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Synthesis and Evaluation of Octyl Methylimidazolium Oleate and Octyl Methylimidazolium Stearate as Lubricant Additives

Thuy Thi Le Bui

Key Research Group: Green Chemistry Process (HUMG-GCP), Department of Oil Refinery and Petrochemical Engineering, Hanoi University of Mining and Geology, 18- Vien Street, Dong Ngac Ward, Ha Noi, Viet Nam.
Email: *thuykhai2001[at]gmail.com*

Abstract: ***The study reports the synthesis of octyl methylimidazolium oleate ([OMIM][Oleate]) and octyl methylimidazolium stearate ([OMIM][Stearate]) from octyl methylimidazolium chloride and fatty acids. The synthesized ionic liquids were characterized using FT-IR and 1H NMR spectroscopy. The effects of reaction temperature, reaction time, and reactant molar ratio on synthesis yield were systematically investigated. The optimum conditions were a [RCOOH]/[OMIM] molar ratio of 1.3, temperatures of 70°C and 78°C, and reaction times of 6 h and 7 h for [OMIM][Oleate] and [OMIM][Stearate], respectively. Under these conditions, yields of 88.5% and 80.7% were obtained. When combined with reduced graphene oxide, the ionic liquids improved dispersion stability in lubricant and enhanced friction reduction. Among the two additives, [OMIM][Oleate] exhibited superior dispersion stability and tribological performance, demonstrating its potential as an environmentally friendly lubricant additive.***

Keywords: Ionic liquids; Octyl methylimidazolium; Oleate; Stearate; Reduced graphene oxide; Lubricant additives; Tribology; Green chemistry

1. Introduction

Currently used additives exhibit excellent anti-friction, anti-wear, and anti-oxidation properties. However, most contain sulfur and phosphorus, which pose environmental concerns and cause corrosion on metallic friction surfaces. This has driven research into developing novel additives to partially or completely replace traditional ones. Ionic liquids (ILs), consisting of cations and anions and remaining liquid at room temperature have been used in many application including catalysts [1,2], solvents [3], both catalyst and solvent [4] . They have emerged as versatile lubricants with exceptional properties [5-7]. Nevertheless, their application is hindered by several drawbacks, including high cost, complex synthesis, poor solubility, corrosivity, and environmental impact [8-10]. To address these challenges, this study synthesizes non-halogenated ILs derived from plant-based long-chain fatty acids, specifically oleic and stearic acids. The long carbon chains of these acids reduce the polarity of the ILs, thereby enhancing their solubility in lubricants [11]. Furthermore, the use of non-halogenated anions significantly mitigates corrosivity. The synthesized ILs are employed in combination with graphene as lubricant additives. Finally, the dispersion stability and lubrication efficiency of these additives are systematically evaluated.

2. Experimental

2.1 Materials

1-Methyl imidazole (99%) was purchased from Merck; 1-Chlorooctane were supplied from Sigma- Aldrich, oleic acid (99%), stearic acid (97%), ethyl acetate (99.5%), hydrogen chloride (37%), ethanol (99.9%), acetone (99%) and potassium hydroxide (85%) were supplied by Guangdong Guanghua Company, China. rGO is synthesized and provided by the laboratory of the Hanoi University of Mining and Geology. Lubricant was supplied by Ba Ria - Vung Tau Chemical Industry Joint Stock Company (Chemico).

2.2 Preparation of ionic liquids

The ionic liquid [OMIM][Oleate] and [OMIM][Stearate] were synthesized from octyl methyl imidazolium chloride ([OMIM]Cl) and oleic/stearic acid. Fatty acids were converted to sodium carbocylate (RCOOK) and then RCOOK reacted with octyl methyl imidazolium chloride.
[OMIM][Oleate] was synthesized by 3 steps:

$C_4H_6N_2 + CH_3(CH_2)_7Cl \rightarrow [C_{12}H_{23}N_2]\ Cl$ ([OMIM]Cl)

