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EXCESS ENTHALPIES FOR *n*-ALKANE/β-CAROTENE+*n*-ALKANE/AOT/WATER SYSTEMS

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The experimental data of excess enthalpies for β-carotene/*n*-alkane+*n*-alkane/AOT/water systems at 298.15 K are reported. The H^E dependence on AOT (sodium *bis*(2-ethylhexyl) sulfosuccinate) concentration and hydrocarbon chain length was investigated. The excess enthalpy was measured using the flow microcalorimeter UNIPAN type 600.

Keywords: β-*carotene, excess enthalpy, flow calorimeter, reversed micelles, sodium bis(2-ethylhexyl) sulfosuccinate*

Introduction

Sodium *bis*(2-ethylhexyl) sulfosuccinate (called commercially Aerosol OT or simply AOT) (Scheme 1) is a surfactant which is able to create the reversed micelles in non-polar solvents [1, 2]. The ability of AOT molecules for aggregating results from the combined action of spatially separated hydrophilic and hydrophobic moieties of this surfactant. Such aggregates are built as inner cores occupied by the hydrophilic head-groups coated by the hydrocarbon tails which are extended into the bulk of non-polar solvent. It has been shown that the peculiar capacity of AOT reversed micelles for a large amount of water depends on the surrounding non-polar medium (solute) and temperature [3]. Water is readily soluble in the polar core of such micelles and forms a so-called water pools which are characterized by *R* parameter defined as: $R=[H_2O]/[AOT]$ [4]. The low *R* values ($R\leq 10$) promotes structures in which water molecules are strongly bounded to the AOT head groups. Contrary, at higher $[H_2O]/[AOT]$ ratios ($R>20$) free water is predominant. The last structures are characteristic for swollen reversed micelles solutions [5, 6]. The ionic nature of interior of AOT micelle easy dissolves water which, as it was mentioned previously can exist as a water bounded to the surfactant polar groups, or as a free water which is able to solute some electrolytes [7]. Knowledge on the electrolyte location in reversed micelles is helpful in their structures exploration.

It is known [8] that micelles as well as reversed micelles and two-layer membrane cells in the vital organisms are distinguished. From the structural point of view systems containing AOT reversed micelles can be considered as a very simple model of the natural biological membranes. Some of the vital functions of human organism are related to many chemical reactions. From among many oxidizing of proteins and/or lipids of the membrane cells belongs to the most important. Antioxidants play a very important role in course of such reactions. In fact they defense organisms against damaging oxidizing reactions effects. The most popular natural antioxidant is β-carotene (Scheme 1) naturally occurring in many vegetables and fruits. β-carotene molecule has 11 conjugate double bonds in the hydrocarbon chain. From the structural point of view β-carotene molecule consists two retinal molecules. As a reagent β-carotene can interacts with other dietary antioxidants like vitamin E and C [9]. Correra *et al*. [3] shown that β-carotene and α-tocopherol (vitamin E) might exert antioxidant action at different positions in the real biological membranes. Namely, α-tocopherol molecules locate on the membrane surface, and β-carotene in its central hydrophobic region. Besides, is possible that β-carotene scavenges peroxyl radicals deeply inside of membrane cells where α-tocopherol scavenges is not so effective.

Knowledge on the antioxidant solubility in reversed micelles and their interactions can help to get to know and understand the analogous processes in biological membranes. D'Aprano *et al*. [10] studied the solubility of retinol and retinal in *n*-heptane/AOT/water reversed micelles by calorimetric method, and suggested that the double C=C bonds interactions with the hydrophilic AOT regions determine retinol and retinal partition between organic and water phases.

Enthalpy of mixing is the thermodynamic function which can be measured directly. Depending on the properties of investigated system, there are in the literature many different calorimeters described. It is noticed the adiabatic [11] and standard Calvet calorimeters [12–14] are recently very popular in thermal effects studies. Among many the flow calorimeters are very popular in liquid systems measurements.

