COSMO-BACKFITTING AS A PROMISING IN SILICO TOOL TO CHARACTERIZE UNDEFINED POLYMERS: ILLUSTRATION OF THE CONCEPT ON THE SOLUBILISATION OF CELLULOSE ACETATE

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Cellulose acetates derived from the renewable cellulose can be used, *inter alia*, to produce membranes by an inexpensive and simple process[1]. The solvents currently used for this process, such as cyclohexane or NMP, are volatile organic compounds and/or harmful to the environment or human health. Since there is a growing demand for more sustainable processes, an effective strategy to find safe and bio-based solvents able to solubilize this polymer is desirable[1].

The COSMO-RS theory (Conductor-like Screening Model for Real Solvents) provides a purely theoretical and computational method for the prediction of solubilities. The chemical potential (μ_S^X) of a solute X in a solvent S is calculated by statistical thermodynamics and quantum chemistry without experimental input (eq. 1). For this purpose, the molecular surface of a molecule is divided into interacting segments whose screening charge densities (σ) can be represented in the so-called σ-profile (p^X) (Fig. 1). The σ-potential (μ_S) describes the affinity of a system to a surface of polarity σ and the combinatorial term ($\mu_{C,S}^X$) considers the effects of size and shape. Solvents, in which the polymer has a low chemical potential, are predicted to be good solvents[2–4].

$$\mu_S^X = \mu_{C,S}^X + \int p^X(\sigma)\mu_s(\sigma) \qquad (1)$$

In order to avoid time-consuming quantum chemical calculations, COSMO-backfitting can also be used to generate a σ-profile, and thus calculate properties, using the fragmentation approach (COSMOfrag). In this approach, the σ-profile of the polymer is a composition of already pre-calculated σ-profiles from a database of 170 000 molecules (Fig. 1,2) Experimentally determined solubilities can be used as references otherwise only relative solubilities are calculated[5,6].

We used both COSMO-RS (via COSMOtherm software) and COSMO-backfitting (via COSMOquick software) to predict the solubility of cellulose acetate DS 2.5 (Degree Substitution). By comparing the predictions with our experimental results, we observed that both approaches are able to predict effective solvents quite well. However, the molecule's structure is not required for the calculations using COSMO-backfitting. Therefore, it's particularly useful for undefined polymer structures, even when they have a broad distribution of molar masses. Further, several non-toxic biosolvents of the polymers could be highlighted.

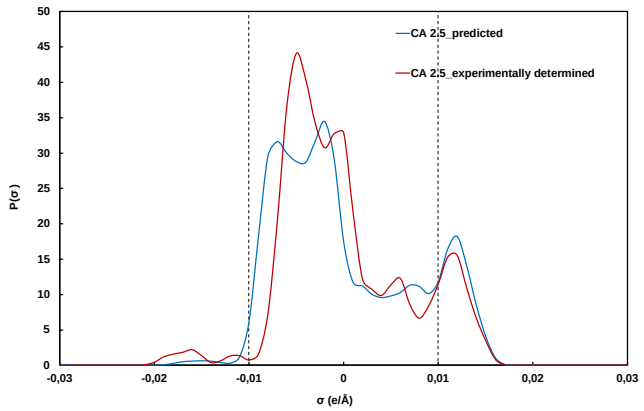

Figure 1: σ-profiles of cellulose acetate DS 2.5 predicted by COSMOtherm (blue curve) and experimentally determined solubility (red curve).

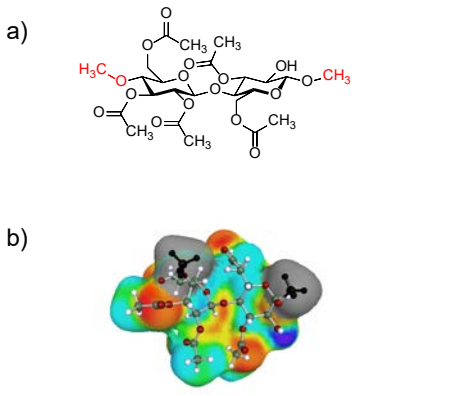

Figure 2: Structure (a) and σ-surface (b) of cellulose acetate DS 2.5.

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Back to Programme