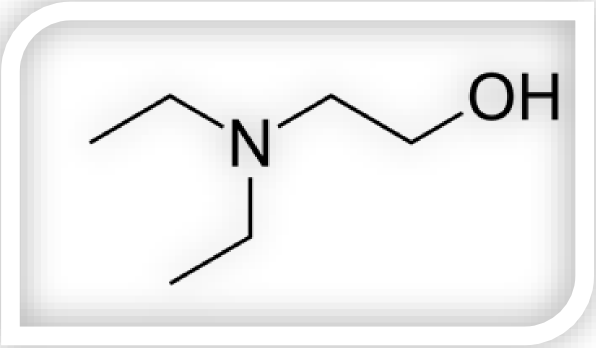
Polarity of the system {water + 2-(diethylamino)ethanol or DEEA} using solvatochromic dyes and excess partial molar enthalpies, at 298.15K.



Palestra no âmbito “Café com Física”
Centro de Física da UC, Departamento de Física
da Universidade de Coimbra, 04 de maio 2022

Maria-Luísa C.J. Moita, Beatriz G. Fialho, Ângela F.S. Santos, Isabel M.S. Lampreia

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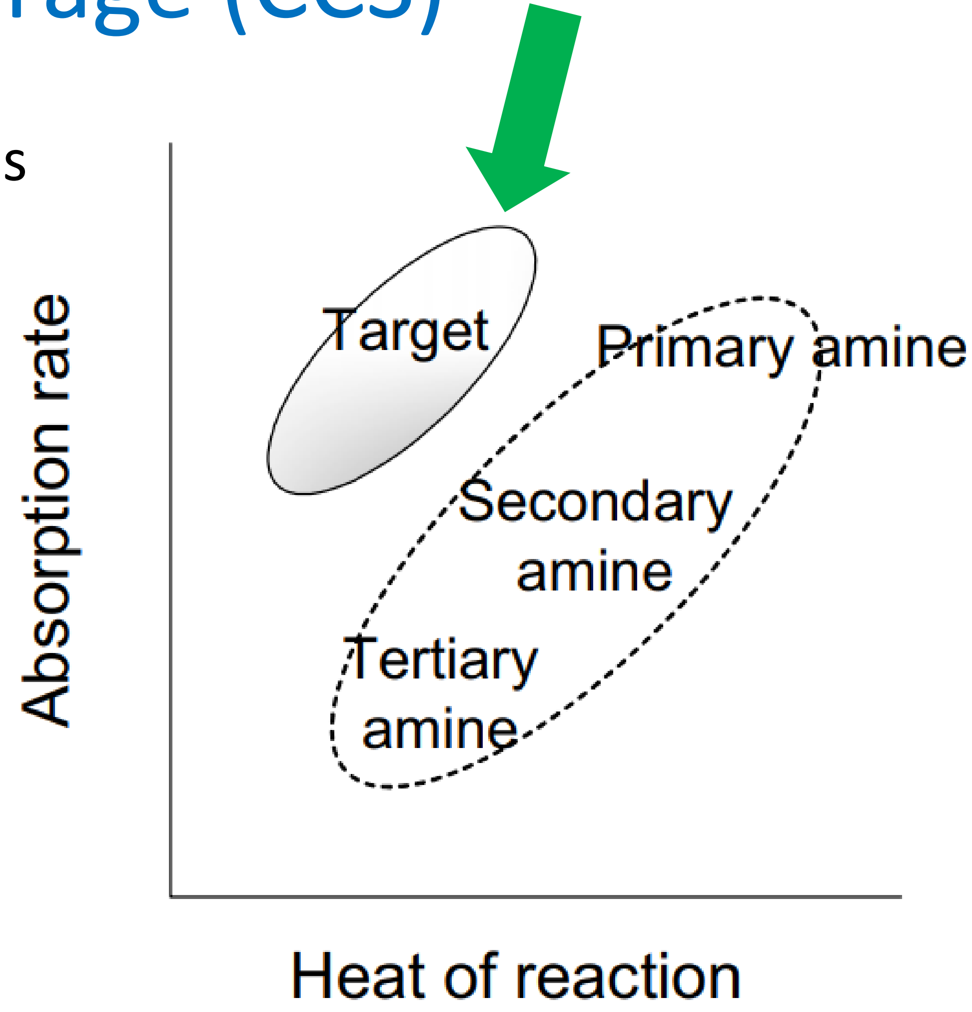
CO_2 Capture and Storage (CCS)

- ✓ The technology of CO_2 capture and storage (CCS) has potential for tackling global warming

- ✓ New target solvents must present:
  - ☐ maximum loading: $\alpha_{CO_2} = \frac{n_{CO_2}}{n_{amine}}$
  - ☐ low heats of reaction
  - ☐ moderately high CO_2 absorption rates

- ✓ This seems to be the case of **aqueous mixtures of alkanolamines**

- ✓ However, the **desorption** energy for CO_2 **and amines regeneration and corrosive nature** and their **degradation** represent a limitation in their application



Primary, secondary and tertiary amines maximum loading

$$CO_2 + 2R_1NH_2 \rightleftharpoons R_1NHCOO^- + R_1NH_3^+$$

$$CO_2 + 2R_1R_2NH \rightleftharpoons R_1R_2NHCOO^- + R_1R_2NH^+$$

The maximum loading is:

0.5 mole CO$_2$/mole amine

Both primary and secondary amines:

- ✓ are weak bases and **form carbamates**
- ✓ **the reaction rates are hight**
- ✓ **The heat absorption is hight**

base catalysis mechanism

$$CO_2 + R_1R_2R_3N + H_2O(l) \rightleftharpoons HCO_3^- + R_1R_2R_3NH^+(aq)$$

- ✓ Lower pK_b values are expected to give faster absorption rates ⟶ **Solvent Polarity (*Basicity*)**
- ✓ Aqueous mixtures decreases the corrosive amines`s nature ⟶ **Water + DEEA binary system**

1 mole CO$_2$/mole amine

Terciary amines:

- ✓ form **bicarbonates** through base catalysis of CO$_2$ hydration
- ✓ **the reaction rates are slow**
- ✓ **the heat absorption is low**

Solvent Polarity

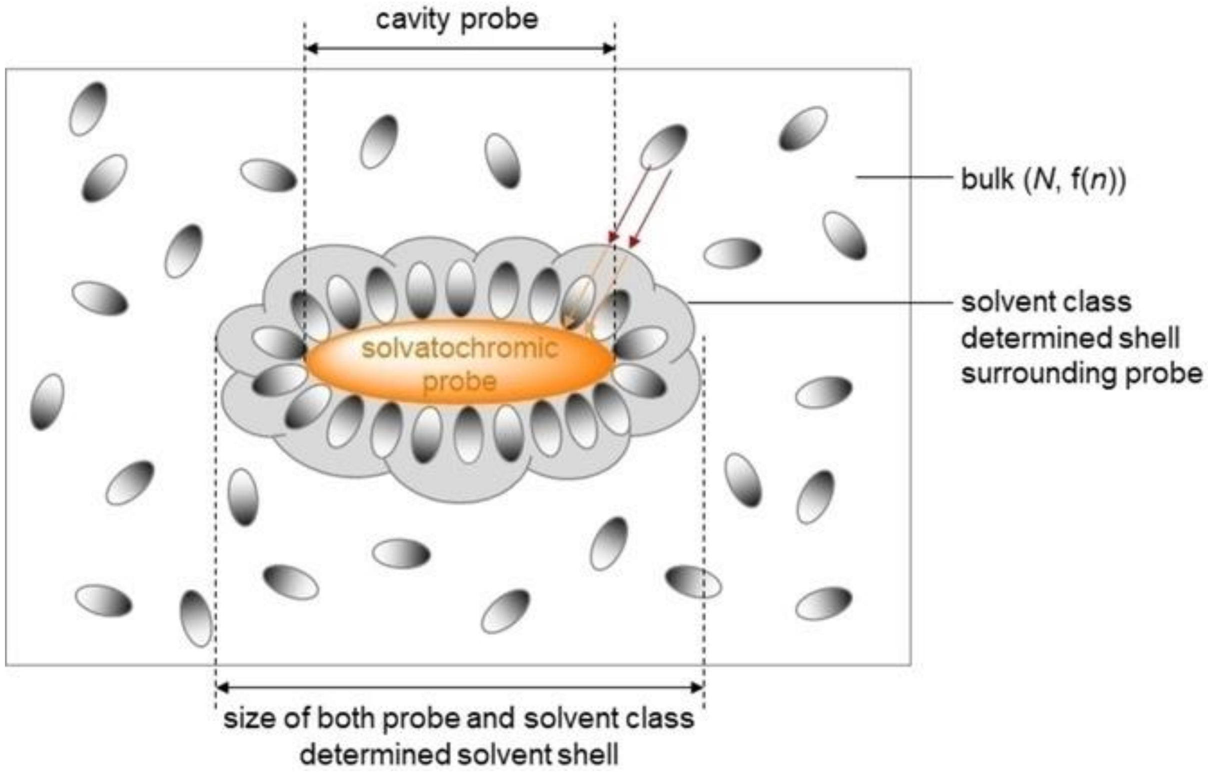
The **"overall solvation capability (or solvation power) for"**

(i) reagents and products

→ chemical equilibria

(ii) reactants and activated complexes

→ reaction rates



Picture from:
S. Spange *et al*., Chemistry—Methods, 1, 42–60, **2021**

(iii) ions or molecules in their ground and first excited state

→ different transitions energies

C. Reichardt, Empirical Parameters of the Polarity of Solvents, *Angew. Chem. Int. Ed. Eng*. **1965**, *4(1)*, 29–40. DOI: 10.1002/anie.196500291. *Angew. Chem.* **1965**, *77(1)*, 30–40. DOI: 10.1002/ange.196500291

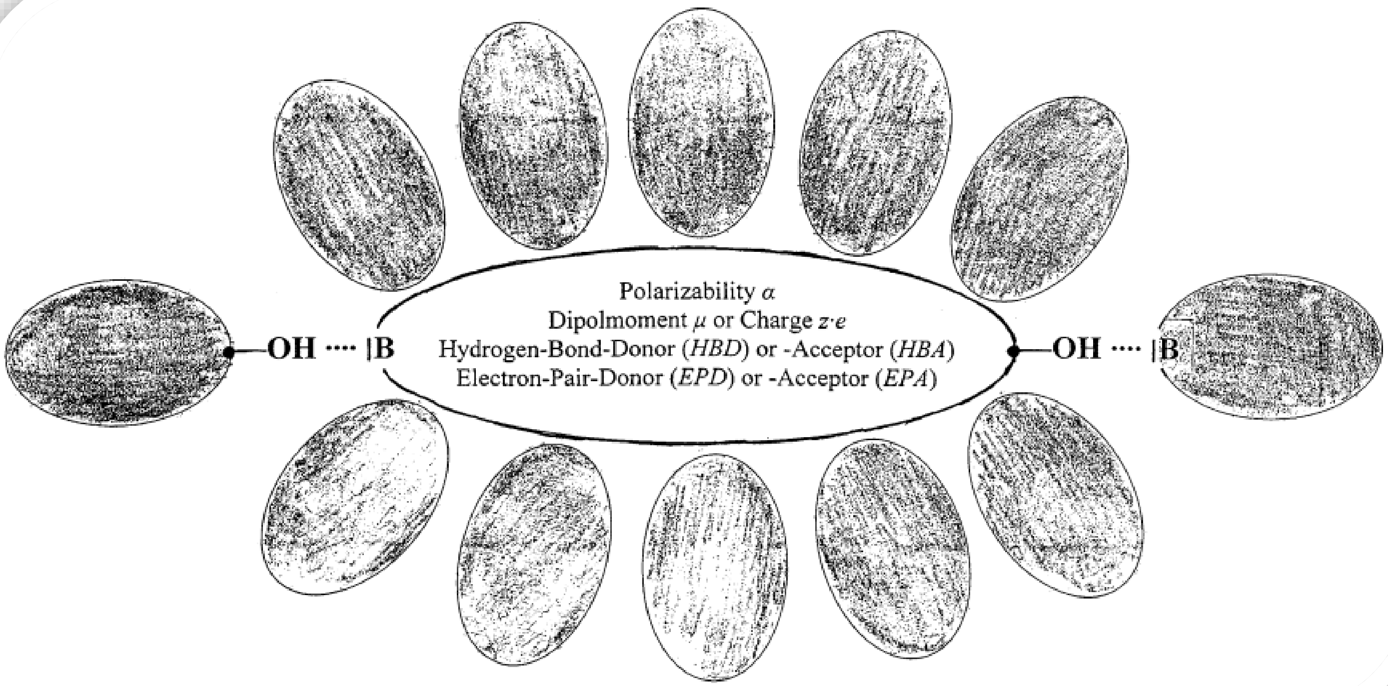
Solvent Polarity

Nonspecific Interaction Forces:

