



# Free energy of solvation and Henry's law solubility constants for mono-, di- and tri-ethylene glycol in water and methane



Richard Olsen<sup>\*</sup>, Bjørn Kvamme, Tatiana Kuznetsova

University of Bergen, Department of Physics and Technology, Allégaten 55, 5007 Bergen, Norway

## ARTICLE INFO

### Article history:

Received 31 August 2015

Received in revised form

5 October 2015

Accepted 8 October 2015

Available online 21 October 2015

### 2010 MSC:

82B80

82D15

70E55

### Keywords:

Glycol

Methane

OPLS

Molecular dynamics

Free energy

## ABSTRACT

Free energy of solvation (i.e. residual chemical potential) and Henry's law solubility constants were estimated for mono ethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG) with water and methane as solvents at both 298 K and 1 atm and at 283 K and 80 atm using molecular dynamics simulations. Three methods of calculating free energies of solvation were compared: free energy perturbation (FEP), thermodynamic integration (TI) and Bennett acceptance ratio (BAR) method. The solubility constants were estimated based on the obtained free energies and were compared to the previously reported values. We found that free energy differences obtained using the three applied methods agreed very well. For both MEG and DEG the estimated solubility constants were within the same order of magnitude as previously reported solubility constants and therefore in good agreement. The estimated solubility constants of TEG were found to be about an order of magnitude smaller than the lowest reported value, and would still yield a reasonable estimate of residual chemical potential due to the logarithmic dependence.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG) are diols commonly used within the industry. Due to their two hydroxyl groups, the glycols can easily form hydrogen bonds to water. Therefore, they are attractive as clathrate hydrate inhibitors, as well as to absorb gas humidity in wet gas streams [1,2]. Since the upper few hundred meters of hydrocarbon systems may be within the hydrate formation region [3] glycols are also important in the field of enhanced oil recovery to prevent hydrate nucleation.

Experimental research on density, viscosity and thermal conductivity has been reported for the various glycols in aqueous environments [4], as well as in other solvents [5], at various temperatures in the range from 290 to 450 K. Reported experiments have obtained volumetric properties (i.e. excess molar volume) of MEG, DEG and TEG in aqueous environments for temperatures ranging between 273 and 363 K [6]. Mutual diffusion

coefficients of aqueous glycols have been measured using Taylor dispersion at temperatures between 303 and 323 K and at mole-fractions ranging from infinite dilution to mole-fractions close to unity [7]. Some research has also been reported on calorimetric measurements of excess enthalpies of aqueous DEG and MEG [8]. Excess Gibbs free energies have been calculated based on measured osmotic coefficients [9]. However, little research has been carried out to determine free energies of solvation (i.e. residual chemical potentials) for MEG, DEG and TEG in aqueous and methane environments.

Free energy of solvation is important to better understand the use of glycols in natural gas dehydration processes and as hydrate inhibitors since it gives crucial information on how thermodynamic processes evolve. In particular, we are interested in water and methane as solvents, both at standard temperatures and pressures and at industrial temperatures and pressures. Furthermore, to calculate the residual chemical potential of such glycols adsorbed to a surface it is common practice to first estimate the free energy difference between the adsorbed glycol and the glycol in the bulk phase. Subsequently, this value can be combined with the free energy difference between the glycol in an ideal gas environment and bulk to find the required residual chemical potential in the

<sup>\*</sup> Corresponding author. Allégaten 55, 5007 Bergen, Norway.  
E-mail address: [richard.olsen@ift.uib.no](mailto:richard.olsen@ift.uib.no) (R. Olsen).

adsorbed state.

In this work, we performed molecular dynamics (MD) simulations of MEG, DEG and TEG at infinite dilution in water, as well as methane, at 298 K and 1 atm and at 283 K and 80 atm. These simulations were used to estimate free energies of solvation at the given temperatures and pressures by applying the methods of free energy perturbation (FEP), thermodynamic integration (TI) and Bennett acceptance ratio (BAR). The obtained free energies were used to estimate Henry's law solubility constants. These were compared to previously reported solubility constants.

Sec. 2 contains some computational details and explanations of methods used throughout the paper. In Sec. 3 we present and discuss our results. Our findings are summarized in Sec. 4.

## 2. Computational details

### 2.1. Software packages

Molecular dynamics (MD) simulations of this work were performed using the 9 Dec 2014 version of LAMMPS [10,11]. To perform thermodynamic integration (TI), free energy perturbation (FEP) and Bennett acceptance ratio (BAR) calculations within LAMMPS, we employed the USER-FEP package.

VMD (Visual Molecular Dynamics) V1.9.1 [12] was used to represent and study molecular structures, as well as molecular motions of the systems.

We used the PackMol software package [13] to create initial system configurations.

