Volume effect of organic solvent on electrochemical Seebeck coefficient of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ in water

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A thermocell with use of the electrochemical Seebeck coefficient ($\alpha \equiv \frac{dE}{dT}$; E and T are the redox potential and temperature, respectively.) is a promising energy harvesting device. α is the key parameter that governs the thermal efficiency (η) of the thermocell. Here, we systematically investigated the variation ($\Delta\alpha$) in α of a redox couple of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ in water, by adding 9 % organic solvent in molar ratio. We found that $\Delta\alpha$ for 11 organic solvents well scale to the molar volume (V). The empirical volume effect is understood in terms of the replacement of water molecules with organic molecules depending on V.

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1. Introduction

To establish a "smart" society, it is crucial to develop novel energy-harvesting technologies that produce electric energy efficiently from human body heat or waste heat near room temperature. A semiconductor-based thermoelectric device, where the Seebeck coefficient ($S_{\mathrm{Seebeck}} \equiv \frac{dE}{dT}$; E and T are the voltage and temperature, respectively) is a key material parameter, is a promising energy-harvesting technology. Bi_2Te_3 (S_{Seebeck} = 0.2 mV/K[1] at room temperature) and PbTe (0.12 mV/K[2] at 300 K) are a prototypical thermoelectric materials with high S_{Seebeck}. Actually, the thermoelectric devices are in practical use for the Peltier cooling and thermal power generation in space vehicles.[3]

On the other hand, several thermocells, which consist of hot and cold electrodes of identical type and solvable redox couples, were proposed in the 1950s and 1960s. Importantly, related research and development are still ongoing.[4–33] The thermocell converts temperature difference (ΔT) to voltage difference (ΔE) between the electrodes via the electrochemical Seebeck coefficient ($\alpha \equiv \frac{dE}{dT}$). Ikeshoji,[4] for example, reported thermocell containing a redox couple of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ or Fe^{2+}/Fe^{3+}. They observed a power density of 2.6

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W/m^2 at ΔT = 72 K in the cell whose electrolyte was aqueous solution containing 0.13 mmol/L $K_4[Fe(CN)_6]$ and 0.85 mmol/L $K_3[Fe(CN)_6]$. We emphasize that α (= - 1.4 mV/K) of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ at room temperature is much higher as compared with S_{Seebeck} of semiconductors, *e.g.*, Bi_2Te_3 (0.2 mV/K) and PbTe (0.12 mV/K). On the other hand, demerit of thermocell is high inner resistance, which causes low thermal efficiency ($\eta = 6.7 \times 10^{-5}$).[4] Nevertheless, from an industrial point of view, the thermocell is still attractive due to its simple device structures and low-cost materials.

From a thermodynamical point of view, α is $\frac{\Delta S}{e}$, where e and ΔS are the elementary charge (≥ 0) and difference in entropies of the system associated with reduction reaction. In the solution system containing electroactive solute, ΔS can be divided into the solute ($\Delta S_{\mathrm{solute}}$) and solvent ($\Delta S_{\mathrm{solvent}}$) components. $\Delta S_{\mathrm{solvent}}$ is ascribed to the variation of the configuration entropy of the solvent molecules within the solvation shell. The reduction reaction of the solute not only changes S_{solute} but also changes S_{solvent} via reconstruction of the solvent structure within the solvation shell.

In this work, we systematically investigated the variation ($\Delta\alpha$) in α of a redox couple of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ in water, by adding 9 % organic solvent in molar ratio. We found that $\Delta\alpha$ for 11 organic solvents well scale to the molar volume (V). The empirical volume effect is understood in terms of the replacement of water molecules with organic molecules depending on V.

