Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

https://chemeng.hust.edu.vn/jca/

Investigation on synthesis of two ammonium based ionic liquids from fatty acids and triethylamine

Thuy Thi Le Bui[1,*], Tien Anh Dang[1], Khun Borin[1], Thanh Nam Ly[1], Trung Tuan Pham[1], Thanh Xuan Thi Phan[1], Ngoc Pham-Cong[2]

[1]*Hanoi University of Mining and Geology, Duc Thang, Bac Tu Liem, Ha Noi*
[2]*Earlham College, 801 National Rd W, Richmond, IN 47374, United State*
**Email: thuykhai2001@gmail.com*

ARTICLE INFO

Received: 07/06/2022
Accepted: 25/07/2022
Published: 20/08/2022

Keywords:

Ionic liquid, synthesis, fatty acid, triethyl amine.

ABSTRACT

Two ionic liquids triethylammonium oleate and triethylammonium stearate were synthesized from fatty acids and triethyl amine using two different methods (one step and three step methods). The yield triethylammonium oleate rearch 68.8-74% (one step method) and 86.3% (three step method) and of triethylammonium stearate rearch 68.7-74.1 (one step method) and 83.5% (three step method). The one step method spends more time but less chemicals and brings higher yield. FT-IR and ^{1}H-NMR spectra of ILs obtained from both method was measured. The results showed that synthesis method doesn't affect on the structure of the products and ILs obtained from one step method has higher purity.

Introduction

Saving energy and protection of environment are essential factors for the sustainability of society and therefore, investigatin of methods for energy saving and environmental protecting are attracting the attention of the whole world to keep the earth clean and green. Using effective lubricants to reduce friction could save ~ 17.5% of the energy used in road transportation, reduce damage to machinery and equipments in the petroleum expoiting and processing, industries, and agriculture.

Ionic liquids (ILs) are ionic compounds with a melting point less than 100°C. ILs are mostly composed of an organic cation, typically containing nitrogen or phosphorus, and a weakly coordinating anion with organic or inorganic nature. Some of the most common cations are imidazolium, phosphonium, pyridinium and ammonium, while some common anions are halogens, BF_4, PF_6, CF_3SO_3 and $N(CF_3SO_2)_2$. The possibility of tuning the chemical and physical properties by changing the structure of anion and cation is a great opportunity to obtain task-specific ILs [1]. Understanding their structural properties [2-4] is essential for a systematic design. Because of their many properties such as thermal stability, non-volatile, good thermal conductivity, and significantly reduce friction and wear, they have been studied and used both as neat lubricating oils and additives for lubricating oils since 2001 [5] to improve wear and friction performance. Investigation on using alkylimidazolium tetrafluoroborates based ionic liquids in steel/steel, steel/aluminium, steel/copper, steel/SiO_2, steel/Si(100), steel/sialon and Si_3N_4/sialon ceramic contacts was conducted and showed excellent friction reduction. In fact, a series of imidazolium have been shown to have a considerably higher stability than a

https://doi.org/10.51316/jca.2023.012

conventional synthetic oil at 200 °C by Minami et al. [6]. More and more reports have showed the potential applications of imidazolium, pyridinium and ammonium ILs as lubricant additives [7-11], especially recently when more ILs have been produced then their applications are more diverse. However, the most limitation of using ionic liquids is their high cost due to complex synthesis methods. So far high cost ILs formed from imidazolium cation and hexafluorophosphate [PF_6^-], tetrafluoroborate [BF_4^-] and triflate [$CF_3SO_3^-$].... anions are most widely used as neat lubricants and additives for lubricants [1]. In addition, hexafluorophosphate [PF_6^-], tetrafluoroborate [BF_4^-] anion could be hydrolysed in the presence of water and release toxic gas (HF). Some ammonium ILs such as bis(2-hydroxyethyl)ammonium and trioctylammonium, methyl-trioctylammonium -based ionic liquids have been used as lubricant additives [1,12-16]. However, preparation and application of low cost ILs based on trietylammonium cation and oleate and stearate anions for lubricants has not published up to now.

