Green Synthesis For Nonionic Surfactants From Poly (EthyleneTerphthalte) Plastic Waste

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Abstract

Efficient solvent free green glycolysis for polyethylene terephthalate plastic waste, in this respect, PET waste was subjected to depolymerization process with trimethylene glycol (1,3-propandiol) (1:3 w/w) in the presence of (1 % w/w) manganese acetate as trans esterification catalyst (1 % w/w), the product is Bis-(3-hydroxy-propyl)-terephthalate, BHPT, as a non-ionic surfactant was separated and characterized by FT-IR and 1HNMR. The surface properties were studied by measuring the surface tension at different concentrations and temperatures. The surface tension, critical micelle concentration (CMC), and surface activities were determined. The surface parameters such as surface excess concentration (rmax), the area per molecule at interface (Amin) and the effectiveness of surface tension reduction (πCMC) were determined from the adsorption isotherms of the prepared surfactant. The thermodynamic data for the micellization and adsorption process were calculated and discussed.

Keywords: Recycling; Glycolysis; waste; Surfactants, thermodynamic; adsorption; PET; Green Synthesis.

1. Introduction

Converting of the plastic waste into useful product is of economical, technical, ethical, and environmental impact, especially with the increasing pressure of keeping the environmental clean the recycling of PET waste is an ecofriendly manner is the only solution, PET is not a hazardous product, but its waste quantity increases drastically. The PET bottle was patented in 1973 by Nathaniel Wyeth and began to be used popularly for the production of disposable soft drink bottles in the 1980s. in 1987, more than 700 million pounds of PET were consumed in their production [1]. PET is semi-crystalline, thermoplastic polyester of characteristic high strength, transparency, and not biodegradability [2]. The overall world production of polyester was about 30 million tons in 2000, this value increased to 55 million in 2012 and most consisted of PET, as a result of the diversity of its applications in a high volume of consumer products, large amount of PET waste is also generated, which includes polymer manufacturing waste as well as the products after the end of their useful life. PET waste can be recycled by different methods like physical recycling and chemical recycling, chemical recycling is the reaction of PET with various reagents to obtain products that are used in the chemical industry [3]. During chemical recycling, PET waste can be depolymerized to base monomers or oligomers. With the use of solvent of depolymerization, generally called solvolysis of polymer, methanolysis [4] and glycolysis [5] are the main possible routes. Water-soluble synthetic surfactants are a family of materials that have been developed commercially and studied scientifically at an accelerating pace in recent years. Many water soluble glycolic polymers, because of their amphipathic structure and surface activity, are used as surface active agents. The study of the surface and thermodynamic properties are important both for basic research and for industrial applications [6-11].
Surfactants or amphiphilic monomers are used together with polymers in a wide range of applications. In areas as diverse as detergents, paints, paper coatings, food and pharmacy, formulations usually contain a combination of a low molecular weight surfactant and a polymer which may or may not be highly surface active [12-15]. In the previous work the recycling of the waste was carried out via the reaction with ethylene glycol and ethanol amine to produce the corresponding surfactant [13]. The aim of the present work is to prepare nonionic surfactant from PET, plastic waste after recovery via reacting the purified waste with trimethylene glycol (1,3-propandiol) in the presence of 1% manganese acetate as transesterification catalyst, via solvent free efficient green recycling, the product is Bis-(3-hydroxy-propyl) terephthalate, BHPT. The surface property of the prepared surfactant was determined at different concentrations and temperatures, thermodynamic parameters were calculated and discussed. The present work deals with green synthesis of water soluble nonionic surfactants from Poly ethyleneterphthalate plastic waste, PET. The thermodynamics and surface properties of the synthesized surfactants are also studied. The main goal and novelty of this work is to convert plastic waste into useful product using solvent free efficient green catalyzed synthesis process instead of traditional chemical recycling this considered as important point from green chemistry point of view.

2. EXPERIMENTAL

2.1. Materials
Poly(ethyleneterphthalate) (PET) waste was collected from beverage bottles, trimethylene glycol (1,3-propandiol), and manganese acetate were obtained from Aldrich Chemical Co., England.

