Quantum Chemical Approach for Condensed-Phase Thermochemistry(IV):

Solubility of Gaseous Molecules

Atsushi Ishikawa^a, Masahiro Kamata^b, and Hiromi Nakai^{a-d,*}

^aResearch Institute for Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan

^bDepartment of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1

Okubo, Shinjuku, Tokyo 169-8555, Japan

^cCREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

^dESICB, Kyoto University, Kyotodaigaku-Katsura, Kyoto 615-8520, Japan

*To whom correspondence should be addressed. E-mail: nakai@waseda.jp

Abstract

The harmonic solvation model (HSM) was applied to the solvation of gaseous molecules and compared to a procedure based on the ideal gas model (IGM). Examination of 25 molecules showed that (i) the accuracy of ΔG_{solv} was similar for both methods, but the HSM shows advantages for calculating ΔH_{solv} and $T\Delta S_{\text{solv}}$; (ii) ΔS_{solv} contributes more than ΔH_{solv} to ΔG_{solv} in the HSM, i.e. the solvation of gaseous molecules is entropy-driven, which agrees well with experimental understanding (the IGM does not show this); (iii) the temperature dependence of Henry's law coefficient was correctly reproduced with the HSM.

Keywords: condensed-phase; quantum chemistry; gaseous solubility; harmonic solvation model; ideal gas model

I. Introduction

The solubility of gaseous molecules is an important parameter in vapor–liquid equilibria in basic physical chemistry and environmental science. Solubility is often expressed by the more clearly defined Henry's law coefficient (HLC). Accurate knowledge of solubility is essential for predicting the environmental behavior of pollutants, since it describes the ability to distribute between vapor- and liquid-phases[1]. Extensive effort has been devoted to accurate estimation of the HLC. However, limited experimental solubility data have been reported, partly owing to difficulties in obtaining accurate data by experimental techniques, such as adsorption effects on the walls of apparatus and analytical limits of detection[2,3]. Altschuh and Brüggemann revealed in 1993 that solubility data has been reported for only 17.4% of approximately 800 environmentally relevant chemicals[3].

The difficulties associated with experimental techniques increase the demand for theoretical and computational methods. In chemical engineering, computer simulations based on property–property relationships (PPRs) or structure–property relationships (SPRs) have been widely used. Quantitative structure–property relationships (QSPRs) are considered accurate models for predicting gaseous solubility or the HLC[4-7]. This method has been successfully applied to various chemical compounds, although the accuracy of the fitting parameters strongly depends on the quality of the experimental data, such as vapor pressure or aqueous solubility, and such data are often unavailable or unreliable.

Theoretical methods, such as molecular dynamics (MD) and Monte-Carlo (MC) simulations, are less dependent on the quality of experimental data[8-10]. Typical approaches are the grand canonical MC with histogram reweighting method, Gibbs–Duhem integration method, isothermal–isobaric (NPT) ensemble

simulation with the Widom test particle insertion method, etc. [11-13]. These simulation techniques give accurate HLCs, and can predict not only the HLC at a fixed temperature, but also its temperature dependence [9,10,14]. However, their accuracy is significantly dependent on the simulation conditions, such as selection of the molecular model (all-atom or united-atom), force field, number of molecules in the simulation box, etc. [15-17]. Particular attention should therefore be paid to the selection of simulation conditions, since the vapor-liquid equilibrium is an intrinsically multi-component system. For example, the Lennard-Jones parameter for solute-solvent pairs should be carefully selected. Several studies have shown that simple formulae, such as the Lorentz-Berthelot rule for estimating Lennard-Jones parameters for different compound pairs, are unsatisfactory for the reliable prediction of gaseous solubility. Several approaches have been proposed to improve the Lorentz-Berthelot rule, however, many require additional information such as polarizability data [18,19]. Force field selection is a difficult problem in vapor-liquid simulations. State-of-the-art force fields, such as polarizable force fields or fluctuation charge, significantly improve the simulation results for liquid systems. However, as reported by Panagiotopoulos, the polarizable force field does not always improve the thermodynamic properties for vapor-liquid equilibria, such as vapor pressure or heat of vaporization [20]. Recent techniques, such as the reaction Gibbs ensemble MC (RGEMC), show promise for circumventing the above-stated force field problem [21,22].

Another theoretical tool used for calculating solubility is the *ab initio* quantum chemistry approach [23,24], which has been applied to the estimation of HLCs [25-27]. However, the current quantum chemistry approach still presents problems in its basic part and needs improvement. Zhang and Zeng have shown that direct

evaluation of the HLC from the Gibbs energy of solvation (ΔG_{solv}) is not sufficiently accurate, and proposed the use of a reference substance and the relative Gibbs energy [28,29]. Another disadvantage of the quantum chemistry method is that the temperature dependence of the HLC is rarely provided. In previous studies employing the quantum chemistry method, HLCs were only evaluated at a fixed temperature and their temperature dependence was not discussed [25-27]. It is widely recognized that the temperature dependence of the vapor–liquid equilibrium can be described with the help of statistical thermodynamics, as shown by Klamt et al. in the Conductor-like Screening Model for Real Solvents (COSMO-RS) approach [30,31]. Temperature-dependent aqueous solubilities were investigated with the COSMO-RS method showing good agreement with experimental data [31-33].

