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, $CH_3OCH_2CH_2OH$, further MC) and propylene glycol (1,2-propanediol, $CH_3CH(OH)CH_2OH$, further PG) are important industrial solvents. They are also structural isomers differing from a molecule of another industrial solvent, ethylene glycol (1,2-ethanediol, $HOCH_2CH_2OH$, further EG), by one 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 $\Delta_{solv}G$ is related to the Ostwald solubility coefficient L of a gaseous solute through equation $\Delta_{solv}G = RT \ln(RT/LP°V_M)$, where V_M is the molar volume of solvent, $P°$ 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: $\Delta_{solv}G = \Delta_{soln}G - \Delta_{vap}G$. In turn, $\Delta_{soln}G$ can be related to the limiting activity coefficient γ_∞ of a given solute in a given solvent: $\Delta_{soln}G = RT \ln \gamma_\infty$. 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 noncovalently 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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In our recent papers [1,5–7] we developed a methodology to describe the solvophobic effect in various solvents on the basis of the values of Gibbs free energy and enthalpy of solvation for low-polar solutes. Now we report new experimental values of the Gibbs free energy of solution and solvation in PG and MC and apply the above mentioned method to compare the strength of the solvophobic effect in these two and other solvents.

2. Experimental

2.1. Available experimental data on the thermodynamic functions of diluted solutions

In our previous paper [8], we have studied the enthalpies of solution in PG and MC for a set of low-polar compounds. No other values of the enthalpies of solution of hydrocarbons and their halogenated derivatives in these solvents were found in literature.

The Gibbs free energy of solvation in PG can be calculated for several low polar solutes from the experimental data reported in literature, though this solvent is much less studied than its homologue, ethylene glycol. Even less data are available for MC. Leitman and Gaile published [9] the values of limiting activity coefficients of several C_6 to C_9 hydrocarbons in PG at $T = (316$ and $324)$ K. In the work [10], the temperature dependences of the solubility of n-heptane in PG and vice versa were studied. (Despite this is not a strict formula, the (liquid + liquid) equilibrium data for poorly soluble compounds expressed in molar fractions can be used to estimate the limiting activity coefficient through equation $\gamma_\infty = x_{22}/x_{21}$, where x_{22} and x_{21} are the molar fractions of compound 2 in two equilibrium phases, and then we can calculate the Gibbs free energy of solvation). Later, the solubilities of n-hexane, n-heptane, n-octane, benzene, toluene, ethylbenzene, o-, m-, and p-xylene in PG were reported [11] at various temperatures. The solubility of phenothiazine was measured in PG [12] and the solubility of pyrene in MC [13]. Limiting activity coefficients of benzene, cyclohexene and cyclohexane in PG were also measured [14] at temperatures $T > 343$ K. Rohrshneider reported [15] (gas + liquid) partition coefficients at $T = 298$ K for a large set of (solute + solvent) systems including octane and toluene dissolved in MC. Later, Park et al. [16] investigated the same set of solutes and solvents using an improved methodology. There are several works on the solubilities of saturated hydrocarbons [17,18] in MC at various temperatures and pressures, but the concentrations at saturation are rather high and these data cannot be used to calculate the Gibbs free energy of solvation related to infinitely diluted solutions. For hydrocarbon-MC systems, VLE data have also been obtained [19,20], but not at $T = 298$ K.

In the present work, novel data for solutions of hydrocarbons and their halogenated derivatives in PG and MC at infinite dilution and $T = 298$ K are obtained using GC headspace techniques. These results are used for both qualitative and quantitative interpretation of solvophobic effects in PG and MC.

2.2. Materials and methods

Propylene glycol and methyl cellosolve with purity > 0.99 were purchased from Acros Organics. All the solutes were at least 0.99 pure grade from Sigma–Aldrich, Acros and Fluka. They have been used without further purification. The absence of significant amounts of impurities has been confirmed by gas chromatography (see table 1).