This study focused on preparing the two low cost ILs triethylammonium oleate and triethylammonium stearate from low cost triethylamine and corresponding fatty acids. The long hydrocarbon chains of the carboxylate in ILs make them to stably disperse in the lubricants and increase the effeciency of additives. In addition, carboxylate ions are stable and not hydrolysed in contact with water. However, the reactions between tertiary amine and high molecular acids are difficult and take long time. Therefore, in this study, triethylammonium oleate and triethylammonium stearate are synthesized by one step and three step methods, FT-IR, and ^{1}H-NMR spectra are measured, reaction performance is evaluated and then the most effective method is selected. Based on the method found in this investigation, similar ILs can be synthesized using triethylamine and fatty acids separated from vegetable oils in the future to minimize the cost.

Materials and methods

Materials

Triethylamine (99%) was supplied by Sigma-Aldrich Company, hydrochloric acid (36-38%), acetone (99%), oleic acid (99.5%), stearic acid (99%), hexane (99%), , ammonia (25%) were provided by Guangdong Guanghua Company, China.

Synthesis of two ionic liquids

Ionic liquids were prepared by the reaction between a tertiary amines and high molecular weigh fatty acids using one step and three step methods.

Triethylammonium oleate

3 step method

$$(C_2H_5)_3N + HCl \rightarrow (C_2H_5)_3NHCl \quad (1)$$

$$RCOOH + NH_4OH \rightarrow RCOONH_4 + H_2O \quad (2)$$

$$RCOONH_4 + (C_2H_5)_3NHCl \rightarrow [RCOO]^-[HN(C_2H_5)_3]^+ + NH_4Cl \quad (3)$$

32.67 g (0.323 mol) of triethylamine was added into a three neck round bottom flask immersed in an ice bath. The flask was connected with a long condenser and a thermometer. 27 mL of HCl 36-38% was slowly dropped during 2 hours. After already dropping, the reaction mixture was stirred and heated at 50^{o}C in 2 hours. The product was obtained by recrystallization in cold diethyl ether. The product is waxy white. The weight of product was determined and used to calculate the yield of process.

19.49 g (0.069 mol) of oleic acid was dissolved in 50mL of acetone and the solution was heated to 50^{o}C until the fatty acids are completely dissolved, 5 mL (in excess amount to oleic acid) of NH3 solution was slowly added for 30 minutes. The reaction mixture was stirred for another 1 hour at 50^{o}C then resulting mixture was cooled and the precipitate was filtered and washed with acetone.

15.56 g (0.052 mol) of ammonium oleate and 7.16 g (0.052 mol) triethylammonium chloride were separately dissolved in acetone. Then two solutions were slowly mixed the together. The reaction mixture was stirred at room temperature for 2 hours. The precipitation of ammonium chloride was filtered and the solution was heated at 60^{0}C to completely evaporate the remain acetone. The remain solution is an ionic liquid of triethylammonium oleate with quite high viscosity.

The weight of products of each step was determined and used to calculate the yield of processes.

One step method

$$RCOOH + (C_2H_5)_3N \rightarrow [RCOO^-][HN^+(C_2H_5)_3] \quad (4)$$

https://doi.org/10.51316/jca.2023.012

53.67 g (0.19 mol) of oleic acid was placed in three neck round bottom flask immersed in an oil bath. The flask was connected with a condenser and a thermometer. 21.23 g (0.21 mol) of triethylamine was dropped slowly into the flask during 1 h. The reaction mixture was stirred at 50°C for 24 hours more. The reaction mixture was stirred at 40°C under vacuum to evaporate any unreacted reactants. The weight of products was determined and used to calculate the yield of process.

Triethylammonium stearate

3 step method

The procedures of synthesis of triethylammonium stearate are similar to those of triethylammonium oleate.

19.596 g (0.069 mol) of stearic acid was dissolved in 50mL of acetone and the solution was heated to 50°C until the fatty acids are completely dissolved, 5 mL (in excess amount to oleic acid) of NH3 solution was slowly added during 30 minutes. The reaction mixture was stirred for another 1 hour at 50°C then resulting mixture was cooled and the precipitate was filtered and washed with acetone.

