Group Contribution Method for Henry's Law Constant of Aqueous Hydrocarbons

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A functional group contribution scheme based on a hydration model predicts Henry's Law constant of aqueous hydrocarbons as a function of temperature and pressure. It uses the direct link of Henry's Law constant with the Gibbs free energy of hydration, as well as its temperature and pressure derivatives accessible from calorimetric and volumetric data. A semitheoretic model inspired by the fluctuation solution theory with five adjustable parameters was used for expressing the temperature and pressure dependence of ten functional contributions. A consistent group contribution scheme for hydration properties at 298 K and 0.1 MPa was taken from literature to constrain the model at reference conditions. Parameters for hydrocarbon functional groups were adjusted by simultaneous correlation of over 1,000 data points on Henry's Law constant and about 550 values on derivative hydration properties (enthalpy, heat capacity, and volume) available in a wide range of temperature and pressure. The resulting group additivity scheme can be used for predicting Henry's Law constant for alkanes, alkenes, alkylcycloalkanes, and alkylbenzenes up to 570 K and up to 100 MPa. Average accuracy of the predictions varies from 20 to 40% at ambient to high temperatures, respectively, and semiquantitative estimates are possible up to the critical point of water.

Introduction

Reliable knowledge of solubility and vapor-liquid partitioning of hydrocarbons in aqueous systems over a wide range of temperature and pressure is essential for conception of industrial operations, as much as for understanding environmental and geological processes. These include, among others, modification of petroleum composition by oil field waters in sedimentary basins, interaction between groundwaters and reservoir fluids, pollution of aquatic and atmospheric environment during storage, transport and treatment of petroleum and natural gas, depollution of petrochemical effluents by air stripping, and the use of high-temperature water as a medium for decomposition of hazardous organic waste. Importantly, many of these operations and processes occur at superambient conditions, thus creating a need for convenient estimation methods allowing to predict the required thermodynamic data. The property of high practical interest is Henry's Law constant (HLC) which is a direct measure of volatility of a given solute in a solution. This property expressed as a function of temperature and pressure is also useful for correlating or predicting solubility of a hydrocarbon in water provided that the fugacity of the coexisting organic phase can be calculated.

HLC is used in various contexts by physical chemists, chemical and environmental engineers, and geochemists. Each community developed its own terminology and approaches specific for the given field and a variety of HLC

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definitions can be found in literature. Unfortunately, the thermodynamic background is not always well understood and available information is sometimes confusing. This is particularly valid regarding the evolution of HLC with temperature and pressure where extrapolations using simple empirical schemes can lead to important systematic errors.

Experimental results allowing calculation of HLC at ambient conditions are available for many common hydrocarbons; much less information was published at superambient conditions and it is not always clear from literature how HLC was determined. In the case of aqueous organic compounds (and hydrocarbons particularly), it is useful to adopt a functional group additive scheme. The reason is obvious: while the number of these compounds is huge, they consist of just a few functional groups. In the chemical thermodynamics of dilute aqueous solutions, this principle has been utilized with success at the temperature of 298 K, and several methods are available that vary in the set of selected functional groups and in the type of thermodynamic property expressed.

Extension of estimation techniques to elevated temperatures faces more difficulty for two reasons. First, there is a lack of reliable experimental results for various solutes in a range of conditions, and second, there is a need of a good thermodynamic model for the description of temperature and pressure dependence of HLC. For aqueous hydrocarbons, little systematic experimental work was performed at superambient conditions with the exception of the major contribution from Tsonopoulos and collaborators (Tsonopoulos and Wilson, 1983; Heidman et al., 1985; Economou et al., 1997; Tsonopoulos, 1999, 2001). Attempts to correlate the data in a range of conditions remained mainly on empirical grounds. Only in the past decade or so, new approaches have appeared inspired by statistical thermodynamics and the theories of near critical dilute solutions that allowed to build high-temperature correlations on a more solid basis. Also, the high-temperature models developed by geochemists for predicting the standard molar properties of aqueous solutes can be adopted for calculation of HLC.

The purpose of this work was to establish a new group contribution scheme for aqueous hydrocarbons that would take into account all types of experimental results for these solutes available in literature. Use of a thermodynamic model related to fluctuation solution theory makes possible reliable calculation of HLC up to the temperature of 573 K and pressures to 100 MPa, and provides realistic predictions in the direction of the critical point of solvent. Practical use of the proposed method is facilitated by a user-friendly software tool presented elsewhere (Majer et al., 2003), which can be obtained free of charge on request provided it will serve for a noncommercial use.

A thermodynamic framework is set relating HLC to the basic thermodynamic functions and the different approaches used in literature for estimating this property are briefly reviewed. This is followed by a presentation of the group contribution scheme and thermodynamic model used for functional groups representation as a function of temperature and pressure. Next, the databases are described which are employed in correlation for establishing adjustable parameters of the model. Finally, the new predictions are discussed and tested against representative high-temperature and high-pressure data.

Thermodynamic Background

The Henry's Law constant K_H is defined as the limit of fugacity/concentration ratio of a solute in a solution (Prausnitz et al., 1999; Sandler, 1999) and has the dimension of pressure

$$K_H(T,p) = \lim_{x_s \to 0} \left(\frac{f_s}{x_s} \right) \tag{1}$$

where f_s is fugacity of the solute and x_s is its molar fraction. This one-phase definition of HLC can be rewritten in two simple relationships. When considering the standard state of ideal gas for the solute, it follows that

$$K_H(T,p) = p\varphi_s^\circ \tag{2}$$

where φ_s° is the fugacity coefficient of solute at infinite dilution, which can be calculated from an equation of state for a solution. Similarly, the introduction of the standard state of pure liquid leads to relationship

$$K_H(T,p) = f_s^\bullet \gamma_s^\infty \tag{3}$$

where $f_s^\bullet$ and γ_s^∞ stand for fugacity of pure liquid solute (real or hypothetical) and the limiting activity coefficient in symmetrical standard state convention, respectively. This latter parameter can be expressed from models characterizing nonideality of a solution in terms of molar excess properties.

HLC is also simply linked with the Gibbs free energy of hydration $\Delta G^\circ_{\text{hyd}}$ corresponding to the transfer of a solute from an ideal gas state at the reference pressure ($p_{\text{ref}} = 0.1$ MPa) to the standard state of infinitely dilute solution at pressure p. (The standard state adopted for aqueous species is unit activity in a hypothetical solution of unit molar fraction referenced to infinite dilution, denoted here with superscript o.) The relationship is obtained by writing relationships for the chemical potential of a solute using the standard state of infinite dilution and that of ideal gas and combining them with the definition of K_H (Eq. 1)

$$RT \ln \left(\frac{K_H(T,p)}{p_{\text{ref}}} \right) = G_s^\circ(T,p) - G_s^{ig}(T,p_{\text{ref}}) = \Delta G^\circ_{\text{hyd}} \tag{4}$$

This equation presents a straightforward connection of HLC to the rigorous system of thermodynamic state functions, and any physicochemical theory of hydration yielding $\Delta G^\circ_{\text{hyd}}$ also allows calculation of HLC. The temperature derivatives of Eq. 4 lead to the enthalpy and heat capacity of hydration

$$RT^2 \left(\frac{\partial \ln K_H}{\partial T} \right)_p = -\left[H_s^\circ(T,p) - H_s^{ig}(T) \right] = -\Delta H^\circ_{\text{hyd}} \tag{5}$$

$$\left(\frac{\partial}{\partial T} \left[RT^2 \frac{\partial \ln K_H}{\partial T} \right] \right)_p = -\left[C^\circ_{p,s}(T,p) - C^{ig}_{p,s}(T) \right] = -\Delta C^\circ_{p,\text{hyd}} \tag{6}$$

and the pressure derivative gives the standard volume of a solute

$$RT\left(\frac{\partial \ln K_H}{\partial p}\right)_T = V_s^\circ(T,p) \tag{7}$$

It follows from Eqs. 5 to 7 that the temperature and/or pressure evolution of HLC can be calculated by integration of derivative hydration properties that can be obtained from calorimetric and volumetric data. The integral of Eq. 7 between saturation pressure of solvent and pressure of the system is known as the Krichevskii-Kasarnovsky equation useful for calculating evolution of solubility with pressure.

Unlike $G_s^\circ(T,p)$, the standard derivative functions $H_s^\circ(T,p)$ and $V_s^\circ(T,p)$ are equal to the partial molar properties at infinite dilution and diverge at the critical point of solvent (Levelt-Sengers, 1991). For hydrophobic solutes, this divergence is generally positive so that the enthalpy of hydration of aqueous hydrocarbons is also positively divergent, and, consequently, the partial temperature derivative of HLC is increasingly negative as $T \to T_{c,w}$. $\Delta H_{\mathrm{hyd}}^\circ$ is most often obtained from the experimentally accessible enthalpies of dissolution and vaporization ($\Delta H_{\mathrm{hyd}}^\circ \approx \Delta H_{\mathrm{sol}} - \Delta H_{\mathrm{vap}}$). Since, at ambient conditions, enthalpy of dissolution of a nonelectrolyte in water is much smaller than the enthalpy of vaporization ($|\Delta H_{\mathrm{vap}}^\circ| > |\Delta H_{\mathrm{sol}}^\circ|$), the enthalpy of hydration is negative ($\Delta H_{\mathrm{hyd}}^\circ \approx -\Delta H_{\mathrm{vap}} < 0$) near room temperature and the temperature slope of HLC is positive. The opposite sign of $\Delta H_{\mathrm{hyd}}^\circ$ at ambient and near critical conditions implies existence of a maximum in HLC at a temperature where $\Delta H_{\mathrm{hyd}}^\circ = 0$, which is generally observed between 373 and 473 K. The pressure derivative of HLC is always positive, increasing strongly at $p \to p_{c,w}$. Using Eq. 2 as a starting point, Japas and Levelt-Sengers (1989) derived a two-parameter equation expressing exactly the evolution of HLC along the saturation line of solvent (w) near its critical point

$$T\ln\left[K_H(T)/f_w^{\mathrm{sat}}\right] = T_{c,w}\ln(p_{c,w}\varphi_{c,s}^\circ/f_{c,w}) + \left[(\partial p/\partial x_s)_{c,V,T}^\circ/\rho_{c,w}^2\right](\rho_w^{\mathrm{sat}} - \rho_{c,w}) \tag{8}$$

The partial derivative of pressure with respect to composition at state of infinite dilution is called the Krichevskii parameter. Its value reflecting interactions between solvent and solute is positive for volatile nonelectrolytes, and is well behaved near the critical point of solvent, which means that Eq. 8 reduces at the critical point to the first term with φ_s° being the only property of solute affecting HLC (Beutier and Renon, 1978). Since temperature and pressure derivatives of the solvent fugacity f_w are well behaved at the critical point, the temperature derivative of HLC along the saturation line of solvent will diverge negatively. According to power laws, the density difference $|\rho_w^{\mathrm{sat}} - \rho_{c,w}|$ is proportional to $|T_w^{\mathrm{sat}} - T_{c,w}|^\beta$ with the critical exponent having a universal value of 0.326 (Sengers and Levelt-Sengers, 1986). Thus, the divergence along the saturation line will be governed by exponent (1-β) and is weaker than that along the isothermal or isobaric path.

For aqueous hydrocarbons that are sparingly soluble in water at most conditions, it is possible to use data on mutual miscibility for obtaining HLC from the equivalence of fugacity of hydrocarbon in organic and aqueous phases

$$f_s^{\mathrm{org}}(T,p) = f_s^{\mathrm{aq}}(T,p) \cong K_H(T,p)x_s^{\mathrm{sol}} \tag{9}$$

Solubility of hydrocarbon in water x_s^{sol} is combined with the fugacity of hydrocarbon in the organic phase that can be solid, liquid, or gaseous. For hydrocarbons in a fluid state, satisfactory results can be obtained from a cubic equation of state (Economou and Tsonopoulos, 1997) with a classical mixing rule adjusted to at least one data point on solubility of water in the organic phase. For solid hydrocarbons or at conditions where water solubility in an organic phase can be neglected, HLC is calculated from the equation

$$K_H(T,p) \cong \frac{p_s^{\mathrm{sat}}\varphi_s^{\mathrm{sat}}\exp\left[V_s(p - p_s^{\mathrm{sat}})/RT\right]}{x_s^{\mathrm{sol}}} \tag{10}$$

where p_s^{sat}, φ_s^{sat}, and V_s are vapor pressure, fugacity coefficient, and molar volume of pure hydrocarbon, respectively. When pressure is low and close to the vapor pressure of solute, Eq. 10 reduces to a simple ratio $K_H = p_s^{\mathrm{sat}}/x_s^{\mathrm{sol}}$.

It should be also mentioned that the term Henry's law constant is often used by environmental engineers for denoting the air-water partition coefficient. This coefficient is defined as a limiting ratio of molar concentrations C_s in air and water and is related to HLC as follows

$$K_{\mathrm{aw}} = \lim_{C_s^{\mathrm{aq}} \to 0}\left(\frac{C_s^{\mathrm{air}}}{C_s^{\mathrm{aq}}}\right) \cong \frac{K_H\rho_w}{RTM_w} \tag{11}$$

The relation is valid exclusively for sparingly soluble compounds at near ambient conditions where air can be approximately described by an ideal gas equation of state and the density of a solution can be considered equal to that of pure solvent.

This outline of basic equations aimed at presenting HLC in a broader thermodynamic context going beyond its restrictive viewing as vapor-liquid partition coefficient along the saturation line of solvent.

Review of Prediction and Correlation Approaches

A number of empirical approaches to the estimation of HLC at 298 K and 0.1 MPa are available using group/bond contribution or structural parameters. Promising methods for correlation at superambient conditions are those making use of the above relationships for activity or fugacity coefficients or for the hydration properties that can be expressed from models for dilute aqueous solutions.

Estimation methods at near ambient conditions

Limiting activity coefficients are popular in engineering applications (Sandler, 1996) and lead directly to HLC after a combination with vapor pressures (Eq. 3). They can be calculated at near ambient conditions from well-established group contribution schemes such as UNIFAC or ASOG, which, however, fail in describing aqueous systems (Eckert and Sherman, 1996). The specific schemes for limiting activity coefficients of aqueous hydrocarbons are less frequent and use structural rather than group parameters (Tsonopoulos and Prausnitz, 1971; Medir and Giralt, 1982). Several linear correlations are available in the literature expressing directly HLC or its analogues such as K_{aw} in terms of group/bond contributions (Hine and Mookerjee, 1975; Meyland and Howard, 1991), solvatochromic parameters (Abraham et al., 1994; Sherman et al., 1996), and topological descriptors (Nirmalakhandan and Speece, 1988; Nirmalakhandan et al., 1997). For the latter two groups of techniques, the determination of parameters is tedious.

