

Performance evaluation of electrodeionization process based on ionic equilibrium with plate and frame modules

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Abstract

The paper describes results of experiments carried out in plate and frame electrodeionization (EDI) modules, aiming to elucidate ion mass transfer phenomena between ion-exchange resin and membrane for more effective desalination. The selective separation rate of different ions in process was investigated with conventional theories such as double electric layer and the Donnan theory to check its consistence. Further, as comparing with ordinary electro dialysis (ED) process, no obvious limiting current point was observed in EDI performance, which was usually used as a criterion for process optimization. Behavior of ion migration in the fluids with different configurations under different operating parameters was also examined and the ionic equilibrium analysis of EDI process was found to be beneficial to determine whether it was in the steady state or in the regeneration stage of operation.

Keywords: Electrodeionization; Plate and frame module; Performance; Ionic equilibrium

1. Introduction

Electrodeionization (EDI) is a combination of ion-exchange resins and electro dialysis (ED) to deionize the water without regeneration chemicals such as strong acid and bases. Conventional ion exchange technology, some of which often

accompanied with reverse osmosis process, can produce ultrapure water with resistivity up to 18 MΩ cm at 25°C. However, the mixed resins are easily saturated with contaminant ions for only a short period of time because of the limited capacity of ion exchange. The exhausted resins must be chemically regenerated and then produce a lot of wastewater containing high contents of waste acids, bases and salts. The electro dialysis

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itself is an effective desalination technology, but it is not economical to treat dilute solutions because of the low current density and concentration polarization. EDI gathers the advantages of both electrodialysis and ion exchange, and can produce ultrapure water continuously and cleanly without any chemical regeneration [1,2].

In EDI process, ions transport occurs mostly through the ion resin and usually is not affected by water resistivity. The mixed ion exchange resin acts a conducting medium in the electric field. When the available ions in the diluted compartments are not sufficient for accommodating the current transport through the solution, a water splitting reaction occurs and then regenerates a relatively high concentration of H^+ and OH^- . These ions are normally considered to be used for regeneration of resins which are saturated for some period of time. These are the unique characteristics of EDI called “continuous electro-regeneration” which is very important for a complete deionization process.

With two different separation processes combined, EDI has a more complicated working principle that varies from both ED and ion exchange. Many researchers have taken consideration in transfer processes of ions in EDI and have given some useful explanations [3–5], but a solid theoretical foundation is still on the way, and requires more investigations. In order to realize a more effective desalination in EDI, this paper aims to elucidate the mass transfer phenomena between ion-exchange resin and membrane and to investigate the selective separation process of different ions with conventional theories such as double electric layer and the Donnan theory to check the consistence.

2. Experimental

Two bench scale apparatus with different electrodeionization modules were employed in this experiment. Module No. 1 with a dimension of 56 cm × 88 cm × 56 cm was used to produce

high-purified water as reagent in the laboratory, while module No. 2 with a dimension of 21 cm × 34 cm × 16 cm was just used for experiment and easy to be dismantled. The configuration of both was plate and frame with compartments sandwiched between the electrodes (titanium-coated ruthenium anode and stainless steel cathode). The resins (Purolite 201 × 7 and 001 × 7, Hangzhou, China) with a mixing ratio of 2 were filled in the diluting compartment that was bounded by the anion membrane and cation membrane (LAOCGF, Hangzhou, China). Normally 5 pairs of heterogeneous ion exchange membrane with low permeability of water were stacked.

All experiments were conducted with the permeate water from the reverse osmosis (RO, with composite membrane, Filmtec, USA) equipment, which was usually lower than 21 $\mu S/cm$ after desalination of tap water. The feed water flowing through the diluting compartment was called as the dilute, while the water discharged from the concentrating compartment facing the cation membrane and anion membrane was defined as the concentrate. The electrode compartment facing the anode or the cathode was for water flowing to remove the waste gas evolved in electrochemistry reactions at the electrodes. The modules usually were operated steadily under a set electric voltage and with the feed flows continuously in the different paths. The Concentrate was mostly recycled with a small part reused to supply the flow in electrode compartment. The effluent from the electrode compartment was finally discharged (see Fig. 1).

