Ciência e Tecnologia
Ministério da Ciência e Tecnologia

Polymeric nanostructures

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Universidade Federal de Pernambuco

VIRTUS IMPAVIDA

polymeric nanostructures

City of Recife,
Capital of the State of Pernambuco

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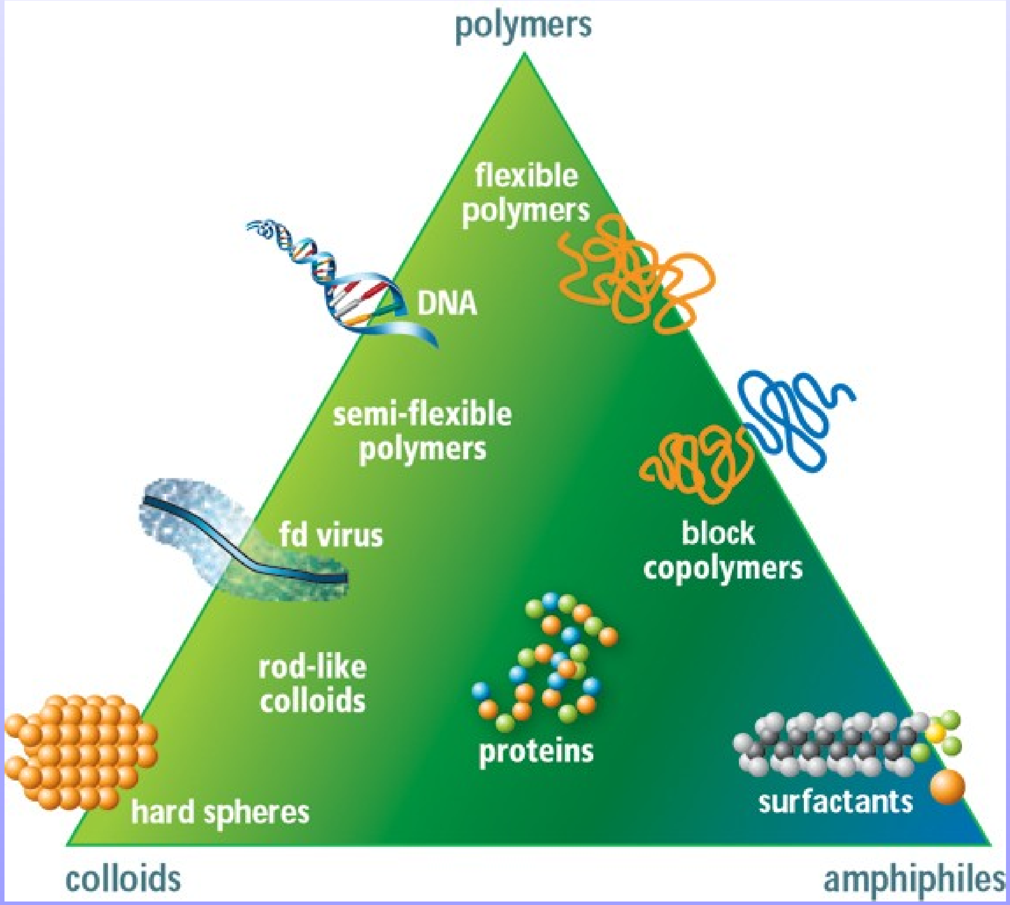
Soft Matter: a large number of possibilities

Phase Diagram

- polymers
- colloids
- surfactants



Conducting

Polymers

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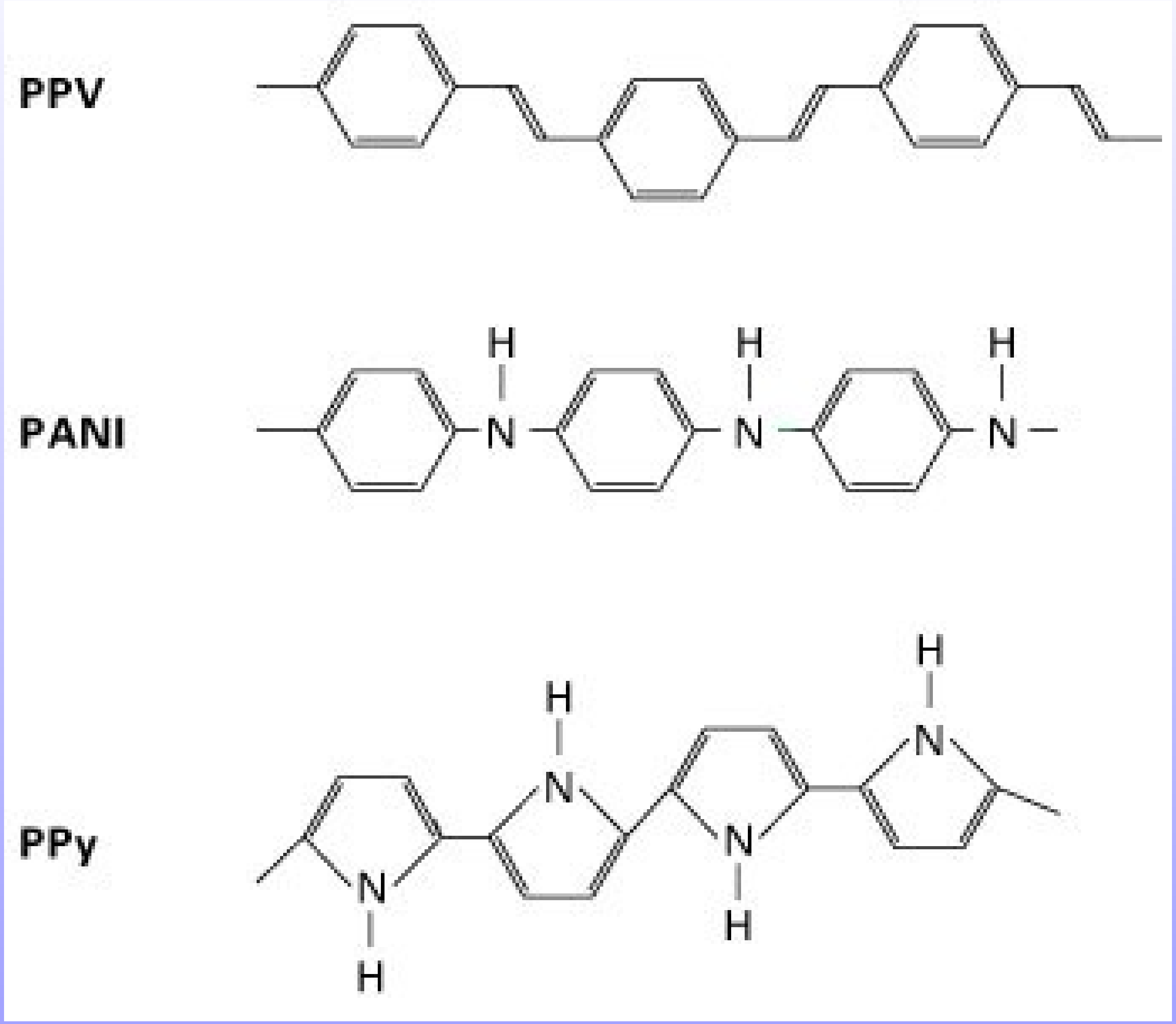

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Conducting polymers as promising materials for:

- OLEDs

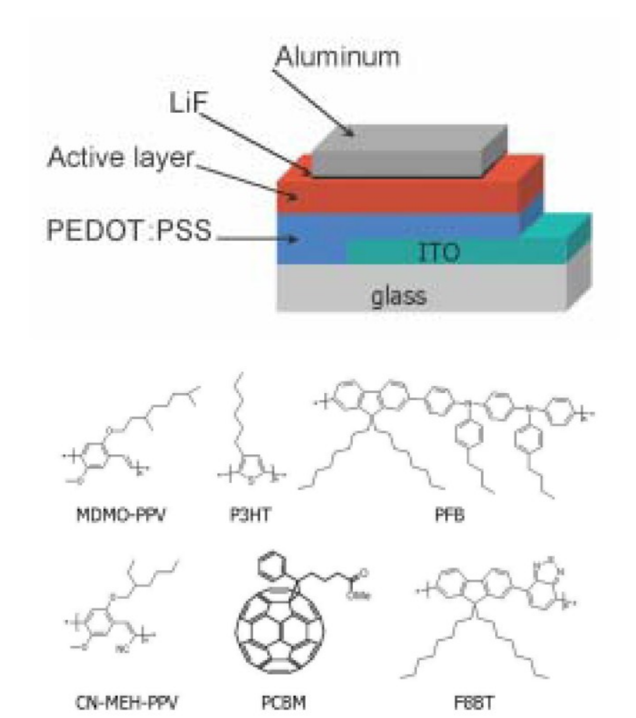

Fig. 1 Schematic structure of a bulk heterojunction photovoltaic device as well as the structural formulae of commonly used compounds in the active layer: poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene-vinylene) (MDMO-PPV); poly-(3-hexylthiophene) (P3HT); poly(9, 9′-dioctylfluorene-co-bis-N,N′-(4-butylphenyl)-bis-N,N′-phenyl-1,4-phenylenediamine) (PFB); poly(2-methoxy-5-ethylhexyloxy-1,4-phenylenecyanovinylene) (CN-MEH-PPV); [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM); and poly(9,9′-dioctylfluorene-co-benzothiadiazole) (F8BT).

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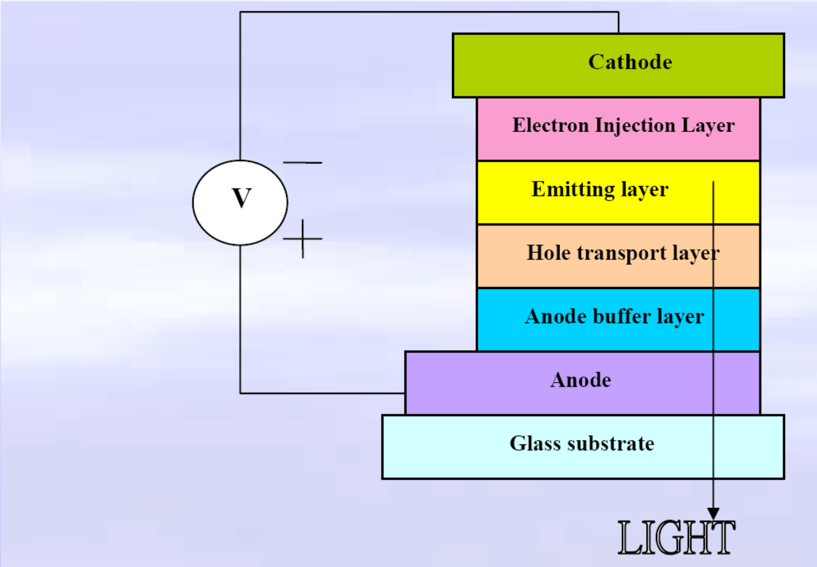


The different layers of the composition of the OLED

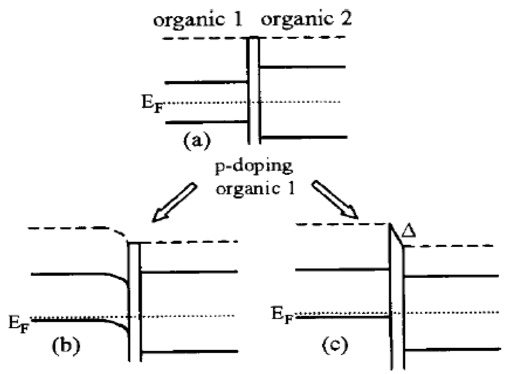
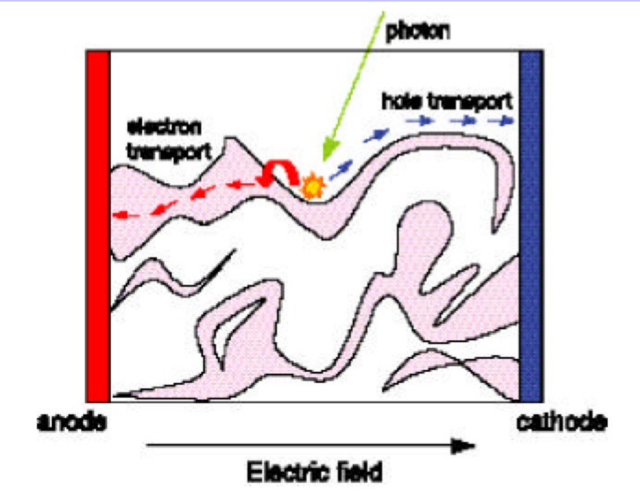


FIG. 1. Scenarios for energy level alignment at organic-organic interfaces when one of the organic materials is *p*-type doped. (a) Both materials undoped; (b) molecular level bending in the doped layer; and (c) interface dipole barrier formation.



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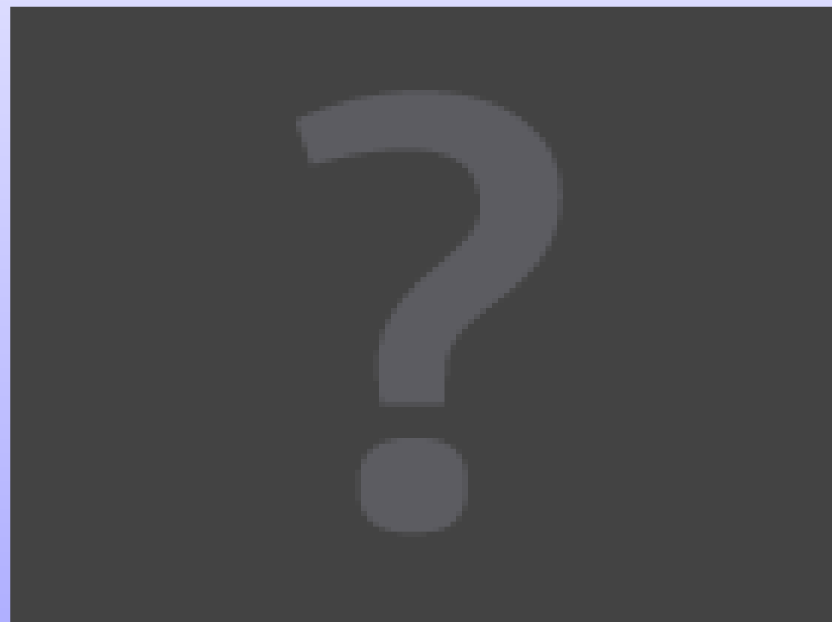
Conducting polymers as promising materials for:

- **electromechanical actuators (“artificial muscles”)**



- **microfluidics: pumps, sphincters, ...**

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Conducting polymers as promising materials for:

- **“electronic nose” type of instruments**

The resistivity of a polymeric film changes after exposure to a vapor:

➔ Use as gas sensors

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Synthetic Metals 102 (1999) 1296–1299

Polypyrrole Based Aroma Sensor*

J.E.G. de Souza[a,b], B.B. Neto[b], F. L. dos Santos[c], C. P. de Melo[c,#], M.S Santos[d], T.B. Ludermir[d]
[a]*Departamento de Química, Universidade Católica de Pernambuco, Recife, PE Brazil*
[b]*Departamento de Química Fundamental,* [c]*Departamento de Física,* [d]*Departamento de Informática, Universidade Federal de Pernambuco, 50670-901, Recife, PE, Brazil*

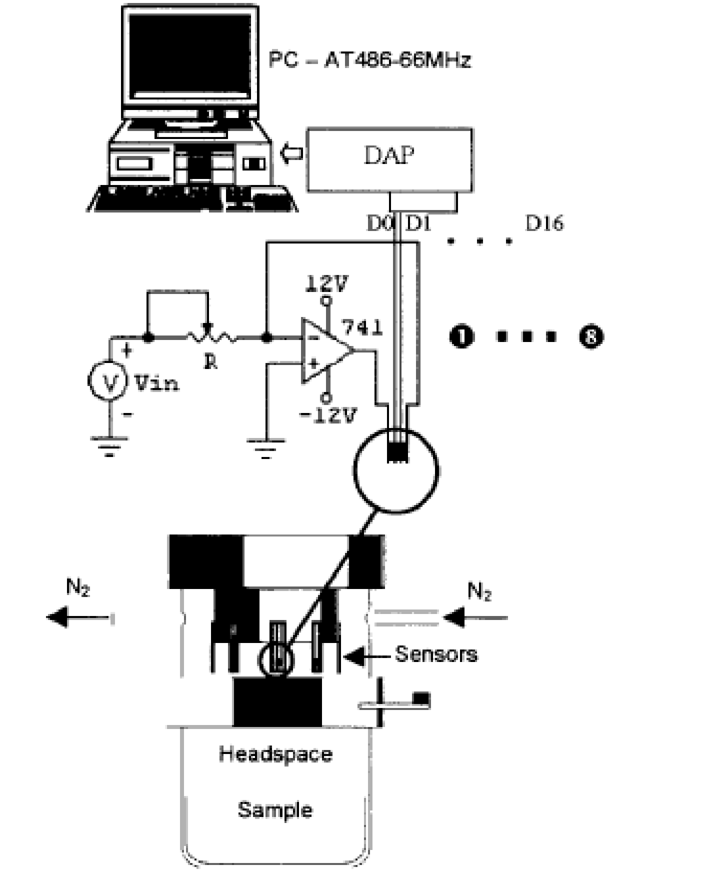

Fig. 1: Diagram of the P-2 prototype, with an indication of the current source for one of sensor units.

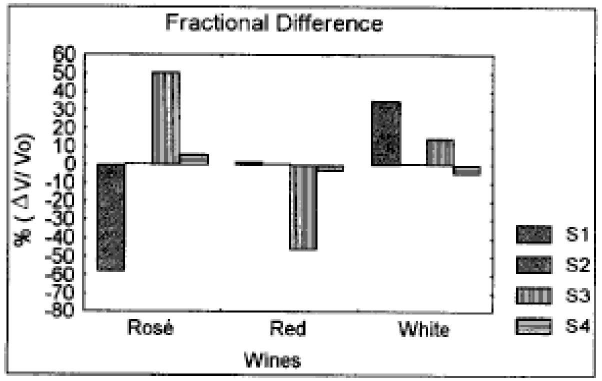

Fig. 3: Fractional change of V_{23} in four of the P-2 sensors after exposure to rosé, red and white wines.

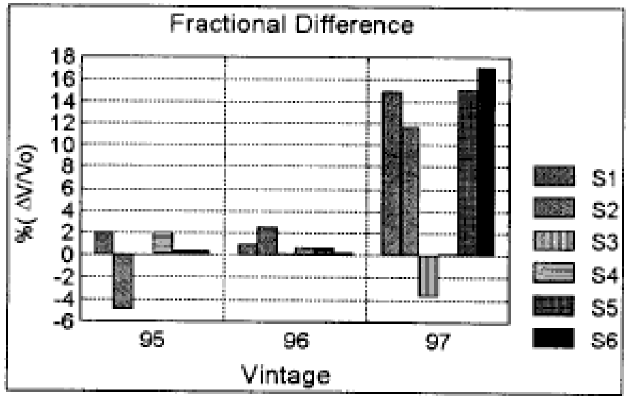

Fig. 4: Fractional change of V_{23} in the P-2 sensors after exposure to red wines of different vintages.

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Sensors and Actuators B 88 (2003) 246–259

Free-grown polypyrrole thin films as aroma sensors

J.E.G. de Souza[a], F.L. dos Santos[b], B.B. Neto[c], C.G. dos Santos[d], M.V.B. dos Santos[c,d], C.P. de Melo[d,*]

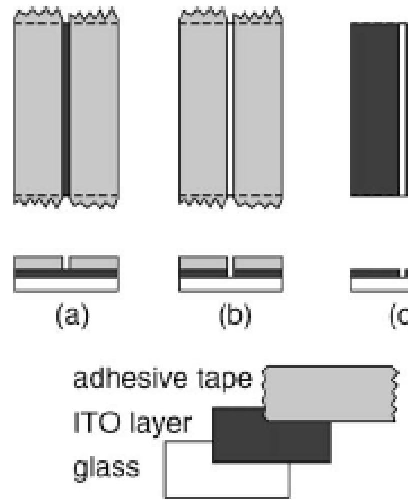

Fig. 1. Preparation of ITO slide for use as substrate: (a) protection of two independent conducting areas; (b) corrosion of ITO in the middle region between adhesive tape strips; (c) ready to use substrate after removal of the adhesive tape.

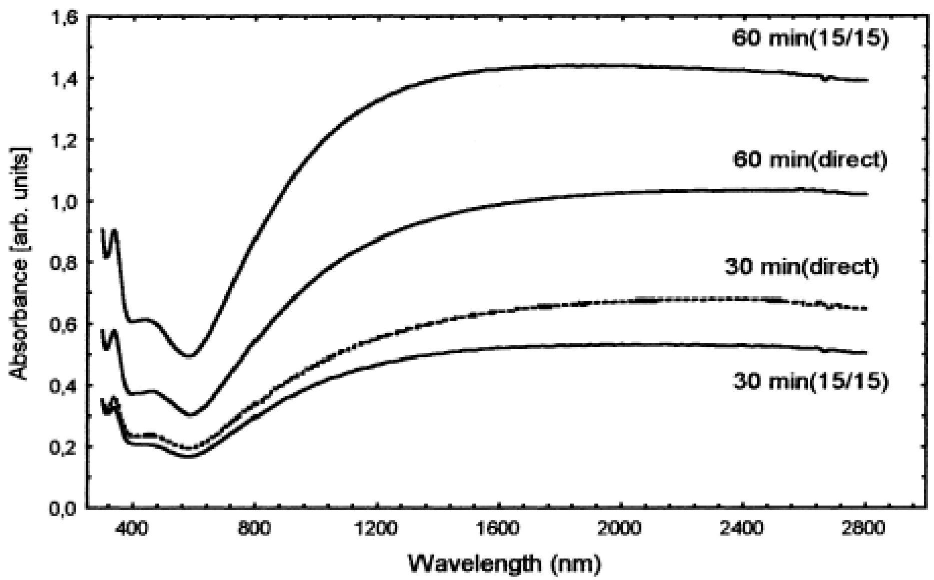

Fig. 6. UV-Vis/NIR absorbance spectra of PPy/ASA films prepared by direct and intermittent polymerization.

