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Micellization of alkylated 1.4-diazabicyclo[2.2.2]octane by nuclear magnetic resonance technique using pulsed gradient of static magnetic field

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ABSTRACT

A phenomenon of micellization of 4-aza-1-tetradecyl-1-azoniabicyclo[2.2.2]octane bromide (AB-14) in aqueous solution has been studied by the methods of nuclear magnetic resonance using magnetic field pulse gradient and fluorimetry. The critical micelle concentration is determined; concentration dependences of percentage of free AB-14 molecules and those associated with micelles as well as radii of micelles and numbers of their aggregation are established. Effect of external and internal translational diffusion of molecules on lifetime of AB-14 molecules in micelles is investigated.

1. Introduction

Studying the nature of interaction of the surfactant (SA) molecules with a dissolvent is one of the main purposes of the micellization theory being reduced to revealing a role of these interaction in both a micellization and an exchange of free and aggregated molecules of SA and an arrival to an equilibrium state between the processes of aggregation and disaggregation of micelles. A method of nuclear magnetic resonance with magnetic field pulse gradient (NMR-MFPG) is largely used in solving these problems. By means of this method, it is possible to determine self-diffusion coefficients (SDC) of the free SA molecules in a solution and those associated in micelles, a critical micelle concentration (CMC), a percentage of free SA molecules and the micelle-forming molecules (MFM), sizes of micelles and a number of their aggregation.

A fast molecular exchange takes place between the free SA molecules and the SA molecules of micelles. The lifetime of a SA molecule makes 10^{-5}–10^{-7} s in a micelle [1–3]. At the same time, the micelles themselves are not long-lived formations: they can both disintegrate and arise again. A time of half-decay of micelles takes the value within the limits of several milliseconds up to several seconds.

The "drop-wise" model of micelles assumes that their geometrical shape is spherical at small concentrations of the SA [4]. It has been shown by thermodynamic and experimental studies that the micelles seem to be liquids: molecules of SA are movable in micelles as in a usual liquid [2]. It is confirmed by the line width of fine NMR spectra of surfactant solutions, which does not change by transferring a solution from a nonmicellar to a micellar state.

The present work has as its objects to examine by using the proton NMR-MFPG method and fluorimetry the concentration dependence of the self-diffusion coefficient of 4-aza-1-tetradecyl-1-azoniabicyclo [2.2.2]octane bromide (AB-14) in deuteroxide solution for both kinds of the SA — outside the micellar formations and inside them, the distribution of surfactant molecules on these kinds, the dependence of the size and the number of aggregation of micelles, the role of external and internal diffusion of surfactant molecules in the process of exchange between their different kinds.

2. Experimental and theoretical procedures

2.1. Chemicals

Bicyclical surfactant AB-14 (Scheme 1) has been synthesized from a solution of 1,4-diazabicyclo[2.2.2]octane and tetradecyl bromide upon a procedure offered in refs. [5,6]. The deuterated water with ^2H isotope content of 99.5% has been taken in order to explore the desired solutions. Cetylpyridinium bromide (CPB) (AppliChem, BioChemica, Germany),

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