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# α-Tocopherol/AOT/alkane/water system

## Calorimetric studies

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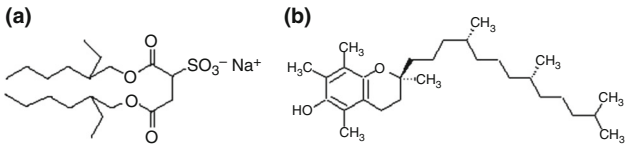
**Abstract** In this paper the calorimetric studies on α-tocopherol/AOT/alkane/water systems are presented. Structural representations of surfactant AOT (a) and α-tocopherol (b) are shown below.




α-Tocopherol (antioxidant) is a form of vitamin E that is preferentially absorbed and accumulated in humans. AOT is an anionic type of surfactant. Its molecule contains two non-polar hydrocarbon tails connected to the polar head. The paper contains new experimental data of heat of mixing ($Q$) for heterogeneous system α-tocopherol/AOT/n-alkane with and without water measured at 309.2 K. The heat of mixing for AOT (sodium bis (2-ethylhexyl) sulfosuccinate) and α-tocopherol solutions in n-alkane (heptane, decane, hexadecane) as the function of surfactant concentration and parameter $R$ given as the water to surfactant molar ratio $R = [H_2O]/[AOT]$ was measured. It can be seen that the $Q$ values grow significantly with temperature increase which indicates on entropic origin of this process. The significant influence of surfactant concentration on $Q$ values was noticed. Unexpectedly, the water presence in the reverse micelles did not have any noticeable influence on the heat of mixing values measured at 309.2 K. There was not noticed the significant hydrocarbon chain length influence on the thermal effect of mixing α-tocopherol and AOT solutions. The thermodynamic parameters: the binding constant ($K$) and the molar enthalpy of transition ($\Delta H^0_{tr}$) of α-tocopherol between solvent and AOT reverse micelles, were calculated from the heat of mixing data as a function of surfactant concentration using the nonlinear regression method. The new calorimetric data measured at 309.2 K were compared to results obtained earlier at 298.2 K, as well as have been discussed in the context of the hydrocarbon chain length and water presence influence on α-tocopherol solubility in AOT reverse micelles. Generally in all investigated systems have been not found a significant influence of water concentration in AOT reverse micelles on α-tocopherol molecules distribution between organic phase and micellar phases. The exothermic values of α-tocopherol molecules transition from organic to micellar phase indicate on spontaneous motion of α-tocopherol towards AOT aggregates. For the systems with n-heptane and n-decane as a solvent, the ($\Delta H^0_{tr}$) values are between −51 and −52 kJ mol$^{-1}$ whereas for n-hexadecane around −43 kJ mol$^{-1}$. Such tendency can be explained through hydrocarbon chains orientation effect existing in hexadecane which probably is responsible for a α-tocopherol molecules freedom motion limitation. Moreover, the solubility of the α-tocopherol in AOT reverse micelles measured with calorimetric technique has been compared to the literature data obtained, respectively, with UV spectrophotometer for reverse micelles, and for phospholipids bilayer by other techniques. Finally, transferring of α-tocopherol from solvent to AOT reverse micelles, intermolecular interactions between α-tocopherol and AOT micelles were discussed, and a privileged place of α-

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tocopherol in the palisade layer of AOT reverse micelle has been deduced.

**Keywords** α-Tocopherol · AOT reverse micelles · Flow calorimetry

## Introduction

It is known that a water addition to a solution of surfactant AOT (sodium bis (2-ethylhexyl) sulfosuccinate) in alkanes and next shaking during a few minutes induces a spontaneous microemulsion formation [1]. Among many, S.P. Moulik research group belongs to the pioneer workers in the field of this type of microemulsions, but not only. They published many essential papers regarding formation, structure, phase behaviour, stability and thermodynamics of water/surfactant/oil systems [2–7] also including some aspects of modelling biological microemulsions [8].

