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A Chemical Study of Aqueous Amine Solvents for Post Combustion Capture by NMR Spectroscopy

Cristina Perinu,[a] Bjørnar Arstad,[b] Aud M. Bouzga,[b] Klaus J. Jens[a]

[a]Faculty of Technology, Telemark University College, Porsgrunn, Norway
[b]SINTEF Materials and Chemistry, Oslo, Norway

cristina.perinu@hit.no

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September 17-20, Bergen, Norway

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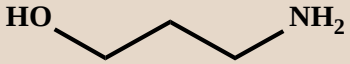
Introduction

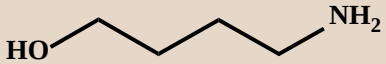
✓ The aim of this work is to get insights into the chemistry of aqueous amine solvents for the CO_2 capture;

✓In this study, **NMR spectroscopy** is used to ***characterize the factors influencing the reactivity*** of the following aqueous primary amines:

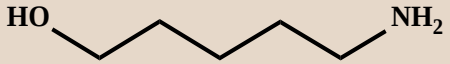
MEA
1-Amino-2-ethanol



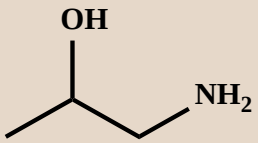
3A1P
3-Amino-1-propanol



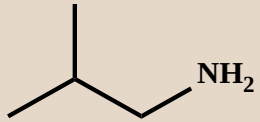
4A1B
4-Amino-1-butanol



5A1P
5-Amino-1-pentanol



1A2P
1-Amino-2-propanol



ISOB
Isobutylamine

✓The ***carbamate formation*** is a critical reaction because it is characterized by fast kinetics but reduced CO_2 absorption capacity and increased desorption/regeneration energy

$$2\ R_1R_2NH + CO_2 \leftrightarrows R_1R_2NCOO^- + R_1R_2NH_3^+$$

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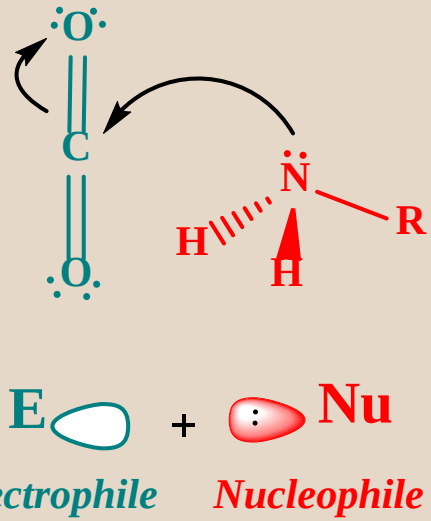
Introduction

Carbamate formation is a nucleophilic addition reaction



•Increased electron density on the nucleophile raises the energy of the electron pair and makes it more available to react;

•The ***reactivity of a nucleophile*** depends on the chemical-structural properties of the molecules, but other factors that interact in a complicated way must also be taken into account, such as ***solvation effects***;

•Considering that the amine nitrogen is the nucleophile involved in the reaction with CO_2, **^{15}N NMR spectroscopy** can give an important contribution in determining the ***electron density on the nitrogen*** and the ***factors influencing the availability of the lone pair electrons***.

•Compared to ^{1}H and ^{13}C, ^{15}N chemical shifts depend not only on the chemical environment of the nuclei (defined by the structure), but also on medium effects.

Experimental methods

- ✓ Aqueous amine solutions at the same concentration (2 mol/l) were prepared:

  1) Qualitative ^{15}N NMR experiments were carried out at 298.15 K to *record the chemical shifts*

  2) Carbamate formation: $NaHCO_3$ was added to these amine solutions, at 1:1 ratio, and the mixture was allowed to get equilibrium over 24 h at 298.15 K.

- ✓ **Quantitative ^{13}C NMR experiments** were carried out at 298.15 K on the amines after carbamate formation *to quantify the amount of carbamate* and of the other species at the equilibrium.