2. Experimental methods

2.1 Preparation of electrolyte

The electrolyte was aqueous solution containing 1 mmol/L $K_4[Fe(CN)_6]$ and 1 mmol/L $K_3[Fe(CN)_6]$ with and without organic solvents. The denominator is the volume of water. The organic solvents are methanol (MeOH), ethanol (EtOH), propan-1-ol (PrOH), tert-butyl alcohol (t-BuOH), ethylene glycol (EG), glycerin, acetone, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), pyridine, 1,4-dioxane (dioxane), tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME), whose molecular structures are shown in Fig. 1. In Table I, we summarized molecular weight (W), molar volume (V), and density (ρ) of the organic solvents. The solvent are purchased and used as received. In the present experiment, the concentration of the organic solvent was fixed at 9 % in molar ratio, which corresponds to 14 - 33 wt % (Table I). The concentration (9 % in molar ratio) was set so that 1 mmol/L $K_4[Fe(CN)_6]$ and 1 mmol/L $K_3[Fe(CN)_6]$ are completely dissolved for all the organic solvents. Actually, we confirmed that 2 mmol/L $K_4[Fe(CN)_6]$ and 2 mmol/L $K_3[Fe(CN)_6]$ were completely dissolved in water

Table I. Molecular weight (W), molar volume (V), and density (ρ) of organic solvents. MeOH, EtOH, PrOH, t-BuOH, EG, DMSO, DMF, dioxane, THF, and DME mean methanol, ethanol, propan-1-ol, tert-butyl alcohol, ethylene glycol, dimethyl sulfoxide, N,N-dimethylformamide, 1,4-dioxane, tetrahydrofuran, and 1,2-dimethoxyethane, respectively. The weight percent (wt%) corresponding to 9 % in molar ratio is also shown.

solvent	$\Delta\alpha$ (mV/K)	W (g/mol)	V (cm^3/mol)	ρ (g/cm^3)	wt%
alcohol					
MeOH	0.04	32.04	40.46	0.80	14.97
EtOH	0.12	46.07	58.39	0.79	20.20
PrOH	0.30	60.10	74.84	0.80	24.82
EG	-0.10	62.07	55.92	1.11	25.43
t-BuOH	0.68	74.12	94.92	0.78	28.94
glycerin	-0.18	92.09	73.09	1.26	33.60
ketone					
acetone	0.37	58.08	73.71	0.79	24.19
DMSO	0.25	78.13	71.03	1.10	30.03
DMF	0.35	73.09	77.43	0.94	28.65
ether					
THF	0.73	72.11	81.10	0.89	28.38
dioxane	0.50	88.11	85.30	1.03	32.62
DME	0.92	90.12	103.89	0.87	33.12
other					
pyridine	0.33	79.10	80.56	0.98	30.29

containing 9 % respective organic solvents, *i.e.*, MeOH, EtOH, PrOH, t-BuOH, EG, glycerin, acetone, DMSO, DMF, pyridine, dioxane, THF, and DME. This result ensures that 1 mmol/L $K_4[Fe(CN)_6]$ and 1 mmol/L $K_3[Fe(CN)_6]$ are completely dissolved in water containing 9 % respective organic solvents.

We further investigated the solubility of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ in pure organic solvent. Except for EG and glycerin, the solubility is negligible since the absorption band due to $[Fe(CN)_6]^{4-}$ or $[Fe(CN)_6]^{3-}$ is absent in visible - violet absorption spectra. In these solvents, the solubility is evaluated less than 0.03 mmol/L. By contrast, solubility of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ is 1.3 and 1.1 mmol/L (1.3 and 0.3 mmol/L) in pure EG (glycerin), respectively.

2.2 Determination of α

α of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ in above-mentioned electrolytes with organic molecules were carefully determined with use of specially-designed thermocell (Fig. 2). The electrolyte was