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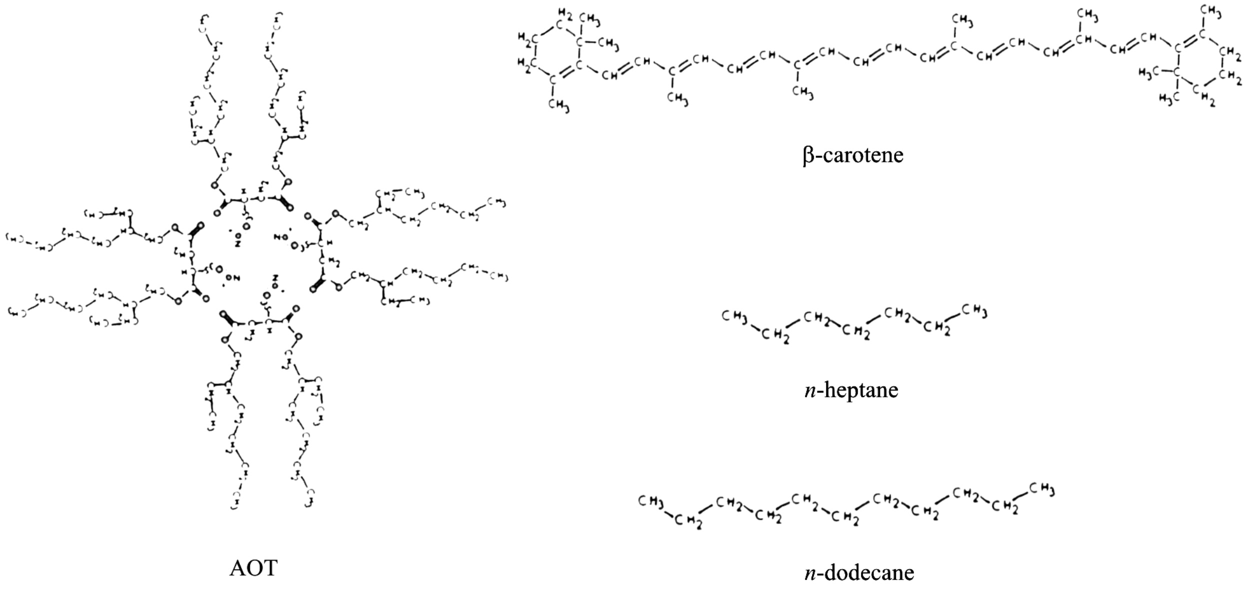

Scheme 1

This paper reports experimental data of the excess enthalpies for *n*-alkane/β-carotene+*n*-alkane/AOT/water systems depending on hydrocarbon chain length, AOT concentration and as a function of R=[H_2O]/[AOT].

Experimental

Materials

High purity sodium *bis*(2-ethylhexyl) sulfosuccinate was purchased from Sigma Co. (99.0%) and used as received without additional purification. The AOT container all time was kept over molecular sieve. β-carotene was purchased from Sigma Co. as 95%, and used without further purification. All alkanes: *n*-heptane (Merck), *n*-octane (Merck), *n*-decane (POCH) and *n*-dodecane (REACHIM) were drying over molecular sieves and than purified by fractional distillation. The final purities checked by GLC were suitable: 99.62% for *n*-heptane; 99.97% for *n*-octane; 99.93% for *n*-decane and 99.65% for *n*-dodecane. Water was used after deionization and bidistillation, its final purity was 99.98%.

Methods

The calorimetric measurements at 298.15 K were carried out with a flow microcalorimeter UNIPAN type 600 [15] using the diathermic method. The calorimetric system was tested by excess enthalpy measurement for binary reference system benzene+cyclohexane at 298.15 K. Obtained results were consistent with literature data [16, 17]. Subsequently, *n*-alkane/β-carotene+*n*-alkane/AOT/water systems were investigated. Concentration of β-carotene in: *n*-heptane, *n*-octane and *n*-decane was $4.85 \cdot 10^{-4}$, and in *n*-dodecane $4.085 \cdot 10^{-4}$ mol L^{-1}. Both solutions: *n*-alkane/β-carotene and *n*-alkane/AOT/water were driven into the calorimetric chamber with the stable flow rates equal 0.609 mL min^{-1} using very precise Shimadzu pumps type LC-10AD (the flow rate accuracy ± 2 μL min^{-1}). The thermal effect occurring in calorimetric vessel during mixing two solutions was electrically detected and recorded till stabilization of the stationary state. The numerical values of calorimetric signal were obtained through the voltage measurements and recorded. On the beginning of each measurement as a standard procedure the *n*-alkane/AOT/water solution (A) at a given R=[H_2O]/[AOT] was mixed with pure *n*-alkane and suitable calorimetric signal was taken as a baseline (U_0). Afterwards, *n*-alkane was replacing with *n*-alkane/β-carotene solution (B), and thermal effect was detected again (U). In a given measurement the same aliphatic hydrocarbon in both solutions was used as a solvent. The excess enthalpy was calculated according the following relation

