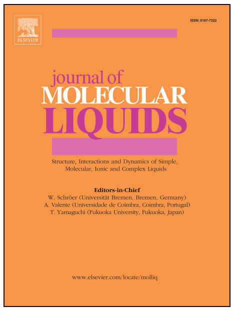

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Stable gasoil/sunflower oil fuel microemulsions prepared by using methylimidazolium based ionic liquids as surfactant

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Abstract

The fuel microemulsions of water in a 4:1 (v:v) blend of gasoil and sunflower oil (respectively) by using of 1-dodecyl-3-methylimidazolium nitrate ([C12mim][NO_3]) and 1-butyl-3-methyl imidazolium nitrate ([Bmim][NO_3] ionic liquids as surfactant and 1-butanol as co-surfactant. Also, the performance of 50:50 wt% blend of the mentioned ionic liquids with Span 80 as surfactant was evaluated in this work. The comparison of the phase diagrams of the samples has revealed a larger single phase region for samples prepared with ionic liquids than the conventional Span 80 surfactant or their blends with Span 80. The dynamic viscosity, and density of two samples with high oily phase content was measured according to the standards showing very close values to the net diesel fuel. DLS analysis indicated a water droplets of 9 nm (upto 70%) for [Bmim][NO_3], 3-6 nm (upto 64-82%) for [C12mim][NO_3], and 331 nm (upto 53%) for systems prepared by Span 80. Meanwhile, a very narrow size distribution was observed for the samples prepared by ionic liquids. No phase separation has been observed for the prepared samples over 6 months on the shelf.

Keywords: Fuel microemulsion; phase diagrams; ionic liquid; gasoil; methylimidazolium; surfactant.

1. Introduction

Diesel engines during the last century have gained a very important place in many industries, especially in road transportation as of their high thermal efficiency [1]. On the other hand, by the increasing of the global concern about the high energy consumption of the world, diesel fuel has entered into the researcher's center of attention. This energy carrier has turned to a major source of releasing the pollutants and suspended particles to the environment. It is believed that the vegetable oils with a good heating power and as a renewable resource for fuel have great potential to reduce the release of the carbon emissive [2]. But, if used directly and without any modification, the high viscosity of these oils cause severe problems in the diesel engines, so they need to be modified by a proper way to overcome their high viscosity problem. Blending of the vegetable oils and diesel fuel has been introduced as a way to reduce its high viscosity problem [3,4]. Another major approach which has been considered to resolve viscosity problem of the vegetable oils as well as to reduce the polluting emissions from the diesel engines is to prepare microemulsion of the diesel (or its blend with vegetable oil) and water. This technique has been introduced as a significant approach to decrease the problems encountered by use of neat diesel fuels [5]. The microemulsions has been very well established mixtures with a macroscopically homogeneous appearance, which do not have a homogeneous structure in microscopic scale, and composed of oil, water and surfactant [6]. These systems are optically clear and thermodynamically stable and formed from two incompatible phases [7]. Regarding the relative amount of the two phases, three type of microemulsions can be formed which include oil dispersed in water (o/w), water dispersed in oil (w/o), and bicontinuous systems. The water in oil (fuel or its blend with vegetable oil) microemulsions (w/o) can be used to improve the high viscosity problem of vegetable oil [8,9] and also in many other research fields [10]. In most of these systems, alcohols such as 1-butanol has been used as co-surfactants that help to emulsify the water in oil as well as can function as fuel [11]. Various commercially available surfactants such as Span 80, Tween 80 or Brij 30 have been employed in many applications [12] as well as fuel microemulsions.

In recent decades, ionic liquids have been widely used as green solvents as well as surfactants in many various applications [13-14]. The properties of these materials as non-conventional solvents can be tuned by changing of the type of cation and anion, which can be investigated by spectroscopic techniques such as fluorescent probe studies [15]. Also, having a low vapor pressure allows these compounds to be used as a good alternative to the volatile solvents in different applications [16]. Ionic liquids have been used as nonpolar or polar phase in microemulsions [17]. Since ionic liquids are safe for the environment and subsequently possess unusual solvent properties, hydrophobic ionic liquids exhibit properties similar to the oil phase for the formation of microemulsions [18]. Microemulsions were prepared by using of hydrophilic ionic liquids such as [Bmim][BF_4] in different organic solvents as nonpolar phase like toluene [19], xylene [17], triethylamine [20], cyclohexane [21] and, hydrophobic ionic liquid [Bmim][BF6] with TX-100 (nonionic surfactant) and water [22].

Ionic liquids have been used in a large variety of applications in chemical industries, such as electrolyte in batteries [23], lubricants [24], synthesis of polymers [25], synthesis of nanoparticles [26], media for biological reactions [27], green solvent and catalysis in synthesis [28-30], purification of gases [31], deep desulfurization of diesel fuel by extraction [32], as a tool for analytical applications [15], such as chromatography [33] etc.

