



Sodyum humat/sles/bitkisel yağların karışımı

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ÖZET

Sodyum humatın iyonik yüzey aktif maddesi olan sodyum lauril eter sülfatla karışımı bitkisel yağ karışımlarıyla 25, 50 ve 75 °C de hazırlandı. Farklı konsantrasyon aralıklarında ve tampon çözelti içerisinde fiziksel teknikler kullanılarak karışım çalışması gerçekleştirildi. Bununla beraber, karışımın karışabilirliği, UV-visible spektrofotometresi ve Fourier dönüşümlü infrared (FTIR) kullanılarak tespit edildi. Çalışmadaki değerler humik asit miktarının %60 dan fazla olduğunda her sıcaklıkta karışabilir olduğunu gösterdi. Farklı sıcaklıklarda karışımın karakteristiğinde önemli bir değişiklik yoktu. Kompleksin oluşum mekanizmasının, karbonil gruplarıyla hidroksil gruplarının arasındaki hidrojen bağı oluşumunu içeren güçlü intermoleküler interaksiyon ile gerçekleştiği düşünülmektedir.

Anahtar Kelimeler: sodyum humat, karışım, yüzey aktif madde, yağ asidi

A blend of sodium humate/sles/herbal oils

ABSTRACT

A blend of sodium humate (SH) with anionic surfactants such as sodium lauryl ether sulfate (SLES) was prepared by solution mixing at medium of herbal oils at 25, 50 and 75°C. Its miscibility studies were carried out by using physical techniques over an extended range of concentration and composition in buffer solution. In addition, to ascertain the state of miscibility of the blends, they were investigated by using UV-visible spectrophotometer and Fourier transform infrared (FTIR). These values revealed that the blend is miscible when the sodium humate content is more than %60 in the blend at all temperatures. There were no important differences in the characteristics of the blends at different temperatures. It was thought that the mechanism of the complex formation is realized by making strong intermolecular interaction like hydrogen bonds between the carbonyl groups in humic acid and hydroxyl groups in fatty acids.

Keywords: Sodium humate, blend, surfactant, fatty acid

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1. INTRODUCTION

Humic substances (HSs) have been said to be the most common polymer on Earth. They account for approximately 80% of organic carbon of the world [1]. HSs are bio-polymers based on carboxyl, hydroxyl and carbonyl units which can reach a high molecular weight (500,000-1,000,000). During humification, HSs are fragmented into small pieces and hydrophilic groups (-OH, -COOH) are produced to make it water soluble, particularly at the high pH (11-12). Their derivatives are polymeric surfactants of the grafted type. They are dispersants for solid particles, as in drilling fluids, among other uses like cosmetic.

The concept of modifying humic substances is based on the methods used for the development of biopolymers with surfactant properties [2]. The sites at the occurrence of modification include the first benzene ring in phenolic structures and hydroxyl groups. The suggested modification methods are designed to enable the addition of hydrophilic sulfonic, hydroxyl or trimethylammonium functional groups, which are likely to affect the surfactant properties. Derivatives of HSs are characterized based on their elemental and functional analysis as well as their UV-vis and FTIR spectra. It is well known that the behavior of humic substances in aquatic solutions depends on their concentration, pH and the concentration of metal ions in the solutions [3] and the same factors determine the influence of humic substances on surface tension and the formation of pseudomicelles. This is because both effects are manifestations of the same solution properties. In addition, it is well known that the properties of humic substances depend on their origin [4]. The development of micellar structures is associated with changes in macromolecules in the solution phase that lead to the exterior of the molecule (molecular aggregates) becoming more hydrophilic and the interior becoming more hydrophobic. This allows a hydrophobic microenvironment that supports the ability of the HSs to solubilize hydrophobic organic molecules like fatty acids.

In this study, sodium humate and water-soluble anionic surfactants with herbal oils was combined as a novel for use in cosmetic [5]. The oils employed were generally fatty acids which are very insoluble in water and tend to be immiscible when water is added. However, under the proper conditions, the oils can be dissolved in water which contains a surfactant such as a petroleum sulfate or a petroleum sulphonate/sodium humate combination.

2. EXPERIMENTAL

2.1. Materials

Sodium humate (SH) was supplied from Sigma-Aldrich Chemical Company. Sodium lauryl ether sulfate (SLES, 70%) and herbal oils (mixing of olive oil, nigella sativa oil and sesame oil) was attained by the market. Other agents used were the entire analytical grade and all solutions were prepared with distilled water.

2.2. Blend Preparation of SLES/Herbal Oils/Sodium Humate

One mixing procedure was to combine the anionic surfactants and the sodium humate and to add herbal oils that had been preheated to a temperature above the melting point of the surfactant. This combination of sodium humate, surfactant and oils were stirred at about 25, 50 and 75°C, respectively. Appropriate amount of SH was dissolved in 50 ml distilled water in a 250 ml four-neck flask, equipped with a mechanical stirrer, a reflux condenser, a funnel and a oxygen line. After being purged with oxygen for 30 min to remove the inert gas dissolved from the system, and certain amount of SLES was introduced to mix with certain amount of oils. Ten minutes later, the remained water was added. The water bath was kept at desired temperatures for 1 h to complete the mixing.

2.3. UV-Visible Spectroscopy

To obtain the E_4/E_6 ratio, the absorbance at 465 nm and 665 nm was measured using SHIMADZU-UV-2401 PC (UV-VIS Recording Spectrometer) on solution of 3.0 mg of each blend in 10 mL of 0.05 mol/L NaHCO_3 .