15.652 g (0.052 mol) of ammonium stearate and 7.16 g (0.052 mol) triethylammonium chloride were separately dissolved in acetone. Then two solutions were slowly mixed the together. The reaction mixture was stirred at room temperature for 2 hours. The precipitation of ammonium chloride was filtered and the solution was heated at 80°C to completely evaporate the remain acetone. The remain solution is triethylammonium oleate with quite high viscosity.

The weight of products of each step was determined and used to calculate the yield of processes.

One step method

$$RCOOH + (C_2H_5)_3N \rightarrow [RCOO^-][HN^+(C_2H_5)_3]$$

53.96 g (0.19 mol) of stearic acid was placed in three neck round bottom flask immersed in an oil bath. The flask was connected with a condenser and a thermometer. 21.23 g (0.21 mol) of triethylamine was dropped slowly into the flask during 1 h. The reaction mixture was stirred at 100°C for 24 hours more. The reaction mixture was stirred at 40°C under vacuum to evaporate any unreacted reactants. The weight of products was determined and used to calculate the yield of process.

Characterization of materials

The FT-IR spectra of the prepared ionic liquids were measured on IRRAffinity-1 Series using potassium bromide compression technique in the range of 400-4000 cm^{-1}. The solid samples were dispersed with dried KBr at a ratio of 1:200 and then pressed into a thin flim under high pressure (removing water vapor by vacuum method). Liquid samples are measured directly without treatment. Nuclear magnetic resonance spectra ^{1}H-NMR was measured using AvanceNEO Spectrometer (at 500 MHz) in $CDCl_3$.

Results and discussion

Yields of IL synthesis

The comparison of yield of two methods of synthesis of triethylammonium oleate and triethylammonium stearate is given in Table 1.

Table 1: Yields of IL synthesis

IL	Over all yield (%)	
	Three step method	One step method
Triethylammonium oleate	68.8-74	86.3
Triethylammonium stearate	68.7-74.1	83.5

It can be seen from the synthesis procedures that the the three step method spends much less time and energy but consumes more chemicals. However, the one step method brings higher yields for both ILs. The total yield depends on the conversion of each step. The higher number of required step the more amount of chemicals lost during whole process.

Characterization of triethylammonium oleate

The structure of triethylammonium oleate is presented in Figure 1.

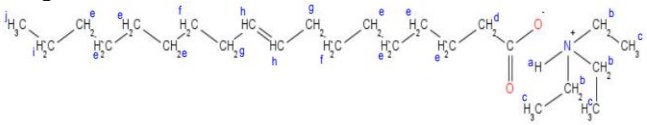

Figure 1: Structure of triethylammonium oleate

The FT-TR spectra of triethylammonium oleate is presented in Figure 2.

https://doi.org/10.51316/jca.2023.012

Method	Spectral data FT-IR ν(cm^{-1})	Spectral data ^{1}H-NMR (500 MHz, *J*(Hz), $CDCl_3$); ^{13}C-NMR (125 MHz, $CDCl_3$)
One step	3020 (sp^2, =C-H), 2922 (C-H of CH_3), 2852 (C-H of CH_2) 1713 (C=O), 1459 (C-H of CH_2) 1398 (C-H of CH_3), 1201 (C-N).	**^{1}H NMR δ(ppm):** 0,87 (*t*, *J* = 5 Hz, 3H, CH_3^h); 1.28 (*t*, *J* = 5 Hz, 2H, CH_2^i); 1.28 (*m*, 2H, CH_2^f); 1.34 (*m*, 3H, CH_3^c) 1.53 (*m* , 2H, CH_2^e); 2.01 (*s*, 2H CH_2^g); 2.22 (*s*, CH_2^d, 2H); 3.15 (m, 2H, CH_2^b); 5.69(m, 1H, CH^h) 9.1-9.6 (m, 1H, NH^a).
Three step	3400 (O-H) 3020 (sp^2 =C-H) 2923 (C-H of CH_3), 2853 (C-H of CH_2) 1707 (C=O), 1460 (C-H of CH_2) 1398 (C-H of CH_3), 1219 (C-N).	**^{1}H NMR δ(ppm):** 0.881-0.913 (*t*, *J* = 5 Hz, 3H, CH_3^h); 1.304-1.240 (*t*, *J* = 5 Hz, 2H, CH_2^i); 1.322-1.86 (*m*, 2H, CH_2^f); 1.4 (*m*, 3H, CH_3^c) ;1.61-1.66 (*m* , 2H, CH_2^e); 2.008-2.077 (*s*, 2H CH_2^g); 2.777-2.95 (*s*, CH_2^d, 2H); 3.094-3.13 (m, 2H, CH_2^b); 5.31-5.37(m, 1H, CH^h) 9.49(m, 1H, NH^a).

