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Microwave-assisted direct synthesis of boronated alkanolamine succinic anhydride esters as potential surfactants for various application

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ABSTRACT

A method of microwave assisted synthesis of a new surfactant family whose hydrophilic head is derived from the ethanolamine adduct of boric acid containing polar $–NR-B(OH)_2$, -O-B(OH)2, and $(OH)_3B \rightarrow NR$-. These compounds were synthesized in two steps. First the boric acid adduct was prepared by reacting ethylene diamine with boric acid and then the adduct was reacted with alkenyl succinic anhydride. The product with boronated alkanol amine showed good yields (>90%). Both reaction steps were carried out by microwave. Boron NMR suggests that probably Boron is mostly in $–O-B(OH)_2$ form (~80%), about 13% as $(OH)_3B \rightarrow NR-(CH_2)_2-O-B(OH)_2$, and approximately 7% in the form of $(OH)_2B-NR-[(CH_2)_2-OH]_2$. The product apparently exhibited good detergency. Parameters characterizing their surface activity (critical micelle concentration, surface tension, and molecular area at the water−air interface) was studied with the dodecenyl succinic anhydride derivative of the Boronated diethanolamine adduct. The compounds show promise for use in organized molecular systems. By altering the hydrocarbon chain length of alkenyl succinic anhydride, the derivatives can be either water or solvent soluble. Hexadecenyl succinic anhydride derivatives are highly oil-soluble, whereas the dodecenyl succinic acid anhydride derivative is primarily water soluble. Total B_2O_3 content in the product is approximately 12.4%. Besides their surface activity, this series of products have a great potential for treating wood for antifungal and anti-termite properties.

1. Introduction

Microwave technique has gone far from its original use of typical industrial drying, and food processing to more chemical applications from synthetic chemistry to analytical processes, including digestion, extraction of samples etc. As microwave irradiation expands its horizons and proves its utility as both a timesaving tool and a novel means to perform challenging transformations, it is becoming an increasingly important method of chemical synthesis in the industrial community. Microwave acceleration has proven to be a valuable tool for any synthetic chemist and will only continue to become more prevalent in the future [1].

In this paper the microwave assisted technique, a green methodology, for the direct esterification of alkenyl succinic anhydride with boronated alkanol amine adducts under solvent free conditions has been discussed. The scope of this method is already expanded for the use of several complex reactions involving aliphatic, aromatic, unsaturated and fatty acid derivatives. The reaction can also be applied to different primary and secondary amines.

This novel experimental method of synthesis was employed for the first time to synthesize borated surfactants for both aqueous and non-aqueous dispersions. This methodology can also be carried out with several other functionalized acids and amines, preferably primary amines.

The conventional condensation method for the esterification or amidation of alkenyl succinic anhydride (ASA) with secondary alkanol amines, di-ethanolamine

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(DEA) for example, generally takes several hours to complete. Moreover, using conventional means of synthesis it is very difficult to get diester or ester-amide forms of the product.

There has been a growing interest in new surfactants over the last few decades not only from a fundamental point of view but also for applications in chemical synthesis and elsewhere. These amphiphilic molecules decrease interactions at interfaces via their surface active properties, and they are classified as ionic, zwitterionic, or nonionic. For that matter the ASA based surfactants are well known in the industry for formulating of lubricants, dispersants for dyes, paper sizing, detergents, dispersion chemicals etc. The ASA based surfactants offer a great versatility to design surfactants for a wide range of solvent systems of varied Hydrophobic Lipophilic Balance (HLB). The two carboxyl groups in ASA allow an unusual amount of flexibility in designing anionic, non-ionic and zwitterionic surfactants. The versatility of such surfactants stems from ASA's ability to react with adducts of either lipophilic or hydrophilic nature, or both [2-7].

In the course of our studies on forming boronated alkanolamine and ASA condensation products, we envisaged a new family of surfactants with hydrophilic heads containing boron atoms. The boronated polar heads of these amphiphilic molecules were derived from the affinity of boron for amine and hydroxyl groups, which were then linked through the acidanhydride group of ASA comprising a long-chain alkenyl group to form an amphiphilic compound by condensation reaction.

The benefit of using microwave technique over the conventional method for the synthesis of such surfactants is to quicken the reaction rate under milder reaction conditions with expected higher yields. Those very specific effects that microwave offers cannot be easily matched using conventional methods [2,3].

We describe here the synthesis, characterization and surface active properties of the condensation reaction product of dodecenyl succinic anhydride and the adduct prepared from the reaction between DEA and Boric Acid (BA).

Boron NMR was used for identifying the most probable nature of Boron linkages in the surfactant molecules.

