

Standard partial molal properties of aqueous alkylphenols and alkyilanilines over a wide range of temperatures and pressures

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Abstract

This article presents methods for predicting the standard partial molar Gibbs energy (standard chemical potential) and related derivative properties of aqueous hydroxy and aminoderivatives of (alkyl)benzenes over a wide range of temperatures and pressures. A thorough literature overview was conducted for collecting all available experimental data resulting from phase equilibrium, calorimetric and volumetric measurements that allow calculation of the thermodynamic properties of hydration. New experimental values are presented for solubility in water of isomeric toluidines and for the partial molal volume of phenol and cresols at high temperatures. Building upon the acquired database several prediction schemes were developed and tested for calculating the standard thermodynamic properties (and namely the Gibbs energy of hydration) of aqueous alkylphenols and alkyilanilines as a function of temperature and pressure. First, a simple group contribution method was proposed for estimations at 298.15 K and 0.1 MPa using the simultaneous treatment of all available data on hydration properties at near ambient conditions. Second, this group contribution method allowed re-adjustment of the parameters of the Helgeson–Kirkham–Flowers model (HKF) using a new procedure proposed recently by Plyasunov and Shock [Plyasunov, A.V., Shock, E.L., 2001b. Correlation strategy for determining the parameters of the revised Helgeson–Kirkham–Flowers model for aqueous nonelectrolytes. *Geochim. Cosmochim. Acta* **65**, 3879–3900]. Third, using the Sedlbauer–O’Connell–Wood equation of state for aqueous species (SOCW), group contributions were determined for predictions at high temperatures and pressures by simultaneous correlation of all available thermodynamic data on hydration properties. The latter method was constrained by the group contributions at 298.15 K and 0.1 MPa making both group contribution schemes consistent at near ambient conditions. The calculations from the HKF and SOCW equations of state and those from the simple thermodynamic integration of the data at 298.15 K and 0.1 MPa were compared for several alkylphenols and alkyilanilines. Equilibrium constants for hydration reactions obtained from the three approaches are in very good agreement at temperatures to at least 400 K. At higher temperatures we assess the accuracy of different predictive schemes and their associated uncertainties. The reliable predictions of the standard chemical potentials to at least 573 K and 100 MPa are possible by the group contribution method using the SOCW equation of state.

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1. Introduction

Hydroxy and aminoderivatives of (alkyl)benzenes (abbreviated here as alkylphenols and alkyilanilines) are commonly a part of oilfield waters or waste effluents from various industrial sources, getting in contact with soil and underground waters. Thermodynamic data of these

aqueous solutes are needed at ambient conditions as well as at elevated temperatures and pressures in order to understand or to design the processes where the phase and chemical equilibria play a significant role (Moore et al., 1995; Dale et al., 1997; Taylor et al., 1997; Sheikhdin et al., 2001; Harrison et al., 2002; Feigenbrugel et al., 2004). These are for example the partitioning of the polar aromatic compounds between the coexisting hydrocarbon-rich phases and deep saline aquifers, the effect of these species to chemical reactions in the brines coming in

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contact with rocks, their transfer between the aquatic and air compartments as well as remediation processes for removal of the hazardous organic pollutants in soils and underground waters. In this context, the thermodynamic properties of prime practical interest for characterizing aqueous solutes are the standard partial molal Gibbs energy of formation, needed in the calculation of chemical equilibria for hydrothermal reactions, and the Gibbs energy of hydration that is closely related to the Henry's law constant important in the phase equilibria calculations. There are many types of experimental data that can be used for their evaluation: the equilibrium constants of chemical reactions

involving aqueous species, vapor–liquid distribution constants, air–water partition coefficients, limiting activity coefficients and solubilities in combination with vapor pressure data. In addition, the data on derivative properties (enthalpies of solution, partial molal heat capacities, and partial molal volumes) resulting from calorimetric and densimetric experiments are useful in determining the functional dependence of the Gibbs energy on temperature and pressure.