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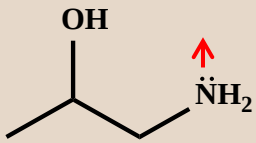
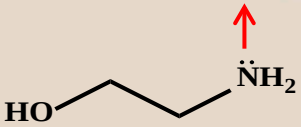
Results

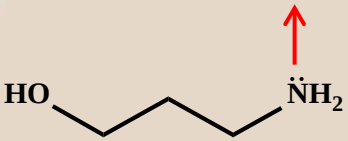
Decreasing reactivity at increasing basicity



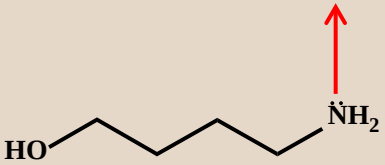
1A2P
1-Amino-2-propanol
(pKa=9.46)



MEA
1-Amino-2-ethanol
(pKa=9.65)



3A1P
3-Amino-1-propanol
(pKa=9.96)



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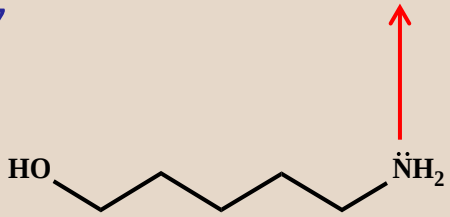
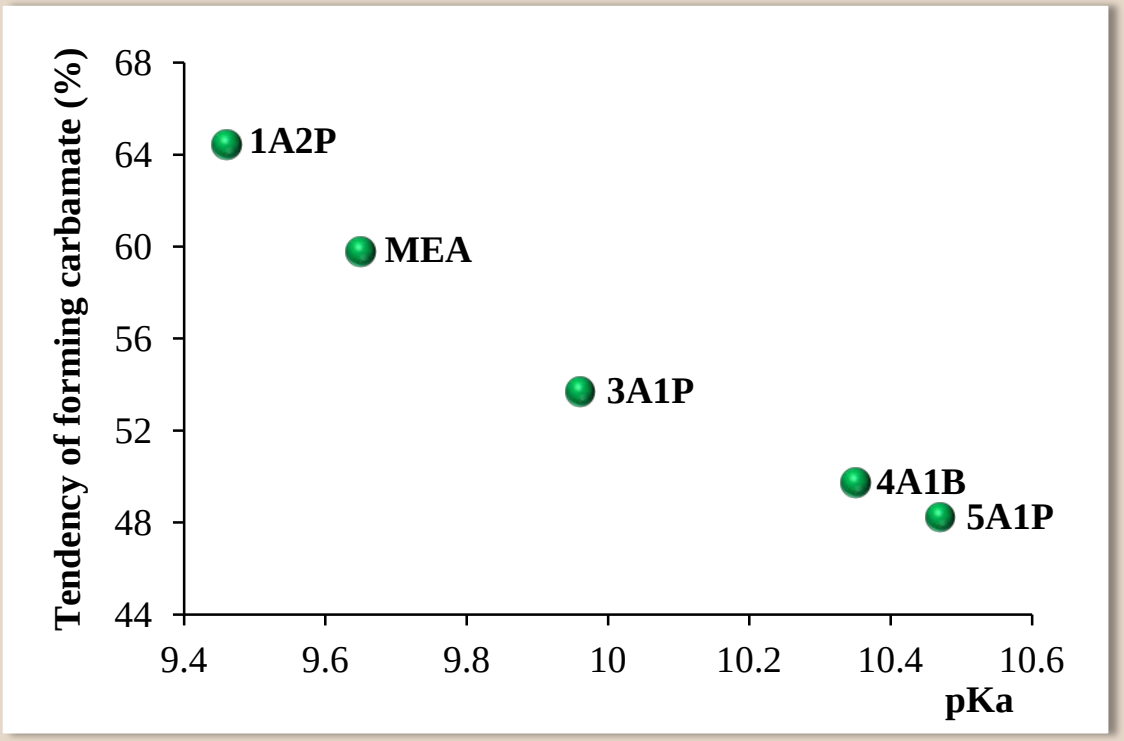
4-Amino-1-butanol
(pKa=10.35)



5A1P
5-Amino-1-pentanol
(pKa=10.47)



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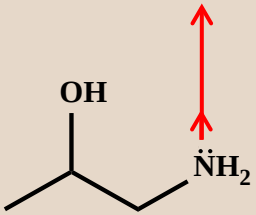
Results

