

The effect of cationic, non-ionic and amphiphilic surfactants on the intercalation of bentonite



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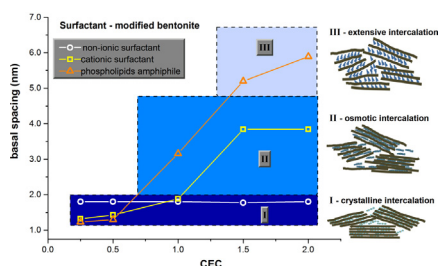
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HIGHLIGHTS

- Three intercalation regions of the bentonite interlayers according to the surfactant type.
- Non-ionic surfactant inhibited intercalation and changed interlayer conformation.
- Lecithin caused extensive bentonite intercalation and increased thermal stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Surfactant–clay interactions are key for the development of new clay applications and inorganic–organic nanocomposites. Bentonite, with montmorillonite as the principal clay mineral constituent, was modified with varying concentrations of hexadecyltrimethylammonium chloride (HDTMA), as a reference cationic surfactant, polypropylene glycol (PPG) 1200 and 2000, as non-ionic surfactants, and lecithin and Topcithin[®], as amphiphilic phospholipid surfactants, according to the cation exchange capacity (CEC). The modified bentonites were characterised by X-ray diffraction, thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectrometry, specific surface area and pore volume. Three intercalation regions have been identified depending on the surfactant. The non-ionic surfactant caused only a crystalline expansion of bentonite interlayers, while the cationic surfactant induced an osmotic intercalation. The amphiphilic lecithin derivatives intercalated more extensively with the bentonite matrix. The TGA and the FTIR spectra showed that, at lower concentrations, the PPGs and HDTMA adopted a disordered conformation that required more energy to degrade, while at higher concentrations, the surfactants were ordered in the interlayer space of the bentonite. The lecithin derivative surfactant had a greater thermal and conformation stability. The specific surface area reduced with increasing surfactant concentrations. This study highlights the effect of surfactant type on the interlayer space of montmorillonite in the perspective of developing novel clay functions.

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1. Introduction

Montmorillonite is a swelling clay whose basal spacing can be adjusted with the use of a surfactant. It is a clay species classified by a 2:1 clay minerals in the smectite group with a dioctahedral character [1]. Montmorillonite is a representative model for a planar, negatively charged colloid with high cation exchange capacity (CEC) [2]; CEC being the quantity of cations available for exchange.

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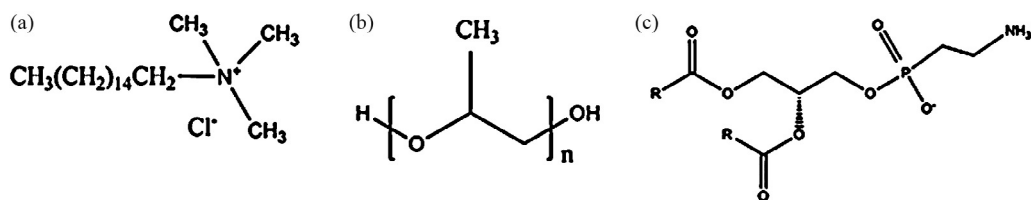


Fig. 1. Chemical structure of (a) hexadecyltrimethylammonium chloride, (b) polypropylene glycol (PPG) and (c) lecithin.

Smectite is a group that includes layered clay minerals with two silica tetrahedral (T) sheets bonded to one central alumina octahedral (O) layer, simplified to a 2:1 clay minerals [1,3]. The swelling of smectites occurs between two TOT layers in agglomerated systems. It is beneficial to intercalate a wide range of guest molecules, such as surfactants, polymers, proteins and dyes [4–7] and to reduce the transmissivity in barrier systems [8]. However, the high adsorption capacity of montmorillonite reduces the efficiency of surfactants, for example superplasticizers of cement paste [9]. Bentonite is a rock with montmorillonite as the main clay mineral constituent obtained by open pit mining [10], and it is mostly used as an industrial raw material for numerous applications such as ceramics, adhesives, catalysts, desiccants, cosmetics and pharmaceutical uses [11]. In geotechnical engineering, bentonite has a range of applications, from trench excavation [12] to pollution control [13].

In the early developments of hybrid inorganic–organic composites, modifications with quaternary alkylammonium ions were first developed to improve the compatibility with less polar matrices [4,5]. The basal spacing was found to increase with the concentration of surfactant dose according to the cation exchange capacity (CEC) [5,14,15], while the specific surface area diminished [16]. The modifications cause conversion of the silicate surface from hydrophilic to organophilic and also reduce the swelling behaviour [17]. The literature on modified clays is still dominated by studies on cationic surfactants. Cationic surfactant is used in environmental remediation [18], but they can be considered toxic [19] and they might not be applicable for certain large scale environmental and biomedical applications [20]. Although there is a large literature on the modifications of montmorillonite with surfactants, there is no specific comparative study with polypropylene glycol as a non-ionic surfactant and lecithin derivatives as amphiphilic surfactant as alternative to the cationic hexadecyltrimethylammonium chloride (HDTMA).