$C_{17}H_{33}COOH + KOH \rightarrow C_{17}H_{33}COOK + H_2O$

$C_{17}H_{33}COOK + [OMIM]Cl \rightarrow [C_{17}H_{33}COO][OMIM]Cl + KCl$

Synthesis of octyl methyl imidazolium chloride

Methylimidazole (0.5 mol) was charged into a three necked round bottom flask immersed in an oil bath. The flask equipped with a thermometer, a reflux condenser, a 250 ml dropping funnel and a magnetic stirrer and was heated to 75°C. Subsequently, 1-chlorooctane (0.52 mol) was added dropwise via a dropping funnel over a period of 1 h. The reaction mixture was maintained under stirring at 75°C for 100 h, yielding a pale red, viscous solution. To remove unreacted starting materials, the resulting mixture was washed three times with acetone (50 mL). After shaking, the mixture was allowed to phase separate, and the lower ionic liquid (IL) layer was collected. Residual solvents were removed by heating at 80°C until a constant weight was achieved, yielding the final product [OMIM]Cl.

Synthesis of OMIM][Oleate] or [OMIM][Stearate]

Oleic acid or stearic acid (0.0231 mol) was added to a flask containing 80 mL of an ethanol solution containing 1.7864 g (0.0319 mol) of KOH. The reaction flask was equipped with a reflux condenser and a thermometer, then heated in an oil bath at 45°C. After stirring at this temperature for 3 h, 9.72

mL (0.0177 mol) of [OMIM]Cl was added, and the mixture was further heated and stirred at the studied temperature and time, resulting in a precipitate. The precipitate was filtered, and 20 mL of ethyl acetate was added to the mixture. The mixture was shaken and heated if necessary to ensure the complete dissolution of the ionic liquid (IL) into the ethyl acetate phase. The mixture was then transferred to a separating funnel, allowed to stand, and the ethyl acetate layer was collected. This washing process was repeated twice. The combined ethyl acetate fractions were distilled to recover the solvent and isolate the IL. The final product was weighed to calculate the reaction yield.

Influence of reaction temperature and reaction time of thesecond step, molar ratio of acid to aliquat on IL synthesis

In this work, in order to investigate the influence of reaction temperature, reaction time *of the third step* and molar ratio of *acid to* [OMIM]Cl on synthesis yield of ionic liquids [OMIM][Oleate] and [OMIM][Sterate]; The reaction temperature, reaction time *of the second step* and RCOOH/[OMIM]Cl molar ratios was varied from 50°C to 70 °C, from 4 h to 8 h and from 1.1 to 1.4, respectively.

Ionic liquid synthesis yield was determined by formula:

$$Y\ (\%) = \frac{m_{IL\,(eq)}}{m_{IL\,(ex)}} x100\% \qquad (1)$$

where: $m_{IL(eq)}$: weight of IL calculated from equation;
$m_{IL(ex)}$: weight of ionic liquid obtained from experiment.

Characterization

FI-IR and NMR spectra of synthesized ionic liquids were measured by FT-IR-1S Shimadzu and NMR Brucker Advance III 500 MHz in $CDCl_3$.

2.3 Evaluation of dispersibility of rGO in lubricant

Reduced graphene oxide (rGO) and ionic liquid [OMIM][Oleate] was mixed to form a dispersion of 0.20 wt% rGO in IL, then this dispersion was added up to 2 wt% to lubricant to form a mixture containing 0.002 wt% rGO and 2 wt% IL denoted as the rGO/[OMIM][Oleate] 0.2%/CBT 2% mixture. The mixture was shaken, stirred and ultrasonic to obtain a homogeneous system. The procedure was repeated with ionic liquid [OMIM][Sterate] to get 2 samples (rGO + IL) 0.2% (Table 1).

Table 1: List of ionic liquids and samples in this research

Ionic liquids	Abbreviation
[OMIM][Oleate]	rGO/[OMIM][Oleate] 0.2%/CBT 2%
[OMIM][Sterate]	rGO/[[OMIM][Sterate]0.2%/ CBT 2%

The UV-VIS of dispersions was measured after mixing at different time intervals. From the UV-VIS measurement results, the relative concentration of solids can be calculated according to formula (2). Based on this relative concentration, the stability of solids in liquids can be assessed:

$$Relative\ con. = \frac{Absorption\ at\ certain\ time}{Absorption\ at\ innitial\ time} * 100\% \qquad (2)$$

2.4 Evaluation of the friction moment reduce ability moment of lubricants containing ionic liquid and graphene

The friction performance of lubricants in drilling fluids is determined (on the EP/Lubricity Tester) according to the technical standard РД VSP-000-PK-650 of the Vietsopetro. The drilling fluid used as a basis for measuring lubrication has a specific gravity of 1.40-1.45 G/cm^3; pH 9-9.5 and has components and rheological parameters according to the technical standard РД VSP-000-PK-637 of the VietsoPetro. The proposed formulation of drilling fluids is a water-based inhibitor solution system.

