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Non-Aqueous Emulsions Stabilised by Nonionic Nonyl Phenol Ethoxylate Reactive Polymerisable Surfactants

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A new series of nonionic polymerisable nonyl phenol ethoxylates (NPEs) has been prepared as organic solvent-soluble surfactants in which straight, branched and cyclic alkyls and phenyl acted as solvophilic segment and polyoxyethylene, or maleate chains as solvophobic segment. The new bifunctional reactive surfactants were prepared by reacting polyoxyethylene 4-nonyl -2-propylene-phenol nonionic reactive surfactant with maleic anhydride followed by esterification with poly (ethylene) glycol. The chemical structure of the prepared surfactants was determined by ^{13}C and ^{1}H NMR analyses. Surface activities of these surfactants in organic solvents including formamide, toluene and aqueous water solvent were determined by surface tension measurement. The results showed that these polymerisable NPE surfactants can reduce the surface tension of both polar and non-polar organic solvents. Stable non-aqueous emulsions of formamide/toluene system was prepared and exhibited excellent stability against coalescence for more than 6 months when stabilised by the modified surfactants. The initial location of the newly prepared reactive surfactants plays a crucial role in determining the type, stability and catastrophic phase inversion point of the resulted oil-in-oil emulsions. Correlation between the stability and the preferred emulsion type with the surface properties of the newly prepared reactive surfactants was addressed.

Keywords: non-aqueous emulsion, surface activity, organic solvent, nonyl phenol ethoxylates, polymerisable surfactants.

1. INTRODUCTION

Emulsions are among the most important classes of colloid science not only from an industrial point of view, but also of great interest in academia [1,2]. They are predominant in foods, cosmetics, pharmaceutics and petroleum production. However, the majority of studies on emulsion systems have been limited to systems containing water and oil, with almost few exceptions [3-6]. A departure from traditional methods and concepts of emulsion technology has resulted in the development of a family of non-aqueous emulsions which possess a variety of interesting and unique properties. Emulsions with no aqueous phase, so-called anhydrous or oil-in-oil emulsions can also be prepared where the selection of the phases depends largely on the polarity of the solvents. Non-aqueous emulsions could provide a promising alternative to conventional aqueous emulsions wherever the presence of water is undesirable; for example, in cleaning systems that are sensitive to formation of corrosion products and other mechanical systems. For such emulsions, it was shown that tailor-made block copolymers are by far the most efficient stabilisers compared to low molecular weight surfactants [6]. Polymerisable non-aqueous emulsions are of interest as nanoreactor systems for the polymerisation of water-sensitive monomers or catalysts. For surfactant-stabilised systems, the major challenge for preparing stable non-aqueous emulsions was to find a suitable stabiliser which is selectively soluble in either of the immiscible oil phases. This required a design of special stabiliser, mostly block copolymers, for each couple of oils [4]. Another strategy was to find a suitable solvent that can replace water and stabilise the system in a similar way utilised in aqueous systems with conventional surfactants. Nonionic surfactants based on the alkyl-aryl phenol ethoxylate type find wide different applications as, for example, emulsifiers, dispersants and foam controlling additives [7-10]. The main reason for their varied applications is that it is possible to control the hydrophobic-hydrophilic balance, and hence interfacial characteristics of such materials, by producing varying lengths of polyethylene oxide chains on a given hydrophobe (e.g. nonyl phenol). Their outstanding chemical and thermal stability expands their applications as emulsifier to extreme conditions which are too severe for other hydrocarbon surfactants [10]. However, they can also have adverse effects on latex properties. The non-polymerisable surfactants adsorbed onto the surfaces of the latexes may desorbed, resulting in latex destabilization when subjected to freeze and thaw cycles, applied shear stress, or high levels of electrolyte. Moreover, the presence of adsorbed surfactants in film-forming polymers can confer water sensitivity on the film which is a drawback for protective coatings and corrosion inhibitors. Using polymerisable surfactants can overcome such a drawback where they can be copolymerised with the main monomer and become covalently bound to form an integral polymeric material. Consequently, desorption of these surfactants from the polymer particles or migration in the polymer film is impeded. Such improvements of latex and polymer properties have been reported for high mechanical stability [11**],** electrolyte stability of the latex [12**],** control of surface charge density [13**],** and a decrease of surfactant migration [14**].** Nonyl phenol ethoxylates, NPEOs, surfactants are essential for emulsification of monomer droplets, fast nucleation of latex particles, and stabilization of latex particles during the course of polymerization and storage **[**15**]**. Alternative surfactants developed to replace NPEOs for emulsion polymerization have been proposed and tested by Fernandez et al. [16]. We present here a method for synthesis of reactive polymerisable NPEOs as organic solvent-soluble surfactants in which straight, branched and cyclic alkyls and phenyl acted as solvophilic segment and single or double chains as solvophobic segment. Surface activities of these surfactants in organic solvents were determined by surface tension measurement. We explore the use of these reactive surfactants in stabilisation of non-aqueous emulsions for potential new applications.

2. EXPERIMENTAL

2.1. Materials

Noigen RN-10 and Noigen RN-20 (polyoxyethylene 4-nonyl -2-propylene-phenol) nonionic reactive surfactant (Daichi Kogyo Seiyaku of Japan manufacture; Montello, distributor) were used as received. Poly(ethylene glycol) having molecular weight 400 (PEG 400), P-toluene sulfonic acid (PTSA), maleic anhydride (MA), toluene (T), formamide (FA), xylene chloroform were purchased from Aldrich and used as received.

2.2. Preparation polyoxyethylene 4-nonyl -2-propyl-phenyl maleic anhydride adducts

Maleic anhydride (2 mol) was reacted with Noigen RN-10 or Noigen RN-20 (1 mol) in the presence of hydroquinone (0.02 g) Noigen RN-10 at 180°C in a nitrogen atmosphere for 24h. The mixture was then poured into chloroform and carefully washed with water (5x50 mL) to remove the unreacted maleic anhydride. The chloroform was evaporated in vacuum, and the reaction yield 94% was obtained as brown oil. The reaction products between MA and Noigen RN-10 or Noigen RN-20 designated as Noigen RN-10-MA and Noigen RN-20-MA, respectively.

2.3. Preparation polyoxyethylene 4-nonyl -2-propyl-phenyl maleate ester

A mixture of freshly distilled PEG 400 (3 mols), Noigen RN-10-MA or Noigen RN-20-MA (1 mol), PTSA (1%) based on total weight of reactants and 100 ml xylene were placed in 0.5 L round-flask fitted with Dean Stark apparatus. The mixture was allowed to heat until the theoretical water was collected through azotropic condensation. Xylene was distilled off from the reaction product by rotary evaporator under reduced pressure. The product was separated by salting out use hot saturated NaCl aqueous solution and extracted with isopropanol using separating funnel. The purified products were isolated after evaporation of isopropanol. The reaction products between PEG 400 and Noigen RN-10-MA and Noigen RN-20-MA designated as Noigen RN-10-MA-PEG 400 and Noigen RN-20-MA-PEG400, respectively.