The use of ionic liquids in microemulsion systems is one of the most important application of these compounds. These compounds have been extensively investigated in the role of polar and nonpolar phase in microemulsion systems [34]. The use of ionic liquids as surfactants is gaining a rapidly increasing attention of the researchers. The first report published in this field is related to the use of room temperature ionic liquid (RTIL) with imidazole head as hydrophilic part and a long hydrophobic tail for emulsion polymerization [14]. Oil recovery [35-36] and oil spill remediation [37], are among the many other examples of applications of ionic liquids as surfactants. The aggregation behavior of alkylimidazolium ionic liquids increases the ability of this category to play the role of surfactant. The use of ionic liquids have exhibited some advantages over organic surfactants in various applications. Among them one can point to the melting points lower than 100 °C, excellent thermal and chemical stability, nonflammable character, miscibility and solubility with many solvents, low toxicity, non-corrosive and recyclable properties [38]. Even though, the most important feature of the ionic liquids as surfactants is the possibility to tune their character by proper selection of the cationic and anionic parts, and also their ability in formation of the very stable micelles without any need for cosurfactant because of the strong interactions between their molecules. The ionic liquids with imidazolium cation have the ability of self-aggregation and act as surfactants [39,40] and also make aggregates such as micelles, vesicles, liquid crystals [41,42], gel and microemulsions [43]. The existence of the strong interactions between the imidazole ring and the co-surfactant molecules is the main advantage of these compounds over the conventional surfactants. This feature can help to immobilize the co-surfactant at the fluid/fluid interface and almost prevents its leakage into the water phase. On the other hand, the aromatic imidazole ring head group is strongly attractive due to the interactions of the π-π system. Finally, because of the possibility to change the structure of ionic liquids and consequently the balance of the hydrophilic-lipophilic parts, one can prepare the surfactants with an optimum performance in any desired application, which is especially important in partitioning in the microemulsions [44].

The main purpose of this work is to synthesis and use some ionic liquids as surfactants for the emulsification of the water in the diesel fuel, and compare their performance with the conventional surfactants, Span 80. Also, the phase diagrams of the microemulsions prepared by these ionic liquid surfactants or their mixtures with Span 80, water and diesel were investigated. Two samples with nearly optimum compositions were selected on the phase diagrams and their physical properties as fuel including dynamic viscosity, density and the size of water droplets were measured according to the relevant standards and compared with the corresponding values for neat diesel fuel.

2. Experimental

2.1. Materials

Gasoil was purchased from a local fuel station. The edible sunflower oil as a vegetable oil was obtained from a local supermarket. 1-methyl imidazole (Merck, >99%), silver nitrate (BDH, 99%), 1-bromobutane and 1-chlordodecan (both from Merck, 98%) were used for the reactions. The solvents used include methanol, ethyl acetate and diethyl ether has been of laboratory grade (purity >98%) and were used after distillation. 1-butanol (Merck, 99%) and Span 80 (Sigma Aldrich Co, 97%) were used without any further purification.

2.2. Methods

FT-IR spectra of synthesized ionic liquids have been measured by using of an infrared spectrometer manufactured by Bruker, Germany, model Tensor 27. The measurements of the FT-IR spectra of the materials has been done as KBr disks. Bruker Avance 400 MHz spectrometer was used to measure the ^{1}HNMR spectra of the materials. Measurement of the ^{1}HNMR spectrum of 1-dodecyl-3-methylimidazolium chloride ([C12mim][Cl]), 1-dodecyl-3-methylimidazolium nitrate ([C12mim][NO_3]) and 1-butyl-3-methylimidazolium bromide ([Bmim][Br]) has been performed in $CDCl_3$ and DMSO-d_6 was used as solvent for the measuring of 1-butyl-3-methylimidazolium nitrate ([Bmim][NO_3]). The dynamic light scattering (DLS) analysis of the samples was performed by the DLS device model Nano ZS ZEN 3600 manufactured by Malvern, UK. The viscosity measurements of the samples were performed with a Lovis digital viscometer device model 2000M manufactured by the Austrian company Anton Paar with a precision of 0.001 mm^2s^{-1}. The density of the liquid samples was measured with a density meter device model DSA5000, manufactured by Anton Paar, Austria, with a precision of 3×10^{-6} $g.cm^{-3}$ and temperature accuracy of ±0.001 °C.

2.2.1. Preparation of the ionic liquids

2.2.1.1. Preparation of [Bmim][Br] and [C12mim][Cl] ionic liquids

To synthesize these ionic liquids, first 2.005 g (24.42 mmol) of 1-methyl imidazole was added into a glass reactor equipped with magnetic stirrer and under an argon atmosphere in an oil bath. Then, the temperature of the oil bath wan raised to 70 °C and and while stirring 26.86 mmol of the related alkyl halide was added dropwise into the reactor via an adding funnel. After stirring for a certain time raw product was obtained, which was then washed several times with a proper solvent and dried in the vacuum oven at 50 °C for 6 h. the detained information regarding the reaction times, washing solvents, physical appearance and reaction yields for each of the prepared ionic liquids are given in Table 1.