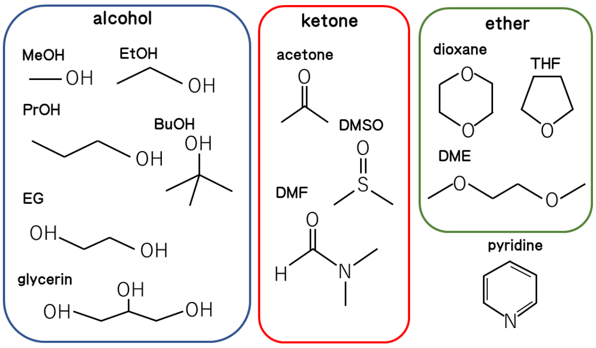

Fig. 1. (Color online) Structures of organic molecules. MeOH, EtOH, PrOH, t-BuOH, EG, DMSO, DMF, dioxane, THF, and DME mean methanol, ethanol, propan-1-ol, tert-butyl alcohol, ethylene glycol, dimethyl sulfoxide, N,N-dimethylformamide, 1,4-dioxane, tetrahydrofuran, and 1,2-dimethoxyethane, respectively.

filled in a ϕ7.3mm polytetrafluoroethylene (PTFE) tube. The both ends are sealed with the Al pedestals, on which Pt plates are attached as anode and cathode. The two electrodes were placed strictly parallel with a distance of 2mm, which causes pseudo one-dimensional thermal gradient within the electrolyte solution. The temperatures ($T_{\rm low}$ and $T_{\rm high}$) of the two electrodes are monitored with T-type thermocouples, which are attached at the pedestals at a distance of 2mm from the electrode-electrolyte interfaces. $T_{\rm low}$ and $T_{\rm high}$ are independently controlled with Peltier modules attached at the bottom of the pedestals. The difference (ΔE) in the redox potential between the electrodes was carefully measured against ΔT (= $T_{\rm high}$ and $T_{\rm low}$) with fixing $T_{\rm low}$. ΔT was less than 13 K. We note that $S_{\rm Seebeck}$ (= - 2 μV/K) of the Al pedestal is negligible as compared with the observed α (= -0.4 ~ -1.6 mV/K).

3. Results

3.1 Electrochemical Seebeck coefficient

Figure 3 shows ΔE against ΔT in aqueous solutions of $[\mathrm{Fe(CN)_6}]^{4-}$/$[\mathrm{Fe(CN)_6}]^{3-}$ with adding 9 ‰ organic solvent. Broken straight lines represent data without organic solvent. The Seebeck coefficient (α_0) without organic solvent is - 1.50 mV/K. The data obtained in the cooling (open symbols) and warming (closed symbols) runs well overlapped to each other, indicating the data is free from thermal deterioration. In the case of (a) alcohol, ΔE shifts to the positive side for primary alcohols (MeOH, EtOH, PrOH, and BuOH) while it shifts to the negative side for secondary (FG) and tertiary (glycerin) alcohols. In the case of primary alcohol, the magnitude of the shift increases with W, *i.e.*, in the order of MeOH, EtOH, PrOH, and BuOH. In the case of (b) ketone, ΔE shifts to the positive side for all the solvents. The magnitude of

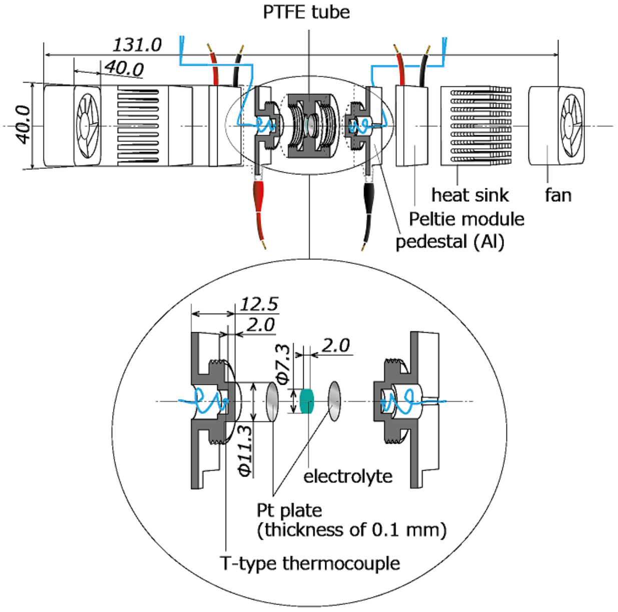

Fig. 2. (Color online) Illustration of specially-designed thermocell. Scales are in mm.

