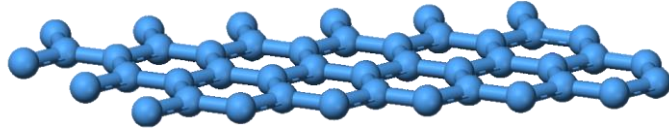




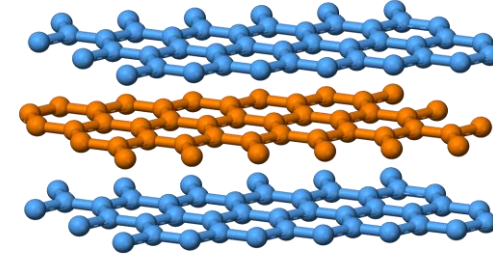
What is Carbon Black?


 **Juliano Fernandes Teixeira**

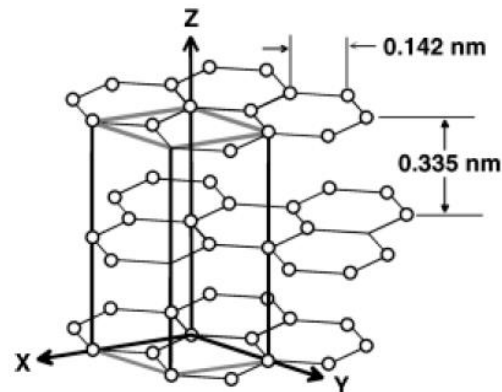
Carbon Black



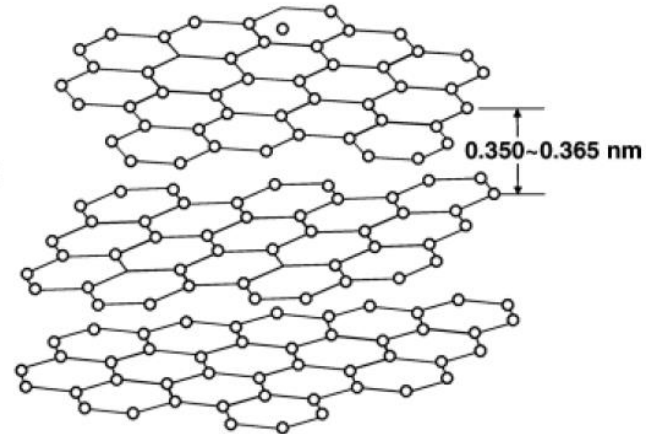
Graphene



Graphite



(a)



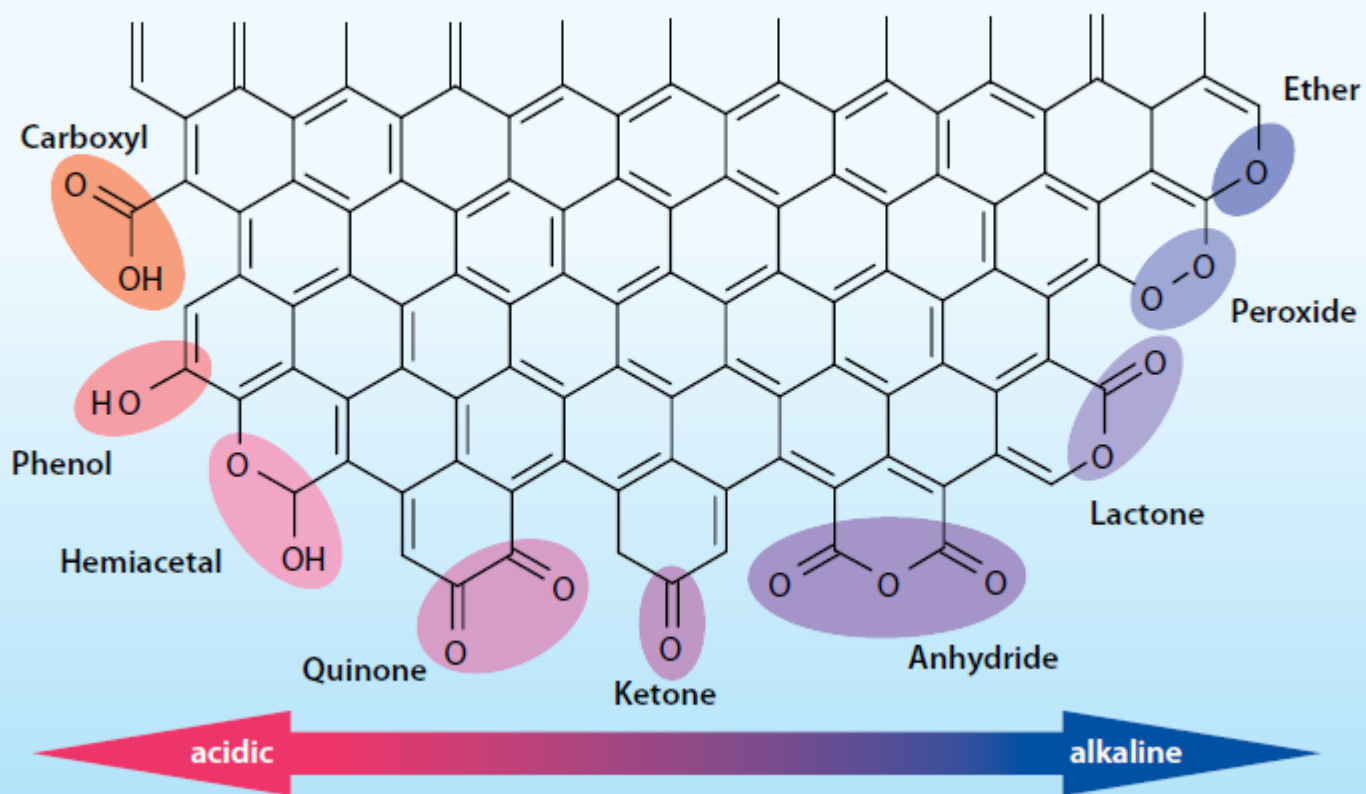
(b)

Atomic structural models of (a) graphite, and (b) carbon black.

It is a fluffy powder of extreme fineness and high surface area, composed essentially of elemental carbon.

Carbon Black

Particle Surface



Applications

Has interesting
conductive properties



Carbon Blacks are the key
to deep jet black paints.