2.4. Characterization of the prepared surfactants

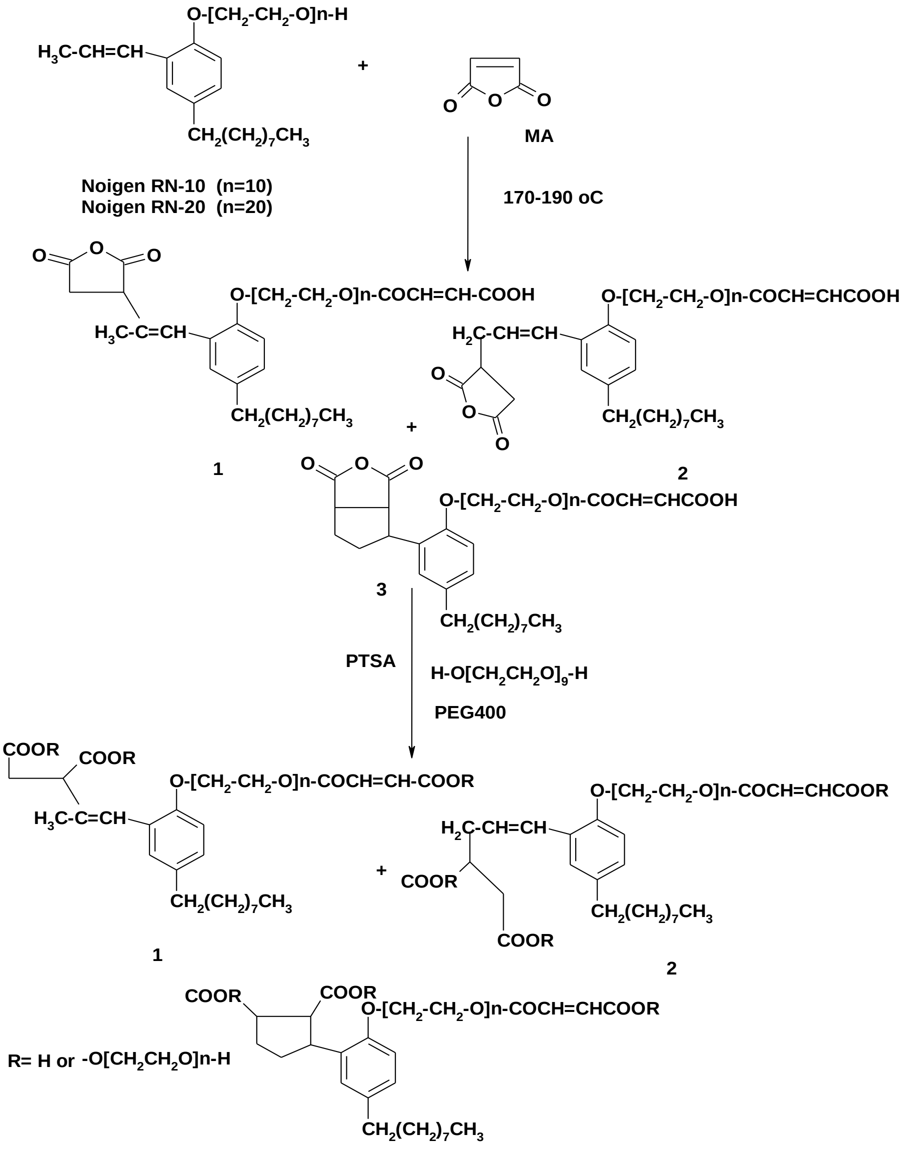
^{1}H-NMR spectra of the prepared polymers were recorded on a 400MHz Bruker Avance DRX-400 spectrometer. The surface tension measurements of the prepared surfactants in water, toluene and formamide were carried out at different molar concentrations and different temperatures (298, 308, 318, and 328 K) by using a ring platinum Kruss K-10 tensiometer (Germany). The surfactants solutions were thermostated in closed cell and measured at high temperature for 3 minutes.

2.5. Non-aqueous emulsion preparation

Simple o/o emulsions were prepared by dissolving a known mass of the liquid reactive surfactant into one liquid which we expect to be the continuous phase of the formed emulsion. The second oil phase was added with the desired volume fraction to the surfactant solution. Note that the surfactant mass is based on the oil in which they dissolve in while the phase volume fraction is based on the total volume of the system. The mixture was then homogenised using a DI-25 basic Yellow-line, IKA (Germany) homogeniser (rotor-stator) with an 18 mm head operating at 13,000 rpm for 2-3 minutes. The emulsion continuous phase was determined by measurement by observation of what happened when a drop of emulsion was added to a volume of each of the pure liquid phases. The emulsions only dispersed in the liquid when its continuous phase matched the liquid to which it was added. Emulsion stabilities against coalescence were monitored by recording the height of any free oil released from the emulsion with time. Emulsions were mounted on a glass slide (Matsunami Glass Ind., Ltd.) and examined by using an optical microscope (BX53, Olympus) equipped with a digital camera (XD200, Flovel Co., Ltd.). The size of the emulsion was determined by calculating the average diameter of 50 droplets. All emulsion were stored at room temperature to monitor their stability with time. The creaming and coalescence stability of o/o emulsions at different conditions was assessed by monitoring the increase with time the position of the clear oil/emulsion interface. Conductivity of emulsions was measured using Accumet Basic AB30 conductivity meter (Fisher Scientific, UK).

3. RESULTS AND DISCUSSION

Recently polymerisable surfactants play important role in colloidal chemistry of polymer latex, formation of aqueous and non-aqueous emulsions [17-21]**.** The polymerisable surfactant molecules should contain vinyl, acrylate, methacrylate and maleate groups as polymerisable moieties. The surfactants contain the polymerisable group either at the hydrophobic tail (T-type) or at the hydrophilic head group (H-type) and form micellar structures in aqueous and non-aqueous solutions. There are different types of polymerisable surfactants were used in aqueous emulsion, miniemulsion and dispersion polymerization to produce polymer latex having superior properties [22-25]. Regular miniemulsion can be defined as aqueous dispersions of surfactant stabilized oil droplets within a size range 50-500 nm prepared by shearing a system containing oil, water, a surfactant, and a strong hydrophobe [22]. It was shown that the hydrophobe acts as an osmotic agent which stabilizes the system against Ostwald ripening. The growth of the droplets by collision is controlled by the density of the surfactant layer: freshly prepared miniemulsions are “critically stabilized” and show a slow, but pronounced, growth whereas a miniemulsion in equilibrium exhibit constant particle size on longer time scales. Up to date, polymerisation reactions in miniemulsion processes are exclusively based on water as the dispersion media. The use of other, organic, but polar, dispersion media is reported [25]. Recently, diblock or triblock copolymers based on poly (ethylene oxide), poly (propylene oxide), poly(ethylene-*co*-butylene), polystyrene, poly(isoprene), polymethylmethacrylate and poly(ethylene glycol) were used to prepare non-aqueous emulsions [6,26,27]. In the present paper our aims were directed to prepare new polymerisable surfactants based on nonionic NPEO surfactants having different hydrophile-lipophile balance (HLB) to apply as emulsifier for non-aqueous systems. In this respect, we attempted to introduce the carboxylic acid group (or anhydride groups) into the oxyethylene chain end of polymerisable APEs to increase the functionality and polymerisable bonds and to increase the surface activity of these compounds. In this respect, we selected Noigen RN-10(20) (polyoxyethylene 4-nonyl -2-propylene -phenol) as nonionic reactive surfactants to modify its chemical structure with MA to produce maleate ester and adducts. The scheme of reaction was illustrated in the Scheme 1.



