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Solution behavior of mixed systems based on novel amphiphilic cyclophanes and Triton X100: Aggregation, cloud point phenomenon and cloud point extraction of lanthanide ions

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ABSTRACT

Aggregation and cloud point (CP) behavior, as well as CP extraction of lanthanide ions have been studied for novel non-ionic cyclophanic surfactants with the varied length of polyoxyethylene and hydrophobic moieties (CnEm) based on calix[4]arene platform in their mixtures with Triton X100 (TX100). The dynamic light scattering data reveal the contribution of the large size lamellar or stack like mixed aggregates in CnEm–TX100 solutions. Aggregation and CP behavior of TX100–CnEm mixed solutions are quite different from those of conventional non-ionic surfactants. The effect of the hydrophobic substituents and polyoxyethylene chains length of CnEm on the CP extraction of La(III), Gd(III) and Lu(III) in the mixed TX100–CnEm micellar solutions is discussed in the correlation with their aggregation and cloud point behavior. The obtained data elucidate the cyclophanic structure of CnEm as the key reason of the formation of large lamellar-like aggregates with TX100, exhibiting the unusual CP behavior and CPE efficiency.

1. Introduction

Cloud point behavior of aqueous solutions of non-ionic surfactants has gained much attention due to its practical and fundamental significance [1–10]. The CP phenomenon is the temperature induced phase separation into aqueous and surfactant-rich phases. This phenomenon is attributed to a dehydration of the polyoxyethylene chains at a definite temperature, which is called CP temperature. The latter value characterizes the key property of non-ionic micellar solutions, closely connected with the surfactant structure [10–14]. The effect of the mixed aggregation on CP phenomenon is also highlighted in the literature [11,15,16].

It is well known that the regularities of self-aggregation well established for conventional surfactants are not valid for biological and pharmacological compounds with indistinctly separated hydrophilic and lipophilic molecular fragments [17]. In particular conventional surfactants associate through the so-called closed model, resulting in the formation of rather small micelle-like aggregates, while biorelevant amphiphiles associate through alternative mechanism, i.e. the open model, resulting in the formation of lamellar or stack structures [17]. The synthesis of diverse amphiphilic molecules on the basis of calix[4]arene platform results in the development of new type of amphiphiles, which can be regarded as the intermediate point between conventional surfactants and some of biological compounds. The specific aggregation mode of cyclophane based amphiphiles is quite different from that of conventional surfactants, which is highlighted in literature [18–21]. Our previous work [22] elucidates the unusual "head-to-tail" self-aggregation mode for watersoluble amphiphilic calix[4]resorcinarene with sulfonatomethyl groups on the upper rim (head) and pentyl radicals (tails) on the lower rim. The hydrophilic and hydrophobic contributions are less strongly marked in this case, indicating that the open model of the aggregation is more suitable. Though the peculiarities of the self-aggregation mode for various watersoluble calixarenes are widely represented in literature [18–24], the relationship between the aggregation mode and colloidal properties, such as cloud point behavior is not properly established.

The cloud point extraction (CPE) procedure is one of the most important applications of cloud point phenomenon in aqueous solutions of non-ionic surfactants [1–6]. The pre-concentration and extraction of lanthanide ions is of particular importance in recent decades due to their extensive application in medicine and technology [6]. Therefore the present work introduces amphiphilic calix[4]arene molecular platform as new candidate for CPE strategy. The particular interest to these aggregates is conditioned by the peculiar structure of calixarenes, providing the pre-organiza-

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