

## RIGOROUS MODELLING AND EXPERIMENTAL RESULTS ON CARBON-DIOXIDE ABSORPTION INTO DIETHANOLAMINE AQUEOUS SOLUTIONS IN PACKED-COLUMNS

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The present work aims to improve the acid-gases removal process using electrolytic solutions of alkanolamines. As a first part, a new rate-based model containing rigorous sub-models for non-ideal thermodynamics, reactions and simultaneous mass and heat transfer has been developed. The model uses Nernst-Planck equations for the liquid film and generalized Maxwell-Stefan equations for the gas film. In the second step a gas-absorption column with random packing for CO<sub>2</sub> capture using aqueous Diethanolamine as solvent has been constructed to generate absorption data in order to validate the model.

The reactive separation under steady-state conditions has been simulated with a rigorous description of diffusion-reaction phenomena in film. The reactions are taken into account in the liquid phase with almost no simplification in terms of reaction mechanism. In the gas film, molecular interactions and diffusional phenomena are taken into account using the generalized Maxwell-Stefan equations. A thermodynamic model “SourWater True Species” has also been developed based on the interactions of true species in aqueous multicomponent electrolytic systems.

In the second part, experimental results of CO<sub>2</sub> absorption by Diethanolamine are given. A 2 m high gas-absorption packed-column with an inside diameter of 50 mm has been constructed. Raschig glass rings (d=5mm) have been used as packing. CO<sub>2</sub> is absorbed from a mixture of air and CO<sub>2</sub> by aqueous DEA (20%wt.) in the counter-current configuration under atmospheric pressure. The feed concentration of CO<sub>2</sub> is fixed at 15%vol. which represents the typical concentration of CO<sub>2</sub> in flue gas. At the steady-state condition, the concentration of CO<sub>2</sub> in liquid and gas phases has been measured along the length of column. The temperature profile has also been obtained for the liquid phase.

### 1. MULTICOMPONENT REACTIVE SEPARATION MODELLING

The design of absorbers has been conventionally based on the equilibrium stage model dividing the column into artificial segments using HETP. The Equilibrium-based model assumes that the leaving liquid and vapour streams in each stage are at thermodynamic equilibrium. In reality, reactive separation processes rarely operate close to thermodynamic equilibrium, since mass and heat transfer are rate-based processes governed by the gradients of chemical potential and temperature.

Authors like Dudukovic and Lee (1998), propose a stage efficiency factor in order to rectify the equilibrium assumption. Lockett (1986) uses the the Murphee efficiency in order to take into account the non-ideal behaviour of phase in terms of mass transfer. However in reactive mixtures with three or more species, component efficiencies are usually very different; some of them have values greater than unity and some less than zero. In fact, there is no fundamental method for estimating efficiencies or HETPs in reactive separation of multicomponent mixtures especially when systems contain a complex chain of chemical reactions. In reactive absorption operations, chemical reactions can lower reactant concentrations, resulting in component efficiencies greater than one.

Traditional models and efficiency approaches are not adequate to describe the reactive separation of multicomponent mixtures. Mass transfer resistances have to be considered by rate-based models with separate balance equations for each phase. The multicomponent interactions can be interpreted as the diffusional competitions of components. Therefore in such systems, the diffusion has to be characterized accurately using generalized Maxwell-Stefan equations. For electrolytic solutions, the impact of ionic charges on diffusion is taken into account using the gradient of electric potentials as the second driving force of diffusion.

When the rate of mass transfer and chemical reaction are quite similar, the influence of chemical reactions on mass transfer cannot be neglected. The use of enhancement factor in order to take into account the impact of reaction on mass transfer as Versteeg et al. (1989, 2007), Gorak et al. (2001), Hikita et al. (1972) and DeCoursey (1982) propose is limited to a few simple reaction schemes, and is not adequate for complex reaction schemes with multiple reversible and parallel reactions. An accurate approach of modelling is then to consider the complete chain of chemical reactions in the reactive phase as well as in the diffusional film near phase interface.

### 1.1 Column rate-based model

The rate-based model follows the principle of a non-equilibrium stage, which is characterized by the actual rates of chemical reactions and multicomponent heat and mass transfer between phases. The model uses the generalized Maxwell-Stefan equations in order to model accurately the multicomponent interactions in electrolytic mixtures. Multiple chemical reactions are explicitly taken into account by writing the complete chain of reactions.