- electrochemical polymerization
- polymerization by vapor phase technique

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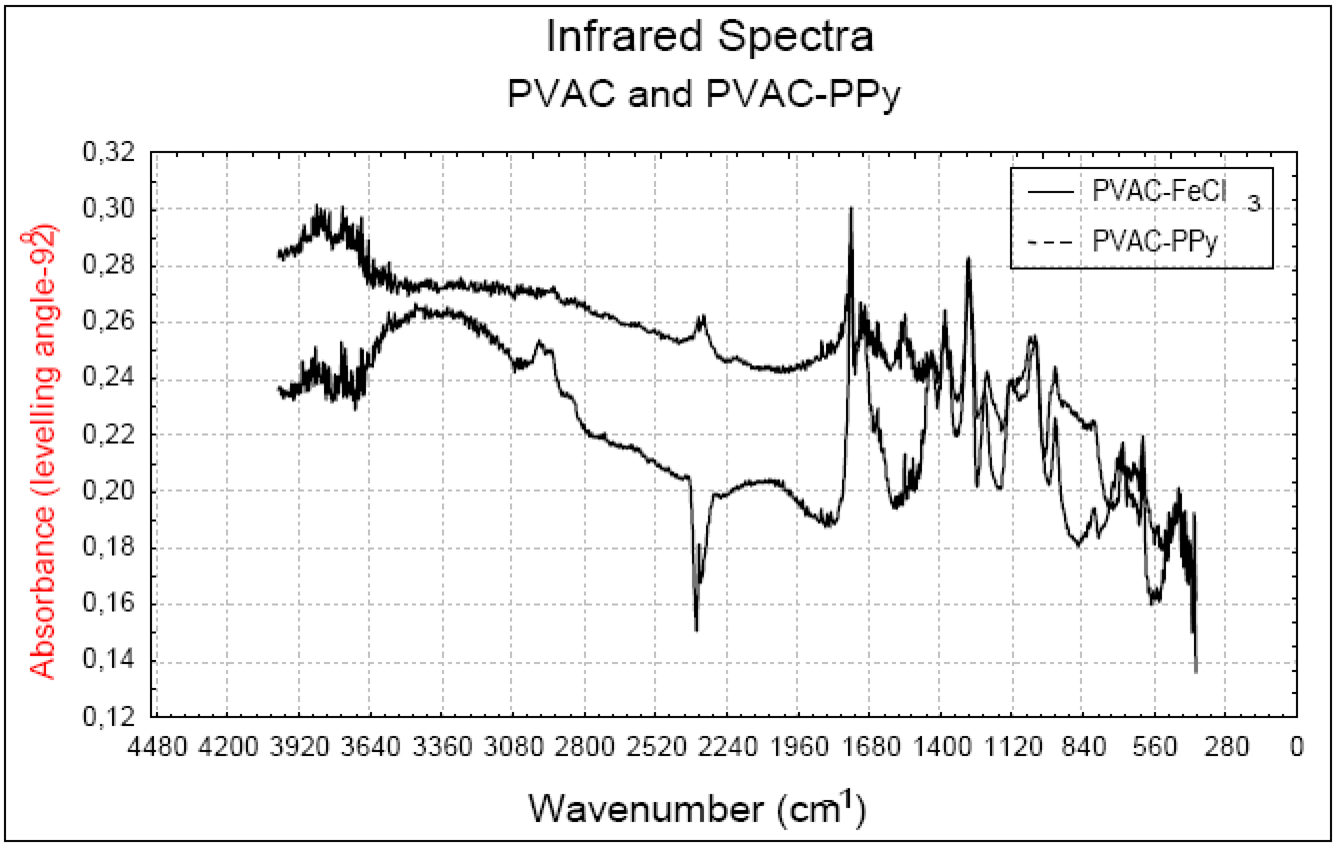

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Synthetic Metals 119 (2001) 383–384

Polypyrrole thin films gas sensors

J.E.G. de Souza[a], F.L. dos Santos[a], B. Barros-Neto[b], C.G. dos Santos[b], C. P. de Melo[b#]
[a]*Universidade Católica de Pernambuco, 50050-900, Recife PE Brazil*
[b]*Universidade Federal de Pernambuco, 50670-901, Recife PE Brazil*

$$f_d = \frac{R_t - R_0}{R_0}$$

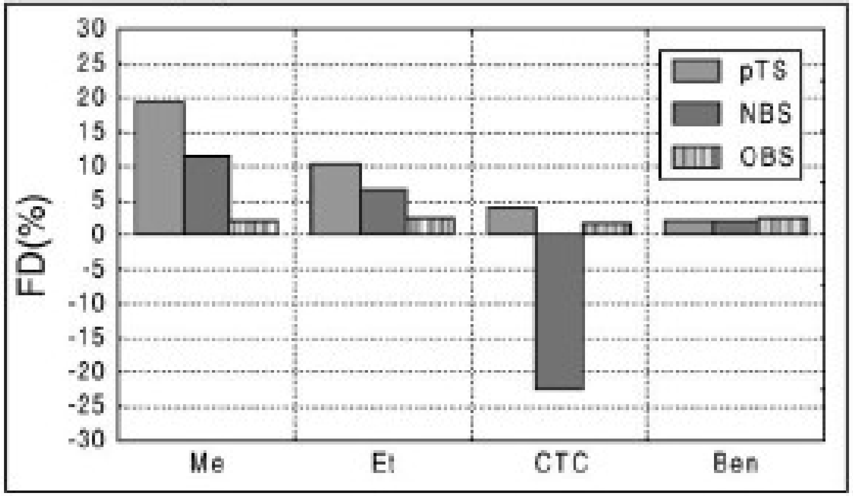

Fig. 2 – Sensitivity of the sensors (the counter-ion effect).

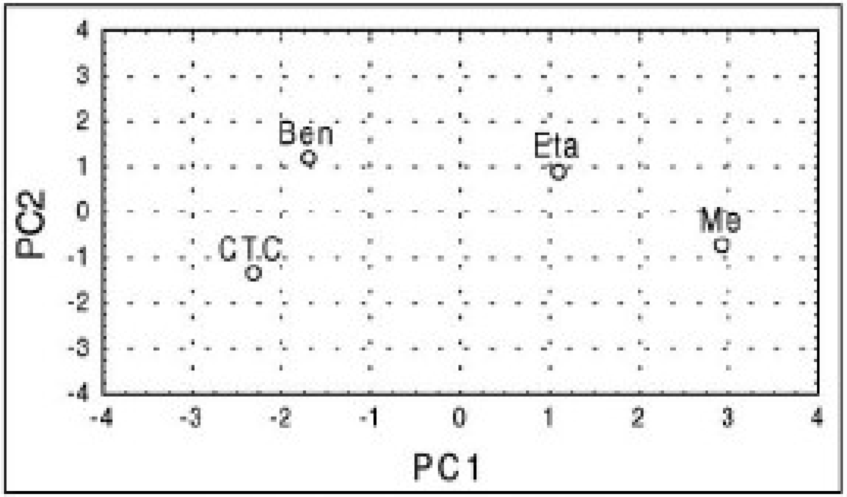

Fig. 3 – PC1 and PC2 scores plot.

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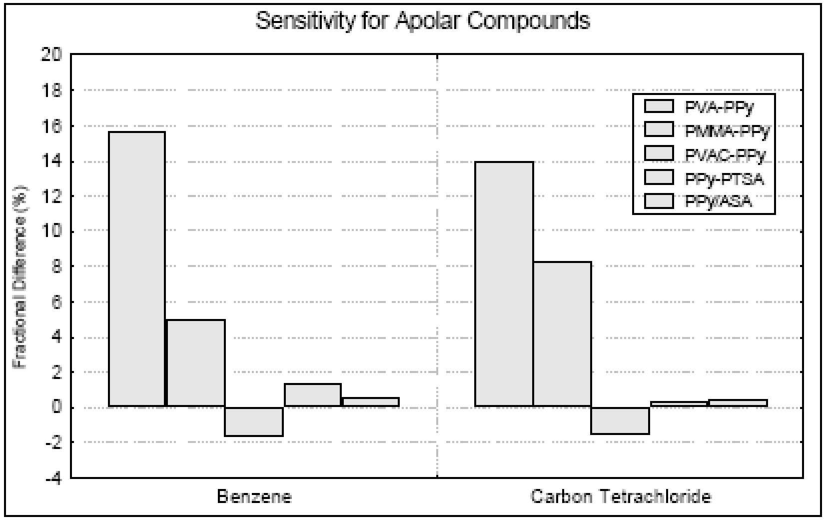

Figure 9

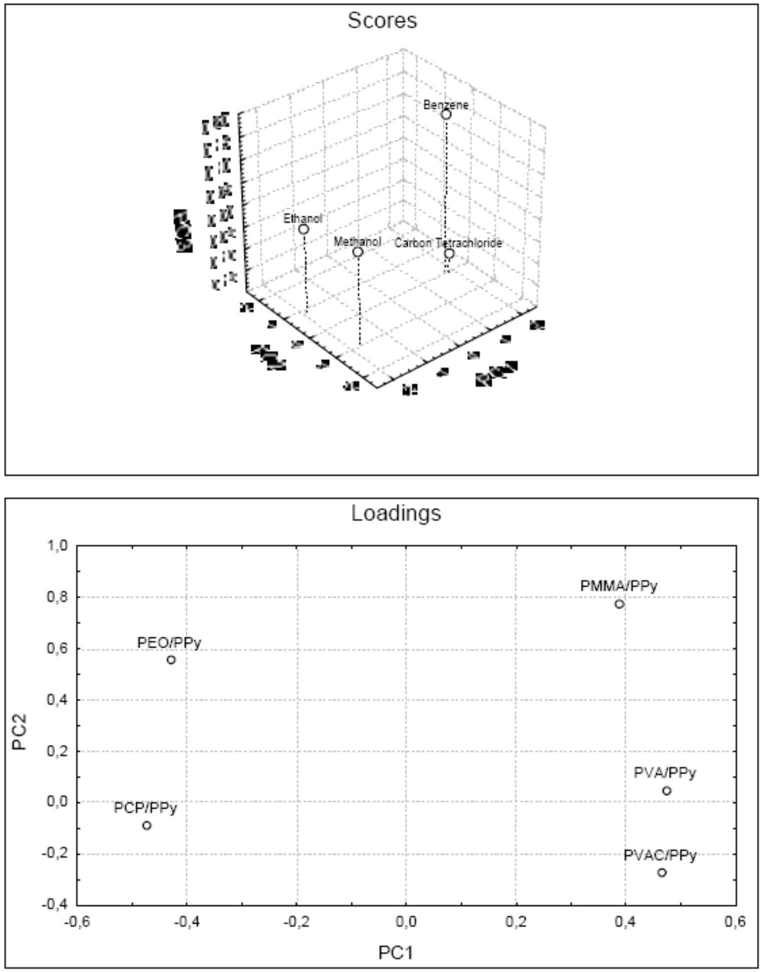

Figure 8

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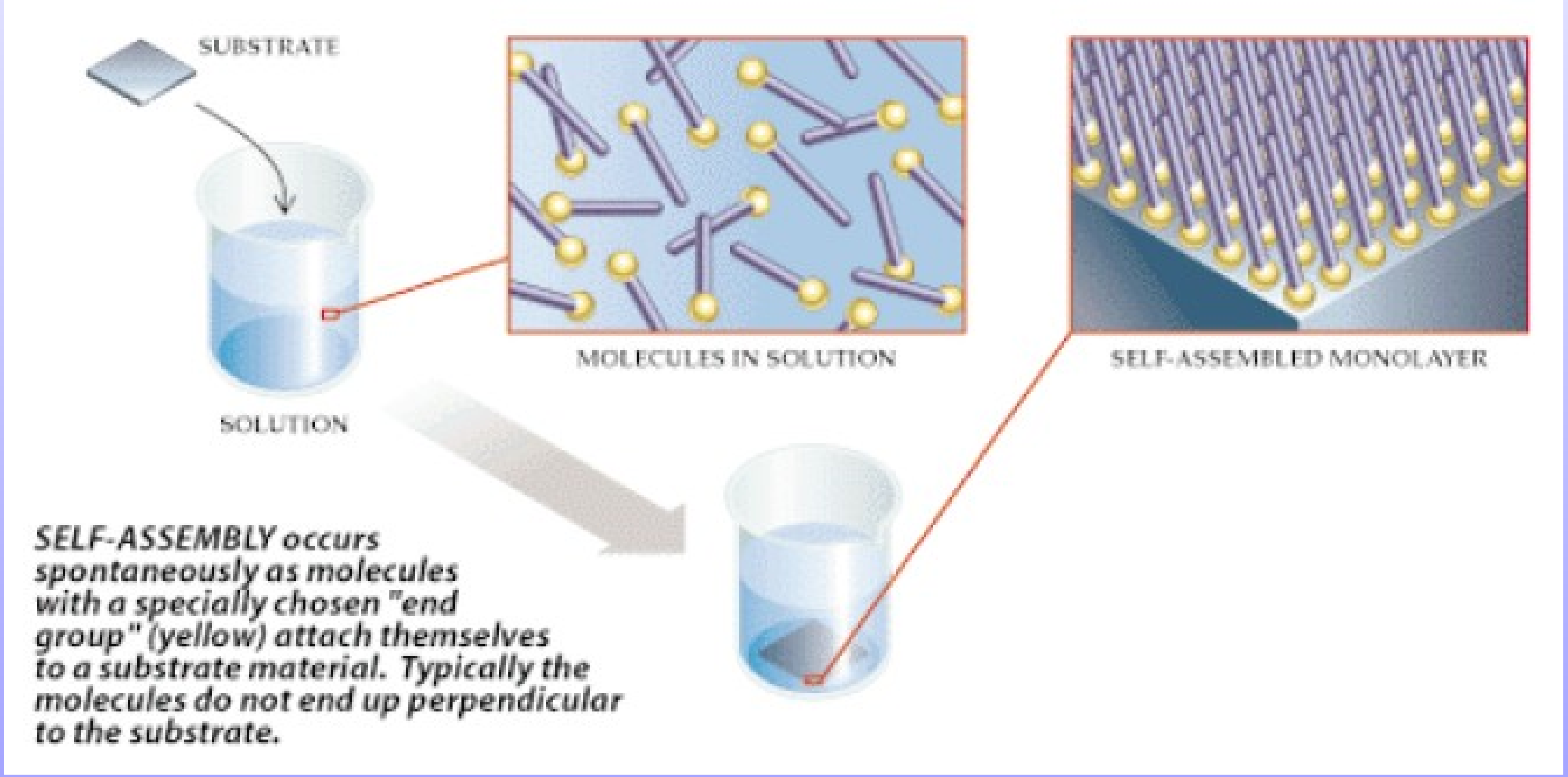
Self-assembly of complex structures



Colloidal Systems

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Colloidal Emulsions and Dispersions

Size distribution of the particles

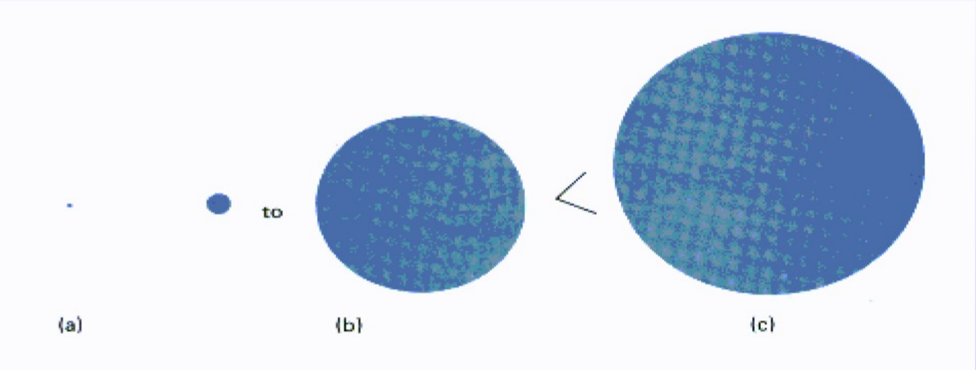

Fig:5.1 Relative particle size: (a) Solute in a solution = 1. (b) Dispersed particles in a colloid = 10 to 100 (c) Suspended particles in a suspension > 100

Table 1.1: Types of dispersions. *Porous solids have a bicontinuous structure while in a solid foam the gas phase is clearly dispersed.

Continuous phase	Dispersed phase	Term	Example
Gas	liquid	aerosol	clouds, fog, smog, hairspray
	solid	aerosol	smoke, dust, pollen
Liquid	gas	foam	lather, whipped cream, foam on beer
	liquid	emulsion	milk
	solid	sol	ink, muddy water, dispersion paint
Solid	gas	porous solids*	
		foam	styrofoam, soufflés
	liquid	solid emulsion	butter
	solid	solid suspension	concrete

Surfactants

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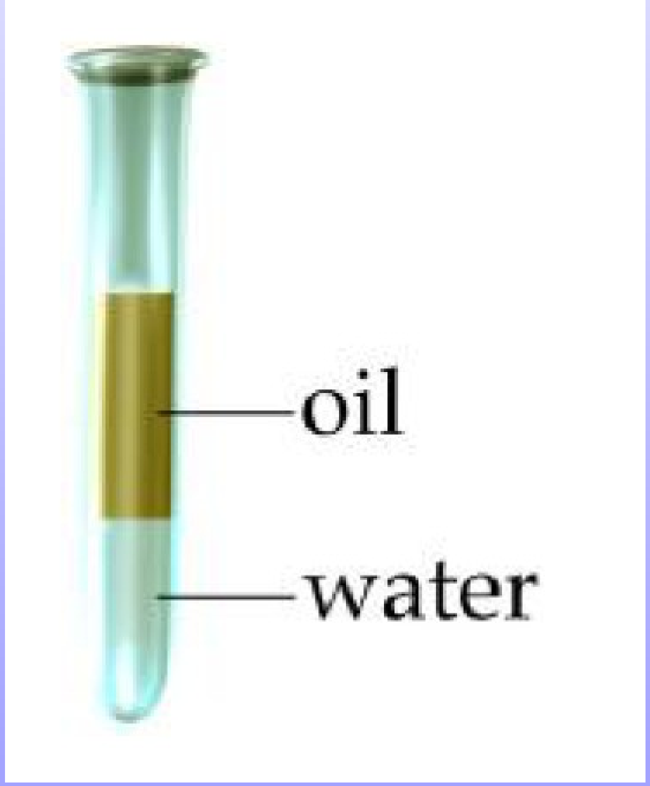
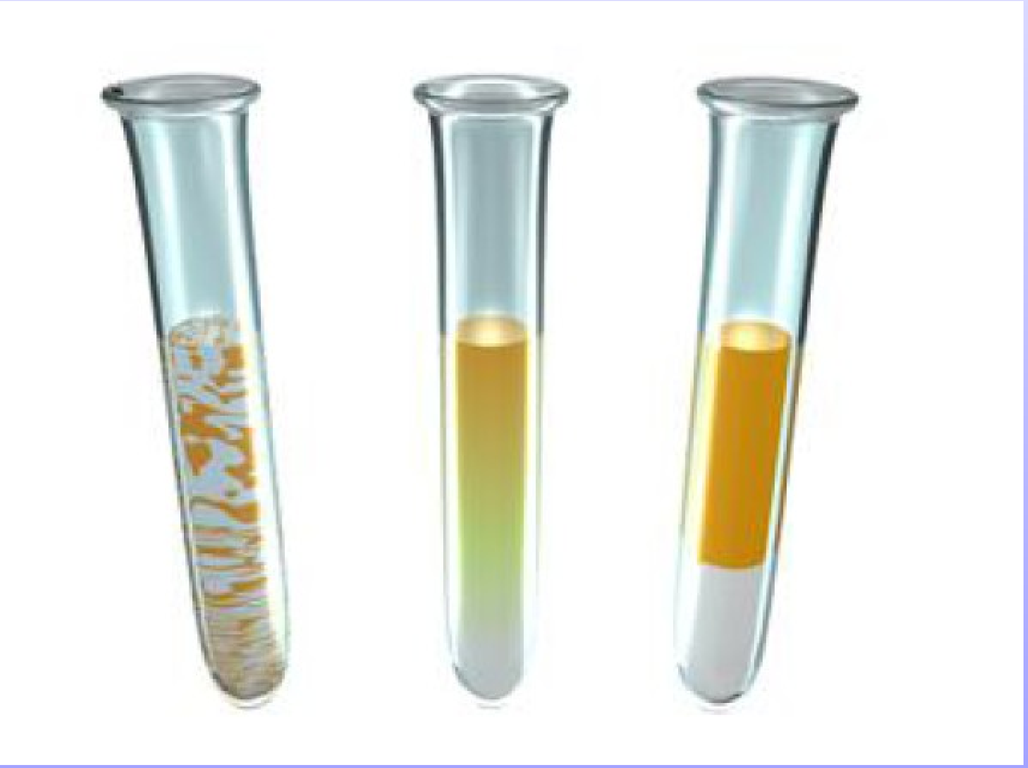
"as different as oil and water"

- **water and oil (fat) do not mix**





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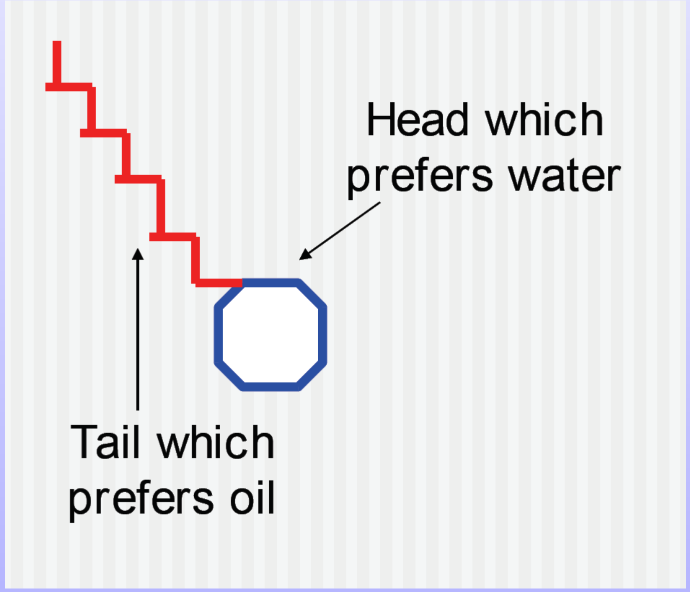
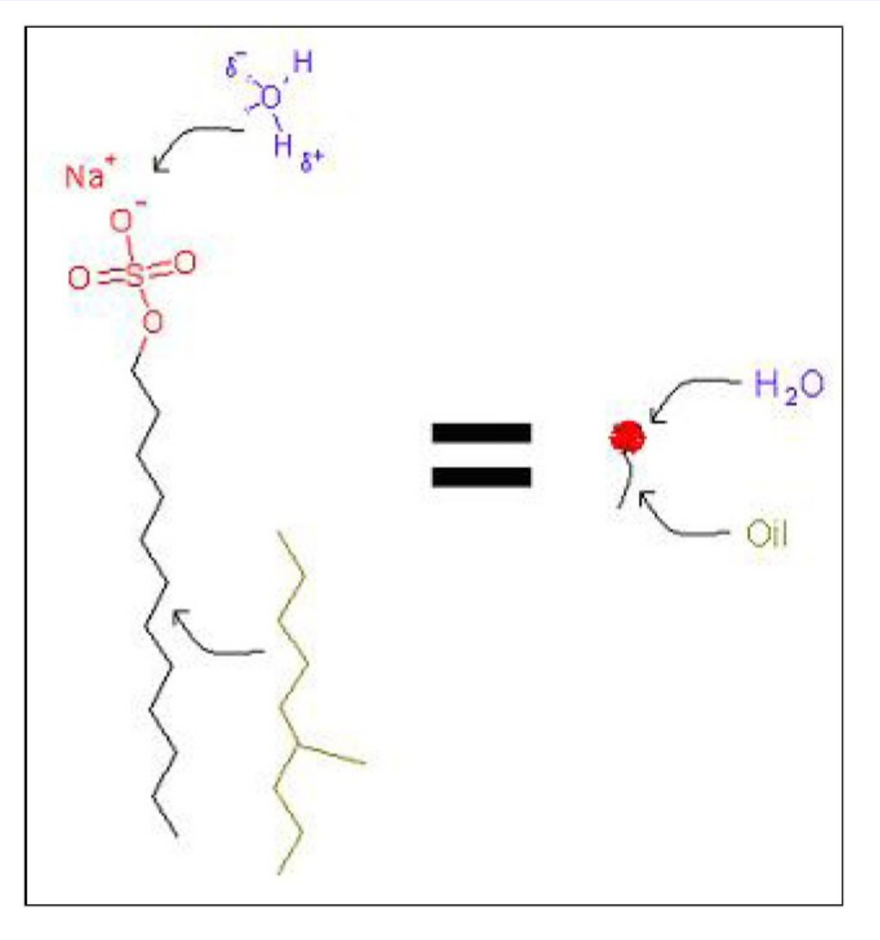
Amphiphilic molecules