Such a three-component system (AOT/alkane/water) is thermodynamically stable although some evidence has recently been obtained suggesting that AOT water-in-oil microemulsions formed in decane can separate into two phases on standing without stirring for a long time (even a few months) [9]. Besides, microemulsions as separate classes of systems containing surfactants aggregates also normal and reverse micelle solutions are selected. Generally it is accepted that the surfactant concentration is the criterion of such selection. The micelles are distinguishable in a narrow surfactant concentration range (usually above critical micellization concentration, CMC). The phenomenon of normal and reverse micelle formation is due to the amphiphilic nature of surfactant molecules, which have separate lyophilic and lyophobic groups. Having both types of such groups makes a surfactant molecule both amphiphilic and amphipathic. A result of the micellization process is the two-phase system formation consisting of the continuous solvent phase and pseudophase containing micellar structures. Such pseudophase formation is a kind of approximation because of dynamic equilibrium between single-phase isotropic of surfactant solution and thermodynamically inverted surfactant aggregates which are in dynamic equilibrium with the surfactant single molecules (surfactant monomers) existing in the solution. Generally, when the solvent appears chemical affinity to surfactant headgroups (which usually are polar) normal micelles are formed whereas in non-polar solvents the reverse micelles formation occurs [10, 11].

Sodium bis (2-ethylhexyl) sulfosuccinate (AOT) is a very popular anionic surfactant whose molecule consists of a polar head-group and two non-polar tails (built with hydrocarbon chains) [1, 9]. The structural formula as well as the size and the shape of AOT reverse micelles formed in aliphatic hydrocarbons or other non-polar solvents have a good representation in the literature [12–16]. Until now reverse micelles made from water and AOT are commonly studied experimentally as models of aqueous microenvironments. They are small enough for individual reverse micelles to also be studied by molecular dynamics simulation, which yields detailed insight into their structure, size and properties [17].

One of the most important among many physicochemical properties is a solvation of a wide range of hydrophilic compounds in the core of reverse AOT micelles. Because of this property, reverse micelles are of interest in nanotechnology [18–20], catalysis and in a variety of fields of study in biology and chemistry also at the molecular level [21–24] recently. In addition, reverse micelles have opened up the possibility of developing new biotechniques to extract proteins from a liquid medium [25], for example. Recently it has been shown that natural membranes except lipid bilayers have some domain areas of reverse micelle structure [26]. It has been recognized that the AOT/n-alkane/water system mimics in a simple way the domain structural peculiarities that have been found in natural membranes as for example micro-surroundings of such biomolecules as enzymatic proteins [27, 28]. According to recent research, the natural cell membranes have a domain structure and except for such domain patterns as lipid rafts, caveoles are present and also some areas having structure of reverse micelles (hexagonal phase second, HII) [27, 28]. This finding opened a new possibility for very simple life-mimicking systems. Although processes in natural cells are very complicated and in their exploration many parameters need to be taken into account, such a simple structural model as reverse micelles is useful at the stage of deducing the fundamental rules occurring as close as possible to the natural conditions. As was mentioned earlier [29] in our investigations, the AOT reverse micelles are discussed as an interface defined by the hydrophobic tailgroups separating the hydrophilic headgroups and water pools (in water-containing reverse micelles) from the organic non-polar solvent phase. The AOT reverse micelles can host a different kind of hydrophilic molecules inside the micelle core and hydrophobic in the palisade layer formed with non-polar tailgroups [10]. This peculiarity of AOT reverse micelles led us to explore the natural antioxidant favourite places in such a model structure of domains of natural membranes as close as possible to the natural structural conditions.

The presented work is an extension of our investigation on natural antioxidant solubility in AOT reverse micelle solutions in alkanes. Previously calorimetric data for β-carotene [30] and α-tocopherol [29] at 298.2 K were reported.

