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# Calorimetric study of solvation of low polar solutes in propylene glycol and methyl cellosolve at 298 K

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ABSTRACT

Enthalpies of solution 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 titration calorimetry. In addition, the enthalpies of solution of poorly soluble solid solutes, naphthalene and biphenyl, in these solvents were determined using indirect method by measuring the enthalpies of solution of liquid mixtures containing them. The enthalpies of solvation from the gas phase were calculated from these data.

The enthalpies of solvation in propylene glycol and methyl cellosolve and previously reported enthalpies of solvation in ethylene glycol were correlated with each other and with molecular parameters of solutes.

## 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 two structural isomers and two important industrial solvents [1]. Methyl cellosolve is used as a solvent in dye and rubber industries, production of cellulose acetate films and laboratory organic synthesis. MC is a toxic compound which can be converted by alcohol dehydrogenase into methoxyacetic acid which can enter the Krebs cycle [2]. In contrast, PG has a very low toxicity for humans.[3] Thus, it is used as a solvent for pharmaceuticals and in food industry, as well as in rubber and polymer production, and as a component of automotive antifreeze. Both MC and PG molecules differ by a methyl group from a molecule of another common industrial solvent, ethylene glycol (1,2-ethanediol, $HOCH_2CH_2OH$, further EG).

The solvent effect on equilibria in chemical reactions, solubility, interfacial distribution properties of dissolved compounds is governed by the Gibbs free energy change. The enthalpy of solvation (transfer of solute from the gas phase into solvent) determines the dependence of the Gibbs energy of solvation on temperature according to Van't Hoff equation. Despite a broad practical use of PG and MC, thermodynamic functions of solvation or solution in these solvents are almost not studied.

Our special interest is the solvophobic effect in self-associated solvents and its influence on the solvation properties. Both MC and PG are self-associated due to intermolecular hydrogen bonds. In our previous papers [4–6] 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. Thus, in this work we have selected a number of such solutes to determine their enthalpies of solution in PG and MC.

Calorimetric measurement of the enthalpies of solution for non-polar solutes in PG is complicated by their low solubility, low speed of dissolution, and a high viscosity of solvent. No values of the enthalpies of solution of hydrocarbons and their halogenated derivatives in PG were found in literature. The solubility of hydrocarbons in MC is higher, but the calorimetric data for their solutions are also very limited.

In the present work, novel thermodynamic data for solutions of hydrocarbons and their halogenated derivatives in PG and MC at infinite dilution and $T = 298$ K are obtained using titration calorimetry technique.

## 2. Experimental

### 2.1. 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

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amounts of impurities has been confirmed by gas chromatography.

### 2.2. Enthalpy of solution measurements

Enthalpies of solution at infinite dilution at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa have been determined using TAM III precision solution calorimeter in 100 ml glass calorimetric vessel equipped with a gold stirrer, a Joule heater and a thermistor. The calorimeter operates under semi-adiabatic condition. The vessel is placed inside a thermostatted metal cylinder, and the temperature change inside the vessel is measured. The vessel exchanges heat with the thermostat in agreement with Newton's law of cooling, which leads to the exponential dependence of the vessel's temperature from time, if no heat is evolved or absorbed due to any physical or chemical processes. In experiments, the heat effects were calculated from temperature vs time curves using Regnault–Pfaundler method [7], which takes into account exponential character of the baseline. This method is integrated into SolCal software used to operate the calorimeter.

For liquid solutes, calorimetric titration method was used. The vessel was initially filled with 100 ml of pure solvent. After thermostatting and heater calibrations, 50–100 μl of solute was added from an electronically operated microsyringe in 5–20 μl portions. The heat effect of each addition was determined from a calorimetric curve. For every solute, the experiments were repeated 2–3 times with a fresh portion of solvent. An average value of enthalpy of solution from all dissolution curves was taken.