- ‘water-loving’ and ‘water-hating’ moieties





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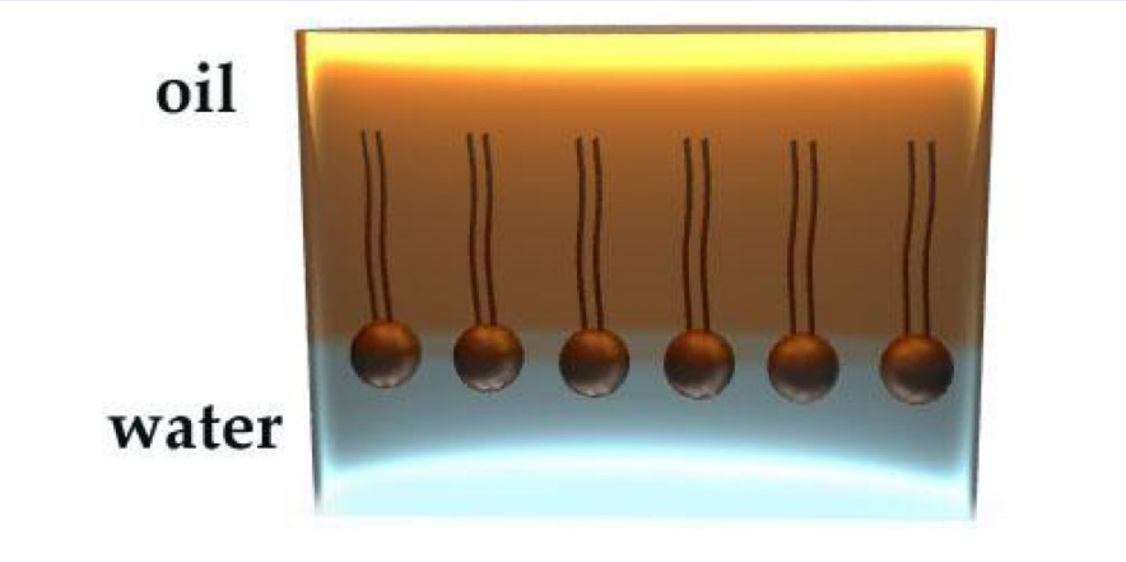
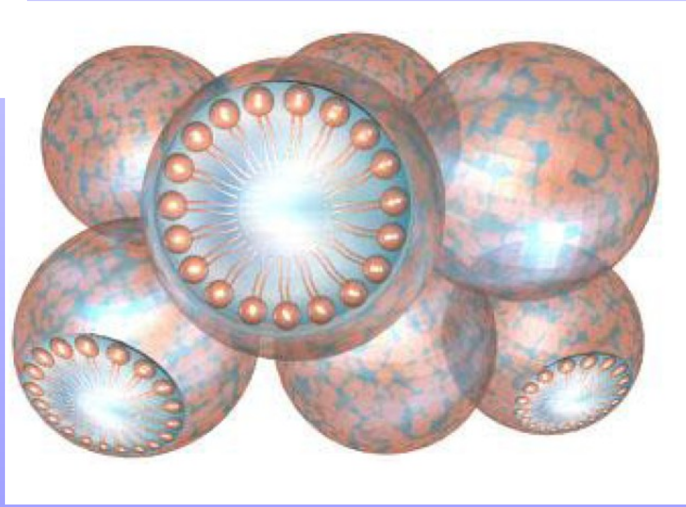
Surfactants are tensoactive molecules





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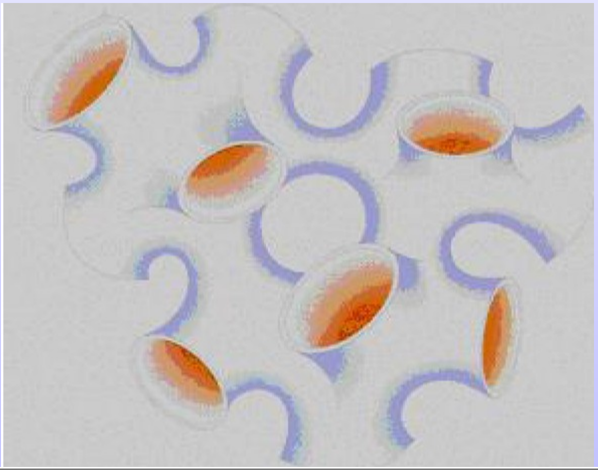
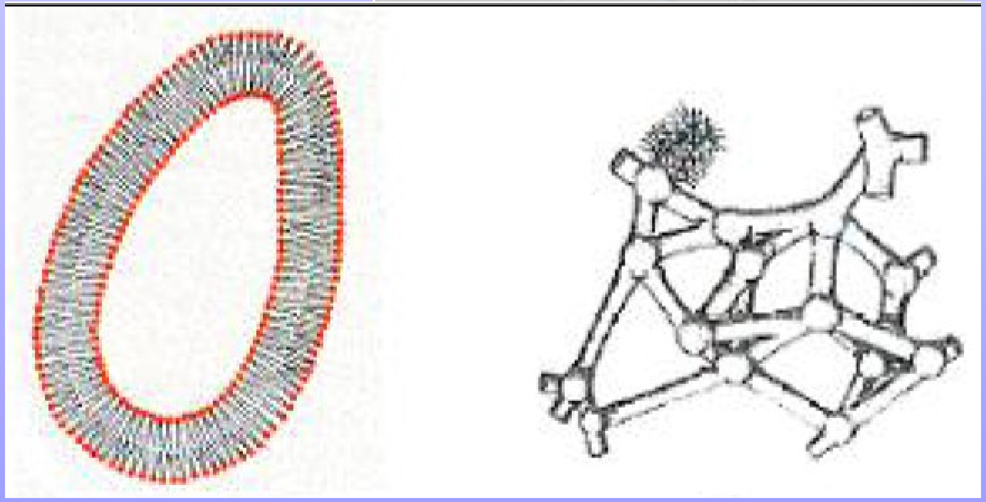
Oil in water:
More complex structures can be formed





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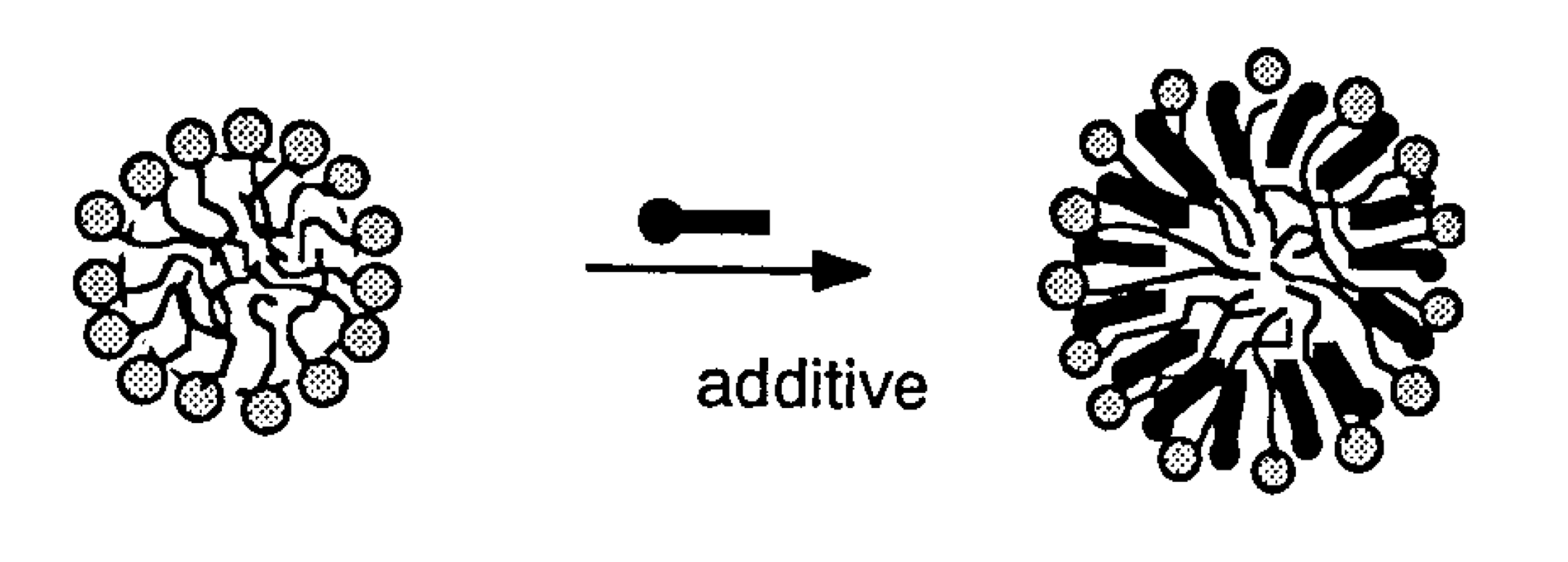
The interior of the micelles as a differentiated micro (or nano?) environment



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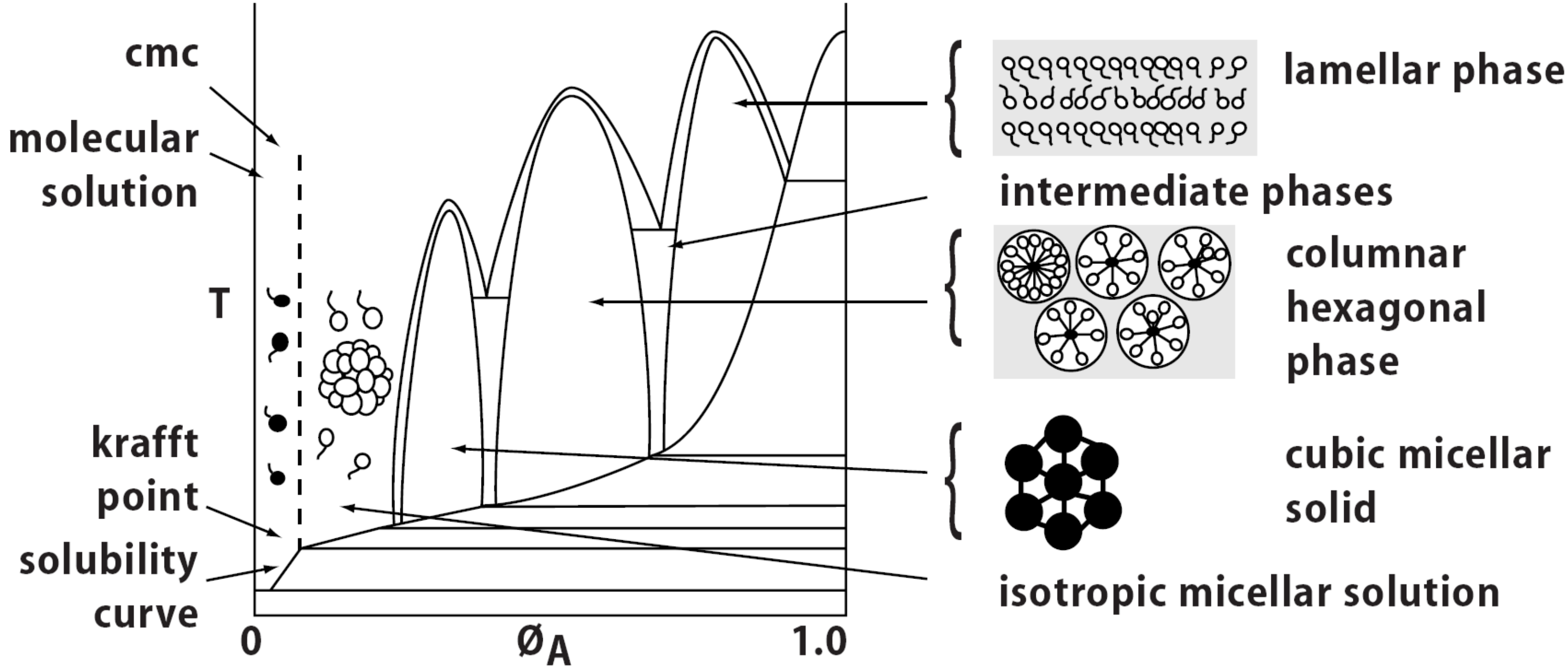
A complex diagram of possibilities



Schematic phase diagram; $\varnothing_A$ is the surfactant volume fraction

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- critical micellar concentration (cmc)

- critical micellar temperature (cmT)

- Krafft point: the triple point where crystals, monomers and micelles co-exist

Electrical Impedance Spectroscopy

(EIS)

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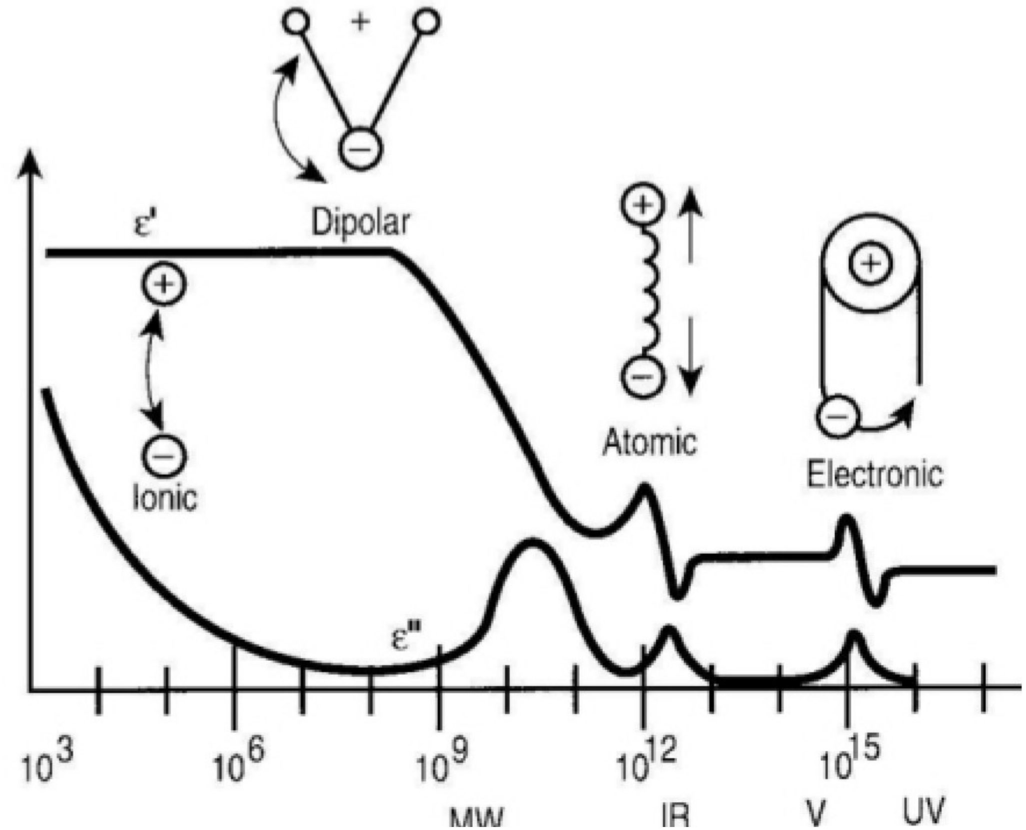
- **EIS: a spectroscopy very suitable to the analysis of polymeric systems**



http://www.psrc.usm.edu/mauritz/dilect.html

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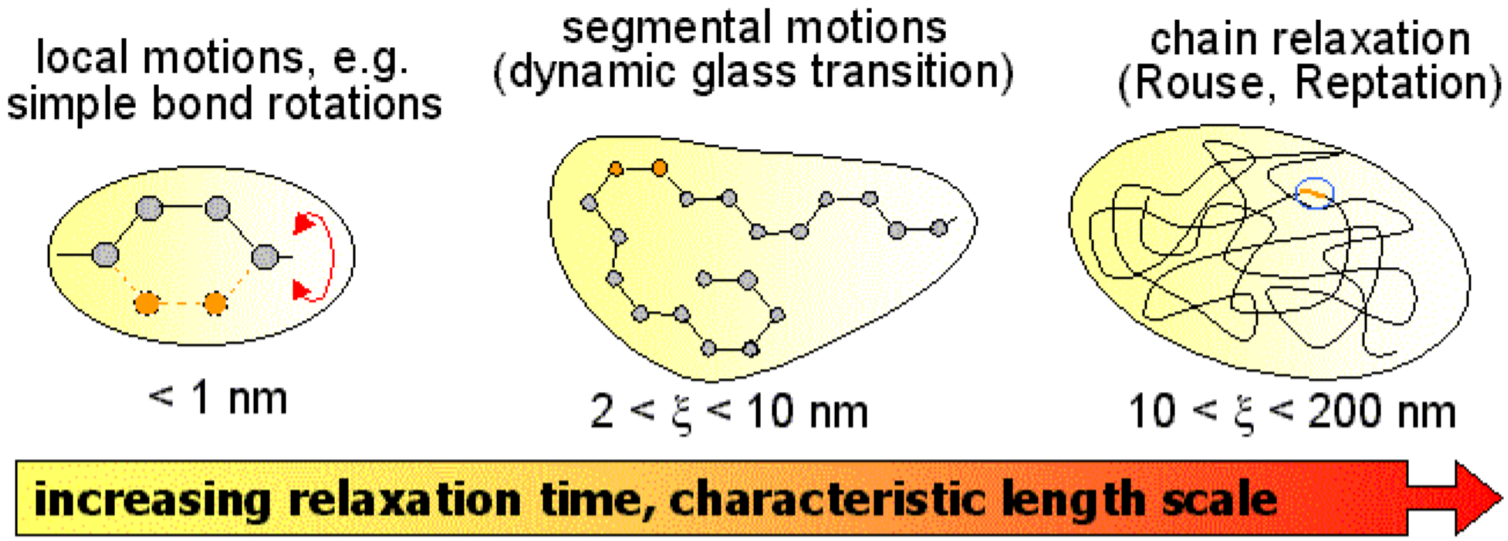
- **different degrees of configurational freedom of a polymeric chain**

Dielectric relaxation spectroscopy (DRS) reveals the molecular dynamics of polymeric materials by the characteristic response of polar groups and ions to a time-dependent electrical field. The extremely wide range in relaxation times is related to typical length scales associated to specific motions (local bond rotations, segmental motions, relaxation of the entire chain).



Nowadays, highly automated spectrometer allow fast and accurate dielectric measurements in a wide frequency range (10^{-3} - 10^{9} Hz) and at temperature usually ranging from -160° - 400°C.

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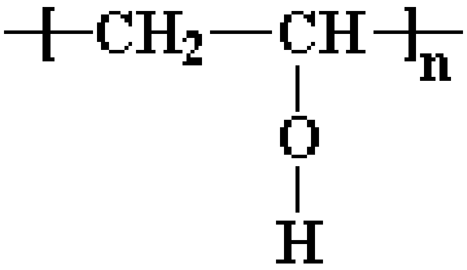
JOURNAL OF APPLIED PHYSICS VOLUME 93, NUMBER 5 1 MARCH 2003

Dielectric spectroscopy of blends of polyvinylalcohol and polypyrrole

H. P. de Oliveira, M. V. B. dos Santos, C. G. dos Santos, and C. P. de Melo[a)]
Departamento de Física, Universidade Federal de Pernambuco, 50670-901 Recife, Pernambuco, Brazil

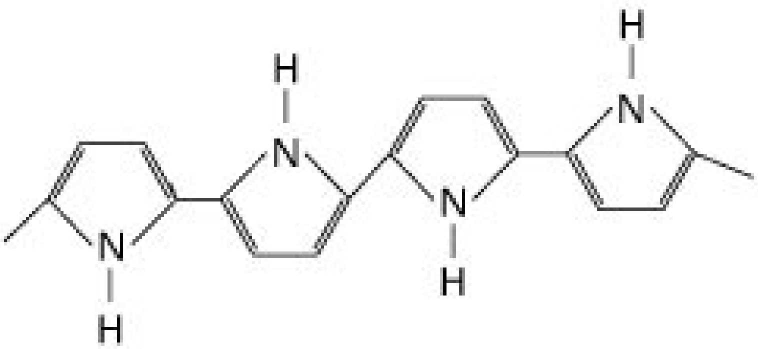
(Received 28 August 2002; accepted 9 December 2002)

Polymeric blends composed of conducting polypyrrole chains dispersed in a matrix of polyvinylalcohol containing ferric chloride represent a class of materials whose electrical behavior is intermediary between those of insulating and conducting polymers. To investigate the transport and polarization characteristics of these films we examine in this work their dielectric relaxation spectrum in the frequency domain. A relaxation in frequency identified in the resistance–reactance diagram is followed as a function of the relative concentration of the two polymers, as different types of dopants are used to promote the conducting behavior of polypyrrole. We also analyze the change in the relative dc and ac contributions to the total conductivity of the samples as the amount of incorporated polypyrrole is increased.
[DOI: 10.1063/1.1542918]



poly(vinyl alcohol)

PPy



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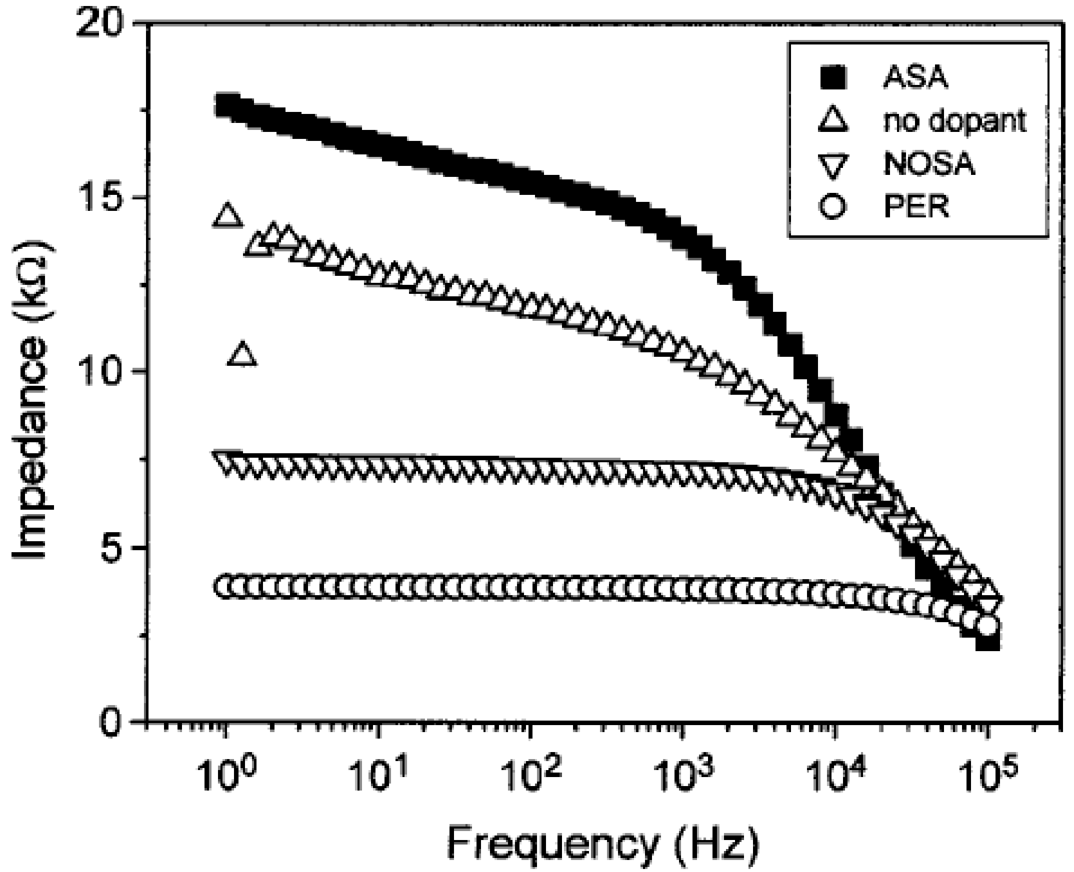

FIG. 7. Comparison of the variation of the impedance as a function of the applied frequency for doped and pristine (PVA+$FeCl_3$+PPY) blends. In each case the matrix was exposed to pyrrole vapor during 60 min.

