

MODELING APPROACHES TO HYDRATION PROPERTIES OF AQUEOUS NONELECTROLYTES AT ELEVATED TEMPERATURES AND PRESSURES

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Received December 16, 2007

Accepted February 18, 2008

Published online April 2, 2008

Dedicated to Professor William R. Smith on the occasion of his 65th birthday.

Thermodynamic models describing temperature and pressure evolution of Henry's law constant and related properties of hydration of aqueous nonelectrolyte solutes are reviewed. The included models cover a broad range spanning from simple van't Hoff-like equations used in environmental chemistry over the more elaborate empirical or semiempirical temperature correlations favored for engineering purposes to complete equations-of-state for hydration properties originating in the theory of near-critical phenomena and developed for modeling of hydrothermal systems. For aqueous organic solutes, the methods are often coupled with the group additivity approximation, leading to complex tools for predicting the properties of solutions containing organic species. The various models were subjected to tests documenting their expected range of applicability at elevated pressures (for acid gases) or at high temperatures (for hydrocarbons and oxygen-containing organic solutes). New developments in the field are discussed and some future needs are envisioned.

Keywords: Aqueous solutions; Henry's law constant; Hydration; Group contributions; Standard thermodynamic properties; Water chemistry; Thermodynamics.

Thermodynamic description of aqueous nonelectrolyte solutes is needed for modeling and/or process design in a variety of applications such as partitioning of chemicals into environmental compartments, cleanup of aqueous effluents by air stripping or by using high-temperature water as a medium for decomposition of hazardous organic waste, in petroleum exploration in sedimentary basins, for chemical speciation and phase equilibrium calculations in power-cycle chemistry and in natural or technological hydrothermal solutions. This array of applications is traditionally covered by several disciplines – environmental chemistry, chemical engineering, geochemistry –

which have developed their own modeling concepts, often without a reference to the achievements reached in the other fields. Major interest for environmental chemists is directed towards the Henry's law constant used in partitioning calculations, usually ignoring its variation with temperature and pressure¹ or describing it by simple thermodynamic integration²⁻⁵. In chemical engineering the property of interest is either the limiting activity coefficient or the Henry's law constant, modeled by semiempirical equations valid up to about 373 K and at saturation pressure^{6,7}, occasionally also at high temperatures⁸⁻¹⁰. The pressure dependence of thermodynamic properties is usually not considered in these models. Full equations-of-state (EOS) for standard thermodynamic properties are needed in hydrothermal and geochemical applications; the EOS approaches have been developed based on the analysis of near-critical phenomena^{11,12}, semiempirical extensions of the Born equation¹³⁻¹⁶ or the fluctuation solution theory¹⁷⁻¹⁹. The target property here is the standard chemical potential of the solute, leading directly to chemical and/or phase equilibrium predictions.

The range of applicability of various approaches reflects typical needs in the respective disciplines, neglecting less crucial factors contributing to the desired property. Obviously the EOS models are most versatile but, on the other hand, they include a number of adjustable parameters to be retrieved from experimental data. Thus the challenge of thermodynamic modeling is, ideally, to provide methods allowing for accurate predictions in a wide range of conditions without the necessity of extensive experimental efforts. Such models would find application in all mentioned disciplines, overriding the crude approximations that are currently often used far beyond their reasonable application limits. The purpose of this paper is threefold: (i) to provide readers with an overview of thermodynamic models for nonelectrolyte aqueous solutes, stressing their common features and theoretical reasoning for semiempirical extensions; (ii) to assess in quantitative terms the errors associated with application of various approaches to the predictions of thermodynamic properties at higher-than-ambient temperatures and pressures; (iii) to discuss the perspectives of thermodynamic modeling in aqueous chemistry.

We start with the necessary brief theoretical background and argue for the merits of representing thermodynamic properties of aqueous solutes in terms of a hydration process. This is followed by an overview of modeling approaches and their application in group contribution methods. To evaluate the errors of different models, representative tests are provided of predictions at high temperatures and pressures for aqueous inorganic gases, hydrocarbons and oxygen-containing organics compared with experimen-

tal data. Finally we discuss the promising approaches to accurate and accessible modeling of aqueous solutes in a wide range of state conditions.

THEORY

The property central to thermodynamic treatment of solutions is the solute standard⁺ chemical potential or standard partial molar Gibbs energy of formation, ΔG_f° . Standard chemical potentials are easily converted to the equilibrium constants of chemical reactions involving aqueous species and, in combination with vapor pressure and other pure solid or liquid data, to limiting activity coefficients, solubility, Henry's law constants and various other vapor-liquid or air-water partition coefficients. The values of ΔG_f° are composed of the Gibbs energy of formation of pure solute, ΔG_f^* , and the property change corresponding to transfer of a solute from the pure state to aqueous solution, which is the Gibbs energy of dissolution, ΔG_s° ,

$$\Delta G_f^\circ = \Delta G_f^* + \Delta G_s^\circ. \quad (1)$$

A special form of Eq. (1) is obtained when the state of pure solute is attributed to the ideal gas, leading to

$$\Delta G_f^\circ = \Delta G_f^{\text{ig}} + \Delta G_h^\circ \quad (2)$$

where ΔG_f^{ig} is the Gibbs energy of formation of a pure solute in the ideal gas standard state and ΔG_h° is the Gibbs energy of hydration. The path selected for determination of ΔG_f° depends mainly on the actual state of a pure solute at a given temperature and pressure, and on the availability of the data. While at near-ambient conditions the input data are known for many solid or liquid solutes as well as for the corresponding dissolution process, the combination of ideal gas and hydration properties is a better option at elevated temperatures, especially for gases and volatile solutes. The reason is that the process of hydration is invariant of (possible) phase transitions during the change of temperature or pressure. Combining Eqs (1) and (2) provides the link between the properties of dissolution and hydration

$$\Delta G_h^\circ = \Delta G_s^\circ + \Delta G_f^* - \Delta G_f^{\text{ig}} = \Delta G_s^\circ + \Delta G_r^* \quad (3)$$

+ Asymmetric standard state of unit activity in a hypothetical solution of unit concentration referenced to infinite dilution. The mole fraction concentration scale was adopted for numerical evaluations in this work.

where ΔG_f° is the residual Gibbs energy, assimilated to standard Gibbs energy of either vaporization or sublimation for liquid and solid solutes, respectively.

