

Enthalpies of solution and enthalpies of solvation of organic solutes in ethylene glycol at 298.15 K: prediction and analysis of intermolecular interaction contributions

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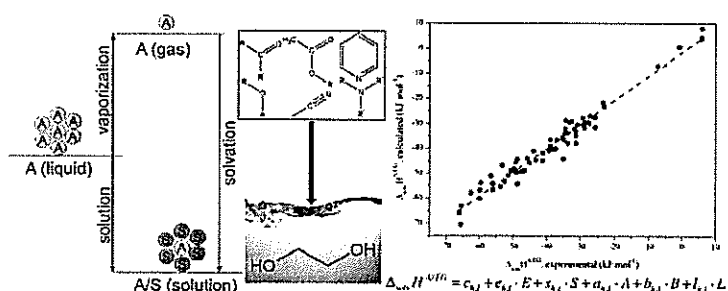
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Graphical abstract



Highlights

- Enthalpies of solution were measured for 28 solutes dissolved in ethylene glycol.
- Enthalpies of solvation were calculated for 68 solutes dissolved in ethylene glycol.
- Equations were derived for predicting enthalpies of solvation in ethylene glycol.
- Enthalpies of specific interactions of solutes in ethylene glycol were determined.
- Enthalpies of specific interactions in ethylene glycol and methanol are equal.

Abstract

Ethylene glycol is one of the most usually used liquid media for realization of different industrial processes. In present work thermochemistry of solvation of inert gases and organic solutes in

ethylene glycol was thoroughly studied using solution calorimetry technique. Enthalpies of solution of 28 organic solutes in ethylene glycol were measured for the first time. Acree and Abraham multi-parameter correlations were successfully applied for description of enthalpies of solvation of number of inert gases and organic compounds in ethylene glycol calculated on the basis of experimental and literature data. Enthalpies of solute-ethylene glycol hydrogen bonding for some ketones, esters, ethers, nitriles, monoatomic aliphatic alcohols, amines and etc. were determined. Linear correlation between enthalpies of solute-ethylene glycol and solute-methanol hydrogen bonding was observed.

Keywords: Ethylene glycol; Solution calorimetry; Enthalpy of solution; Enthalpy of solvation; Multi-parameter correlation; Hydrogen bond.

1. Introduction

Ethylene glycol (ethanediol-1,2) is an organic compound which is widely used in industry. Ethylene glycol and its mixtures with water can be utilized as antifreeze, heat transfer agent or as a medium for micelle formation processes [1, 2]. As to chemical synthesis, ethylene glycol is a precursor to polyester fibers and resins. Besides, ethylene glycol is used as a thermodynamic inhibitor of natural gas hydrates formation in pipelines [3].

Most of physical and chemical properties of ethylene glycol are attributed to intermolecular hydrogen bonds in bulk phase. As well as water, ethylene glycol molecules are capable of formation of spatial network of intermolecular H-O...H hydrogen bonds [4], which is one of reasons of poor solubility of non-polar solutes in ethylene glycol media. Relatively high viscosity causes additional obstacles to solubility measurements. Therefore, solvation processes in ethylene glycol are studied insufficiently full.

The aim of present work is examination of enthalpies of transfer of solute molecule from gas phase to infinitely diluted solution in ethylene glycol (solvation process). Enthalpies of solvation provide valuable information about solute-solvent intermolecular interactions. As an example, solvation enthalpies values are used to assess solvent influence on reaction kinetics and equilibria [5-7].

Since experimental measurement of solvation enthalpies in ethylene glycol is difficult for some solutes, a predictive solvation correlation should be ascertained. A multi-parameter correlations between solvation enthalpies and several solute properties were proposed earlier by Abraham *et al* [8]. To date such correlations are available for number of solvents [8-27] including self-associated solvents: water [8], monoatomic aliphatic alcohols [8, 15, 16, 18, 19,

23], acetic acid [26] and formamide [25]. Abraham multi-parameter correlations for enthalpy of solvation of noble gases and organic solutes are expressed by following equations:

$$\Delta_{\text{solv}}H^{AEG} = c_{h,l} + e_{h,l} \cdot E + s_{h,l} \cdot S + a_{h,l} \cdot A + b_{h,l} \cdot B + l_{h,l} \cdot L \quad (1)$$

$$\Delta_{\text{solv}}H^{AEG} = c_{h,v} + e_{h,v} \cdot E + s_{h,v} \cdot S + a_{h,v} \cdot A + b_{h,v} \cdot B + v_{h,v} \cdot V \quad (2)$$

Solute descriptors in Eqs. (1) and (2) represent ability of solute molecule interact with solvent molecules in bulk liquid media. E descriptor refers to the excess molar refraction of solute; S is a dipolarity/polarizability solute parameter; A and B represent overall hydrogen bond acidity and basicity, respectively; L is a logarithm of gas-to-hexadecane partition coefficient at 298.15 K and V is a characteristic volume of solute molecule [28]. Coefficients $c_{h,x}$, $e_{h,x}$, $s_{h,x}$, $a_{h,x}$, $b_{h,x}$, $l_{h,x}$ and $v_{h,x}$ represent complementary properties of the process and can be calculated by linear regression analysis. Abraham model was implemented not only for predicting solvation enthalpies, but also for gas-to-solvent [29, 30] or water/blood-to-tissue/membrane [31-33] partition coefficients.