2.2. Recycling Process
PET waste was depolymerized with 1,3-propandiol (PG), at weight ratio of PET to Glycol (PG) (1:3 wt.% of PET: wt% of Glycol) using of manganese acetate as transesterification catalyst (1.0 % by weight based on weight of PET). The reaction mixtures were heated under vigorous stirring in nitrogen atmosphere at temperature about 170–190 °C for 4 h. and at 200 °C for 2 h. The temperature of the reaction was then lowered to 100 °C for 1 h. The mixture was allowed to cool to room temperature. at the end of the reaction, saline water was added to the reaction mixture with vigorous agitation followed by phase separation, the product, poly (bis (2-Hydroxy ethylene) terephthalate) (BHPT) was obtained in organic layer as a white viscous product (83% yield), which have the chemical structure as showed in figure (1 ). The general diagram for the green synthesis procedure as presented in figure 2.

2.3. Elemental and Spectroscopic Analysis
Elemental and spectroscopic analyses were carried out in the Micro Analytical Center of Cairo University. The fine chemicals were purchased from Aldrich Co. The reactions were monitored using TLC and the resultant compounds were crystallized and then extra purified using a column chromatography technique.

2.4. Infrared Spectroscopic Analysis
The purified synthesized compounds were analyzed using ATI Mattson Genesis Series FTIR spectrophotometer. The samples were investigated as thin film between two KBr discs.

2.5. Nuclear Magnetic Resonance Spectroscopic Analysis
The prepared surfactants were dissolved in chloroform, CDCl₃, and analyzed using Jeol NMR spectrometer model JNM-EX (270 MHz) as another spectroscopic technique for determining the chemical structure.

2.6. Surface Property Characterizations
Cloud point of 2% of the prepared surfactant aqueous solutions were determined visually by testing the temperature at which turbidity was observed. The same temperature was determined at which turbidity disappeared on cooling. The average of the results was taken as the cloud point of the system [13-15]. The surface tension measurements of the prepared surfactants were carried out at different molar concentrations and different temperature (303 k, 313k, 323k, and 333k) by using platinum tensiometer. The surface tension was determined using a Kruss K-12 tensiometer.

Figure 1. the chemical scheme of the green synthesis process for the Bis-(3-Hydroxy- Propyl) Terephthalate, BHPT compound.
Figure 2. The Flow Diagram of the solvent free green synthesis Processes.

**Table 1.** Elemental analysis of the Prepared Compound from PET waste

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Molecular Formula (Mol.F)</th>
<th>Molecular Weight (Mol.wt.)</th>
<th>C %</th>
<th>H %</th>
<th>O %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>C_{14}H_{18}O_{6}</td>
<td>282.3</td>
<td>59.5</td>
<td>6.4</td>
<td>33.98</td>
</tr>
<tr>
<td>Found</td>
<td>281.6</td>
<td>59.1</td>
<td>5.3</td>
<td>32.6</td>
<td></td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1. Chemistry: Synthesis of Bis-(3-hydroxypropyl)-terephthalate, BHPT

PET (1%w/w) and an tri molecular ratio of 1,3-propane diol (3 %w/w) were refluxed in the presence of manganese acetate (0.1 % wt. %) as a catalyst for 6 hours at temperature (190-200 °C) as mentioned before Part 2.2. The reaction mixture was cooled to 100 °C, then to room temperature, saline water was added to remove glycol the product residue is a white viscous product, this compound was extra purified using column chromatography with 83% yield. figure 1 show the chemical structure of the product and scheme of the synthesis process, the obtained compound has the elemental analysis as given in table 1.

