# Ionic liquids as novel surfactants for potential use in enhanced oil recovery

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**Abstract**−The screening and use of benign chemicals for enhanced oil recovery (EOR) applications is important because of their properties and relationship to the embedded fluids. We investigated a special type of ionic liquids (ILs) called "Ammoeng" for potential use in surfactant EOR to replace the currently used surfactants that have many disadvantages. The interfacial tension (IFT) between a representative oil sample from Saudi reservoirs and solutions of Ammoeng™ ILs at different concentrations in 10 wt% NaCl aqueous solutions were measured as a function of temperature. It was found that the IFT values decreased with the increase of IL concentration. However, the effect of temperature on the IFT depended on the type of IL. Ammoeng™ 102 gave the lowest IFT values among the screened ILs. The comparison of the results to those resulting from TritonX100, a commercially used surfactant, showed that the IFT values using Ammoeng™ 102 were smaller than the corresponding values when TritonX100 was used at the same conditions. The possibility of having a synergetic effect when using a mixture of Ammoeng™ 102 and Triton X 100 was also investigated. The results showed that the IFT values depended on the total concentration, the surfactant to IL mass ratio, and the temperature.

Key words: Enhanced Oil Recovery, Interfacial Tension, Ionic Liquids, Ammoeng 102, Triton X-100

## INTRODUCTION

As worldwide energy needs continue to grow, there is a concern that the demand for energy may outstrip the supply of energy. Technologies for improving the efficiency of petroleum production will become increasingly valuable. In petroleum field exploitation, generally oil recovered from original oil in place (OOIP) after water flooding is only 30-50%. Advanced methods are required to acquire this unrecoverable oil. New technology applications such as enhanced oil recovery method have been the aim [1,2]. Chemical EOR operations are increasingly applied in oil fields as tertiary-oil-recovery methods. In the literature, there are excellent comprehensive studies on chemical flooding [3-7]. The chemical flooding processes are classified into three main categories: surfactant flooding (SF), polymer flooding (PF) and alkaline flooding (AF). Surface-active agents or surfactants are an important class of chemical compounds used in different sectors of modern industry, such as food, pharmaceutical, cosmetics and petroleum industries. These compounds are able to reduce surface and interfacial tensions, as well as to form and stabilize oil in water or water in oil emulsions. Structurally, they are amphiphilic molecules that comprise both hydrophobic and hydrophilic moieties, the apolar component usually being a carbon chain, whereas the polar part, more variable, can be ionic (anionic or cationic) or non-ionic [8]. The enormous market demand for surfactants is currently met by numerous synthetic, mainly petroleum-based, chemical surfactants. These compounds are usually toxic to the environment and non-biodegradable. They may bio-accumulate and their production, processes and by-products can be environ-

mentally hazardous [9]. Due to environmental issues and restrictive laws, the demand for biodegradable and non-toxic surfactants is increasing.

The mechanism of oil displacement by surfactant and alkaline flooding depends on reducing the interfacial tension between crude oil and formation brine, whereas polymer flooding results in controlling the mobility of reservoir fluids [10,11]. In general, chemical flooding application in the field occurs using pre-flush (low salinity brine) injection to the reservoir followed with chemical solutions. The low salinity pre-flush can be considered as buffer between high salinity formation brine in the reservoir and chemical solutions. The chemical solutions are aimed to reduce IFT between the reservoir fluids For example Bo Gao and Sharma found that Geminis surfactant reduces IFT between brine solution and crude oil to less than 0.001 dynes/cm [12]. Simjoo et al. [13] examined the foaming properties of selected commercial surfactants used in the petroleum industry, namely Dowfax 8390, C12-15 Enordet, Petrostep SB, and C14-16 AOS.

In a typical surfactant-based flooding process applied in petroleum fields, surfactant solutions are injected into an appropriate site, away from the production well, in order to create very low interfacial tensions that will enable the mobilization of oil trapped in the reservoir, when other nonchemical methods fail to improve the extraction efficiency [14]. Normally, a mobile zone should be maintained, with propitious mobility ratios, which can be achieved by incorporating polymers and alkali in the surfactant formulation, thus characterizing the ASP mixtures or solutions. An oil bank is then formed by the mobilized oil, which is ultimately driven to the production well for enhanced recovery. In contrast, oil reservoirs could be damaged by insoluble residues left by the surfactant and/or polymer-based formulations, with obvious environmental impacts. In view

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of this, a continuously developing line of research aims to propose novel chemical systems to be used in EOR activities, with the purpose of minimizing or even eliminating this problem. The paramount importance of surfactant-based chemical systems, however, has been demonstrated by numerous academic studies and technological operations throughout the years [14].

In surfactant flooding, adsorption phenomena like chain interactions in solution and self-assembly, which affect interfacial tension and interfacial rheology and occur within the reservoir porous medium, play an essential role in determining the final oil recovery factor [15,16]. The efficiency of the process is reduced because of surfactant loss by adsorption, impairing the reduction of interfacial tension between residual water and crude oil, which ultimately renders the process technically unviable. The literature reports that surfactants should be used at concentrations above the CMC for ionic molecules [17,18] and around the CMC value for nonionic ones [19]. Chromatographic separation effects involving the surfactant molecules take place during specific applications, as in surfactant-alkaline flooding, lead to the loss of surfactants. Material loss is also caused by adsorption on reservoir rocks, precipitation and changes in rock wettability [20].

