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Prediction of the vapor–liquid distribution constants for volatile nonelectrolytes in water up to its critical temperature

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Abstract—The distribution of solutes between coexisting liquid and vapor phases of water can be expressed by the distribution constant, K_D, defined as

$$K_D = \lim_{x \to 0} \frac{y}{x},$$

where y and x stand for the mole fraction concentrations of a solute in vapor and liquid phases, respectively. Research reported here is concerned with the prediction of this property, K_D, for volatile nonelectrolytes, over the whole temperature range of existence of the vapor–liquid equilibrium for water, i.e. from 273 K to the critical temperature at 647.1 K. A simple empirical method is proposed to extrapolate the values of K_D from 298 K to 500–550 K. Calculations at higher temperatures are based on the theoretical relation that establishes the proportionality between $RT \ln K_D$ and the Krichevskii parameter, A_{Kr}, which is the single most important property of a solute at near-critical conditions, and can be evaluated using the method proposed here. The comparison of predicted and experimental values of K_D and A_{Kr} for a few well-studied solutes reveals the satisfactory performance of the proposed method. It appears that the accuracy of predictions in the framework of this method is limited mainly by the accuracy of the values of the thermodynamic functions of hydration of solutes at 298 K, and that the best way to improve the quality of predictions of K_D and A_{Kr} is to increase the inventory of accurate calorimetric enthalpy and heat capacity data for aqueous solutes at 298 K. We stress that the values of the Krichevskii parameter, such as those generated in this study, are of crucial importance for reliable predictions of the chemical potential and its derivatives (V_2^o, Cp_2^o) for aqueous solutes at near-critical and supercritical conditions. Values of K_D and A_{Kr} are predicted for many inorganic volatile nonelectrolytes and some halogenated derivatives of methane and ethene. We show that both $\ln K_D$ and A_{Kr} for aqueous organic solutes follow group additivity systematics, and we derive a set of corresponding group contribution values for several functional groups (material point, CH_3, CH_2, CH, C, $C = C$, $HC = CH$, $C \equiv C$, HC_{ar}, C_{ar}, C_{fus}, OH, O, S, SH, CO, COO, COH, COOH, CN, F, Cl, Br, NH_2, NH, N, etc.). *Copyright © 2003 Elsevier Ltd*

1. INTRODUCTION

If a hydrothermal solution exists in equilibrium with a gaseous phase, or, in other words, if boiling occurs, then the dissolved compounds fractionate between coexisting liquid and vapor phases. Solutes that are more volatile than the solvent will concentrate in the vapor phase, whereas nonvolatile compounds (salts, or metal oxides and sulfides, for examples) dominate the liquid phase. This fractionation of solutes between coexisting liquid and gaseous phases is recognized as a major factor in the evolution of hydrothermal systems, affecting the acidity/alkalinity, oxidation states, salt and volatile compound contents, isotopic compositions of phases, the fate of "ore" elements, etc. (Drummond and Ohmoto, 1985; Barnes and Seward, 1997; Giggenbach, 1997; Scott, 1997; Seward and Barnes, 1997; Roedder and Bodnar, 1997; Heinrich et al., 1999; Shmulovich et al., 1999 among many others).

Highly accurate thermodynamic data characterizing the be-

havior of dissolved compounds along the liquid–vapor equilibrium curve for water are known (Alvarez et al., 1994; Fernández-Prini et al., 2003) for a few gases (He, Ne, Ar, Kr, Xe, H_2, N_2, O_2, CO, CO_2, H_2S, CH_4, C_2H_6, SF_6). Many more compounds may be of interest for hydrothermal geochemistry in connection with the eternal geochemical problem of redistribution of chemical elements in natural processes. The presence of aqueous solutions in meteorite parent bodies, terrestrial planets and icy satellites means that the distribution of nonelectrolytes between liquid and vapor phases of H_2O has had consequences throughout the history of the solar system.

These considerations determine the goal of this contribution: to provide a quantitative framework for describing the fractionation of volatile nonelectrolytes between coexisting phases of water by delivering reliable estimates of vapor–liquid distribution constants for these solutes at infinite dilution up to the critical temperature of water, T_c. At T_c the compositions of the coexisting vapor and liquid phases of water become identical and, therefore, the vapor–liquid equilibrium is terminated. The values of the gas-liquid critical constants for pure water used in this contribution are taken from Levelt Sengers et al. (1985): the critical temperature $T_c = 647.096$ K, the critical pressure P_c

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= 22.064 MPa; the critical density ρ_c = 322 kg · m^{-3}. Volatile nonelectrolytes under consideration in this work consist of many inorganic and organic compounds. However, the approach developed is not applicable to neutral ionic pairs like HCl and NaCl, neutral compounds containing metals (solutes like Hg, AgCl, ZnBr$_2$, Sn(OH)$_2$, all metal-organic species), and hydroxides like H$_4$SiO$_4$ and B(OH)$_3$. An essential factor in excluding these species is the inapplicability of corresponding-state correlations employed in this study, see below, to describe the strong deviations from ideality for interactions between water and these solutes. Another limitation is the consideration of pure water as a solvent, in contrast to natural hydrothermal solutions which are practically always multicomponent mixtures. Nevertheless, the limiting case of pure water is a foundation on which more elaborate approaches should rest.

An additional reason to work with the vapor–liquid distribution constants arises from our interest in predicting the properties of aqueous solutes over a wide range of the state parameters (Plyasunov et al., 2000a,b). Typically, experimental data are available at ambient conditions, i.e., at low temperatures and high water densities. Therefore, we need data at very low (the range of validity of the virial equation of state truncated at the second coefficient) and intermediate densities. In our view, the vapor–liquid distribution coefficients (rather than Henry's constants or partial molar derivatives of the chemical potential of a solute) are the properties for which accurate predictions can be made at temperatures up to the critical temperature of water, mainly due to theoretical constraints on variations of these properties at near-critical conditions.

2. THERMODYNAMICS OF VAPOR–LIQUID DISTRIBUTION OF SOLUTES IN WATER

A rigorous and modern account of the problem of the distribution of solutes between coexisting vapor and liquid phases of water was made in the geochemical literature by Alvarez et al. (1994). The partitioning of solutes between coexisting vapor (or gaseous phase, or steam) and liquid phases of water can be described by either Henry's constant, k_H, or by the distribution constant, K_D. The following definition of Henry's constant is employed here (note that the term "Henry's constants" has become quite generic, with its definitions being different, for example, in environmental chemistry and chemical engineering. An operating definition is necessary to escape any misunderstandings):

$$k_H = \lim_{x \to 0} \frac{f_2}{x}, \tag{1}$$

where f_2 stands for the fugacity of a solute, and x represents the concentration (in mole fraction) of a solute in a liquid phase. Therefore, Henry's constant is defined as the limiting value of the fugacity/concentration ratio for a solute along the vapor–liquid coexistence curve for pure water, and k_H, defined in this way, is only temperature dependent. At the critical point of a solvent k_H has a quite definite value, specific for each solute.

For a solute at infinite dilution the vapor–liquid distribution constant is defined as:

$$K_D = \lim_{x \to 0} \frac{y}{x}, \tag{2}$$

where y and x stand for the mole fraction concentrations of a solute in vapor and liquid phases, respectively. Obviously, K_D is defined only along the vapor–liquid coexistence curve for water. At the critical point of a solvent K_D = 1 for all solutes.

The following relations connect K_D, k_H, and the standard chemical potentials of a solute in the coexisting vapor ($\mu_{2,v}^o$) and liquid ($\mu_{2,l}^o$) phases, and in the state of the ideal gas ($\mu^{\otimes}$) at the same temperature:

$$RT\ln k_H = \mu_{2,l}^o - \mu^{\otimes} \tag{3}$$

and

$$RT\ln K_D = \mu_{2,l}^o - \mu_{2,v}^o. \tag{4}$$

In other words, Henry's constant is proportional to the difference between the standard chemical potentials of a solute in the liquid phase of water and in the ideal gas state, whereas the distribution constant is proportional to the difference between the standard chemical potentials of a solute in the coexisting vapor and liquid phases of water. As the difference between the chemical potentials in the vapor phase and in the ideal gas state defines the fugacity of a solute, it follows that there is the following relation between K_D and k_H (Alvarez et al., 1994):

$$k_H = K_D \cdot \Phi_2^o \cdot P_1^o, \tag{5}$$

where Φ_2^o stands for the fugacity coefficient of a solute at infinite dilution, and P_1^o is the vapor pressure of pure water.

Basically, Eqn. 5 indicates that to evaluate the distribution constant of a solute, one has to know its fugacity coefficient and its Henry's constant as functions of temperature. This way of evaluating of K_D from predicted Φ_2^o and k_H data is hardly practical if one has to cover the whole temperature range of the vapor–liquid equilibrium of pure water, from the triple point temperature, 273.16 K, to the critical temperature, T_c = 647.1 K. Indeed, if one considers a nonpolar solute, for example, then at ambient conditions its thermodynamic properties in the liquid phase of water are determined by the so-called "hydrophobic hydration." As a result, for such a solute both the enthalpy and entropy of hydration are negative, whereas the heat capacities of hydration have positive values, quickly decreasing with increasing temperature. However, at near-critical conditions the picture is quite different: all derivatives of the standard chemical potential of a solute (the partial molar enthalpy, entropy, heat capacity, etc.) diverge, i.e., quickly increase (for nonpolar compounds in water), going to infinite values on the way to the critical point of water. The typical temperature course of the standard partial molar heat capacity of a hydrophobic solute at the saturated vapor pressure is qualitatively depicted in Figure 1 by the thick solid line. This complicated temperature dependence of the thermodynamic functions of a solute makes accurate predictions of Henry's constant over the whole temperature range of the existence of the vapor–liquid equilibrium for water a very challenging task.

Equally (and maybe even more) difficult is the prediction of the fugacity coefficient of a solute. Values of Φ_2^o describe the deviations from ideality (when Φ_2^o = 1) of interactions between water and a solute in the vapor phase at the limit of infinite
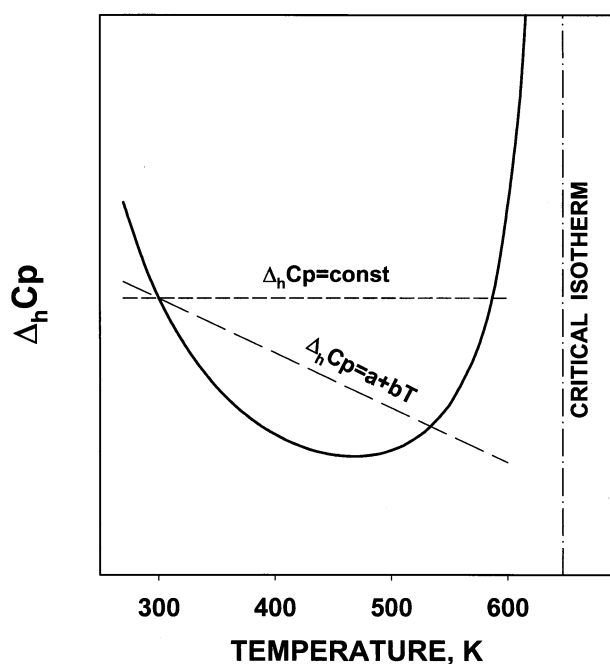
Fig. 1. A typical temperature dependence of the standard partial molar heat capacity of hydration, $\Delta_h C_p^o(T)$, for a hydrophobic solute at the saturated water vapor pressure (solid line). The merits of different approximations for $\Delta_h C_p^o(T)$ are discussed in the text.

dilution with respect to a solute. At very low water densities, say, way below 0.01 g $\cdot$ cm^{-3}, or at T $<<$ 480 K along the vapor–liquid coexistence curve for water, an approximation of ideal mixing is expected to be satisfactory for interactions between water and volatile nonelectrolytes. However, as the density of water in the vapor phase increases, one has to consider sequences of interactions ("collisions") between molecules of water and a solute. At rather low water densities, say, below 50 kg $\cdot$ m^{-3}, or at T $<$ 570 K for the vapor–liquid equilibrium for water, mainly binary interactions of one water molecule with one molecule of a solute will contribute to the deviations from ideal mixing in the gaseous phase. As the density of the coexisting vapor phase goes up, then the probability of simultaneous "collisions" of two water molecules with a molecule of a solute increases and has to be taken into consideration. For aqueous gaseous mixtures involving nonpolar compounds a rather accurate account of the deviations from ideality (but not very close to the critical point of water!) can be done using the cubic equations of state, see Fernández-Prini and Crovetto (1989); Akinfiev (1997); Fernández-Prini et al. (2003). However, in general the problem of accurate prediction of Φ_2^o up to the critical density of the solvent cannot be handled in a simple way due to the complicated picture of intermolecular interactions between water and the solute.

Fortunately, recent advances in the theory of infinitely diluted mixtures near the critical point of a solute enable a significant simplification of the problem of predicting the vapor–liquid distribution constants through the direct employment of Eqn. 5, which is exactly the subject of this contribution.

The region around the critical point of a solvent was recognized long ago (for an edifying historical account see Levelt

Sengers, 1976, 2002) as a particular space with seemingly paradoxical properties, which are in principal contradictions with the predictions of the otherwise successful so-called "classical" equations of state, from which the Van der Waals equation is the best known example. ("Classical" equations assume that the Helmholtz energy of a system can be given by an analytical function around the critical point of the system, which turned out not to be the case. Nevertheless, the investigations of the "classical" variant of the near-critical theory of mixtures were extremely fruitful for elucidation of unusual properties of mixtures close to the critical point of a system, because conclusions of such an analysis are qualitatively valid for strongly-diverging derivatives of the chemical potential of a solute). The fundamental reason for the "anomalous" behavior of near-critical systems is the universal development of long-range ordering close to the critical point, where peculiarities of solvent-solute interactions and the molecular structure of the solute, which determine the thermodynamic properties of a solute away from the critical point, no longer matter. A pioneering analysis of the thermodynamics of infinitely diluted critical solutions was done by Krichevskii and his colleagues in the USSR (Krichevskii, 1967, 1975; Rozen, 1969, 1976 and others) using the "classical" variant of the near-critical theory. (Note that many important results were first obtained in the Netherlands at the turn of 20th century, but for a number of reasons were not appreciated by contemporary scientists and forgotten for more than a half of century, see Levelt Sengers, 1976, 2002). Further important investigations of the properties of near-critical mixtures were done for both "classical" and "nonclassical" variants of the theory, for reviews see Levelt Sengers (1991a,b). The most important for the purposes of this presentation are the asymptotic relations, first derived by Japas and Levelt Sengers (1989), that must be valid for the temperature dependence of Henry's constants and distribution constants of an infinitely dilute solute close to the critical point of the solvent:

$$RT\ln\frac{k_H}{f_1} = A_{Kr}\frac{\rho(1) - \rho_c}{\rho_c^2} + D, \qquad (6)$$

and

$$RT\ln K_D = 2A_{Kr}\frac{\rho(1) - \rho_c}{\rho_c^2}, \qquad (7)$$

Here $\rho(1)$ stands for the density of liquid water (in mol $\cdot$ l^{-1}) and ρ with the subscript c stands for the critical density of water (ρ_c = 322 kg $\cdot$ m^{-3} = 17.87 mol $\cdot$ l^{-1}); f_1 represents the fugacity of pure water; D is a proportionality constant. The parameter A_{Kr} has a special place in the thermodynamics of near-critical solutions, and it was called by Levelt Sengers (1991a) the Krichevskii parameter. This parameter is given by the relation

$$A_{Kr} = \left(\frac{\partial P}{\partial x}\right)_{T,V,x=0}^c, \qquad (8)$$

with P and V being the pressure and volume of a system; the superscript c indicates that the evaluation is done at the critical point of the pure solvent. The Krichevskii parameter ubiquitously appears in most applications of near-critical theory and

governs such seemingly different problems as the initial coordinates of the critical lines, the sign and magnitude of the partial molar properties of a solute, etc. In other words, the Krichevskii parameter is the fundamental thermodynamic property of a solute at conditions corresponding to the critical temperature and the critical density/pressure of the solvent, and any successful thermodynamic model has to reproduce its value correctly. Therefore, one of the motivations for this paper is to derive values of the Krichevskii parameter for as many volatile nonelectrolytes in water as possible.

Returning to Eqns. 6 and 7, we note that these relations state that close enough to the critical point of the pure solvent the left hand sides of Eqns. 6 and 7 must be linear functions of the liquid water density, with the value of the slope dictated by the Krichevskii parameter. The theoretical analysis employed to derive these relations can not specify the temperature range of validity of these limiting, and therefore called "asymptotic," equations. Only comparison with experimental data may reveal the temperature range of applicability of relations given by Eqns. 6 and 7. Such an analysis for aqueous systems was done by the USA and Argentine groups of researchers (Harvey et al., 1990; Alvarez et al., 1994; Harvey et al., 1998; Fernández-Prini et al., 2003). They reached the conclusions that for Henry's constants the temperature range of validity of the near-critical asymptotic relations may be very small, within a few K from the critical point of water. However, it turned out that for the distribution constants the slope is nearly constant over 100–150 K (in some cases up to 200 K) below the critical point of water. This finding is empirical, but it is supported by the large variety of experimental results we have today, exemplified by the experimental data shown in Figure 2.[1]

There are two main implications of this finding.

(1) Eqn. 7 may be used to check the internal consistency of high-temperature data on the compositions of coexisting vapor and liquid phases as done by Fernández-Prini et al. (2003) when deriving the recommended values of K_D and k_H for a few gases in water. One of the conclusions reached by these authors is that there are no accurate experimental K_D and k_H data for hydrogen sulfide in water at temperatures in excess of 450 K. Reported literature K_D data for aqueous H_2S at high temperatures (Kozintseva, 1964; Suleimenov and Krupp, 1994) are shown in Figure 3. According to Eqn. 7 values of the $T\ln K_D$ function at T>500 K should fall on a straight line from the origin of the $T\ln K_D$ - $(\rho(l)-\rho_c)$ plane. Available experimental data show considerable scatter and, what is of more concern, do not extrapolate to the origin of the coordinates, at least at temperatures in excess of 550 K. New experimental investigations of the vapor–liquid distribution would be useful for a compound of such major importance for hydrothermal geochemistry as H_2S.

(2) Another use of Eqn. 7 is for extrapolating the values of the distribution constants toward the critical point of the sol-
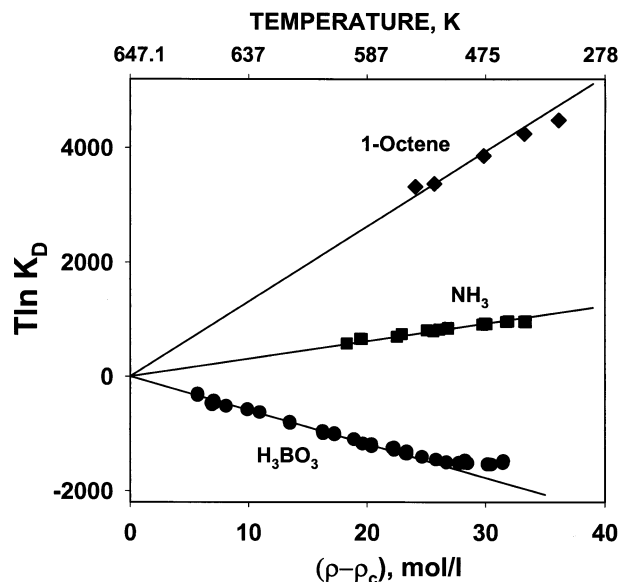

Fig. 2. Examples of validity of the asymptotic relation, given by Eqn. 7, far away from the critical point of water. Vapor–liquid distribution constants for 1-octene, ammonia, and boric acid are taken from Economou et al. (1997); Jones (1963); and Kukuljan et al. (1999), respectively.

vent. From the discussion given above, it follows that the asymptotic slope, in other words the value of the Krichevskii parameter for the solute under question, can be reliably estimated from K_D data at temperatures between 500 and 550 K, i.e., 100–150 K below the critical temperature of water, T_c. This means that if one measures, or is able to evaluate, values of the distribution constants up to 550 K, then the values of K_D at higher temperatures, all the way to T_c, can be reliably predicted.
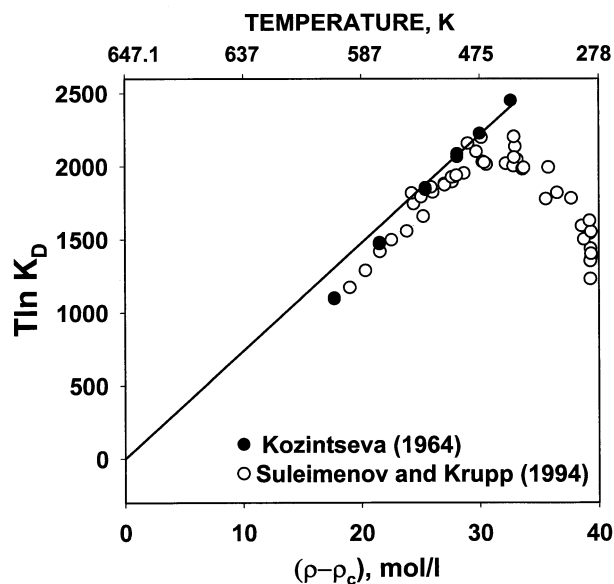
Fig. 3. The use of Eqn. 8 for checking the internal consistency of literature K_D data for H_2S. The solid line shows the asymptotic slope recommended by Fernández-Prini et al. (2003).