2.3. Measurement of limiting activity coefficients

Limiting activity coefficients in PG and MC solutions were determined by GC headspace analysis using PerkinElmer Clarus

TABLE 1
Source and purity of the chemicals.

Chemical name	Mass fraction purity	Source
Propylene glycol	0.99	Acros Organics
Methyl cellosolve	0.99	Sigma–Aldrich
n-Hexane	0.99	Sigma–Aldrich
n-Heptane	0.99	Acros Organics
n-Octane	0.99	Sigma–Aldrich
n-Nonane	0.99	Acros Organics
n-Decane	0.99	Acros Organics
n-Undecane	0.99	Acros Organics
Methylcyclopentane	0.995	Sigma–Aldrich
Cyclohexane	0.995	Acros Organics
Methylcyclohexane	0.99	Acros Organics
Cyclooctane	0.99	Sigma–Aldrich
Cyclohexene	0.99	Acros Organics
1,7-Octadiene	0.99	Acros Organics
4-Vinyl-1-cyclohexene	0.995	Fluka
Benzene	0.99	Sigma–Aldrich
Toluene	0.998	Sigma–Aldrich
Ethylbenzene	0.99	Fluka
o-Xylene	0.99	Sigma–Aldrich
m-Xylene	0.99	Sigma–Aldrich
p-Xylene	0.99	Sigma–Aldrich
p-Cymene	0.99	Acros Organics
Fluorobenzene	0.99	Acros Organics
Chlorobenzene	0.996	Acros Organics
Bromobenzene	0.99	Acros Organics
Naphthalene	0.99	Acros Organics

580 chromatograph with a headspace autosampler. The samples of equilibrium vapor phase were taken from thermostated $(T = 298$ K) 22 ml vials containing 5 ml of solution or pure substance and transferred to the gas chromatograph.

The ratio of areas of chromatographic peaks in experiments with a solution and with pure solute (denoted as A) is equal to the ratio of vapor pressures $p^{A/S}/p_{sat}^A$ of solute A over its dilute solution in solvent S and over pure A. The limiting activity coefficient $\gamma_\infty^{A/S}$ is given by: $\gamma_\infty^{A/S} = p^{A/S}/(p_{sat}^A \cdot x^{A/S})$, where $x^{A/S}$ is the molar fraction of A in solution. We made a correction of initial molar fraction of solute for the quantity of evaporated solute. Measurements were carried out at 3 to 4 different concentrations of every solute in the range (0.1 to 1.5) vol% and repeated 2 times for each concentration. No significant difference between the values of the activity coefficients at different concentrations in this range was observed. An average value of the Gibbs free energy of solution $\Delta_{soln}G^{A/S} = RT \ln \gamma_\infty^{A/S}$ from all measurements with the same dissolved compound was taken. The Gibbs free energy of solvation can be calculated using a formula $\Delta_{solv}G^{A/S} = \Delta_{soln}G^{A/S} - \Delta_{vap}G^A$, where the Gibbs free energy of vaporization $\Delta_{vap}G^A = -RT \ln p_{sat}^A$. The values of p_{sat}^A were taken from EPA database [21]. Results are presented in tables 2 and 3. The standard pressure is 1 bar and the standard state for solutions is a hypothetical ideal solution with unit molar fraction of a solute. Relatively large uncertainties were observed in the case of solvation of alkanes in PG (up to 16% for hexane, or ±0.4 kJ · mol^{-1} in the Gibbs energies scale). This is apparently because of a low speed of dissolution of poorly soluble alkanes in viscous PG. It takes a long time to reach the vapor–liquid equilibrium in these systems. In our experiments, we subjected the solutions to vigorous shaking in a vortex. Without this step, alkanes almost did not dissolve, which can be judged by the chromatographic peak areas.

3. Discussion

A comparison of the obtained results with literature values can be made for some systems. The data for solvation of octane and