The friction reduction indicates the lubricity of lubricants in drilling fluids and is calculated according to the following formula:

$$\text{Friction moment reduction} = \frac{(f_1 - f_2) * 100}{f_1}\ x\%$$

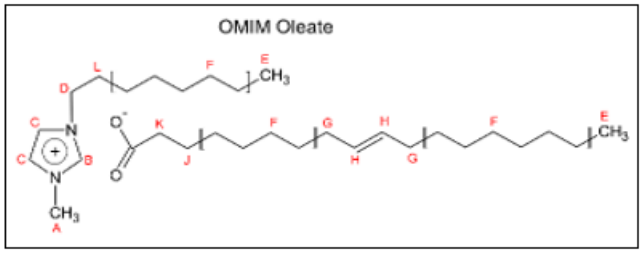
Where: f_1 readings on the meter without adding lubricant additives; f_2 readings on the meter with adding lubricant additives.

The friction reduction was measured at room temperature and after heating (at 130°C during 16 h) for evaluate the stablility of the lubricanr containing additives.

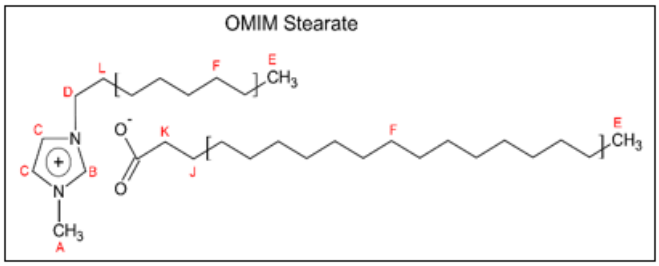
3. Results and Discussion

3.1 Characterization of triethyl ammonium oleate [OMIM][Oletate] and triethyl ammonium stearate [OMIM][Stearate]

Structure of [OMIM][Oleate] and [OMIM][Stearate] are given in Fig, 1. The FT-IR spectra provide clear evidence of the structural components of the synthesized ionic liquids (ILs). The absorption band at 3771 cm^{-1} is assigned to the O-H stretching vibration of residual water within the ILs. In the aromatic region, peaks at 3148 cm^{-1} and 3147 cm^{-1} correspond to the C=C-H stretching of the imidazolium rings. A distinct peak at 3006 cm^{-1} in the [OMIM][Oleate] spectrum confirms the presence of sp^2 =C-H stretching from the oleate ions, a feature notably absent in [OMIM][Stearate]. Aliphatic chain characteristics are observed through asymmetric and symmetric C-H stretching at 2921 cm^{-1} and 2952 cm^{-1}. Furthermore, the presence of C=O and COO^- groups in [OMIM][Oleate] and [OMIM][Stearate] is confirmed by peaks at 1732–1733 cm^{-1} and 1561–1562 cm^{-1}, respectively. The broad signals between 1460 cm^{-1} and 1480 cm^{-1} result from the overlapping CH_2/CH_3 bending vibrations and the signature N-CH_3 vibration of the quaternary ammonium headgroup. Finally, the sharp peaks at 721–722 cm^{-1} represent the rocking vibrations of long hydrocarbon chains (≥4 consecutive groups), consistent with the alkyl structures of both the metyl octhyl imidazolium cation and the fatty acid anions.



(a)



(b)

Figure 1: Structure of [OMIM][Oletate] (a) and [OMIM][Stearate] (b).

^{1}H NMR δ(ppm) of [OMIM][Oletate]:
0.860-0.888 (t, 6H, CH_3^E), 1.222-1.301 (m, 30H của CH_2^F), 1.607-1.621 (m, 2H, CH_2^J), 1.852-1.881 (m, 2H, CH_2^L), 1.999-2.044 (m, 4H, CH_2^G), 2.193-2.225 (t, 2H, CH_2^K), 4.072 (s, 3H, N-CH_3^A), 4.279-4.309 (t, 2H, CH_2^D), 5.323-5.367 (m, 2H, CH^H), 7.079-7.082 (d, 2H, CH^C), 11.561 (s, 1H, CH^B).