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[1] It may be worth noting that the relation given by Eqn. 7 is not applicable over extended temperatures for solutes for which the value of the Krichevskii parameter is close to zero, and that other terms in the Helmholtz energy expansion dominate the properties of such mixtures at near-critical conditions. An example of such "unusual" behavior was observed experimentally and explained for D_2O in water by Japas et al. (1995).

This circumstance greatly simplifies the evaluation of K_D by means of Eqn. 5 using extrapolated or predicted values of Φ_2^o and k_H. Indeed, at temperatures below 550 K the density of saturated water vapor is rather low, less than $40 \text{ kg} \cdot \text{m}^{-3}$, and the first-order correction for deviations from ideality, the second virial coefficient approximation, will be sufficient for predicting accurate values of Φ_2^o, see Section 3. Concerning k_H, we note that its accurate evaluation at temperatures below 550–570 K is a far less demanding exercise compared to its prediction over the whole temperature range up to T_c. A simple approximation of the temperature course of the standard partial molar heat capacity of hydration, $\Delta_h C_p^o$, which completely ignores the diverging near-critical branch of $\Delta_h C_p^o$, is accurate enough for evaluating k_H up to 550 K by means of a thermodynamic integration, see Section 4.

With the preceding discussion in mind, here is what we have done: simple methods are proposed on an essentially empirical basis for evaluating Φ_2^o and k_H for many nonelectrolytes in water over a limited temperature range, up to 550 K. This information is used to calculate values of K_D using Eqn. 5 over the same temperature range. Assuming from the empirical observations that the slope of the distribution constants versus liquid water density at temperatures between 500 and 550 K is close to the asymptotic near-critical slope, we estimate the Krichevskii parameter for a wide variety of aqueous solutes. Finally, we correlate the values of K_D over the whole temperature range of existence of the vapor–liquid equilibrium for water. These calculations are done for many inorganic and organic compounds, and for the latter a group contribution approximation was employed to represent values of A_{Kr} and ln K_D.

3. EVALUATION OF THE FUGACITY COEFFICIENT OF A SOLUTE AT INFINITE DILUTION, Φ_2^o, UP TO 550 K

The values of the fugacity coefficient of a component of a mixture can be calculated from equations of state, EoS, describing the volumetric properties of the mixture. The problems with mixtures involving water are that they are particularly difficult to describe by means of simple few-parameter EoS due to a variety of forces (dispersion, electrostatic, chemical) contributing to the potential energy of interactions between the polar molecule of water and other molecules. However, there is a universal equation of state, the so-called virial equation of state, given as a polynomial series in inverse volume, that is valid for all systems, including mixtures:

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \ldots + , \qquad (9)$$

where $B(T)$, $C(T)$, ... are the temperature dependent properties, called the second, third, ... virial coefficients. Contrary to the empirically-introduced equations of state, the virial EoS can be theoretically derived from statistical mechanics (Mason and Spurling, 1969), with $B(T)$, $C(T)$, ... relating to the potential energy of intermolecular interactions. Importantly, the composition dependence of virial coefficients is given rigorously by the theory, with the following relation valid for the second virial coefficient of a mixture, B_m, as an example:

$$B_m = \sum_i \sum_j y_i y_j B_{ij}, \qquad (10)$$

with B_{ij} designating the second virial coefficient between interacting components i and j of a mixture of unlimited number of components, and y standing for the mole fraction of a component in a mixture.

As discussed in the previous Section, at low densities only binary interactions contribute significantly to the deviations of thermodynamic properties of mixtures from ideality. So, we assume that at temperatures below 550–570 K, i.e., at pure water densities below $50 \text{ kg} \cdot \text{m}^{-3}$, the virial equation of state truncated at the second virial coefficient (i.e., neglecting ternary and higher interactions) will be adequate for representing the properties of the vapor phase. The virial equation of state truncated at the second virial coefficient gives the following relation for the fugacity coefficient of a solute at infinite dilution (Prausnitz et al., 1986):

$$\ln\Phi_2^o = (2B_{12} - B_{11})\frac{P}{RT}, \qquad (11)$$

where B_{11} is the second virial coefficient of pure water; B_{12} is the cross second virial coefficient for interactions between water and a solute; P, as before, stands for pressure.

Therefore, the task of predicting Φ_2^o values for solutes at infinite dilution in water vapor at T < 550 K is essentially the task of evaluating B_{11} and B_{12}. The second virial coefficient of water, B_{11}, is sufficiently well known over extremely wide temperature ranges (Wagner and Pruß, 2002; see Appendix A). However, evaluating the second cross virial coefficients for interactions between water and other solutes is a challenge. Our attempts to tackle this problem are reported elsewhere (Plyasunov and Shock, 2003; Plyasunov et al., 2003). Here we give a brief outline of the procedure proposed to evaluate and predict the values of the second cross virial coefficients for interactions involving water.

The practical option to reproduce or predict values of the second virial coefficients is to employ corresponding-states correlations. The corresponding-states principle in its simplest formulation, which descends from pioneering discoveries of Van der Waals, postulates the existence of a universal EoS in the reduced variables (with the reduced temperature, volume and pressure, T_R, V_R and P_R, defined by $T_R = T/T_c$, $V_R = V/V_c$ and $P_R = P/P_c$, where T_c, V_c and P_c stand for critical temperature, volume and pressure, respectively), which all substances will obey. A comparison with experimental PVT data, see, for example Prausnitz et al. (1986), showed that this formulation is accurate only for rare gases and small nonpolar compounds, like methane, with spherically symmetric force fields. The subsequent theoretical analysis showed the necessity to account for the nonspherical shape and electric properties of interacting molecules, for the formation of "hydrogen bonds" or chemical associates, etc. (Prausnitz et al., 1986). A number of semiempirical corresponding-states correlations are published in the chemical engineering literature to evaluate the second virial coefficients of pure substances. We employed the Tsonopoulos correlation (Tsonopoulos, 1974; Tsonopoulos and Heidman, 1990), which can be extended to mixtures, or to cross interactions, by means of only one mixture-specific parameter. Elsewhere (Plyasunov et al., 2003) we present a method to

estimate this mixture-specific parameter and, therefore, to predict B_{12} values for interactions between water and a number of volatile nonelectrolytes. The use of the Tsonopoulos correlation for calculating B_{12} requires knowledge of many properties: critical temperatures, pressures, volumes, acentric factors, dipole moments, "hydrogen-bonding" parameters for both components of a binary mixture, the mixture-specific parameter, etc. So, instead of tabulating these parameters, it was decided to fit the values of B_{12} correlated by means of the Tsonopoulos method with a simple analytical relation valid for the square-well potential (SWP):

$$B_{12} = \frac{2}{3} \pi N_A \sigma_{12}^3 \left\{ 1 - (\lambda_{12}^3 - 1)\left(\exp\left[\frac{\varepsilon_{12}}{k_B T} - 1\right]\right)\right\},$$

(12)

where $N_A = 6.02214 \cdot 10^{23}$ stands for Avogadro's number and k_B represents Boltzmann's factor; σ_{12}, ε_{12}/k_B, λ_{12} are the SWP-parameters, representing the collision diameter in Å $(10^{-10}$ m), the depth of the potential well in K, and the well width in collision diameters, respectively. A more detailed description of the procedure used is given in Plyasunov et al. (2003). Parameters of the square-well potential were determined for interactions between water and many inorganic and organic compounds. For organic compounds the group contribution approximation was employed to represent B_{12} values, therefore, the SWP-parameters were evaluated for functional groups as well.

4. EVALUATION OF HENRY'S CONSTANT, k_H, up to 550–570 K

Different methods can be used for estimating Henry's constant at elevated temperatures including approaches based on electrostatic considerations (Shock et al., 1989; Shock and Helgeson, 1990), or extensions of near-critical theories (Harvey and Levelt Sengers, 1990; Harvey, 1996), etc. However, the simplest and most universal way of estimating k_H at temperatures up to 550–570 K seems to be the method of thermodynamic integration.

This method exploits the connection between Henry's constant and the Gibbs energy of hydration (i.e., the Gibbs energy change associated with transfer of one mole of a compound from the state of the ideal gas at the reference pressure of 0.1 MPa to the state of the standard aqueous solution, defined as the state of unit activity in a hypothetical solution of unit molality referenced to infinite dilution at any temperature and pressure) given by the following relation:

$$\Delta_h G^\circ(T) = RT\ln k_H - RT\ln\frac{1000}{M_w} \approx RT\ln k_H - RT\ln(55.51),$$

(13)

where $M_w = 18.015268$ g · mol^{-1} (Wagner and Pruß, 2002) stands for the molar mass of water, and the second term is needed for conversion between the molality concentration scale employed for the Gibbs energy of hydration to the mole fraction concentration scale, which is used for Henry's constant. Note that the value of k_H has to be converted into the bar pressure units, because the standard pressure for the ideal gas is 0.1 MPa = 1 bar. Values of the Gibbs energy of hydration can

be calculated by thermodynamic integration from a reference isotherm:

$$\Delta_h G^\circ(T) = \frac{T}{T_r}\Delta_h G^\circ(T_r) - \frac{T - T_r}{T_r}\Delta_h H^\circ(T_r)$$

$$+ \int_{T_r}^{T} \Delta_h C_p^\circ(T)dT - T\int_{T_r}^{T}\frac{\Delta_h C_p^\circ(T)}{T}dT,$$

(14)

where $\Delta_h H^\circ(T_r)$ is the standard partial molar enthalpy of hydration at the reference isotherm, and $\Delta_h C_p^\circ(T)$ stands for the temperature-dependent standard partial molar heat capacity of hydration. The natural selection for the reference isotherm is 298.15 K, where most experimental determinations of the thermodynamic functions of hydration are performed. Some explanation may be necessary. Note that Henry's constant is defined as only a temperature-dependent function along the vapor–liquid equilibrium of water, regardless of the pressure increases along this path. Strictly speaking, $\Delta_h C_p^\circ(T)$ values used in Eqn. 14 should be isobaric values at some pressure, P, in excess of the saturated water vapor pressure, P_1°, and the additional term,

$$\int_{P}^{P_1^\circ} V_2^\circ(T, P)dP,$$

should be employed to bring the calculated values of $\Delta_h G^\circ(T)$ to the saturated water vapor pressure. However, for the sake of simplicity the pressure correction is omitted from Eqn. 14 because its effect at temperatures 273–550 K is minor. As a matter of fact, this small correction is implicitly included into the parameters of the heat capacity function proposed below.

The values of the heat capacities of hydration at T > 373 K are known only for a few nonelectrolytes. However, accurate calculations of $\Delta_h G^\circ(T)$ at elevated temperatures do not require exceedingly accurate $\Delta_h C_p^\circ(T)$ values. This fortunate circumstance is due to the particular form of Eqn. 14. Indeed, systematic errors in $\Delta_h C_p^\circ(T)$ will result in systematic errors in both integrals in Eqn. 14 and these errors to a great extent cancel when calculating $\Delta_h G^\circ(T)$. Therefore, the practical option is to look for a simple but general approximation for $\Delta_h C_p^\circ(T)$, the use of which will allow calculations of $\Delta_h G^\circ(T)$ up to 550 K with, say, accuracy of $\pm$ 0.05 log units, if one log unit is defined as $\Delta G^\circ/(\ln 10 \cdot RT)$.

The approximation that the standard partial molar heat capacity of hydration does not depend on temperature, i.e., that

$$\Delta_h C_p^\circ(T) = \Delta_h C_p^\circ(298),$$

(15)

allows accurate calculations of $\Delta_h G^\circ(T)$ up to 400–450 K, but not at higher temperatures that are of interest in this study. The departures resulting from using Eqn. 15 to calculate values of $\Delta_h G^\circ(T)$ in log units are shown as dashed curves in Figure 4. Note that for larger compounds such as *n*-octane (Fig. 4b), this approximation fails dramatically even at relatively low temperatures, resulting in errors in the $\Delta_h G^\circ(T)$ value corresponding to 0.41 log units at temperature 450 K. Explaining why this approximation is unsatisfactory, especially for hydrophobic species, is helped by Figure 1. The integral of Eqn. 14,
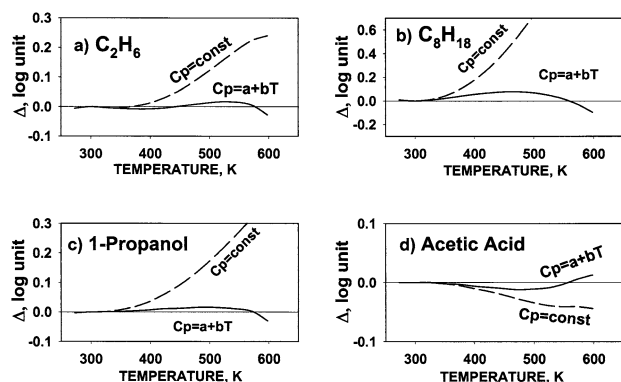
Fig. 4. The performance of approximations to the standard partial molar heat capacity of hydration given by Eqn. 15 (dashed line) and Eqn. 16 (solid line) for calculating $\Delta_h G^o(T)$ for some solutes by the method of thermodynamic integration. Differences are given as departures in log units as described in the text.

$$\int_{T_r}^{T} \Delta_h C_p^{\circ}(T) dT,$$

is given by the area under the solid line in Figure 1, and the approximation that $\Delta_h C_p^{\circ}(T) = \Delta_h C_p^{\circ}(298\ \text{K})$, which is shown by the horizontal short-dash line, generally gives a poor evaluation for this integral, although the upper limit of integration may matter in how poor this evaluation will be.

The next simplest approximation, namely that the standard partial molar heat capacity of hydration depends linearly on temperature (but must reproduce the experimental value of $\Delta_h C_p^{\circ}$ at 298.15 K), i.e., that

$$\Delta_h C_p^{\circ}(T) = a + bT, \tag{16}$$

turns out to be sufficient for calculating $\Delta_h G^o(T)$ up to 570 K. This conclusion was checked by fitting the temperature dependence of the Gibbs energy of hydration for more than 30 solutes, spanning the range from nonpolar rare gases to strongly-polar alcohols, amines, carboxylic acids and amides, and from small solutes like ammonia or oxygen to large ones like n-octane or benzene (Table 1). Some examples are shown by the solid curves in Figure 4. Returning to Figure 1, it can be seen that this approximation, which usually overestimates $\Delta_h C_p^{\circ}$ at lower temperatures and underestimates it at higher ones, gives a reasonable value of the

$$\int_{T_r}^{T} \Delta_h C_p^{\circ}(T) dT$$

integral, i.e., the area under the solid line. Certainly the optimal value of b (or the slope in Fig. 1) varies with the upper limit of integration, which was in our case fixed at 573 K.

Using Eqn. 16, the analytical expression for $\Delta_h G^o(T)$, consistent with Eqn. 14, is given by

$$\Delta_h G^o(T) = \frac{T}{T_r} \Delta_h G^o(T_r) - \frac{T - T_r}{T_r} \Delta_h H^o(T_r)$$
$$+ a\left(T - T_r - T \ln\frac{T}{T_r}\right) - \frac{b}{2}(T - T_r)^2. \tag{17}$$

To perform calculations, one needs, in addition to $\Delta_h G^o(T)$ and $\Delta_h H^o(T)$ data at the reference isotherm $T_r = 298.15$ K, the values of the parameters a and b of the heat capacity function, Eqn. 16. If an experimental $\Delta_h C_p^{\circ}$ value is available at the reference temperature, then only one parameter, say, b, has to be known independently, with the parameter a given then by

$$a = \Delta_h C_p^{\circ}(T_r) - b \cdot T_r. \tag{18}$$

We attempted to find a way to estimate the b parameter from information readily available at $T_r = 298.15$ K. To meet this goal, we selected a training set of solutes, for which reliable values of Henry's constant at temperatures up to 570 K are either measured directly or can be calculated using experimental $\Delta_h C_p^{\circ}(T,P)$ and $V_2^{\circ}(T,P)$ data. When searching empirical correlations, it is important to work with a representative array of data. In our case, the training set needed to include solutes of different sizes and shapes (neon, benzene, n-octane as examples), and greatly varying in strengths of water-solute interactions (argon, ammonia, acetic acid, etc.). The selected set is presented in Table 1. Numbers in parentheses in various columns of Table 1 show uncertainties, given as a number of significant figures, so, 19.44(3) means 19.44 ± 0.03 and $-0.07(37)$ means -0.07 ± 0.37. The optimal values of the b coefficient of Eqn. 16 for each solute were determined by the least squares fit of $\Delta_h G^o(T)$ data using fixed values of $\Delta_h G^o(T_r)$, $\Delta_h H^o(T_r)$, and $\Delta_h C_p^{\circ}(T_r)$. However, the uncertainties of the b coefficients given in Table 1 include contributions, calculated using usual rules of error propagation, arising from uncertainties in the values of the thermodynamic functions at the reference isotherm 298.15 K. A quick analysis of the b results in Table 1 shows that there is a strong negative correlation between $\Delta_h C_p^{\circ}(298)$ and the coefficient b: the larger the $\Delta_h C_p^{\circ}(298)$ datum the more negative the value of b is. The second observation is that for compounds with similar $\Delta_h C_p^{\circ}(298)$ values the coefficient b seems to depend on polarity of the solute, and for polar compounds the values of b are less negative. This could be seen by comparing b results for argon and ethanol, two solutes with similar $\Delta_h C_p^{\circ}(298)$ values of ~ 200 J $\cdot$ K^{-1} mol^{-1}.

Accepting values of the Gibbs energy of hydration at 298.15 K, 0.1 MPa, $\Delta_h G^o(298)$, as an approximate measure of the polarity of a solute, we propose the following empirical correlation for the b coefficient:

$$b = b_o + b_1 \cdot \Delta_h C_p^{\circ}(298) + 10^3 \cdot b_2 \cdot \Delta_h G^o(298), \tag{19}$$

where the dimensions of $\Delta_h C_p^{\circ}(298)$ are J $\cdot$ K^{-1} $\cdot$ mol^{-1} and those of $\Delta_h G^o(298)$ are kJ $\cdot$ mol^{-1}. The fit of data in Table 1 gives the following values of the coefficients of Eqn. 19: $b_o = 0.210$ J $\cdot$ K^{-2} $\cdot$ mol^{-1}; $b_1 = -2.84 \cdot 10^{-3}$ K^{-1}; $b_2 = -8.04 \cdot 10^{-6}$ K^{-2}. Illustrating the quality of the correlation given by Eqn. 19 is hampered by the fact that b depends on two parameters. If one defines the auxiliary quantity Π as

$$\Pi = b - 10^3 \cdot b_2 \cdot \Delta_h G^o(298), \tag{20}$$

then there should be a linear relation between Π and $\Delta_h C_p^{\circ}(298)$, because from Eqn. 19 it follows that

$$\Pi = b_o + b_1 \cdot \Delta_h C_p^{\circ}(298). \tag{21}$$

The quality of the correlation is seen in Figure 5, where

Table 1. The training set of solutes employed to test the methods of predicting k_H at high temperatures together with thermodynamic functions of hydration at 298.15 K, 0.1 MPa and parameters a and b for Eq no. 16.