If a solute is volatile and poorly soluble, we should make a correction in order to account for the heat loss due to evaporation of a part of the solute molecules to a free volume of the calorimetric vessel. The standard molar enthalpy of solution obtained from calorimetric curves $\Delta H_{\mathrm{obs}}$ is equal to the sum of heat effects of dissolution and evaporation of some part of a solute:

$$\Delta H_{\mathrm{obs}} = (1-\varphi)\Delta_{\mathrm{soln}}H^{\mathrm{A/S}} + \varphi\Delta_{\mathrm{vap}}H^{\mathrm{A}} \qquad (1),$$

where $\Delta_{\mathrm{soln}}H^{\mathrm{A/S}}$ is the molar enthalpy of solution of solute A in solvent S, $\Delta_{\mathrm{vap}}H^{\mathrm{A}}$ is the enthalpy of evaporation of A, $\varphi$ is the molar fraction of solute in the vapor phase that can be calculated by equation:

$$\varphi = \frac{1}{\left(1 + \mathrm{RT}\nu_{\mathrm{S}} / \left(p_{\mathrm{sat}}^{\mathrm{A}} \gamma_{\infty}^{\mathrm{A/S}} V_{\mathrm{free}}\right)\right)} \qquad (2)$$

Here $p_{\mathrm{sat}}^{\mathrm{A}}$ is the saturated vapor pressure of pure substance A, $\gamma_{\infty}^{\mathrm{A/S}}$ is the limiting activity coefficient of A dissolved in S, $V_{\mathrm{free}}$ is the volume of the free space in the calorimetric vessel, $\nu_{\mathrm{S}}$ – number of moles of solvent in the vessel.

However, in all the cases except for saturated hydrocarbons dissolved in PG, the contribution of evaporation process to the measured enthalpies of solution is very small. For example, even for volatile hexane in MC the estimated value of $\varphi\Delta_{\mathrm{vap}}H^{\mathrm{A}}$ is only 0.05 kJ·mol$^{-1}$, which is less than the uncertainty of the experiment. Thus, we assumed that $\Delta H_{\mathrm{obs}} = \Delta_{\mathrm{soln}}H^{\mathrm{A/S}}$. For alkanes and cyclohexane in PG, which have a poor solubility and low liquid–gas distribution coefficient, we calculated the corrected values of $\Delta_{\mathrm{soln}}H^{\mathrm{A/S}}$ by Eq. (1) using literature values of $\Delta_{\mathrm{vap}}H^{\mathrm{A}}$ [8], $p_{\mathrm{sat}}^{\mathrm{A}}$ [9], and the values of $\gamma_{\infty}^{\mathrm{A/S}}$ estimated from the solubilities reported in literature [10].

Solid solutes were placed in sealed glass ampoules, which were then broken inside a calorimetric vessel with the solvent. The heat effect of dissolution following ampoule break was measured. However, the process of complete dissolution took up to several hours. The results were very sensitive to the method of calculation since the baseline is not absolutely stable on such a long timescale. The values of $\Delta_{\mathrm{soln}}H^{\mathrm{A/S}}$ can differ by up to 3–4 kJ·mol$^{-1}$ depending on which moment is thought to be the end of dissolution and which part of the baseline after dissolution is chosen.

To obtain more accurate results, we developed another experimental method. Given that we want to find the molar enthalpy of solution $\Delta_{\mathrm{soln}}H^{\mathrm{A/S}}$ of a solid compound A in a solvent S, but A has a poor solubility in S. We choose one of the solvents (let us denote it by B) in which compound A has the best solubility and prepare a concentrated (but not saturated) solution (A + B) in this solvent with the molar fraction of A $x_{\mathrm{A}}$. It is important for B to be relatively well soluble in S, otherwise the results can be inaccurate. Then we measure the molar enthalpy of solution of the mixture (A + B) by means of titration calorimetry in solvent S ($\Delta_{\mathrm{soln}}H^{\mathrm{A+B/S}}$) and in another (reference) solvent R ($\Delta_{\mathrm{soln}}H^{\mathrm{A+B/R}}$). The molar enthalpies of solution for compound B must be measured separately in both solvents S and R ($\Delta_{\mathrm{soln}}H^{\mathrm{B/S}}$ and $\Delta_{\mathrm{soln}}H^{\mathrm{B/R}}$). If all solutions are very diluted and we can neglect the interactions between the molecules of A and B, then the following relationship is correct (due to the fact that enthalpy is a function of state):

