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UV-VIS and FTIR spectroscopic analyses of inclusion complexes of nonylphenol and nonylphenol ethoxylate with β-cyclodextrin

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ABSTRACT

A study of inclusion complexation of liquid non-ionic surfactants, nonylphenol (NP) and nonylphenol 9 mole ethoxylate (NP9EO), with β-cyclodextrin (β-CD), was carried out by mass spectrometry, surface tension, and ultraviolet–visible (UV-VIS) and Fourier transform infrared (FTIR) spectroscopies. The inclusion complexation was effectuated by heating at 80 °C and filtration of aqueous NP + β-CD and NP9EO + β-CD suspensions. The mass spectrometry and surface tension measurements revealed that NP and NP9EO form inclusion complexes with β-CD and β-CD possesses a higher affinity for NP. These results are supported by the data from UV-VIS spectroscopic analyses that have indicated that a three times greater amount of NP is entrapped into β-CD than NP9EO. This phenomenon has been associated with the smaller size and a higher degree of hydrophobicity of NP that favours its entrapment into β-CD as compared to that of NP9EO. At the structural level, the data from FTIR spectroscopic study have indicated that alkyl chains of NP and NP9EO can form van der Waals interactions with the cavity of β-CD. Moreover, NP and NP9EO seem to cause a reorganization of the intramolecular hydrogen bonds and change of the hydration of β-CD, but did not appear to strongly interact with C–C, C–O–C, and OH groups of β-CD. Together these results suggest that the formation of inclusion complexes by NP and NP9EO with β-CD molecules could constitute an effective and advantageous technique to remove liquid non-ionic surfactants from wastewater due to the non-toxic character of β-CD to humans and the environment.

1. Introduction

Cyclodextrins are polycyclic glucose oligosaccharides resulting from the degradation of starch by bacterial enzymes (Bizzigotti et al., 1997; McCray and Brusseau, 1998; Saenger et al., 1998). There are three common types of cyclodextrins (α-, β-, and γ-cyclodextrins), which are constituted of six, seven, or eight glucose units respectively, linked by α-1,4-glucosidic bonds (Bizzigotti et al., 1997; McCray and Brusseau, 1998; Saenger et al., 1998; Szente et al., 1999). The doughnut-shaped structure

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of cyclodextrins is characterized by the presence of glucose residues in a C_1 conformation with hydroxyl groups arranged around the outer rim (Fig. 1) (Bizzigotti et al., 1997; Saenger et al., 1998; Szente et al., 1999). Cyclodextrin molecules have a hydrophobic and non-polar cavity that contains the oxygen-bridge and hydrogen atoms, which may permit the solibilization of non-polar and low-polarity organic molecules of appropriate size and shape through the formation of water-soluble inclusion complexes (Bender and Komiyama, 1978; Bizzigotti et al., 1997; McCray and Brusseau, 1998; Saenger et al., 1998; Szente et al., 1999). The chemical properties of cyclodextrins combined with their non-toxic character to humans have led to their use in pharmaceuticals, as food additives, as well as in the environmental decontamination procedures of wastewater, aquifer, air, and soil (Bizzigotti et al., 1997; Szejtli, J., 1987). Particularly, cyclodextrins and their derivatives, such as hydroxypropyl-β-cyclodextrin and carboxymethyl-β-cyclodextrin, have been used to remove contaminants by the formation of inclusion complexes or enhance the solubility of several compounds (Bizzigotti et al., 1997; Brusseau et al., 1997; Gao et al., 2006; Ko et al., 2000; Liang et al., 2007; McCray and Brusseau, 1998; Murai et al., 1998; Oláh et al., 1998; Szente and Szejtli, 1999; Wang and Brusseau, 1993, 1995a,b).

