IEAGHG

PCCC-8

LSPC
Laboratoire de sécurité des procédés chimiques

About benchmarking of amino acid (AA) performance for CO_2 absorption

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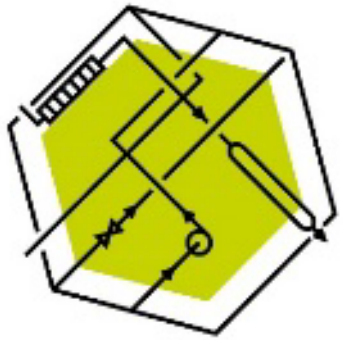
Rouen

LSPC at a glance



LSPC
Laboratoire de sécurité des procédés chimiques

12 researchers in chemical engineering

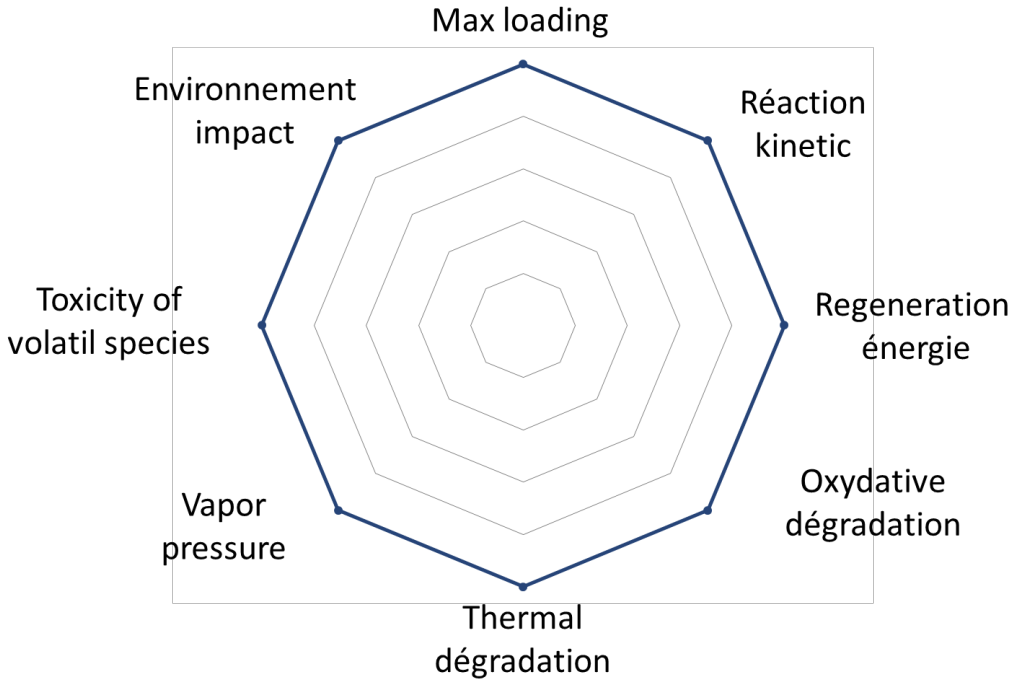
- Process Safety
- Biomass valorization
- CO_2 capture and valorization

Expertise

- Heat and mass transfer
- Calorimetric approach
- Kinetic determination

The quest of the ideal solvent…

- Rapid reaction with CO2
- Low regeneration energy
- High absorption capacity
- No degradation
- No toxicity
- Regeneration without loss



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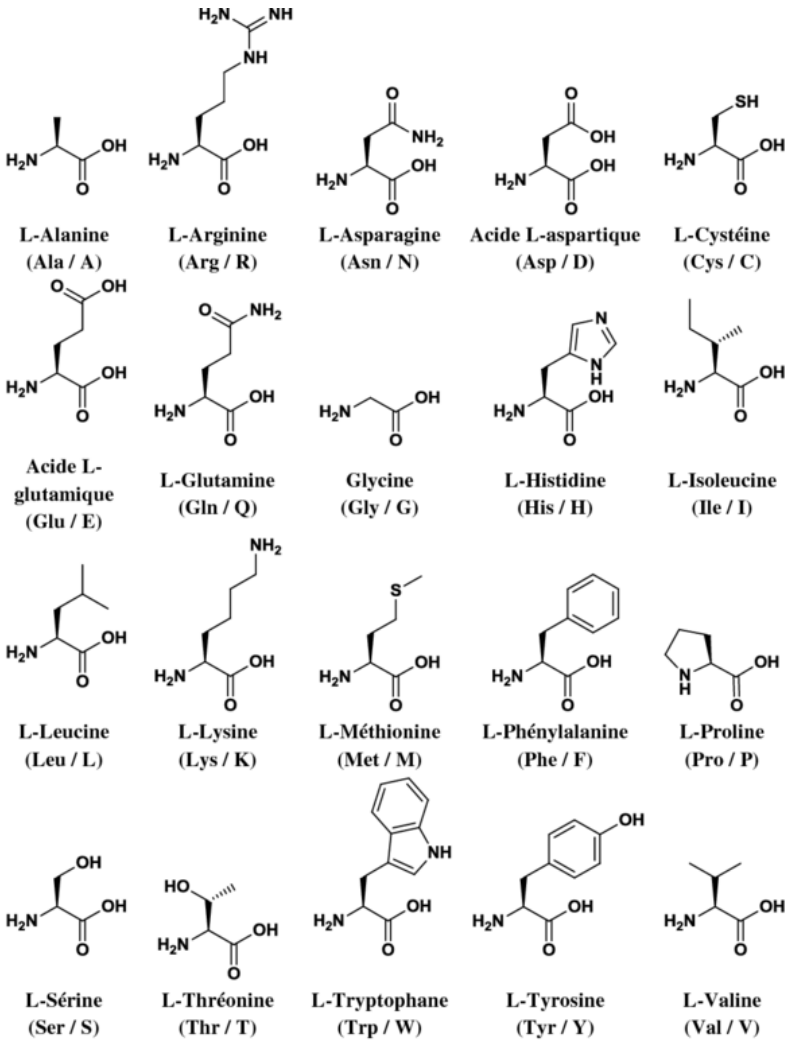
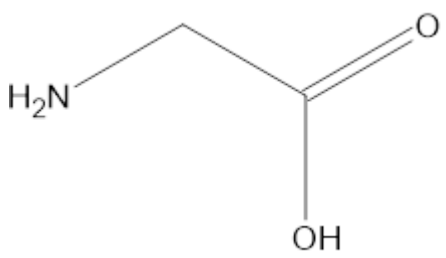
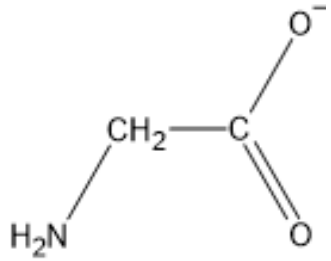
More than 500 amino acids exist in nature.



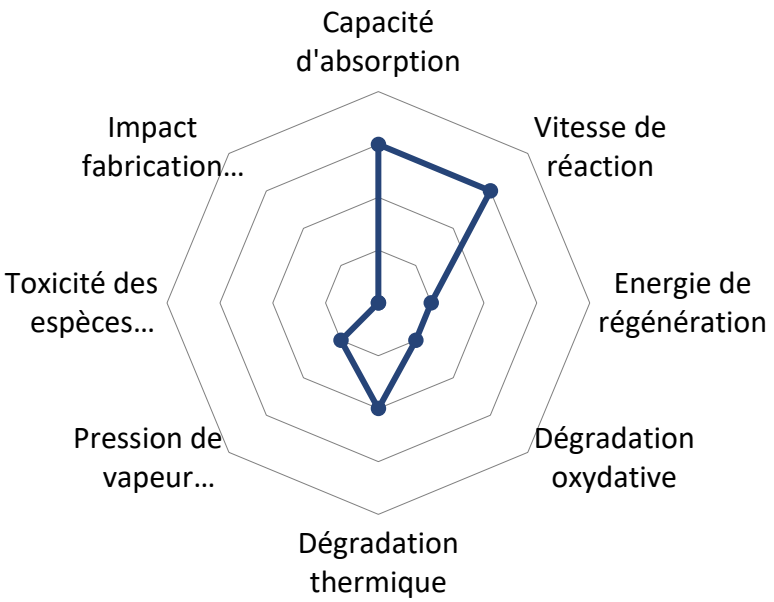
- Same reaction system as primary and secondary alkanolamines
- Possible high reaction rates
- Low oxidative degradation
- High absorption capacity
- Possibility of synthesizing them in an eco-responsible way
- Low toxicity
- Very low volatility





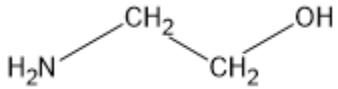
Glycine (Gly)