Compound	Formula	$\Delta_h G^{o\,a,b}$	$\Delta_h H^{o\,a,b}$	$\Delta_h C_p^{o\,a,c}$	a^c	b^d	$\Delta_h G^o$ (T) sources
Helium	He	19.44(3)[e]	−0.7(2)[f,g]	130(10)[f,e]	182	−0.17 ± 0.15	[h]
Neon	Ne	19.07(3)[e]	−3.8(2)[f,i]	145(10)[f]	278	−0.44 ± 0.16	[h]
Argon	Ar	16.28(3)[e]	−12.0(1)[f,i]	200(10)[f]	373	−0.58 ± 0.15	[h]
Krypton	Kr	14.83(3)[e]	−15.3(1)[f,i]	220(10)[f]	443	−0.75 ± 0.15	[h]
Xenon	Xe	13.44(3)[e]	−19.0(2)[f,i]	250(10)[f]	440	−0.64 ± 0.16	[h]
Hydrogen	H_2	17.73(3)[j]	−4.0(5)[j]	140(15)[j]	236	−0.32 ± 0.23	[h]
Nitrogen	N_2	18.21(3)[k]	−10.4(3)[k]	214(10)[k]	388	−0.58 ± 0.16	[h]
Oxygen	O_2	16.55(3)[l]	−12.1(1)[l,m,f]	200(5)[l,f,g]	339	−0.47 ± 0.09	[h]
Carbon monoxide	CO	17.19(3)[n]	−10.8(3)[n]	215(10)[n]	386	−0.57 ± 0.16	[h]
Sulfur hexafluoride	SF_6	20.62(10)[i]	−20.7(5)[g]	311(25)[g]	467	−0.53 ± 0.37	[h]
Carbon dioxide	CO_2	8.41(5)[o]	−19.7(1)[p,r]	180(10)[s]	305	−0.42 ± 0.15	[h]
Hydrogen sulfide	H_2S	5.66(10)[t]	−18.0(15)[t]	144(10)[u]	247	−0.35 ± 0.27	[h]
Ammonia	NH_3	−10.1(1)[v,w]	−35.4(2)[x]	39(5)[y]	−13	0.17 ± 0.09	[z]
Methane	CH_4	16.26(3)[aa]	−13.1(1)[f,bb]	216(10)[s,cc]	368	−0.51 ± 0.14	[h]
Ethane	C_2H_6	15.57(5)[dd]	−19.4(5)[dd]	280(20)[dd]	411	−0.44 ± 0.28	[h]
Propane	C_3H_8	16.1(1)[dd]	−22.9(3)[dd]	330(30)[dd]	444	−0.38 ± 0.43	[ee]
n-Butane	C_4H_{10}	16.6(2)[dd]	−25.9(3)[dd]	385(20)[dd]	589	−0.69 ± 0.29	[ee]
n-Pentane	C_5H_{12}	17.5(3)[dd]	−28.8(3)[dd]	454[ff]	778	−1.09 ± 0.44	[ee]
n-Hexane	C_6H_{14}	18.1(4)[dd]	−31.6(4)[dd]	518[ff]	967	−1.51 ± 0.45	[ee]
n-Heptane	C_7H_{16}	18.9(4)[dd]	−36.2[ff]	582[ff]	1080	−1.67 ± 0.54	[ee]
n-Octane	C_8H_{18}	19.4(5)[dd]	−39.9[ff]	646[ff]	1213	−1.90 ± 0.56	[ee]
Ethene	C_2H_4	13.25(10)[dd]	−16.5(3)[dd]	210(20)[dd]	440	−0.67 ± 0.29	[z]
Propene	C_3H_6	12.9(2)[dd]	−21.6(3)[dd]	280(30)[dd]	398	−0.39 ± 0.43	[ee]
1-Butene	C_4H_8	13.6(2)[dd]	−24.9(4)[dd]	366[ff]	676	−1.04 ± 0.44	[ee]
1-Hexene	C_6H_{12}	15.1(3)	−31.7[ff]	494[ff]	957	−1.55 ± 0.54	[ee]
1-Octene	C_8H_{16}	16.7[ff]	−39.2[ff]	622[ff]	1225	−2.02 ± 0.56	[ee]
Cyclohexane	C_6H_{12}	13.0(2)[dd]	−33.1(3)[dd]	410(30)[dd]	629	−0.73 ± 0.43	[ee]
Benzene	C_6H_6	4.3(2)[dd]	−31.7(3)[dd]	290(15)[dd]	436	−0.49 ± 0.23	[ee]
Toluene	C_7H_8	4.6(2)[dd]	−36.3(3)[dd]	340(30)[dd]	513	−0.58 ± 0.43	[ee]
Methanol	CH_4O	−13.2(2)[dd]	−45.1(2)[dd]	114(5)[dd]	138	−0.08 ± 0.10	[gg]
Ethanol	C_2H_6O	−13.0(2)[dd]	−52.6(2)[dd]	199(5)[dd]	264	−0.22 ± 0.10	[gg]
1-Propanol	C_3H_8O	−12.4(2)[dd]	−57.7(2)[dd]	268(6)[dd]	402	−0.45 ± 0.15	[gg]
1-Propanamine	C_3H_9N	−10.4(5)[hh]	−55.8(10)[hh]	231(15)[hh]	251	−0.07 ± 0.31	[gg]
Acetic acid	$C_2H_4O_2$	−21.0(5)[gg]	−52.8(20)[hh]	105(10)[gg]	84	0.07 ± 0.37	[gg]
Propanoic acid	$C_3H_6O_2$	−20.4(9)[gg]	−56.5(20)[hh]	160(10)[hh]	168	−0.03 ± 0.37	[gg]
Propanamide	C_2H_7NO	−31.5(10)[gg]	−73.4(30)[gg]	168(10)[gg]	185	−0.06 ± 0.59	[gg]

[a] At 298.15 K, 0.1 MPa,[b] $kJ \cdot mol^{-1}$,[c] $J \cdot K^{-1} \cdot mol^{-1}$,[d] $J \cdot K^{-2} \cdot mol^{-1}$,[e] Krause and Benson (1989),[f] Olofsson et al. (1984),[g] Hallén and Wadsö (1989),[h] Fernández-Prini et al. (2003),[i] Dec and Gill, (1985a),[j] Wilhelm et al. (1977),[k] Rettich et al. (1984),[l] Rettich et al. (2000),[m] Dec and Gill, (1984a),[n] Rettich et al. (1982),[o] Crovetto, (1991),[p] Berg and Vanderzee, (1978),[r] Gill and Wadsö (1982),[s] Hnedkovsky and Wood, (1997),[t] Cox et al. (1989),[u] Barbero et al. (1982),[v] Clegg and Brimblecombe (1989),[w] Kawazuishi and Prausnitz (1987),[x] Vanderzee and King (1972),[y] Allred and Woolley (1981),[z] Plyasunov et al. (2000b),[aa] Rettich et al. (1981),[bb] Dec and Gill (1984b),[cc] Dec and Gill (1985b),[dd] Plyasunov and Shock (2000a),[ee] Plyasunov and Shock (2000b),[ff] group contribution value from Plyasunov and Shock (2000a),[gg] Plyasunov et al. (2001),[hh] Cabani et al. (1981).

"experimental" Π values, calculated from Eqn. 20, are plotted as filled circles against $\Delta_h C_p^o(298)$, and all "predicted" values of Π fall on the solid line, which is given by Eqn. 21. Note that the error bars show the uncertainties of the "experimental" points due to uncertainties in both the b coefficients and $\Delta_h C_p^o(298)$ values. Given the success of Eqn. 19 for the large and diverse set of compounds in Table 1, which contains results for polar and nonpolar solutes of spherical, linear and ring shapes, we expect that Eqn. 19 can be applied to various aqueous compounds.

To launch the procedure of estimating high-temperature k_H values for aqueous solutes described above, one needs to know the values of the thermodynamic functions of hydration at 298.15 K. Experimental values of $\Delta_h G^o(298)$ are available for many compounds from vapor–liquid and liquid-liquid equilibria studies, whereas experimental determinations of $\Delta_h H^o(298)$ and $\Delta_h C_p^o(298)$ are often not available. Therefore, general methods for estimating the standard partial molar enthalpy and heat capac-

ity of hydration at 298.15 K would be useful. This task is in general far from simple. One possible approach to the problem is outlined in Appendix B. The method assumes the existence of "universal" correlations between the values of $\Delta_h G^o$, $\Delta_h H^o$, and $\Delta_h C_p^o$ at 298.15 K, with deviations from these "universal" correlations depending on the chemical composition of a solute (see Appendix B for details). Fit results are given in Table B1, and numerical values of universal terms and atomic contributions to $\Delta_h H^o(298)$ and $\Delta_h C_p^o(298)$ are given in Table B2.

5.. CALCULATION OF VAPOR–LIQUID DISTRIBUTION CONSTANTS, K_D, UP TO Tc

5.1. Calculation of K_D at Temperatures up to 550 K

5.1.1. Expected Accuracy of K_D Predictions

According to Eqn. 5 the uncertainty of K_D depends on uncertainties in Φ_2^o and k_H as follows:
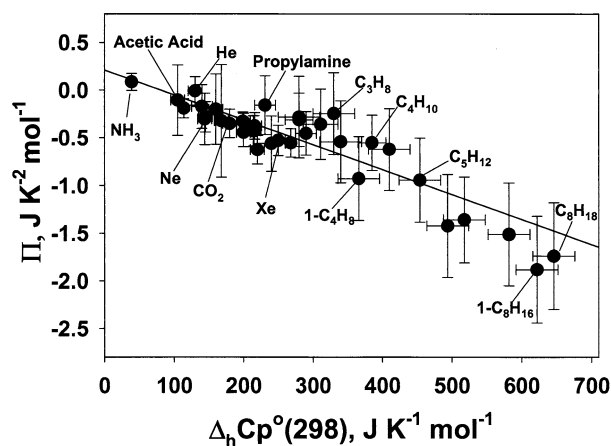
Fig. 5. The relation between the "experimental" (filled circles, calculated using Eqn. 20) and correlated (solid line, given by Eqn. 21) values of the quantity Π, see text. Error bars show the uncertainties of the "experimental" data due to uncertainties of $\Delta_h C_p^o(298)$ values and the b coefficients.
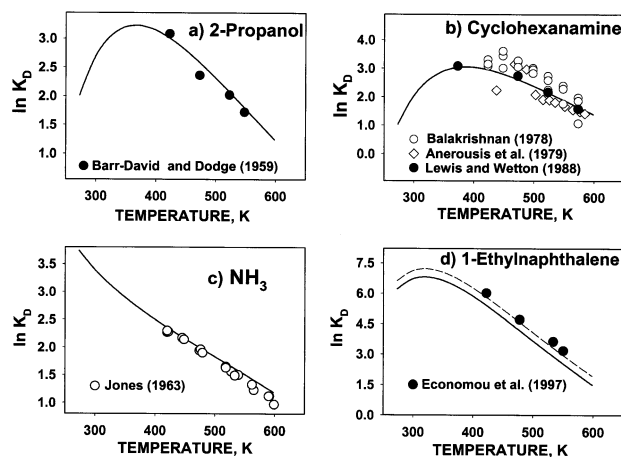

Fig. 6. Comparison of experimental (various symbols) and predicted (solid lines) values of the vapor–liquid distribution constants for some aqueous solutes. The dashed line shows predictions for 1-ethylnaphthalene with a different value of $\Delta_h G^o$ employed, see text.

$$\delta \ln K_D = [(\delta \ln \Phi_2^o)^2 + (\delta \ln k_H)^2]^{0.5}, \quad (23)$$

where δ stands for the uncertainty in each quantity. Let us discuss the expected errors in $\ln \Phi_2^o$ and $\ln k_H$ values.

From Eqn. 11, ignoring rather small errors in the second virial coefficients of pure water, B_{11}, we obtain

$$\delta \ln \Phi_2^o = \frac{2P_1^o}{RT} \delta B_{12}. \quad (24)$$

The errors in predicted B_{12} values, δB_{12}, are larger at low temperatures. However, the vapor pressure of water is rather low at ambient temperatures, and, therefore, the resulting errors in $\ln \Phi_2^o$ are also small at these conditions. For example, even an error as large as 3000 $cm^3 \cdot mol^{-1}$ in B_{12} around 300 K will result in an error of less than 0.01 in $\ln \Phi_2^o$. Both absolute values and uncertainties of the predicted B_{12} values are much larger for polar compounds. Some representative estimates of δB_{12} and $\delta \ln \Phi_2^o$ for nonpolar and polar solutes are given in Table 2.

There are several contributions to the errors in predicted k_H values. First, there is an "intrinsic" error due to the approximate character of Eqn. 16 for the temperature dependence of the standard partial molar heat capacity of hydration. This "intrinsic" error is appreciable for larger hydrophobic solutes and it is less for polar solutes. Second, errors in predicted values of k_H also arise because of uncertainties in the values of $\Delta_h G^o$, $\Delta_h H^o$,

Table 2. Expected uncertainties in the predicted in K_D values.

T,K	δB_{12}^a	$\delta \ln \Phi_2^o$	$\delta \ln k_H^b$	$\delta \ln K_D$
350	30–200[c]	0.001–0.006	0.02–0.03	0.02–0.03
450	15–50[c]	0.008–0.024	0.09–0.23	0.10–0.24
550	10–20[c]	0.027–0.054	0.24–0.73	0.25–0.73

[a] The lesser value refers to a typical nonpolar solute (n-pentane), and the larger value referes to a strongly polar compound (methanol).
[b] The lesser and larger values refer to "well-studied" and "poorly-studied" solutes, respectively; see text.
[c] Units: $cm^3 \cdot mol^{-1}$.

and $\Delta_h C_p^o$ at the reference isotherm. Considering all these sources of errors to be independent, we obtain the estimates of $\delta(\ln k_H)$ shown in the fourth column of Table 2. The smaller and larger error estimates refer to "well-studied" and "poorly-studied" solutes, for which the "intrinsic" errors are similar, but the uncertainties of $\Delta_h G^o(298)$, $\Delta_h H^o(298)$, and $\Delta_h C_p^o(298)$ are different. In these examples, values of $\delta \Delta_h G^o(298)$ are equal to ± 0.2 and ± 0.5 $kJ \cdot mol^{-1}$, $\delta \Delta_h H^o(298)$ are ± 0.5 and ± 2.0 $kJ \cdot mol^{-1}$, and $\delta \Delta_h C_p^o(298)$ are equal to ± 10 and ± 30 $J \cdot K^{-1} \cdot mol^{-1}$ for the "well-studied" and "poorly-studied" solutes, respectively. Very often, uncertainties in $\Delta_h G^o(298)$, $\Delta_h H^o(298)$ and $\Delta_h H^o(298)$, $\Delta_h C_p^o(298)$ pairs are correlated (if the enthalpy is determined from the temperature dependence of the Gibbs energy, or the heat capacity is evaluated from the temperature course of enthalpy data), therefore, we believe that the uncertainties of predicted $\ln k_H$ values in Table 2 are overestimated. However, in the case of solutes for which both $\Delta_h H^o(298)$ and $\Delta_h C_p^o(298)$ are estimated as described in Appendix B, the values of $\delta \ln k_H$ may bear large uncertainties.

From this discussion it follows that the main contributions to the uncertainties of predicted K_D values, $\delta(\ln K_D)$, listed in the last column of Table 2, arise from uncertainties in Henry's constants, $\delta(\ln k_H)$.

5.1.2. Examples of K_D Predictions

To perform the most stringent test of our methods to predict K_D values, only the thermodynamic functions of hydration at 298 K were employed, and the parameter b of Eqn. 17 was estimated using the empirical correlation with $\Delta_h G^o(298)$ and $\Delta_h C_p^o(298)$, according to Eqn. 19. In all cases the Tsonopoulos (1974) correlation was employed to calculate Φ_2^o, with the mixture-specific parameters k_{12} evaluated according to Plyasunov et al. (2003). Calculated values of K_D are compared with high-temperature experimental data in Figure 6 for 2-propanol, cyclohexanamine, ammonia and 1-ethylnaphthalene.

For 2-propanol (Fig. 6a) the values of $\Delta_h G^o$, $\Delta_h H^o$ and $\Delta_h C_p^o$ at 298 K are taken from our earlier compilation (Plya-

sunov and Shock, 2000a). The high-temperature K_D values are calculated by us from isothermal xy data (compositions of coexisting liquid and vapor phases) reported by Barr-David and Dodge (1959) as follows: first, we calculated values of concentration quotients, $Q = y/x$, for diluted solutions, where $x < 0.09$ (5 points at each isotherms), then we extrapolated these results to infinite dilution assuming the validity of approximation $\ln Q = \ln K_D + kx$, where k stands for the proportionality coefficient. The resulting $\ln K_D$ values are expected to have uncertainties of 0.1–0.2 in ln units.

For cyclohexanamine the values of the thermodynamic functions of hydration at 298 K are taken from Bergström and Olofsson (1975). As amines are used to regulate pH values of boiling water in steam power plants, there are 3 sets of experimental K_D values for cyclohexanamine at high temperatures. The scatter of experimental results is obvious in Figure 6b. The most accurate set of K_D values was reported by Lewis and Wetton (1988), who worked with low concentrations of solutes and employed dilute NaOH solutions to suppress the ionization of amines. Our prediction describes these data closely.

For ammonia the values of $\Delta_h G^o$, $\Delta_h H^o$ and $\Delta_h C_p^o$ at 298 K are collected in Table 1. The results of K_D predictions are compared in Figure 6c with experimental values measured by Jones (1963). Only above 550 K departures become significant.

The final example is presented for 1-ethylnaphthalene (Fig. 6d), with experimental K_D values evaluated from compositions of coexisting vapor and liquid phases measured along the three-phase equilibrium by Economou et al. (1997). The solid line in Figure 6d shows the calculated K_D results, which are obtained using the following data for the thermodynamic functions of hydration at 298 K, all calculated from the group contribution values of Cabani et al. (1981): $\Delta_h G^o = -1.91$ kJ $\cdot$ mol^{-1}, $\Delta_h H^o = -52.1$ kJ $\cdot$ mol^{-1} and $\Delta_h C_p^o = 429$ J $\cdot$ K^{-1} $\cdot$ mol^{-1}. One can see the systematic deviations between the experimental and predicted data. Changing the value of the Gibbs energy of hydration at 298 K to $\Delta_h G^o = -0.90$ kJ $\cdot$ mol^{-1} as determined by Altschuh et al. (1999), improves the agreement between experimental and calculated values as indicated by the dashed line in Figure 6d. This example demonstrates the importance of the accuracy of the thermodynamic properties of a solute at the reference isotherm.

In general, these examples confirm the success of the procedure proposed to predict the values of the vapor–liquid distribution constants of aqueous solutes up to 550 K, provided that there are reliable values of the thermodynamic functions of hydration for a solute of interest at 298 K.

5.2. Evaluation of the Krichevskii Parameter, A_{Kr}

As discussed in Section 2, the values of K_D at temperatures above 500 K already belong to the asymptotic slope given by Eqn. 7. This empirical finding introduces a simple way to evaluate the Krichevskii parameter, A_{Kr}, by using Eqn. 7 to calculate A_{Kr} from predicted K_D values at temperatures around 500, 525 and 550 K. The higher the temperature, the larger the uncertainties in the predicted K_D and, therefore, A_{Kr}, values are. On the other hand, there is always the possibility that, for a particular solute, the K_D value at lower temperature, say, 500 K, will deviate from the one given by the asymptotic relation. As a compromise, we gave equal weights to data at 500, 525,

and 550 K, when averaging A_{Kr} results calculated at these temperatures. Using values of $\delta \ln K_D$ obtained above, we estimate the uncertainties in the predicted values of A_{Kr} to be around $\pm$ 7 MPa and $\pm$ 20 MPa for the "well-studied" and "poorly-studied" solutes (as defined in Section 5.1.1), respectively, at least for hydrophobic solutes with positive values of A_{Kr}. Of course, large errors in the values of the thermodynamic functions of hydration of a solute at 298 K will result in errors of the predicted values of the Krichevskii parameter that are larger than these estimates, reemphasizing the importance of high-quality thermodynamic data at the reference isotherm.

In Table 3 we compare predicted and "experimental" values of the Krichevskii parameter for some aqueous solutes. Predictions were done for compounds for which there are both independent values of A_{Kr} reported in the literature and reliable values of the thermodynamic functions of hydration at 298 K. Predicted values of A_{Kr} are collected in Table 3, together with their estimated uncertainties, given in parentheses as the number of significant figures, so, 168.6(70) means 168.6 ± 7.0. The uncertainty of the calculated value of the Krichevskii parameter represents the standard deviation from the mean (calculated from K_D at 3 temperatures, 498, 523 and 548 K), if this standard deviation exceeds the minimal expected uncertainty of A_{Kr}. Otherwise, the uncertainties are given as $\pm$ 7.0 or $\pm$ 20 MPa. The values of $\Delta_h G^o$, $\Delta_h H^o$ and $\Delta_h C_p^o$ at 298 K employed in the calculations are given in footnotes in Table 3 for solutes not listed in Table 1. The necessary values of the fugacity coefficients are calculated using the square-well potential parameters for compounds or organic functional groups from Plyasunov et al. (2003).

Methods of calculating A_{Kr}, other than from variations of K_D in accordance with Eqn. 7, require accurate experimental data at near-critical conditions. We discussed methods for evaluating the Krichevskii parameter elsewhere (Plyasunov and Shock, 2001b), which may be consulted for further details about the abbreviations used in Table 3: CRL stands for the method of evaluating from the initial slopes of the critical line in a binary system; DB from dew-bubble curves; K_D from high-temperature vapor–liquid distribution constants; V_2^o from values of the partial molar volumes at near-critical conditions, obtained from highly accurate measurements of dilute solutions using a vibrating-tube densimeter; and PVTX from the volumetric studies of binary systems in the neighborhood of the critical point of water. "Global fit" means that the value of A_{Kr} is obtained through the overall fit of V_2^o, $\Delta_h G^o$, $\Delta_h H^o$ and $\Delta_h C_p^o$ data, including those at near-critical conditions, in the framework of the Fluctuation Solution Theory based model (Plyasunov et al., 2000b). The most accurate A_{Kr} results were obtained for a few solutes by Fernández-Prini et al. (2003) and Alvarez et al. (1994) after critical evaluation of high-temperature vapor–liquid equilibrium data ("gas solubility"). Our estimates of the Krichevskii parameters for these solutes are not completely independent of these publications. Indeed, we used $\Delta_h G^o$ results up to 570 K from these works when deriving Eqn. 19, which represents the core of our method to extrapolate k_H data up to 550 K. Nevertheless, the comparison for these solutes is valid, since we did not used their $\Delta_h G^o$ data at near-critical conditions, and our K_D predictions are absolutely independent of K_D data given by Fernández-Prini et al. (2003) and Alvarez et al. (1994). Methods for evaluating the Krichev-

Table 3. Calculated and "experimental" values of the Krichevskii parameter for some aqueous nonelectrolytes.