Data for phenolic compounds were summarized and treated using the HKF thermodynamic model by Dale et al. (1997), allowing predictions of the standard partial molal Gibbs energy of formation as well as the Gibbs

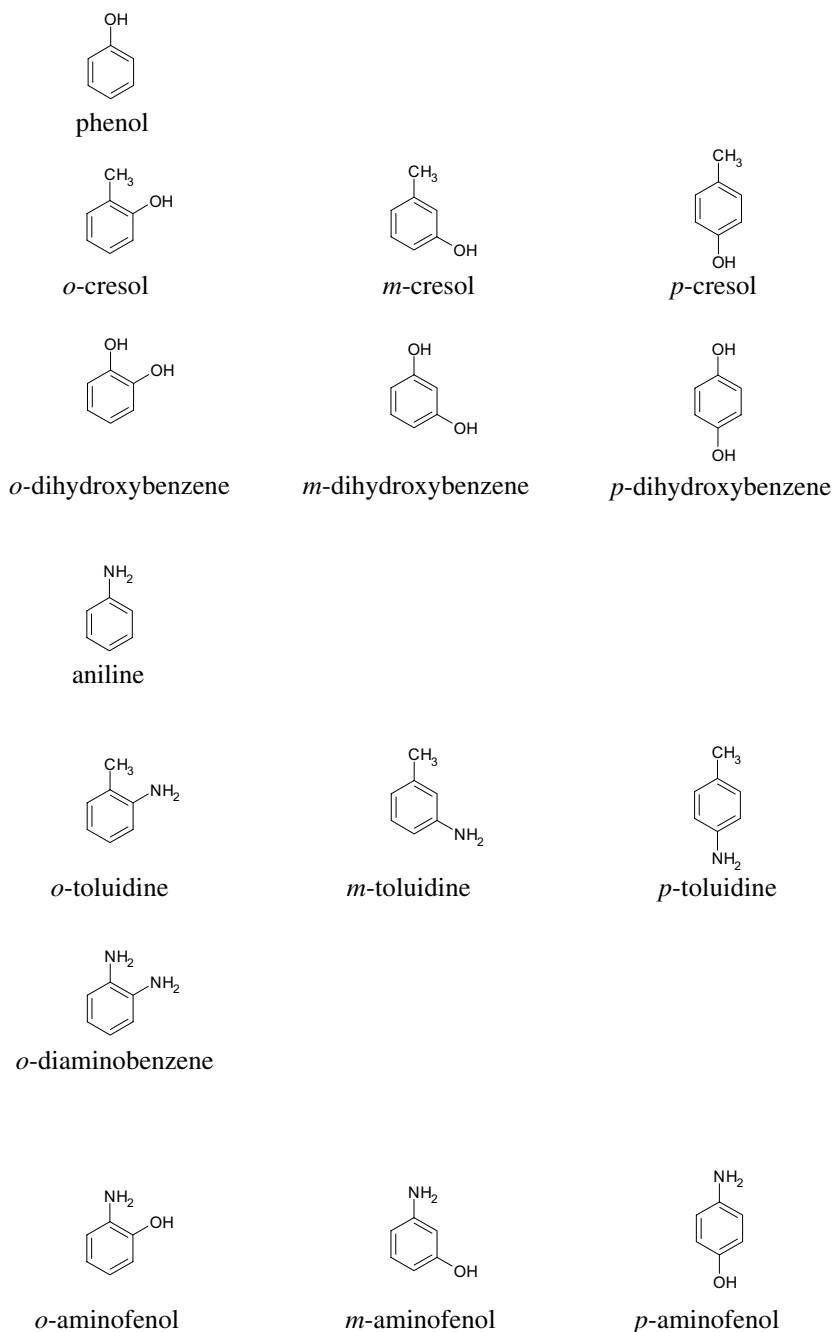


Fig. 1. Molecular structures and the trivial names of principal solutes treated in this study.

energy of hydration in a wide range of conditions. These estimations were based purely on the experimental data at temperatures below 373 K and at ambient pressure since no other information was available at that time. Large amount of new data became, however, available in the last few years, namely for the derivative properties (partial molal volumes and heat capacities) of phenol, cresols, and dihydroxybenzenes at temperatures to 623 K, allowing a test and refinement of Dale et al. (1997) predictions for phenolic solutes. At the same time, analogous data were also obtained for aminoderivatives of aromatic hydrocarbons (aniline, toluidines, diamminobenzenes, and aminophenols), suggesting a possibility of parallel treatment for this class of solutes.