The compilation of hydration properties for aqueous organics expressed in terms of group contributions at 298 K and 0.1 MPa was established by Cabani et al. (1981) on the basis of extensive experimental work performed by solution chemists. These data, largely ignored by the engineering community, allow a straightforward calculation of HLC (Eq. 4). Plyasunov and Shock (2000a) published a comprehensive update of Cabani's work for hydrocarbons and alcohols presenting the most exhaustive overview of experimental values available, as well as new values of group contributions.

Correlation as a function of temperature and pressure

Since the HLC exhibits a maximum in temperature, any extrapolation from near ambient data by a polynomial-like equation can be a failure. For a correlation or prediction over a wide range of temperature and/or pressure, it is necessary to use relationships giving a realistic description of the derivative hydration properties (Eqs. 5 to 7). Several authors presented empirical equations for correlating HLC of gases in water along the saturation line of solvent respecting negative divergence of the temperature derivative of HLC at the critical point of solvent (see, for example, Krause and Benson (1989), Fernandez-Prini and Crovetto (1989), and Crovetto (1991)).

Harvey and Levelt-Sengers (1990) added an empirical term to Eq. 8, which allowed correlation of HLC down to room temperature. They have also shown (Harvey et al., 1991) that this relationship is not restricted to the solvent saturation line, but can be applied for correlating HLC and hydration properties as a function of temperature and pressure

$$T\ln\left[K_H(T,p)/f_w\right] = A + B(\rho_w - \rho_{c,w}) + CT\rho_w\exp\left[(273.15 - T)/50\right] \quad (12)$$

This simple three-parameter equation is not, however, flexible enough for allowing quantitative description of the standard derivative hydration properties using Eqs. 5 to 7 (Harvey, 1998; Sedlbauer and Majer, 2000). For engineering applications, Harvey (1996) proposed a simplified form of Eq. 12 for correlation along the saturation line of solvent, where calculation of water density is not necessary

$$T\ln\left[K_H(T)/p_w^{\mathrm{sat}}\right] = A + B(T - T_{c,w})^{0.355} + CT^{0.59}\exp(T_{c,w} - T) \quad (13)$$

The parameters were presented for several gases in water including light hydrocarbons. This equation was also used by Economou et al. (1997) and by Plyasunov and Shock (2000b) for correlation of HLC for aqueous hydrocarbons.

The approaches based on the link between HLC and the Gibbs free energy of hydration (Eq. 4) were explored first using the scale particle theory (Pierotti, 1976)

$$RT\ln\left(\frac{K_H(T,p)}{p_{\mathrm{ref}}}\right) = G_c + G_i + RT\ln\left(V^{\mathrm{ig}}/V_w\right) \quad (14)$$

In this relationship the three terms express the contribution for creating a cavity in the solvent, the interaction between solvent and solute and the standard term, respectively. Schulze and Prausnitz (1981) have expressed G_c and G_i as a function of molecular parameters and temperature for correlating HLC of gases in water.

Another way of expressing hydration properties is inspired by the fluctuation solution theory based on the work of O'Connell and collaborators (for example, O'Connell, 1971; O'Connell et al., 1996). The spatial integral of the infinite dilution solute-solvent correlation function $C^{\circ}_{s,w}$ can be related to the so-called modified Krichevskii parameter $A^{\circ}_{s,w}$ defined as the ratio of V°_s and the point mass volume

$$1 - C^{\circ}_{s,w} = A^{\circ}_{s,w} = \frac{V^{\circ}_s}{\kappa_w RT} = \lim_{n_s \to 0}\left(\frac{\partial p}{\partial n_s}\right)_{T,V}\frac{V}{RT} \quad (15)$$

where κ_w is the compressibility of water and n_s is the mole number of solute in the volume of solution V. This dimensionless parameter changes much less with density of solvent than the partial molar volume and is well behaved in the critical region of water. It can be used for expressing the fugacity coefficient of solute at infinite dilution (O'Connell et al., 1996) allowing to calculate HLC from Eq. 2. When rewriting the $A^{\circ}_{s,w}$ parameter in the form of a virial expansion in density, we get

$$A^{\circ}_{s,w} = \lim_{n_s \to 0}\left(\frac{\partial(pV/RT)}{\partial n_s}\right)_{T,V} = 1 + \left(\frac{2}{M_w}\right)\rho_w B_{s,w} + \ldots \quad (16)$$

where $B_{s,w}$ is the second cross virial coefficient. An analogous procedure can be adopted for pure water where solvent-solvent interactions are expressed in terms of a modulus $A_{w,w}$

$$A_{w,w} = 1 + \left(\frac{2}{M_w}\right)\rho_w B_{w,w} + \ldots \quad (17)$$

Subtracting Eq. 17 from 16 and introducing an empirical parameter d related to the ratio of cavity-creating sizes for solute and solvent leads to the relationship

$$A^{\circ}_{s,w} = dA_{w,w} + (1-d) + \rho_w\left(\frac{2}{M_w}\right)(B_{s,w} - dB_{w,w}) + \ldots \quad (18)$$

Several ways have been proposed how to express $A^{\circ}_{s,w}$ and to obtain subsequently hydration properties by integration. Plyasunov and collaborators (Plyasunov et al., 2000a,b; 2001) have added an empirical term to approximate the contribution of higher virial terms resulting in a relationship with three adjustable parameters. The necessity to know or to estimate the second cross virial coefficient is a complication namely for solutes of low volatility. Sedlbauer et al. (2000) have proposed a version of Eq. 18 where virial expansion is replaced by a sum of exponentials in T and ρ_w

$$A^{\circ}_{s,w} = dA_{w,w} + (1-d) + \rho_w\{a + b(\exp[\vartheta\rho_w]-1) + c\exp[\Theta/T] + \delta(\exp[\lambda\rho_w]-1)\} \quad (19)$$

where a, b, c, d are four adjustable parameters, $\delta = 0.35$a and υ, Θ and λ are generalized constants that were obtained earlier (Sedlbauer et al., 2000) from analysis of a large amount of data on various aqueous solutes. This relationship has a correct ideal gas limit for low densities and is analytically integrable to obtain properties on the Gibbs free energy level (see the Appendix). The particular functional form has been inspired by an older model of O'Connell et al. (1996). Although this development was originally made in connection with an application in geochemistry, we found this approach appealing also as a basis for prediction of HLC over a wide range of temperature and pressure.

New Group Contribution Model

The basic idea of our approach is to calculate HLC from a hydration model whose parameters are adjusted with the use of the Gibbs free energy data, resulting mainly from solubility measurements, and also with the use of data on the derivative properties obtained from calorimetric and volumetric measurements. The adopted model for expression of HLC as a function of temperature and pressure provides realistic behavior at near critical and low density conditions. Because prevailing amount of existing accurate experimental results is available at or near to ambient conditions, we considered it is also useful to constrain the model at the reference conditions $T_{\text{ref}} = 298.15$ K and $p_{\text{ref}} = 0.1$ MPa using representative recommendations of $\Delta G^{\circ}_{\text{hyd}}(T_{\text{ref}},\ p_{\text{ref}})$ that were taken from literature. For this purpose, we have selected the recent group contribution method by Plyasunov and Shock (2000a), which is based on a very thorough evaluation of all available data related to hydration of aqueous hydrocarbons at 298.15 K and 0.1 MPa.

A hydration property $\Delta Y^{\circ}_{\text{hyd}}(T,p)$ $(Y = G,H,S)$ can be expressed by a relationship

$$\Delta Y^{\circ}_{\text{hyd}}(T,p) = \Delta Y^{\circ}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}}) + \left[\Delta Y^{\circ}_{\text{hyd}}\right]^{T,p}_{T_{\text{ref}},p_{\text{ref}}} \quad (20)$$

where the second term corresponds to the change of hydration property between the reference state and T, p of interest. In the case of the Gibbs free energy of hydration Eq. 20 can be written as

$$\Delta G^{\circ}_{\text{hyd}}(T,p) = \Delta G^{\circ}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}}) + \left[\Delta H^{\circ}_{\text{hyd}}\right]^{T,p}_{T_{\text{ref}},p_{\text{ref}}} - \left[T\Delta S^{\circ}_{\text{hyd}}\right]^{T,p}_{T_{\text{ref}},p_{\text{ref}}} \quad (21)$$

which can be rearranged in the form

$$\Delta G^{\circ}_{\text{hyd}}(T,p) = \Delta G^{\circ}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}}) - (T - T_{\text{ref}})\Delta S^{\circ}_{\text{hyd}}[T_{\text{ref}},p_{\text{ref}}] + \int_{T_{\text{ref}}}^{T} \left(\Delta C^{\circ}_{p,\text{hyd}}\right)^{p_{\text{ref}}} dT - T\int_{T_{\text{ref}}}^{T} \left(\Delta C^{\circ}_{p,\text{hyd}}\right)^{p_{\text{ref}}} d\ln T + \int_{p_{\text{ref}}}^{p} \left(V^{\circ}_{s}\right)^{T} dp \quad (22)$$

where the superscripts p_{ref} and T indicate the constant variable at which the integration is performed. The two reference state terms are expressed from an independent scheme available in literature (lit) (Plyasunov and Shock, 2000a), while the sum of three integrals is obtained from our temperature dependent model (mod). Then one can simplify Eq. 22 to

$$\Delta G^{\circ}_{\text{hyd}}(T,p) = \Delta G^{\circ\,\text{lit}}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}}) - (T - T_{\text{ref}})\Delta S^{\circ\,\text{lit}}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}}) + \Delta G^{\circ\,\text{mod}}_{\text{hyd}}(T,p) - \left[\Delta G^{\circ\,\text{mod}}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}}) - (T - T_{ref})\Delta S^{\circ\,\text{mod}}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}})\right] \quad (23)$$

The entropy of hydration $\Delta S^{\circ\,\text{lit}}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}})$ is calculated simply as

$$\Delta S^{\circ\,\text{lit}}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}}) = \left[\Delta H^{\circ\,\text{lit}}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}}) - \Delta G^{\circ\,\text{lit}}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}})\right]/T_{\text{ref}} \quad (24)$$

from the group contributions tabulated for $\Delta G^{\circ\,\text{lit}}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}})$ and $\Delta H^{\circ\,\text{lit}}_{\text{hyd}}(T_{\text{ref}},p_{\text{ref}})$ by Plyasunov and Shock (2000a). Regarding the temperature-dependent model, $\Delta G^{\circ\,\text{mod}}_{\text{hyd}}$ and $\Delta S^{\circ\,\text{mod}}_{\text{hyd}}$ are obtained from equations

$$\Delta G^{\circ\,\text{mod}}_{\text{hyd}} = \int_{p_{\text{ref}}}^{0} RTd\ln p + \int_{0}^{p} V^{\circ}_{s}\,dp + \Delta G^{\circ\,\text{cor}}_{\text{hyd}} \quad (25)$$

$$\Delta S^{\circ\,\text{mod}}_{\text{hyd}} = \left(\frac{\partial \Delta G^{\circ\,\text{mod}}_{\text{hyd}}}{\partial T}\right)_{p} \quad (26)$$

where V°_{s} is expressed from Eq. 19. An empirical correction term $\Delta G^{\circ\,\text{cor}}_{\text{hyd}}$ with one adjustable parameter e is needed since the simple volumetric equation is not sufficient for describing quantitatively the thermodynamic hydration properties at subcritical conditions

$$-\left(\frac{\partial^2 \Delta G^{\circ\,\text{cor}}_{\text{hyd}}}{\partial T^2}\right)_{p} = \left(\frac{\partial \Delta S^{\circ\,\text{cor}}_{\text{hyd}}}{\partial T}\right)_{p} = \frac{\Delta C^{\circ\,\text{cor}}_{p,\text{hyd}}}{T} = \frac{e(T - T_c)^2}{T(T - \Phi)} \qquad T < T_c \quad (27)$$

where Φ is again a general constant. The contribution of the correction term is decreasing with increasing temperature and it vanishes at the critical temperature of solvent ($\Delta G^{\circ\,\mathrm{cor}}_{\mathrm{hyd}} = \Delta H^{\circ\,\mathrm{cor}}_{\mathrm{hyd}} = \Delta C^{\circ\,\mathrm{cor}}_{p,\mathrm{hyd}} = 0\ T \geq T_c$) thus providing integration constants for Eq. 27. Detailed expressions for thermodynamic functions of hydration are available in the Appendix.

An assumption of functional group additivity allows to determine any thermodynamic function of hydration of an aqueous organic molecule as a sum of structural contributions

$$\Delta Y^{\circ}_{\mathrm{hyd}} = Y_{\mathrm{SS}} + \sum_{i=1}^{N} n_i Y^{\circ}_{s,i} \qquad (28)$$

where N is the total number of functional groups present in a given compound, n_i is the number of occurrences of each specific functional group, and $Y^{\circ}_{s,i}$ stands for the Y property of the i-th group. Y_{SS} accounts for the intrinsic contribution to the Y property that is equal to the contribution of a point mass. This term is derived from theory (Ben-Naim, 1987) and can be evaluated using only thermodynamic functions of pure solvent.

There are two basic features crucial for success of any functional group contribution scheme operating over a range of conditions: a suitable selection of a set of functional groups and the quality of thermodynamic model, representing the evolution of $Y^{\circ}_{s,i}$ group properties with T and p. In the choice of appropriate functional groups one has to take into account several constraints. The first one is the validity of the assumption of structural additivity. The more complex is the set of selected groups, the better the resulting scheme can reflect effects of different structures and the method is the more accurate. The second constraint is that we are limited in the selection of functional groups by the amount of available experimental results, which may be used for model parameterization. This is often not compatible with the first requirement, because the use of aggregated groups increases the number of contributions and, hence, demands more data. The third constraint is the fact that, for calculating HLC as a function of temperature and pressure, we use also the values of $\Delta G^{\circ}_{\mathrm{hyd}}(T_{\mathrm{ref}},p_{\mathrm{ref}})$ and $\Delta H^{\circ}_{\mathrm{hyd}}(T_{\mathrm{ref}},p_{\mathrm{ref}})$ resulting from some previously established group contribution scheme taken over from literature. The reliability of predictions at reference conditions 298.15 K and 0.1 MPa is crucial since these values largely affect accuracy of results at superambient conditions, particularly through the term $\Delta S^{\circ}_{\mathrm{hyd}}(T_{\mathrm{ref}},p_{\mathrm{ref}})(T - T_{\mathrm{ref}})$ (Eq. 23). The complexity of a functional group selection applied for T, p dependent model should not be higher than that used at T_{ref} and p_{ref}, and the selection of group contributions in both schemes should be as close as possible. In our group contribution scheme we utilize the same set of functional groups as proposed by Cabani et al. (1981) and later re-evaluated for hydrocarbons at ambient conditions by Plyasunov and Shock (2000a): C, CH, CH_2 and CH_3 for alkanes, c-CH and c-CH_2 for cycloalkanes, CH_{ar} and C_{ar} for benzene and alkylbenzenes, C = C for alkenes, and H_π for a hydrogen atom attached to the double bond. The only correction for proximity effects in this first-order group contribution scheme is considered for *ortho*substituted dialkylbenzenes and *cis*-1,2-dialkylcycloalkanes. For these compounds, Plyasunov and Shock introduced a "pseudo-group" I(C-C), which we have not used in the T, p dependent model due to lack of data on relevant compounds. The functional group values at $T_{\mathrm{ref}} = 298.15$ K and at $p_{\mathrm{ref}} = 0.1$ MPa of Plyasunov and Shock (2000a) that were used in this study are summarized in Table 1, while the five parameters for each functional group in the T, p dependent model are given in Table 2. The database of hydration properties applied for adjusting parameters of the functional groups in the latter model and calculation procedure are described below.

