Enthalpies and Gibbs free energies of solvation in ethylene glycol at 298 K: Influence of the solvophobic effect

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ABSTRACT

Enthalpies of solution of low-polar substances: aliphatic and aromatic hydrocarbons, including alkanes, cycloalkanes, alkylbenzenes, naphthalene, biphenyl, and halobenzenes in ethylene glycol were measured at temperature $T = 298.15$ K using semi-adiabatic solution calorimetry. For some of these systems, previously unknown values of limiting activity coefficients were also determined using GC headspace analysis. Consideration of compensation plots of the Gibbs free energy vs enthalpy of solvation shows that the behavior of solutions in ethylene glycol is different from that of solutions in non-associated aprotic solvents. The Gibbs energies of solvation are significantly increased relative to the enthalpies, which is the sign of the solvophobic effect. The contribution of the solvophobic effect into the Gibbs energies of solvation of various substances was quantified using an extrathermodynamic approach. A linear correlation between this quantity and a molecular volume of dissolved compound was found. The solvophobic effect in ethylene glycol is stronger than in monohydric alcohols, weaker than in formamide and much weaker than in water. It is also entropy-driven and does not affect the enthalpies of solution of the studied substances in ethylene glycol.

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1. Introduction

Ethylene glycol (EG) HOCH$_2$CH$_2$OH is a polar protic organic solvent, which is widely used in industry. Most of it is used as a component of automotive antifreeze, engine coolants, and in synthesis of polymers (mainly polyethylene terephthalate). Besides a low price, a very important feature of EG is that it is miscible with water in any proportion and is very hygroscopic. Thus, EG also finds its application as a desiccant, particularly to prevent formation of gas hydrates in pipelines.

Strong affinity between EG and water is due to the similarity in structure of the liquid phase of these two solvents. Both molecules simultaneously have proton acceptor and donor sites. In the bulk phase, each molecule of EG in average engages in slightly lower than four hydrogen bonds [1], as well as each molecule in liquid water [2]. Molecular dynamics simulations show [3] that in liquid EG molecules form a water-like three-dimensional network of hydrogen bonds. Among other dihydric alcohols, which may exhibit similar behavior, EG is the simplest compound that has the highest concentration of hydrogen bonds in the bulk phase and should therefore be the most water-like.

A very important and interesting phenomenon observed in aqueous solutions is the hydrophobic effect. It has diverse manifestations, most notably affecting thermodynamic properties of solutions. In EG, similar (solvophobic [4]) effects take place. Apolar substances have low solubilities and high values of the Gibbs energy of dissolution in both solvents, while highly polar organic solutes, which are capable to form hydrogen bonds, are well-soluble in both water and EG. The hydrophobic effect is a driving force of micelle formation processes in solutions of amphiphilic substances. In EG, formation of micelles from nonionic [4] and cationic [5] surfactants has been observed.

Some other properties of EG and solutions in it have been used to show the presence of solvophobic effects [6], such as a low value of isothermal compressibility, dependencies of excess heat capacity and surface thermodynamic functions [7] of solutions from concentration.

However, thermodynamic properties of solutions in EG have not been studied extensively enough, despite their interesting characteristics and industrial importance of mixtures containing ethylene glycol. The enthalpies of solution are unknown even for the simplest organic molecules. The aim of the present work is to extend our knowledge about thermodynamic properties (enthalpies and Gibbs free energies at 298.15 K) of solution of low polar compounds in EG and the solvophobic effect which takes place in them. The values of thermodynamic functions of solution are not only of interest in order to compare the behavior of EG and aqueous solutions, but

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List of symbols

ΔH enthalpy change
ΔG Gibbs free energy change
R the gas constant
T temperature
p pressure or vapor pressure
x mole fraction
V volume
V_x^A characteristic molecular volume of compound A
γ activity coefficient
ν number of moles
δg solvent parameter used in Eq. (4)

Superscripts
A   solute
S   solvent
EG   ethylene glycol
A/S   infinitely dilute solution of solute A in solvent S

Subscripts
solv   solvation
soln   solution
vap   vaporization
solv(nonsp)   non-specific solvation
s.e.   solvophobic effect
sat   saturated vapor
∞ infinite dilution

may also serve as the basis for development of predictive models to calculate various properties of solutions and mixtures, or design of separation and synthetic processes.

