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Attempts to Predict Absorption Equilibria

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How do we predict absorption equilibria?



Capture capacity for amine-CO₂ system

The net capacity is defined as the difference between equilibrium concentrations at the absorption and stripping partial pressures.

With CO₂ partial pressure change of 5 bar to 1 bar:

- i. At 70 °C, 4.5 M MDEA solution has a net CO₂ pickup of 30 vol/vol (0.297 mole/mole).
- ii. At 60 °C, 4.1 M MEA solution has a net CO₂ pickup of 5 vol/vol.

In a chemical reaction,



the thermodynamic equilibrium constant is defined as:
$$K = \frac{[C][D]}{[A][B]}$$

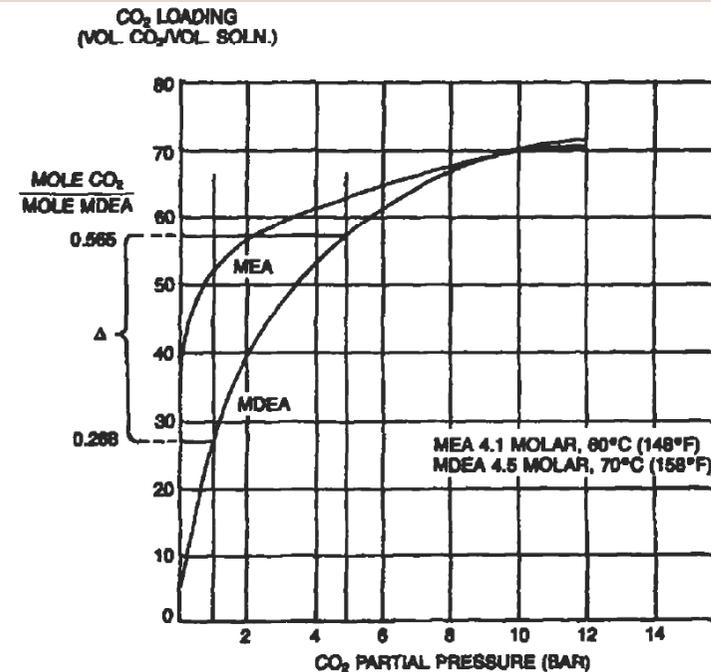


Figure 2-8. CO₂ solution isotherms in MEA and MDEA (Meissner and Wagner, 1983). Reprinted with permission from Oil & Gas Journal, Feb. 7, 1983. Copyright Pennwell Publishing Company.



How do we predict absorption equilibria?