MEA 30 %

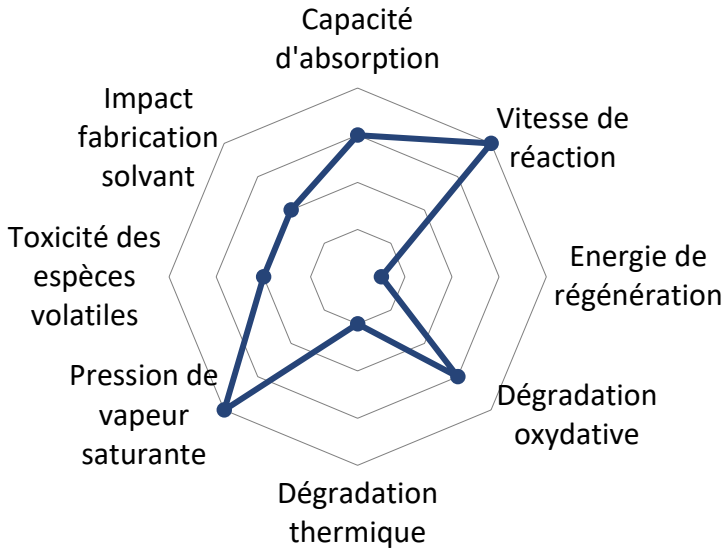


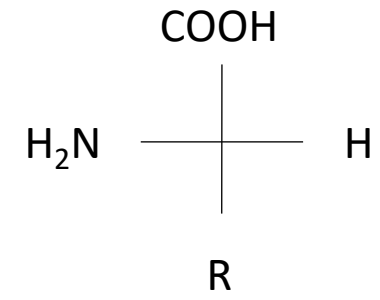
$k_2 \simeq 7000$ L/mol·s à 298 K

Energie de régénération $\simeq$ 3,5 GJ/t_{CO2}

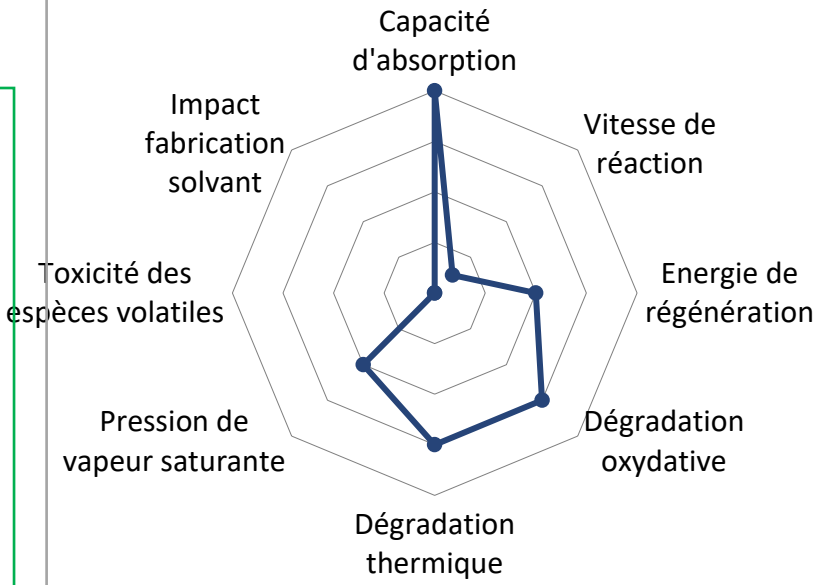


Sels d'acides aminés



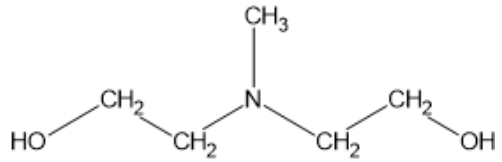


MDEA 30 %



$k_2 \simeq 8$ L/mol·s à 298 K

Energie de régénération $\simeq$ N/A



Aim of this work :

- Assess the influence of the counter-ion on viscosity, density and kinetics.
- Model viscosities based on the molecular structure of aminocarboxylate ions.
- Explore the potential of mixtures of tertiary amines and amino acid salts to minimize regeneration energy while rapidly absorbing CO_2.

Measurement of physical properties for glycinate solutions

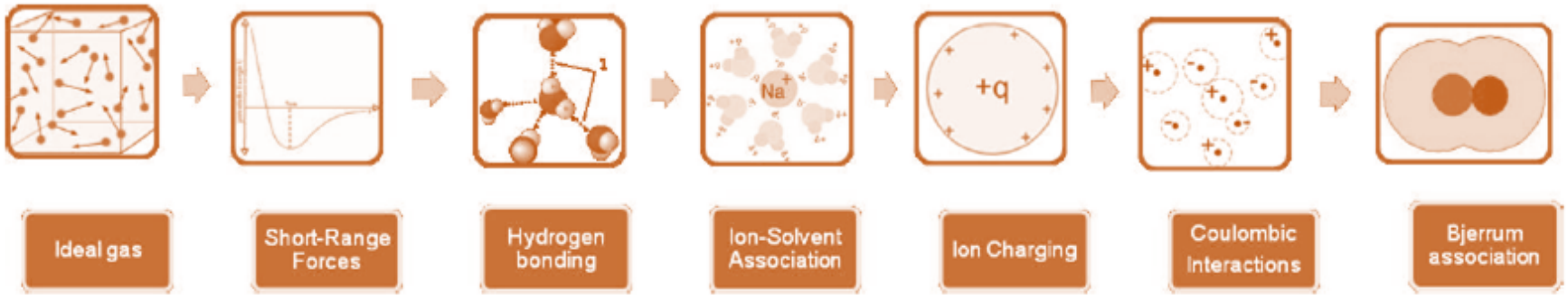
Viscosity
&
Density

Mass fraction range [4 % mass - 40 % mass].

Temperature range [288.15 K - 323.15 K].

electrolytic solutions = **multiple interactions**:
- ion-ion interactions
- ion-solvent interactions
- solvent-solvent interactions

is not just a two-body problem :
Seat of a system of complex interactions between several bodies.



(Kontogeorgis et al., 2018)

Bibliographic correlations for density of Gly

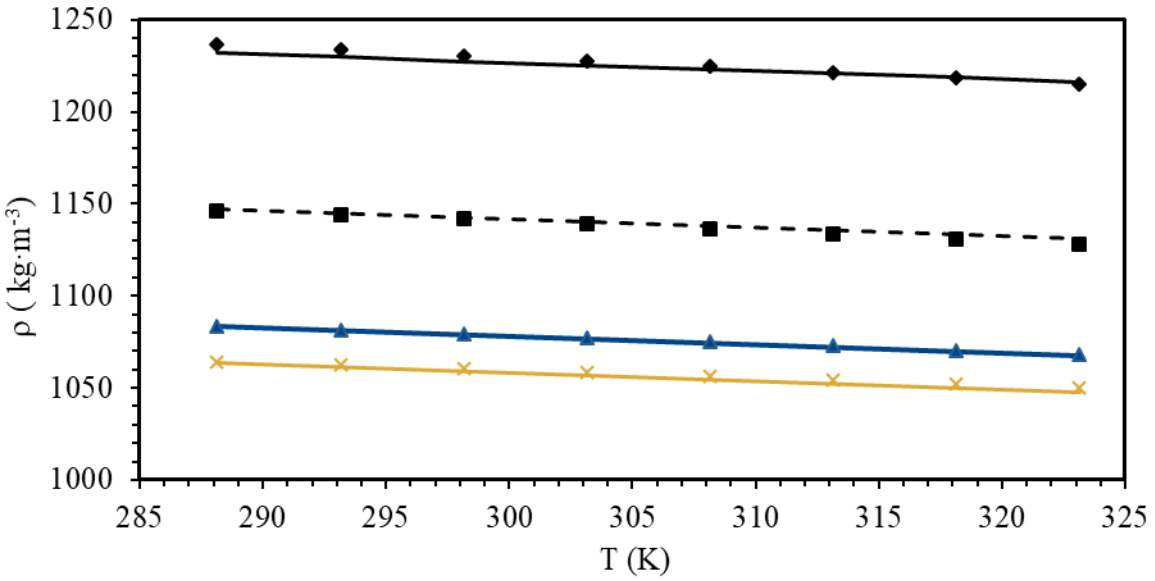
Solution aqueuse	Auteurs	Équation	Température (K)	Concentration
GlyNa	(S. Lee et al., 2005)	$\rho = A_1 + A_2 \cdot T + A_3 \cdot T^2$ *Eq. II-13*	303 – 353	10 – 50 % mass.
GlyNa	(Harris et al., 2009)	$\rho = A_0 \cdot T + A_1$ *Eq. II-14*	298,15 – 353,15	1 – 30 % mass.
Sels d'acides aminés et de potassium	(Holst et al., 2008)	$\rho = A_1 \cdot T + A_2 \cdot C + A_3$ *Eq. II-15*	298,15 – 333,15	0,2 – 3,5 M
GlyNa + pipérazine	(Shaikh et al., 2015)	$\rho = A_1 + A_2 \cdot T + A_3 \cdot T^2$ *Eq. II-16*	298,15 – 343,15	GlyNa: 0,0348 – 0,0177 (fraction molaire) Pipérazine: 0,0348 – 0,0177 (fraction molaire)
Mélange d'anhydrase carbonique et de L-lysine	(Suleman & Fosbøl, 2020)	$\rho = \rho_{H_2O} \cdot (k_1 + k_2 \cdot W_{PL} + k_3 \cdot W_{CA} + k_4 \cdot T)$ *Eq. II-17*	303 – 353	W_{PL} = 0,296 – 0,489 (fraction massique) W_{CA} = 0 – 3,4 g/L

