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The physicochemical properties of CTAB solutions in the presence of α-tocopherol

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ABSTRACT

The electrolytic conductivity, electrophoretic mobility and zeta potential (LDV - laser Doppler velocimetry method) as well as the particles size distribution (DLS - dynamic light scattering method) were determined in the cetyltrimethylammonium bromide (CTAB) solutions (0.25–25.00 mM) at different concentrations of α-tocopherol (0–11.6 mM). The measurements were made at 25 °C and 30 °C. It was found that α-tocopherol (vitamin E) modifies the physicochemical properties of CTAB micellar solutions – the potential carrier of bioactive substances. The electrolytic conductivity of CTAB solutions was lowered by the addition of α-tocopherol. Particularly, the effect was observed in the concentration range 0.25–2.5 mM, i.e. in the vicinity of CMC. The critical micelle concentration (CMC) of CTAB solutions determined from the conductivity data decreased with the increasing vitamin E content due to the mixed aggregates formation. At the same time the electrophoretic mobility and zeta potential increased as a result of higher degree of the mixed aggregates dissociation. This effect was observed for all surfactant concentrations at both temperatures. The hydrodynamic diameter of mixed CTAB/α-tocopherol particles increased from 7–8 nm for the CTAB solutions to 50–60 nm for those containing vitamin E. The information about the aggregates size and their electrokinetic properties can be useful in predicting the encapsulation of biomolecules in the surfactant micelles and their transport by different membranes.

1. Introduction

Vitamin E is often used as a component of different pharmaceuticals and cosmetic products. There are many different forms of vitamin E. The most active of them is α-tocopherol commonly used as an effective antioxidant in the protection of cellular membranes from lipid peroxidation by free radicals. It acts synergistically with the other antioxidants such as vitamins A and C in preventing photoageing and skin photocarcinogenesis [1]. Alpha-tocopherol possesses anti-inflammatory properties, promoting wound healing [2]. On the molecular level, vitamin E affects the transcription of inflammatory genes. Its activity is related to the modulation of signaling pathways involved in upregulation of genes and the inhibition of the activity of enzymes involved in eicosanoid biosynthesis. In the case of α-tocopherol, the second mechanism is primary [3]. The reactive oxygen and nitrogen metabolites, eicosanoids and cytokines belong to the substances which are overproduced in the inflammatory state. Anti-inflammatory activity of vitamin E includes free-radicals scavenging, inhibition of cyclooxygenase-2 (COX-2) expression and lowering the C-reactive protein (CRP) level [4,5]. Additionally, vitamin E can enhance the antitumor activity of drugs [6]. Within the cell, α-tocopherol partitions into the hydrophobic core of the cell membrane. This is due to its very low solubility in water [7,8]. The precise locations and arrangements of α-tocopherol molecules in biological membranes are unknown. However, the model investigations indicate that they are oriented with a long axis parallel to the lipid hydrocarbon chains [9].

There are many ways of delivering vitamin E to the human organism. Selection among them depends on the detected deficiencies and the patient's individual requirements. In cosmetology, dermatology and pharmacy, micro/nano-emulsions are often used as the carriers of active substances, especially in transdermal transport [6,10,11]. Currently, there is an observed tendency to minimize the size of the domains of active substances present in the specimens and create, e.g., a nano-emulsion, to ensure the effectiveness of their action. This should result in an increase in their bioavailability. Amphiphilic substances (like surfactants) can be used in these systems as drug carriers [12]. Cetyltrimethylammonium bromide (CTAB) is a cationic surfactant, which additionally shows antimicrobial activity [13–15]. It occurs in pharmaceutical investigations, e.g., as a stabilizer of emulsion or a

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compound used in encapsulation [16,17]. The molecules of α-tocopherol are mainly hydrophobic. Hydrophilic properties due to the presence of a hydroxyl group in the aromatic ring are weak [18]. As a consequence, α-tocopherol is poorly-soluble in water [9].

On the nanoscale the penetration of active particles through the skin, their biodistribution, rate of excretion and toxicity can be evaluated from the analysis of their properties, such as shape, size, surface charge and surface composition. Many modern analytical methods like dynamic light scattering (DLS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) are involved in the evaluation of morphological properties of the systems containing bioactive substances [19]. Some authors have also investigated electrical properties of the systems used as food components, cosmetics or pharmaceuticals to obtain information about their composition and stability [6,17,20–22].

The aim of this paper was to investigate the interfacial and bulk properties of a cationic surfactant (cetyltrimethylammonium bromide, CTAB) solution in the presence of α-tocopherol in a wide range of the CTAB to α-tocopherol ratios at two temperatures. This was accomplished by measuring electrolytic conductivity, electrophoretic mobility and particle size. Studies were carried out not only to investigate the solubilization of vitamin E in the CTAB aggregates but also to determine physicochemical properties of the system.

2. Materials and methods

2.1. Materials

Cetyltrimethylammonium bromide (CTAB) and α-tocopherol (vitamin E) were purchased from Sigma Aldrich (Germany). The reagents were analytical grade and used as received. Redistilled filtrated (Whatman Anodisc Membrane Filter with 0.02 μm pores size) water with the electrolytic conductivity of 0.11 10^{-2} mS cm^{-1}, was used for preparation of the solutions.

