계면 활성제와 고분자 물질의 상호작용

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1. 서 론

계면활성제 (Surfactant) 는 세제, 화장품, 의약품 등 최종 제품뿐 아니라 유화중합 (Emulsion polymerization), Mineral processing 등에 광범위하게 사용되어지며 많은 경우 제품의 특성을 조절하기 위하여 고분자 (polymer) 와 함께 쓰여진다. 그러나 계면활성제와 고분자를 같이 사용할 경우 전기적 상호작용 (Electrical interaction), 소수기에 의한 상호작용 (Hydrophobic interaction), 입체 상호작용 (Steric interaction), 수소결합 (Hydrogen bonding)등에 의해 Complex 를 형성하거나 Solvent medium 의 특성을 변화시켜 Solubility, Viscosity, Surface charge, Colloidal stability, Surface hydrophobicity and hydrophilicity, Interfacial tension 등에 영향을 미친다. 따라서 계면활성제와 고분자를 같이 사용할 경우 이들 사이의상호작용이 최종 제품에 미치는 영향을 파악하는 것은 매우 중요하다.

먼저 계면활성제와 고분자간의 상호작용의 중요성이 다음과 같은 대표적인 System들을 통해 인식될것이며 계속해서 이러한 상호작용의 근원및 연구방법이 논의될 예정이다.

- o Pharmaceutical Formulation (or Cosmetic Formulation)
- o Latex Particle Production
- o Adhesion
- o Filtration
- o Enhance Oil Recovery
- o Mineral Processing

2. 계면활성제와 고분자 상호작용이 중요한 대표적인 Systems

2-1. Pharmaceutical Formulation

Surfactant - Drug substance 의 용해도 증가

Polymer - Viscosity modifier, Suspension stabilizer

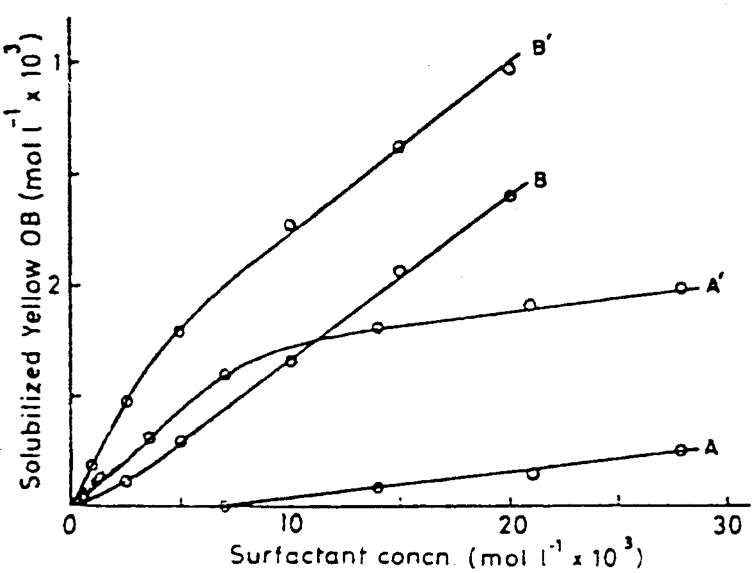


Fig. 1 Effect of PVP addition on the solubilization of an oil-soluble dye, Yellow OB, in surfactant solutions at 30°C:A, NaDS;, dodecyl-(oxyethylene)-ether. The primes refer to the addition of 0.1 % PVP to the corresponding surfactant solutions.