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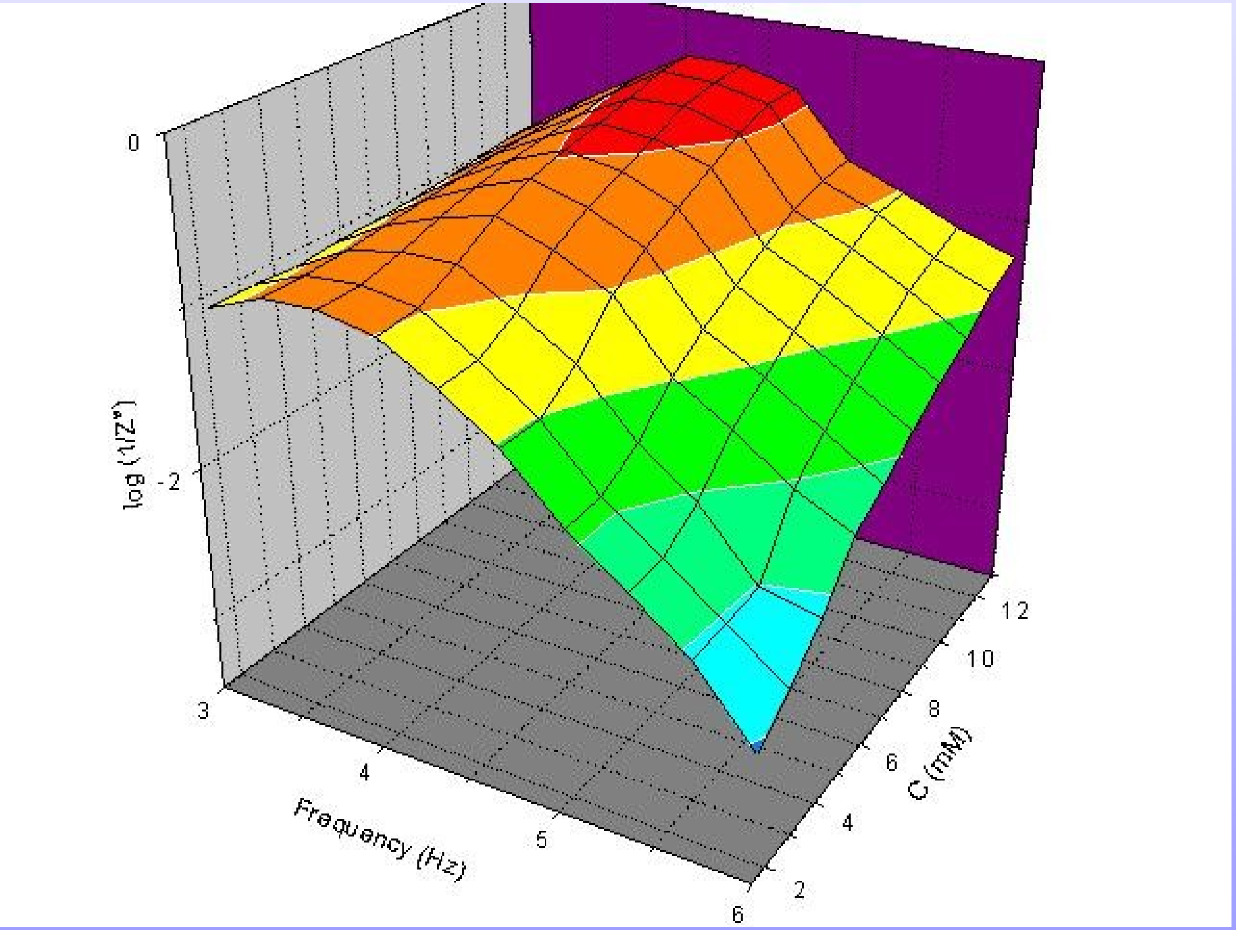
EIS:
a 3D map of the electrical response of colloidal systems



Critical Micellar Concentration

(cmc)

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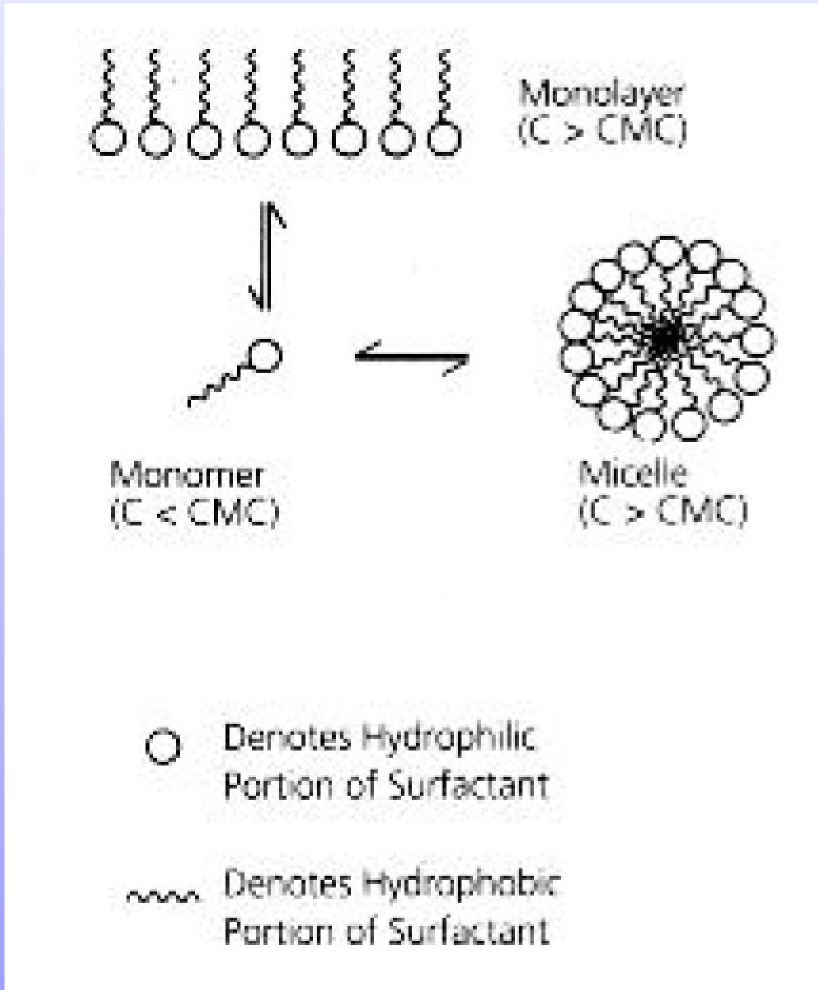
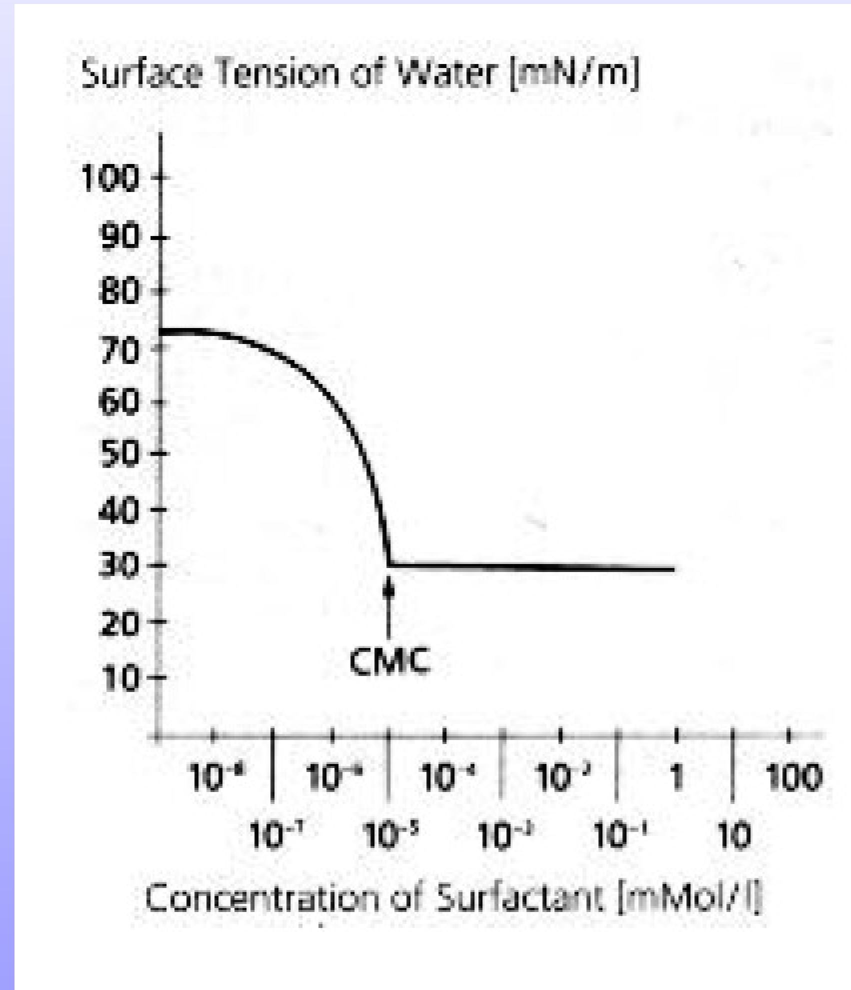
- **cmc as a structural phase transition**





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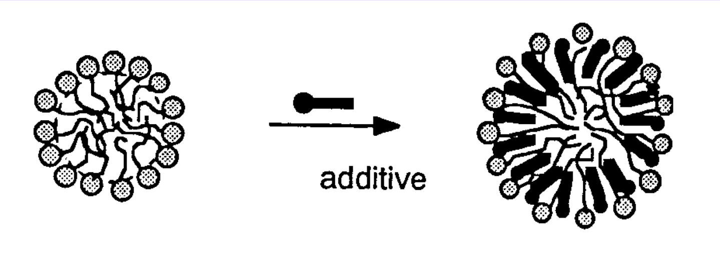
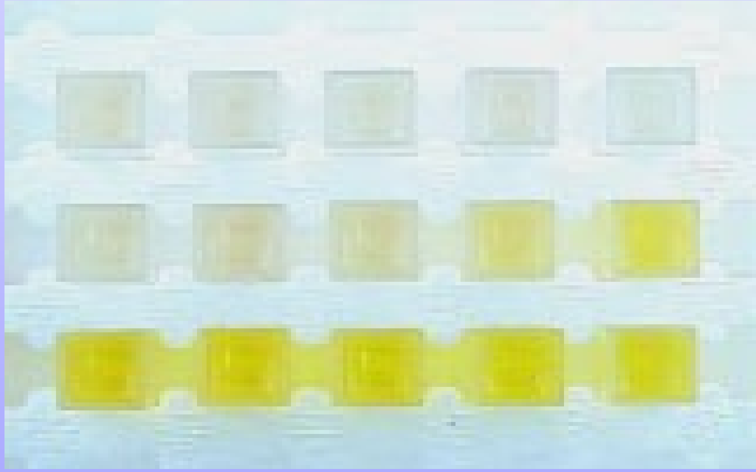
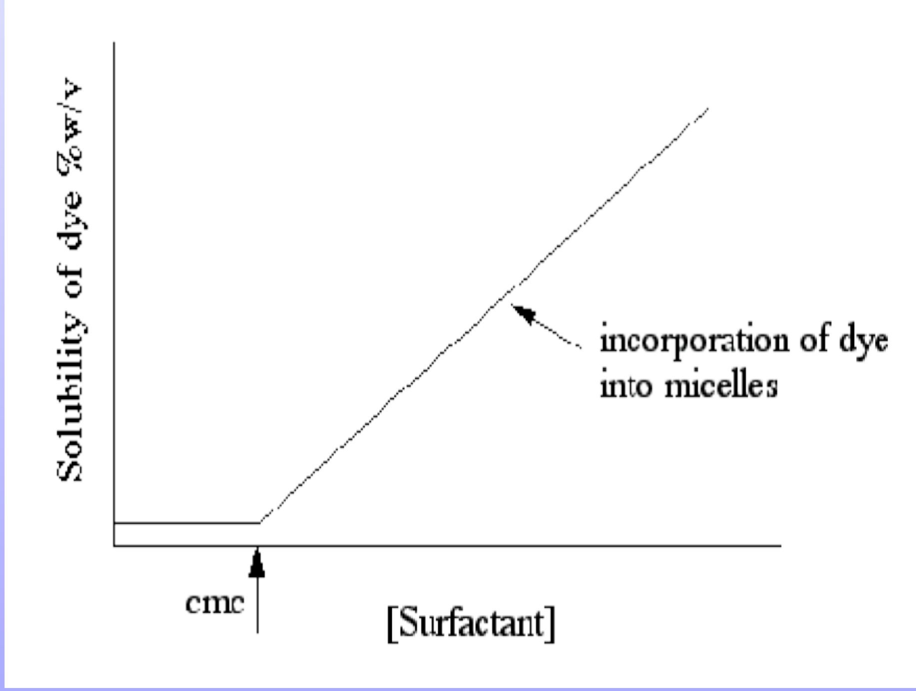
• **the absorption (removal) of contaminants in the interior of micelles when c > cmc**







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- **cmc: a very important parameter**

ANALYTICAL SCIENCES APRIL 1998, VOL. 14 379

Determination of Critical Micelle Concentration of Anionic Surfactants by Capillary Electrophoresis Using 2-Naphthalenemethanol as a Marker for Micelle Formation

Hiroshi NAKAMURA†, Akira SANO and Kiyomi MATSUURA

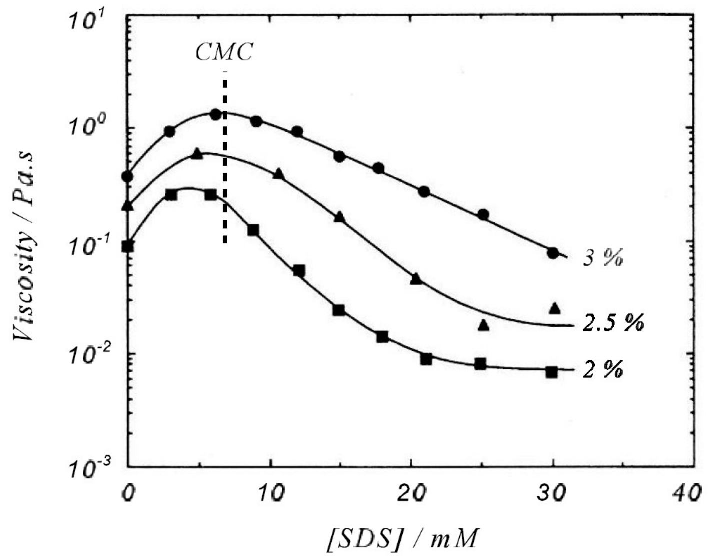

Figure 2.2 Effect of SDS concentration on the viscosity of HEUR solutions of different concentrations. Reproduced from [16].

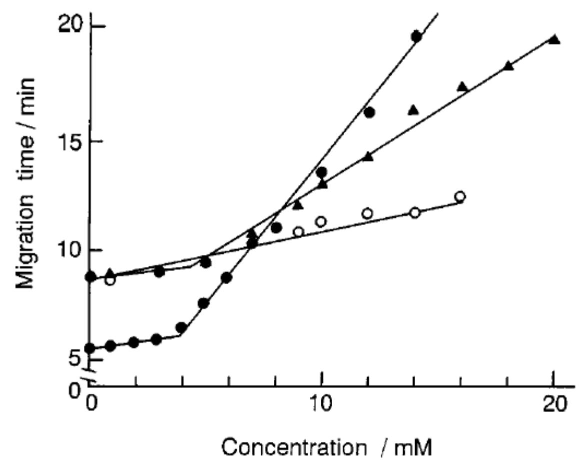

Fig. 1 Effect of marker compounds on determination of CMC of SDS by CE. Marker: ○, toluene; ●, 2-naphthalene-methanol; ▲, 2-naphthol.

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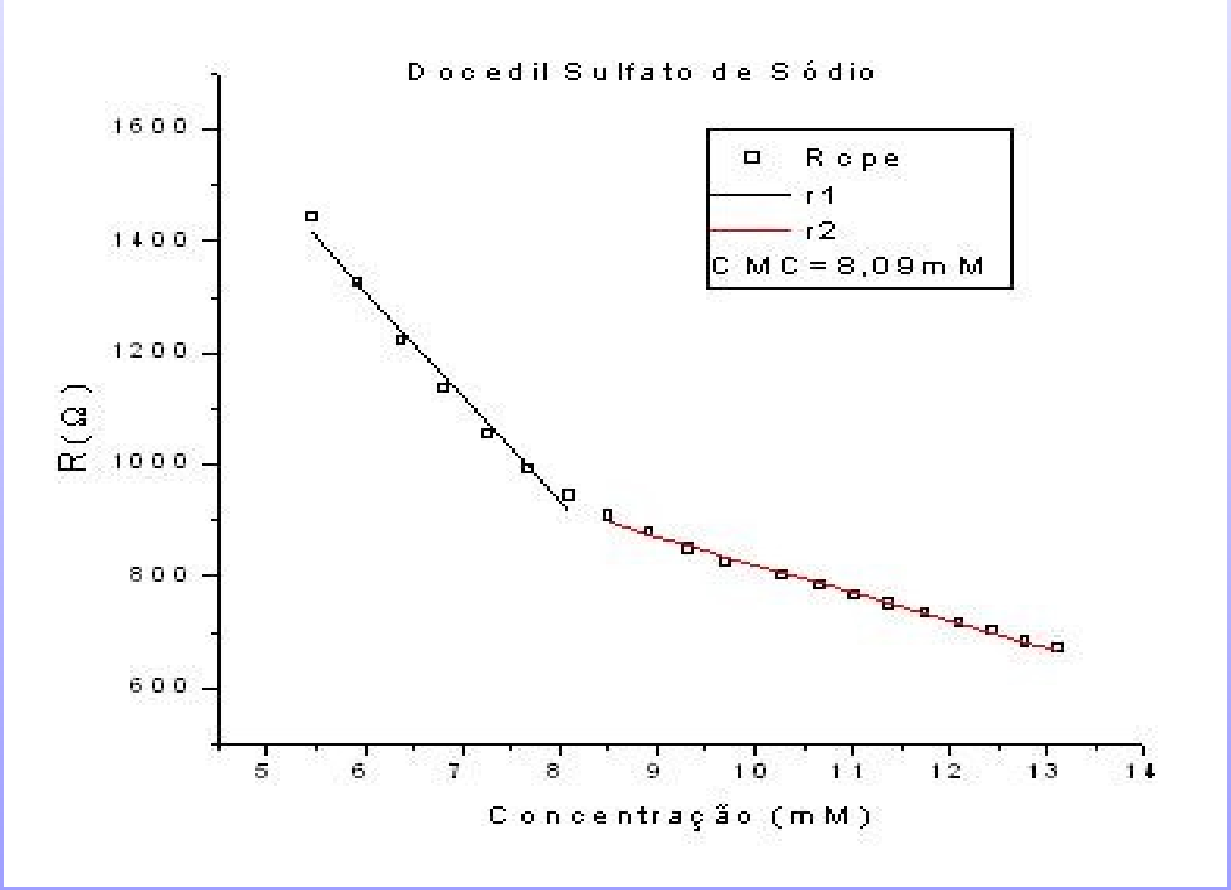
- **EIS as a competitive technique for the determination of the cmc in different systems**



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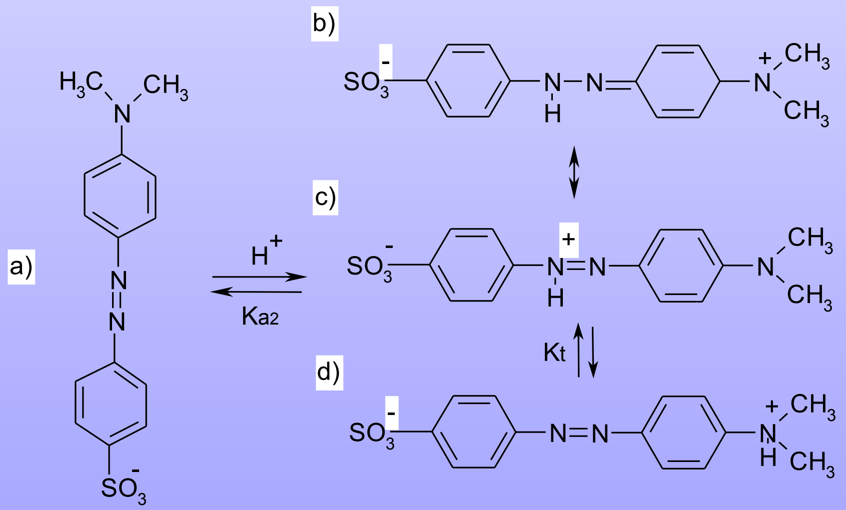
- **EIS as a competitive technique for the determination of the cmc in different systems**



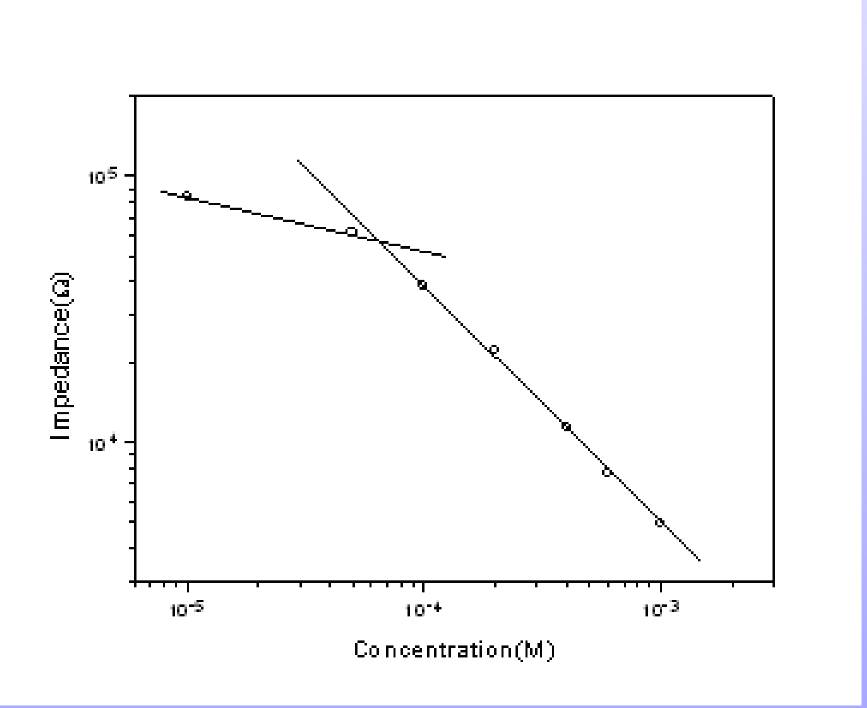


Figura 6 –Z'(f=1 MHz) do alaranjado de metila a diferentes concentrações.

Metallic Colloidal Suspensions

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The beautiful colors of medieval stained glasses

An ancient technique

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Nanostructures: quantum confinement effects

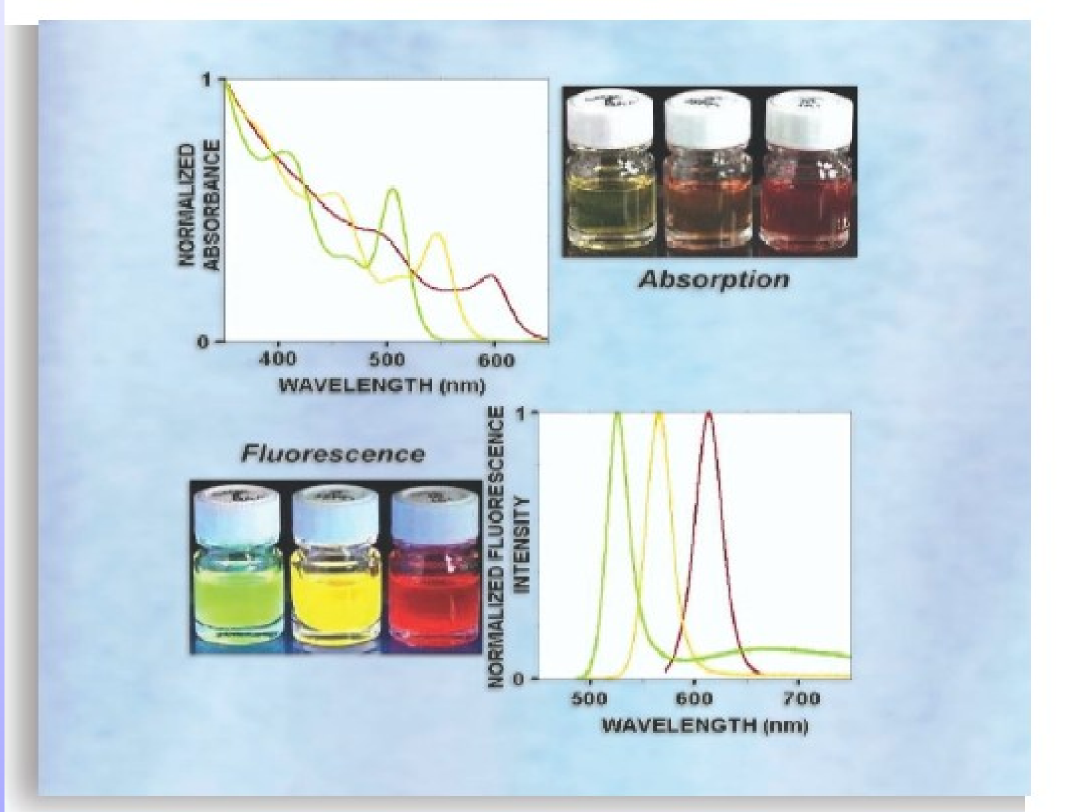

Figure 1 : Absorption (upper part) and emission (lower part) of CdSe nanocrystals with diameters of 2.8 nm (green), 3.8 nm (yellow), 5 nm (red).

