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International Journal of Pharmaceutics 353 (2008) 52–55

INTERNATIONAL JOURNAL OF PHARMACEUTICS

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The spectrophotometric study of the binding of vitamin E to water + dimethyl sulfoxide and water + diethyl sulfoxide containing reversed micelles

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Received 24 July 2007; received in revised form 25 September 2007; accepted 9 November 2007
Available online 17 November 2007

Abstract

The effect of dimethyl sulfoxide (DMSO) and its nearest homologue diethyl sulfoxide (DESO) as a polar cosolvents on the binding of vitamin E to water + DMSO (DESO) containing reversed micelles of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) has been investigated by a spectrophotometric method.

The results suggest that compare with water without organic cosolvent-containing reversed micelles in this case an increase of binding constant of vitamin E in reversed micelles takes place.

The results obtained shown that with the addition of DMSO and DESO it will be possible to monitoring a penetration of vitamin E into micellar core.

Keywords: Vitamin E; Reversed micelles; Dimethyl sulfoxide; Diethyl sulfoxide; UV–vis spectroscopy

1. Introduction

It is well known that the antioxidant action of vitamin E significantly depends upon its location in the membrane bilayer (Fukuzawa et al., 1981; Burton and Ingold, 1986; Niki, 1989). On one hand the phenolic hydroxyl group of vitamin E acts as a capture of peroxyl radicals. Recently, on the basis of numerical kinetic investigation, it was shown that the pro-oxidant activities of vitamin E mostly due to the reduction of hydroperoxides by vitamin E (Tavadyan et al., 2007). On the other hand the existence of a long hydrophobic phytyl side chain allows one to monitor the location of vitamin E in the membrane bilayer and hence to vary its antioxidant action.

One of approaches to study such types problems is the application of surfactants leading to the formation of water-containing reverse micelles. In this respect it is worthy to note that an elegant approach based on the spectrophotometric method has been developed (Ceraulo et al., 1999; Avellone et al., 2002) to evaluate the distribution of vitamin E between apolar organic (heptane) and water containing reversed micelles of sodium bis(2-ethylhexyl) sulfosuccinate (AOT). The main result of that works was that for solely water as polar medium containing reversed micelles the increase of the size of the water domain leads to the decrease of Nernstain distribution constant (K).

In this work instead of just water as a polar solvent a mixture of water with DMSO and DESO has been used. Our interest to study these systems arises from various reasons. Recently we have shown that not only DMSO but also DESO reveal biomedical significance (Markarian et al., 2004, 2006). Also on the basis of FTIR studies it has been shown that H-bonded intermolecular complex formation between vitamin E and DMSO (DESO) occurs. Moreover, from the analysis of IR data it was concluded that DESO compare with DMSO forms more stronger complex with vitamin E (Melik-Ohanjanyan et al., 2006). On the other hand it was shown that both DMSO and DESO have significance influence on micellization of sodium dodecyl sulfate in aqueous solutions (Markarian et al., 2005a). Moreover, the aggregation numbers and radii of micelles, the hydrophilic group area, and the parameters of

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doi:10.1016/j.ijpharm.2007.11.019

critical compaction of micelles have been calculated from the data on fluorescence quenching (Harutyunyan and Markarian, 2007).

2. Materials and methods

Vitamin E (97%) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT 98%) obtained from Sigma–Aldrich, and *n*-heptane from Macrochem, Holland. DESO was prepared and purified according to the literature (Markarian and Tadevosyan, 2002), distilled under vacuum and stored on molecular sieves. DMSO was commercially available from LACHEMA N.P. Brno.

The micellar solutions were prepared by weight dissolving AOT in heptane. Vitamin E was added to these solutions in order to obtain a solubilizate molal concentration of about $1.4 \times 10^{-4}\,\mathrm{mol\,kg^{-1}}$. The same ratio, of different polar solvent (water, water + DMSO, DESO mixtures) to AOT, *R*, equals to 10 was obtained by adding appropriate amounts of water and water + sulfoxide mixture solvent to the vitamin E/AOT/heptane systems.