→ Instantaneous Dipole/Induced Dipole Forces (Dispersion or London Forces)
→ Dipole/Induced Dipole Forces (Induction or Debye Forces)
→ Dipole/Dipole Forces (Orientation or Keesom Forces)
→ Ion/Dipole Forces (Coulomb Forces)

Specific Interaction Forces:

→ *HBD* or/and *HBA* Interactions
→ *EPD*/*EPA* or Charge–Transfer Interactions
→ Solvophobic Interactions (only in highly structured solvents such as water)



"This **overall solvation capability** depends on the action of all possible, nonspecific and specific, intermolecular solute/solvent interactions"

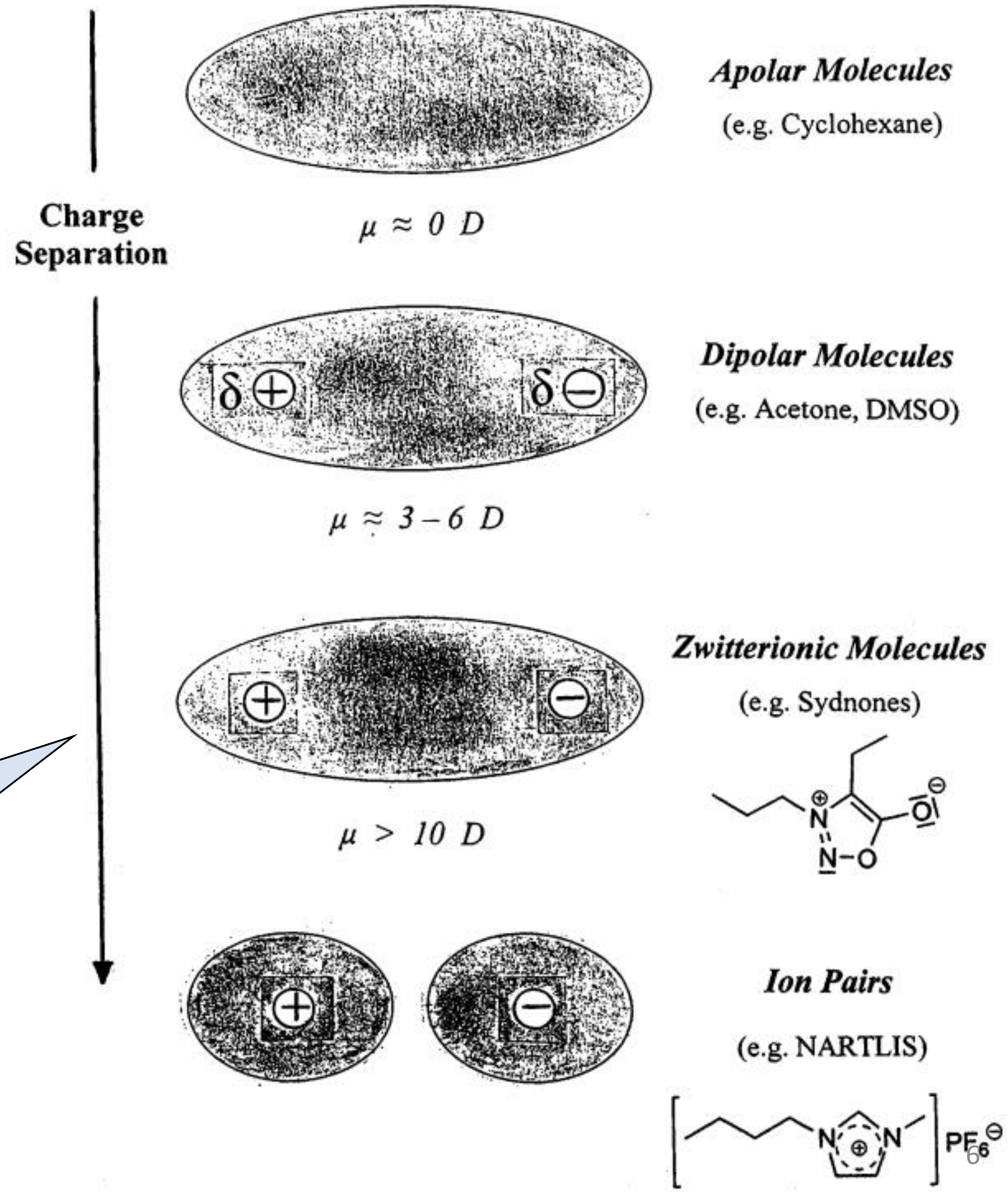
Polarity definition:
IUPAC committee responsible for the edition of the Glossary of Terms Used in Physical Organic Chemistry, 1994

C. Reichardt, *Organic Process Research & Development* 11, 105−113, **2007**

Sequence of solutes with increasing charge separation

Dipole moment:

$\mu = q.d$

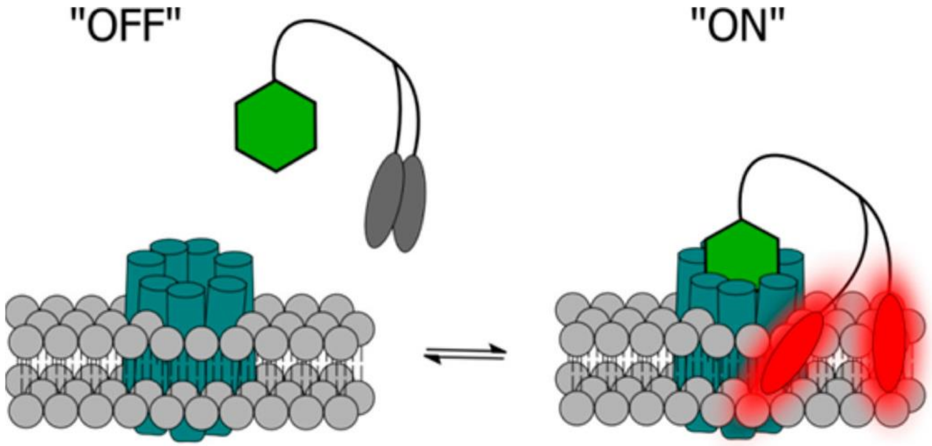


Molecular probes or dyes

- ✓ Solvent polarity cannot be measured by means of macroscopic physical solvent parameters such as relative permittivities, dipole moments, etc.

- ✓ Solvent polarity is better measured empirically by means of convenient, well-known, **solvent-sensitive reference processes that reflect all possible solute-solvent interactions**

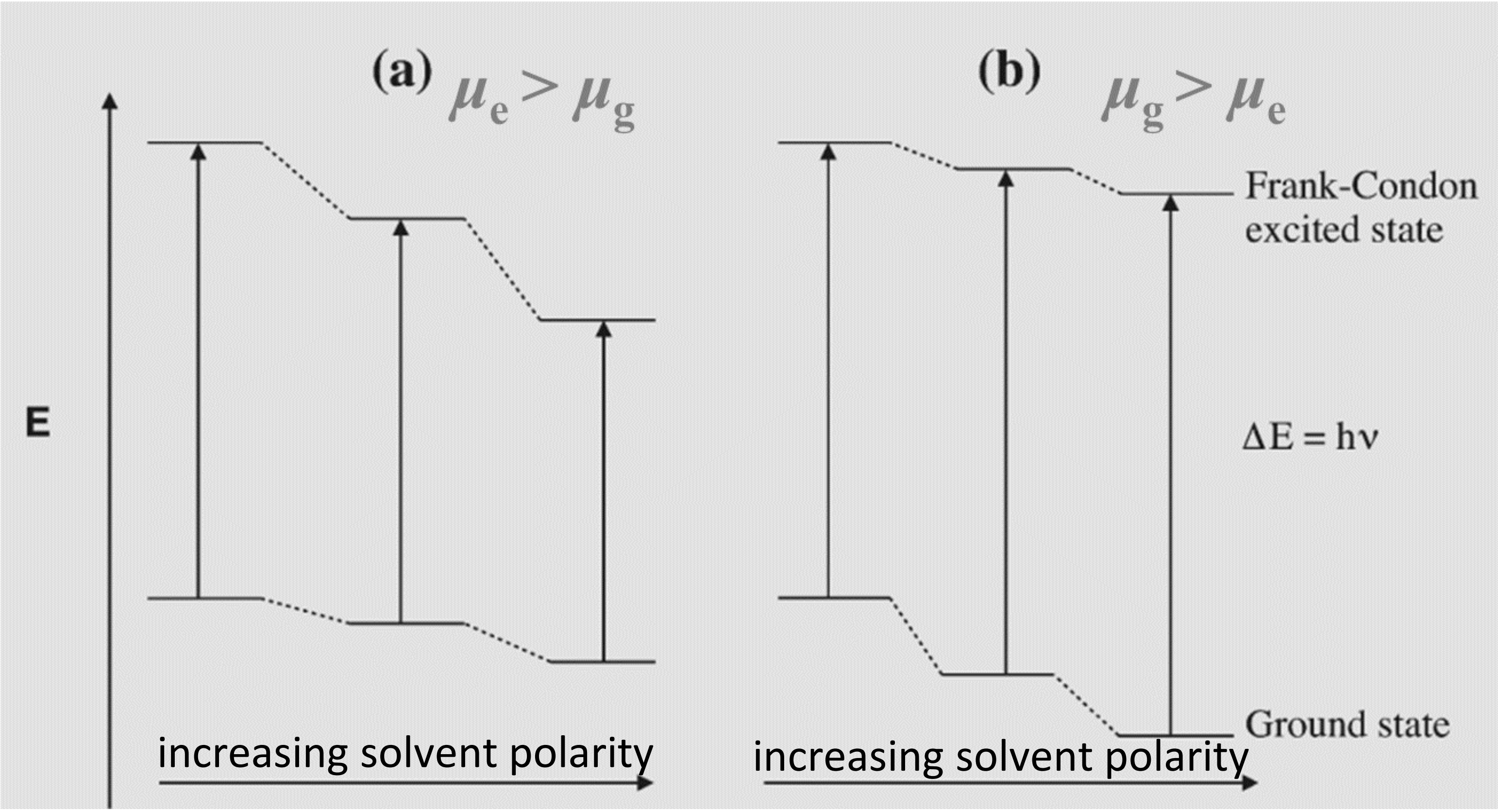
- ✓ It is necessary to choose **Molecular Probes** (standard solutes) that **reflect** all specific and non-specific solute-solvent interactions



J. Am. Chem. Soc. 2015, 137, 1, 405-412

Transition Energy of Molecular Probes (*I*) and Solvatochromism

$$(I)_S + h.\nu \rightleftharpoons (I)_S{}^*$$



(a) Positive solvatochromism: the UV-vis transition energy shifts to lower energy (longer wavelength) …