As it was mentioned earlier, experimental research of solvation in ethylene glycol is difficult. At the moment only a few publications concerning solvation enthalpies in ethylene glycol are available. In this paper we have used solution calorimetry technique for quantitative studies of solvation processes in ethylene glycol media. Enthalpies of solution of different types of organic molecules in ethylene glycol were measured at 298.15 K. Multi-parameter equations (1) and (2) were applied for description of 68 solute to ethylene glycol solvation enthalpies which were determined from the experimental and literature thermochemical data. With values of gas-to-liquid partition coefficients for 44 solute-ethylene glycol systems, collected earlier by Abraham et al [34], predictive equations for solvation enthalpies and solvation free Gibbs energies in ethylene glycol will be available.

Polar molecule can easily form solute-solvent hydrogen bonds when being dissolved in ethylene glycol. Hydrogen bonding in solution governs physical-chemical properties of solute while hydrogen bond enthalpy represents strength of intermolecular interactions. Enthalpy of hydrogen bonding can be evaluated by IR-spectroscopy technique. However, spectroscopic method has a number of restrictions. At first, shift of wave number of solute molecule functional groups should be significant to detect. Secondly, if solute-solvent H-bonded complex is strong (free Gibbs energy of hydrogen bonding is significantly below 0), then band of “free” characteristic group of solute molecule will be undetectable due to full complexation. We chose more universal thermodynamic approach, proposed earlier by Solomonov *et al* [35], to calculate solute-ethylene glycol hydrogen bonds. Obtained values were compared with hydrogen bond

enthalpies in methanol media which has only one O-H group in molecule and another scheme of self-association than ethylene glycol.

2. Experimental

2.1. Chemicals

Ethylene glycol with purity grade more than 0.99 was supplied by Sigma-Aldrich and was used without further purification. All studied solutes were purchased from Sigma-Aldrich, Acros Organics and Panreac. Solute were purified according to standard methods [36] or were used without purification (see Table 1). Diethyl ether and tetrahydrofuran were pre-dried with CaCl_2 and then refluxed and distilled over sodium. Aliphatic amines (except diethylamine) were pre-dried with KOH and then distilled over calcium hydride. Pyridine derivatives were dried with BaO followed by fractional distillation. Purity of chemicals was checked by gas chromatographic analysis (Agilent 7890B). Amount of water in chemicals was measured by Karl Fischer titration [37] and was found not to exceed 0.1 mass %. More detailed information about sources, purity grades, methods of purification and water mass fractions in ethylene glycol and solutes are given at Table 1.

2.2. Solution calorimetry

The standard enthalpies of solution at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa were measured using TAM III precision solution calorimeter. Detailed description of procedure was reported elsewhere [38, 39]. Calorimetric titration method was used for dissolution process. Solvent was placed into 100 ml glass calorimetric vessel equipped with a gold stirrer, a Joule heater and a thermistor. After thermostating and heater calibrations, 50-100 μl of solute were added from an electronically operated microsyringe in solvent by 5–15 μl portions. As long as concentration of solute was very low, we could consider solution as extremely diluted. The heat effect of each addition was determined from a calorimetric curve. Finally, an average value of enthalpy of solution from all dissolution curves was derived. In addition, the concentration measurements of solution enthalpies were carried out. Analysis of the experimental values measured at different molalities (from 0.9 mmol kg^{-1} up to 11.5 mmol kg^{-1}) of solute did not reveal any concentration dependence of solution enthalpies within boundaries of their uncertainties.

3. Results and Discussion

Enthalpies of solution at infinite dilution of 28 organic compounds in ethylene glycol at 298.15 K measured in this work are presented at Table 2. Values of $\Delta_{\text{soln}}H^{A/EG}$ for ketones, esters, ethers and nitriles are above zero. At the same time dissolution process of amines in ethylene glycol is exothermic. Aliphatic amines have more negative solution enthalpies than pyridine and its methyl derivatives. It means that aliphatic amines form stronger intermolecular interactions with ethylene glycol than other solutes. Solution enthalpies of oxygen containing compounds and nitriles slightly increase with elongation of alkyl chain length in molecule. All studied solutes refer to proton acceptor compounds and they can form hydrogen bonds with hydrogen atom of OH-groups of the solvent. Different sign of $\Delta_{\text{soln}}H^{A/EG}$ values shows that dissolution process is complicated and consists of several contributions: (i) breaking of solute-solute intermolecular interactions (infinite dilution conditions) (endothermic processes); (ii) breaking of solvent-solvent (cavity formation) intermolecular interactions (endothermic processes); (iii) intermolecular interactions between solute and solvent molecules (exothermic process).