2. Experimental

2.1. Available data on the thermodynamic functions of diluted solutions in EG

Low solubility and low speed of dissolution of non-polar compounds in EG complicates calorimetric measurement of their enthalpies of solution. Also, a high viscosity of the solvent impedes stirring of solution in a calorimetric cell. In part because of these difficulties, the enthalpies of solution of hydrocarbons and their halogenated derivatives in EG have not been determined previously. Even for polar organic substances, only a few values of enthalpies of solution in EG were measured, namely for n-alcohols [8,9] and tetraalkylammonium halogenides [10].

Gibbs free energies of solution in EG are known for much more solutes, including apolar compounds. They can be calculated from gas–liquid distribution or limiting activity coefficients. In paper [11], 44 gas-EG partition coefficients of noble gases, alkanes, alkenes, arenes and a few polar compounds were collected from literature sources. Some additional new values were reported in a later compilation [12]. Additionally, partition coefficients for many various organic compounds in the n-heptane–EG biphasic system were measured [11,13,14]. Since EG and heptane are poorly soluble in each other, one can find a gas-EG partition coefficient if both heptane-EG and gas-heptane partition coefficients are known.

In the present work, novel thermodynamic data obtained using calorimetric and GC headspace techniques are reported. These results are used for both qualitative and quantitative interpretation of solvophobic effects in EG.

2.2. Materials and methods

Ethylene glycol with purity >0.999 was purchased from Acros Organics. All the solutes were at least 0.99 pure grade from Sigma–Aldrich, Acros and Fluka. They were used without further purification. The absence of significant amounts of impurities was confirmed by gas chromatography.

2.2.1. Enthalpy of solution measurements

Enthalpies of solution 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. For liquid solutes, calorimetric titration method was used. The vessel was initially filled with 100 ml of pure EG. After about an hour of 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. Solid solutes were placed in sealed glass ampoules, which were then broken inside a calorimetric vessel with EG. The heat effect of dissolution following the ampoule break was measured. For every solute, the experiments were repeated 2–3 times with a fresh portion of solvent. Since most of the solutes we studied were volatile and poorly soluble, a correction was made 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 molar enthalpy of solution obtained from calorimetric curves ΔH_{obs} is equal to the sum of heat effects of dissolution and evaporation of some part of a solute:

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

where $\Delta_{soln}H^{A/S}$ is the molar enthalpy of solution of solute A in solvent S, $\Delta_{vap}H^A$ is the enthalpy of evaporation of A, φ is the molar fraction of solute in the vapor phase that can be calculated by equation $\varphi = 1/\left(1 + RT\nu_S/\left(p_{sat}^A\gamma_\infty^{A/S}V_{free}\right)\right)$. Here p_{sat}^A is the saturated vapor pressure of pure substance A, $\gamma_\infty^{A/S}$ is the limiting activity coefficient of A dissolved in S, V_{free} is the volume of the free space in the calorimetric vessel, ν_S is the number of moles of solvent in the vessel.

We calculated the values of $\Delta_{soln}H^{A/S}$ from the results of calorimetric measurements using literature values of $\Delta_{vap}H^A$ [15], p_{sat}^A [16], and literature [12] or measured as described below values of $\gamma_\infty^{A/S}$. For each solute, an average value of enthalpy of solution from all dissolution curves was taken. The results along with the experimental uncertainties $u(\Delta_{soln}H^{A/EG})$ are given in Table 1. The contribution of evaporation process ($\varphi\Delta_{vap}H^A$, Eq. (1)) to the measured enthalpies of solution is also provided, it is very small for relatively well-soluble aromatic solutes and significantly large for saturated compounds.

2.2.2. Measurements of limiting activity coefficients

Limiting activity coefficients in EG solutions were determined by GC headspace analysis using PerkinElmer Clarus 580 chromatograph with Turbomatrix HS-16 headspace autosampler. The samples of equilibrium vapor phase were taken from thermostated (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 A is equal to the ratio of vapor pressures $p^{A/S}/p_{sat}^A$ of solute A over its dilute solution in S and over pure A. The limiting activity coefficient $\gamma_\infty^{A/S}$ is given by: $\gamma_\infty^{A/S} = p^{A/S}/\left(p_{sat}^A \cdot x^{A/S}\right)$, 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 different concentrations of every solute in the range

Table 1
Experimental values of enthalpies of solution in EG, vaporization and solvation in EG at $T = 298.15$ K and atmospheric pressure.