(b) Negative solvatochromism: the UV-vis transition energy shifts to higher energy (shorter wavelength) …

as the solvent polarity is increased

S. Rutan *et al.*, Applied Spectroscopy, 55,372A-370A, **2001**

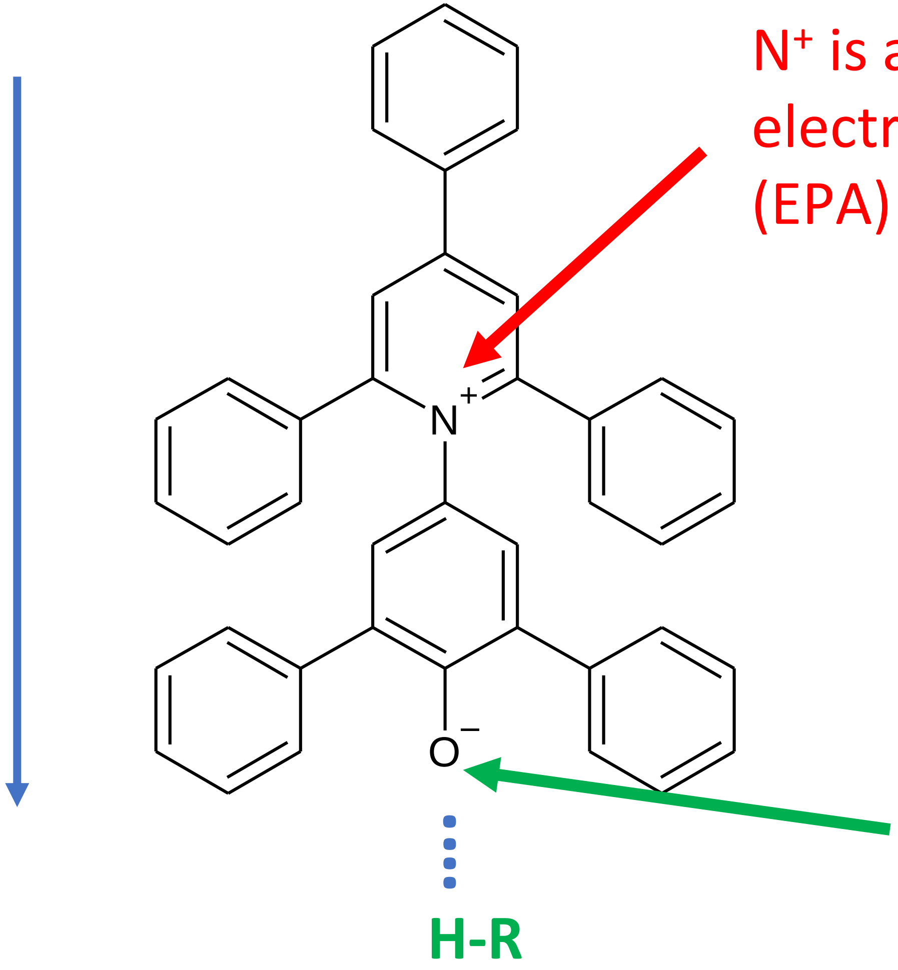
$$E_T/\text{kcal}\cdot\text{mol}^{-1} = \frac{h.c.N_A}{\lambda_{max}} = \frac{28591}{\lambda_{max}}$$

Reichardt Betaine and $E_T(30)$ parameter

RB (30) - Large polarizable aromatic π electron system (44 π electrons)

Large permanent dipole moment,

$\mu_g = 15\ D$



N^+ is a very weak electron-pair acceptor (EPA)

RB (30)- Measures the solvent dipolarity/polarizability and acidity

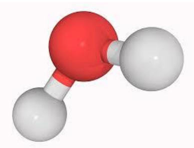
O^- group is a strong electron-pair donor (EPD), *i. e.* strong Hydrogen-bond acceptor (HBA)

Reichardt betaine dye and the solvatochromic parameter normalised

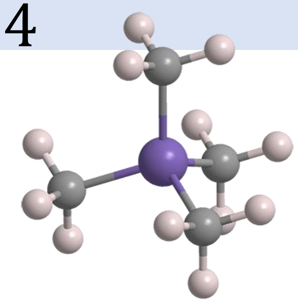
- ✓ **a change in the solvent polarity will lead to differential stabilization of the ground and excited states**, and thus, **a change in the energy gap between these electronic states.**

$$E_T^N = \frac{E_T(\text{solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})}$$

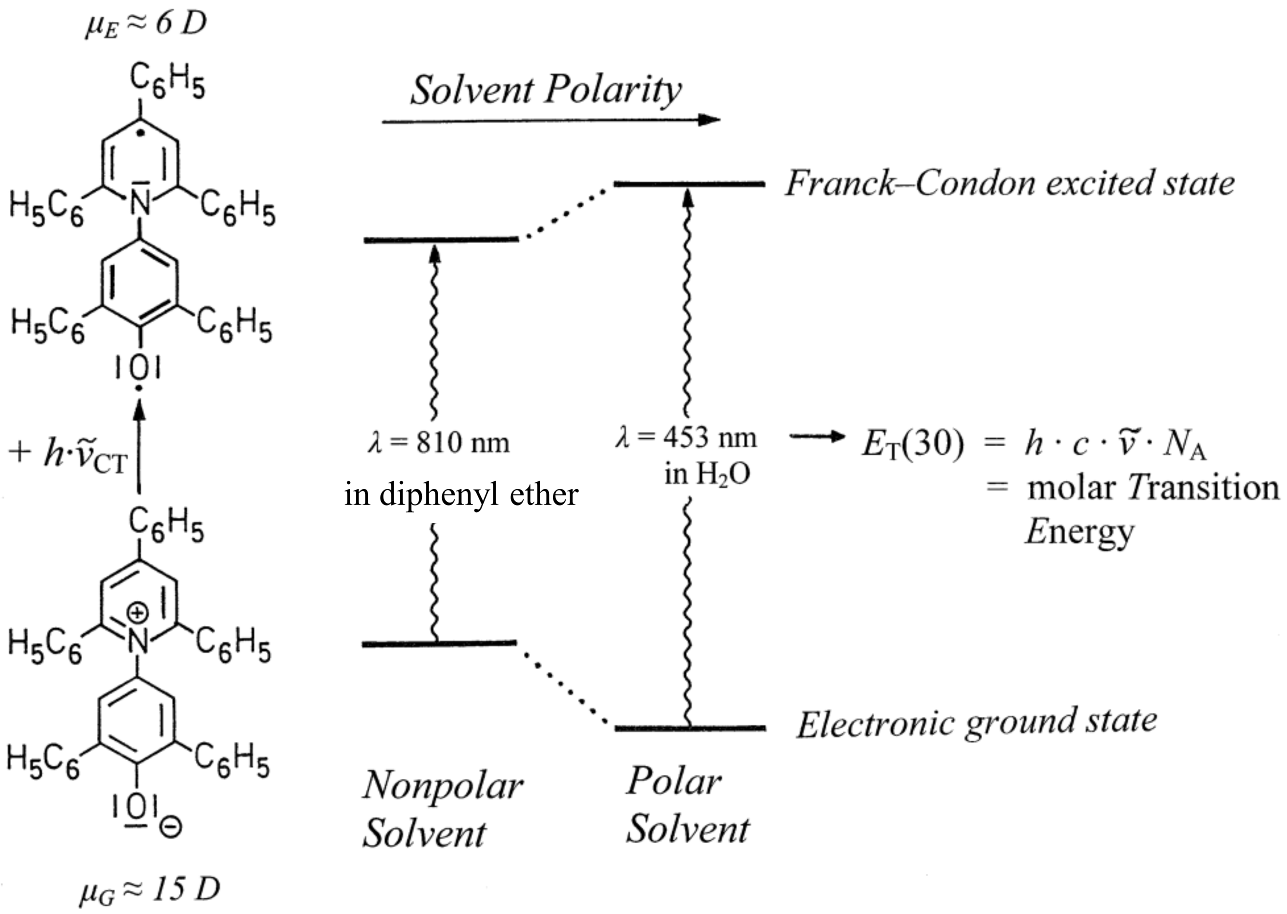
$$= \frac{E_T(\text{solvent}) - 30.7}{32.4}$$



E_T^N (water) = 1

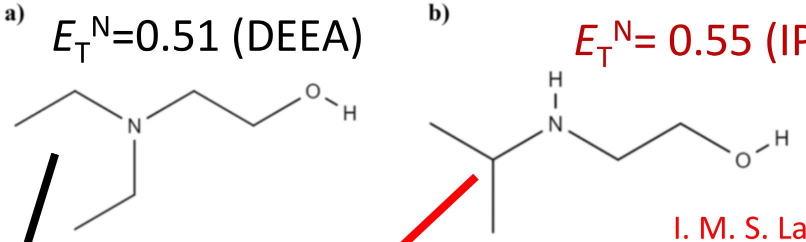


E_T^N (TMS) = 0



C. Reichardt, *Pure Appl. Chem.*, 76, 1903–1919, **2004**

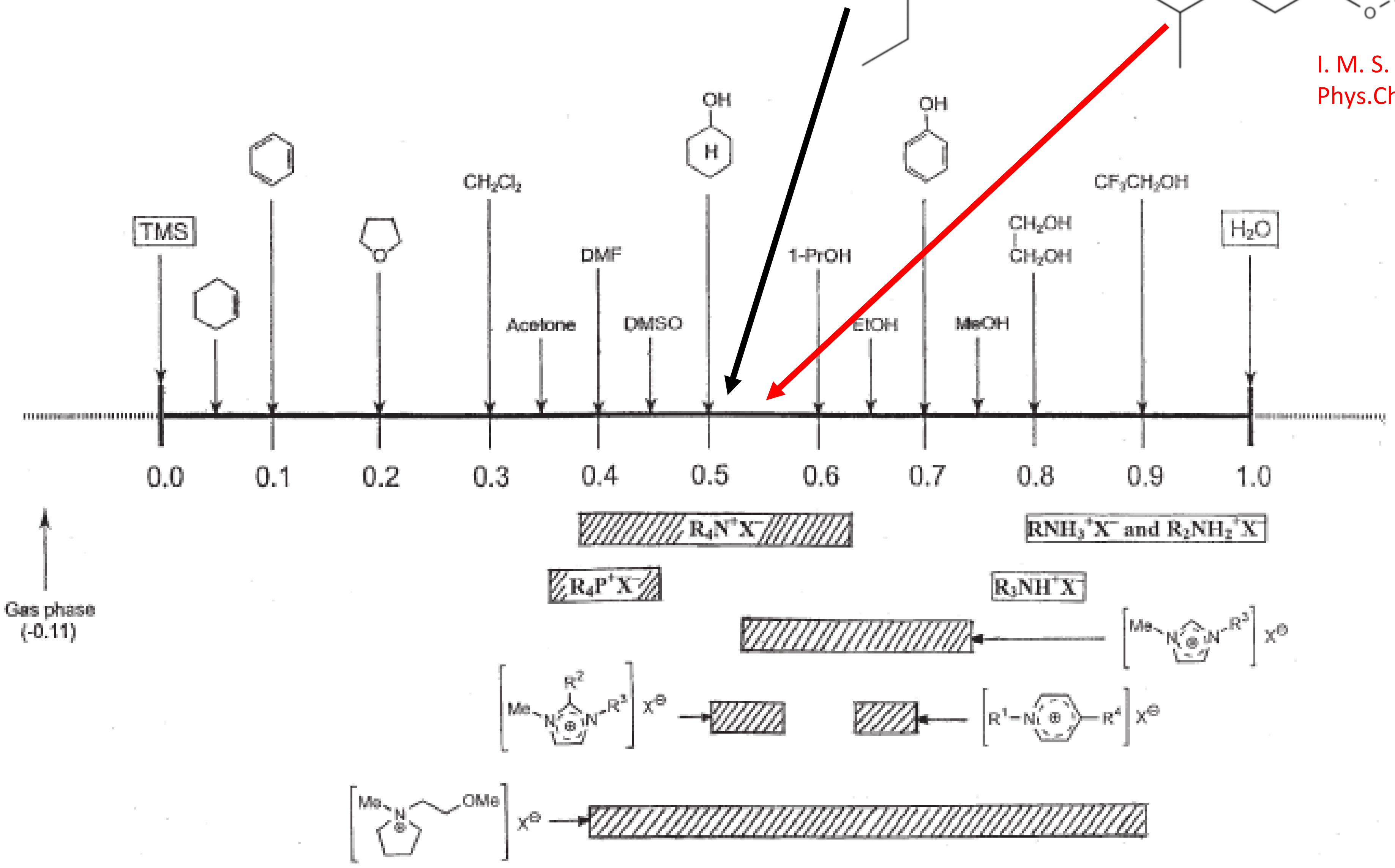
Scale of solvent polarity



E_T^N=0.51 (DEEA)

E_T^N= 0.55 (IPAE)

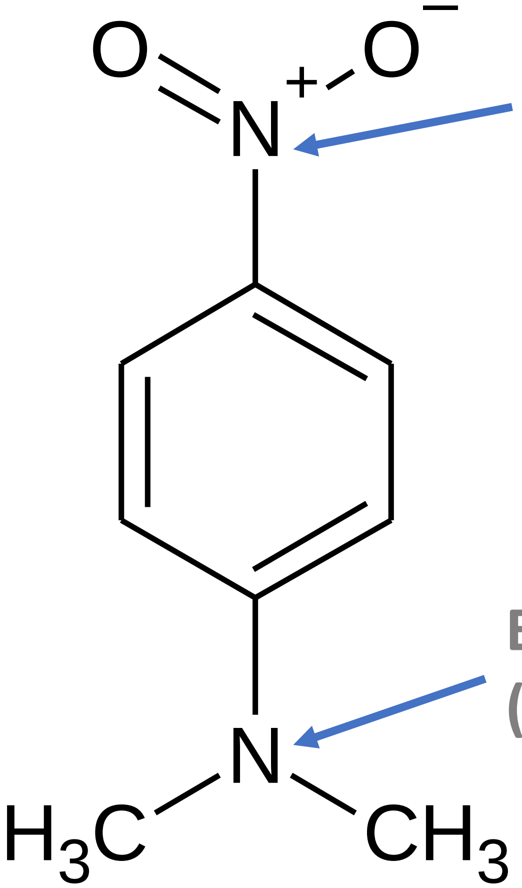
I. M. S. Lampreia *et al*.
Phys.Chem.Chem.Phys., 18, 17506, 2016