Enthalpies of solvation of solute A in ethylene glycol were obtained by Eq. (3) from enthalpies of solution measured in this work and taken from literature [40-48]. Totally, solvation enthalpies for 68 compounds were determined.

$$\Delta_{\text{solv}}H^{A/EG} = \Delta_{\text{soln}}H^{A/EG} - \Delta_{\text{cr,l}}^{\text{s}}H^{\text{A}}, \quad (3)$$

where $\Delta_{\text{cr,l}}^{\text{s}}H^{\text{A}}$ is an enthalpy of sublimation of solid solute or enthalpy of vaporization of liquid solute at 298.15 K. Enthalpies of sublimation and vaporization data were taken from [49]. Calculated enthalpies of solvation are given at Table 3. Further, we have analyzed these data using multi-parameter correlations approach proposed by Acree and Abraham. Also, we have studied contributions of different types of intermolecular interactions to the enthalpies of solvation, including hydrogen bonding term.

3.1. Abraham model correlations for solutions in ethylene glycol

Multi-parameter equations with L and V descriptors were arranged based on 68 solute-ethylene glycol solvation enthalpy data points. List of solutes contains different classes of non-electrolyte compounds: inert gases, aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, alcohols, ketones, nitriles, ethers, esters, amines, etc. Because of sufficient diversity of solutes, Abraham model equations should have good predictive capability:

$$\Delta_{\text{solv}}H^{A/EG} (\text{kJ} \cdot \text{mol}^{-1}) = -4.334(1.050) - 8.369(2.082)E + 2.702(1.805)S - 32.656(2.731)A - 29.069(2.096)B - 7.067(0.384)L \quad (4)$$

with (N=68, R²=0.961, F=308, SD=3.11 kJ·mol⁻¹);

$$\Delta_{\text{solv}}H^{AIEG} \text{ (kJ}\cdot\text{mol}^{-1}\text{)} = 4.409(1.601) - 16.227(2.124)E - 3.945(2.138)S - 35.848(3.123)A - 30.652(2.338)B - 27.524(1.728)V \quad (5)$$

with (N=68, R²=0.951, F=240, SD=3.50 kJ·mol⁻¹).

Coefficients e , s , a , b , l and v in Eqs. (4) and (5) were calculated by linear regression analysis. Solute descriptors are given at Table 3 along with enthalpies of solvation magnitudes. Solvation enthalpies, provided at Table 3, were calculated on the basis of solution enthalpies measured in this work, if opposite is not denoted. Experimental values of $\Delta_{\text{solv}}H^{AIEG}$ are plotted vs. $\Delta_{\text{solv}}H^{AIEG}$ calculated by Eqs. (4) and (5) (Figs. 1 and 2). These equations can be used for estimation of unknown solvation enthalpies in ethylene glycol.

Usually, standard deviation for correlations (1) and (2) does not exceed 3 kJ·mol⁻¹. However, there were reported standard deviations 3.68 kJ·mol⁻¹ (with L descriptor) and 4.04 kJ·mol⁻¹ (with V descriptor) for water [8] and 3.55 kJ·mol⁻¹ (with V descriptor) for methanol [15]. For ethylene glycol we observe standard deviations 3.11 kJ·mol⁻¹ (for Eq. (4)) and 3.5 kJ·mol⁻¹ (for Eq. (5)) as well. It can be explained by reduced solubility of non-polar compounds in associated via hydrogen bonds solvents, which is caused by additional energy costs for breaking intermolecular solvent-solvent hydrogen bonds.

3.2. Analysis of enthalpies of solvation in ethylene glycol

It seems interesting to compare enthalpies of solvation of different solutes in ethylene glycol and in methanol. Molecule of ethylene glycol has the same ratio of carbon atoms number to oxygen atoms number as a molecule of methanol. However, methanol is able to self-associate in chain-like H-bonded structures, when case of ethylene glycol is more complicated. It is generally accepted that ethylene glycol forms three-dimensional network of hydrogen bonds in liquid phase [4].

It was reported earlier [41] that there was a single linear correlation between enthalpies of solvation of alkanes, aromatic hydrocarbons and their halogenated derivatives in ethylene glycol and in methanol. We compared enthalpies of solvation of more polar molecules in ethylene glycol, measured in this work, and methanol (Fig. 3). Values of enthalpies of solvation in methanol were taken from literature [15, 50, 51]. Linear correlation was observed:

$$\Delta_{\text{solv}}H^{AIEG} = 1.03 \cdot \Delta_{\text{solv}}H^{AICH_3OH} + 1.85 \quad (\text{N}=51, \text{R}^2=0.986, \text{SD}=1.73 \text{ kJ}\cdot\text{mol}^{-1}) \quad (6)$$

Since data set of solvation enthalpies in methanol is significantly larger than in ethylene glycol and range of values of solvation enthalpies in methanol is vast (from -64.9 to 5.9 kJ·mol⁻¹), this correlation could be one more instrument for prediction of unknown values of solvation

enthalpies of various compounds in ethylene glycol. For solutions in other aliphatic monoatomic alcohols similar correlations were also observed.

3.3. Enthalpies of specific interactions of solute with ethylene glycol

When we consider solution of polar solute in polar solvent, we should take specific interactions (i.e., hydrogen bonding, coordinate bonding) into account. Solute-solvent interactions play a key role in reactivity of solute. Reaction centers of solute molecules are bonded specifically with the solvent. Such solute-solvent hydrogen bonds will break during a chemical reaction (taken place in the solution). Therefore, it is important to estimate thermodynamic functions of solute-solvent specific interactions correctly.