Solute (A)	$\Delta_{soln}H^{A/EG}$ (kJ mol^{-1})	$\Delta_{vap}H^{A}$ (kJ mol^{-1}) [15]	$\varphi\Delta_{vap}H^{A}$ (kJ mol^{-1})	$u(\Delta_{soln}H^{A/EG})$ (kJ mol^{-1})	$\Delta_{solv}H^{A/EG}$ (kJ mol^{-1})
Hexane	8.5	31.4	1.44	0.5	−22.9
Heptane	9.5	36.6	0.88	0.3	−27.1
Octane	10.7	41.6	0.52	0.5	−30.9
Nonane	11.8	46.5	0.30	0.5	−34.7
Cyclohexane	7.3	33.1	0.42	0.3	−25.8
Methylcyclohexane	7.7	35.1	0.38	0.5	−27.4
Benzene	2.09	33.9	0.05	0.1	−31.8
Toluene	2.70	38.0	0.05	0.1	−35.3
Ethylbenzene	3.55	42.4	0.02	0.1	−38.9
o-Xylene	3.65	42.9	0.02	0.3	−39.3
m-Xylene	3.6	42.7	0.02	0.3	−39.0
p-Xylene	3.75	42.3	0.02	0.3	−38.7
Fluorobenzene	1.05	34.5	0.04	0.1	−33.4
Chlorobenzene	1.92	40.3	0.01	0.1	−38.4
Bromobenzene	0.92	44.8	<0.01	0.1	−43.9
Naphthalene	18.5	72.3	<0.01	1	−53.8
Biphenyl	17.6	82.9	<0.01	1	−65.3

0.1–1.5 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 $\Delta_{solv}G^{A/S} = \Delta_{soln}G^{A/S} - RT \ln p_{sat}^{A}$. The values of p_{sat}^{A} were taken from EPA database [16]. Results are presented in Table 2. The standard states are 1 bar fugacity of gaseous solute A and the hypothetical ideal solution with unit molar fraction of A.

3. Discussion

3.1. Thermodynamic functions of solvation in ethylene glycol

No measured or calculated values of the enthalpies of solution for the studied substances in EG were found in literature to make a comparison with our results. In contrast, the Gibbs free energies of solvation in EG can be calculated from the literature data on Ostwald solubility coefficients. Our results are in good agreement with these values (last column of Table 2). Thus, we did not determine limiting activity coefficients of all those solutes for which we measured the enthalpies of solution, and use literature data in further discussion. Only for three studied compounds the Gibbs energies of solvation were unknown: fluorobenzene, chlorobenzene and iodobenzene. The Ostwald solubility coefficients in EG for these substances were predicted using a PCA model [18], but the results recalculated into the values of $\Delta_{solv}G^{A/EG}$ and given in parentheses in the last column of Table 2 are in total disagreement

with the experiment. It seems that solvation in EG cannot be adequately described with the solvent parameters used in the current version of this model. We can also compare these values with the prediction of LSER model [12], which gives better agreement with the experiment.

It is interesting to compare the values of thermodynamic functions of solvation in EG with those in methanol. A molecule of EG has the same ratio of carbon atoms number to oxygen atoms number as a molecule of methanol. However, they have completely different hydrogen bonding patterns. The molecules of methanol can only form intermolecular hydrogen bonds – with one other molecule as a HB-donor and with another one as a HB-acceptor, while EG can form both intermolecular and intramolecular bonds and has two proton donating sites, which enables it to form a complicated branched network of hydrogen bonds in liquid state. In addition, EG is more polar than methanol as measured by various solvent polarity scales such as π^* [19] or SPP scale [20].

The comparison of thermodynamic functions of solvation in two solvents shows that the values of $\Delta_{solv}H^{A/EG}$ (Table 1) and $\Delta_{solv}H^{A/CH_3OH}$ for the same solute A are linearly correlated (Fig. 1a). For the Gibbs energies of solvation, the correlation is worse, and it may be more proper to consider two separate correlations for aliphatic and aromatic solutes (Fig. 1b). It is important that for all solutes the Gibbs energies of solvation in EG are higher than those in methanol.

However, without additional analysis it is not clear whether the high values of the Gibbs energies of solvation of apolar compounds in EG are related to the solvophobic effect caused by high affinity of solvent molecules to each other (like in water) or can be explained in terms of unfavorable solute–solvent van der Waals interactions

Table 2
Experimental values of limiting activity coefficients and Gibbs free energies of solution and solvation in EG at $T = 298$ K.[e]