Choice : using w instead of C

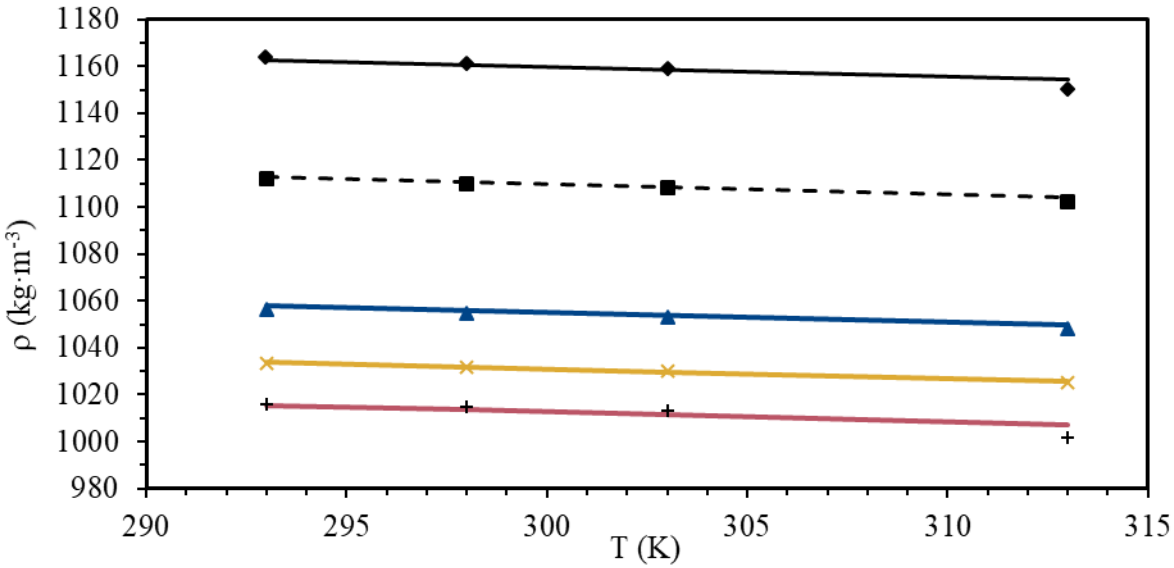
density measurement

$$\rho\left(\frac{kg}{m^3}\right) = k'_1 \times T(K) + k'_2 \times w(mass\ fraction) + k'_3$$

GLyK



GLyNa



◆ $w = 0{,}2901$; ■ $w = 0{,}2027\ K$; ▲ $w = 0{,}1074$; X $w = 0{,}0652$; + $0{,}0330$

Viscosity measurement : modelling appraoch

Einstein (1906)

$$\eta = \eta_0 \cdot (1 + 2{,}5 \cdot \theta)$$

Solutions with MES

Glasstone et al. (1941)

$$\eta = \frac{h \cdot N_A}{V} \cdot e^{\frac{\Delta G^*}{R \cdot T}}$$

Transition state theory
Energy barrier

Jones et Dole (1929)

$$\frac{\eta}{\eta_0} = 1 + A \cdot \sqrt{C} + B \cdot C + D \cdot C^2$$

Ionic force opposing movement in $\sqrt{C}$
Empirical terms B and D

Modèle n°1

$$\eta = k_1 \cdot exp\left(\frac{k_2 \cdot exp(k_3 \cdot w))}{R \cdot T}\right) \cdot exp(k_4 \cdot w)$$

Model similar to that of Holst et al.
Allowance for expansion = > w

Modèle n°3

$$\eta = k_{12} \cdot exp\left(k_{13} \cdot w + k_{14} \cdot w^2 + \frac{k_{15}}{T}\right)$$

Model based on a combination of the Glasstone et al.
Energy barrier independent of w

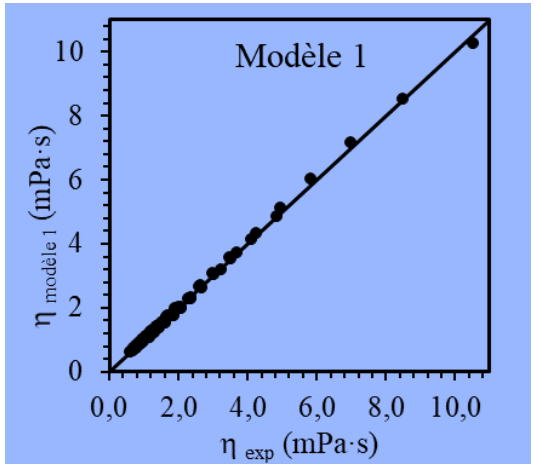
Modèle n°2

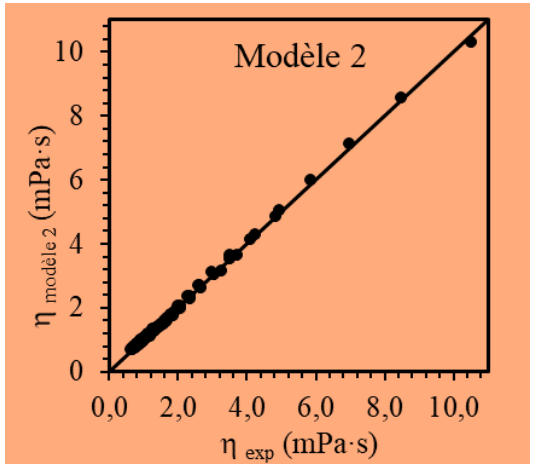
$$\eta = k_5 \cdot \left(1 + k_6 \cdot w^{0.5} + k_7 \cdot w + k_8 \cdot w^{1.5}\right) exp\left(\frac{k_9 \cdot \left(1 + w + k_{10} \cdot w^{1.5} + k_{11} \cdot w^2\right)}{R \cdot T}\right)$$

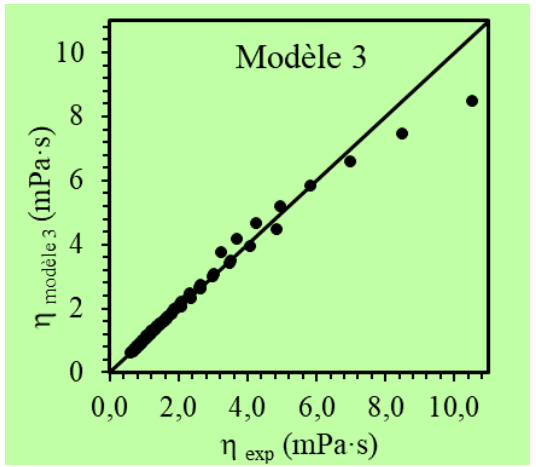
Combination of the Jones and Dole model and that of Glasstone et al.
Energy barrier dependent on w

Delanney, A., Ledoux, A., Estel, L., Villegas, G. C., & Baret, C. (2023). *Journal of Chemical & Engineering Data*, *68*(6), 1267-1278. https://doi.org/10.1021/acs.jced.2c00773