Typically three types of data result from the most common phase equilibrium measurements: limiting activity coefficients, solubility, or Henry's law constant. Thermodynamic relations linking these properties with the standard Gibbs energy of dissolution or hydration are obtained from appropriate phase equilibrium conditions²⁰. For the limiting activity coefficient γ^∞ of a liquid solute in the symmetric standard state convention⁺⁺,

$$\Delta G_s^\circ = RT \ln \gamma^\infty . \quad (4)$$

In the case of liquid or solid chemicals exhibiting low solubility in water and immiscibility in the non-aqueous phase, the Gibbs energy of dissolution is conveniently expressed by the relationship

$$\Delta G_s^\circ = RT \ln x_{\text{sat}} \gamma^{\text{H}} . \quad (5)$$

where x_{sat} is the solubility at saturation and γ^{H} is the solute activity coefficient in the asymmetric standard state, which is usually considered as unity. Henry's law constant k_{H} is related to the Gibbs energy of hydration by the equation

$$\Delta G_{\text{h}}^\circ = RT \ln (k_{\text{H}}/p^\circ) \quad (6)$$

where $p^\circ = 101325 \text{ Pa}$ is the ideal gas standard pressure. Equations (1)–(6) constitute the basis for mutual transformations of experimentally accessible data and properties desired for thermodynamic modeling¹². Finally it should be mentioned that a particular form of standard chemical potential is often used in geochemistry, called the apparent standard partial molar Gibbs energy of formation, $\Delta G_f^{\circ, \text{app}}$ and representing a difference between the standard chemical potential at the temperature and pressure of the system and that of constituents at some reference T_r, p_r

$$\Delta G_f^{\circ, \text{app}}(T, p) = \Delta G_f^\circ(T_r, p_r) + \left[G_f^\circ \right]_{T_r, p_r}^{T, p} . \quad (7)$$

++ Symmetric standard state of pure substance in liquid state (real or hypothetical) at temperature and pressure of the system.

This concept is applied with advantage in the calculation of equilibrium constants because the change in ΔG_f° attributed to constituent elements between T, p and T_r, p_r cancels out in any mass-balanced process¹⁵. Thus the properties of constituent elements need to be known only at T_r, p_r .

As we argue above, the Gibbs energy of hydration is the most appropriate quantity for expressing solute behavior in a wide range of temperatures and pressures due to its unambiguous standard state, which is the ideal gas. ΔG_h° can be subjected to usual thermodynamic derivations, leading to other hydration properties – enthalpy of hydration ΔH_h° , heat capacity of hydration $\Delta C_{p,h}^\circ$, and volume of hydration which is by virtue equal to the standard molar volume V°

$$\Delta H_h^\circ = -T^2 \left(\partial(\Delta G_h^\circ / T) / \partial T \right)_p \quad (8)$$

$$\Delta C_{p,h}^\circ = \left(\partial \Delta H_h^\circ / \partial T \right)_p = T \left(\partial^2 \Delta G_h^\circ / \partial T^2 \right)_p \quad (9)$$

$$\Delta V_h^\circ = V^\circ = \left(\partial G_h^\circ / \partial p \right)_T. \quad (10)$$

It follows from Eqs (8)–(10) that the data on derivative properties of hydration may be of significant importance in the description of temperature and pressure evolution of ΔG_h° . Indeed the development of currently the most general modeling approaches was guided by experimental data at elevated conditions including the critical region of water that resulted mainly from calorimetric and volumetric experiments performed over the last two decades or so. These models often start with the definition of Gibbs energy

$$\Delta G_h^\circ(T, p) = \Delta G_h^\circ(T_r, p_r) + \left[\Delta H_h^\circ \right]_{T_r, p_r}^{T, p} - \left[T \cdot \Delta S_h^\circ \right]_{T_r, p_r}^{T, p} \quad (11)$$

which, after some rearrangements, leads to the formula

$$\begin{aligned} \Delta G_h^\circ(T, p) = & \Delta G_h^\circ(T_r, p_r) + (T_r - T) \Delta S_h^\circ(T_r, p_r) + \\ & + \int_{T_r}^T \left[\Delta C_{p,h}^\circ \right]_{p_r} dT - T \int_{T_r}^T \left[\Delta C_{p,h}^\circ \right]_{p_r} d \ln T + \int_{p_r}^p \left[V^\circ \right]_T dp \end{aligned} \quad (12)$$

where $\Delta S_h^\circ(T_r, p_r) = \left(\Delta H_h^\circ(T_r, p_r) - \Delta G_h^\circ(T_r, p_r) \right) / T_r$ is the entropy of hydration at reference conditions.

Even with a good thermodynamic model, nonelectrolyte organic solutes with their tremendous variety are basically untreatable by the usual experiment–correlation process. Fortunately, it is well established at near-ambient conditions that the group additivity approach permits reasonably accurate predictions of standard thermodynamic properties of aqueous organic compounds. It has been shown that this approximation can be used with success also at the above standard conditions^{21–23}, which greatly enhances our ability of predictions. Under the assumption of group additivity, any thermodynamic function of hydration of an aqueous organic substance is determined as a sum of structural contributions. The basic equation takes the form

$$Y_h^o = Y_{SS} + \sum_{i=1}^N n_i Y_{h,i}^o + \delta Y_h^o \quad (13)$$

where N is the total number of pre-defined groups present in a given molecule, n_i is the number of occurrences of each specific group, and $Y_{h,i}^o$ stands for the property Y of the i -th group. Y_{SS} accounts for the intrinsic contribution to the Y property that is equal to the contribution of a material point and can be evaluated using only thermodynamic quantities of pure solvent^{24,25}. If each group is considered independent of its neighbors, the first two terms define the basic group contribution method. Typical basic groups are, e.g., CH_3 and CH_2 groups in hydrocarbon backbones. Structural and proximity effects induced by particular arrangement of basic groups in a given molecule are hidden in the last term, δY_h^o , which includes the sum of higher-order corrections to the basic group additivity approximation. Group contribution methods differ in the definition of basic groups and in that they may or may not include higher-order corrections^{5,21–23}.

