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Hydrolysis-condensation kinetics of 3-(2-amino-ethylamino)propyl-trimethoxysilane

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ABSTRACT

The kinetics of the hydrolysis and self-condensation reactions of 3-(2-amino-ethylamino)propyl-trimethoxysilane (DAMS) were investigated by *in situ* ^{29}Si NMR spectroscopy using pure water and an alcoholic (80:20 w/w ethanol/water) solvent mixture as reaction media. In both media, the reactivity of the silane was strongly influenced by the pH of the medium during the initial stage of the reaction. The silanols produced by hydrolysis in water were much more stable than those produced in the alcoholic solvent mixture, the latter of which were susceptible to self-condensation, yielding siloxane bridges. The active silanol reactivity (SR), which is a simple parameter that reflects the silanol content in the solution as a function of the reaction time, was proposed for evaluating the reactivity of a solution of DAMS. SR was maintained at a good level (high silanol group concentration) when pure water was used as the reaction medium. The pH of the reaction appears to be the predominant parameter for determining the SR during the first 2 h, regardless of the reaction solvent.

1. Introduction

Organofunctional silanes are commonly used as surface modifiers in various industrial applications and have been particularly used in glass-based materials [1,2]. More recently, these alkoxysilanes have been successfully used for the surface modification of natural fibers, which bear surface hydroxyl groups [3–6]. Grafting of alkoxysilanes onto such hydroxyl-bearing surfaces often occurs via intermediate silanols, formed by the hydrolysis of silanes with water or atmospheric moisture. The silanols, once formed, either can be adsorbed onto the substrate, or may undergo self-condensation to yield polysiloxane structures. Grafting efficiency is maximized by promoting the hydrolysis reaction while limiting the self-condensation process, given that the latter phenomenon decreases the reactivity of the silane solution [1].

The conventional surface modification process is carried out in a mixture of organic solvent and water. The relative ratio of the solvents has a direct effect on the reaction yields (hydrolysis vs. self-condensation); in particular, the solvent composition affects the relative abundance of various species and the reactivity of the solution [7,8]. Many other parameters also influence the reactions between the alkoxysilanes and water [7], such as the temperature [9], pH [10], and concentration of the silane [11,12].

In most cases, both industrial applications and literature studies deal only with the preparation of 1% or 2% w/w silane solutions in mixed alcohol–water solvents [13,14]. The molar ratio of water added to the medium is generally rather low relative to the number of hydrolysable groups, with a maximum of 20% w/w water. Organic solvents are used to improve the miscibility between water and the silane as necessary [1].

NMR spectroscopy (especially, ^{29}Si NMR) has been reported to be a powerful tool for investigating the kinetics of the reactions occurring with organosilanes (both hydrolysis and self-condensation) [9,13,15-21]. Most current studies have been conducted at a concentration of 10% w/w to facilitate the detection of low concentration species and for fast reaction kinetics. This analytical technique is the only one that allows the direct *in situ* observation of the evolution of the ratios of the different silane-born structures in the medium, including transient species. For this purpose, a commonly used nomenclature refers to silane structures as being of the M, D, T, or Q types depending on the number of Si–O– bridges formed by the silicon atom studied; these notations correspond to 1, 2, 3, or 4 Si–O– bridges, respectively. Glaser and Wilkes [22] introduced a slightly different notation by adding the index “i” to the existing notation, where i is the number of siloxane (Si–O–Si) linkages attached to the silicon atom of interest. Therefore, when considering 3-(2-amino-ethylamino)propyl-trimethoxysilane (DAMS) belonging to the T family structure group, i is equal to 0 in the case of uncondensed silanes and silanols. Herein, the notations T^0_H and T^0_R are used to denote the silane and silanol units, respectively. For dimers or end chain units, i takes the value 1 (T^1). T^2 indicates parts of a linear chain, whereas T^3 is associated to totally condensed species belonging to a tri-dimensional network. The structures of the DAMS molecules corresponding to each of these notations are presented in Fig. 1. T^0_H and T^1 are considered as the most

