



# Thermodynamics of solvation in propylene glycol and methyl cellosolve



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## ABSTRACT

Limiting activity coefficients of low-polar substances: aliphatic and aromatic hydrocarbons, including alkanes, cycloalkanes, alkylbenzenes, and halobenzenes in two solvents, propylene glycol and methyl cellosolve, were measured at temperature  $T = 298.15$  K using gas chromatographic headspace analysis technique. The Gibbs free energies of solvation were calculated from these data and analyzed together with the enthalpies of solvation for the same systems. It was shown that the Gibbs free energies of solvation in propylene glycol are significantly lower than in its homologue ethylene glycol, and in methyl cellosolve they are lower than in propylene glycol. This difference is mainly due to the solvophobic effect, which strength is decreasing in the same order: ethylene glycol > propylene glycol > methyl cellosolve. The contribution of the solvophobic effect into the Gibbs free energies of solvation can be determined using a Gibbs free energy versus enthalpy of solvation plot. This contribution is shown to grow up linearly with the molecular volume of a solute in propylene glycol and methyl cellosolve, as well as in ethylene glycol and in monohydric alcohols.

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## 1. Introduction

Methyl cellosolve (2-methoxyethanol,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ , further MC) and propylene glycol (1,2-propanediol,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$ , further PG) are important industrial solvents. They are also structural isomers differing from a molecule of another industrial solvent, ethylene glycol (1,2-ethanediol,  $\text{HOCH}_2\text{CH}_2\text{OH}$ , further EG), by one  $\text{CH}_2$  group.

The process of solvation of a molecule by transferring it from the gas phase into solvent can be described in terms of thermodynamic functions. The standard molar Gibbs free energy of solvation  $\Delta_{\text{solv}}G$  is related to the Ostwald solubility coefficient  $L$  of a gaseous solute through equation  $\Delta_{\text{solv}}G = RT \ln(RT/LP^\circ V_M)$ , where  $V_M$  is the molar volume of solvent,  $P^\circ$  is the standard pressure, and the molar fraction based standard state is used for solution. For solid and liquid solutes, it is the difference of the standard molar Gibbs free energies of dissolution at infinite dilution and vaporization of a solute:  $\Delta_{\text{solv}}G = \Delta_{\text{soln}}G - \Delta_{\text{vap}}G$ . In turn,  $\Delta_{\text{soln}}G$  can be related to the limiting activity coefficient  $\gamma_\infty$  of a given solute in a given solvent:  $\Delta_{\text{soln}}G = RT \ln \gamma_\infty$ . Knowledge of the values of solvation properties is useful for optimization of industrial processes and for the development of models of solutions. However, the Gibbs free energies of solvation in PG and MC have been unknown for almost any compound.

In the bulk liquid phase, both MC and PG molecules are able to form hydrogen bonds with each other. The molecules of PG have two hydroxyl groups and can form a branched three-dimensional network of hydrogen bonds similar to that of ethylene glycol. The molecule of MC has only one hydroxyl group and is unable to form similar structures. Though not studied yet, the mechanism of self-association of liquid MC should be similar to that of monohydric alcohols forming chain linear and cyclic hydrogen-bonded aggregates. Such difference in the structure of the liquid phase should lead to a significant difference in solvation properties of these two isomeric solvents.

An interesting feature of self-associating solvents is the solvophobic effect. Compounds which are unable to be a donor neither an acceptor of hydrogen bonds have an increased Gibbs free energy of solvation and, therefore, a decreased solubility in solvents that form intermolecular hydrogen bonds. Such solutions are also characterized with low entropies of solvation and increased heat capacity in comparison with solutions of the same compounds in aprotic organic solvents. Such behavior is known as the solvophobic effect [1,2] and is similar to the hydrophobic effect in water. The solvophobic effect can stabilize micelles, vesicles or other non-covalently bonded structures in non-aqueous media. Formation of micelles in PG has been studied, in particular, on the sample of nonylphenoxypolyethoxyethanol [3]. However, the solvophobic effect induced by PG is much weaker than the hydrophobic effect in water, and PG is able to denaturate or weaken the hydrophobically bonded structure of proteins [4] like other organic solvents.

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