One of the most serious problems associated with the quantum chemistry method when applied to vapor–liquid phase co-existing systems is its insufficient description of the liquid-phase entropy. Recently, we proposed a novel quantum chemical model aimed at accurate thermodynamic property calculation in the condensed-phase [34]. The method is called the harmonic solvation model (HSM), since the solute's motion in the solvent environment is expressed by the harmonic oscillator. The calculation of thermodynamic properties, such as enthalpy, entropy, and Gibbs energy, are improved with the HSM, especially the entropy term.

In the present study, we used the HSM to calculate the HLC of simple gaseous molecules. One advantage of the HSM over conventional quantum chemistry methods is that ΔH_{solv} and ΔS_{solv} can be accurately evaluated as well as ΔG_{solv} . Previous studies applying quantum chemistry methods to the solubility problem mainly focus on ΔG_{solv} without detailed discussion of individual enthalpy and entropy contributions, although ΔH_{solv} and ΔS_{solv}

clearly have different physical and chemical origins[35]. Such discussion would be advantageous in calculating the temperature dependence of the HLC, since it is mainly determined by ΔS_{solv} .

II. Theoretical Aspects

A. HSM

In the quantum chemistry method, vapor-phase thermodynamic properties are calculated from the set of equations formulated by the kinetic theory of gas under the ideal gas assumption; the ideal gas model (IGM). In the IGM, the motion of gaseous molecules is separated into vibrational, rotational, and translational components, whose energies (E_{vib} and E_{rot} , respectively) and entropies (S_{vib} , S_{rot} , and S_{trans} , respectively) are expressed by Eqs. (1)–(5).

$$E_{\text{vib}} = N_{\text{A}} k_{\text{B}} T \sum_i^{3N-6} \frac{h\nu_i}{k_{\text{B}} T} \left\{ \frac{1}{2} + \frac{\exp(-h\nu_i / k_{\text{B}} T)}{1 - \exp(-h\nu_i / k_{\text{B}} T)} \right\}, \quad (1)$$

$$E_{\text{rot}}^{\text{IGM}} = E_{\text{trans}}^{\text{IGM}} = \frac{3}{2} N_{\text{A}} k_{\text{B}} T = \frac{3}{2} RT, \quad (2)$$

$$S_{\text{vib}} = N_{\text{A}} k_{\text{B}} \sum_i^{3N-6} \left[\frac{(h\nu_i / k_{\text{B}} T) \exp(-h\nu_i / k_{\text{B}} T)}{1 - \exp(-h\nu_i / k_{\text{B}} T)} - \ln \{1 - \exp(-h\nu_i / k_{\text{B}} T)\} \right], \quad (3)$$

$$S_{\text{rot}}^{\text{IGM}} = R \left\{ \frac{1}{2} \ln ABC + \frac{3}{2} \ln T - \ln \sigma + \text{const.} \right\}, \quad (4)$$

$$S_{\text{trans}}^{\text{IGM}} = R \left\{ \frac{3}{2} \ln M + \frac{5}{2} \ln T - \ln p + \text{const.} \right\}. \quad (5)$$

N_{A} , k_{B} , h , and R are the Avogadro, Boltzmann, Planck, and gas constants, respectively. p and T are pressure and temperature, and the vibrational frequencies $\{\nu_i\}$, mass M , rotational constants $\{A, B, \text{ and } C\}$, and symmetry number σ are system-dependent variables. The enthalpy and Gibbs energy are given by

$$H = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}} + W \quad (6)$$

and

$$G = H - TS = H - T(S_{\text{elec}} + S_{\text{vib}} + S_{\text{rot}} + S_{\text{trans}}), \quad (7)$$

respectively, where work $W = pV$. Note that S_{elec} is zero in the ground electronic state for closed-shell molecules. In the condensed-phase, rotational and translational motions are restricted by solute-solvent interactions. Consequently, expressions for rotational and translational energies and entropies based on the IGM (Eqs.(2), (4), and(5)) are inappropriate in the condensed-phase. It should be noted that many quantum chemistry programs employ the IGM formulae for the calculation of condensed-phase thermodynamic properties.

To adequately express these effects, the HSM treats the rotational and translational motions corresponding to solute-solvent interactions as harmonic oscillators[34]. By applying the harmonic oscillator model to the translational and rotational motions, their energy and entropy contributions become

$$E_{\text{trans/rot}}^{\text{HSM}} = \frac{1}{2} N_A k_B T \sum_{i \in \text{trans/rot}}^3 \frac{h\nu_i}{k_B T} \left\{ \frac{1}{2} + \frac{\exp(-h\nu_i/k_B T)}{1 - \exp(-h\nu_i/k_B T)} \right\} \quad (8)$$

and

$$S_{\text{trans/rot}}^{\text{HSM}} = N_A k_B \sum_{i \in \text{trans/rot}}^3 \left[\frac{(h\nu_i / k_B T) \exp(-h\nu_i / k_B T)}{1 - \exp(-h\nu_i / k_B T)} - \ln \{1 - \exp(-h\nu_i / k_B T)\} \right], \quad (9)$$

respectively. Note that $S_{\text{trans/rot}}^{\text{HSM}}$ is identical to $S_{\text{vib}}^{\text{IGM}}$ (Eq.(3)). Therefore, a key difference between the IGM and HSM is the treatment of the solute rotational and translational motions in the condensed-phase; in the IGM, the rotational and translational modes, which normally correspond to the six lowest modes, are omitted when evaluating the thermal contribution from vibrational motion. In contrast, all motions of the solute molecules are treated as harmonic vibrations in the HSM. Therefore, the rotational and translational energies and entropies were evaluated according to the vibrational formulae.