Amine-CO₂ VLE
experiments

Liquid speciation
method

NMR spectroscopy

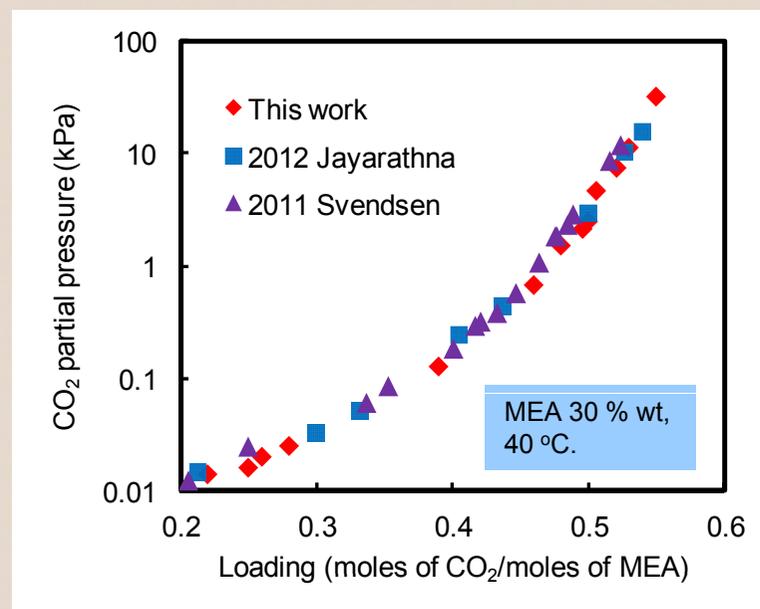
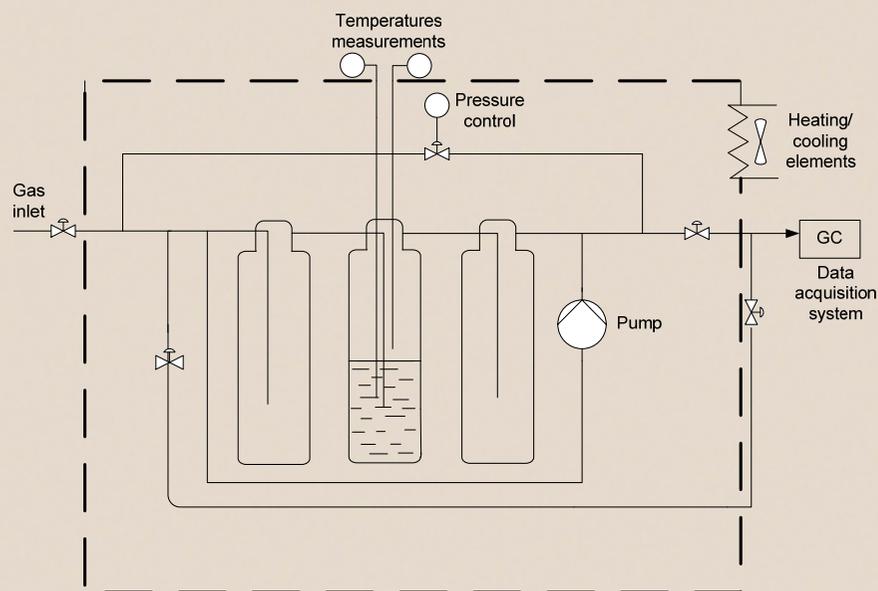
Molecular structure
relationship



1. Amine-CO₂ VLE solubility experiments