Table 1.Detailed reaction and workup conditions for the synthesis of [Bmim][Br] and [C12mim][Cl] ionic liquids

ionic liquid	alkyl halide	reaction time	washing solvent	appearance	yield

[Bmim][Br]	1-butyl bro mide	24h	ethyl acetate	yellow viscose oil	94%
[C12mim][Cl]	1-chlorododecane	72h	diethyl ether	white waxy solid	82%

2.2.1.2. Preparation of [Bmim][NO$_3$] and [C12mim][NO$_3$]

In a 100 mL flask, 2.5 mmol of the each of ionic liquids synthesized as in the section 1.1 was dissolved in 30 mL methanol at 20 °C. A solution of 2.5 mmol silver nitrate in 20 mL methanol was then added dropwise to the ionic liquid solution under vigorous stirring in the darkness. The formed silver halide was immediately appeared as precipitate. The stirring of the reaction mixture was continued for another one hour. Then the mixture was filtered though a buchner funnel, and the precipitate was washed with an additional 30 mL aliqout of methanol. The filtrate was then rotaevaporated at 50 °C to remove methanol. The resultant product was further dried in the vacuum oven at 40 °C for 24 h. The appearance of the both of ionic liquids was yellow viscose oil. The yield of reaction for [Bmim][NO$_3$] and [C12mim][NO$_3$] has been 95% and 45%, respectively.

2.2.2. Characterization of ionic liquids

The ionic liquids were prepared via the methods already reportd in the literature with some modifications [46,47], and characterized by using of ^{1}HNMR and FT-IR spectra.

The FT-IR spectra of the [Bmim][Br] and [Bmim][NO$_3$] are depicted in Fig. 1. As in Fig. 1a, the peaks appearing in the range of 2736- 2960 cm^{-1} and 3074-3142 cm^{-1} are attributed to the stretching vibrations of the aliphatic and aromatic C-H bonds, respectively. The peak related to the stretching vibrations of C = N bond in imidazole ring are appeared in 1636 cm^{-1}. The peaks of stretching vibrations of C=C bonds of the aromatic imidazole ring is observed at 1568 cm^{-1}. The peaks appearing in the 1462 cm^{-1} and 1379 cm^{-1} are assigned to the bending vibrations of CH_2 and CH_3 groups in the butyl chains. The peak in 1168 cm^{-1} could be attributed to the C-N bond.

For the synthesis of the [Bmim][NO$_3$] ionic liquid, the [Bmim][Br] was subjected to the ion exchange reaction with silver nitrate, and the reaction completion was monitored by formation and precipitation of the silver bromide. For comparison, the FT-IR spectra of the [Bmim][NO$_3$]

along with the its precursor [Bmim][Br] is depicted in Fig.1. As it can be seen in the Fig.1, the main difference between these two spectra (Fig.1a and Fig.1b) is in the peak appeared in the range of 1300-1379 cm^{-1}, which can be attributed to the stretching vibrations of the NO_3 group.

The ^{1}HNMR spectra of the [Bmim][Br] is ilustrated in Fig. 2. The triplet peak at 0.96 ppm is related to the protons of the CH_3 of the butyl group. The multiplet peaks at 1.43 ppm and 1.88 ppm are related to the protons on the C2 and C3 carbons (the middle two -CH_2 moieties) of the butyl group. The peak of the protons in -CH_2-N- is appeared at 4.34 ppm with a triplet splitting pattern. The singlet peak appearing in 4.1 ppm is related to the protons of the CH_3-N group. The protons of the imidazole ring are produced peaks at 10.26 ppm, related to -N-CH-N- as a singlet peak and two doublet peaks at 7.63 ppm and 7.75 ppm which are assigned to the -N-CH-CH-N- protons.