The vibrational frequency in the condensed-phase is obtained using the framework of the self-consistent reaction field (SCRF) procedure. In the HSM, the Hessian matrix is evaluated by fixing solute cavities since interactions between a solute molecule and its cavities are presumed to be solute–solvent interactions. After the Hessian matrix evaluation, vibrational, rotational, and translational energies and entropies are evaluated.

In the present study, ΔG_{solv} was calculated using the following formula in both the IGM and HSM;

$$\Delta G_{\text{solv}} = \left[E_{\text{elec}}^{\text{sol}} + E_{\text{vib}}^{\text{sol}} + E_{\text{rot}}^{\text{sol}} + E_{\text{trans}}^{\text{sol}} + pV - T \left(S_{\text{elec}}^{\text{sol}} + S_{\text{vib}}^{\text{sol}} + S_{\text{rot}}^{\text{sol}} + S_{\text{trans}}^{\text{sol}} \right) \right] - \left[E_{\text{elec}}^{\text{gas}} + E_{\text{vib}}^{\text{gas}} + E_{\text{rot}}^{\text{gas}} + E_{\text{trans}}^{\text{gas}} + pV - T \left(S_{\text{elec}}^{\text{gas}} + S_{\text{vib}}^{\text{gas}} + S_{\text{rot}}^{\text{gas}} + S_{\text{trans}}^{\text{gas}} \right) \right] = \Delta H_{\text{solv}} - T \Delta S_{\text{solv}} \quad (10)$$

where both vapor- and liquid-phase Gibbs energies include all components.

B. Solubility and HLC

The vapor- and liquid-phase chemical potentials are written as

$$\mu_{i,\text{vap}}(p, T) = \mu_{i,\text{vap}}^\circ(p, T) + RT \ln(p_i / p_0) \quad (11)$$

and

$$\mu_{i,\text{liq}}(p, T, x_i) = \mu_{i,\text{liq}}^\circ(p, T) + RT \ln a_i = \mu_{i,\text{liq}}^\circ + RT \ln \gamma_i x_i, \quad (12)$$

respectively, where p_i and p_0 are the partial pressure of compound i and the reference pressure, respectively; a_i is the activity of i ; and γ_i and x_i are the activity coefficient and solubility (in molar fraction) of i , respectively [14,36,37]. Since these chemical potentials are equal at vapor–liquid equilibrium,

$$\mu_{i,\text{vap}}^\circ + RT \ln(p_i / p_0) = \mu_{i,\text{liq}}^\circ + RT \ln \gamma_i x_i. \quad (13)$$

p_i and x_i are therefore related by

$$p_i = K_i x_i, \quad (14)$$

in which

$$K_i(p, T) = p_0 \gamma_i \exp \left[\frac{\mu_{i,\text{liq}}^\circ(p, T) - \mu_{i,\text{vap}}^\circ(p_0, T)}{RT} \right]. \quad (15)$$

The HLC $H_i(p, T)$ is defined as the limiting value of $K_i(p, T)$ as [38]

$$H_i(p, T) = \lim_{x_i \rightarrow 0} \left(\frac{p_i}{x_i} \right) = \lim_{x_i \rightarrow 0} K_i(p, T). \quad (16)$$

$H_i(p, T)$ depends on both pressure and temperature, but its pressure dependence is negligible. Therefore, we consider only its temperature dependence.

In MD and MC simulations, the HLC is calculated via the excess chemical potential (at infinite dilution)

μ_{ex}^{∞} . This corresponds to the non-ideality of the solution, i.e. solute–solvent interactions. Since γ_i is related to

μ_{ex}^{∞} as $\gamma_i = \exp(\mu_{\text{ex}}^{\infty} / RT)$, the HLC is calculated as

$$H_i(T) = p_0 \exp\left(\frac{\mu_{\text{ex}}}{RT}\right) = \rho_i RT \exp\left(\frac{\mu_{\text{ex}}^{\infty}}{RT}\right), \quad (17)$$

where ρ_i is the density of i in the liquid-phase. In the quantum chemistry method, the ideal and non-ideal parts of

ΔG_{solv} are treated together as the whole solvation free energy $\Delta\mu_{\text{solv}}$. The HLC is calculated as

$$H_i(T) = p_0 \exp\left(\frac{\mu_{i,l}^{\circ} - \mu_{i,g}^{\circ} + \mu_{\text{ex}}^{\infty}}{RT}\right) = p_0 \exp\left(\frac{\Delta\mu_{\text{solv}}}{RT}\right). \quad (18)$$

In many cases, the reference state is taken as the standard condition for solution (1 mol/L) and in this case p_0

becomes RT . This definition was also applied in the present study, i.e. the solvation chemical potential (or Gibbs

energy) is defined as the Gibbs energy of transferring 1 mol/L vapor-phase molecules into solution[39]. Since many

experimental and theoretical studies report the HLC as

$$\ln H_i(T) = \frac{\Delta\mu}{RT} + \ln RT, \quad (19)$$

we have done the same herein.