REVIEW OF THERMODYNAMIC MODELS

A major part of experimental data related to standard chemical potential were obtained close to reference conditions of 298 K and 0.1 MPa. Modeling interpretation of these data is possible, at least for organic solutes, within the structural additivity assumption. A great number of methods has been developed to meet this task, their summary being beyond the scope of this work: the reader may consult recent reviews^{26,27} or specialized journals such as *QSAR & Combinatorial Science*. It is obvious from Eq. (12) that predictions of thermodynamic properties at T_r , p_r crucially affect the accuracy of predictions also at elevated temperatures – the model applied at

T_r, p_r is thus an inherent and important part of any model for hydration properties applied in a wide range of conditions. In this context we need to mention at least the ongoing extensive efforts of Plyasunov et al.²⁸⁻³⁰, leading to careful reviewing of experimental data on various solute classes and development of a group contribution method at reference conditions that became a basis for recent high-temperature modeling efforts^{23,31,32}.

Starting with reference data, a thermodynamic model valid in a broader range of conditions can be obtained by suggesting some functional form for $\Delta C_{p,h}^\circ$ and V° in Eq. (12). The simplest approximation is that $\Delta C_{p,h}^\circ = V^\circ = 0$, leading to the well-known van't Hoff equation

$$\begin{aligned}\Delta G_h^\circ(T) &= \Delta G_h^\circ(T_r, p_r) + (T_r - T)\Delta S_h^\circ(T_r, p_r) = \\ &= \Delta H_h^\circ(T_r) - T\left(\left(\Delta H_h^\circ(T_r) - \Delta G_h^\circ(T_r)\right) / T_r\right).\end{aligned}\quad (14)$$

Note that there is no pressure dependence in Eq. (14), allowing calculation of the hydration properties just close to the saturation line of water. Equation (14) is often used in environmental applications^{2,5}, usually in an empirical format expressed for the Henry's law constant, e.g.,

$$\ln(k_H / p^\circ) = \Delta G_h^\circ / RT = A + B / T \quad (15)$$

where the adjustable constants A, B can be related to $\Delta G_h^\circ(T_r, p_r)$ and $\Delta H_h^\circ(T_r, p_r)$. A better assumption is that $\Delta C_{p,h}^\circ(T) = \Delta C_{p,h}^\circ(T_r) = \text{const}$, $V^\circ = 0$, transforming Eq. (12) to

$$\begin{aligned}\Delta G_h^\circ(T) &= \Delta H_h^\circ(T_r) + (T - T_r)\Delta C_{p,h}^\circ(T_r) - \\ &- T\left(\left(\Delta H_h^\circ(T_r) - \Delta G_h^\circ(T_r)\right) / T_r + \ln(T / T_r)\Delta C_{p,h}^\circ(T_r)\right).\end{aligned}\quad (16)$$

Equation (15) is used, usually again in an empirical form via the Henry's law constant, in environmental or engineering correlations reaching to higher temperatures^{3,7}.

A physically realistic modeling of hydration properties at high temperatures and pressures requires more sophisticated assumptions about the heat capacity and volume of hydration. Major developments in this field occurred during the last two or three decades, starting with the landmark works of Helgeson et al.¹³⁻¹⁵ that were proposed originally for aqueous ions but extended also to nonelectrolyte solutes^{33,34} and have been used in many, mainly geochemical, applications. A few other promising thermodynamic models for nonelectrolytes have been proposed on the background

of various theoretical considerations^{10,17–19,35}. It should be emphasized that all these models are more or less empirical. However, the leading terms of the equations always arise from some theoretical considerations and these fundamental assumptions are a prerequisite for their success, determining the possible application range of the model.

One of the first theories that can be applied in the description of hydration properties is the scaled particle theory²⁴

$$\Delta G_h^o = G_{ca} + G_{in} + RT \ln(V^{ig}/V_w) \quad (17)$$

where the last expression on the right-hand side is the standard state term, representing the hydration of a point mass. V_w is molar volume of water solvent, V^{ig} is molar volume of the ideal gas, G_{ca} stands for the cavity-creation contribution and G_{in} is the contribution due to solute-solvent interaction. Expressions for G_{ca} and G_{in} are available from the theory. However, the equations include also properties that are generally unknown and have to be estimated on empirical grounds. Although its use in practical calculations is limited, the scaled particle theory remains an important source of inspiration in model developments.

The Born equation provides an access to hydration properties of aqueous ions

$$\Delta G_h^o = \omega \left(\frac{1}{\epsilon_w} - 1 \right) \quad (18)$$

where ω is parameter related to ion size and charge and ϵ_w is the dimensionless (relative) dielectric permittivity of water. Equation (18) has served as a background for establishing several semiempirical equations, namely the Helgeson-Kirkham-Flowers (HKF) model^{13–15}. HKF combines the Born equation with an empirical “non-solvation” contribution, reconciling the simple model of hydration with reality¹⁵. Extension of this model to nonelectrolytes was done by analogy, assuming ω as an additional adjustable parameter³³. The resulting equations for standard molar volume and heat capacity in the HKF framework are

$$V^o = a_1 + \frac{a_2}{\psi + p} + \left(a_3 + \frac{a_4}{\psi + p} \right) \frac{1}{T - \Theta} - \frac{\omega}{\epsilon_w^2} \left(\frac{\partial \epsilon_w}{\partial p} \right)_T \quad (19)$$

$$\left[C_p^o \right]_{p_r} = \left[\Delta C_{p,h}^o \right]_{p_r} + C_p^{ig} = c_1 + \frac{c_2}{(T - \Theta)^2} + \omega T \left(\frac{\partial}{\partial T} \frac{1}{\epsilon_w^2} \left(\frac{\partial \epsilon_w}{\partial T} \right) \right)_p \quad (20)$$