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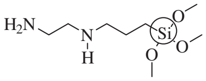
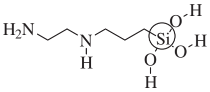
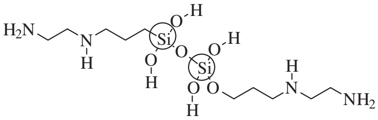
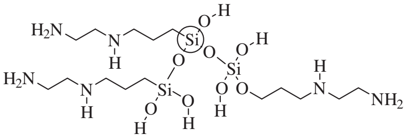
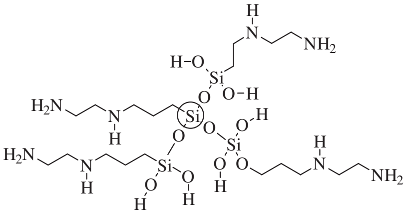
Reference under Glaser and Wilkes' [22] notation	Chemical structure
T^0_R **3-(2-amino-ethylamino)propyl-trimethoxysilane**	
T^0_H **3-(2-amino-ethylamino)propyl-silanetriol**	
T^1	
T^2	
T^3	

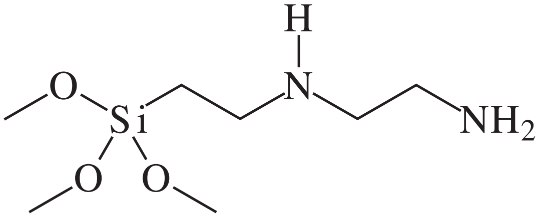
Fig. 1. Structure of DAMS and its hydrolysis and self-condensation products. The silicon atom of interest is encircled.

interesting species for reactions with OH-rich substrates because hydroxyl moieties remain available in these structures for linking with such surfaces. Compounds possessing T^2 groups are also theoretically reactive with OH-bearing surfaces; however, steric hindrance may impede such a reaction. Finally, the T^3 species, which are totally condensed, are unsuitable for surface grafting.

In situ ^{29}Si NMR spectroscopy has been particularly applied to the study of the behavior of γ-amino-propyl-triethoxy-silane (APES) and γ-diethylene-triamino-propyl-trimethoxy-silane (TAS), in water/alcohol solutions [23]. The high reactivity of aminosilanes makes them particularly interesting since it has been demonstrated that the presence of the amine functionality in these molecules produces a catalytic effect on the hydrolysis reaction in the presence of water. Moreover, aminosilanes exhibit excellent solubility in water, which could allow for the possibility of working in a purely aqueous medium; this in turn could offer important environmental advantages. This is particularly important within the context of the modification of natural fibers.

Based on the aforementioned considerations, our aim is to investigate the possibility of using aminosilanes for the modification of cellulose using pure water as a medium. Herein, the kinetics of the hydrolysis and self-condensation reactions of the aminosilane molecule, 3-(2-amino-ethylamino)propyl-trimethoxysilane (DAMS, structure below), in pure water were compared with the kinetics in an 80/20 w/w ethanol/water mixture. The effect of pH was evaluated in both media. The reactions were monitored by *in situ* ^{29}Si NMR spectroscopy for a period of 48 h.

To the best of our knowledge, there is currently only one report on amino-bearing silane in pure water; however, that study focused on blending [15]. The *in situ* observation of the hydrolysis and condensation structures formed by DAMS has been reported in one study; however, in that study, observations were made in an alcoholic medium only [16].



DAMS

2. Experimental

2.1. Materials

Reactions were carried out in two different media: (i) pure deuterium oxide was used as a model for a purely aqueous medium and (ii) a solution of deuterium oxide and ethanol-d_6 (20:80 w/w) was used as an aqueous alcoholic solvent. In both media, experiments were performed under two different pH conditions: (i) at an unmodified pH of 10.5 and (ii) at a pH of 4 after the addition of an adequate volume of glacial acetic acid. The choice of pH values was motivated by our previous studies involving other silane coupling agents, which showed that the self-condensation reaction was accelerated in basic pH, whereas acidic pH stabilizes the formation of silanol-bearing derivatives.