E_T^N

C. Reichardt, *Green Chem*., 7, 339 (2005)

NN-4-NA and the dipolarity/polarizability solvent parameter



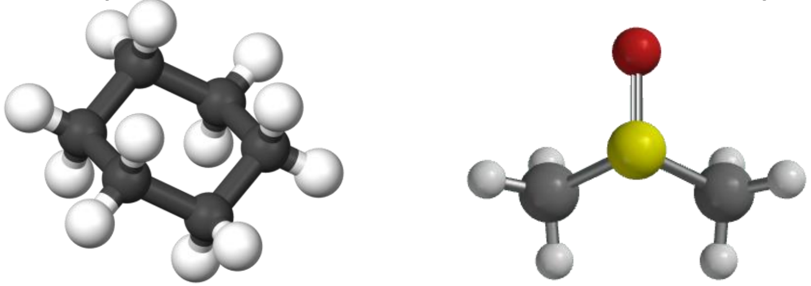
Electron-pair acceptor (EPA)

Electron-pair donor (EPD)

NN-4-NA - Measures the solvent dipolarity/polarizability

$$\boldsymbol{\pi}^* = \frac{\tilde{\nu}\,(\mathbf{NN-4-NA}) - \mathbf{28.18}}{\mathbf{-3.52}}$$

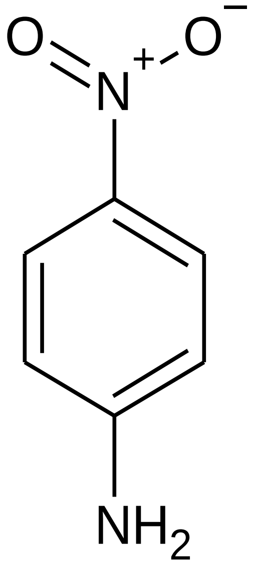
$\boldsymbol{\pi}^*$ = 0 for cyclohexane and $\boldsymbol{\pi}^*$ = 1 for dimethyl sulfoxide



M. J. Kamlet et al., (1977). Journal of the American Chemical Society, 99, 6027–6038, **1977**
doi:10.1021/ja00460a031

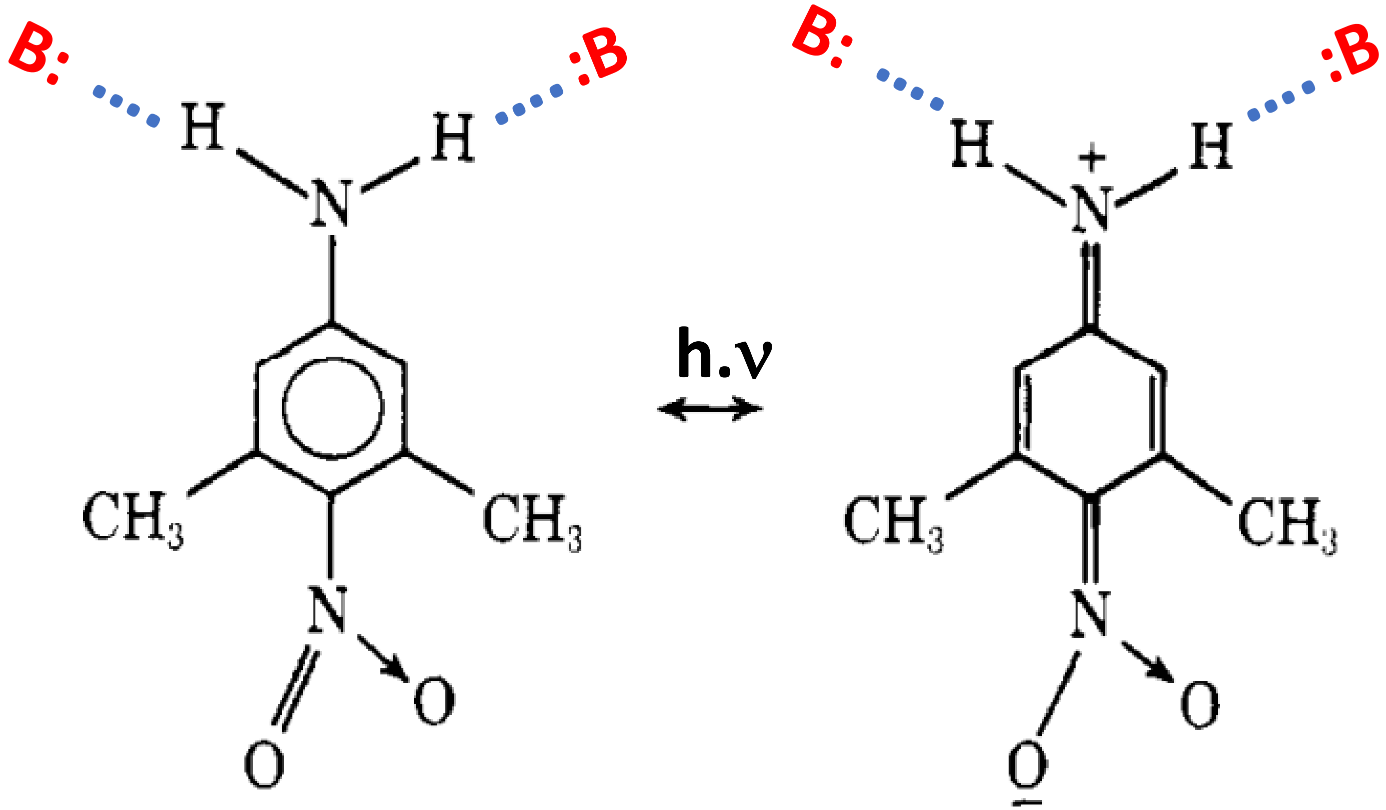
4-NA molecular probe

N is an electron-pair acceptor (EPA)

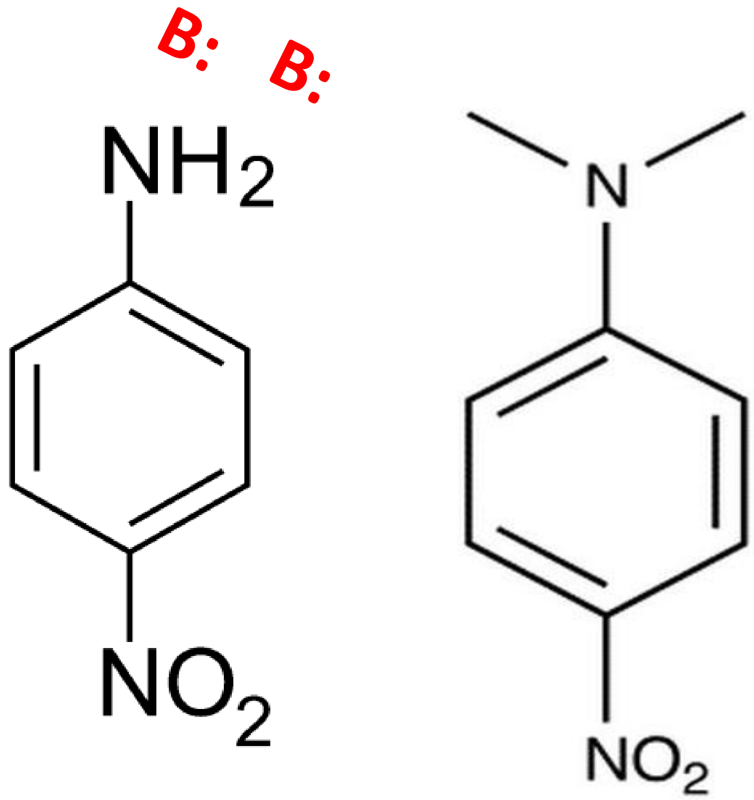


N is an electron-pair donor (EPD)

H (in R-NH_2) are good electron-pair acceptors and can form hydrogen-bonds (HB) with EPD (Bases)

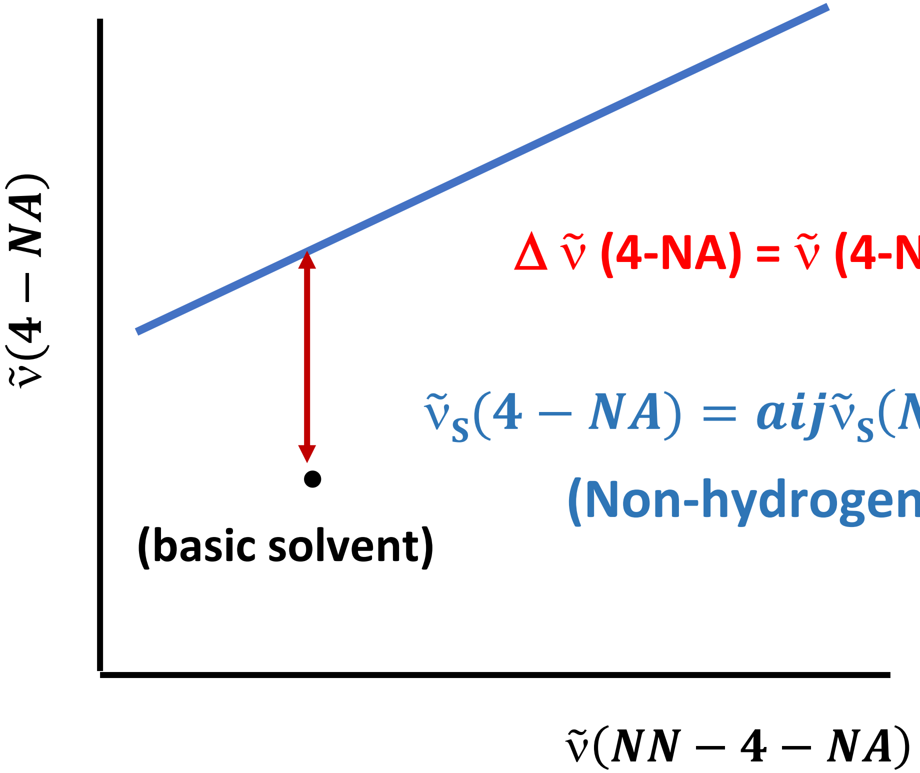


(4-NA and NN-4-NA) and determination of the solvatochromic β parameter



$$\beta = \frac{\mathbf{0.9841}\,\tilde{\mathrm{v}}(\boldsymbol{NN-4-NA}) + \mathbf{3.49} - \tilde{\mathrm{v}}(4-NA)}{2.759}$$