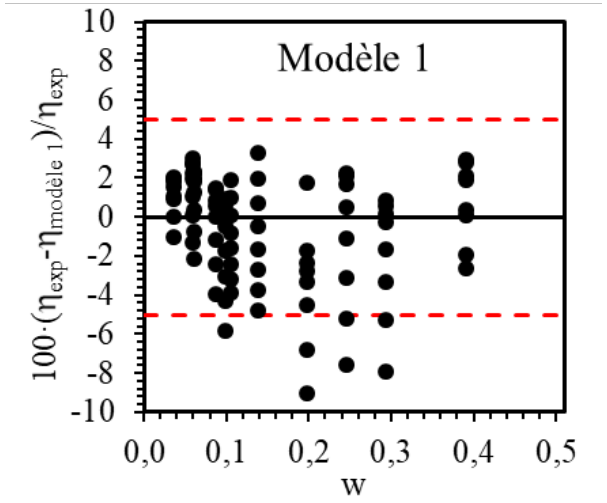
Results

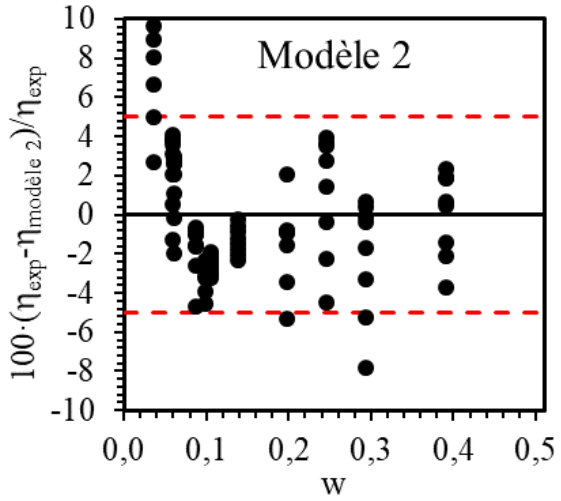


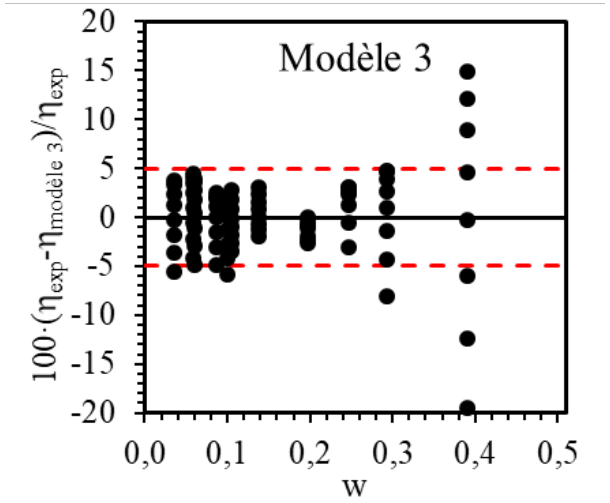




Strong interactions between cations @ high concentraton

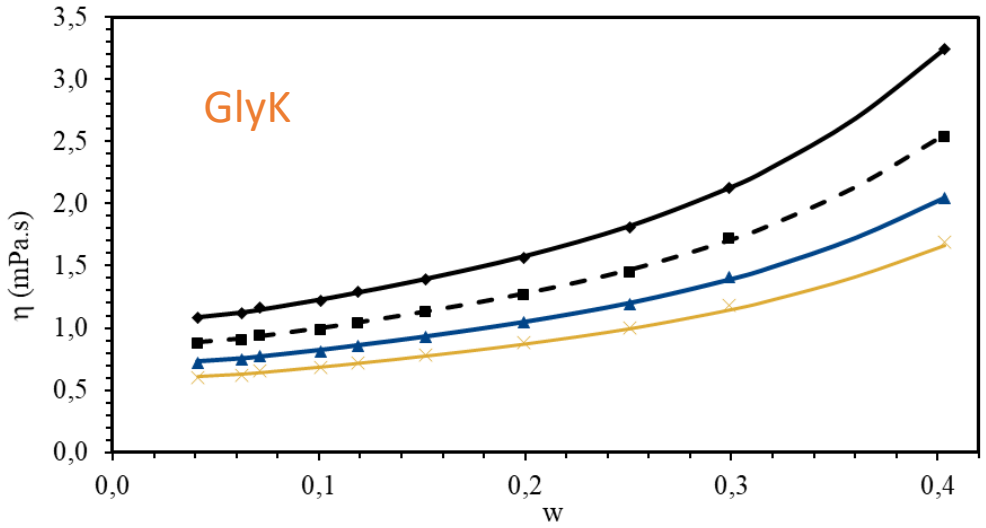


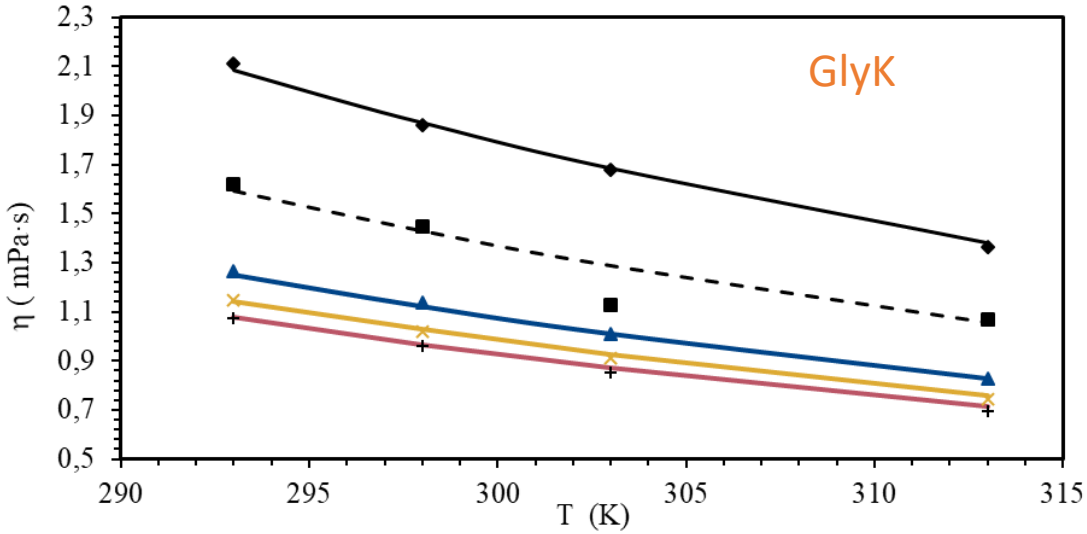


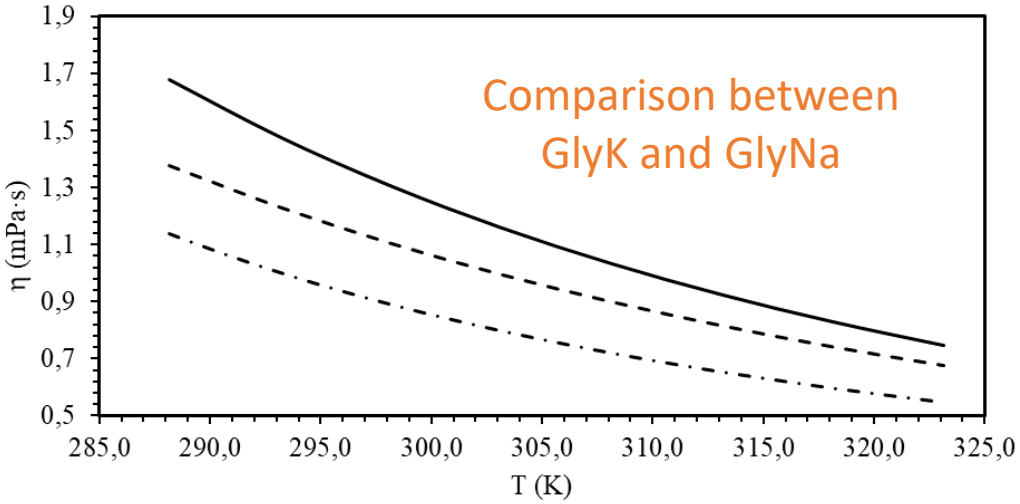


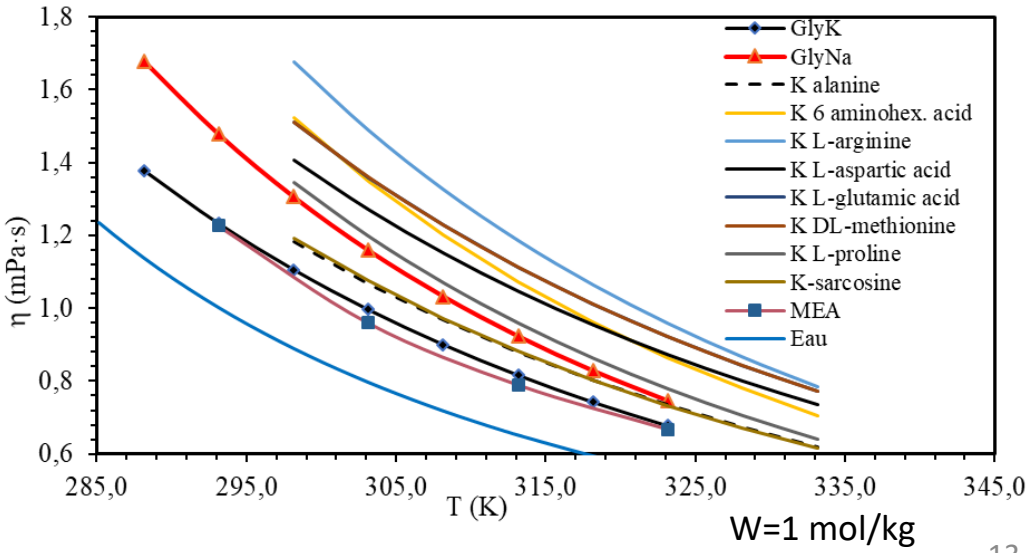
Delanney, A., Ledoux, A., Estel, L., Villegas, G. C., & Baret, C. (2023). *Journal of Chemical & Engineering Data*, *68*(6), 1267-1278. https://doi.org/10.1021/acs.jced.2c00773