Methodology of calculation of enthalpies of specific interactions of solute with proton-acceptor solvent was described elsewhere in detail [35, 52, 53]. Since there was no significant contribution of solvophobic effect to enthalpy of solvation in ethylene glycol [41], we can denote enthalpy of solvation as a sum of enthalpy of non-specific solvation and enthalpy of specific interaction:

$$\Delta_{\text{solv}}H^{A/EG} = \Delta_{\text{solv(nonsp)}}H^{A/EG} + \Delta_{\text{int(sp)}}H^{A/EG} \quad (7)$$

So, to calculate enthalpies of specific interactions of solute with ethylene glycol, we need to know $\Delta_{\text{solv}}H^{A/EG}$ and $\Delta_{\text{solv(nonsp)}}H^{A/EG}$ values. $\Delta_{\text{solv}}H^{A/EG}$ can be calculated by Eq.(3). To estimate enthalpy of non-specific interactions we should apply Eq. (8) proposed earlier [35]:

$$\begin{aligned} \Delta_{\text{solv(nonsp)}}H^{A/EG} = & \Delta_{\text{solv(nonsp)}}H^{A/S_1} + V_X^A \cdot (\delta_{\text{cav}}h^{EG} - \delta_{\text{cav}}h^{S_1}) + \\ & + \left(a^R + b^R \cdot \sqrt{\delta_{\text{cav}}h^{EG}} \right) \left(\Delta_{\text{solv(nonsp)}}H^{A/S_R} - \Delta_{\text{solv(nonsp)}}H^{A/S_1} - V_X^A \cdot (\delta_{\text{cav}}h^{S_R} - \delta_{\text{cav}}h^{S_1}) \right) \end{aligned} \quad (8)$$

where a^R and b^R are empiric coefficients related to standard solvent S_R , V_X^A is a characteristic volume of solute molecule [28] and $\delta_{\text{cav}}h^S$ is a specific relative cavity formation enthalpy in solvent S and, in turn, is calculated by Eq. (9).

$$\delta_{\text{cav}}h^{EG} = \frac{\Delta_{\text{soln}}H^{C_nH_{2n+2}/EG}}{V_X^{C_nH_{2n+2}}} \quad (9)$$

Solvents S_1 and S_R must not interact specifically with solute. Moreover, it is desirable to have a large data set of solvation enthalpies in standard solvents. Because of this, cyclohexane was chosen as S_1 solvent. As for S_R , carbon tetrachloride was used for proton-donating solutes (alcohols) while for other solutes benzene was chosen. Parameter $\delta_{\text{cav}}h^{EG}$ was calculated based on enthalpy of solution of *n*-octane in ethylene glycol and was taken as $8.65 \cdot 10^{-2} \text{ kJ} \cdot \text{cm}^{-3}$. Calculated values of $\Delta_{\text{int(sp)}}H^{A/EG}$ are given at Table 4. We compared specific interactions of the same solutes with ethylene glycol and methanol (Fig. 4). Enthalpies of specific interactions with methanol were either taken from literature (if available) or calculated using the similar approach.

Solute-solvent specific interactions are spontaneous forces. Therefore, value of free Gibbs energy of specific interactions is negative at isothermal-isobaric conditions. So, if positive values of enthalpy of specific interactions is observed – value of entropy of specific interactions should be positive. In that case, as it can be seen from Table 4, specific interactions of tetrahydrofuran, alcohols and nitrogen containing solutes with ethylene glycol are enthalpically driven. For other solutes positive value of enthalpy of specific interactions is due to large energy cost of reorganization of ethylene glycol induced by solute dissolution.

Value of $\Delta_{\text{int(sp)}}H^{A/EG}$ is constant for individual class of solutes within the Eq. (8) uncertainty ($\approx 2 \text{ kJ}\cdot\text{mol}^{-1}$). Similar result was obtained for solutions in methanol. Relationship at Fig. 4 represents various classes of compounds, such as ketones, esters, nitriles, monoatomic alcohols, nitrogen containing compounds etc. Both enthalpies of non-specific and specific interactions of solutes with ethylene glycol and methanol are correlated, which is shown by linear relationship (Eq. (10)):

$$\Delta_{\text{int(sp)}}H^{A/EG} = 0.92 \cdot \Delta_{\text{int(sp)}}H^{A/CH_3OH} - 1.85 \quad (\text{N}=26, \text{R}^2=0.967, \text{SD}=1.60 \text{ kJ}\cdot\text{mol}^{-1}) \quad (10)$$

4. Conclusion

In this work values of enthalpies of solution of set of polar compounds in ethylene glycol were measured at 298.15 K and 0.1 MPa. Measured and literature data were used for search of correlations between solvation enthalpies and properties of solute molecules. In that way, Abraham general solvation model was successfully applied for ethylene glycol as a solvent.

Magnitudes of enthalpies of specific interactions of various polar or low polar solutes with ethylene glycol were calculated. For aliphatic alcohols, for strong proton acceptors like dimethyl sulphoxide, aliphatic and aromatic amines enthalpies of specific interactions are below zero. For ketones, esters, ethers and nitriles these values are positive or close to zero. Priority of enthalpic or entropic contributions to Gibbs energy of specific interactions can be analyzed based on this data. It was shown that enthalpies of non-specific and specific interactions of solutes with ethylene glycol and methanol are in good agreement with each other.