III. Computational Details

The solvation of 25 small molecules, such as H₂, N₂, CO₂, hydrocarbons (methane, ethane, propane etc.), and haloalkanes (CH₃F, CH₃Cl, etc.), with water was examined. Geometry optimizations were carried out at the second order Møller–Plesset perturbation (MP2) level with an aug-cc-pVTZ basis set. The electronic energies were evaluated at the CCSD(T) level with an aug-cc-pVTZ basis set.

The electronic energy in solution was evaluated by the SCRF method, where the conductor-like polarizable continuum model (CPCM) was used. In the CPCM calculations, Bondi's van der Waals radii scaled by $\alpha = 1.2$ were used throughout. The repulsion and dispersion terms were evaluated by the method of Floris and Tomasi[40,41]. The cavitation energy equation defined by Pierotti includes both enthalpy and entropy contributions in the IGM [42]. The entropy contribution mainly arises from the translational entropy difference between the vapor- and liquid-phases. When the whole cavitation energy is included in the solvation Gibbs energy, the translation entropy component is counted twice in the solvation entropy. This is problematic in the HSM calculations, since the vapor- and liquid-phase entropy difference is explicitly taken into account by Eq.(9). For this reason, we only added the enthalpy contribution of the cavitation energy to the solvation enthalpy in the HSM calculations.

Thermodynamic contributions were calculated by the IGM and HSM. All vapor-phase calculations were carried out using Gaussian09, and PCM calculations were carried out using Gaussian09 and GAMESS2013[43,44]. HSM calculations were carried out by our own program connected with the GAMESS software.

Experimental solvation data were taken from the following sources: (i) the IUPAC Solubility Data Series[45], (ii) a review by Wilhelm, Battino, and Wilcock[46], and (iii) data compiled by Sander in which the HLC and

$d \ln H_i / d(1/T)$ were reported with original references[47]. Values of $d \ln H / d(1/T)$ were used for the estimation of ΔH_{solv} from the relationship

$$\frac{d \ln H_i}{d(1/T)} = \frac{-\Delta H_{\text{solv}}}{R}. \quad (20)$$

When the HLC is given in $\text{kPa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$, it is converted to other frequently used units as follows,

$$H'_i [\text{atm} \cdot \text{L} \cdot \text{mol}^{-1}] = 1.0 \times 10^1 H_i [\text{kPa} \cdot \text{m}^3 \cdot \text{mol}^{-1}], \quad (21)$$

$$H''_i [\text{GPa}] = 1.0 \times 10^{-6} \rho [\text{kg} \cdot \text{m}^{-3}] / MW [\text{kg} \cdot \text{mol}^{-1}] \cdot H_i [\text{kPa} \cdot \text{m}^3 \cdot \text{mol}^{-1}], \quad (22)$$

where ρ and MW are the density and molecular weight of the solvent, respectively. Solvent density is taken from

Ref.[48], where density is fixed to that at 20 °C.

IV. Results and Discussion

ΔG_{solv} was calculated for the 25 molecules under standard conditions (25 °C, 1 atm) with the IGM and HSM. Enthalpy and entropy contributions, i.e. ΔH_{solv} and ΔS_{solv} , were also evaluated. The thermodynamic properties and $\ln H_i$ values calculated from ΔG_{solv} are shown in Table 1.

As seen from Table 1, the IGM shows reasonable agreement with experimental ΔG_{solv} (mean absolute deviation (MAD) of 4.54 kJ/mol). The largest deviation from experimental values was obtained for CF_4 , -10.33 kJ/mol. Note that the accuracy of the IGM calculations is similar to those in previous studies employing the PCM; Takano and Houk reported an MAD of 5.64 kJ/mol for ΔG_{solv} calculated by the PCM for neutral species [49]. ΔG_{solv} calculated by the HSM shows similar accuracy to that obtained with the IGM, but slightly larger deviation; the MAD and largest deviation were calculated as 7.02 and -22.28 kJ/mol (the latter for CF_2Cl_2), respectively. As a result, $\ln H_i$ is of similar accuracy for the IGM and HSM since with MADs of 1.80 and 2.83, respectively. The IGM and HSM therefore show similar accuracy for ΔG_{solv} and HLC for neutral gaseous molecules.

Conversely, the IGM and HSM show significantly different results for ΔH_{solv} and ΔS_{solv} . The IGM shows large deviation from experimental values for ΔH_{solv} (MAD of 22.66 kJ/mol). Likewise, $T\Delta S_{\text{solv}}$ shows significant errors (MAD of 26.04 kJ/mol). However, the HSM shows good accuracy for both ΔH_{solv} and ΔS_{solv} (MADs of 6.33 and 6.02 kJ/mol, respectively). Thus, the accuracy of the entropy component was improved more than 4-fold with the HSM. Because the conventional PCM scheme only concentrates on the accuracy of ΔG_{solv} , parameters such as cavity radius were optimized to reproduce experimental ΔG_{solv} . Accurate individual ΔH_{solv} and ΔS_{solv} components are then not guaranteed, as clearly shown by the above results. The HSM improves the accuracy of ΔS_{solv} more

significantly than the IGM, and the overall accuracy of ΔG_{solv} is similar to or moderately lower than that of the IGM. ΔH_{solv} also shows reasonable agreement with experimental values, better than ~ 10 kJ/mol on average. These results show that correct decomposition of ΔG_{solv} into ΔH_{solv} and ΔS_{solv} is possible with the HSM.