Results for viscosity of Gly









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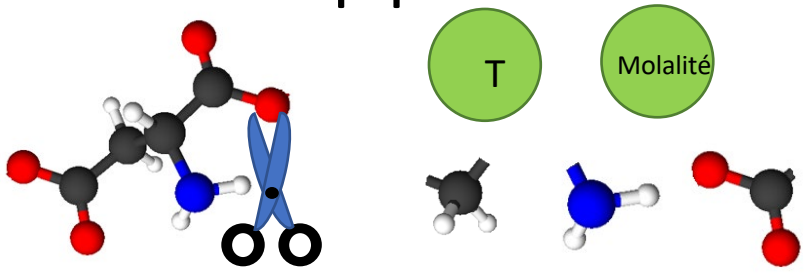
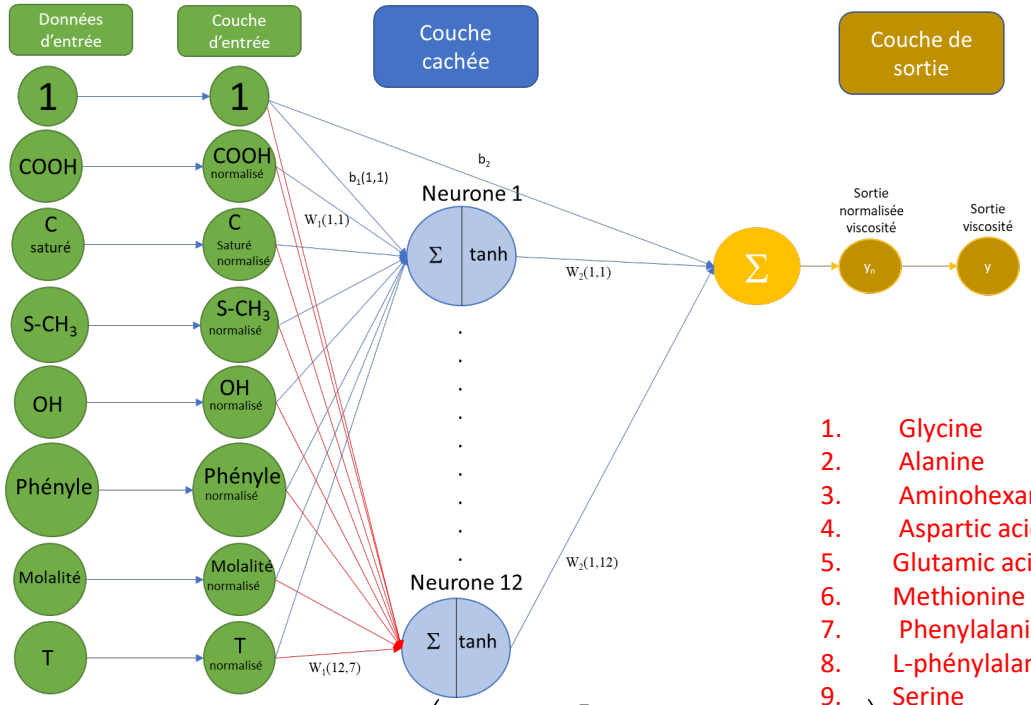
ANN Approach



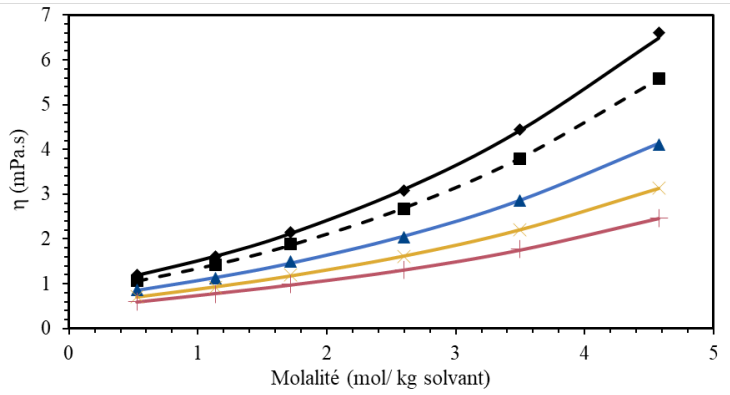


1. Glycine
2. Alanine
3. Aminohexanoic acid
4. Aspartic acid
5. Glutamic acid
6. Methionine
7. Phenylalanine
8. L-phénylalanine
9. Serine

$$y_{norm}(x) = b_2 + \sum_{i=1}^{n_c} W_2(1,i) \cdot f\left(b_1(i,1) + \sum_{j=1}^{7} W_1(i,j) \cdot x_{norm}(j,1)\right)$$

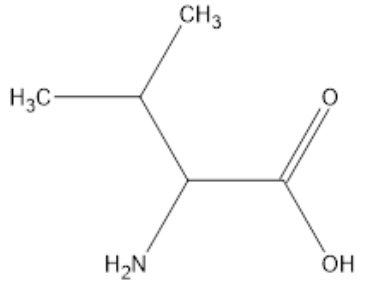
$$\text{Fonction d'activation } f(x) = \tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}}$$

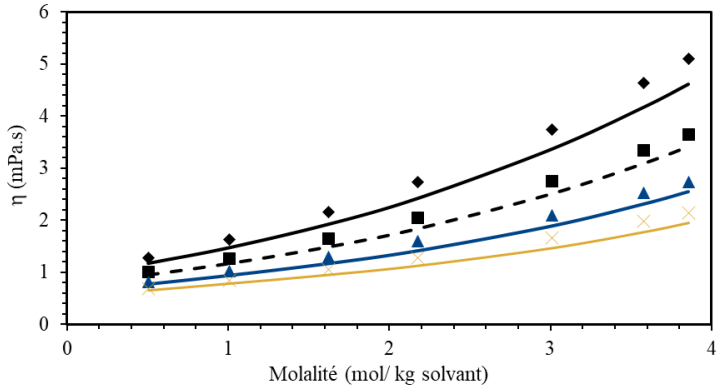
Distribution of 330 data sets - Aqueous solutions of 9 potassium amino acid salts



Performance sur l'ensemble des données	
AARD	1,42 %
MSE	$7{,}20 \cdot 10^{-4}$
RMSE	$2{,}68 \cdot 10^{-4}$ Pa·s
Déviation maximale	10,8 %
Proportion de données avec un écart relatif ≤ 5 %	97,0 %