The linear velocity of the diluate and concentrate was controlled around 0.15 cm/min in module No. 1, while 0.26 cm/min in module No. 2. For both modules, the operating pressure was set below 0.1 MPa, in which the pressure for the diluting compartment was a little higher than others to prevent the reverse transfer due to the concentration difference. When resistivity of the dilute and conductivity of the concentrate were measured on line during the experiments,

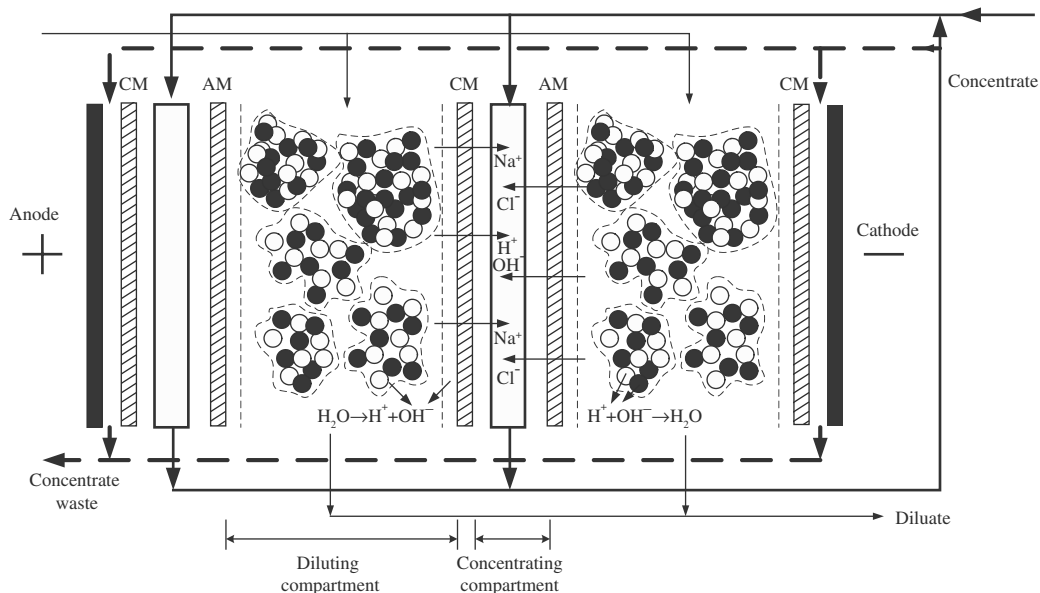


Fig. 1. Diagram of the electrodeionization module. The mixed ion-exchange resins are randomly filled in the diluting compartment bounded by anion membrane (AM) and cation membrane (CM).

the samples from different compartments were picked up simultaneously for analysis. Metallic ions were determined by means of Inductively Coupled Plasma (ICP, IRIS Intrepid, USA). Anions were determined by means of Ionic Chromatography (IC) using a Metrohm 792 Compact IC with conductivity detection. Sometimes, the conductivity of samples was re-measured by a DDS-11A conductivity meter (Reiz, Shanghai, China).

3. Results and discussion

3.1. Voltage–current curve

The voltage–current curve of module No. 1 is shown in Fig. 2, where the triangles and diamonds refer to the ED and EDI process, respectively. For comparison, the spacer and membranes of the ED and EDI used here was the same except that there were no ion exchange resins in the diluting compartment of ED. When the electric current was higher than 3A in the electro dialysis process, there was an inflection point on the

voltage–current curve that made the slope ascend. This current at the inflection point was called limiting current which was the maximum current

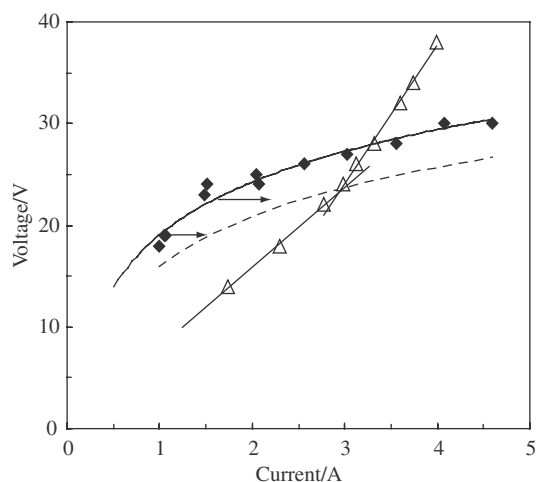


Fig. 2. Voltage–current curve of the EDI and ED process. The diamond represents the EDI process, the triangle represents the ED process. The dashed line represents the current increases by about 1.6 times after 5 h operation under the same voltage.