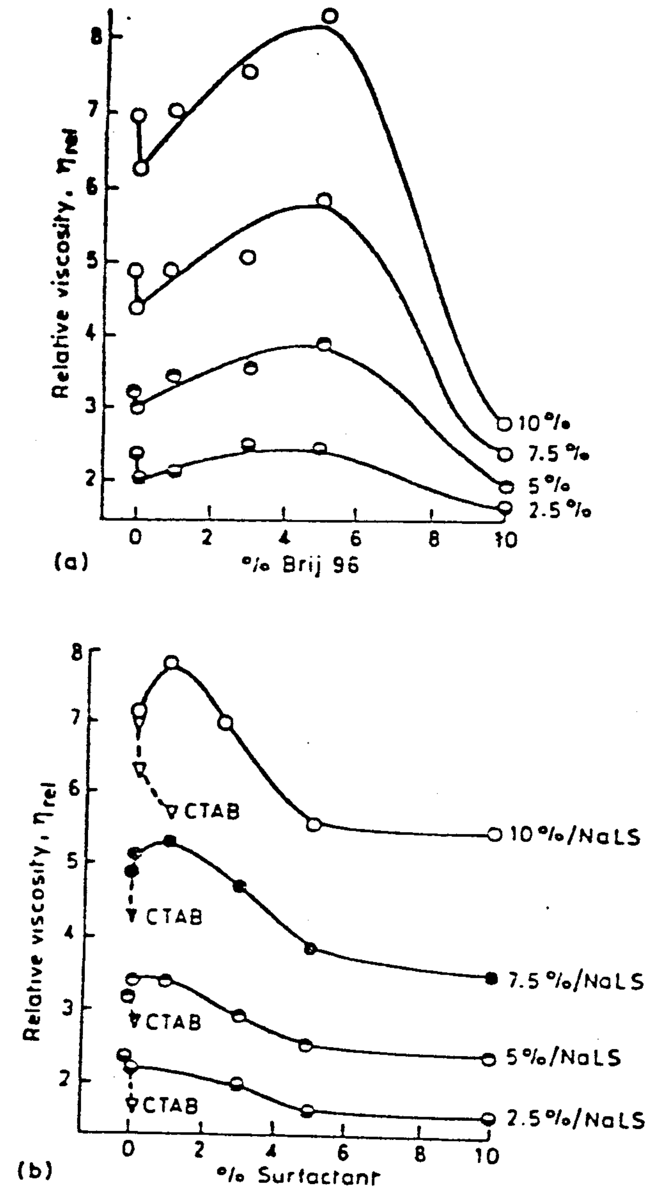


Fig. 2 Relative viscosity of gum arabic aolutions (a) in the presence of increasing concentrations of Brij 96, concentrations of gum arabic as shown on plots, and (b) in the presence of sodium laurysulphate (NaLS) and cetyltrimethylammonium bromide (CTAB) at the concentrations of gum shown, from 2.5 % to 10 %.

2-2. Latex Particle Production

Surfactant - Solubilization of reactant, Stabilizer of Latex

Polymer - Latex

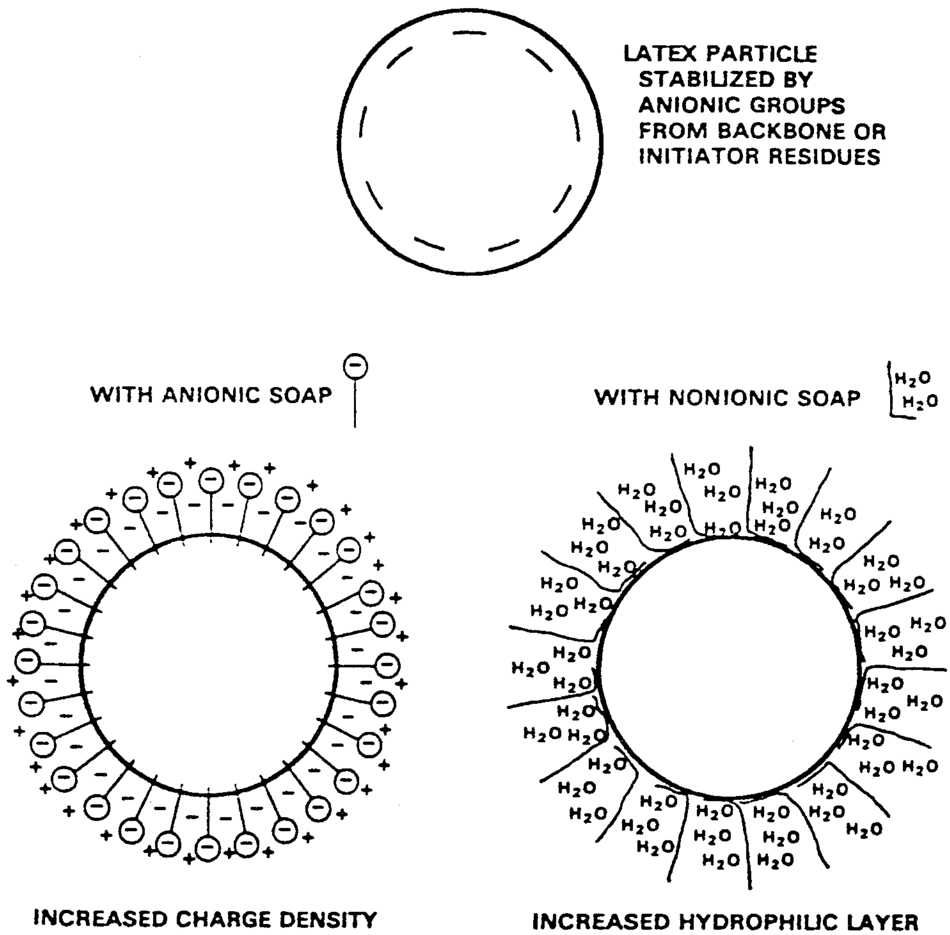


Fig. 3 Schematic representation of surfactant stabilization.