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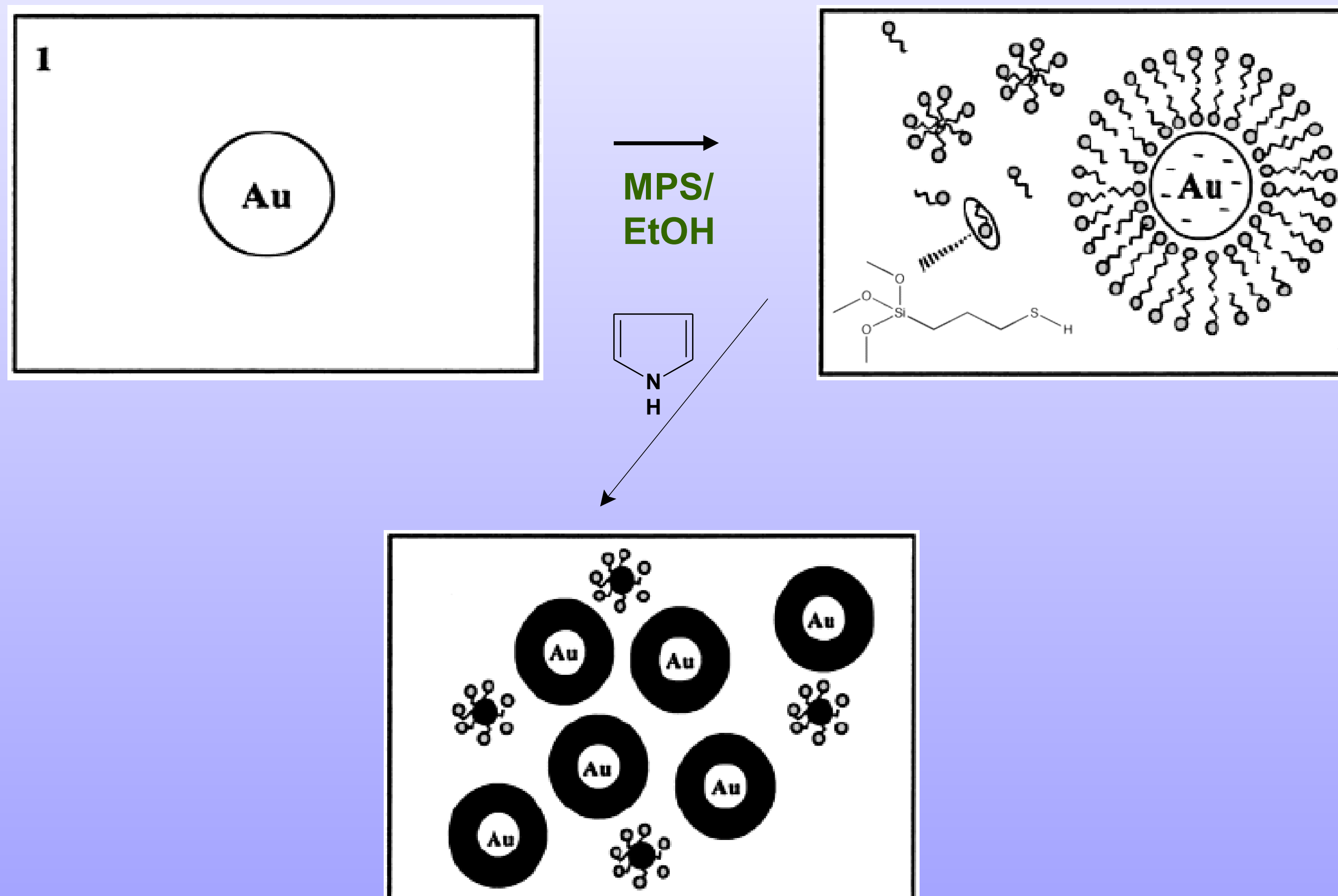
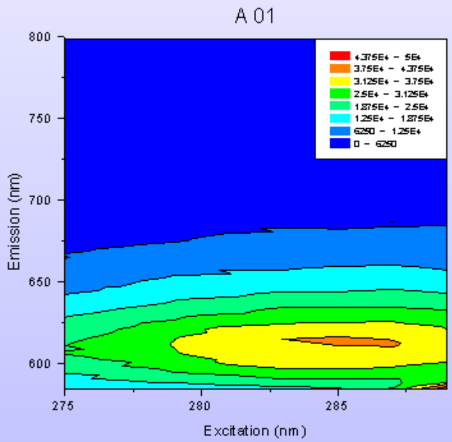
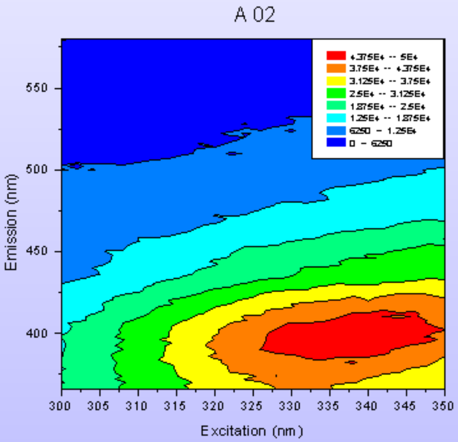
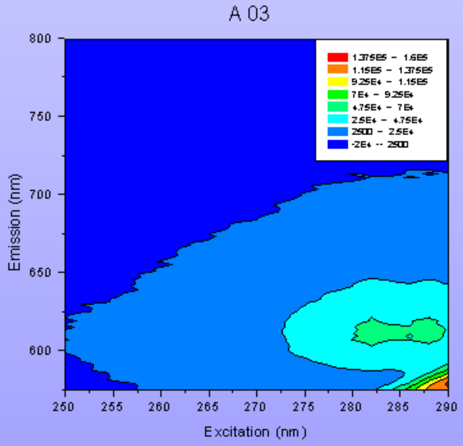
Synthesis

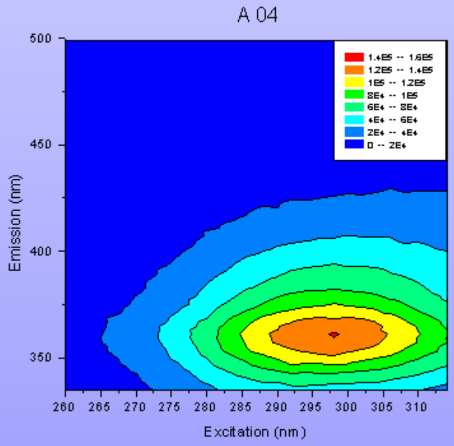


Luminescence Matrices

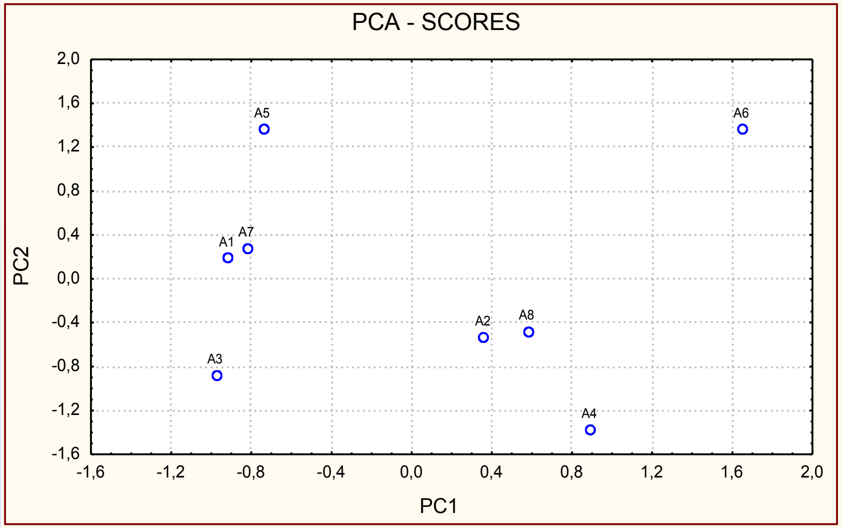


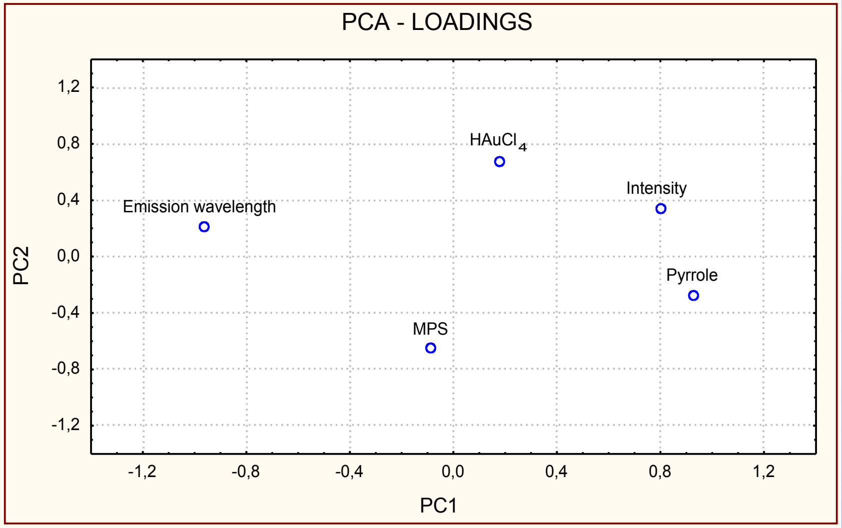






Principal Components Analysis





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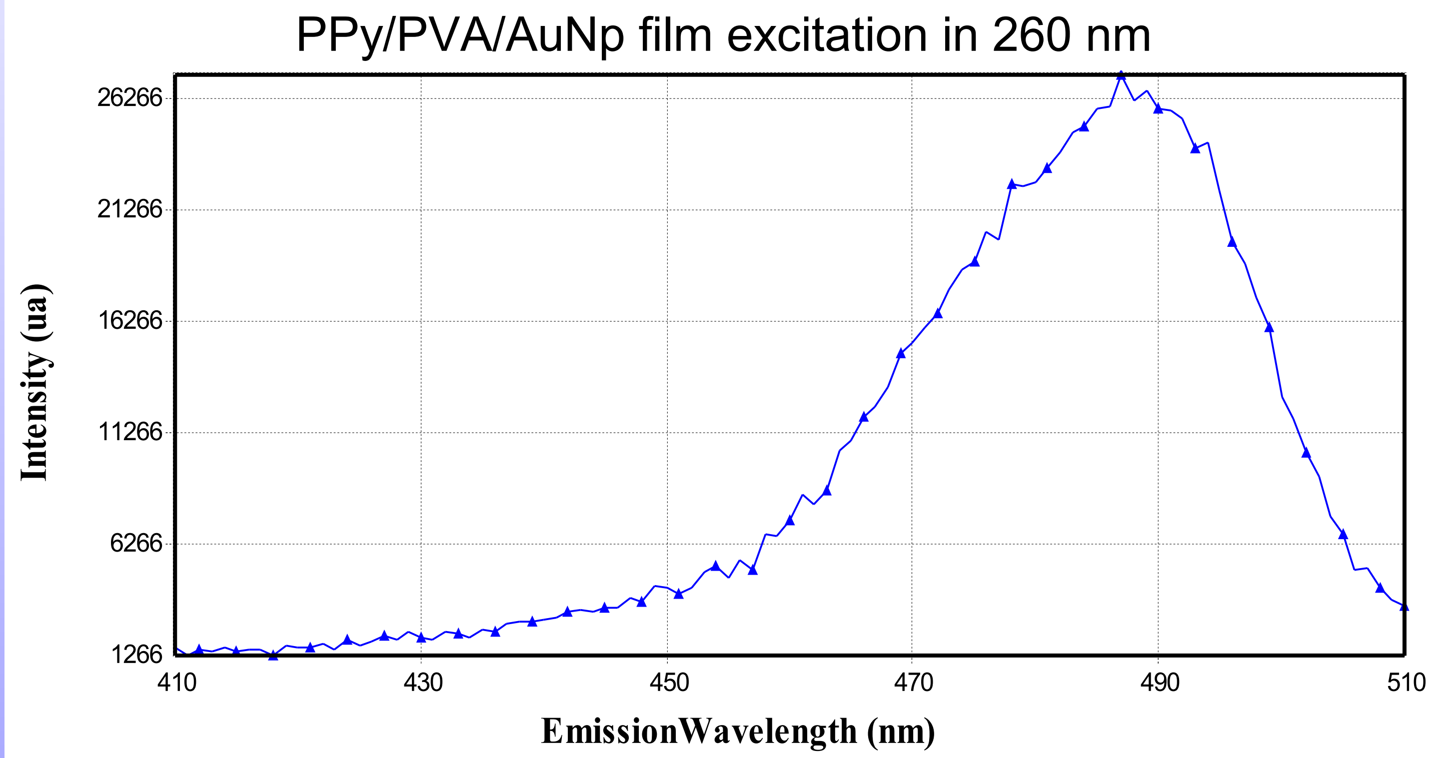
It is possible to tune the position and the intensity of the photoluminescence



PPy/PVA/AuNp film

Magnetic Colloids

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Preparation of the Surfactant-PPY micelles

- **Use a standard surfactant (Lutrol F68, a block copolymer of polyethylene and polypropylene glycol).**
- **After pyrrole is introduced into the solution, it can become incorporated into the micelles by energetic stirring.**
- **When ferric chloride (an oxidant) is introduced in the medium, polymerization begins both inside and outside the micelles.**
- **It is possible to separate the polymeric chains dispersed in the solution, leaving only the PPY chains trapped inside the micelles.**

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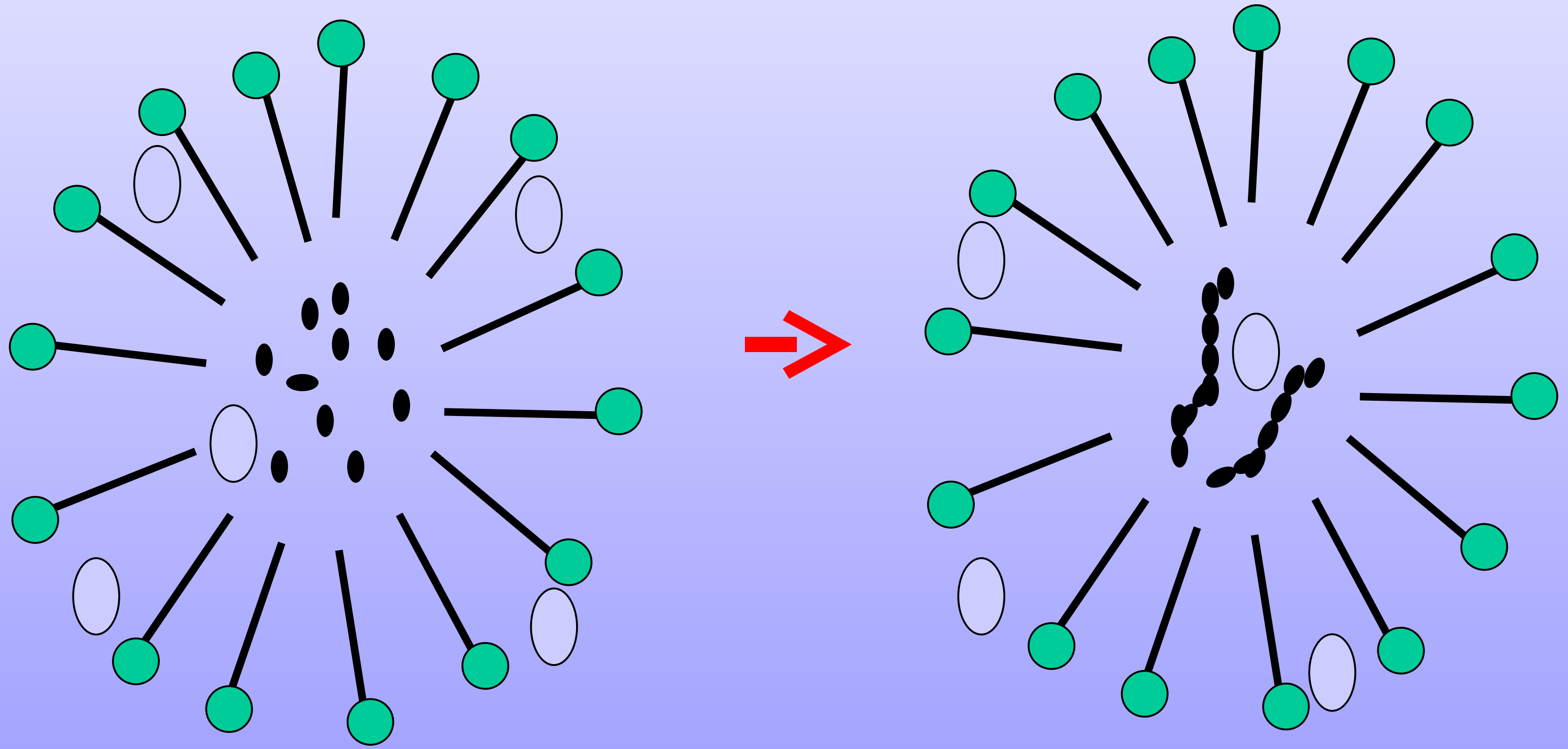
Polymerization also occurs inside the micelles

(emulsion polymerization)



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Advantages of emulsion polymerization include:

- The water phase allows the heat to be removed from the system

  →increase in the rate of many reaction methods

- Polymer molecules are contained within the particles → viscosity does not depend on molecular weight and remains close to that of water

- No need to alter or further process the final product, that can be used as obtained

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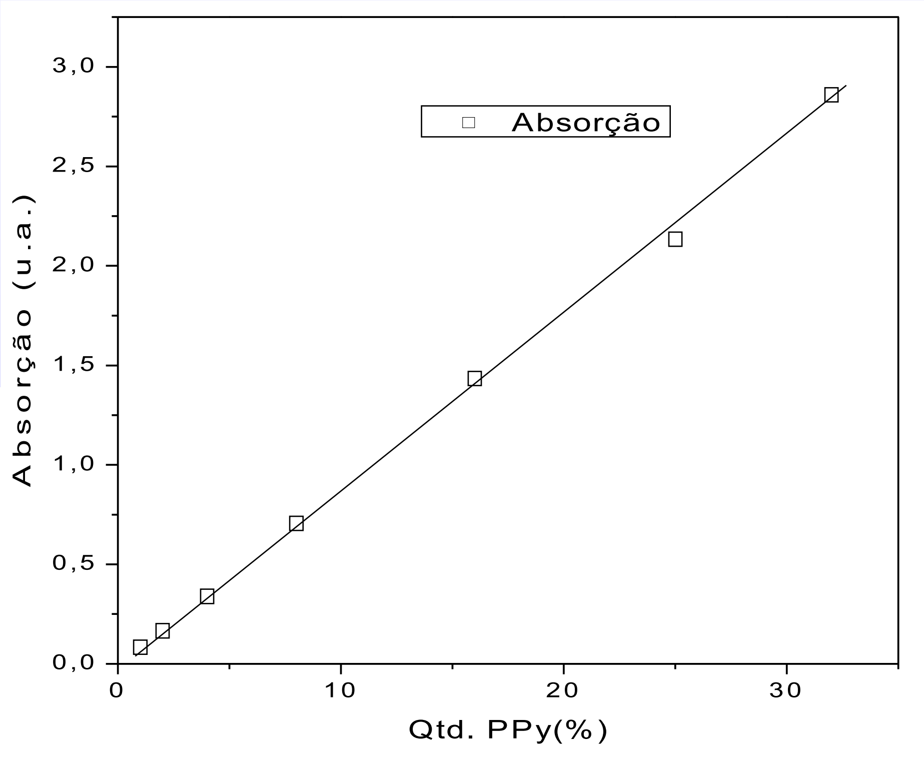
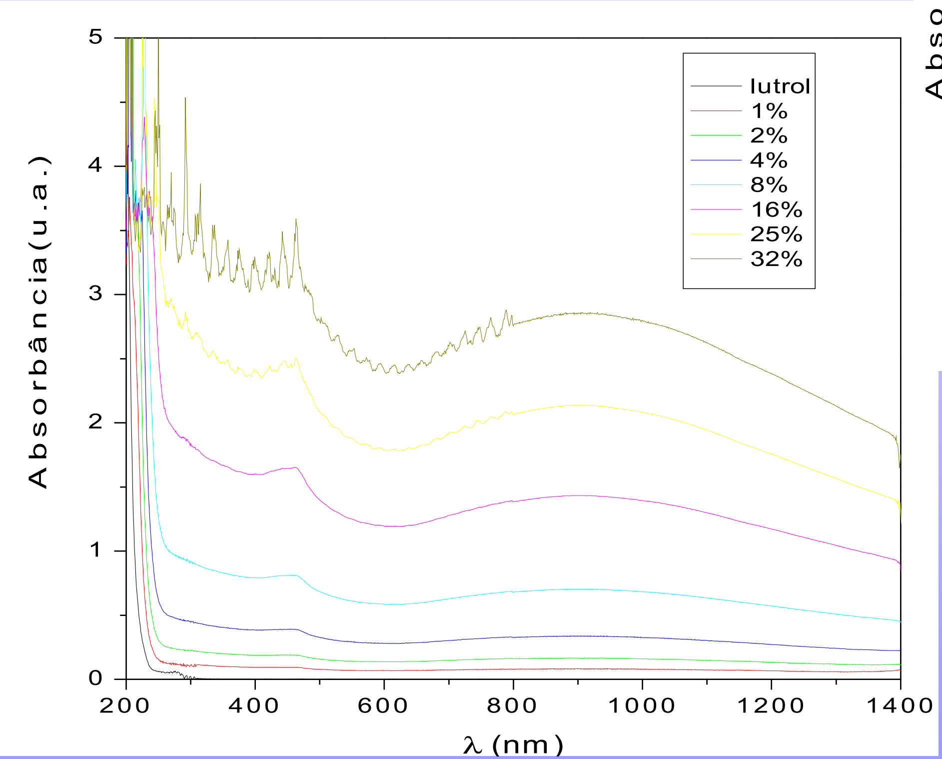
Lutrol-PPY samples





Absorbance Results

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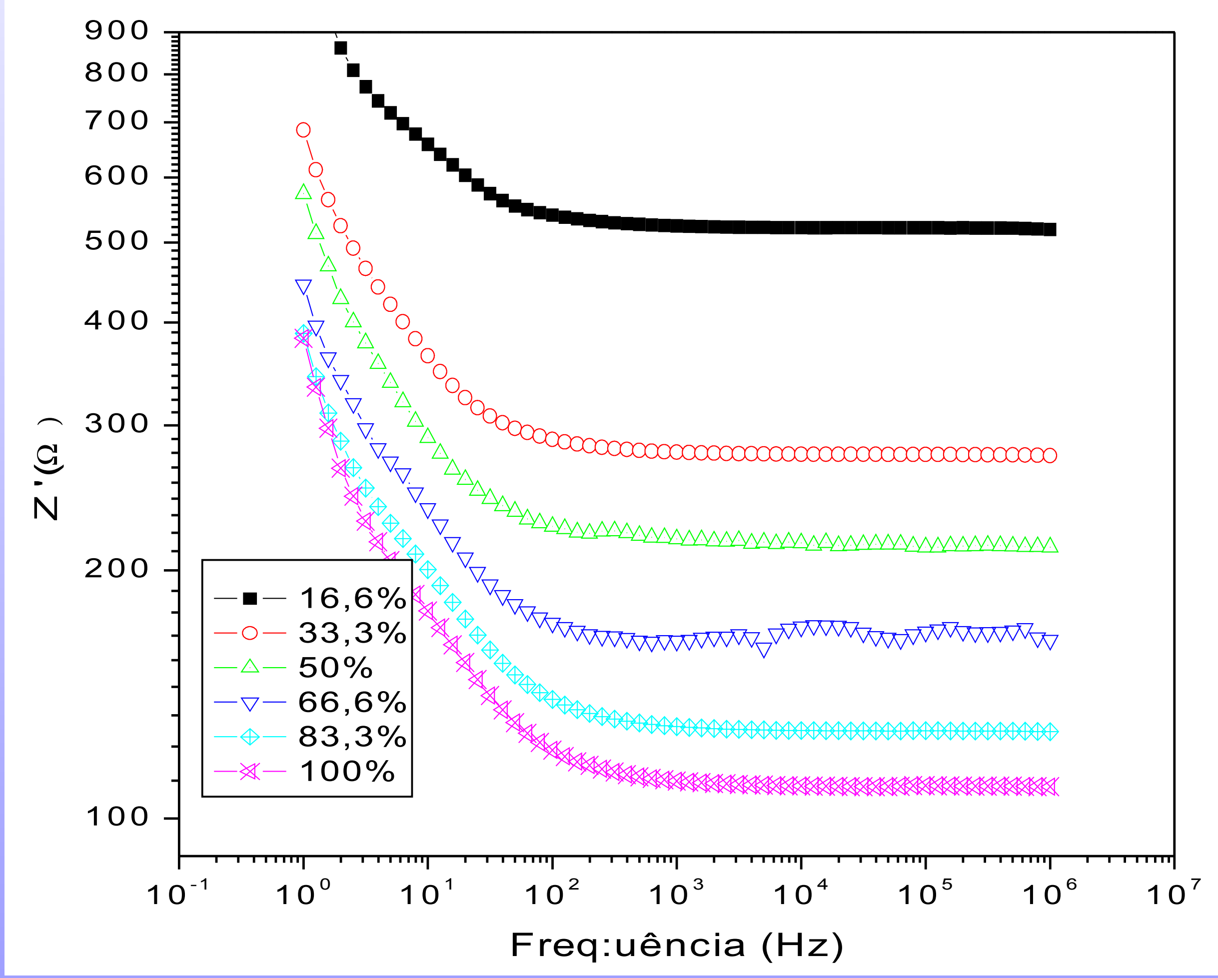
Lutrol-PPY samples