### 2.2. Models

All-atom Optimized Potentials for Liquid Simulations (OPLS) force-field parameters [14–24] were assigned to MEG, DEG, TEG and CH<sub>4</sub> (methane). OPLS force-fields utilize harmonic bonds and angles of the form

$$E_{bond} = \sum_{i \in \text{bonds}} K_i^r (r_i - r_{0,i})^2,$$

and

$$E_{ang} = \sum_{i \in \text{angles}} K_i^\theta (\theta_i - \theta_{0,i})^2,$$

where  $K_i$  are force constants,  $r_{0,i}$  and  $\theta_{0,i}$  are equilibrium bond lengths and angles. Dihedral angles of TEG are modeled by

$$E_{dih} = \frac{1}{2} \sum_{i \in \text{dih.}} \sum_{n=1}^4 V_{n,i} [1 + (-1)^{n+1} \cos(n\phi_i)],$$

where  $V_{n,i}$  are force constants and  $\phi_i$  are dihedral angles. Short-range and long-range interactions are modeled using 12-6 Lennard–Jones potentials and Coulomb potentials, respectively, of the form

$$E_{LJ+C}^{ij} = \left[ 4\varepsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} + \frac{e^2 q_i q_j}{4\pi\epsilon_0 r_{ij}} \right] f_{ij},$$

where  $\varepsilon_{ij}$ ,  $\sigma_{ij}$  are Lennard–Jones parameters,  $q_i$ ,  $q_j$  are partial charges,  $r_{ij}$  is the distance between atom  $i$  and  $j$ , and

$$f_{ij} = \begin{cases} 1 & \text{if } i, j \text{ in separate molecules} \\ 0.5 & \text{if } i, j \text{ separated by 3 bonds} \\ 0 & \text{if } i, j \text{ separated by } < 3 \text{ bonds} \\ 1 & \text{else.} \end{cases}$$

Water was modeled using flexible Simple Point Charge (fSPC) force-field parameters [25]. In fSPC, bonds are described by

$$E_{bond} = D_m \left\{ \left[ 1 - e^{-\rho_m \Delta r_1} \right]^2 + \left[ 1 - e^{-\rho_m \Delta r_2} \right]^2 \right\} + c \{ \Delta r_1 + \Delta r_2 \} \Delta r_3 + b (\Delta r_3)^2 + d \Delta r_1 \Delta r_2, \quad (1)$$

where  $\Delta r_1$  and  $\Delta r_2$  are the two H–O bond length perturbations, while perturbations of H–H atomic separations are described by  $\Delta r_3$ . In our simulations higher order cross terms,  $\Delta r_1 \Delta r_3$ ,  $\Delta r_2 \Delta r_3$ ,  $\Delta r_1 \Delta r_2$  were ignored (this has little impact on the water–water and water–glycol interactions, which are important in our work).

We employed geometric mixing rules to obtain pair interactions,  $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$  and  $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$  (which are preferred mixing rules within the OPLS force-field specification). All parameters used are listed in the appendix.

### 2.3. Free energy calculations

Gibbs free energy difference between glycol in solvent and glycol in the gas phase (i.e. solvation free energy) was calculated using FEP, TI and BAR. In TI [26] free energy is estimated by

$$\Delta G \equiv G(\lambda = 1) - G(\lambda = 0) = \int_0^1 d\lambda \left\langle \frac{\partial U_{\text{int}}}{\partial \lambda} \right\rangle_\lambda,$$

where  $\langle \dots \rangle_\lambda$  in our case was a second order interpolation function of 400 time-averages, where

$$\frac{\partial U_{\text{int}}}{\partial \lambda} \approx \frac{E_{LJ+C,s}(\lambda + \delta\lambda) - E_{LJ+C,s}(\lambda)}{\delta\lambda},$$

with  $\delta\lambda = 125\text{ps}/50000 \text{ ps}$ .

For FEP with volume correction [27] the free energy is calculated as

$$\Delta G = -\frac{1}{\beta} \sum_{i=1}^{400} \ln \frac{\langle V e^{-\beta \delta E(\lambda)} \rangle_{\lambda_i}}{\langle V \rangle_{\lambda_i}} \approx \sum_{i=1}^{400} \Delta G_i, \quad (2)$$

where

$$\delta E(\lambda) \equiv E_{LJ+C,s}(\lambda + \delta\lambda) - E_{LJ+C,s}(\lambda),$$

with  $\beta^{-1} \equiv k_B T$  where  $k_B$  is the Boltzmann constant.

In the BAR method,  $\mathcal{W}(\Gamma)$  is inserted as an undetermined function of the configurational coordinates,  $\Gamma$ , in the ratio between two partition functions:

$$\frac{Q_0}{Q_1} = \frac{Q_0 \int d\Gamma \mathcal{W} e^{-\beta(U_0+U_1)}}{Q_1 \int d\Gamma \mathcal{W} e^{-\beta(U_0+U_1)}} = \frac{\langle \mathcal{W} e^{-\beta U_0} \rangle_1}{\langle \mathcal{W} e^{-\beta U_1} \rangle_0}, \quad (3)$$

where  $U_0$  and  $U_1$  are the potentials at state 0 and 1, respectively. Thus, the free energy difference between states 0 and 1 becomes

Download English Version:

<https://daneshyari.com/en/article/201158>

Download Persian Version:

<https://daneshyari.com/article/201158>

[Daneshyari.com](https://daneshyari.com)