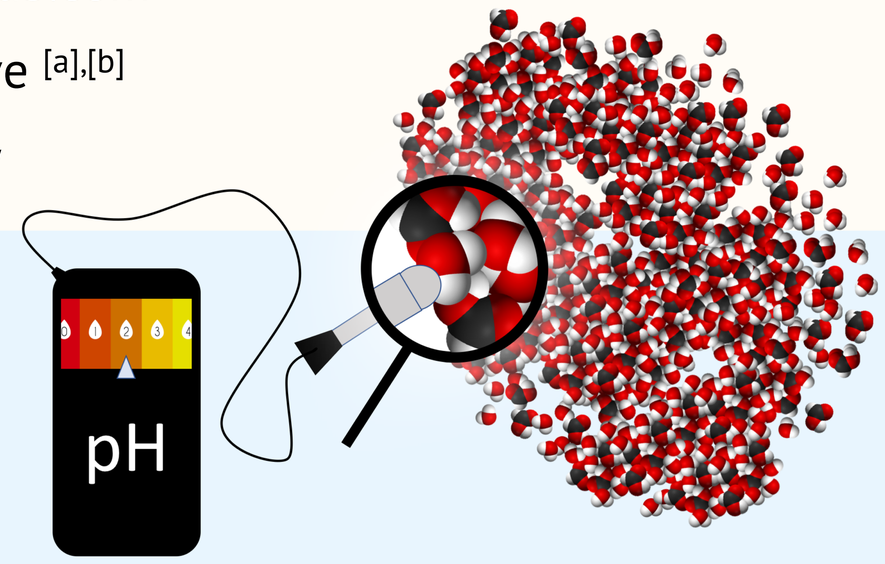
# How to Modify the Acidity of Charged Droplets?

mari.ojakivi@ut.ee | www.kruvelab.com

M. Ojakivi [a]; J. Liigand [a]; A. Kruve [a],[b]

[a] University of Tartu, Institute of Chemistry, Estonia
[b] Free University of Berlin, Institute of Chemistry and Biochemistry, Germany




## INTRODUCTION

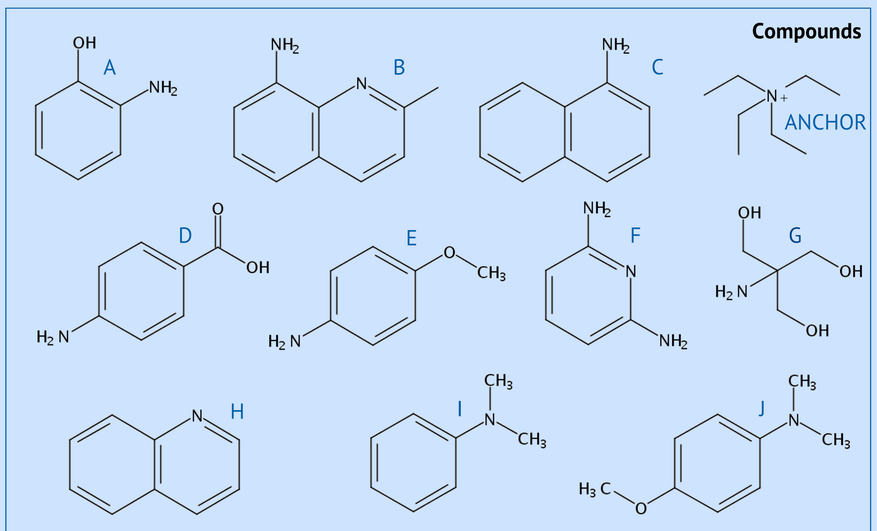
The concept of acidity in confined spaces is up to date poorly understood; especially, in case of media violating electro-neutrality. Here, we describe the acidity of charged droplets via their ability to protonate simple nitrogen bases and we propose ways to modify the protonation efficiency.

**We studied the effect of:**

- Bulk-phase pH
- Surface charge type
  - Different counter-ions
- Wrong-way-round ionization

## METHODS

**Compounds**




$pK_a^{H_2O}$ = 2.7…9.0 $pK_a^{MeOH}$ = 5.2…10.3

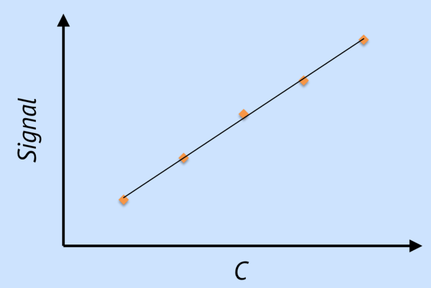
**Additives**

Formic acid
Acetic acid
Oxalic acid
TFA
Citric acid
Ammonium acetate
Ammonium formate
Ammonium fluoride
Ammonia
Hydrazine

These additives were mixed to give different solvent compositions – 28 in water and 14 in methanol.

$pH^{H_2O}$ = 1.4…10.3 $pH^{MeOH}$ = 3.6…12.2

**Measurements**




Calibration graph was prepared for all of the compounds in all solvent compositions.