The presence of functional group amide is shown by a wide peak 1201 cm^{-1} (one step method) (1219 cm^{-1} (three step method)). The bands of wave numbers at 2922 cm^{-1} (2923 cm^{-1}) and 2852 cm^{-1} (2853 cm^{-1}) are the asymmetric and symmetric (C-H) stretching vibrations due to aliphatic methyl groups [17,18]. C=C and C=O stretching is shown by wave numbers (3010 cm^{-1}) and (1713 cm^{-1} or 1707 cm^{-1}). The band at wave number 721 cm^{-1} is due to the C-N stretching vibration [19].

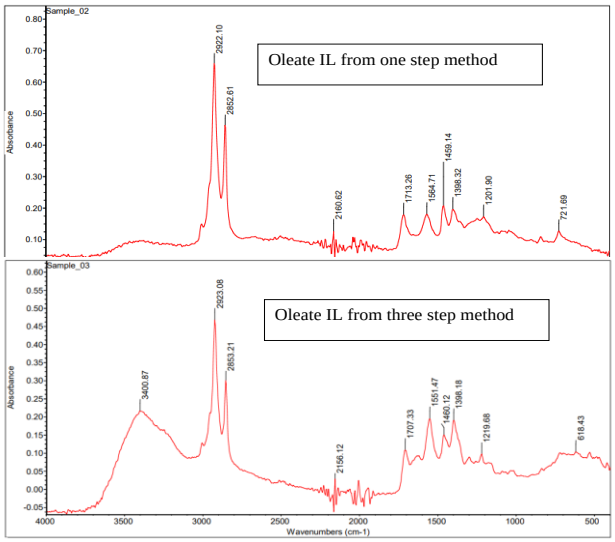

Figure 1: FT-IR spectra of IL triethylammonium oleate obtained by one step and 3 step methods

Table 2: FT-IR and ^{1}H-NMR spectroscopy results of triethylammonium oleate

The ^{1}H-NMR spectra of triethylammonium oleate products are shown in Figure 3,4.

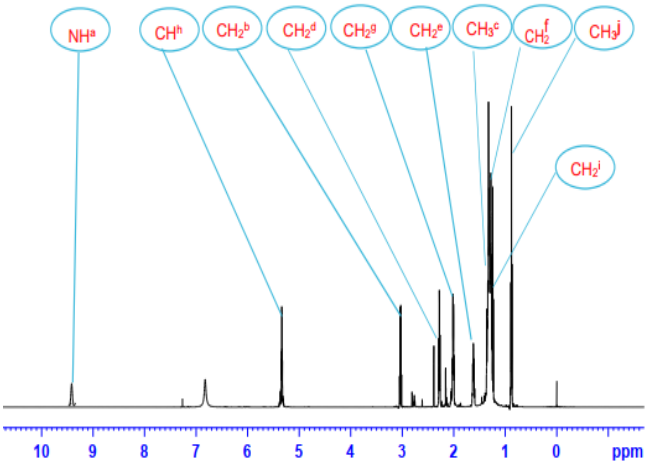

Figure 3: ^{1}H NMR of IL triethylammonium oleate obtained by 3 step method

https://doi.org/10.51316/jca.2023.012

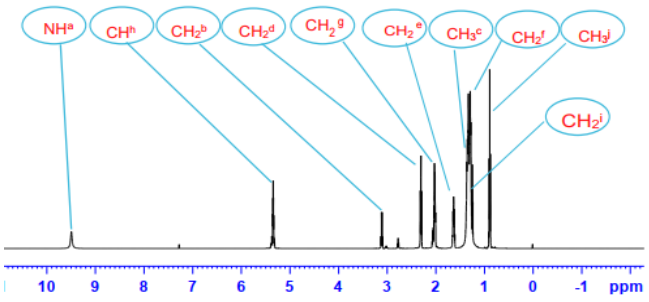

Figure 4: ^{1}H NMR IL triethylammonium oleate by one step method

The similar characteristic peaks of IR and ^{1}H-NMR spectra of two products (triethylammonium oleate) synthesized by one and 3 step methods were observed. This shows that synthesis method doesn't not affect on the strucrute of ionic liquid.