^{1}H NMR δ(ppm) of [OMIM][Stearate]:
0.860-0,892 (t, 6H, CH_3^E); 1.244-1.323 (m, 38H, CH_2^F); 1.621-1.650 (m, 2H, CH_2^J); 2.207-2.238 (2H, CH_2^K); 4.074 (s, 3H, N-CH_3^A); 4.278-4.308 (t, 2H, CH_2^D)**,** 7.109-7.127 (d, 2H, CH^C), 11.382 (s, 1H, CH^B).

From the results of FT-IR and NMR spectra, two ionic liquids were successfully synthesized.

3.2 Influence of factors on synthesis of [OMIM][Oleate] and [OMIM][Stearate]

Influence of reaction temperature on IL synthesis performance
The results in Fig. 2 showed that [OMIM][Oleate] synthesis yield increases dramatically from 68.1% to about 83.63% when increasing the reaction temperature from 50ºC to 70ºC, the and the yield increase more slowly at temperature of 78ºC (89.1%). When temperature increases from 50ºC to 70ºC and then to 78 ºC [OMIM][Stearate] synthesis efficiency increases rapidly from 60,2% to 69.1% and then to 80.7%. The suitable temperatures for synthesizing [OMIM][oleate] and [OMIM][Stearate] are 70ºC and 78ºC, respectively.

Similar to trimethyl ammonium ionic liquids [12], the higher temperature is required for reaction of sodium stearate with aliquat compared to reaction of sodium oleate with aliquat because both stearate ionic liquid and sodium stearate have higher melting temperatures than [OMIM][oletate] and sodium oleate. They have lower viscosity and mobility than corresponding compounds of oleic acid at the same temperature.

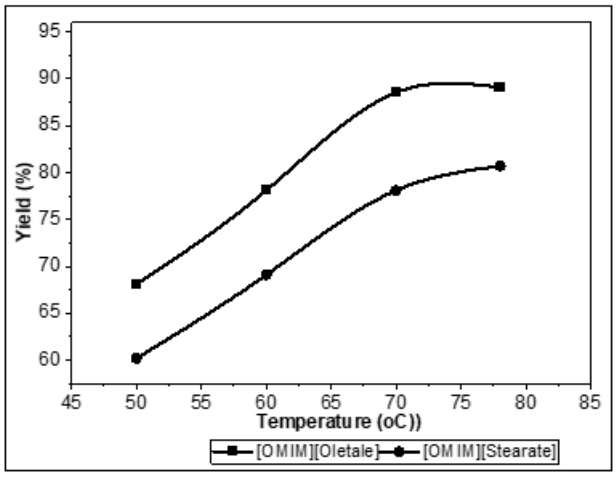


Figure 2: Influence of reaction temperature on the synthesis efficiency of [Aiquat][oleate] and [OMIM][Stearate] (molar ratio [RCOOH]/[OMIM]= 1.3; 6 h for [OMIM][oleate] and 7 h for [OMIM][Stearate]).

Influence of reaction time on IL synthesis performance
Ionic liquids [OMIM][Oletate] and [OMIM][Stearate] were synthesized at temperatures of 70 ºC and 78 ºC, respectively with the molar ratio of [RCOOH] to [OMIM] is 1.3 and at different time intervals from 4 hours to 8 hours. The results are presented in Fig. 3.

It can be seen that [OMIM][Oletate] synthesis efficiency increases from 66,2% to 88.53% with increasing the reaction time from 4 hours to 6 hours. However, when increasing the reaction time from 6 to 8 hours, the reaction slightly increases. When increasing the time from 4 hours to 7 hours the [OMIM][Stearate] yield increases rapidly from 53.3% to 80.7% and then slightly change with increasing the reaction time to 8 hours.