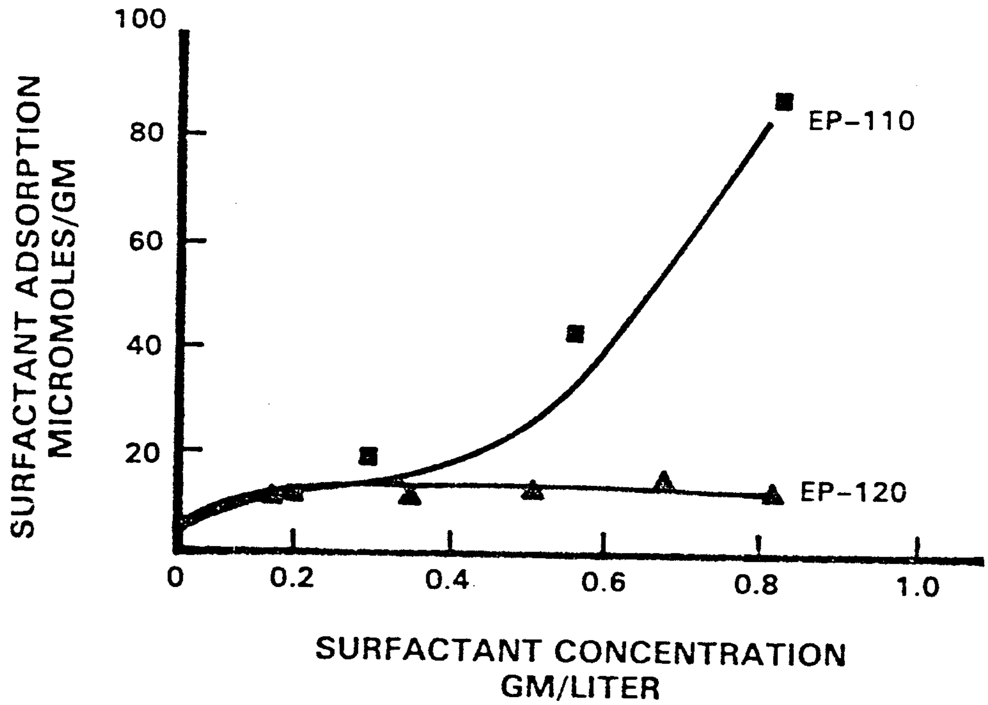


Fig. 4 Adsorption isotherms of Alipal EP-110 and Alipal EP-120 surfactants at the 85:15 VA/BA latex-water interface.

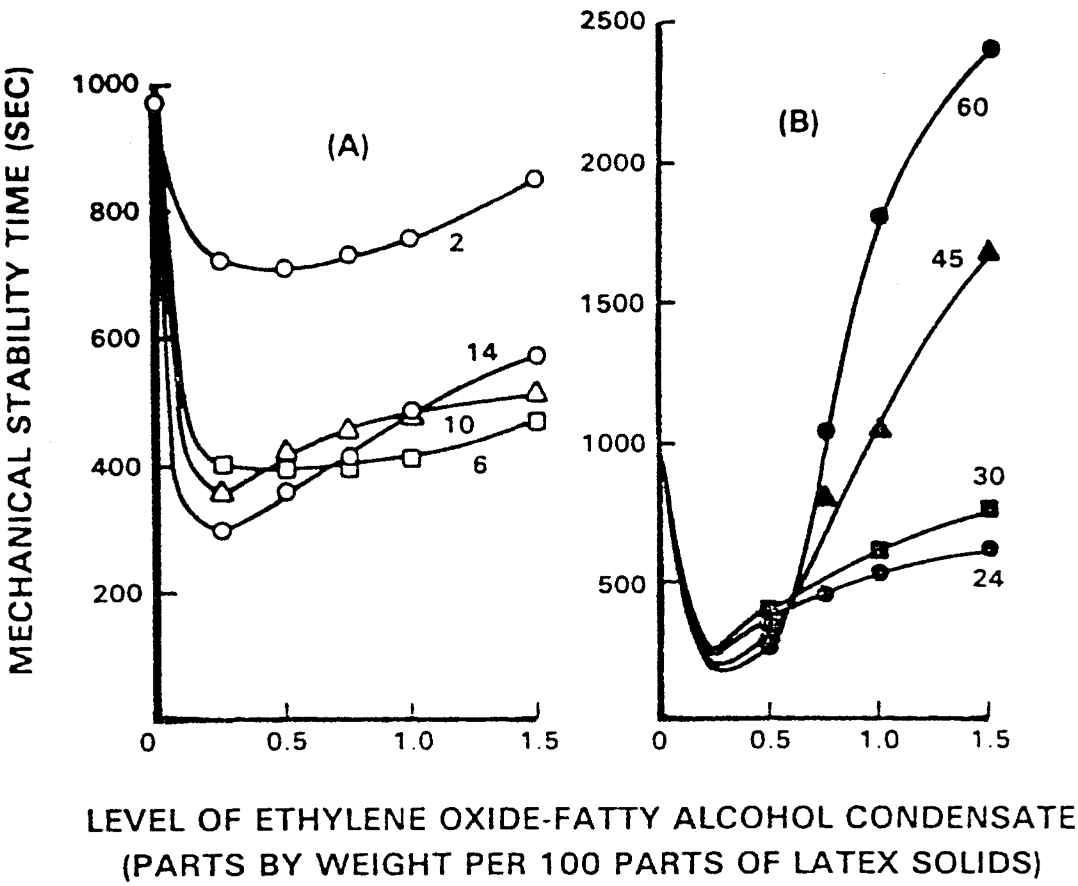


Fig. 5 Effect of added ethylene oxide/fatty alcohol condensates on mechanical stability of natural rubber latex. Levels of condensate are expressed in parts by weight. Numbers appended to curves indicate overall ethylene oxide/fatty alcohol mole ratio in comdensate.

