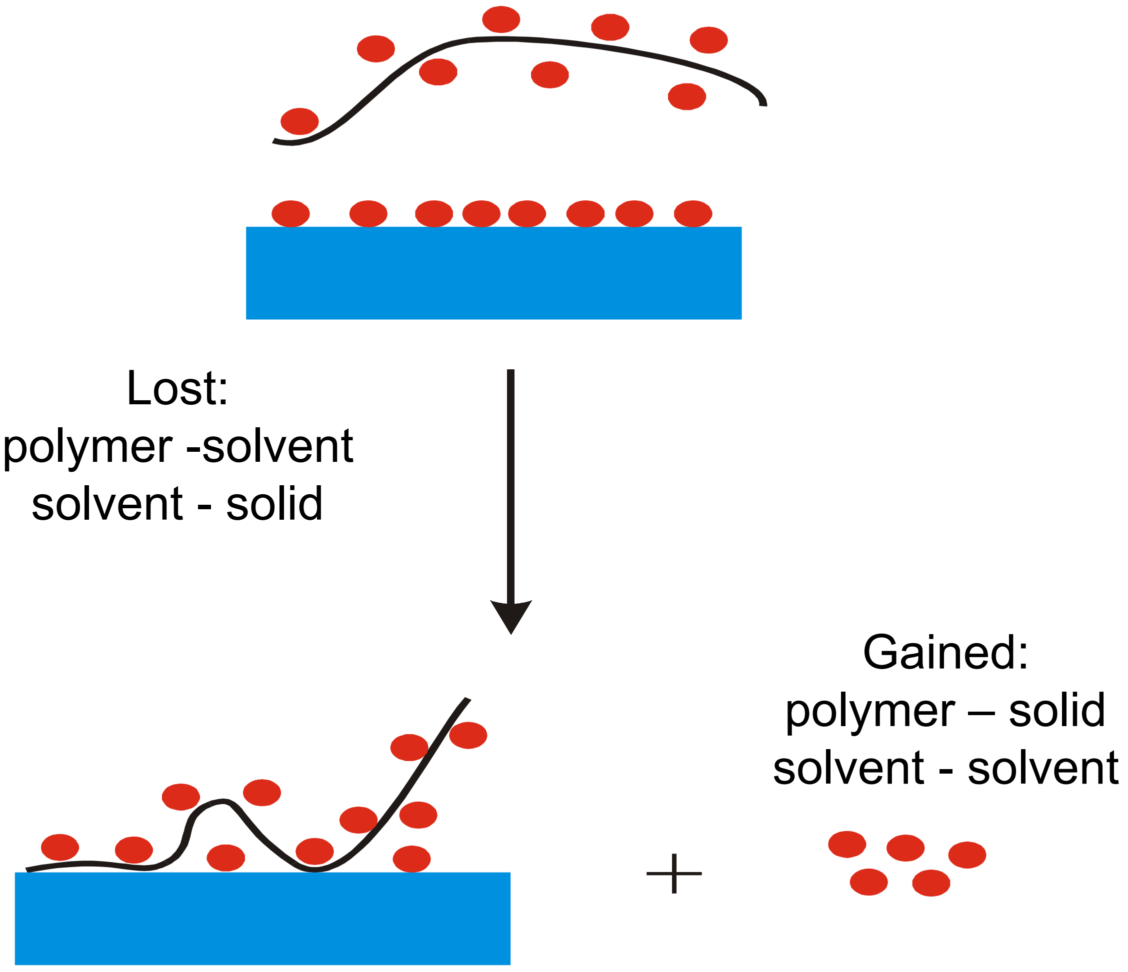
Polymer adsorption

Lecture 5

Adsorption of Polymers



Lost:
polymer -solvent
solvent - solid

Gained:
polymer – solid
solvent - solvent

Why are Polymers Adsorbed?