This work adapts the two-film theory to a non-equilibrium stage (Fig. 1) and the influence of column internals and hydrodynamics is described through the calculation of film thicknesses ( $\delta_L$  and  $\delta_G$ ). A non-equilibrium stage consists of the well-mixed phases and two diffusional film regions adjacent to the interface.

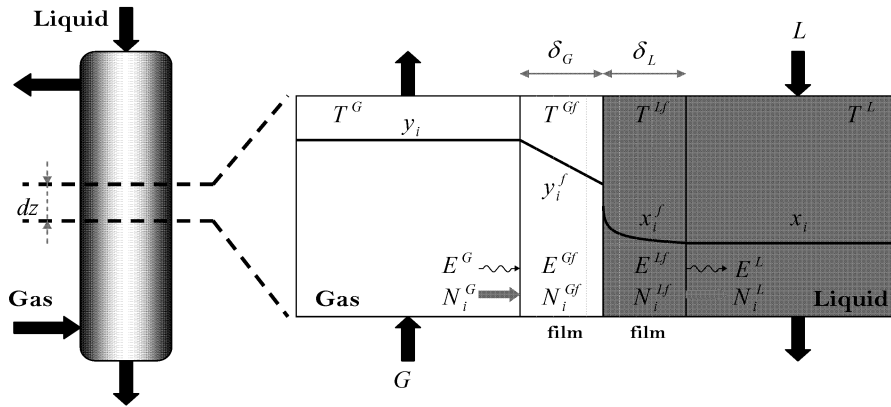


Fig. 1: Non-equilibrium stage in reactive separation column (two-film model)

The component material balances in a differential element of the two-phase volume in the packing are written for both phases under steady-state condition (EQ. 1 and 2). Due to the presence of chemical reactions at instantaneous equilibrium, the chemical equilibrium conditions have to be verified in liquid (EQ. 3). The bulk phase balances are completed by the summation of mole fractions. Here the liquid phase equations are described. The gas phase system follows the same set of equations but without reaction term.

$$\frac{d}{dz}(Lx_i) + \left( -N_i^L \cdot a_e + \sum_{k=1}^{nrc} \nu_{ik} \cdot r_k \cdot \mathcal{E}^* + \sum_{k=1}^{nre} \nu'_{ik} \cdot \chi_k \right) \cdot A_c = 0 \quad (i=1, nc) \quad (1)$$

$$\frac{d}{dz}(L.H^L) + (Q^L - E^L).a_e.A_c = 0 \quad (2)$$

$$K_k^{ch} = \prod_{i=1}^{nc} (a_i)^{\nu'_{ik}} \quad (k = 1, nre) \quad (3)$$

$$\sum_{i=1}^{nc} x_i = 1 \quad (4)$$

In the above equations, index  $i$  represents a true specie of mixture (ionic or molecular). The flux terms ( $N_i^L$ ,  $E^L$ ) are determined at the boundary of film layer ( $\delta_G$ ,  $\delta_L$ ) by the transfert model. The hydrodynamic parameters such as  $a_e$  (exchange surface) and  $\varepsilon^*$  (holdup) are given using experimental correlations. The enthalpies ( $H^L$ ), activities ( $a_i$ ), and chemical equilibrium constants ( $K^{ch}$ ) are calculated using appropriate thermodynamic models for electrolytic solutions. The choice of kinetic models for the calculation of reaction rates ( $r_k$ ) is very important especially in the case of reactive absorption where reaction rates are so high.

The set of equations are completed, considering the molar and heat balances for fluxes at the phase interface. At the phase interface, the thermodynamic equilibrium is also assumed (Eq. 5).  $K_i$  values are evaluated for true species (ions and molecules), taking into account fugacities in both phases and activity coefficients in liquid phase. The activity coefficients are provided by Mather's method (McGregor and Mather, 1995) which is a modified method of Pitzer. "SourWater True Species" thermodynamic model has been developed based on physical interaction of true species in electrolytic mixtures, in order to model phase equilibrium independently from instantaneous reactions at the phase interface.

$$y_i^I - K_i .x_i^I = 0 \quad (i = 1, nc) \quad (5)$$

The boundary conditions for column model are the pressure, the temperature and the compositions of liquid and gas inlets. In our previous paper (Ahmadi et al., 2010), the complete set of equations describing Liquid-Vapour multicomponent reactive separation for non-electrolytic systems and its numerical resolution has been studied. In the present work, the same model is expanded to electrolytic systems.