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Figure captions

Fig. 1. Comparison of calculated by Eq. (4) and experimental data of solvation enthalpies in ethylene glycol.

Fig. 2. Comparison of calculated by Eq. (5) and experimental data of solvation enthalpies in ethylene glycol.

Fig. 3. Relationship between enthalpies of solvation of organic solutes in ethylene glycol and methanol.

Fig. 4. Relationship between enthalpies of specific interactions of different polar solutes in ethylene glycol and methanol.

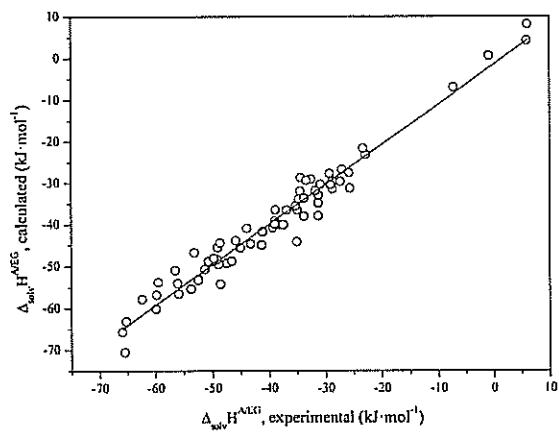


Fig 1

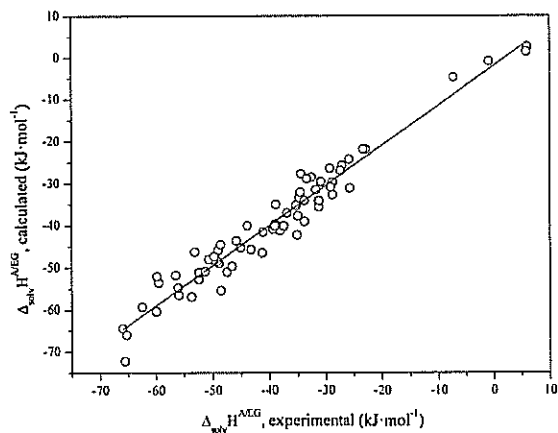


Fig 2

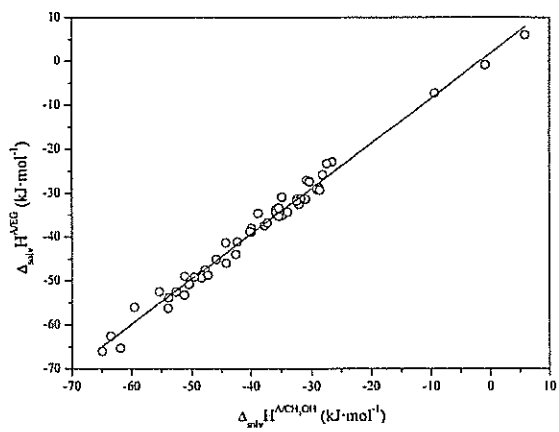


Fig 3

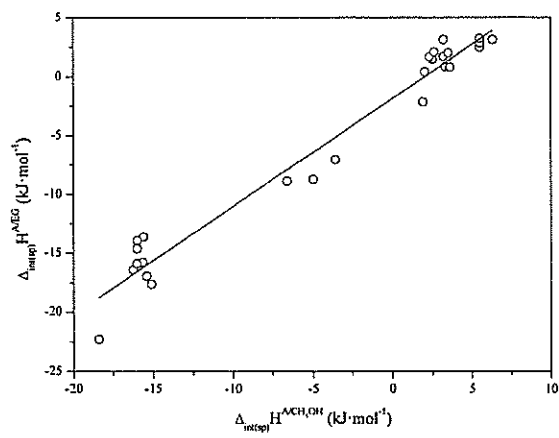


Fig 4

Table 1 Sources, purity grades, methods of purification and mass fraction of water in ethylene glycol and solutes.

Chemical name	Source	CAS number	Molecular weight	Mass fraction purity stated by supplier	Purification method	Final mass fraction purity	Analysis method	Mass fraction of water
Ethylene glycol	Sigma-Aldrich	107-21-1	62.07	0.99	None	-	-	0.0010
Acetone	Panreac	67-64-1	58.08	0.995	None	-	-	0.0008
Butanone	Panreac	78-93-3	72.11	0.995	None	-	-	0.0005
Pentan-2-one	Sigma-Aldrich	107-87-9	86.13	0.995	None	-	-	0.0004
Heptan-2-one	Sigma-Aldrich	110-43-0	114.19	0.99	Distillation	0.998	GC	0.0004
Methyl acetate	Sigma-Aldrich	79-20-9	74.08	0.995	None	-	-	0.0002
Ethyl acetate	Sigma-Aldrich	141-78-6	88.11	0.997	None	-	-	0.0001
Propyl acetate	Sigma-Aldrich	109-60-4	102.13	0.99	Distillation	0.994	GC	0.0002
Butyl acetate	Sigma-Aldrich	123-86-4	116.16	0.99	Distillation	0.995	GC	0.0002
Tetrahydrofuran	AcrosOrganics	109-99-9	72.11	0.99	Distillation	0.994	GC	0.0008
1,4-Dioxane	AcrosOrganics	123-91-1	88.11	0.995	None	-	-	0.0010
Diethyl ether	AcrosOrganics	60-29-7	74.12	0.99	Distillation	0.995	GC	0.0004
Acetonitrile	AcrosOrganics	75-05-8	41.05	0.995	None	-	-	0.0003
Propionitrile	AcrosOrganics	107-12-0	55.08	0.99	Distillation	0.996	GC	0.0004
Butyronitrile	AcrosOrganics	109-74-0	69.11	0.99	Distillation	0.995	GC	0.0004
Pyridine	Sigma-Aldrich	110-86-1	79.1	0.998	None	-	-	0.0009
2-Methylpyridine	Sigma-Aldrich	109-06-8	93.13	0.98	Distillation	0.994	GC	0.0009
3-Methylpyridine	Sigma-Aldrich	108-99-6	93.13	0.99	Distillation	0.996	GC	0.0007
4-Methylpyridine	Sigma-Aldrich	108-89-4	93.13	0.99	Distillation	0.996	GC	0.0007

