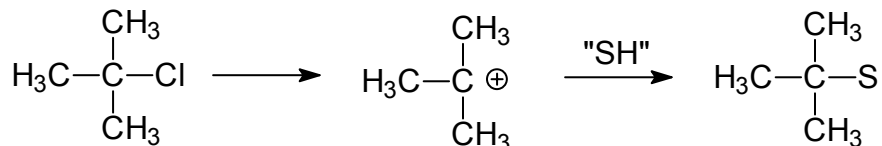Other LFER's

(i)   Solvent polarity

It has been known for many years that S_N1 reactions take place more rapidly in the more polar solvents. Grunwald and Winstein suggested that a scale of "solvent ionizing power" could be established by measuring the rate of solvolysis of t-butyl chloride in various solvent media.


(where "SH" = solvent)

Grunwald-Winstein equation:

$$\log\left(\frac{k}{k_0}\right) = mY \quad \text{original version}$$

$$\log\left(\frac{k}{k_0}\right) = mY + lN \quad \text{more recent extension}$$

where k_0 refers to the reaction in 80% EtOH:H_2O and k to the solvent in question. The parameter m is defined as 1.00 for the t-butyl chloride solvolysis, and measures the sensitivity of various reactions (e.g. solvolysis of other substrates) to change in solvent.

Solvent	Y
(100%)EtOH	-2.033
90% EtOH	-0.747
80% EtOH	(0.00) (defined)
50% EtOH	1.655
30% EtOH	2.721
Water	3.493
MeOH	-1.090
i-PrOH	-2.73
t-BuOH	-3.26
HCOOH	2.054
CH_3COOH	-1.639
$HCONH_2$	0.604

When it was realized that there was some solvent assistance to the solvolysis of t-butyl chloride, a new scale was constructed based on rates of solvolysis of 1-adamantyl tosylate; this led to Y_{OTs} values.
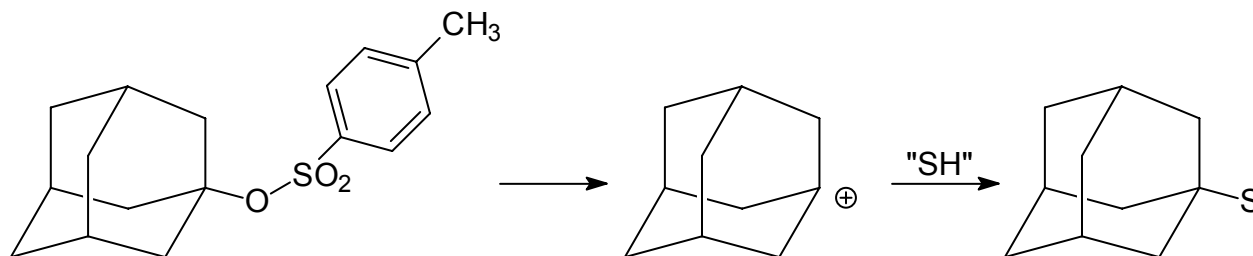
To apply the Grunwald-Winstein approach to a reaction:
   plot log (k/k_0) vs Y
   If the correlation is at least approximately linear, determine 'm'
   If m is "small" (i.e. 0.0 to 0.2) the reaction probably does not involve ionization
   If m is "large" (i.e. 0.9 to 1.2) the reaction probably does involve ionization.

There are problems with this approach
   the substrate of interest may not dissolve in all the solvents of interest to an extent which permits kinetics
   the reaction may be too slow (effectively may not happen) in some solvents of interest
   there are limits on generality: as the RX gets more different from tBu-Cl or Ad-OTs one sees less parallels in behavior.

Other parameters have been proposed as measures of solvent polarity. Two are based on spectroscopic measurements.
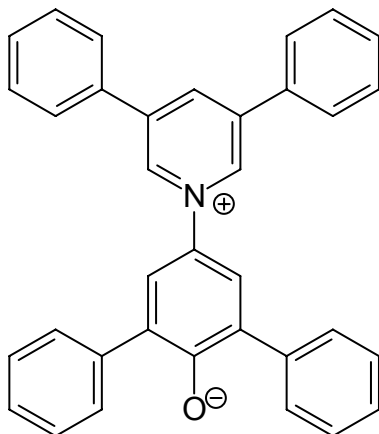   The **Z** parameter is derived from the UV-visible absorption spectrum of the pyridinium salt
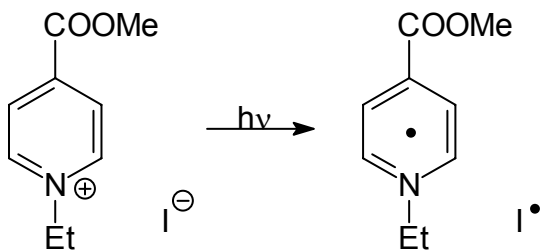
This absorption involves charge transfer and leads to a large drop in polarity. Transfer from a non-polar to a polar solvent raises the necessary excitation energy.