### 1.2 Mass and heat transfer model

In addition to the bulk balances, the transfer model in film is also applied in order to provide the differential molar and heat balances in films (EQ. 6 and EQ. 7). The chemical equilibrium conditions have also to be verified for the film reactions at instantaneous equilibrium (EQ. 8).

$$\nabla N_i^{Lf} = \sum_{k=1}^{nrc} \nu_{ik} .r_k + \sum_{k=1}^{nre} \nu'_{ik} .\chi_k^f \quad (i = 1, nc) \quad (6)$$

$$\nabla E^{Lf} = 0 \quad (7)$$

$$K_k^{ch} = \prod_{i=1}^{nc} (a_i^f)^{\nu'_{ik}} \quad (k = 1, nre) \quad (8)$$

The generalized Maxwell-Stefan equations (EQ. 9) provide a rigorous modelling of multicomponent interactions in non-ideal phase (Taylor and Krishna, 1993; Wesselingh et al., 1997). In electrolytic mixtures, the impact of electrical forces is also taken into account as the second driving force for diffusion. In dilute mixtures, generalized Maxwell-Stephan equations are reduced to Nernst-Planck equations by neglecting diffusional interactions (EQ. 10).

$$\frac{x_i^f}{RT^f} \nabla \mu_i^f + x_i^f z_i \frac{F}{RT^f} \nabla \phi_e = - \sum_{j=1}^{nc} \frac{(x_i^f N_j^{Lf} - x_j^f N_i^{Lf})}{C_i^L D_{ij}^L} \quad (i = 1, nc - 1) \quad (9)$$

$$N_i^{Lf} = -\nabla x_i^f C_i^L D_{in}^{\circ} - \nabla \phi_e C_i^L D_{in}^{\circ} x_i^f z_i \frac{F}{RT^{Lf}} + x_i^f N_n^{Lf} \quad (i = 1, nc - 1) \quad (10)$$

Where,  $i$  represents a true specie (ionic or molecular).

Considering the electrical potential gradients demands complementary information that we call electroneutrality condition. It is written as follow,

$$\sum_{i=1}^{nc} x_i^f z_i = 0 \quad (11)$$

In this work, the multicomponent interactions in gas phase have been described using Generalized Maxwell-Stefan equations. In the liquid film, Nernst-Planck equations have been adapted because of lack of access to multicomponent ionic diffusivities.

The energy equations express the heat transfer in film by integrating the conductive and convective heat flows in film:

$$E^{Lf} = \left[ -\lambda \nabla T^{Lf} + \sum_{i=1}^{nc} N_i^{Lf} h_i^{Lf} \right] \quad (12)$$

The boundary conditions for the transfer model are at phase interface and at the diffusional film thicknesses.

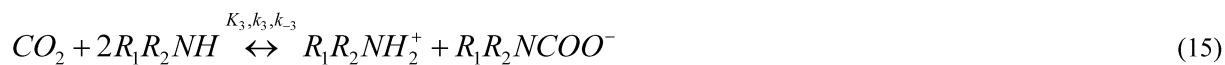
## 2. ACID GASES REMOVAL PROCESS

After the removal of  $\text{NO}_x$  and  $\text{SO}_x$  from the flue gases coming from a power plant, the gas mixture contains a variety of different polluting compounds such as sour gases and can not be emitted directly into the atmosphere. These exhaust gases have to be treated in absorption columns. Our objective is to provide a selective removal unit of acid-gases such as  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{COS}$ , using different amine solvents. As an example, the  $\text{CO}_2$  capture in packed-bed unit using aqueous Diethanolamine as solvent has been investigated.