that could be employed in conventional industrial electrodialysis [6–8]. If the potential required to produce this current was exceeded, the extra current would be carried by other processes, first by transport of anions through the cationic membrane and then at a higher potentials, by water dissociation. In ED process, these undesirable processes consumed more power without producing any separation and decreased the current efficiency of the process. The current efficiency of electrodialysis is the separation achieved per unit of power consumed and can be defined by

$$\eta = \frac{zFQ(C_0 - C_1)}{I} \quad (1)$$

where z is the valence, F is the Faraday's constant, Q is the flux per cell, C_0 is the feed concentration, C_1 is the diluate concentration. Usually, ED current efficiency was always in the range of 70–90% from early results [6]. But in EDI, as the current increased, the flux and concentration were much lower than that in ED, therefore caused a lower current efficiency value. A low current efficiency around 7–19% which was moderate for EDI process was obtained in this experiment. Low current efficiency was bad for ED process but might be suitable for EDI process since the dissociated hydrogen and hydroxyl were extremely useful for resin regeneration. Therefore, EDI might be the special case of ED process and its voltage–current correlation should be very different from that of ED.

From Fig. 2, no inflection point which represented the limiting current was found in EDI process. Its voltage–current curve was similar to that of bipolar membranes. Since bipolar membrane usually consist of an anionic and as cationic membrane laminated together, the EDI module might be compared to a thick bipolar in which the resins used as the close packing between the membranes and then laminated. Therefore the special voltage–current curve could be explained from the behavior of bipolar membrane. Noted in

the previous reports, the experimental voltage–current relationship of bipolar membrane occurring water splitting was not consistent with the Ohm's law $R = U/I$ and could be given by [9,10]

$$\varphi = a + b \ln I \quad (2)$$

where φ is voltage, I is current, a and b are parameters concerning the temperature and the steady velocity of water dissociation or forming. Usually, a and b can be treated as constant. From this equation, an exponential curve between φ and I should be found which is consistent with the results showed in Fig. 2. By calculating experimental data, a mathematic relationship of $\varphi = 19.063 + 7.463 \ln(I)$ was obtained.

The dashed line in Fig. 2 was observed from the experiment. It indicated that the voltage–current curve of module No. 2 tended to drift towards the right direction of the abscissa during operation, which showed the current increased by about 1.6 times after 5 h operation under the same voltage. This was also different from the conventional ED process. As the water splitting in the electrodeionization, the resulted extra ions such as H^+ and OH^- were very active to transfer through solution and membrane and thus might reduce the resistance of both solution and membrane boundary layer. Another reason might be that a strong concentration polarization at the surface of resins happened in this situation.

3.2. Ionic equilibrium

The function of ion exchange resins in the electrodeionization was also found to be much different from that in conventional demineralizer. In EDI, resins not only functioned as an ion exchanger but also transported ions to the surface of the ion exchange membrane. Since the quality of the final product was dependent on the transport of ions from the diluate to the concentrate, the ionic equilibrium was analyzed here to evaluate the performance of the resins

