Surface-active solutes
“Surface-active agents”
“Surfactants”

Lecture 2
Etymology

<table>
<thead>
<tr>
<th>English</th>
<th>Greek</th>
<th>Latin</th>
</tr>
</thead>
<tbody>
<tr>
<td>oil</td>
<td>lipo-</td>
<td>oleo-</td>
</tr>
<tr>
<td>water</td>
<td>hydro-</td>
<td>aqua-</td>
</tr>
<tr>
<td>solvent</td>
<td>lyo-</td>
<td>solvo-</td>
</tr>
<tr>
<td>both</td>
<td>amphi-</td>
<td></td>
</tr>
<tr>
<td>flow</td>
<td>rheo-</td>
<td></td>
</tr>
<tr>
<td>affinity</td>
<td>-philic</td>
<td></td>
</tr>
<tr>
<td>lack-of-affinity</td>
<td>-phobic</td>
<td></td>
</tr>
<tr>
<td>nature</td>
<td>-pathic</td>
<td></td>
</tr>
<tr>
<td>science</td>
<td>-logy</td>
<td></td>
</tr>
</tbody>
</table>

English meanings are not literal translations, but interpretations of how the words are understood in this branch of science.

Technical terms (neologisms) are formed by combinations of these words, such as the following adjectives:

- **amphipathic** = combining both natures (oil and water understood)
- **amphiphilic** = with affinity for both (oil and water understood)
- **hydrophilic** = with affinity for water
- **lipophilic** = with affinity for oil
- **lyophilic** = with affinity for the solvent
- **lyophobic** = lack of affinity for the solvent
Classification of surfactants

Classified by the hydrophilic group:

• Anionic
  • Carboxylic
  • Sulfuric esters
  • Alkane sulfonic acids
  • Alkyl aromatic sulfonic acids
  • Others: Phosphates, phosphoric acids, …
• Cationic
  • Amine salts (primary, secondary, and tertiary)
  • Quaternary salts
• Nonionic
  • Ethers
  • Esters
  • Amides
• Amphoteric
Adsorption lowers the energy

At the air/liquid interface:

Lowers surface tension.

At the solid/liquid interface:

Stabilizes dispersions.
Adsorption of surfactant decreases the work needed for:

- Spreading and wetting.
- Emulsification and dispersion.
Ionic surfactants produce charged surfaces.

Nonionic surfactants produce protective coatings.
Adsorption at water and organic surfaces

**Air**

**Water**

**Oil**

**Water**

Strong adsorption, substantial lowering of surface tension.

Little adsorption, little lowering of surface tension.

Strong adsorption, substantial lowering of interfacial tension.
Lowering of surface tensions with surfactants

The surface tension drops but reaches a limit:

![Graph showing the lowering of surface tensions with surfactants. The graph plots surface tension (mJ/m²) against concentration of surfactant. There are two lines: one for Sucrose, which remains constant at ~0.05%, and one for Soap, which decreases from 72 mJ/m² to 35 mJ/m² as the concentration increases.](image-url)
Surfactants can create their own “surface”
- Micelles

Adsorption and micellization are competing processes.
Physical properties of surfactant solutions

The critical micelle concentration.
Surfactant “phases”

These terms come from the old soap makers literature.

Different liquid crystal phases “look” different.
Phase diagrams can be constructed

(Consider taking the ACS short course on emulsions for much more information.)
A widely used additive that combines both high molecular weight and basic function is polyisobutylene succinimide, marketed as OLOA 1200 by the Chevron Chemical Co. It provides low-temperature sludge and varnish control in gasoline engines and effective dispersancy in diesel engine, natural gas engine, and marine cylinder lubricants.
Oil “electrolytes” form inverse micelles

The micelle core is highly polar.

The diameters are 10’s of nanometers.

Single polymer molecules may be sufficient.
Linear conductivity of nonpolar electrolytes?

The conductivity of weak electrolytes should vary with the square root of concentration.

\[ \lambda = 58.6 \times \text{concentration} \]
Creation of charged micelles:

Micelles exchange ions with each other and with surfaces.

The equilibrium is a dynamic balance.
Adsorption is a slow process

The adsorption of surfactants is much! slower than is estimated by molecular diffusion.

Time is required for molecules to rearrange at the solid/liquid interface.
Adsorption of ionic surfactants

At the air/liquid interface:

Lowers surface tension.

At the solid/liquid interface:

Charges the particle and stabilizes the dispersion.
Model of a charged particle in suspension

The loosely held countercharges form the “electrical double layer.”