Scheme 1. Synthesis of Noigen-MA-PEG surfactants.

There are three different adducts proposed to form during reaction of MA with Noigen. The reaction between MA and terminated vinyl or propylene polymers produced succinate terminated polymers according Alder-ene reaction, which is generally promoted by a Lewis acid [28]. The reaction can be conducted in the presence of a radical quencher [i.e., hydroquinone, p-cresol, or 2,6-di-tertbutyl- 4-methylphenol (DTBMP)] without using a Lewis catalyst and found that the addition of MA is highly effective for achieving a high selectivity reaction in order to yield succinate functionalized polymers (selectivity 97%) [29]. The polymerisation inhibitor hydroquinone in addition reaction examined is highly recommended, because of the polymerization of propylene C=C double bonds. In the present work the reaction between Noigen and MA was carried out in the presence of hydroquinone to produce Noigen adducts 1 and 2 (scheme 1). Adduct 3 can be formed according to 1, 3-hydrogen shift mechanism [30, 31]. The reaction can be completed by the ene cyclo-addition reaction at high temperatures or by a hydrogen abstraction reaction on the α-CH_2 [32, 33]. The radical addition reaction yielded products that have many complicated structures and the large portion of the products become insoluble. However, in the present system the products were soluble in organic solvents and the insoluble product was not obtained. The reactions products of Noigen-MA adduct were reacted with PEG-400 to produce Noigen-MA-PEG polymeric surfactants as illustrated in the experimental section and scheme 1.

The molecular structures of the polymerisable Noigen, Noigen- MA and Noigen MA-PEG surfactants were confirmed by ^{1}H and ^{13}C NMR spectroscopy. In this respect, Noigen RN-20-MA-PEG400 were represented in Figures 1,2. Assignments of the various chemical shift peaks were made based on the labeling of the structure shown in Scheme 1. It can be noticed that the main Noigen RN-20 structure remains in the product spectra; also, the disappearance of conjugated –CH=CH- (propylene group) peak at 6.1 ppm from spectra of Noigen RN-10 - MA and appearance of new peak at 4.6 ppm (isolated $H_2C=C$ bond) indicated the formation of adduct 1. On the other hand, the disappearances of peak at 0.71 ppm (CH_3 of propylene group) indicated the formation of adduct 3. It can be noticed that the main Noigen RN-10 structure remains in the product spectra; also, the methylene triplet peak at 4.04 ppm due to - CH_2OCO attached to ester group also, -COOH moiety can be detected in both Noigen RN-10-MA and Noigen RN-20-MA spectra at 11.72 ppm. Since the hydroxyl terminal group appeared at 3.02 ppm of Noigen RN-10 is consumed during the reaction, the methylene triplet peak at 3.65 – 3.72 ppm due to -OCH_2CH_2O- is shifted downfield. It was also determined that, and Noigen RN-20-MA spectra, Figure 1, proton resonance signals characteristic to maleic acid derivatives were observed at chemical shifts $\delta = 6.3\pm0.6$ ppm, and signals of protons adjacent to oxygen atoms were shifted downfield by $\Delta\delta = 0.4\pm0.6$ ppm after acylation. The integrations of the most important peaks for Noigen RN-10, Noigen RN-10-MA and Noigen RN-20-MA were determined and the data indicated that the formation of adduct 3. In this respect, it was found that the disappearance of OH end group peak (F peak) at 3.05 ppm (integration area 2.1) and appearance of new peak (L- peak) at 11.6-11.72 ppm (integration area 5.8) for Noigen RN-10-MA indicated that the integration ratio between OH and COOH group is 1: 3. The data indicated that the one OH group was replaced with three carboxylic groups and elucidated the formation of both ester and adduct end group. The formation of Noigen-MA-PEG was confirmed from their spectra (Figures 1**).** The spectra indicated the disappearance of COOH moiety at 11.72 ppm and formation of the methylene triplet peak ester at 3.9 ppm. Integrals of individual ^{1}H NMR signals were successfully used to evaluate the purity of the surfmers, and isolated surfmers usually contained less than 2% of by-products. Another route to determine the chemical structures of the modified polymerisable surfactants was based on ^{13}CNMR data (Figure 2). The data of Noigen – MA-PEG 400 indicated the appearance of peaks at 20, 26.2, 45.6 and 172.2 which proved the formation of esters group among Noigen, MA and PEG 400 as illustrated in Scheme 1.

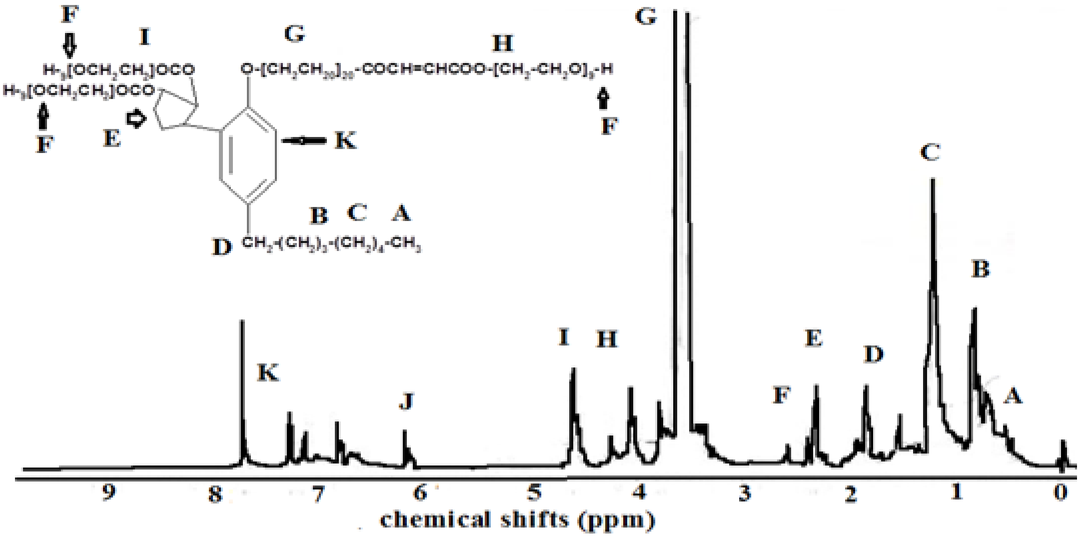


Figure 1. ^{1}HNMR spectrum of Noigen RN-20-MA-PEG400.

