Ribitol and Xylitol: Explaining the Differences in Physical Chemical Properties

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The diastereomeric pentoses xylitol [1] and ribitol [2] show some remarkable differences in their physical properties in the solid state. Though xylitol has the lowest melting point (T = 93° C) it has a higher density (ρ = 1.540 g/cm³) than ribitol (T = 102° C, ρ = 1.488 g/cm³).

Based on accurate X-ray diffraction data we have performed experimental electron density studies and rigid-body TLS analyses, in order to analyse the interplay between entropy and enthalpy contributions to the free energy, and thereby explain the observed differences in physical properties.

Topological analyses of the electron densities show that the chemical bonds of the two pentoses are identical. Though the compounds have different hydrogen bond patterns, they most likely have very similar crystal packing energy. A result in accordance with calorimetric measurements and interaction energies derived from periodic DFT calculations.

Assuming that the translational and librational molecular normal modes are harmonic and uncoupled from the motion of neighbouring molecules we find the difference in vibrational entropy in the solid state to be 6 J mol^{-1} K^{-1}, a result that accounts quantitatively for the difference in melting point.

[1] Kim H. S., Jeffrey G. A., *Acta Cryst*., 1969, B**25**, 2607-2613. [2] Kim H.S., Jeffrey G. A., Rosensten R. D., *Acta Cryst*., 1969, B**25,** 2223-2230.

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