Microemulsions are also potential candidates in enhanced oil recovery, especially because of the ultra-low interfacial tension values attained between the contacting oil and water microphases that form them. In the early 1970's, Healy and Reed reported on some fundamentals of microemulsion flooding, especially viscosity, interfacial tension and salinity [21,22]. The British Petroleum (BP) oil company devised a method whereby co-injection of a low-concentration mixture of surfactant and biopolymer is effected. Austad et al. [23,24] investigated the importance of understanding the interactions existing within specific polymer surfactant and microemulsion systems applied in EOR. Their studies evolved during the 1990's on chemical flooding of oil reservoirs, with detailed reports on positive and negative effects of chemicals in oil recovery [25,26]. In these reports, they have compared cationic, anionic and nonionic surfactants, showing that cationics are more efficient. Morrow and Mason report on researches that indicate the use of surfactants expanding from laboratory to field tests [27]. However, though many results are obtained for specific reservoirs, much has yet to be understood. The surfactant CMC is an important property that must be observed when designing its EOR application. Because the CMC decreases with increasing salinity at relatively low temperatures (ambient to 40 °C), the oil recovery from oil-wet carbonate rock is delayed, which does not seem to be case when temperature is increased to around 70 °C. Also, certain surfactants are more capable of changing the rock wettability from oil-wet to more water-wet conditions, like the cationic ones derived from coconut oil, and to less oil wet conditions, like the ethoxylated nonionic and anionic structures. Babadagli [28] reports on the dynamics of capillary imbibition effected in Berea sandstone and Indiana limestone by mixtures of Triton® X-100 (a polyethoxylated nonionic surfactant), sodium chloride and polyacrylamide in different compositions, further enhanced by the action of heat, providing information on specific conditions that cause weak or strong capillary imbibition in both water- and oil-wet matrices. Babadagli [29] compared different EOR processes (water flooding, thermal, and chemical with surfactant, with polymer and with NaCl brine) in the same rock samples with respect to oil viscosity, matrix wettability and matrix boundary conditions. It is important that careful selection of surfactant structures and identification of the effects that surfactant properties have on capillary imbibition must always guide the implementation of the EOR process [30].

In microemulsion injection, a high concentration of surfactant is required to produce self-assembled structures, such as spherical droplets similar to micelles that are able to solubilize or dissolve the oil in a reservoir. This process occurs by incorporating a certain amount of oil in the core of the droplets, thereby promoting miscibility in the overall system. Surface tensions between oil and water are then reduced with the microemulsion injection into the reservoir, improving the oil recovery efficiency, also because of the relatively high viscosity of microemulsions [31].

Li et al. proposed a new type of flooding system, involving worm-like micelles, formed by the anionic surfactant sodium oleate, in sodium phosphate solutions [32]. Laboratory simulation flooding experiments were performed to investigate the effects of flooding with the worm-like micelle system. The results showed that the oil recovery was as high as 32.7%.

Some successful results have been acquired from the implementation of surfactant flooding for some conventional oil reservoirs worldwide; however, huge surfactant loss through flowing in the porous media and relevant issues of adsorption and reactions between reservoir rock and surfactant are considered as serious drawbacks [33].

Frequently, an ultra-low interfacial tension value ($<10^{-3}$ mN/m) is required [34]. For a chemical flooding system, a surfactant alone may not be able to significantly reduce the interfacial tension to $10^{-3}$ mN/m, and use of other chemicals such as co-surfactant (usually an alcohol), alkali, polymer and salt may be necessary [35]. Chemical flooding can observably enhance oil recovery more than water flooding, but it has also faced new problems owing to the environment and the cost of surfactant. Therefore, there has been an increased drive to use natural surface-active components as surfactants.

Zhang et al. [36] reported the synthesis of hydrophobically modified sodium humate surfactants with different chain lengths. The effects of alcohol and alkaline on the interfacial tension of oil/water interface were also reported. Ultra-low interfacial tension related to EOR was obtained at the crude oil/water interface from the mixture solution of the surfactant, $Na_3PO_4 \cdot 12H_2O$ and n-propanol. The experimental results show that hydrophobic modification of sodium humate surfactants causes low interfacial tension at the crude oil/water interface as compared with that of the single sodium humate. While the interfacial tension of the sodium humate/crude oil interface could reach to $10^{-1}$ mN/m, the interfacial tension of the modified surfactant/crude oil system, in aqueous solution, decreases so much that sometimes it is less than $10^{-4}$ mN/m.

Ionic liquids are composed of ions only and have a freezing point of less than 100 °C. The cation is from organic source while the anion could be organic or inorganic [37]. ILs have distinctive physical and chemical properties that make them potential replacement for volatile organic solvents, such as their very low vapor pressure, high chemical and thermal stabilities, and ability to dissolve many polar, non-polar, organic and inorganic compounds [38]. ILs are being examined for different industrial applications, e.g., separation, electrochemical processes, biochemical, catalysis, and syntheses [39-50].

ILs called "Ammoeng" represent acyclic ammonium salts that contain cations with oligoethylenglycol units of different chain length. These ILs are readily available in technical quantities for reasonable prices and hence, represent an interesting alternative to the much more expensive and often not yet listed imidazolium-based ILs [51]. In addition, Ammoeng ionic liquids have gained interest for commercialization due to their surfactant properties. These ILs have amphiphilic structure containing both hydrophobic (long alkyl side chain) and hydrophilic (hydroxyl) groups.

Kohlmann et al. [52] utilized the IL AMMOENG™ 101 as a feasible co-solvent for the continuous biocatalytic synthesis of (R)-2-octanol. They reported excellent process stability of the biocatalysts. Utilization of AMMOENG™ 101 increased substrate concentration, and improved space time yields and turnover numbers of the cofactor by factors of 3 and 6, respectively. Moreover, 80% less waste was generated, while producing the same amount of product. Manic et al. [53] reported the use of Cocos alkyl pentaethoxi methyl ammonium methylsulfate (AMMOENG100) for the purpose of extraction of linoleic acid from soybean oil. Liquid-liquid phase equilibrium was measured for binary (IL/soybean oil) as well as ternary (IL/soybean oil/linoleic acid) mixtures, as a function of temperature and composition. The influence on distribution coefficients and separation factor of temperature, initial acid content of the oil and solvent to oil ratio were studied. AMMOENG100 was chosen due to its extremely low miscibility with soybean oil, complete miscibility and low viscosity and cost. Guo et al. [54] reported the establishment of an efficient protocol for enzymatic production of diglycerides by means of the tunable property of ILs. They found that a single IL system was insufficient to achieve remarkably higher yield of desired products than conventional solvents. The authors thus resorted to binary IL systems based on the observations of the characteristics of enzymatic glycerolysis in single IL system. The binary IL systems are constructed with one IL with better diglycerides generation selectivity and another IL being able to achieve high conversion of oil. A preliminary parameter optimization was then conducted for selected binary IL system: trioctylmethylammonium bis(trifluoromethylsulfonyl)imide/Ammoeng 102. Kohlmann et al. [55] showed that ILs represent a promising alternative to conventional cosolvents as biocompatible solubilizers for biocatalysis. This was shown using water miscible ILs to facilitate the stereoselective reduction of hardly water soluble, aliphatic ketones catalyzed by the alcohol dehydrogenase from Lactobacillus brevis. Ten ILs were screened for activity and solubility. Improved storage stabilities besides improved enzyme activities, as well as reduced substrate surplus and product inhibitions were found, while applying the most promising AMMOENG™ 101 in more detailed investigations. Batch reactions with cofactor regeneration via a glucose dehydrogenase showed increased reaction rates, thus underlining the positive influence of AMMOENG™ 101. Rodriguez et al. [56] reported the first-time usage of an isolated thermo stable Baeyer-Villiger monooxygenase (phenylacetone monooxygenase, PAMO) in the presence of ILs. They studied stability, activity and selectivity of PAMO as an oxidative enzyme in the presence of different ionic liquids. They found that the addition of some specific ILs, such as Ammoeng™ 102, can significantly enhance the E-value in the oxidation of racemic benzylketones. Moreover, the use of ILs increases the optimal substrate concentration for performing Baeyer-Villiger oxidation, thereby