### 2.1 Chemical reactions of $\text{CO}_2$ in aqueous alkanolamines

When  $\text{CO}_2$  is absorbed in an aqueous solution of a primary or secondary amine, the following scheme of reactions may occur:





The reaction between  $CO_2$  and DEA (EQ. 15) follows the mechanism of zwitterion through the formation of unstable specie known as zwitterion ( $R_1R_2NH^+COO^-$ ). The global kinetic constant of zwitterion mechanism is estimated using EQ. 20. The corresponding kinetic constants are given by Versteeg and Oyevaar (1989) as well as Littel et al. (1992) regarding to Table 1.

$$k_3 = \left[ \frac{1}{k'_1} + \frac{1}{[R_1R_2NH] \frac{k'_1 k'_2}{k'_{-1}}} \right]^{-1} \quad (20)$$

Table 1: Kinetic constants of Zwitterion mechanism

Reference	T (°C)	$k'_1$	$k'^1_1 \cdot k'^2_2 / k'^2_{-1}$
Versteeg and Oyevaar (1989)	25	3170	720
Littel et al. (1992)	30	4360	1300
	45	7310	1360

The reactions 13, 14 and 15 are reversible and controlled by kinetics, while the reactions 16-19 are reversible at instantaneous equilibrium. The kinetic and equilibrium constants for the reactions 13 and 14 are given by Pinsent et al. (1956); for the reactions 17, 18 and 19 are given by Edwards et al. (1978); and for the reaction 16 is given by Kent and Eisenberg (1976).

## 2.2 Experimental investigation

**Packed column.** A gas-absorption column of 50mm inside diameter and 2m height has been constructed. The height of packing is 1 m and it contains Raschig glass rings of 5mm diameter. The height of packing is divided into 5 segments of 20 cm (Fig. 2a). A special Teflon connection has been designed and placed between segments to be able to analyze liquid and gas samples along the column (Fig. 2b). Gas mixture is introduced below the packing. A centrifugal pump with 0-60 L.h<sup>-1</sup> capacity of discharge is used to send the liquid from 300 L storage tank to the top of the packing. Gas flow rates are monitored by two flow meters. All flow rates are monitored and can be regulated. Gas samples are first transported by pipelines to a chilled mirror hygrometer (DewMaster DM-C1) in order to measure the absolute humidity. Then, passing by a dry Calcium sulphate filter, they finally reach the infrared (I.R.) ADC-MGA-3000 Multi-Gas analyzer ( $\pm 0.02\%$ vol.). Liquid samples are taken by accurate gas-proof and transported to the CO<sub>2</sub> content analysis cell. Liquid temperatures are measured at the inlet, outlet and between segments, to obtain liquid temperature profile in the column.

**Sampling Teflon connection.** The segments of packing are separated by the sampling Teflon connection (Fig. 2b). Referring to Fig. 2b, the top chamber is conceived for liquid sampling and temperature measurement in liquid. The bottom chamber is directed to the gas sampling pipelines and reaches the hygrometer and the I.R. analyzer.