Increasing reactivity at increasing electron density



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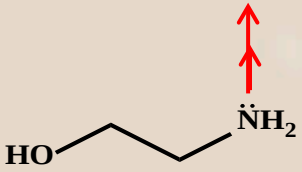

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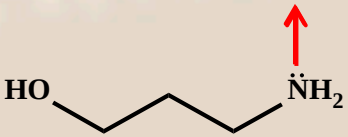

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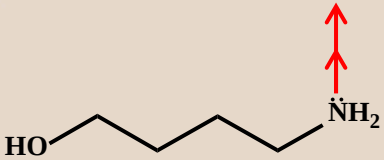

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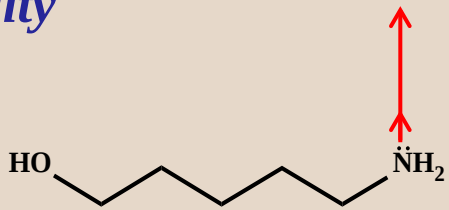

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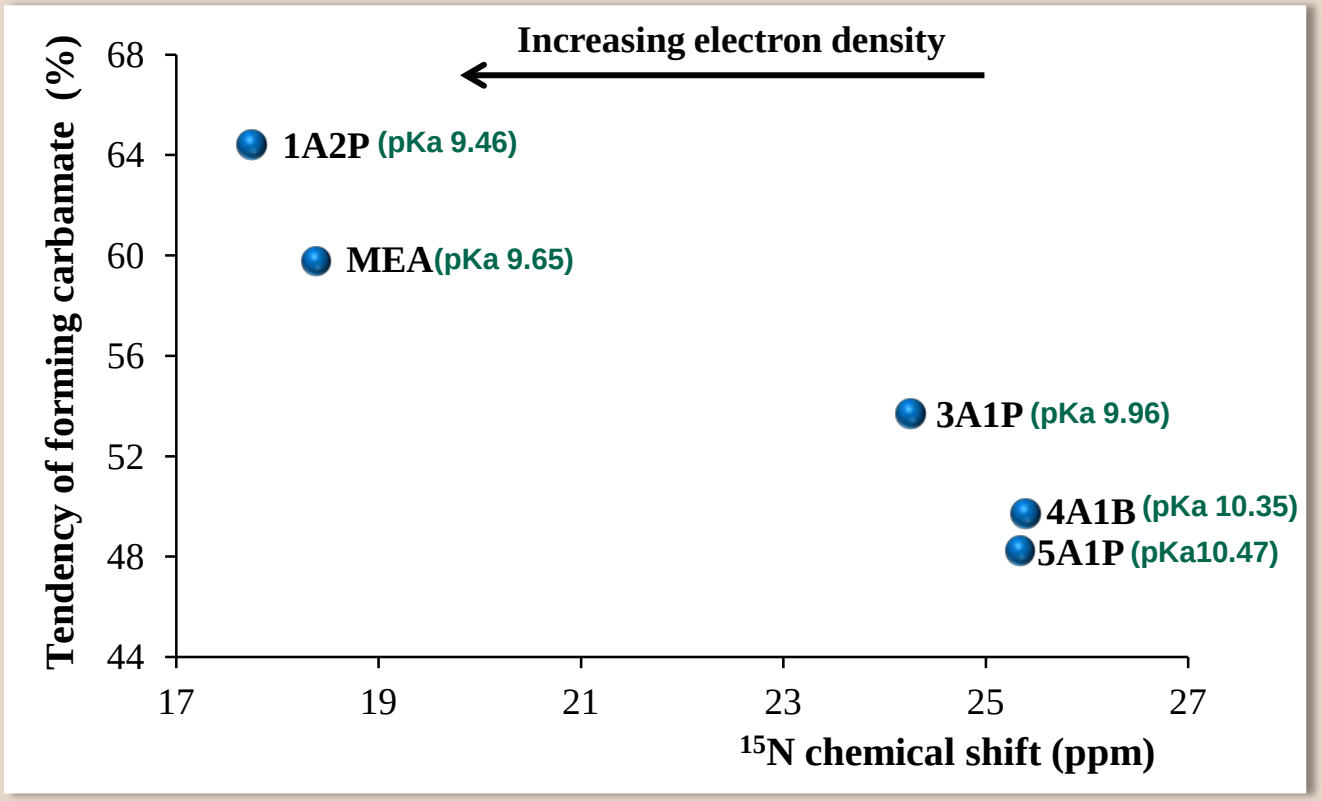