Valine

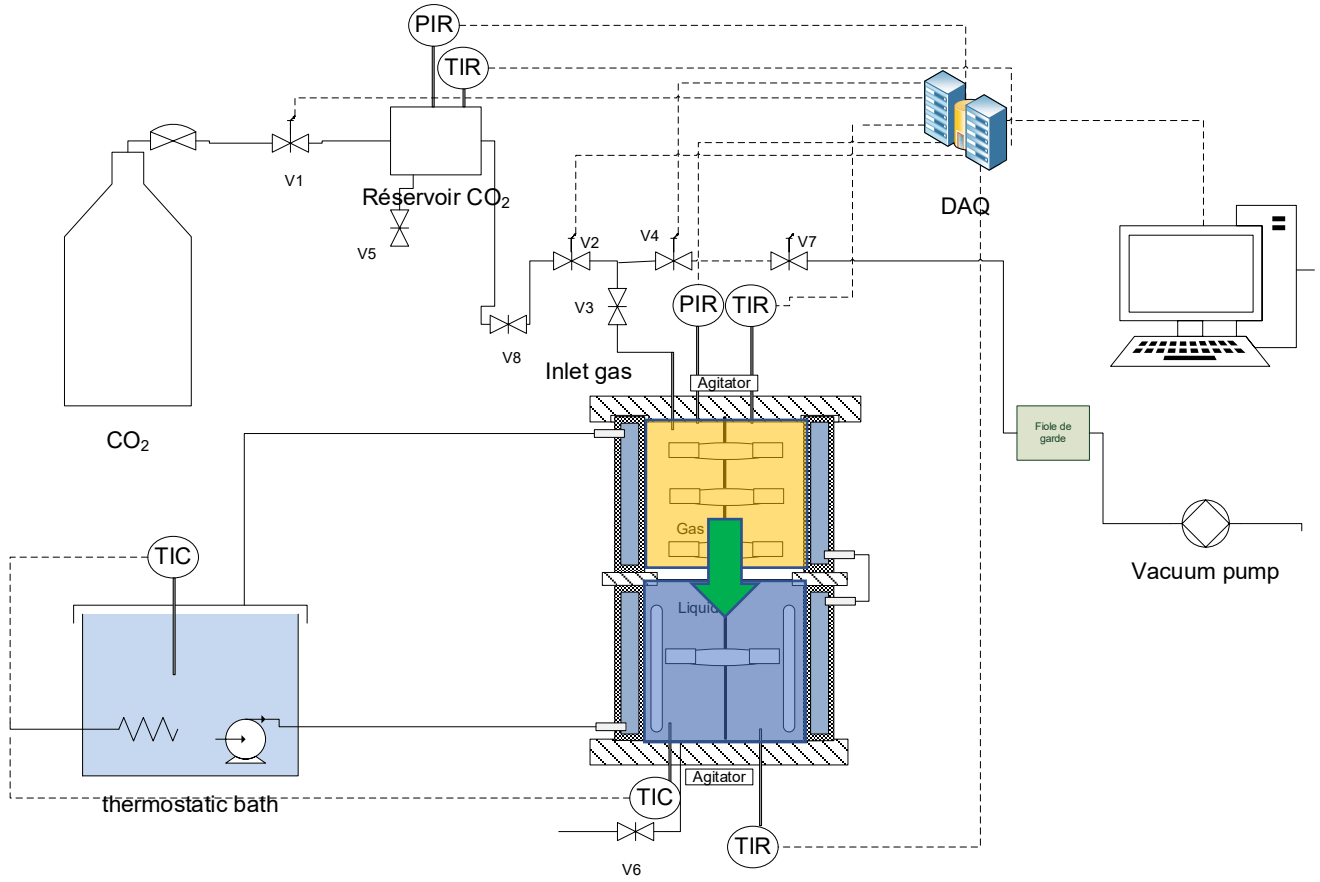




AARD	9,03 %
MSE	0,0700
RMSE	0,2646 Pa·s
Déviation maximale	13,3 %

Delanney, A., Ledoux, A., & Estel, L. (2023).. *Industrial & Engineering Chemistry Research*, *62*(41), 16589-16603. https://doi.org/10.1021/acs.iecr.3c02083

Absorption kinetic method



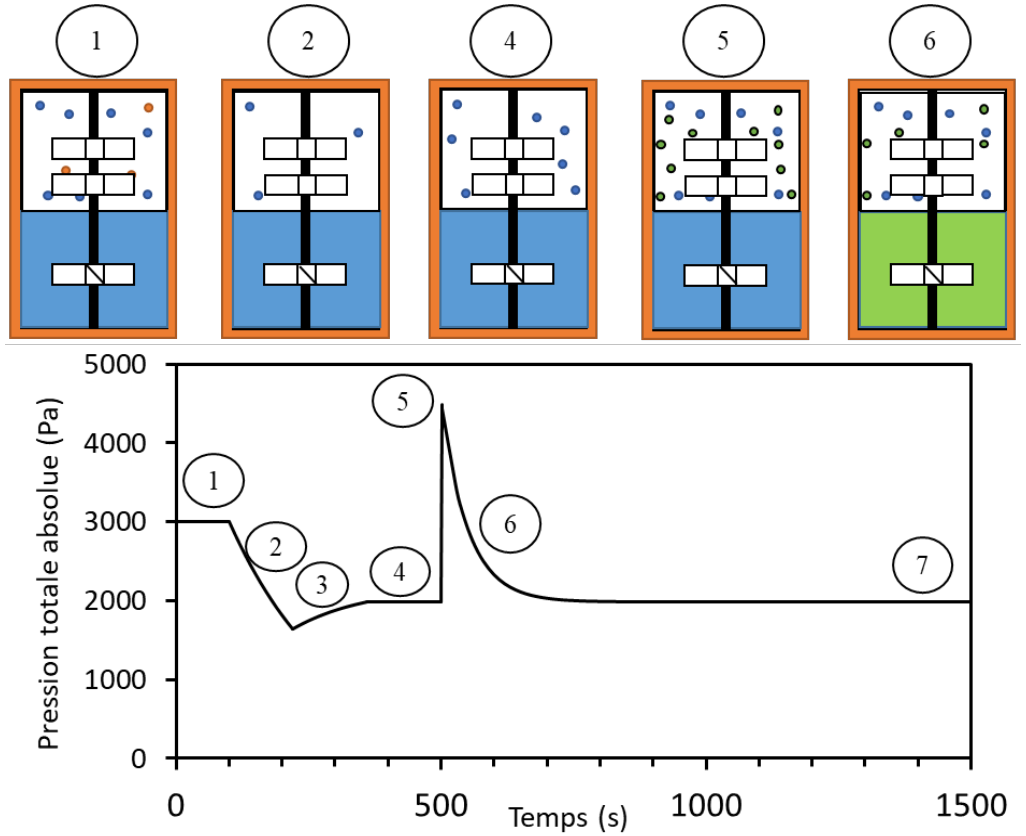
Characteristics of the Lewis cell

-Volume: 1.14 L

-Gas/liquid transfer surface: 47.9 cm2

-2 independent stirring shafts

-Temperature control



Hydrodynamic characterisation of the device

$$Sh = 0,171 \cdot Re^{0,646} \cdot Sc^{0,333}$$

$$Sh = \frac{k_l \cdot d_s}{D_{co_{2,l}}} \qquad Sc = \frac{\eta}{\rho \cdot D_{co_{2,l}}} \qquad Re = \frac{N_l \cdot \rho \cdot d_s^2}{\eta}$$

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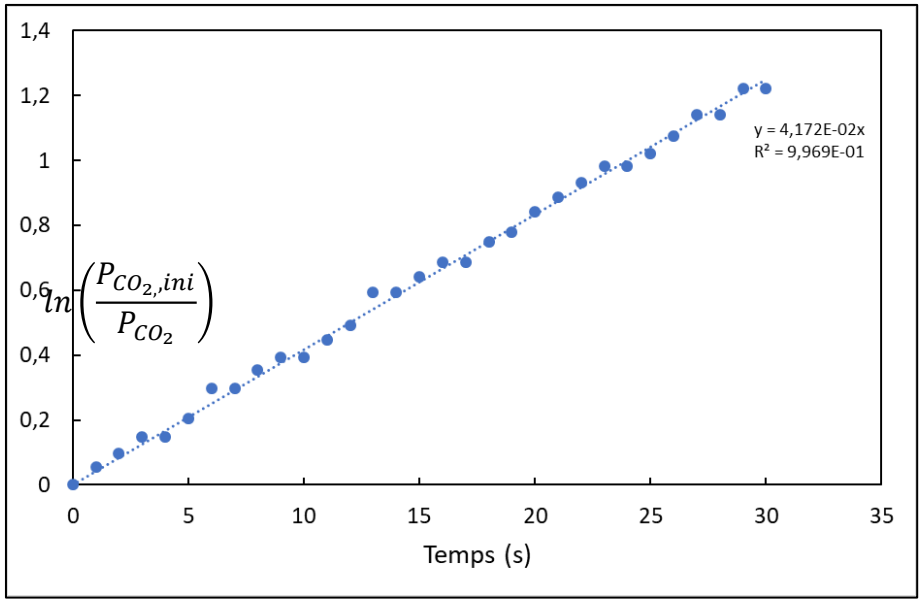
Identification of k_{ov}

- **Bilan de matière en CO_2 :**

$$ln\left(\frac{P_{CO_2,ini}}{P_{CO_2}}\right) = \frac{A \cdot R \cdot T}{V_g} \cdot \frac{\sqrt{k_{ov} \cdot D_{CO_2}}}{He_{CO_2}} \cdot t$$

$$r_{CO_2} = -k_{ov} \cdot C_{CO_2}$$

Determining of the slopede $ln\left(\frac{P_{CO2}}{P_{CO2,ini}}\right)$ vs t



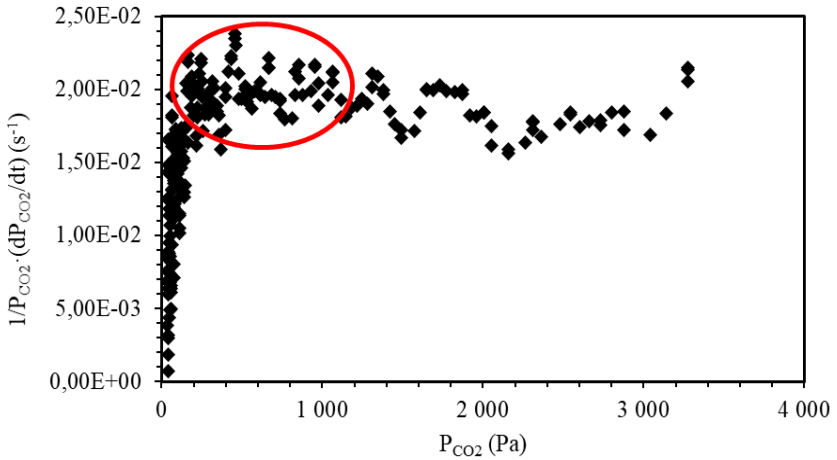
- **Estimation of He_{CO_2}:** $log\left(\frac{He_{CO_2}}{He_{CO_2,pure\ water}}\right) = \sum(h_i + h_g) \cdot C_i$

(Schumpe et al (1993) h_i et h_g obtained by analogy N_2O-CO_2)

- **Estimation de D_{CO_2} et D_B :** $(D_i \cdot \eta^{\alpha})_{sol} = (D_i \cdot \eta^{\alpha})_w$