The structure of the obtained compound, BHPT was verified form their IR spectra. The spectra of BHPT figure 3 shows the presence of strong band at 3399 cm⁻¹, in the spectra, indicates the termination of the products with hydroxyl groups. On the other hand, the band observed at 829 cm⁻¹ for all depolymerized PET

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is assigned to –CH out-of-plane bending of p-substituted phenyl. This band confirms the presence of phenyl rings in depolymerized products. The presence of strong peaks at 1717 cm\(^{-1}\) and 1192 cm\(^{-1}\), which were assigned for C=O stretching and C-O stretching of ester groups, indicates the incorporation of ester groups in all depolymerized PET products. A further confirmation for the product compound from the reaction of PET with 1,3-propane diol is given by its \(^1\)HNMR spectrum, with the following signals: (CDCl\(_3\)) \(\delta\) ppm: 2.22-2.24 (m, 4H, 2CH\(_2\)), 3.52-3.54 (t, 4H, 2CH\(_2\)), 4.32-4.34 (t, 4H, 2CH\(_2\)), 4.80 (2H, 2OH, D\(_2\)O exchangeable), 7.88 (s, 4H, Ar-H), as it showing in figure 4 the presence of the signals at chemical shifts 7.88 ppm, represent p-substituted phenyl group indicating the incorporation of aromatic hydrophobic part in the structure. The signal observed at 4.8 ppm in the spectra of BHPT, which represent OH group, indicate the presence of terminal OH in the obtained BHPT sample.

3.2. Surface Activity Characterization

The surface Activity of the Prepared Surfactant due to the presence of the hydrophobic effect, surfactant molecules adsorb at interfaces, even at low surfactant concentrations. As there will be a balance between adsorption and desorption (due to thermal motions), the interfacial condition requires some time to establish. This difference is due to the difference in hydrophilic-lipophilic balance (HLB) of the surfactants. The HLB values were calculated by using the general formula for nonionic surfactants, [16-20].

\[
\text{HLB} = \frac{\text{MH}}{\text{MH} + \text{ML}} \times 20,
\]

Where MH is the formula weight of the hydrophilic portion of the surfactant molecule and ML is the formula weight of the hydrophobic portion. HLB and molecular weight values of nonionic surfactants prepared from PET plastic waste were calculated and listed in Table 2. Classical equations derived by Griffin and Davies were used to calculate the HLB number of surfactants, [21, 29] however, these equations consider only the chemical compositions, and the effect of position isomerism is not taken into account. Because HLB is difficult to determine experimentally, the cloud point of the prepared surfactants was used to represent the hydrophilic-lipophilic balance. The cloud point is defined as the temperature at the surfactant loses sufficient water solubility and a cloudy dispersion observed [21, 29]. Above this temperature, the surfactant also ceases to perform some or all of its normal functions. So cloud point can be used to limit the choice of nonionic surfactants for application in certain processes. A suggestion was made to regard the cloud point in solution of nonionic surfactant as a pseudo phase inversion. For polyoxyethylene-type surfactant, the cloud point and the phase inversion temperature (PIT) are directly correlated when surfactant alone is dispersed in water. PIT is defined as the temperature at which the hydrophilic-lipophilic property of surfactant just balances at the interface. [23-31]. A study on the effect of structural changes in the surfactant molecule on its cloud point [19,20] indicates that, at constant oxyethylene content the cloud point is lowered due to decreased molecular weight of the surfactant and increasing length of the hydrophobic group. In this respect, the cloud points of the prepared surfactants were determined and listed in Table 2. Accordingly, the prepared BHPT surfactants were highly water soluble surfactants. The surface activity of surfactants can be determined by measuring surface or interfacial tensions versus time for a freshly

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**Figure 3.** IR spectrum for the prepared compound BHPT from PET, waste

**Figure 4.** \(^1\)HNMR spectrum for the prepared compound BHPT from PET, waste.
formed surface. The micellization and adsorption of surfactants are based on the critical micelle concentrations (CMC), which was determined by the surface balance method. The CMC values of the prepared surfactants were determined at 303 K, 313 K, 323 K, and 333K from the change in the slope of the plotted data of surface tension (γ) versus the natural logarithm of the solute concentration and listed in Table 2. Adsorption isotherms are illustrated in figure 5. The isotherms are used for estimating surface activity and confirming the purity of the studied surfactants. It is of interest to mention that all obtained isotherms showed one phase, which is considered as an indication on the purity of the prepared surfactants. The listed data shows that the CMC decreases with measuring temperature for the investigated non-ionic monomeric surfactants. The reduction in CMC values is due to the decrease in the solubility of the surfactants. The direct determination of the amount of surfactant adsorbed per unit area of liquid-gas or liquid-liquid interface, although possible, is not generally under taken because of the difficulty of isolating the interfacial region from the bulk phase for purpose of analysis when the interfacial region is small, and of measuring the interfacial area when it is large. Instead, the amount of material adsorbed per unit area of interface is calculated indirectly from surface or interfacial tension measurements.