Consider the thermodynamics of adsorption:

$$\Delta G_a = \Delta H_a - T\Delta S_a$$

For adsorption to occur:

$$\Delta G_a < 0$$

Polymers loose conformational entropy on adsorption thus:

$$T\Delta S_a < 0$$

For adsorption to take place, ΔH_a must be large and negative.

$$\left|\Delta H_a\right| > \left|T\Delta S_a\right|$$

Acid-Base Interactions

The degree of acid-base interaction is measured by the enthalpy of adduct formation. Drago proposed the following relation:

$$-\Delta H_{ab} = E_a E_b + C_a C_b$$

where $-\Delta H_{ab}$ is the enthalpy of adduct formation per mole.

E_a and C_a are empirically determined parameters for the acid. E_b and C_b are empirically determined parameters for the base.

The magnitudes of the *E* parameters can be interpreted as measures of the susceptibility of the molecule for electrostatic interaction; the magnitudes of the *C* parameters can be interpreted as measures of the susceptibility for covalent interactions (similar to the concept of “hard” and “soft” acids and bases.)

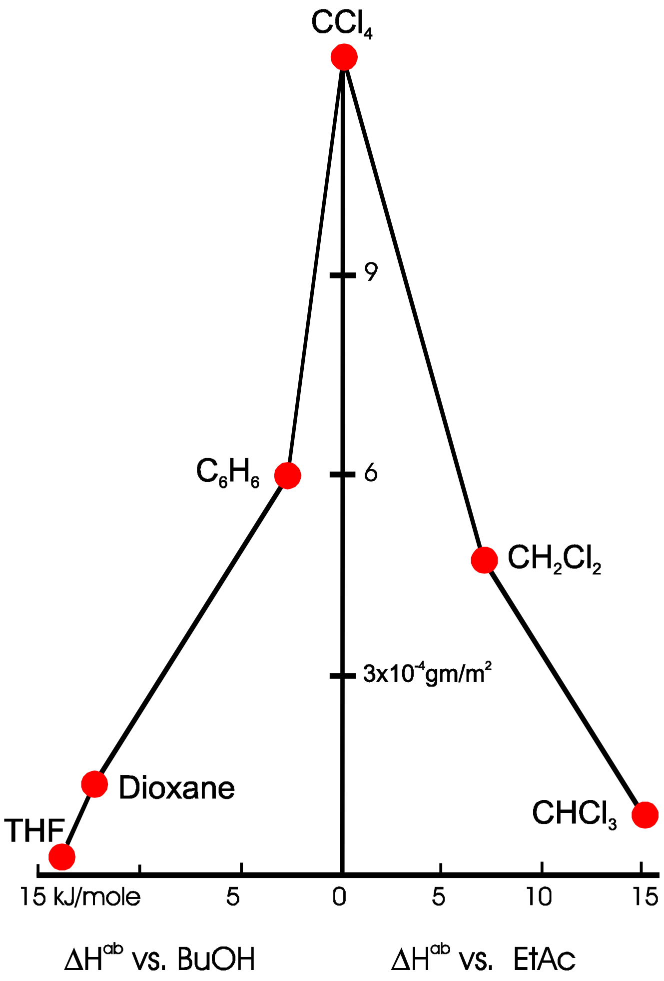
Drago E and C Parameters for a Variety of Molecular Bases

Bases	C_b	E_b
Pyridine	13.09	2.39
Ammonia	7.08	2.78
Methylamine	11.41	2.66
Dimethylamine	17.85	2.33
Trimethylamine	23.6	1.652
Ethylamine	12.31	2.80
Diethylamine	18.06	1.771
Triethylamine	22.7	2.03
Acetonitrile	2.74	1.812
p-Dioxane	4.87	2.23
Tetrahydrofuran	8.73	2.00
Dimethyl sulfoxide	5.83	2.74
Ethyl acetate	3.56	1.994
Methyl acetate	3.29	1.847
Acetone	4.76	2.018
Diethyl ether	6.65	1.969
Isopropyl ether	6.52	2.27
Benzene	1.452	1.002
p-Xylene	3.64	0.851