Solute (A)	$\gamma_{\infty}^{A/EG}$	$u(\gamma_{\infty}^{A/EG})$	$\Delta_{soln}G^{A/EG}$ (kJ mol^{-1})	$\Delta_{solv}G^{A/EG}$ (kJ mol^{-1})	$\Delta_{solv}G^{A/EG}$ (kJ mol^{-1}) from literature
Benzene	32	3	8.6	3.5	3.5[a]
Toluene	93	6	11.2	3.1	1.7[a], 3.6[b]
Fluorobenzene	32	5	8.6	2.9	(−14.0[c], 4.4[d])
Chlorobenzene	40	4	9.1	−1.1	(−7.2[c], 1.0[d])
Bromobenzene	45	5	9.4	−3.4	−3.3[a]
Iodobenzene	42	5	9.3	−7.0	(−28.7[c], −4.5[d])
Naphthalene	238	25	13.6	−9.0	−9.2[a]

[a] Calculated from gas-liquid partition coefficients compiled in ref [12].
[b] Calculated from gas-liquid partition coefficient measured in ref [17].
[c] Estimated using a PCA model [18].
[d] Estimated using LSER equation [12].
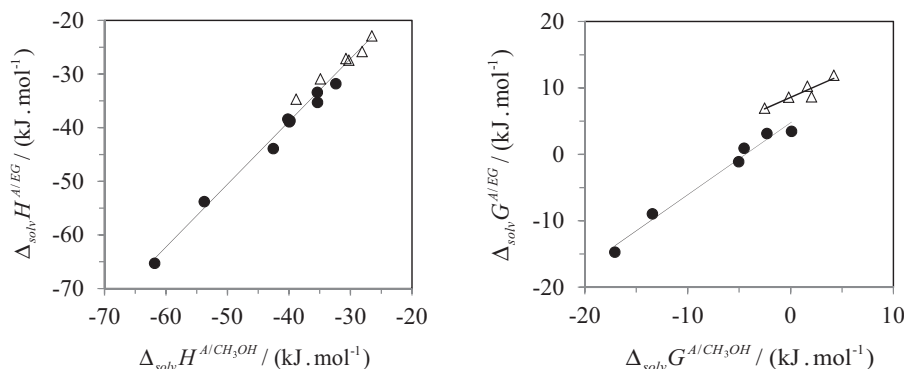[e] Standard uncertainty for temperature $u(T) = 0.2$ K.

Fig. 1. Comparison of (a) enthalpies of solvation (b) Gibbs free energies of solvation of non-polar solutes in EG and in methanol at $T = 298$ K. Triangles are aliphatic, circles are aromatic solutes.

(like in aprotic polar solvents). In a recent paper [21], we proposed a criterion to indicate the presence of the solvophobic effects and a method quantify the contribution of the solvophobic effect into the Gibbs energies of solvation of various compounds.

3.2. A method to quantify the strength of the solvophobic effect

We considered [21] the relationship between the Gibbs free energies and enthalpies of solvation of nonelectrolytes. It was found that the Gibbs energy and enthalpy of solvation for many compounds with different structures dissolved in various non-associated solvents (no intermolecular hydrogen bonding between solvent molecules) are linearly correlated. For example, 978 solute–solvent pairs consisting of solutes and solvents with different structure, polarity, molecular size and shape follow the relationship $\Delta_{solv}G^{A/S} = 0.627\Delta_{solv}H^{A/S} + 16.3$ (1) with $\sigma = 1.6$ kJ mol^{-1}, $R^2 = 0.9768$ [22]. The accuracy of a correlation for a group of solutes that belong to a single class of organic compounds is higher, while the coefficients are almost the same. For example, a correlation for linear alkanes C$_1$–C$_8$ dissolved in 34 different solvents (101 data points) is given by:

$$\Delta_{solv}G^{A/S} = 0.632\Delta_{solv}H^{A/S} + 15.6,$$
$$\sigma = 0.75 \text{ kJ} \cdot \text{mol}^{-1}, \quad R^2 = 0.9890. \tag{2}$$

For solutions in self-associated solvents such as alcohols, formamide or water data points appreciably deviate from these correlations [21], so that the Gibbs energy of solvation is always higher than for a solution in non-associated solvent with the same enthalpy of solvation.