The correlation between experimental and theoretical ΔH_{solv} , ΔS_{solv} , and ΔG_{solv} values obtained by the IGM and HSM are plotted in Figure 1. It can be seen that the HSM improves the accuracy of both ΔH_{solv} and ΔS_{solv} significantly. The IGM underestimates ΔS_{solv} considerably, since ideal gas behavior is assumed in the both vapor- and liquid-phases. These results indicate that the IGM performs well for ΔG_{solv} , but its enthalpy and entropy contributions are not as accurate.

To analyze the solvation process in more detail, ΔH_{solv} and $T\Delta S_{\text{solv}}$ contribution to ΔG_{solv} with the IGM and HSM was evaluated, as shown in Figure 2. Five molecules from hydrocarbons, haloalkanes, and small inorganic molecules are shown as examples. The HSM results indicate that rather small ΔG_{solv} results from the summation of a large negative ΔH_{solv} contribution and large positive $T\Delta S_{\text{solv}}$ contribution. This is in good agreement with experimental understanding, i.e. ΔH_{solv} induces the solvation of gaseous molecules via solute-solvent interactions while $T\Delta S_{\text{solv}}$ inhibits solvation since releasing solute molecules into the vapor-phase is entropically favorable. Enthalpic and entropic contributions are of similar magnitude, although $T\Delta S_{\text{solv}}$ contributions slightly exceed those of ΔH_{solv} in non-polar solutes such as CH_4 and PH_3 as a result of smaller solute-solvent interactions. This also correlates with experimental understanding of the solvation of small non-polar molecules, i.e. these processes are entropy-driven[35]. As shown in these examples, the correct decomposition of ΔG_{solv} into enthalpy and entropy contributions is useful for better understanding of the solvation process, since these components have completely

different physical origins; larger ΔH_{solv} signifies stronger solute–solvent interactions, while larger ΔS_{solv} indicates more significant loss of freedom in the liquid-compared to the vapor-phase. This result also indicates that the reasonable accuracy of ΔG_{solv} with the IGM is achieved because of the error cancellation of ΔH_{solv} and ΔS_{solv} , where ΔH_{solv} and ΔS_{solv} are significantly overestimated and underestimated, respectively.

Finally, the temperature dependence of the HLC was investigated. In Figure 3, $\ln H_i$ calculated with the IGM and HSM vs. temperature T is plotted, together with the experimental values. Here, four sets of molecules were employed, (A) alkanes; CH_4 , C_2H_6 , C_3H_8 , and C_4H_{10} , (B) haloalkanes; CH_3F , CH_3Cl , and CH_3Br , (C) C_2 -hydrocarbons; C_2H_6 , C_2H_4 , and C_2H_2 , and (D) small inorganic molecules; H_2 , N_2 , CO , and N_2O . To observe the temperature dependence more clearly, relative $\ln H_i$ values at 288 K (the lowest temperature at which experimental data are available) were taken.

As shown in Figure 3, $\ln H_i$ increases in the order C_4H_{10} , C_3H_8 , C_2H_6 , CH_4 for hydrocarbons. The HSM results correctly reproduce this trend, although the increase in $\ln H_i$ is slightly underestimated. On the contrary, the IGM predicts a decrease in $\ln H_i$ with increasing temperature. For haloalkanes, both the IGM and HSM show increasing $\ln H_i$ with temperature, although the increase in $\ln H_i$ is significantly underestimated with the IGM. Again, the HSM shows reasonable agreement with experimental results in all cases. For small inorganic molecules, the HSM successfully reproduces the experimental order of increasing HLC with temperature ($\text{N}_2\text{O} > \text{CO} > \text{N}_2 > \text{H}_2$), although this was not the case for C_2 -hydrocarbons (correct order: $\text{C}_2\text{H}_6 > \text{C}_2\text{H}_4 > \text{C}_2\text{H}_2$). This inaccuracy results from insufficient treatment of short-range solute–solvent interactions, such as explicit coordination of solvent molecules or intermolecular hydrogen bond formation. Description of these interactions is possible by treating

several explicit solvent molecules quantum chemically, known as the cluster–continuum approach[50].

The HSM results indicate that the HLC increases with temperature, meaning gaseous solubility decreases at higher temperature since the solubility is inversely proportional to the HLC. This is inaccordance with experimental results, but the IGM fails to reproduce it. This is because the IGM does not give the correct ΔS_{solv} since the temperature dependence of ΔG_{solv} and the HLC is mainly governed by the entropy component.

V. Conclusions

In the present study, the HSM, which aims to produce accurate thermodynamic properties of condensed-phase molecules, was applied to calculation of the HLC, which is equivalent to the solubility of gaseous molecules. The solvation of 25 molecules with water was examined using both the HSM and IGM.