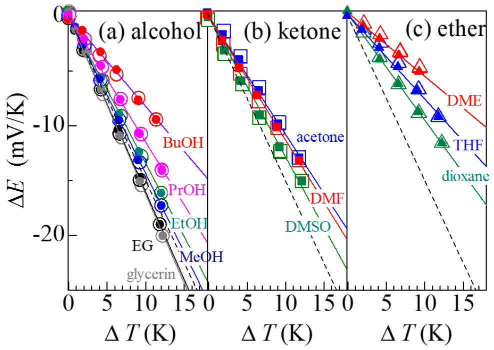

Fig. 3. (Color online) Difference (ΔE) in the redox potential against difference (ΔT) in temperature in aqueous solutions of $[\mathrm{Fe(CN)_6}]^{4-}/[\mathrm{Fe(CN)_6}]^{3-}$ with adding 9 % organic solvent: (a) alcohol, (b) ketone, (c) ether. Open and closed symbols represent data obtained in the cooling and warming runs, respectively. Error bars (≤ 0.01 mV) are within the symbol size. Solid straight lines are results of least-squares fittings. Broken straight lines represent data without organic solvent.

the shift, however, does not increase with W, but in the order of DMSO ($W = 78.13$), DMF (73.09), and acetone (58.08). In the case of (c) ether, ΔE shifts to the positive side for all the solvent. The magnitude of the shift does not increase with W, but in the order of dioxane ($W = 88.11$), THF (72.11), and DME (90.02).

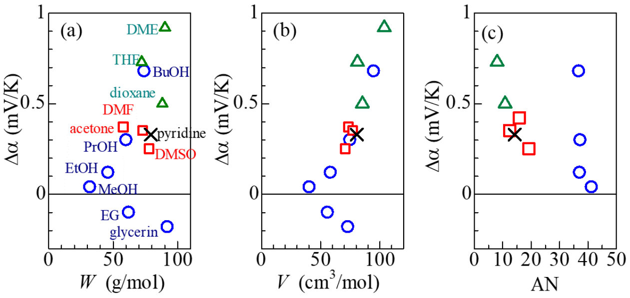

Fig. 4. (Color online) Variation ($\Delta\alpha$) of electrochemical Seebeck coefficient (α) by adding 9 % organic solvent in molar ratio against (a) molecular weight (W), (b) molar volume (V) and (c) acceptor number (AN). Circles, squares, triangles and cross represent alcohol, ketone, ether, and pyridine, respectively.

3.2 Scaling relation in organic solvent effect ($\Delta\alpha$)

We define the organic solvent effect ($\Delta\alpha$) as $\Delta\alpha = \alpha - \alpha_0$, where α and α_0 (= -1.50 mV/K) are the values with and without organic solvent, respectively. Figure 4(a) shows correlation between $\Delta\alpha$ and W for 13 organic solvents. Solvents other than EG and glycerin shows positive correlation in the $\Delta\alpha$ - W plane. The distribution of data, however, is rather wide. In addition, $\Delta\alpha$ of ketones (circles) and ether (triangles) does not increase in the order of W. Figure 4(b) shows correlation between $\Delta\alpha$ and V (= $\frac{W}{\rho}$). The distribution of data points is much narrower in the $\Delta\alpha$ - V plane than that that in the $\Delta\alpha$ - W plane. Thus, we empirically found that $\Delta\alpha$ for 11 organic molecules well scales V. We will call the relation as *empirical volume effect*.

Weaver *et al.*[34] reported a linear relationship between the reaction entropy of Ru redox species in organic solvents and their acceptor number (AN).[35] AN measures Lewis basicity of the solvent, and hence, relates to the electrostatic interaction between the redox ion and solvent. So, we investigate the correlation between $\Delta\alpha$ and AN [Fig. 4(c)]. However, the correlation between $\Delta\alpha$ and AN is much poorer than that between $\Delta\alpha$ and V [Fig. 4(b)]. In the present experiment, the reaction entropies of $[\mathrm{Fe(CN)_6}]^{4-}/[\mathrm{Fe(CN)_6}]^{3-}$ in water containing 9 % organic solvent were investigated. Then, AN of the added organic molecule is not the determinative parameter of the electrochemical reaction of the solute - water - organic solvent system.