These exceptions from a general rule can be used as a probe of the solvophobic effect. Increased values of the Gibbs free energy of solvation mean a decreased solubility of apolar species. The solvophobic effect may contribute to both the entropic and enthalpic components of the Gibbs free energy of solvation. In the absence of hydrogen bonding between solute and solvent [23,24], we can represent thermodynamic functions of solvation as the sum of contributions of non-specific van der Waals intermolecular interactions that corresponds to a "normal" behavior of solvent and of the solvophobic effect:

$$\Delta_{solv}G^{A/S} = \Delta_{solv(nonsp)}G^{A/S} + \Delta_{s.e.}G^{A/S}$$
$$\Delta_{solv}H^{A/S} = \Delta_{solv(nonsp)}H^{A/S} + \Delta_{s.e.}H^{A/S}. \tag{3}$$

For non-associated solvents that follow the linear Gibbs energy–enthalpy relationship (Eq. (2)), $\Delta_{s.e.}G^{A/S} = \Delta_{s.e.}H^{A/S} = 0$. In associated solvents, the values of $\Delta_{solv(nonsp)}G^{A/S}$ and $\Delta_{solv(nonsp)}H^{A/S}$ should follow the same relationship,

$\Delta_{solv(nonsp)}G^{A/S} \approx 0.632 \Delta_{solv(nonsp)}H^{A/S} + 15.6,$ while $\Delta_{s.e.}G^{A/S}$ is non-zero and $\Delta_{s.e.}H^{A/S}$ can be non-zero.

Thermodynamic functions of solvation in associated solvents also show deviations from other general extrathermodynamic relationships. In the previous studies [25,26], we have shown that the values of the Gibbs free energies of solvation in non-associated solvents for solutes forming no hydrogen bonds with the solvent can be satisfactorily described using the following equation:

$$\Delta_{solv}G^{A/S} = \Delta_{solv}G^{A/S_0} + \left(\delta g^S - \delta g^{S_0}\right) \cdot V_x^A +$$

$$+\left[a + b\sqrt{\delta g^S}\right] \cdot \left[\left(\Delta_{solv}G^{A/S_R} - \Delta_{solv}G^{A/S_0}\right) - \left(\delta g^{S_R} - \delta g^{S_0}\right) \cdot V_x^A\right];$$

$$a = -\frac{\sqrt{\delta g^{S_0}}}{\sqrt{\delta g^{S_R}} - \sqrt{\delta g^{S_0}}};$$
$$b = \frac{1}{\sqrt{\delta g^{S_R}} - \sqrt{\delta g^{S_0}}}. \tag{4}$$

Here $\Delta_{solv}G^{A/S_0}$, $\Delta_{solv}G^{A/S_R}$ are the Gibbs free energies of solvation of solute A in the standard solvents S_0 and S_R, which should not form hydrogen bonds with the molecules of A (typically, S_0 is n-hexadecane and S_R can be, for example, benzene or dimethyl sulfoxide), V_x^A is the characteristic molecular volume of A, which is calculated using an additive scheme from atomic contributions [27], and δg^S, δg^{S_R}, δg^{S_0} are solvent parameters reflecting non-specific interactions of solvent molecules with other (solvent and solute) molecules.

In self-associated solvents, this equation can describe only the non-specific contribution into the Gibbs free energy of solvation $\Delta_{solv(nonsp)}G^{A/S}$. This can be used to find the magnitudes of $\Delta_{s.e.}G^{A/S}$ for various solutes and solvents. The only parameter of solvent in Eq. (4), δg^S, is determined from the Gibbs energy of non-specific solvation of n-octane in solvent S. If the solvent S is self-associated, one must take into account the contribution of the solvophobic effect into the Gibbs energy of solvation:

$$\delta g^S = \frac{\Delta_{solv(nonsp)}G^{C_8H_{18}/S} - \Delta_{solv}G^{C_8H_{18}/C_{16}H_{34}}}{V_x^{C_8H_{18}}} =$$
$$= \frac{\Delta_{solv}G^{C_8H_{18}/S} - \Delta_{s.e.}G^{C_8H_{18}/S} - \Delta_{solv}G^{C_8H_{18}/C_{16}H_{34}}}{V_x^{C_8H_{18}}} \tag{5}$$

$(C_8H_{18} = \text{n} - \text{octane}, \ C_{16}H_{34} = \text{n} - \text{hexadecane}).$

In our previous paper [21], we assumed that for alkanes dissolved in monohydric alcohols the solvophobic effect enthalpy is small and can be neglected, so we were able to find the value of $\Delta_{s.e.}G^{C_8H_{18}/S}$ directly from the Gibbs energy vs enthalpy of solvation plot: it equals the deviation of a data point for octane from the line (Eq. (2))

for non-associated solvents. However, in water and formamide the solvophobic effect affects the enthalpies of solvation [28], and we used different approaches to calculate δg^S.