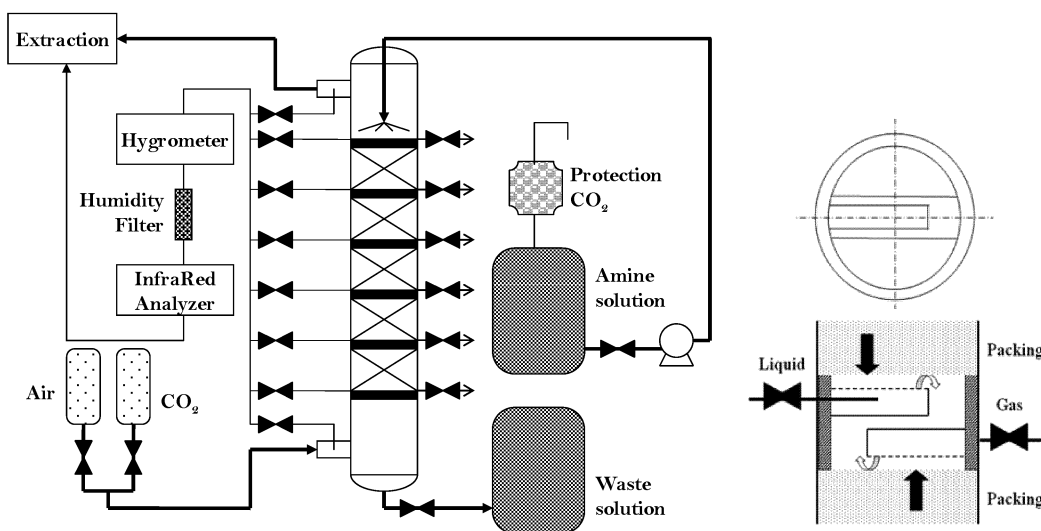


Fig. 2: (a) process flow diagram (b) Sampling connection between segments

**CO<sub>2</sub> content analysis in liquid.** Liquid samples are transported to the analysis cell to determine the total dissolved CO<sub>2</sub> in liquid solution. The method consists of acidifying a well measured volume of amine sample with phosphoric acid which liberates carbon dioxide from the amine solution. All ions containing carbon are now transformed to gaseous CO<sub>2</sub> and their mole number can be calculated by monitoring the total pressure above the solution. The CO<sub>2</sub> content analysis in liquid is provided with  $\pm 0,003\text{mol.L}^{-1}$  of accuracy.

**Operational conditions.** CO<sub>2</sub> is absorbed from a mixture of air and CO<sub>2</sub> by aqueous DEA (20% wt) in the counter-current configuration under atmospheric pressure. Fig. 2a illustrates the process flow diagram. The liquid solution is sent into the column without gas flow rate in order to prewet the column for 15 minutes. Then the liquid flow rate is fixed to  $11.9\text{ m}^3.\text{m}^{-2}.\text{h}^{-1}$ , and gas mixture is introduced containing  $0.85\text{ Nm}^3.\text{h}^{-1}$  dry-air and  $0.15\text{ Nm}^3.\text{h}^{-1}$  of pure CO<sub>2</sub>. Hence, a feed concentration of CO<sub>2</sub> at 15% is provided which represents the typical concentration of CO<sub>2</sub> in the flue gas. The inlet and outlet CO<sub>2</sub> concentration in gas, as well as liquid and gas temperatures are monitored periodically during the experiment until the steady-state condition is gained. In about

30 minutes the steady-state condition is reached; and hence the concentrations of CO<sub>2</sub> in liquid and gas phases, as well as the liquid temperature are measured along the column.

### 3. RESULTATS AND DISCUSSIONS

The simulation of CO<sub>2</sub> capture in packed-column has been conducted with the same operating conditions as the experiment. Gas and liquid flow rates are the same as described in the above section. Inlet composition of CO<sub>2</sub> in gas is fixed at 14.46%vol. and liquid and gas inlet temperatures are set respectively to 18.7°C and 19.1°C.

Fig. 3a shows the experimental results on CO<sub>2</sub> %vol. (Error = ±0.02%vol.) in gas along the column together with the simulation results. The CO<sub>2</sub> percentage in gas is reduced in column from 14.46%vol. to 5.49%vol. and the absorption is almost linear. Liquid temperature is increasing inside packing from top to bottom because of exothermic chemical reactions (Fig. 3b).

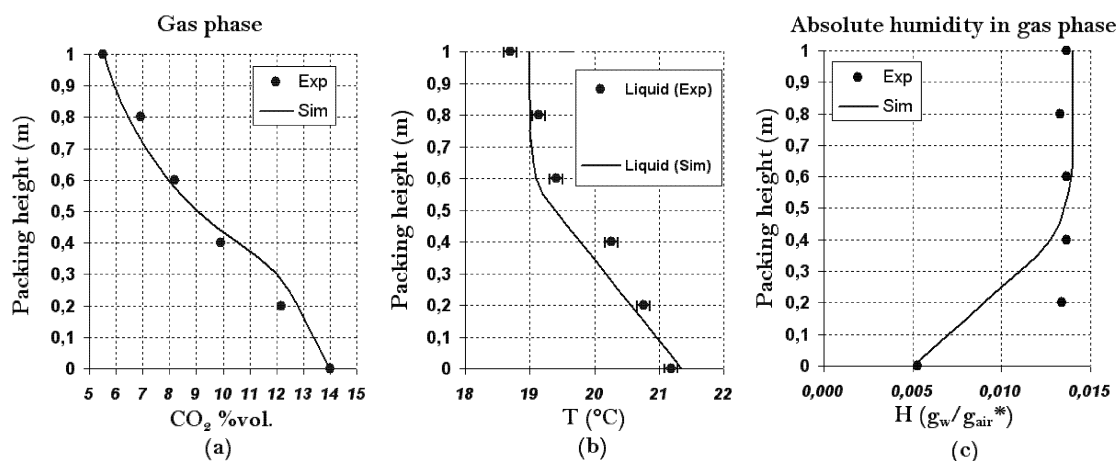


Fig. 3: (a) experimental results on CO<sub>2</sub> (%vol.) profile in gas phase, (b) Temperature profiles in liquid and gas [points: experiment, lines: simulation]