extending the biocatalytic repertoire of PAMO for synthetic applications. Ribot et al. [57] reported a method for the gelation of the amphiphilic quaternary ammonium oligoether-based ionic liquid Ammoeng™ 100 with water. This approach allows the preparation of thermo-reversible ionogels with high ionic conductivity (up to 60 mS cm$^{-1}$), remarkable mechanical properties (storage moduli above 10$^5$ Pa-a value comparable to the mechanical properties of some rubbers), and melting points in the range from $-20$ to 53 °C. These properties can be easily tuned in a broad range by varying the water (and/or inorganic salts) concentration in the ionogels. The reported method is a very convenient way to prepare ionogels because it is based on simple and inexpensive materials, namely Ammoeng™ 100 and water (no volatile organic solvents involved). Infrared measurements suggested that the observed gelation phenomenon might occur via the formation of a hydrogen bonded network between water and Ammoeng™ 100. Devi et al. [58] investigated the use of a variety of ILs as reaction media for the production of biodiesel by enzymatic methanolysis of rapeseed oil. The IL Ammoeng™ 102, was found to be capable of forming oil/IL biphasic reaction system by mixing with substrates, which is highly effective for the production of biodiesel with more than 98% biodiesel yield and nearly 100% conversion of oil. Dreyera et al. [59] reported the extraction of catalytically active biomolecules using ionic liquid-based aqueous two-phase systems composed of the IL Ammoeng™ 110 and K$_2$HPO$_4$/KH$_2$PO$_4$. This process represents a powerful tool for the integration of several process steps into one unit operation within downstream processing. Jimenez and Bermudez reported the friction and wear behavior of grade 3 titanium against AISI 52100 steel, in the presence of six ILs lubricants, four imidazolium ILs, and two quaternary ammonium salts, the chloride derivative AMMOENG™ 101 and the dihydrogenphosphate AMMOENG™ 112, and compared with that of a mineral base oil. At room temperature, all ILs gave similar mean friction values, below 0.20, with a 60% reduction with respect to the mineral oil.

The green character of ILs has been usually related to their negligible vapor pressure; however, their toxicology data have been very limited until now [60]. Several authors [60-65] already mentioned this lack of toxicological data in the literature. Although ILs will not evaporate and thus will not cause air pollution, it does not mean that they will not harm the environment if they enter **the aquatic system**. Most ILs are water soluble and they may enter the aquatic environment by accidental spills or effluents. The most commonly used ILs, [bmim][PF$_6$] and [bmim][BF$_4$], are known to decompose in the presence of water, and as a result hydrofluoric and phosphoric acids are formed [66]. Therefore, both toxicity and ecotoxicity information, which provides metabolism and degradability of ILs, are also required to label them as green solvents or investigate their environmental impact. The ecotoxicological studies performed to understand the effects of different ILs on enzymatic activities, cells and microorganisms are utilized to obtain LC$_{50}$ levels (lethal concentration). Decreasing LC$_{50}$ values indicate higher toxicities according to the toxicity classes of Hodge and Sterner scale (1956) [67]. This scale indicates that the LC$_{50}$ value (in terms of mg/L) of 10 or less shows that the chemical is extremely toxic, LC$_{50}$ value between 10 and 100 shows that chemical is highly toxic, LC$_{50}$ value between 100 and 1,000 shows that chemical is slightly toxic, and finally LC$_{50}$ value between 1,000 and 10,000 means that chemical is practically

nontoxic. The impact of ILs on aquatic ecosystems is highly important since some ILs have a high solubility in water. Maginn [68] provided the $LC_{50}$ levels for two imidazolium-based ILs with Daphnia magna, common fresh water crustaceans. Since D. magna are filter feeders at the base of the aquatic food chain, their responses to ILs are essential to understand how these new solvents may impact an environmental ecosystem. As ILs, 1-n-butyl 3-methylimidazolium cation with $PF_6$ and $BF_6$ anions was used. These two ILs are as toxic to Daphnia as benzene and even far more toxic than acetone, but much less toxic than ammonia, chlorine, phenol, etc. Wells and Coombe [69] also provided the results of freshwater ecotoxicity tests of some common ILs with imidazolium, ammonium, phosphonium and pyridinium cations on invertebrate D. magna and the green alga Pseudokirchneriella subcapitata (formerly known as Selenastrumcapricornutum). The results were reported using medium effective concentration ($EC_{50}$) values. The toxicity values of the most toxic IL were four orders of magnitude more than the least toxic IL. There was a relation between the order of toxicity and alkyl side chain length of the cation. For alkyl methylimidazolium ILs with C4 side chain constituents showed moderate toxicity, whereas the C12, C16, and C18 species were very highly toxic to both organisms under investigation. Pyridinium, phosphonium, and ammonium species with C4 side chain constituents had also only moderate toxicity, whereas C6 and longer side chains showed significant increases in toxicity. It was shown that the least toxic ionic liquids' ecotoxicity was comparable to hydrocarbons' such as toluene and xylene. The most toxic ionic liquids are many orders of magnitude more acutely ecotoxic than organic solvents such as methanol, tert-butyl methyl ether, acetonitrile, and dichloromethane. The authors also emphasized that simple acute ecotoxicity measurements are not enough to fully characterize the full impact of a solvent released to the environment but were only part of the environmental impact assessment. There were also some studies on toxicity of ILs performed on animals such as the nematode model organism (Caenorhabditis elegans) [freshwater pulmonate snails (Physa acuta) [71], Fischer 344 rats [72] and zebra fish (Danio rerio) [73]. One of the most important points that must be taken into account during the toxicological study of the ILs is the purity of the IL studied. Therefore, different authors [74] attached significant importance to proper analyzing techniques. ILs are introduced under the concept of green chemistry in all research papers due to their nonvolatile nature. The environmental persistence of commonly used ILs, along with their possible toxicity should be taken into account. There are still very few results about the eco-toxicological effect of ILs, and they can be evaluated more satisfactorily as green solvents or not after more data on the subject will be provided [75]. The possible toxic and non-biodegradable nature of the existing ILs has also led to the development of new types of nontoxic and biodegradable ILs [76-81].