Table 1. Group Contributions for Calculating $\Delta G^{\circ\,\mathrm{lit}}_{\mathrm{hyd}}$ (T_{ref}, p_{ref}) and $\Delta H^{\circ\,\mathrm{lit}}_{\mathrm{hyd}}$($T_{\mathrm{ref}}$, p_{ref})(Plyasunov and Shock, 2000a)

Functional Group	$\Delta G^{\circ\,\mathrm{lit}}_{\mathrm{hyd}}(T_{\mathrm{ref}}, p_{\mathrm{ref}})$ (kJ·mol^{-1})	$\Delta H^{\circ\,\mathrm{lit}}_{\mathrm{hyd}}(T_{\mathrm{ref}}, p_{\mathrm{ref}})$ (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*	3.91	−3.7
c-CH**	−1.03	−2.4
c-CH_2	0.83	−5.36
C_{ar}†	−3.85	−0.67
CH_{ar}	−0.65	−5.00
I(C − C)	−1.01	2.0
Y_{SS}‡	17.92	−2.29

*Hydrogen atom bound to alkene group.
**Prefix c-denotes a cycloalkane group.
†A group with subscript ar is a part of aromatic ring.
‡Standard state term.

Experimental Database

For determining parameters of the temperature dependent model, we have established a database consisting of HLC and

Table 2. Group Contributions for Calculating Parameters of the T, p Dependent Model

Functional Group	$a_i \times 10^3$ (m^3·kg^{-1}·mol)	$b_i \times 10^4$ (m^3·kg^{-1}·mol)	$c_i \times 10^6$ (m^3·kg^{-1}·mol)	d_i	$e_i \times 10$ (J·K^{-2}·mol^{-1})
C	−34.6310	9.4034	−53.9212	−7.3260	−13.7921
CH	−6.5437	1.8156	−16.9215	−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
$C = C$	−10.2988	−9.5352	−12.9835	11.4045	1.4871
H_π	2.8400	3.1911	9.2357	−3.1496	0.5847
c-CH	−16.9864	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	−21.3460	−1.3723	−4.9993
CH_{ar}	0.6924	0.5168	−5.0903	0.3337	−1.0754

Table 3. Database of Experimental Values

Compounds	Total No. of Exp. Values (No. of Compounds)			
	x_s^{sol}	$\Delta H_{\mathrm{hyd}}^{\circ}$	$C_{p,s}^{\circ}$	V_s°
Alkanes	295 (8)	63 (6)	1 (1)	5 (1)
Alkenes	291 (5)	6 (3)	3 (3)	—
Cycloalkanes	27 (3)	12 (2)	—	6 (1)
Alkylbenzenes	445 (7)	56 (6)	16 (2)	72 (6)
Alcohols	—	—	44 (16)	286 (22)
Total	1,058 (23)	137 (17)	64 (22)	369 (30)

related derivative properties (enthalpies and heat capacities of hydration and standard molar volumes (Eqs. 5 to 7)) for aqueous alkanes, alkenes, cycloalkanes, and alkylbenzenes. It has been found in test correlations that the amount of available data for aqueous hydrocarbons was not sufficient to allow parameterization of the quaternary carbon functional group (C), and also parameters for CH, C = C and H_{π} functional groups were subject to substantial numerical instability. To improve determination of these groups, we have included in the fit also the data on V_s° and $\Delta C_{p,\mathrm{hyd}}^{\circ}$ of aqueous alcohols that are available in literature as a function of temperature. The contribution for the alcoholic OH group was also evaluated, but is not presented in the context of this publication.

Included in the database were primary literature sources, and, in several cases, also recommended data from representative compilations in order to strengthen the presence of less common groups. The numbers of compounds and data points

Table 4. Database of Hydrocarbon Solubility in Water

Hydrocarbon	Temp. (K)	Pres. (MPa)	Solubility (Molar Fraction)	No. of Points	Ref.
			Alkanes		
Ethane	311−444	50	$1.07\times10^{-3} - 2.79\times10^{-3}$	5	Culberson and McKetta (1950)
	573	30−100	$2.0\times10^{-2}-2.5\times10^{-2}$	2	Danneil et al. (1967)
	273−573	*0.1−8.6*	–	*13*	Fernandez Prini and Crovetto (1989)
	344	50	1.3×10^{-3}	1	Dhima et al. (1998)
Propane	285−422	0.5−19.2	$8\times10^{-5}-6.9\times10^{-4}$	45	Kobayashi and Katz (1953)
	288−411	0.1−3.5	$1.2\times10^{-5}-3.1\times10^{-4}$	71	Azarnoosh and McKetta (1958)
	344	0.5−1.2	$5.5\times10^{-5}-1.2\times10^{-4}$	8	Wehe and McKetta (1961a)
Butane	311−511	50	$7.8\times10^{-5}-1.6\times10^{-3}$	7	Reamer et al. (1952)
	273−523	*0.1−3.4*	–	*11*	Carroll and Mather (1997)
	344	50	1.0×10^{-4}	1	Dhima et al. (1998)
Pentane	573	15−70	$3.3\times10^{-3}-4.3\times10^{-3}$	5	Connoly (1966)
	277−303	0.1	$10\times10^{-6}-1.1\times10^{-5}$	4	Nelson and De Ligny (1968)
	278−309	0.1	$3\times10^{-5} - 3\times10^{-5}$	3	Pierotti and Liabastre (1972)
	273	0.1	1.6×10^{-5}	1	Polak and Lu (1973)
	313−423	0.1−2.1	$10\times10^{-6}-7.4\times10^{-5}$	6	Price (1976)
	367−589	0.62−20.7	$2.3\times10^{-5}-5.1\times10^{-3}$	19	Gillespie and Wilson (1982)
	288−308	0.1	$1.0\times10^{-5}-1.1\times10^{-5}$	4	Jönsson et al. (1982)
	273—453	0.02−3.6	$1.0\times10^{-5}-1.9\times10^{-4}$	8	Jou and Mather (2000)
n-Hexane	277−328	0.1	$2.7\times10^{-6}-4.6\times10^{-6}$	5	Nelson and De Ligny (1968)
	273	0.1	3.4×10^{-6}	1	Polak and Lu (1973)
	293	0.1	3.1×10^{-6}	1	Busantseva et al. (1976)
	313−425	0.1−1.3	$2.1\times10^{-6}-2.2\times10^{-5}$	9	Price (1976)
	288−308	0.1	$2.1\times10^{-6}-2.2\times10^{-6}$	4	Jönsson et al. (1982)
	313−333	0.1	$1.5\times10^{-6}-1.7\times10^{-6}$	2	Bittrich et al. (1983)
	311−473	0.1−3.5	$2.4\times10^{-6}-1.9\times10^{-4}$	7	Tsonopoulos and Wilson (1983)
	573	20	3.8×10^{-3}	1	Brunner et al. (1993)
	373−464	0.4−3	$6.1\times10^{-6}-1.9\times10^{-4}$	5	Barrufet et al. (1996)
2-Methylpentane	573	15−70	2.7×10^{-3}	4	Connoly (1966)
	273	0.1	4.0×10^{-6}	1	Polak and Lu (1973)
	313−423	0.1−1.4	$2.9\times10^{-6}-2.4\times10^{-5}$	6	Price (1976)
n-Heptane	568	17−70	2.0×10^{-3}	4	Connoly (1966)
	561−583	24.8	$2\times10^{-3}-3.1\times10^{-3}$	4	O'Grady (1967)
	277−318	0.1	$3.5\times10^{-7}-4.3\times10^{-7}$	4	Nelson and De Ligny (1968)
	273-298	0.1	$7.9\times10^{-7}-6.1\times10^{-7}$	2	Polak and Lu (1973)
	293−313	0.1	$3.0\times10^{-6}-1.0\times10^{-5}$	2	Busantseva et al. (1976)
	313−424	0.1−0.9	$4.7\times10^{-7}—7.9\times10^{-6}$	6	Price (1976)
	288−308	0.1	$4.5\times10^{-7}-4.8\times10^{-7}$	4	Jönsson et al. (1982)
n-Octane	278−318	0.1	$2.6\times10^{-7}-3.9\times10^{-7}$	3	Nelson and De Ligny (1968)
	273	0.1	2.1×10^{-7}	1	Polak and Lu (1973)
	293	0.1	1.9×10^{-7}	1	Busantseva et al. (1976)
	298−423	0.1−0.7	$8.3\times10^{-8}-1.9\times10^{-6}$	6	Price (1976)
	288−308	0.1	$9.6\times10^{-8}-1.0\times10^{-7}$	4	Jönsson et al. (1982)
	293−343	0.1	$1.4\times10^{-7}-2.7\times10^{-7}$	3	Burris and MacIntyre (1985)
	311−553	0.1−8.9	$1.2\times10^{-7}-6\times10^{-4}$	6	Heidman et al. (1985)
	394−500	0.3−1.3	$3.0\times10^{-6}-2\times10^{-5}$	4	Rahman and Barrufet (1995)
	298−473	6.5	$1.4\times10^{-4}-3\times10^{-5}$	5	Miller and Hawthorne (2000)

included for individual properties for different classes of hydrocarbons and for alcohols are given in Table 3. A detailed listing of data sources with temperature and pressure intervals can be found in Tables 4–7.

Henry's Law constant

The data on HLC have been retrieved from phase equilibrium determinations in water-hydrocarbon systems as a function of temperature. We tried to avoid using HLC published in literature, since it is not usually clear how the values were obtained. As a rule, we have calculated HLC systematically from experimental data on solubility of a hydrocarbon in water and the fugacity of organic phase using Eq. 9. The values of x_s^{sol} are typically between 10^{-4} and 10^{-8} at near ambient conditions, but increase considerably with temperature. Also, deviations from the Henry's Law must be expected. The solubility data above 573 K were therefore omitted due to large uncertainties connected with conversion of solubility measurements to HLC. Since methodology of calculating $f_s^{\mathrm{org}}(T,p)$ was similar to that used by Plyasunov and Shock

Table 4. Database of Hydrocarbon Solubility in Water (Continued)

Hydrocarbon	Temp. (K)	Pres. (MPa)	Solubility (Molar Fraction)	No. of Points	Ref.
Decane	*298*	*0.1*	2.0×10^{-9}	*1*	Baker (1959)
	298	*0.1*	2.5×10^{-9}	*1*	Franks (1966)
	298	*0.1*	6.6×10^{-9}	*1*	Krasnoshchekova and Gubercrits (1973)
	298	*0.1*	1.1×10^{-9}	*2*	Mackay and Shiu (1975)
	298	*0.1*	$2.3 \times 10^{-8} - 1.6 \times 10^{-7}$	*1*	Becke and Quitzsch (1977)
	374–576	*0.1 – 11.2*	$5.1 \times 10^{-7} - 5.0 \times 10^{-5}$	*4*	Economou et al. (1997)
			Alkenes		
Ethene	308–379	0.8–53.1	$2.0\times10^{-4}-4.8\times10^{-3}$	53	Bradbury et al. (1952)
	297–346	0.10–0.13	$4.5\times10^{-5}-1.1\times10^{-4}$	14	Morrison and Billet (1952)
	311–394	0.1–3.7	$2.7\times10^{-5}-1.9\times10^{-3}$	46	Davis and McKetta (1960)
	311–411	3.4–34.4	$1.3\times10^{-3}-5.6\times10^{-3}$	35	Anthony and McKetta (1967)
	439–573	10–94.5	$4.0\times10^{-3}-4.9\times10^{-2}$	12	Sanchez and Lentz (1973)
Propene	311–411	1.6 – 33	$8.1\times10^{-4}-2.3\times10^{-3}$	34	Li and McKetta (1963)
	441–573	12.6–97	$2.9\times10^{-3}-3.3\times10^{-2}$	12	Sanchez and Lentz (1973)
	293–323	0.1	$5.7\times10^{-5}-1.2\times10^{-4}$	12	Serra et al. (1998)
1-Butene	311–411	0.4–41.4	$2.2\times10^{-4}-6.1\times10^{-4}$	6	
	311–428	0.4–69	$2.3\times10^{-4}-1.1\times10^{-3}$	52	Leland et al. (1955)
	311–378	0.4–2.1	$2.2\times10^{-4}-\ \ 4\times10^{-4}$	3	Wehe and McKetta (1961b)
1-Hexene	293	0.1	1.0×10^{-5}	1	Busantseva et al. (1976)
	311–494	0.2–24.8	$1.2\times10^{-5}-4.5\times10^{-3}$	5	Economou et al. (1997)
1-Octene	311–550	0.1–9.3	$5.0\times10^{-7}-9.8\times10^{-4}$	6	Economou et al. (1997)
			Alkylcyclohexanes		
Cyclohexane	563–573	13.9–19	5.9×10^{-3}	2	Rebert and Hayworth (1967)
	313–482	0.03–3.6	$1.5\times10^{-5}-4.9\times10^{-4}$	6	Tsonopoulos and Wilson (1983)
	274–323	0.1	$1.3\times10^{-5}-1.5\times10^{-5}$	8	de Hemptinne et al. (1998)
Methylcyclohexane	*313–422*	*0.1–0.7*	$3.3 \times 10^{-6} - 4.5 \times 10^{-5}$	6	Price (1976)
	299–444	*1.6*	$3.0 \times 10^{-6} - 7.1 \times 10^{-5}$	6	Jose (2001)
Ethylcyclohexane	311–553	0.1–8.8	$1.1\times10^{-6}-2.4\times10^{-3}$	*6*	Heidman et al. (1985)
Butylcyclohexane	366–550	0.1–7.1	$1.9\times10^{-7}-4.2\times10^{-4}$	5	Economou et al. (1997)
			Alkylbenzenes		
Benzene	278–314	0.1	$4.0-10^{-4}-4.6\times10^{-4}$	8	Bohon and Claussen (1951)
	273–342	0.1	$3.9\times10^{-4}-6.0\times10^{-4}$	23	Arnold et al. (1958)
	274–338	0.1	$4.1\times10^{-4}-5.9\times10^{-4}$	11	Alexander (1959b)
	298–336	0.1	$3.9\times10^{-4}-5.4\times10^{-4}$	15	Franks et al. (1963)
	377–477	6.9–34.5	$1.0\times10^{-3}-9.9\times10^{-3}$	8	Thompson and Snyder (1964)
	533–554	10–80	$162\times10^{-2}-3.7\times10^{-2}$	8	Connoly (1966)
	277–295	0.1	$3.9\times10^{-4}-4.1\times10^{-4}$	10	Leinonen (1972)
	298–328	0.1	$4.2\times10^{-4}-5.6\times10^{-4}$	2	Bradley et al. (1973)
	273	0.1	3.9×10^{-4}	1	Polak and Lu (1973)
	278–293	0.1	$4.1\times10^{-4}-4.2\times10^{-4}$	9	Brown and Wasik (1974)
	294	0.1	4.0×10^{-4}	1	Chey and Calder (1975)
	328–348	0.1	$9.2\times10^{-4}-1.5\times10^{-3}$	2	Price (1976)
	273–299	0.1	$4.0\times10^{-4}-4.2\times10^{-4}$	7	May (1977)
	283–293	0.1	$3.8\times10^{-4}-4.0\times10^{-4}$	2	Ben-Naim and Wiff (1979)
	288–318	0.1	$3.5\times10^{-4}-4.3\times10^{-4}$	5	Sanemasa et al. (1981)
	281–306	0.1	$3.9\times10^{-4}-4.4\times10^{-4}$	3	Dutta-Choudhury et al. (1982)
	278–318	0.1	$3.6\times10^{-4}-4.1\times10^{-4}$	4	Sanemasa et al. (1982)
	313–333	0.1	$5.0\times10^{-4}-6.9\times10^{-4}$	2	Bittrich et al. (1983)
	273–343	0.1	$4.0\times10^{-4}-5.9\times10^{-4}$	12	May et al. (1983)
	313–473	0.03–3.0	$4.4\times10^{-4}-5.4\times10^{-3}$	4	Tsonopoulos and Wilson (1983)
	374–477	0.3–3.2	$1.0\times10^{-3}-6.1\times10^{-3}$	8	Anderson and Prausnitz (1986)