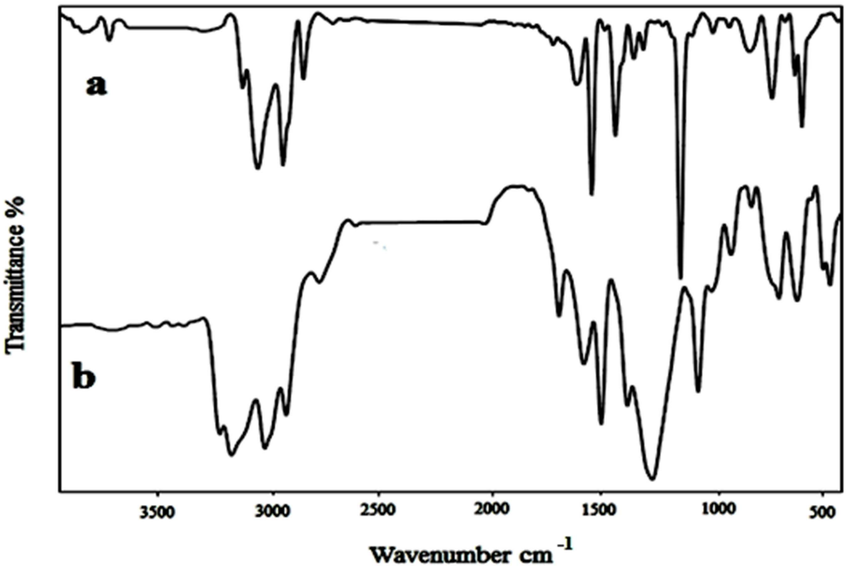

Fig. 1. The FTIR spectra of (a) [Bmim] [Br] (b) [Bmim][NO_3]

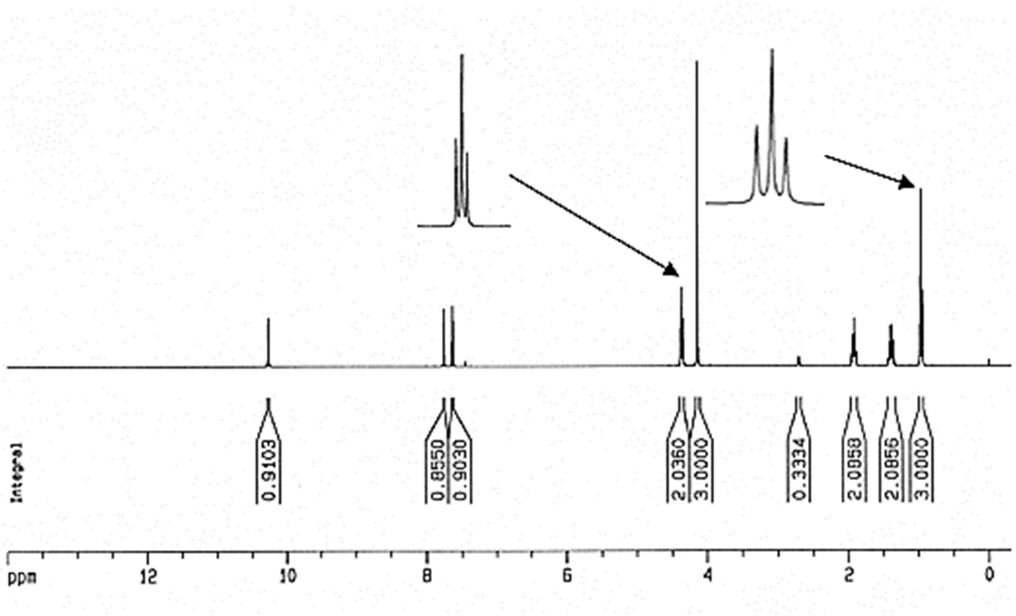

Fig. 2. The ^{1}HNMR spectra of [Bmim][Br]

The FT-IR spectra of the [C12mim][Cl] and [C12mim][NO_3] are shown in Fig. 3. As in Fig. 3a, the peaks appearing in the range of 2850- 2916 cm^{-1} and 3057-3144 cm^{-1} are assigned to the stretching vibrations of the aliphatic and aromatic C-H bonds, respectively. The peak related to the stretching vibrations of C = N bond in imidazole ring are appeared in 1643 cm^{-1}. The peaks of stretching vibrations of C=C bonds of the aromatic imidazole ring is observed at 1572 cm^{-1}. The peaks appearing in the 1468 cm^{-1} and 1359 cm^{-1} are assigned to the bending vibrations of CH_2 and CH_3 groups in the dodecyl chains. The peak in 1171 cm^{-1} could be attributed to the C-N bond. For preparation of the [C12mim][NO_3], the same procedure as used for [Bmim][NO_3] ionic liquid has been employed and, the [C12mim][Cl] was subjected to the ion exchange reaction with silver nitrate. For comparison, the FT-IR spectra of the [C12mim][NO_3] along with the its precursor [C12mim][Cl] is depicted in Fig.3. As it can be seen in the Fig.3, similar to the other ionic liquid the main difference between these two spectra (Fig.3a and Fig.3b) is in the peak appeared in the range of 1300-1400 cm^{-1}, which can be attributed to the stretching vibrations of the NO_3 group.

The ^{1}HNMR spectra of the [C12mim][Cl] is ilustrated in Fig. 4. The triplet peak at 0.8 ppm is assigned to the protons of the CH_3 group in the dodecyl chain. The multiplet peaks at 1.28-1.8

ppm are attributed to the protons of the methylene groups on the carbons number C2 to C11 of the dodecyl chain. The protons of the methyl group on the N atom of the imidazole ring (CH_3-N) has created a singlet peak appearing in 4 ppm. The peak of the protons on the methylene group directly connected to the N atom of the imidazole ring (-CH_2-N-) is observed at 4.2 ppm which has a triplet splitting pattern. The other two protons of the imidazole ring -N-CH-CH-N- are produced two doublet peaks at 7.8 ppm and 7.9 ppm. The peak representing of the -N-CH-N- proton of the imidazole ring is observed at 10.5 ppm as a singlet peak.