Compound	Formula	A_{Kr}[a,b]	Literature A_{Kr}[a] results
Helium	He	168.5(70)	168.4[c] K_D; 167.0[d] K_D
Neon	Ne	173.7(70)	186.3[c] K_D; 177.9[d] K_D
Argon	Ar	163.0(70)	171.7[c] K_D; 170.9[d] K_D; 130[c] CRL; 170.1[f] Global fit
Krypton	Kr	156.1(70)	169.2[c] K_D; 163.7[d] K_D
Xenon	Xe	148.4(70)	150.3[c] K_D; 148.7[d] K_D; 150.6[f] Global fit; 166(15)[g] V_2^o
Hydrogen	H_2	162.0(70)	169.9[c] K_D; 163.2[d] K_D; 150[e] CRL
Nitrogen	N_2	171.7(70)	177.5[c] K_D; 171.0[d] K_D; 180[e] CRL
Oxygen	O_2	166.1(70)	171.2[c] K_D; 163.6[d] K_D; 140[e] CRL
Carbon monoxide	CO	161.9(70)	174.3[c] K_D
Sulfur hexafluoride	SF_6	213.0(70)	214.5[c] K_D
Carbon dioxide	CO_2	121.7(70)	124.3[c] K_D; 118.2[d] K_D; 100[e] CRL; 127.2[f] Global fit; 130(10)[g] V_2^o
Hydrogen sulfide	H_2S	96.6(70)	98.0[c] K_D; 103[d] K_D; 100.9[f] Global fit; 105(10)[g] V_2^o
Ammonia	NH_3	44.4(70)	40[d] K_D; 47.1[f] Global fit; 52(10)[g] V_2^o; 42[h,i] (CRL); 43[j,i] (CRL)
Tetrafluoromethane	CF_4	202.8(70)[k]	210(20)[g] (CRL)
Methane	CH_4	162.6(70)	164.6[c] K_D; 158.2[d] K_D; 150[e] CRL; 166.1[f] Global fit; 163(10)[g] V_2^o
Ethane	C_2H_6	162.9(70)	159.3[c] K_D; 194(40)[g] DB
Propane	C_3H_8	153.8(70)	160(20)[g] CRL; 153(40)[g] DB
n-Pentane	C_5H_{12}	164.4(70)	181(30)[g] CRL; 180(40)[g] DB
n-Hexane	C_6H_{14}	169.0(70)	151(15)[g] CRL; 197(40)[g] DB; 170(10)[g] V_2^o; 96.4[l] PVTX
n-Heptane	C_7H_{16}	176.4(70)	234(40)[g] CRL; 167(40)[g] DB; 115.1[m] PVTX
n-Octane	C_8H_{18}	178.4(71)	191(7)[n,i] K_D; 127.5[m] PVTX
n-Dodecane	$C_{12}H_{26}$	191(12)[o]	152(30)[g] CRL
Ethene	C_2H_4	141.3(70)	142.6[f] Global fit; 176(15)[g] V_2^o
Propene	C_3H_6	135.8(70)	132(25)[g] CRL
l-Hexene	C_6H_{12}	149(20)	152(4)[n,i] K_D
l-Octene	C_8H_{16}	163(20)	177(10)[n,i] K_D
Cyclohexane	C_6H_{12}	145.3(70)	152(25)[g] CRL; 130(15)[g] V_2^o
Benzene	C_6H_6	93.6(70)	66(25)[g] CRL; 95(10)[g] V_2^o; 52.4[m] PVTX
Toluene	C_7H_8	100.0(70)	105(10)[g] V_2^o; 137.7[p] PVTX and CRL
Ethanol	C_2H_6O	37.7(70)	52(25)[g] CRL; 42[q,i] K_D
2-Propanol	C_3H_8O	52.9(70)[f]	50[r,i] K_D
Dimethylamine	C_2H_7N	78.7(70)[s]	75[t,i] K_D
Diethylamine	$C_4H_{11}N$	79.6(70)[u]	80[t,i] K_D
Piperidine	$C_5H_{11}N$	52.0(70)[v]	57[w,i] K_D; 67[t,i] K_D
Cyclohexanamine	$C_6H_{13}N$	55.3(70)[x]	57[w,i] K_D; 63[t,i] K_D; 53[y,i] K_D
2-(Diethylamino)ethanol	$C_6H_{15}NO$	35.9(70)[z]	41[t,i] K_D; 35[y,i] K_D

[a] MPa,[b] our evaluation from K_D using the method outlined in the text,[c] Fernández-Prini et al. (2003),[d] Alvarez et al. (1994),[e] Harvey et al. (1990),[f] Plyasunov et al. (2000b),[g] Plyasunov and Shock (2001b),[h] Rizvi and Heidemann (1987),[i] Our calculations of A_{Kr},[j] Sassen et al. (1990),[k] At 298 K: $\Delta_h G^o = 20.98$ kJ $\cdot$ mol^{-1} (Scharlin and Battino, (1994)), $\Delta_h H^o = -14.54$ kJ $\cdot$ mol^{-1}; $\Delta_h C_p^o = 268$ J $\cdot$ K^{-1} $\cdot$ mol^{-1} (Hallén and Wadsö, (1989)),[l] Abdulagatov et al. (2001),[m] Abdulagatov et al. (1998),[n] Heidman et al. (1985),[o] At 298 K: $\Delta_h G^o = 22.45$ kJ $\cdot$ mol^{-1}, $\Delta_h H^o = 54.96$ kJ $\cdot$ mol^{-1}; $\Delta_h C_p^o = 902$ J $\cdot$ K^{-1} $\cdot$ mol^{-1}, group contribution values (Plyasunov and Shock, (2000a)),[p] Kiselev et al., 2002,[q] Barr-David and Dodge (1959),[r] At 298K: $\Delta_h G^o = -11.93$ kJ $\cdot$ mol^{-1}, $\Delta_h H^o = -58.5$ kJ $\cdot$ mol^{-1}; $\Delta_h C_p^o = 272$ J $\cdot$ K^{-1} (Plyasunov and Shock, 2000a),[s] At 298 K: $\Delta_h G^o = -9.97$ kJ $\cdot$ mol^{-1}. $\Delta_h C_p^o = 194$ J $\cdot$ K^{-1} $\cdot$ mol^{-1} (Cabani et al. 1981); $\Delta_h H^o = -54.0$ kJ $\cdot$ mol^{-1} (Parker, 1965),[t] Balakrishnan (1988),[u] At 298 K: $\Delta_h G^o = -9.06$ kJ $\cdot$ mol^{-1}, $\Delta_h H^o = -65.12$ kJ $\cdot$ mol^{-1}; $\Delta_h C_p^o = 371$ J $\cdot$ K^{-1} $\cdot$ mol^{-1} (Cabani et al., 1981),[v] At 298 K: $\Delta_h G^o = -13.42$ kJ $\cdot$ mol^{-1}, $\Delta_h H^o = -65.41$ kJ $\cdot$ mol^{-1}; $\Delta_h C_p^o = 319$ J $\cdot$ K^{-1} $\cdot$ mol^{-1} (Cabani et al. 1981),[w] Lewis and Wetton (1988),[x] At 298 K: $\Delta_h G^o = -13.6$ kJ $\cdot$ mol^{-1}, $\Delta_h H^o = -66.2$ KJ $\cdot$ mol^{-1}; $\Delta_h C_p^o = 325$ J $\cdot$ K^{-1} $\cdot$ mol^{-1} (Bergström and Olofsson, 1975),[y] Anerousis et al. (1979),[z] At 298 K: $\Delta_h G^o = -19.7$ kJ $\cdot$ mol^{-1}, $\Delta_h H^o = -78.5$ kJ $\cdot$ mol^{-1} (preliminary results of our data evaluation); $\Delta_h C_p^o = 358$ J $\cdot$ K^{-1} $\cdot$ mol^{-1} (Cabani et al. 1981).

skii parameter, other than from K_D data, typically give values of A_{Kr} with relatively large uncertainties: we expect the typical uncertainty to be ± 25–40 MPa for CRL data, ± 40 MPa for DB data, ± 10–15 MPa for V_2^o data.

In our opinion, data in Table 3 strongly suggest that the method proposed allows evaluation of the Krichevskii parameter for many aqueous solutes with accuracy close to the best determinations currently available. We would like to emphasize the expected high accuracy of estimates of A_{Kr} from K_D data, where uncertainty of most determinations is less than ± 20 MPa. This level of accuracy is difficult to achieve when calculating A_{Kr} from, say, the initial slopes of the critical line or from the slope of dew-bubble curves, as a direct consequence of the differentiation of experimental data of limited accuracy. We used this method to calculate the values of the Krichevskii parameter for many inorganic compounds and halogenated

derivatives of methane and ethane. The results obtained are collected in Tables 4–6 together with necessary auxiliary data ($\Delta_h G^o$, $\Delta_h H^o$, $\Delta_h C_p^o$ at 298.15 K and parameters of the square-well potential).

5.3. Group Contribution Values of the Krichevskii Parameter for Aqueous Organic Solutes

5.3.1. Applicability of the Group Contribution Approximation for the Krichevskii Parameter of Aqueous Solutes

Using the method outlined above we evaluated values of the Krichevskii parameter in water for several members of the homologous series of normal alkanes and 1-alcohols. The results are shown in Figure 7, where values of A_{Kr} are plotted

Table 4. Thermodynamic properties of hydration at 298.15, 0.1 MPa for some inorganic compounds together with Krichevskii parameter and values of the C_o parameter (Eqn. 42) as well as the parameters for the square-well potential (Eqn. 12).

Solute	$\Delta_h G^{o a,b}$	$\Delta_h H^{o a,b}$	$\Delta_h C_p^{o a,c}$	$A_{Kr}{}^d$	C_o	$\lambda_{12}{}^e$	$\sigma_{12}{}^{e,f}$	$\varepsilon_{12}/k_B{}^{e,g}$
He[h]	19.44(3)[i]	−0.7(2)[i]	130(10)[i]	167.63	−35.13	—	2.35[j]	0
Ne[h]	19.07(3)[i]	−3.8(2)[i]	145(10)[i]	185.78	−88.65	1.454	2.533[k]	61.6[k]
Ar[h]	16.28(3)[i]	−12.0(1)[i]	200(10)[i]	175.16	−90.52	1.455	2.734[l]	211[l]
Kr[h]	14.83(3)[i]	−15.3(1)[i]	220(10)[i]	174.30	−111.38	1.454	3.21	253
Xe[h]	13.44(3)[i]	−19.0(2)[i]	250(10)[i]	149.74	−16.14	1.454	3.36	298
Rn	11.60(5)[m]	−21.4(10)[m]	293(15)[m]	125.8	6.69	1.458	3.49	337
SF$_6$[h]	20.62(10)[i]	−20.7(5)[i]	311(25)[i]	219.27	−155.85	1.358	3.74	308
N$_2$[h]	18.21(3)[i]	−10.4(3)[i]	214(10)[i]	177.95	−59.89	1.436	3.17	202
H$_2$[h]	17.73(3)[i]	−4.0(5)[i]	140(15)[i]	165.24	−29.38	1.454	2.38	111
NF$_3$	17.7(2)[n]	−15.5(20)[i]	293(50)[i]	163.3	−16.70	1.351	3.36	317
D$_2$	17.57(5)[o]	−4.6(5)[o]	160(20)[o]	156.0	−24.16	1.533	2.94	91.0
N$_2$F$_4$	17.5(1)[n]	−20.5(20)[n]	(260)[p]	195.9	−68.91	1.308	3.67	368
O$_2$	16.55(3)[i]	−12.1(1)[i]	200(5)[i]	170.82	−57.04	1.443	3.10	185
CD$_4$	16.30(3)[q]	−13.0(5)[q]	206(15)[q]	166.2	−39.22	1.438	3.25	241
CO[h]	17.19(3)[i]	−10.8(3)[i]	215(10)[i]	179.72	−103.90	1.398	3.19	215
NO	15.49(5)[n]	−11.9(10)[n]	190(30)[n]	157.3	−31.12	1.212	3.04	429
PH$_3$	11.91(10)[m]	−16.6(10)[m]	174(20)[m]	147.3	−38.45	1.356	3.25	418
AsH$_3$	11.69(10)[m]	−17.1(15)[m]	180(30)[m]	146.0	−38.42	1.401	3.38	410
NO$_2$	11.6(10)[r]	(−17.5)[p]	(193)[p]	143.1	−33.65	1.245	3.27	687
O$_3$	10.9(10)[n]	(−17.3)[p]	(189)[p]	133.7	−19.75	1.294	3.23	447
COS	9.5(10)[m]	(−15.0)[p]	(200)[p]	105.3	13.56	1.328	3.33	492
N$_2$O	9.2(1)[n]	−21.4(10)[n]	(180)[p]	138.2	−36.55	1.345	3.21	459
CO$_2$[h]	8.41(5)[i]	−19.7(1)[i]	180(10)[i]	121.23	−2.05	1.355	3.19	468
Cl$_2$	6.9(3)[n]	−23.4(10)[n]	(230)[p]	106.1	4.38	1.421	3.43	419
H$_2$Se	6.1(2)[m]	−15.7(20)[m]	76(30)[m]	114.6	−33.18	1.380	3.25	48
H$_2$S[h]	5.66(10)[i]	−18.0(15)[i]	144(10)[i]	98.86	−6.26	1.324	3.10	554
NOCl	1.1(1)[s]	(−27.6)[p]	(178)[p]	81.1	6.52	1.225	2.64	996
Br$_2$	0.8(3)[s]	−33.5(30)[s]	(179)[p]	106.2	−33.33	1.398	2.58	814
SO$_2$	−0.51(10)[n]	−27.0(3)[n]	155(10)[n]	69.5	11.33	1.249	3.07	857
N$_2$O$_3$	0.0(20)[r]	(−34.0)[p]	(188)[p]	94.7	−15.51	1.193	3.20	834
N$_2$O$_4$	0.0(20)[r]	(−37.0)[p]	(214)[p]	101.7	−25.05	1.286	3.52	702
ClO$_2$	0.0(2)[n]	−27.8(30)[n]	(175)[p]	71.7	13.89	1.216	2.80	1010
I$_2$	−2.4(30)[t]	(−37.5)[p]	(180)[p]	93.9	−36.45	1.401	2.49	1068
HCN	−5.0(10)[u]	−24.4(30)[u]	(81)[p]	36.1	26.75	1.183	2.72	1286
HN$_3$	−6.2(5)[n]	−33.0(30)[n]	(107)[p]	54.1	−0.19	1.183	2.80	1272
HNO$_2$	−9.6(5)[n]	−40.5(30)[n]	(111)[p]	52.9	−16.32	1.197	2.92	1296
NH$_3$	−10.1(1)[n]	−35.4(2)[n]	39(5)[n]	44.4	−10.40	1.248	2.04	1391
HF	−23.6(5)[s]	−49.0(5)[s]	−16(10)[v]	−16.1	4.60	1.209	2.48	1527
H$_2$O$_2$	−28.5(5)[n]	−54.9(5)[n]	19(10)[n]	−34.5	3.97	1.205	2.42	2052
N$_2$H$_4$	−31.3(5)[n]	−61.1(5)[n]	−34(10)[n]	−32.4	−10.85	1.226	2.28	1791

[a] At 298.15 K, 0.1 MPa,[b] kJ · mol^{-1},[c] J · k^{-1} · mol^{-1},[d] MPa,[e] From Plyasunov et al. (2003) unless otherwise indicated,[f] 10^{-10} m,[g] K,[h] K_D from Fernández-Prini et al. (2003) at 273–623 K were used,[i] see Table 1 for data sources,[j] from B_{12} at 200–1200 K (Hodges et al. 2002a),[k] from B_{12} at 200–1400 K (Hodges et al. 2002b),[l] from B_{12} at 200–2000 K (Hodges et al. 2002b),[m] Wilhelm et al. (1977),[n] see Table B1 for data source,[o] Muccitelli and Wen (1978),[p] calculated using the method outlined in Appendix B,[q] Gomes and Grolier (2001),[r] Schwartz and White (1983),[s] Wagman et al. (1982),[t] Benlhima et al. (1989) + Cox et al. (1989),[u] Kotlik and Lebedeva (1974),[v] Parker (1965).

against the number of the methylene groups, CH$_2$, in the structure of each solute. The compounds with zero methylene groups are ethane for n-alkanes and methanol for 1-alkanols, respectively. The uncertainty brackets represent the standard deviation from the mean, if it exceeds the expected minimal uncertainty of the evaluated A_{Kr} value, ± 7 MPa. The results suggest that the group additivity approximation holds for the Krichevskii parameter of aqueous organic solutes. Therefore, we adopted the group additivity approximation as an economic way to represent the A_{Kr} values for aqueous organic solutes.

The finding that the Krichevskii parameter follows the group additivity approximation is hardly surprising. Indeed, the properties of aqueous organic solutes both at high water densities, for example, the Gibbs energy of hydration, see Cabani et al. (1981); Plyasunov and Shock (2000b), and at low water densities, for example, the second cross virial coefficients, see

Plyasunov et al. (2003), are consistent with the group additivity approximation at different temperatures. So, one would expect that the Krichevskii parameter for aqueous organic solutes, as the property defined at the critical values of the density and temperature of water, can also be represented by a sum of the functional group contributions.

5.3.2. Krichevskii Parameter for an Ideal Gas (Material Point) as a Solute

When discussing the group contribution method for any property, it is always a useful idea to consider first the limiting case of a compound without any groups at all. This is the case of a material point, or a point mass, or an ideal gas, an abstract substance devoid of size and any interactions with themselves or with other compounds, including water. Group additivity
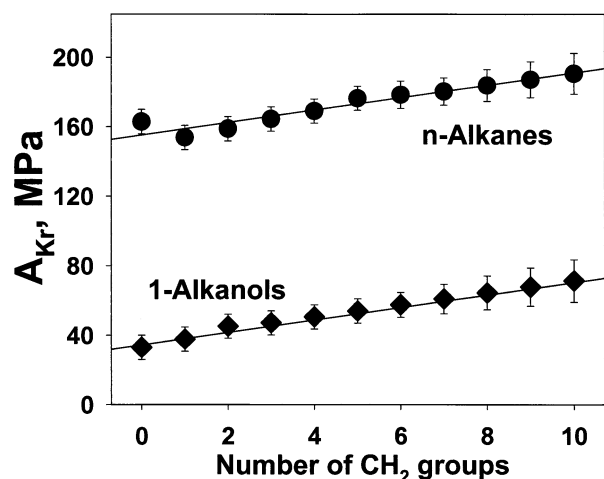
Fig. 7. Predicted values of A_{Kr} for members of homologous series of n-alkanes (filled circles) and 1-alkanols (filled diamonds) in water.

models for high-temperature properties of aqueous compounds, developed during the last decade beginning with the works from R. H. Wood laboratory (Criss and Wood, 1996; Yezdimer et al., 2000), include this contribution. Our point here is that the value of the Krichevskii parameter for an ideal gas in water, or in any other solvent, is not equal to zero, but has a finite positive value. Or in other words, counterintuitive as it may sound, the addition of a small amount of an ideal gas to a solvent at constant values of temperature and volume, equal to their critical values, see Eqn. 8, will increase the pressure of the system.

We are aware of two ways to evaluate the value of the Krichevskii parameter for an ideal gas (or for a material point, we do not distinguish between them).

1.). The first way: starting from Eqn. 4 one writes

$$RTlnK_D = \mu^o_{2,l} - \mu^o_{2,v} = \Delta_h G^o(l) - \Delta_h G^o(v), \quad (25)$$

where $\Delta_h G^o(l)$ and $\Delta_h G^o(v)$ denote the Gibbs energy of hydration of a solute in coexisting liquid and vapor phases, respectively. Based on theoretical models, see, for example, Pierotti (1976), the transfer of a material point (designated by mp) from an ideal gas to the standard aqueous solution is accompanied by a nonzero change of the Gibbs energy, equal to (for the mole fraction concentration scale):

$$\Delta_h G^o(mp) = RTln\frac{RT}{V^o_1}, \quad (26)$$

where V^o_1 stands for the molar volume of the solvent. Therefore, for the material point we have

$$RTlnK_D(mp) = RTln\frac{V^o_1(v)}{V^o_1(l)} = RTln\frac{\rho(l)}{\rho(v)}, \quad (27)$$

with subscripts v and l denoting, as before, the coexisting vapor and liquid phases of the solvent. The limiting behavior of the distribution constant for a material point at the solvent critical point can be found as follows (using the expansion $ln(1 + x) \approx x$ if $x \ll 1$ and ignoring higher order terms):

$$\lim_{T \to T_c} RTln\frac{V^o_1(v)}{V^o_1(l)} = \lim_{T \to T_c} RTln\frac{V^o_{1,c} + \delta V(v)}{V^o_{1,c} + \delta V(l)}$$

$$= \frac{RT_c}{V^o_{1,c}}(\delta V(v) - \delta V(l)), \quad (28)$$

where T_c and $V^o_{1,c}$ stand for the critical temperature and volume of the solvent; $\delta V(v) = V^o_1(v) - V^o_{1,c}$ and $\delta V(l) = V^o_1(l) - V^o_{1,c}$, with $V^o_1(v)$ and $V^o_1(l)$ being the molar volumes of coexisting vapor and liquid phases of the solvent, respectively. This equation should be compared with the following statement for the variations of K_D close to the critical point of the solvent

$$RTlnK_D = A_{Kr}(\delta V(v) - \delta V(l)), \quad (29)$$

which was obtained by Japas and Levelt Sengers (1989) and is a "precursor" of Eqns. 6 and 7. The comparison reveals that for the material point

$$A_{Kr}(mp) = \frac{RT_c}{V^o_{1,c}}. \quad (30a)$$

2). The second way: the theory of near-critical phenomena in dilute solutions (Chang et al., 1984) states that at the critical point of solvent, when approaching it along any path but the critical line of a binary system, one has

$$\lim_{x \to 0} \frac{V^o_2}{\kappa_T} = A_{Kr} \cdot V^o_{1,c}, \quad (31)$$

where κ_T stands for the isothermal compressibility of the pure solvent.