$$\Delta_{\mathrm{soln}}H^{\mathrm{A/S}} = \frac{\Delta_{\mathrm{soln}}H^{\mathrm{A/R}} + \left(\begin{array}{l} \Delta_{\mathrm{soln}}H^{\mathrm{(A+B)/S}} - \Delta_{\mathrm{soln}}H^{\mathrm{(A+B)/R}} \\ \quad - (1-x_{\mathrm{A}})\left(\Delta_{\mathrm{soln}}H^{\mathrm{B/S}} - \Delta_{\mathrm{soln}}H^{\mathrm{B/R}}\right) \end{array}\right)}{x_{\mathrm{A}}} \qquad (3).$$

Here the enthalpy of solution of solid A in solvent R, $\Delta_{\mathrm{soln}}H^{\mathrm{A/R}}$ must be known or measured. If we choose a solvent in which A has a good solubility, then the value of $\Delta_{\mathrm{soln}}H^{\mathrm{A/R}}$ can be measured with a good precision. It is also important to use a mixture with a high value of $x_{\mathrm{A}}$, because the uncertainties of four measured enthalpies of solution are divided by $x_{\mathrm{A}}$ making the error of $\Delta_{\mathrm{soln}}H^{\mathrm{A/S}}$ inversely proportional to it. This approach resembles that used by Desnoyers et al. [11] for a liquid solute (benzene) to determine its enthalpy of solution in water-rich binary aqueous-organic solvent.

In our experiments, we prepared the mixtures of naphthalene and biphenyl with tetrahydrofuran with the molar fraction of a solute around 0.2. The enthalpies of solution of tetrahydrofuran in PG, MC, and cyclohexane were measured and found to be 1.57, 1.20, and 3.31 kJ·mol$^{-1}$ respectively. Solid aromatic hydrocarbons rapidly dissolve in other hydrocarbons, and cyclohexane has been chosen as (reference) solvent R. For both solid naphthalene and biphenyl, the enthalpies of solution in cyclohexane were measured (22.7 and 23.8 kJ·mol$^{-1}$ respectively). The enthalpies of solution of the liquid mixtures in PG, MC, and cyclohexane were also measured, and the enthalpies of solution of naphthalene and biphenyl in PG and MC have been calculated by Eq. (3). To verify our method, two additional measurements were conducted for the mixture of biphenyl with tetrahydrofuran dissolved in acetone and pure tetrahydrofuran dissolved in acetone. From these experiments and Eq. (3), the enthalpy of solution of biphenyl in acetone was found to be 19.1 kJ·mol$^{-1}$, while a direct measurement gives 19.3 kJ·mol$^{-1}$.

The results of measurements along with the standard deviations $u(\Delta_{\mathrm{soln}}H^{\mathrm{A/S}})$ are given in Tables 1–3. The standard state for liquid (at $T = 298$ K) solutes is the pure liquid and for solids at $T = 298$ K it is the pure solid substance.

## 3. Discussion

The existing literature calorimetric data on the considered systems are limited to the excess enthalpies of mixtures of MC with cyclohexane [12–14] at several temperatures including $T = 298.15$ K, and the enthalpies of mixing of MC with n-hexane, n-heptane, n-octane, and n-decane at $T = 323.15$, 348.15, and 373.15 K [15]. An estimated value of the enthalpy of solution of