$$H^{\mathrm{E}} = \frac{\Delta U k}{\Sigma n} \quad [\mathrm{J\ mol^{-1}}] \qquad (1)$$

where $\Delta U = U_0 - U$ [V] is a voltage corresponding to the thermal effect; U_0 [V] and U [V] are the voltages corresponding to the basic line and to the calorimetric signal suitable at the stationary state; k [W V^{-1}] – is a calibration constant, $\Sigma n=n_A+n_B$ [mol s^{-1}] is the total molar flow of solutions A and B. Calibration constant k was determined using electric method in details described elsewhere [15]. The precision of the H^E determination is estimated to be within ±2 J mol^{-1}.

Results and discussion

The experimental data of excess enthalpies for *n*-alkane/β-carotene+*n*-alkane/AOT/water systems are presented on Figs 1 and 2. Precise H^E values are given in Table 1.

The following regularity has been observed for systems without water: the excess enthalpy increased rapidly from –59.5 to 58.1 kJ mol^{-1} for solutions in *n*-heptane and *n*-dodecane as a solvents. Unexpectedly for all systems containing water (with R<5.9–36.6>) the H^E increasing or decreasing depending on *n*-alkane was observed. For a chosen system: *n*-heptane/β-carotene +*n*-heptane/AOT/water excess enthalpy as a function of AOT concentration was measured and rapid decreasing of the exothermic effect with surfactant concentration increasing was detected (Fig. 2). For systems containing *n*-decane and *n*-dodecane all H^E values were positive (endothermic) and rapidly decreased with parameter R=[H$_2$O]/[AOT] increasing, whereas for systems with *n*-heptane and *n*-octane all H^E values were negative (exothermic) and increased rapidly with R increasing.

According to the literature [1, 2] the AOT micelle volume increases with increasing of water to AOT molar concentration ratio. Moreover, is necessary to note that for longer *n*-alkane chains the so-called short order orientation effect is observed [18, 19]. It is important to emphasize that in calorimetric experiment we observe the total thermal effect which occurs during mixing two pure liquids or two solutions. Such effect consists of a few contributions. We assumed that for systems investigated in this paper three main contributions to H^E can be distinguished:

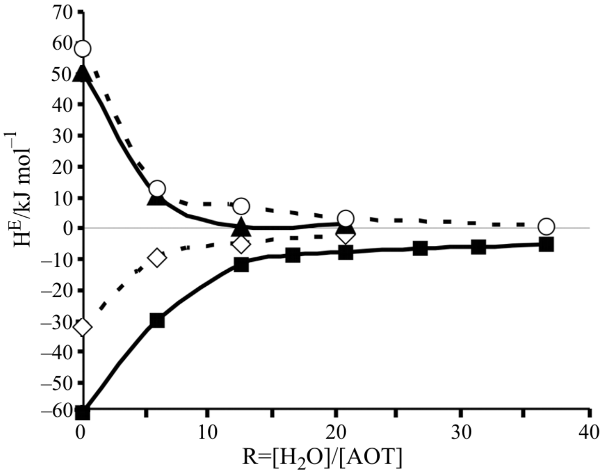

Fig. 1 Excess enthalpy for *n*-alkane/β-carotene+*n*-alkane/AOT/water systems at 298.15 K. —■— – *n*-heptane; --◇-- – *n*-octane; —▲— – *n*-decane; --○-- – *n*-dodecane