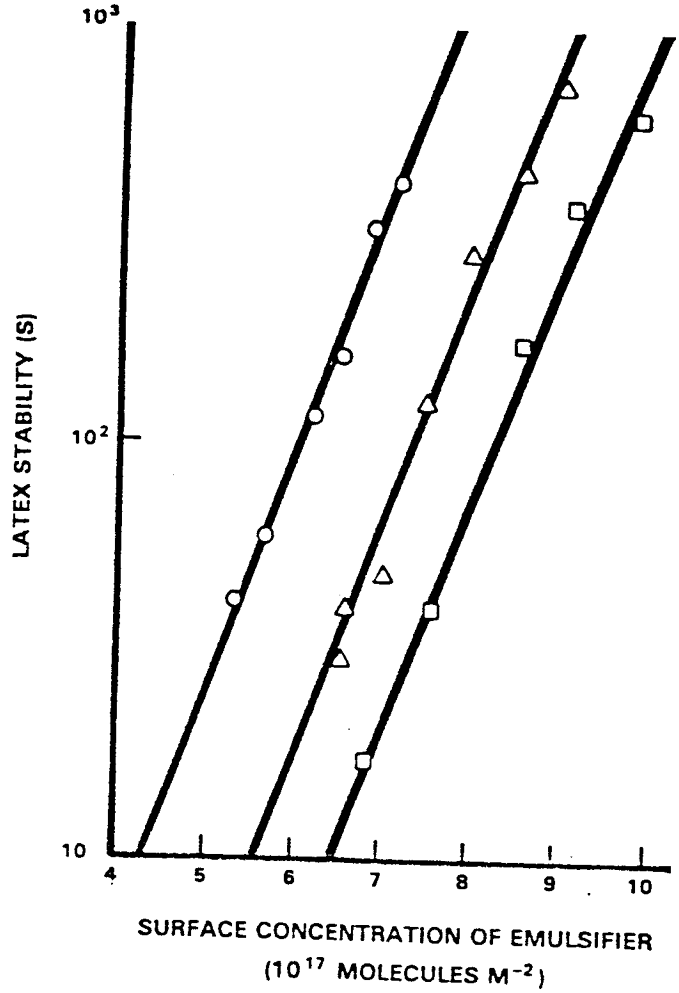
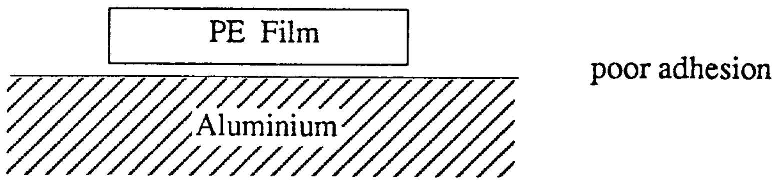


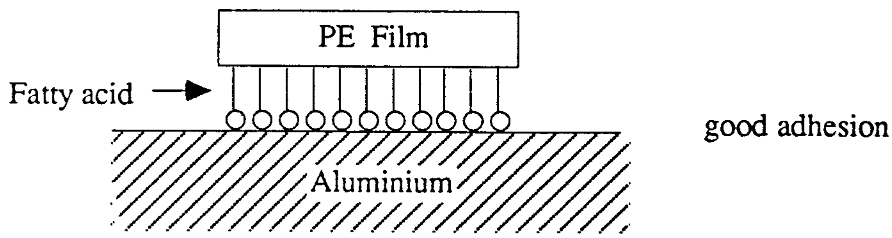
Fig. 6 Mechanical stability of 45 % (w/w) PVC lattices as a function of particle size and emulsifier level. Latex particle diameters : form left to right, 123 nm, 202 nm, 283 nm.

2-3. Adhesion

Surfactant - Surface modifier

Polymer - Substrate, Coating material





Surface Energy of Aluminium

γs = 64.3 dynes/cm

γds = 28.8 dynes/cm

γps = 35.5 dynes/cm

Surface Energy of PE

γs = 32.82 dynes/cm

γds = 32.10 dynes/cm

γps = 0.72 dynes/cm

2-4. Filtration

Surfactant - Surface modifier

Polymer - Membrane filter

TABLE 1. Influence of Tween 80 concentration on elution of poliovirus type 1 adsorbed to membrane filters in the presence of 1.0 M NaCl at pH 4

% Tween 80	% of adsorbed virus eluted by :			
	Primary eluent		3% beef extract, pH 9	
	Mean	SD	Mean	SD
0[a]	0	0	87	20
0.001	8	7	101	5
0.005	91	7	13	4
0.01	93	7	7	5
0.05	99	4	4	2
0.1	104	7	3	2