Lacrama et al. [82] used the recently launched spectral-structure activity relationship (S-SAR) analysis to investigate the vectorial anionic-cationic model of a generic ionic liquid, along with the associated algebraic correlation factor in terms of the measured and predicted activity norms. The reliability of the present scheme is tested by assessing the Hansch factors, i.e., lipophylicity, polarizability and total energy, to predict the ecotoxicity endpoints of wide types of ionic liquids with ammonium, pyridinium, phosphonium, choline and imidazolium cations on the aquatic bacteria Vibrio fischeri. The results, while confirming the cationic dominant influence when only lipophylicity is considered, demonstrate that the anionic effect dominates all other more specific interactions. It was also proved that the S-SAR vectorial model predicts considerably higher activity for the ionic liquids than for its anionic and cationic subsystems separately, in all considered cases. Moreover, through applying the least norm-correlation path principle, the complete toxicological hierarchies are presented, unfolding the ecological rules of combined cationic and anionic influences in ionic liquid toxicity. Ribot et al. [83] disclosed a new and convenient method to prepare ion gels with a reverse thermo responsive behavior (i.e., mechanical moduli and viscosity increase with temperature), enhanced $\sigma$, and tunable gelation point in a broad temperature range. These ion gels are based on simple and inexpensive materials, namely Ammoeng™ 111 and water (no volatile organic solvents are involved). The obtained ion gels revealed storage moduli above $10^3$ Pa and $\sigma$ up to 3 mS cm$^{-1}$; these values are comparable to the values of other reported ion gels. Their reverse thermo responsiveness and gelation mechanism are most likely to be related to the lower critical solution temperature (LCST) behavior of poly(propylene oxide) moieties present in the Ammoeng™ 111 and to the formation of a hydrogen bonded phase-segregated network between water and the amphiphilic Ammoeng™ 111. The observed enhanced $\sigma$ upon addition of water might be related to the well-known phenomenon of dissociation of ions upon addition of polar solvents (water) into ionic compounds (Ammoeng™ 111), which generally promotes an increase in s in electrolytes. After taking into account limitations related to their electrochemical stability (due to the reactivity and narrow electrochemical window of water) and potential toxicity of the Ammoeng™ 111, the new ion gels may be interesting candidates to be tested in applications ranging from electrochemical devices, to injectable polymers in medicine.

Bosmann reported that although Ammoeng™ 100 is very toxic to fish, it has an $LD_{50}>2,000$ mg/kg in mice. There are ILs around that are not too toxic, and once we have learned what structural features cause toxicity, we can make our new ILs even less toxic [84].

Frade et al. [85] reported the toxicological evaluation of over 80 ionic liquids from different classes of cations and anions. The work was performed on confluent human colon cancerous cells, a suitable model for cytotoxicity studies. They found that, in general, the toxicity of the cation increases when longer alkyl chains are present. The introduction of a COOH group or ether functionality leads to a great reduction of ILs toxicity. They also found that the type of anion can affect strongly toxicity of the ionic liquid, and some seem to have a bigger impact in the overall toxicity than others. The authors concluded that based on a comparison of all toxicological data there are potential good candidates for building human friendly ionic liquids.

Peric et al. [86] indicated that though ILs are considered as nonvolatile and thus cannot contribute to the air pollution, the water solubility of many ILs is not negligible. The potential release of ILs into aquatic and terrestrial environment may lead to water and soil pollution and related risks. So, it is important to evaluate ecotoxicity, biodegradability, bioaccumulation and environmental fate of these chemicals. They reported that the quaternary ammonium compounds were less toxic than the imidazolium and pyridinium analogues. Generally speaking, all of the aquatic toxicity tests showed that the head group (cationic part of the molecule) was responsible for the toxicity of the ILs. In most cases there was no influence of the anionic

part of the ILs molecule to the toxicity. The side chains on the head groups were proven to have a very strong influence on the toxicity. The longer and more branched the side chain is, the more toxic is the IL. Most toxic ILs have an alkyl chain with more than eight carbons. These results point to the fact that some ILs may be more toxic than the commonly used organic solvents, and not as green as expected.

Dumitrescu [87] reported the acute toxicity caused by zebrafish (Danio rerio) exposure to various concentrations of tetrabuthylammonium bromide. The ionic liquid's acute toxicity on zebrafish was assessed according to the lethal effects after a 96-hour exposure. A histopathological examination was performed on individuals from the control group and on all the dead fish. The results of the acute toxicity test reveal that the $LC_{50}$ value after 96 hours is between 2,500 and 3,000 mg $L^{-1}$. The values obtained for tetrabuthylammonium bromide are much smaller than the data obtained for $LC_{50}$ at 96 hours for other solvents like acetone (30,642 mg $L^{-1}$), dimethylformamide (12,220 mg $L^{-1}$), but much bigger than the toluene (60-313 mg $L^{-1}$), benzene (203 mg $L^{-1}$), phenol (5 mg $L^{-1}$), etc.