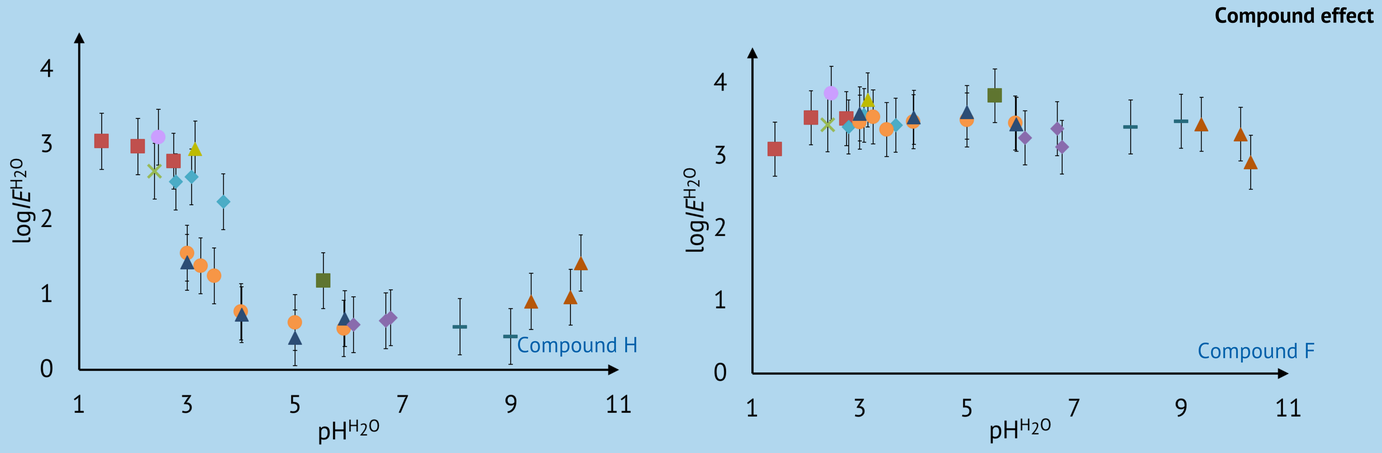
**Calculations**

$$\log IE(\mathrm{M}) = \log\left(\frac{slope([\mathrm{M+H}]^+)}{slope(\mathrm{Et_4N^+})} \times \frac{IC(\mathrm{M})}{IC(\mathrm{Et_4N^+})}\right) + \log IE(\mathrm{Et_4N^+})$$

The ionization efficiency value (log*IE*(M)) for each compound in all solvent compositions was calculated as above. Higher log*IE* value refers to higher concentration of protonated compound in droplets.