β =1 in hexamethylphosphoramide

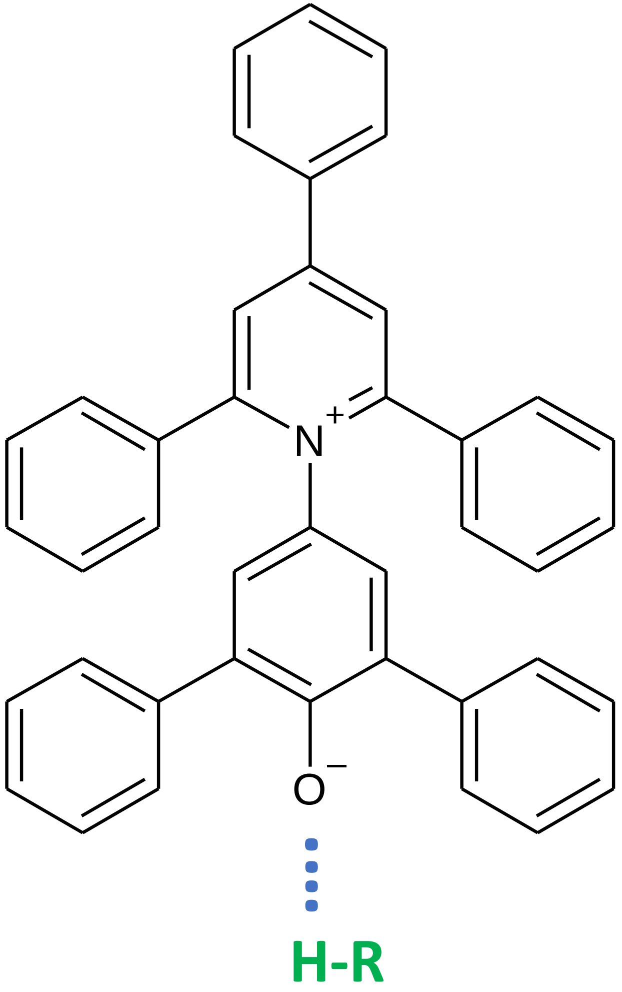


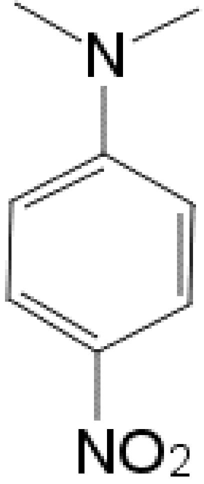
$\Delta\,\tilde{\mathrm{v}}$ (4-NA) = $\tilde{\mathrm{v}}$ (4-NA)$_{exp}$ – $\tilde{\mathrm{v}}$ (4-NA)$_{calc}$

$\tilde{\mathrm{v}}_S(\boldsymbol{4-NA}) = \boldsymbol{aij}\tilde{\mathrm{v}}_S(\boldsymbol{NN-4-NA})$**+ b$_{ij}$**

(Non-hydrogen-bonding solvents)

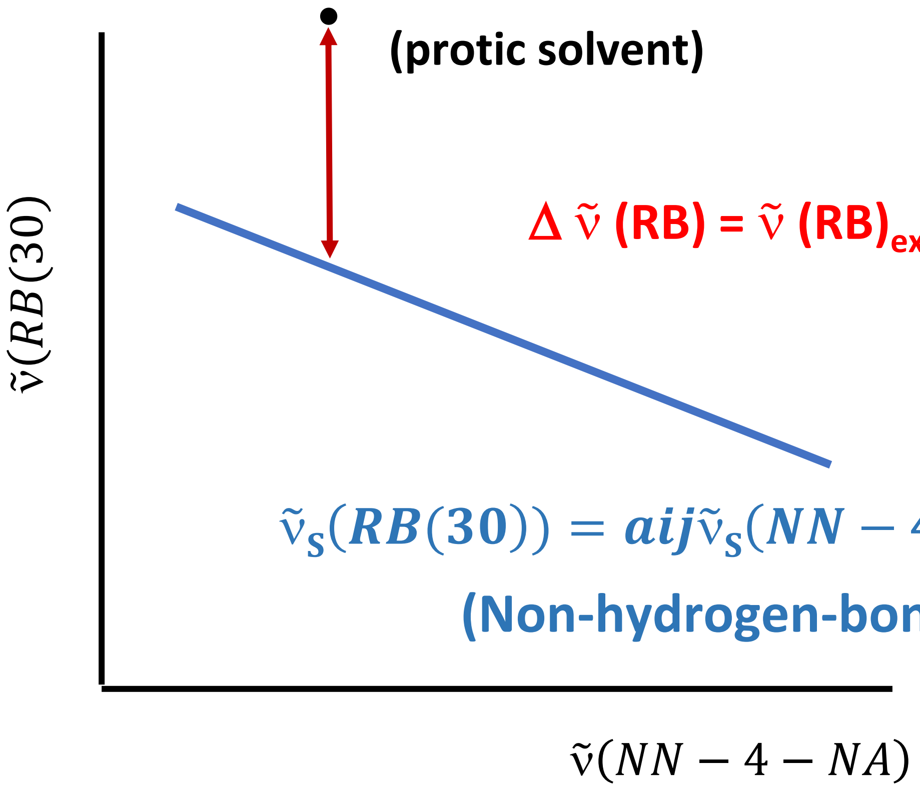
(RB(30) and NN-4-NA) and determination of the solvatochromic α parameter





$$\alpha = \frac{\mathbf{1.318}\,\tilde{\nu}(\boldsymbol{NN-4-NA}) - \mathbf{47.7} + \tilde{\nu}(RB(30))}{5.47}$$

$\alpha = 1$ in methanol



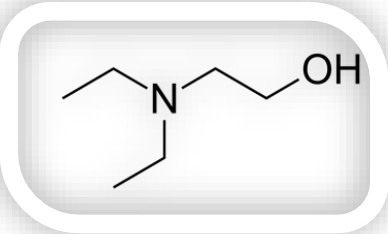
(protic solvent)

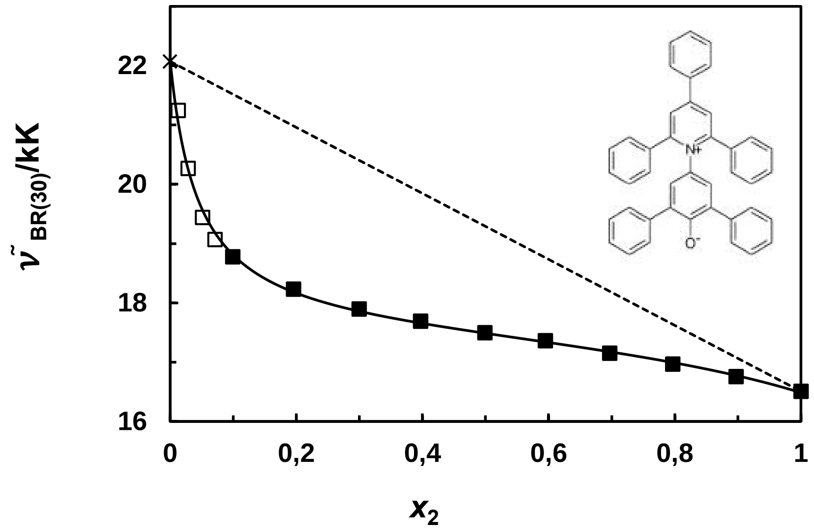
$\Delta\,\tilde{\nu}$ (RB) = $\tilde{\nu}$ (RB)$_{exp}$ − $\tilde{\nu}$ (RB)$_{calc}$

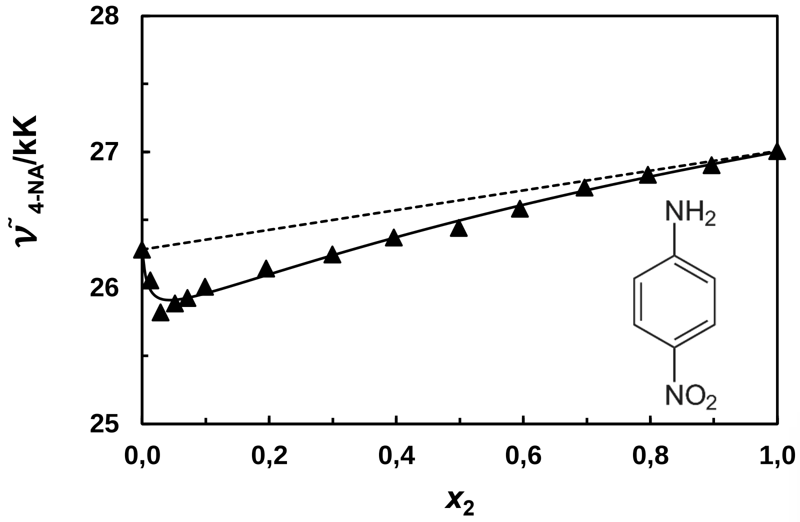
$\tilde{\nu}_S(\boldsymbol{RB(30)}) = \boldsymbol{aij}\tilde{\nu}_S(\boldsymbol{NN-4-NA})$ + b_{ij}

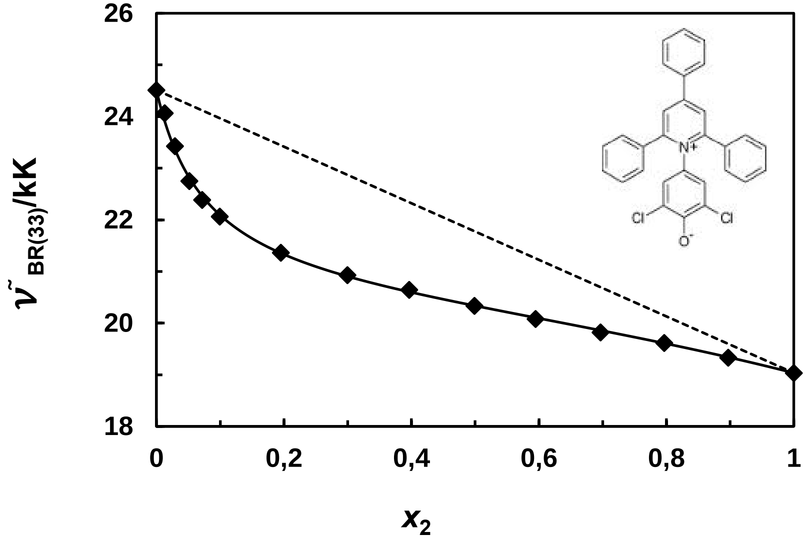
(Non-hydrogen-bonding solvents)

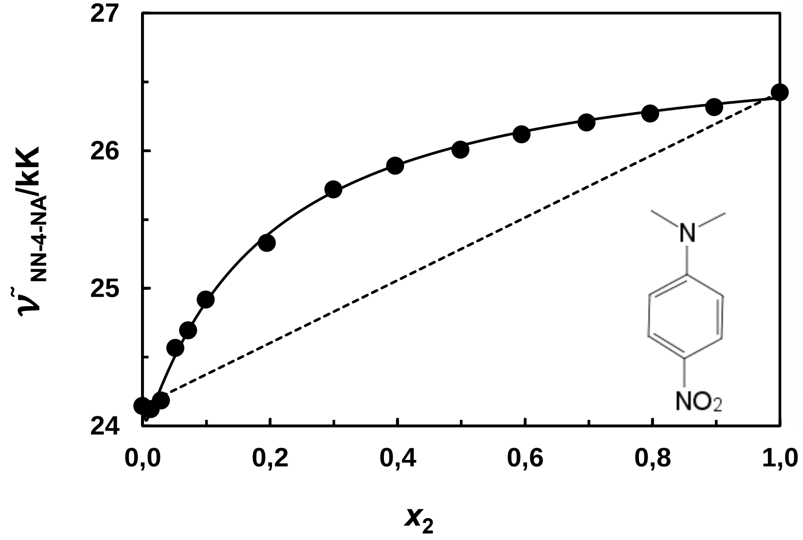
Wavenumber data obtained for system: {water + DEEA} at 298.15 K











UV-1800 SHIMADZU

Preferential Solvation Model of E. Bosch *et al.*

$$\boldsymbol{I}(\mathrm{S1})_2 + 2\mathrm{S2} \leftrightarrows \boldsymbol{I}(\mathrm{S2})_2 + 2\mathrm{S1}$$

$$\boldsymbol{I}(\mathrm{S1})_2 + \mathrm{S2} \leftrightarrows \boldsymbol{I}(\mathrm{S12})_2 + \mathrm{S1}$$

I **= Molecular Probe**

S1=Solvent 1; S2=Solvent 2; S12=Solvent 12

$$\tilde{\nu} = A + \frac{B(x_2)^2 + C(1-x_2)x_2}{(1-x_2)^2 + D(x_2)^2 + E(1-x_2)x_2}$$

$$\boldsymbol{A} = \tilde{\nu}_1 \qquad \boldsymbol{C} = f_{12/1}(\tilde{\nu}_{12} - \tilde{\nu}_1)$$

$$\boldsymbol{B} = f_{2/1}(\tilde{\nu}_2 - \tilde{\nu}_1)$$

298.15 K	***A*^{a}/kK**	***B*/kK**	***C*/kK**	***D* = $f_{2/1}$**	***E* = $f_{12/1}$**	**$f_{12/2}$**	***N*^{b}**	***R*$^{2\,c}$**	**σ_{fit}/kK^{d}**	***F*^{e}**
BR(30)	22.07^{f}	-46.86	-104.05	8.39	23.53	2.80	15	0.99	0.09	164037
BR(33)	24.52	-43,16	-54.03	7,87	14.36	1.82		0.99	0.06	414819
4-NA	26,28	117.33	-57.7	163.29	112.27	0.69		0.98	0.05	1139440
NN-4-NA	23.65	4425.64	-78.9	1981.93	320.58	0.16		0.99	0.04	1323560

[a] Fixed $\tilde{\nu}_1$ for $x_2 = 0$; [b] Number of experimental data; [c] Determination coefficient; [d] Standard deviation of the fit; [e] Statistical parameter *F*; [f] Value from lit.