The values of $\Delta_{s.e.}G^{A/S}$ for various solutes in water, aliphatic monohydric alcohols, and formamide were found to be linearly correlated with the characteristic molecular volume of the solute: $\Delta_{s.e.}G^{A/S} = k^S V_x^A + b^S$, where the coefficients k^S and b^S are dependent on solvent nature. Using this method, we can quantitatively study the solvophobic effect in EG on the basis of measured and literature values of thermodynamic functions of solvation.

3.3. Gibbs free energy of the solvophobic effect in ethylene glycol

In Fig. 2, we compare the Gibbs free energies and enthalpies of solvation of compounds from Table 1 in EG. A straight line corresponds to the correlation between the Gibbs energies and enthalpies of solvation in non-associated solvents (Eq. (2)). We observe a strong deviation of the data points from the line, and its magnitude is greater than for the solutions of the same compounds in methanol and other monohydric alcohols, but less than for their aqueous solutions.

The Gibbs energies are increased due to the solvophobic effect, and its contributions have been determined using the approach given above. The value of δg^{EG} can be estimated in two different ways, which give the same result. We may note that the succession of solvents in δg^S scale of solvent non-specific interactions power is similar to the π^* polarity scale. This scale is based on
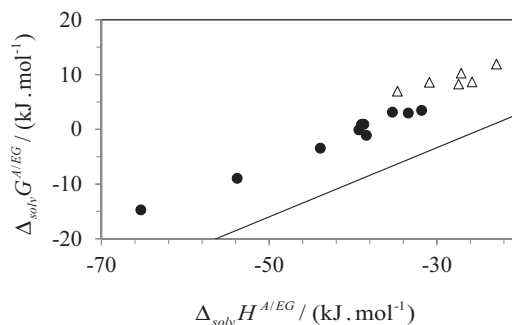

Fig. 2. Gibbs free energies vs enthalpies of solvation of low-polar solutes in EG at $T = 298$ K. Triangles are aliphatic, circles are aromatic solutes. The line corresponds to a linear relationship (2) for solutions in non-associated solvents.

solvatochromic characteristics and also reflects the ability of solvent molecules to interact with dissolved molecules. Moreover, the Gibbs free energies of solvation of some non-polar solutes in non-associated solvents were correlated with π^* parameter [29]. Since the π^* value for hexadecane is about zero, as well as its δg^S value, we can suggest that the ratio of π^* values [19] for EG (0.92) and water (1.09), which equals 0.844, can be an estimate for the ratio of δg^S values for the same solvents: $\delta g^{EG} = 0.844 \delta g^{H_2O} \approx 4.85 \cdot 10^{-2}$ kJ $\cdot$ cm^{-3}. This value was taken for further calculations. Another way is to make an assumption that, like in monohydric alcohols, the enthalpic part of the solvophobic effect $\Delta_{s.e.}H$ for solvation of

Table 3
Gibbs free energies of the solvophobic effect in EG at $T = 298$ K and thermodynamic data[a] used in their calculation.

Solute	V_x^A (cm^3 mol^{-1} 10^2)	$\Delta_{solv}G^{A/EG}$ (kJ mol^{-1})	$\Delta_{solv}G^{A/C_{16}H_{34}}$ (kJ mol^{-1})	$\Delta_{solv}G^{A/DMSO}$ (kJ mol^{-1})	$\Delta_{s.e.}G^{A/EG}$ (kJ mol^{-1})
Helium	0.0680	27.6	20.9	25.9	3.3
Argon	0.1900	23.2	14.9	21.8	3.9
Xenon	0.3290	18.1	8.8	15.8	5.2
Hydrogen	0.1086	25.1	17.8	23.5	3.6
Nitrogen	0.2222	25.4	16.6	23.3	4.7
Methane	0.2495	21.6	12.9	19.3	4.8
Ethane	0.3904	18.7	8.2	14.8	6.8
Propane	0.5313	14.9	5.0	13.0	5.6
Butane	0.6722	13.9	1.8	10.3	7.6
Hexane	0.9540	11.9	−4.2	7.3	10.2
Heptane	1.0949	10.3	−7.1	5.5	11.0
Octane	1.2358	8.6	−10.0	2.5	12.6
Nonane	1.3767	7.0	−12.9	1.1	13.1
Decane	1.5176	3.9	−15.8	−1.0	12.7
Isooctane	1.2358	10.7	−6.7	5.9	11.4
Cyclohexane	0.8454	8.7	−5.9	4.4	9.2
Methylcyclohexane	0.9863	8.3	−7.5	2.7	10.8
Ethylcyclohexane	1.1272	6.4	−10.5	0.9	11.5
Hex-1-ene	0.9110	10.6	−3.7	5.8	9.7
Isoprene	0.7271	10.4	−1.0	4.6	9.1
Cyclohexene	0.8024	7.2	−6.2	1.4	9.8
Benzene	0.7164	3.5[*]	−4.9	−2.1	8.0
Toluene	0.8573	3.1[*]	−8.0	−4.4	10.5
Ethylbenzene	0.9982	0.9	−10.6	−5.6	10.2
o-Xylene	0.9982	−0.1	−11.5	−7.0[*]	10.4
m-Xylene	0.9982	0.8	−10.9	−6.1[*]	10.5
p-Xylene	0.9982	0.9	−10.9	−6.0[*]	10.5
Fluorobenzene	0.7341	2.9[*]	−5.9	−3.7	8.9
Chlorobenzene	0.8388	−1.1[*]	−9.9	−7.1	8.7
Bromobenzene	0.8914	−3.4[*]	−12.1	−9.5	8.8
Iodobenzene	0.9746	−7.0[*]	−15.1	−13.2	8.9
Naphthalene	1.0854	−9.0[*]	−19.5	−17.6	11.5
Biphenyl	1.3242	−14.7	−23.3	−22.4	10.8
Anthracene	1.4544	−22.4	−32.2	−30.9	12.1
Phenanthrene	1.4544	−20.7	−31.3	−31.9	14.1
Acenaphthene	1.2586	−14.7	−26.0	−23.1	12.0
Pyrene	1.5846	−28.4	−38.8	−38.6	13.7