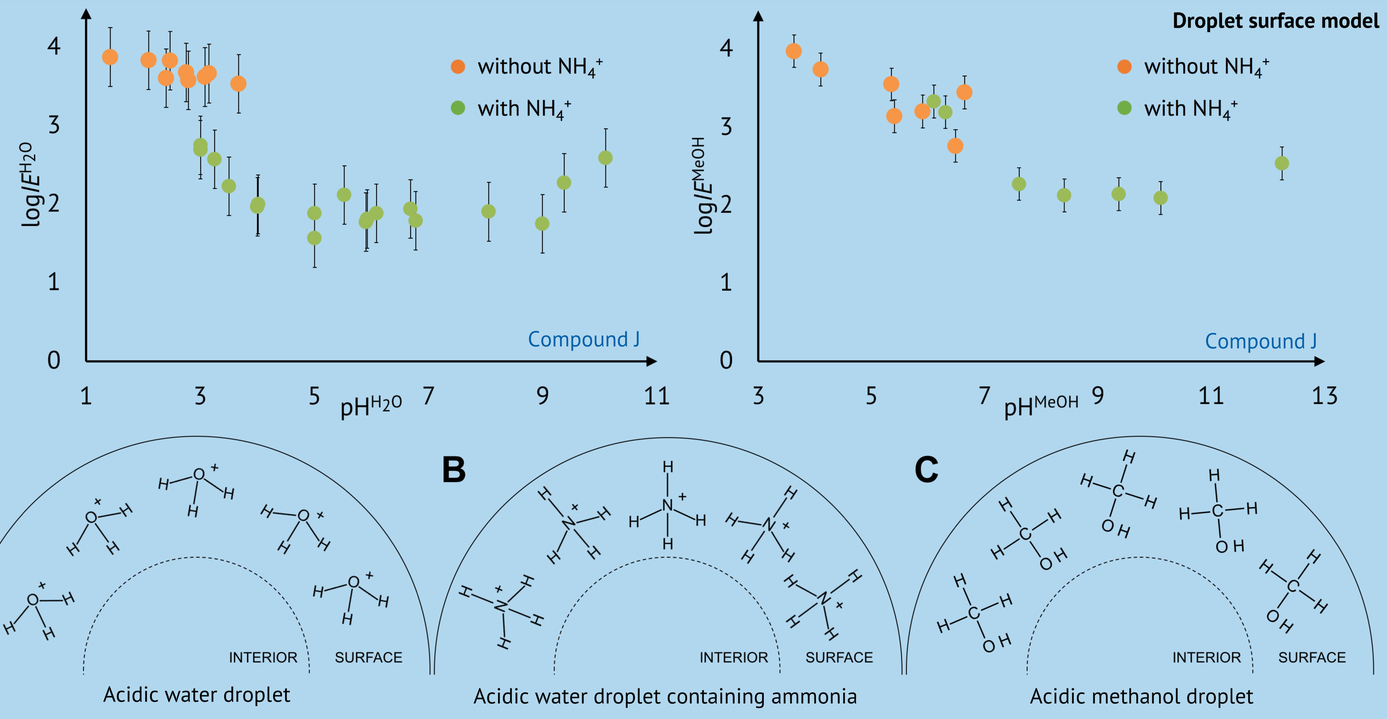
## RESULTS

**Compound effect**



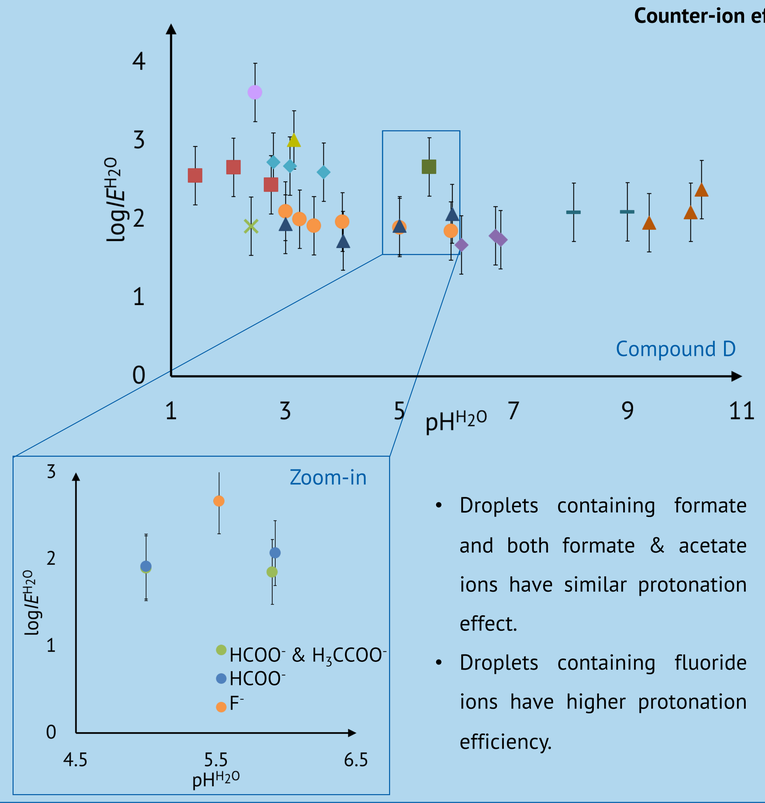

- Protonation of most of the compounds is strongly dependent on the solvent composition.
- Protonation of some compounds is not affected by the acidity of the droplets.

**Droplet surface model**



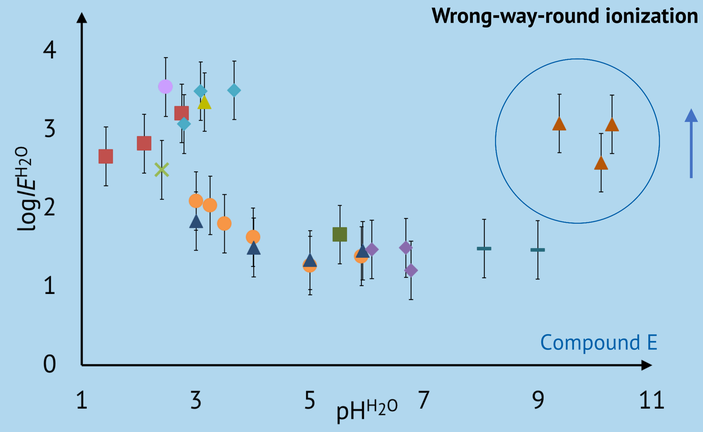

- Protonation efficiency in charged water droplets depends on the ionic content of the surface of the droplet.
- Protonation efficiency in charged methanol droplets depends more on the bulk-phase pH.

**Counter-ion effect**




- Droplets containing formate and both formate & acetate ions have similar protonation effect.
- Droplets containing fluoride ions have higher protonation efficiency.

**Wrong-way-round ionization effect**




- Observed for 6 compounds out of 10 in water.
- Observed for 1 compound out of 10 in methanol.
- Hypothesis: kinetic effect?

## REFERENCES


- Ojakivi et al DOI: 10.1002/slct.201702269
- Kruve et al DOI: 10.1021/ac404066v
- Oss et al DOI: 10.1021/ac902856t
- Enami et al DOI: 10.1021/jz101402y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