Impedance results for aqueous solutions



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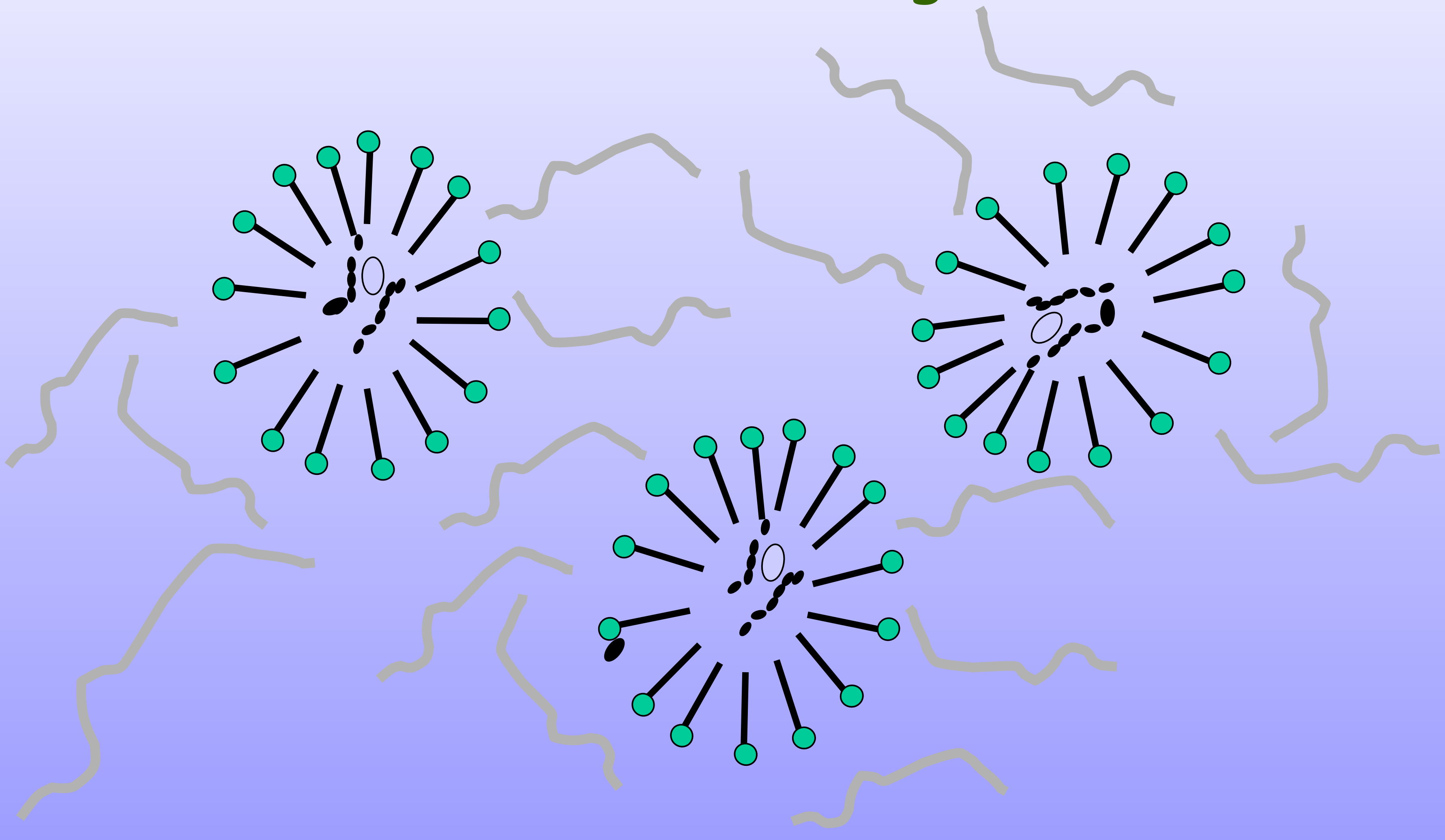
Lutrol-PPY samples:
effect of introducing PVA



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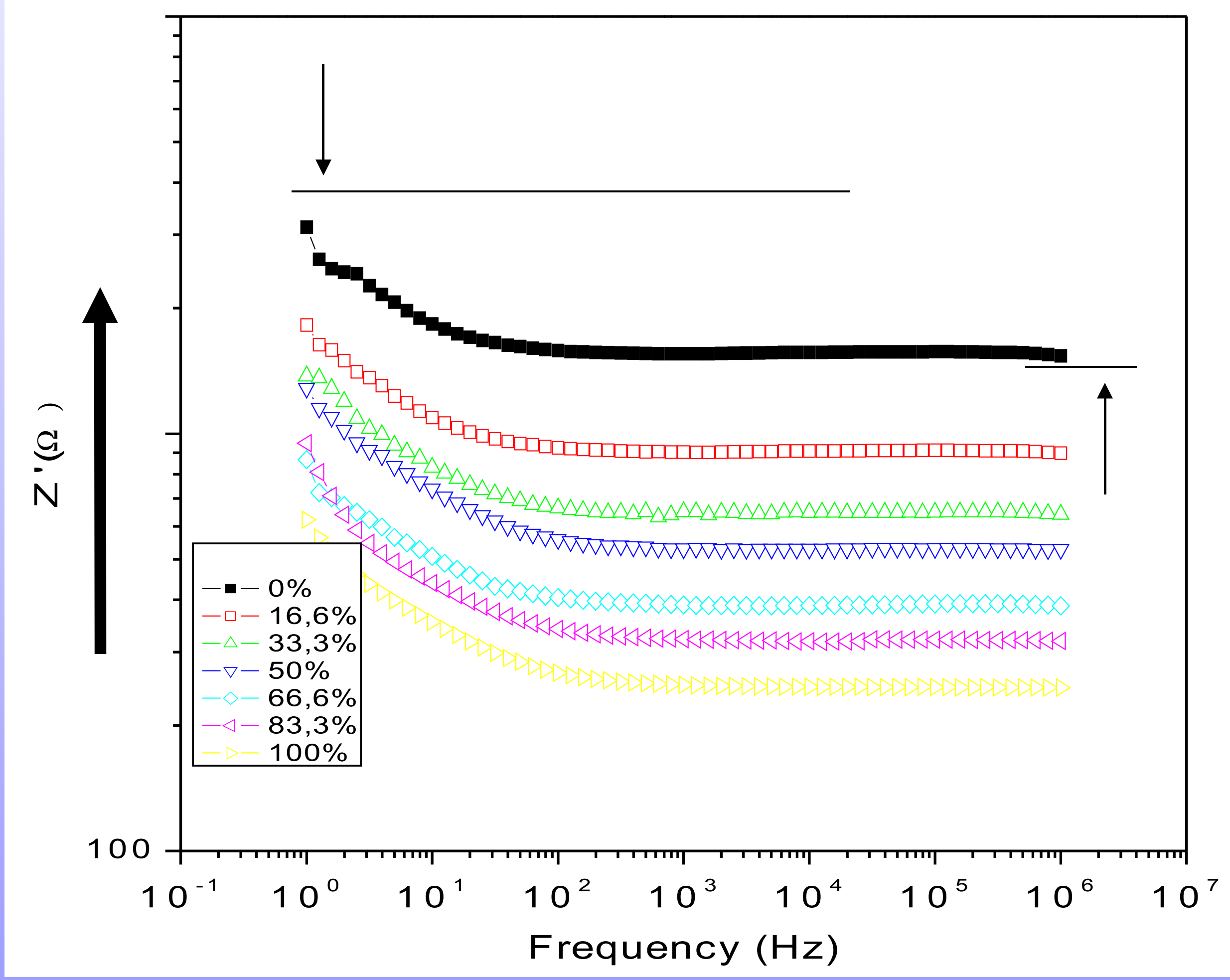
Lutrol-PPY samples: effect of introducing PVA

Impedance results for aqueous solutions containing PVA



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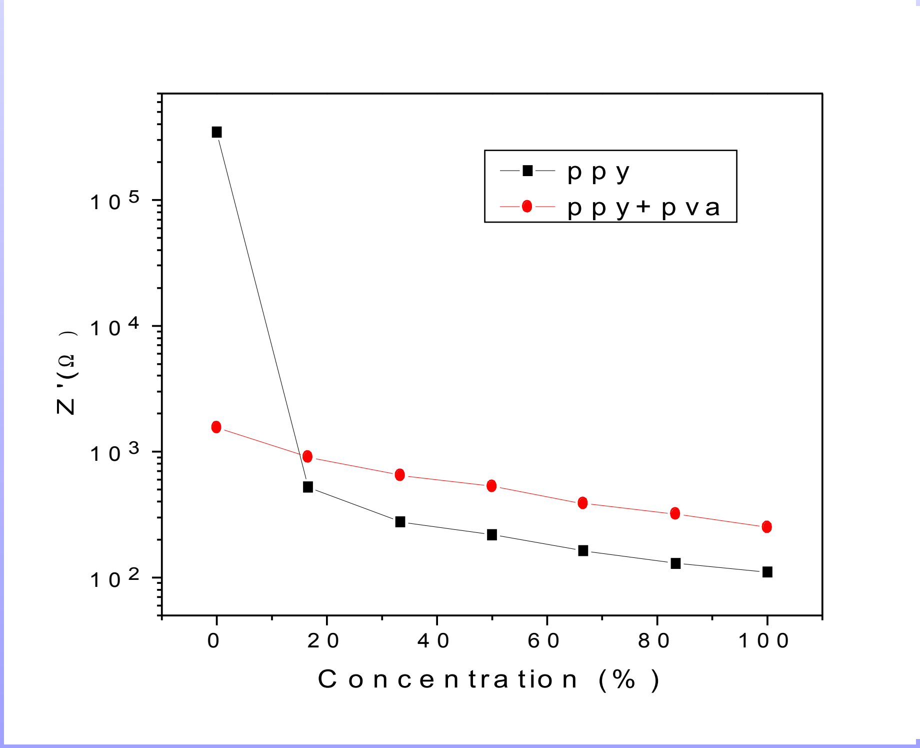
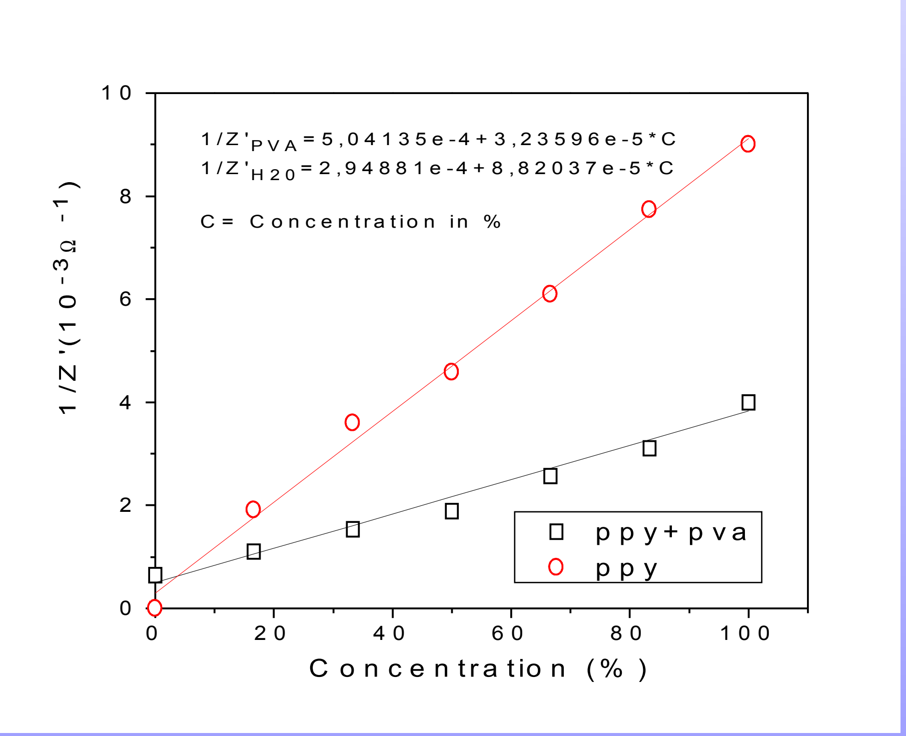
Introduction of PVA into the solution limits the range of variation of the impedance of the Lutrol-PPY solutions





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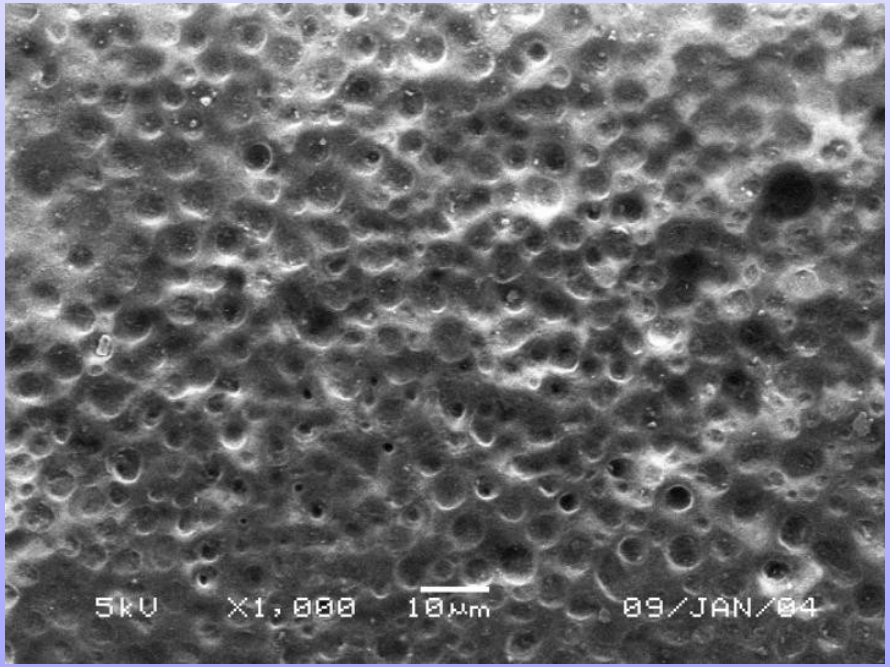
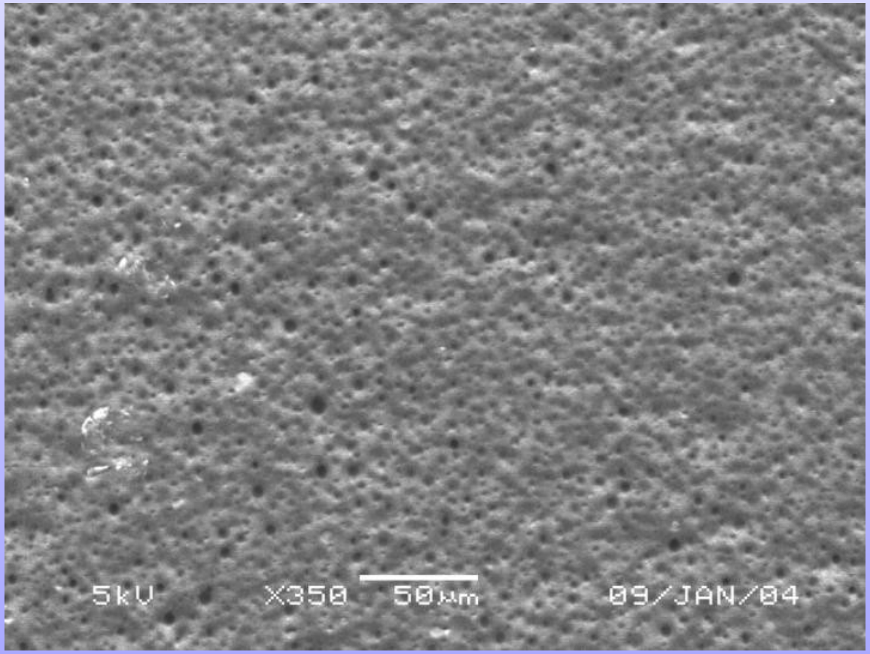
PVA films containing Lutrol-PPY nanoparticles





SEM images

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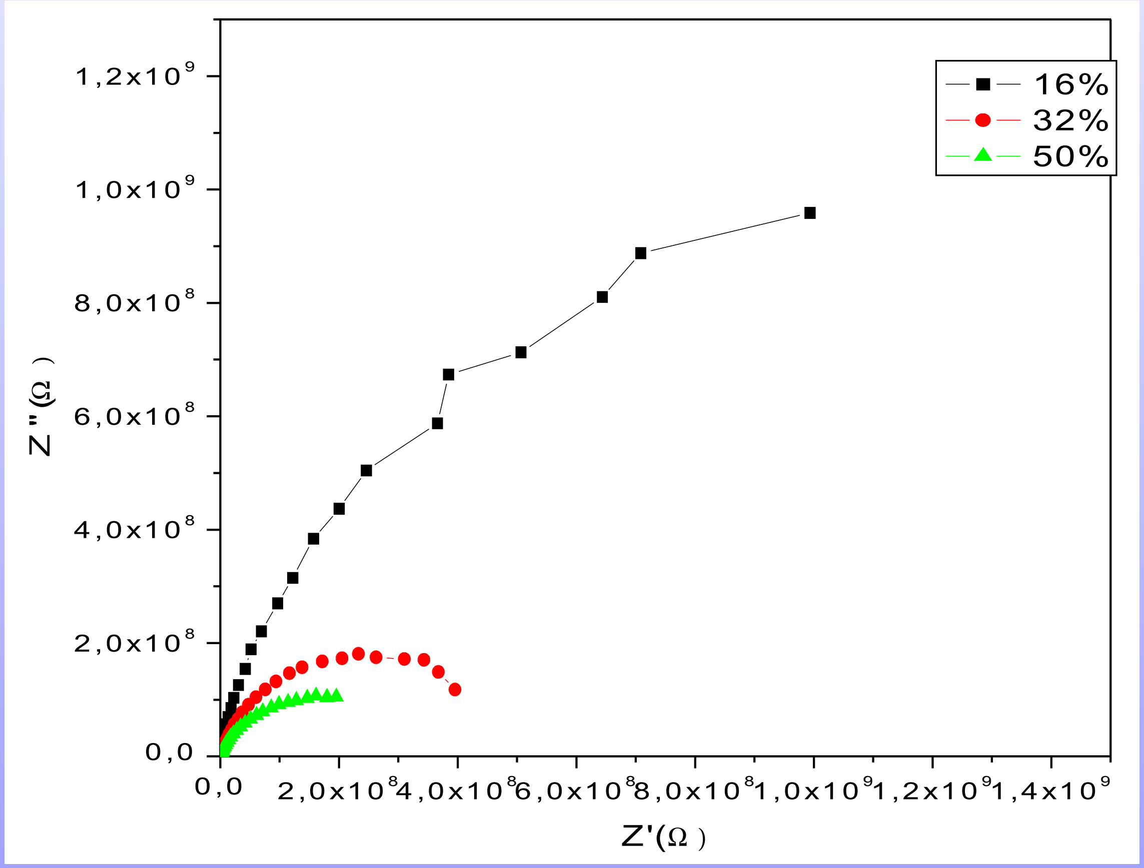
PVA films containing Lutrol-PPY nanoparticles

Impedance results for PVA films containing Lutrol-PPY nanoparticles (RX diagram)



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Preparation of the micelles with a magnetic core

- **To obtain the iron nanoparticles, we have used NH_4OH (ammonium hydroxide), $FeCl_3.6H_2O$ (ferric chloride hexahydrate) and $FeSO_4.7H_2O$ (ferrous sulfate heptahydrate).**

- **Under a N_2 atmosphere and by controlling the pH, the Fe nanoparticles are formed and can be magnetically separated from the solution.**

- **The magnetic particles can are incorporated into the micelles using the methods described before for the pure Lutrol-PPY case.**

Preparation of Lutrol-PPY micelles with a magnetic core

Sample	Pyrrole (μL)	Iron (mL)	Pyrrole (%)	Iron(%)
S1	173	0	100	0
S2	147	0.1	85	10
S3	121	0.25	70	25
S4	95	0.4	55	40
S5	69	0.55	40	55
S6	43.25	0.7	25	70
S7	17.3	0.85	10	85
S8	0	1	0	100

Table I: Summary of the SDS-Fe-PPY solutions investigated in this work. The total volumes of each individual solution used (see text) are indicated; and the percent columns refer to the relative amount of pyrrole [Iron] present in a given solution compared to the maximum amount used (in sample S1 [S8]).