In this paper are reported the new calorimetric results on α-tocopherol solubility in AOT/n-heptane/water, AOT/n-decane/water and AOT/n-hexadecane/water systems measured at 309.2 K. Obtained data are compared to results at 298.2 K for AOT/n-heptane/water reported previously [29] and then discussed in the context of the temperature, and alkane chains length influence on α-tocopherol solubility in AOT reverse micelles, as well as the water contents influence on its localization in AOT reverse micelles. The presented data indicate that: (1) the molar enthalpy of transfer of α-tocopherol from the solvent to AOT reverse micelles decreases in the order: n-heptane > n-decane ≫ n-hexadecane; (2) the significant influence of temperature on the molar enthalpy of transition ($\Delta H^0_{tr}$) of α-tocopherol between solvent and AOT reverse micelles has been noticed; (3) it has been confirmed that the palisade layer is the privileged place of α-tocopherol localization in domain structure mimicking with AOT reverse micelles. The paper also contains a comparison of calorimetric data [30] to the literature data obtained with UV spectrophotometry [31] as well as for natural cell membrane structures like the phospholipid bilayer obtained by other techniques [32–34].

## Experimental

### Materials and methods

99% aerosol OT was purchased from Sigma-Aldrich Co., USA, and vacuum-dried at 25 °C for 24 h, and then the AOT container was kept over molecular sieves. α-Tocopherol was obtained from SIGMA as 95%, and continuously kept at temperature between 2 and 8 °C as well as protected from air and light. For calorimetric measurements, solvents and water were prepared as follows: n-heptane, n-decane and n-hexadecane (Merck) were dried over molecular sieves and then purified by fractional distillation (distillation in n-hexadecane case was done under vacuum). The final purity checked by GLC was 99.97% for n-heptane and n-decane, and 99.95% for n-hexadecane. Water was deionized and bidistilled from a laboratory supply.

All investigated solutions were prepared gravimetrically using a balance with ± 0.00005 g accuracy.

### Calorimetric measurements

The flow microcalorimeter UNIPAN 600 [35] was used for the heat of mixing measurements in all investigated systems. Using the diathermic (stable state) method, thermal effects occurring during mixing two solutions (suitable antioxidant and surfactant in n-alkane) were detected at 309.2 K. Two peristaltic pumps were used to drive both investigated solutions into the calorimetric chamber. During all experiments (including calibration), the flow rates of α-tocopherol/n-alkane and AOT/n-alkane solutions were constant and equal 0.2 mL $min^{-1}$. The numeric value of the flow rate was chosen in order to assure the occurrence of the totality of the thermal effect inside the calorimeter chamber (vessel). Before each heat of mixing measurement ($Q$) as a standard procedure, the base line signal ($U_0$) was detected. During base line detection, one pump drove solvent (n-alkane) and the second AOT/n-alkane solution at a given suitable molality. In this way, the base line detection caused the main thermal effect correction with heat of dilution of the AOT/n-alkane solution. The calibration procedure using electric method was described elsewhere in details [35].

The thermal effects occurring in the calorimetric vessel during base line detection ($U_0$), as well as during mixing the two solutions ($U$) were measured in terms of voltage, and recorded. Afterwards, collected data were processed to calculate the heat of mixing effect using the prescribed way [35]. In all measurements, accuracy of the thermal effects determination is estimated to be within ± 2 J $mol^{-1}$.

The amount of water dissolved in AOT solutions is given with R parameter defined as a ratio of water to AOT molality ($R = [H_2O]/[AOT]$). The heat of mixing ($Q$) was measured as the surfactant concentration function for different $R$. In all investigated systems, α-tocopherol solution concentration was invariable and equal to 0.02 mol $kg^{-1}$. The molalities of AOT solutions were above CMC characteristic for a given solvent and below 0.4 mol $kg^{-1}$. They were above the suitable CMC value to be sure that surfactant molecules are aggregated in reverse micelles structure. The numerical values of CMC for AOT reverse micelle formation in n-alkane used as solvents are given in Table 1. To avoid eventual phase separation, the AOT solutions with R higher than 10 were continuously mixed with a magnetic stirrer until the mixing chamber dosage was reached. Shimadzu pumps LC-10AD (the flow rate accuracy ± 2 μL $min^{-1}$) were used for driving both solutions into the calorimetric vessel.

