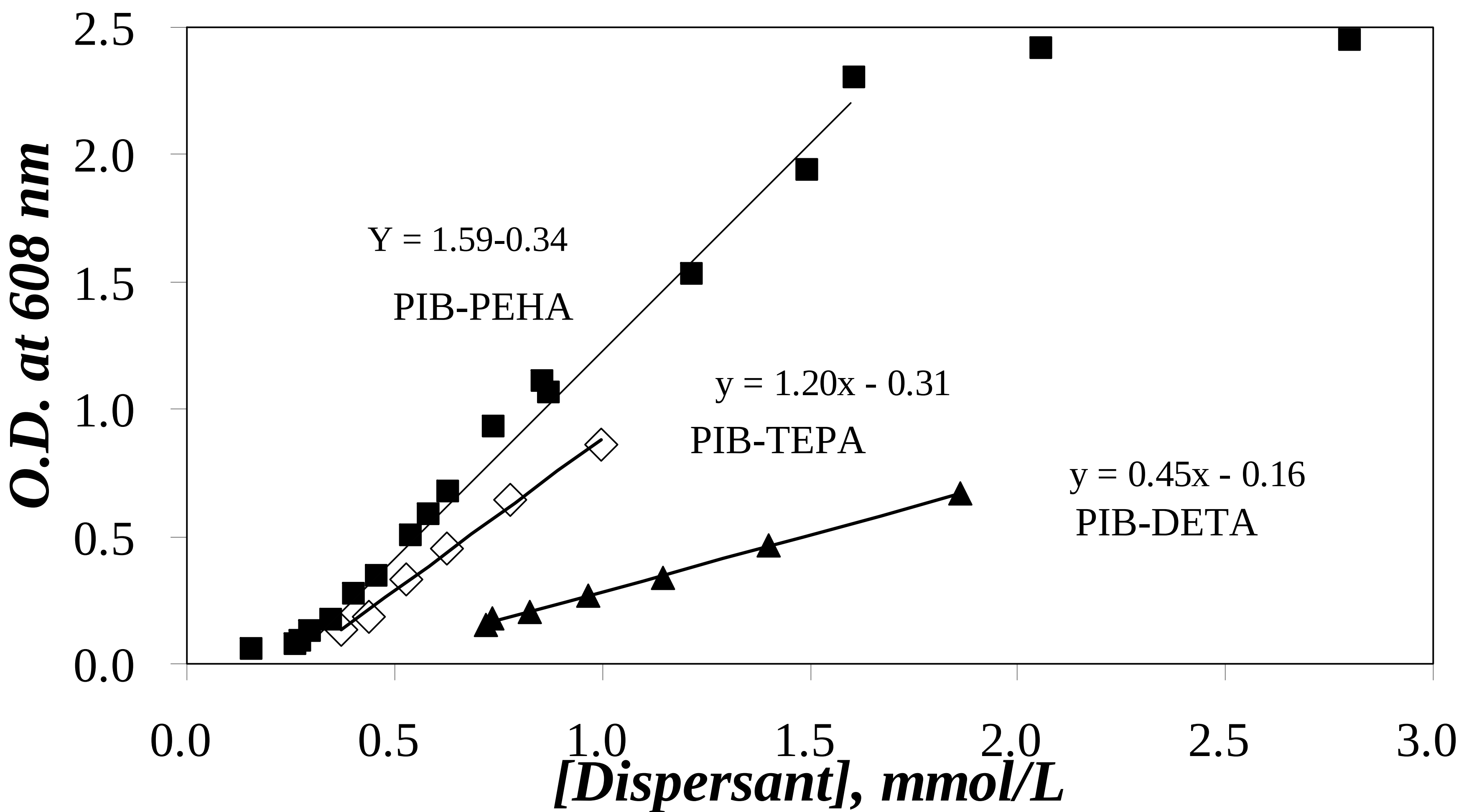
Dispersant + TBPE $\rightleftarrows$ DisTBPE (complex)



TBPE
(pH indicator)