[a]All solutions contained 1.0 M NaCl buffered with 0.05 M KHP adjusted to pH4

2-5. Enhance Oil Recovery

Surfactant - Low interfacial tension generator

Polymer - Mobility buffer

$$N_{ca} = \eta v / \gamma \phi$$

N_{ca} = Capillary number

η = Viscosity of the displacing fluid

v = Velocity of the displacing fluid

γ = Interfacial tension

ϕ = Porosity of the porous medium

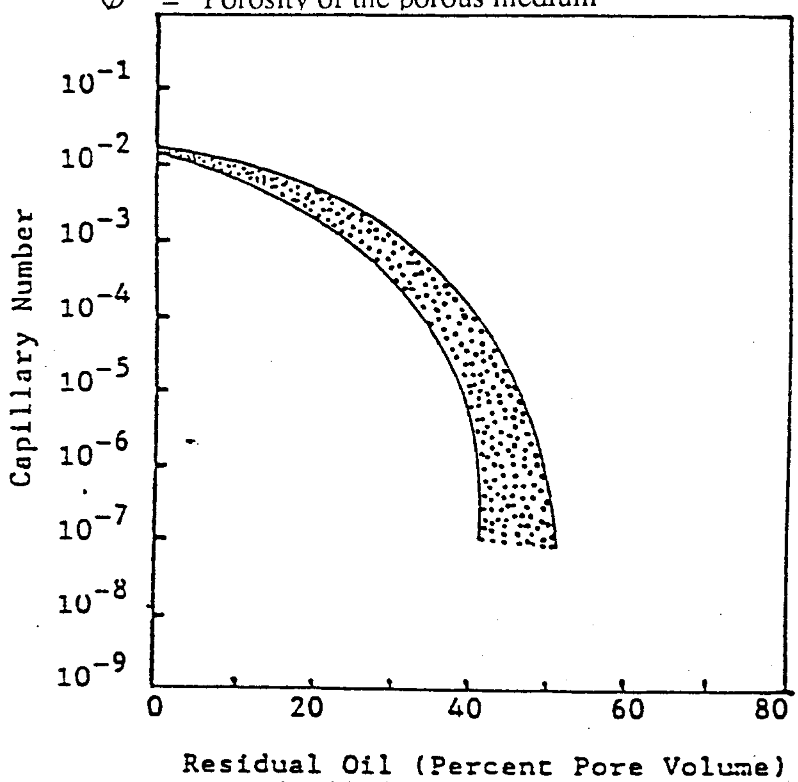


Fig. 7 Dependence of residual oil saturation on capillary number.

				Tertiary Oil Recovery
2500 ppm Polymer Solution with 0.02% TRS 10-80	Brine (1.0%)	Oil (n-hexane)	Brine (1.0%)	75 %

Modified Polymer Flooding with a Small Amount of Surfactant

2500 ppm Polymer Solution	Brine (1.0%)	Oil (n-hexane)	Brine (1.0%)	33 %

Polymer Flooding

0.02 % TRS10-80 Solution	Brine (1.0%)	Oil (n-hexane)	Brine (1.0%)	15 %

Flooding with Surfactant Solution

Fig. 8 A schematic presentation of oil displacement experiments.

2-6. Mineral Processing

Surfactant - Collector (imparting hydrophobicity selectively, to the desired particles), Frothers

Polymer - Depressant, Activator

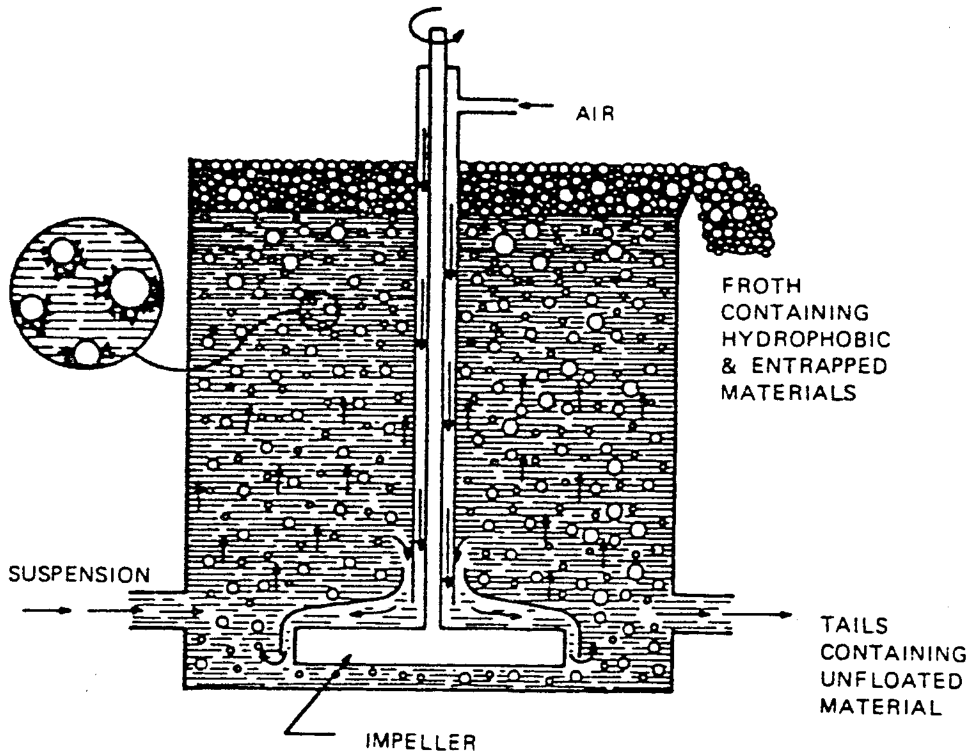


Fig. 9 Schematic representation of a flotation cell.

