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Synthesis and application of trialkyl methyl ammonium oleate and trialkyl methyl ammonium stearate as additives for lubricants

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ABSTRACT

This research aims to synthesize bio-based ionic liquids (ILs) derived from Aliquat and long-chain fatty acids (oleic and stearic acid) to enhance the dispersion stability and tribological performance of reduced graphene oxide (rGO) in lubricant oils. The [Aliquat][Oleate] and [Aliquat][Stearate] ionic liquids were synthesized via a two-step method, with their molecular structures successfully verified through FT-IR and ^{1}H-NMR spectroscopy. Experimental results indicated that [Aliquat][Stearate] required more rigorous synthesis conditions (90°C for 9 hours) compared to [Aliquat][Oleate] (85°C for 8 hours) at an optimal molar ratio of [RCOOH]/[Aliquat] = 1.3. Under these parameters, high yields of 80.1% and 83.2% were achieved, respectively. Furthermore, the synthesized ILs significantly improved the stability of rGO within the lubricant base. Tribological testing demonstrated that additives formulated with rGO and ILs effectively minimized the friction moment of the motor; specifically, additives containing [Aliquat][Oleate] and [Aliquat][Stearate] yielded friction reductions of 64% and 60%, respectively, compared to 58% for pure rGO. These findings highlight the practical significance of using ionic liquids as effective surfactants to prevent rGO aggregation, offering a robust solution for developing high-performance, stable nano-lubricants for industrial engine applications.

Introduction

Friction causes energy loss, machine surface damage, reduces equipment lifespan, and causes significant damage, especially in harsh environments such as deep drilling and inclined drilling in oil and gas exploration. Therefore, investigation on improving the efficiency of lubricating systems for machinery and equipment working in harsh environments is of great interest. Among them, ionic liquids and graphene are considered as two of the most promising material groups [1-6].

Graphene, with its layered structure, has superior lubricating capabilities. Ionic liquids, which were used as catalysts and solvents for many reactions and processes [7,8], have been found to act as both lubricants and friction-reducing additives. A synergistic effect was observed when both ionic liquids and graphene were used as lubricating additives [9]. The effectiveness was higher than using each material individually. Ionic liquids are effective

in lubricating and help disperse graphene, reducing graphene agglomeration. Many vegetable oils based lubricants are currently used and some fatty acid-based ionic liquids have been used as effective lubricating additives [10]. Triethyl ammonium and octyl ammonium carboxylate ionic liquids have been also synthesized for lubricating additives [11,12].

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In this study, two ionic liquids were synthesized from aliquat (a mixture of trioctyl methyl ammonium chloride and tridecyl methyl ammonium chloride) and oleic acid or stearic acid using two-step methods. The influence of solvent, temperature, time, and acid/aliquat molar ratio were studied, and suitable conditions for the synthesis of the ionic liquids were proposed.

Experimental

Materials

Aliquat (97%) was purchased from Merck; 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 [10]. Lubricant was supplied by Ba Ria - Vung Tau Chemical Industry Joint Stock Company (Chemico)..

Experimental

Preparation of ionic liquids

The ionic liquid [Aliquat][Oleate] and [Aliquat][Stearate] were synthesized from aliquat (a mixture of trioctylmethyl ammonium chloride and tridecylmethyl ammonium chloride) and oleic/stearic acid. Firstly, fatty acids were converted to sodium carboxylate (RCOOK) and then RCOOK reacted with aliquat.

$RCOOH + KOH \rightarrow RCOOK + H_2O$ (1)

$RCOOK + (C_8H_{17})_3CH_3NCl \rightarrow [RCOO]^-[(C_8H_{17})_3CH_3N]^+ + KCl$ (2)

In the first step, 0.0231 mol of oleic acid or stearic acid and 100 mL aqueous solution of KOH 0.319 M were introduced to a three neck flask. The reaction flask was connected to a reflux condenser and a thermometer and heated in a water bath or oil bath. The reaction mixture was stirred at 45°C for 3 hours. In the second step, a determined amount of aliquat was added, and the mixture was further heated and stirred at the studied temperature and time. The mixture was transferred to a separating funnel and separated into two phases. The organic phase containing IL was separated and washed with 100 mL of distilled water at 45°C, washing process was repeated 6 times to remove KCl, RCOOK, and any excess KOH. The resulting liquid was then dried to obtain a slightly yellowish viscous liquid. Weighed and the yield calculated.

