ASCORBIC ACID AND ITS RADICAL OXIDATION PRODUCTS IN HOMOGENEOUS AND MICROHETEROGENEOUS SYSTEMS

I investigated the influence of different factors like the presence of oxygen or transient metal ions, pH, and microenvironment on the stability of ascorbic acid. These studies have revealed that according to the expectations the presence of transient metal ions, which influence can be inhibited by introducing chelating agent to the system, e.g. EDTA, is the main factor lowering the stability of ascorbic acid. Furthermore the stability of ascorbic acid decreases with increasing pH of a solution, which determines the AsA form in the system (protonated or monoanionic). The stability of ascorbic acid depends also on its microenvironment. Among the investigated micellar systems stabilized by ionic surfactants (SDS, AOT) and nonionic ones (Brij 35, Igepal CO-720) the biggest and also the most complex effect on the stability of ascorbic acid I observed for a simple micellar solution of Igepal CO-720. I have assigned this effect to the formation of hydrogen bonds between the AsA molecule and the ethoxyl groups of the surfactant. On the other hand ascorbic acid showed higher stability in reverse micelles of AOT/n-hepthane in comparison to both homogeneous aqueous solution and the simple micellar solution. I observed negligible decrease of the stability of AsA with increasing the size of the water pool of reverse micelles.

I also investigated the influence of the presence of simple micelles on acid-base equilibrium of ascorbic acid, i.e. on the pKa_1 value of AsA. The pKa_1 value of ascorbic acid undergoes the highest shift towards acidic pH for the simple micellar solutions of AOT, what is the result of H^+ ions attraction to the negatively charged molecules and the micellar structures of the surfactant. This effect is additionally enhanced by the structure of AOT molecule and high charge density on the micellar surface. The pKa_1 value undergoes also significant decrease in the presence of the simple micelles of Igepal CO-720, what is connected to the formation of hydrogen bonds between AsA and ethoxyl groups of the surfactant. In the simple micellar solution of Brij 35 the pKa_1 value of AsA is similar to that in homogeneous aqueous solution, despite the fact that Brij 35 also contains the ethoxyl groups. In this case the higher number of the ethoxyl groups in Brij 35 comparing to Igepal CO-720 results in an increase of the electron density on O-H bond in AsA molecule, what

makes difficult the release of the proton and causes the inhibition of the dissociation process and increase the AsA pKa_1 value.

I have proposed two methods allowing the estimation the pH "sensed" by ascorbic acid introduced into the reverse micelles of AOT. Both methods are based on the strong dependence of AsA form present in a solution on pH. The first method utilizes the dependence of the position of AsA maximum absorption band on the pH of solution, while the second method utilizes the contribution of AsA monoanion form in the absorption band on pH. In the AOT reverse micelles pH is shifted towards lower values with the increase of w_0 parameter due to tendency of AsA to locate close to the AOT hydrophilic groups or even to penetrate deeper among the surfactant chains, where the protons from the water phase are also attracted.

In a next step I investigated the influence of the presence of simple micelles on the reactivity of the ascorbyl radical. I did not observe any significant effect of AOT simple micelles on generation or decay process of an ascorbyl radical in comparison to the homogeneous aqueous solution. However the presence of the simple micelles of Igepal CO-720 accelerates the disproportionation of ascorbyl radicals in comparison to the homogeneous aqueous solution. This effect can be explained by the tendency of AsA to locate in the interface and to form hydrogen bonds with ethoxyl groups of the surfactant.

In the main part of the Thesis I investigated the kinetics of the radiation-induced generation and decay, via disproportionation reaction, of ascorbyl radicals in the reverse micellar systems stabilized by AOT/n-heptane or Igepal CO-520/cyclohexane. In both cases I used the hydroxyl radical to oxidize ascorbic acid and in both cases I have observed the characteristic absorption band of ascorbyl radicals at 360 nm. I have corrected the rate constants of ascorbyl radical disproportionation by the f factor expressing the content of micellar phase in the system. In the reverse micellar systems of AOT the rate constant of ascorbyl radical formation is lower than in homogeneous aqueous solution and increases with increasing of water-pool size of micelles (w_0). I have observed the increase of the ascorbyl radical decay with increasing of water-pool size of reverse micelles at constant concentration of reverse micelles in the system. The rate constant of ascorbyl radical

disproportionation increases and approaches the value observed in homogeneous aqueous solutions with increasing of water content in the system. The latter effect is due to the increase of the probability of generation at least two ascorbyl radicals in one reverse micelle.

The decay of the absorption band peaking at 360nm in reverse micelles of Igepal CO-520/cHx differs from that observed in the reverse micelles of AOT/n-heptane. Namely the band decays in two steps – slow and fast one. I have assigned the fast step to the decay of the adduct of hydroxyl radicals to the phenyl ring of the surfactant molecule. Such an adduct exhibits an absorption band in range 300 – 360 nm. The slower decay, which proceeds according to the second order kinetics, I have assigned to the disproportionation of ascorbyl radicals. The rate constant of the ascorbyl radicals disproportionation in the reverse micellar solutions of Igepal CO-520 decreases with increasing of w_0 parameter, i.e. with increasing the size of micellar aggregate, what is the opposite effect to that observed in the reverse micelles of AOT. This can be rationalized by the fact that molecules of Igepal CO-520 forming reverse micelles are packed much more densely than those of AOT, thus both regions aqueous and polar are well separated. The decrease of the rate constant of ascorbyl radical disproportionation with the increase of w_0 parameter I have then ascribed to the separation of AsA between the phases of the system. In the reverse micelles of Igepal CO-520 most part of ascorbic acid molecules is located at the interface or even bound with polyoxyethylene chains of the surfactant. Hence the ascorbyl radicals are formed mainly at the interface where their disproportionation is slower as their mobility is limited.

To check whether the ascorbic acid is really bound with the polyoxyethylene chains of Igepal I have measured the spin-lattice relaxation constants of AsA, T_1, by means of ^1H NMR method. The experiment has allowed to determine the molar fractions of the free AsA and AsA bound with surfactant, which are 0,84 and 0,16 respectively.