Homogeneous multicomponent solids (solid solutions) could represent a viable alternative that could provide a better understanding and controlling of the structure-property relationships in drugs, in order to optimize their properties for practical applications. These phases consist of different molecular constituents randomly occupying equivalent crystallographic sites; and, more important, according to Vegard's law, the stoichiometry of the solid solutions allow changes in the concentration of each component without limitation to integer values. Those changes in composition are often accompanied by a continuous variation in some physical and/or chemical properties (e.g., density, solubility, stability, reactivity). One of the main requirements for the solid solution formation is based on geometrical approaches, which consider the shape of the host and guest molecules; and the packing density in the mixed crystal as well as the symmetry of the crystalline structure of the pure components. Solid solutions occur between isomorphic materials, which means the same space group and unit cell dimensions and/or substantially the same type and position of atoms or functional groups; or isostructural materials, having the same structure but not necessarily the same size or chemical composition of the unit cell. In the case of organic solid solutions, the similarity between the molecular forms is not only a condition, but the foremost and enough condition for the component solubility. The vast land of mixed crystals includes several applications, for example, in engineering organic field and pharmacological field. Lamivudine and emtricitabine are nucleoside analogues reverse transcriptase inhibitor antiretroviral drugs, which have extremely similar molecular structures, differing by a single fluorine atom. Due to these structural and molecular resemblances, lamivudine and emtricitabine are good candidates for producing a solid solution with physicochemical properties controlled by the stoichiometry. Following this hypothesis, it was verified the formation of a nonconventional solid-solution, whose crystalline structure is not defined by any of the individual constituents, but by the one of the lamivudine hydrate with emtricitabine as a solute. The crystalline structures of two members of the solid-solution were determined showing a non-uniform distribution of the solute among the independent molecules of the asymmetric unit of the lamivudine hydrate structure. Thermal analysis investigations confirmed that the physicochemical properties (for example the melting point) could be control through the variation of the emtricitabine content.

Keywords: solid-solution, antiretroviral, solvate