Beside the HKF equation of state (Tanger and Helgeson, 1988), used predominantly by geochemists for the thermodynamic description of hydrothermal systems, new models have been published recently allowing calculation of the standard thermodynamic properties of aqueous solutes (e.g., O'Connell et al., 1996; Plyasunov et al., 2000a,b; Sedlbauer et al., 2000). A group contribution concept is often applied for estimating properties of organic aqueous solutes at the reference conditions of $T_r = 298.1$ K and $p_r = 0.1$ MPa (e.g., Hine and Mookerjee, 1975; Cabani et al., 1981; Meylan and Howard, 1991; Plyasunov and Shock, 2000a, 2001a; Plyasunov et al., 2004, 2005, 2006) or over a wide range of conditions (Amend and Helgeson, 1997; Yezdimer et al., 2000; Plyasunov and Shock, 2000b; Sedlbauer et al., 2002) making these new schemes fully predictive. It is therefore desirable to determine in such new models contributions for hydroxy and amino groups on aromatic rings using the new experimental data obtained in the last 10 years or so.

The purpose of this study was: (i) to extend the database for aqueous alkylphenols and alkylanilines by new experimental measurements, (ii) to collect all thermodynamic data for the given classes of compounds and use them for the development of new group contribution schemes for aqueous alkylphenols and alkylanilines at ambient and at elevated conditions, and (iii) to refine the HKF predictions for aqueous alkylphenols and alkylanilines and compare them with the results of the group contribution high-temperature model.

This article is structured as follows. After a brief introduction to thermodynamic modeling in aqueous solutions of organic compounds we present in Section 3 new solubility data leading to the Henry's law constant of aqueous toluidines at near ambient conditions and the standard partial molal volumes of phenol and cresols at high temperatures. Follows a summary and comments on primary literature sources that allow the calculation of the thermodynamic properties of hydration (Gibbs energy, enthalpy, heat capacity, and partial molal volume). The group contributions at the reference conditions of $T_r = 298.1$ K and $p_r = 0.1$ MPa are then determined from the experimental results at near ambient conditions ($T < 373$ K). New parameters are listed for the HKF equation of state based

on the new data. Parameters of the group contribution SOCW model are obtained by regression of thermodynamic data at $T < 623$ K. Finally, the differences between the Gibbs energy results calculated from the different approaches are quantified and the effect of the derivative properties of investigated compounds on their high-temperature behavior is discussed. For the sake of clarity the molecular structures of most compounds treated in this study are depicted in Fig. 1.

2. Theory

The standard¹ partial molal Gibbs energy of formation (or the standard chemical potential for short) of a solute ΔG_f° at a temperature T and pressure p can be expressed by integration using its known reference value $\Delta G_f^\circ[T_r, p_r]$ and the standard entropy, $S^\circ[T_r, p_r]$

$$\begin{aligned} \Delta G_f^\circ[T, P] = & \Delta G_f^\circ[T_r, p_r] + (T_r - T) \cdot S^\circ[T_r, p_r] \\ & + \int_{T_r}^T C_p^\circ dT - T \cdot \int_{T_r}^T C_p^\circ d \ln T \\ & + \int_{p_r}^p V^\circ dp. \end{aligned} \quad (1)$$