3.3 Comparison with literature

Recently, Kim *et al.*[5] reported that addition of organic solvent, such as MeOH and EtOH, enhances α of $[\mathrm{Fe(CN)_6}]^{4-}/[\mathrm{Fe(CN)_6}]^{3-}$ in negative direction. For example, $\Delta\alpha$ = - 1.4 mV/K

(-1.5 mV/K) when 20 wt% MeOH (20 wt% DMF) is added to the aqueous solution. Their results apparently contradict with the present results; $\Delta\alpha \geq 0$ when 15 wt% MeOH (29 wt% DMF) is added to the aqueous solution. We investigated the effect of the concentration (wt%) of the organic solvent on $\Delta\alpha$: $\Delta\alpha$ monotonously increases with wt% with keeping positive value. Therefore, the slight difference in wt% cannot explain the serious discrepancy.

We note that the solute concentration in the experiment performed by Kim *et al.*$^{5)}$ was 400 mmol/L, which is two order higher than that (1 mmol/L) in the present experiment. We note that 400 mmol/L is close to the solubility of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ in water at 298 K. We tried to dissolve 400 mmol/L $[Fe(CN)_6]^{4-}$ and 400mmol/L $[Fe(CN)_6]^{3-}$ in water containing 20 wt% MeOH or 20 wt% DMF. In both cases, a part of the solute remained at the bottom of the beaker. This means that the actual solute concentration is the same as the solubility of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$, which strongly depend on the electrode temperature. In addition, the solute concentration influences α, even if water is only used as solvent. Then, the negative-$\Delta\alpha^{5)}$ may be ascribed to the difference in the actual solute concentration between the high (T_{high}) and low (T_{low}) temperature electrodes.

4. Discussion

Now, let us consider the origin of the empirical volume effect as observed. From a thermodynamic point of view, α is $\frac{\Delta S}{e}$, where ΔS in entropies (S) of the system associated with reduction reaction. ΔS can be divided into the solute ($\Delta S_{\mathrm{solute}}$) and solvent ($\Delta S_{\mathrm{solvent}}$) components. In the present redox system, *i.e.*, $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ in water with organic solvent, $\Delta S_{\mathrm{solute}}$ is ascribed to variation of configuration entropy (S_{3d}) of the $3d$ electrons and vibrational entropy (S_{vib}) of the internal mode. It is well known that Fe ion takes the low spin state in $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. Then, ΔS_{3d} is easily evaluated at - 0.15 meV/K.$^{36)}$ On the other hand, ΔS_{vib} is evaluated at - 0.17 meV/K.$^{37)}$ Then, $\Delta S_{\mathrm{solvent}}$ (= ΔS - ΔS_{3d} - ΔS_{vib}) becomes - 1.18 meV/K.

If no organic solvent is added, $\Delta S_{\mathrm{solvent}}$ is ascribed to variation of the configuration entropy of water within the solvation shell around $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$. Prampolini *et. al.*$^{38)}$ investigated the water structure around $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ by means of quantum mechanical and molecular dynamics calculations. They found that water molecules get closer to $[Fe(CN)_6]^{4-}$ than to $[Fe(CN)_6]^{3-}$, reflecting the higher charge of $[Fe(CN)_6]^{4-}$. The radius of first solvation shell (~ 5.8 Å) of more charged $[Fe(CN)_6]^{4-}$ is smaller than that (~ 6.1 Å) of less charged $[Fe(CN)_6]^{3-}$. Then, the water molecules in the first solvation shell of $[Fe(CN)_6]^{4-}$ are considered to be more closely packed. Actually, the number of molecules found within 5 Å is 17 for $[Fe(CN)_6]^{4-}$ and 11 for $[Fe(CN)_6]^{3-}$. Such water structures suggest that S_{solvent}

around $[\mathrm{Fe(CN)_6}]^{4-}$ is smaller than that around $[\mathrm{Fe(CN)_6}]^{3-}$. Then, $\Delta S_{\mathrm{solvent}}$ is expected to be negative, consistently with the observation ($\Delta S_{\mathrm{solvent}}$ = - 1.18 meV/K).