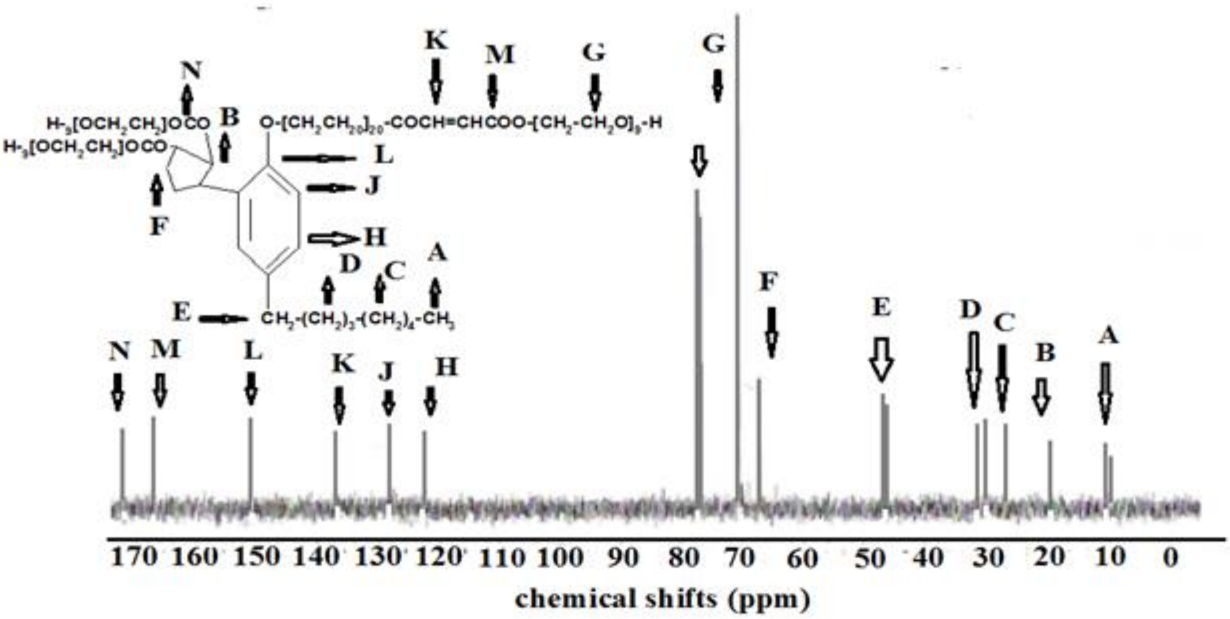


Figure 2. ^{13}CNMR spectra of Noigen RN-20-MA-PEG400.

3.1. Surface activity and solubility of surfactants in organic solvent

The nature of the traditional surfactants is based on the chemical antipathy of the surfactant tail and head, and on their opposite sympathy for water molecules as a solvent. Information about relative size, configuration, degree of association and stability of the aggregates is required if these surfactants are to be used in industrial applications. Surfactant solutions in different organic solvents show that not only the surface adsorption of the surfactants at the interfaces but also the presence of aggregates depends on the surfactant structure, particularly on the relative size of the hydrophobic and polar moieties [34]. Surfactant molecules which dissolve in organic solvent are generally contained both a solvophobic group and a solvophilic group in the same molecule. The hydrocarbon alkyl or phenyl tail, hydrophobic in water, may be the solvophilic group providing solubility in organic solvents. The surfactants are expected to adsorb at the organic solvent/air surface to form a monolayer in which the solvophobic segment of the surfactant tilts away from the surface. In the present system, the modification of Noigen RN-10 and Noigen RN-20 with MA and PEG yields different hydrophobicity, hydrophilicity, chain flexibility and solubility due to the difference of inter- and intramolecular interactions with water or organic solvents. The distortion of the solvent structure can also be decreased (and the free energy of the solution reduced) by aggregation of the surface-active molecules into clusters (micelles) while their hydrophilic or hydrophobic groups are directed towards the polar and nonpolar solvents, respectively. Micellization and aggregation are therefore an alternative mechanism for adsorption of the surfactant at the interfaces for removing the lipophobic groups from contact with the solvent, thereby reducing the free energy of the system. The micellization, aggregation and adsorption of surfactants are based on the critical micelle and critical aggregation concentrations (cmc or cac), which were determined by the surface balance method. The cmc and cac values of the prepared polymerisable surfactants were determined in water, hexane and formamide at 298, 308, 318 and 328K from the change in the slope of the plotted data of surface tension (γ) *versus* the solute concentration (ln C). The obtained data is summarized in Table 1. The main difference between these data and that for common surfactants in aqueous solutions is that the initial surface tensions of the pure organic solvents are much lower than that of pure water. Surface activity results (cmc, cac, γ_{cmc} and γ_{cac}) of each modified Noigen surfactants in saturated solutions of various solvents are presented in Tables 1. It is evident that the cac values increase and then decrease with an increase of polarity of organic solvents, which agrees with the idea that excessive solubility increases the concentration to obtain minimum surface tension.

The effectiveness of the surfactants was expressed by the maximum reduction of surface tension of the organic solvents which calculated from the equation, $\Delta\gamma = \gamma_{solvent} - \gamma_{solution}$; where $\gamma_{solvent}$ is the surface tension of pure solvent, and $\gamma_{solution}$ is the surface tension of the saturated solution (γ_{cmc} and γ_{cac}). The $\Delta\gamma$ values of the prepared surfactants were determined in water, formamide and hexane and listed in Tables 1**.** The data indicated that the Noigen surfactants are not as effective in organic solvents to reduce the surface tension as in water because of the initial surface tension of organic solvents, 19–43 mN/m for most of hydrocarbon solvents, is much lower than that of pure water (72.2 mN/m, 25 ^{o}C). Careful inspection of data indicated that there is a close relationship between the structure of the solvophobic and solvophilic constituents of surfactant molecules, the property of organic solvents (miscibility, salvation power, polarity) and the surface activity of surfactants. It was observed that the Noigen-RN20 surfactants reduced the surface tension of both water and organic solvent more than modified Noigen RN-10 at lower concentrations.

Table 1. Surface properties of the prepared surfactants based on Noigen RN-20 at different temperatures.

designation	Theoretical Molecular Weights (mol/L)	Temp. (K)	cac mol/L		cmc mol/L $*10^4$	γ_{cac} mN/m		γ_{cmc} mN/m	$\Delta\gamma$ mN/m		
			FA $*10^4$	T		FA	T		water	FA	T
NOIGEN RN-20	1140	298	0.9	0.35	0.88	44.2	26.1	38.6	33.6	14.0	2.1
		308	0.6	0.22	0.65	43.1	25.2	37.7	33.4	14.7	2.7
		318	0.3	0.18	0.43	42.2	24.7	36.8	31.7	15.0	2.8
		328	0.08	0.12	0.21	40.3	23.1	35.7	31.8	16.5	4.1
Noigen RN-20 -MA	1321	298	0.080	0.33	0.42	47.2	25.8	34.1	38.1	11.0	2.4
		308	0.050	0.22	0.21	43.1	24.1	33.2	37.9	14.7	4.1
		318	0.010	0.11	0.12	42.1	23.2	31.9	36.6	15.1	4.3
		328	0.009	0.08	0.07	41.2	22.1	31.1	36.1	15.6	5.1
Noigen RN-20 -MA-PEG400	2467	298	0.02	0.03	0.24	41.1	23.1	30.5	41.7	17.1	5.1
		308	0.01	0.02	0.10	40.3	22.3	28.2	42.9	17.5	5.6
		318	0.005	0.01	0.05	39.2	21.9	26.1	42.4	18.0	5.6
		328	0.001	0.005	0.03	38.1	21.1	24.3	42.9	18.7	6.1