Table 4. Database of Hydrocarbon Solubility in Water (Continued)

Hydrocarbon	Temp. (K)	Pres. (MPa)	Solubility (Molar Fraction)	No. of Points	Ref.
	293–323	0.1	$3.9\times10^{-4}-4.0\times10^{-4}$	4	Cooling et al. (1992)
	303–373	0.1–0.3	$4.2\times10^{-4}-9.5\times10^{-4}$	8	Chen and Wagner (1994)
	472–523	3.5–7.7	$5.0\times10^{-3}-1.5\times10^{-2}$	3	Stevenson et al. (1994)
	303–313	0.1	$4.3\times10^{-4}-4.8\times10^{-4}$	3	Zou et al. (1997)
	473–548	2.7–17.2	$5.7\times10^{-3}-2.6\times10^{-2}$	6	Chandler et al. (1998)
	279–323	0.1	$3.8\times10^{-4}-4.5\times10^{-4}$	6	de Hemptinne et al. (1998)
	323–473	6.5–40	$3.3\times10^{-4}-5.0\times10^{-3}$	7	Miller and Hawthorne (2000)
Toluene	303	0.1	1.1×10^{-4}	1	Gross and Saylor (1931)
	273–318	0.1	$1.2\times10^{-4}-1.4\times10^{-4}$	12	Bohan and Claussen (1951)
	553–573	15–60	$1.2\times10^{-2}-3.2\times10^{-2}$	7	Connoly (1966)
	278–318	0.1	$1.2\times10^{-4}-1.3\times10^{-4}$	5	Pierotti and Liabastre (1972)
	318–328	0.1	$1.4\times10^{-4}-1.7\times10^{-4}$	2	Bradley et al. (1973)
	293	0.1	1.4×10^{-4}	1	Polak and Lu (1973)
	279–293	0.1	$1.1\times10^{-4}-1.2\times10^{-4}$	8	Brown and Wasik (1974)
	294	0.1	9.4×10^{-5}	1	Chey and Calder (1975)
	283–293	0.1	$1.1\times10^{-4}-1.1\times10^{-4}$	2	Ben-Naim and Wiff (1979)
	283–303	0.1	$1.3\times10^{-4}-1.8\times10^{-4}$	7	Schwarz and Miller (1980)
	288–318	0.1	$1.0\times10^{-4}-1.2\times10^{-4}$	3	Sanemasa et al. (1981)
	283–306	0.1	$1.1\times10^{-4}-1.2\times10^{-4}$	2	Dutta-Choudhury et al. (1982)
	288–318	0.1	$1.0\times10^{-4}-1.1\times10^{-4}$	3	Sanemasa et al. (1982)
	313–333	0.1	$1.4\times10^{-4}-1.6\times10^{-4}$	2	Bittrich et al. (1983)
	372–473	0.16–2.4	$2.9\times10^{-4}-2.7\times10^{-3}$	6	Anderson and Prausnitz (1986)
	278–318	0.1	$1.3\times10^{-4}-1.4\times10^{-4}$	4	Smith et al. (1989)
	298	*0.1–200*	$1.09\times10^{-4}-1.28\times10^{-4}$	*5*	Sawamura et al. (1989)
	273–363	0.1	$1.6\times10^{-4}-2.5\times10^{-4}$	10	Stephenson (1992)
	303–373	0.1–0.3	$1.2\times10^{-4}-2.7\times10^{-4}$	8	Chen and Wagner (1994)
	294–473	0.1–5	$9.8\times10^{-5}-2.5\times10^{-3}$	8	Yang et al. (1997)
	473–548	2.5–17.2	$2.4\times10^{-3}-1.3\times10^{-2}$	5	Chandler et al. (1998)
	553–573	15.1 – 30.5	$1.4\times10^{-2}-2.7\times10^{-2}$	8	Haruki et al. (2000)
	298–473	5	$1.1\times10^{-4}-1.9\times10^{-3}$	5	Miller and Hawthorne (2000)
	273–323	*0.1–200*	$1.08\times10^{-4}-1.46\times10^{-4}$	*34*	Sawamura et al. (2001)
Ethylbenzene	273–316	0.1	$3.5\times10^{-5}-3.9\times10^{-5}$	9	Bohon and Claussen (1951)
	273	0.1	3.3×10^{-5}	1	Polak and Lu (1973)
	278–293	0.1	$3.0\times10^{-5}-3.3\times10^{-5}$	9	Brown and Wasik (1974)
	283–293	0.1	$3.4\times10^{-5}-3.6\times10^{-5}$	2	Ben-Naim and Wiff (1979)
	283–293	0.1	$3.0\times10^{-5}-3.1\times10^{-5}$	2	Schwarz and Miller (1980)
	283–318	0.1	$3.0\times10^{-5}-3.6\times10^{-5}$	5	Sanemasa et al. (1981)
	288–318	0.1	$2.7\times10^{-5}-3.3\times10^{-5}$	3	Sanemasa et al. (1982)
	311–553	0.1–8.6	$3.2\times10^{-5}-3.7\times10^{-3}$	6	Heidman et al. (1985)
	283–318	0.1	$3.0\times10^{-5}-3.6\times10^{-5}$	15	Owens et al. (1986)
	298	*0.1–150*	$2.9\times10^{-5}-3.6\times10^{-5}$	*6*	Sawamura et al. (1989)
	303–373	0.14–0.2	$2.9\times10^{-5}-8.5\times10^{-5}$	8	Chen and Wagner (1994)
	273–323	*0.1–150*	$2.6\times10^{-5}-3.6\times10^{-5}$	*25*	Sawamura et al. (2001)
m-Xylene	273–313	0.1	$3.3\times10^{-5}-3.7\times10^{-5}$	8	Bohon and Claussen (1951)
	344–540	0.15–6.8	$5.9\times10^{-5}-4.9\times10^{-3}$	7	Pryor and Jentoft (1961)
	273	0.1	3.3×10^{-5}	1	Polak and Lu (1973)
	293–343	0.1	$2.7\times10^{-5}-6.4\times10^{-5}$	3	Chernoglazova and Simulin (1976)
	288–318	0.1	$2.7\times10^{-5}-3.1\times10^{-5}$	3	Sanemasa et al. (1982)
	373–473	0.15–1.1	$1.4\times10^{-4}-9.7\times10^{-4}$	6	Anderson and Prausnitz (1986)
	298–473	6	$2.9\times10^{-5}-8.8\times10^{-4}$	5	Miller and Hawthorne (2000)
p-Xylene	273–316	0.1	$2.6\times10^{-5}-3.8\times10^{-5}$	11	Bohon and Claussen (1951)
	360–556	0.14–8.8	$7.8\times10^{-5}-7.6\times10^{-3}$	5	Pryor and Jentoft (1961)
	273	0.1	2.8×10^{-5}	1	Polak and Lu (1973)
	283–293	0.1	$3.2\times10^{-5}-3.2\times10^{-5}$	2	Ben-Naim and Wiff (1979)
	288–318	0.1	$2.7\times10^{-5}-3.0\times10^{-5}$	3	Sanemasa et al. (1982)
	303–373	0.14–0.2	$2.9\times10^{-5}-8.8\times10^{-5}$	8	Chen and Wagner (1994)
	298–422	0.14–50	$1.6\times10^{-5}-1.4\times10^{-4}$	18	Knauss and Copenhaver (1995)
Propylbenzene	*298*	*0.1–150*	$8.2\times10^{-6}-9.6\times10^{-6}$	*5*	Sawamura et al. (1989)
	273–323	*0.1–150*	$8.2\times10^{-6}-1.2\times10^{-5}$	*23*	Sawamura et al. (2001)
Butylbenzene	*280–318*	*0.1*	$1.7\times10^{-6}-2.5\times10^{-6}$	*11*	Owens et al. (1986)
	303–373	*0.14–0.2*	$2.2\times10^{-6}-1.1\times10^{-5}$	*8*	Chen and Wagner (1994)
m-Diethylbenzene	311–550	0.1–7.07	$4.3\times10^{-6}-3.0\times10^{-3}$	6	Economou et al. (1997)
p-diisopropylbenzene	311–550	0.1–7.5	$3.7\times10^{-7}-7.1\times10^{-4}$	6	Economou et al. (1997)
Hexylbenzene	*278–302*	*0.1*	$1.0\times10^{-7}-1.1\times10^{-7}$	*23*	May et al. (1983)
	280–318	*0.1*	$9.2\times10^{-8}-1.4\times10^{-7}$	*9*	Owens et al. (1986)

(2000b), as well as the data used, we give here only the most salient features of the procedure. The cubic equation of state of Strycek and Vera (1986) was used for 23 hydrocarbons included in the database with the binary interaction parameter k_s adjusted to representative vapor pressure data. The van der Waals mixing rule was applied with the parameter k_{sw} adjusted to the data on solubility of water in the organic phase. Recent measurements of solubilities of water in ethylbenzene at high temperature (Guillaume et al., 2001) completed the data listed by Plyasunov and Shock. Since no information is available for solubility of water in 2-methylpentane and *p*-xylene above 298 K, the data for water in hexane and *m*-xylene were used instead, respectively. The cubic equation of state reproduces the data on water solubility in organic phase within 10 to 20%, which is consistent with the typical scatter of experimental results. Once the parameters k_s and k_{sw} were determined, the fugacity was calculated at T, p corresponding to experimental points of hydrocarbon solubility in water for getting HLC. No data above the pressure of 100 MPa were included since the fugacity calculation by a cubic equation of state can fail at these extreme pressures. More detailed information on the procedure of calculating HLC can be found in the thesis by Bergin (2002).

The summary of calculated HLC is presented in Table 4. The bulk of the database consisted of 1,058 data points included in the regression calculations. These primary data were completed by six values of HLC for each of the three solutes (2,2-dimethylpropane, 2-methylpropene, 1,3-butadiene) calculated between 273 and 343 K from a correlation presented by Wilhelm et al. (1977). No primary data on solubilities as a function of temperature were found in literature for these three compounds, yet they contain groups that are otherwise underrepresented in the database. About 200 additional data points (printed in italics) were used as a testing set for assessment of predictive capabilities of the new group contribution scheme (see below).

Derivative properties

The derivative properties $\Delta H^\circ_{\rm hyd}$, $\Delta C^\circ_{p,\rm hyd}$ and V°_s are obtained from results of calorimetric and volumetric experiments with dilute aqueous solutions. The data for aqueous hydrocarbons are rare at near ambient conditions where their determination is complicated due to low solubility of hydrocarbons in water; they are, however, quite frequent for aqueous alcohols. Particularly, a limited amount of high temperature data is available due to measurements performed at the University of Delaware (Wood and collaborators) and at the Blaise Pascal University in Clermont-Ferrand, France (Majer and collaborators). The data on derivative properties extended in a few cases (hexane, cyclohexane, benzene and toluene) to 643 K and supercritical pressure of 30 MPa. The purpose of their inclusion was to guide correlation of HLC correctly in the direction of the critical point; however, no near critical experimental results were considered.