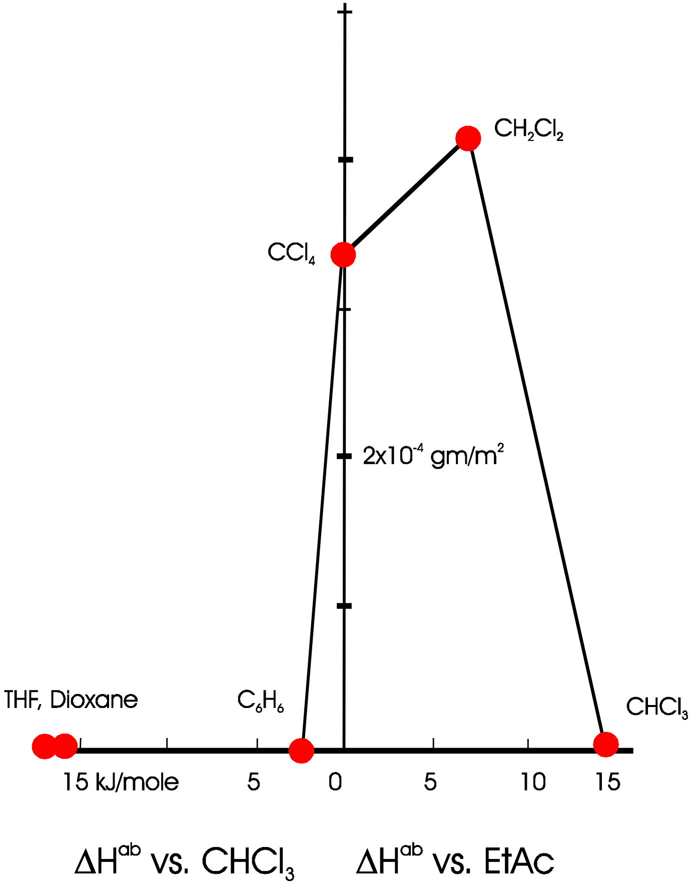
Drago E and E Parameters for a Variety of Molecular Acids

Acids	C_a	E_a
Iodine	2.05	2.05
Iodine monochloride	1.697	10.43
Thiophenol	0.405	2.02
p-*tert*-Butylphenol	0.791	8.30
p-Methylphenol	0.826	8.55
Phenol	0.904	8.85
p-Chlorophenol	0.978	8.88
tert-Butyl alcohol	0.614	4.17
Trifluoroethanol	0.922	7.93
Pyrrole	0.603	5.19
Isocyanic acid	0.528	6.58
Sulfur dioxide	1.652	1.88
Antimony pentachloride	10.49	15.09
Chloroform	0.325	6.18
Water	0.675	5.01
Methylene chloride	0.02	3.40
Carbon tetrachloride	0.00	0.00

Adsorption of PMMA on Silica



Adsorption of Cl-PVC on $CaCO_3$



The Acidity and Basicity of Solid Surfaces

Solid	E_a (kcal/mol)$^{1/2}$	C_a (kcal/mol)$^{1/2}$
Silica	4.2 ± 0.1	1.16 ± 0.02
Rutile	5.7 ± 0.2	1.02 ± 0.03
α-Ferric oxide	4.5 ± 1.1	0.8 ± 0.2

Techniques:

- Inverse gas chromatography
- Rates of liquid wicking
- Flow calorimetry

Gutmann Acceptor-Donor Numbers

(1) The Acceptor Number (AN) is a measure of the acid strength.

Measure the electron shift in the P-O bond of triethylene phosphorous oxide when it interacts with the material in 1,2 dichloroethane. The acceptor number of hexane is set to 0. The acceptor number of $SbCl_5$ is set to 100.

(2) The Donor Number (DN) is a measure of the base strength.

Characterize the base strength of a material by measuring the heat of reaction with $SbCl_5$ in 1,2 dichloroethane.