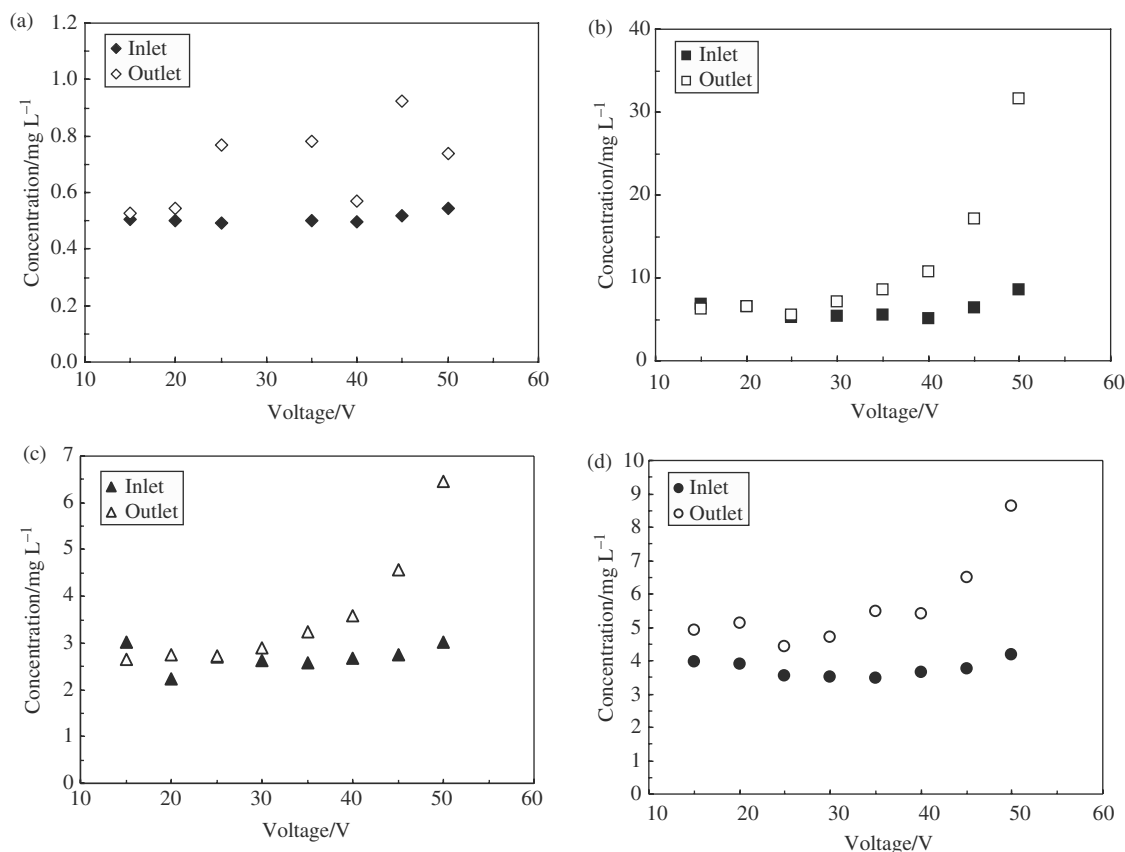


Fig. 3. Variation of ion concentration on voltage between inlet and outlet of the dilute compartment: (a) fluorine, (b) chlorine, (c) nitrate and (d) sulfate.

fixed in the compartment. Fig. 3 compared the behavior of different ions entering in and going out of the EDI module.

At low voltage below 30 V, as shown in Fig. 3a–c, the concentration of F^- , Cl^- and NO_3^- ions between the inlet and outlet of module No. 1 were balanced because resin regeneration consumed almost all the H^+ and OH^- ions produced in the electric field. The regeneration rate was equal to transport rate and the absorption effect of resins dominated. When the voltage increased gradually, the concentration of F^- , Cl^- , NO_3^- and SO_4^{2-} ion in the outlet was significantly higher than that in the inlet, respectively. It seemed that a higher voltage often caused a stronger water

splitting, then more H^+ and OH^- came to exchange with the ions of resins absorbed before and made them escape faster. For example, if one anion resin macromolecule absorbed three counter-ions, it could be regenerated by dissipating one counter-ion at the low voltage. As the voltage increasing, the other counter-ions were also dissociated and came into dilute product in the outlet. Therefore the ionic equilibrium analysis of EDI could be used to determine whether the module was in the steady state or in the regeneration stage of operation and to decide when the operating voltage should be adjusted, which controlled how high the current efficiency could be obtained in the desalination process. The F^- data in Fig. 3a is

somewhat scattered because the fluorin concentration was lower than others in the experiment and might be affected more by the former leftover in IC column.