The differences in surface activity of surfactants are based on the high adsorption of a high concentration of of modified Noigen RN-20-MA and Noigen RN-20-MA-PEG400 at the organic solvent/air interface. A possible explanation is that a maleic anhydride and PEG chain favor sufficient solubility, yet a long poly (oxyethylene) chain of modified Noigen RN-20 surfactants arranged in zigzag conformation is easier to bend than a short poly (oxyethylene) chain of modified Noigen RN-10. Because of the increasing steric hindrance between the bending long poly (oxyethylene) chains, a long poly (oxyethylene) chain may be unfavorable for high packing density of Noigen RN-20 chains at the interface. Moreover, long poly(oxyethylene) chains have the contribution to maximize the mutual immiscibility and incompatibility between the Noigen RN-20 chain and solvent, to promote Noigen RN-20 chain escaping from the bulk of organic solvent, and thus to increase adsorption. In general, the surface tension reduction depends mostly on the length of the solvophilic group of Noigen, which exhibits a great reduction when the length of the single poly(oxyethylene) is long enough. The data listed in Table 1 indicated that the high reduction in surface tension of toluene was obtained with Noigen RN-20-MA-PEG400. This can be attributed to the solubility of the surfactants is controlled by the structural similarity between the solvophobic portion of the solute molecule and the solvent molecules. The modification of Noigen -RN 20 with MA and PEG400 prevented the coiling of poly (oxyethylene) chains and increase the interaction between the phenyl ring of Noigen with toluene solvent, so it shows relatively higher surface activity. While the branching chain effect of Noigen RN-10-MA-PEG400 of the solvophilic segment which increases the steric hindrance between the surfactant molecules, leading to a lower density of surfactant chains at the organic solvent/air interface. This different ability in lowering the surface tension of organic solvents might be not only caused by insufficient solubility, but also due to the increased steric hindrance of poly(oxyethylene), phenyl and propyl, cyclopentyl groups in surfactant molecules as shown in scheme 1. It is believed that an increase of the solvophobic part in surfactant molecules may decrease the solubility and lead to closer packing at the solvent/air interface.

The relation between the efficiency of Noigen surfactants to reduce the surface tension ($\Delta\gamma$) of water, toluene and formamide and temperature of measurements were represented in Figures 3. The data indicated that the reduction in surface tension increased for toluene and formamide and decreased for water with increasing the temperature. On the other hand Noigen -RN20-MA-PEG 400 surfactants achieved good results in reduction of surface tension of water, toluene and formamide with increasing the temperature. These data indicated high surface activity of Noigen -RN20-MA-PEG 400 surfactant. This can be attributed to the increase in the radius of gyration of the surfactant molecule and interaction between solvophilic part of surfactants and solvents result of increasing the temperature [35-37]. The data indicated that Noigen surfactants reduced the surface tension of solvents in the order water>formamide>toluene. According to the literature, aggregation behavior of surfactants in non-polar solvents, such as toluene, is a consequence of dipole–dipole and ion interactions between the surfactant molecules [38]. As no hydrophobic interaction should be expected, only enthalpy effects should then be the main contribution to aggregation of the surfactant molecules. Consequently, these effects could arise from the formation of inter- or intramolecular hydrogen bonds between the hydrogen of the terminal -OH group and the oxygen on any of the ethoxylate groups, either from the same molecule or from a neighboring one.

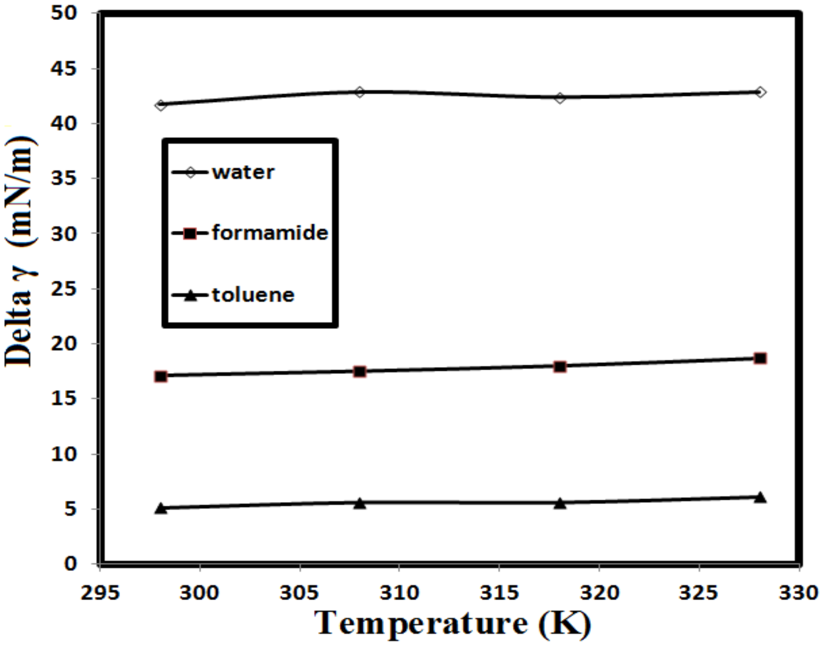


Figure 3. Relation between reduction of surface tension and temperature for Noigen RN-20-MA-PEG400.

Therefore, it is the length of the central and terminal ethoxylate groups that must be taken as the actual length of the surfactant molecule. Consequently, the remaining part of the molecule fills the space between Noigen surfactant monomers, forming a compact aggregate which completely excludes solvent [39]. This process can prevented toluene to penetrate into the inner surfactant core and decrease the surface activity of the modified Noigen surfactants in nonpolar toluene solvent.

3.2. Fabrication of non-aqueous emulsions using Noigen RN-20-MA- PEG400 surfactant

We have explored the possibility of stabilising formamide-toluene non-aqueous emulsion system using the synthesized Noigen RN-10-MA- PEG400 and Noigen RN-20-MA- PEG400 polymerisable surfactants. We have shown in previous study that modified Noigen RN-10 and RN20 polymerisable surfactants can stabilise water based simple oil/water emulsions [40].

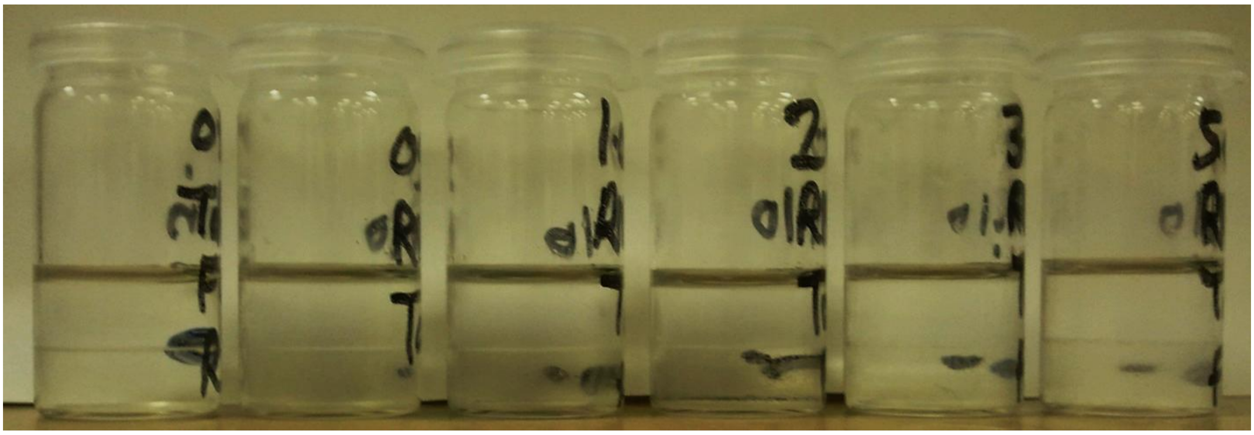


Figure 4. Digital image for toluene-formamide system stabilised with different concentrations of parent Noigen RN20 without modification (from left to right, 0.1, 0.2, 0.3 0.5, 1 and 3 wt.%). Image taken after 10 minutes from homogenisation.