<i>n</i> -Butylamine	Sigma-Aldrich	109-73-9	73.14	0.99	Distillat ion	0.994	GC	0.0005
<i>sec</i> -Butylamine	Sigma-Aldrich	13952-84-6	73.14	0.99	Distillat ion	0.995	GC	0.0006
<i>tert</i> -Butylamine	Sigma-Aldrich	75-64-9	73.14	0.995	None	-	-	0.0005
<i>n</i> -Hexylamine	Sigma-Aldrich	111-26-2	101.19	0.99	Distillat ion	0.994	GC	0.0002
Piperidine	Sigma-Aldrich	110-89-4	85.15	0.99	Distillat ion	0.994	GC	0.0006
Diethylamine	Sigma-Aldrich	109-89-7	73.14	0.995	None	-	-	0.0008
Di- <i>n</i> -propylamine	Sigma-Aldrich	142-84-7	101.19	0.99	Distillat ion	0.995	GC	0.0007
Di- <i>n</i> -butylamine	Sigma-Aldrich	111-92-2	129.24	0.99	Distillat ion	0.995	GC	0.0007
Triethylamine	Sigma-Aldrich	121-44-8	101.19	0.99	Distillat ion	0.995	GC	0.0003
Acetophenone	Sigma-Aldrich	98-86-2	120.15	0.99	Distillat ion	0.997	GC	0.0002

Table 2 Enthalpies of solution (with number of measurements (N) and uncertainties (u)) of various organic solutes in ethylene glycol measured in this work at 298.15 K and 0.1 MPa ($\text{kJ}\cdot\text{mol}^{-1}$).

Solute (A)	N	$\Delta_{\text{soln}} H^{\text{A/EG}}$	$u (\Delta_{\text{soln}} H^{\text{A/EG}})^a$
Propanone (l) ^b	8	2.53	0.10
Butanone (l)	8	3.42	0.03
Pentan-2-one (l)	8	4.60	0.11
Heptan-2-one (l)	8	6.13	0.03
Methylacetate (l)	7	3.46	0.09
Ethylacetate (l)	8	3.87	0.08
Propylacetate (l)	9	4.84	0.16
Butylacetate (l)	8	5.64	0.03
Tetrahydrofuran (l)	8	0.68	0.09
1,4-Dioxane (l)	7	3.50	0.03
Diethylether (l)	8	1.56	0.06
Acetonitrile (l)	8	3.71	0.09
Propionitrile (l)	8	4.10	0.15
Butyronitrile (l)	8	4.69	0.08
Pyridine (l)	8	-5.35	0.07
2-Methylpyridine (l)	10	-6.78	0.17
3-Methylpyridine (l)	10	-5.41	0.10
4-Methylpyridine (l)	9	-5.87	0.13
<i>n</i> -Butylamine (l)	9	-17.58	0.10

<i>sec</i> -Butylamine (l)	8	-16.51	0.11
<i>tert</i> -Butylamine (l)	9	-19.27	0.26
<i>n</i> -Hexylamine (l)	10	-14.57	0.21
Piperidine (l)	9	-13.20	0.30
Diethylamine (l)	8	-16.00	0.27
Di- <i>n</i> -propylamine (l)	10	-14.94	0.25
Di- <i>n</i> -butylamine (l)	10	-13.00	0.26
Triethylamine (l)	10	-12.59	0.28
Acetophenone (l)	8	4.79	0.02

^aUncertainty is calculated as a standard deviation of the mean.

^bPhysical state of solute at 298.15 K (l – liquid).

^cStandard uncertainties u are $u(T) = 0.01$ K, $u(p) = 10$ kPa.

Table 3 Values of enthalpies of solvation in ethylene glycol (kJ mol^{-1}) for 68 solutes along with solute descriptors.