Information on the solubility of CO₂ in a amine solution is required for solvent evaluation.

Normally this will involve measuring partial pressures of CO₂ during equilibrium at different CO₂-amine concentrations.

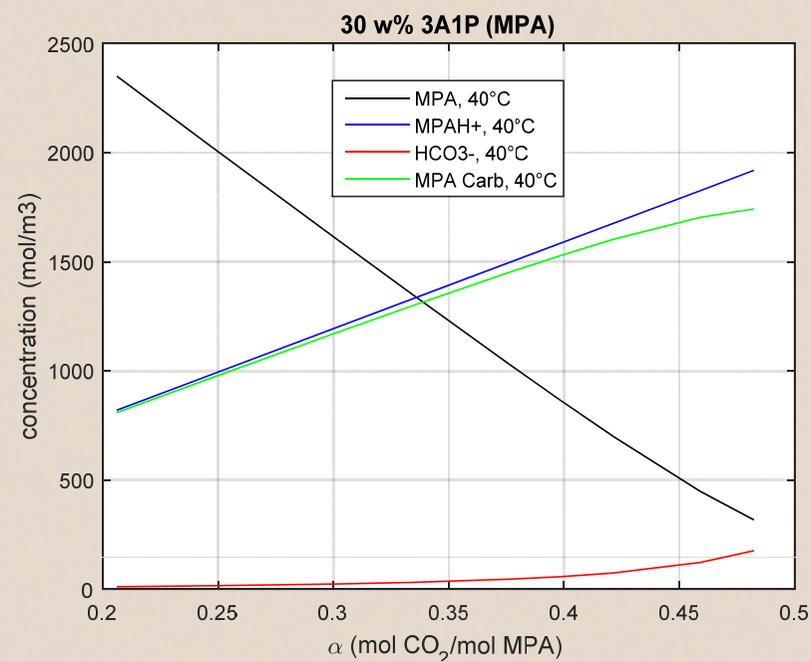
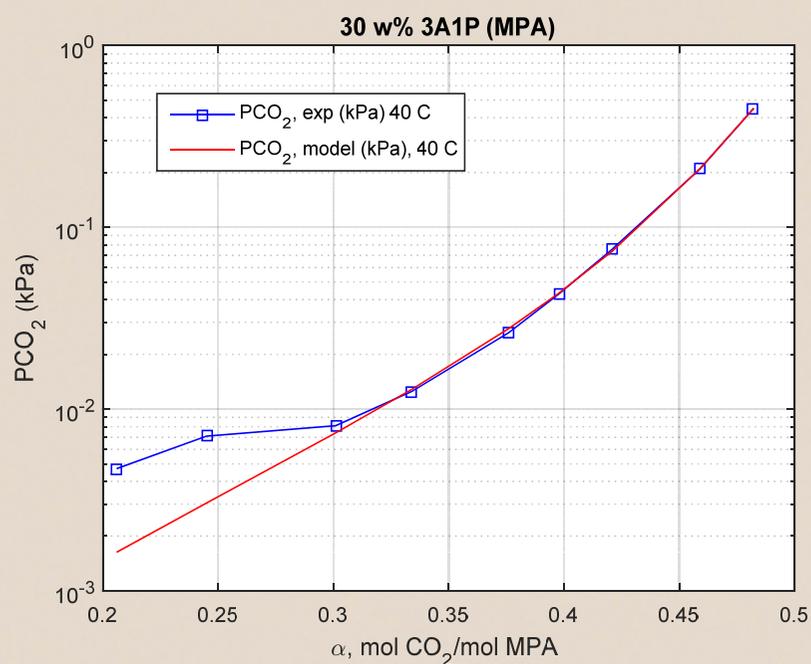