A simultaneous counter-current transfer of CO<sub>2</sub> and water between phases is taking place, showing the multicomponent character of mass transfer. As we see in fig. 3c, the gas phase is rapidly saturated with water vapor at the bottom. The evaporation of water also cools down the liquid in the lowest segments and lowers the impact of exothermic reaction on the liquid temperature profile. The experimental values of absolute humidity (Fig. 3c) have been measured with an error of  $\pm 1 \times 10^{-4}$  gw.gair<sup>-1</sup>.

### 4. CONCLUSIONS AND PERSPECTIVES

An extended column rate-based model for the reactive separation in multicomponent electrolytic systems has been developed. The model takes into account the simultaneous heat and mass transfer in the diffusional field near the phase interface as well as the complete chain of chemical reactions in film and in phase. The thermodynamic models for the calculation of phase equilibria as well as physico-chemical parameters are based on the interactions of the true species of mixture (all ionic and molecular components in the mixture).

The absorber has a good performance and presents no operating challenges. The experimental observations are very close to the simulation results and they validate the model. The Raschig glass rings have been used as packing because of the wide knowledge about their properties in the literature. The model can be applied for other solvents as well as other packings. The calculations of phase equilibria are also suitable for multi-amines systems. Hence, the rate-based model can be applied for the simulation of acid-gases removal by mixed amines such as DEA, MEA, TEA and MDEA.

The CO<sub>2</sub> absorption can also be run with higher concentrations of DEA, in order to evaluate the capacity of model to handle higher transfer rates and higher concentration profiles in the separation column.

The rich amine solvent is generally regenerated in a stripping tower and circulated back to the absorber. The energy costs associated with the amine regeneration is high because of the high formation enthalpy of carbamate. The column rate-based model presented in this work can be applied with some modifications to the stripping towers. Hence, the optimization of stripping towers would also be a subject of research in future.

### Notations

$A_c$	cross section of column ( $m^2$ )
$a_e$	effective surface ( $m^2 m^{-3}$ )
$a_i$	activity coefficient
$C_i$	concentration ( $mol m^{-3}$ )
$D_{in}^o$	diffusion in pure solvent ( $m^2 s^{-1}$ )
$D_{ij}$	binary diffusion ( $m^2 s^{-1}$ )
$E$	heat flux ( $J m^{-2} s^{-1}$ )
$F$	Faraday constant
$H$	molar enthalpy of mixture ( $J mol^{-1}$ )
$h_i$	partial molar enthalpy ( $J mol^{-1}$ )
$K^{ch}$	chemical equilibrium constant
$K_i$	dimensionless gas-liquid equilibrium constant
$L$	liquid flow rate ( $mol s^{-1}$ )
$nc$	total number of components in mixture
$N_i$	molar flux ( $mol m^{-2} s^{-1}$ )
$Q$	heat loss flux ( $J m^{-2} s^{-1}$ )
$R$	constant of ideal gas ( $J mol^{-1} K^{-1}$ )
$r_k$	reaction rate ( $mol m^{-3} s^{-1}$ )
$T$	temperature (K)
$x_i, y_i$	mole fraction ( $mol mol^{-1}$ )
$z$	column height (m)
$z_i$	ionic charge
$\delta$	film thickness (m)
$\epsilon^*$	liquid holdup ( $m^3 m^{-3}$ )
$\lambda$	thermal conductivity ( $J s^{-1} m^{-1} K^{-1}$ )
$\mu_i$	chemical potential ( $J mol^{-1}$ )
$v, v'$	stoichiometric coefficients
$\phi$	electrical potential (V)
$\chi_k$	conversion rate of the instantaneous equilibrium reaction k ( $mol m^{-3} s^{-1}$ )

*Index and numbers:* f (film), G (gas), I (interface), L (liquid)

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