The symbols a_{1-4} and c_{1-2} stand for six adjustable parameters in the “non-solvation” part, ω is the only adjustable parameter in the “hydration” part of equations, $\Theta = 228$ K and $\Psi = 260$ MPa are general constants. Despite its success, this model is subject to some deficiencies that hamper its application for nonelectrolyte solutes. First, the leading term in equations at high temperatures (close to the critical region of water) is the relative permittivity of water and its derivatives, which was shown to be incorrect by the theory of near-critical phenomena³⁶. Second, the model includes 7 adjustable parameters that can rarely be obtained from experimental data with reasonable numerical stability³⁷. Instead, the method was suggested by the authors that allows for empirical estimation of all or some of these parameters from reference data^{33,34}.

Another approach to modeling of hydration properties is represented by a broad family of the so-called density models suggested originally for correlating ionization or association constants of weak electrolytes in aqueous solutions. An example here is the concept of the total equilibrium constant that was applied, e.g., in the international formulation for the ionization constant of pure water³⁸. Again the same type of equations can be extended by analogy also for the description of nonelectrolyte hydration, e.g.

$$\Delta G_h^o / RT = \sum_{j=0}^3 a_j T^{-j} + \ln \rho_w \sum_{j=0}^2 b_j T^{-j} \quad (21)$$

where ρ_w is water density and a_j, b_j are adjustable parameters. Derivations of Eq. (21) with respect to temperature and pressure (Eqs (8)–(10)) lead to derivative properties of hydration and allow for assimilating some of the parameters to the values of these properties at reference conditions. A large number of adjustable parameters remains the main problem of density models that are otherwise flexible and accurate¹².

Japas and Levelt-Sengers³⁹ investigated the asymptotic behavior of the Henry’s law constant near the critical point of water and derived the expression for the limiting temperature dependence of the Gibbs energy of hydration¹¹

$$\Delta G_h^o = RT \ln f_w + a + b(\rho_w - \rho_{c,w}) + \dots \quad (22)$$

where a and b can be related to the reference properties of hydration, f_w is water fugacity and $\rho_{c,w}$ its critical density. By adding an empirical function of temperature to represent behavior far from the critical region, a three-

parameter equation was obtained that was successful in correlation of the Henry's law constant of volatile solutes down to room temperature^{9,10} but failed for the description of derivative properties of hydration³⁷.

Recently, use was made of the fluctuation solution theory (FST) which relates the spatial integral of the standard state solvent-solute direct correlation function $C_{w,i}^{\circ}$ with a dimensionless parameter $A_{w,i}^{\circ}$, often called the modified Krichevskii parameter⁴⁰ (notation here is for i -th solute species, to be distinguished from the water solvent)

$$1 - C_{w,i}^{\circ} = \frac{V_i^{\circ}}{\kappa_w RT} A_{w,i}^{\circ} \quad (23)$$

Both the standard molar volume of solute and solvent compressibility diverge at the solvent critical point, but their ratio remains finite and relatively well behaved. In addition, $A_{w,i}^{\circ}$ after some rearrangement can be expressed in terms of a virial expansion valid for low solvent densities^{17,35}

$$A_{w,i}^{\circ} = \lim_{n_i \rightarrow 0} \left(\frac{\partial(pV/RT)}{\partial n_i} \right)_{T,V} = 1 + (2/M_w) \rho_w B_{w,i} + \dots \quad (24)$$

where $B_{w,i}$ is the second cross (water-solute) virial coefficient. An analogous procedure can be adopted for the pure solvent where the water-water direct correlation function is linked with the $A_{w,w}$ parameter and a similar virial series is obtained. By comparing the virial expansions for aqueous solute and for pure water one obtains the equation

$$A_{w,i}^{\circ} = 1 + d(A_{w,w} - 1) + \rho_w (2/M_w) (B_{w,i} - dB_{w,w}) + \dots \quad (25)$$

where the d parameter has been introduced as a scaling factor related to the difference between the "cavity-creating" volume of solute and that of water molecule. Equation (25) established a basis for several thermodynamic models describing the difference of the virial terms. The approach of Plyasunov et al.¹⁷ is explicit and requires the knowledge of $B_{w,i}$ and $B_{w,w}$ at the input, approximating the higher-order terms empirically. This way of anchoring the low-density limit of the model allows reduction of the number of adjustable parameters, but limits the use of the equation to volatile nonelectrolytes for which the data on cross virial coefficients are available or can be estimated and the virial expansion is quickly converging. The approaches of Sedlbauer, O'Connell and Wood¹⁸ (SOCW) and Akinfiev and Diamond¹⁹ do not include explicitly virial coefficients and can be applied

to all types of solutes at the cost of a higher number of adjustable parameters.

Of the FST models, SOCW EOS has found most applications in nonelectrolyte modeling so far. It is based on a volumetric formula inspired by generalized observations of O'Connell³⁵ from which the SOCW equation is¹⁸

$$V^o = RT\kappa_w + d(V_w - RT\kappa_w) + RT\kappa_w\rho_w(a + b(\exp[\vartheta\rho_w] - 1) + c\exp[\theta/T] + \delta(\exp[\lambda\rho_w] - 1)) \quad (26)$$

where V_w , ρ_w and κ_w are molar volume, density and isothermal compressibility of water, respectively, and the general coefficients valid for all solutes are $\vartheta = 0.005 \text{ m}^3/\text{kg}$, $\theta = 1500 \text{ K}$, $\lambda = -0.01 \text{ m}^3/\text{kg}$. Adjustable parameters are a , b , c and d , parameter δ is determined depending on the charge of a particle ($\delta = 0.35a$ for neutral molecules). Equation (26) is in fact modeling the hydration process by a series of perturbation effects due to insertion of an ideal gas molecule into water solvent ($RT\kappa_w$), growing it to a "water-like" molecule with the size adjusted to mimic the intrinsic volume of a solute ($d(V_w - RT\kappa_w)$), and then changing its potential field from solvent-solvent to solute-solvent interaction (the third term on the right-hand side of Eq. (26)). The Gibbs energy of hydration is expressed at any given temperature by