Reinforcement
of rubber

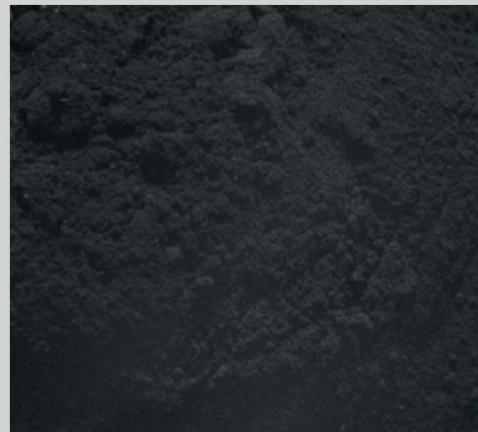
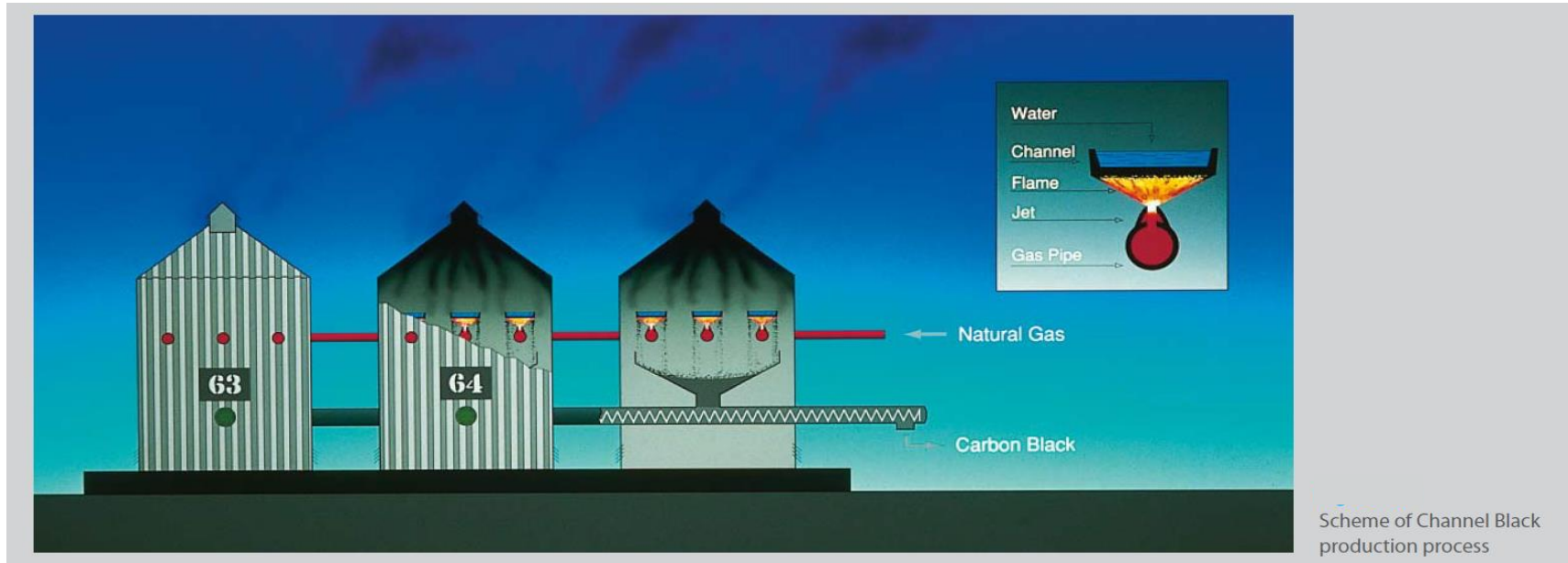


The coatings industry, fine-particle
types are used for obtaining a
deep jet black color.
Absorb UV light and convert it into
heat
Makes polyethylene more resistant
to UV radiation.



Manufacturing Process

Incomplete combustion of natural gas.



1) Powder Carbon Black



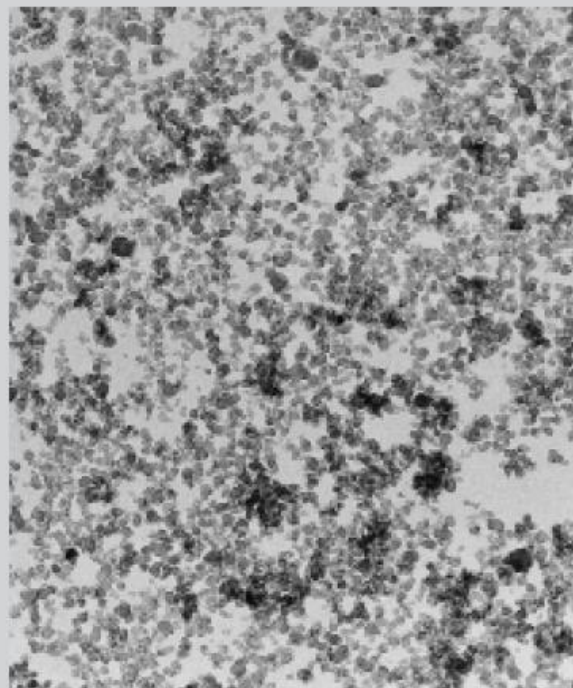
2) Dry-Pelletized Carbon Black



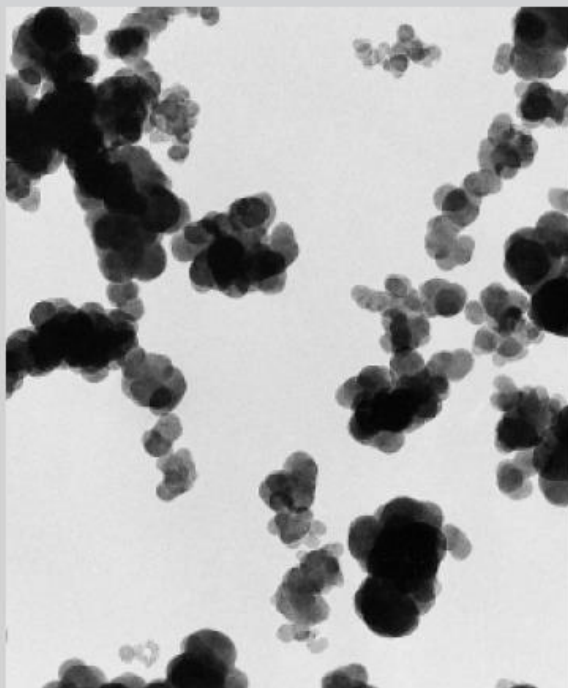
3) Wet-Pelletized Carbon Black

Different sizes

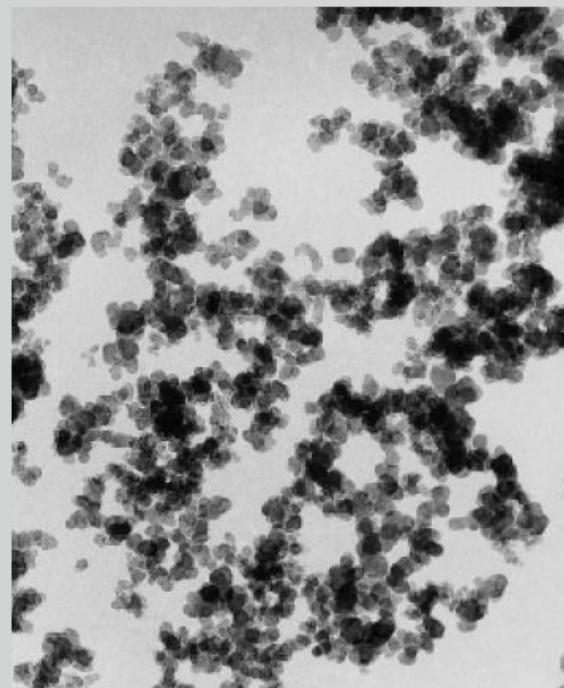
Furnace Blacks of varying particle size and structure.