Among other amine-CO₂ systems investigated are:

- i. 3-amino-1-propanol (3A1P)
- ii. 4-amino-1-butanol (4A1P)
- iii. 5-amino-1-pentanol (5A1P)

Concentration related equilibrium model was used to represent the experimental data.





2. Determination of K_{app} using wet chemical method (WCM)

A method to determine species present during CO₂-amine-water reactions is developed.

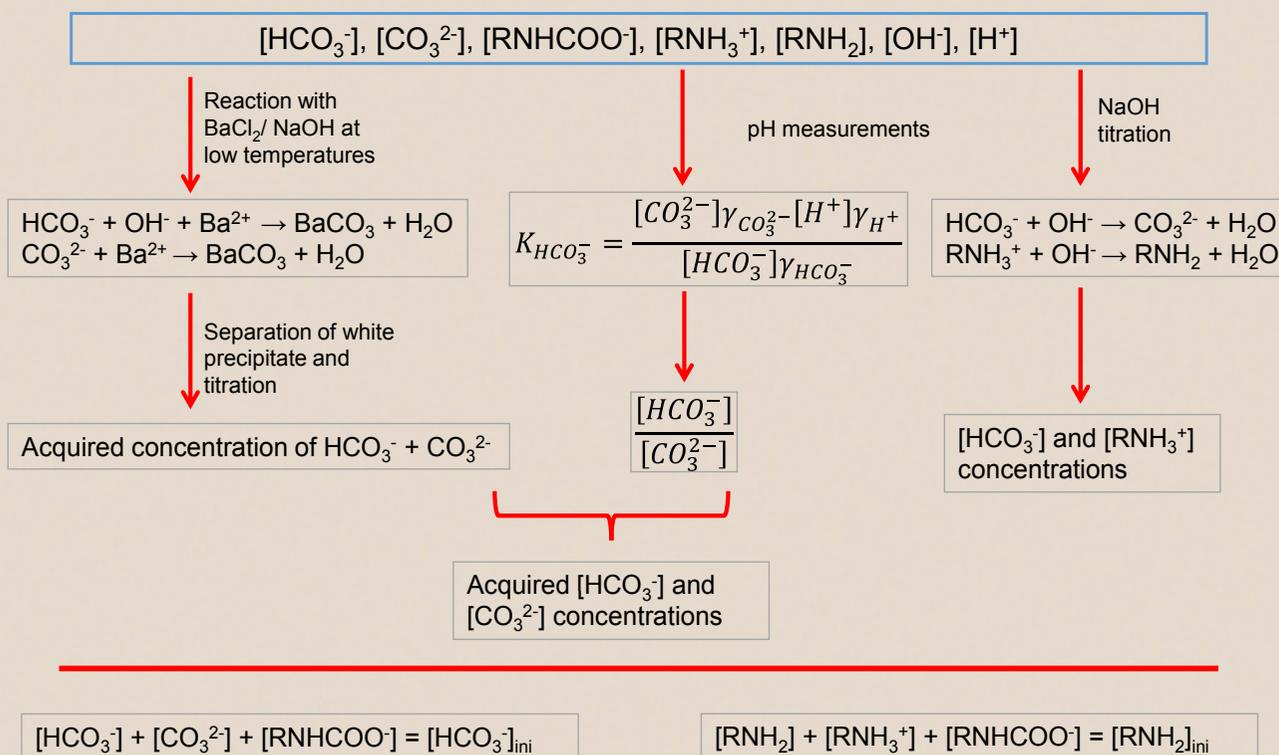




Table 1. Aqueous species speciation in a HCO_3^- -loaded MEA solution at 25 °C.

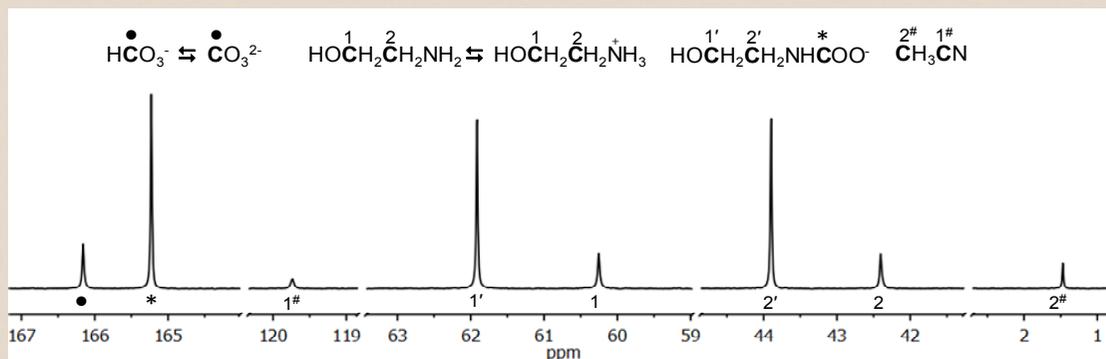
$[\text{HCO}_3^-]_{\text{ini}}/[\text{RNH}_2]_{\text{ini}}$	0.50		0.75		1.00	
	WCM	NMR	WCM	NMR	WCM	NMR
$[\text{HCO}_3^-]$	0.015 ± 0.001	0.016	0.032 ± 0.003	0.033	0.074 ± 0.005	0.068
$[\text{CO}_3^{2-}]$	0.044 ± 0.004	0.046	0.047 ± 0.010	0.053	0.075 ± 0.005	0.065
$[\text{RNHCOO}^-]$	0.103 ± 0.002	0.109	0.161 ± 0.011	0.152	0.172 ± 0.007	0.193
$[\text{RNH}_2]$	0.184 ± 0.011	0.169	0.100 ± 0.001	0.108	0.077 ± 0.008	0.058
$[\text{RNH}_3^+]$	0.038 ± 0.007	0.042	0.063 ± 0.006	0.053	0.070 ± 0.003	0.061
$K_{\text{HYD}a}$ (mol/L)	0.027 ± 0.003	0.025	0.020 ± 0.002	0.023	0.033 ± 0.004	0.021
Ionic strength (mol/L)	0.248		0.342		0.447	

A study by Chan and Danckwerts found that the $K_{\text{HYD}a}$ value of **0.0342 mol/L** at an ionic strength of 0.531 mol/L. A $K_{\text{HYD}a}$ value of **0.033 mol/L** at ionic strength of 0.447 mol/L was calculated in this method.