[*] Calculated from limiting activity coefficients measured in the present work.

[a] All the values of the Gibbs free energies of solvation except marked with an asterisk were calculated from Ostwald solubility coefficients compiled in refs [12,18].
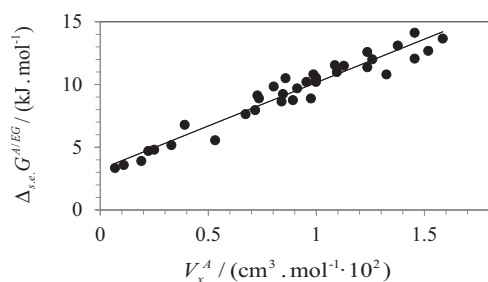
Fig. 3. Relationship between the Gibbs free energies of solvophobic effect in EG and characteristic molecular volumes of solutes.

octane in EG is zero, and the deviation of $\Delta_{solv}G^{C_8H_{18}/EG}$ from the line in Fig. 2 has purely entropic origin and equals $\Delta_{s.e.}G^{C_8H_{18}/EG}$. Then $\Delta_{s.e.}G^{C_8H_{18}/EG} = 12.5\,\mathrm{kJ \cdot mol^{-1}}$, and $\delta g^{EG} = 4.90 \cdot 10^{-2}\,\mathrm{kJ\,cm^{-3}}$. It should be said that the uncertainty of enthalpy of solvation of octane can lead to the uncertainty of δg^{EG} value up to $0.5 \cdot 10^{-2}\,\mathrm{kJ\,cm^{-3}}$. However, such uncertainty does not lead to significantly different results when we use the δg^{EG} value in Eq (4).

Calculated values of the Gibbs free energies of the solvophobic effect in EG and the data that have been used to calculate them are given in Table 3.

As noted above, the values of $\Delta_{s.e.}G^{A/S}$ for various solutes A in water, monohydric alcohols, and formamide have been shown [21,28] to correlate linearly with the characteristic volume of a solute molecule V_x^A. In EG, we also observe a linear correlation with V_x^A (Fig. 3) for solutes with different atomic composition, structure, and shape, including inert gases, alkanes, cycloalkanes, alkenes, mono- and polycyclic aromatic hydrocarbons and their halogenated derivatives:

$$\Delta_{s.e.}G^{A/EG}/(\mathrm{kJ \cdot mol^{-1}}) = (6.92 \pm 0.30)V_x^A/(\mathrm{cm^3 \cdot mol^{-1} \cdot 10^2}) + (3.24 \pm 0.29) \quad (6)$$