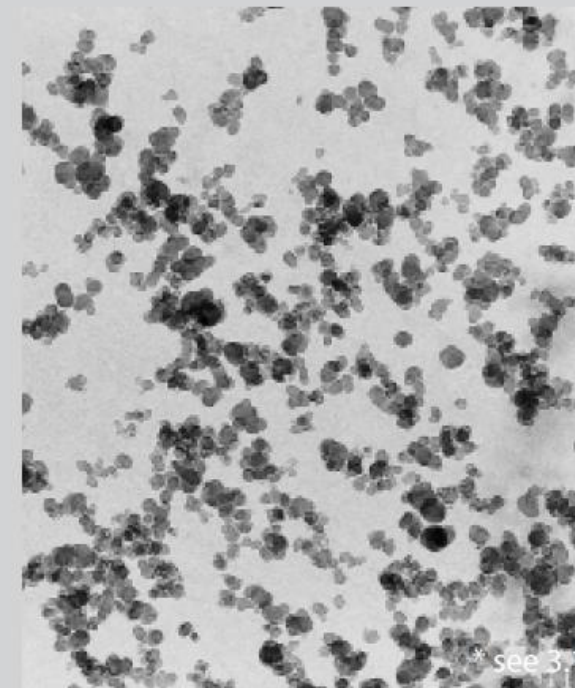
1) Furnace Black, fine primary particle size



2) Furnace Black, coarse primary particle size



3) High-structure Furnace Black



4) Low-structure Furnace Black

Different types

Carbon Black Morphology

ASTM designation	Particle size ^a , D_{wm} , ^b nm	Aggregate size ^a , D_{wm} , ^b nm	D_{st} , ^c nm	Surface area ^a , m^2/g
N110	27	93	76–111	143
N220	32	103	95–117	117
N234	31	109	74–97	120
N326	41	108	98	94
N330	46	146	116–145	80
N339	39	122	96–125	96
N351	50	159	127	75
N375	36	106	91	105
N550	93	240	220–242	41
N660	109	252	227–283	34
N774	124	265	261	30
N990	403	593	436	9

^a Measured by TEM.

^b D_{wm} = weight mean diameter = $\Sigma nd^4 / \Sigma nd^3$.

^c Stokes diameter by centrifugal sedimentation from various sources.



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Effect of cationic surfactant and block copolymer on carbon black particle surface charge and size

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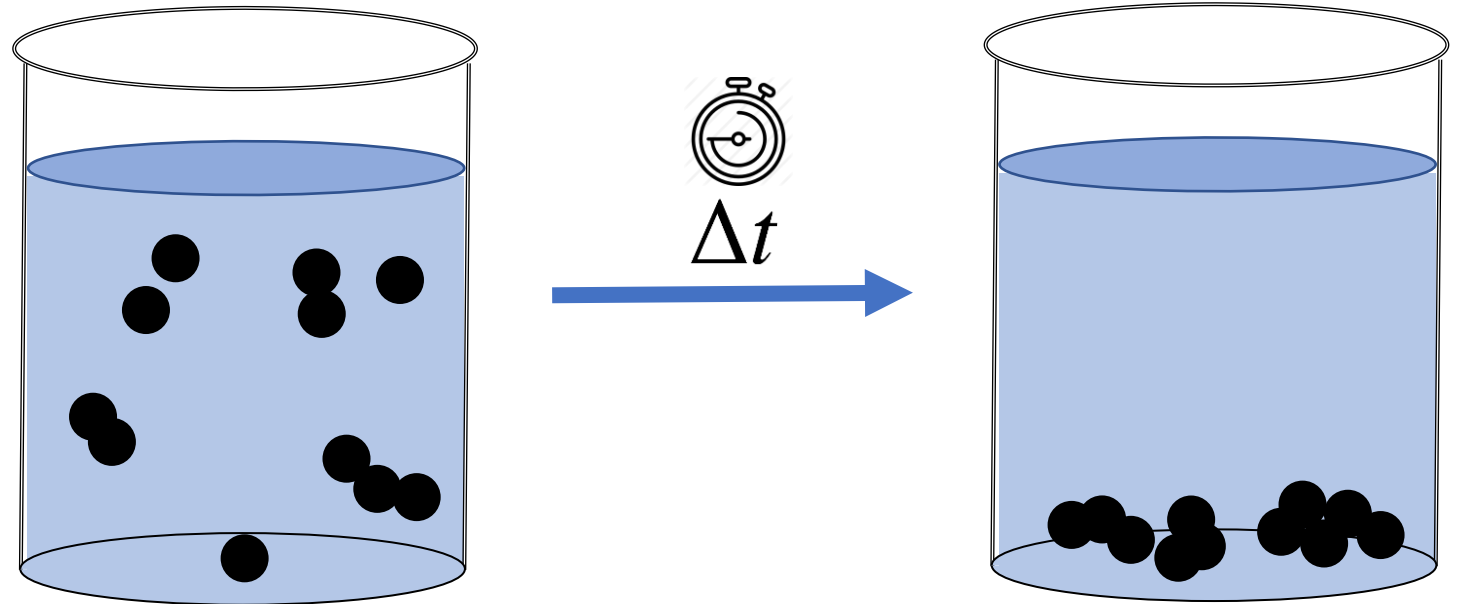
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Available online 18 January 2006

Purpose of the article

● Primary Particles

●●● Aggregates



Investigate the effects of cationic surfactant, block copolymer, pH of the aqueous phase and the preparation mode on size reduction and surface charge modification of carbon black particles aqueous dispersions.

Materials

Carbon Black N234

Size: 17 – 40 nm

Composition: 96.29% C, 0.48% H, 0.20% N, 1.53% O and 1.50% S

Cetyltrimethylammonium chloride (CTAC)

CMC: 1.45 mM

Cationic surfactant

Polystyrene oxide diblock (SE10-10)

Molecular weight of polystyrene block = 1000 g/mol

Molecular weight of oxide block 1000 g/mol

$C_{aap} = 20$ mg/L

Non-ionic copolymer

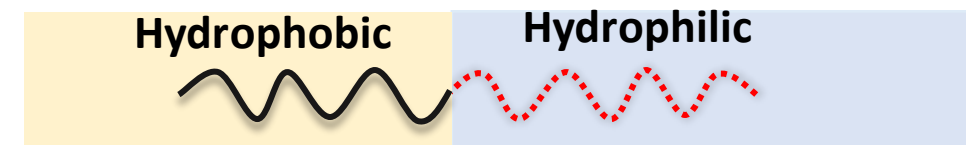
Polyethylene oxide diblock (SE 10-30)

Molecular weight of polystyrene block = 1000 g/mol

Molecular weight of oxide block 3000 g/mol

$C_{aap} = 64$ mg/L

Non-ionic copolymer



Preparation

Carbon Black (20 mg/L)
Distilled water

Sonificate on ultrasonic device for 5 min

Carbon Black (20 mg/L)
CTAC (1 – 70 mg/L)

Carbon Black (20 mg/L)
SE 10-10 (1 – 900 mg/L)

Carbon Black (20 mg/L)
SE 10-30 (1 – 5000 mg/L)

In all experiments, the salt concentration $\text{NaCl} = 10^{-3}\text{M}$ was kept constant

Dispersions were shaken at ambient temperature, for 24 h to reach the equilibrium adsorption.