Most data on enthalpies of hydration (Table 5) at near ambient conditions were derived from articles by the groups of I. Wadsö at the University of Lund and S. J. Gill at the University of Colorado. They obtained $\Delta H^\circ_{\rm hyd}$ combining unique calorimetric data on dissolution of hydrocarbons in water with enthalpies of vaporization. The high-temperature values were determined from recent experimental data on $\Delta H_{\rm sol}$ and the residual enthalpies of pure hydrocarbons $\Delta H_{\rm res} = H_s^\bullet - H_s^{\rm ig}$ calculated using the corresponding state method of Lee and Kesler (1975) as described by Degrange (1998)

$$\Delta H^\circ_{\rm hyd} = \lim_{x_s \to 0} (\Delta H_{\rm sol}/x_s) + \Delta H_{\rm res}. \tag{29}$$

Table 5. Standard Molar Enthalpies of Hydration

Hydrocarbon	Temp. (K)	Pres. (MPa)	No. of Points	Ref.
Hydrocarbons				
Ethane	273–323	0.1	11	Naghibi et al. (1987)
	288–308	0.1	2	Dec and Gill (1985)
	288–308	0.1	2	Olofsson et al. (1984)
Propane	273–323	0.1	11	Naghibi et al. (1987)
	288–308	0.1	2	Dec and Gill (1985)
	288–308	0.1	2	Olofsson et al. (1984)
Butane	288–308	0.1	2	Dec and Gill (1985)
	288–308	0.1	2	Olofsson et al. (1984)
	273–318	0.1	9	Naghibi et al. (1987)
2-Methylpropane	288–308	0.1	2	Dec and Gill (1985)
	273–318	0.1	9	Naghibi et al. (1987)
2,2-Dimethylpropane	288–308	0.1	2	Dec and Gill (1985)
Hexane	288–308	0.1	2	Gill et al. (1976)
	573–643	20–30	5	Degrange (1998)
Ethene	288–308	0.1	2	Dec and Gill (1985)
1-Propene	288–308	0.1	2	Dec and Gill (1985)
1-Butene	288–308	0.1	2	Dec and Gill (1985)
Cyclopropane	288–308	0.1	2	Dec and Gill (1985)
Cyclohexane	288–308	0.1	4	Gill et al. (1976)
	573–643	10–30	6	Degrange (1998)
Benzene	288–308	0.1	5	Gill et al. (1975)
	573–643	10–30	12	Degrange (1998)
	523–623	10–30	5	Pardo (2000)
Toluene	288–308	0.1	4	Gill et al. (1976)
	573–643	10–30	8	Degrange (1998)
	523–623	10–30	4	Pardo (2000)
Ethylbenzene	523–623	10–30	5	Pardo (2000)
o-Xylene	523–623	10–30	5	Pardo (2000)
m-Xylene	523–623	10–30	4	Pardo (2000)
p-Xylene	523–623	10–30	4	Pardo (2000)

Values of partial molar volumes at infinite dilution V°_s (Table 6) obtained mainly from density measurements on vibrating tube densimeters are numerous and present over 20% of the database with the data both at near ambient and high-temperature conditions. Heat capacities of hydration were calculated as a difference between the experimental partial molar heat capacity at infinite dilution $C^\circ_{p,s}$ and the heat capacity of an ideal gas $C^{\rm ig}_{p,s}$ estimated from the group contribution method of Joback, as presented in the monograph of Reid et al. (1988). Most data for $C^\circ_{p,s}$ resulted from flow calorimetric experiments on the Picker-type flow calorimeters performed at near ambient conditions and for three compounds also at elevated temperatures (Table 7). For both V°_s and $C^\circ_{p,s}$, we have mainly included primary data sources listing measurements at several temperatures. Multiple sources presenting the data at 298.15 K only were avoided with an exception of four compounds for volumes and 12 compounds for heat capacities where we also included values from representative compilations by Hoiland (1986) and Cabani et al. (1981). These secondary data were used for com-

Table 6. Standard Molar Volumes

	Temp. (K)	Pres. (MPa)	No. of Points	Reference
Hydrocarbons				
Hexane	373−643	20−30	5	Degrange (1998)
Cyclohexane	373−643	10−30	6	Degrange (1998)
Benzene	278−318	0.1	5	Sakurai (1990)
	278−353	0.6	5	Makhatadze and Privalov (1988)
	373−643	10−30	16	Degrange (1998)
	523−623	10−30	4	Pardo (2000)
Toluene	278−318	0.1	5	Sakurai (1990)
	278−353	0.6	5	Makhatadze and Privalov (1988)
	373−643	10−30	7	Degrange (1998)
	523−623	10−30	4	Pardo (2000)
Ethylbenzene	278−318	0.1	5	Sakurai (1990)
	523−623	10−30	5	Pardo (2000)
o-Xylene	523−623	10−30	4	Pardo (2000)
m-Xylene	523−623	10−30	3	Pardo (2000)
p-Xylene	523−623	10−30	4	Pardo (2000)
Alcohols				
Methanol	273−333	0.1	6	Alexander (1959a)
	278−318	0.1	3	Nakajima et al. (1975)
	278−348	0.1	4	Makhatadze et al. (1990)
	278−318	0.1	5	Sakurai et al. (1994)
	323−573	0.1−13.5	14	Xiao et al. (1997)
Ethanol	273−333	0.1	6	Alexander (1959a)
	274−323	0.1	4	Makhatadze and Privalov (1989)
	278−318	0.1	3	Nakajima et al. (1975)
	278−318	0.1	5	Sakurai et al. (1994)
1-Propanol	273−333	0.1	6	Alexander (1959a)
	274−323	0.1	4	Makhatadze and Privalov (1989)
	278−318	0.1	3	Nakajima et al. (1975)
	278−318	0.1	5	Sakurai et al. (1994)
	278−313	0.1	4	Hoiland (1980)
	298−523	28	8	Criss and Wood (1996)
2-Propanol	278−318	0.1	5	Sakurai et al. (1994)
	278−318	0.1	5	Sakurai (1988)
	278−313	0.1	4	Hoiland (1980)
	283−298	0.1	2	Roux et al. (1980)
	301−523	0.1−28	7	Schulte et al. (1999)
1-Butanol	273−333	0.1	4	Alexander (1959a)
	274−323	0.1	4	Makhatadze and Privalov (1989)
	278−318	0.1	3	Nakajima et al. (1975)
	278−318	0.1	5	Sakurai et al. (1994)
	278−313	0.1	4	Hoiland (1980)
	274	0.1	1	Franks and Smith (1968)
2-Butanol	278−318	0.1	5	Sakurai et al. (1994)
	278−313	0.1	4	Hoiland (1980)
	274.15	0.1	1	Franks and Smith (1968)
2-Methyl-1-Propanol	278−318	0.1	5	Sakurai et al. (1994)
	298	0.1	1	Hoiland (1986)
2-Methyl-2-Propanol	278−318	0.1	8	Sakurai et al. (1994)
	278−318	0.1	7	Sakurai (1987)
	274	0.1	1	Franks and Smith (1968)
	298	0.1	1	Hoiland (1986)
1-Pentanol	273−333	0.1	4	Alexander (1959a)
	274−323	0.1	4	Makhatadze and Privalov (1989)
	278−318	0.1	3	Nakajima et al. (1975)
	278−318	0.1	5	Sakurai et al. (1994)
	278−313	0.1	4	Hoiland (1980)
	298−413	19	8	Inglese and Wood (1996)
2,2-Dimethyl-1-propanol	283	0.1	1	Roux et al. (1980)
2-Methyl-2-Butanol	278−318	0.1	5	Sakurai et al. (1994)
	278−318	0.1	5	Sakurai (1989)
	298	0.1	1	Cabani et al. (1981)
	283−298	0.1	2	Roux et al. (1980)
1-Hexanol	278−318	0.1	5	Sakurai et al. (1994)
	278−313	0.1	4	Hoiland (1980)
2-Pentanol	278−313	0.1	4	Hoiland (1980)
2-Hexanol	278−313	0.1	4	Hoiland (1980)
1,3-Propanediol	278−318	0.1	3	Nakajima et al. (1975)

Table 6. Standard Molar Volumes (Continued)

	Temp. (K)	Pres. (MPa)	No. of Points	Reference
	278–313	0.1	4	Hoiland (1980)
1,3-Butanediol	273–333	0.1	4	Alexander (1959a)
1,4-Butanediol	278–318	0.1	3	Nakajima et al. (1975)
	278–313	0.1	4	Hoiland (1980)
	298–523	28	8	Criss and Wood (1996)
1,5-Pentanediol	278–318	0.1	3	Nakajima et al. (1975)
	301–523	0.1–28	7	Schulte et al. (1999)
1,6-Hexanediol	278–318	0.1	3	Nakajima et al. (1975)
	278–313	0.1	4	Hoiland (1980)
	298–523	28	8	Criss and Wood (1996)
1,7-Heptanediol	278–313	0.1	4	Hoiland (1980)
2-Propen-1-ol	298	0.1	1	Cabani et al. (1981)
Cyclohexanol	301–523	0.1–28	7	Schulte et al. (1999)
Benzyl alcohol	301–523	0.1–28	7	Schulte et al. (1999)

pounds including group contributions that are only scarcely present in the data set, namely the quaternary and ternary carbon functional groups and the unsaturated bond, in order to improve representation of these functional groups in the correlation.

Results and Discussion

The model equations from the Appendix can be used if all of the five adjustable parameters *a*, *b*, *c*, *d*, and *e* are known for a given solute. Because the model linearly depends on adjustable parameters, the group contribution scheme is applied most easily by calculating each parameter as a sum of parameters for functional groups present in the solute of interest, such as

$$a = \sum_{i=1}^{N} n_i a_i \qquad \text{and so on} \qquad (30)$$

where a_i is the parameter for *i*-th functional group. The point mass (standard state) contribution to a given property (Eq. 28) is already included in the equations in the Appendix. Parameters of the functional groups were obtained by simultaneous correlation of data on hydration properties of aqueous hydrocarbons and alcohols obtained as described above. For the sake of consistency, the most abundant data on HLC were converted before correlation to $\Delta G^{\circ}_{\mathrm{hyd}}$ using Eq. 4. The ob-

Table 7. Standard Molar Heat Capacities

	Temp. (K)	Pres. (MPa)	No. of Points	Reference
		Hydrocarbons		
2,2-Dimethylpropane	298	0.1	1	Cabani et al. (1981)
Ethene	298	0.1	1	Cabani et al. (1981)
1-Propene	298	0.1	1	Cabani et al. (1981)
2-Methyl-1-propane	298	0.1	1	Cabani et al. (1981)
Benzene	278–413	0.6	8	Makhatadze and Privalov (1988)
Toluene	278–413	0.6	8	Makhatadze and Privalov (1988)
		Alcohols		
Methanol	278–348	0.1	4	Makhatadze and Privalov (1990)
Ethanol	278–348	0.1	4	Makhatadze and Privalov (1989)
1-Propanol	278–348	0.1	4	Makhatadze and Privalov (1989)
	303–523	28	3	Inglese and Wood (1996)
2-Propanol	283–298	0.1	2	Roux et al. (1980)
1-Butanol	278–348	0.1	4	Makhatadze and Privalov (1989)
2-Methyl-1-Propanol	298	0.1	1	Cabani et al. (1981)
2-Methyl-2-Propanol	298	0.1	1	Cabani et al. (1981)
1-Pentanol	278–348	0.1	4	Makhatadze and Privalov (1989)
2-Methyl-2-Butanol	298	0.1	1	Cabani et al. (1981)
	283–298	0.1	2	Roux et al. (1980)
2,2-Dimethyl-1-Propanol	298	0.1	1	Cabani et al. (1981)
	283	0.1	1	Roux et al. (1980)
1,4-Butanediol	303–523	28	4	Inglese and Wood (1996)
1,6-Hexanediol	303–523	28	4	Inglese and Wood (1996)
2-Propene-1-ol	298	0.1	1	Cabani et al. (1981)
2-Butene-1-ol	298	0.1	1	Cabani et al. (1981)
3-Butene-1-ol	298	0.1	1	Cabani et al. (1981)
4-Pentene-1-ol	298	0.1	1	Cabani et al. (1981)

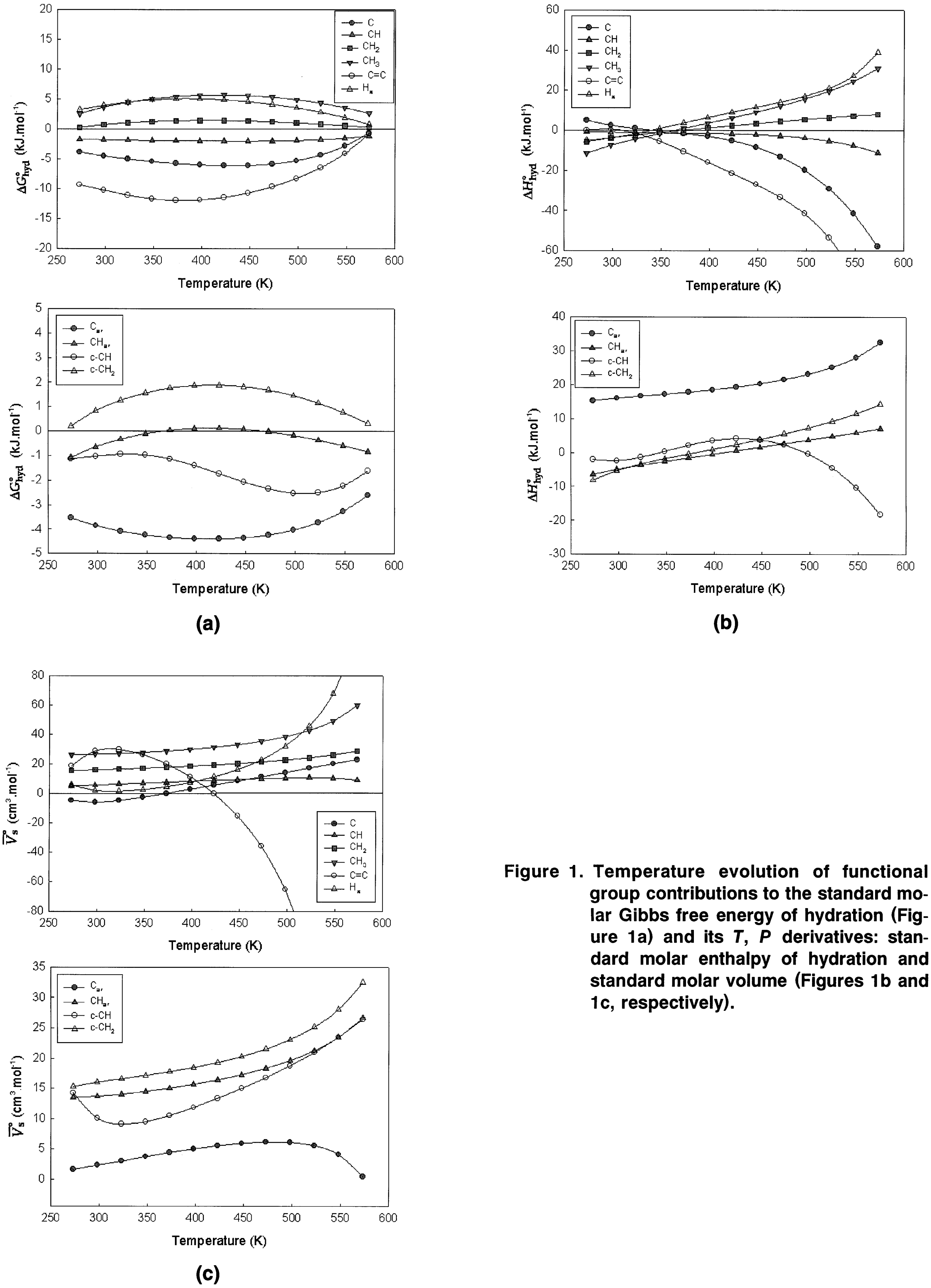

Figure 1. Temperature evolution of functional group contributions to the standard molar Gibbs free energy of hydration (Figure 1a) and its *T*, *P* derivatives: standard molar enthalpy of hydration and standard molar volume (Figures 1b and 1c, respectively).