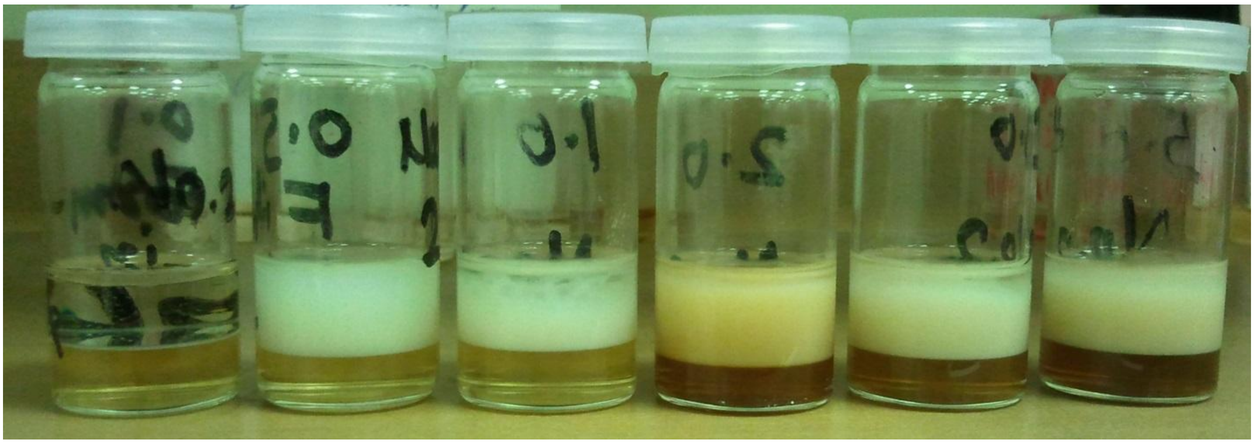


Figure 5. Digital image for toluene-formamide system stabilised with different concentrations of Noigen RN-10-MA- PEG400 (from left to right, 0.1, 0.2, 0.3 0.5, 1 and 3 wt.%). Image taken after 1 month from homogenisation.

Polymerisation in non-aqueous microemulsions was studied in a system containing formamide, the anionic surfactant AOT (bis(2-ethyl-hexyl) sulfosuccinate sodium salt), sodium bromide and either of the monomers hexyl methacrylate or styrene at 60°C [41]. It was reported that non-aqueous emulsions of different oils can be stabilised by a mixture of unmodified Noigen RN10 and clay nanoparticles where the addition of the solid clay improved the emulsion stability [42]. Moreover, non-aqueous simple and multiple emulsions were successfully stabilised by only surface modified silica nanoparticles without any surfactants [43]. In the current study, we have performed preliminary experiments to investigate the ability of the parent unmodified reactive surfactant Noigen RN10 and RN20 to stabilise the formamide-toluene emulsions. Using either surfactants at 0.1-3 wt.% in formamide and 50:50 vol.% of the oil phases did not give any stable emulsions and a complete phase separation was observed within 10 minutes of homogenisation the mixture at high shear power.

This means that the unmodified Noigen RN10 or RN20 surfactants did not adsorb at the oil-oil interface due to their low surface activity. Figure 4 shows a digital image for the resulted system where the two phases are completely separated. Using the modified surfactant Noigen RN-10-MA- PEG400 with the same oils shown above, the emulsions were formed but with less stability against coalescence over the time. Figure 5 represents the physical shape of the obtained equal volume toluene-in-formamide emulsions after stabilisation with 0.1-3 wt.% of Noigen RN-10-MA- PEG400 dissolved in formamide. It transpires that modification of the parent Noigen RN10 reactive surfactant has a remarkable effect of its surface activity in the oils used in the emulsions which is in a good agreement with the results obtained and discussed above.

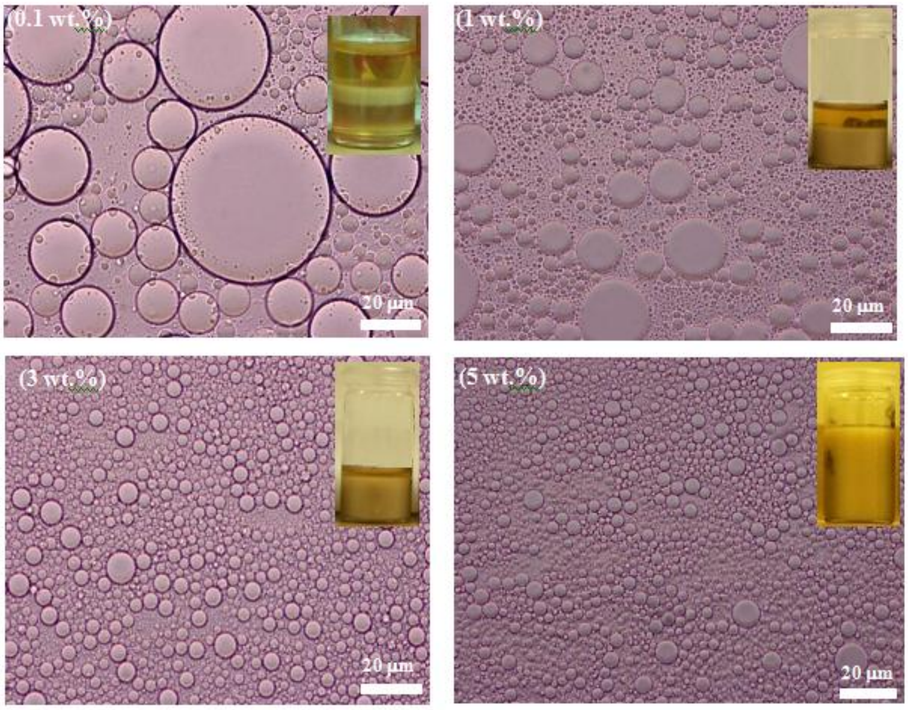


Figure 6. Optical images for equal volumes formamide-in-toluene emulsions as a function of Noigen RN-20-MA- PEG400 concentrations in (wt.%) given, initially added to toluene. The insets digital images are for the corresponding shape of the resulted emulsions.

We explore further the ability of the other newly prepared surfactant Noigen RN-20-MA-PEG400 in stabilising the formamide-toluene emulsion system at different concentrations. Figure 6 shows the change in shape and droplet sizes of equal volumes of formamide-in-toluene emulsions stabilised by 0.1, 1, 3 and 5 wt.5 of Noigen RN-20-MA- PEG400 initially dissolved in toluene. The resulted emulsion type was formamide-in-toluene (fa/tol) as inferred from the drop test method. As mentioned above, we expected from our findings that this surfactant will have the highest interfacial activity when it is dissolved in toluene rather than formamide. As can be seen in figure 6 the size of formamide drops is remarkably reduced (from ~50 μm to ~ 3 μm) upon increasing the surfactant concentration indicative of the excellent ability of this surfactant to partition at the formamide-toluene interface. It is also clear that the stability of the resulted emulsions against coalescence and sedimentation was greatly enhanced by increasing the concentration of the surfactant in the system (see the shape of emulsions in the insets of Figure 6).