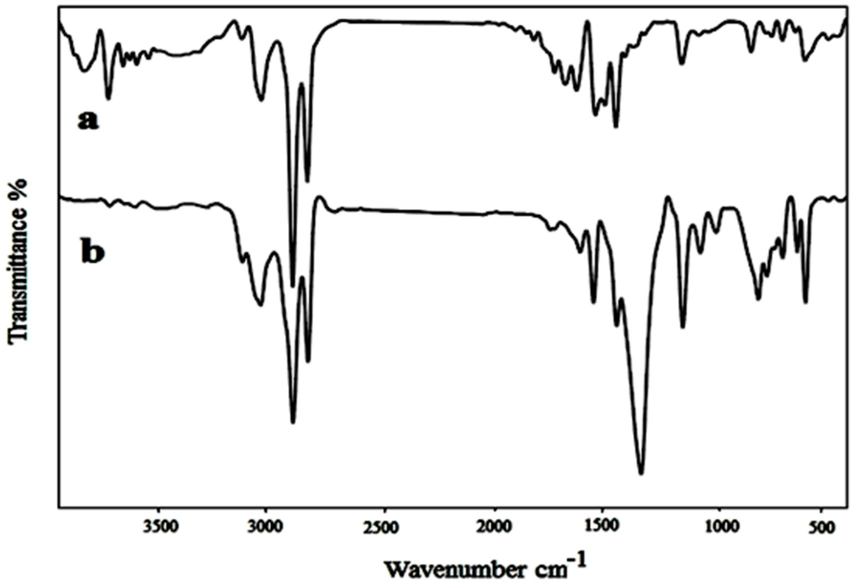

Fig. 3. The FTIR spectra of (a)［C12mim］［Cl］(b) [C12mim][NO_3]

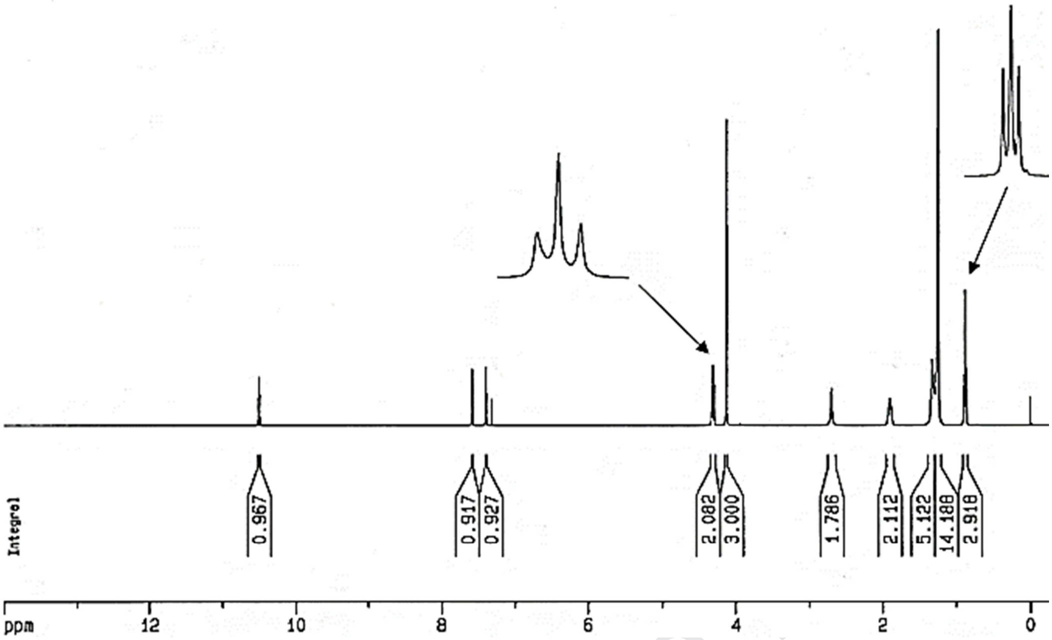

Fig. 4. The ^{1}HNMR spectra of [C12mim][Cl]

2.2.3. Preparation of microemulsions

The microemulsions were prepared so that to keep the mass fraction of the surfactant in the mixture of oil and surfactant, parameter γ, at constant value of 0.05, which was calculated by Eq. 1.

$$\gamma = \frac{S}{S+O} \qquad \text{Eq. 1}$$

To prepare the microemulsion system, at first the oil phase was prepared by mixing of gasoil and sunflower oil with volume ratio of 4 to 1, which was then mixed with a certain mass of desired surfactant to get required γ value as calculated via Eq. 1. Then, a certain amount of distilled water as aqueous phase, was added into the oil phase (with various weights) and the mixture was stirred at 750 rpm in room temperature for 5 min, which was then titrated with co-surfactant to determine phase changes. Here, the conventional Span 80, 1-butyl-3-methylimidazolium nitrate, 1-dodecyl-3-methyl-imidazolium nitrate ionic liquids and the blends of each of these ionic liquids with Span 80 with a ratio of 50:50, were examined as surfactant.