$$\Delta G_h^o = \int_{p^o}^p RT \ln p + \int_0^p V^o dp + \Delta G_h^{o \text{ cor}} \quad (27)$$

where p^o is the standard pressure of ideal gas. Correction term $\Delta G_h^{o \text{ cor}}$ applies at temperatures below critical temperature of water ($T_c = 647.126 \text{ K}$) and arises due to inadequacy of the volumetric equation (26) to describe accurately the pressure change of hydration Gibbs energy in both gas and liquid phases in a two-phase subcritical region. Appropriate derivations of ΔG_h^o lead to other thermodynamic properties of hydration (Eqs (8)–(10)), e.g., to the heat capacity of hydration

$$\begin{aligned} \Delta C_{p,h}^o &= -T(\partial^2 \Delta G_h^o / \partial T^2)_p = -T \int_0^p \left(\frac{\partial^2 V^o}{\partial T^2} \right) dp + \Delta G_h^{o \text{ cor}} = \\ &= -T \int_0^p \left(\frac{\partial^2 V^o}{\partial T^2} \right) dp + \frac{e(T - T_c)^2}{T - \Theta} \end{aligned} \quad (28)$$

where the last term represents the empirical correction factor obtained from derivation of $\Delta G_h^{o\text{ cor}}$ and includes one additional adjustable parameter e ($\Theta = 228$ K is a general constant). Full expressions of the SOCW EOS for various hydration properties can be found in the literature^{12,18,23,31}.

Apart from reference data, the group contribution approximation can be applied also on thermodynamic models describing the change of hydration properties with temperature and pressure. Parameters of the model are then assigned not to a particular solute but rather to a basic group or higher-order correction, in the same manner as in the group contribution schemes at T_r , p_r . This approach was undertaken by Amend and Helgeson²¹ with the HKF EOS, Yezdimer et al.²² with the SOCW EOS and the combined group/bond contribution method and Sedlbauer et al.^{23,31,32} using again the SOCW model with a more elaborate set of groups and including some higher-order corrections. Evaluation of model parameters for structural groups in the latter methods was based on simultaneous correlations of a large body of data on several properties of hydration. The objective function for this purpose is defined as

$$S = \sum_j \sum_i \left[(Y_i^{o\text{ cal},j} - Y_i^{o\text{ exp},j}) / \sigma Y_i^{o,j} \right]^2 \quad (29)$$

where $Y_i^{o\text{ exp},j}$ is the experimental value of a hydration property, $Y_i^{o\text{ cal},j}$ is calculated from the SOCW model, $\sigma Y_i^{o,j}$ is the estimated uncertainty of a given data point, summation with index i relates to the order of the data and summation with index j goes over all included properties (ΔG_h^o , ΔH_h^o , $\Delta C_{p,h}^o$, V^o). The databases of experimental results on hydration properties for organic nonelectrolytes that were used for parameter regressions include several thousands data points retrieved from original literature sources^{23,31,32}.

DISCUSSION AND CONCLUSIONS

The Henry's law constants of gaseous solutes are typically presented along the saturation line of the solvent because most data are actually obtained from gas solubility at saturation conditions. Several correlation models are used for this purpose in chemical engineering literature (e.g., refs⁸⁻¹⁰). A representative correlation of this type has been published recently for 14 gases in water by Fernandez-Prini et al.⁹, based on careful evaluation of major part of available gas solubility data. However, the calculations of hydration properties are often needed also at conditions far from saturation such as for solubility and vapor-liquid distribution of CH_4 , CO_2 and H_2S in aqueous systems modeling the geological sequestration of acid gases in

deep aquifers after their separation from natural gas. Pressures at such systems may easily reach up to 100 MPa and the calculated Henry's law constant must be corrected for pressure difference. This so-called Poynting correction is sometimes neglected, introducing a considerable error to the calculations. Using the full EOS approach avoids the problem, with the advantage of extending the data set for parameter determinations also by data on derivative properties of hydration via thermodynamic links (Eqs (8)–(10)) and simultaneous regression (Eq. (29)). The SOCW model was applied to this purpose for main constituents of natural gas (CH_4 , CO_2 , H_2S) up to the critical point of water and at pressures up to 100 MPa⁴¹, using the same set of solubility data as Fernandez-Prini et al.⁹ and adding the available experimental results for derivative properties of hydration in a wide range of conditions. The results in terms of ΔG_h° are displayed in Figs 1–3 for the saturation pressure and at 20 and 50 MPa isobars. The calculations at p_{sat} agree within experimental uncertainty with the correlation of Fernandez-Prini et al.⁹ while at high pressures there are significant differences of several kJ/mol and increasing with temperature. In terms of k_H this leads to relative error of about 30% between p_{sat} and 20 MPa and about 100% between p_{sat} and 50 MPa, the error being approximately the same at all temperatures

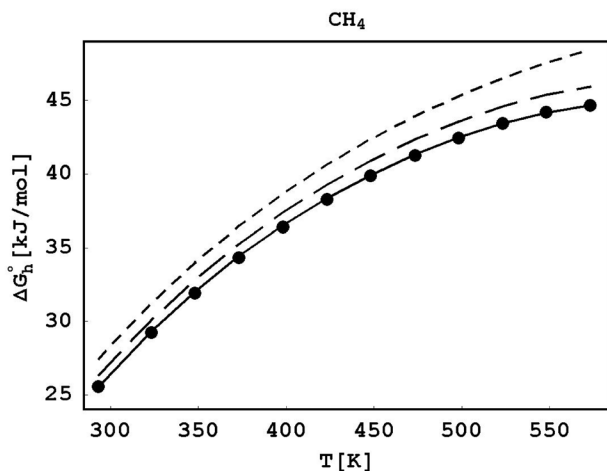


FIG. 1

Gibbs energy of hydration of aqueous CH_4 as a function of temperature at p_{sat} (solid line), 20 MPa (long-dash line) and 50 MPa (short-dash line). The lines were calculated using the SOCW EOS and parameters from Tables I and II. Points were generated at selected temperatures from the recommended correlation of the Henry's law constant valid at p_{sat} ⁹