The UV–vis spectrophotometric determinations were carried out with a Specord 50PC spectrophotometer in the wavelength range from 200 to 360 nm. All measurements were performed at constant temperature equal to $25.0 \pm 0.3\,°\mathrm{C}$ using a thermostating device (LAUDA A100) attached to spectrophotometer. As a background it was used the polar solvent/AOT/heptane systems at the same composition.

3. Results and discussion

It has been considered (Avellone et al., 2002) that UV–vis absorption spectroscopy is a suitable technique to provide direct information on the location of vitamin E in the water/AOT/heptane system. UV absorption band of vitamin E (α-tocopherol; Fig. 1) as an aromatic group-containing compound exhibits fine vibrational structure in non-polar solvents, such as heptane or cyclohexane. On the other hand, in relatively polar solvent chloroform and in methanol the fine structure is vanished and just broad absorption is observed. These observations provided to develop an elegant approach for studying the local microenvironments of vitamin E in micelles and membranes. Particularly, (Avellone et al., 2002) have quantitatively described the partitioning of vitamin E between water containing reversed micelles and organic solvent (heptane) on the basis of monitoring the intensities of the absorbance ratio (*S*) at two appropriately selected wavelengths (292 and 298 nm).

$$S = \frac{\varepsilon_{292}}{\varepsilon_{298}} \tag{1}$$

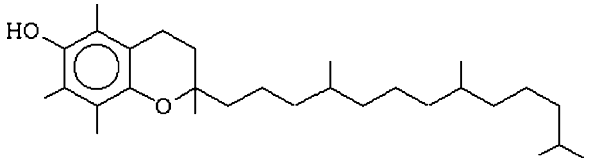

Fig. 1. Molecular structure of vitamin E.

where the experimental *S* value results from the contribution of the fraction of vitamin E solubilized in micelles (X_m) and in the organic solvent ($1 - X_\mathrm{m}$):

$$S = X_\mathrm{m} S_\mathrm{m} + (1 - X_\mathrm{m}) S_0 \tag{2}$$

where S_m and S_0 are the *S* values when vitamin E is totally solubilized in the reversed micelles and in the pure organic solvent, respectively.

Further treatment (Avellone et al., 2002) with involving of distribution constant (*K*) of vitamin E between the organic and micellar pseudo-phases

$$K = \frac{n_\mathrm{m}}{n_0 m_\mathrm{s} P_\mathrm{A}} \tag{3}$$

results in the following equation:

$$S = S_0 + \frac{(S_\mathrm{m} - S_0) K P_\mathrm{A} m_\mathrm{s}}{1 + K P_\mathrm{A} m_\mathrm{s}} \tag{4}$$

In Eqs. (3) and (4) n_m and n_0 are the moles of the solubilizate in the micellar and in the organic phases, m_s the molal concentration of the surfactant (AOT) and P_A is the surfactant (AOT) molecular weight (expressed in kg).

In our case when instead of alone water as a polar solvent water + DMSO (DESO) mixtures have been used the question regarding the behavior of organic cosolvent and hence the structure of micellar solution is rising.

In principle, for AOT/oil/(water + organic cosolvent) reverse micelles one can consider a possibility of organic cosolvent partition between micellar phase and bulk solvent which depends particularly on the polarity and type of organic cosolvent (Lee et al., 2004; Walderhaug and Johannessen, 2006). However, from the results obtained by (Walderhaug and Johannessen, 2006) it follows that the higher polarity of alcohol as an organic cosolvent the more alcohol remains in core of micelle.

Thus it is reasonable to assume that for DMSO (DESO) containing solutions this tendency is more emphasized according to their values of dielectric constants (ε): 46.6 for DMSO and 44.1 for DESO (Gabrielian and Markarian, 2004) which are higher than those for methanol and ethanol: 32.6 and 24.5, respectively, at 20 °C. Moreover, the peculiar strong intermolecular interactions between sulfoxides' and water molecules, especially in the concentration range used in this work provide an additional background to assume that in fact DMSO (DESO) are remaining in the micellar core. In addition one has to take into account that the solubility of DMSO and DESO in heptane is negligible. Thus it is reasonable to suggest that high values of dielectric constants on the one hand and structural peculiarities of water + DMSO (DESO) mixtures on the other hand allows one to treat the results on the basis of the above presented model.