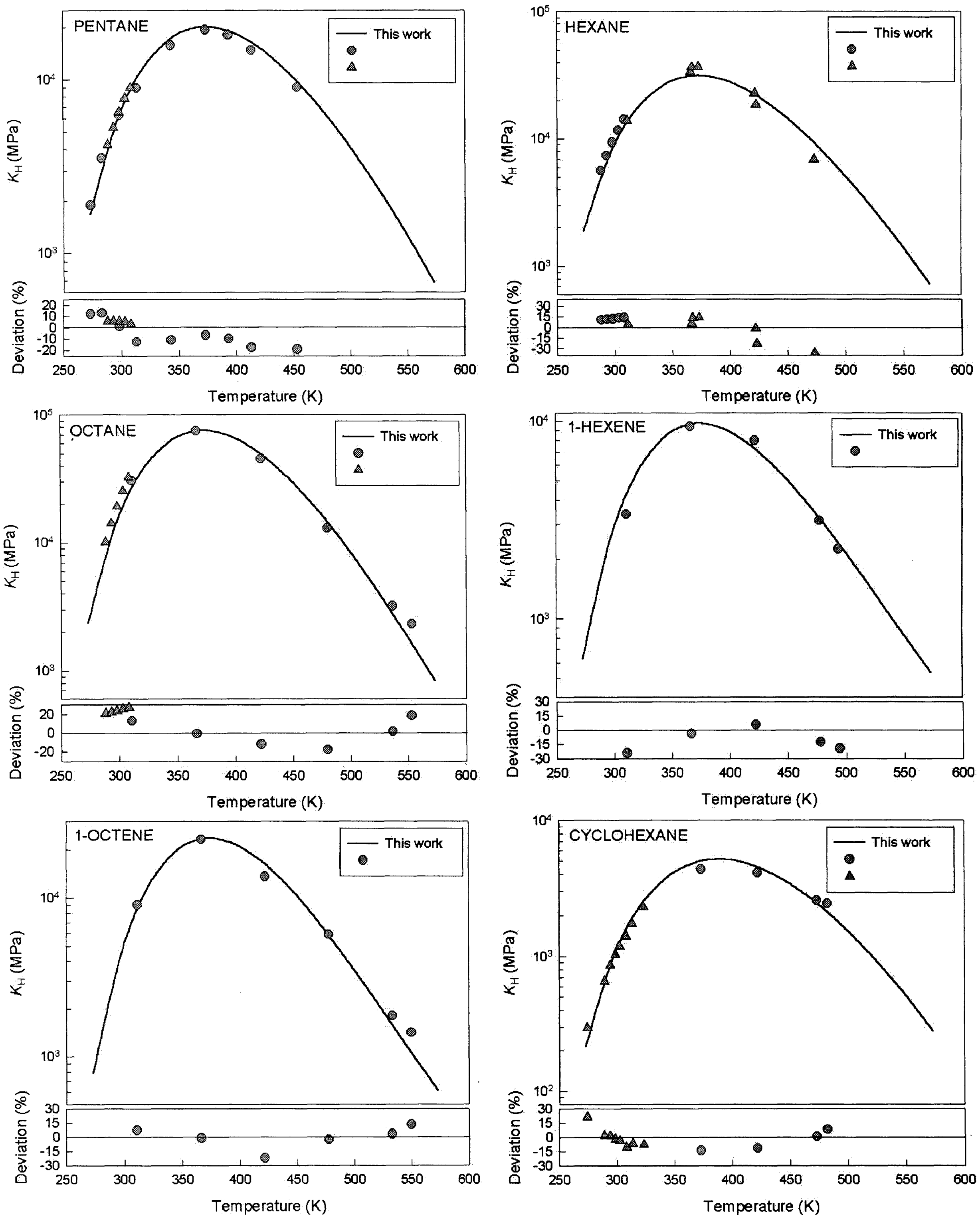

Figure 2a. Henry's Law constant calculated with the new model vs. experimental data along the saturation line of water: pentane, hexane, octane, 1-hexene, 1-octene, cyclohexane, butylcyclohexane, benzene, toluene, ethylbenzene, *m*-diethylbenzene, *p*-diisopropylbenzene.

References: *pentane*, — this work, ● Jou and Mather (2000), ▲ Jönsson et al. (1982); *hexane*, — this work, ● Jönsson et al. (1982), ▲ Tsonopoulos and Wilson (1983); *octane*, — this work, ● Heidman et al. (1985), ▲ Jönsson et al. (1982); *1-hexene*, — this work, ● Economou et al. (1997); *1-octene*, — this work, ● Economou et al. (1997); *cyclohexane*, — this work, ● Tsonopoulos and Wilson (1983), ▲ de Hemptinne et al. (1998); *butylcyclohexane*, — this work, ● Economou et al. (1997); *benzene*, — this work, ● Tsonopoulos and Wilson (1983), ▲ Anderson and Prausnitz (1986), ■ Chen and Wagner (1994a), ▼ Chandler et al. (1998); *toluene*, — this work, ● Anderson and Prausnitz (1986), ▲ Chen and Wagner (1994b), ■ Chandler et al. (1998); *ethylbenzene*, — this work, ● Heidman et al. (1985), ▲ Owens et al. (1986), ■ Chen and Wagner (1994c); *m-diethylbenzene*, — this work, ● Economou et al. (1997); *p-diisopropylbenzene*, — this work, ● Economou et al. (1997).

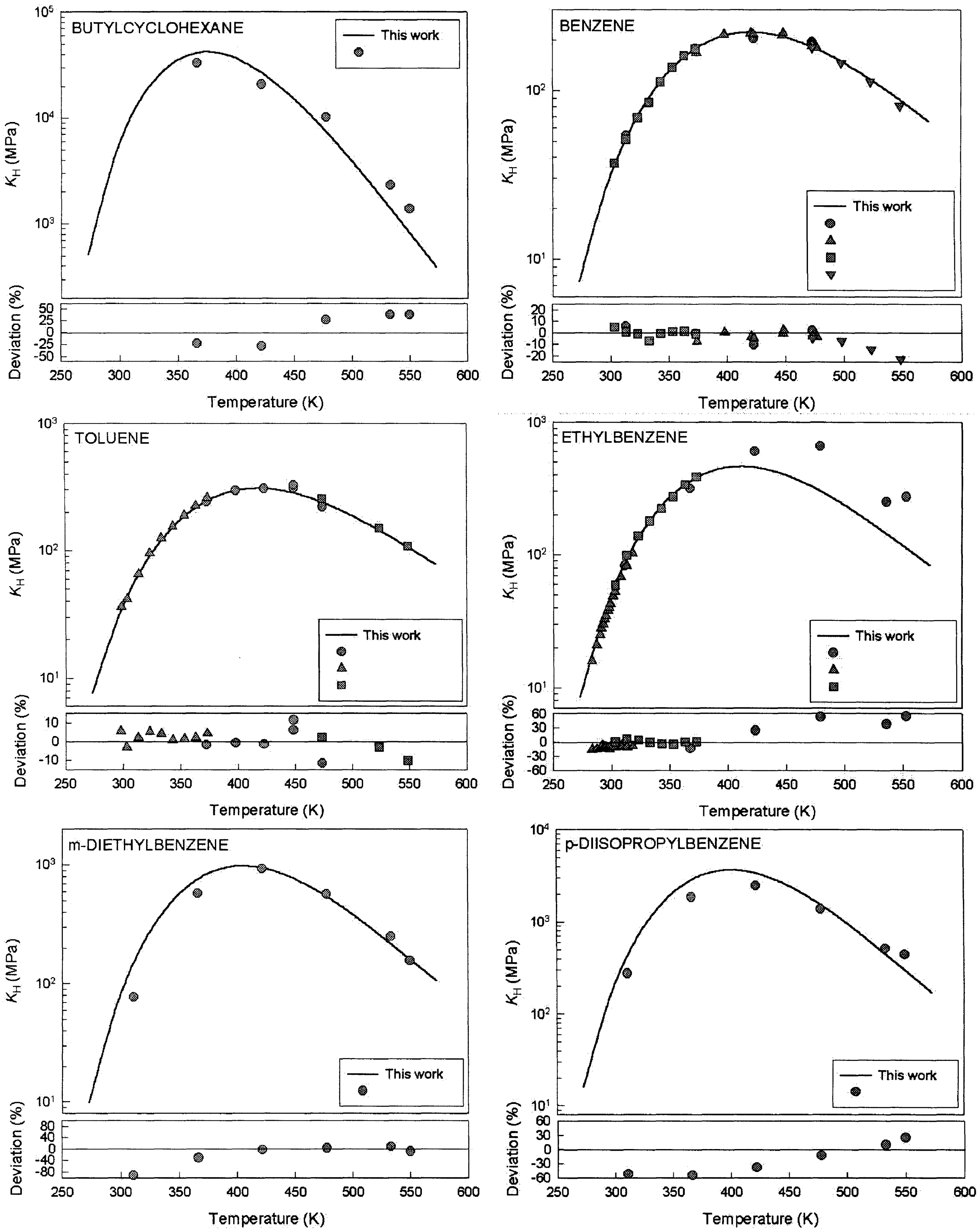

Figure 2b. Henry's Law constant calculated with the new model vs. experimental data along the saturation line of water: pentane, hexane, octane, 1-hexene, 1-octene, cyclohexane, butylcyclohexane, benzene, toluene, ethylbenzene, *m*-diethylbenzene, *p*-diisopropylbenzene.

References: *pentane*, — this work, ● Jou and Mather (2000), ▲ Jönsson et al. (1982); *hexane*, — this work, ● Jönsson et al. (1982), ▲ Tsonopoulos and Wilson (1983); *octane*, — this work, ● Heidman et al. (1985), ▲ Jönsson et al. (1982); *1-hexene*, — this work, ● Economou et al. (1997); *1-octene*, — this work, ● Economou et al. (1997); *cyclohexane*, — this work, ● Tsonopoulos and Wilson (1983), ▲ de Hemptinne et al. (1998); *butylcyclohexane*, — this work, ● Economou et al. (1997); *benzene*, — this work, ● Tsonopoulos and Wilson (1983), ▲ Anderson and Prausnitz (1986), ■ Chen and Wagner (1994a), ▼ Chandler et al. (1998); *toluene*, — this work, ● Anderson and Prausnitz (1986), ▲ Chen and Wagner (1994b), ■ Chandler et al. (1998); *ethylbenzene*, — this work, ● Heidman et al. (1985), ▲ Owens et al. (1986), ■ Chen and Wagner (1994c); *m-diethylbenzene*, — this work, ● Economou et al. (1997); *p-diisopropylbenzene*, — this work, ● Economou et al. (1997).

jective function for optimization had the following form

$$F = \sum_{i=1}^{O}\left(\frac{\Delta G_{\rm hyd}^{\circ,\rm exp} - \Delta G_{\rm hyd}^{\circ,\rm calc}}{\sigma \Delta G^{\circ}_{\rm hyd}}\right)_i^2 + \sum_{j=1}^{P}\left(\frac{\Delta H_{\rm hyd}^{\circ,\rm exp} - \Delta H_{\rm hyd}^{\circ,\rm calc}}{\sigma \Delta H^{\circ}_{\rm hyd}}\right)_j^2 + \sum_{k=1}^{Q}\left(\frac{\Delta C_{p,\rm hyd}^{\circ,\rm exp} - \Delta C_{p,\rm hyd}^{\circ,\rm calc}}{\sigma \Delta C^{\circ}_{p,\rm hyd}}\right)_k^2 + \sum_{l=1}^{R}\left(\frac{V_s^{\circ,\rm exp} - V_s^{\circ,\rm calc}}{\sigma V^{\circ}_{s}}\right)_l^2 \qquad (31)$$

where $\sigma \Delta Y^{\circ}_{\rm hyd}$ is the estimated uncertainty of a given data point, and O, P, Q and R are the numbers of data points for each property. The variables $Y^{\circ,\rm exp}$ were derived from experimental data, while those denoted as $Y^{\circ,\rm calc}$ were calculated from Eq. 23 for $\Delta G^{\circ}_{\rm hyd}$ and for $\Delta H^{\circ}_{\rm hyd}$ analogously from the relationship

$$\Delta H^{\circ}_{\rm hyd}(T,p) = \Delta H^{\circ\,\rm lit}_{\rm hyd}(T_{\rm ref},p_{\rm ref}) + \Delta H^{\circ\,\rm mod}_{\rm hyd}(T,p) - \Delta H^{\circ\,\rm mod}_{\rm hyd}(T_{\rm ref},p_{\rm ref}) \qquad (32)$$

for maintaining consistency with the enthalpic data at the reference conditions generated from the group contributions determined by Plyasunov and Shock (2000a). Expressions used for $C^{\circ}_{p,\rm hyd}$ and V°_s are directly the model equations listed in the Appendix, without any constraint at the reference conditions. In this way we obtained five parameters of the temperature-dependent SOCW model for ten hydrocarbon functional groups in Table 2 (the value of the OH group is considered only as provisional). Compared to the reference state group contribution scheme, we omitted the correction for proximity effect I(C-C) due to an insufficient amount of data at elevated conditions for relevant hydrocarbon structures. However, the correction at reference conditions also probably accounts for most of the proximity effect at higher temperature and, thus, the distinction is made for *ortho*dialkylbenzenes and *cis*-dialkylcycloalkanes in our high-temperature predictions.