Preferential Solvation Model of E. Bosch *et al.*

Component 1: water
Component 2: DEEA

$$f_{2/1} = \frac{x_2^s/x_1^s}{(x_2/x_1)^2}$$

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{(x_2/x_1)}$$

$$f_{12/2} = \frac{f_{12/1}}{f_{2/1}}$$

Preferential Solvation Order:

BR(30): S12>S2>S1

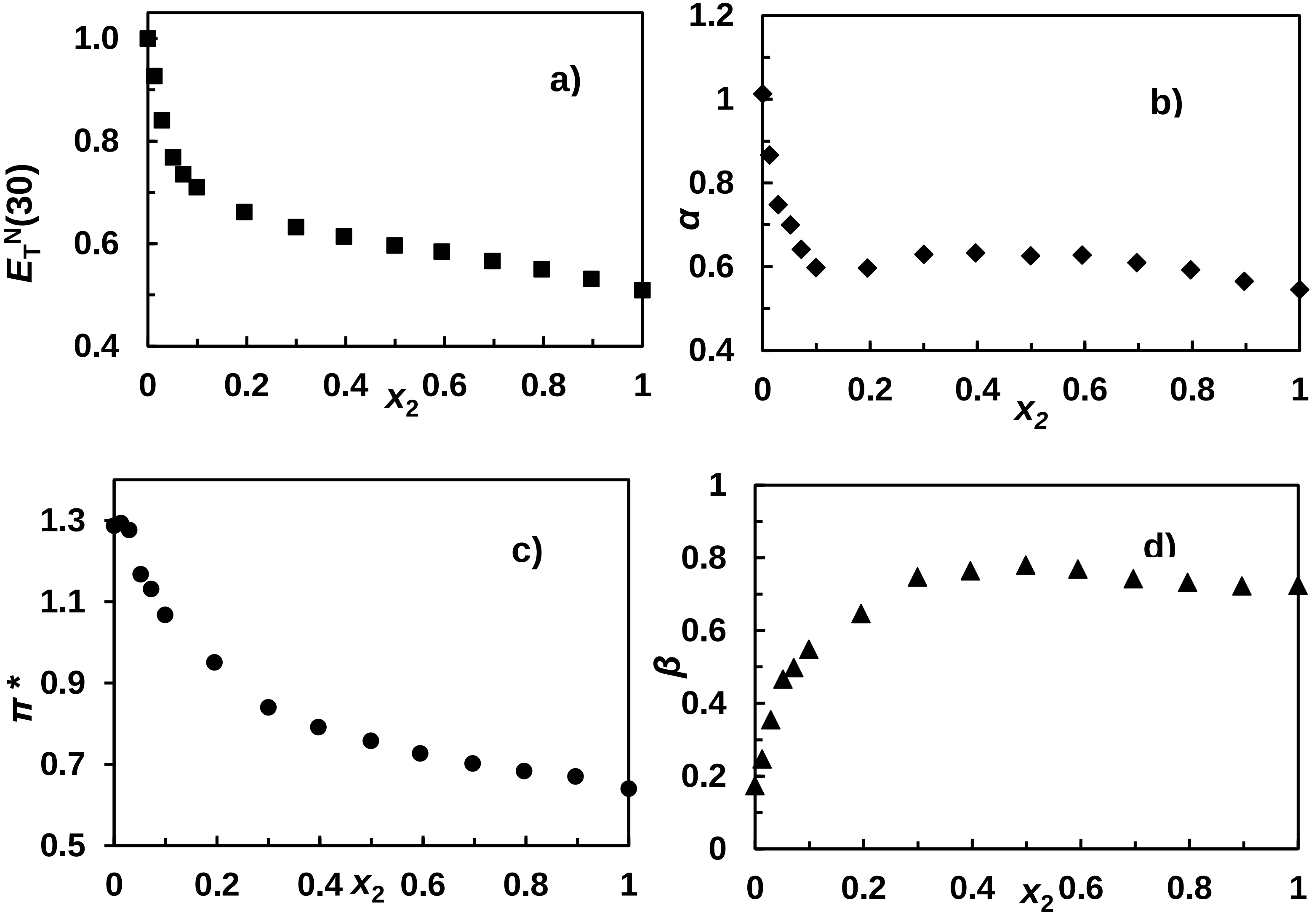
BR(33): S12 ≅ S2>S1

4-NA and NN-4-NA: S2>S12>S1

x_{i}- mole fraction of i in the bulk

x_{i}^{s}- mole fraction of i in the cybotatic region

Solvatochromic parameters for system: {water + DEEA}

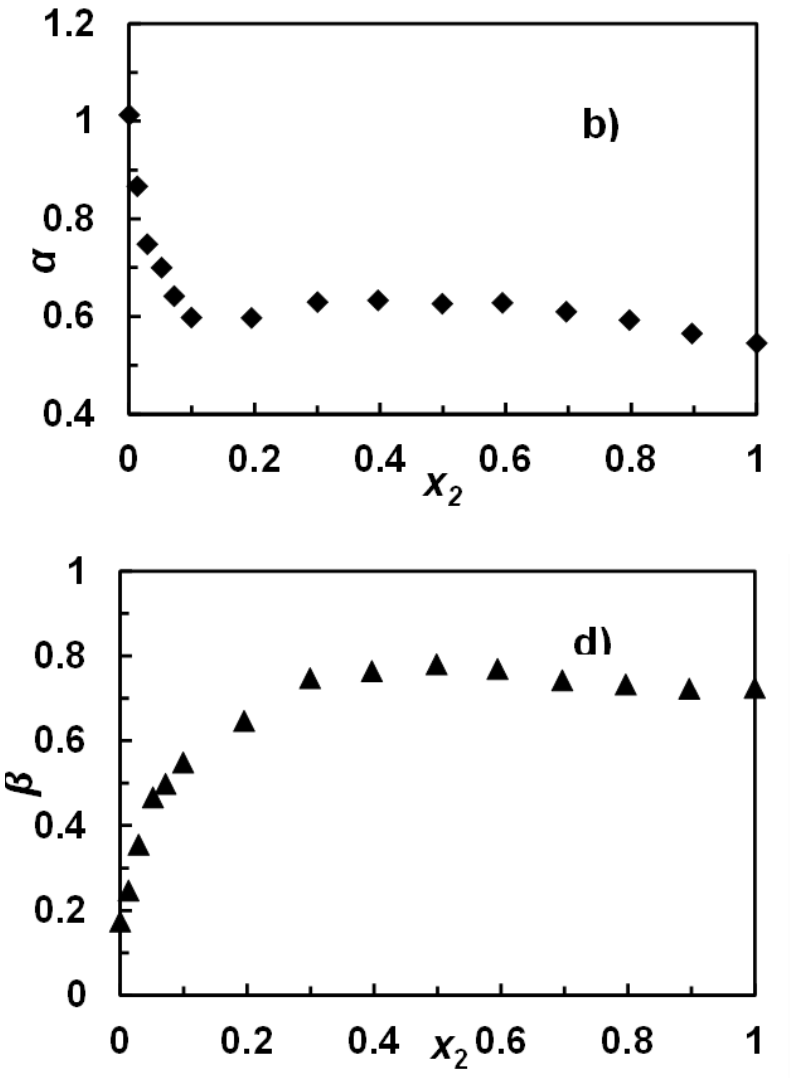


- ✓ $a) E_T^N(30)$ jointly measuring the dipolarity/polarizability and the acidity of the solvent, depicts a sharp decrease until $x_2 \cong 0.1$ followed by a slight decrease up to $x_2 = 1$

- ✓ b) and c) the separation of solvent effects allows to infer that, until $x_2 = 0.1$, the main interaction mechanism is driven by α since the π^* parameter presents a very slight increase in the water very-rich region.

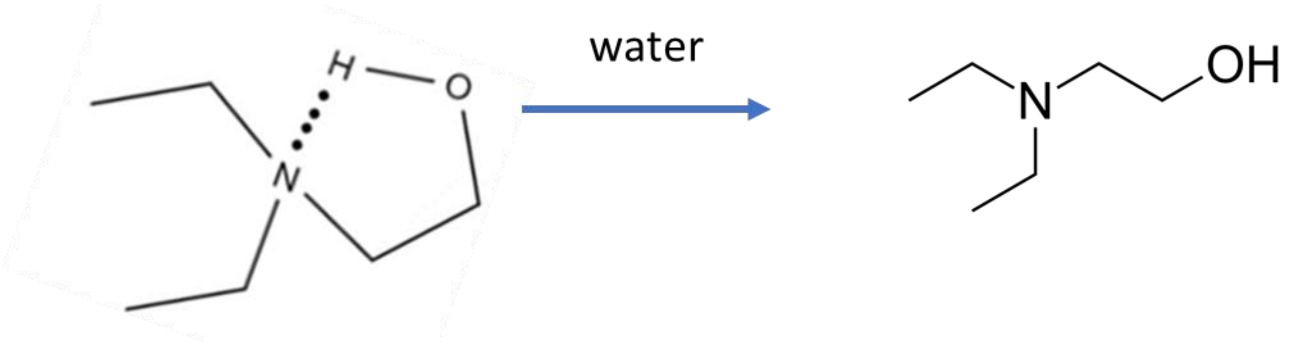
- ✓ d) in the range of mole fractions $0.3 < x_2 < 0.7$ (observed in β) a slight synergistic effect is observed

Solvatochromic parameters for system: {water + DEEA}

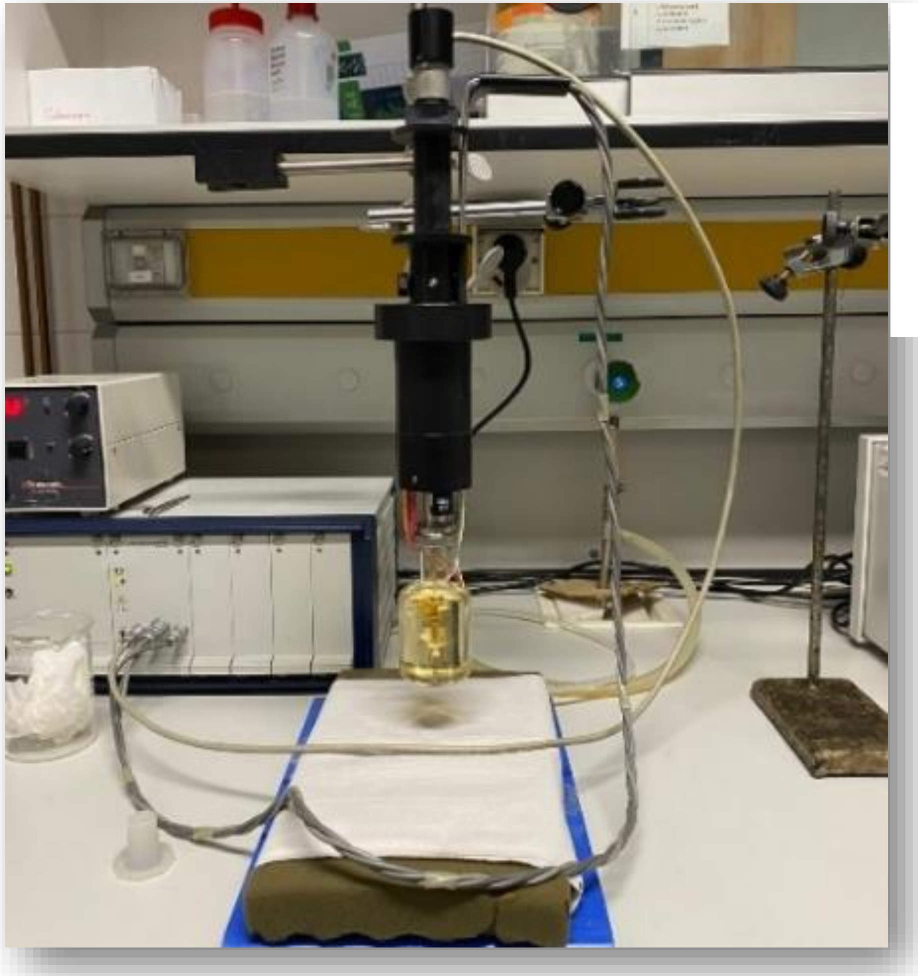


- ✓ Starting from the pure DEEA the addition of water molecules produces an increase in the acidity of the solvent and a simultaneous increase in basicity, in the composition range ($0.5 < x_2 < 1$)