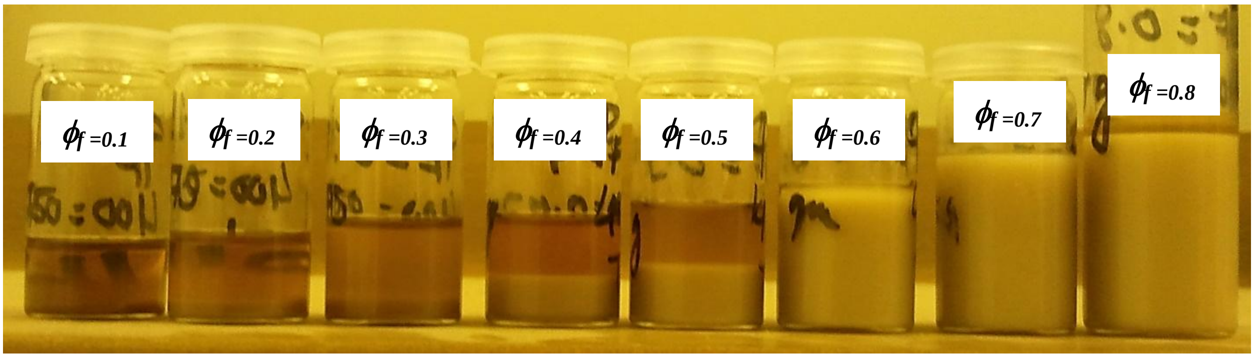


Figure 7. Formamide in toluene emulsion as a function of ϕ_f (given). Emulsions were stabilised by fixed concentration of Noigen RN-10-MA- PEG400 at 3 wt.% in toluene.

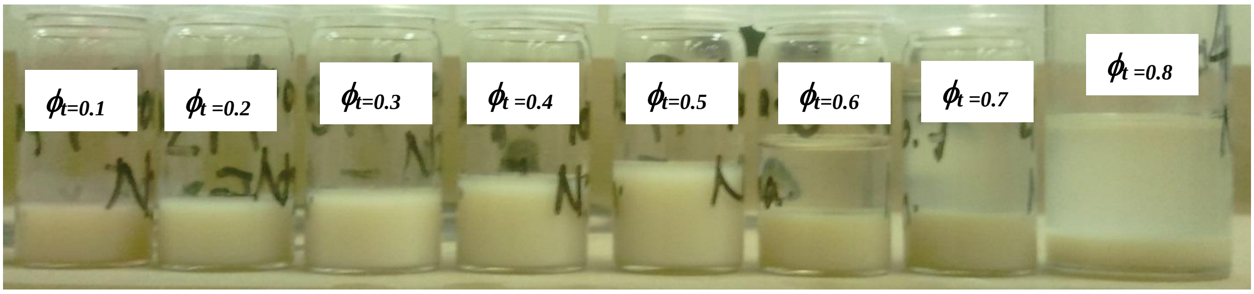


Figure 8. Toluene in formamide emulsion as a function of ϕ_t (given). Emulsions were stabilised by fixed concentration of Noigen RN-10-MA- PEG400 at 3 wt.% in formamide.

Catastrophic phase inversion of emulsions, from w/o to o/w or vice versa, can be achieved in surfactant-stabilised systems by changing the oil/water volume ratio. It has been argued that this type of conversion, known as catastrophic inversion, only occurs in emulsions containing surfactant and co-surfactant and is accompanied by dramatic changes in properties of the emulsions, including viscosity and drop size [1].

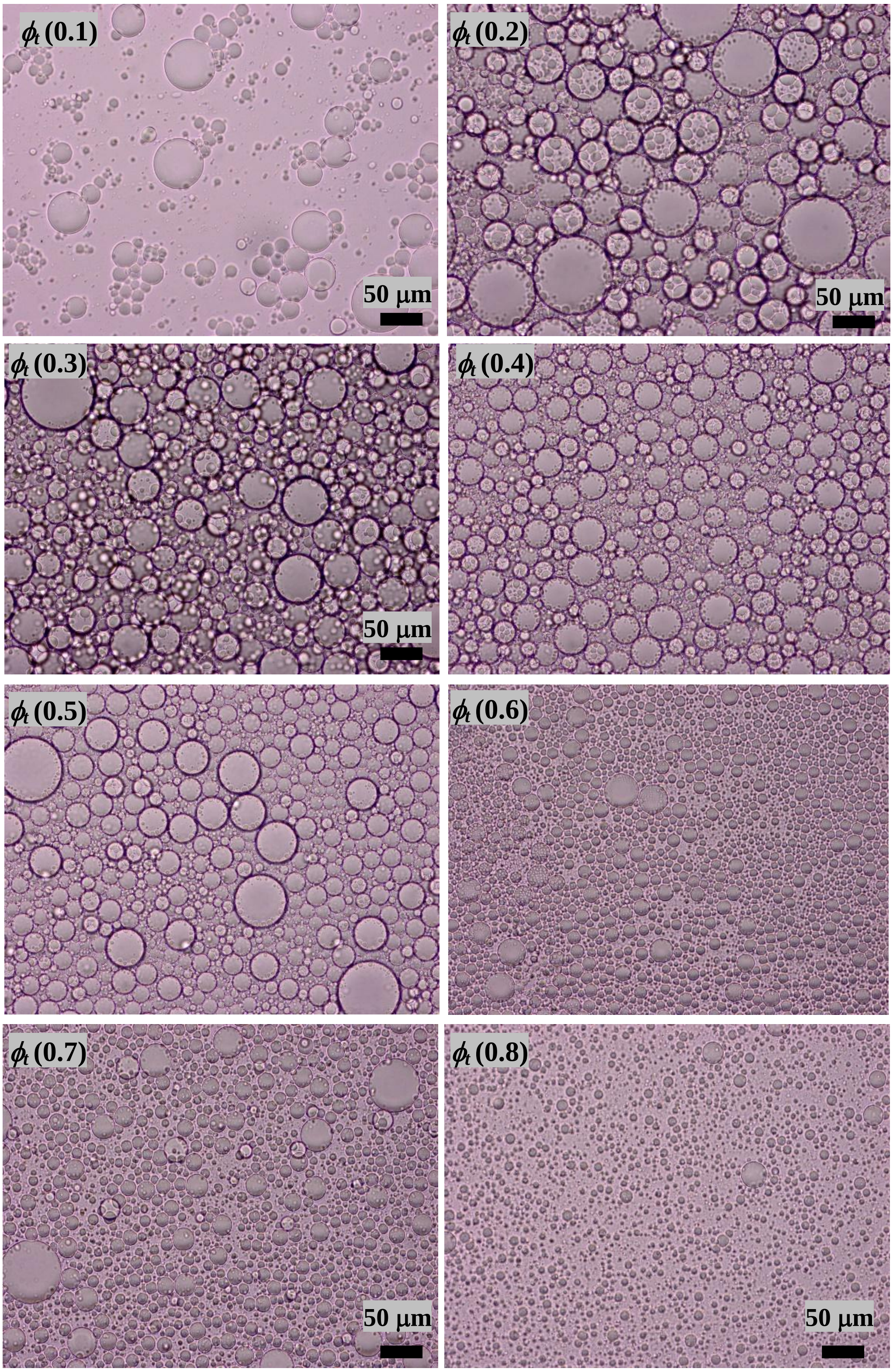


Figure 9. Evolution of equal volumes formamide-in-toluene emulsion drops sizes as a function of volume fraction of formamide (ϕ_f). Emulsions were stabilised by 3 wt.% Noigen RN-20-MA-PEG400 surfactant dissolved in toluene.