Experimental techniques

Transmission electron microscopy → Morphology and size of carbon particle in vacuum dried dispersions

Dynamic Light Scattering (DLS) → Measure the size of carbon particles

Zeta potential → Surface charge of carbon black dispersion

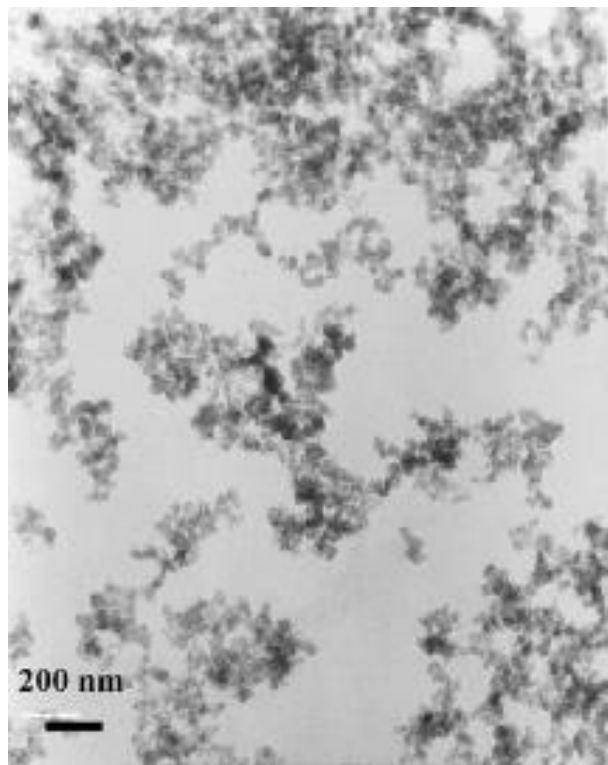
Size distribution

(pH = 6.1 ± 0.1)

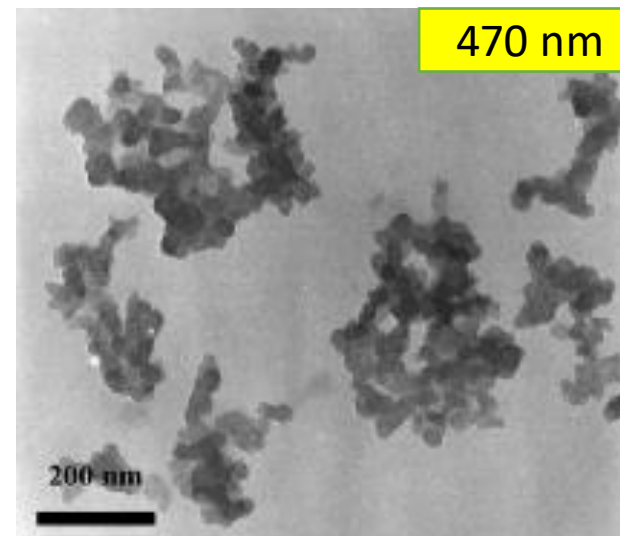
Sieved fractions of the N234 sample

Sieve size (mm)	Amount sieved (wt.%)
1	10.68
0.5	27.4
0.25	18.0
0.125	17.9
Below 0.125	25.9

Sieving the sample



TEM micrograph of N234 sample before sieving.



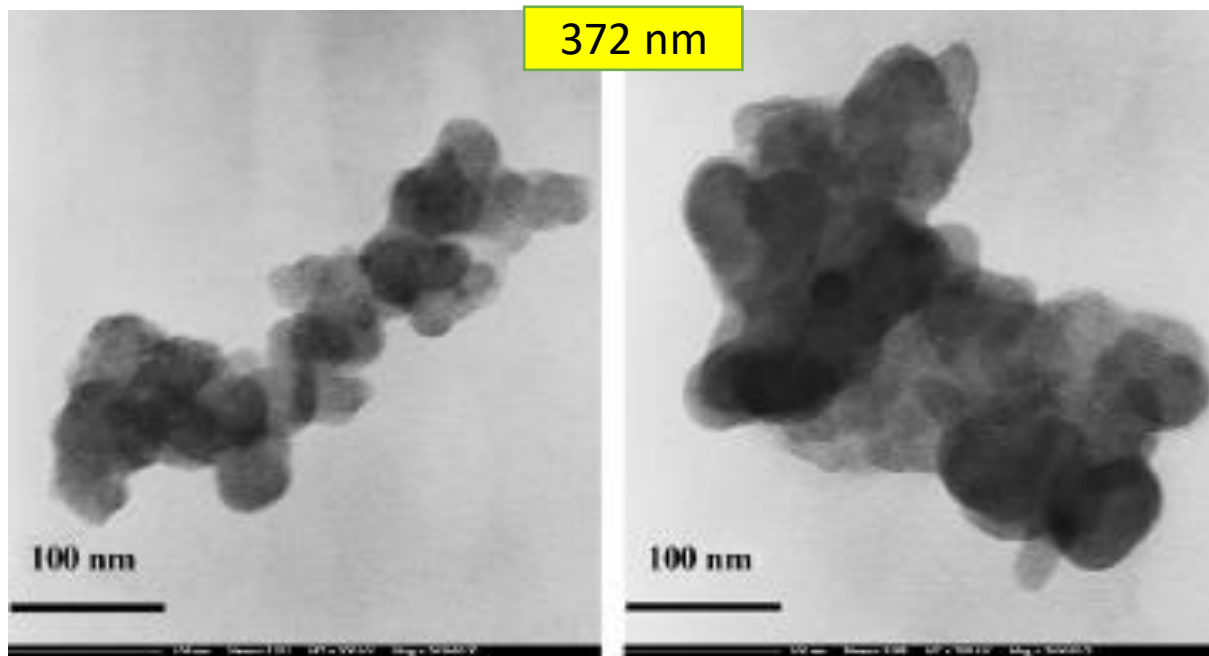
TEM micrograph of N234 sample after sieving.

In the following, we will consider only the carbon black fine fraction, obtained by sieving (mesh size $\leq 125 \mu\text{m}$).

Effect of cationic surfactant

Obs: In all experiments: surfactant concentration < CMC

copolymer-carbon weight ratio = 1



Before TEM analysis, the mean particle diameter = 170 nm

The increase when going from aqueous médium to vacuum dried, is driven by capillary forces, which become operative and overcome the electrical repulsive forces.