3.3. Influence of operating voltage on module resistance

Fig. 4 showed the changes of module resistance with concentrate conductivity. As the concentrate conductivity increased, the resistance of module No. 2 decreased obviously. The conductivity capability of the concentrate was more critical than that of the dilute because the dilute compartment was full of the resins in solution which had enough ions for electric current transportation. Also from Fig. 4, the electrical resistance seemed to decrease if the voltage of the module increased. Since the rate of mass transfer from the dilute to the resin J was obviously affected by the voltage of module, the result could be explained by the double electric layer theory with equation given below [11]

$$J = -zCU \frac{d\varphi}{dx} \quad (3)$$

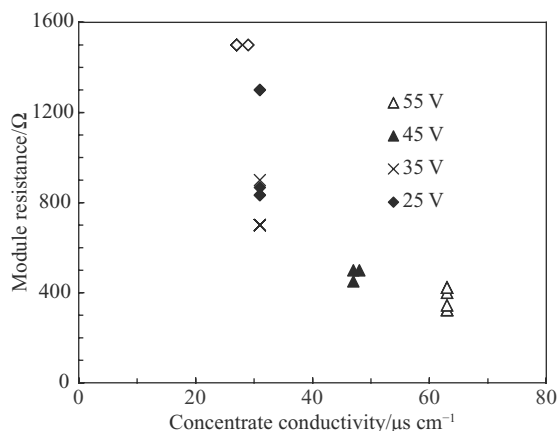


Fig. 4. Change of module resistance vs. concentrate conductivity and voltage. The different signs represent different voltages. There are more than five data at the fixed voltage, which are overlapped.

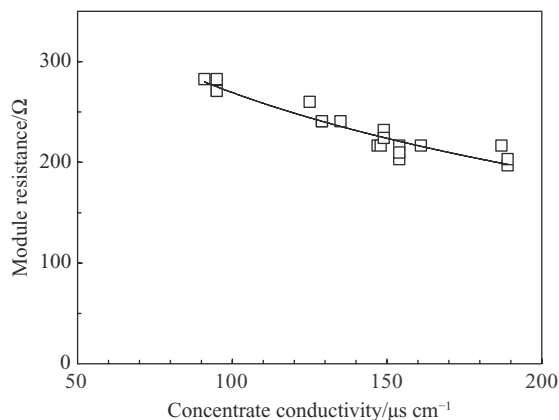


Fig. 5. Influence of concentrate conductivity on module resistance at 65 V. The curve of module resistance vs. concentrate conductivity was more leveled than that at lower voltage shown in Fig. 4.

where z is the valence, C is the concentration, U is the coefficient related to diffusion coefficient, φ is the voltage. From Eq. (3), the rate of mass transfer should increase with the operating voltage. This meant more ions transferred from the dilute to the resin phase and then enriched within its matrix, therefore the conductivity of resin phase increased, which pulled down the total resistance of module in the meantime. The overlapped data at one fixed voltage shown in Fig. 4 was obtained at a relatively low voltage no more than 55 V. The results at a higher voltage of 65 V were presented in Fig. 5. With the higher operating voltage here, the curve of module resistance vs. concentrate conductivity was more leveled and the decreasing range of resistance of 280–180 Ω was smaller than that of Fig. 4 which ranged from 1500 to 300 Ω . But the change of concentration conductivity showed a wider range, which demonstrated more active ions in the concentrate compartment. A 65 V voltage might be enough to support strong water splitting with large amounts of hydrogen and hydroxyl dissociated, and the transportation of these ions took place of the resin absorption which dominated in the process. This was proved to be true with a pH

value change in the concentrate, and was consistent with the results from elsewhere [12].

3.4. Influence of operated voltage on ions rejection

In EDI process, there are various mass transfer processes including ions transfer from liquid phase to resins phase, ions transfer in the resins phase, ions transfer from liquid phase to membrane phase and ions transfer in membrane [11]. Due to the influence of the electric field, cations in solution are attracted to the cathode, and anions are attracted to the anode. While solutes move into the membrane phase, the Donnan effect should be taken into consideration [6]. Therefore the mechanism of ions rejection is very complicated. At the same time, water splitting reaction occurs on the surface of mixed ion exchange resins and at the interface between ion exchange membrane and solution. H^+ and OH^- produced are then able to regenerate the mixed ion-exchange resins during operation. Therefore water dissociation is critical for the removal of most ions such as Mg^{2+} , Ca^{2+} , Na^+ , Cl^- , NO_3^- and SO_4^{2-} , which might be absorbed on the resins before.