The ^{1}H-NMR results showed that the purity of IL obtained from 1 step method is higher than that of IL from 3 step method. Similar IR spectra results were received (Table 2). Combination of ILs yield and ^{1}H-NMR spectra it is recommended that the one step method should be used to synthesize triethylammonium oleate.

Characterization of triethylammonium stearate IL

The structure of triethylammonium stearate is presented in Figure 5.

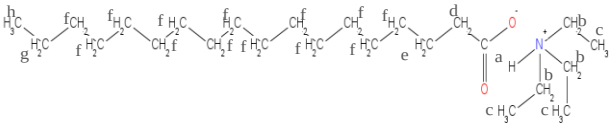

Figure 5. Structure of triethylammonium steate

The result FT-IR spectrum of IL triethylammonium stearate is given in Figure 6. Similarly, the bands of wave numbers at 2916 cm^{-1} (2919 cm^{-1}) and 2849 cm^{-1} (2850 cm^{-1}) are the aliphatic asymmetric and symmetric (C-H) stretching vibrations due to methyl groups. The band appear at 1210 cm^{-1} (1220 cm^{-1}) are assigned to vibration of C-N group. C=O stretching is shown by wave numbers 1714 cm^{-1} (1712 cm^{-1}). The band at wave number 720 cm^{-1} is due to the C-N stretching vibration.

It can be seen from IR and ^{1}H-NMR spectra that synthesis method doesn't not affect on the strucrute of triethylammonium stearate. This is shown by the appearance of all triethylammonium stearate characteristic peaks in IR and ^{1}H-NMR spectra.

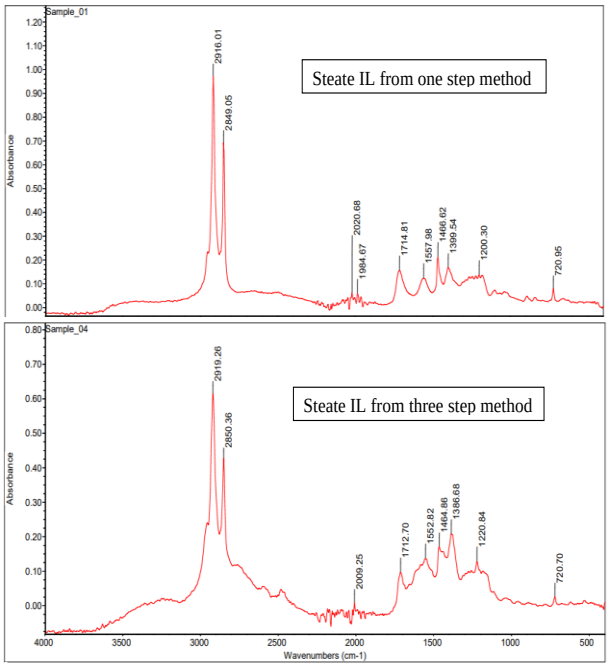

Figure 6: FT-IR of IL triethylammonium stearate

The NMR spectra of triethylammonium steate IL are shown in Figure 7,8.