For an ideal gas (or material point) as a solute we have

$$V^o_2(mp) = \kappa_T RT. \quad (32)$$

Eqn. 32 may be obtained through the link between V^o_2 and the solute-solvent direct correlation function integral, C^o_{12} (O'Connell, 1990, 1994):

$$C^o_{12} = 1 - \frac{V^o_2}{\kappa_T RT}. \quad (33)$$

As the material point (no size, zero value of the solute-solvent potential energy of interactions) and solvent molecules are uncorrelated, then

$$C^o_{12} = 0 \quad (34)$$

and, therefore, we again come to Eqn. 32. Combining Eqns. 31 and (32) at the critical point of a solvent we obtain

$$A_{Kr}(mp) = \frac{RT_c}{V^o_{1,c}}, \quad (30b)$$

which is identical to Eqn 30a.

For the particular case of water we obtain $A_{Kr}(mp) = 96.17(90)$ MPa, where the main contribution to the uncertainty is due to ~1% uncertainty of the $V^o_{1,c}$ value (Levelt Sengers et al., 1985).

An anonymous reviewer of the original manuscript proposed a very simple and lucid way to obtain Eqn. 30: "Think of the definition of the Krichevskii parameter: $A_{Kr} = (\partial P/\partial x)_{VT}$. Fill a cell with 1 mol of a critical fluid, and ask what happens if an

infinitesimal amount of the fluid is replaced by a perfect gas. The gas just fills the space and does not see the fluid, which remains critical at the same temperature. Within two lines you will find the pressure increase, as we as the expression" (30). This is a very clear explanation from the point of view of physics, and the credit for it should be given to the anonymous reviewer.

5.3.3. Values of the Krichevskii Parameter for Functional Groups of Aqueous Organic Compounds

In accordance with the logic outlined above, the group contribution approximation for the Krichevskii parameter should be given as

$$A_{Kr} = A_{Kr}(mp) + \sum_i p_i A_{Kr,i} = \frac{RT_c}{V_{1,c}^o} + \sum_i p_i A_{Kr,i}, \quad (35)$$

where p_i stands for the number of a functional group i in the structure of a compound, and $A_{Kr,i}$ represents the contribution of the group i to the value of the Krichevskii parameter for this compound.

We treat every functional group as an individual compound, and used the procedure outlined above to evaluate the values of A_{Kr} for these functional groups. Note that to convert a functional group to an individual compound one should add the properties of the material point to the properties of the functional group. Then one uses the thermodynamic properties ($\Delta_h G^o$, $\Delta_h H^o$, $\Delta_h C_p^o$) of this "pseudo compound" to launch the procedure of evaluating A_{Kr} and $\ln K_D$. The final operation is to convert the properties of the "pseudo compound" to the properties of the functional group under consideration by extracting the values of A_{Kr} and $\ln K_D$ for the material point from the evaluated A_{Kr} and $\ln K_D$ data for the "pseudo compound."

For illustration of this procedure we consider the determination of the Krichevskii parameter for the OH functional group. The necessary parameters, $\Delta_h G^o$, $\Delta_h H^o$, $\Delta_h C_p^o$ λ_{12}, σ_{12}, ε_{12}/k_B, are given in Table 7. All the calculations are done for temperatures of 498.15, 523.15, and 548.15 K.

a). The first step is the calculation of $\ln \Phi_2^o$. Using Eqn. 12 we obtain B_{12} results equal to -171.8, -146.7, and -126.6 cm^3 · mol^{-1}. The values of B_{11} and the saturated water vapor pressure at these three temperatures are equal to -171.5, -148.3, -129.5 cm^3 · mol^{-1} and 2.550, 3.976, 5.946 MPa, respectively. Inserting these values in Eqn. 11 we obtain the values of $\ln \Phi_2^o$ of -0.106, -0.133, and -0.161.

b). The second step is the calculation of the Henry constant for the OH group by means of Eqn. 13. To begin with, we convert the functional group OH to the "pseudo compound" OH by adding the properties of the material point (the first group in Table 7) to those of the group OH. Therefore, for the "pseudo compound" OH we obtain at 298.15 K: $\Delta_h G^o = -25.40 + 7.96 = -17.44$ kJ · mol^{-1}, $\Delta_h H^o = -39.79 - 2.29 = -42.08$ kJ · mol^{-1}, and $\Delta_h C_p^o = 6 + 0 = 6$ J · K^{-1} · mol^{-1}. The parameter b of Eqn. 16 is determined from the correlation 19: b = $+0.333$ J · K^{-2} · mol^{-1} and then the parameter a of Eqn. 16 is calculated by means of Eqn. 18: a = -93.3 J · K^{-1} · mol^{-1}. Now all the necessary coefficients are known, and one calculates by means of Eqn. 17 the following values of the Gibbs energy of hydration of the "pseudo compound" OH at

498.15, 523.15, and 548.15 K: -2.38, -0.82, and $+0.63$ kJ · mol^{-1}, respectively. The corresponding values of $\ln k_H$ (Henry' constant is in bar units) are equal to 3.443, 3.827, and 4.155, as calculated from Eqn. 13.

c). The third step is the calculation of the vapor–liquid distribution constant for the "pseudo compound" OH by means of Eqn. 5. We will not forget to convert the water pressure to bar units. Values of $\ln K_D$ for temperatures of 498.15, 523.15, and 548.15 K are: 0.310, 0.277, 0.231.

d). The final step is the calculation of the Krichevskii parameter from these K_D results by means of Eqn. 7. Evaluations from $\ln K_D$ at these three temperatures result in the following values of A_{Kr}: 7.22, 7.26, and 6.92 MPa. By averaging these values, we finally accept for the "pseudo compound" OH the Krichevskii parameter equal to 7.13 MPa. To obtain A_{Kr} for the functional group OH, we extract from the obtained result the value of A_{Kr} for the material point equal to 96.17 MPa: 7.13–96.17 = -89.0 MPa, which is the value of the Krichevskii parameter for the group OH.

Values of the Krichevskii parameters for different functional groups, evaluated using this procedure, are given in Table 7 together with all relevant thermodynamic data ($\Delta_h G^o$, $\Delta_h H^o$, $\Delta_h C_p^o$ at 298.15 K and parameters of the square-well potential for B_{12}) for each group. Only the CH$_2$ group was treated differently. For this group the value of the Krichevskii parameter was determined from A_{Kr} values for the first ten members of homologous series of n-alkanes and 1-alkanols, see Figure 7. For some functional groups (CH$_3$, CH$_2$, CH, C = C, HC$_{ar}$, OH, CO, etc.) the values of the thermodynamic functions of hydration at 298.15 K are based on our comprehensive compilation of experimental data (Plyasunov and Shock, 2000a, 2001a) and are, probably, the most reliable values currently available. However, for many groups in Table 7 the values of $\Delta_h G^o$, $\Delta_h H^o$, $\Delta_h C_p^o$ are estimated by us from a single compound, therefore, we consider results for such groups to be preliminary. The preliminary results are shown in italics.

Some comments concerning group selection may be necessary. The C$_{ar}$-C$_{ar}$ group was found necessary to "construct" some aromatic compounds, because biphenyl, for example, is not identical to the sum of 10 HC$_{ar}$ and 2 C$_{ar}$ groups, so, it was decided to consider it as a sum of 10 HC$_{ar}$ groups and 1 C$_{ar}$-C$_{ar}$ group. The "fused" carbon group, C$_{fus}$, is necessary for polyaromatic hydrocarbons. We also define as separate groups CF$_3$, CCl$_3$ (completely halogenated groups) to account for possible nearest-neighbor effects, when the properties of two or more functional groups in close proximity due to intermolecular interactions differ from the properties of the same groups in "isolated" states (this is why we treat halogenated derivatives of methane and ethane as individual compounds; Tables 5 and 6). In general, we suggest using these groups to "construct" only monofunctional noncyclic compounds. The reason is that the simple first order group contribution method considered here may fail for polyfunctional compounds (i.e., containing more than one polar group, like OH, COH, NH, COO, etc.) due to its ignorance of proximity effects. As every cyclic compound bears different amount of "strain" energy, depending on its structure and elemental composition, each representative structure has to be treated separately. Of course, cyclic and polyfunctional solutes may be treated as

Table 5. Thermodynamic properties of hydration at 298.15, 0.1 MPa for some halogenated derivatives of methane together with Krichevskii parameter and values of the C_o parameter (Eqn. 42) as well as the parameters for the square-well potential (Eqn. 12).

Solute	$\Delta_h G^{oa,b}$	$\Delta_h H^{oa,b}$	$\Delta_h C_2^{oa,c}$	A_{Kr}^{d}	C_o	λ_{12}^{e}	$\sigma_{12}^{e,f}$	$\varepsilon_{12}/k_B^{e,g}$
CH_4	16.26(3)[h]	−13.1(1)[h]	216(10)[h]	164.52[i]	−37.70[i]	1.449	3.29	230
CH_3F	7.0(1)[h]	−18.1(20)[h]	151(40)[h]	108.9	−8.53	1.257	3.27	586
CH_3Cl	5.6(1)[h]	−23.2(10)[h]	195(40)[h]	103.6	−3.34	1.267	3.15	710
CH_3Br	4.5(3)[h]	−25.5(10)[h]	183(30)[h]	106.5	−14.07	1.258	3.15	737
CH_3I	4.1(5)[h]	−29.4(30)[h]	(206)[j]	112.9	−22.59	1.263	3.28	736
CH_2F_2	6.6(1)[k]	−19.8(20)[k]	(164)[j]	108.4	−8.35	1.232	3.29	667
CH_2Cl_2	2.2(3)[h]	−30.5(10)[h]	(249)[j]	83.2	16.15	1.298	3.47	671
CH_2Br_2	−0.2(3)[h]	−32.4(20)[h]	(201)[j]	83.8	−4.23	1.264	3.36	829
CH_2I_2	−2.1(5)[h]	−41.6(40)[h]	(232)[j]	98.5	−34.76	1.292	3.62	840
CH_2FCl	4.7(1)[h]	−21.7(20)[h]	154(40)[h]	101.1	−9.85	1.264	3.42	663
CH_2ClBr	1.0(5)[l]	(−31.0)[j]	(223)[j]	82.1	7.78	1.253	3.31	827
CH_2ClI	0.3(5)[h]	−35.8(40)[h]	(242)[j]	90.6	−5.08	1.261	3.40	815
CHF_3	10.9(2)[h]	−19.6(10)[h]	232(50)[h]	133.3	−14.81	1.244	3.33	538
$CHCl_3$	3.4(3)[h]	−32.1(10)[h]	(308)[j]	84.2	27.04	1.273	3.36	775
$CHBr_3$	−1.6(5)[h]	−35.8(30)[h]	(228)[j]	76.2	2.23	1.294	3.65	752
CHF_2Cl	8.4(2)[h]	−24.6(10)[h]	236(60)[h]	125.2	−13.47	1.261	3.42	573
$CHCl_2Br$	1.7(3)[h]	−32.4(30)[h]	(278)[j]	77.2	25.82	1.273	3.58	719
$CHClBr_2$	0.1(5)[h]	−33.3(30)[h]	(250)[j]	75.3	14.47	1.273	3.45	824
CF_4	21.0(1)[h]	−14.5(2)[h]	268(20)[h]	202.8	−60.84	1.373	3.51	264
CCl_4	8.2(3)[h]	−32.4(30)[h]	(390)[j]	108.6	26.55	1.367	4.01	463
CF_3Cl	17.3(2)[h]	−21.5(5)[h]	278(25)[h]	192.1	−61.61	1.309	3.58	372
CF_3Br	15.4(5)[m]	(−20.1)[j]	(261)[j]	171.2	−43.44	1.301	3.63	412
CF_2Cl_2	14.4(2)[h]	−26.0(5)[h]	315(15)[h]	169.6	−38.75	1.309	3.69	436
$CFCl_3$	11.2(5)[n]	−19.8(20)[n]	(330)[j]	102.2	42.61	1.314	3.78	492

[a] At 298.15 K, 0.1 MPa,[b] kJ · mol^{-1},[c] J · K^{-1} · mol^{-1},[d] MPa,[e] Values from Plyasunov et al. (2003),[f] 10^{-10} m,[g] K, see Table B1 for data sources,[i] K_D from Fernández-Prini et al. (2003) at 273–623 K are used,[j] calculated using the method outlined in Appendix B,[k] Abraham et al. (2001),[l] Tewari et al. (1982) + Stephenson and Malanowski (1987),[m] Cabani et al. (1981),[n] Hunter-Smith et al. (1983).

individual compounds, if all necessary auxiliary data are available for such calculations.

We note that values of the Krichevskii parameter are positive for most hydrocarbon groups and negative for all functional groups except CF_3. There is at least a qualitative correlation of A_{Kr} for a functional group with the strength of interactions between water and that functional group, and the most negative values of the Krichevskii parameter are for the groups that are expected to form hydrogen bonds with water like $CONH_2$, NH, COOH, OH, etc.

5.4. Temperature Dependence of the Vapor–Liquid Distribution Constants up to the Critical Temperature of Water

5.4.1. The General Analytical Form of the Correlating Equation

The temperature dependence of K_D over the whole temperature range of interest, i.e., between $T = 273.15$ K and $T_c = 647.096$ K, can be accurately reproduced by the following five-parameter equation (Alvarez et al., 1994; Fernández-Prini et al., 2003):

$$\ln K_D = \frac{E}{T} \cdot f(v) + (F + G \cdot v^{2/3} + H \cdot v) \cdot \exp\left(\frac{T_o - T}{100}\right) + I,$$

$$(36)$$

where $v = (1 - T/T_c)$; $T_o = 273.15$ K; $f(v) = \rho(1)/\rho_c - 1$; and E, F, G, H, I are the solute-specific coefficients. Alvarez et al. (1994) pointed out that one of the coefficients is not independent, since $K_D = 1$ at $T = T_c$, therefore,

$$I = -F \cdot \exp\left(\frac{T_o - T}{100}\right) \approx -0.023767 \cdot F. \quad (37)$$

As temperature approaches the critical temperature of a solvent, the contributions of the last terms in the right hand side of Eqn. 36 become exceedingly small, and the asymptotic relation, given by Eqn. 7, is recovered. The coefficient E is related to the Krichevskii parameter (Fernández-Prini et al., 2003) by

$$E = \frac{2A_{Kr}}{R\rho_c} \quad (38)$$

Although Eqn. 36 is successful for description of the temperature dependence of K_D of aqueous solutes, we decided to modify it to make it more suitable for group contribution approximation. We explicitly include in the correlating equation the "ideal gas" or "material point" term, with the general form of the equation to be

$$\ln K_D = n \cdot \ln\left(\frac{\rho(1)}{\rho(v)}\right) + \psi(v), \quad (39)$$

where n is a scaling coefficient to the material point term; and $\psi(v)$ is a not-yet-specified function of $v = (1 - T/T_c)$, which should become exceedingly small close to the critical point of water to recover the asymptotic form given by Eqn. 7. For the material point (or ideal gas) n = 1 and $\psi(v) = 0$. Eqn. 39 without the last term is practically identical to the equation

Table 6. Thermodynamic properties of hydration at 298.15, 0.1 MPa for some halogenated derivatives of ethene together with Krichevskii parameter and values of the C_o parameter (Eqn. 42) as well as the parameters for the square-well potential (Eqn. 12).

Solute	$\Delta_h G^{oa,b}$	$\Delta_h H^{oa,b}$	$\Delta_h C_p^{oa,c}$	A_{Kr}^d	C_o	λ_{12}^e	$\sigma_{12}^{e,f}$	$\varepsilon_{12}/k_B^{e,g}$
C_2H_4	13.25(10)[h]	−16.5(3)[h]	240(20)[h]	141.3	−19.42	1.413	3.46	332
C_2H_3Cl	7.6(3)[h]	−24.6(20)[h]	(248)[i]	113.3	−0.45	1.295	3.36	587
$1,1\text{-}C_2H_2Cl_2$	8.2(5)[h]	−25.8(20)[h]	(300)[i]	107.6	18.03	1.249	3.49	649
$1,2\text{-}C_2H_2Cl_2$	0.5(5)[h]	−32.8(5)[h]	258(10)[h]	71.4	28.39	1.355	3.78	504
C_2HCl_3	5.3(5)[h]	−32.4(20)[h]	(344)[i]	93.3	28.56	1.283	3.66	658
C_2F_4	16.0(5)[j]	−17.3(20)[j]	296(40)[j]	150.0	−0.67	1.354	3.66	342
C_2Cl_4	7.1(3)[k]	−41.5(30)[k]	407(50)[k]	134.6	−15.74	1.359	4.07	523

[a] At 298.15 K, 0.1 MPa, [b] kJ · mol^{-1}, [c] J · K^{-1} · mol^{-1}, [d] MPa, [e] Values from Plyasunov et al. (2003), [f] 10^{-10} m, [g] K, [h] see, Table B1 for data sources, [i] calculated using the method outlined in Appendix B, [j] Wilhelm et al.(1977), [k] Knauss et al. (2000).

$$\ln K_D = m \cdot \ln\left(\frac{\rho(v)}{\rho(1)}\right), \quad (40)$$

widely used by a number of research groups, most prominently by those of Styrikovich and Martynova in the USSR (Martynova, 1964, 1979; Styrikovich, 1969), for successful correlation of vapor–liquid distribution constants at elevated temperatures, with m often called "the hydration number" of a solute. Eqn. 39 is also related to equations that assume the proportionality of the standard chemical potential of solutes and the logarithm of the density of a solvent (Marshall, 1970; Marshall, 1972; Marshall and Mesmer, 1984). Without exploring these interconnections, we note that previous attempts to derive Eqn. 40 used the idea of hydrate formation. We obtain Eqn. 39 by scaling the rigorous equation for the material point and adding the low-temperature $\psi(v)$ function. The theory says that this form is correct in the neighborhood of the critical point of a solvent (Japas and Levelt Sengers, 1989). A vast amount of experimental K_D data, which were successfully correlated by Eqn. 40, provides ample empirical evidence that Eqn. 39 will be successful for most volatile and nonvolatile aqueous solutes.

Preliminary tests showed that the satisfactory form of the low-temperature function $\psi(v)$ can be obtained by the following relation

$$\psi(v) = v^3 \cdot (C_o + C_1 \cdot v + C_2 \cdot v^2). \quad (41)$$

Therefore, for individual compounds the $K_D(T)$ correlating equation is given by

$$\ln K_D = n \cdot \ln\left(\frac{\rho(1)}{\rho(v)}\right) + v^3 \cdot (C_o + C_1 \cdot v + C_2 \cdot v^2). \quad (42)$$

The coefficient n, the scaling factor of A_{Kr} of a solute compared to that of the material point, is related to the Krichevskii parameter (in MPa) by means of:

$$n = A_{Kr}\frac{V_{1,c}^o}{RT_c} \approx \frac{A_{Kr}}{96.17}. \quad (43)$$

5.4.2. Additional Constraints on Coefficients of the Correlating $K_D(T)$ Equation

In the spirit of the method proposed above to evaluate K_D values at elevated temperatures, we want to provide consistency of the coefficients of Eqn. 42 with the values of $\Delta_h G^o$ and $\Delta_h H^o$ at 298.15 K and 0.1 MPa. This can be done through the link between K_D, k_H and $\Delta_h G^o$, see Eqn. 5 and (13). At 298 K one can neglect deviations of the fugacity coefficient, Φ_2^o, from 1 (if a solute is similar to water, then the error introduced by this is less than 5 J · mol^{-1} for $\Delta_h G^o$ and less than 50 J · mol^{-1} for $\Delta_h H^o$), accepting that

$$\ln K_D = \ln k_H - \ln P_1^o - \ln \Phi_2^o \approx \ln k_H - \ln P_1^o. \quad (44)$$

Combining Eqns. 13 and 42 yields analytical relations for $\Delta_h G^o$ and $\Delta_h H^o$:

$$\frac{\Delta_h G(T)}{RT} = \ln P_1^0 - \ln\frac{1000}{M_W} + n \cdot \ln\left(\frac{\rho(1)}{\rho(v)}\right) + v^3 \cdot (C_o + C_1 \cdot v + C_2 \cdot v^2) \quad (45)$$

and

$$-\frac{\Delta_h H(T)}{RT^2} = \frac{d \ln P_1^0}{dT} + n \cdot \left(\frac{1}{\rho(1)} \cdot \frac{d\rho(1)}{dT} - \frac{1}{\rho(v)} \cdot \frac{d\rho(v)}{dT}\right)$$
$$+ 3 \cdot v^2 \cdot \left(\frac{dv}{dT}\right) \cdot ((C_o + C_1 \cdot v + C_2 \cdot v^2)) + v^3 \cdot (C_1 + 2 \cdot C_2 \cdot v) \cdot \left(\frac{dv}{dT}\right), \quad (46)$$

where

$$\frac{dv}{dT} = -\frac{1}{T_c},$$

and analytical statements for $\ln P_1^o$, $d\ln P_1^o/dT$, $\rho(1)$, $d\rho(1)/dT$, $\rho(v)$, and $d\rho(v)/dT$ are given in Appendix A.