What happens if organic solvent is added to the system? We note that the solubility of the positive-$\Delta\alpha$ organic solvents, *i.e.*, MeOH, EtOH, PrOH, t-BuOH, acetone, DMSO, DMF, pyridine, dioxane, THF, and DME, is less than 0.03 mmol/L. The small solubility suggests small solvation effect with $[\mathrm{Fe(CN)_6}]^{4-}$ and $[\mathrm{Fe(CN)_6}]^{3-}$. Then, these organic molecules do not directly coordinate with $[\mathrm{Fe(CN)_6}]^{4-}/[\mathrm{Fe(CN)_6}]^{3-}$, when mixed with water. In other words, the organic molecules do not influence $\Delta S_{\mathrm{solute}}$. We rather consider that the organic molecule influence $\Delta S_{\mathrm{solvent}}$ via spatial replacement of water molecules in proportion to its molar volume (V). In the displaced volume, the variation of configuration entropy ($\Delta S_{\mathrm{water}}$) of the water molecule is replaced by that ($\Delta S_{\mathrm{organic}}$) of the organic molecule. Then, $\Delta\alpha$ is proportional to $\Delta S_{\mathrm{organic}}$ - $\Delta S_{\mathrm{water}}$. $|\Delta S_{\mathrm{water}}|$ is expected to be larger than $|\Delta S_{\mathrm{organic}}|$, since the degree of freedom of water arrangement is larger than that of organic molecule. Then, we expect that $\Delta S_{\mathrm{organic}} - \Delta S_{\mathrm{water}} > 0$. Thus, our picture well explains the observed positive correlation between $\Delta\alpha$ and V [Fig. 4(b)].

More precisely, we obtain $\Delta\alpha = v\frac{\Delta S_{\mathrm{organic}}-\Delta S_{\mathrm{water}}}{e}$, where v (= $\frac{V}{180+V}$) is the volume fraction of organic molecule. This qauation, however, fails to explain the nonlinear or threshold behaver between $\Delta\alpha$ and V [Fig. 4(b)]. One possible explanation is that organic molecules prefer to be outside of the solvation shell. In small-v region, there is no organic molecules in the solvation shell, and hence, has no effect on α. In high-v region, however, the organic molecules are push to the solvation shell to causes the nonlinear behavior.

Finally, let us comment on the exceptional negative $\Delta\alpha$ observed in EG and glycerin. We emphasize that EG and glycerin shows finite solubility of $\mathrm{K_4[Fe(CN)_6]}$ and $\mathrm{K_3[Fe(CN)_6]}$, making in sharp contrast with the other 11 organic molecules. The finite solubility suggests strong solvation effect with $[\mathrm{Fe(CN)_6}]^{4-}$ and $[\mathrm{Fe(CN)_6}]^{3-}$. Then, these organic molecules tend to coordinate with $[\mathrm{Fe(CN)_6}]^{4-}$ and $[\mathrm{Fe(CN)_6}]^{3-}$, when added into the electrolyte. Such a coordination may cause the exceptional negative $\Delta\alpha$ as observed.

5. Conclusion

In conclusion, we systematically investigated the variation ($\Delta\alpha$) in α for a redox couple of $[\mathrm{Fe(CN)_6}]^{4-}/[\mathrm{Fe(CN)_6}]^{3-}$ in water, by adding 9 % organic solvent in molar ratio. We found that $\Delta\alpha$ for 11 organic molecules well scale to the molar volume (V). The empirical volume effect is understood in terms of the replacement of water molecules with organic molecules depending on V. Our results indicate that the solvent effect on α is significant. We belive an appropriate combination of redox pair and organic molecule could enhance the magnitude of α.

Acknowledgments

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