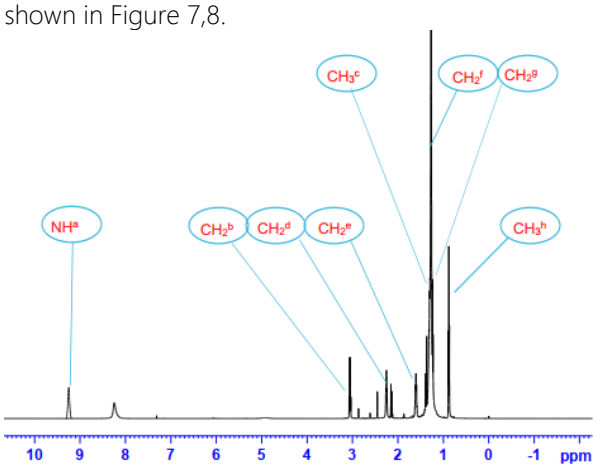

Figure 7: 1H NMR of IL triethylammonium stearate by 3 step method

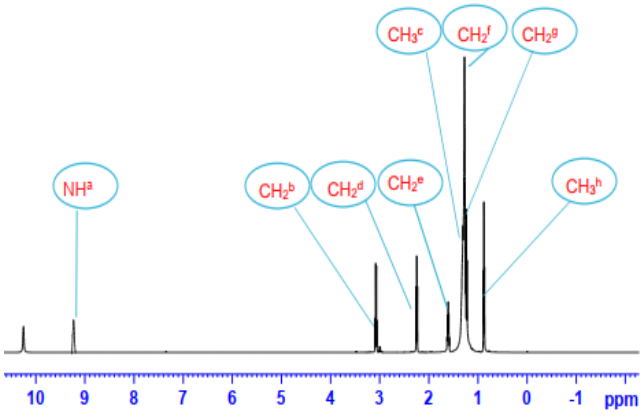

Figure 8: 1H NMR of IL triethylammonium stearate by one step method

https://doi.org/10.51316/jca.2023.012

Similar to the ^{1}H NMR of triethylammonium oleate the 1H NMR results of triethylammonium stearate showed that the purity of IL obtained from 1 step method is also higher than that of IL from 3 step method. Similar FT-IR spectra results were received. It is recommended from ILs yield and NMR spectra that the one step method should be used to synthesize triethylammonium stearate.

Table 3: FT-IR and ^{1}H-NMR spectroscopy results of triethylammonium stearate

Method	Spectral data FT-IR ν(cm^{-1})	Spectral data ^{1}H-NMR (500 MHz, *J*(Hz), $CDCl_3$)
One step	2916 (C-H of CH_3), 2849 (C-H of CH_2) 1714 (C=O), 1466 (C-H of CH_2) 1399 (C-H of CH_3), 1200 (C-N).	**^{1}H NMR δ(ppm):** 0-0.0891 (*t*, *J* = 5 Hz, 3H, CH_3^h); 1.227-1.24 (*t*, *J* = 5 Hz, 2H, CH_2^g); 1.252-1.293 (*m*, 2H, CH_2^f); 1.05-1.391 (*m*, 3H, CH_3^c) 1.58-1.615 (*m* , 2H, CH_2^e); 2.41-2.65 (*s*, 2H CH_2^d); 3.075-3.083 (*s*, CH_2^b, 2H); 9.281 (m, 1H, NH^a)
Three step	2919 (C-H of CH_3), 2850 (C-H of CH_2) 1712 (C=O), 1464 (C-H of CH_2) 1386 (C-H of CH_3), 1220 (C-N).	**^{1}H NMR δ(ppm):** 0,87 (*t*, *J* = 5 Hz, 3H, CH_3^h); 1.21 (*t*, *J* = 5 Hz, 2H, CH_2^g); 1.28 (*m*, 2H, CH_2^f); 1.34 (*m*, 3H, CH_3^c) 1.53 (*m* , 2H, CH_2^e); 2.26 (*s*, 2H CH_2^d); 3.15 (*s*, CH_2^b, 2H); 9.1-9.6 (m, 1H, NH^a)

Conclusion

Two ILs triethylammonium oleate and triethylammonium stearate can be synthesized by three step and one step methods. The spectra show that of obtained ILs have all the typical the characteristic peaks and the synthesis method does not affect on the structure of ionic liquids. Each method has one its advantages and disadvantages. Three step method needs much less time and spends less energy but consumes more chemicals. The over all yields of two ionic liquids obtained by one step method are higher than by three step method. In addition, the ^{1}H NMR results showed that the purity of IL obtained from 1 step method is higher than that of IL from 3 step method due to the higher number of required step the more amount of chemicals lost during whole process. IT-IR spectra results were received. It is recommended that the one step method should be used to synthesize triethylammonium oleate and triethylammonium stearate.