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 second step* and molar ratio of acid to aliquat on synthesis yield of ionic liquids [Aliquat][Oleate] and [Aliquat][Stearate]; The reaction temperature, reaction time *of the second step* and RCOOH/aliquat molar ratios was varied from 60 ^{o}C to 90 ^{o}C, from 5 h to 9 h and from 1.1 to 1.4, respectively.

Ionic liquid synthesis yield was determined by formula [11]:

$$Y\ (\%) = \frac{m_{IL\ (eq)}}{m_{IL\ (ex)}} * 100\% \qquad (1)$$

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

Characterization

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

Evaluation dispersibility of rGO in lubricant

Reduced graphene oxide (rGO) and ionic liquid [Aliquat][Oleate] was mixed to form a dispersion of 0.20 wt% rGO in IL, then this mixture was added at a concentration of 2 wt% to the lubricant to form a mixture containing 0.002 wt% rGO and 2 wt% IL denoted as the rGO/[Aliquat][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 [Aliquat][Stearate] to get 2 samples (rGO + IL) 0.2% (Table 1).

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

Ionic liquids	Abbreviation
[Aliquat][Oleate]	rGO/[Aliquat][Oleate] 0.2%/CBT 2%
[Aliquat][Stearate]	rGO/[Aliquat][Stearate]0.2%/CBT2%

The UV-VIS of dispersions was measured after mixing at different time intervals [12]. From the UV-VIS measurement results, the relative concentration of solids can be calculated according to formula (2). Based on this relative concentration, the dispersibility of rGO in liquids can be assessed:

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

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 [13]. 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 (3):

$$\text{Friction moment reduction} = \frac{(f_1 - f_2)*100}{f_1} * \% \quad (3)$$

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 lubricant containing additives.

Results and discussion

Characterization of triethyl ammonium oleate [Aliquat][Oleate] and triethyl ammonium stearate [Aliquat][Stearate]

Structure of [Aliquat][Oleate] and [Aliquat][Stearate] are given in Fig., 1. The FT-IR spectra of the ionic liquids (ILs) exhibit several characteristic absorption bands. The signals at 3379 cm^{-1} and 3389 cm^{-1} are assigned to the O-H stretching vibrations of residual water within the ILs. The presence of the sp^2 =C-H bond from the oleate ions is confirmed by a distinct band at 3004 cm^{-1} in the spectrum of [Aliquat][Oleate], which is notably absent in the [Aliquat][Stearate] spectrum.

Aliphatic asymmetric and symmetric C-H stretching vibrations appear at 2921 cm^{-1} (2915 cm^{-1}) and 2952 cm^{-1} (2850 cm^{-1}) for [Aliquat][Oleate] and [Aliquat][Stearate], respectively, corresponding to the methyl and methylene groups. The presence of the carboxylate functionality is confirmed by the C=O stretching at 1734–1735 cm^{-1} and the COO$^-$ asymmetric stretch at 1563–1557 cm^{-1}. Furthermore, the bands between 1460 cm^{-1} and 1480 cm^{-1} are attributed to the bending (deformation) of CH_3 and CH_2 moieties from both the Aliquat cation and the fatty acid chains, overlapping with the signature N-CH_3 vibration of the quaternary ammonium headgroup. Finally, the sharp peaks at 720 cm^{-1} and 721 cm^{-1} are characteristic of the rocking vibrations of long hydrocarbon chains (containing at least four consecutive groups), consistent with the extended alkyl structures of both the Aliquat cation and the fatty acid anions.