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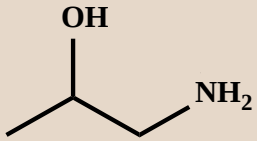
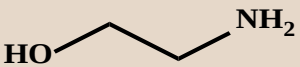
Results

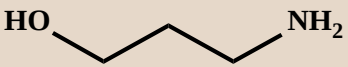
Factors influencing the ^{15}N chemical shifts



1A2P
1-Amino-2-propanol



MEA
1-Amino-2-ethanol



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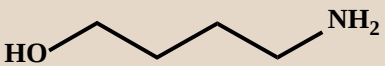

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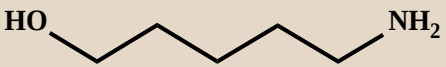
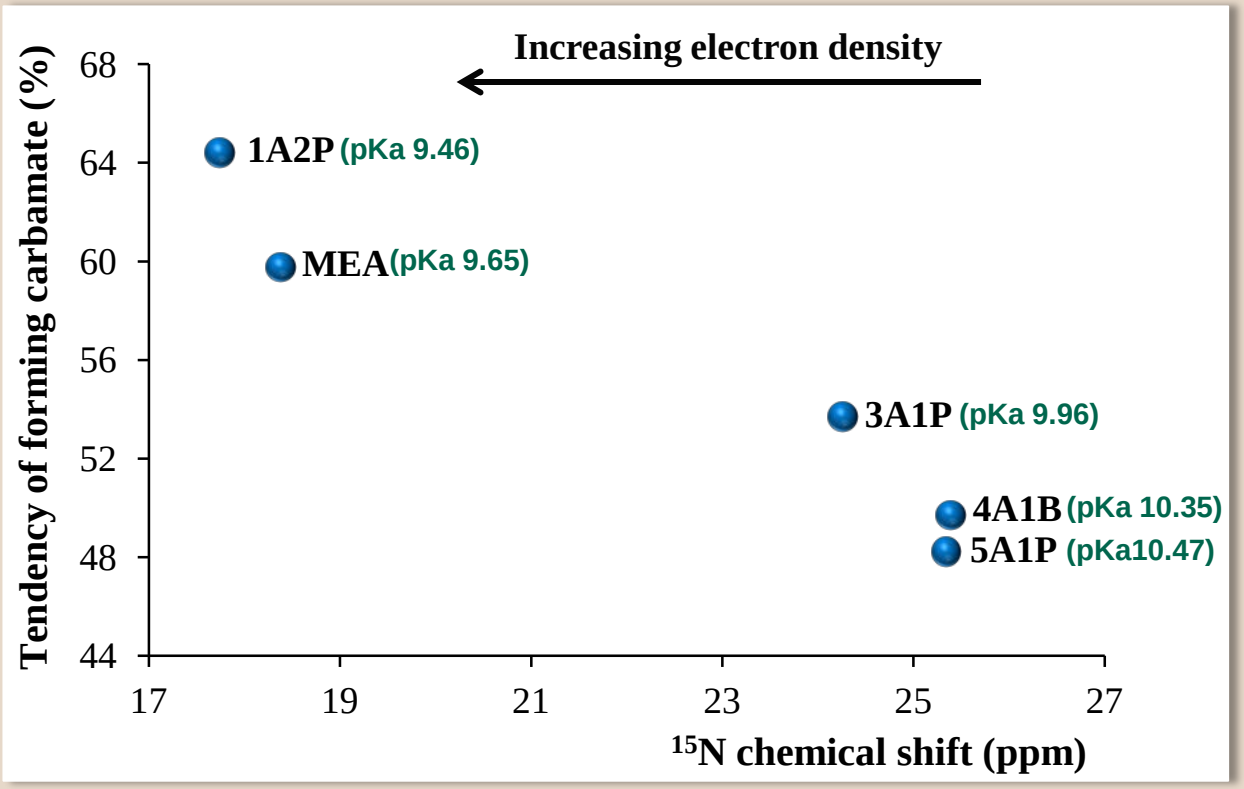
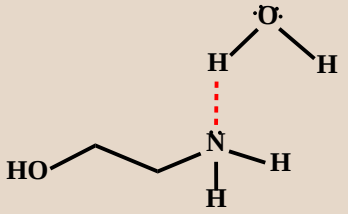