\[
\Gamma_{\text{max}} = \frac{1}{RT} \left( -\frac{\partial \gamma}{\partial \ln c} \right)\]

(1)

where \((-\partial \gamma / \partial \ln c)\) is the slope of the plot of \(\gamma\) versus \(\ln c\) at a constant temperature \((T)\), and \(R\) is the gas constant in J mol\(^{-1}\)K\(^{-1}\). The surface excess concentration at surface saturation is a useful measure of the effectiveness of adsorption of surfactant at the liquid-gas or liquid-liquid interface, since it is the maximum value which adsorption can attain. The \(\Gamma_{\text{max}}\) values were used for calculating the minimum area \(A_{\text{min}}\) at the aqueous-air interface, the area per molecule at the interface provides information on the degree of the packing and the orientation of the adsorbed surfactant molecules, when compared with the dimensions of the molecule as obtained by use of models. From the surface excess concentration, the area per molecule at interface is calculated using the following Equation:

\[
A_{\text{min}} = \frac{10^{16}}{N \Gamma_{\text{max}}} \]

(2)

where \(N\) is Avogadro’s number. The surface tension values at CMC were used to calculate values of surface pressure (effectiveness). The effectiveness of surface tension reduction, \(\pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}}\), where \(\gamma_0\) is the surface tension of water and \(\gamma_{\text{CMC}}\) is the surface tension of solution at CMC [22-25] was determined at different temperatures. The values of \(\pi_{\text{CMC}}\) show that, the most efficient one is that gives the greater lowering in surface tension at the critical micelle concentration. The effectiveness increases with increasing the length of carbon chain in the hydrophobic moiety. Efficiency \(\pi_{\text{CMC}}\) is determined by the concentration (mol / L) capable to suppress the surface tension by 20 dyne/cm. The efficiency of the prepared surfactants, listed in Table 2, it increases with increasing temperature. Careful inspection of data indicated that the prepared surfactants based on PET plastic waste have high \(A_{\text{min}}\) values, this observation was referred to the presence of hydrophilic ends on the side of the prepared surfactant which reflect on the packing of the surfactants at the air-water interface. This can be attributed to the behavior of surfactants with hydrophilic groups at opposite ends of the molecule which show large area per molecule at the interface and are probably lying flat at the interface with both hydrophilic groups in contact with the aqueous phase. Careful inspection of data, indicates that, \(A_{\text{min}}\) of the surfactants have two opposite relations with the temperature. The \(A_{\text{max}}\) may be increased or decreased with increasing the temperature. In polyoxyethylated nonionic the lack of significant temperature effect may be resulted from two compensating effects [21,32]. Decrease in \(A_{\text{min}}\) at the surface due to increased dehydration of the hydrophilic group at higher temperature; and increase in \(A_{\text{min}}\) as a result of enhanced molecular motion at higher temperature. In the present system, it was found

Figure 5. The adsorption isotherms of the BHPT surfactants prepared from Plastic waste.
that the $A_{\text{mic}}$ increases with increase in temperature, as would be expected from the increased thermal agitation of the molecules in the surface film. When the area of hydrophilic group is greater than that of the hydrophobic chain, the larger the hydrophilic group, the smaller of the amount adsorbed at surface saturation [21-32].

3.3. Thermodynamic Parameters of Micellization of the Prepared Surfactants

The formation of micelles in aqueous solutions is generally viewed as a compromise between the tendency for alkyl chains to avoid energetically unfavorable contacts with water and the desire for the polar parts to maintain contact with the aqueous environment [21-29]. The ability for micellization processes depends on the change on thermodynamic parameters, (enthalpy $\Delta H$, entropy $\Delta S$, and free energy $\Delta G$) of micellization. Thermodynamic parameters of micellization of the prepared non-ionic surfactants were calculated and listed in Table 3.

Table 3. Thermodynamic parameters of micellization of nonionic surfactants derived from used cooking oil.