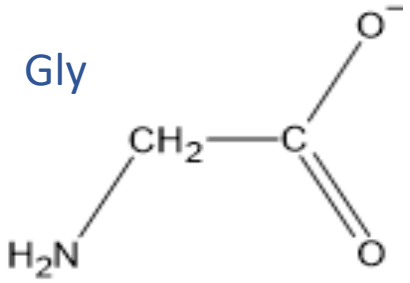
$\frac{\sqrt{k_{ov} \cdot D_{CO_2}}}{He_{CO_2}}$ k_{ov}

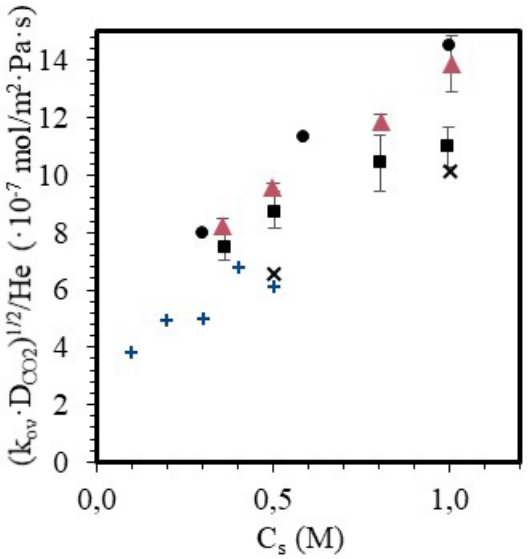
In PFO conditions :

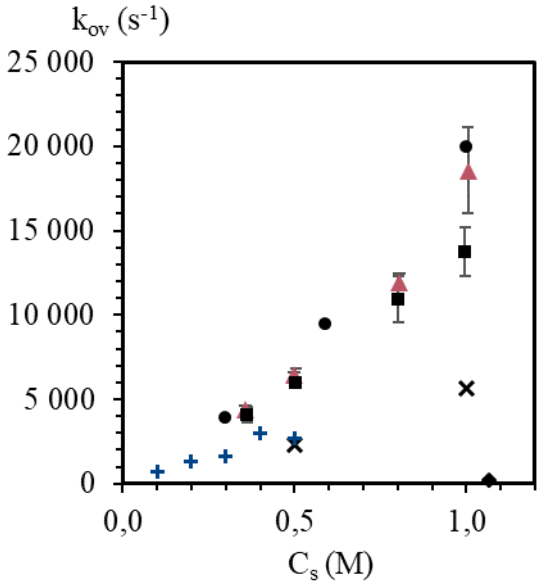


Absorption kinetic results

Gly



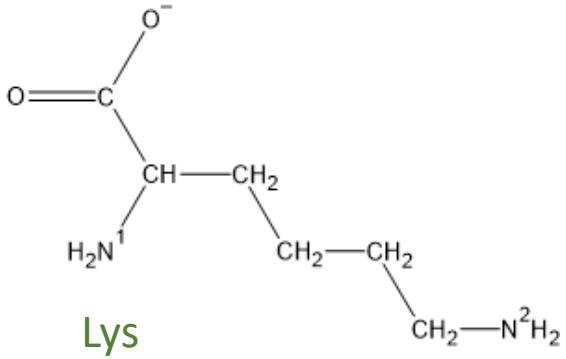


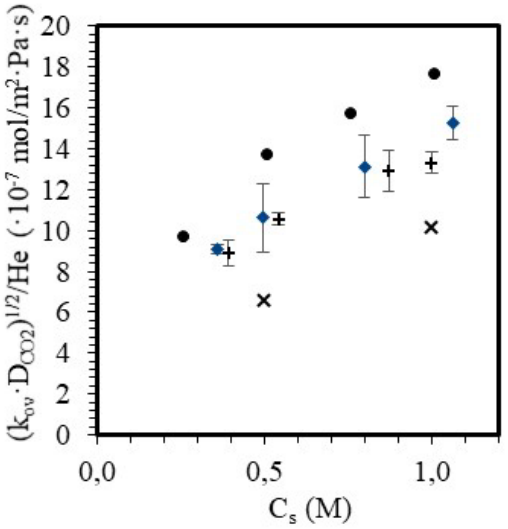


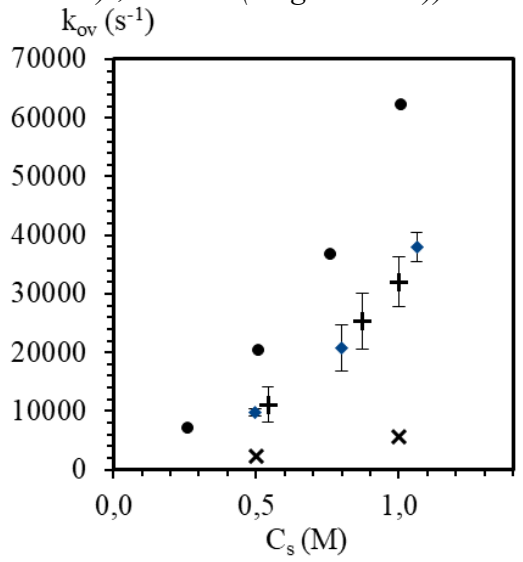
the absorption rates of GlyNa solutions are between 7% and 21% lower than those of GlyK

(● GlyK (Portugal et al.) ; + GlyK (Vaidya et al.) ; ◆ GlyNa (Lee et al.) ; ▲ GlyK (this work) ; ■ GlyNa (Ce travail) ; X MEA (Ying et Eimer))

Lys







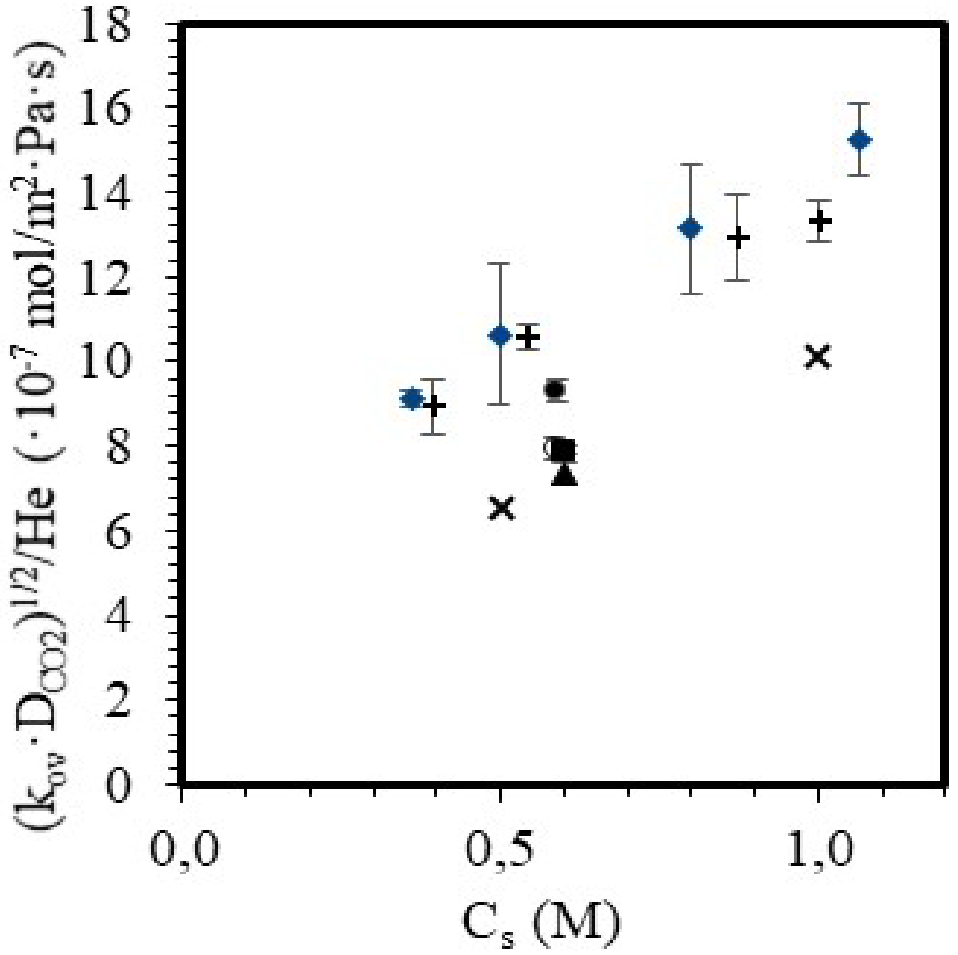
LysK > LysNa ≥ GlyK > GlyNa

(● LysK (Shen et al.) ; ◆ LysK (this work) ; + LysNa (Ce travail) ; X MEA (Ying et Eimer))

Promoting effect : activation of MDEA by AA

- MDEA 20 % + LysK 0,6 M
- MDEA 20 % + LysNa 0,6 M
- MDEA 20 % + glyK 0,6 M
- MDEA 20 % + GlyNa 0,6 M