2. Materials and method

2.1. *Reagents*

Dodecenyl Succinic Anhydride (DDSA), Aldrich Chemicals, USA; Hexadecenyl Succinic Anhydride (HDSA), Dixie Chemicals, USA; Octadecenyl Succinic Anhydraide (ODSA), Milliken Chemicals, USA, and Diethanol Amine (DEA) Sigma-Aldrich, USA used for the experiment were of at least 90% active technical grade quality. Boric Acid powder (BA) of Etimine USA Inc. used for the preparation of adducts was of 99.9% purity. High purity Ethylenediamine (EDA) of Sigma Aldrich, USA was used NMR study.

2.2. *Apparatus*

For the present study a standard 0.9 kW microwave oven was equipped in-house to be able to handle a reaction volume of 500ml. ^{11}B NMR spectroscopy was performed at 21°C (room temperature) using a 300 MHz (300 DPX Bruker) spectrometer. A DuNouy tensiometer was used for the determination of surface tension at 25 ºC.

2.3. *Procedure*

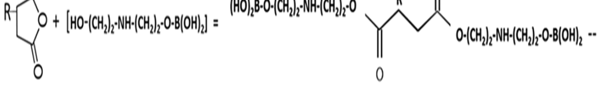
The experimental goal was to develop a microwave-assisted synthesis of a new series of boron containing surfactants of the present study that could be performed in a domestic microwave oven that was a faster, greener alternative to the traditional synthesis. The microwave oven used was suited for the esterification and amidation chemistry containing boron at a mini-scale rather than microscale level under solventless conditions that allowed the synthesis to take place involving green chemistry as well.

The reaction scheme used for the synthesis of the surfactants of the present series, the boronated alkanol amine esters of ASA, primarily involved two steps.

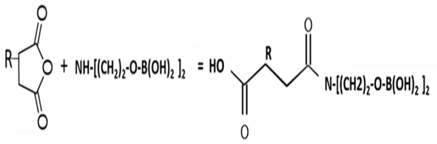
The first step of reaction was to form Boric Acid (BA) and diethanolamine (DEA) adduct by allowing them to react at 2:1 molar ratio. The reaction between BA and DEA offers many possibilities for the way BA can react with DEA.

$2B(OH)_3 + HN\text{-}[(CH_2)_2OH]_2 = (OH)_2B\text{-}N[(CH_2)_2OH)_2 + HN\text{-}[(CH_2)_2\text{-}O\text{-}B(OH)_2]_2 + (OH)_3B{\rightarrow}NH\text{-}(CH_2\text{-}CH_2\text{-}OH)_2 + (OH)_2B\text{-}(CH_2)_2\text{-}NH\text{-}(CH)_2\text{-}OH$ -------

The second step was to allow BA-DEA adduct thus formed to react with 0.5 molar quantity of ASA following a condensation reaction. Such reaction can also offer multiple possibilities the way BA-DEA adducts can combine with ASA under intimate microwave heating conditions. The most probable condensation reaction products that could possibly be formed under microwave assisted synthesis, are shown below:



(1)



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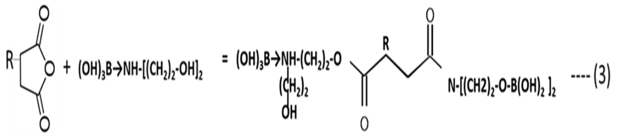

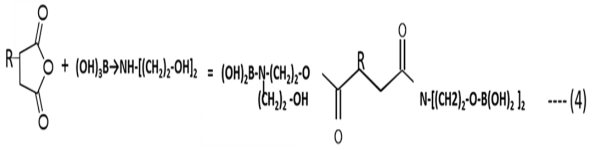

The same condition of synthesis was applied for the synthesis of DDSA, HDSA and ODSA derivatives of the DEA-BA adducts. The DDSA derivative appeared water dispersible whereas the HDSA and ODSA derivatives are more solvent soluble. In this communication all discussions are on the DDSA-DEA-BA product only as full characterization of HDSA and ODSA are still in progress.

In view of its Lewis acid nature, boric acid associates readily with the atom of oxygen and nitrogen of –(OH) and –(NR_2) groups where R being alkyl, alkanol, etc. The addition of BA into DEA is exothermic in nature. Using the Microwave setup the reaction between BA and DEA (at a 2:1 molar ratio) to prepare BA-DEA adduct under a solventless condition, was followed in a stepwise addition mode. For each addition of BA into DEA, the mixture was exposed to microwaves for approximately thirty seconds. It is to be noted, for microwave assisted reactions exposure of reactants under controlled heating conditions is always beneficial [8,9]. Upon completion of addition of BA, the mixture was further heated for another few minutes until the bubbling was visibly slowed down. The solventless preparation method is very tricky and difficult to handle. However, it is worth mentioning that a small addition of xylene or toluene is always helpful for the ease of transfer and handling, which can be distilled off at the end of the process. The BA-DEA adduct thus formed was allowed further to react with DDSA by mixing DDSA slowly into BA-DEA. The final molar composition between BA, DEA and DDSA was maintained at 4:2:1. The mixture was exposed to microwave heating for approximately 10 minutes to obtain mostly diester forms of DDSA as shown in equation (1). Due to the very sticky nature of the product, a small addition of xylene or toluene can always be useful as mentioned above. The average molecular weight of the final product was approximated as 350.