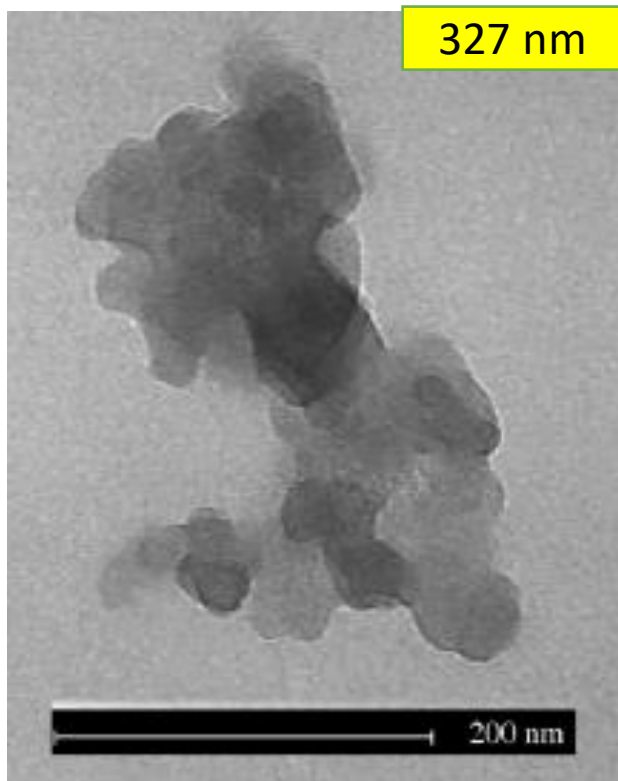
TEM micrographs of carbon black aggregate in 20 mg/L of CTAC surfactant

NaCl = 10^{-3} M

(pH = 6.1 ± 0.1)

Effect of non-ionic PS-PEO diblock copolymer

copolymer-carbon weight ratio = 15



The reduction on size is due to the complete coverage of carbon surface by a thin Polymer layer, screening carbon-carbon attraction

Comparing with cationic surfactant. The reduction is due either electrostatic or steric repulsion.

TEM micrographs of carbon black aggregate in presence of SE 10-10

$\text{NaCl} = 10^{-3} \text{ M}$

$(\text{pH} = 6.1 \pm 0.1)$

Effect of pH on dispersion of carbon black (aqueous solution)

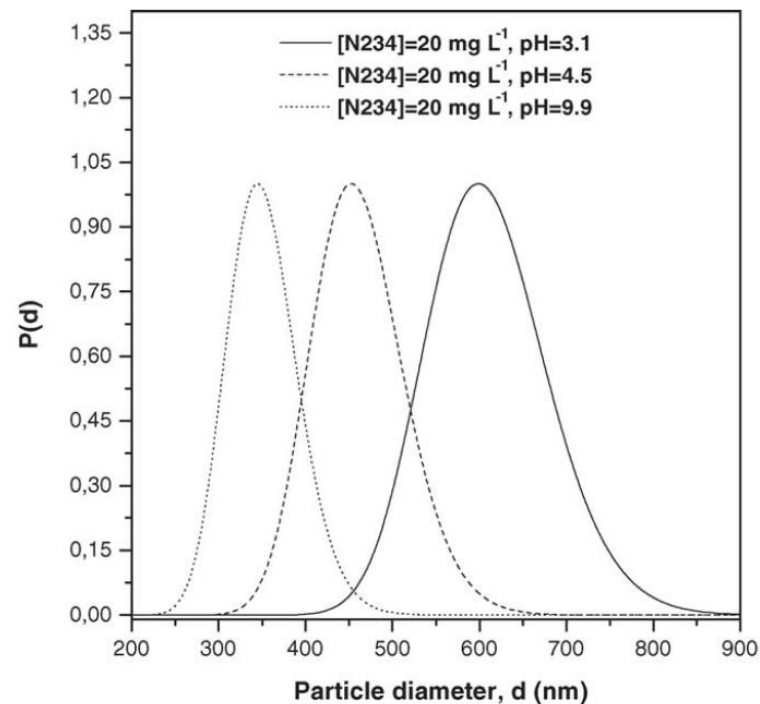


Fig. 6. Effect of pH of the aqueous phase on the size distribution of N234 carbon dispersion in the absence of additives. $P(d)$ is the relative probability of a particle of diameter d , describing the log-Gaussian particle size distribution in the unimodal analysis (see Eq. (11)). The maximum of the $P(d)$ curve corresponds to the mean particle diameter, $\langle d \rangle$, and the $P(d)$ broadness is related to the particle size polydispersity index $\mu_2/(\Gamma)^2$.

The reduction on size
with increase on pH

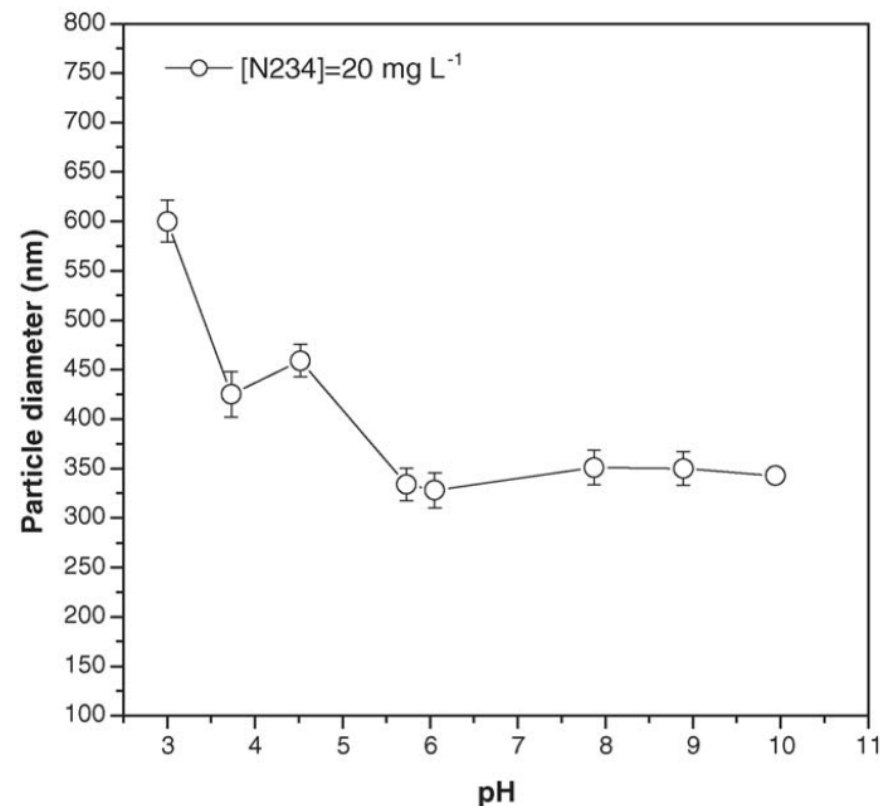


Fig. 7. Variation of the N234 carbon particle size with the pH of the aqueous phase, in the absence of surfactant molecules.

This result is due to the increase of the ionization of acidic carbon surface groups (carboxylic and phenolic groups) leading to electrical force repulsion between the negatively charged carbon particles.

