EFFECT OF THE SATURATION DEGREE OF A NANOCRYSTALLINE CELLULOSE AEROGEL WITH MEFENAMIC ACID ON THE PROBABILITY OF ITS REACTION WITH SUPERCRITICAL CARBON DIOXIDE WITHIN THE AEROGEL PORES

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In this work, we investigated the phenomenon of reaction blocking between mefenamic acid (MA) and carbon dioxide (CO_2) confined within the pores of a nanocrystalline cellulose (NCC) aerogel. The present work continues a series of our studies devoted to the conformational equilibria of MA and its chemical reactivity toward supercritical carbon dioxide ($scCO_2$), both in bulk solution and under conditions of aerogel confinement. In our recent work [1], we have found that the chemical reaction between MA and CO_2 can proceed via two distinct pathways: in bulk solution — nucleophilic attack by CO_2 on the MA carbonyl oxygen, and under the confined geometry of NCC aerogel pores — attack by CO_2 on the MA amino-group. In present work we checked if blocking the chemical reaction within the aerogel pores can be achieved by increasing the degree of pore saturation with the MA instead using the inhibitors. For this we increased the aerogel saturation degree with dopant by its impregnation at higher temperatures. It allowed us increasing the MA concentration retained in aerogel by one order of magnitude as compared to that achieved in [1]. A combination of low-temperature nitrogen sorption and IR spectroscopy revealed that with increasing aerogel saturation, the probability of forming an amorphous MA phase inside the aerogel pores increases, while the amount of retained CO_2 markedly decreases. In turn, the formation of the amorphous MA phase within the pores accompanied with arising the intermolecular hydrogen bonds between MA molecules – specifically those involving the amino-group. It is precisely this feature that acts as the key factor blocking the reaction proceeding through the amino-group attack. Moreover, we showed that the conformational equilibrium of MA released from MA-doped NCC aerogel differs from that observed in bulk MA/$scCO_2$ saturated solution. This divergence arises primarily from the combined effects of confinement within the pores of NCC aerogel and its ability to form hydrogen bonds with MA molecules retained inside them.

1. R.D. Oparin, M.A. Krestyaninov, D. V. Ivlev, A.A. Dyshin, M.S. Kuz'mikov, M.G. Kiselev, Reaction mechanism between carbon dioxide and mefenamic acid in saturated solution and within the confinement of a nanocrystalline cellulose aerogel, J. Mol. Liq. 435 (2025) 128146. https://doi.org/10.1016/J.MOLLIQ.2025.128146

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