Samples were prepared with a balance between the amount of PPY and Fe

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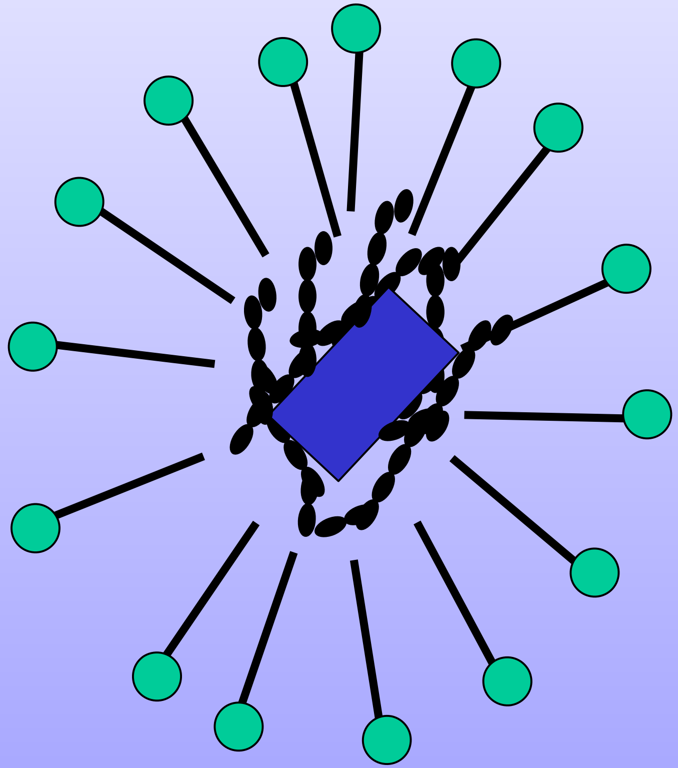
Lutrol-PPY nanoparticles with a magnetic core



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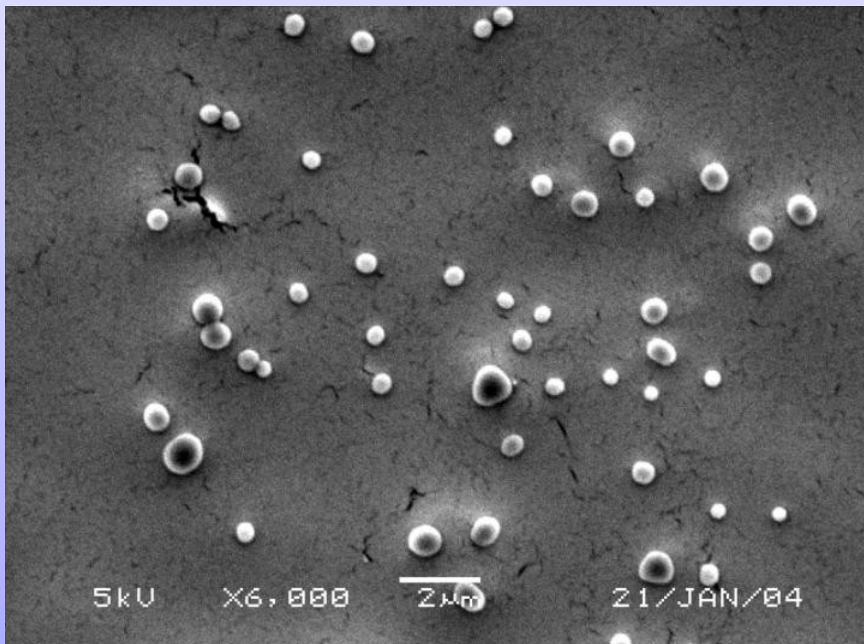
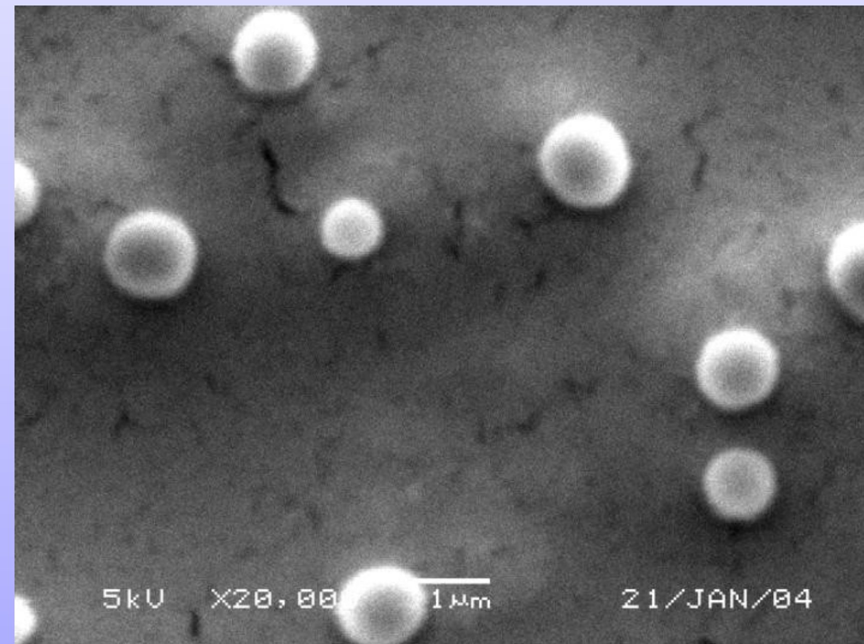
Lutrol-PPY nanoparticles with a magnetic core





SEM images for samples with a significant amount of PPY

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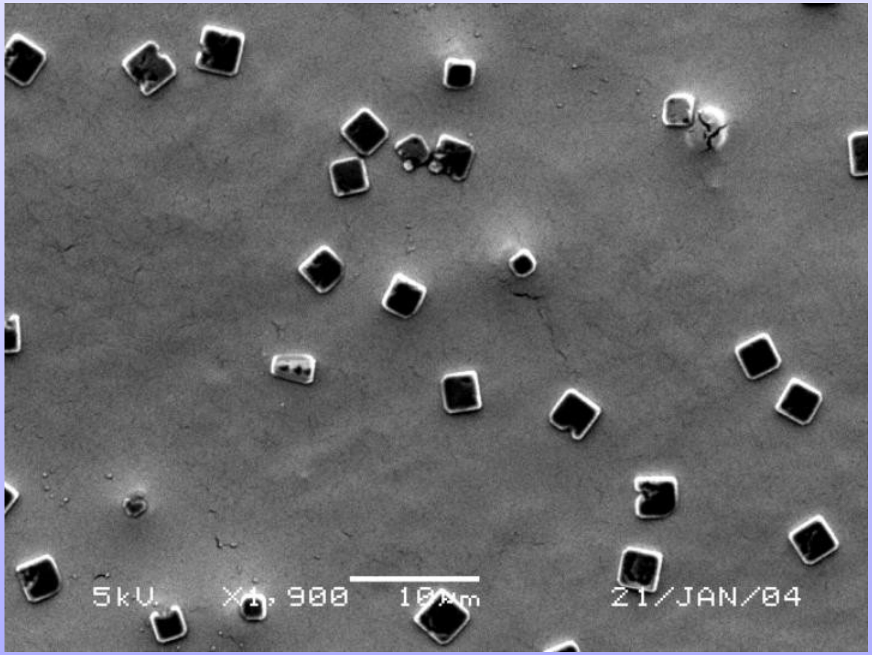
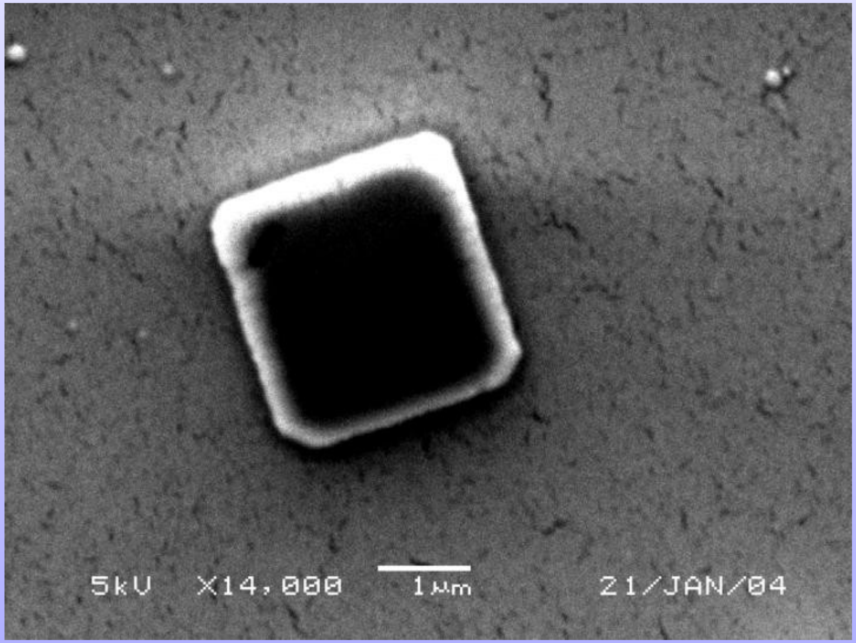
Lutrol-PPY nanoparticles with a magnetic core





SEM images:
significant change in shape when amount of PPY is reduced

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DIELECTRIC CHARACTERIZATION OF COLLOIDAL SURFACTANT-IRON-POLYPYRROLE PARTICLES

H. P. de Oliveira[1], C. A. S. Andrade[2] and C. P. de Melo[1*]

[1] Departamento de Física, [2] Pós-Graduação em Ciência de Materiais

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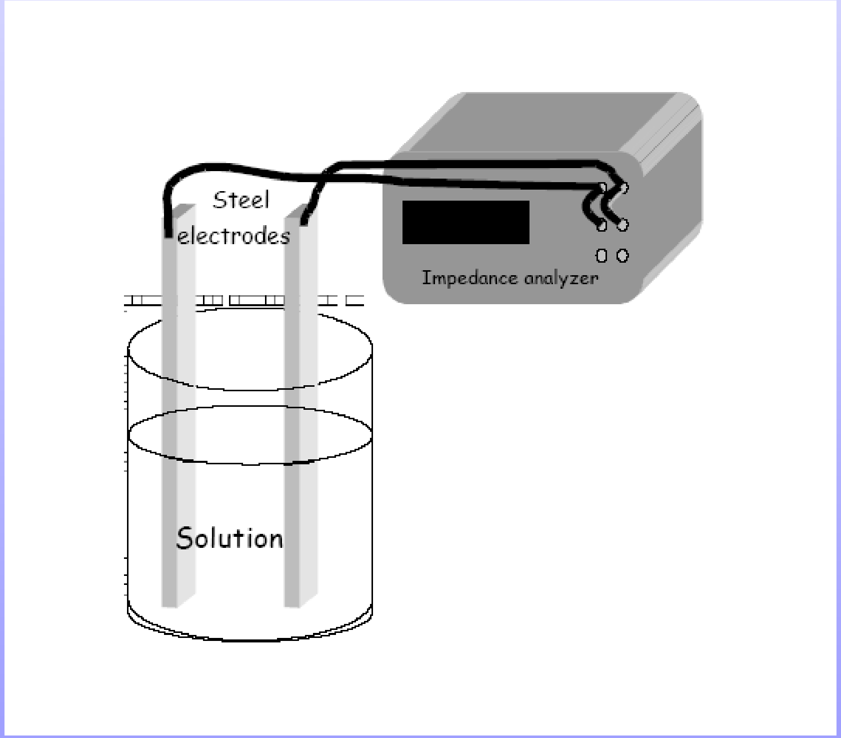

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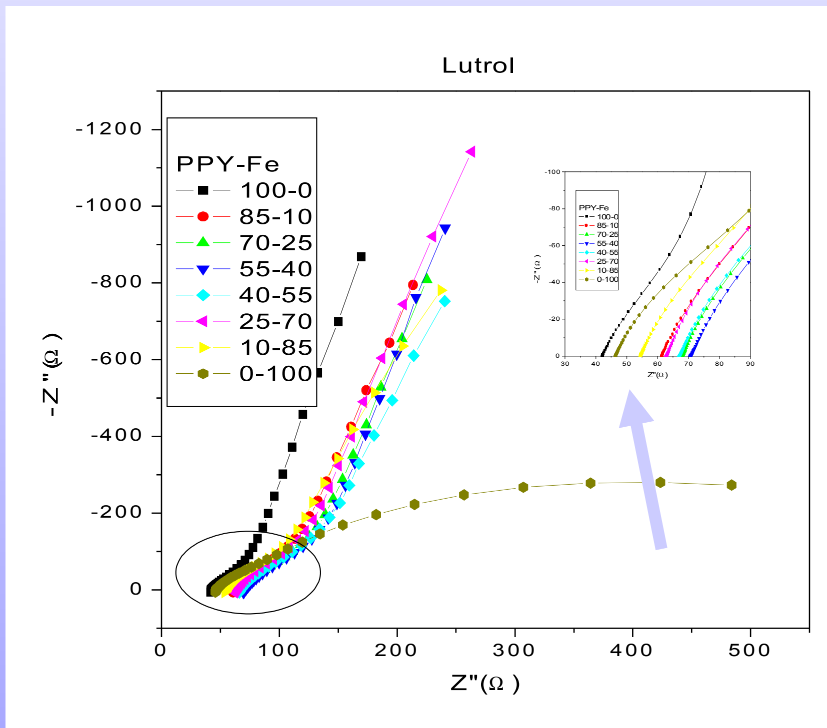
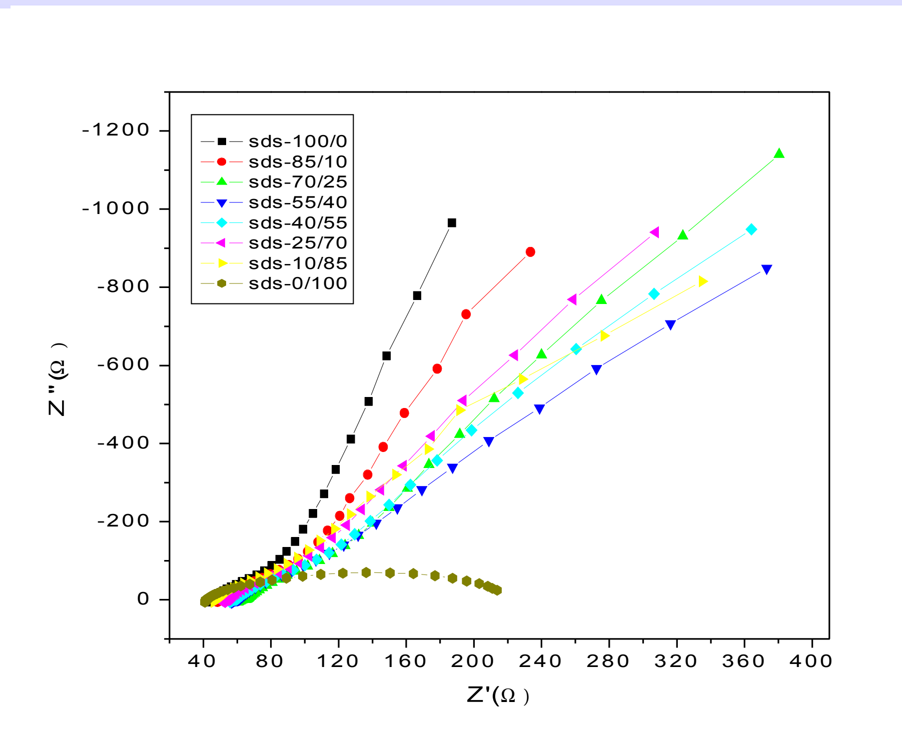
Surfactant-PPY nanoparticles with a magnetic core

Dielectric response for different surfactants





Lutrol

Sodium dodecyl sulfate

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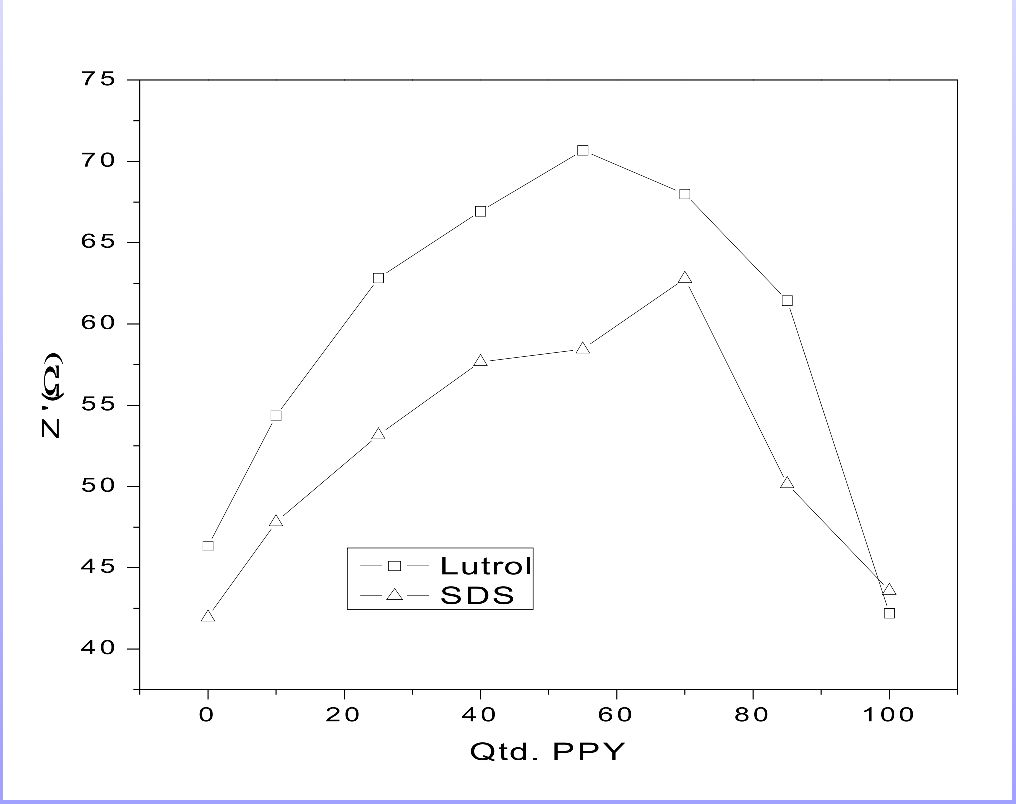
Surfactant-PPY nanoparticles with a magnetic core

Dielectric response for different surfactants



It is possible to get a balance between the conductive and the magnetic properties

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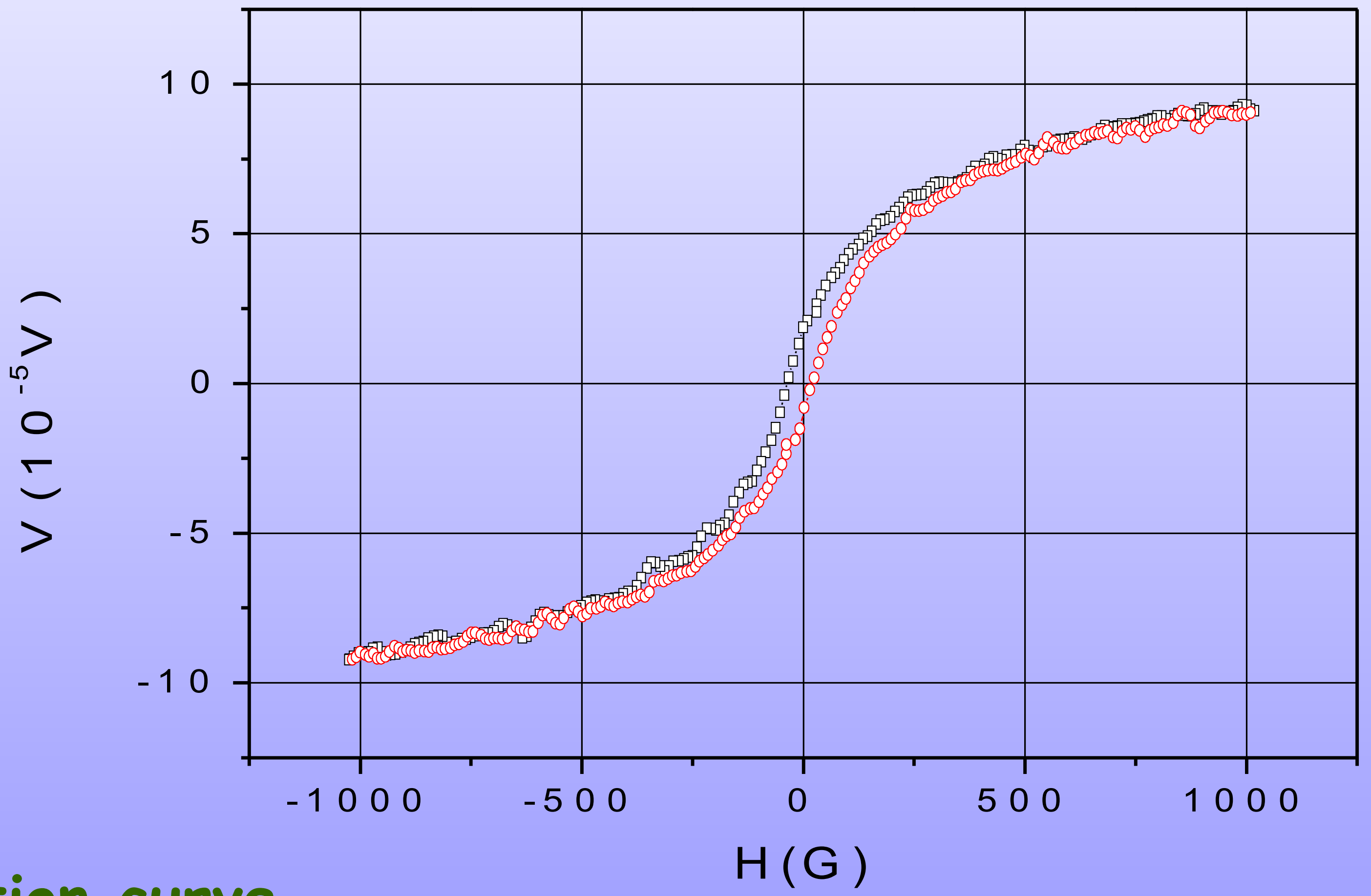
Surfactant-PPY nanoparticles with a magnetic core



Magnetization curve

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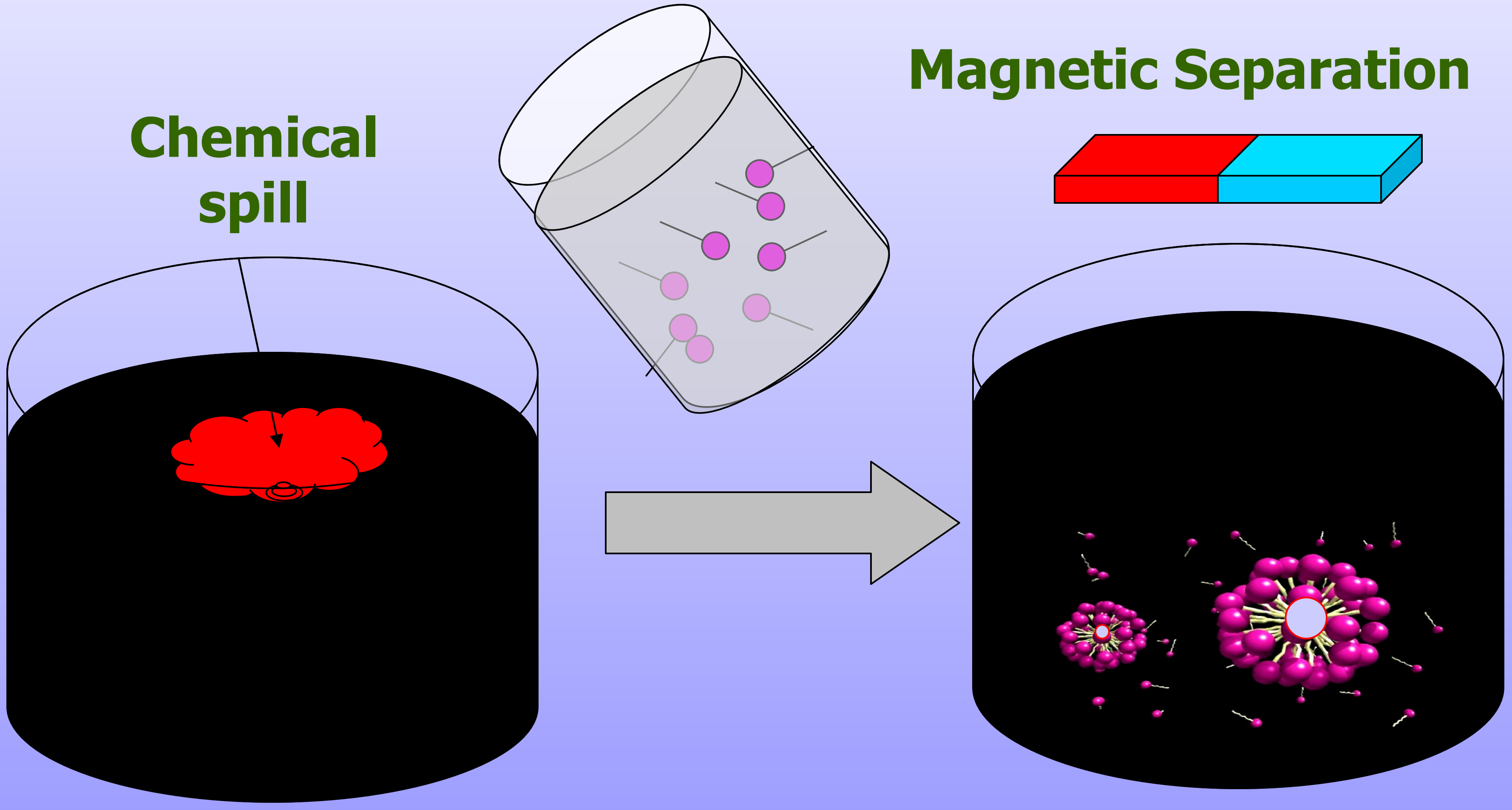
Possible Applications:
Cleaning up of chemical spillages



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Surfactant-PPY nanoparticles

- Lutrol-PPY micelles:
  - ✓ samples with “tunable” conducting properties (as measured by the impedance level)
- Lutrol-PPY micelles in the presence of PVA:
  - ✓ the range of impedance variation is more limited
  - ✓ it is possible to obtain solid films
- Introduction of magnetic iron nanoparticles:
  - ✓ balance between metallic and dielectric properties

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Possible uses of water-based micellar systems containing polymers and metallic nanoparticles:

- **anti-corrosive protection**
- **electromagnetic shielding ("stealth technologies")**
- **use in medical diagnosis**

Possible Applications:

Cleaning up of chemical spillages

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Possible Applications:
Cleaning up of chemical spillages

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INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS

J. Phys. D: Appl. Phys. 37 (2004) 2054–2059 PII: S0022-3727(04)77606-8

Colloidal dispersions of maghemite nanoparticles produced by laser pyrolysis with application as NMR contrast agents

Sabino Veintemillas-Verdaguer[1], Maria del Puerto Morales[1], Oscar Bomati-Miguel[1], Carmen Bautista[1], Xinqing Zhao[1,6], Pierre Bonville[2], Rigoberto Pérez de Alejo[3], Jesus Ruiz-Cabello[3], Martin Santos[4], Francisco J Tendillo-Cortijo[4] and Joaquin Ferreirós[5]

Figure 7. Coronal T2-weighted fast spin echo images pre- (*a*) and 10 min post- (*b*) injection of the colloid. Arrows sign liver (L), spleen (S) and brain (B) uptake.