5A1P
5-Amino-1-pentanol

Reduced electron density on the nitrogen at increasing basicity is due to:

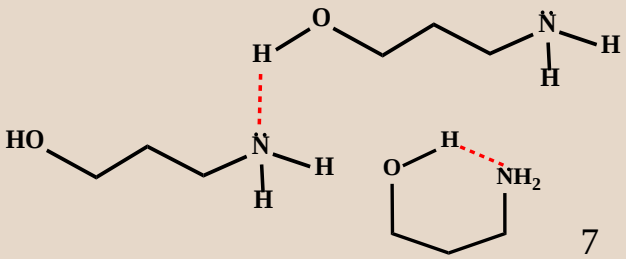


1) Solvents interactions



$$RNH_2 + H_2O \leftrightarrows RNH_3^+ + OH^-$$

2) Hydroxyl group interactions



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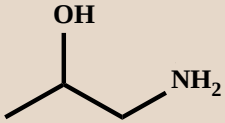
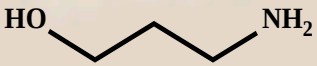
Results

Factors influencing the reactivity

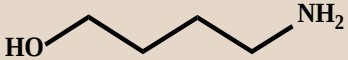


1A2P
1-Amino-2-propanol

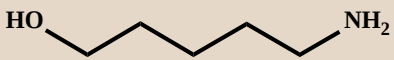
MEA
1-Amino-2-ethanol



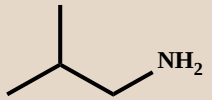
3A1P
3-Amino-1-propanol



4A1B
4-Amino-1-butanol

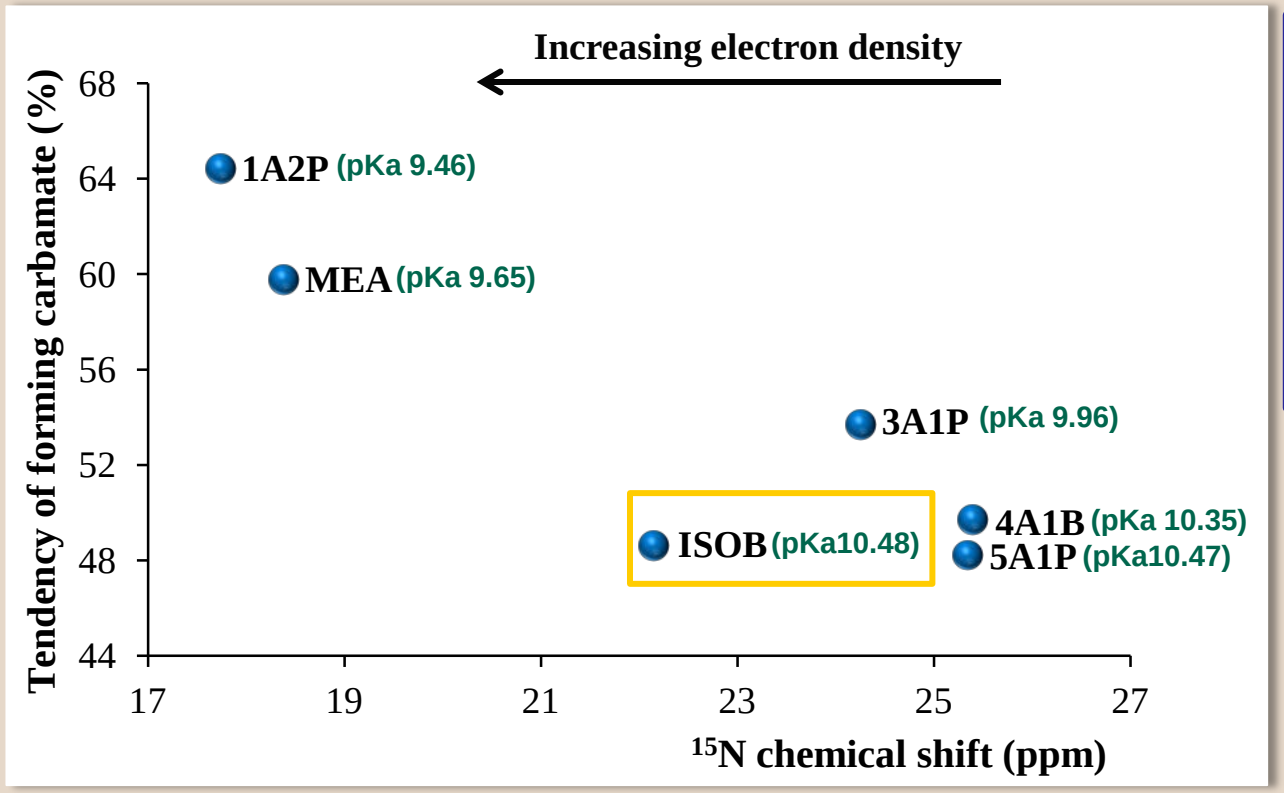


5A1P
5-Amino-1-pentanol

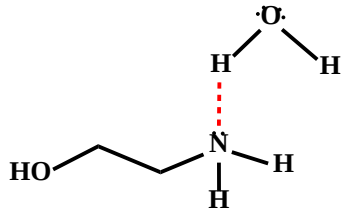


ISOB
Isobutylamine

Stronger the base => More favourable the solvation
=> Reduced the reactivity

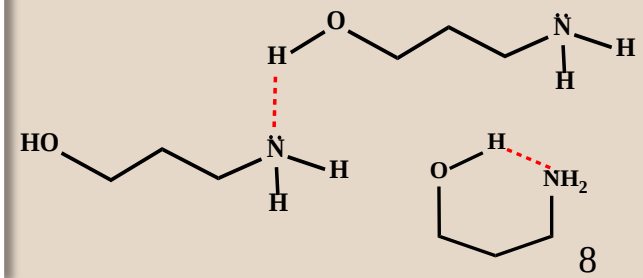


1) Solvents interactions



$RNH_2 + H_2O \leftrightarrows RNH_3^+ + OH^-$

2) Hydroxyl group interactions



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Conclusions

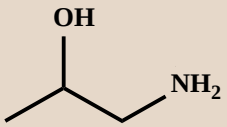
• To improve the efficiency of the amine-based Post Combustion CO_2 Capture technology, insights into the chemistry involved into the reaction of CO_2 with aqueous amine solvents is a key task;