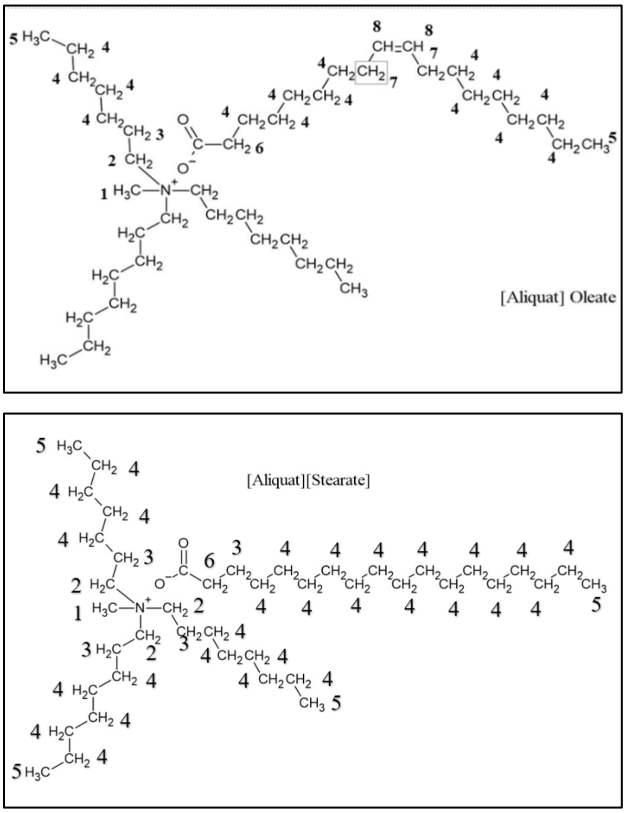

Figure.1. Structure of [Aliquat][Oleate] and [Aliquat][Stearate]

^{1}H NMR δ(ppm) of [Aliquat][Oleate]:

0.869-0.893(t, 12H, CH_3^5), 1.267-1.345 (m, 50H of CH_2^4), 1.587-1.646 (m, 8H, CH_2^3), 2.00 (m, 4H, CH_2^7), 2.173 (m, 2H, CH_2^6), 3.223 (s, 3H, N-CH_3^1), 3.291- 3.299 (t, 6H, CH_2^2), 5,334 (m, 2H, CH^8).

^{1}H NMR δ(ppm) of [Aliquat][Stearate]:

0.858-0,894 (12H, CH_3^5); 1.255-1.354 (58H, CH_2^4); 1.655-1.613 (8H, CH_2^3); 2.285-2.316 (2H, CH_2^6); 3.299 (3H, CH_3^1); 3.372-3.389 (6H, CH_2^2).

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

Influence of factors on synthesis of [Aliquat][Oleate] and [Aliquat][Stearate]

Influence of reaction temperature on IL synthesis performance

The experiments were performed in 6 h with [Aliquat][Stearate] and in 7 h with [Aliquat][Stearate] at different temperatures using the same [RCOOH]/[Aliquat] molar ratio of 1:1.3 (Fig 2A).

The results showed that when increasing the reaction temperature from 70°C to 80°C, the [Aliquat][Oleate] synthesis yield increases dramatically from 62.1% to about 83.7% and continues to increase more slowly to a temperature of 90°C and 100 °C. Similarly, [Aliquat][Stearate] synthesis efficiency increases rapidly from 50.2% to 73.1% and then to 90.5% with increasing the temperature from 70°C to 80°C and then to 90 °C; when temperature continues to increase to a of 100°C the efficiency is constant.

Influence of reaction time on IL synthesis performance

Ionic liquids [Aliquat][Oleate] and [Aliquat][Stearate] were synthesized at temperatures of 80 °C and 90 °C, respectively with the molar ratio of [RCOOH] to [Aliquat] is 1.3 and at different time intervals from 5 hours to 9 hours. The results are presented in Fig. 2B.