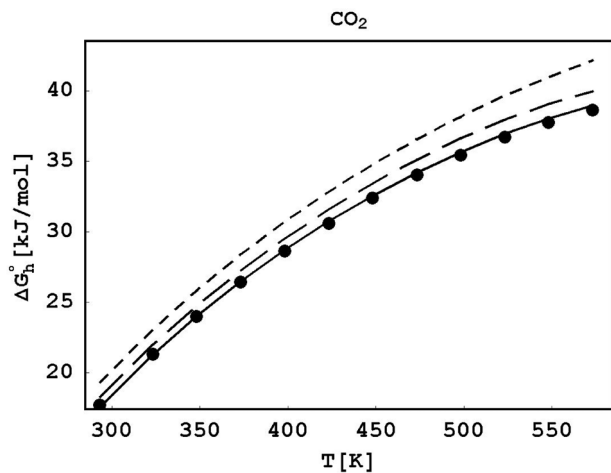


FIG. 2

Gibbs energy of hydration of aqueous CO_2 as a function of temperature at p_{sat} (solid line), 20 MPa (long-dash line) and 50 MPa (short-dash line). For details, see Fig. 1

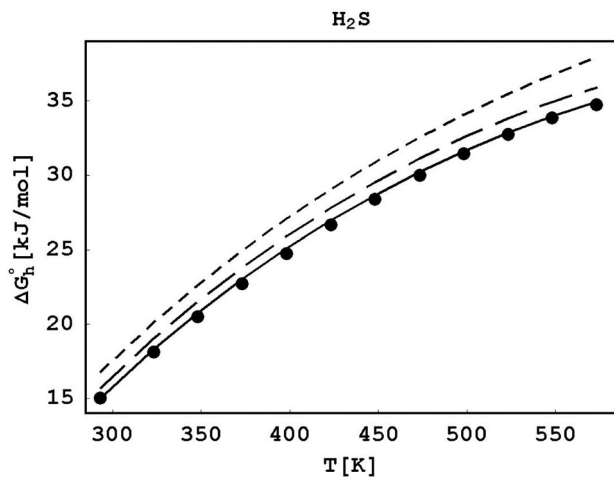


FIG. 3

Gibbs energy of hydration of aqueous H_2S as a function of temperature at p_{sat} (solid line), 20 MPa (long-dash line) and 50 MPa (short-dash line). For details, see Fig. 1

and for all tested solutes. For the difference between p_{sat} and the 100 MPa isobar (not shown in the figures), the relative difference in k_{H} reaches almost 300% for all tested gases. The EOS approach is clearly justified here, as it is in other applications dealing with solutes at higher pressures³⁷.

Gibbs energies of hydration of aqueous hydrocarbons and oxygen-containing organic solutes are shown as a function of temperature at p_{sat} in Figs 4 and 5, respectively. Various prediction methods are included in the graphics for testing. There are two graphs for each solute with different temperature ranges, 573 K in the left column and 473 K in the right one,

TABLE I
Values of $\Delta G_{\text{h}}^{\circ}(T_{\text{r}}, p_{\text{r}})$ and $\Delta H_{\text{h}}^{\circ}(T_{\text{r}}, p_{\text{r}})$ for selected groups²⁸⁻³¹ and gases³⁴

Group or solute	$\Delta G_{\text{h}}^{\circ}(T_{\text{r}}, p_{\text{r}})$, kJ mol ⁻¹	$\Delta H_{\text{h}}^{\circ}(T_{\text{r}}, p_{\text{r}})$, kJ mol ⁻¹
C	-4.50	2.6
CH	-1.79	-0.9
CH ₂	0.72	-3.76
CH ₃	3.63	-7.54
C=C	-10.23	0.6
H _{π} ^a	3.91	-3.7
c-CH ^b	-1.03	-2.4
c-CH ₂	0.83	-5.36
C _{ar} ^c	-3.85	-0.67
CH _{ar}	-0.65	-5.00
OH	-25.34	-40.47
CO	-22.68	-23.24
O	-15.40	-15.60
OH _{phi} ^d	-19.11	-27.51
Y _{SS} ^e	17.92	-2.29
CH ₄	26.25	-13.10
CO ₂	18.24	-20.40
H ₂ S	15.62	-18.35

^a Hydrogen atom bound to alkene group. ^b Prefix c- denotes a cycloalkane group. ^c A group with subscript ar is a part of aromatic ring. ^d A group with subscript phi is directly bound to aromatic ring. ^e Standard state term.

providing a window in which the tested methods are usually applied. The left column displays the results of the group contribution method using the SOCW EOS^{23,31,32}, calculations by the HKF EOS with parameters for single solutes from Shock and Helgeson⁴², and the HKF-based group contribution method by Amend and Helgeson²¹. Right column includes again the SOCW group contribution method; results of thermodynamic integration with Eq. (16) and reference data from the group contribution scheme of Plyasunov et al.²⁸⁻³⁰, a model using Eq. (15) with parameters for individual solutes from Staudinger and Roberts², and the group contribution method with Eq. (14) where $\Delta G_h^o(T_r, p_r)$ comes from Plyasunov et al.²⁸⁻³⁰ and $\Delta H_h^o(T_r, p_r)$ from Kühne et al.⁵. The methods were selected for testing