Gutmann Acceptor-Donor Numbers

Acidic Solvents	AN kcal mol^{-1}	Basic Solvents	DN kcal mol^{-1}	Basic Solvents	DN kcal mol^{-1}
Hexane (reference solvent)	0	1,2-Dichloroethane		Tetrahydrofuran	20.0
Diethyl ether	3.9	Benzene	0.1	Diphenylphosphonic chloride	22.4
Tetrahydrofuran	8.0	Sulfuryl chloride	0.1	Trimethyl phosphate	23.0
Benzene	8.2	Thionyl chloride	0.4	Tributyl phosphate	23.7
Carbon tetrachloride	8.6	Acetyl chloride	0.7	Dimethoxyethane	~24
Diglyme	9.9	Tetrachloroethylene carbonate	0.8	Dimethylformamide	26.6
Glyme	10.2	Benzoyl fluoride	2.3	*N*-Methyl-2-caprolactam	27.1
HMPA	10.6	Benzoyl chloride	2.3	*N*-Methyl-2-pyrrilidinone	27.3
Dioxane	10.8	Nitromethane	2.7	*N,N*-Dimethylacetamide	27.8
Acetone	12.5	Dichloroethylene carbonate	3.2	Dimethyl sulfoxide	29.8
N-Methyl-2-pyrrolidinone	13.3	Nitrobenzene	4.4	*N,N*-Diethylformamide	30.9
DMA	13.6	Acetic anhydride	10.5	*N,N*-Diethylacetamide	32.2
Pyridine	14.2	Phosphorous oxychloride	11.7	Pyridine	33.1
Nitrobenzene	14.8	Benzonitrile	11.9	Hexamethylphosphoramide	38.8
Benzonitrile	15.5	Selenium oxychloride	12.2	Hydrazine	44.0
DMF	16.0	Acetonitrile	14.1	Ethylenediamine	55.0
Dichloroethane carbonate	16.7	Sulfolane (tetramethylene sulfone)	14.8	Ethylamine	55.5
PDC	18.3	Dioxane	14.8	Isopropylamine	57.5
CH_3CN	18.9	Propanediol 1,2-carbonate	15.1	*tert*-Butylamine	57.5
DMSO	19.3	Benzyl cyanide	15.1	Ammonia	59.0
Methylene chloride	20.4	Ethylene sulfite	15.3	Triethylamine	61.0
Nitromethane	20.5	Isobutyronitrile	15.4		
Chloroform	23.1	Propionitrile	16.1		
Isopropyl alcohol	33.5	Ethylene carbonate	16.4		
Ethyl alcohol	37.1	Phenylphosphonic difluoride	16.4		
Formamide	39.8	Methyl acetate	16.5		
Methyl alcohol	41.3	n-Butyronitrile	16.6		
Acetic acid	52.9	Acetone	17.0		
Water	54.8	Ethyl acetate	17.1		
CF_3COOH	105.3	Water	18.0		
CH_3SO_3H	126.3	Phenylphosphonic dichloride	18.5		
$SbCl_5$ as ref. in DCE	100	Diethyl ether	19.2		

W.B. Jensen
The Lewis Acid-Base Concepts:
An Overview
Wiley-Interscience: NY; **1980**