Dispersion size of carbon black in CTAC and SE solution

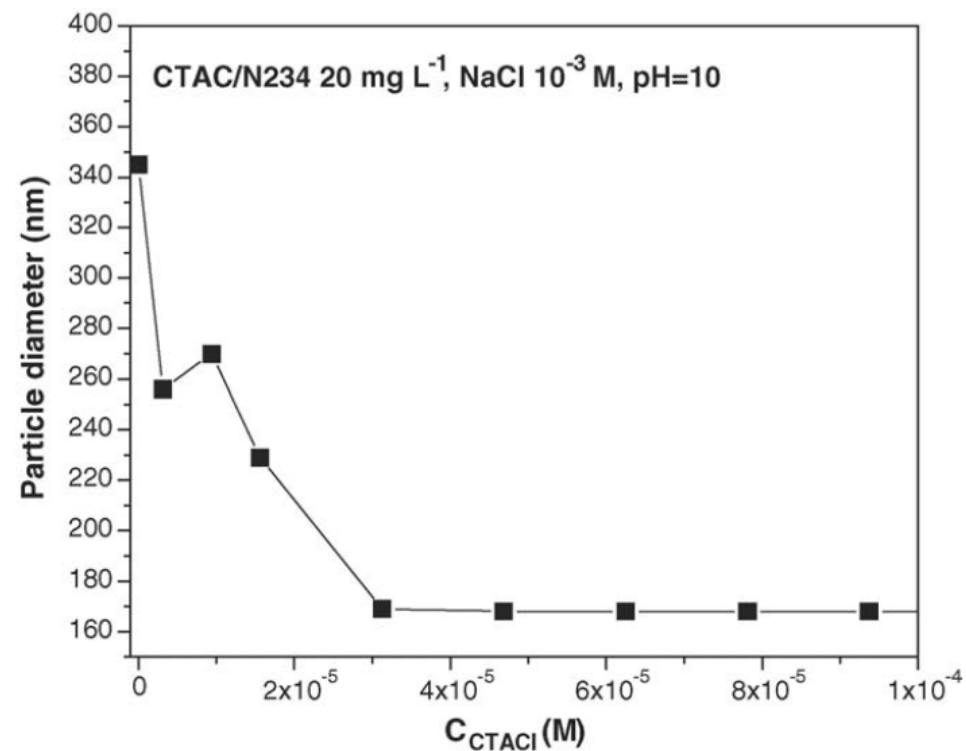


Fig. 8. Variation of the N234 carbon particle size with the concentration of CTAC.

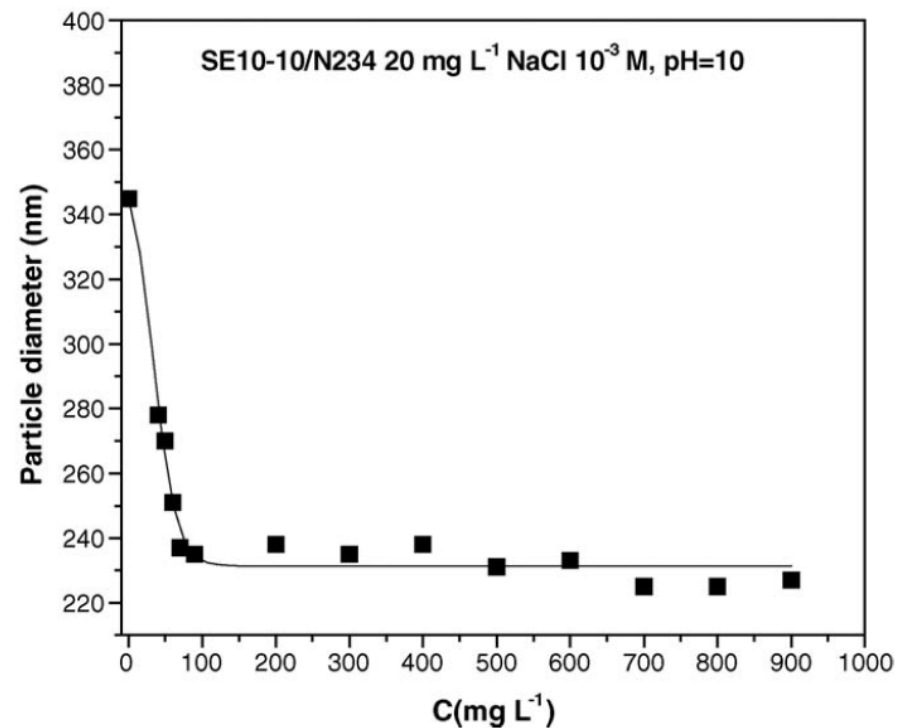
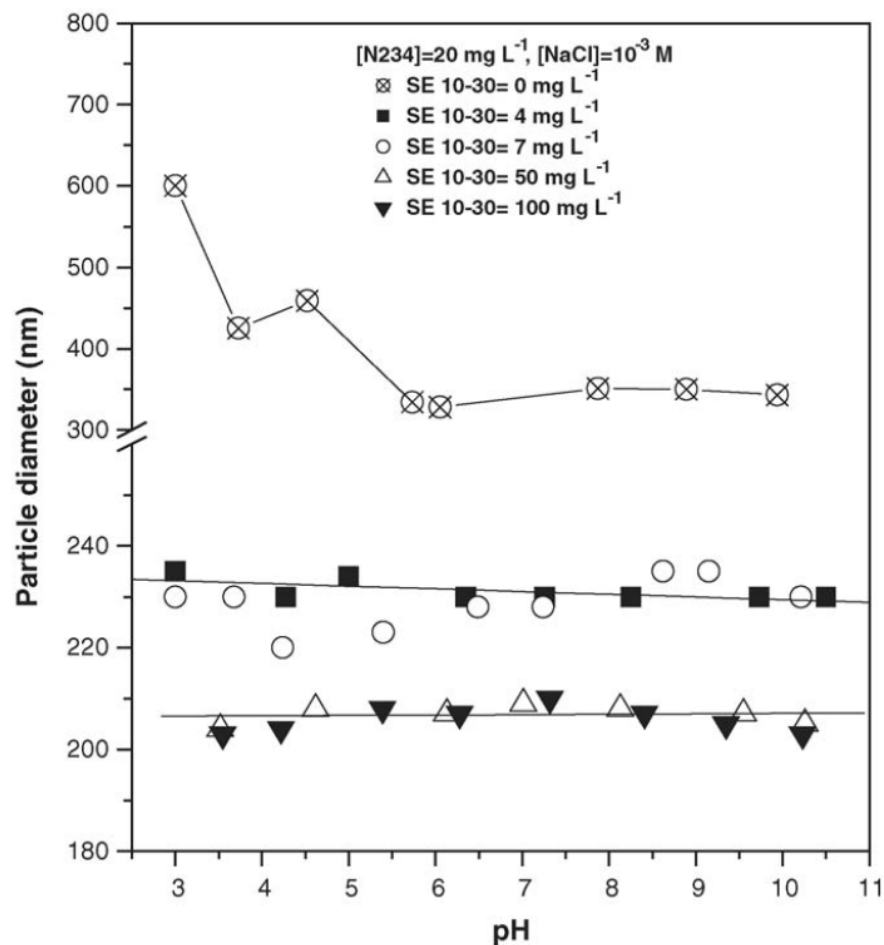


Fig. 9. Variation of the N234 carbon particle size with the concentration of SE 10-10 surfactant.

Effect of pH on dispersion of carbon black with SE 10-30 solution



The particle diameter decrease with increasing [SE 10-30], but does not change with the pH

Such decrease in carbon particle size results from copolymer adsorption on the solid surface providing hence steric repulsion between particles.