## Results and discussion

Our investigation was focused on the system: α-tocopherol/n-alkane/AOT/water. Normal alkanes: n-heptane, n-decane and n-hexadecane were used as solvents. The experimental heat of mixing data ($Q$) for α-tocopherol/n-alkane solution with AOT/n-alkane/water system measured calorimetrically at 309.2 K as a function of AOT molality and R parameter are present in Fig. 1. $Q$ values recorded in all systems were strongly exothermic and decreasing with

**Table 1** CMC for AOT reversed micelle formation in alkane solvents

| Solvent | CMC/mM | | | |
|---|---|---|---|---|
| | Experimental value | Method of measurement | Literature data | Method of measurement |
| Heptane | 0.42 (298.2 K) | UV–vis | 0.54 (298 K)[a] | UV–vis |
| Decane | 0.91 (298.2 K) | Refractometry | – | – |
| | 0.62 (298.2 K) | UV–vis | – | – |
| | – | – | 0.73 (297)[b] | X-ray scat. |
| | 0.55 (309.2 K) | Refractometry | – | – |
| Hexadecane | – | – | 0.001 (298 K)[c] | Conductivity |

[a] [43]

[b] [44]

[c] [45]

AOT concentration. A particularly rapid decrease is observed in the range of AOT concentrations below 0.05 mol kg$^{-1}$. In all studied systems, we did not notice any influence of water dissolved in AOT reverse micelles on $Q$ values.

The results obtained at 309.2 K for n-heptane were compared to data obtained previously at 298.2 K [30] (Fig. 2). It can be seen that the $Q$ values grow significantly with temperature increase which indicates on entropic origin of this process. The significant influence of surfactant concentration on $Q$ values was noticed. Unexpectedly the water presence in the reverse micelles did not have any noticeable influence on the heat of mixing values measured at 309.2 K (see Fig. 2a). In contrary, the surfactant concentration increase from 0.02 to 0.11 mol kg$^{-1}$ caused a significant decrease in heat of mixing values. Similar regularity has been observed in the systems containing n-decane and n-hexadecane as solvents. There was not noticed the significant hydrocarbon chain length influence on the thermal effect of mixing α-tocopherol and AOT solutions (Fig. 1).

The total thermal effect concomitant with two solutions mixing as a function of surfactant concentration can be discussed in the context of α-tocopherol molecule distribution between AOT reverse micelles and bulk solvent. Magid et al. [36] proposed a thermodynamic model describing phenol solvation in AOT reverse micelles measured with the UV method. According to it, Yekta et al. [37] and Kwan et al. [38] made the assumption that the mean number of molecules binding to a single micelle can be described by the Poisson distribution function and they

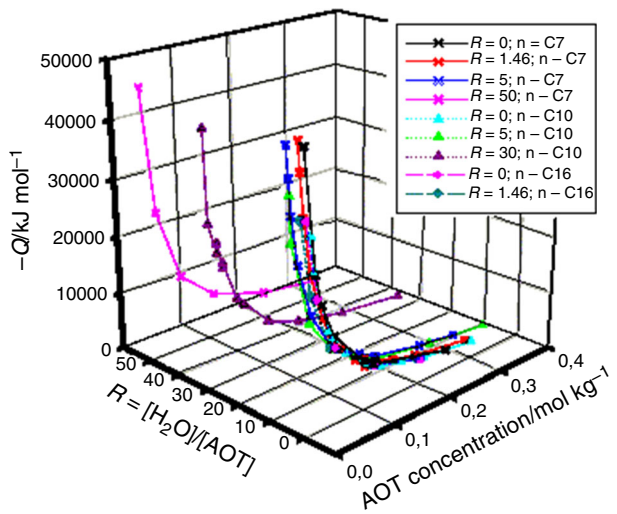


**Fig. 1** Heat of mixing at 309.2 K of 0.02 mol kg$^{-1}$ α-tocopherol/n-alkane with AOT/n-alkane solution as a function of surfactant solution concentration and $R$ parameter