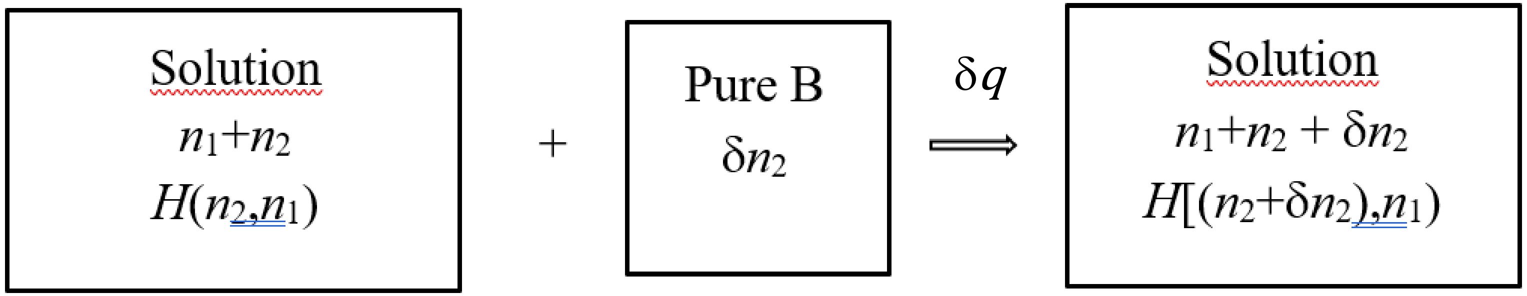
This feature is probably due to the breaking of the intramolecular N•••HO bond in DEEA, increasing the electron pair donor ability (basicity) as well as the hydrogen-bond donor ability of the solvent



Excess partial molar enthalpies, H_i^{E} $(i = 1 \text{ or } 2)$



A semi-adiabatic isoperibol thermometric precision solution calorimeter with a resolution in temperature around 1 μK



Solution

n_1+n_2

$H(n_2,n_1)$

$+$

Pure B

δn_2

$\xrightarrow{\delta q}$

Solution

$n_1+n_2+\delta n_2$

$H[(n_2+\delta n_2),n_1)$

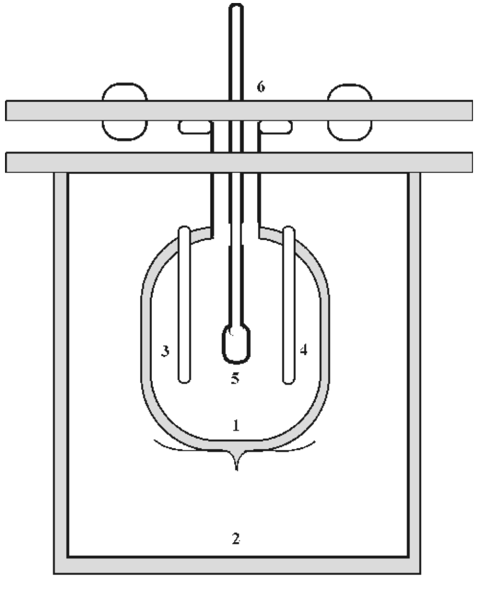
Schematic view of the experimental procedure of obtaining partial molar enthalpy of the component 2 of a binary mixture (1+2)

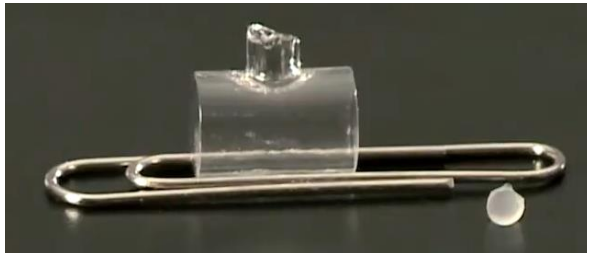
$$\delta q = H[(n_2+\delta n_2),n_1) - H(n_2,n_1) - \delta n_2 H_2^0$$

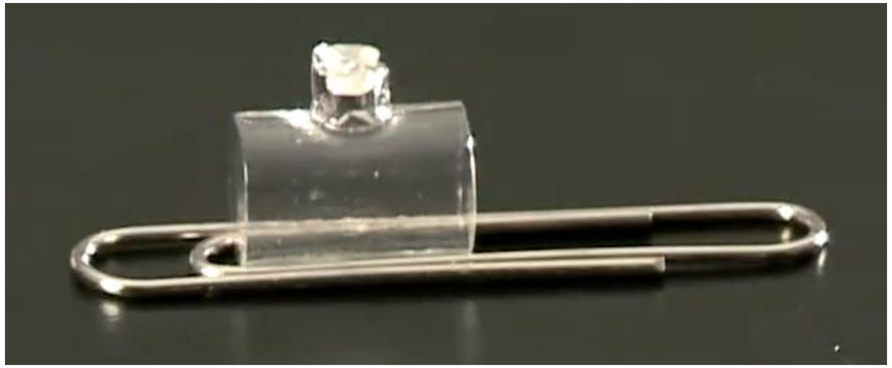
$$\delta q/\delta n_2 \quad = (\partial H/\partial n_2)_{T,P,n_1} - H_2^0 = H_2^{\mathrm{E}}$$

$$H_i^{\mathrm{E}} = (\partial H^{\mathrm{E}}/\partial n_i)_{P,T,n_j}$$

Isoperibol solution calorimeter and ampoule weighing and filling process

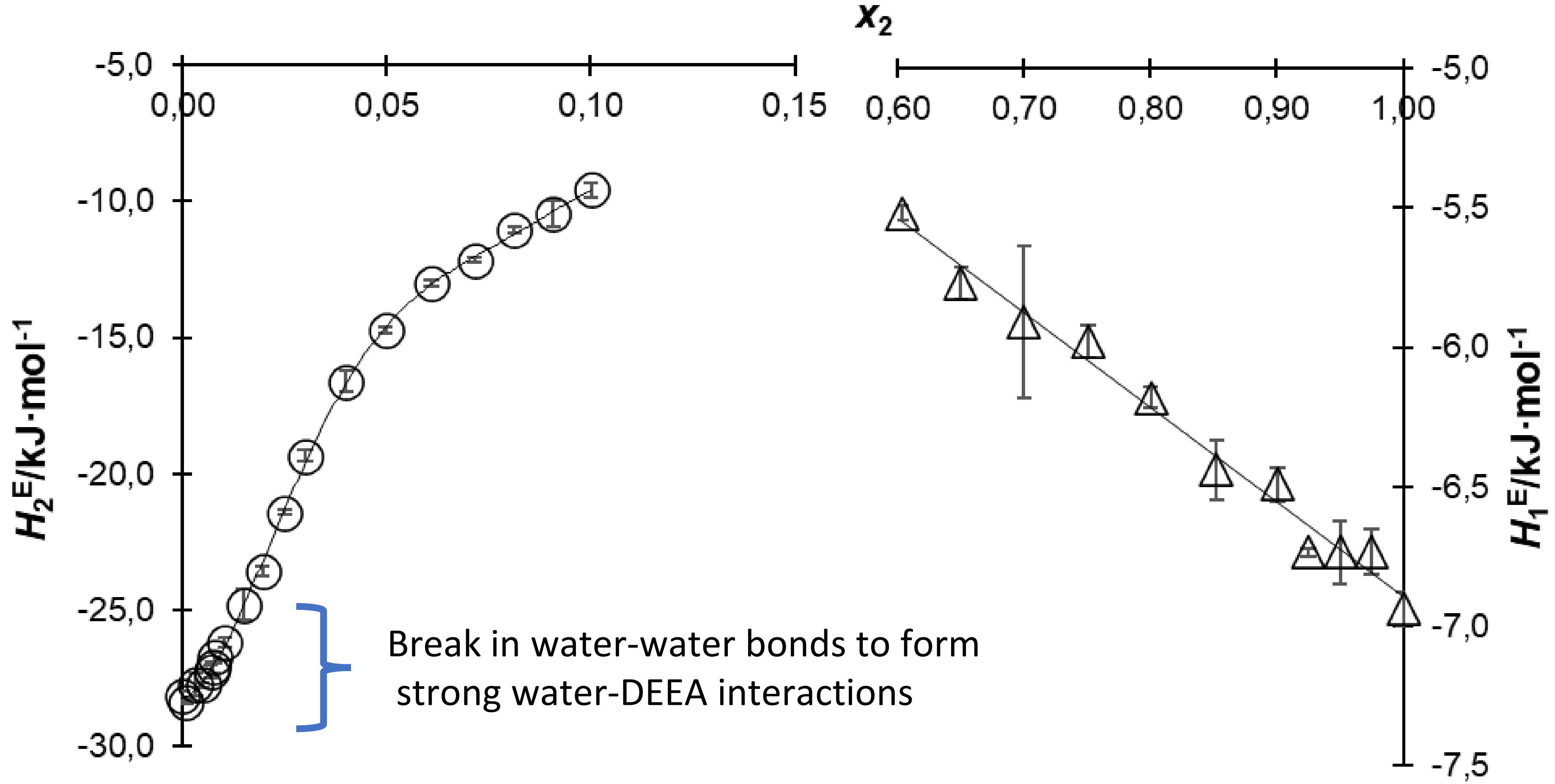






https://youtu.be/gRoxxnDI7r8

Excess partial molar enthalpies, $H_{\mathrm{i}}^{\mathrm{E}}$ $(\mathrm{i} = 1 \text{ or } 2)$



Break in water-water bonds to form strong water-DEEA interactions

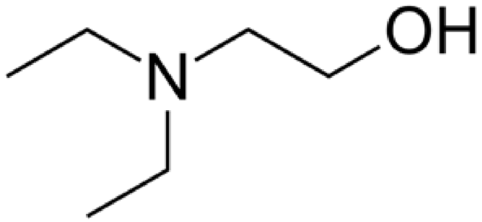
- ✓ Both exothermic processes, but the left process is more negative at infinite dilution
- ✓ On left: Very strong hydrophilic interactions water-DEEA with a change in aggregation pattern at $x_2 \approx 0.02$ and the hydrophobic behaviour prevails giving rise to “aggregative species”

Limiting excess partial molar enthalpies, $H_i^{\mathrm{E},\infty}$ $(i = 2)$

✓ the branching effect induces more negative $H_2^{\mathrm{E},\infty}$ values

branched amphiphilic

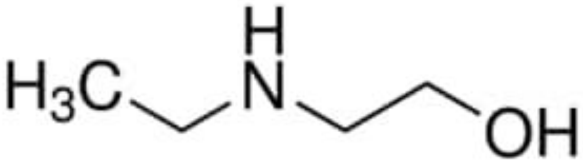
$H_2^{\mathrm{E},\infty}$ / $kJ.mol^{-1}$



2-(Diethylamino)ethanol (DEEA)

– 28.2

non- branched amphiphilic



2-(Ethylamino) ethanol (EEA)