$$Z = \frac{2.859 x 10^4}{\lambda_{max} / nm} \quad \text{(Z in kcal/mol)}$$

Another widely used measure is ET based on the solvatochromic dye

which also undergoes excitation to a less polar excited state when it absorbs UV-visible light

$$E_T = \frac{2.859 x 10^4}{\lambda_{max} / nm} \quad \text{(E_T in kcal/mol)}$$
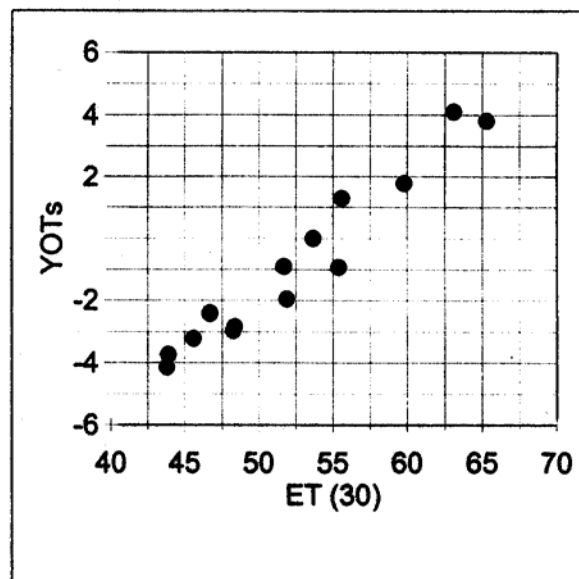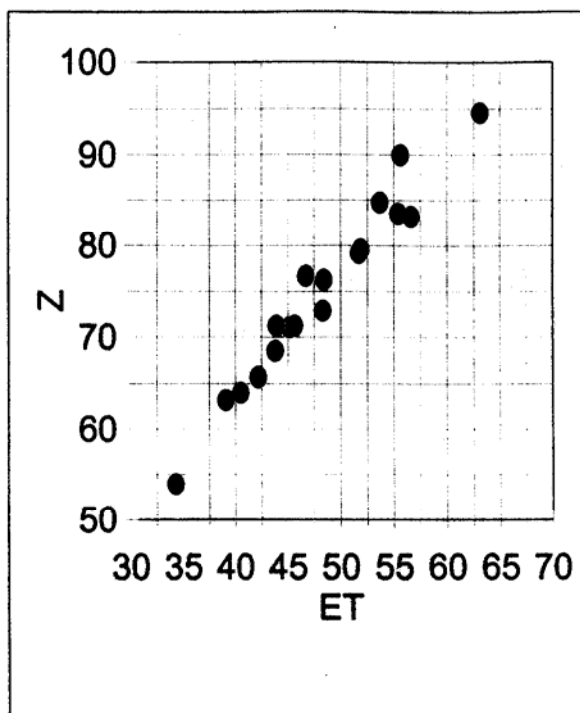
Some othere solvation parameters

$\varepsilon \equiv$ dielectric constant

$\dfrac{\varepsilon - 1}{2\varepsilon + 1} \equiv$ Kirkwood function (a theoretically based function expressing

how the energy of an ion or dipole depends on the dielectric constant).
These measures of solvent polarity are related, though not exactly.

Y, YOTs. Z and ET (30) values for some solvents

Solvent	Y	Y_{OTs}	Z	ET(30)	ε	(ε-1)/(2ε+1)
CF_3COOH		4.57			40.2	0.48
H_2O	3.5	4.1	94.6	63.1	78.4	0.49
$(CF_3)_2CHOH$		3.82		65.3		
HCOOH	2.1	3.04			58	0.49
H_2O-EtOH 1 1)	1.7	1.29	90	55.6		
CF_3CH_2OH	1.0	1.77		59.8	26.7	0.47
$HCONH_2$	0.6		83.3	56.6	111	0.49
80% EtOH	0.0	0.0	84.8	53.7		
MeOH	-1.1	-0.92	83.6	55.4	32.5	0.48
AcOH	-1.6	-0.9	79.2	51.7	6.15	0.39
EtOH	-2.0	-1.96	79.6	51.9	24.5	0.47
90% dioxane	-2.0	-2.41	76.7	46.7		
iso-PrOH	-2.7	-2.83	76.3	48.4	19.9	0.46
95% acetone	-2.8	-2.95	72.9	48.3		
t-BuOH	-3.3	-3.74	71.3	43.9	12.5	0.44
MeCN	-3.21		71.3	45.6	37.5	0.48
Me_2SO			71.1	45.1	46.7	0.48
$HCONMe_2$	-4.14		68.5	43.8	37	0.48
Acetone			65.7	42.2	20.7	0.46
HMPA			40.9			
CH_2Cl_2			40.7			
Pyridine			64.0	40.5	12.4	0.44
$CHCl_3$			63.2	39.1	4.8	0.36
PhCl				37.5	5.6	0.38
THF				37.4	2.6	0.26
Dioxane				36.0	2.2	0.22
Et_2O				34.5	4.3	0.34
C_6H_6			54	34.3	2.3	0.23
PhMe				33.9	2.4	0.24
CCl_4				32.4	2.2	0.22
n-Octane				31.1		
n-Hexane				31.0	1.9	0.19
Cyclohexane				30.9	2	0.20