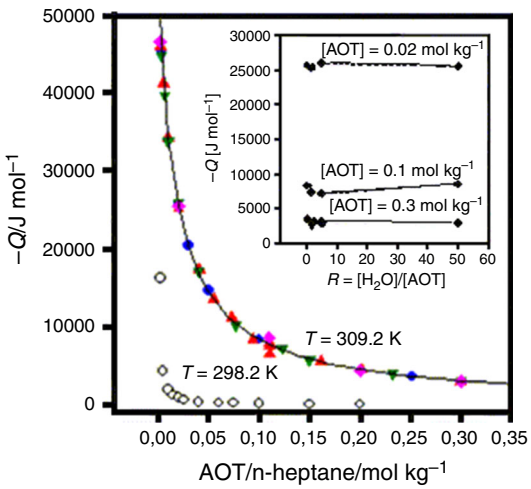


**Fig. 2** Heat of mixing of 0.02 mol kg$^{-1}$ α-tocopherol/n-heptane with AOT/n-heptane/water solution as a function of AOT/n-heptane concentration: o—data at 298.2 K [29]; filled points mark data at 309.2 K (where: blue dots, red triangles, green triangles and pink diamonds mark data for $R$ = 0; 1.46; 5 and 50). **a** Heat of mixing of 0.02 mol kg$^{-1}$ α-tocopherol/n-heptane with AOT/n-heptane/water solution as a function of $R$ at 309.2 K for chosen AOT/n-heptane concentrations

**Table 2** Thermodynamic parameters for α-tocopherol transfer from n-alkane to AOT reversed micelles

| Model | Solvent | $T$/K | $R^b$ | $Q_f$/kJ mol$^{-1}$ | $Q_b$/kJ mol$^{-1}$ | K/kg mol$^{-1}$ | $\Delta H^0_{tr}$/kg mol$^{-1}$ | $K'^c$ |
|---|---|---|---|---|---|---|---|---|
| Nernstian law[a] | n-$C_7$ | 298.2 | 0 | – | – | 45.9 | −20.197 | 103.2 |
| Present model | n-$C_7$ | 298.2 | 0 | 20.418 | −1.936 | 51.5 | −22.354 | 115.8 |
| | | 309.2 | 0 | 52.281 | −0.033 | 51.9 | −52.314 | 116.7 |
| | | 309.2 | 1.46 | 51.664 | −0.271 | 50.5 | −51.935 | 113.6 |
| | | 309.2 | 5.0 | 51.786 | −0.153 | 50.3 | −51.939 | 113.1 |
| | | 309.2 | 50.0 | 51.610 | −0.162 | 50.3 | −51.771 | 113.1 |
| | n-$C_{10}$ | 309.2 | 0 | 50.460 | −0.399 | 63.2 | −50.859 | 142.2 |
| | | 309.2 | 5 | 51.295 | −0.601 | 64.0 | −51.896 | 143.9 |
| | | 309.2 | 30 | 43.895 | −1.017 | 38.4 | −42.879 | 86.4 |
| | n-$C_{16}$ | 309.2 | 0 | 42.285 | −0.079 | 44.0 | −42.356 | 99.0 |
| | | 309.2 | 1.46 | 42.878 | −0.196 | 48.9 | −43.074 | 110.0 |

[a] [30]

[b] $R = [H_2O]/[AOT]$

[c] $K' = K/M_{AOT}$

defined the ratio of the concentration of molecules bonded with micelles to molecules unbound as directly proportional to the total surfactant concentration. The proportionality coefficient was the association constant with the same value for each association step. D'Aprano et al. [39] successfully used this model for describing thermal effects connected with n-pentanol transition from heptane to AOT/heptane/water systems.