Solute (A)	E	S	A	B	L	V	$\Delta_{\text{sol}} H^{A/EG}$
Helium	0.000	0.000	0.000	0.000	-1.741	0.0680	6.0 ^a
Argon	0.000	0.000	0.000	0.000	-0.688	0.1900	-0.9 ^a
Xenon	0.000	0.000	0.000	0.000	0.378	0.3290	-7.3 ^a
Hydrogen	0.000	0.000	0.000	0.000	-1.200	0.1086	5.9 ^b
<i>n</i> -Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	-22.9 ^c
<i>n</i> -Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	-27.1 ^c
<i>n</i> -Octane	0.000	0.000	0.000	0.000	3.677	1.2358	-30.9 ^c
<i>n</i> -Nonane	0.000	0.000	0.000	0.000	4.182	1.3770	-34.7 ^c
Cyclohexane	0.310	0.100	0.000	0.000	2.964	0.8454	-25.8 ^c
Methylcyclohexane	0.244	0.060	0.000	0.000	3.319	0.9863	-27.4 ^c
2-Chloro-2-methylpropane	0.142	0.300	0.000	0.030	2.273	0.7946	-23.3 ^d
2-Chloro-2-methylbutane	0.171	0.270	0.000	0.150	2.858	0.9355	-28.8 ^d
3-Chloro-3-methylpentane	0.207	0.390	0.000	0.130	3.520	1.0764	-33.8 ^d
Diethyl ether	0.041	0.250	0.000	0.450	2.015	0.7309	-25.6 ^e
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	-31.3 ^e
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	-35.1 ^e
Propanone	0.179	0.700	0.040	0.490	1.696	0.5470	-28.8 ^e
Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	-31.3 ^e
Pentan-2-one	0.143	0.680	0.000	0.510	2.755	0.8288	-33.8 ^e
Heptan-2-one	0.123	0.680	0.000	0.510	3.760	1.1106	-41.3 ^e
Methyl acetate	0.142	0.640	0.000	0.450	1.911	0.6057	-29.1 ^e
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	-31.2 ^e
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	-35.0 ^e
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	-38.1 ^e
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	-29.3 ^e

Propionitrile	0.162	0.900	0.020	0.360	2.082	0.5451	-32.6 ^e
Butyronitrile	0.188	0.900	0.000	0.360	2.548	0.6860	-34.5 ^e
Triethylamine	0.101	0.150	0.000	0.790	3.040	1.0538	-47.5 ^e
Nitromethane	0.313	0.950	0.060	0.310	1.892	0.4237	-34.4 ^f
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	-37.4 ^g
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	-41.1 ^g
Propan-1-ol	0.236	0.420	0.370	0.480	2.031	0.5900	-45.1 ^g
Butan-1-ol	0.224	0.420	0.370	0.480	2.601	0.7309	-48.9 ^g
Propan-2-ol	0.212	0.360	0.330	0.560	1.764	0.5900	-43.2 ^h
Butan-2-ol	0.217	0.360	0.330	0.560	2.338	0.7309	-46.6 ^h
Pentan-1-ol	0.219	0.420	0.370	0.480	3.106	0.8718	-52.5 ^g
Hexan-1-ol	0.210	0.420	0.370	0.480	3.610	1.0127	-56.0 ^g
Heptan-1-ol	0.211	0.420	0.370	0.480	4.115	1.1536	-60.0 ^g
Ethylene glycol	0.404	0.900	0.580	0.780	2.661	0.5078	-66.0 ⁱ
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	-31.8 ^e
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	-35.3 ^e
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9980	-38.9 ^e
<i>o</i> -Xylene	0.663	0.560	0.000	0.160	3.939	0.9980	-39.3 ^e
<i>p</i> -Xylene	0.613	0.520	0.000	0.160	3.839	0.9980	-38.7 ^e
<i>m</i> -Xylene	0.623	0.520	0.000	0.160	3.839	0.9980	-39.0 ^e
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	-53.8 ^e
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3242	-65.3 ^e
Fluorobenzene	0.477	0.570	0.000	0.100	2.788	0.7341	-33.4 ^e
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	-38.8 ^e
Bromobenzene	0.882	0.730	0.000	0.090	4.041	0.8914	-43.9 ^e
Acetophenone	0.818	1.010	0.000	0.480	4.501	1.0140	-48.6 ^e
<i>N</i> -Methylimidazole	0.589	0.950	0.000	0.800	3.805	0.6772	-59.8 ^f
<i>N</i> -Methylpyrrol	0.559	0.790	0.000	0.310	2.923	0.7180	-36.8 ^f
Pyridine	0.631	0.840	0.000	0.520	3.022	0.6753	-45.9 ^e
2-Methylpyridine	0.598	0.750	0.000	0.580	3.422	0.8162	-49.3 ^e
3-Methylpyridine	0.631	0.810	0.000	0.540	3.631	0.8162	-49.9 ^e
4-Methylpyridine	0.630	0.820	0.000	0.540	3.640	0.8162	-50.8 ^e
Piperidine	0.422	0.460	0.100	0.690	3.304	0.8043	-52.5 ^e
Acetic acid	0.265	0.640	0.620	0.440	1.816	0.4648	-51.4 ^k
Dimethylsulfoxide	0.522	1.740	0.000	0.880	3.459	0.6130	-56.2 ^l
2-Phenylethanol	0.811	0.860	0.310	0.650	4.628	1.0569	-65.6 ^m
<i>n</i> -Butylamine	0.224	0.350	0.160	0.610	2.618	0.7720	-53.2 ^e
<i>sec</i> -Butylamine	0.170	0.320	0.160	0.630	2.410	0.7720	-49.1 ^e
<i>tert</i> -Butylamine	0.121	0.290	0.160	0.710	2.493	0.7720	-49.8 ^e
<i>n</i> -Hexylamine	0.197	0.350	0.160	0.610	3.655	1.0538	-59.6 ^e