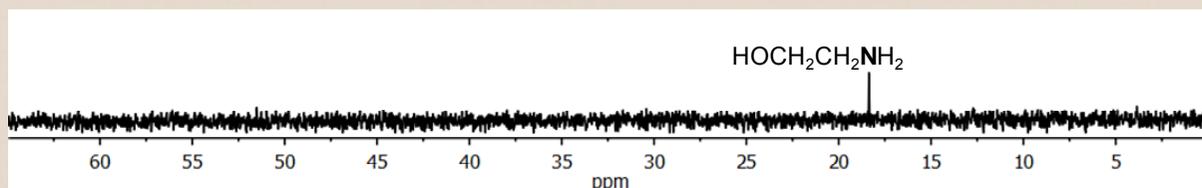
3. NMR spectroscopy

- A non-invasive analytical method that allows direct measurements of the specific nuclei of atoms of compounds
- Peak areas are directly proportional to the number of nuclei contributing to the signals and, with some care, quantitative analyses of compounds are hence possible (e.g ^1H and ^{13}C NMR experiments).



Quantitative ^{13}C NMR spectrum of an amine- CO_2 - H_2O system

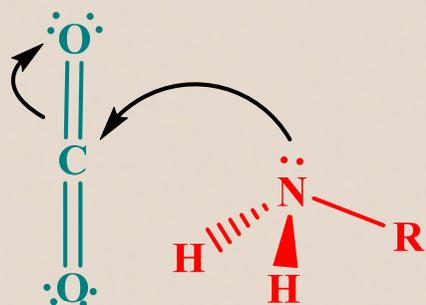
- By means of qualitative ^{15}N -NMR experiments, the relative electron density on the ^{15}N nucleus (which is directly involved into the reaction with CO_2) of amines can be measured to investigate factors influencing the carbamate-forming reactions.



Qualitative ^{15}N NMR spectrum of MEA



Carbamate formation is a Lewis acid-base and a nucleophilic addition reaction



- Increased electron density on the Lewis base (nucleophile) raises the energy of the electron pair and makes it more available to react;

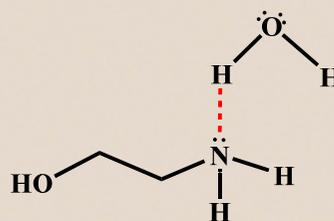
- The *reactivity of a Lewis base (nucleophile)* depends not only on the chemical-structural properties of the molecules, but also on other factors such as solvation etc.



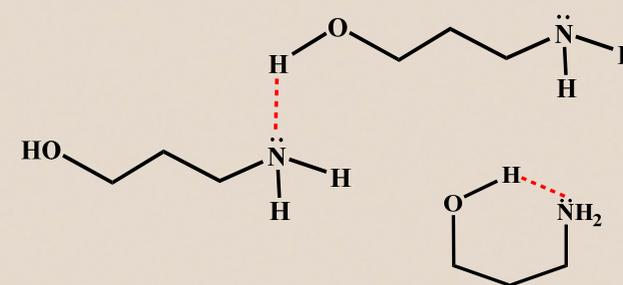
Electrophile
(Lewis acid)

Nucleophile
(Lewis base)