In the present paper, the total value of heat of mixing of two solutions: α-tocopherol/n-heptane with AOT/n-heptane has been considered as the sum of a two contributions: heat of dilution of α-tocopherol and the heat of α-tocopherol and AOT intermolecular interaction. It needs to be noticed that the heat of dilution of AOT solution was covered in the base line. When AOT concentration tends to infinite dilution, the α-tocopherol/n-heptane solution is mixed with almost pure solvent. Thus, at AOT infinite dilution we can discuss the calorimetrically measured heat of mixing as a sum of the contributions of α-tocopherol solution dilution and the intermolecular interactions between α-tocopherol and AOT molecules. Following Magid et al. [36], we assumed that the mean number of α-tocopherol molecules connected to one AOT reverse micelle is described in the terms of the Poisson distribution function. The final relation used in the numerical analysis with nonlinear regression of heat of mixing experimental data was the following:

$$Q_{tot} = Q_f + (Q_b - Q_f)KC_{AOT}(1 + KC_{AOT})^{-1} \quad (1)$$

where $Q_{tot}$ is the total heat of mixing value (experimental data), $Q_f$ is a heat of dilution of α-tocopherol solution, $Q_b$ is the heat of α-tocopherol and AOT intermolecular interaction, $K$ is the binding constant of α-tocopherol molecule solubilized in the AOT reverse micelles and $C_{AOT}$ is the AOT molality. The experimental data ($Q_{tot}$) are correlated to Eq. (1) with three fitted parameters: $Q_b$, $Q_f$ and $K$ suitable. In the nonlinear regression procedure, values of binding constant ($K$) and the heats contributed to $Q_{tot}$ ($Q_f$, $Q_b$) were obtained. The molar enthalpy of transition ($\Delta H^0_{tr}$) of α-tocopherol from solvent to AOT reverse micelles was calculated as a difference between $Q_b$ and $Q_f$. The numerical values of all fitted parameters and $\Delta H^0_{tr}$ are given in Table 2.

Reported in previous paper [30], experimental data registered at 298.2 K were analysed with the procedure described above and compared to binding constant and molar enthalpy of transition values founding in NLREG procedure employed to Nernstian law formalism [29]. As it can be seen in Table 2 obtained in both procedures, parameters $K$ and ($\Delta H^0_{tr}$) for α-tocopherol/n-heptane/AOT system are comparable and we conclude that the procedures are compatible.

Next the α-tocopherol distribution constants ($K'$) were calculated using the relation:

$$(K') = \frac{K}{M_{AOT}} \quad (2)$$

where $K$ is a binding constant, $M_{AOT}$ is a surfactant molecular weight.

The obtained values are given in Table 2. For systems with n-heptane as solvent, the difference between distribution constant values obtained at 309.2 and 298.2 K is not significant. For systems with $R = 0$, the distribution constant value ($K'$) changes in order heptane < decane ≫ hexadecane. Additionally the lack of any dependence between the distribution constant and the $R$ parameter can be noticed in the systems with n-heptane as solvent. For n-decane $K'$ value doesn't change with $R$ in the range $R < 0 \div 5 >$ and then decreases for $R = 30$. For

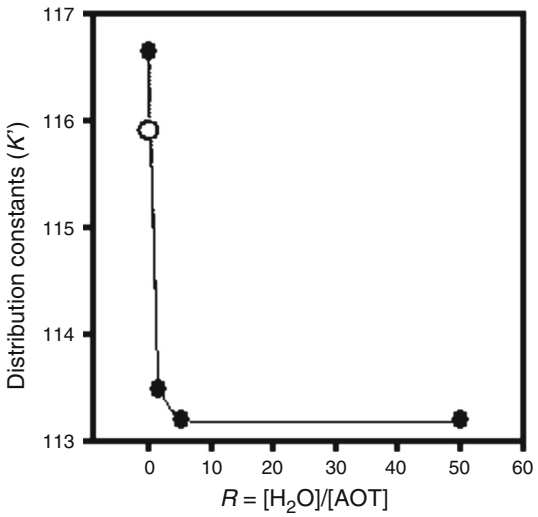


**Fig. 3** Distribution constant ($K'$) for a-tocopherol transferring between organic phase and AOT reverse micelles as a $R$ parameter function calculated for n-heptane as solvent. Filled circles—309.2 K; open circle—298.2 K

