Solubilities of oxygen and carbon dioxide in PDMS oils by computer simulation

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Bioconversion reactions involving whole cells are usually characterized by low volumetric productivities in aqueous media, due to the low solubility of both the substrates and the reaction products in water. In order to overcome this problem, organic solvents have been used as substrate/product pools, including some environmentally friendly substances in view of their low volatility and toxicity [1].

Silicone oils have successfully been used as production medium in conversion of sterols to steroids with whole cells in monophasic and biphasic systems [1]. For the process scale-up, a number of physical properties of the system are needed, such as viscosity of the production medium and solubility of metabolic gases (oxygen and carbon dioxide) in the organic solvent.

Polydimethylsiloxane (PDMS) and polymethylphenylsiloxane have been the most used silicone oils in production media for bioconversion reactions. In the case of polydimethylsiloxane, oils with kinematic viscosities of around 20 cSt are common (molecular weight of 2000). Solubilities of oxygen and carbon dioxide in such silicone oils are very scarce as well as their prediction by molecular simulation.

Makrodimitri *et al* [2] have developed a united atom force field for the calculation of structural and thermodynamic properties of pure PDMS. Using this force field, they have obtained, by simulation, solubilities of oxygen in PDMS (with an average molecular weight of around 6000), as well as solubilities and diffusion coefficients of other penetrant gases, such as *n*-alkanes, *n*-perfluoroalkanes and noble gases [3].

This work focused on prediction of the properties of silicone oils of short to moderate chain length (8 to 25 monomers, which corresponds to a molecular weight between around 750 and 2000) by computer simulation, in particular the solubility of oxygen and carbon dioxide in these liquids. Two different force fields were tested against experimental measurements of density for the shortest dimethylsiloxanes methyl terminated: Gromos-43 A1 and the force field developed by Makrodimitri *et al* specifically for PDMS.

Henry's constants for the dissolution of oxygen and carbon dioxide in PDMS oils were obtained as a function of temperature by computer simulation using both the force fields tested. The calculations were done for PDMS with three different chain lengths: 8, 16 and 25 monomers [$(CH_3)_2SiO$ units] with methyl termination in all cases. The force field developed by Makrodimitri *et al* provides the best description of the PDMS oils studied both in terms of density and gas solubility. Liquid structure and interaction between gas solute and solvent were also investigated by simulation.

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