• **^{15}N NMR spectroscopy** can be a useful tool to **characterize the reactivity of the amines**. In particular, in this study an experimental evidence of the water solvation effects on the nucleophilic reactivity of the amines is provided.

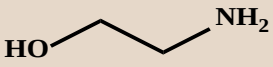
• **For the aqueous primary amines under study, it has been demonstrated that increasing reactivity at decreasing basicity is due to solvation effect:**

✓Increasing basicity of a molecule leads to a more favourable solvation, so that the observed reactivity is reduced because, before a nucleophilic attack, complete desolvation is required.

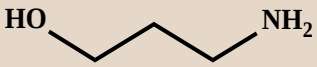
✓The hydroxyl function in β-position to the nitrogen increases the nucleophilic reactivity of the amines due to the electrowithdrawal property that reduces the basicity and, consequently, the solvation effects.



1A2P
1-amino-2-propanol



MEA
1-amino-2-ethanol



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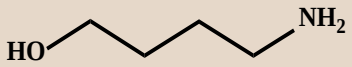
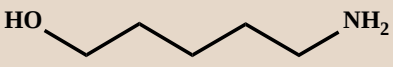
3-amino-1-propanol



4A1B
4-amino-1-butanol



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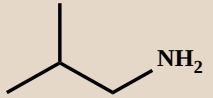
5-amino-1-pentanol



ISOB
Isobutylamine

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Acknowledgements

The financial support provided by the Research Council of Norway (CLIMIT grant nr. 199890) and the assistance by the SINTEF NMR lab, including staff, are gratefully acknowledged.

Thank you for your attention!