We recorded the UV-spectra for all DMSO (DESO)/water mixtures, at fixed *R* equals to 10, with the increase of AOT concentration ($\mathrm{mol\,kg^{-1}}$). Our investigations were restricted with one fixed $R = 10$ as we are interested to reveal the effect of polar cosolvent DMSO and DESO as well as due to restricted solubility of vitamin E in aqueous solutions of these sulfoxides.

The spectra obtained for the system DMSO/water and DESO/water as polar mixed solvent with 1:1 volume ratio with

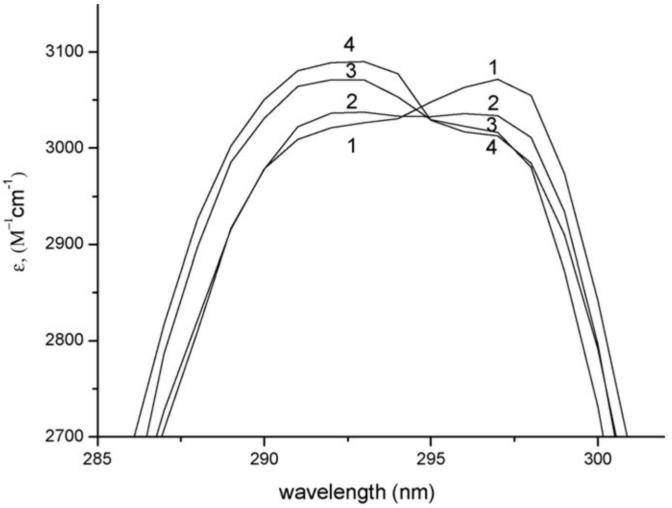

Fig. 2. UV spectra of water + DMSO/AOT/*n*-heptane microemulsions at 1DMSO/1H_2O volume ratio and fixed $R = 10$ at various AOT concentrations: (1) $m_{AOT} = 0.106\,mol\,kg^{-1}$; (2) $m_{AOT} = 0.227\,mol\,kg^{-1}$; (3) $m_{AOT} = 0.530\,mol\,kg^{-1}$; (4) $m_{AOT} = 0.956\,mol\,kg^{-1}$, $t = 25\,°C$.

AOT/*n*-heptane at fixed *R* value ($R = 10$) and various AOT concentrations are shown in Figs. 2 and 3. As it follows from these figures with the increase of the AOT concentration the rising of lower wavelength band takes place indicating the increase of solubilized amount (X_m) of vitamin E. The same picture is observed for 1DMSO:5water mixed solvent as polar solvents.

It should be noted that for high content of DMSO (DESO) the systems are not suitable for spectroscopic measurements because of non-homogeneity of solutions.

This observations are similar with those reported earlier for the system water/AOT/*n*-heptane at $R = 10$ (Avellone et al., 2002).

Although we kept $R = 10$ fixed, however it should be noted that, in fact the DMSO (DESO)/water mixtures exhibit strong deviations from ideality, e.g. excess molar volumes are negative over the whole range of composition (Markarian et al., 2005b). Therefore, it is clear that the polar sulfoxide/water mixture encapsulated into the micellar core is characterized with less volume. Obviously, on the other hand the existing competitive interactions occurring in this system will have certain effect on the hydration degree of the surfactant head groups as well.