At the reference temperature, 298.15 K, one obtains the following linear relations between $\Delta_h G^o$ and $\Delta_h H^o$ (both in kJ · mol^{-1}) and the coefficients of Eqn. 42:

$$\Delta_h G^o = -18.513 + 26.4600 \cdot n + 0.388721 \cdot C_o + 0.209617 \cdot C_1 + 0.113036 \cdot C_2 \quad (47)$$

and

Table 7. Thermodynamic properties of hydration at 298.15, 0.1 MPa for functional groups of organic compounds together with Krichevskii parameter and values of the C_o parameter (Eqn. 42) as well as the parameters for the square-well potential (Eqn. 12). Results considered preliminary are given in italics.

Group	$\Delta_h G^{o a,b}$	$\Delta_h H^{o a,b}$	$\Delta_h C_p^{o a,c}$	$A_{Kr}^{\ d}$	C_o	$\lambda_{12}^{\ e}$	$\sigma_{12}^{\ e,f}$	$\varepsilon_{12}/k_B^{\ e,g}$
Material point[h]	7.96[i]	−2.29[i]	0[i]	96.17[j]	0.0	—	0	0
CH_3	3.63[i]	−7.54[i]	132[i]	29.39	−12.31	1.430	2.788	283.8
CH_2	0.72[i]	−3.76[i]	64[i]	3.55[k]	5.04[l]	1.430	2.226	271.4
CH	−1.79[i]	−0.9[i]	−2[i]	−14.89	8.60	1.439	1.73	260
C	−4.50[i]	2.6[i]	−63[i]	−40.15	24.59	1.464	−2.421	265.7
$C(CH_3)_2$	2.76[m]	−12.48[m]	201[m]	18.79	9.59	1.420	2.957	261.4
$C(CH_3)_3$	6.39[m]	−20.02[m]	333[m]	48.65	0.84	1.394	3.668	304
$H_2C=CH$	*1.5[n]*	*−10.5[n]*	*170[n]*	*7.8*	*12.91*	*1.348*	*2.96*	*446*
HC=CH	*−2.41[n]*	*−6.8[n]*	*105[n]*	*−29.8*	*40.20*	*1.341*	*2.51*	*525*
$H_2C=C$	*−2.41[n]*	*−6.8[n]*	*105[n]*	*−29.7*	*39.85*	*1.356*	*2.58*	*504*
HC=C	*−6.32[n]*	*−3.1[n]*	*40[n]*	*−67.4*	*67.56*	*1.348*	*1.89*	*702*
C=C	*−10.23[i]*	*−0.6[i]*	*−25[i]*	*−105.3*	*95.92*	*1.368*	*1.54*	*753*
C_2H_2	*1.5[o]*	*−12.31[o]*	*150[o]*	*6.26*	*4.94*	*1.368*	*3.39*	*404*
HC=C	*−4.45[p]*	*−8.89[p]*	*85[p]*	*−34.4*	*33.08*	*1.304*	*2.72*	*662*
C=C	*−8.36[i]*	*−5.19[i]*	*20[i]*	*−71.3*	*58.10*	*1.404*	*2.48*	*647*
HC_{ar}	−0.65[i]	−5.00[i]	48[i]	0.29	−2.65	1.435	2.202	439
C_{ar}	−3.85[i]	−0.67[i]	−50[i]	−20.5	−1.76	1.376	1.63	859
C_{fus}	*−2.4[q]*	*−2.3[q]*	*−21[q]*	*−7.9*	*−7.69*	*1.449*	*0.77*	*1419*
C_{ar}—C_{ar}	*−4.56[r]*	*1.3[r]*	*−185[r]*	*8.1*	*−62.38*	*1.430*	*0.52*	*1910*
Cyclic CH_2	0.83[i]	−5.36[i]	79[i]	6.89	−0.06	1.435	2.294	316
CF_3	*6.6[s]*	*−4.3[s]*	*130[s]*	*47.0*	*−23.81*	*1.303*	*3.02*	*314*
CCl_3	*−4.7[t]*	*−19.3[t]*	*(225)[t]*	*−36.0*	*52.70*	*1.285*	*3.28*	*647*
N	*−24.5[u]*	*−26.8[u]*	*−128[u]*	*−95.8*	*2.17*	*1.354*	*2.51*	*816*
NH	*−25.2[v]*	*−34.8[v]*	*−70[v]*	*−85.3*	*−8.76*	*1.295*	*2.68*	*928*
NH_2	*−23.0[w]*	*−37.4[w]*	*−27[w]*	*−63.5*	*−24.71*	*1.276*	*2.70*	*988*
O	*−15.6[x]*	*−22.1[x]*	*−77[x]*	*−39.2*	*−30.76*	*1.308*	*2.49*	*780*
HS	*−9.2[y]*	*−14.9[y]*	*(38)[y]*	*−40.9*	*12.95*	*1.298*	*2.69*	*815*
S	*−13.7[x]*	*−14.1[z]*	*−36[z]*	*−68.1*	*21.38*	*1.301*	*2.72*	*818*
COO	*−20.3[aa]*	*−22.7[aa]*	*−50[aa]*	*−94.4*	*27.14*	*1.253*	*2.94*	*920*
F	*−4.6[bb]*	*−8.3[bb]*	*19[bb]*	*−17.7*	*2.38*	*1.330*	*2.34*	*515*
Cl	*−5.1[cc]*	*−13.7[cc]*	*67[cc]*	*−11.8*	*−6.31*	*1.327*	*2.50*	*814*
Br	*−7.1[dd]*	*−15.7[dd]*	*51[dd]*	*−19.2*	*−6.08*	*1.293*	*2.51*	*852*
I	*−7.5[ee]*	*−19.6[ee]*	*(74)[ee]*	*−12.8*	*−14.70*	*1.296*	*2.76*	*810*
COH	*−18.3[ff]*	*−22.3[ff]*	*−41[ff]*	*−76.5*	*10.42*	*1.236*	*2.85*	*1043*
CO	*−22.68[gg]*	*−23.2[gg]*	*−93[gg]*	*−98.7*	*10.93*	*1.232*	*2.76*	*1266*
CN	*−21.5[hh]*	*−24.9[hh]*	*6[hh]*	*−111.6*	*48.61*	*1.206*	*2.75*	*1354*
NO_2	*−20.5[ii]*	*−25.9[ii]*	*18[ii]*	*−101.6*	*41.73*	*1.210*	*2.87*	*1231*
$CONH_2$	*−44.3[kk]*	*−60.8[kk]*	*−37[kk]*	*−153.5*	*−17.90*	*1.188*	*3.08*	*1829*
CONH	*−48.8[ll]*	*−56.3[ll]*	*−108[ll]*	*−205.6*	*30.00*	*1.190*	*3.14*	*1703*
CON	*−46.9[ll]*	*−46.3[ll]*	*−210[ll]*	*−207.4*	*34.79*	*1.220*	*3.08*	*1430*
COOH (Acid)	*−33.0[mm]*	*−43.0[mm]*	*−32[mm]*	*−141.2*	*36.03*	*1.355*	*2.49*	*1136*
H-COOH	*−29.4[nn]*	*−44.6[nn]*	*50[nn]*	*−118.9*	*26.86*	*1.369*	*2.31*	*1352*
OH	−25.40[i]	−39.79[i]	6[i]	−89.0	6.14	1.182	2.56	1349

[a] At 298.15 K, 0.1 MPa,[b] kJ · mol^{-1},[c] J · K^{-1} · mol^{-1},[d] MPa,[e] from Plyasunov et al. (2003) unless otherwise indicated,[f] 10^{-10} m,[g] K,[h] for a material point n = 1, G=H=F=O,[i] Plyasunov and Shock (2000a),[j] see Eq. (34),[k] by optimization of A_{Kr} for n-alkanes and 1-alkanols,[l] by optimization of ln K_D for the CH_2 group as calculated from ln K_D data for n-alkanes and 1-alkanols,[m] as a sum of values for CH_3 and C groups from Plyasunov and Shock (2000a),[n] as a sum of values for C=C and H groups from Plyasunov and Shock (2000),[o] as the values for ethyne from Plyasunov and Shock (2000a) minus the contribution of the material point,[p] as a sum of values for C=C and H groups from Plyasunov and Shock (2000a),[q] calculated from data for naphthalene (Cabani et al. 1981),[r] calculated from data for biphenyl: $\Delta_h G^o = -3.1$ kJ · mol^{-1} (Cabani et al. 1981); $\Delta_h H^o = -51$ kJ · mol^{-1}; $\Delta_h C_p^o = 295$ J · K^{-1} · mol^{-1} (our preliminary evaluation),[s] calculated using data for trifluoroethanol from Table B1,[t] calculated using data for 1,1,1-trichloroethane from Table B1,[u] calculated using data for trimethylamine from Table B1,[v] calculated using data for dimethylamine from Table B1,[w] calculated using data for methylamine from Table B1,[x] calculated using data for diethyl ether from Table B1,[y] calculated using data for ethanethiol from Table B1,[z] calculated using data for dimethylsulfide from Table B1,[aa] calculated using data for methyl acetate from Table B1,[bb] calculated using data for fluoromethane from Table B1,[cc] calculated using data for 1,3-dichloropropane from Table B1,[dd] calculated using data for bromomethane from Table B1,[ee] calculated using data for iodomethane from Table B1,[ff] calculated using data for acetaldehyde: $\Delta_h G^o = -6.7$ kJ · mol^{-1}; $\Delta_h C_p^o = 91$ J · K^{-1} · mol^{-1} (Cabani et al. 1981); $\Delta_h H^o = -32$ kJ · mol^{-1} (our preliminary evaluation),[gg] Plyasunov and Shock (2001a),[hh] calculated using data for acetonitrile from Table B1,[ii] calculated using data for nitromethane from Table B1,[kk] calculated using data for acetamide from Table B1,[ll] our preliminary evaluation,[mm] calculated using data for acetic acid from Table B1,[nn] calculated using data for formic acid from Table B1.

$$\Delta_h H^o = -44.064 + 41.8239 \cdot n + 0.996405 \cdot C_o$$
$$+ 0.716414 \cdot C_1 + 0.482907 \cdot C_2. \quad (48)$$

Solving the system of Eqns. 47 and (48) relative to the coef-

ficients C_1 and C_2, one obtains analytical statements for these coefficients of Eqn. 42, which automatically provide consistency with the values of the Gibbs energy and enthalpy of hydration at 298.15 K, 0.1 MPa:

$$C_1 = 195.562 + 23.853 \cdot \Delta_h G^o - 5.58336 \cdot \Delta_h H^o$$

$$- 3.70886 \cdot C_o - 397.631 \cdot n \quad (49)$$

and

$$C_2 = -198.877 - 35.3869 \cdot \Delta_h G^o + 10.354 \cdot \Delta_h H^o$$

$$+ 3.43891 \cdot C_o + 503.294 \cdot n. \quad (50)$$

One has to remember that relations 47–50 are obtained using the approximations that at the reference isotherm, 298.15 K, $\Phi_2^o = 1$ and $d\Phi_2^o/dT = 0$. Therefore, these relations will be inaccurate for cases where errors due to these approximations exceed the uncertainties of $\Delta_h G^o$ and $\Delta_h H^o$ at 298 K (examples of these cases are highly accurate measurements of solubility in water for a few gases, see Fernández-Prini et al., 2003). However, for the overwhelming majority of solutes errors introduced due to these approximations are of little practical concern.

There are two reasons why we did not explore the possibility of providing consistency between the coefficients of the K_D-correlating equation and the values of the standard partial molar heat capacity of hydration of a solute at 298 K. First, the "intrinsic" error of approximation given by Eqn. 44 appears to exceed the experimental uncertainty of $\Delta_h C_p^o$. Second, even for the best studied solutes K_D values can be successfully reproduced by the four-term Eqn. 41, and it appears that there is no need for an additional term.

5.4.3. The Fitting Procedure and the Coefficients of Eqn. 42 for Individual Solutes

We employ the four-term Eqn. 42 together with the three constraints, which are discussed in the previous Sections, to correlate the temperature dependence of the vapor–liquid distribution constants for aqueous solutes. As a result, the value of only one coefficient of Eqn. 42, chosen to be C_o, is determined by the least-squares procedure. The value of the coefficient n is fixed using the accepted value of the Krichevskii parameter (see Section 5.2) in accordance with Eqn. 43, and Eqns. 49 and (50) allow us to fix values of the coefficients C_1 and C_2. In the spirit of this approach, we collect in Tables 4–6 values of $\Delta_h G^o$, $\Delta_h H^o$, A_{Kr} for each of the solutes rather than values of n, C_1, C_2, because all these properties are linearly related. Two sets of the generated ln K_D data are employed in the least-square fit for each solute. The first set consists of the ln K_D values at 273–498 K generated as discussed in Section 5.1. In addition, the ln K_D values at 573, 598 and 623 K are calculated by means of Eqn. 7 using the accepted value of the Krichevskii parameter for the solute under consideration.

A slightly different procedure was employed for gases, for which accurate values of K_D are recommended over the whole temperature range of interest by Fernández-Prini et al. (2003). In these cases we employ ln K_D values at 273– 623 K as recommended by these authors. We also require consistency with the selected values of $\Delta_h G^o$ and $\Delta_h H^o$ at 298.15 K. As we want to describe ln K_D data for these solutes as close to the recommended values as possible, we allow two parameters, A_{Kr} and C_o, to be freely adjustable. As a result, the values of the Krichevskii parameter obtained differ from those in Fernández-Prini et al. (2003). However, the difference is small,

less than 6 MPa for all solutes and less than 3 MPa for 9 from 14 solutes. When employing Eqn. 42 to calculate the vapor–liquid distribution constants, A_{Kr} results from Table 4, not from Table 3, should be used. For the 14 solutes the maximal difference between the recommended and our fitted values is less than 0.02 log unit at temperatures between 273 and 600 K for 12 solutes, and is less than 0.04 log unit for all solutes at all temperatures (273 to 623 K). Slight variations within the expected accuracy of the accepted values of $\Delta_h G^o$, $\Delta_h H^o$, $\Delta_h C_p^o$ at 298 K could improve the goodness of the fit at low temperatures. However, this was decided not to be worthwhile, especially taking into account that recommendations of Fernández-Prini et al. (2003) at T < 333 K, as admitted by these authors, are not in perfect agreement with highly accurate data available in this temperature range.

5.4.4. The Fitting Procedure and the Coefficients of Eqn. 42 for Functional Groups of Organic Compounds in Water

As discussed above, a property of an individual organic compound can be represented as the sum of the properties of functional groups times the number of these groups in the structure of the compound plus the corresponding property of the material point:

$$\Xi = \Xi(mp) + \sum_i p_i \Xi_i, \quad (51)$$

Ξ is the property of interest, and p_i stands for the number of a functional group i in the structure of a compound.

There are many reasons to expect the applicability of the group contribution approximation to ln K_D values for aqueous organic solutes. Indeed, Henry's constant for these compounds follow group additivity both at 298 K and at elevated temperatures (Cabani et al., 1981; Plyasunov and Shock, 2000b). In addition, because B_{12} data can be reproduced by the group contribution method (Plyasunov et al., 2003), it follows from Eqn. 11 that $\ln \Phi_2^o$ must be consistent with the additivity principle at least up to 550 K, the expected temperature range of validity of Eqn. 11. Taking into account Eqn. 5, these results ensure the applicability of the group contribution method to ln K_D up to 550 K. On the other hand, if the Krichevskii parameter for organic solutes can be represented as the sum of contributions of functional groups, then it follows from Eqn. 7 that the same is true for ln K_D at temperatures in excess of 500–550 K. Likewise, one can show that all the coefficients of Eqn. 42 will follow the group contribution approximation.

Again, we treat every functional group as an individual compound, and use the procedure outlined above to evaluate the values of the coefficient F for functional groups of organic solutes. As in the case of individual compounds, values of the coefficients C_1 and C_2 can be calculated from Eqns. 49 and (50). Note again that first a functional group has to be converted to an individual compound by adding the properties of the material point to the values of $\Delta_h G^o$, $\Delta_h H^o$, and A_{Kr} for this functional group. Then the values of $\Delta_h G^o$, $\Delta_h H^o$, and A_{Kr} for a "pseudo compound" constructed in this way are employed to evaluate the necessary coefficients C_1 and C_2 using Eqns. 49 and (50). These C_1 and C_2 coefficients for the "pseudo compound" are identical to ones for the functional group, because

C_1 and C_2 for the material point are both equal to zero. We discussed in Section 5.3.3 the procedure for evaluating A_{Kr} and ln K_D values for the "pseudo compound." The resulting A_{Kr} and ln K_D data are employed in the fit to determine the coefficient C_0, which has a numerical value identical for both the "pseudo compound" and the functional group under consideration. The reader who is willing to employ our group contribution method for calculating K_D values for organic solutes in water should follow these procedures to calculate correctly the necessary C_1 and C_2 values.

Only for the CH_2 group was the procedure slightly different, with ln K_D values being determined from the values of ln K_D generated for the first ten members of homologous series of *n*-alkanes and 1-alkanols.

All restrictions on the use of the group contributions discussed for the case of A_{Kr} also apply for the case of the coefficients of the ln K_D correlating equation. It is known that the group contribution method may be inaccurate for the first few members of a homologous series. In this case the solutes with low carbon number may better be treated as individual compounds.

6. DISCUSSION

This work is concerned with the evaluation of the vapor–liquid distribution constants, K_D, for many aqueous solutes over the whole temperature range of existence of this equilibrium, i.e., from 273 K to the critical temperature of water, $T_c = 647.1$ K. The vapor–liquid distribution constant, rather than Henry's constants or the derivatives of the chemical potential appears to be the property for which accurate prediction of high-temperature values can be made. This unique position of distribution constants arises from two main factors. First, there are theoretical constraints on the temperature variations of this property at T>500–550K. Second, the relatively short temperature extrapolation of values of the chemical potentials of solutes from 300 to 500–550 K is rather routine in hydrothermal geochemistry. Combination of these two factors allows the accurate prediction of K_D all the way up to the critical temperature of water.

K_D values may be directly employed for modeling the distribution of solutes between the coexisting vapor and liquid phases of water. In addition, values of K_D for nonpolar compounds can be combined with fugacity coefficients of these compounds evaluated from the cubic equations of state to obtain values of Henry's constants, k_H, for aqueous solutes at temperatures up to T_c. This route appears to be the most accurate way to calculate k_H for nonpolar solutes at temperatures in excess of 550 K. It is not expected that the traditional cubic equations of state can be used to evaluate Φ_2^o for polar solutes in water. However, for a few polar solutes, for example ethanol, *n*-propylamine, etc., accurate values of k_H at high temperatures can be calculated by the thermodynamic integration of experimental $C_{p,2}^o$ and V_2^o data. In these cases the combination of K_D and k_H allows evaluation of Φ_2^o, and such data are scarce for polar solutes in water. In other words, the relation between k_H, K_D, and Φ_2^o, given by Eqn. 5, if explored properly, can supply a wealth of thermodynamic information.

The single property that governs the thermodynamics of dilute near-critical mixtures is the Krichevskii parameter, A_{Kr}.
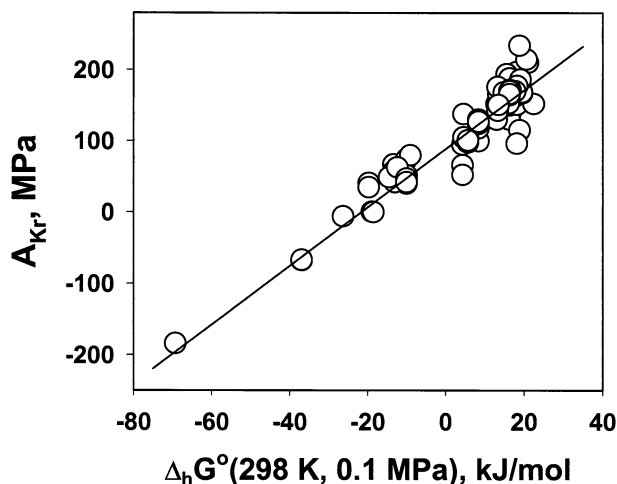

Fig. 8. The correlation between A_{Kr} and $\Delta_h G°$ for aqueous solutes. "Experimental" values of A_{Kr}, given by circles, are those collected in Plyasunov and Shock (2001b) and in Table 3. The solid line is consistent with the correlating equation given by Plyasunov and Shock (2001b).

As one of many examples of its utility, we mention that the derivatives of the chemical potential of a solute (V_2^o, $C_{p,2}^o$) at near-critical conditions are proportional to the Krichevskii parameter. Therefore, even approximate values of A_{Kr} will be very helpful in improving the reliability of predictions of the thermodynamic properties of aqueous solutes at high temperatures. So far the Krichevskii parameter was a rather exotic property with accurate values available for a very few aqueous solutes. This contribution provides estimates of A_{Kr} for many volatile nonelectrolytes in water, using methods that appear to be accurate as judged by comparison of predictions with the limited set of "experimental" A_{Kr} values currently available. The expected uncertainty of the predicted values of the Krichevskii parameter is comparable to that of the best "experimental" A_{Kr} data. As a matter of fact, we expect that the accuracy of A_{Kr} prediction is mainly limited by the accuracy of the thermodynamic functions of hydration for solutes at 298.15 K. If data for $\Delta_h G°$, $\Delta_h H°$, or $\Delta_h C_p^o$ at 298.15 K employed in the calculations are inaccurate, then the evaluated A_{Kr} values may be seriously in error.