Peric et al. [86] have studied the toxic effect on aquatic organisms of a new family of water soluble protic ILs that are composed of ammonium substituted organic salts. The cationic moiety is mono-, di- or trihydroxyethylammonium, while the anionic moiety is an alkylcarboxylate. The results show no toxicity to aquatic organisms, with $EC_{50}$ values being between 460 and 2,600 mg $L^{-1}$ for the tests of aquatic toxicity. According to the EU regulation they have no toxic effects on aquatic organisms (all of the $EC_{50}$ are above the limit value of 100 mg $L^{-1}$). Within this group of protic ILs the toxicity increases with the increase of complexity of the molecule. Comparing the $EC_{50}$ values obtained for the aprotic ILs it can be seen that the new protic ILs are less toxic than the aprotic ILs studied up to date.

The biodegradation potential of ILs in aqueous media and soil has been addressed in many works [86,87]. Peric et al. [86] have studied the biodegradability in water of three ILs from the new family of protic ILs, derived from substituted ammonium salts (hydroxyethylammonium formate, diydroxyethylammonium propionate, and trihydroxyethylammonium pentanoate). Almost all of the analyzed protic ILs were shown to be readily biodegradable with biodegradation rates of 57 to 86% in a 28 days period. These results can be due to the fact that these PILs do not show toxicity towards microorganisms and also to their non-cyclic simple structure. Even though they have cations and anions composed of short alkyl chains (≤C5), these chains have hydroxyl and carboxyl functional groups, which can increase the biodegradability rate, in accordance with the findings of other authors related to ester and amide functional groups [85]. Peric et al. [86] have performed other type of studies of biodegradability of ILs in soil. The results indicate that the biodegradation rate ranges between 60 and 90%, with the most complex ILs showing the lowest biodegradation rate. The ILs from the new family of protic ILs are clearly less toxic than the ILs derived from imidazolium, pyridinium, pyrrolidium, etc., and also less toxic than the conventional solvents, with a notable rate of biodegradation in water and soil. This can be a path to follow regarding a synthesis of really green ILs, formed by a pair of organic ions, with simple (short and lineal) structure and functional groups which facilitate biodegradation.

Several studies conducted in the last decade investigated the effect of ILs on IFT and consequently its impact on the increase of the production of oil [87]. The synergetic effect of these surfactants was also investigated regarding their effect in lowering the IFT and their contribution towards the assessment of recovery [87].

Lago et al. [88] investigated the suitability of several ILs as effective replacements for conventional surfactants in EOR. However, they did not use real reservoir fluid. Instead the reservoir fluid was modeled as a ternary system of water (pure water or aqueous solution of NaCl) plus the ionic liquid trihexyl(tetradecyl)phosphonium chloride plus dodecane. Determination of its liquid-liquid phase equilibrium indicates the formation of a Winsor type III system, with a tri-phasic region and adjacent biphasic regions. The interfacial tensions in the system corroborate the ability of the IL to act as a surface active agent, as desirable for its use in an EOR process. They also reported measured values of relevant transport properties such as viscosity and density for the equilibrium phases. Hezave et al. [89] examined the use of 1-dodecyl-3-methylimidazolium chloride as the IFT reducing agent and its dynamic IFT with one of the Iranian crude oils under different conditions. The obtained results revealed that the critical micelle concentration between the crude oil and formation brine was obtained at a very low concentration of 100 ppm. Unlike traditional surfactants, this IL-based surfactant was found to be more effective for higher saline formation water. In addition, several core flooding experiments were performed to find both tertiary oil recovery efficiency and IL adsorption on the rock surfaces, which indicated promising results. Different mechanisms were proposed for interfacial tensions reduction using 1-dodecy-3-methylimidazolium chloride as the surface active agent, which helps preparing formulations of practical application of the ILs for EOR. Hezave et al. [90] investigated the effect of 1-dodecyl-3-methylimidazolium chloride as a new kind of surfactant on IFT of heavy crude oil and water for possible application in the chemical EOR processes. The obtained results showed that the used IL introduced a rather a low CMC of about 250 ppm. The results showed that IFT was decreased significantly when IL solution was prepared by formation brine (consisted of mono and divalent ions especially negative). In general, the obtained results revealed that IL concentration of 250 ppm in formation brine leads to IFT value of 1.2 mN/m (about 80 times reduction). In addition, an increase in the temperatures leads to an increase in the measured IFT. The authors concluded that the used IL can be a good candidate for the chemical EOR processes since not only it can reduce the IFT for the heavy crude oil/water system but also was able to well tolerate the harsh conditions of salinity.

In this work ammonium-based ILs, namely Ammoeng™, were investigated for possible use in surfactant EOR. The IFT values for solutions of different ILs in brine and deionized water and representative Saudi oil sample were measured. The effect of type of IL, concentration of IL, and temperature on the measured IFT was studied. Moreover, IFT of mixtures of Ammoeng and TritonX100 in brine and deionized water and representative Saudi oil sample values were measured at different concentrations and temperatures.