TABLE II
Parameters of the SOCW EOS for selected groups^{23,31,32} and gases⁴¹

Group or solute	$a \times 10^3$ m ³ /(kg mol)	$b \times 10^4$ m ³ /(kg mol)	$c \times 10^6$ m ³ /(kg mol)	d	$e \times 10$ J/(K ² mol)
C	-34.631	9.4034	-53.921	-7.3260	-13.792
CH	-6.5437	1.8156	-16.922	-0.9492	-3.9136
CH ₂	-0.0244	0.7216	-8.9576	0.3416	-1.8264
CH ₃	7.2778	-0.1571	-1.9499	1.4268	-0.0177
C=C	-10.299	-9.5352	-12.984	11.404	1.4871
H _π	2.8400	3.1911	9.2357	-3.1496	0.5847
c-CH	-16.986	4.8289	5.0487	-3.3563	-0.9028
c-CH ₂	3.0612	0.1108	-7.6472	0.7839	-1.2200
C _{ar}	-9.1549	2.2106	-21.346	-1.3723	-4.9993
CH _{ar}	0.6924	0.5168	-5.0903	0.3337	-1.0754
OH	5.5214	-0.4407	9.0281	0.9743	1.6262
CO	-12.020	2.6884	-13.796	-1.2068	-43.412
O	-9.7673	2.2722	2.8822	-1.5357	-10.024
OH _{phi}	10.949	-3.1873	15.067	3.2721	3.6873
CH ₄	3.9020	2.0984	-2.4163	0 ^a	-0.7465
CO ₂	3.1504	1.5963	-9.6580	0.40748	-1.9086
H ₂ S	1.3670	1.6967	-12.882	0.44352	-2.8164

For explanation of symbols, see Table I. ^a Not significant at the 95% confidence level.

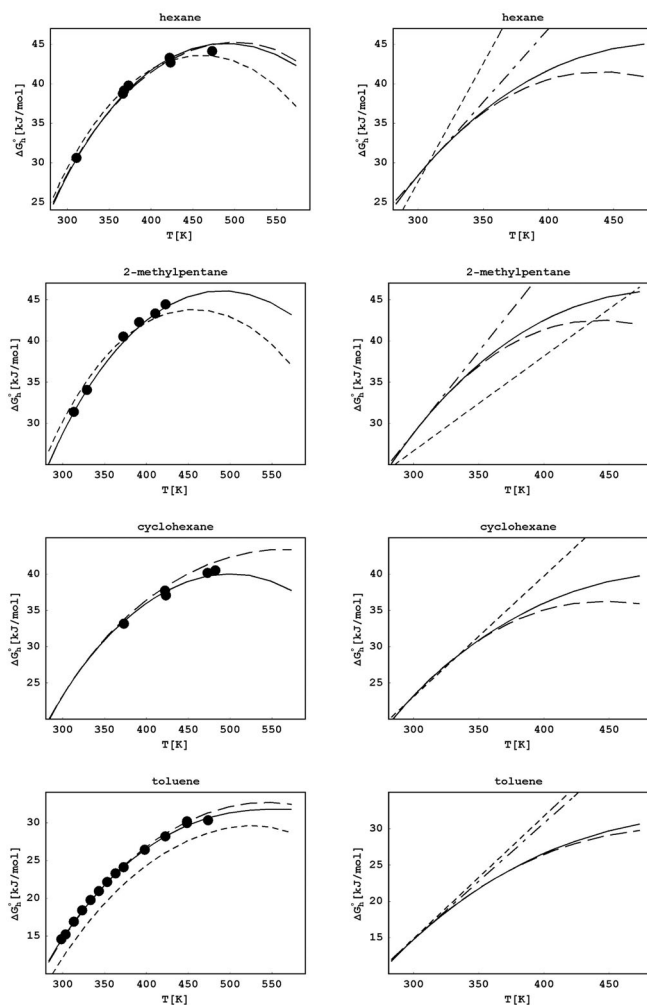


FIG. 4

Gibbs energy of hydration of aqueous hydrocarbons as a function of temperature at p_{sat} . Left column: group contribution SOCW EOS with parameters from Tables I and II (solid line); HKF EOS with parameters from Shock and Helgeson⁴² (long-dash line); group contribution HKF EOS with parameters from Amend and Helgeson²¹ (short-dash line); representative experimental data taken from literature^{43–45} (points). Right column: group contribution SOCW EOS with parameters from Tables I and II (solid line); group contribution method with Eq. (16) and reference data from Plyasunov and Shock²⁸ (long-dash line); Eq. (15) with parameters from Staudinger and Roberts² (short-dash line); group contribution method with Eq. (14), $\Delta G_h^0(T_r, p_r)$ from Plyasunov and Shock²⁸ and $\Delta H_h^0(T_r, p_r)$ from Kühne et al.⁵ (dashed-and-dot line)