The electric potential between the particle surface and the liquid at infinite distance is called the zeta potential.

The description of the charged particle contains the zeta potential and a measure of how “thick” is the electrical double layer.
Electric charge on carbon black particles in oil

![Graph showing the electric charge on carbon black particles in oil. The graph plots Zeta Potential (mV) on the y-axis against OLOA 1200 in dodecane (% weight) on the x-axis. The data points are shown as black dots, and a smooth curve connects them.]
Zeta potential and adsorption

OLOA 1200 on Carbon black (2% vol) in Isopar

Zeta Potential (mV)

Surface coverage

Surface coverage
Charging of particles in nonpolar liquids
Nonpolar, electrocratic applications:

- Carbon in engine oils:
  
- Liquid immersion printing:
  
- Electrophoretic displays:

http://www.autoshop-online.com/auto101/eng1.html
## Commonly used surfactants

<table>
<thead>
<tr>
<th>Chemical Class</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Anionic</td>
<td></td>
</tr>
<tr>
<td>Alkyaryl sulfonates</td>
<td>Detergents, emulsifiers</td>
</tr>
<tr>
<td>Fatty alcohol sulfates</td>
<td>Detergents, emulsifiers</td>
</tr>
<tr>
<td>Lignosulfonates</td>
<td>Dispersants</td>
</tr>
<tr>
<td>Alkali soaps of tall oil</td>
<td>Anionic emulsifiers</td>
</tr>
<tr>
<td>Alkali soaps of rosin</td>
<td>Anionic emulsifiers</td>
</tr>
<tr>
<td>Dialkylsulfosuccinates</td>
<td>Wetting agents</td>
</tr>
<tr>
<td>2. Cationic</td>
<td></td>
</tr>
<tr>
<td>Alkyltrimethylammonium chloride</td>
<td>Emulsifier, corrosion, inhibitor, textile softener, antibacterial agent, detergent</td>
</tr>
<tr>
<td>3. Nonionic</td>
<td></td>
</tr>
<tr>
<td>Alkanolamides</td>
<td>Detergents, foam stabilizers</td>
</tr>
<tr>
<td>Glyceryl esters</td>
<td>Emulsifiers</td>
</tr>
<tr>
<td>Ethylene-oxide condensates of alkylphenols</td>
<td>Emulsifiers</td>
</tr>
<tr>
<td>Ethoxylated alkylphenols</td>
<td>Detergents, wetting agents, emulsifiers, dispersants</td>
</tr>
<tr>
<td>Ethoxylated fatty esters</td>
<td>Food emulsifiers (oil in water)</td>
</tr>
<tr>
<td>Fatty esters</td>
<td>Food emulsifiers (water in oil)</td>
</tr>
<tr>
<td>Polyalkylsuccinimides</td>
<td>Oil-soluble dispersants</td>
</tr>
<tr>
<td>Lecithins</td>
<td>Oil-soluble dispersants</td>
</tr>
<tr>
<td>Metal soaps</td>
<td>Oil-soluble dispersants</td>
</tr>
</tbody>
</table>
Large volume surfactants

- Fatty alcohols and alkylphenol ethoxylates:

\[
\begin{align*}
R\text{--OH} & \quad R\text{--OH} \\
& \quad \underset{\text{(OCH}_2\text{CH}_2\text{)}_n\text{OH}}{\text{--}}
\end{align*}
\]

- Alkanolamides:

- Alkylbenzene sulphonates

- Fatty alcohol and fatty alcohol ether sulphates:

\[
\begin{align*}
R\text{--OSO}_3\text{Na}
\end{align*}
\]
Surfactant structure

Structure affects adsorption, stability, solubility, and temperature dependence, etc.

Effect of structure on adsorption and micellization

The linear molecule is more effective at lowering interfacial tension at low concentrations, but forms micelles easily.

The branched molecule is not as effective at lowering interfacial tension, but does not form micelles so readily and therefore gets to a higher concentration in solution.
Bancroft’s Rule

“The emulsifier stabilizes the emulsion type where the continuous phase is the medium in which it is most soluble.”

A hydrophilic solute in an O/W emulsion.  
A hydrophilic solute in a W/O emulsion.

The long tail on the surfactant is to represent the longer range interaction of a “hydrophilic” molecule through water.
The HLB Schema

Variation of type and amount of residual emulsion with HLB number of emulsifier.