References

1. María-Dolores Bermúdez, Ana-Eva Jiménez, José Sanes and Francisco-José Carrión, Molecules 14 (2009) 2888-2908. https://10.3390/molecules14082888
2. Dupont, J. On the solid, J.Braz. Chem. Soc. 15 (2007) 341-350. https://10.1590/s0103-50532004000300002
3. Brenecke, J.F., Rogers, R.D., Seddon, K.R., Eds.; ACS Symposium Series 975 (2007) 86-101. https://10.1021/bk-2007-0975.ch007
4. Consorti, C.S.; Suarez, P.A.Z.; de Souza, R.A.; Farrar, D.H.; Lough, A.J.; Loh, W.; da Silva, L.H.M.; Dupont, J. Phys. Chem. B 109 (2005) 4341-4349. https://doi.org/10.1021/jp0452709
5. Ye, C.F.; Liu, W.M.; Chen, Y.X.; Yu, L.G. Chem. Commun. (2001) 2244-2245. https://10.1039/B106935G
6. Minami, I.; Kamimuram, H.; Mori, J. Synth. Lubr. 24 (2007) 135-147. https://doi.org/10.1002/jsl.36
7. Yue Yang, Fanhan Liu, Shaole Song, Honghu Tang, Shitian Ding, Wei Suna, Shuya Lei, Shengming Xu, Lubricants 1 (2013) 3-21, https://doi.org/10.3390/lubricants1010003
8. Nicole Do¨rr, Proc IMechE Part J: J Engineering Tribology 226 (11) 889–890. https://10.1177/1350650112464332
9. Jeewan Singh, Sukhpal Singh Chatha, Rakesh Bhatia, Materials Today: Proceedings 56 (2022) 2659–2665. https://10.1016/j.matpr.2021.09.228
10. Zhaozhao Yang, Bian Guo, Yijing Liang, Qing Huang, Feizhou Li, Ruozheng Wang, Xiaoyan Yan, Bo Yu, Qiangliang Yu, Meirong Cai, Journal of Molecular Liquids 363 (2022) 119837. https://doi.org/10.1016/j.molliq.2022.119837
11. P. Oulego, D. Blanco, D. Ramos, J.L. Viesca b,c, M. Díaz, A. Hernández Battez, Journal of Molecular Liquids 272 (2018) 937–947, https://doi.org/10.1016/j.molliq.2018.10.106

12. Tulia Espinosa, José Sanes, Ana-Eva Jiménez, María-Dolores Bermúdez, Wear 303 (2013) 495–509. https://doi.org/10.1016/j.wear.2013.03.041
13. Ghassan M.J. Al Kaisy, M. Ibrahim A. Mutalib, T V V L N Rao, Adolfo Senatore, Tribology International 160 (2021) 107058.
14. M.D. Avil´es , R. Pamies , J. Sanes , J. Arias-Pardilla , F.J. Carrion, M.D. Bermúdez, Tribology International 158 (2021) 106917 https://doi.org/10.1016/j.triboint.2021.107058
15. Raimondas Kreivaitis, Arturas Kupcinskas, Audrius Zunda, Thi Na Ta, Jeng Haur Horng, Wear (2022) 492-493 204217. https://doi.org/10.1016/j.wear.2021.204217
16. J. L. Viesca, M.T. Mallada b, D. Blanco, A. Fern andez-Gonz alez, J. Espina-Casado c, R. Gonz alez, Tribology International 116 (2017) 422–430. https://doi.org/10.1016/j.triboint.2017.08.004
17. Bui, T. T. L. A. D. Nguyen, S. Ho-Van and H. T. N. Uong. Journal of Applied Polymer Science 133 (2016) 43920. https://doi.org/10.1002/app.43920
18. Bui, T. T. L. H. T. N. Uong, L. V. Nguyen and N. C. Pham. Chemical and Biochemical Engineering Quarterly 32 (2018) 41. https:10.15255/CABEQ.2017.1193
19. Bui, T. T. L, H. T. N. Uong, D. K. Nguyen, D. T. K. Hoang and G. Vo-Thanh. Korean Journal Chemical Engineering 37 (2020) 2262. https://doi.org/10.1007/s11814-020-0659-2