Fig. 6 presents the influence of operating voltage on rejection of some ions. The rejection of divalent ions except sulfate was higher than 98% when operating voltage was above 25 V. The sequence to selective separation rate of different univalent ions was Ca^{2+} , Mg^{2+} , $K^+ > NO_3^- > Cl^- > Na^+$ in the experiment, which was consistent with the relative order in conventional ion exchange process such as $SO_4^{2-} > NO_3^- > Cl^-$ and $Ca^{2+} > Mg^{2+} > K^+ > Na^+$. Therefore, it was the absorption of ion exchange resin that controlled the separation sequence of different ions, which could also be affirmed by the results of Fig. 7. The case of SO_4^{2-} was abnormal partly because its concentration in the feed was low, which could not be change in tap water. As the complication of multi-ions situation added more difficulties to judge, a single-species testing

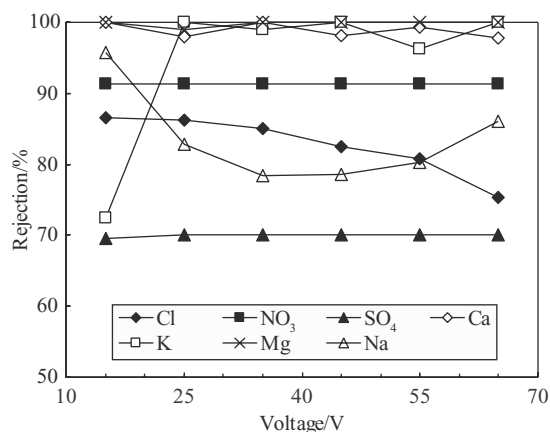


Fig. 6. Influence of operated voltage on ion rejection. The ion rejection was calculated by $R (100\%) = 100 \times (C_0 - C_1)/C_0$, where C_0 is the feed concentration, C_1 is the product concentration.

deserves to perform in the following experiments. Further, the composition ratio of cation exchange resin to anion exchange resin might cause special separation behavior and should be carefully studied later. For the lowest concentration of Ca^{2+} and Mg^{2+} shown in these figures, the resin absorption might be the most donations

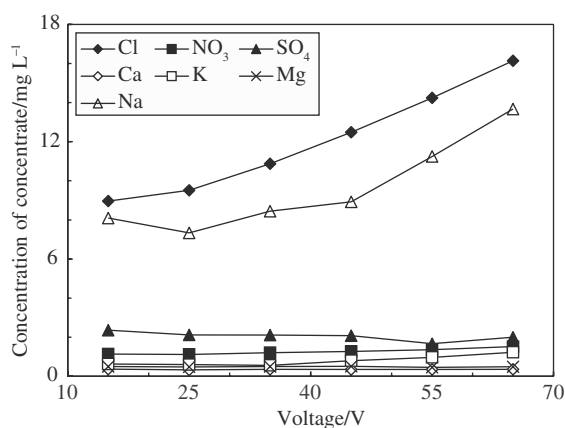


Fig. 7. Influence of operated voltage on the concentration of concentrate. The sequence from high to low is $Cl^- > Na^+ > SO_4^{2-} > NO_3^- > K^+ > Mg^{2+} > Ca^{2+}$.

and should be paid more attention in practical production to prevent scale forming which would be very harmful to EDI separation.

4. Conclusion

The mass transfer phenomena obtained by two bench scale EDI modules were evaluated concerning the concentration variation of different ions at different operating voltage. The main results are

- Compared with ordinary electrodialysis (ED) process, no obvious limiting current point was observed in EDI performance. The relationship between voltage and current can be expressed as $\varphi = 19.063 + 7.463 \ln(I)$.
- The ionic equilibrium analysis of EDI could be used to determine the steady state of the operating system and to select the optimum operation voltage which would enhance the current efficiency in the desalination process.
- At a lower voltage no more than 55 V, the resistance of EDI decreased obviously as the concentrate conductivity increased. At the higher operating voltage of 65 V, the curve of module resistance vs. concentrate conductivity was more leveled, and the change of concentration conductivity showed a wider range, demonstrating more active ions in the concentrate compartment.
- The sequence to selective separation rate of different univalent ions was Ca^{2+} , Mg^{2+} , $\text{K}^+ > \text{NO}_3^- > \text{Cl}^- > \text{Na}^+$ in the experiment, which was consistent with the relative order in conventional ion exchange.

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