1) Solvent interactions

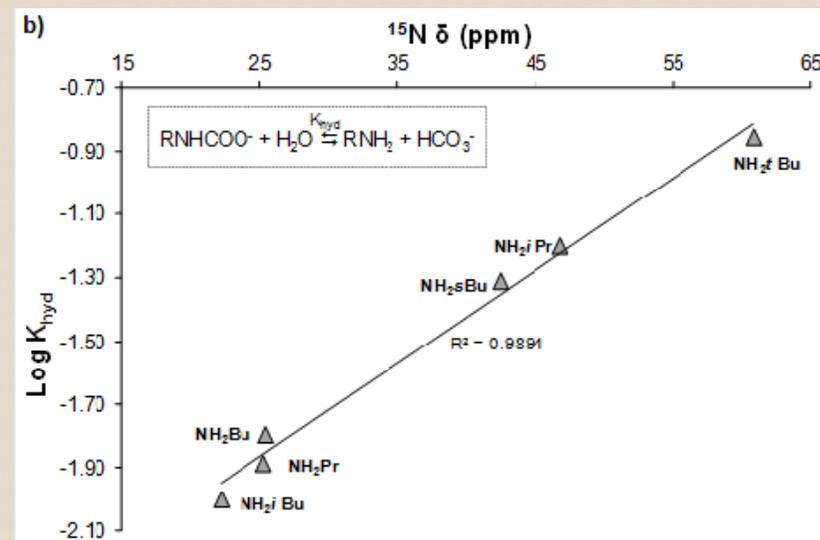
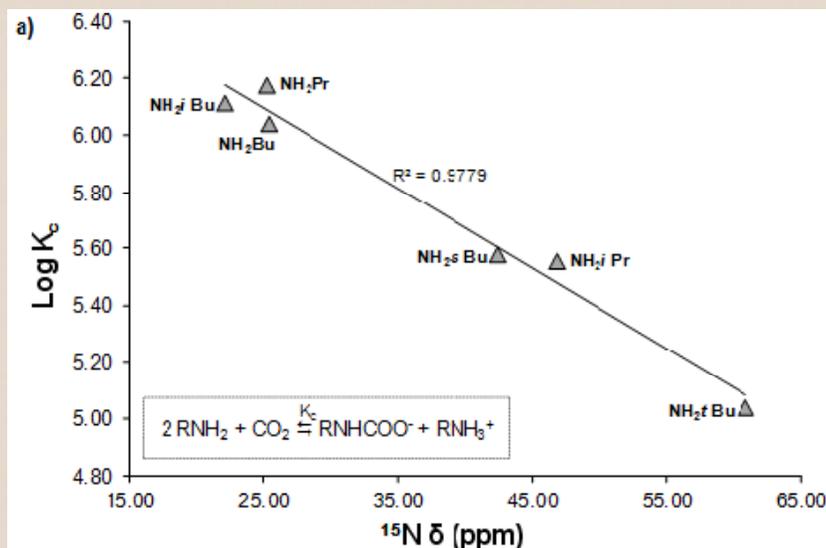


2) Hydroxyl group interactions





Correlation of ^{15}N NMR chemical shift values δ (ppm) with reaction equilibrium constants



- A linear relation for carbamate formation (a) and carbamate hydration/stability (b) vs δ ppm value
- Higher δ ppm value (less relative electron density) leads to less carbamate formation.
 - At increasing steric hindrance at the α -C to N: less electron density on the N atom
 - Back donation of N-centred electron density to α -C bonded $-\text{CH}_3$ groups; e.g. NH_2 -s-Bu, NH_2 -i-Pr, NH_2 -t-Bu



4. Molecular structure-activity relationship



The electron density on N atom of the reacted amine influences the reaction with CO_2 and the stability of carbamate.

R. W. Taft (1952) introduced an empirical parameter which describes the **polar effect** (σ^*) of substituents.

Polar effect : atoms or groups of atoms attached to the functional group have the ability to withdraw or donate electrons through the bonds. These can distort the electron density distribution of the molecules.



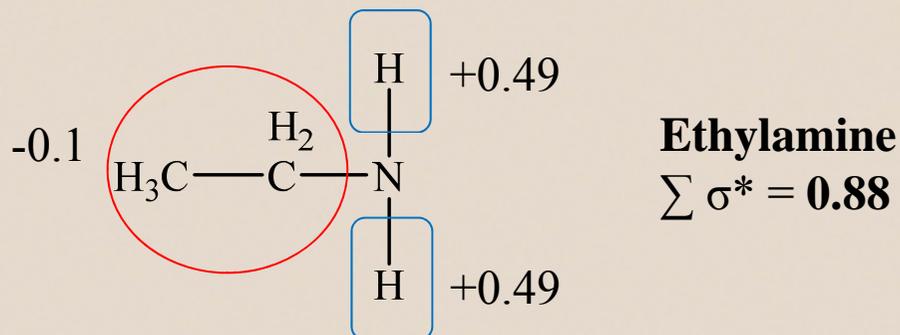


Substituent	H	CH ₃	C ₂ H ₅	n-C ₃ H ₇	i- C ₃ H ₇	n- C ₄ H ₉	i- C ₄ H ₉	s- C ₄ H ₉	t- C ₄ H ₉
σ^*	+0.49	0	-0.100	-0.115	-0.190	-0.130	-0.125	-0.210	-0.300

- A Positive σ^* value is attributed to electron withdrawing.
- A Negative σ^* value is attributed to electron donating.