It can be seen that when the [RCOOH]/[Aliquat] molar ratio is fixed, [Aliquat][Oleate] synthesis efficiency increases from 63,2% to 83.7% when increasing the reaction time from 5 hours to 7 hours. However, when increasing the reaction time from 7 to 9 hours, the reaction is steady. The [Aliquat][Stearate] yield increases rapidly from 51.3% to 80.5% with increasing the time from 5 hours to 8 hours and then slightly change with increasing the reaction time to 9 hours.

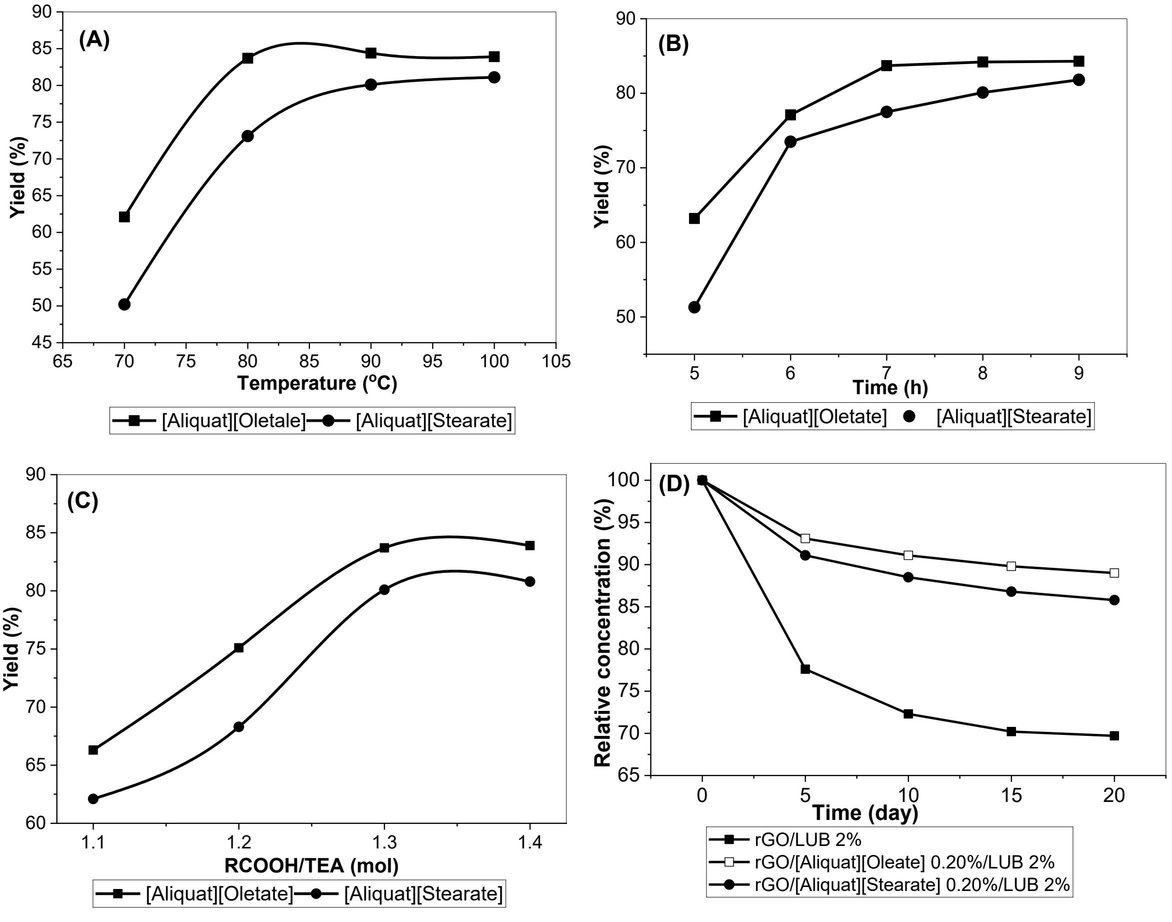

Figure 2. Influence of (A) reaction temperature on the synthesis efficiency of [Aiquat][oleate] and [Aliquat][Stearate] (molar ratio [RCOOH]/[Aliquat]= 1.3; 7 h for [Aliquat][oleate] and 8 h for [Aliquat][Stearate]); (B) reaction time on the synthesis yield of [Aliquat][Oleate] and [Aliquat][Stearate] (molar ratio [RCOOH]/[Aliquat]= 1.3; temperature 80 °C with [Aliquat][Oleate] and 90°C with [Aliquat][Stearate]); (C) [RCOOH]/[Aliquat] molar ratio on IL synthesis performance (7 h for [Aliquat][oleate] and 8 h for [Aliquat][Stearate], temperature 80 °C with [Aliquat][Oleate] and 90°C with [Aliquat][Stearate]); (D) 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%.

The results show that [Aliquat][Stearate] formation requires a longer time than that of [Aliquat][Oleate]. This can be due to 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 [11]. In order to get the synthesis efficiency of over 80%, [Aliquat][Oleate] needs 7 hours while [Aliquat][Stearate] needs 8 hours.

The variation in reaction temperature and time between [Aliquat][Oleate] and [Aliquat][Stearate] is primarily governed by the physical properties of the fatty acid anions. Experimental data indicates that

[Aliquat][Stearate] requires more rigorous conditions, specifically 90oC for 9 hours, compared to [Aliquat][Oleate] which requires 85oC for 8 hours. This is due to the higher melting points and higher viscosities of sodium stearate and the resulting stearate-based ionic liquid. At a given temperature, these saturated structures exhibit lower molecular mobility; conversely, the double bond present in the oleate chain reduces the internal viscosity of the medium, facilitating a more efficient ion exchange at lower temperatures and shorter time intervals. Similar results were also observed when triethyl ammonium oleate and triethyl ammonium stearate was synthesized in 6h at 45 °C and in 7h at 55 °C [11].