To evaluate the integrals, expressions for the standard molal volume $V^\circ = V^\circ(T, p)$ and for the standard molal heat capacity $C_p^\circ = C_p^\circ(T, p_r)$ are needed. Experimental data and models for these properties can be thus used for an easy and accurate extrapolation of the standard chemical potential at the reference conditions T_r and p_r to high temperatures and pressures. Prime position among methods of this type belongs to the revised Helgeson–Kirkham–Flowers equations (Tanger and Helgeson, 1988) adapted to organic aqueous compounds by Shock and Helgeson (1990). New generation of models appeared in the last decade that was inspired by the Fluctuation Solution Theory and based on the work of O'Connell and collaborators (O'Connell et al., 1996; Plyasunov et al., 2000a,b; Sedlbauer et al., 2000). The approach presented by the last authors (Sedlbauer–O'Connell–Wood) has been applied for data representation and for predictions in a variety of aqueous systems, nonelectrolyte and ionic (Majer et al., 2000; Sedlbauer and Majer, 2000, 2004; Yezdimer et al., 2000; Sedlbauer et al., 2002; Sedlbauer and Wood, 2004).

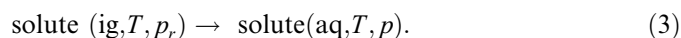
Standard chemical potential is the crucial property for predicting thermodynamic constants characterizing chemical equilibria in systems involving aqueous solutions. However, for data representation and for modeling phase equilibria it is convenient to work in terms of the Gibbs energy of hydration, defined as

$$\Delta_h G^\circ = \Delta G_f^\circ(T, p) - \Delta G_f^{\text{ig}}(T, p_r), \quad (2)$$

where ΔG_f^{ig} is the Gibbs energy of formation of pure solute in an ideal gas phase at reference pressure $p_r = 0.1$ MPa.

¹ The standard state adopted here for aqueous species is unit activity in a hypothetical one molal solution referenced to infinite dilution.

$\Delta_{\text{h}}G^{\circ}$ thus corresponds to the change in free energy associated with the transfer of a solute molecule from an ideal gas phase to an aqueous solution at the standard state of infinite dilution



The appropriate equilibrium constant K_{hyd} for this hydration reaction is given by

$$\Delta_{\text{h}}G^{\circ} = -RT \ln K_{\text{hyd}} = -2.303RT \log K_{\text{hyd}} \quad (4)$$

The temperature and pressure derivatives of $\Delta_{\text{h}}G^{\circ}$ provide a link with the corresponding standard derivative properties: enthalpy of hydration $\Delta_{\text{h}}H^{\circ}$, heat capacity of hydration $\Delta_{\text{h}}C_p^{\circ}$, and standard partial molal volume V°

$$T^2 \left(\frac{\partial(\Delta_{\text{h}}G^{\circ}/T)}{\partial T} \right)_p = -\Delta_{\text{h}}H^{\circ}, \quad (5)$$

$$\left(\frac{\partial}{\partial T} \left[T^2 \frac{\partial(\Delta_{\text{h}}G^{\circ}/T)}{\partial T} \right] \right)_p = -\Delta_{\text{h}}C_p^{\circ}, \quad (6)$$

$$\left(\frac{\partial \Delta_{\text{h}}G^{\circ}}{\partial p} \right)_T = V^{\circ}. \quad (7)$$

Note that in the last relationship V° replaces $\Delta_{\text{h}}V^{\circ}$ since the Gibbs energy of an ideal gas in Eqs. (2) and (3) is at constant pressure p_r .

The reason for using a hydration-based representation is that most data such as Henry's law constant, limiting activity coefficient, solubility, enthalpy of solution, etc. are actually obtained in experiments close to a hydration process; these data are interconnected with the above properties of hydration by common thermodynamic relations and can be easily converted. The rearrangement to the partial molal properties of formation (necessary for the G and H functions) requires only ideal gas phase properties that are well known. Treating just hydration-specific effects also allows development of more sensitive and accurate models, as shown, e.g., by Plyasunov et al. (2000a,b) or Sedlbauer et al. (2000).