The IGM and HSM show good agreement with experimental values for ΔG_{solv} . The MADs for ΔG_{solv} are 5.60 and 7.02 kJ/mol, respectively. On the contrary, the IGM fails to reproduce experimental values for ΔH_{solv} and ΔS_{solv} , but the HSM shows considerable improvement. The MADs for $\{\Delta H_{\text{solv}}, T\Delta S_{\text{solv}}\}$ are $\{21.98, 6.33\}$ and $\{90.47, 20.18\}$ in kJ/mol for the IGM and HSM, respectively. For most of the examined compounds, ΔS_{solv} contribution to ΔG_{solv} is larger than that of ΔH_{solv} with the HSM, and vice versa for the IGM. The HSM results indicate that the solvation of gaseous molecules is entropy-driven, which agrees well with experimental understanding.

When correct ΔS_{solv} values were obtained, the temperature dependence of the HLC was predicted accurately. Experimentally, the HLC decreases as temperature increases. This tendency was correctly reproduced by the HSM but not the IGM.

Acknowledgements

Some calculations were performed at the Research Center for Computational Science (RCCS), the Okazaki Research Facilities, and the National Institutes of Natural Sciences (NINS). This study was supported in part by the Core Research for Evolutional Science and Technology (CREST) program from the Japan Science and Technology (JST) Agency, the Grants-in-Aid for Challenging and Exploratory Research “KAKENHI 15K13629”, the Strategic Programs for Innovative Research (SPIRE), and the Computational Materials Science Initiative (CMSI) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

- [1] J.J. Carroll, J. Chem. Educ. 70 (1993) 91.
- [2] D. Mackay, W.Y. Shiu, J. Phys. Chem. Ref. Data 10 (1981) 1175.
- [3] J. Altschuh, R. Bruggemann, H. Santl, G. Eichinger, et al., Chemosphere 39 (1999) 1871.
- [4] J. Hine, P.K. Mookerjee, J. Org. Chem. 40 (1975) 292.
- [5] C.J. Russell, S.L. Dixon, P.C. Jurs, Anal. Chem. 64 (1992) 1350.
- [6] A.R. Katritzky, Y.L. Wang, S. Sild, T. Tamm, et al., J. Chem. Inf. Comput.Sci. 38 (1998) 720.
- [7] K.U. Goss, Fluid Phase Equilib. 233 (2005) 19.
- [8] R.J. Sadus, J. Phys. Chem. B 101 (1997) 3834.
- [9] A.Z. Panagiotopoulos, J. Phys.: Condens. Matter.12 (2000) R25.
- [10] I.G. Economou, Fluid Phase Equilib. 183 (2001) 259.
- [11] J.M. Stubbs, B. Chen, J.J. Potoff, J.I. Siepmann, Fluid Phase Equilib. 183 (2001) 301.
- [12] T.I. Morrow, E.J. Maginn, Fluid Phase Equilib. 217 (2004) 97.
- [13] J. Vrabec, J. Stoll, H. Hasse, Mol. Simul.31 (2005) 215.
- [14] D. Frenkel, B. Smit, Understanding Molecular Simulations, Academic Press, 2002.
- [15] M. Lísal, W.R. Smith, K. Aim, Fluid Phase Equilib. 226 (2004) 161.
- [16] C.J. Wu, X.F. Li, J.X. Dai, H. Sun, Fluid Phase Equilib. 236 (2005) 66.
- [17] H. Yuan, S. Murad, C.J. Jameson, J.D. Olson, J. Phys. Chem. C. 111 (2007) 15771.
- [18] G.C. Boulougouris, J.R. Errington, I.G. Economou, A.Z. Panagiotopoulos, et al., J. Phys. Chem. B 104 (2000) 4958.
- [19] T. Schnabel, J. Vrabec, H. Hasse, J. Mol. Liq. 135 (2007) 170.
- [20] A.Z. Panagiotopoulos, N. Quirke, M. Stapleton, D.J. Tildesley, Mol. Phys. 63 (1988) 527.
- [21] W.R. Smith, B. Triska, J. Chem. Phys. 100 (1994) 3019.
- [22] M. Lísal, W.R. Smith, I. Nezbeda, J. Phys. Chem. B 103 (1999) 10496.
- [23] J. Tomasi, M. Persico, Chem. Rev. 94 (1994) 2027.
- [24] J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev. 105 (2005) 2999.

- [25] G. Schüürmann, J. Comput. Chem. 21 (2000) 17.
- [26] E.J. Delgado, J.B. Alderete, J. Chem. Inf. Comput. Sci. 42 (2002) 559.
- [27] E.J. Delgado, J.B. Alderete, J. Chem. Inf. Comput. Sci. 43 (2003) 1226.
- [28] X. Zhang, Y. Zeng, Fluid Phase Equilib. 376 (2014) 234.
- [29] Y. Zeng, X. Chen, D. Zhao, H. Li et al., Fluid Phase Equilib. 313 (2012) 148.
- [30] A. Klamt, F. Eckert, Fluid Phase Equilib. 172 (2000) 43.
- [31] A. Klamt, F. Eckert, Fluid Phase Equilib. 217 (2004) 53.
- [32] S. Oleszek-Kudlak, M. Grabda, E. Shibata, F. Eckert, et al., Environ. Toxicol.Chem. 24 (2005) 1368.
- [33] B. Schroeder, L.M.N.B.F. Santos, I.M. Marrucho, J.A.P. Coutinho, Fluid Phase Equilib. 289 (2010) 140.
- [34] H. Nakai, A. Ishikawa, J. Chem. Phys. 141 (2014) 174106.
- [35] J.H. Hildebrand, R.L. Scott, The solubility of nonelectrolytes, Reinhold Publishing, New York, 1950.
- [36] E.J. Baum, Chemical Property Estimation; Theory and Application, CRC Press, 1997.
- [37] D. Kondepudi, Introduction to Modern Thermodynamics, John Wiley & Sons, 2007.
- [38] J.M. Smith, H.C. Van Ness, M.M. Abbott, Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, New York, 2001.
- [39] A. Ben-Naim, Solvation Thermodynamics, Plenum Press, New York, 1987.
- [40] F.M. Floris, J. Tomasi, J. Comput. Chem. 10 (1989) 616.
- [41] F.M. Floris, J. Tomasi, J.L.P. Ahuir, J. Comput. Chem. 12 (1991) 784.
- [42] R.A. Pierotti, Chem. Rev. 76 (1976) 717.
- [43] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, et al., Gaussian 09, Revision C.01. Gaussian Inc, Wallingford, CT, 2009.
- [44] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, et al., J. Comput.Chem. 14 (1993) 1347.
- [45] IUPAC, Solubility Data Series, Pergamon, 1972.
- [46] E. Wilhelm, R. Battino, R.J. Wilcock, Chem. Rev. 77 (1977) 219.
- [47] R. Sander, Atmos. Chem. Phys. Discuss. 14 (2014) 29615.
- [48] CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL., 2014.