Diethylamine	0.154	0.300	0.080	0.690	2.395	0.7720	-48.7 ^e
Di- <i>n</i> -propylamine	0.124	0.300	0.080	0.690	3.351	1.0538	-56.5 ^e
Di- <i>n</i> -butylamine	0.107	0.300	0.080	0.690	4.349	1.3356	-62.5 ^e
Triethylamine	0.101	0.150	0.000	0.790	3.040	1.0538	-47.5 ^e

^a Taken from ref. [48].

^b Taken from ref. [47].

^c Calculated from solution enthalpies from the ref. [41].

^d Calculated from solution enthalpies from the ref. [42].

^e Calculated from solution enthalpies measured in this work.

^f Calculated from solution enthalpies from the work [46].

^g Calculated from solution enthalpies from the ref. [43].

^h Calculated from solution enthalpies from the ref. [45].

ⁱ Calculated from the enthalpy of vaporization of ethylene glycol [49].

^j Calculated from solution enthalpies from the ref. [40].

^k Calculated from solution enthalpies from the ref. [44].

^l Calculated from solution enthalpies from the ref. [50].

^m Calculated from solution enthalpies from the ref. [51].

Table 4 Enthalpies of solution of organic solutes in carbon tetrachloride, benzene and cyclohexane at 298.15 K required for Eq. (9) and calculated enthalpies of specific interactions of solutes with ethylene glycol and methanol (kJ·mol⁻¹).

Solute (A)	$\Delta_{\text{soln}} H^{A/\text{CCl}_4}$ ^a	$\Delta_{\text{soln}} H^{A/\text{C}_6\text{H}_6}$	$\Delta_{\text{soln}} H^{A/\text{C}_6\text{H}_{12}}$	$\Delta_{\text{int(sp)}} H^{A/\text{EG}}$	$\Delta_{\text{int(sp)}} H^{A/\text{CH}_2\text{OH}}$
Tetrahydrofuran		-31.08 ^b	-28.70 ^b	-2.2	1.9 ^c
1,4-Dioxane		-39.03 ^b	-30.98 ^b	2.5	5.5 ^c
Propanone		-30.08 ^b	-21.09 ^b	0.4	2.0 ^f
Butanone		-34.27 ^b	-26.69 ^b	1.5	2.5 ^f
Pentan-2-one		-37.61 ^b	-31.30 ^b	1.7	2.3 ^f
Heptan-2-one		-46.44 ^b	-40.67 ^b	2.1	2.6 ^f
Methylacetate		-31.28 ^b	-23.94 ^b	0.9	3.3 ^f
Ethylacetate		-34.74 ^b	-27.86 ^b	1.7	3.2 ^f
Propylacetate		-38.52 ^b	-32.87 ^b	3.1	3.2 ^f
Butylacetate		-41.84 ^b	-37.40 ^b	0.8	3.6 ^f
Acetonitrile		-31.23 ^b	-17.93 ^b	2.0	3.5 ^f
Propionitrile		-35.30 ^d	-23.40 ^b	2.9	5.5 ^f
Butyronitrile		-39.09 ^d	-29.10 ^b	3.3	5.5 ^f
Methanol	-19.80		-16.90 ^b	-17.6	-15.1 ^c
Ethanol	-24.28		-17.50 ^b	-14.6	-16.0 ^c
Propan-1-ol	-27.90		-22.50 ^b	-16.9	-15.4 ^c
Butan-1-ol	-34.53		-27.70 ^b	-13.9	-16.0 ^c
Propan-2-ol	-26.40		-20.80 ^b	-16.4	-16.3 ^c
Pentan-1-ol	-37.82		-31.80 ^b	-15.8	-15.6 ^c
Hexan-1-ol	-42.20		-36.40 ^b	-15.9	-16.0 ^c
Acetophenone		-53.89 ^b	-42.66 ^b	3.1	6.3 ^c
Pyridine		-40.20 ^b	-32.01 ^b	-7.1	-3.6 ^g
2-Methylpyridine		-42.43 ^b	-35.92 ^b	-8.9	-6.6 ^g
Dimethylsulfoxide		-48.08 ^c	-35.40 ^b	-8.7	-5.0 ^c

<i>n</i> -Butylamine	-33.13 ^e	-29.51 ^b	-22.3	-18.4 ^e
Triethylamine	-37.06 ^b	-33.80 ^b	-13.6	-15.6 ^g

^a Taken from ref. [11].

^b Taken from ref. [12].

^c Calculated in this work. Enthalpies of solution in methanol were taken from refs. [15, 52, 56].

^d Calculated from solution enthalpies from the ref. [53].

^e Calculated from solution enthalpies from the ref. [52].

^f Taken from ref. [53].

^g Taken from ref. [52].

^h Calculated from solution enthalpies from the ref. [57].