In the case of organic solutes it is often useful to adopt a functional group additivity scheme. The reason is obvious: while the number of organic structures is large, they consist of just a few functional groups. In the thermodynamics of dilute aqueous solutions this principle has been adopted with success at temperature of 298 K and several methods are available varying in the set of selected functional groups and in the type of evaluated thermodynamic properties (e.g., Hine and Mookerjee, 1975; Cabani et al., 1981; Meylan and Howard, 1991; Plyasunov and Shock, 2000a). This approach can be applied also at elevated temperatures and pressures, where the functional group contributions need to be expressed in terms of an equation of state such as the HKF model (Amend and Helgeson, 1997) or the SOCW model (Yezdimer et al., 2000; Sedlbauer et al., 2002), or using another empirical representation (Plyasunov and Shock, 2000b). Again, the hydration properties are preferred for this treatment because the properties of ideal gas do not need to be considered in the resulting func-

tional group contributions. It should also be noted that fundamentally correct group additivity scheme applies a general equation

$$\Delta_{\text{h}}X^{\circ} = X_{\text{SS}} + \sum_{i=1}^N n_i X_i^{\circ}, \quad (8)$$

where N is the total number of functional groups present in a given solute, n_i is the number of occurrences of each specific functional group, and X_i° stands for the X property of the i th group. The term X_{SS} accounts for the intrinsic contribution to the X property that is equal to the contribution of hydration of a point mass. This term is derived from theory (Ben-Naim, 1987) and can be evaluated using only thermodynamic functions of pure solvent (Majer et al., 2004). Functional groups can be represented by a set of first-order or higher-order contributions (such as steric corrections for proximity effects), depending on the amount of data available for parameterization and the required predictive accuracy of the method.

When using a group contribution concept it is convenient to determine at first the group contributions at the reference T_r , p_r from the data at near ambient conditions that are relatively abundant and of reasonable accuracy. The parameters of the model representing the standard thermodynamic properties over a wide range of temperatures and pressures can be obtained with the help of these reference data, as demonstrated for the HKF model by Plyasunov and Shock (2001b). It is of course preferable to formulate the model for superambient conditions again in terms of group contributions, temperature and pressure dependent this time, which are expressed by a sound, theoretically founded equation. The parameters of these functional dependencies should be determined using simultaneously all the thermodynamic data available in a wide range of conditions. In addition, a provision should be made to provide a consistency between the group contribution schemes for the reference state of T_r , p_r and for superambient conditions, ideally the two methods should yield identical results at 298 K and 0.1 MPa. This is the approach we have adopted in this study using the SOCW model (Sedlbauer et al., 2000), presented in Appendix A, in its group contribution form described by Sedlbauer et al. (2002).

3. Experimental

In this section are presented: (i) new experimental data for solubilities and the calculated Henry's law constants of *o*-, *m*-, and *p*-toluidines determined between 293 and 323 K at the Institute of Chemical Technology Prague, (ii) the standard partial molal volumes of aqueous phenol and of *o*-, *m*-, and *p*-cresols obtained at 573 and 623 K and at pressures between 10 and 31 MPa from density measurements performed at the Blaise Pascal University in Clermont-Ferrand. All studied solutes were purchased

from Fluka in purity of at least 99% in mass and used without further purification.

3.1. Solubility measurements

Aqueous solubilities were measured by a conventional batch contacting technique as described by Benes and Dohnal (1999). Apparatus consisted of several jacketed 50 cm³ glass equilibrium cells connected in series whose temperature was maintained constant to 0.01 K with help of a Luda C6 CP (Germany) thermostat. A cooling unit ANKL Kryo (Czech Republic) was used during measurements at 298.15 K. Serial connection allowed obtaining simultaneously multiple data points at one temperature; six cells were connected in series for measurement at 298.15 K while only three cells were used at temperatures of 313.15 and 323.15 K. By reducing the number of cells during measurements at higher temperatures we wanted to prevent the possible temperature gradient due to uneven distance of the cells from the thermostat. Outer walls of the cells were covered by cellulose wool for isolation.

Studied compounds were added in excess to the cells containing demineralized water and magnetically stirred for approximately two days. Then the heterogeneous system was allowed to settle under a controlled temperature for approximately one day. The organic phase was always liquid except for *p*-toluidine, solid at the lowest experimental temperature.