$$n = 37,\ \sigma = 0.70\,\mathrm{kJ\,mol^{-1}},\ R^2 = 0.9398.$$

If we change the value of δg^{EG} in a range of its uncertainty from $4.35 \cdot 10^{-2}\,\mathrm{kJ\,cm^{-3}}$ to $5.35 \cdot 10^{-2}\,\mathrm{kJ\,cm^{-3}}$, a linear correlation of $\Delta_{s.e.}G^{A/FA}$ with V_x^A holds, and its slope and intercept stay in the range of their uncertainties in Eq (6) (if we assume $\delta g^{EG} = 4.35 \cdot 10^{-2}\,\mathrm{kJ\,cm^{-3}}$, the correlation equation will be $\Delta_{s.e.}G^{A/EG} = 7.05V_x^A + 3.46$, and if $\delta g^{EG} = 5.35 \cdot 10^{-2}\,\mathrm{kJ\,cm^{-3}}$, it will be $\Delta_{s.e.}G^{A/EG} = 6.77V_x^A + 3.02$). Single values of $\Delta_{s.e.}G^{A/EG}$ change by no more than $0.7\,\mathrm{kJ\,mol^{-1}}$: for example, if instead of $\delta g^{EG} = 4.85 \cdot 10^{-2}\,\mathrm{kJ\,cm^{-3}}$ we take $\delta g^{EG} = 4.35 \cdot 10^{-2}$ or $5.35 \cdot 10^{-2}\,\mathrm{kJ\,cm^{-3}}$, then the Gibbs free energy of the solvophobic effect of octane will be 13.2 or $12.0\,\mathrm{kJ\,mol^{-1}}$ respectively instead of $12.6\,\mathrm{kJ\,mol^{-1}}$.

The magnitude of the slope of this correlation (6.91) is between those for similar correlations in methanolic (5.17) [21] and formamide solutions (8.88) [28], and is much lower than that in aqueous solutions (22.0) [30]. The intercepts have very close values for EG, formamide, and water, while for methanol it almost equals zero. Thus, the Gibbs solvophobic effect energy in EG for any solute will be higher than for the same solute in aliphatic alcohols and lower than in formamide or water.

In Fig. 4, the residual part of the Gibbs energy of solvation in EG arising from nonspecific van der Waals solute–solvent interactions, $\Delta_{solv(nonsp)}G^{A/EG}$, is plotted against the enthalpies of solvation in EG for all substances from Table 1. The points on the plot corresponding to both aliphatic and aromatic solutes fall on or near the line expressed by Eq. (2). The root mean square deviation for 17 values of $\Delta_{solv(nonsp)}G^{A/EG}$ from Eq. (2) equals $0.8\,\mathrm{kJ\,mol^{-1}}$. This value is less than possible experimental errors in the magnitudes of enthalpies of solution of alkanes. Now, after the contribution of the solvophobic effect into the Gibbs energy is excluded, relationship between the residual part of the Gibbs energy and enthalpy of solvation is
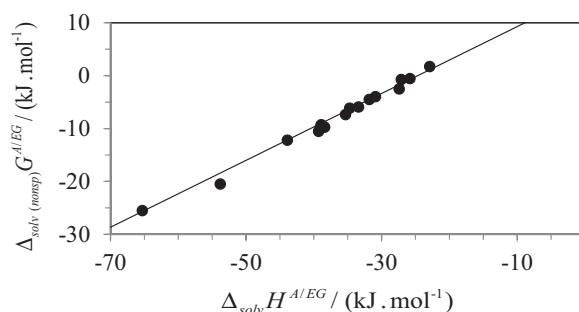

Fig. 4. Plot of the Gibbs free energies of nonspecific solvation in EG vs enthalpies of solvation in EG. The line corresponds to Eq. (2), the same line is shown in Fig. 2.

the same as in non-associated solvents. It means that the solvophobic effect does not have a significant influence on the enthalpies of solvation in EG. In this sense EG is similar to monohydric alcohols, while in water and formamide the values of $\Delta_{s.e.}H^{A/S}$ were found to be non-zero [21,28].

4. Conclusion

In the work, the values of the enthalpies of solution for a number of low-polar substances in EG at temperature $T = 298.15\,\mathrm{K}$ have been measured for the first time. Limiting activity coefficients and Gibbs free energies of solvation have also been determined for some of these systems.

Analysis of newly determined and literature data on thermodynamic functions of solution and solvation in EG shows the presence of strong solvophobic effect, which reduces their solubility. Solvophobic effect in EG is entropy-driven and does not affect the enthalpies of solution of the studied substances. Such behavior of thermodynamic functions of solutions in ethylene glycol is similar to the solutions in monohydric alcohols, while the hydrophobic effect in water also influences the values of the enthalpies of solution. At the same time, the solvophobic effect is stronger in EG than in methanol and other monohydric alcohols, weaker than in formamide and much weaker than in water. As in other associated solvents we have studied, the Gibbs free energy of solvophobic effect in EG correlates linearly with the molecular volume of a solute.

Acknowledgement

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