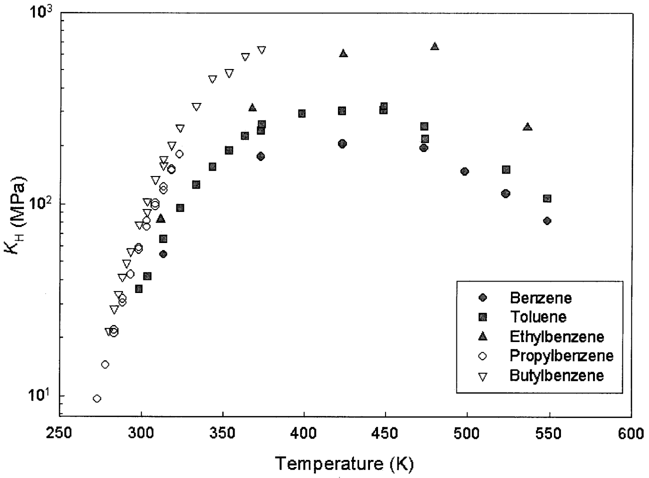

Figure 3a. Henry's Law constant of homologous series of alkylbenzenes: test of methylene group addition.

Displayed are experimental data from major sources.

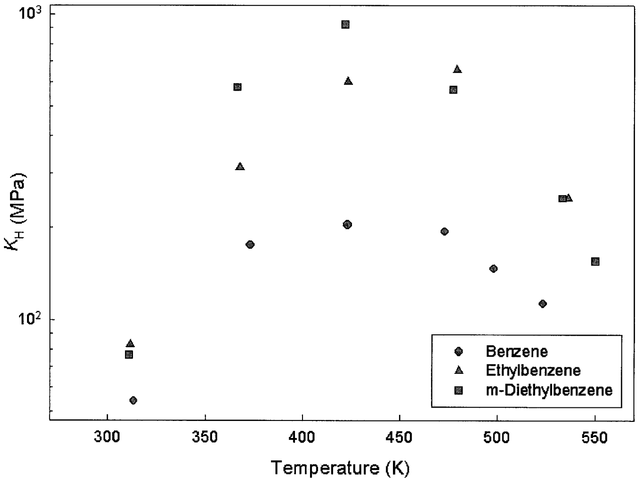

Figure 3b. Henry's Law constant of benzene, ethylbenzene and *m*-diethylbenzene: test of ethyl group substitution.

Displayed are experimental data from major sources.

The estimated uncertainties σY° in Eq. 31 play a role of weighting factors reflecting reliability of experimental data and error margin within which we want to reproduce the given property. In assignment of these weighting factors it is inevitable to also take into account the inherent error of the functional group additivity assumption. The weighting scheme employed here intended to yield the most reliable predictions over the entire temperature and pressure range, and to balance the impact of different properties on the overall fit. The uncertainties were therefore assigned to each property in such a way that, on average, the data on this property were described by our model at the limits of the estimated uncertainty. In the case of $\Delta G^{\circ}_{\rm hyd}$ the data sources on HLC were divided into five classes depending on data quality (which sometimes changed with temperature) and the assignment of uncertainties was done using a simple relation $\sigma \Delta G^{\circ}_{\rm hyd} = 0.2 + 0.1 \cdot C$ [kJ/mol] where C is the uncertainty class ranging from 1 to 5. This error margin corresponds to about 10–40% relative error in K_H. The uncertainties assigned to derivative properties were in most cases somewhat higher than the expected experimental errors in calorimetric and volumetric data. The data of highest accuracy were those available for standard molar volumes and heat capacities of aqueous alcohols near ambient conditions. However, directly using experimental uncertainties associated with these data in our simultaneous correlation would lead to overweighting of derivative properties at the expense of a good fit to HLC. The values of σY° for derivative properties were finally set to 8% for $\Delta H^{\circ}_{\rm hyd}$ (but at least 1.2 kJ/mol), 5% for $\Delta C^{\circ}_{p,\rm hyd}$ (at least 13 J/K/mol), and 0.8% for V°_s (at least 0.5 cm^3/mol). It should be noted that the adopted weighting scheme at the same time provides an assessment of the expected prediction uncertainties of K_H and of the derivative hydration properties for aqueous hydrocarbons which were treated by our group con-

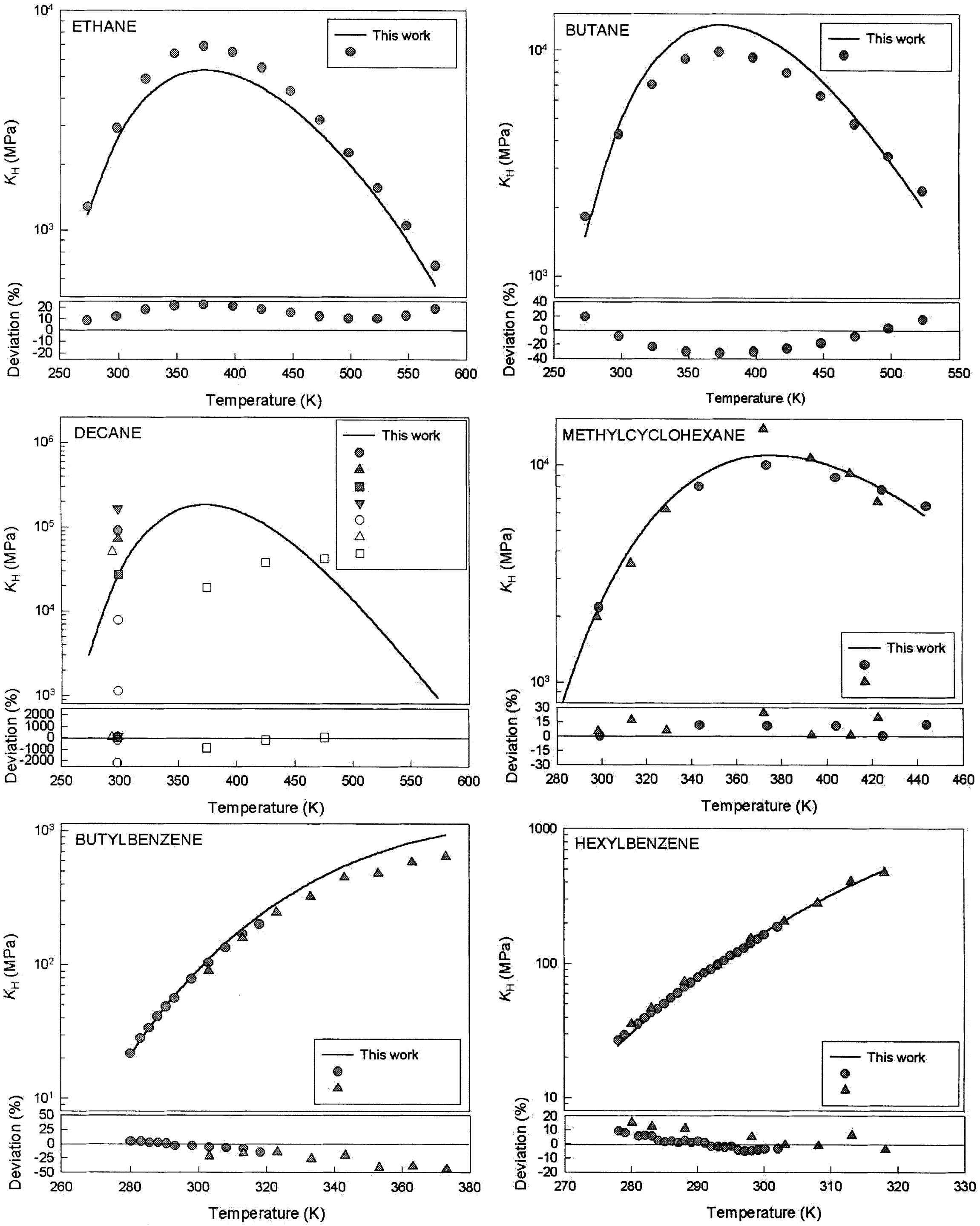

Figure 4a. Tests of calculated Henry's Law constant vs. experimental data excluded from regression along the saturation line of water: ethane, butane, decane, methylcyclohexane, butylbenzene and hexylbenzene.

References: *ethane*, — this work, ● Fernandez Prini and Crovetto (1989); *butane*, — this work, ● Carroll and Mather (1997); *decane*, — this work, ● Baker (1959); ▲ Franks (1966), ▼ Krasnoshchekova and Gubercrits (1973), ○ Mackay and Shiu (1975), △ Becke and Quitzsch (1977), □ Economou et al. (1997); *methylcyclohexane*, — this work, ● Jose (2001), ▲ Price (1976); *butylbenzene*, — this work, ● Owens et al. (1986), Chen and Wagner (1994c); *hexylbenzene*, — this work, ● May et al. (1983), ▲ Owens et al. (1986).

tribution procedure, or which are reasonably similar by their structure to our training set used in correlation.

The plots of temperature evolution of the functional group contributions to $\Delta G^{\circ}_{\mathrm{hyd}}$ and to its first derivatives calculated along the saturation line of water are given in Figure 1. Structural elements governing total $\Delta G^{\circ}_{\mathrm{hyd}}$ for hydrocarbons (methyl, methylene, c-CH_2 and CH_{ar} groups) exhibit a maximum in the range from 400 K to 450 K that is consistent with

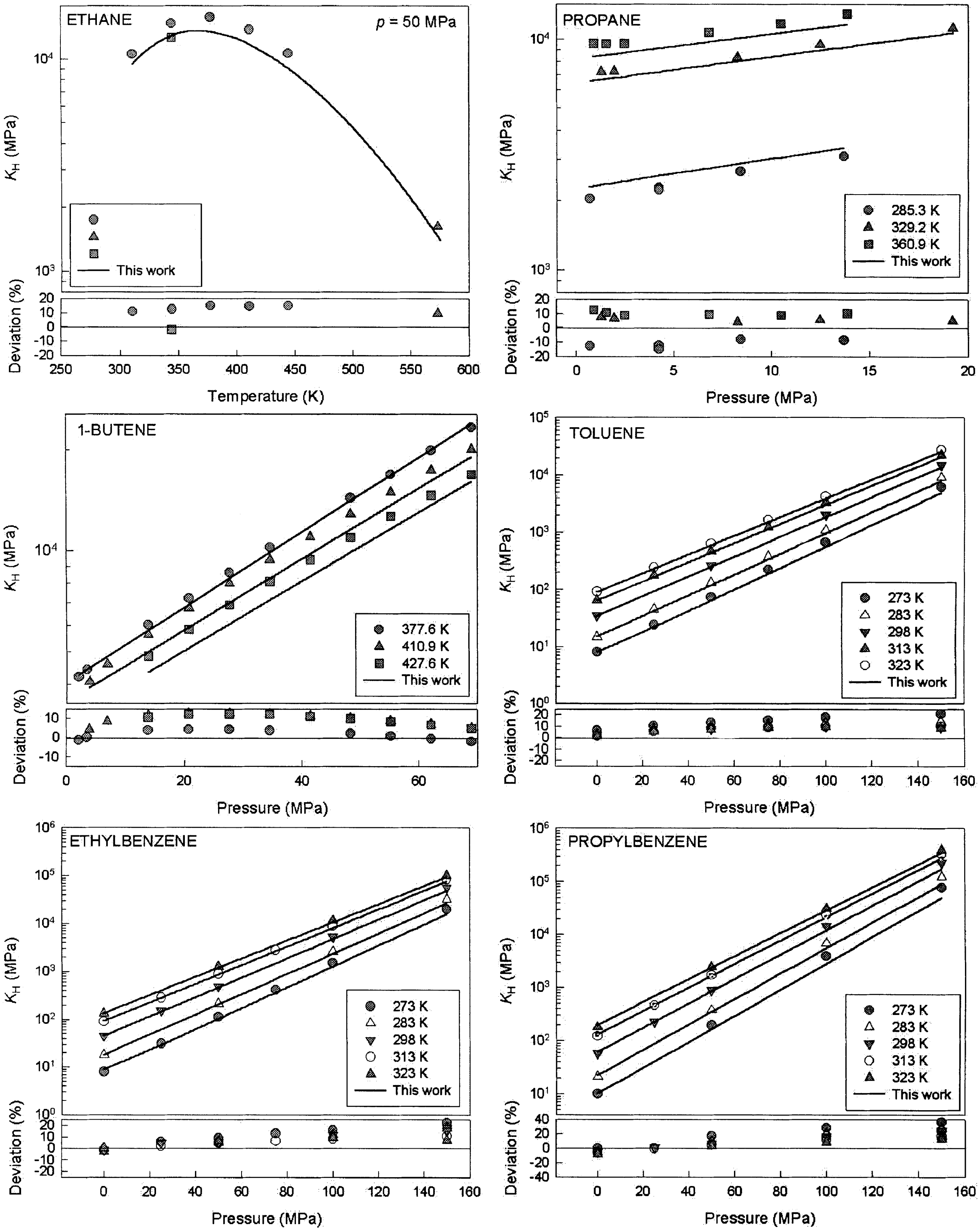

Figure 4b. Tests of calculated Henry's Law constant vs. experimental data at elevated pressures.

Ethane, propane (Kobayashi and Katz, 1953), 1-butene (Leland et al., 1955): data for these three compounds were included in regression. Toluene, ethylbenzene, propylbenzene (all Sawamura et al., (2001)): data for these three compounds were not included in regression.

References: *Ethane*: ● Culberson and McKetta (1950), ▲ Danneil et al. (1967), ■ Dhima et al. (1998), — this work.

the occurrence of maximum in HLC for hydrophobic solutes. The trend is reversed mainly for the $C=C$ contribution of alkenes, which mimics behavior of polar (hydrophilic) compounds. This is, however, not surprising due to an easy polarization of the double bond. The temperature evolution of functional groups for derivative properties also follows expected paths and are in accordance with our previous findings (Yezdimer et al., 2000). Prevailing hydrophobic character of hydrocarbons dictates positive divergence of the leading functional groups for V_s° and $\Delta H_{\mathrm{hyd}}^\circ$ near the critical point of a solvent.

Figure 2 compares predicted HLC with representative literature data along the saturation line of water for several compounds reflecting variety of hydrocarbon structures present in the database. For convenience, the graphs also include deviation plots in terms of percentage difference between the literature and predicted HLC. It follows from Figure 2 that our group contribution scheme provided prediction of HLC in the limits of uncertainties, as estimated above, for all test solutes with the exception of ethylbenzene at elevated temperatures. The reason for this discrepancy is that data of Heidman et al. (1985) do not comply with the group additivity assumption. Figure 3a displays in detail experimental HLC for benzene, toluene, ethyl-, propyl- and butylbenzene. Considering additivity of the CH_2 group addition, the difference between toluene and any other higher alkylbenzene should be the same at each temperature. This approximately holds true at lower temperatures, but the results of Heidman et al. seem to deviate from this path at temperatures over 400 K. Figure 3b shows variation of HLC of benzene, ethylbenzene, and diethylbenzene where the differences between neighbor pairs should again be comparable at the same conditions. The experimental data from both plots on ethylbenzene at high temperatures seem to be much too high, although we do not dare to draw any final conclusion before some new experimental results supplement the only existing high-temperature study on this solute.

