Determination of conformational and dehydration contributions to change of entropy of cholesterol water solvent

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Earlier in works [1, 2] spectral photosensitivity of the heterojunction silicon – cholesterol aqueous solution were investigated. The expansion of spectral photosensitivity to the short waves was observed. This is caused by the process of self-organization of molecules of cholesterol water solvent on the surface of silicon because of conformational changes of macromolecules. Conformational changes may be controlled by entropy factors.

In this work the theoretical model of the self-organization process was constructed and both conformational and dehydration contributions to the entropy change were determined in the experiment.

The Gibbs free energy of aggregation of cholesterol molecules in water is given by:

$$\Delta G=-T\,\Delta S$$

because the enthalpy effect of aggregation of nonelectrolytes in polar solvents is negligible small $\Delta H=0$ [3].

Assuming that, for aggregation, surface area cannot be higher than 50% of the total surface area of the cavity accommodating the cholesterol molecule in the aqueous phase [4], $\Delta G=37$kJ/mole, the absolute value of the entropy aggregation of cholesterol molecules in water at 300 K equals

$$\Delta S_{agg} \le 120\text{J/(K·mole)}.$$

The entropy of aggregation ΔS_{agg} is the entropy of dehydration of the cholesterol molecule, which is equal to the molar entropy of evaporation of water aggregation under standard conditions [5].

Experimentally, the aggregation entropy can be determined from the number of evaporated molecules by calculating the partition function for the water-cholesterol solution, which can be represented as a system of contacts [6]:

$$\Delta S_{total} = R\ln[(C_a M_w/M_{ch}\,RT)cN],$$

where M_w and M_{ch} are the molecular weights of water and cholesterol, respectively, $c=1.8\text{x}10^{-6}$ is the solubility of cholesterol in water [7], N is number of evaporated water molecules; ΔS_{total} is the total change in the entropy.

To determine N we measured the dependence of the weight of the evaporated water m on the time during the aggregation of cholesterol molecules at 300K. The aggregation of cholesterol molecules in the form of globules and

mesomorphic textures was observed at t=20h, when the water evaporation approaches to the constant value [8].

Using N measured in our experiment and c, we calculated the total entropy:

$$\Delta S_{total} = 300 J/(K \cdot mole).$$

The total entropy change is associated with conformational changes in the solution ΔS_{conf} and with dehydration of the cholesterol molecules ΔS_{dehydr}:

$$\Delta S_{total} = \Delta S_{conf} + \Delta S_{dehydr}$$

where $\Delta S_{dehydr} \leq 120 J/(K \cdot mole)$, therefore ΔS_{conf} lies within the range:

$$180 J/(K \cdot mole) < \Delta S_{conf} < 300 J/(K \cdot mole).$$

Since $\Delta S_{conf} > \Delta S_{dehydr}$, the entropy controlled aggregation of cholesterol molecules in water is due predominantly to conformational conversions of the structure of the cholesterol aqueous solution. These conformational changes of macromolecules might be used for creating molecular devices [9].

References

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