2.2.4. Ternary phase diagram

A ternary phase diagram is an equilateral triangle which consists of three vertices, that each one is representing the percentage of the each of the three components [45]. The ternary phase diagrams of the system was plotted so that the two vertices at the bottom of triangle represented the percentage of the diesel/sunflower oil/surfactant mixture at the right side and the aqoeous phase at the left side. Meanwhile, the upper vertex was representing the percentage of the co-surfactant (1-butanol) phase.

3. Result and discussion

3.1. Phase diagram study

The solubilization of the water in the gasoil/ oil blend as two incompatible phases require the use of an emulsifier or surfactant [48]. The surfactants facilitates the expansion of the interface during the formation of microemulsion and stabilizes the dispersed phase in continous phase and control the convergence of microemulsion [49]. The surfactant has also an amphipathic effect which confines each droplet and prevents their coagulation.

One of the most important points in microemulsion studies is the used detection method for indentifying of the phase changes, which has been done by visual inspection in this work. The triangle diagrams was used here which is an equilateral triangle, and typically the top of that shows co-surfactant and in its lower vertices the nonpolar phase is increased from left to right. To ensure the same effect from the amount of surfactant in all samples, the parameter γ which represents the mass fraction of the surfactant in oil-surfactant mixture, has been kept the same for all samples. The mixture of gasoil and sunflower oil (sunflower oil) (80:20wt%) and surfactant by taking into account the γ value of 0.05 was used as oil phase and distilled water as polar phase. The all samples were prepared under the same conditions of stirring speed at the room temperature with 1-butanol as co-surfactant, until the stable one phase system was titrated. Samples were prepared by using of conventional surfactant, Span 80, [Bmim][NO_3] and [C12mim][NO_3] ionic liquids. Also for the better investigation of the effect of ionic liquids, a blend with a weight ratio of 50:50 of surfactant Span 80 with each of these ionic liquids by keeping the same value of γ=0.05, were prepared and investigated here. In the Fig. 5 the phase diagrams for microemulsion systems prepared in the presence of the conventional surfactant Span 80, [Bmim][NO_3] and [C12mim][NO_3] ionic liquids, 50:50 blend of Span 80 and each of these ionic liquids have been illustrated.

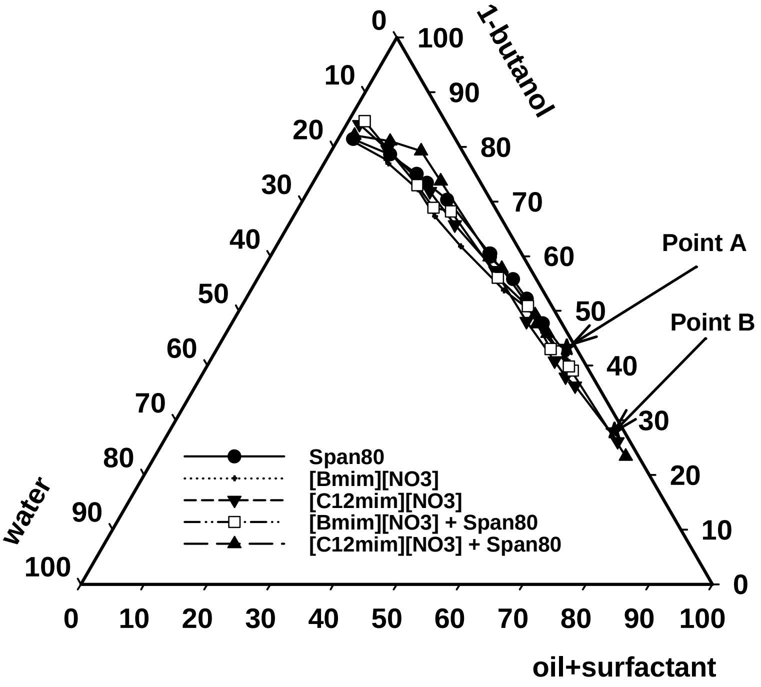

Fig. 5. The phase diagram of gasoil/sunflower oil (80:20 wt %), water, surfactant (Span 80, ionic liquids and their blends with Span 80) and 1-butanol with γ=0.05 at room temperature and stirring speed of 750 rpm

3.2. Stability of samples prepared with ionic liquids

The stability of the samples prepared with ionic liquids were investigated at different time intervals, showing significant stability. These sample were stable for over 6 months without any phase separation. After 6 months, only in one of the samples phase sepration has been observed. Given that the ionic liquids used in this project are based on imidazolium cation, because of this, the cation contributed to the stability of these systems which had a strong interaction between the imidazole ring and the co-surfactant, which resulted in the stability of the formed micells and the prevention of water leakage into the solution. Especially if the chain of ionic liquid is longer, it can act as better surfactant and cause self-accumulation of imidazolium ionic liquids [44].