Calibration of Dispersants Concentration

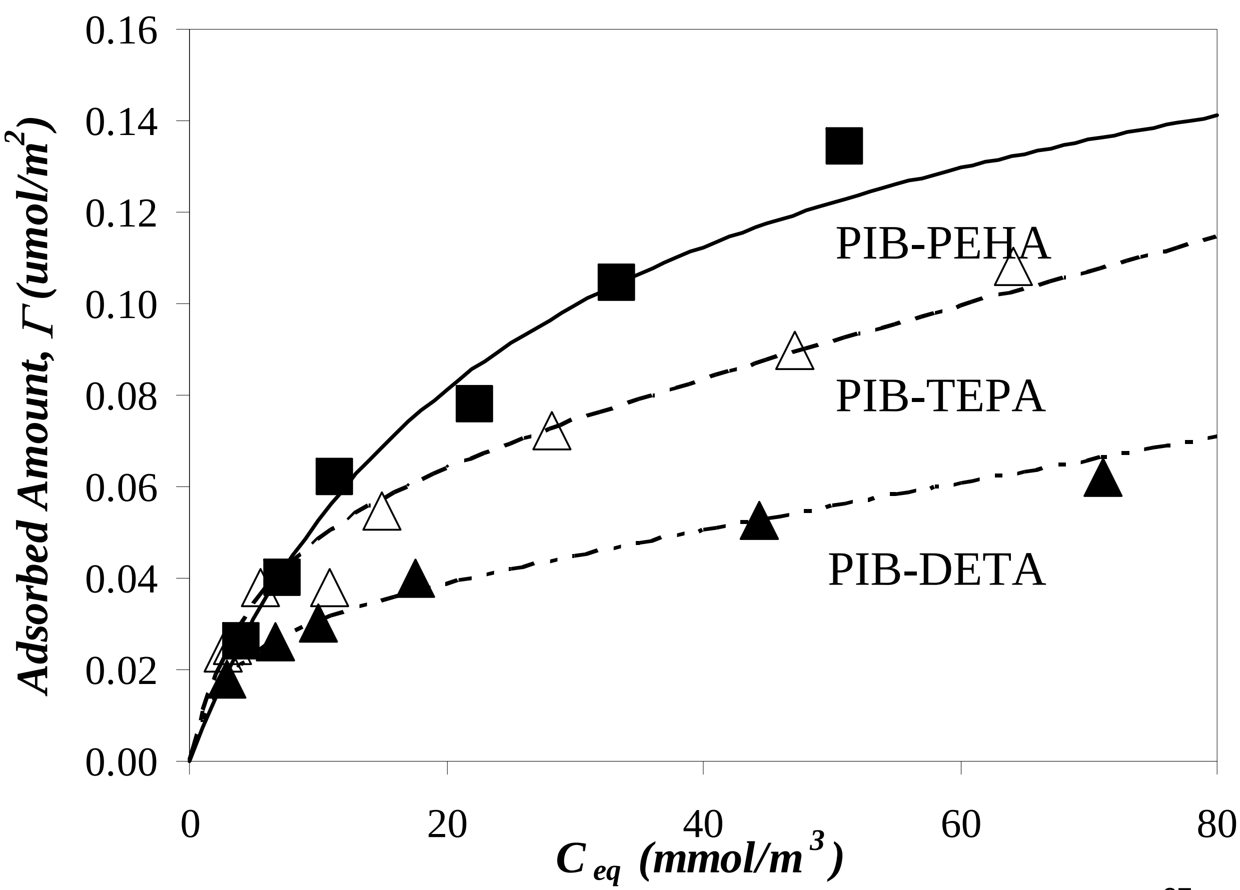


Adsorption Isotherm

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

Γ: 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

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

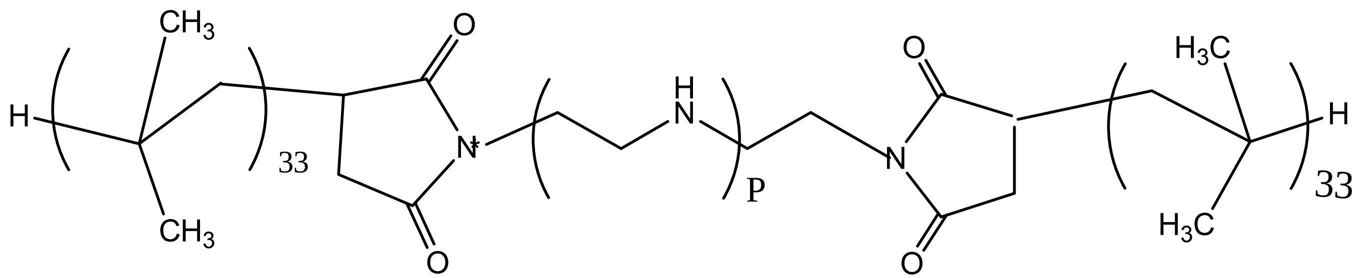
Γ1, Γ2 : ***maximum amount of dispersant adsorbed*** **at saturation**

K1 , K2 : **equilibrium constants of the two sites**

	Γ_1 (mol.m^{-2})	K_1 (m^3.mol^{-1})	$\Gamma_2 K_2$ (m)
PIB-DETA	1.70×10^{-7}	43	1.13×10^{-7}
PIB-TEPA	6.31×10^{-8}	193	6.91×10^{-7}
PIB-PEHA	3.35×10^{-8}	336	4.82×10^{-7}

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

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