All solutions for the NMR studies were kept at pH 8.5.

3. Results and discussions

By conventional means, formation of diesters or amide-ester of alkenyl succinic anhydride does not happen easily with alkenyl succinic anhydride and DEA. Depending on the reaction conditions, they generally form mono esters, mono-amides or their mixtures. Under a solventless condition, the microwave assisted synthesis of ester derivatives of DDSA, HDSA or ODSA using DEA-BA adducts was found very beneficial. Besides a faster rate, it was able to form mostly diesters. All reactions of the present study are primarily characterized by the formation of nonpolar ester linkages with intramolecular –NR-$B(OH)_2$, -O-B(OH)2, and $(OH)_3B \rightarrow NR$ B−N bonds. Furthermore the DEA-BA adduct is comprised of all possible boron linkages either via –O-, or –NR-, which constitutes the common reaction precursor for the surfactants of the present series. In this communication we'll discuss mainly the product DDSA-DEA-BA.

For ^{11}B NMR studies all samples were kept at pH 8.5. Chemical shifts from ^{11}B NMR spectra of DDSA-DEA-BA, BA and Ethylenediamine (EDA) complex of BA (BA-EDA) at pH 8.5 (Figure 1) suggested that the intramolecular linkages thus formed between B, O and N in the compound of DDSA-DEA-BA could be a mixture of all possible forms as shown above (Eqn. 1-4), of which –O-$B(OH)_2$ type was most prevalent. In Figure 2 the integrated areas of each individual fractions indicated that the linkages viz. –O-$B(OH)_2$ was found to be about 80% or more with a small fraction of $(OH)_2B$-NR- and $(OH)_3B \rightarrow NH$- type. The ratio of the individual linkage types thus formed in DDSA-DEA-BA appeared to be 80% of type (1), 13% of type (2) and 7% of type (3) and (4).

It was indeed a lucky coincidence that the chemical shift, δ, of Boric Acid does not change very abruptly between pH 4-9 (between 19-17 ppm) [10]. The δ drops very sharply only between pH 9.5-10. Therefore the observed δ values at lower ppm for DDSA-DEA-BA product were indicative of the true changes in the Boron environment and they were indeed different from BA under similar pH conditions. A comparison of chemical shifts of BA, BA-EDA and DDSA-DEA-BA are presented in Table 1.

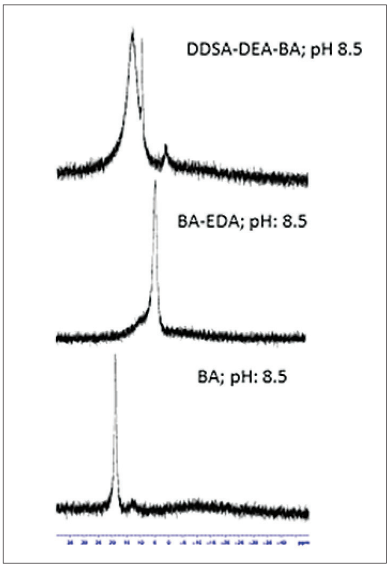

Figure 1. ^{11}B NMR of (A) boric acid alone; (B) boric acid complexed with ethylenediamine (EDA) and the product DDSA-DEA-BA at pH 8.5

It is to be noted that the sequential addition of 2 molar equivalent of boric acid gave better results than the addition of whole amount at a time. The chemical shift data also suggested the derivative of DDSA (1) was largely formed due to the identical nature of both –O-B- linkages and a small fraction might have undergone to form amide as shown in (2). A small peak at δ = 0.89ppm suggests that the DDSA-DEA-BA derivative may also contain a small fraction of the structures (3) and (4).

