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Complexes of 1-Hexadecyl-4-aza-1-azoniabicyclo[2.2.2]octane Bromide with Transition Metal Nitrates. Micelle-Forming, Solubilizing, and Adsorption Properties

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Abstract—Amphiphilic complexes of 1-hexadecyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide (D-16) with nitrates of transition metals (La^{3+}, Cu^{2+}, Ni^{2+}, and Co^{2+}) have been synthesized and characterized. Absorption spectrophotometry in the UV, visible, and IR regions, as well as ^1H NMR spectroscopy, have been employed to study their spectral properties in water and organic media. Adsorption properties and micelle-forming and solubilizing abilities of the amphiphilic complexes have been investigated in aqueous solutions by the methods of tensiometry and conductometry, as well as by solubilization of a water-insoluble dye (Orange OT). The values of the critical micelle concentration, adsorption parameters at a water/air interface, and solubilization capacity *S* of complex micelles have been determined. It has been shown that the most pronounced decrease in the critical micelle concentration (as large as two to three times) and differences in the adsorption characteristics and the *S* values as compared with those of ligand D-16 are observed for complexes of copper and lanthanum. The *S* values for these complexes are 1.3–2.5 and 3–6.5 times higher than those for D-16 and cetyltrimethylammonium bromide, respectively.

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INTRODUCTION

Cationic surfactants (CSs) are among the most in-demand and promising surfactants. Owing to their specific structure, namely, the presence of positively charged head groups, the structures of cationic centers (N, S, or P) and substituents located at them, hydrophobicity, the number of hydrocarbon radicals, and types of counterions, CSs possess high adsorption and biological activities and pronounced anticorrosion, catalytic, antistatic, and complexation properties. CSs are, for all these reasons, used in medical and sanitary practice, as well as in the oil-extracting, cosmetics, and fabric industries [1–4].

The incorporation of a metal fragment into an amphiphilic molecule is a method for modifying the structure of CSs with the aim to enhance their functional properties. This approach makes it possible not only to affect the properties primordially inherent in CSs, i.e., their surface activity and ability to form aggregates of different morphologies and bind (solubilize) hydrophobic substances, but also to enhance the redox activity of a compound and change the value of its charge.

We have synthesized and, using a set of physicochemical investigation methods, studied the properties of new metal-containing surfactants based on monoquaternized (hexadecyl-containing) derivative of 1,4-diazabicyclo[2.2.2]octane (DABCO) and nitrates of transition metals (Cu^{2+}, Ni^{2+}, Co^{2+}, and La^{3+}). 1-Hexadecyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide (D-16) was selected as a ligand because of its pronounced tendency toward the formation of aggregates, which have high solubilization capacity, catalytic and biological activity, and relatively low toxicity [5–8]. Moreover, the presence of the tertiary nitrogen atom in the bicycle head group of D-16 enables this surfactant to form complexes with metals. This all makes it possible to obtain new amphiphilic compounds capable of forming various supramolecular ensembles and exhibiting a high polyfunctional activity.