Common Polymeric Stabilizers

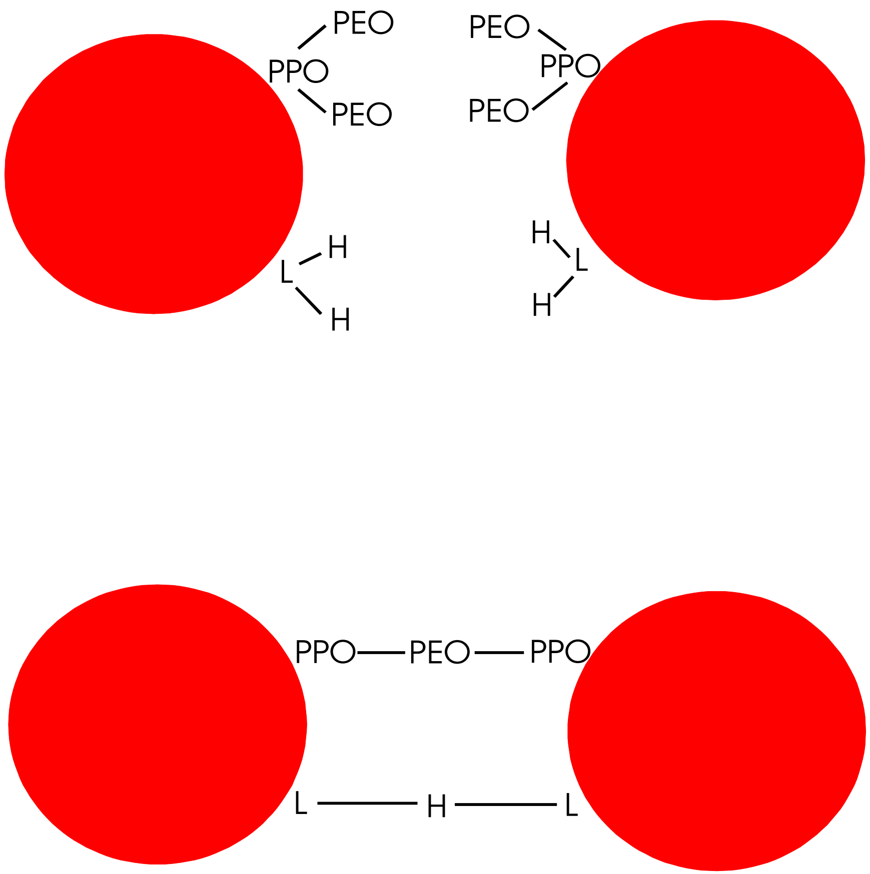
Aqueous dispersions

Anchor polymer	Stabilizing moieties
Polystyrene	Poly(oxyethylene)
Poly(vinyl acetate)	Poly(vinyl alcohol)
Poly(methyl methacrylate)	Poly(acrylic acid)
Poly(acrylonitrile)	Poly(methacrylic acid)
Poly(dimethylsiloxane)	Poly(acrylamide)
Poly(vinyl chloride)	Poly(vinyl pyrrolidone)
Poly(ethylene)	Poly(ethylene imine)
Poly(propylene)	Poly(vinyl methyl ether)
Poly(lauryl methacrylate)	Poly(4-vinylpyridine)

Nonaqueous dispersions

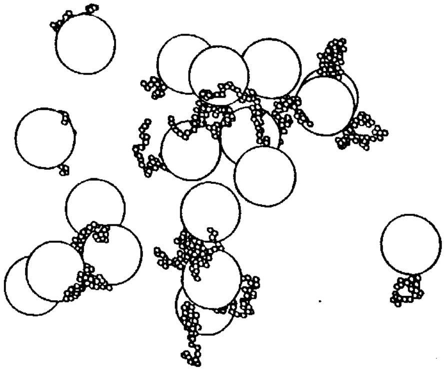
Anchor polymer	Stabilizing moieties
Poly(acrylonitrile)	Polystyrene
Poly(oxyethylene)	Poly(lauryl methacrylate)
Poly(ethylene)	Poly(12-hydroxystearic acid)
Poly(propylene)	Poly(dimethylsiloxane)
Poly(vinyl chloride)	Poly(isobutylene)
Poly(methyl methacrylate)	Cis-1,4-poly(isoprene)
Poly(acrylamide)	Poly(vinyl acetate)
	Poly(methyl methacrylate)
	Poly(vinyl methyl ether)

Polymers for Dispersing and for Flocculation



Polymer Flocculants

Add a polymer that will "bridge" between two particles:



If a polymer is adsorbed and if the particles are not completely covered, then the polymer acts as a flocculant!

The efficiency of flocculation goes roughly as $\approx \Theta(1-\Theta)$

If the coverage is large, the polymer acts as a stabilizer.