The intercalation of bentonite with non-ionic surfactants has a variety of applications in the oil industry [21,22]. Non-ionic surfactant based organo-bentonites are more chemically stable than cationic surfactant based ones, and greater interlayer spacings are achievable by hydrogen bonding between the oxide and the SiO₂ surface [23]. The interaction of bentonite with polypropylene glycol (PPG, also called polypropylene oxide), has not been studied extensively and there is no current consensus on its swelling effect. PPG has been used as a swelling agent for the synthesis of mesoporous materials [24], but is known from the oil and gas industry as a swelling inhibitor [21,22]. Recent molecular dynamics investigations support the hypothesis that non-ionic surfactants are swelling inhibitors [22,25]. Polypropylene glycols are also well-known components of shrinkage-reducing admixtures of concrete [26].

Lecithin possesses both hydrophilic and hydrophobic functional groups, thus it belongs to the group of amphiphilic phospholipid surfactants which have a wide range of applications, e.g. as a surface active agent in baked goods, food supplements and pharmaceuticals [27], as a component of drilling fluid [28] and of hybrid nanomaterials for drug and fragrance delivery [29,30], as an adsorbent for herbicide on clay–liposomes complexes for ground-water treatment [31], and for general biomedical applications [32].

Phospholipids are electrostatically attached to the silicate surface [33,34]. Amphiphilic surfactants are known for their greater montmorillonite basal spacing than the cationic surfactants [34,35], but the reasons are not well understood.

This study combines for the first time the analyses of the basal spacing, thermal behaviour and FTIR spectroscopy of sodium bentonite modified with HDTMA as well as with the less often reported PPG and lecithin derivatives.

2. Materials and methods

2.1. Materials

The clay mineral was sodium activated bentonite, composed of 80% montmorillonite, with a typical chemical composition of: SiO₂ 54.2%, Al₂O₃ 18.8%, Fe₂O₃ 5.0%, CaO 4.9%, MgO 3.7%, NaO 3.0%, K₂O 0.6%, TiO₂ 0.7% (obtained from Macromin Kentish Minerals, UK). It was preferred to a pure montmorillonite, because its composition is closer to those used in practical applications, especially in geotechnical engineering. Thus bentonite is the investigated material in this study, any reference to montmorillonite or smectite indicates other literature results.

The CEC of the sodium activated bentonite was 90 mequiv./100 g. Hexadecyltrimethylammonium chloride solution (HDTMA, CH₃(CH₂)₁₅N(CH₃)₃Cl (Fig. 1a), at 25% concentration, was chosen as a reference cationic surfactant with a molar mass of 320 g/mol, a density of 0.968 g/ml at 25 °C (obtained from Sigma–Aldrich, UK). It has a valence of one, thus it has one molar equivalent. It is toxic to aquatic life [19]. HDTMA intercalation of montmorillonite is well known and served as a reference point to compare with the polypropylene glycol (PPG) and the lecithin derivatives. Two PPGs with a unit formula of C₃H₈O₂ were tested, one at 1200 g/mol (obtained from Sigma–Aldrich, UK) and one at 2000 g/mol (obtained from VWR International, UK) (Fig. 1b). Both had a density of 1 g/ml. The lecithin (obtained from MP Biomedical, UK) was obtained from refined soy; the fatty acids were 70% L- α -phosphatidylcholine (C₁₁H₂₂NO₈P), the molecular mass was 760 g/mol (Fig. 1c) and one valence.

Topcithin[®] is a form of lecithin supplied by Cargill for larger scale applications in the food, cosmetic and oil industries. It was produced from non-genetically modified soy phospholipids and contained 12% phosphatidylcholine, 10% phosphatidylinositol, 8% phosphatidylethanolamine and 7% phosphatidic acid. The measured density of Topcithin was 0.998 g/cm³. Both lecithin and Topcithin[®] do not present a toxicological risk to humans and the environment.

2.2. Modified bentonite preparation

The bentonite was modified at 0.25, 0.50, 1.00, 1.50 and 2.00 CEC by adjusting the molar quantity of HDTMA, lecithin and Topcithin[®], while it was modified additionally at 0.05 and 0.10 CEC for the PPGs, due to their larger molecular mass. The CEC of the bentonite given to 90 mequiv./100 g, 1 CEC meant 90 mmol surfactant per 100 g of bentonite. Deionised water was added to the bentonite mixture to

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