- [49] Y. Takano, K.N. Houk, *J. Chem. Theory Comput.* 1 (2005) 70.
- [50] D.G. Truhlar, J.R. Pliego, in: B. Mennucci, R. Cammi (Eds.), *Continuum Solvation Models in Chemical Physics*, John Wiley & Sons Ltd, England, 2007, p. 338.

Tables and Figures

Table 1. ΔH_{solvs} , $T\Delta S_{\text{solvs}}$, ΔG_{solvs} , and $\ln H_i$ calculated by the IGM and HSM. Deviation from experimental values [45] are shown in parentheses.

	ΔH_{solvs} (kJ/mol)			$T\Delta S_{\text{solvs}}$ (kJ/mol)			ΔG_{solvs} (kJ/mol)			$\ln H_i$		
	IGM	HSM	Exptl.	IGM	HSM	Exptl.	IGM	HSM	Exptl.	IGM	HSM	Exptl.
Methane	4.87 (+17.92)	-14.11 (-1.07)	-13.04	0.01 (+21.37)	-18.77 (+2.59)	-21.36	11.03 (+2.71)	4.66	8.32 (-3.66)	5.36 (-1.10)	2.79 (+1.47)	4.26
Ethane	7.67 (+27.10)	-13.82 (+5.62)	-19.43	-0.05 (+26.97)	-26.04 (+0.98)	-27.02	7.71 (+0.13)	12.22	7.59 (+4.63)	4.02 (-0.05)	5.84 (-1.87)	3.97
Propane	11.64 (+33.80)	-12.88 (+9.29)	-22.16	0.78 (+31.07)	-32.43 (-2.14)	-30.29	12.58 (+4.45)	19.56	8.13 (+11.42)	5.29 (-1.10)	8.80 (-4.61)	4.19
Butane	14.99 (+40.33)	-13.13 (+12.21)	-25.34	-0.58 (+33.38)	-38.02 (-4.06)	-33.96	17.29 (+8.67)	24.90	8.62 (+16.28)	7.88 (-3.50)	10.95 (-6.57)	4.38
CH ₃ F	-4.19 (+13.94)	-24.20 (-6.07)	-18.13	0.06 (+17.25)	-29.33 (-12.14)	-17.19	-4.26 (-3.31)	5.13	-0.94 (+6.07)	-0.81 (+1.34)	2.98 (-2.45)	0.53
CH ₃ Cl	-5.17 (+17.98)	-26.82 (-3.66)	-23.16	0.06 (+20.86)	-28.63 (-7.83)	-20.80	-5.23 (-2.88)	1.81	-2.35 (+4.16)	-1.20 (+1.16)	1.64 (-1.68)	-0.04
CH ₃ Br	-6.10 (+19.43)	-28.27 (-2.74)	-25.53	0.04 (+22.11)	-24.51 (-2.43)	-22.07	-6.14 (-2.68)	-3.77	-3.46 (-0.31)	-1.57 (+1.08)	-0.61 (+0.12)	-0.49
C ₂ H ₂	-2.79 (+12.00)	-19.79 (-5.00)	-14.79	-0.40 (+14.32)	-17.68 (-2.95)	-14.73	-2.39 (-2.32)	-2.11	-0.07 (-2.04)	-0.05 (+0.93)	0.06 (+0.82)	0.88
C ₂ H ₄	3.86 (+19.20)	-17.46 (-2.13)	-15.34	0.00 (+20.63)	-28.26 (-7.63)	-20.63	7.30 (+2.01)	10.80	5.29 (+5.50)	3.85 (-0.81)	5.26 (-2.22)	3.04
Propene	6.78 (+34.99)	-17.85 (10.37)	-28.22	-0.37 (+32.04)	-35.48 (-3.06)	-32.42	7.15 (+2.95)	17.63	4.20 (+13.43)	3.79 (-1.19)	8.02 (-5.42)	2.60
H ₂	4.62 (+8.72)	-8.48 (-4.39)	-4.10	0.00 (+13.87)	-12.26 (+1.60)	-13.87	6.34 (-3.43)	3.78	9.77 (-5.99)	3.47 (+1.38)	2.43 (+2.42)	4.85
N ₂	4.48 (+14.78)	-11.98 (-1.67)	-10.31	0.00 (+20.50)	-15.29 (+5.21)	-20.51	6.20 (-4.00)	3.32	10.20 (-6.88)	3.41 (+1.61)	2.25 (+2.77)	5.02
CO	6.60 (+17.73)	-11.49 (-0.36)	-11.13	-0.01 (+20.40)	-17.15 (+3.25)	-20.40	6.61 (-2.66)	5.66	9.27 (-3.61)	3.57 (+1.08)	3.19 (+1.46)	4.65