Earlier we (Plyasunov and Shock, 2001b) proposed a linear correlation between the Krichevskii parameter for aqueous solutes and the Gibbs energy of hydration of those solute at 298.15 K as a way of estimating A_{Kr} (Fig. 8). This correlation was considered purely empirical. However, using the formalism outlined in this work, one obtains the following statement for A_{Kr}:

$$A_{Kr} = \frac{\rho_c^2}{\rho - \rho_c}\{\Delta_h G°(T_r) - \Delta_h S°(T_r)(T - T_r) + \int_{T_r}^{T} \Delta_h C_p^o(T)dT$$

$$- T\int_{T_r}^{T}\frac{\Delta_h C_p^o(T)}{T}dT - RT\ln\frac{\Phi_2^o P_1^o}{(1000/M_w)}\} \quad (52)$$

This equation shows that there is indeed the linear relation

between A_{Kr} and $\Delta_h G^o(298)$, if the reference temperature T_r is chosen to be 298 K. In addition, as shown in Appendix B, existing experimental $\Delta_h G^o$, $\Delta_h H^o$, and $\Delta_h C_p^o$ data at 298 K are strongly correlated. On the other hand the term containing Φ_2^o is relatively small. All these considerations suggest that the correlation between A_{Kr} and $\Delta_h G^o(298)$ must have some merit. Nevertheless, the method outlined in this work provides a more thermodynamically sound way of evaluating A_{Kr}.

7. CONCLUSIONS

This work presents the results of prediction of the vapor–liquid distribution constants, K_D, for many aqueous solutes up to the critical temperature of water. We propose a simple method for evaluating K_D using readily available information, namely the values of the thermodynamic functions of hydration for a solute at 298.15 K and 0.1 MPa. The comparison of our predictions with a few available K_D data at high temperatures reveals the satisfactory performance of the proposed method. The present method can be used for evaluating the Krichevskii parameter, which governs the thermodynamics of a solute in the neighborhood of the critical point of a solvent, for volatile nonelectrolytes in water. It appears that the accuracy of predictions of both vapor–liquid distribution constants and the Krichevskii parameter are limited mainly by the accuracy of the values of the thermodynamic functions of hydration of solutes at 298 K, and that the best way to improve the quality of predictions of K_D and A_{Kr} is to increase the inventory of accurate calorimetric enthalpy and heat capacity data for aqueous solutes at 298 K. Values of K_D and A_{Kr} are predicted for many inorganic volatile nonelectrolytes and halogenated derivatives of methane and ethene. We show that both ln K_D and A_{Kr} for aqueous organic solutes follow group additivity and we derive a set of the corresponding group contribution values for several functional groups (material point, CH_3, CH_2, CH, C, $C = C$, $HC = CH$, $C≡C$, HC_{ar}, C_{ar}, C_{fus}, OH, O, S, SH, CO, COO, COH, COOH, CN, F, Cl, Br, NH_2, NH, N, etc.).

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Appendix A. Some Properties of Water from the IAPWS Formulation

The International Association for the Properties of Water and Steam (IAPWS) adopted in 1995 a new formulation of the thermodynamic properties of water, with the formal publication following in 2002 (Wagner and Pruß, 2002). We used this formulation to calculate the properties of water.

a). The temperature dependence of the second virial coefficient of water, B_{11}, in units $cm^3 \cdot mol^{-1}$, is given by the following statement:

$$B_{11}(\tau) = \frac{10^3}{M_w} \cdot \frac{1}{\rho_c} \sum_{i=1}^{7} n_i \cdot \tau^{t_i}, \qquad (A1)$$

where M_w stands for the molar mass of water, $M_w = 18.015268$ g · mol^{-1}; $\rho_c = 322$ kg · mol^{-1} is the critical density of water; $\tau = T_c/T$, with $T_c = 647.096$ K being the critical temperature of water; and values of n_i and t_i are given in Table A1. All numerical values are from Wagner and Pruß (2002). Eqn. A1 supplies B(T) values that are reasonable up to very high temperatures, even up to 12000 K. The following values (up to six significant figures), which were provided to us by Prof. Wagner, can be used to verify calculations: 300 K, $B_{11} = -1201.30$ $cm^3 \cdot mol^{-1}$; 1273 K, $B_{11} = -6.70720$ $cm^3 \cdot mol^{-1}$; 12000 K, $B_{11} = 10.8451$ $cm^3 \cdot mol^{-1}$.

b). Pressure along the vapor–liquid equilibrium for water, P_1° in MPa, is given by:

$$\ln\left(\frac{P_1^\circ}{P_c}\right) = \frac{T}{T_c}[a_1 \upsilon + a_2 \upsilon^{1.5} + a_3 \upsilon^3 + a_4 \upsilon^{3.5} + a_5 \upsilon^4 + a_6 \upsilon^{7.5}], \quad (A2)$$

and the temperature derivative of the pressure, in MPa · K^{-1}, is

$$\frac{dP_1^\circ}{dT} = -\frac{P_1^\circ}{T}\left[\ln\left(\frac{P_1^0}{P_c}\right) \right.$$
$$+ a_1 + 1.5a_2\upsilon^{0.5} + 3a_3\upsilon^2 + 3.5a_4\upsilon^{2.5}$$
$$\left. + 4a_5\upsilon^3 + 7.5a_6\upsilon^{6.5} \right], \quad (A3)$$

Table A1. Coefficients of Eqns. A1 to A7.

i	t_i	n_i	a_i	b_i	c_i
1	−0.5	$0.125\ 335\ 479\ 355\ 23 \times 10^{-1}$	−7.859 517 83	1.99274064	−2.03150240
2	0.875	$0.789\ 576\ 347\ 228\ 28 \times 10^1$	1.844 082 59	1.09965342	−2.68302940
3	1	$-0.878\ 032\ 033\ 0.35\ 61 \times 10^1$	−11.786 649 7	−0.510839303	−5.38626492
4	4	−0.668 565 723 079 65	22.680 741 1	−1.75493479	−17.2991605
5	6	0.204 338 109 509 65	−15.961 871 9	−45.5170352	−44.7586581
6	12	$-0.662\ 126\ 050\ 396\ 87 \times 10^{-4}$	1.801 225 02	$-6.74694450.10^5$	−63.9201063
7	7	−0.107 936 009 089 32			

$v = (1 - T/T_c)$, $P_c = 22.064$ MPa, and the numerical values of coefficients a_i are collected in Table A1.

c). Saturated liquid density, $\rho(l)$, in $kg \cdot m^{-3}$, and its temperature derivative, are given by:

$$\rho(l) = \rho_c(1 + b_1 v^{1/3} + b_2 v^{2/3} + b_3 v^{5/3} + b_4 v^{16/3} + b_5 v^{43/3} + b_6 v^{110/3})$$

(A4)

and

$$\frac{d\rho(l)}{dT} = -\frac{\rho_c}{3T_c}(b_1 v^{-2/3}$$
$$+ 2b_2 v^{-1/3} + 5b_3 v^{2/3} + 16b_4 v^{13/3} + 43b_5 v^{40/3}$$
$$+ 110b_6 v^{107/3}) \quad (A5)$$

where the numerical values of coefficients b_i are collected in Table A1.

c). Saturated vapor density, $\rho(v)$, in $kg \cdot m^{-3}$, and its temperature derivative, are given by:

$$\rho(v) = \rho_c \cdot Exp(c_1 v^{2/6} + c_2 v^{4/6} + c_3 v^{8/6} + c_4 v^{18/6} + c_5 v^{37/6} + c_6 v^{71/6})$$

(A6)

and

$$\frac{d\rho(v)}{dT} = -\frac{\rho(v)}{6T_c}(2c_1 v^{-4/6}$$
$$+ 4c_2 v^{-2/6} + 8c_3 v^{12/6} + 18c_4 v^{12/6} + 37c_5 v^{31/6} +$$
$$71c_6 v^{65/6}) \quad (A5)$$

where the numerical values of coefficients c_i are collected in Table A1.

Note that the Eqns. A2–A7 are not exactly the IAPWS formulation, which results in equations for the properties of the coexisting phases that are too complicated and lengthy. They are auxiliary equations, endorsed by the authors of the IAPWS formulation, and the difference between results from Eqns. A2–A7 and the IAPWS formulation is said to be extremely small.

Appendix B. Empirical Correlations for Estimating the Standard Partial Molar Enthalpy and the Heat Capacity of Hydration of Neutral Compounds at 298.15 K, 0.1 MPa

For many neutral compounds there are no experimental determinations of the standard partial molar heat capacity in water. The reasons may be numerous: a calorimetric experiment is expensive; many neutral compounds have low solubility in water and only a few laboratories in the world have the expertise and equipment for making accurate calorimetric measurements for such compounds (Gill and Wadsö, 1982; Olofsson et al., 1984; Dec and Gill, 1985; Hallén and Wadsö, 1989). In addition to calorimetric determinations, values of the partial molar heat capacities may be obtained from solubility measurements performed over extended temperature ranges by means of the double differentiation of the Gibbs energy of solution (Wilhelm et al., 1977; Rettich et al., 1981, 1984, 2000). However, this method requires extreme accuracy and, probably, will be of no use for compounds undergoing chemical reactions in water (chlorine, COS, NO_2, for example), or dissociation (HNO_2), polymerization (HF), or decomposition (NH_2Cl, HN_3), where even moderate uncertainties in the values of the thermodynamic and kinetic constants of side reactions will strongly compromise the reliability of data interpretation.

Typically, values of the enthalpy of hydration are available for a large number of compounds, either from calorimetric measurements or from determinations of solubility at different temperatures. Still, there are many neutral compounds for which the experimental determinations of the enthalpy of hydration are of uncertain quality or lacking altogether.

These gaps can be overcome by methods to estimate the standard partial molar heat capacity of hydration, $\Delta_h C_p^o$, and enthalpy of hydration, $\Delta_h H^o$, for neutral compounds at 298.15 K and 0.1 MPa. For organic compounds, group contribution methods may be successful for predicting the thermodynamic functions of hydration. However, a general estimation method must account for how the chemical compo-
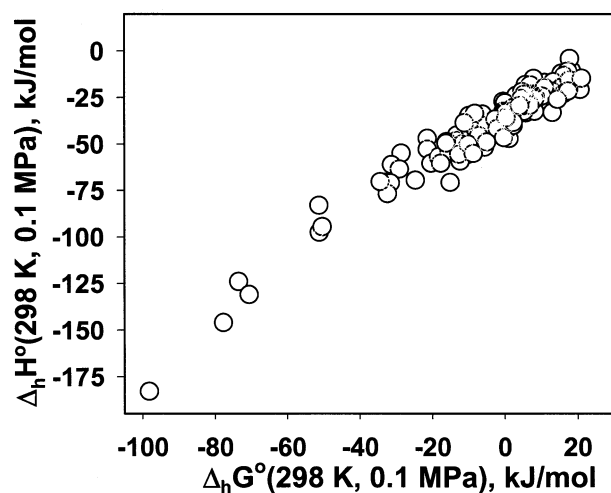

Fig. B1. The correlation between $\Delta_h G^o$ and $\Delta_h H^o$ values at 298 K for compounds listed in Table B1.

sition and the structure determine the thermodynamic properties of a compound. For example, at 298 K the Gibbs energies of hydration of ethanol and dimethyl ether, two compounds of identical composition, C_2H_6O, differ by ~ 13 kJ $\cdot$ mol^{-1} (in other words the equilibrium constants for identical reactions involving these compounds will differ by ~ 190 times!).

Evidently chemical composition alone does not determine the thermodynamic functions of hydration of a compound, and ways must be devised to account for the different chemical structures of compounds and details of their interactions with water, a fundamental problem that has yet to be solved. Possible empirical approaches to the problem of estimation of $\Delta_h H^o$ and $\Delta_h C_p^o$ are outlined here. The starting point for this discussion is the fact, mentioned above, that compounds of identical composition but different structures have markedly different values of Gibbs energy of hydration, $\Delta_h G^o$. In this sense, values of $\Delta_h G^o$ can serve as explicit proxies of chemical composition, structure of a compound, and strength of water-solute interactions. From a pragmatic point of view, values of the Gibbs energy (contrary to the heat capacity and enthalpy) are the most readily available of all thermodynamic functions of hydration, because they are experimentally measured for several hundred chemical compounds, at least at 298 K.

There is a definite correlation between the values of $\Delta_h G^o$ and $\Delta_h H^o$ for neutral compounds at 298.15 K and 0.1 MPa, as shown in Figure B1. Unfortunately, this correlation is of low accuracy: it describes 118 $\Delta_h H^o$ data points in Table B1 (see below) with a standard deviation of 6.6 kJ $\cdot$ mol^{-1} and for 42 compounds (more than 1/3 of all solutes in Table B1) the difference between the experimental and fitted results exceeds 6 kJ $\cdot$ mol^{-1}. A more accurate approximation can be built on the assumption that deviations from the (presumably universal) correlation between $\Delta_h G^o$ and $\Delta_h H^o$ depend on the elemental chemical composition of individual solutes. Mathematically this can be expressed as:

$$\Delta_h H^o = f(\Delta_h G^o) + \sum_{i=1} b_i \, n(i) + \sum_{i=1} c_i \, n(i)^2 + \ldots, \quad (B1)$$

where $f(\Delta_h G^o)$ is some universal function of the Gibbs energy of hydration; the index i stands for the chemical elements constituting a given solute, so i = C,H,O,N,S,F,Cl,...; $n(i)$ represents the number of atoms of a particular chemical element in a formula of a compound; and b_i and c_i are numerical constants, specific for each chemical element i under consideration.

To determine an appropriate functional form of $f(\Delta_h G^o)$, and to retrieve the optimal values of the numerical coefficients, we selected a set of data, that contains 118 experimental $\Delta_h G^o$ and $\Delta_h H^o$ values for diverse chemical compounds in the C-H-O-N-S-F-Cl-Br-I system (Table B1). This set contains both inorganic and organic compounds. We

Table B1. Experimental values of $\Delta_h H^o$ and $\Delta_h C_p^o$ and those fitted by means of Eqns. B1 and B2.

Compound	Formula	$\Delta_h G^{oa}$	$\Delta_h H^{oa}$ Experimental	Calculated	Δ	$\Delta_h C_p^{ob}$ Experimental	Calculated	Δ
Compounds in the subsystem H-N-O							
Nitrogen	N_2	18.21(3)[c]	−10.4(3)[c]	−10.2	−0.2	214(10)[c]	200	14
Oxygen	O_2	16.55(3)[d]	−12.0(1)[d,e,f]	−9.8	−2.2	200(5)[d,f,g]	200	0
Hydrogen	H_2	17.73(5)[h]	−4.0(5)[h]	−6.8	2.8	140(15)[h]	161	−21
Nitrogen oxide	NO	15.49(5)[h]	−11.9(10)[h]	−11.5	−0.4	190(30)[h]	188	2
Dinitrogen oxide	N_2O	9.2(1)[h]	−21.4(10)[h]	−20.3	−1.1	143(50)[h]	183	−40
Nitrous acid	HNO_2	−9.6(5)[i]	−40.5(30)[i]	−38.1	−2.4		111	
Hydrogen azide	HN_3	−6.2(5)[j]	−33.0(30)[j]	−36.5	2.6		107	
Ammonia	NH_3	−10.1(1)[k,l]	−35.4(2)[m]	−36.5	1.1	39(5)[n]	69	−30
Ozone	O_3	10.9(10)[o]	−16.8(30)[o]	−17.3	0.5		189	
Hydrogen peroxide	H_2O_2	−28.5(5)[o]	−54.9(5)[o]	−55.5	0.6	19(10)[p,q]	6	13
Hydrazine	N_2H_4	−31.3(5)[o]	−61.1(5)[o]	−63.9	2.8	−34(10)[r]	8	−42
Compounds in the subsystem H-C-N-O							
Carbon monoxide	CO	17.19(3)[s]	−10.8(3)[s]	−7.6	−3.2	215(10)[s]	205	10
Carbon dioxide	CO_2	8.41(5)[t]	−19.7(1)[u,v]	−17.6	−2.1	180(10)[w]	183	−3
Formic acid	CH_2O_2	−21.4(5)[x]	−46.9(20)[o]	−49.1	2.2	50(10)[y]	55	−65
Nitromethane	CH_3NO_2	−8.9(5)[z]	−35.7(10)[y]	−42.4	7.3	150(20)[aa]	131	19
Methane	CH_4	16.26(3)[bb]	−13.1(1)[f,cc]	−12.9	−0.2	216(10)[w,dd]	212	4
Methanol	CH_4O	−13.2(2)[ee]	−45.1(2)[ee]	−41.7	−3.4	114(5)[ee]	107	7
Urea	CH_4N_2O	−51.3(20)[ff+gg]	−83 (6)[ff+gg]	−91.2	8.2	30(20)[hh]	−36	66
Methylamine	CH_5N	−11.4(3)[o]	−47.2(10)[o]	−42.7	−4.5	105(5)[y]	129	−24
Ethyne	C_2H_2	7.89(15)[ee]	−14.6(3)[ee]	−17.1	2.5	150(20)[ee]	161	−11
Acetonitrile	C_2H_3N	−9.9(5)[ii]	−34.7(5)[y]	−38.7	4.0	138(10)[jj]	109	29
Ethene	C_2H_4	13.25(10)[ee]	−16.5(3)[ee]	−16.4	−0.1	240(20)[ee]	220	20
Acetic acid	$C_2H_4O_2$	−21.4(5)[x]	−52.8(20)[y]	−54.0	1.2	100(10)[y]	107	−7
Acetamide	C_2H_5NO	−32.7(15)[y]	−70.6(20)[kk+ll]	−68.8	−1.8	95(5)[y]	80	15
N-Methylformamide	C_2H_5NO	−29.1(10)[mm]	−63.5(20)[kk+nn]	−64.9	1.4	92(10)[y]	84	8
Glycine	$C_2H_5NO_2$	−73.5(20)[oo+pp]	−124 (5)[qq+pp]	−122.2	−1.8	−51(20)[rr+ss]	−42	−9
Ethane	C_2H_6	15.57(5)[ee]	−19.4(2)[ee]	−18.3	−1.1	280(20)[ee]	260	20
Ethanol	C_2H_6O	−13.0(2)[ee]	−52.6(2)[ee]	−46.4	−6.2	199(5)[ee]	165	34
Ethanediol	$C_2H_6O_2$	−33.0(10)[tt]	−72.3(20)[h]	−70.2	−2.1	114(10)[y]	93	21
Dimethylamine	C_2H_7N	−10.0(3)[y]	−52.2(20)[o]	−46.2	−6.0	194(10)[y]	189	5
2-Aminoethanol	C_2H_7NO	−31.6(20)[uu]	−71.0(20)[vv]	−71.3	0.3	91(15)[y]	101	−10
Ethylenediamine	$C_2H_8N_2$	−32.4(20)[ww]	−76.8(10)[xx+nn]	−74.9	−1.9	93(10)[xx]	116	−23
Propionitrile	C_3H_5N	−8.1(5)[y]	−39.7(10)[y]	−41.8	2.1	208(15)[jj+ss]	172	36
Propene	C_3H_6	12.9(2)[ee]	−21.6(3)[ee]	−21.6	0.0	280(30)[ee]	267	13
Cyclopropane	C_3H_6	11.0(1)[ee]	−23.3(4)[ee]	−23.2	−0.1	310(20)[ee]	258	52
Acetone	C_3H_6O	−8.2(3)[yy]	−41.5(3)[yy]	−43.0	1.5	158(10)[yy]	187	−29
Methyl acetate	$C_3H_6O_2$	−5.1(3)[zz]	−40.1(5)[aaa]	−43.0	2.9	214(10)[jj]	223	−9
Alanine	$C_3H_7NO_2$	−70.6(20)[oo+pp]	−131 (6)[oo+pp]	−123.2	−7.8	24(20)[rr+ss]	35	−11
Propane	C_3H_8	16.1(1)[ee]	−22.9(3)[ee]	−22.8	−0.1	330(30)[ee]	307	23
Propylamine	C_3H_9N	−10.4(5)[y]	−55.8(10)[y]	−51.5	−4.3	231(15)[y]	230	1
2-Methoxyethanol	$C_3H_8O_2$	−20.4(5)[y]	−60.4(10)[y]	−61.7	1.3	187(10)[y]	183	4
Glycerol	$C_3H_8O_3$	−51.2(20)[a+eee]	−97.5(20)[ddd]	−99.2	1.7	124(15)[ddd+ss]	85	39
Trimethylamine	C_3H_9N	−5.6(5)[y]	−51.7(10)[o]	−47.0	−4.7	268(15)[eee]	253	15
Succinic acid	$C_4H_6O_4$	−50.4(30)[ff+ggg]	−94.5(30)[xx+ggg]	−98.6	4.1	94(15)[xx+ss]	107	−13
Tetrahydrofuran	C_4H_8O	−6.6(5)[y]	−47.3(5)[y]	−46.4	−0.9	211(10)[y]	250	39
2-Butanone	C_4H_8O	−7.2(3)[yy]	−45.5(3)[yy]	−47.0	−1.5	234(10)[yy]	240	6
1,4-Dioxane	$C_4H_8O_2$	−13.2(5)[y]	−48.0(5)[y]	−55.6	7.6	127(10)[y]	219	−92
Morpholine	C_4H_9NO	−24.7(10)[hhh]	−69.5(15)[y]	−70.0	0.5	142(10)[iii+ss]	202	−60
Diethyl ether	$C_4H_{10}O$	1.1(5)[y]	−47.0(20)[y]	−43.1	−3.9	315(50)[y]	320	−5
1,2-Dimethoxyethane	$C_4H_{10}O_2$	−12.3(5)[y]	−59.3(10)[y]	−58.5	−0.8	244(10)[y]	274	−30
Pyridine	C_5H_5N	−11.7(5)[y]	−49.9(10)[y]	−47.6	−2.3	228(10)[y]	218	10
Tetrahydrofuran	$C_5H_{10}O$	−51.5(5)[y]	−48.9(10)[y]	−49.9	1.0	286(10)[iii]	299	−13
Xylose	$C_5H_{10}O_5$	−77.3(3)[kkk+lll]	−146 (5)[lll+mmm]	−145.9	−0.1	100(30)[mmm+ss]	126	−26
Phenol	C_6H_6O	−18.3(10)[ooo]	−56.9(10)[y]	−56.4	−0.5	211(10)[y]	221	−10
Aniline	C_6H_7N	−15.4(10)[ppp]	−54.0(10)[qqq]	−56.1	2.1	199(10)[y]	236	−37
4-Methylpyridine	C_6H_7N	−12.7(5)[y]	−55.5(10)[y]	−53.5	−2.0	277(10)[y]	261	16
Cyclohexane	C_6H_{12}	13.0(2)[ee]	−33.1(3)[ee]	−36.2	3.1	410(30)[ee]	402	8
Cyclohexanol	$C_6H_{12}O$	−15.1(3)[ee]	−70.7(7)[ee]	−64.4	−6.3	340(15)[ee]	326	14
Glucose	$C_6H_{12}O_6$	−98.2(30)[kkk+lll]	−183 (6)[lll+mmm]	−183.8	0.8	132(30)[nnn+ss]	139	−7
4-Methylphenol	C_7H_8O	−17.7(10)[y]	−60.4(10)[y]	−60.7	0.3	259(10)[y]	269	−10
Compounds containing S							
Sulfur dioxide	SO_2	−0.51(10)[m]	−27.0(3)[m]	−25.4	−1.6	155(10)[m]	158	−3
Hydrogen sulfide	H_2S	−5.66(10)[sss]	−18.0(15)[sss]	−17.9	−0.1	144(10)[ttt]	154	−10
Methanethiol	CH_4S	3.1(3)[uuu]	−23.8(30)[uuu]	−25.0	1.2		186	