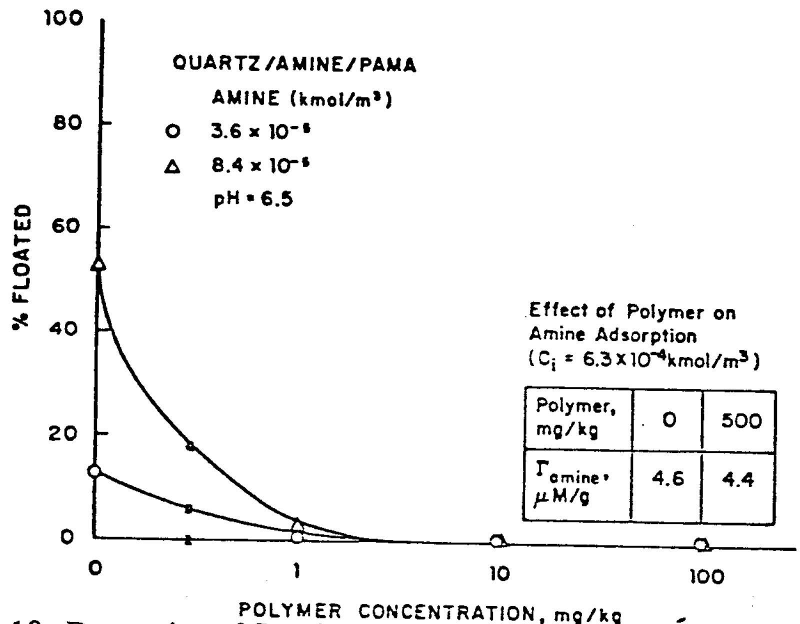


Fig. 10 Depression of flotation of quartz using dodecylamine by the cationic polymer PAMA at natural pH. Adsorption of sulfonate in the presence and absence of polymer is shown in the inset.

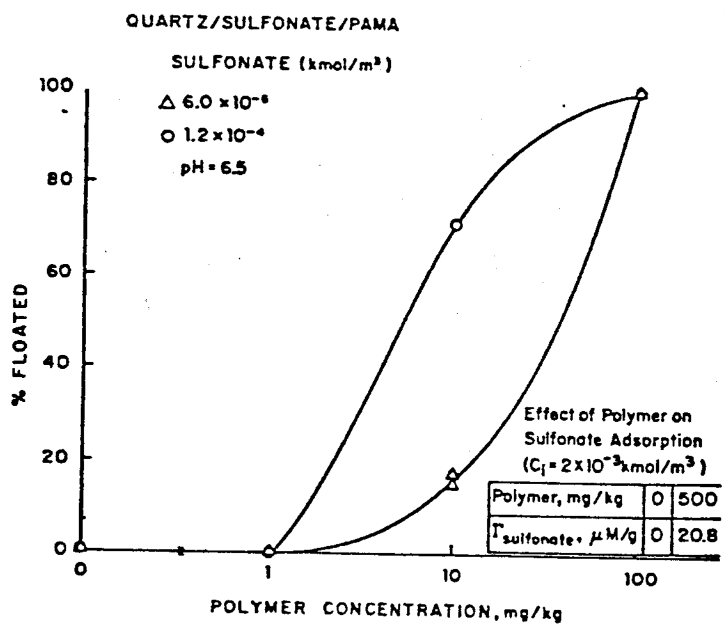


Fig. 11 Activation of flotation of quartz dodecylsulfonate by the cationic polymer PAMA at natural pH. Adsorption of sulfonate in the presence and absence of polymer is shown in the inset.