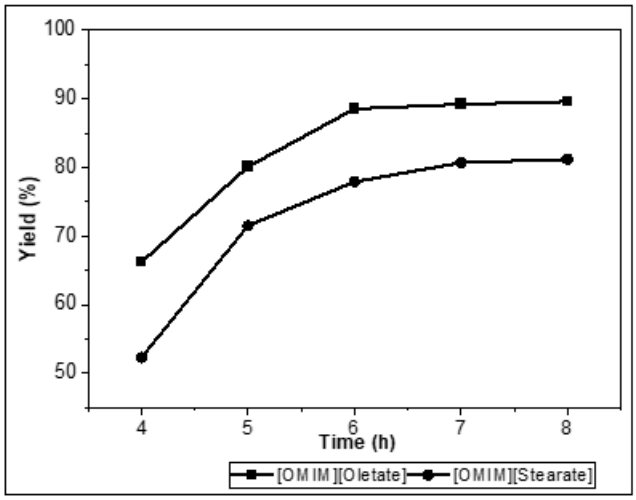


Figure 3: Influence of reaction time on the synthesis yield of [OMIM][Oletate] and [OMIM][Stearate] (with molar ratio [RCOOH]/[OMIM]= 1.3; temperature 70 ºC with [OMIM][Oletate] and 78ºC with [OMIM][Stearate])

It can be seen from the results that [OMIM][Oletate] eware formed faster than [OMIM][Stearate]. This can propsed that the presence of a double bond in oleic acid which results in the decrease in viscosity and mobility of the ionic liquid and, therefore, reaction time is reduced [12].The suitable time for

synthesizing [OMIM][Oletate] and [OMIM][Stearate] are 6 hours and 7 hours.

Influence of [RCOOH]/[OMIM] molar ratio on IL synthesis performance

[OMIM][Oleate] and [OMIM][Stearate] were synthesized at 80°C in 7 h and at 90°C in 7 h. Reactions were carried out with different [RCOOH]/[OMIM] molar ratios of 1.1; 1.2; 1.3; 1.4.

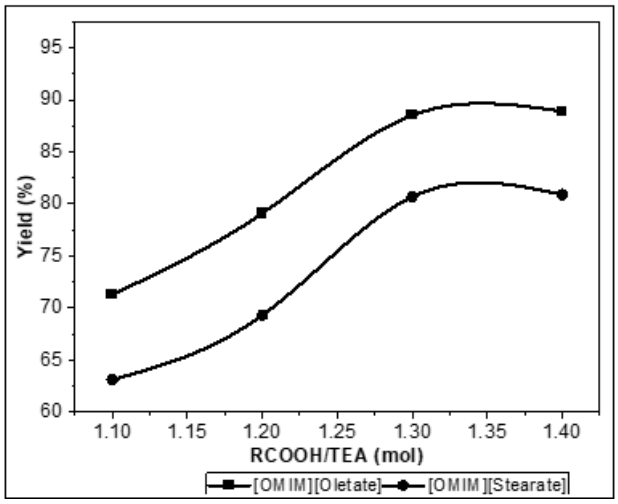


Figure 4: Influence of [RCOOH]/[OMIM] molar ratio on IL synthesis performance (6 h for [OMIM][oleate] and 7 h for [OMIM][Stearate], temperature 70 °C with [OMIM][Oletate] and 78°C with [OMIM][Stearate])

The results in Fig. 4 show that the yields of [OMIM][Oleate] and [OMIM][Stearate] increase from 66.3% and 62.1% to 83.7 % and of 80.1 %, with increasing the [RCOOH]/[OMIM] molar ratio and reaches the maximum value at 1.3. This is due an excess amount of one of reactants will shift the equilibrium to form the products. In this work an excess amount of RCOOH, which is cheaper and more environmentally safe was used for this purpose.

Tab. 2 presents the suitable conditions for synthesizing the two ionic liquids [OMIM][oleate] and [OMIM][Stearate].

Table 2: Optimal conditions for the synthesis of [OMIM][oleate] and [OMIM][Stearate]

No	Parameters	Ionic liquids	
		[OMIM] [Oletate]	[OMIM] [Stearate]
1	Solvent	Ethanol	Ethanol
2	Temperature (oC)	70	78
3	Time (h)	6	7
4	[RCOOH]/[TEA] (mol)	1.3	1.3
	Yield (%)	88.53	80.7