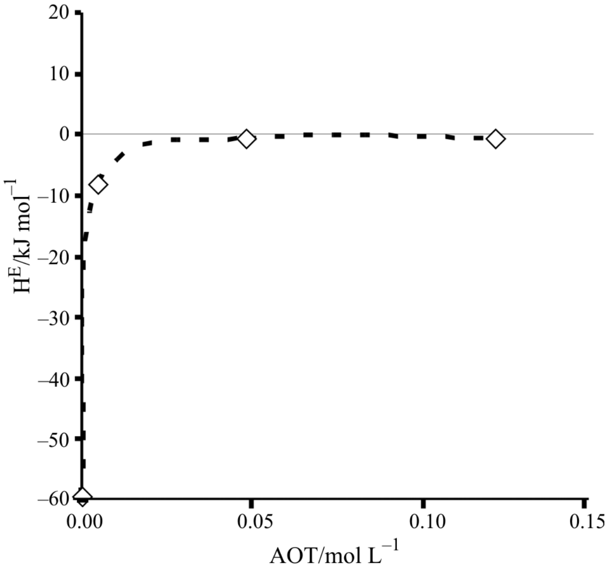

Fig. 2 Excess enthalpy for *n*-heptane/β-carotene+*n*-heptane/AOT depending on AOT molar concentration

Table 1 The excess enthalpy experimental values

R=[H$_2$O]/[AOT]	ΔH^E/kJ mol^{-1} for β-carotene+			
	n-heptane	*n*-octane	*n*-decane	*n*-dodecane
0	–59.5	–32.1	50.6	58.1
5.9	–29.9	–9.3	10.6	12.8
12.5	–11.7	–5.2	0.5	7.4
16.6	–8.8	–	–	–
20.7	–7.8	–1.9	1.4	3.2
26.6	–6.5	–	–	–
31.2	–5.9	–	–	–
36.6	–5.2	–	–	0.5

- First contribution is connected with volume of AOT reversed micelle. When micelles radii increase (*R* increases) it causes larger density of AOT 2-ethylhexyl chains around reversed AOT micelles, and as a consequence worse β-carotene molecules access to their palisade layer. This effect should appears as a higher positive contribution to the excess enthalpy for bigger than for smaller micelles.
- Second contribution arises from the short order orientation effect for *n*-hydrocarbon chains in the liquid-state. During *n*-alkane mixing with another liquid component its order is destroyed. This effect as a positive contribution to the excess enthalpy of mixing should be discussed.
- Third contribution is connected with β-carotene and *n*-hydrocarbon competition in access to palisade layer of AOT reversed micelle. When the length of *n*-hydrocarbon increases (from *n*-heptane to *n*-dodecane) the geometrical similarity (size and volume, Scheme 1) of *n*-hydrocarbon to β-carotene molecule increases and as a consequence increases competition between them in access to palisade layer. According to such assumption for short *n*-alkane chains smaller contribution to heat of mixing should be expected comparing to longer chains.

Conclusions

The excess enthalpies for: *n*-heptane/β-carotene+*n*-heptane/AOT/water; *n*-octane/β-carotene+*n*-octane/AOT/water; *n*-decane/β-carotene+*n*-decane/AOT/water; *n*-dodecane/β-carotene+*n*-dodecane/AOT/water as a function of R=[H_2O]/[AOT] were measured. The excess enthalpies for *n*-alkanes at R=0 increases in order: *n*-heptane<*n*-octane<*n*-decane<*n*-dodecane. It is agreeable with assumption on competition between β-carotene and hydrocarbon molecules in access to palisade layer of AOT reversed micelles. Our results for systems containing *n*-decane and *n*-dodecane confirmed assumption on the AOT micelles volume influence on the H^E. For systems with these *n*-alkanes the endothermic effects of mixing decreasing rapidly with R increasing. It confirmed hypothesis on a worse access of β-carotene molecules to the palisade layer of AOT reversed micelles with water concentration increasing. Rapid H^E decreasing with surfactant concentration increasing was observed for *n*-heptane/β-carotene+*n*-heptane/AOT system.

Nomenclature

H^E	molar excess enthalpy (kJ mol^{-1})
R	water to AOT ratio parameter
ΔU	voltage corresponding to the thermal effect (V)
U_0	voltage corresponding to the basic line (V)
U	voltage corresponding to the calorimetric signal (V)
k	calibration constant (W V^{-1})

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