Table B1. continued

Compound	Formula	$\Delta_h G^{\circ a}$	$\Delta_h H^{\circ a}$			$\Delta_h C_p^{\circ b}$		
			Experimental	Calculated	Δ	Experimental	Calculated	Δ
Ethanethiol	C_2H_6S	3.1(3)[vvv]	−28.5(30)[vvv]	−29.9	1.4		234	
Dimethylsulfide	C_2H_6S	1.5(5)[vvv]	−31.5(2)[www]	−31.3	−0.2	228(10)[www+ss]	231	−3
Dimethyldisulfide	$C_2H_6S_2$	0.1(5)[vvv]	−34.7(3)[www]	−33.8	−0.9	286(15)[www+ss]	272	14
Diethylsulfide	$C_4H_{10}S$	1.2(5)[vvv]	−40.2(3)[www]	−41.4	1.2	318(15)[www+ss]	322	−4
Diethyldisulfide	$C_4H_{10}S_2$	1.0(5)[vvv]	−41.3(5)[www]	−42.8	1.5	363(20)[www+ss]	365	−2
Dimethyl sulfoxide	C_2H_6SO	−34.4(10)[xxx]	−70.3(20)[xxx]	−70.1	−0.9	97(10)[y]	101	−4
	Compounds containing F							
Sulfur hexafluoride	SF_6	20.62(10)[h]	−20.7(5)[g]	−20.1	−0.6	311(25)[g]	316	−5
Dinitrogen tetrafluoride	N_2F_4	17.5(1)[h]	−20.5(20)[h]	−22.7	2.2		260	
Nitrogen trifluoride	NF_3	17.7(2)[h]	−15.5(20)[h]	−15.8	0.3	190(50)[h]	224	69
Fluoromethane	CH_3F	7.0(1)[h]	−18.1(20)[h]	−21.5	3.4	151(40)[h]	159	−8
Trifluoromethane	CHF_3	10.9(2)[yyy]	−19.6(10)[yyy]	−20.5	0.9	232(50)[yyy]	199	33
Tetrafluoromethane	CF_4	21.0(1)[h]	−14.5(2)[g]	−13.7	−0.8	268(20)[g]	262	6
1,1-Difluoroethane	$C_2H_4F_2$	7.45(10)[yyy]	−23.1(20)[yyy]	−27.2	4.1	230(40)[yyy]	214	16
1,1,1,2-Tetrafluoroethane	$C_2H_2F_4$	10.2(1)[yyy]	−24.2(20)[yyy]	−27.1	2.9	280(50)[yyy]	243	37
Trifluoroethanol	$C_2H_3F_3O$	−10.1(5)[y]	−50.1(20)[y]	−47.0	−3.1	200(20)[zzz]	186	14
	Compounds containing Cl							
Chlorine	Cl_2	6.9(3)[o]	−23.4(30)[o]	−20.0	−3.4		230	
Chlorine dioxide	ClO_2	0.0(2)[y]	−27.8(30)[y]	−27.7	−0.1		175	
Nitrogen trichloride	NCl_3	5.7(15)[aaaa]	−33.2(50)[aaaa]	−28.7	−4.5		315	
Dichloroamine	$NHCl_2$	−8.3(20)[aaaa]	−33.5(50)[aaaa]	−39.2	5.7		165	
Chloramine	NH_2Cl	−11.2(20)[aaaa]	−38.6(50)[aaaa]	−39.8	1.2		115	
Hypochlorous acid	$HClO$	−16.1(20)[bbbb]	−48.7(40)[bbbb]	−41.9	−6.8		108	
Chloromethane	CH_3Cl	5.6(1)[y]	−23.2(10)[y]	−23.8	0.6	195(40)[y]	207	−12
Dichloromethane	CH_2Cl_2	2.2(3)[cccc]	−30.5(10)[dddd+nn]	−28.9	−1.6		249	
Chloroform	$CHCl_3$	3.4(3)[cccc]	−32.1(10)[dddd+nn]	−30.0	−2.1		308	
Carbon tetrachloride	CCl_4	8.2(3)[cccc]	−32.4(30)[eeee,ffff]	−28.1	−4.3		390	
Chlorofluoromethane	CH_2ClF	4.7(1)[y]	−21.7(20)[y]	−25.7	4.0	154(40)[y]	198	−44
Chlorodifluoromethane	$CHClF_2$	8.4(2)[yyy]	−24.6(10)[yyy]	−23.7	−0.9	236(60)[yyy]	238	−2
Chlorotrifluoromethane	$CClF_3$	17.3(2)[gggg]	−21.5(5)[hhhh]	−17.6	−3.9	278(25)[hhhh]	299	−21
Dichlorodifluoromethane	CCl_2F_2	14.4(2)[gggg]	−26.0(5)[hhhh]	−20.9	−5.1	315(15)[hhhh]	333	−18
Chloroethylene	C_2H_3Cl	7.6(3)[y]	−24.6(20)[y]	−23.2	−1.4		248	
1,1-Dichloroethylene	$C_2H_2Cl_2$	8.2(5)[eeee]	−25.8(20)[eeee]	−24.9	−0.9		300	
1,2-Dichloroethylene	$C_2H_2Cl_2$	0.5(5)[eeee]	−32.8(5)[iiii]	−35.3	2.5	258(10)[iiii]	276	−18
Trichloroethylene	C_2HCl_3	5.3(5)[eeee]	−32.4(20)[eeee]	−29.6	−2.8		344	
Chloroethane	C_2H_5Cl	5.3(5)[y]	−23.2(20)[y]	−28.9	5.7		237	
1,3-Dichloropropane	$C_3H_6Cl_2$	0.0(10)[iiii]	−37.3(5)[iiii+nn]	−40.6	3.3	325(10)[iiii+ss]	319	6
1,4-Dichlorobutane	$C_4H_8Cl_2$	−1.7(30)[iiii]	−41.2(5)[iiii+nn]	−47.1	5.9	392(10)[iiii+ss]	351	41
1,1-Dichloroethane	$C_2H_4Cl_2$	4.4(3)[ffff]	−29.9(30)[ffff]	−31.9	2.0		296	
1,1,1-Trichloroethane	$C_2H_3Cl_3$	6.9(3)[ffff]	−29.1(30)[ffff]	−31.9	2.8		357	
1,1,2-Trichloroethane	$C_2H_3Cl_3$	−0.5(3)[ffff]	−32.4(30)[ffff]	−38.4	6.0		311	
1,1,1,2-Tetrachloroethane	$C_2H_2Cl_4$	2.3(3)[ffff]	−39.9(30)[ffff]	−38.1	−1.8		401	
1,1,2,2-Tetrachloroethane	$C_2H_2Cl_4$	−1.7(3)[ffff]	−41.6(30)[ffff]	−41.6	0.0		376	
2-Chloroethanol	C_2H_5ClO	−16.2(20)[kkkk+llll]	−49.5(30)[mmmm+llll]	−51.8	2.3		175	
	Compounds containing Br							
Bromomethane	CH_3Br	4.5(3)[y]	−25.5(10)[y]	−25.7	0.2	183(30)[y]	188	−5
Dibromomethane	CH_2Br_2	−0.2(3)[ffff]	−32.4(20)[ffff]	−33.0	0.6		201	
Tribromomethane	$CHBr_3$	−1.6(5)[eeee]	−35.8(30)[eeee]	−37.5	1.7		228	
1,2-Dibromoethane	$C_2H_4Br_2$	−1.0(5)[nnnn+oooo]	−37.7(40)[nnnn+nn]	−38.7	1.0		245	
1,1,2,2-Tetrabromoethane	$C_2H_2Br_4$	−8.7(20)[pppp]	−55.1(30)[pppp]	−52.1	−3.0	296(30)[pppp+ss]	295	1
Bromodichloromethane	$CHBrCl_2$	1.7(3)[eeee]	−32.4(30)[eeee]	−32.5	0.1		278	
Dibromochloromethane	$CHBr_2Cl$	0.1(5)[eeee]	−33.3(30)[eeee]	−35.0	1.7		250	
Bromobenzene	C_6H_5Br	2.3(5)[qqqq]	−38.3(30)[rrrr+nn]	−37.2	−1.1		328	
	Compounds containing I							
Iodine	I_2	−2.7(30)[ssss]	−36.6(40)[ssss]	−37.7	1.1			
Iodomethane	CH_3I	4.1(5)[tttt]	−29.4(30)[tttt]	−29.8	0.4			
Diiodomethane	CH_2I_2	−2.1(5)[uuuu]	−41.6(40)[uuuu]	−42.1	0.5			

include our estimate of the accuracy of the experimental data, shown in parentheses as the number of significant figures; that is, 10.2(3) means 10.2 ± 0.3 and −50.0(20) means −50.0 ± 2.0. To make this set of

solutes as diverse as possible we tried to include compounds containing chemical elements in various oxidation states (for example, Cl₂, HClO, CHCl₃, etc.) and to include compounds of different structures (for

Table B1. continued

| Compound | Formula | $\Delta_h G^{\circ a}$ | $\Delta_h H^{\circ a}$ | | | $\Delta_h C_p^{\circ b}$ | | |
			Experimental	Calculated	Δ	Experimental	Calculated	Δ
Chloroiodomethane	CH_2ICl	0.3(5)[uuuu]	−35.8(40)[uuuu]	−35.3	−0.5			
Iodobenzene	C_6H_5I	−0.3(5)[rrrr+oooo]	−46.5(40)[rrrr+oooo]	−43.2	−3.3			

[a] $kJ \cdot mol^{-1}$,[b] $J \cdot K^{-1} \cdot mol^{-1}$,[c] Rettich et al. (1984),[d] Rettich et al., 2000,[e] Dec and Gill, 1984a,[f] Olofsson et al., 1984,[g] Hallén and Wadsö, 1989,[h] Wilhelm et al., 1977,[i] Becker et al., 1996,[j] D'Orazio and Wood, 1963,[k] Clegg and Brimblecombe, 1989,[l] Kawazuishi and Prausnitz, 1987,[m] Vanderzee and King, 1972,[n] Allred and Woolley, 1981,[o] Wagman et al., 1982,[p] Giguere and Carmichael, 1962,[q] Giguere et al., 1955,[r] Bushnell et al., 1937,[s] Rettich et al., 1982,[t] Crovetto, 1991,[u] Berg and Vanderzee, 1978,[v] Gill and Wadsö, 1982,[w] Hnedkovsky and Woody, 1997,[x] Khan et al., 1995,[y] Cabani et al., 1981,[z] Park et al., 1987,[aa] Stern and Swearingen, 1970,[bb] Rettich et al., 1981,[cc] Dec and Gill, 1984(b),[dd] Dec and Gill, 1985b,[ee] Plyasunov and Shock (2000a),[ff] Jakil and Hook, 1981,[gg] Wit et al., 1983,[hh] Desnoyers et al., 1976,[ii] Benkelberg et al., 1995,[jj] Hovorka et al., 1999,[kk] Sijpkes et al., 1989,[ll] Wadsö, 1965,[mm] Zielkiewicz, 1998,[nn] Majer and Svoboda, 1985,[oo] Kruif et al., 1979,[pp] Fasman, 1975,[qq] Ngauv et al., 1977,[rr] Hakin et al., 1994,[ss] the Benson method was used to estimate the ideal gas heat capacity,[tt] Suleiman and Eckert, 1994,[uu] Touhara et al., 1982,[vv] Kim et al., 1987,[ww] Schmelzer and Quitzsch, 1973,[xx] Nichols, 1963,[yy] Plyasunov and Shock, 2001a,[zz] Kieckbush and King, 1979,[aaa] Nilsson and Wadso, 1986,[bbb] To et al., 1999,[ccc] Tang and Munkewitz, 1991,[ddd] Bastos et al., 1988,[eee] Bergström and Olofsson, 1977,[fff] Robinson et al., 1942,[ggg] Silva et al., 2001,[hhh] Sovova and Boublik, 1986,[iii] Tremaine et al., 1997,[jjj] Kiyohara et al., 1975,[kkk] Goldberg and Tewari, 1989,[lll] Oja and Suuberg, 1999,[mmm] Jasra and Ahluwalia, 1982,[nnn] Galema et al., 1993,[ooo] Abd-El-Bary et al. 1986,[ppp] Jayasinghe et al., 1992,[qqq] Nichols and Wadsö, 1975,[rrr] Goldberg and Parker, 1985,[sss] Cox et al., 1989,[ttt] Barbero et al., 1982,[uuu] Murakami et al., 1987,[vvv] Przyazny et al., 1983,[www] Bastos et al., 1991,[xxx] Lai et al., 1995,[yyy] Zheng et al., 1997,[zzz] Rochester and Symonds, 1973,[aaaa] Holzwarth et al., 1984,[bbbb] Huthwelker et al., 1995,[cccc] Hoff et al., 1993,[dddd] Larsen and Magid, 1974,[eeee] Tse et al., 1992,[ffff] Wright et al., 1992,[gggg] Scharlin and Battino, 1994,[hhhh] Naghibi et al., 1987,[iiii] Hallén, 1993,[jjjj] Leighton and Calo, 1981,[kkkk] Gothard et al., 1973,[llll] Stull, 1947,[mmmm] Gierycz et al., 1985,[nnnn] Stephenson, 1992,[oooo] Stephenson and Malanowski, 1987,[pppp] Gooch et al., 1972,[qqqq] Shiu and Mackay, 1997,[rrrr] Borisover et al., 1991,[ssss] Palmer et al., 1985,[tttt] Hunter-Smith et al., 1983.

example, propene and cyclopropane, both having formula C_3H_6). A least-squares fit was employed to determine the optimal form of the correlating equation, which appears to be as follows:

$$\Delta_h H^\circ = a_0 + a_1 \Delta_h G^\circ + a_2 (\Delta_h G^\circ)^2 + \sum_{i=1} b_i n(i). \quad (B2)$$

The inclusion of the term quadratic in $\Delta_h G^\circ$ improves the description of data for compounds with $\Delta_h G^\circ < -50 \ kJ \cdot mol^{-1}$. However, terms quadratic in composition (the last summation in Eqn. B1) were found to be unnecessary. Numerical values of the parameters are given in Table B2. The array of 118 $\Delta_h H^\circ$ data points is described with a standard deviation of 3.0 $kJ \cdot mol^{-1}$ as compared with 6.6 $kJ \cdot mol^{-1}$ when the elemental composition is ignored, and the difference between the experimental and fitted results exceed 6 $kJ \cdot mol^{-1}$, twice the standard deviation, for only 7 compounds as compared with 42 when only $\Delta_h G^\circ$ is used as a variable.

A similar approach can be employed to correlate $\Delta_h C_p^\circ$ values of neutral compounds. The optimal form of the correlating equation was found to be

Table B2. Parameters of Eqns. B2 for $\Delta_h H^\circ$ and B3 for $\Delta_h C_p^\circ$, together with their uncertainties at the 0.95 confidence level, shown in parentheses as the number of significant figures.

Parameter	$\Delta_h H^\circ$	$\Delta_h C_p^\circ$
a_0	−17.87(196)	
a_1	0.891(60)	7.68(55)
a_2	$-3.27(125) \cdot 10^{-3}$	−3.27(64)
b_C	−1.16(57)	20.6(37)
b_H	−1.87(35)	5.9(30)
b_O	−2.91(100)	16.9(80)
b_N	−3.72(118)	12.8(111)
b_S	−1.24(155)	40.4(107)
b_F	−2.99(59)	8.2(68)
b_{Cl}	−4.04(79)	50.1(94)
b_{Br}	−5.05(134)	32.1(161)
b_I	−8.72(321)	40[a]

[a] This value is estimated from the average between values for Cl and Br.

$$\Delta_h C_p^\circ = a_1 \Delta_h G^\circ + a_2 \Delta_h H^\circ + \sum_{i=1} b_i n(i). \quad (B3)$$

The set employed to determine the numerical values of the fitting parameters contained 82 $\Delta_h C_p^\circ$ data. Where necessary, the values of $\Delta_h C_p^\circ$ were calculated from experimentally measured values of the standard partial molar heat capacity, $C_{p,2}^\circ$, using the relation

$$\Delta_h C_p^\circ = C_{p,2}^\circ - C_p(ig), \quad (B4)$$

where $C_p(ig)$ stands for the heat capacity of a compound in the ideal gas state. In a few cases, the values of $C_p(ig)$ are estimated using the Benson group contribution method (Reid et al., 1987). The resulting values of parameters of Eqn. B3 are given in Table B2. The array of 82 $\Delta_h C_p^\circ$ data is described with a standard deviation of 26 $J \cdot K^{-1} \cdot mol^{-1}$, and the difference between the experimental and fitted results exceed 50 $J \cdot K^{-1} \cdot mol^{-1}$, or about twice the standard deviation, for 5 compounds.

The worst cases for correlation seem to be cyclic compounds (1,4-dioxane, morpholine, cyclopropane, etc.) and compounds forming hydrogen bonds with water (urea, amines, alcohols, but not polyamines and polyols). For cyclic compounds the various ring geometries provide different amounts of strain energies, which contribute to the values of the thermodynamic functions of hydration, and no single universal "cyclic correction" is able to improve the fit. Attempts to introduce simple corrections for the presence of hydroxyl and amine groups resulted in only a modest improvement of the quality of the fit, and were determined not to be worthwhile. One may speculate that the (relative) failure of this correlation for urea is due to strong intramolecular amine-amine interactions within this compound. In any case, it appears that a real improvement can be reached only by introduction of a much more elaborate atom/group contribution scheme including second-order structural corrections, which is exactly what we are trying to avoid by pursuing the simplest correlating method possible.

One of the reviewers pointed out that this model is physically unrealistic. We admit that it is a purely empirical correlation, developed out of necessity to move forward in a situation where no satisfactory methods seem to exist. Certainly, the argument that "something is better than nothing" is weak. A development of more sound ways to predict the hydration properties of many compounds would be of definite value for many branches of science, including not least the hydrothermal geochemistry. Still, we would like to note that the approach based on elemental composition, that ignores the structure and the valent type of elements, may not be so naïve and undefendable. For

example, a number of methods are proposed in the literature for predicting gas-liquid critical temperatures (see Yan et al., 2003). Most of them require 40–160 parameters and limited only by organic compounds in the C-H-O-N-S-halogens system. Compared to these monsters, the Wilson-Jasperson method, which uses only 9 elemental, or atomic, contributions and up to 12 secondary corrections, may appear an inadequate dwarf. However, an independent test (Yan et al., 2003) showed that the Wilson-Jasperson atomic model results in about the same quality of description of known data as the other methods and deliver the best predictive values of critical temperatures. In addition, contrary to the other methods, it is applicable to both inorganic and organic compounds in the C-H-O-N-S-halogens system.