## MATERIALS AND METHODS

Ammoeng ILs with reported purity of >95% were supplied by Solvent Innovation (Cologne, Germany now Merck, KgA). Triton X 100 of 99% was supplied by Sigma-Aldrich (Germany). Sodium
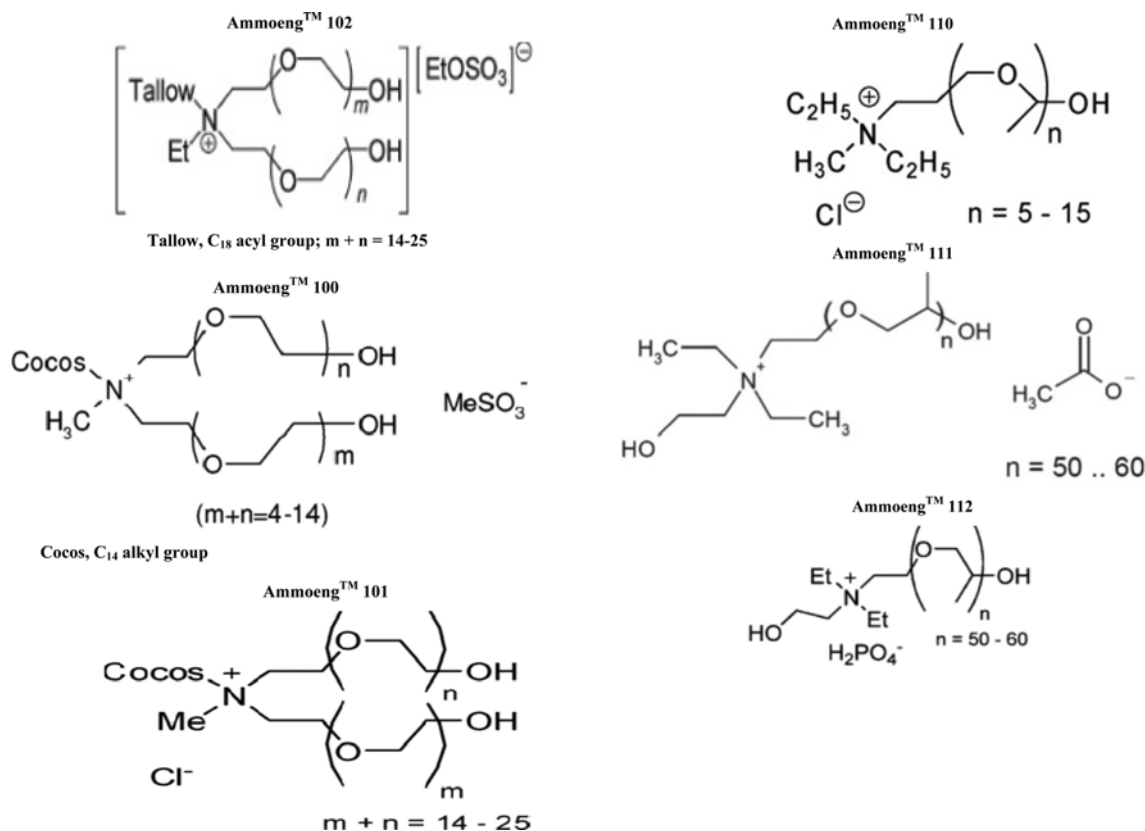
Scheme 1. Structure of selected Ammoeng™ ILs used in this study.

Table 1. Physical properties of selected Ammoeng ILs used in this study

| IL | Chemical Formula | Melting point (°C) | Density (g/cm³) | Viscosity (cP) | pH | Solubility in water |
|---|---|---|---|---|---|---|
| AMMOENG 102 | Tetra-alkyl ammonium sulfate | <25 | 1.08 | _____ | 6-8 | Soluble |
| AMMOENG 110 | Quaternary ammonium chloride | <25 | 1.08 | _____ | 6-8 | Soluble |
| AMMOENG 111 | Quaternary ammonium acetate (poly[oxy(methyl-1,2-ethandiyl)]-alpha-(diethyl-hydroxyethylammonio)ethyl]-acetate) | <25 | 1.04 | _____ | 7.5-9.5 | Not soluble |
| AMMOENG 112 | (Poly[oxy(methyl-1,2-ethandiyl)]-alpha-(diethyl-hydroxyethylammonio)ethyl]-dihydrogenphosphate) | <-65 | 1.04 | 1695 | 7.5-9.5 | Soluble |
| AMMOENG 120 | Quaternary ammonium sulfate | 8-10 | 0.99 | 808 | 5-6 | Partially soluble |
| AMMOENG 130 | 1-Octadecanaminium,N,N-dimethyl-N-octadecyl-, chloride (1 : 1) | | | | | Not soluble |

chloride and calcium chloride were supplied by KSU main store and were of 99% purity. All chemicals were used without any further purification.

Several Ammoeng ILs were screened to test their suitability for use in EOR, Scheme 1. Important physical properties for the tested ILs are listed in Table 1. The screening was based on solubility in water or brine, e.g. 10 wt% NaCl in water. A proper surfactant must have at least partial solubility in water or brine. IFT values measurement were then taken for the successful ILs. The IL that gave the minimum IFT values at reservoir conditions was chosen for further investigation.

To prepare brine, NaCl was used because it is the typical salt found mainly in petroleum reservoirs. The 10 wt% NaCl solution in deionized water was used to represent the typical condition of brine which exists in most petroleum reservoirs in Saudi Arabia. The unit used for the concentration of the IL or surfactant is ppm, based on weight of materials used. The concentrations were 0, 100, 200, 500, and 2,000 ppm.

For surfactant-ionic liquid solutions different weight ratios were used for each overall concentration. The used surfactant was Triton X 100 and the IL used after screening was Ammoeng 102. The applied temperature started from ambient temperature up to the reservoir temperature (from 23 °C to 80-90 °C).

The IFT measurements were taken using Kruss Pendant Drop apparatus DSA100 (Germany). The reported accuracy of the measured IFT is ±0.01 mN/m. This equipment is capable of measuring

surface tension and IFT at various conditions of pressures and temperature. To test the equipment and procedure used, IFT values for water and selected standards were measured and compared to values reported in the literature. There was excellent agreement between the two sets of values.

The Saudi crude oil sample used in this study was characterized by measuring its specific gravity (0.886), and viscosity (12 cP). All the parameters were measured at King Abdul-Aziz City for Sciences and Technology (KACST). **The composition of the sample was determined using Perkin-Elmer 2400 Series II CHNS/O Analyzer**: carbon=81.29 wt%, hydrogen=9.13 wt%, nitrogen=0.70 wt% and the total sulfur content=2.56 wt%. The ashpaltenes content was 5.6 wt%.

## RESULTS AND DISCUSSION

We started by screening the available Ammoeng ILs for being suitable for use in surfactant EOR by measuring their solubility in deionized water and 10 wt% NaCl brine. It was found that most of the Ammoeng ILs were soluble in water and in brine, Table 1. However, some of these ILs formed an emulsion in water and thus were discarded from IFT measurement experiments.

Then IFT between aqueous solutions of the soluble ILs and the oil was measured at atmospheric pressure and different temperatures. It was found that IFT values for some ILs are high and increase with temperature. This means that these IL are not suitable for the use in surfactant EOR. Fig. 1 shows good examples for this type of behavior. Other ILs have high IFT values that decrease with the increase of temperature, but their value at typical reservoir temperature was higher than the acceptable limit (Fig. 1).