The first part of Figure 4a displays comparison of predicted and experimental results along the saturation line of water for several data sets that were not included in correlation (ethane, butane, n-decane, methylcyclohexane, butylbenzene, and hexylbenzene). Predicted lines show a fair consistency with the experimental points, except for very large disagreement with data on n-decane. This solute has been studied mainly at ambient conditions, but, even at those conditions, the scatter of various reported results is in several orders of magnitude. The authors of the only available high-temperature data set (Economou et al., 1997) noticed appealing inconsistency of their HLC with the homologous additivity scheme, which is also a reason for the discrepancy with our prediction. Since the model description of most experimental data for n-alkanes is good up to octane and reasonable even for dodecane (for which new experimental results were obtained by Bergin (2002)), we consider in agreement with Economou et al. the data for decane as doubtful. A similar problem, although in a lesser extent, was observed also for 1-decene from the same literature source.

Finally, Figure 4b includes a set of plots for HLC by the group contribution scheme compared to data for ethane, propane, 1-butene, toluene, ethylbenzene, and propylbenzene at pressures remote from the saturation line of water (high-pressure data for the three alkylbenzenes are also new database additions and were not included in correlation). Predictions tend to somewhat shifted pressure effects compared to experimental values, namely at very low temperatures, but the differences are within estimated uncertainty limits to at least 150 MPa for all test solutes.

In concluding the discussion on expected errors, we would like to emphasize once more what are the sources of uncertainties associated with high-temperature predictions of HLC. There are model errors and extrapolation uncertainty, connected mainly with functional groups for which only few data were available at elevated conditions such as groups in branched chains. A major source of error is, however, the assumption of group additivity in the adopted scheme, which sets the limits for appropriate use of the group contribution method. This uncertainty affects mainly the reference values of $\Delta G_{\mathrm{hyd}}^{\circ,\mathrm{lit}}(T_{\mathrm{ref}}, p_{\mathrm{ref}})$ and $\Delta S_{\mathrm{hyd}}^{\circ,\mathrm{lit}}(T_{\mathrm{ref}}, p_{\mathrm{ref}})$ determining the error at both reference level by $\Delta G_{\mathrm{hyd}}^{\circ,\mathrm{lit}}(T_{\mathrm{ref}}, p_{\mathrm{ref}})$ and at high temperatures additionally by $(T - T_{\mathrm{ref}})\Delta S_{\mathrm{hyd}}^{\circ,\mathrm{lit}}(T_{\mathrm{ref}}, p_{\mathrm{ref}})$ term in Eq. 23. Plyasunov and Shock (2000a) estimated these errors to be at least 0.5 kJ/mol and 8 J/K/mol, respectively, which transforms to 20% relative uncertainty in K_H at 298 K, 40% at 400 K, and about the same at 500 K (relative error in HLC $\delta K_H / K_H$ is given by $(\exp[\delta(\Delta G_{\mathrm{hyd}}^\circ)/RT] - 1)$, in linear approximation by $\delta(\Delta G_{\mathrm{hyd}}^\circ)/RT$). This effect is in most part included in the estimate of uncertainties utilized in the regression as stated above, but, in predictions beyond the classes of compounds considered in correlation, it may lead to important additional errors. This is true namely for alkanes with over twelve carbon atoms, for which the predictions of $\Delta G_{\mathrm{hyd}}^{\circ,\mathrm{lit}}(T_{\mathrm{ref}}, p_{\mathrm{ref}})$ from the group contribution scheme by Plyasunov and Shock (2000a) are inappropriate. While the method of Plyasunov and Shock suggests a continuing increase in hydrophobic nature with an increasing carbon number, available experimental data on solubility of long chain alkanes (Baker, 1959; Franks, 1966; Sutton and Calder, 1974; Bergin, 2002) indicate that this trend is much weaker for n-alkanes with over twelve carbon atoms. This effect may be explained by structural collapse of the long chains, which might be folding and thus decreasing their hydrophobic surface (Tsonopoulos, 1999). A simple group contribution method is therefore not recommended for predicting HLC of hydrocarbons containing more than twelve carbon atoms in the backbone aliphatic chain.

The group contribution model presented in this article is rather complex. To facilitate its use in potential applications we decided to implement the equations and parameters reported here into a software tool, which is free for a noncommercial use and is presented in a separate paper (Majer et al., 2002).

Conclusions

Available literature data for HLC and for the related derivative properties of aqueous hydrocarbons at elevated conditions were collected and converted to standard molar thermodynamic functions of hydration. The prepared databases were used for establishing a group contribution method, based on the SOCW thermodynamic model. Parameters of the model equations are reported for ten hydrocarbon functional groups: C, CH, CH_2, CH_3, c-CH, c-CH_2, CH_{ar}, C_{ar}, $C=C$, and H_π, leading to predictions of HLC and of the related standard molar thermodynamic properties of hydration at elevated temperature and pressure for aqueous alkanes, alkenes, cycloalkanes, and (alkyl)benzenes. The predictions are provided to at least 570 K and 100 MPa and for compounds including up to twelve carbon atoms in the aliphatic backbone chain. Our interest was not to quantitatively reproduce the behavior of HLC in the close vicinity of the critical point of water. In such a case the approach proposed here by Japas and Levelt-Sengers (1989) should be preferred. However, considering the physically reasonable temperature extrapolation of presented group contributions, we believe that in most cases the results provided by our scheme will be semiquantitatively correct even at near critical conditions.

In addition to practical calculations the group contribution scheme can be employed as a consistency check for new experimental determinations on HLC, solubility or other related properties for alkanes/alkenes up to C_{12}, and for (alkyl)cyclohexanes/benzenes with one to three alkyl chains up to typically C_6. While it is clear that group additivity assumption has its limitations, it is well-established thermodynamic regularity and any large disagreement calls for a physically sound explanation.

The new group contribution method is intended as a basis for later extensions, covering also polar and ionic organic functional groups. An important advantage of our scheme regarding this task is a consistent methodology and data representation in terms of hydration properties. The employed thermodynamic model is capable of the description of all types of solutes and since the hydrocarbon functional group contributions were evaluated here with a high confidence level, it will be possible to keep them unchanged in the correlations of data for any newly included groups.

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Notation

A = modified Krichevskii parameter
B = second virial coefficient, m^3/kg
C = molar concentration, mol/dm^3
$C_{s,w}$ = integral of the solute-water direct correlation function
C_p = heat capacity, J/K/mol
f = fugacity, Pa
G = Gibbs free energy, J/mol
H = enthalpy, J/mol
K_H = Henry's law constant, Pa
M = molar mass, kg
n = number of moles
p = pressure, Pa
R = gas constant, J/K/mol
S = entropy, J/K/mol
T = temperature, K
V = volume, m^3
x = molar fraction

Greek letters

α = coefficient of thermal expansion, K^{-1}
δ = relative error
γ = activity coefficient
Δ = finite change
κ = isothermal compressibility, Pa^{-1}
ρ = density, kg/m^3
σ = absolute error
φ = fugacity coefficient

Subscripts

air = air
aq = aqueous
aw = air-water
c = critical
s = solute
SS = standard state
sol = dissolution
hyd = hydration
ref = reference conditions
res = residual
vap = vaporization
w = water

Superscripts

$\circ$ = standard state of unit concentration referenced to infinite dilution
∞ = infinite dilution in the symmetrical standard state convention
calc = calculated value
cor = correction
exp = experimental value
ig = ideal gas standard state
lit = literature value
mod = calculated from model
sat = saturation
sol = dissolution

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Appendix: Summary of the SOCW Thermodynamic Model

Equation 19 in the main text can be rearranged into a volumetric form using the definition of the modified Krichevskii parameter (Eq. 15)

$$V_s^{\circ} = RT\kappa_w + d(V_w - RT\kappa_w) + RT\kappa_w\rho_w\{a + b(\exp[\vartheta\rho_w] - 1) + c\exp[\theta/T] + \delta(\exp[\lambda\rho_w] - 1)\} \quad \text{(A1)}$$

where V_w, ρ_w, and M_w are molar volume, specific density, and molar mass of water, respectively, and general coefficients valid for all solutes are $\upsilon = 0.005$ m^3/kg, $\theta = 1{,}500$ K, and $\lambda = -0.01$ m^3/kg. Adjustable parameters are a, b, c, and d, and parameter δ is determined depending on the charge of a particle ($\delta = 0.35a$ for neutral molecules). Equation A1 is in fact modeling a series of perturbation effects due to insertion of a point mass into water solvent ($RT\kappa_w$), growing it to a "water-like" molecule with 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 righthand side of Eq. A1).

The process of hydration is defined as a transfer of solute molecule from the ideal gas standard state at given T and pressure $p_{\text{ref}} = 0.1$ MPa to aqueous solution at T, p. Corresponding change in the Gibbs free energy is expressed by Eq. 25. Full form of Eq. 25 in the framework of the SOCW model is given by Sedlbauer et al. (2000)

$$\begin{aligned}\Delta G^{\circ}_{\text{hyd}} = \Delta G^{\circ\,\text{cor}}_{\text{hyd}} &+ RT\ln\left[\frac{\rho_w RT}{M_w p_{\text{ref}}}\right]\\ &+ d\left(G_w - G_w^{\text{ig}} - RT\ln\left[\frac{\rho_w RT}{M_w p_{\text{ref}}}\right]\right)\\ &+ RT\left\{\rho_w(a + c\exp[\theta/T] - b - \delta) + \frac{b}{\vartheta}(\exp[\vartheta\rho_w] - 1)\right.\\ &\left. + \frac{\delta}{\lambda}(\exp[\lambda\rho_w] - 1)\right\} \qquad \text{(A2)}\end{aligned}$$

Appropriate derivations of $\Delta G^{\circ}_{\text{hyd}}$ lead to other thermodynamic properties of hydration

$$\begin{aligned}\Delta H^{\circ}_{\text{hyd}} = \Delta H^{\circ\,\text{cor}}_{\text{hyd}} &+ RT(T\alpha - 1) + d\big[H_w - H_w^{\text{ig}}\\ &- RT(T\alpha - 1)\big] + RT\theta c\exp[\theta/T]\frac{\rho_w}{T}\\ &- RT^2\left(\frac{\partial\rho_w}{\partial T}\right)_p\{a + b(\exp[\vartheta\rho_w] - 1) + c\exp[\theta/T]\\ &+ \delta(\exp[\lambda\rho_w] - 1)\} \qquad \text{(A3)}\end{aligned}$$

$$\Delta S^{\circ}_{\text{hyd}} = (\Delta H^{\circ}_{\text{hyd}} - \Delta G^{\circ}_{\text{hyd}})/T \qquad \text{(A4)}$$

$$\Delta C^{\circ}_{p,\text{hyd}} = \Delta C^{\circ\,\text{cor}}_{p,\text{hyd}} + \left(2RT\alpha_w + RT^2\left(\frac{\partial\alpha_w}{\partial T}\right)_p - R\right) + d\left\{C_{p,w} - C_{p,w}^{\text{ig}} - \left[2RT\alpha_w + RT^2\left(\frac{\partial\alpha_w}{\partial T}\right)_p - R\right]\right.$$

$$-T\left(\begin{array}{l} 2R\left(\frac{\partial\rho_w}{\partial T}\right)_p(a + b(\exp[\vartheta\rho_w] - 1) + c\exp[\theta/T] + \delta(\exp[\lambda\rho_w] - 1\} - c\exp[\theta/T]\frac{\theta}{T}\\ + Rc\exp[\theta/T]\theta^2\frac{\rho_w}{T^3} + RT\left(\frac{\partial\rho_w}{\partial T}\right)_p^2(\vartheta b\exp[\vartheta\rho_w] + \lambda\delta\exp[\lambda\rho_w])\\ + RT\left(\frac{\partial^2\rho_w}{\partial T^2}\right)_p\{a + b(\exp[\vartheta\rho_w] - 1) + c\exp[\theta/T] + \delta(\exp[\lambda\rho_w] - 1)\}\end{array}\right) \qquad \text{(A5)}$$

where G_w, H_w, and $C_{p,w}$ are the molar Gibbs free energy, enthalpy and heat capacity of water, G_w^{ig}, H_w^{ig}, and $C_{p,w}^{\text{ig}}$ are the same properties of water in ideal gas standard state at temperature T, and $\alpha_w = -[1/\rho_w(\partial\rho_w/\partial T)_p]$ is the coefficient of thermal expansion. Thermodynamic properties of pure water needed in calculations were obtained in this study from the equation of state by Hill (1990). Correction terms in Eqs. A2–A5 apply at temperatures below critical temperature of water $T_c = 647.126$ K and arise due to inadequacy of the simple volumetric Eq. A1 to describe accurately pressure change of K_H in both gas and liquid phases in a two-phase subcritical region. For nonelectrolyte solutes, this correction is expressed by an empirical function with one additional adjustable parameter e

$$\Delta S^{\circ\,\text{cor}}_{\text{hyd}} = e\left(T - T_c - \frac{T_c^2}{\Phi}\ln\left[\frac{T}{T_c}\right] + \frac{(T_c - \Phi)^2}{\Phi}\ln\left[\frac{T - \Phi}{T_c - \Phi}\right]\right) \qquad \text{(A6)}$$

$$\begin{aligned}\Delta H^{\circ\,\text{cor}}_{\text{hyd}} = e\Big\{&(2T_c - \Phi)(T_c - T) + 1/2(T^2 - T_c^2)\\ &+ (T_c - \Phi)^2\ln\left[\frac{T - \Phi}{T_c - \Phi}\right]\Big\} \qquad \text{(A7)}\end{aligned}$$

$$\Delta G^{\circ\,\text{cor}}_{\text{hyd}} = \Delta H^{\circ\,\text{cor}}_{\text{hyd}} - T\Delta S^{\circ\,\text{cor}}_{\text{hyd}} \qquad \text{(A8)}$$

$$\Delta C^{\circ\,\text{cor}}_{p,\text{hyd}} = \frac{e(T - T_c)^2}{(T - \Phi)} \qquad \text{(A9)}$$

where $\Phi = 228$ K is a general constant. Correction functions are zero by definition at $T \geq T_c$. All thermodynamic properties that appear in the above equations should be applied in their basic SI units when using parameters from Table 2 in the text.

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