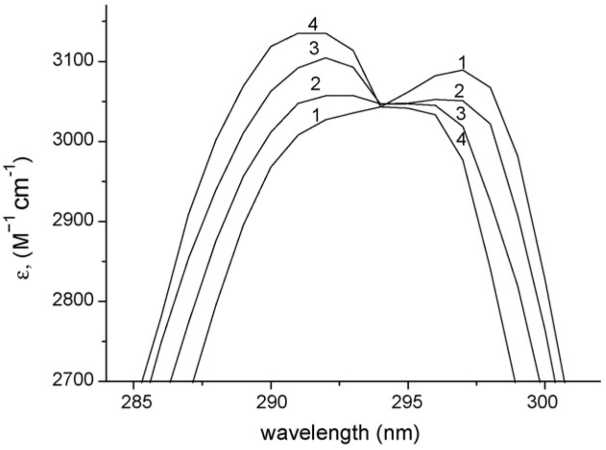

Fig. 3. UV spectra of water + DESO/AOT/*n*-heptane microemulsions at 1DESO/5H_2O volume ratio and fixed $R = 10$ at various AOT concentrations: (1) $m_{AOT} = 0.106\,mol\,kg^{-1}$; (2) $m_{AOT} = 0.227\,mol\,kg^{-1}$; (3) $m_{AOT} = 0.530\,mol\,kg^{-1}$; (4) $m_{AOT} = 0.956\,mol\,kg^{-1}$, $t = 25\,°C$.

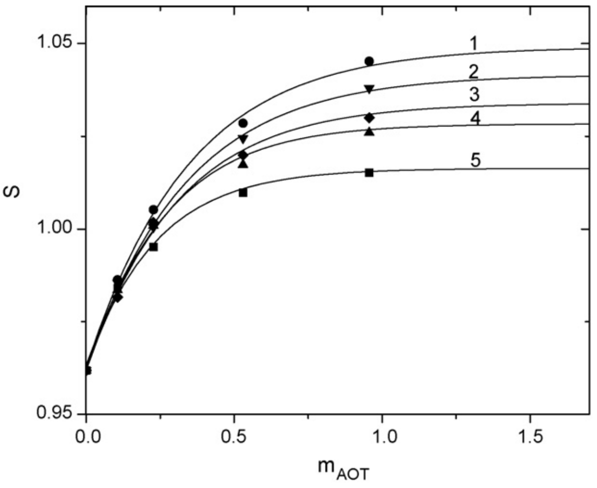

Fig. 4. Typical spectrophotometric data (*S*, m_{AOT}) and fitting curves of vitamin E in polar phase/AOT/*n*-heptane at two selected *R* values (5 $R = 0$, 1–4 $R = 10$), polar phase: (1) H_2O, (2) 1DMSO/5H_2O, (3) 1DESO/5H_2O, (4) 1DMSO/1H_2O, $t = 25\,°C$.

A non-linear regression analysis of Eq. (4) gives to dependences depicted in Fig. 4. The derived quantities are summarized in Table 1.

As it follows from Table 1 in microemulsions with the addition of DMSO or DESO to the polar phase an increase of distribution constant (*K*) takes place. Thus one can conclude that in the presence of sulfoxide promotes the binding ability of vitamin E and the increase of solubilized amount of vitamin E in micelles. To interpret this observation one has to take into account several reasons.

Because of the competitive strong intermolecular interactions between sulfoxides and water molecules (Markarian et al., 2005b) a less hydration of the surfactant head groups occurs. The latter causes a decrease of the size of the water/DMSO (DESO) domain encapsulated within the reversed micelles. As a result the solubility of vitamin E in micelles is increased.

In addition, one cannot exclude a direct interaction between vitamin E and sulfoxide's molecule through H-bond mechanism. The latter is more pronounced for DESO containing system as in this case a more strong H-bonded complex is formed (Melik-Ohanjanyan et al., 2006).

Table 1
Fitting parameters for partitioning of vitamin E polar phase-containing reversed micelles (at fixed $R = 10$) and apolar organic solvent, heptane ($t = 25\,°C$)

R	Polar phase	S_m	*K*
0	–	1.017 ± 0.001	10.1 ± 1.1 (10.6 ± 2.9)[a]
10	H_2O	1.049 ± 0.002	6.3 ± 0.1 (6.8 ± 0.7)[a]
	1DMSO/5H_2O	1.042 ± 0.001	6.7 ± 0.6
	1DMSO/1H_2O	1.028 ± 0.002	7.9 ± 0.3
	1DESO/5H_2O	1.034 ± 0.001	7.2 ± 0.2

[a] Data presented by Avellone et al., 2002.

We believe that the above-mentioned factors provide an appropriate explanation for the observed phenomenon.

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