PS-PEO copolymer adsorbs onto carbon particles by its hydrophobic part (PS block) and extends its hydrophilic part (PEO block) into the aqueous medium, leading to stable dispersions.

Fig. 10. Effect of pH of the aqueous phase on the N234 carbon particle size in the absence and the presence of various concentrations of SE 10-30 surfactant.

Zeta Potential of carbon black (aqueous solution) varying pH

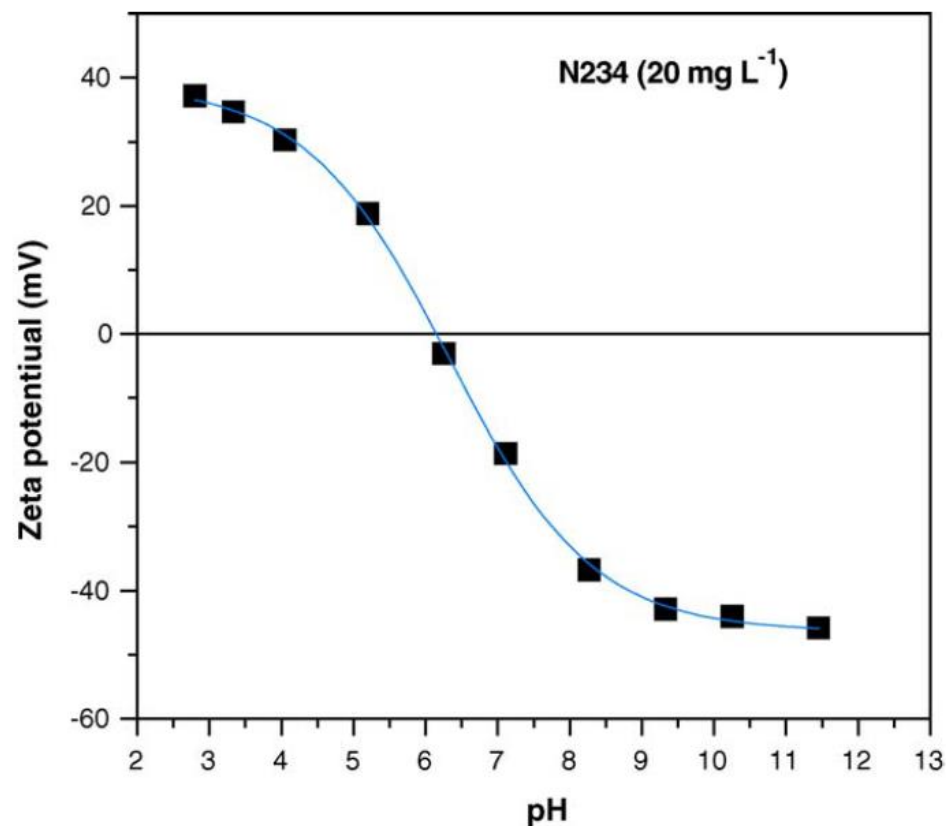
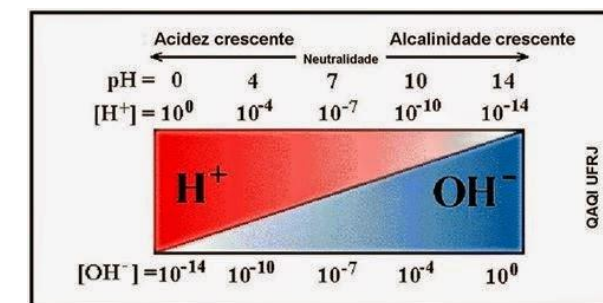
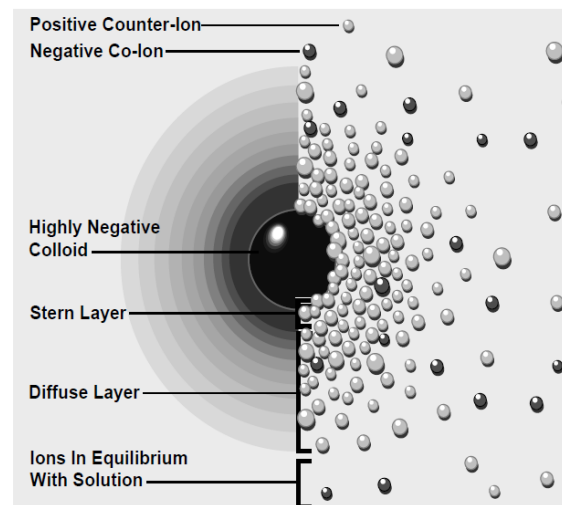


Fig. 11. Variation of the zeta potential with the pH of N234 aqueous dispersions (NaCl = 10⁻³ M), in the absence of additives.

Since the N234 carbon sample used in the present study was not heated or treated with liquid oxidants, it is likely that the basic functionality (positively charged particles) may be due to organic Sulphur.

Indicates that H⁺ and OH⁻ ions are the potential determining ions (PDI), i.e. ionic species of the aqueous medium that enter the inner part of the electrical **double layer** and undergo specific interaction with the surface.



Zeta Potential: carbon black with CTAC

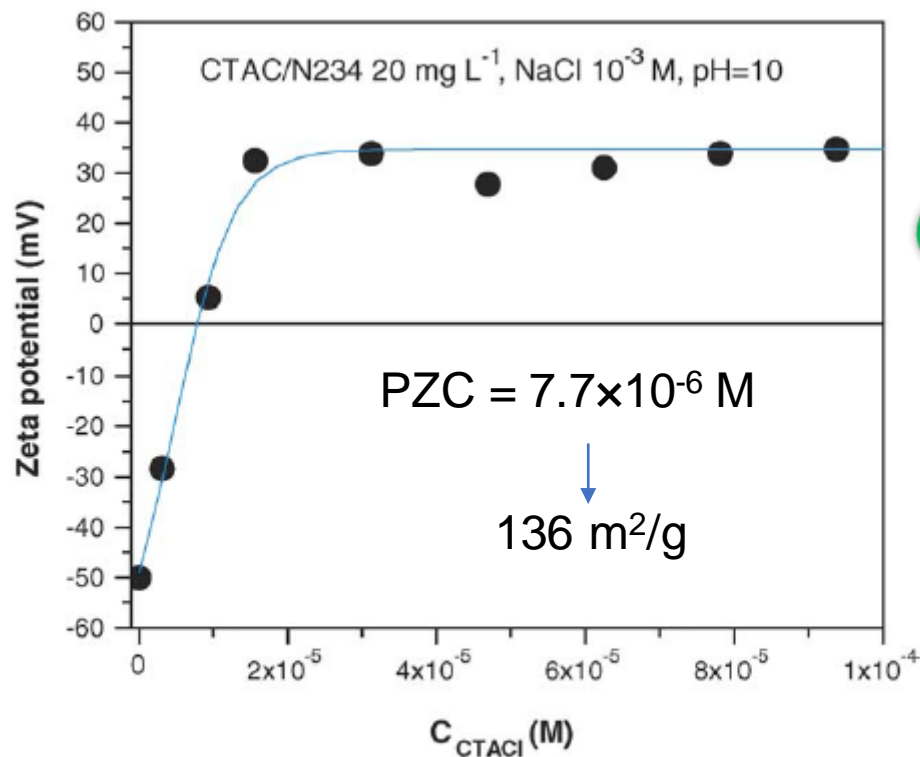
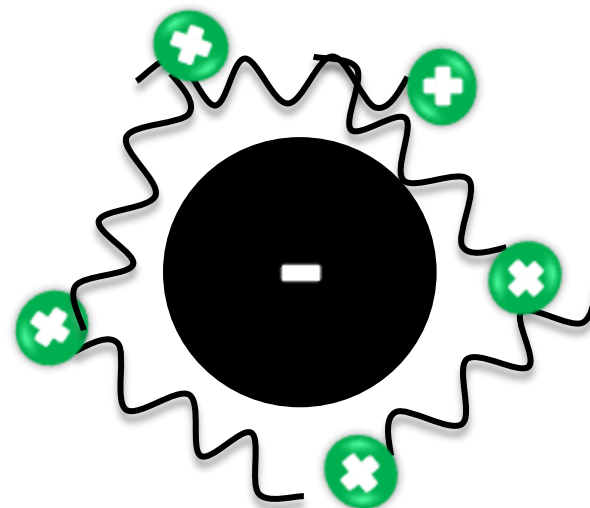