n-hexadecane systems $K'$ are stable for $R < 0 \div 1.46 >$. Generally in all investigated systems have been not found a significant influence of water concentration in AOT reverse micelles on α-tocopherol molecules distribution between organic phase and micellar phases (Fig. 3 and Table 2). This finding indicates that the privileged place of α-tocopherol molecules in AOT reverse micelles is the micellar palisade layer between the alkyl chains of surfactant. Moreover, the small values of $Q_b$ indicate that intermolecular interactions between α-tocopherol and AOT are rather weak. As a consequence, α-tocopherol molecules move towards the external part of the palisade layer and they do not compete with water molecules (in the systems with $R > 0$) for the binding sites at the water surfactant interface. The exothermic values of α-tocopherol molecules transition from organic to micellar phase indicate on spontaneous motion of α-tocopherol towards AOT aggregates. For the systems with n-heptane and n-decane as a solvent, the ($\Delta H^0_{tr}$) values are between −51 and −52 kJ mol$^{-1}$ whereas for n-hexadecane around −43 kJ mol$^{-1}$. Such tendency can be explained through hydrocarbon chains orientation effect existing in hexadecane [40, 41] which probably is responsibly for a α-tocopherol molecules freedom motion limitation.

On the basis of the presented data, we can say that the thermodynamic parameters of α-tocopherol solution in AOT reverse micelles obtained from calorimetric data led us to deduce that α-tocopherol is preferentially solubilized in the palisade layer, not inside AOT reverse micelles. Such hypothesis was postulated in our previous paper [29] ($K'$ values are independent of the R parameter for a different AOT molality). Our findings also confirmed results obtained by Avellone et al. [31] who investigated the binding of α-tocopherol to water-containing reverse micelles using UV–vis spectrophotometry, as well as by Fukuzawa et al. [32], Urano et al. [33] and Wassall et al. [34] who found that vitamin E molecules are located in the hydrophobic part of the phospholipid bilayer of cell membranes. Recently Gunaseelan et al. [42] published results referring to α-tocopherol solubility in water/surfactant/octane system. Although they used a different kind of surfactants (forming regular micelles), their results are consistent with our data presented in this paper.

## Conclusions

In this paper, the new calorimetric studies on α-tocopherol/n-alkane/AOT system at 309.2 K are presented. Using the flow calorimetric method, the α-tocopherol solubility in AOT reverse micelles, both with and without water, was investigated. Using the experimental heat of mixing data, the binding constant and the heat of dilution of α-tocopherol as well as the heat of α-tocopherol and AOT intermolecular interaction at $R = 0$, 1.46, 5.0, 30 and 50 with nonlinear regression were calculated. The obtained results were compared to data at 298.2 K.

The present paper is a continuation of our investigations on α-tocopherol solubility in the AOT/n-heptane/water system. Previously it has been postulated that α-tocopherol molecules are located preferentially in the palisade layer of AOT reverse micelles. Present data are in a good agreement with the literature UV absorption spectroscopy data, as well as with results published for phospholipids bilayer structure.

As it has been emphasized previously, the knowledge on α-tocopherol localization in such a simple model of interface as AOT reverse micelles may be useful in mimicking the domain structural peculiarities in the presence of antioxidant molecules.

The presented data indicate that α-tocopherol molecules are located between palisade layers of AOT reverse micelles towards its external part. In addition, it has been postulated not competition in the interaction with the polar heads of the AOT between molecules of water that were located in the interior of micelles, and α-tocopherol in the palisade layer. Data presented in this paper indicate also that AOT reverse micelles mimic some aspects of the domain structure of biomembranes successfully.

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