2.4. Fourier Transforms Infrared (FTIR) Spectrum

To analyze the chemical and/or physical interactions after producing the blend polymer, IR spectra were scanned by Shimadzu's FTIR-8000 instrument over wave number range of 4000–400 cm^{-1} . FTIR data analysis was made by Shimadzu's Irsolution 1.30 software.

3. RESULTS AND DISCUSSION

Figure 1 illustrates the infrared spectra of some samples in the range 4000 cm^{-1} –600 cm^{-1} . FTIR spectrometry has been proven to be a very powerful technique to detect the intermolecular interaction between three organic materials. The intermolecular interaction through hydrogen bonding can be characterized by FTIR, because the specific interaction affects the local electron density and the corresponding frequency shift can be observed [6]. In FTIR spectra the shift of the bands derived from

the groups which can be involved to hydrogen bonds suggests that the interactions between SH, SLES and oils occur by it. The IR hydroxyl stretching range of SH/SLES/oils is sensitive to the hydrogen bonding formation. SH as a hydrogen donor forms hydrogen bond with sulfate group from SLES and herbal oils. The sulfate group in SLES contains a proton-accepting moiety ($-\text{SO}_3^-$), while SH presents carboxylic groups as side groups. Therefore, a hydrogen-bonding interaction may take place between these chemical moieties in a blend of SH, SLES and oils. The formation of hydrogen bonds between three different macromolecules competes with the formation of hydrogen bonds between molecules of the same structure. The molecular structure of SLES reveals that the 1700 and 1600 cm^{-1} bonds refer to the vibration of $\text{C}=\text{N}$, and $\text{C}=\text{C}$ and the stretching vibration of the $-\text{CH}=\text{}$ is evident at 3600 and 3000 cm^{-1} , as shown in curves (from a to f) in Figure 1.

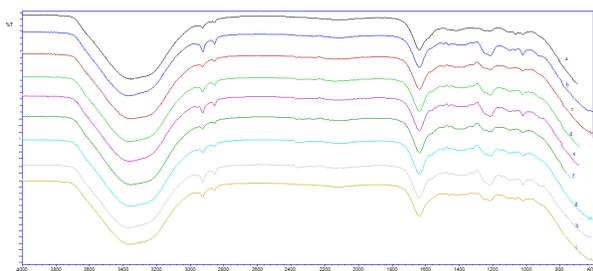


Figure 1. The FTIR spectra of (a) 5% SLES at 25°C, (b) 10% SLES at 25°C, (c) 15% SLES at 25°C, (d) 5% SLES at 50°C, (e) 10% SLES at 50°C, (f) 15% SLES at 50°C, (g) 5% SLES at 75°C, (h) 10% SLES at 75°C, (i) 15% SLES at 75°C.

The UV/Vis spectra of the blend of SH/SLES/oils were recorded at the range of 200–800 nm (Figure 2). The ratio E4/E6 of the diluted humic substances extracted from the peat were used in the characterization of humic (HA) and fulvic acids (FA). The E4/E6 ratio was much larger for the FA fractions than for the HA fractions. The larger E4/E6 values were associated with lower molecular weights [7]. This E4/E6 ratio is inversely related to the degree of condensation of the aromatic groups in humic substances [8], so that a high ratio would reflect a low degree of aromatic condensation and the presence of relatively large proportions of aliphatic structures. Although all samples didn't indicate any sharp end point, they exhibited a slight projection characterizing humic substances at 450–470 nm [9]. This projection reflects the unsaturated parts of humic substances or their absorbance with double bands ($\text{C}=\text{C}$, $\text{C}=\text{O}$ and $\text{N}=\text{N}$) of aromatic groups [10]. The changes in the projection observed in the blend of SH/SLES/oils were attributed to those in the concentration of aromatic compounds. In conclusion, these changes came from the structure of the characteristic differences in the humification process [11].

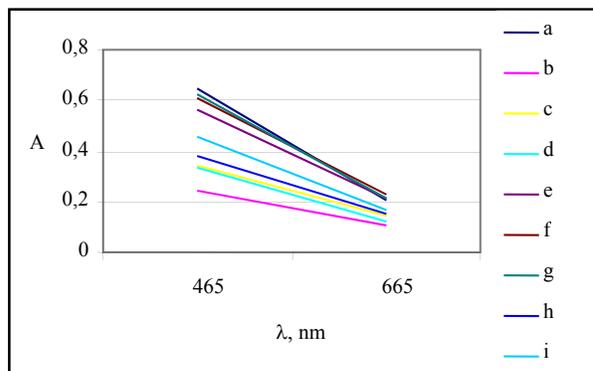


Figure 2. UV-vis spectra of blend of SH/SLES/oils.

Chromophores being responsible for the absorbance include unbound electrons such as oxygen, sulfur, halogen atoms [12]. Absorbance is mainly formed due to the aromatic ring structures [13]. Moreover, the rotation of molecules and intermolecular interactions affect the spectra [14].

4. CONCLUSIONS

This paper focused on the interactions of SH/SLES/herbal oils blended as surface-active substance. SLES was miscible with SH due to intermolecular hydrogen bonding between hydroxyl and amine of humic substances and sulfate group in SLES with carboxylic group of herbal oils. The IR spectra of the blends proved that hydrogen-bonding interaction occurred between SH, SLES and oil. The temperature increased with an increase of SLES content, which indicates that these blends are able to form a miscible phase due to the formation of intermolecular hydrogen bonding between hydroxyl and amine of SH and sulfate group in SLES. Humic substances isolated from natural environments found to have a significant impact on the surface tension of the solutions as the concentration of these compounds increased. However, industrially produced humic materials had little or no impact on the surface tension of their solutions. Finally, the results of this study suggest that modification of the methods used to derive humic substances can allow significant increases in the surfactant properties of humic substances.

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