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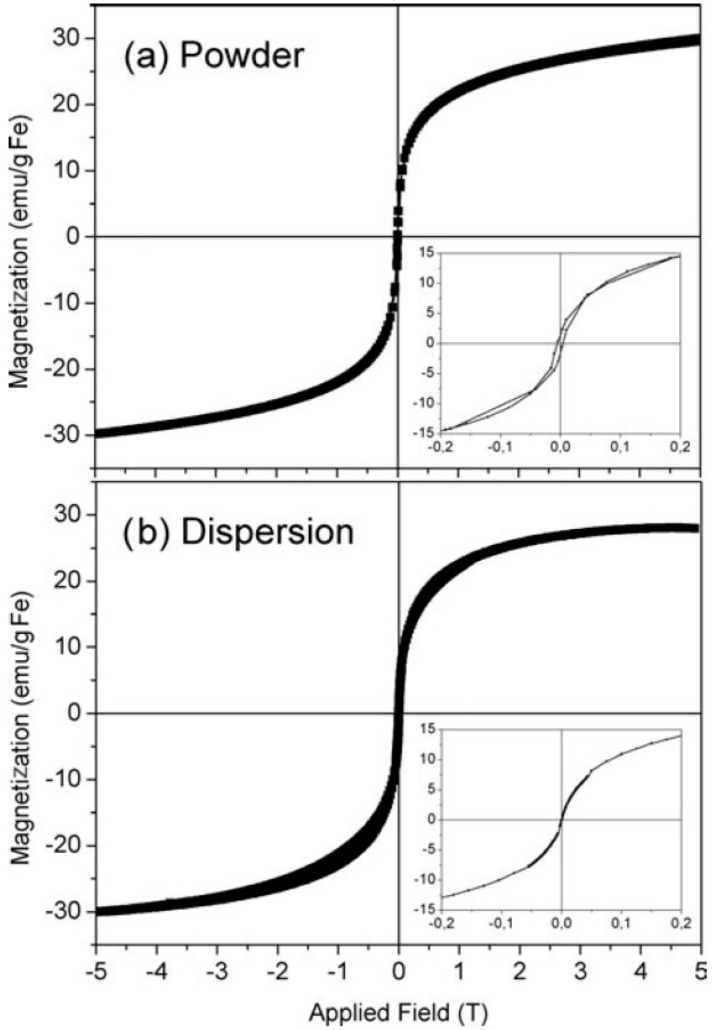

Figure 4. Magnetization curves at room temperature for the iron oxide nanoparticles obtained by laser pyrolysis (*a*) and the suspension resulting by dispersing and coating with dextran (*b*). A detailed view of the low field region is given in a inset.

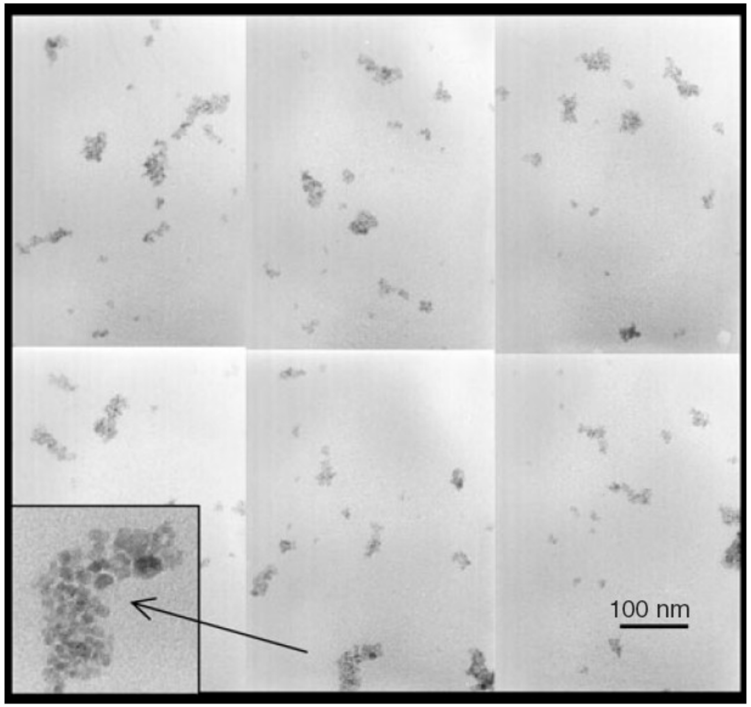

Figure 5. Composition formed from six TEM micrographs of the colloidal dispersion. A detailed view of one 50 nm aggregate is shown in a inset.

Application

for systems

of biological interest

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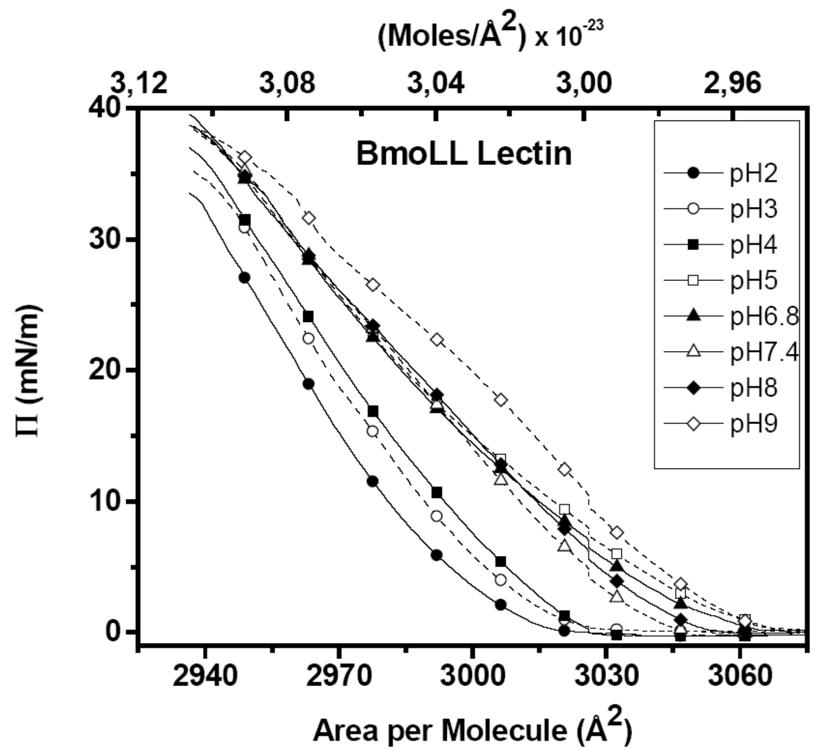
DIELECTRIC PROPERTIES of *Bauhinia monandra* and *Concanavalin A* LECTIN MONOLAYERS

PART I

Cesar A. S. Andrade[1,2]; Adam Baszkin[3]; Nereide S. Santos-Magalhães[4,5]; Luana C. B. B. Coelho[5]; Celso P. de Melo[2*]



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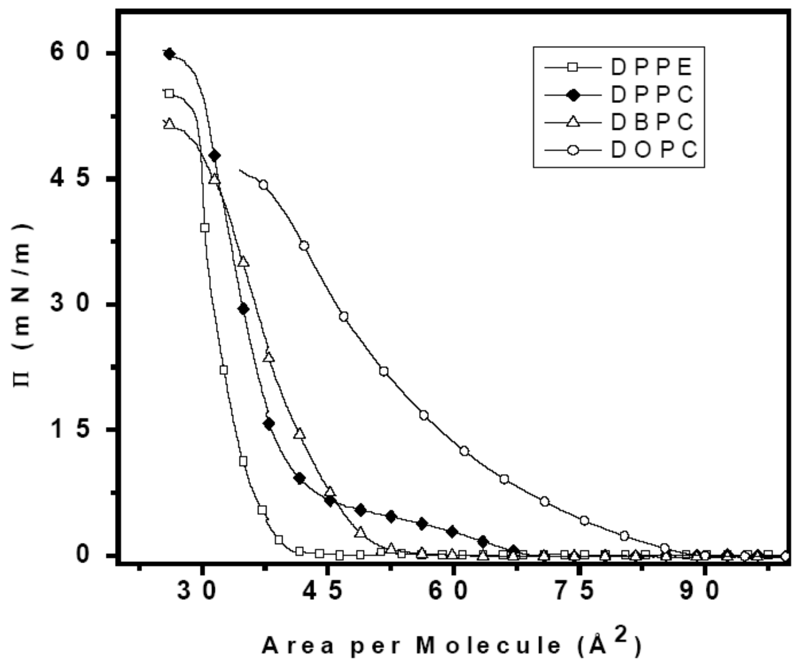
MIXED MONOLAYERS of *Bauhinia monandra* and *Concanavalin A* LECTINS with PHOSPHOLIPIDS

PART II

Cesar A. S. Andrade[1,2]; Adam Baszkin[3]; Nereide S. Santos-Magalhães[4,5]; Luana C. B. B. Coelho[5]; Celso P. de Melo[2*]



USE OF POLYANILINE NANOPARTICLES IN ALL-POLYMER ELECTRONICS

Micro (and nano) fluidics

Figure 9: Microcontact printing

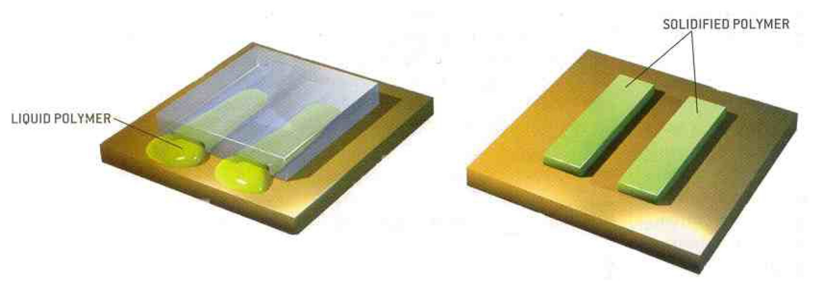
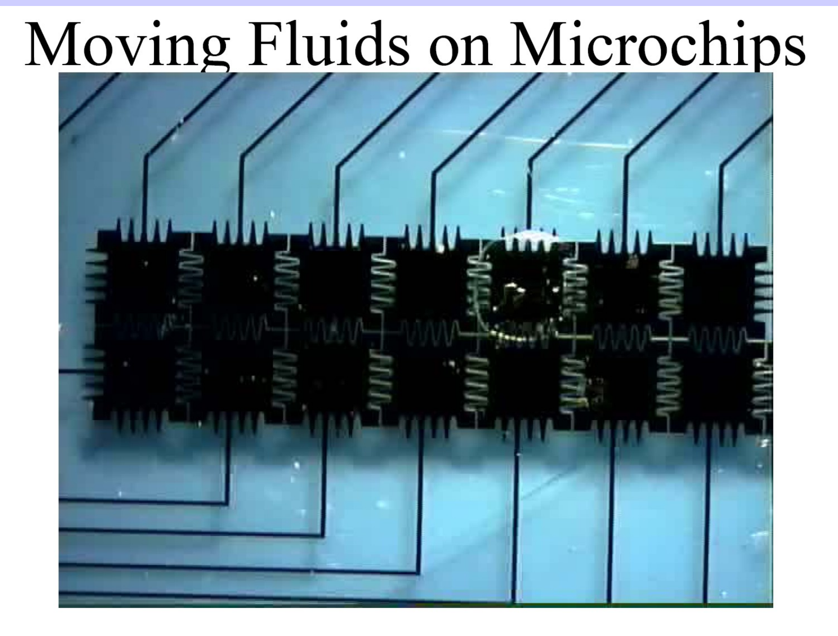


Figure 10: Micromolding in capillaries



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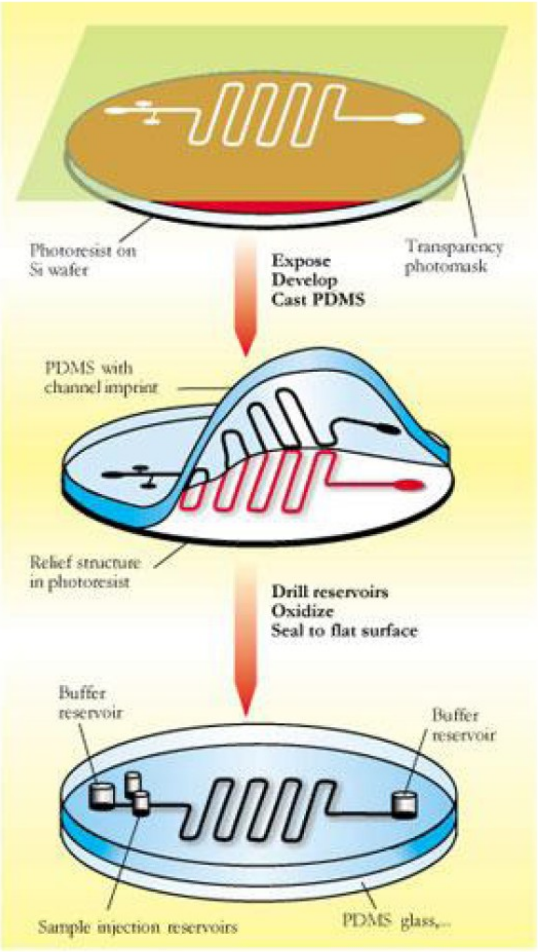
Fabricating Microfluidic Devices



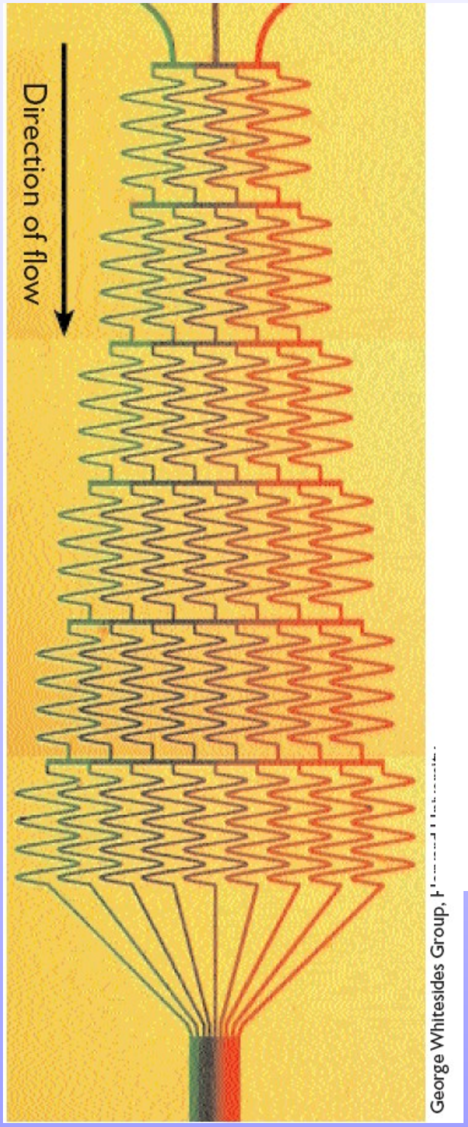


Figure 4. Photograph of a microfluidic device used for studying concentration gradients in a network of branching serpentines, in which three dyes are injected at the top before combining in a single channel at the bottom.

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How to connect the all-polymer circuit to the external world?

Microfluidics can be used for the preparation of Au nanowires

ELSEVIER

COLLOIDS AND SURFACES A

Colloids and Surfaces A: Physicochem. Eng. Aspects 223 (2003) 177–183

www.elsevier.com/locate/colsurfa

Linear aggregation of gold nanoparticles in ethanol

Jianhui Liao[a], Yu Zhang[b], Wei Yu[a], Lina Xu[a], Cunwang Ge[a], Jinhong Liu[a], Ning Gu[a,*]

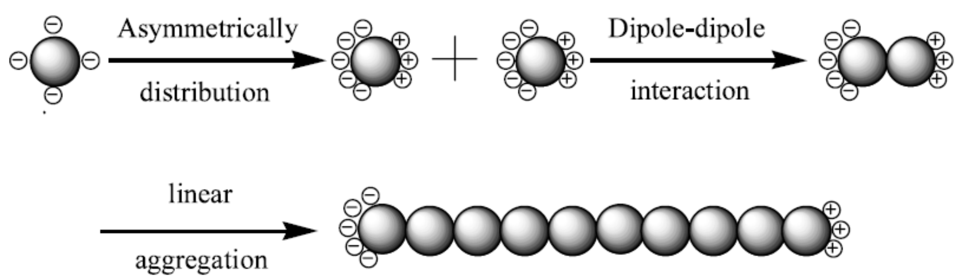

Fig. 5. The schematic illustration of the self-assembly process of gold nanoparticle chains based on the dipole assembly model.

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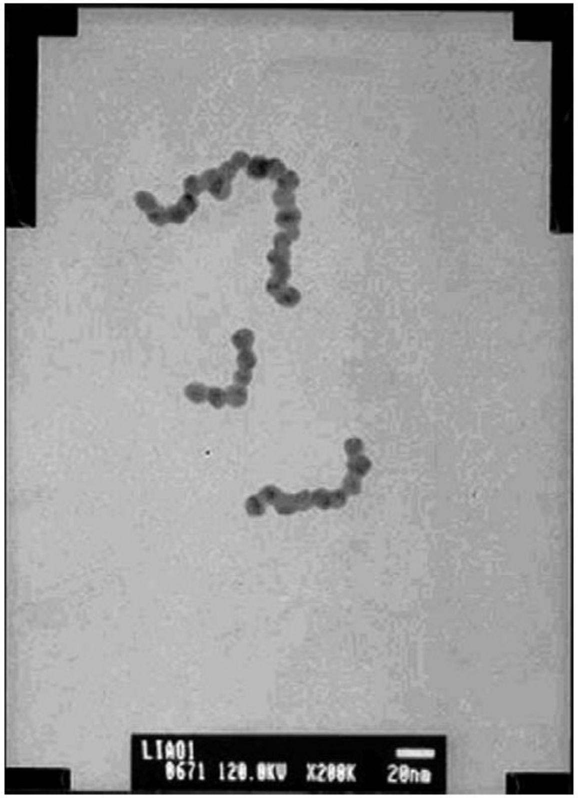

Fig. 1. A TEM photograph of chain-like nanoparticle aggregates deposited on a microgrid covered with a very thin carbon film.

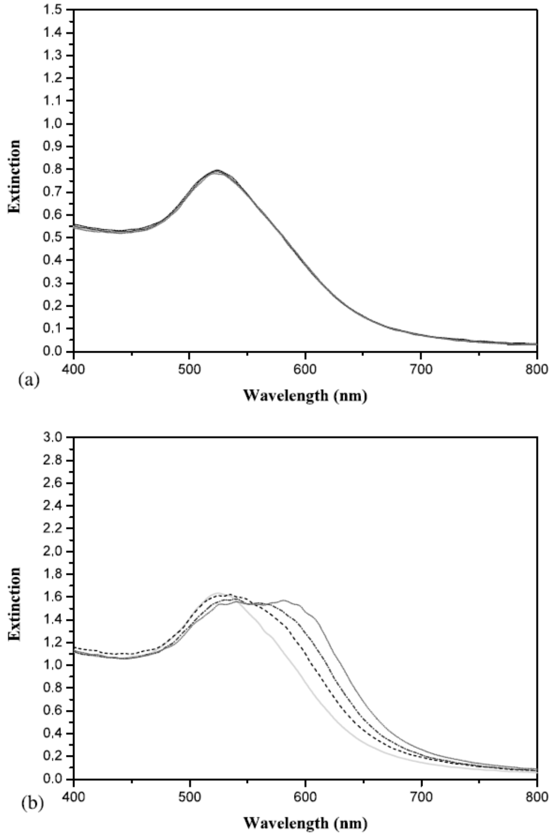

Fig. 4. Kinetics of chain-like aggregation of gold nanoparticles in ethanol with the particle concentration of 1.98×10^{15} ml^{-1} (a) and 4.95×10^{15} ml^{-1} (b). The recorded times corresponding with the solid lines, dashed lines, dash dot lines and short dot lines are 3 h, 1, 3 and 5 days, respectively.

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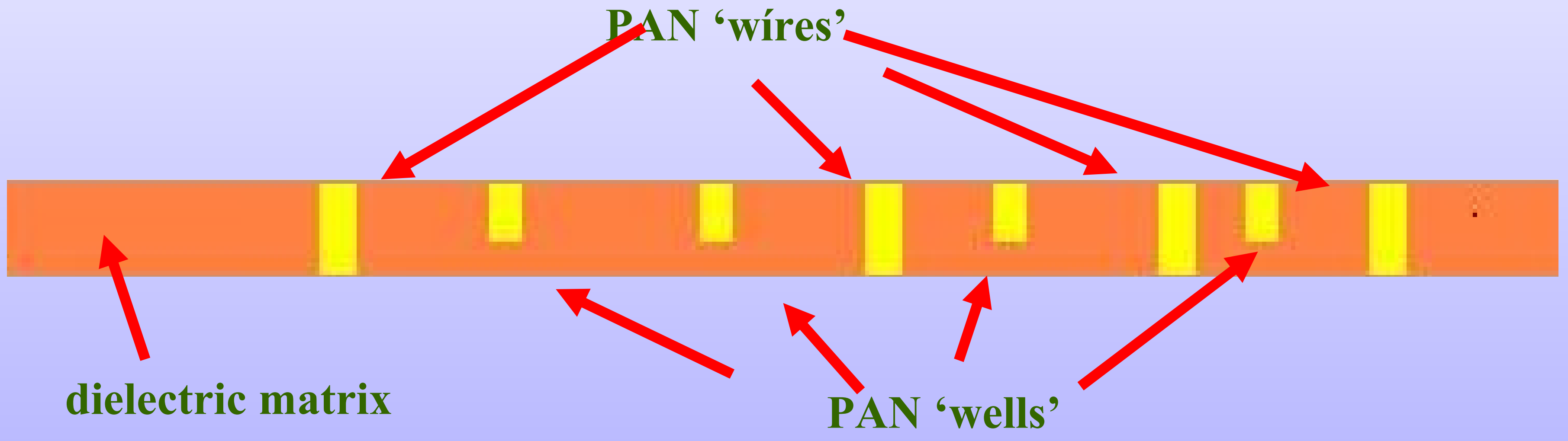
PAN nanowires in a dielectric matrix



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✓ **Emulsion polymerization methods allow the preparation of micelles containing conducting polymers and metallic nanoparticles**

✓ **Such systems can find application in:**

- **anti-corrosive protection**
- **electromagnetic shielding ("stealth technologies")**
- **medical diagnosis**
- **environmental site remediation**
- **spectral control**

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Summary:

- **composite polymeric nanostructures:**
  - ✓ **hybrid organic-inorganic systems**
  - ✓ **materials with controlled degree of conductivity**
  - ✓ **biological systems**
- **composite polymeric nanostructures appear as promising materials for:**
  - ✓ **OLEDs**
  - ✓ **mechanical actuators**
  - ✓ **electronic noses**

Ciência e Tecnologia
Ministério da Ciência e Tecnologia

Polymeric nanostructures

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VIRTUS IMPAVIDA