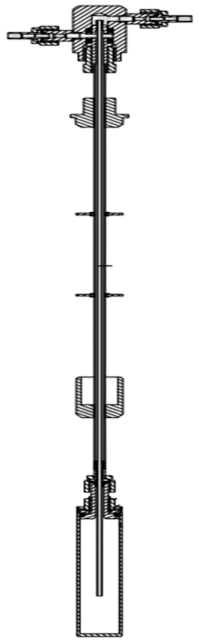
- ❑ Good activation of MDEA
- ❑ Strong effect of viscosity

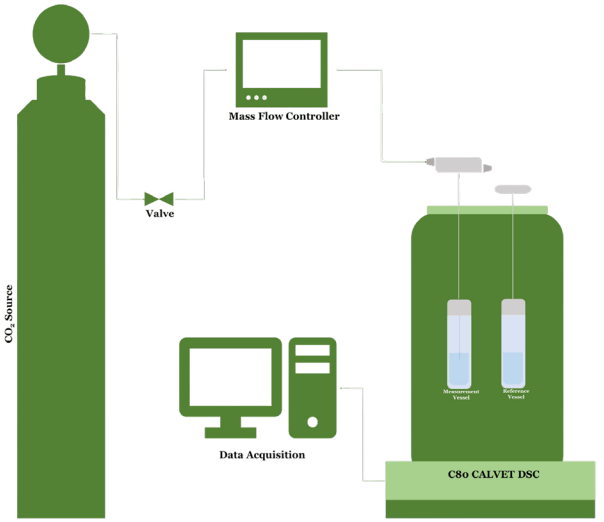


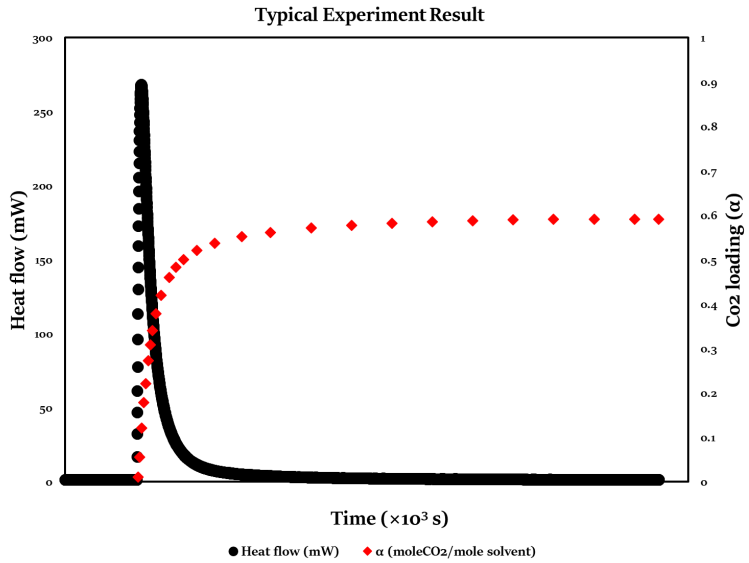
(◆ LysK; + LysNa ; ● LysK + MDEA 20 % ; ■ LysNa + MDEA 20 % ; O GlyK + MDEA 20 % ; ▲ GlyNa + MDEA 20 % ; X MEA (Ying et Eimer))

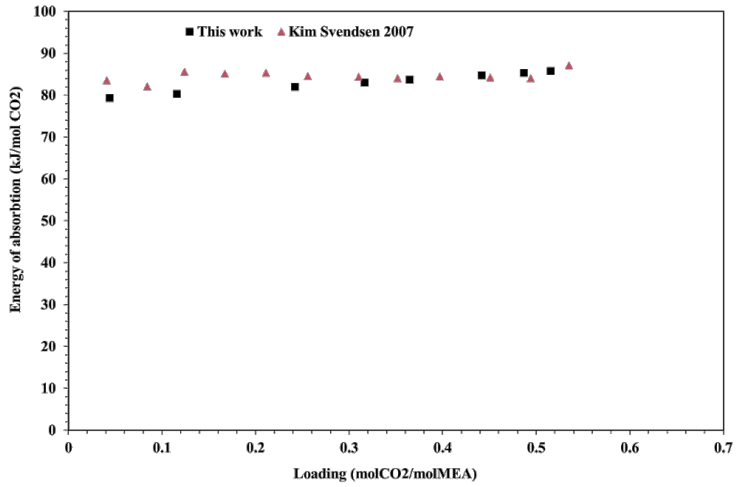
LSPC Laboratoire de sécurité des procédés chimiques

Heat of absorption : Calorimetric approach



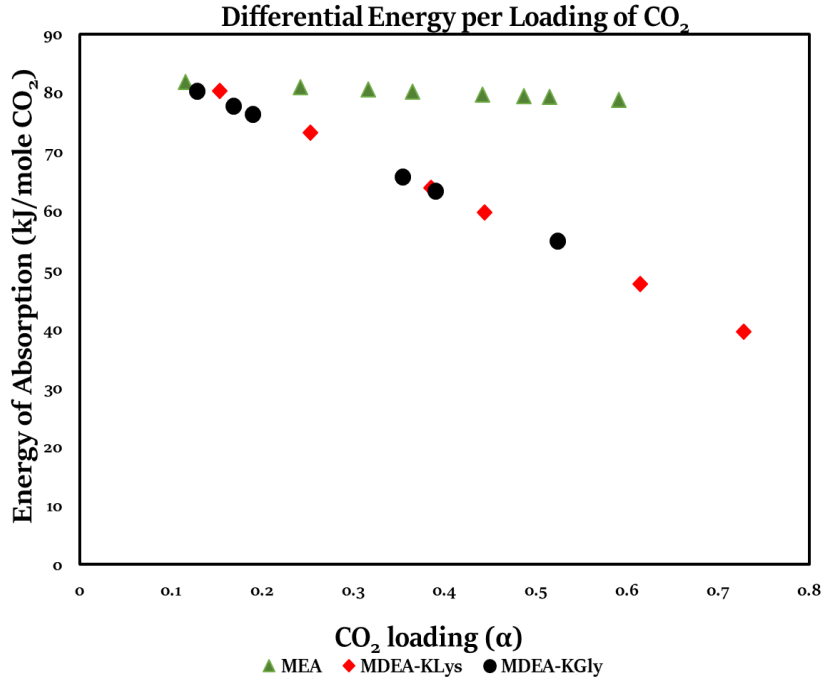






Heat of absorption : Calorimetric approach

Solvents	Classifications
30 wt.% Monoethanolamine-aqueous (MEA)	Primary amine
20 wt.% Methyldiethanolamine, 10 wt.% Potassium Lysinate-aqueous (MDEA+Klys)	Blend-Tertiary amine (MDEA), Primary amine (lysine)
20 wt.% Methyldiethanolamine, 10 wt.% Potassium Glycinate-aqueous (MDEA+KGly)	Blend-Tertiary amine (MDEA), Primary amine (glycine)



Sel d'acide aminé	Concentration	α (mol de CO_2 / mol)	Enthalpie de désorption (kJ/mol CO_2)	T (K)	Source
GlyNa	10 % mass.	0	72,5 59,5	313,15 323,15	(Salazar et al., 20
ProK	7,5 % mass.	0 – 0,80	54,3	298,37-313,83	(Majchrowicz & Brilman, 2012)
LysK	37,7 % mass.	0,58 1,2	70 55	313-343	(Zhao, Shen, et a 2017)
LysK	32,9 % mass.	0,40 1,20	110 58	313 313	(Zhao, Bian, et a 2017)
SarK	3,5 M (37,9 % mass.[a])	0,20	66,7	313	(Aronu et al., 201
AlaK	2,5 M (28,1 %mass.[b])	0–0,68 0–0,57	53,26 66,13	298 313	(Lim et al., 2012
ProK	2,5 M (33,4 % mass.[c])	0–0,66 0–0,62	90,20 86,17	298 313	

[a] Fraction massique calculée à partir des valeurs de densité à 298 K prise dans la publication de Aronu et al. (Aronu et al., 2012)

[b] Fraction massique calculée à partir des valeurs de densité à 298 K prise dans la publication de Holst et al. (Holst et al., 2008)

[c] Fraction massique calculée à partir des valeurs de densité à 298 K prise dans la publication de Shen et al. (Shen et al., 2015)

- The DSC measurement was developed: accurate measurement
- MEA showed constant differential heat.
- MDEA + LysK and MDEA + GlyK showed decreasing heat, suggesting less energy required for higher mole uptakes

Conclusions and perspectives

- Solid modelling of physical properties of AA
- Validation of the higher absorption rate of aqueous lysinate and glycinate solutions compared to aqueous MEA solutions
- Aqueous sodium solutions absorb less quickly than their potassium counterparts
- Good positioning of AAs in terms of absorption energy

❖Absorption energy : focus on influence of loading

❖Analytical approach for speciation during absorption (in situ NMR)

❖Work on degradation based on FTCIR analysis (Fourier-transform ion cyclotron resonance)