<table>
<thead>
<tr>
<th>Temp. K.</th>
<th>303 k</th>
<th>313 k</th>
<th>323 k</th>
<th>333 k</th>
<th>$\Delta S_{\text{mic}}$ J K$^{-1}$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BHPT</td>
<td>17.2</td>
<td>61.5</td>
<td>19.6</td>
<td>61.3</td>
<td>22.1</td>
</tr>
</tbody>
</table>

The thermodynamic parameters of micellization are the standard free energies $\Delta G_{\text{mic}}$, enthalpies $\Delta H_{\text{mic}}$, and entropies $\Delta S_{\text{mic}}$, of micellization for nonionic surfactants.

$$\Delta G_{\text{mic}} = RT \ln \text{CMC}$$

(3)

Values of $\Delta S_{\text{mic}}$ were obtained from Equation (4) by invoking the values of $\Delta G_{\text{mic}}$ at 303K, 313 K, 323 K, and 33 K.

$$\frac{\partial \Delta G_{\text{mic}}}{\partial T} = -\Delta S_{\text{mic}}$$

(4)

In addition, $\Delta H_{\text{mic}}$ was calculated from $\Delta G_{\text{mic}}$ and $\Delta S_{\text{mic}}$ by applying Equation (5) [29-32]:

$$\Delta H_{\text{mic}} = \Delta G_{\text{mic}} + T \Delta S_{\text{mic}}$$

(5)

The values of $\Delta G_{\text{mic}}$, $\Delta H_{\text{mic}}$, and $\Delta S_{\text{mic}}$ for the prepared surfactants are calculated and are listed in Table 3. Analyzing the thermodynamic parameters of micellization leads to the fact that micellization process is spontaneous ($\Delta G_{\text{mic}} < 0$). On the other hand, the data reveal that (- $\Delta G_{\text{mic}}$) increases with increasing temperature from 303K to 333 K. The data listed in Table 3 show that $\Delta S_{\text{mic}}$ values are all positive, indicating increased randomness in the system upon transformation of the nonionic surfactant molecules into micelles or increasing freedom of the hydrophobic chain in the nonpolar interior of the micelles compared to aqueous environment [29-32].

3.4. Thermodynamic Parameters of adsorption of the Prepared Surfactants

The thermodynamic parameters values of adsorption, $\Delta G_{\text{ad}}$, $\Delta H_{\text{ad}}$, and $\Delta S_{\text{ad}}$ were calculated via Equations (6), (7), and (8), respectively, [29-32].

$$\Delta G_{\text{ad}} = RT \ln \text{CMC} - 0.6023 H_{\text{CMC}} A_{\text{min}}$$

(6)

$$\frac{\partial \Delta G_{\text{ad}}}{\partial T} = -\Delta S_{\text{ad}}$$

(7)

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The following conclusions can be extracted from the previous discussion:

4. Conclusions

The following conclusions can be extracted from the previous discussion:

1. Polyethylene terephthalate Plastic waste PET, can be easily recycled via solvent free efficient green synthesis in the presence of catalyst.
2. The produced compounds were separated with high yield, Purified, and characterized by FT-IR, \(^1\)HNMR.
3. The obtained compounds act as nonionic surfactants of highly surface activities.
4. The surface and thermodynamic parameters indicate that the prepared surfactants based on PET waste favor adsorption than micellization.
5. The prepared surfactant, BHPT derived from used PET waste have more negative values of \(\Delta G_{ad}\).
6. This observation indicates that the BHPT surfactants favor the adsorption than mercerization.

The values of \(\Delta S_{ad}\) are all positive and have greater values than \(\Delta S_{mic}\) for nonionic surfactants. This may reflect the greater freedom of motion of the hydrophobic chains at the planar air-aqueous solution interface compared to that in the relatively cramped interior beneath of the convex surface of the micelle. This indicates that the steric factor inhibits micellization more than do adsorption for nonionic surfactants. On the other hand, the positive values of \(\Delta H_{ad}\) are much lower than the corresponding values of \(\Delta H_{mic}\). This indicates that the dehydration-breaking of hydrogen bonds- at adsorption is easier than at micellization \([14,15,32]\).

References