Optimum for O/W

Emulsion breaker

10

Optimum for W/O

Volume and type of emulsion

O/W

W/O

HLB

Colloidal Dispersions © 2005
Surface Active Solutes
## HLB Scale

<table>
<thead>
<tr>
<th>Lipophilic End of Scale</th>
<th>Hydrophilic end of scale</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stearane</strong></td>
<td><strong>Sucrose</strong></td>
</tr>
<tr>
<td>Soluble in oil;</td>
<td>Insoluble in oil;</td>
</tr>
<tr>
<td>insoluble in water</td>
<td>soluble in water</td>
</tr>
<tr>
<td>Nonspreading on water</td>
<td>Increases surface</td>
</tr>
<tr>
<td>substrate</td>
<td>tension in aqueous solution</td>
</tr>
</tbody>
</table>

| **Steric Acid**         | **Sodium Stearate**      |
| Soluble in oil;         | Soluble in oil;          |
| insoluble in water      | and in hot water         |
| Spreads on water        | Reduces surface tension  |
| substrate               | of aqueous solutions     |

| **Sodium Laurate**      | **Sodium Sulfate**       |
| Slightly oil-soluble;   | Insoluble in oil;        |
| soluble in water        | soluble in water         |
| Reduces interfacial     | Does not affect the      |
| tension at oil–water    | surface tension in       |
| interface               | aqueous solution         |

<table>
<thead>
<tr>
<th><strong>Stabilizes water in oil emulsions</strong></th>
<th><strong>Stabilizes either type of emulsion</strong></th>
<th><strong>Stabilizes oil in water emulsions</strong></th>
<th><strong>Does not stabilize emulsions</strong></th>
<th><strong>Decreases the stability of emulsions</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HLB Scale</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Phase inversion temperature

30°C 40°C 50°C 60°C 70°C 75°C 80°C 90°C 100°C

Water Emulsion Oil

HLB and the Phase Inversion Temperature

![Graph showing the relationship between HLB number (at 25°C) and Phase Inversion Temperature (°C). The graph includes two sets of data points: Cyclohexane/Water and Water/Cyclohexane.](image-url)
Particles as emulsion stabilizers

Almost all particles are only partially wetted by either phase.

When particles are “adsorbed” at the surface, they are hard to remove – the emulsion stability is high.

Crude oil is a W/O emulsion and is old!!
Polymer Adsorption

Lost:
- polymer - solvent
- solvent - solid

Gained:
- polymer – solid
- solvent - solvent
Drago E and C Parameters for a Variety of Molecular Bases

<table>
<thead>
<tr>
<th>Bases</th>
<th>$C_b$</th>
<th>$E_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>13.09</td>
<td>2.39</td>
</tr>
<tr>
<td>Ammonia</td>
<td>7.08</td>
<td>2.78</td>
</tr>
<tr>
<td>Methylamine</td>
<td>11.41</td>
<td>2.66</td>
</tr>
<tr>
<td>Dimethylamine</td>
<td>17.85</td>
<td>2.33</td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>23.6</td>
<td>1.652</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>12.31</td>
<td>2.80</td>
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<tr>
<td>Diethylamine</td>
<td>18.06</td>
<td>1.771</td>
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<tr>
<td>Triethylamine</td>
<td>22.7</td>
<td>2.03</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>2.74</td>
<td>1.812</td>
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<tr>
<td>$p$-Dioxane</td>
<td>4.87</td>
<td>2.23</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>8.73</td>
<td>2.00</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>5.83</td>
<td>2.74</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>3.56</td>
<td>1.994</td>
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<tr>
<td>Methyl acetate</td>
<td>3.29</td>
<td>1.847</td>
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<tr>
<td>Acetone</td>
<td>4.76</td>
<td>2.018</td>
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<tr>
<td>Diethyl ether</td>
<td>6.65</td>
<td>1.969</td>
</tr>
<tr>
<td>Isopropyl ether</td>
<td>6.52</td>
<td>2.27</td>
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<tr>
<td>Benzene</td>
<td>1.452</td>
<td>1.002</td>
</tr>
<tr>
<td>$p$-Xylene</td>
<td>3.64</td>
<td>0.851</td>
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</table>
Drago E and E Parameters for a Variety of Molecular Acids