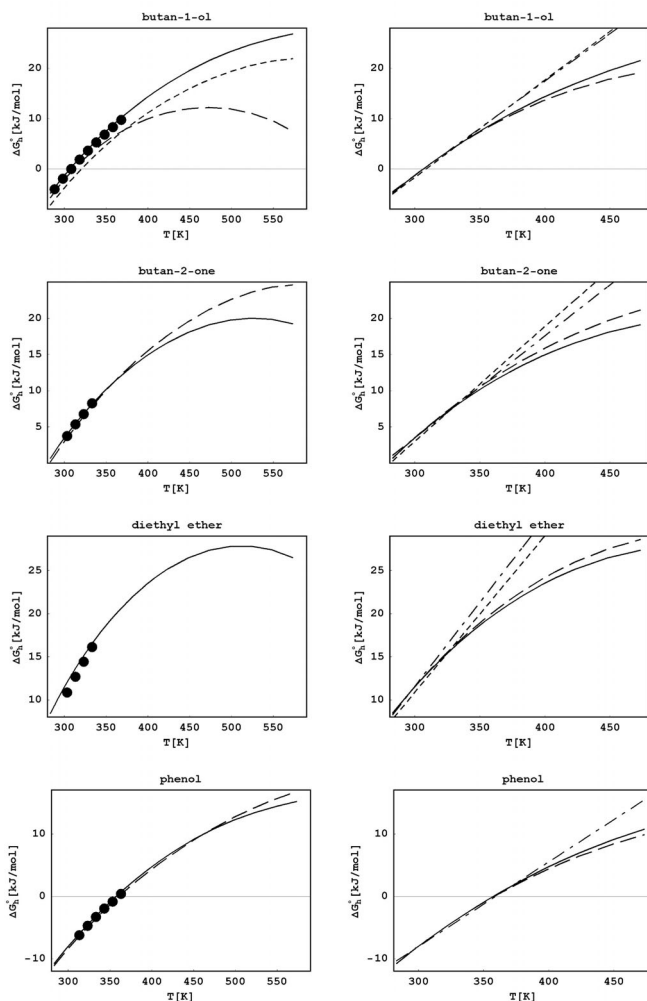


FIG. 5

Gibbs energy of hydration of aqueous oxygen-containing organics as a function of temperature at p_{sat} : Left column: group contribution SOCW EOS with parameters from Tables I and II (solid line); HKF EOS with parameters from Shock and Helgeson^{42,50} (long-dash line); group contribution HKF EOS with parameters from Amend and Helgeson²¹ (short-dash line); representative experimental data taken from literature^{7,46,47} (points). Right column: group contribution SOCW EOS with parameters from Tables I and II (solid line); group contribution method with Eq. (16) and reference data from Plyasunov et al.^{29,30} (long-dash line); Eq. (15) with parameters from Staudinger and Roberts² (short-dash line); group contribution method with Eq. (14), $\Delta G_{\text{h}}^{\circ}(T_{\text{r}}, p_{\text{r}})$ from Plyasunov et al.^{29,30} and $\Delta H_{\text{h}}^{\circ}(T_{\text{r}}, p_{\text{r}})$ from Kühne et al.⁵ (dashed-and-dot line)

based upon their broader significance so that mainly the group contribution schemes or substantial compilations of model parameters for individual species were included. Representative experimental data taken from literature are displayed in the left-column graphs, in the right-column figures this role of “experimental reference” is played by the results of the SOCW group contribution method which generally describes the data within their experimental uncertainty. Experimental results are only shown as a guidance, the sources were selected either for reaching to highest temperatures or for covering the largest temperature range. The data for hexane and cyclohexane were taken from Tsonopoulos and Wilson⁴³, methylpentane from Price⁴⁴, toluene from Chen and Wagner⁴⁵, for butan-1-ol the “pseudo data” were generated from the recommended correlation of Dohnal et al.⁷, butan-2-one and diethyl ether were obtained from Atik et al.⁴⁶, and data for phenol from Tabai et al.⁴⁷.

The results in Figs 4 and 5 underline the advantages of EOS-based approaches that provide physically realistic predictions of hydration properties to much higher temperatures (and also pressures) compared with methods based on reference data and applying simplified thermodynamic integration. Using Eq. (14) or (15) is fairly accurate at temperatures below 323 K, occasionally also at higher temperatures but then the disagreement may be larger at temperatures below 298 K, such as in the case of cyclohexane or phenol. Equation (16) at the cost of one additional parameter allows good predictions to temperatures below 373 K and still reasonable to some 410–430 K. Both equations do not provide estimation of pressure dependence. Correlations for individual solutes may suffer from an uncertain quality of model parameters such as in the case of the HKF model for butan-1-ol or the parameterization of Staudinger and Roberts for hexane and 2-methylpentane. Group contribution methods avoid this problem by averaging the results for many solutes in parameter regression so that misleading data for some compounds cannot disqualify the resulting description of structural groups. On the other hand, the group contribution assumption cannot itself ensure reliable predictions, very important is the design of the additivity scheme and mainly the careful treatment of experimental data used in determination of model parameters for groups at reference conditions as well as at high temperatures and pressures.

Thermodynamic models for hydration properties based on the EOS approach possess a strong application potential not only in the traditional fields of hydrothermal solutions and power-cycle chemistry, but also for the common engineering or environmental purposes. The reasons prevent-

ing these models so far from widespread utilization include data availability, method deficiency and tricky implementation:

i) A higher number of adjustable parameters in the EOS requires sufficient experimental data of good quality to be available for parameterization. Although the possibility of simultaneous regression with data on derivative properties is of considerable help, it is sometimes difficult to obtain statistically significant and physically reasonable parameters. Fortunately, in the case of aqueous organics, the group contribution approximation proved recently to be a viable tool at least up to 573 K and 100 MPa^{21,23}. Still a lot of work is ahead in compilation, recalculation and critical evaluation of experimental data from diverse literature sources as exemplified by the meticulous efforts of Plyasunov et al.²⁸⁻³⁰ or Dohnal et al.^{7,48}.

ii) The possibility of utilizing also derivative data for parameterization of EOS is of great advantage. However, it also puts a strain on a model: it has to be flexible and accurate not only at integral level (chemical potential or the Gibbs energy of hydration), but also for its derivatives. The models that are comparably precise in correlation of ΔG_h^0 may significantly differ in the quality of description, if parameterized mainly with derivative data. None of the existing EOS is able of describing the data for all experimental properties within their experimental uncertainties, namely if the experiments were of top quality and data reach to higher temperatures³⁷. However, in the application-oriented approach this is not much of a problem because the target property is always ΔG_h^0 . A more important model deficiency is associated with the group contribution schemes that more or less fail in the case of complex organic solutes with several polar functional groups at close separation where the structural and/or proximity effects become pronounced²⁷. More sophisticated methods that eliminate such effects are needed, most of all at reference conditions²⁷.

iii) Compared with engineering temperature-dependent correlations the hydration EOS are difficult for implementation not only due to long equations, but mainly because of the need for calculating the properties of pure solvent so that the user must have a fundamental equation-of-state for water. It is possible to overcome this trouble by providing a software tool implementing EOS for both solute and solvent as was done with considerable success in the case of the HKF model⁴⁹. On-line application with a Java-based calculator is in preparation also for the SOCW group contribution method.

This work was supported by the Grant Agency of the Czech Republic under contract No. 104/08/0758.

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