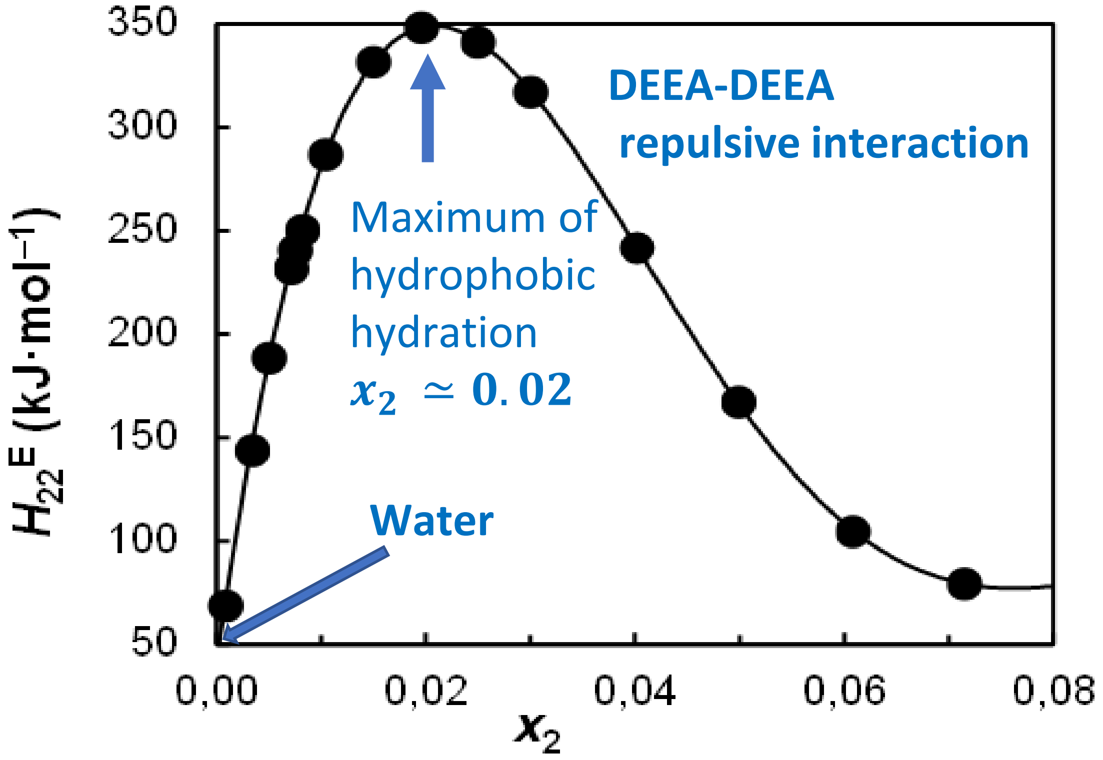
-21.4

DOI: 10.1021/je960304u

Energetic contributions of solute *i*-solute *i* interactions, $H^{\mathrm{E}}_{i,i}$ $(i = 1 \text{ or } 2)$

$$H^{\mathrm{E}}_{11\text{ or }22} = (n_1 + n_2)\left(\partial H^{\mathrm{E}}_{1\text{ or }2}/\partial n_{1\text{ or }2}\right)_{T,P,n_{2\text{ or }1}} = (1 - x_{1\text{ or }2})\ \left(\partial H^{\mathrm{E}}_{1\text{ or }2}/\partial x_{1\text{ or }2}\right)_{T,P}$$

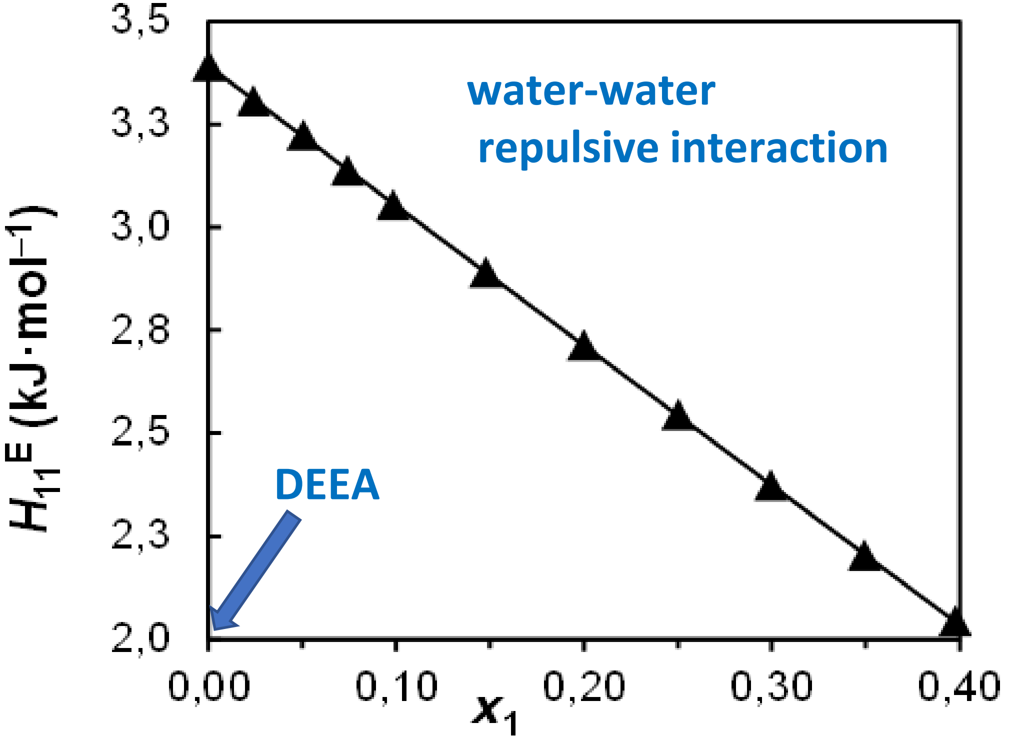
$H^{\mathrm{E}}_{i,i}$ signifies the effect of additional *i* molecules on the value of H^{E}_{i}



DEEA-DEEA repulsive interaction

Maximum of hydrophobic hydration $\boldsymbol{x_2 \simeq 0.02}$

Water



water-water repulsive interaction

DEEA

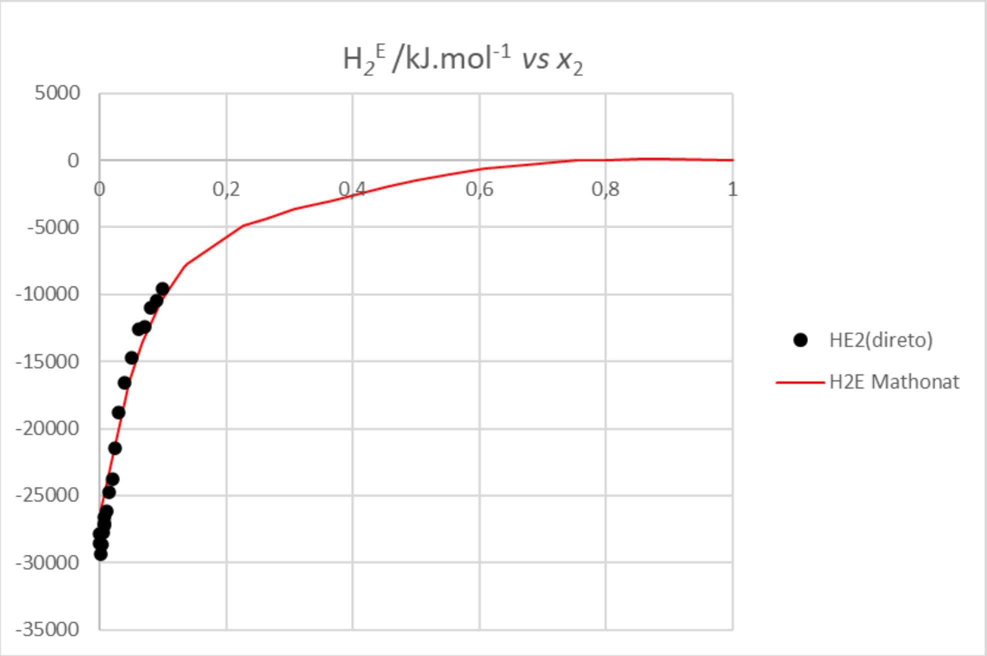
✓ DEEA-DEEA and water-water interactions are both “repulsive” in terms of enthalpy

Multicomponent linear regression analysis

Separating the global solvent effects

$$H_2^{\mathrm{E}} = 4.8(\pm 2) - 18.4(\pm 0.9)\pi^* - 10.0(\pm 1)\alpha + 18.2(\pm 1)\beta$$

$$(N = 20; R^2 = 0.998; \sigma_{\mathrm{fit}} = 0.3; F = 2664)$$



Mathonat, C. *et al.*, *J. Chem. Eng. Data*; 42: 993-995, **1997**

- ✓ π^* and α contributions are both negative
- ✓ β contribution is positive and is very important in the range: $0.8 < x_2 < 1$

General conclusions

- ✓ **The details of water- DEEA interactions** were elucidated from the behavior of the second and third derivatives of Gibbs Energy

- ✓ The polarity characterization of the water-DEEA solvent system allowed to conclude that **this mixture is promising for CO_2 capture** in the mole fractions range **0.3** < $x_{DEEA} < 0.6$

- ✓ The correlation between H^{E}_{DEEA} and the solvatochromic parameters revealed that the **solvent dipolarity/polarizabiliy and acidity** favor exothermic DEEA-water interactions

N,*N*-diethylethanolamine (DEEA) **30%** + H_2O 70%

α_{CO_2} = 0.83

ΔH (kJ/mole of CO_2)= -73.17

T= 313.15 K

Hadri H. *et al*. Applied Energy, 185, 1433-1449, **2017**

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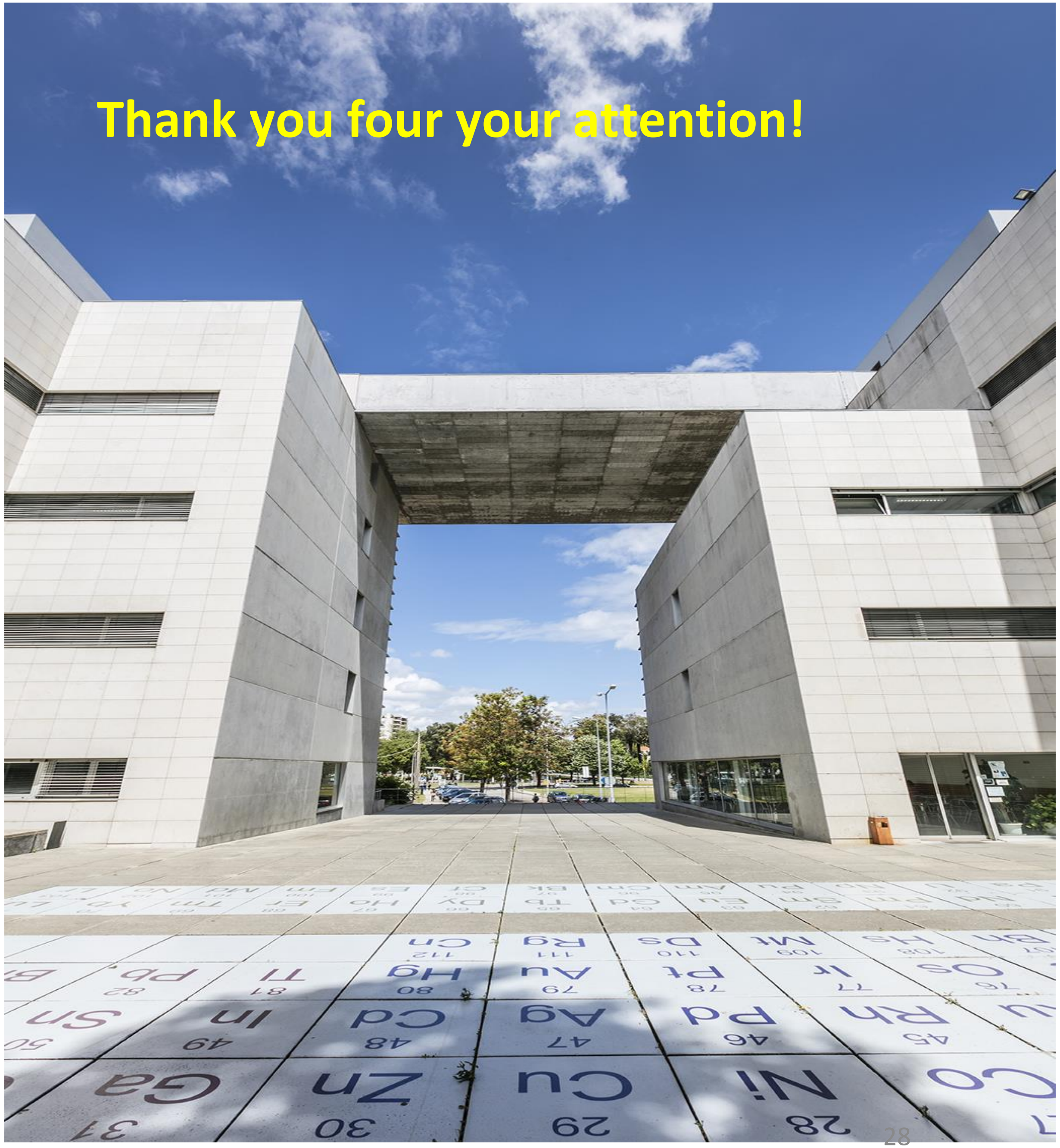

Thank you four your attention!