It is believed that the spontaneous curvature of the mixed surfactant-co-surfactant layer around drops changes with the oil/ water ratio due to a change in the composition of the layer after partitioning between bulk phases is complete. One emulsion type is then favoured over the other as the volume fraction of, say, water (ϕ_w) is increased. In emulsions stabilised by only one pure surfactant, inversion does not occur; instead high internal phase gel emulsions form upon increasing the volume fraction of dispersed phase. According to our knowledge there is no comprehensive information about the phase inversion of non-aqueous oil/oil emulsions.

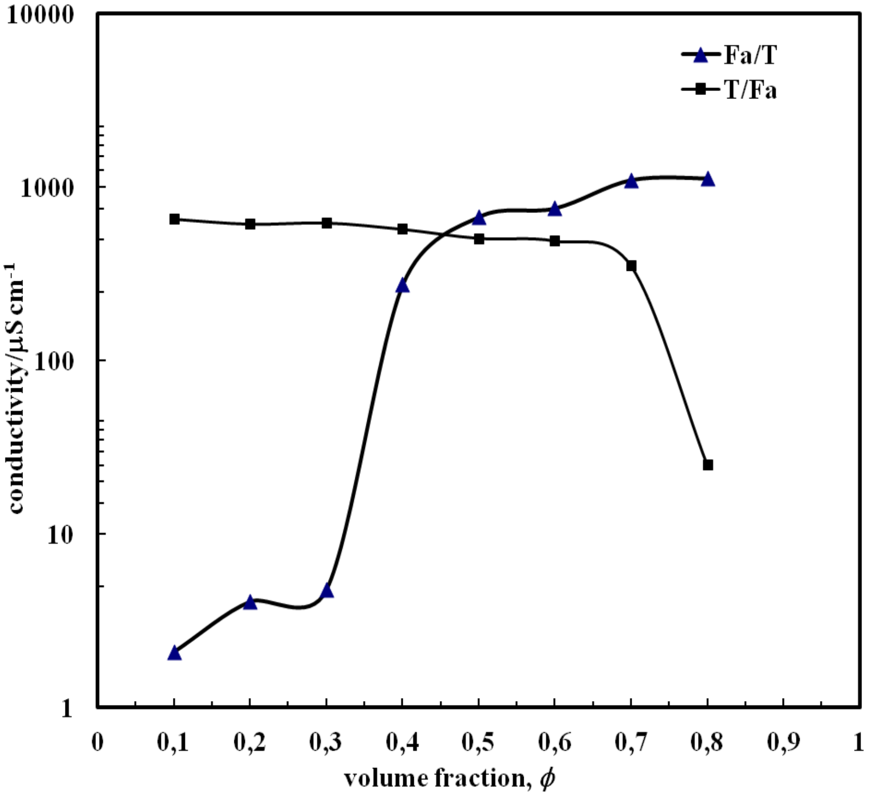


Figure 10. Conductivity of equal volumes formamide-toluene systems as a function of volume fraction of either formamide (ϕ_f) or toluene (ϕ_t). Emulsions were stabilised by 3 wt.% Noigen RN-20-MA- PEG400 surfactant dissolved initially in either toluene or formamide.

We have investigated the effect of volume fraction of formamide in emulsions stabilised by fixed concentration of Noigen RN-10-MA- PEG400 at 3 wt.% dissolved initially in toluene. The appearance of the resulted emulsions are shown in Figure 7 where the phase inversion did not occur in this emulsion. The only effect that we noticed is the increasing of the creaming stability of the emulsions by increasing the ϕ_f . Catastrophic phase inversion was observed for emulsions prepared with same concentration of Noigen RN-10-MA- PEG400 but dissolved in formamide and then altering the volume fraction of toluene (Figure 8). The emulsion has inverted from toluene-in-formamide (tol/fa) to formamide-in-toluene (fa/tol) between ϕ_t = 0.5 and 0.6. For the other surfactant Noigen RN-20-MA- PEG400, we have also achieved phase inversion only in formamide-in-toluene emulsions by changing the volume fraction of formamide as can be seen in Figures 9 and 10. The phase inversion point was between ϕ_f = 0.3 and 0.4 and the emulsion inverted from fa/tol to tol/fa. This results suggested that the preferred emulsions for such s system is tol/fa i.e, the surfactant prefer to dissolve initially in formamide to give the highest interfacial activity. Figure 9 represent the change in droplet sizes of the emulsions as a function of ϕ_t where it is clear that the size of the inverted tol/fa emulsions became smaller at $\phi_t > 0.5$ which gives a creaming stability to the emulsions after the phase inversion point. It was generally accepted that for water based emulsions systems with surfactants, the emulsions became less stable around the phase inversion point which did not happen in our oil/oil system with the modified surfactant. Figure 10 depicts the change in conductivity of the emulsions as a function of the volume fraction of either formamide or toluene with Noigen RN-20-MA- PEG400 surfactant. Conductivity can help determining the catastrophic phase inversion point where a sudden change in its value occurs. The conductivity of pure formamide is very high (~ 2500 μS cm^{-1}) while it is very low for pure toluene (< 1.0 μS cm^{-1}). For toluene-in-formamide emulsions shown in Figure 10, the conductivity remained unchanged up to volume fraction of toluene of 0.7 indicative that the preferred emulsion again is toluene-in-formamide.

4. CONCLUSIONS

A series of nonionic polymerisable NPE derivatives were designed and modified. These surfactants can reduce the surface tension organic polar solvent such as formamide and non-polar organic solvent such as toluene, exhibit surfactant properties in these solvents, and add new trend to use as emulsifier for organic non-aqueous solvents and their potential applications. It was found that the polymerisable surfactants based on NPEs have low efficiency to reduce the surface activity of toluene because of stronger incompatibility between the substituted solvophobic groups of the NPE surfactant and the toluene at interface. The modification of NPE surfactants with MA and PEG 400 can improve both solubility and surface activity of these surfactants in polar aqueous and organic solvent (formamide). Stable non-aqueous emulsions of formamide/toluene system was prepared and exhibited excellent stability against coalescence for more than 6 months when stabilised by Noigen RN-20-MA-PEG400 surfactant. The initial location of the newly prepared reactive surfactants plays a crucial role in determining the type, stability and catastrophic phase inversion point of the resulted oil-in-oil emulsions. The obtained stable non-aqueous emulsions, or their polymeric materials if one or both oils is a monomer, will open up interesting avenues of research particularly those applications that require the absence of water as coating, paints and anticorrosion areas.

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