<table>
<thead>
<tr>
<th>Acids</th>
<th>$C_a$</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodine</td>
<td>2.05</td>
<td>2.05</td>
</tr>
<tr>
<td>Iodine monochloride</td>
<td>1.697</td>
<td>10.43</td>
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<tr>
<td>Thiophenol</td>
<td>0.405</td>
<td>2.02</td>
</tr>
<tr>
<td>$p$-tert-Butylphenol</td>
<td>0.791</td>
<td>8.30</td>
</tr>
<tr>
<td>$p$-Methylphenol</td>
<td>0.826</td>
<td>8.55</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.904</td>
<td>8.85</td>
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<tr>
<td>$p$-Chlorophenol</td>
<td>0.978</td>
<td>8.88</td>
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<tr>
<td>tert-Butyl alcohol</td>
<td>0.614</td>
<td>4.17</td>
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<tr>
<td>Trifluoroethanol</td>
<td>0.922</td>
<td>7.93</td>
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<tr>
<td>Pyrrole</td>
<td>0.603</td>
<td>5.19</td>
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<tr>
<td>Isocyanic acid</td>
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<td>6.58</td>
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<td>Sulfur dioxide</td>
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<td>1.88</td>
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<tr>
<td>Antimony pentachloride</td>
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<td>15.09</td>
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<td>3.40</td>
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<tr>
<td>Carbon tetrachloride</td>
<td>0.00</td>
<td>0.00</td>
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</table>
Adsorption of PMMA on Silica

![Graph showing adsorption of PMMA on Silica]
<table>
<thead>
<tr>
<th>Acidic Solvents</th>
<th>AN kcal mol⁻¹</th>
<th>Basic Solvents</th>
<th>DN kcal mol⁻¹</th>
<th>Basic Solvents</th>
<th>DN kcal mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane (reference solvent)</td>
<td>0</td>
<td>1,2-Dichloroethane</td>
<td>0.1</td>
<td>Tetrahydrofuran</td>
<td>20.0</td>
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<tr>
<td>Diethyl ether</td>
<td>3.9</td>
<td>Benzene</td>
<td>0.1</td>
<td>Diphenylphosphonic chloride</td>
<td>22.4</td>
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<tr>
<td>Tetrachloroethane</td>
<td>8.0</td>
<td>Sulfuryl chloride</td>
<td>0.1</td>
<td>Tributyl phosphate</td>
<td>23.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>8.2</td>
<td>Thiethyl chloride</td>
<td>0.4</td>
<td>Tributyl phosphate</td>
<td>23.7</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>8.6</td>
<td>Acetyl chloride</td>
<td>0.7</td>
<td>Dimethyl ether</td>
<td></td>
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<td>Dihyde</td>
<td>9.9</td>
<td>Tetrachloroethane</td>
<td>0.8</td>
<td>Dimethylformamide</td>
<td>26.6</td>
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<td>Glyme</td>
<td>10.2</td>
<td>Benzyl fluoride</td>
<td>2.3</td>
<td>N-Methyl-2-cyanoacetic acid</td>
<td>27.1</td>
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<tr>
<td>DMSO</td>
<td>10.6</td>
<td>Benzyl chloride</td>
<td>2.3</td>
<td>N-Methyl-2-pyrrolidinone</td>
<td>27.3</td>
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<tr>
<td>Acetone</td>
<td>10.8</td>
<td>Nitromethane</td>
<td>2.7</td>
<td>N,N-Dimethylformamide</td>
<td>27.8</td>
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<tr>
<td>N-Methyl-2-pyrrolidinone</td>
<td>13.3</td>
<td>Nitrobenzene</td>
<td>4.4</td>
<td>N,N-Dimethylacetamide</td>
<td>30.9</td>
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<td>DMA</td>
<td>15.6</td>
<td>Acetic anhydride</td>
<td>10.5</td>
<td>N,N-Dimethylacetamide</td>
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<td>Pyridine</td>
<td>15.7</td>
<td>Phosphorus oxychloride</td>
<td>11.7</td>
<td>Pyridine</td>
<td>33.1</td>
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<tr>
<td>Nitrobenzene</td>
<td>14.8</td>
<td>Benzimidazole</td>
<td>11.9</td>
<td>Hexamethylphosphoramide</td>
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<tr>
<td>Benzimidazole</td>
<td>15.5</td>
<td>Selenium oxychloride</td>
<td>12.2</td>
<td>Hydrazine</td>
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<td>Acetonitrile</td>
<td>14.1</td>
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<td>Dichloroethane carbonate</td>
<td>16.7</td>
<td>Sulfolene (tetramethylene sulfoxime)</td>
<td>14.8</td>
<td>Etylendiamine</td>
<td>55.5</td>
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<td>PDC</td>
<td>18.3</td>
<td>Dioxane</td>
<td>14.8</td>
<td>Isopropylamine</td>
<td>57.5</td>
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<td>CICCN</td>
<td>18.9</td>
<td>Propanol-1,2-carbonate</td>
<td>15.1</td>
<td>tert-Butylamine</td>
<td>57.5</td>
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<td>DMAD</td>
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<td>Ethylene sulfide</td>
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<td>Triethylamine</td>
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<tr>
<td>Nitromethane</td>
<td>20.5</td>
<td>Isobutyronitrile</td>
<td>15.4</td>
<td></td>
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<tr>
<td>Chloroform</td>
<td>23.1</td>
<td>Propionitrile</td>
<td>16.1</td>
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<td></td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>33.5</td>
<td>Isobutyronitrile</td>
<td>16.4</td>
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<tr>
<td>Ethyl alcohol</td>
<td>37.1</td>
<td>Phenylphosphonic difluoride</td>
<td>16.4</td>
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<td>Formamide</td>
<td>39.8</td>
<td>Methyl acetate</td>
<td>16.5</td>
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<tr>
<td>Methyl alcohol</td>
<td>41.3</td>
<td>n-Butyronitrile</td>
<td>16.6</td>
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<td>Acetic acid</td>
<td>52.9</td>
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<td>Water</td>
<td>54.8</td>
<td>Ethyl acetate</td>
<td>17.1</td>
<td></td>
<td></td>
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<tr>
<td>CF₃COOH</td>
<td>105.3</td>
<td>Water</td>
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<td>CH₃SO₂H</td>
<td>126.3</td>
<td>Phenylyphosphonic dichloride</td>
<td>18.5</td>
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<td></td>
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<tr>
<td>SMe₂, in DCE</td>
<td>100</td>
<td>Diethyl ether</td>
<td>19.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