2 Dispersibility of rGO in lubricant

To evaluate the role of ionic liquids in increasing the stability of rGO in lubricants, mixture of rGO and [OMIM][Oleate] or [OMIM][Stearate] was dispersed in lubricant and the dispersibility of rGO in lubricant mixed with and without ionic liquids was evaluated. Ionic liquids used to are made up of the same cation. It can be seen from the results in Figure 5 that rGO relative concentration in lubricant mixed with ionic liquids decreased slower than without ionic liquids. For example, after 5 days and 20 days, the relative concentration of rGO in lubricant decreased from approximately 100% (0 days) to 77.6% and 69.7% while concentration of rGO in [OMIM][Oleate]+lubricant and [OMIM][Stearate] + lubricant decreased from 100% (0 days) to 95.5% and 93.5% (5 day) and to 92.6% and 89.4& (20 days), respectively. It is observed that the stability of rGO in the lubricant mixed with [Oleate] based ionic liquid is higher than in the lubricant mixed with [Stearate] IL.

[OMIM][Oleate] made of unsaturated fatty acid anion is more polar and contains high electron density π bonds, so that it is easily compatible with rGO which has polar O-H groups.

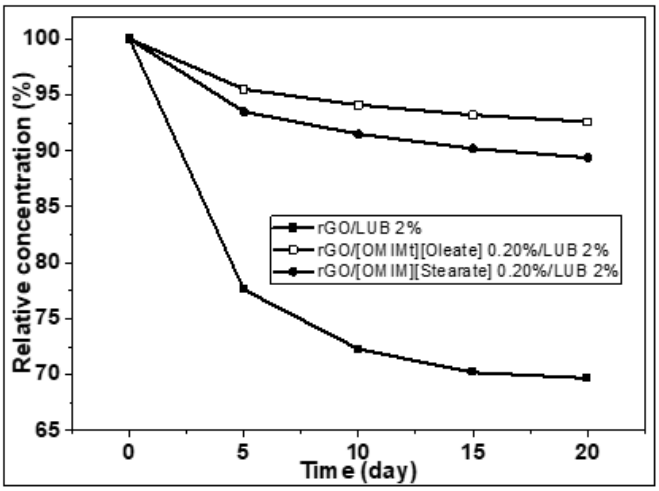


Figure 5: Influence of structure of ionic liquid on the dispersibility of rGO in IL and lubricants: GO concentration in IL is 0.20%; IL concentration in lubricant is 2%.

3.3 Friction performance of lubricants before calcination

Tribology performance of lubricant containing rGO and ionic liquids [OMIM][Oleate] decreased is better than of lubricant containing [OMIM][Stearate] more than lubricant containing only rGO. For example, friction moment decreases of lubricant+rGO, lubricant + rGO + [OMIM][Oleate] and lubricant +rGO + [OMIM][Stearate] are 58%, 71% và 69% before calcination.

Similarly lubricant+rGO, lubricant + rGO + [OMIM][Oleate] and lubricant +rGO + [OMIM][Stearate] decrease the friction moment 54%, 63% và 61% after calcination.

Table 3: Friction reduction results of additive samples containing rGO and ionic liquids

Abbreviation	Reduction in friction moment of lubricant containing rGO and ionic liquid (%)	
	Before calcination	After calcination *
rGO/LUB 2%	58	54
rGO/[OMIM][Oleate] 0.20%/LUB 2%	71	63
rGO/[OMIM][Stearate] 0.20%/LUB 2%	69	61

* at 130°C during 16 h

It is due to the decrease in friction moment is closely correlated with the stability of the ionic liquids in the lubricant. The stability of rGO in lubricants mixed ionic liquids also depends on the structure of ILs. The data in Table 3 also shows that when using IL together with rGO, the frictional moment is reduced more than when using rGO alone

and rGO is most stable in the ionic liquid [OMIM][Oleate] than in [OMIM][Stearate].

4. Conclusion

Two ionic liquids, [OMIM][Oleate] and [OMIM][Stearate], were successfully synthesized and confirmed by FT-IR and 1H NMR analyses. The optimum synthesis conditions were identified for both products, with [OMIM][Stearate] requiring a higher reaction temperature than [OMIM][Oleate]. The synthesized ionic liquids effectively improved the dispersion stability of reduced graphene oxide in lubricant and enhanced friction reduction compared with graphene alone. Among the investigated additives, [OMIM][Oleate] demonstrated the best overall performance, indicating its potential as an environmentally friendly lubricant additive for tribological applications.

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