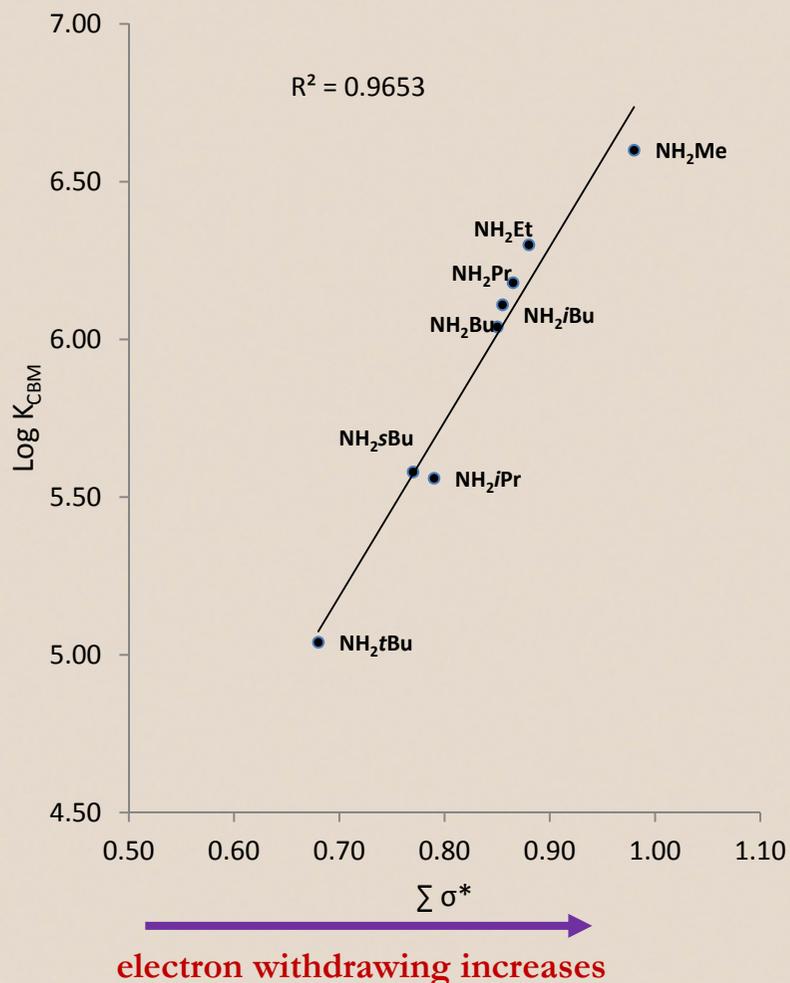
These effects are independent of reactions.

For a molecule consisting of many substituents, the balancing effects is additive ($\sum \sigma^*$).

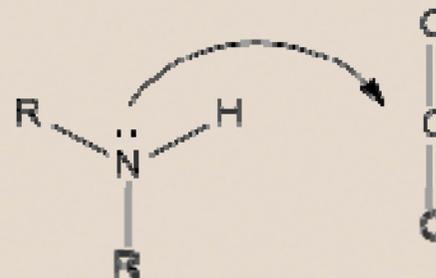




K_{CBM} against $\sum\sigma^*$



- $\sum\sigma^*$ - a measure of the electron withdrawing or releasing ability of substituents.
- $\sum\sigma^*$ vs K_{CBM} is a linear relationship
- Reactivity of aqueous amine with CO₂ can be described by the electronic effect.





Conclusions and Outlook

- Concentration based VLE modelling was successfully demonstrated.
- Liquid speciation method developed.
- ^{15}N NMR method development
 - Deeper understanding of equilibrium reactions
- Correlations between equilibrium constants (K_{CBM} and K_{HYD}) and Taft polar substituent constants ($\sum\sigma^*$) were established.



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Thank you for your attention