W.B. Jensen
The Lewis Acid-Base Concepts: An Overview
Wiley-Interscience: NY, 1980
# Common Polymeric Stabilizers

<table>
<thead>
<tr>
<th>Anchor polymer</th>
<th>Stabilizing moieties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>Poly(oxyethylene)</td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td>Poly(vinyl alcohol)</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>Poly(acrylic acid)</td>
</tr>
<tr>
<td>Poly(acrylonitrile)</td>
<td>Poly(methacrylic acid)</td>
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## Nonaqueous dispersions

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Sources of surfactants
Surfactant Companies

1. Surfactant Producers
3M Corp.
Air Products And Chemicals, Inc.
Akzo Nobel Surfactants America
Albemarle Corp.
Arizona Chemical
BASF Corp.
BFGoodrich Personal Care
(Noene)
CK Witco (Crompton)
Clariant Corporation
The Cognis Group
Croda Inc.
DeForest Enterprises, Inc.
The Dow Chemical Co.
Dow Corning
DuPont
EAC Chemicals
Ethox Chemicals
Goldschmidt AG (Degussa)
Henkel KGaA (The Henkel Group)
Heterene Inc.
Huntsman Corp.
ICI in North America
Jeneil Biosurfactant Company
Lambent Technologies
Libra Chemicals Ltd
LidoChem, Inc.
Lonza Inc.
MacDermid, Inc.
McIntyre Group Ltd.
Montello Inc.
National Starch and Chemical Company
Nikko Chemicals
Novo Nordisk A/S
Petroferm, Inc.
PILOT Chemical Company
Procter & Gamble Chemicals
Rhodia
Rohm and Haas
Shell Chemical
Stepan Co.
Taiwan Surfactant Co.
Tomah Products, Inc.
Uniqema

2. Surfactant Distributors
Barton Solvents
The M.F. Cachat Company
Casey Chemicals
Dawn Chemical Corp.
New Life Chemical & Equipment
Norman, Fox & Co.
Novo Pacific Corp.
Schibley Chemical Company
Spectrum Laboratory Products, Inc.
Surfactants, Inc.
Thornley Company
Van Waters & Rogers (Vopak USA)

For this and other information, visit the Surfactants Virtual Library (http://www.surfactants.net/).
Dispersants

DISPERSING POWDERS IN LIQUIDS

RALPH D. NELSON, Jr.,
Consultant Engineering Services Division,
E.I. du Pont de Nemours & Co., Inc., Newark, Delaware, U.S.A.

ELSEVIER
**Typical Entries**

### Table C-7: Nonionic and Cationic Class Characteristics

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Colloidal Dispersions © 2005
## Typical Entry

### Span

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**Remarks:** Emulsifiers. Lipophilic surfactants, insoluble or dispersible in water but generally soluble in oils or organic solvents. Used as o/w emulsion stabilizers and thickeners. Used in the textile industry as fiber lubricants and softeners, used as oil additives for corrosion inhibition. Food emulsifiers.
Surface Active Solutes

Chemcyclopedia
Bibliography for Surfactants