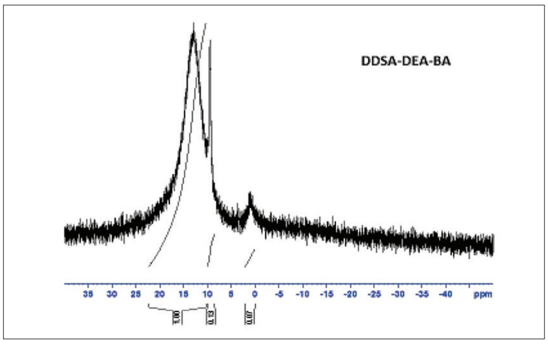

Figure 2. Integrated fractions of each possible Boron linkages, viz. –O-B$(OH)_2$, $(OH)_2$B-NR- and $(OH)_3$B → NH- formed in DDSA-DEA-BA

Table 1. Chemical shift data for Boric Acid, complex form of Boric Acid and ethylenediamine, and the dodecenyl Succinic Acid esters of Diethanolamine and Boric Acid (DDSA-DEA-BA) adduct at pH 8.5.

	BA, pH 8.5	BA-EDA, pH 8.5	DDSA-DEA-BA, pH 8.5		
Chemical Shift, δ ppm	19.42	3.55	12.82 (80%)	9.45 (13%)	0.89 (7%)

Although there was no proper quantitative evaluation of its detergency yet, this is also to be noted, the water dispersion of DDSA-DEA-DA apparently showed very good foam forming and dirt removal characteristics.

We thus measured the surface properties of DDSA-DEA-BA at various concentrations in water using conventional methods [11]. Surface tensions were measured at the air-water interface under ambient conditions. The surface tension versus concentration profile is shown in Figure 2. Critical micelle concentration (cmc) was calculated from the point of intersection of the two best-fit slopes of Ln C vs. σ plot. Plots of surface tension vs. Ln [surfactant] display two major regions (Figure 3): Region A - a steep, almost linear, where surface tension continuously falls with the increase in surfactant concentration, and Region B - showing an abrupt leveling at the critical micelle concentration (CMC). Conventional theory assumes that the air/water interface is saturated with surfactant throughout Region-A [11-13]. It is this key assumption that allows the calculation of the area-per-molecule via application of the Gibbs equation (i and ii) where Γ= the surface excess; dσ/d(ln*c*) = the slope of line-A; and N = Avogadro's number. If the area-per-molecule were continuously decreasing in Region-A, instead of remaining constant owing to saturation, a unique area obviously could not be obtained.

$$\Gamma = -\frac{1}{RT}\cdot\left(\frac{\delta\sigma}{\delta lnC}\right) \quad ..... (i) \qquad Area = 1/N\Gamma \quad ......(ii)$$

The shape of the curve shown in Figure 3 is characteristic of a surfactant, and the values of the parameters of surface activity are obtained using the above equations (See Table 2). It was observed that the DDSA-DEA-BA surfactant have reduced surface pressures equivalent to those for liquid alkanes [14] of similar hydrocarbon chain (~0.6 nm^2).

Table 2. Surface Properties of DDSA-DEA-BA

Surfactant	cmc (mM) at 25 ºC	Surface tension (σType equation here.) at cmc (mN/m)	Surface excess (m^{-2})	Molecular area (nm^2)
DDSA-DEA-BA	1.65	26.3	3.1x10^{-6}	0.533

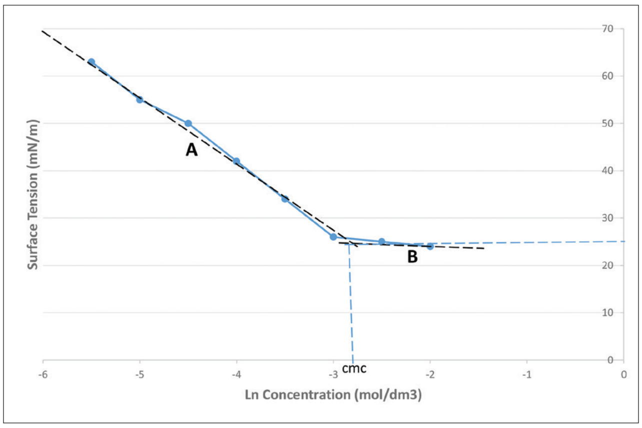

Figure 3. Variation of the surface tension (mN·m^{-1}) with Ln[Concentration] (mol·dm^{-3}) for the water solution of the DDSA-DEA-BA at 300 K

4. Concluding remarks

In conclusion from the very basic evaluation of the DDSA-DEA-BA surfactant containing non-polar head groups containing Boron, we have demonstrated the method of synthesis of a new series of surfactants employing microwave technique. Their structures contain intramolecular –O-B-$(OH)_2$ and $(OH)_2$ - B-NR-bonds, giving rise to a stable amphiphilic molecule with very good surfactant properties. The results of surface properties offer an excellent possibility for such compounds in the areas of detergents and dispersion formulations for various anti-fungal and insecticide applications, and also for formulating both water and oil dispersible wood-treatment chemicals.

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