N ₂ O	-1.59 (+19.58)	-20.09 (+1.08)	-21.17	-0.01 (+22.42)	-24.08 (-1.65)	-22.43	-1.58 (-2.84)	4.00	1.26 (+2.74)	0.27 (+1.15)	2.52 (-1.10)	1.42
PH ₃	-1.05 (+15.57)	-21.29 (-4.67)	-16.62	0.00 (+20.57)	-21.13 (-0.56)	-20.57	-1.05 (-5.00)	-0.17	3.95 (-4.12)	0.48 (+2.02)	0.84 (+1.66)	2.50
CH ₂ ClCl	-8.24 (+13.47)	-31.38 (-9.67)	-21.70	0.07 (+18.50)	-31.97 (-13.54)	-18.43	-8.31 (-5.04)	0.59	-3.27 (+3.86)	-2.44 (+2.03)	1.15 (-1.56)	-0.41
CHF ₃	-5.84 (+20.89)	-26.81 (-0.09)	-26.73	0.05 (+29.50)	-26.14 (+3.31)	-29.45	-5.89 (-8.61)	-0.67	2.72 (-3.39)	-1.47 (+3.47)	0.64 (+1.36)	2.00
CF ₃ Cl	0.97 (+14.38)	-21.95 (-8.54)	-13.41	0.05 (+22.76)	-23.62 (-0.92)	-22.71	0.91 (-8.38)	1.67	9.30 (-7.63)	1.27 (+3.39)	1.58 (+3.08)	4.66
CF ₂ Cl ₂	-0.01 (+14.55)	-25.72 (-11.15)	-14.56	0.08 (+21.92)	-28.40 (-6.55)	-21.85	-0.09 (-7.37)	2.68	7.29 (-4.61)	0.87 (+2.98)	1.99 (+1.86)	3.85
CF ₄	2.74 (+17.80)	-18.37 (-3.31)	-15.06	0.05 (+28.13)	-9.10 (+18.98)	-28.08	2.68 (-10.33)	-9.27	13.02 (-22.28)	1.99 (+4.17)	-2.83 (+8.99)	6.16
SF ₆	0.32 (+20.30)	-24.04 (-4.06)	-19.98	0.27 (+32.88)	-30.33 (+2.28)	-32.62	3.49 (-9.14)	6.29	12.63 (-6.34)	2.32 (+3.68)	3.45 (+2.55)	6.00
C ₂ F ₄	3.11 (+35.89)	-20.30 (12.48)	-32.78	0.14 (+40.95)	-28.50 (+12.31)	-40.81	2.97 (-5.06)	8.20	8.03 (+0.18)	2.11 (+2.04)	4.22 (-0.07)	4.15
C ₃ F ₆	4.93 (+25.15)	-22.66 (-2.44)	-20.22	-1.25 (+31.17)	-41.02 (-8.60)	-32.43	6.18 (-6.03)	18.36	12.21 (+6.16)	3.40 (+2.43)	8.32 (-2.49)	5.83
Isobutene	10.20 (+34.88)	-17.16 (+7.52)	-24.68	2.24 (+31.76)	-39.43 (-9.91)	-29.52	7.96 (+3.12)	22.27	4.84 (+17.43)	4.12 (-1.26)	9.89 (-7.03)	2.86
1-Butene	2.89 (+56.16)	-24.63 (28.64)	-53.27	-0.30 (+55.76)	-40.13 (+15.93)	-56.06	3.19 (+0.40)	15.49	2.79 (+12.70)	2.19 (-0.16)	7.16 (-5.13)	2.03
MAD	22.66	6.33		26.04	6.02		4.54	7.02		1.80	2.83	
Max. dev.	+56.16	+28.64		+55.76	+18.98		-10.33	-22.28		+4.17	+8.99

Figure 1. Comparison of experimental and theoretical (IGM and HSM) ΔG_{solv} , ΔH_{solv} , and $T\Delta S_{\text{solv}}$ values.

Figure 2. Contribution of ΔH_{solv} and $T\Delta S_{\text{solv}}$ to ΔG_{solv} for (A) hydrocarbons, (B) haloalkanes, and (C) small inorganic molecules. Under standard conditions (298.15 K, 1 atm). Experimental values (Ref.[45]) and IGM and HSM computational results are shown.

Figure 3. Relative temperature dependence of HLC for (A) alkanes, (B) haloalkanes, (C) C_2 -hydrocarbons, and (D) small inorganic molecules. Experimental values were taken from Ref.[47], and theoretical values were obtained using the IGM and HSM.

Enthalpic and Entropic Contributions to Gaseous Solubility