Fig. 2 shows that IFT for Ammoeng 102 in 10 wt% NaCl brine is much smaller than that for any other tested Ammoeng IL. In addition, the IFT values decrease with the increase of temperature and reach as low as 2.3 mN/m at reservoir temperature. The IFT values decrease with the increase of IL concentration at the same temperature. Moreover, the IFT value of the IL in brine is much smaller than that in deionized water at the same conditions (Fig. 2).

To compare the behavior of Ammoeng 102 with commercially available surfactants we measured the IFT of solutions of Triton X-100 in water and 10 wt% NaCl brine. In a previous study Triton
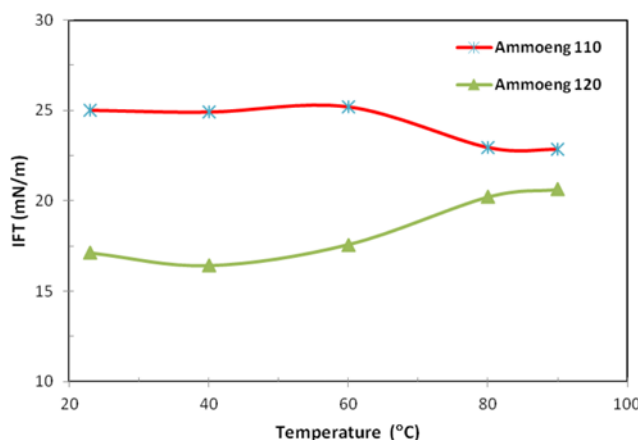


**Fig. 1. IFT as a function of temperature for Ammoeng 110 and Ammoeng 120, 500 ppm in 10 wt% NaCl aqueous solution.**
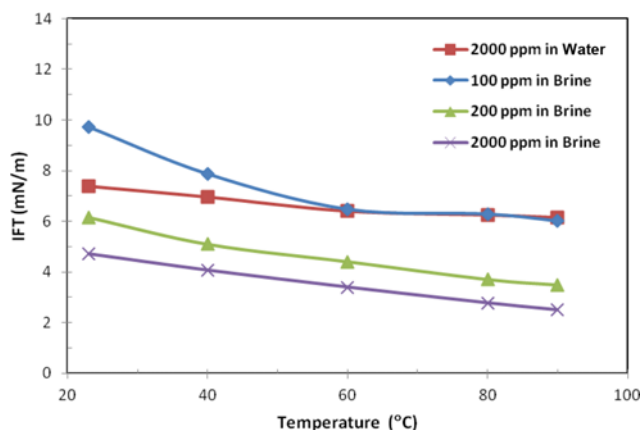
**Fig. 2. IFT as a function of temperature for Ammoeng 102 in water and 10 wt% NaCl brine.**
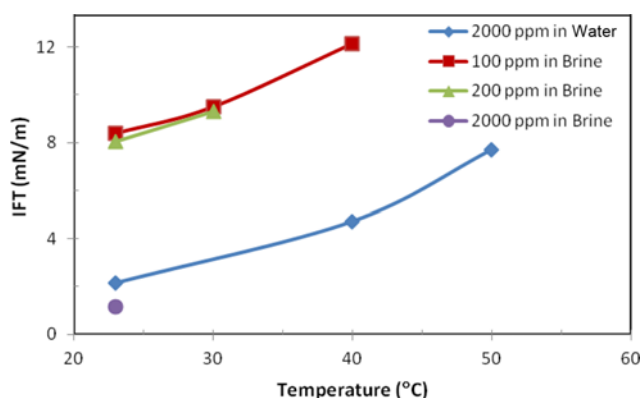


**Fig. 3. IFT as a function of temperature for Triton X 100 in deionized water and 10 wt% NaCl brine.**

X100 gave the best results when compared to other available surfactants [91,92]. The results are shown in Fig. 3. It is clear from the figure that the IFT increases with the increase of temperature and decreases with the increase of the surfactant concentration. It should be noted that the appearance of a cloud point at low temperature precluded taking more IFT measurements, e.g. at 2,000 ppm in 10 wt% NaCl the cloud point appears near 30 °C.

It can be noted from Fig. 2 and Fig. 3 that IFT values for Ammoeng 102 solutions and oil below 40 °C are higher than the corresponding values for Triton X 100 at the same conditions. However, above 40 °C and up to the reservoir temperature the opposite is true. This means that Ammoeng 102 is more suitable to be used as a surfactant in EOR than Triton X 100.

To investigate the possibility of having a synergetic effect when using a mixture of Ammoeng and Triton X 100, we measured IFT values for the same oil sample with different mixtures of the IL and surfactant at different total concentrations and different IL/surfactant ratios. The results are shown in Fig. 4-7 for 100 ppm, 200 ppm, 2,000 ppm in 10 wt% NaCl brine, and 2,000 pm in deionized water, respectively.

For 100 and 200 ppm total concentration mixtures in 10 wt% NaCl brine, it is clear that pure Ammoeng 102 is better than any mixture containing Triton X 100 (Fig. 4 and Fig. 5). As expected the IFT of the mixture in brine with oil decreases with the increase
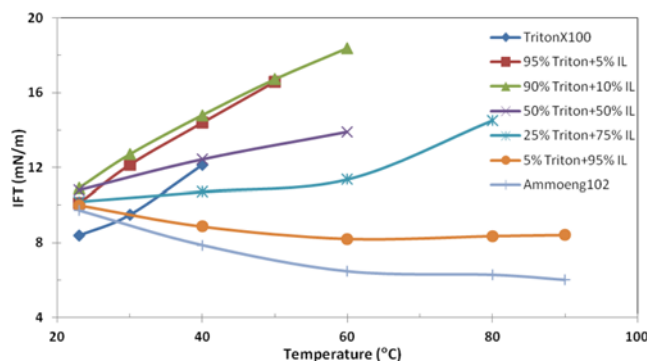
**Fig. 4. IFT as a function of temperature for a mixture of Triton X 100 and Ammoeng 102 of a total concentration of 100 ppm in 10 wt% NaCl brine.**
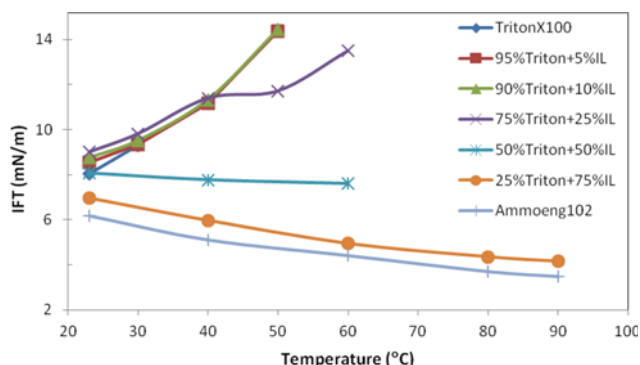