3.3. Viscosity and Density study

The viscosity and density of the diesel fuel are among the very important parameters for its performance. As detailed in the Table 2, the four fuel microemulsion samples of S1 to S4 were prepared according to the compositions of the components as indicated by the two points of A and B as marked on the phase diagram in Fig. 5. The criterion of choice for these two points has been having the higher percentage of the oil phase, as well as the lowest co-surfactant consumption. Indeed, these two points are chosen so that the samples prepared by these compositions and related surfactant or ionic liquid to form one phase microemulsions. The above four samples were differed regarding the type of materials used as surfactant or emulsifier. Considering the phase diagram of the systems with each of the surfactants, the samples of S1, S2 and S3 were prepared according to the composition of the components in point A, while the sample S4 was prepared as the compositions in point B. Span 80 was employed as surfactant in the preparation of sample S1 and the sample S2 was prepared by using of [Bmim][NO_3] ionic liquid as emulsifier. The samples S3 and S4 are prepared by using of [C12mim][NO_3] ionic liquid as emulsifier. The density of the samples S1 to S4 were measured at different temperatures and given in the Table 3.

Table 2.The general specification samples S1 to S4

Sample No	**S1**	**S2**	**S3**	**S4**
composition point	A	A	A	B
emulsifier	Span 80	[Bmim][NO_3]	[C12mim][NO_3]	[C12mim][NO_3]

Table 3.The density of samples S1-S4, neat gasoil and 4:1(v:v) gasoil/sunflower oil blend at different temperatures

Temperature (°C)	**S1 (A) (g/mL)**	**S2 (A) (g/mL)**	**S3 (A) (g/mL)**	**S4 (B) (g/mL)**	**Gasoil (g/mL)**	**gasoil:sunflower oil (g/mL)**
15	0.841282	0.843816	0.842081	0.848774	0.837349	0.853857
20	0.837527	0.840058	0.838501	0.845081	0.833869	0.850364
30	0.829919	0.832475	0.830988	0.837643	0.826930	0.843383
40	0.822204	0.824772	0.823280	0.828858	0.819895	0.836412

As it is revealed by the data in Table 3, the sample S4 has indicated the highest density among these samples. The dynamic viscosity for the samples S1 to S4 were measured at different temperatures (15, 20, 30 and 40 °C) and plotted versus temperature in Fig. 6. As it can be seen from the Fig. 6, the sample S4, which is prepared by using of [C12mim][NO_3] ionic liquid as emulsifier and composition as in the point B, exhibited a higher viscosity than other samples. As expected, the viscosity of the samples were decreased with increasing of the temperature. Also the difference between the viscosity of the samples S1 to S4 were reduced with increasing of the temperature. For the samples prepared with the composition of the point A, which has different surfactants, no significant difference in viscosities has been observed, this in indicating that these three surfactants have imparted almost the same level of effects regarding the changes in the viscosity of the samples, but which is a bit higher for the inonic liquid with longer length hydrophobic chain ([C12mim][NO_3]) than shorter one ([Bmim][NO_3]). As expected, the viscosity of the gasoil-sunflower oil blend has been higher than net gasoil. The microemulsification of the water in the gasoil-sunflower oil blend has caused a significant decrease in its viscosity, but which is still higher than the viscosity of the neat gasoil. Anyway, the viscosity of the all of fuel microemulsions has been in the accepatable range for the diesel fuel.

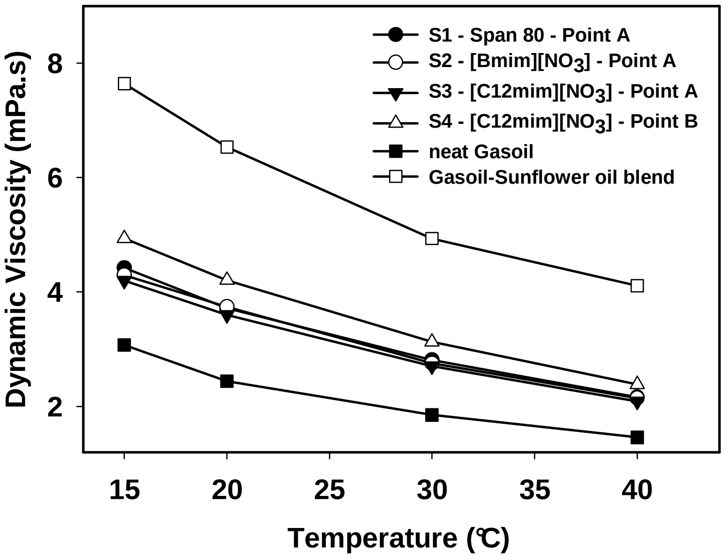

Fig. 6. The dynamic viscosity of the samples S1-S4 (detailed in Table 2), neat gasoil and gasoil-sunflower oil blend (4:1) versus temperature

According to the ASTM D1298 standard, the density of diesel oil at 15 °C temperature should be between 0.82 to 0.86 g/cm^3. Also according to the ASTM D445 the kinematic viscosity of the diesel fuel at temperature of 37.5 °C must be between 2.0 to 2.5 mm^2/s. Hence, the measured data indicate that the density and viscosity of the prepared fuel microemulsion samples are in the desirable range and near to the values for the neat diesel fuel.