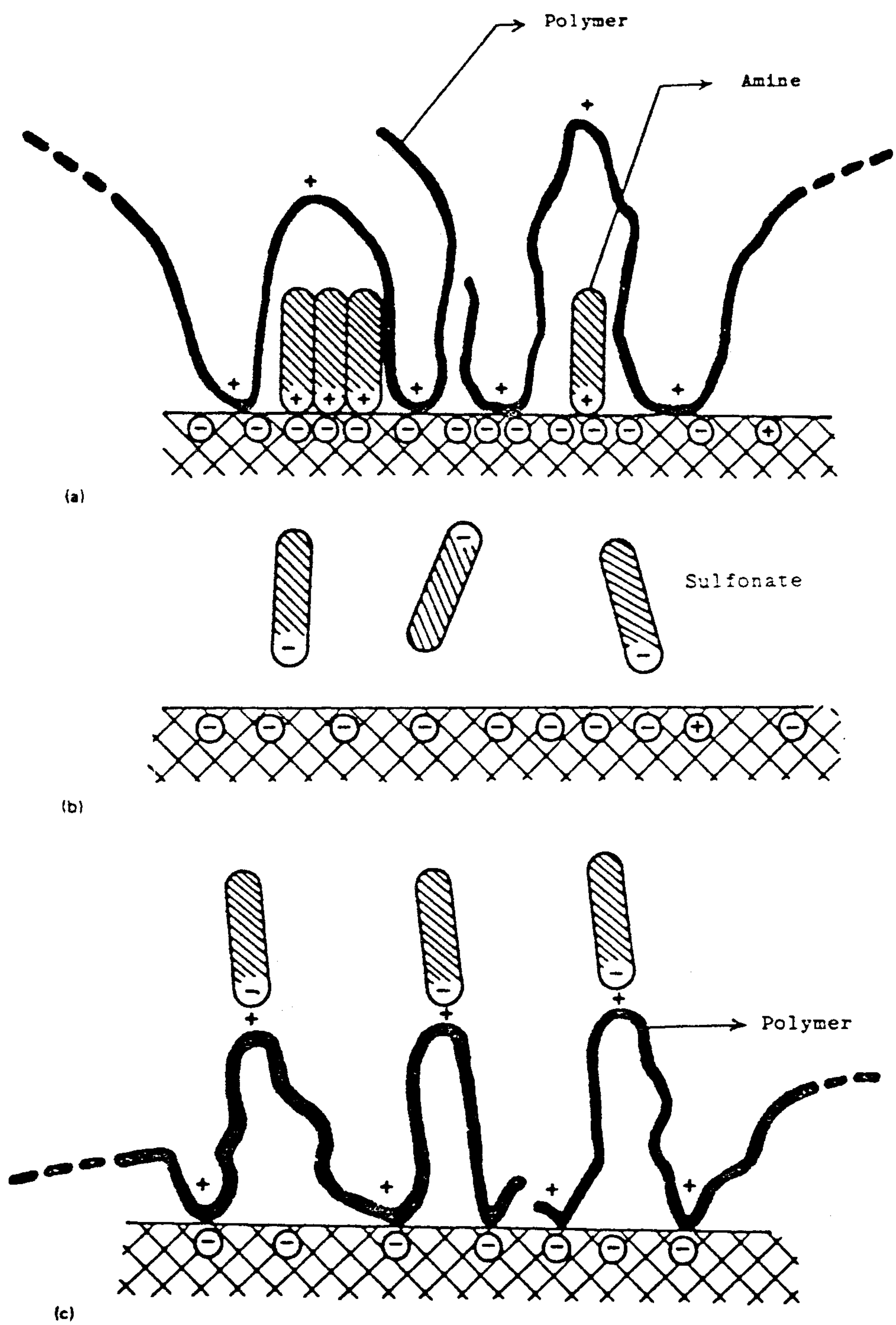


Fig. 12

3. 계면활성제와 고분자 상호작용의 근원

앞에서 본것과 같은 계면활성제와 고분자 상호작용에 의한 특성변화에 대한 연구는 1950년대 중반부터 현재까지 계속해서 이루어졌고 많은연구 진전이 있었다. 이러한 상호작용은 크게 세가지 유형으로 나눌수가 있다:

1) Ionic surfactant-nonionic polymer interaction (or Nonionic surfactant - ionic polymer interaction),
2) Oppositely charged surfactant-polymer interaction,
3) Simiarly charged surfactant-polymer interaction.

3-1. Ionic surfactant-nonionic polymer interaction

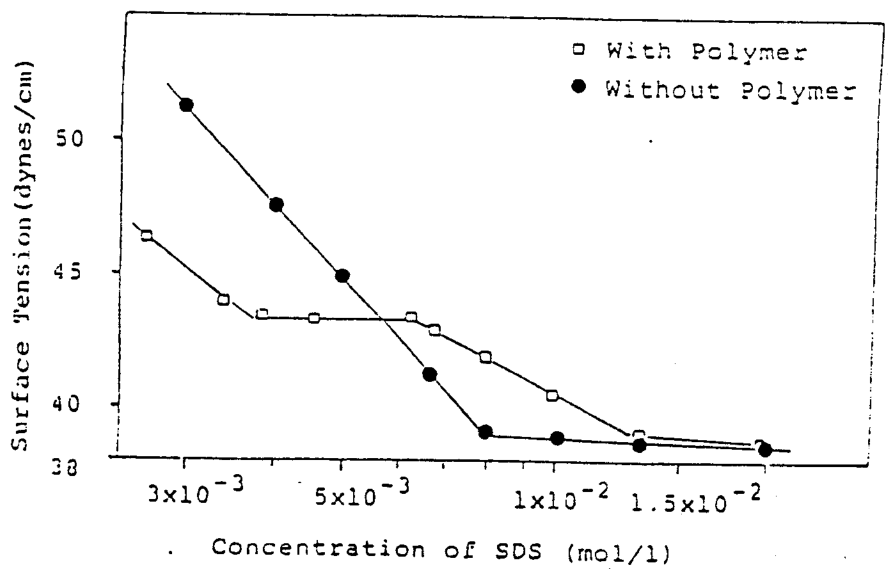
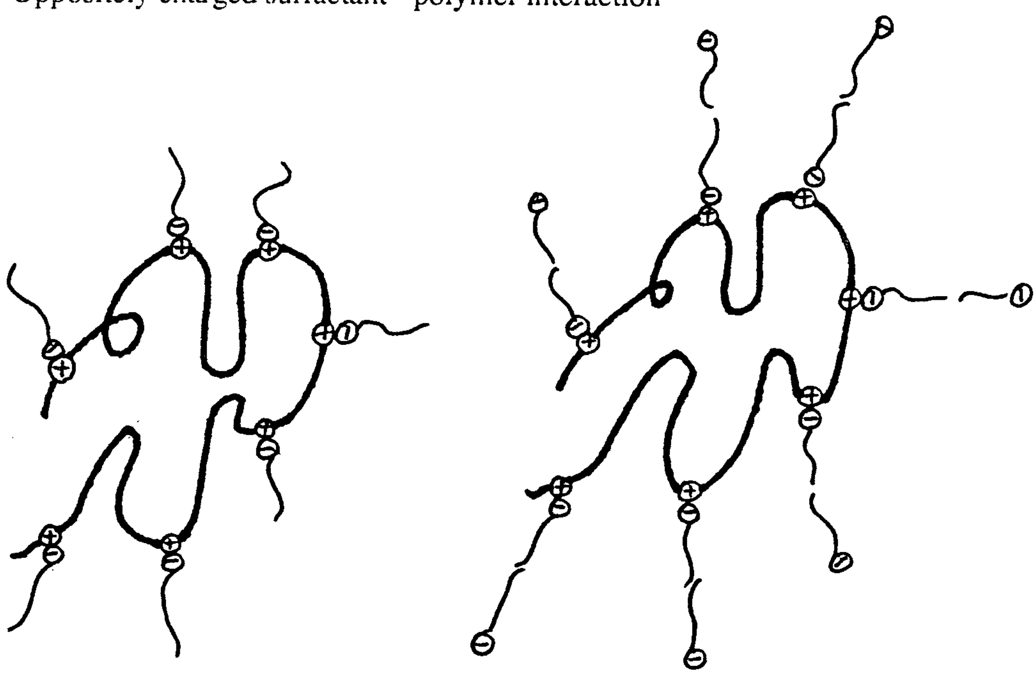