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

Synthesis processes of [Aliquat][Oleate] and [Aliquat][Stearate] were performed at 80°C in 7 h and at 90°C in 7 h. Reactions were carried out with different [RCOOH]/[Aliquat] molar ratios of 1.1; 1.2; 1.3; 1.4. The results are presented in Fig. 2C.

The obtained results show that when the [RCOOH]/[Aliquat] molar ratio increasing from 1.1 to 1.3, the yields of [Aliquat][Oleate] and [Aliquat][Stearate] increase from 66.3% and 62.1% to 83.7 % and of 80.1 %, respectively. The performance does not increase further with increasing the molar ratio. It can be seen that at the molar ratio [RCOOH]/[Aliquat] of 1.3, the yields of [Aliquat][Oleate] and [Aliquat][Stearate] reaches the high values. This can be explained as to shift the equilibrium, it is necessary to use an excess amount of one of reactants. Here the excess amount of RCOOH was chosen because this component is cheaper and more environmentally safe.

From the above results, the optimal conditions for synthesizing the two ionic liquids [Aliquat][oleate] and [Aliquat][Stearate] can be summarized in Table 2.

Table 2. Optimal conditions for the synthesis of [Aliquat][oleate] and [Aliquat][Stearate]

No	Parameters	Ionic liquids	
		[Aliquat] [Oleate]	[Aliquat] [Stearate]
1	Solvent	Water	Water
2	Temperature (°C)	85	90
3	Time (h)	7	8
4	[RCOOH]/[Aliquat] ratio (mol)	1.3	1.3
	Yield (%)	83.2	80.1

Dispersibility of rGO in lubricant

In this section, 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 [Aliquat] and 2 anions: oleate and stearate. The results in Figure 2D show that the rGO concentration in all samples decreased over time, however, the rGO concentration in lubricant mixed with ionic liquids decreased slower than without ionic liquids. For example, after 5 days, the relative concentration of rGO in lubricant, [Aliquat][Oleate]+lubricant and [Aliquat][Stearate] + lubricant decreased from approximately 100% (0 days) to 77.6%, 93.1% and 91.1%, respectively. After 20 days, the relative concentration of rGO in lubricant, [Aliquat][Oleate]+lubricant and [Aliquat][Stearate] + lubricant decreased from approximately 100% (0 days) to 69.7%, 89% and 85.8%, respectively. It can be concluded that the rGO disperses in the group [Oleate] based ionic liquid mixture more stable than in [Stearate] based IL mixture.