3.4. Studying the size of water droplets

In the fuel microemulsion systems, the size of water droplets and their size distribution is an important parameter affecting the stability of these systems. The more smaller water droplets and more narrower distribution, the greater stability will be observed for the system. The size and size distribution of the water droplets in the prepared fuel microemulsions were measured by using of dynamic light scattering technique (DLS). In the Fig. 7 the DLS graphs of the fuel microemulsions prepared in this work (samples S1 to S4) are illustrated. According to the Fig. 7, all of the samples has exhibited water droplets with a trimodal size distributions.

Table 4.The size and relative ratios of the modals of the water droplets in samples S1 to S4 measured by DLS

sample	modal 1		modal 2		modal 3		total
	mean diameter (nm)	relative ratio (%)	mean diameter (nm)	relative ratio (%)	mean diameter (nm)	relative ratio (%)	mean diameter (nm)
S1	0.9	6.3	2.3	40.0	331	53.7	6.1
S2	8.7	70.4	1403	29.6	—	—	10.7
S3	3.3	64.5	935	32.1	4928	3.4	59
S4	1.3	7.4	6.1	82.3	235	10.3	154

The Fig. 7 also indicate that the size and size distribution of water droplets in the systems with the composition in point A has been 9 nm (upto 70%) for [Bmim][NO_3] and 3 nm (upto 64%) for [C12mim][NO_3], also for the microemulsions with the composition in point B has been 6 nm (upto 82%) for systems containing [C12mim][NO_3] and 331 nm (upto 53%) for systems prepared by Span 80.

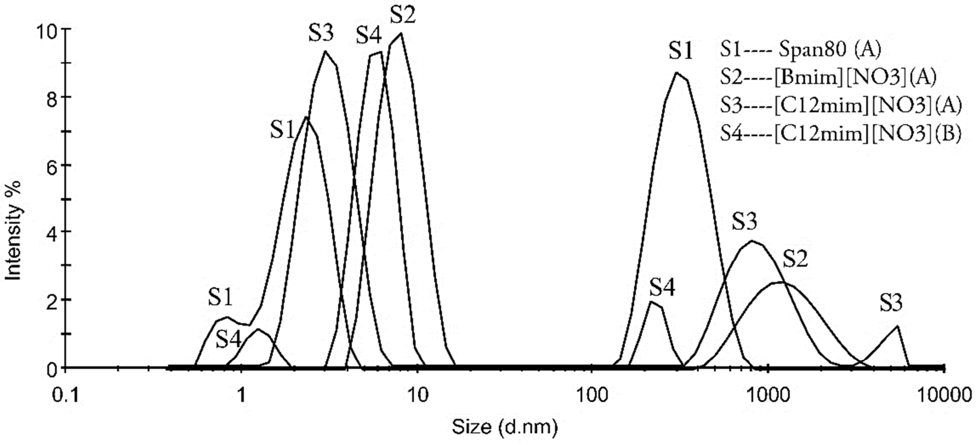

Fig. 7. DLS size distribution graphs of samples S1 to S4

4. Conclusion

The synthesized ionic liquids of 1-dodecyl-3-methylimidazolium nitrate ([C12mim][NO_3]) and 1-butyl-3-methylimidazolium nitrate ([Bmim][NO_3] were successfully used as surfactant for the preparation of the fuel microemulsion of gasoil/sunflower oil (80:20), water and1-butanol as co-surfactant. The phase diagrams of the systems indicated a wider single phase region, indicating of the better performance of these ionic liquids compared to the conventional Span 80 surfactant. The longer length of the hydrophobic chain on the ionic liquid imparted a bit higher viscosity on the system, but no significant difference has been seen on the phase diagrams. The size of water droplets formed inside of microemulsions prepared by ionic liquids with longer hydrophobic chain has been smaller than the microemulsions of ionic liquids with shorter chains, which is attributed to the higher stability of the micelles formed in these systems.

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Highlights

- Methylimidazolium based ionic liquids is used as surfactant in emulsifying of water in diesel/sunflower oil blend.
- The prepared microemulsions has been stable for 9 months on the shelf.
- The ionic liquids exhibited performances comparable to the commercial surfactants such as Span80.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: