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Aggregation and counter ion binding ability of sulfonatocalix[4]resorcinarenes in aqueous solutions

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Abstract

¹H NMR spectroscopy, ¹H NMR spin-lattice relaxation, conductivity and pH-metric titration data have been used to study the aggregation and counter-ion binding of tetrasulfonatocalix[4]resorcinarenes with methyl (H₈XNa₄) and amyl (H₈YNa₄) substituents. The data obtained reveal the self-aggregation of H₈YNa₄ driven by hydrophobic interactions. The NMR relaxation data indicate that Gd³⁺ is bound by both H₈XNa₄ and H₈YNa₄. The Gd³⁺ ions were found to induce the aggregation of H₈YNa₄ with critical association concentration (CAC) value less than in case of its self-aggregation. Using Gd³⁺ as a probe of counter-ion binding with the aggregate interface it was found out that binding of quaternary ammonium cations (QUATs) with H₈YNa₄ aggregates and SDS aggregates is quite different, while binding of inorganic ions by both types of aggregates is similar. The most outstanding peculiarity of QUATs binding with H₈YNa₄ aggregates is selective recognition of QUATs, possessing trimethylammonium group, detected by NMR relaxation method.

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1. Introduction

One of the objectives of supramolecular chemistry is to mimic nature in its development of specific receptor molecules [1]. The specificity of recognition phenomena in turn is resulted from multiple weak forces, coming into play in supramolecular self-assembled systems [2]. Therefore, a water-soluble calixarenes and resorcinarenes capable to self-organization are of particular importance. The self-assembly of amphiphilic particles in aqueous solution changes many physical chemical properties of solution, that is why various methods have been used to study the self-aggregation phenomena, including NMR spectroscopy [3], NMR relaxation [4], electrical conductivity [5], surface tension [6,7], self-diffusion measurements [8], small-angle neutron scattering [9]. The self-assembly of an amphiphilic calixarenes results in the formation of the charged aggrega-

tes [10–12] (anionic or cationic), that is why binding with counter-ions plays major role in their stability. For example, the binding of counter-ions to alkyl sulfate micelles resulting in the efficient screening of surfactant's charge and thus mediating sphere-to-rod transition of micelle architecture [13–15] is driven by electrostatic interaction, while the adsorption of 1,3-dioctyloxy-calix[4]arene-crown-6-ether at the micellar interface of cesium dodecylsulfate provides most efficient screening of surfactant's charge under cesium counter-ions entrapping [9]. Therefore, a binding of self-aggregated water-soluble calixarenes with counter-ions is of great importance, because it should differ from the counter-ion binding in well-known alkyl sulfate anionic micelle.

The water-soluble sulfonatocalix[4]resorcinarene (H₈XNa₄) is known as receptor for both organic and lanthanide ions [16,17]. The sulfonatocalix groups are able to bind lanthanide ions and the π -donor hydrophobic cavity provides the opportunity of an inclusion of organic cations [17]. Trivalent lanthanides have attractive spectroscopic

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