The superior dispersibility of rGO in oleate-based ionic liquids is supported by the high electron density π bonds and increased polarity of the unsaturated fatty acid anion. These structural features allow for enhanced compatibility with rGO through π- π stacking and interactions with its polar O-H groups. This behavior is quantitatively confirmed by UV-Vis spectroscopy and sedimentation data: after 20 days, the relative concentration of rGO in the [Aliquat][Oleate] lubricant mixture remained at 89%, whereas the [Aliquat][Stearate] mixture dropped to 85.8% and the pure lubricant fell to 69.7%. This experimental evidence demonstrates that the ionic liquid acts as an effective surfactant to prevent rGO aggregation.

Friction performance of lubricants before calcination

Friction moment of the lubricant containing rGO and ionic liquids [Aliquat][Oleate] decreased more than of lubricant containing [Aliquat][Stearate] before *calcination* more than lubricant containing only rGO. For example, of lubricant, [Aliquat][Oleate]+lubricant and [Aliquat][Stearate] + lubricant decrease the friction moment 58%, 64% and 60%.

The similar results were observed with of lubricant containing rGO and ionic liquid after calcination.

There is a direct correlation between the stability of the rGO dispersion and the resulting tribological performance of the lubricant. When rGO is stabilized by [Aliquat][Oleate], which showed the highest stability in dispersion tests, it achieved a friction moment reduction of 64%, compared to 60% for the less stable [Aliquat][Stearate] system and 58%

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for rGO alone. This relationship is further proven by performance tests after calcination at 130°C for 16 hours, where the more stable oleate system maintained a 62% reduction, significantly outperforming the pure rGO system which dropped to 54%.

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/[Aliquat][Oleate] 0.20%/LUB 2%	64	62
rGO/[Aliquat][Stearate] 0.20%/LUB 2%	60	57

***** at 130°C during 16 h

The physicochemical impact of the anion structure is significant, as the unsaturated oleate chain prevents tight molecular packing, resulting in lower viscosity and better flowability compared to the saturated stearate chain. In practical applications such as high-pressure drilling or complex environments, the non-volatile nature and high thermal stability of these ionic liquids ensure that the lubricating film remains intact. The synergistic combination allows the ionic liquid to maintain surface adsorption under high shear stress while the rGO flakes provide additional protection against the extreme pressures typically encountered in deep drilling operations.

Conclusion

In this research, two ionic liquids, [Aliquat][Oleate] and [Aliquat][Stearate] were successfully prepared and characterized by IR and NMR spectra. The suitable conditions for synthesizing ionic liquids are 7h and 85 °C with [Aliquat][Oleate] and 8 h and 90 °C with [Aliquat][Stearate]. To shift the equilibrium toward ionic liquid products, two methods were used employed: using an excess amount of fatty acids (molar ratio [RCOOH]/[Aliquat]= 1.3) and using water solvent that dissolves co-product KCl but does not dissolve ionic liquids. The obtained ionic liquids was used together with rGO as additive for lubricant. Ionic liquids are found to increase the stability of rGO in lubricant, and therefore, decrease the friction moment of motor followed technical standard РД VSP-000-PK-650 of the Vietsopetro. Lubricant containing rGO and ionic liquids [Aliquat][Oleate] decreases friction moment more than lubricant containing rGO and [Aliquat][Stearate] and more than lubricant containing only rGO.

The ionic liquid and rGO contribute to friction reduction through complementary but distinct mechanisms. rGO functions as a solid lubricant with a layered structure that provides an easy-shear physical barrier between rubbing surfaces to prevent direct metal-to-metal contact. In contrast, the ionic liquid serves a dual role: first, as a surfactant that prevents the agglomeration of rGO to ensure a homogeneous additive distribution, and second, as a liquid lubricant that forms a high-strength adsorption film on the motor's metal surfaces to further minimize friction.

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