

Physico-chemical interaction patterns of oxidized polyvinyl alcohol fraction with 4- and 5-aminosalicylic acids

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Abstract

The interaction of the oxidized fraction of polyvinyl alcohol (OF of PVA) with 4- and 5-aminosalicylic acids (4- and 5-ASA) in aqueous solutions was examined by ultraviolet spectroscopy. OF of PVA is obtained by oxidation of polyvinyl alcohol in an aqueous medium affected by hydrogen peroxide (363 K, [PVA] = 3.5% wt., [H₂O₂] = 1 mol/l, t_{oxid.} = 45 min), further separated from the solution by acetone addition. The average molecular weight of the oxidized fraction of PVA, calculated from the experimentally found value of the characteristic viscosity using the Mark-Kun-Houwink equation, amounted to 4.5 kDa. It was found that the addition of the original (non-oxidized) polyvinyl alcohol to aqueous solutions of 4- and 5-ASA does not change their UV spectra. At the same time, the introduction of an oxidized fraction of polyvinyl alcohol into aqueous solutions of aminosalicylic acids leads to spectral changes, indicating intermolecular interactions and complexation. By the method of molar ratios, it was shown that in dilute aqueous solutions OF of PVA forms complex 1 : 1 compounds with 4-ASA and 5-ASA, i.e., one molecule of 4- or 5-aminosalicylic acid accounts for one carboxyl group of the oxidized PVA fraction. Using this method, in the 291-316 K temperature range, the stability constants (K) of the resulting complex compounds were calculated. The results analysed demonstrated that the oxidized fraction of polyvinyl alcohol forms strong enough complexes with 4- and 5-aminosalicylic acids: the K values in the temperature range under study vary within (1-7)·10⁴ l/mol. It was found out that with increasing temperature, the values of stability constants of complex compounds decrease. The study of the temperature dependence of K made it possible to determine the standard values of the changes in the Gibbs energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) of complexing. Negative values of thermodynamic parameters indicate a spontaneous process of formation of complexes, their exothermicity and the resulting constraints of the movements of molecules.

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