Fig. 12. Variation of the N234 carbon particle zeta potential with the concentration of CTAC.



CMC: 1.45 mM

Above the PZC leads successively to the formation of a monolayer, followed by the formation of clusters or micelles. The formation of clusters, which is due to the lateral interaction between the alkyl chains of the adsorbed surfactant molecules, leads to stable carbon aqueous dispersions having minimal particle size.

Point of zero charge (PZC), i.e. the CTAC concentration at which all the solid surface acidic groups are neutralized by the surfactant molecules

Zeta Potential: carbon black with SE

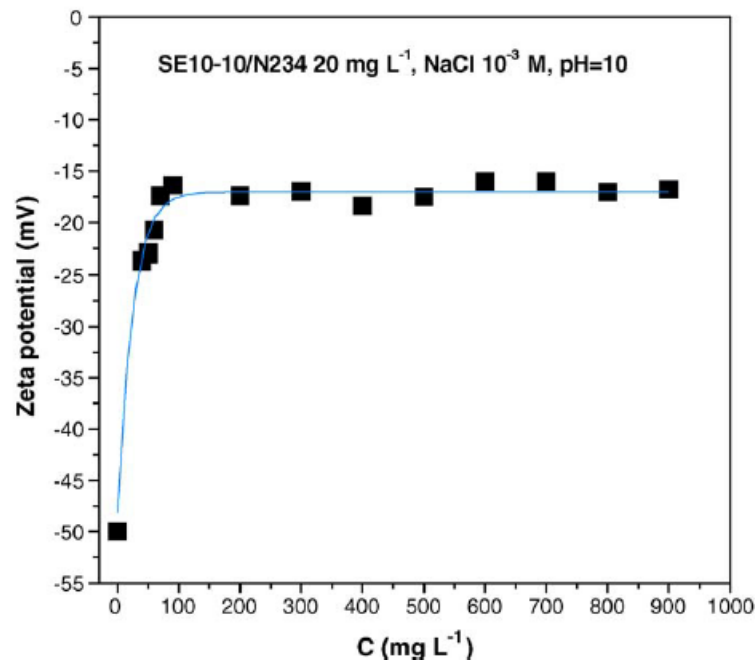


Fig. 13. Variation of the N234 carbon particle zeta potential with the concentration of SE 10-10 surfactant.

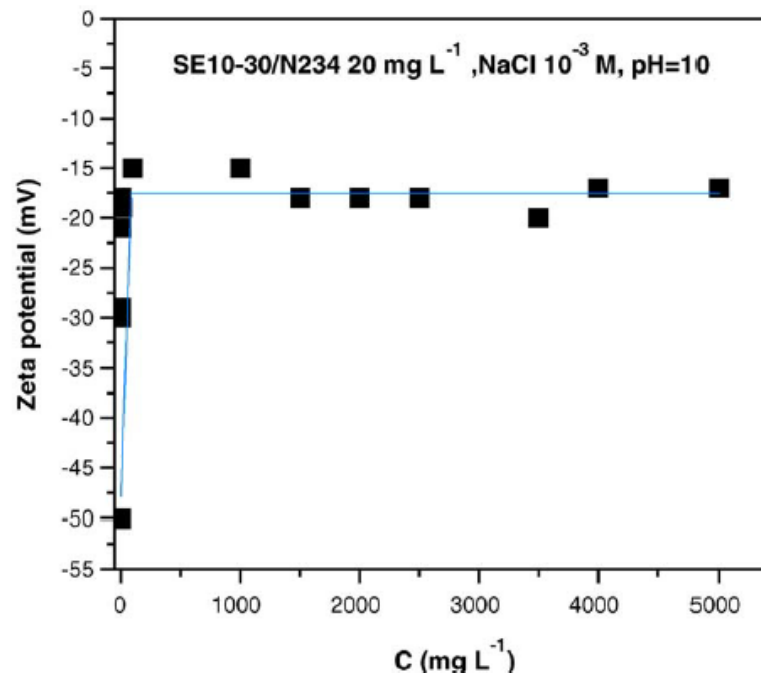


Fig. 14. Variation of the N234 carbon particle zeta potential with the concentration of SE 10-30 surfactant.

Results indicate that the adsorbed PEO blocks on carbon surface are close together and stretch into the solution. The presence of polymer barrier leads in turn to steric repulsions between carbon particles.

Adsorbed polymer layer having a thickness $L_z = 10.14$ nm.

Plateau values for the two polymeric amphiphiles indicate that adsorption PS-PEO block copolymer from water on carbon surface is mainly controlled by the hydrophobic PS block and is less dependent on the hydrophilic PEO block.

Conclusions

Vacuum dried dispersions (TEM):

	particle size change from
• CTAC/carbon black (weight ratio = 1):	470 to 372 nm
• SE 10 – 10/carbon black (weight ratio = 15):	470 to 327 nm

In aqueous solution (DLS) (pH = 10)

	particle size change from
• CTAC($0 - 1 \times 10^{-4}$) + carbon black (20 mM):	340 to 170 nm
• SE 10 – 10 (0 – 900 mg/L) + carbon black (20 mM):	340 to 230 nm

CTAC or PS-PEO adsorption from water on carbon surface lead to electrostatic or steric repulsion avoiding hence carbon–carbon attraction and limiting the aggregate size.

Conclusions

Carbon surface charge (Zeta potential) (pH = 10)

- CTAC($0 - 1 \times 10^{-4}$) + carbon black (20 mM):
- SE 10 – 10 (0 – 900 mg/L) + carbon black (20 mM):

change on surface charge

-50 to +35 mV

-50 to -18 mV

Figures Reference:

Kirk-othmer Encyclopedia of Chemical Technology. Vol. 4. Carbon Black

<https://www.thecarycompany.com/media/pdf/specs/orion-what-is-carbon-black.pdf>

Article:

<https://www.sciencedirect.com/science/article/abs/pii/S0927775705009672>

Thank you!