**Fig. 5. IFT as a function of temperature for a mixture of Triton X 100 and Ammoeng 102 of a total concentration of 200 ppm in 10 wt% NaCl brine.**
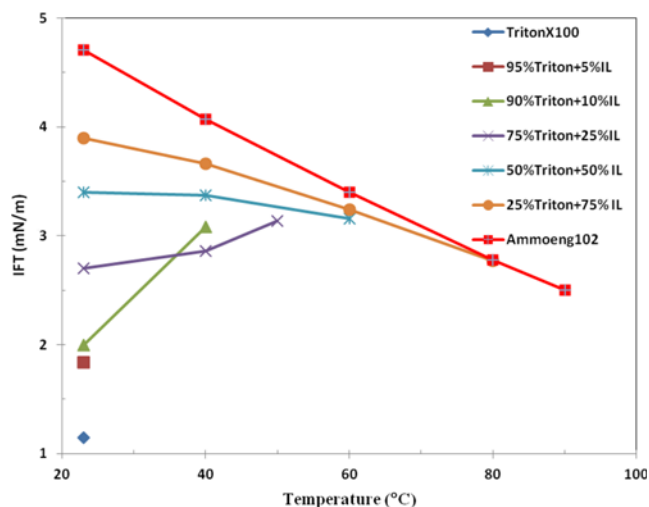


**Fig. 6. IFT as a function of temperature for a mixture of Triton X 100 and IL Ammoeng 102 of a total concentration of 2,000 ppm in 10 wt% NaCl brine.**



**Fig. 7. IFT as a function of temperature for a mixture of Triton X 100 and Ammoeng 102 IL of a total concentration of 2,000 ppm in deionized water.**

X 100 to Ammoeng 102. This ratio depends on the total concentration, 1 : 3 and 1 : 1 for 100 and 200 ppm, respectively. Below this ratio the effect of temperature is reversed.

For the 2,000 ppm total concentration mixtures in 10 wt% NaCl brine, it is clear that pure Ammoeng 102 is better than a mixture containing Triton X 100 only for surfactant to IL mass ratio of 3 : 1 or higher and at temperatures higher than 60 °C (Fig. 6). However, close to the reservoir temperature Ammoeng is as effective as 1 : 3 surfactant to IL mass ratio. The cloud point temperature increased with the increase of the IL to surfactant ratio, which enabled measurement of more IFT values. To study the effect of brine on the behavior of IL/surfactant mixture we measured the IFT values for 2,000 ppm total concentration mixtures in deionized water (Fig. 7). The IFT values in 10 wt% NaCl brine are less than the corresponding values in deionized water at the same conditions. However, the cloud point temperatures in deionized water are higher than the corresponding values in brine, which means that more data points can be measured.

**CONCLUSIONS**

A special type of Ammoeng ILs was investigated for the potential use in surfactant EOR. The interfacial tension between a representative oil sample from Saudi reservoirs and solutions of different Ammoeng ILs at different concentrations in 10 wt% NaCl aqueous solutions was measured as a function of temperature. Some of the tested ILs gave very high IFT values, even at high concentration of the IL. Moreover, the measured IFT increased with the increase of temperature. In all cases, the IFT values decreased with the increase of IL concentration. Ammoeng 102 gave the least IFT values, which decreased with the increase of temperature.

IFT values for solutions of a commercially available surfactant, namely TritonX100 with the same oil sample, were measured as a function of temperature and surfactant concentration and compared to values obtained using Ammoeng 102. The comparison showed that the IFT values when using the IL were smaller than the corresponding values for the surfactant at the same conditions. Also, the IFT values for all used chemicals in 10 wt% NaCl brine were

of the total concentration. For example, at 40 °C the IFT equals 10.6, 7.6, and 3.3 for surfactant to IL mass ratio of 1 : 1 and total concentration of 100, 200, and 2,000 ppm in 10 wt% NaCl brine, (Figs. 4-6). It can be also noted that the IFT of the mixture increases with the increase of temperature for a certain value of the ratio of Triton
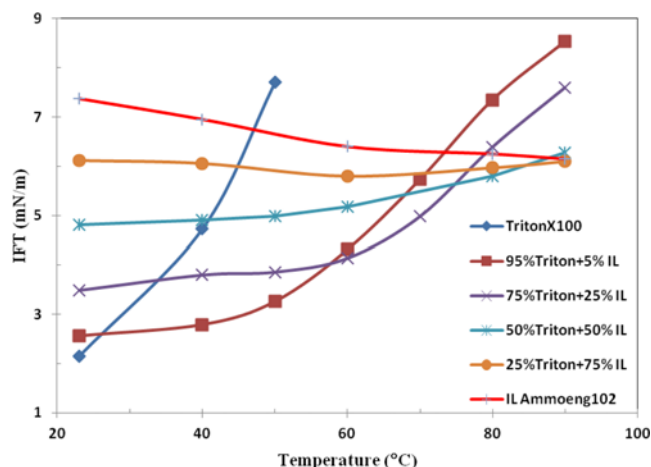
less than those in deionized water under the same conditions.

The possibility of having a synergetic effect when using a mixture of Ammoeng 102 and Triton X 100 was investigated. The results showed that the IFT values depended on the total concentration, the surfactant to IL mass ratio, and the temperature. At the reservoir temperature solutions of Ammoeng 102 in brine gave the best results.

Enhanced oil recovery depends on the contact of three phases, namely, oil, aqueous solution, and rocks. Flooding experiments using the tested ILs must be done to determine the possibility of using these ILs in surfactant EOR.

## ACKNOWLEDGEMENTS

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