Fig. 13 Surface tension depending on SDS concentration with and without polymer (Polyethylene glycol, 0.02 M)

- Nonionic polymer 는 Surfactant micelle 안에 용해된다.
- Surfactant 의 Hydrophobic part 가 Polymer 에 흡착되고 Hydrophilic part 가 물분자쪽으로 배열됨으로써 계면활성제-고분자의 Complex 가 Polyelectrolyte 처럼 작용.
- 고분자가 계면활성제의 Micelle 를 위한 Nucleating agent 로 작용함으로써 고분자 부재시보다 적고 Dimer 보다는 큰 계면활성제의 Cluster 로써 계면활성제를 안정화시킨다. - 혼합형의 계면활성제-고분자 Micelle 형성.

3-2. Oppositely charged surfactant - polymer interaction



o Head to head 상호작용에 의한 Complex 형성 (Turbidity 증가및 침전)

o Tail to tail 상호작용에 의한 Polyanion 형성 (re-solubilization)

3-3. Similarly charged surfactant-polymer interaction

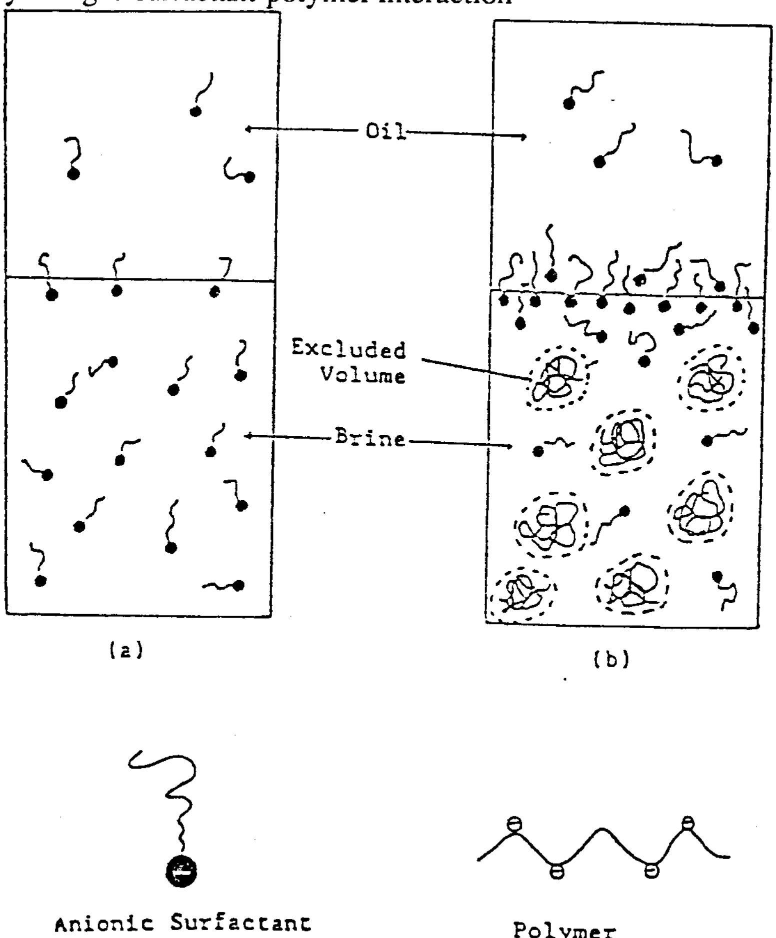


Fig. 14 A schmatic presentation of the excluded volume effect of polymer on surfactant solution : (a) in the absence of polymer ; (b) in the presence of polymer

o Polymer 의 Excluded volumn effect 에 의한 Surfactant 의 농도 증가 효과

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