Certain surfactants possessing lipophilic characteristics such as alkylphenol ethoxylates (APEOs), nonyphenol ethoxylates (NPEOs), and nonylphenol (NP) may be entrapped into the cavity of cyclodextrins (Hoai et al., 2003; Szente et al., 1999). NPEOs are APEOs constituted by a core phenol substituted in para position, with a chain radical containing nine carbon atoms (Fig. 2) (Berryman et al., 2004; Crescenzi et al., 1995). APEOs and NPEOs have been extensively used in the preparation of household cleaning products, pesticides formulation, wetting and dispersing agents, and emulsifiers in the last 50 years (Li et al., 2004; Planas et al., 2002; Tsuda et al., 2000). Annual world production of APEOs has been estimated at approximately 300,000 tons, of which approximately 80% was nonylphenol ethoxylates (Berryman et al., 2004; Houde et al., 2002; Li et al., 2004). Of this amount, it has been estimated that about 60% was released to the aquatic environment (Naylor et al., 1992). The frequent use of APEOs has inspired a great interest in removing these nonylphenols from the environment due to the stability and toxicity of its biodegradation metabolites. Wastewater treatment may lead to the shortening of the ethoxylate chains of NPEOs, whereas aerobic degradation may transform NPEOs to nonylphenol carboxylic acids (NPECs) (Ahel et al., 1994). The biodegradation products (nonylphenol mono- and diethoxylates, and NPECs) may be completely biodegraded to nonylphenol, which is more resistant to biodegradation and more toxic than APEOs. NPECs and NP are dangerous endocrine disruptors that can affect the development of testes and cause the feminization of male fish, reproductive disorders, and prostate cancer (Blom et al., 1998; Brian et al., 2005; Giwercman et al., 1993; Jobling and Sumpter, 1993; Purdom et al., 1994; Routledge and Sumpter, 1996; Skinner, 2005; White et al., 1994). Therefore, the removal of NPEOs, NPECs, and NP from wastewater may have multiple advantages for the environment and human health.

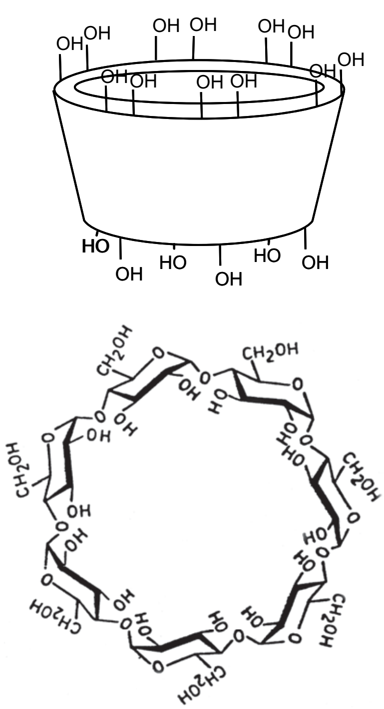

Fig. 1 – Scheme of structure of β-cyclodextrin.

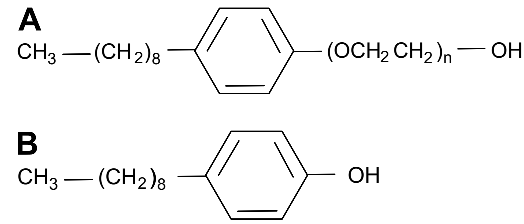

Fig. 2 – Scheme of general structures of (A) nonyphenol ethoxylates, and (B) nonylphenol.

The present study was undertaken to investigate the inclusion complexations of nonylphenol and nonylphenol 9 mole ethoxylate (NP9EO) with β-cyclodextrin (β-CD). Therefore, the inclusion complexes β-CD-NP and β-CD-NP9EO were characterized by mass spectrometry, surface tension, ultraviolet–visible (UV–vis) and Fourier transform infrared (FTIR) spectroscopies.

2. Materials and methods

2.1. Materials

β-Cyclodextrin (98%) and nonylphenol were purchased from Sigma–Aldrich Canada Ltd (Oakuill, Ontario), nonylphenol 9 mole ethoxylate from Univar Canada Ltd (Dorval, Quebec), methanol optima grade from Fisher Scientific Co. (Nepean, Ontario), and HPLC grade water from JT Baker (Philipsburg, NJ). All these products were used without additional purification.

2.2. Inclusion complexations

The inclusion complexations of NP and NP9EO with β-CD were effectuated by a method similar to that used for inclusion