2.2. Preparation of the surfactant solutions

CTAB solutions at 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 2.00, 4.00, 6.00, 12.00 and 25.00 mM concentrations were prepared by dissolving an appropriate amount of surfactant in water.

Alpha-tocopherol was added to these solutions to obtain the concentrations equal to 0.3, 0.7, 1.3, 1.7, 2.2, 2.9, 5.8 and 11.6 mM. In this way the systems with different molar ratios of CTAB to α-tocopherol (see Table S1 in Supporting Material) were obtained. All the samples were mixed vigorously and then conditioned for 24 h at a temperature of either 25 or 30 °C (±0.1 °C) while gentle stirring.

For 1.00 mM and 25.00 mM CTAB concentrations and the highest vitamin E content (Fig. 1) the amount of solubilized fraction was evaluated by weight. In the photos of samples 1 and 3 only a narrow beam of laser light can be seen which is characteristic of a microemulsion system. For samples 2 and 3 the bright cone of scattered light (called the Tyndall cone) is observed because of light scattering by colloidal particles. In addition, for sample 2 unsolubilized vitamin E can be seen.

As a result, it was possible to determine the minimum CTAB/α-tocopherol mole ratio which was needed for the total solubilization of vitamin E (Table S1).

2.3. Determination of particle size distribution

The dynamic light scattering method was used for determination of the particle size distribution in the systems [23–25]. The measurements were made by means of the Zetasizer Nano ZS (Malvern Instruments, UK) apparatus, equipped with a He—Ne laser beam (633 nm) as a source of light. The non-invasive back-scatter technique (173° backscatter detection) was involved. The apparent hydrodynamic diameters ($d_{h,app}$) of the aggregates were obtained from the analysis of the peak location on the particle size distribution by a number of particles to avoid possible influence of contaminants and differential polydispersity of studied systems. The particle size distribution by the intensity of scattered light, which is the main information derived from the dynamic light scattering method, is very sensitive to even a small number of incidental big particles. The mean hydrodynamic diameter (Z-average) is a representative value for the homogeneous systems at the Polydispersity Index (PDI) value lower than 0.5. The Polydispersity Index is a measure of the width of particles size distribution. Its value is within the range of 0 to 1. The higher the PDI, the less homogeneous the system is [23].

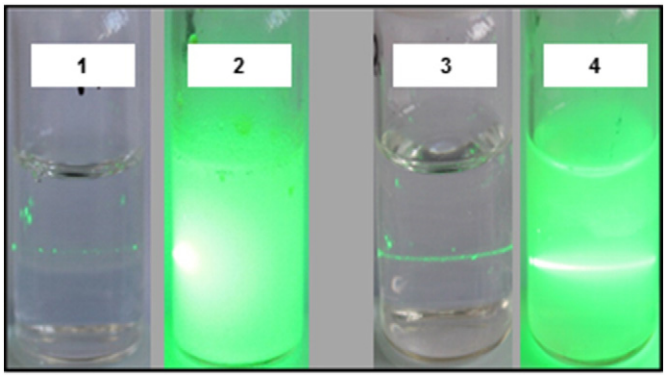

Fig. 1. Photos of the light scattering (laser wavelength 532 nm) by the samples of 1) 1.00 mM CTAB, 2) 1.00 mM CTAB/11.6 mM α-tocopherol (the real concentration of vitamin E: 7.3 mM), 3) 25.00 mM CTAB, 4) 25.00 mM CTAB/11.6 mM α-tocopherol (totally solubilized vitamin E).

The average result (i.e., the particles size distribution) was calculated by the software from six measurement repetitions. Each measurement comprised 12 sub-runs [23]. A multiple narrow mode (high resolution) was used as an analysis model for the data processing. This model is pointed out by the apparatus software as being appropriate for the samples where multi-peak particles size distribution could be obtained [26].

The input data for the dynamic light scattering technique are the dispersant viscosity (η) and the refractive index (RI) of both the dispersant and dispersed materials. For the micelles (with and without α-tocopherol) dispersed in the aqueous solution, the refractive index was that for the saturated CTAB aqueous solution at 25 °C (i.e., RI = 1.3478). For the dispersant (CTAB bulk solution) the values of η and RI were calculated by the apparatus software for the critical micelle concentration.

2.4. Measurement of electrophoretic mobility and electrolytic conductivity

The electrophoretic mobility distribution was determined by means of the Zetasizer Nano ZS device (Malvern Instruments, UK). The apparatus uses the LDV method (laser Doppler velocimetry) in connection with the PALS (phase analysis light scattering) technique and the fast and slow changes of electric field in the M3 system [26–28]. The electrokinetic (zeta) potential is calculated using the Henry's equation:

$$U_e = \frac{v}{E} = \frac{\varepsilon\zeta}{\eta} f(\kappa a) \quad (1)$$

where U_e denotes the electrophoretic mobility, v is the velocity of the dispersed particles, E is the electric field strength, ε is the permittivity of the dispersing medium, ζ is the zeta potential, η is the viscosity of the dispersing medium, and $f(\kappa a)$ denotes the Henry's function. For the aqueous systems the Smoluchowski approximation ($f(\kappa a) = 1$) is applied to the above formula [29].