Samples of the saturated solutions (about 20 cm³) were withdrawn using a syringe through a glass wool filter for analysis. The first portion of the withdrawn aqueous phase was always discarded in order to avoid possible adsorption effects on glass wool. Samples were diluted to reach concentration range where the Lambert–Beer law is obeyed (absorbance less than 0.8) and analyzed by spectrophotometry using a computer-interfaced UV absorbance detector LCD 2084 ECOM (Czech Republic). The concentrations were established on the basis of the previous measurements with three calibration solutions. Two to three solubility determinations were performed at each temperature with the reproducibility of results being typically about 1% and lower at the highest temperature. Tables 1a–1c list the results of new measurements in terms of molar fraction x_s with their average absolute deviations s_x , the literature data are also listed for comparison. In addition, the temperature dependence of solubility data is depicted in Fig. 2. The solubility of *o*-toluidine published by Huyskens et al. (1975) at 298.15 K was by 4% lower than the value obtained in this work. Chiou et al. (1982) reported data for *o*-toluidine and *m*-toluidine at 293.15 K; in the case of *m*-toluidine their value does not seem to be quite consistent with our result at 298.15 K. The solubility of *p*-toluidine published by Hashimoto et al. (1984) at 298 K is by 24% lower in comparison with the value from this study. Our results in combination with the literature values indicate that the solubilities increase with increasing temperature. This is a type of behavior typical for hydrophilic solutes unlike

Table 1a
Solubility of *o*-toluidine

<i>T</i> (K)	$x_{\text{sol}} \cdot 10^2$	$s_x \cdot 10^2$	$p_{\text{sat}}^{\text{d}}$ (MPa)	k_{H}^{e} (kPa)
298.15	0.2907 ^a	0.0030	0.0401	14.3
313.15	0.2975 ^a	0.0025	0.121	42.1
323.15	0.3066 ^a	0.0012	0.236	79.7
293.15	0.2788 ^b		0.0269	10.0
298.15	0.2804 ^c		0.0401	14.8

^a This study.

^b Chiou et al. (1982).

^c Huyskens et al. (1975).

^d p_{sat} calculated from the correlation of selected experimental data described below.

^e Henry's law constant determined as described in the last paragraph of Section 4.1.1.

Table 1b
Solubility of *m*-toluidine

<i>T</i> (K)	$x_{\text{sol}} \cdot 10^2$	$s_x \cdot 10^2$	$p_{\text{sat}}^{\text{c}}$ (MPa)	k_{H}^{d} (kPa)
298.15	0.2543 ^a	0.0036	0.0341	13.8
313.15	0.2601 ^a	0.0021	0.106	42.1
323.15	0.2751 ^a	0.0011	0.211	79.2
293.15	0.2563 ^b		0.0226	9.1

^a This study.

^b Chiou et al. (1982).

^c p_{sat} calculated from the correlation of selected experimental data described below.

^d Henry's law constant determined as described in the last paragraph of Section 4.1.1.

Table 1c
Solubility of *p*-toluidine

<i>T</i> (K)	$x_{\text{sol}} \cdot 10^2$	$s_x \cdot 10^2$	$p_{\text{sat}}^{\text{c}}$ (MPa)	k_{H}^{d} (kPa)
298.15	0.1399 ^a	0.0017	0.0237	17.2
313.15	0.2624 ^a	0.0016	0.1004	39.5
298	0.1126 ^b		0.0234	21.1

^a This study.

^b Hashimoto et al. (1984).

^c p_{sat} calculated from the correlation of selected experimental data described below.

^d Henry's law constant determined as described in the last paragraph of Section 4.1.1.

that for the hydrophobic organic compounds which exhibit a minimum in solubility at a near ambient temperature (typically between 293 and 323 K). The values for *o*-toluidine are higher compared to the two other isomers suggesting an increase of solubility due to CH₃ and OH proximity effect. A different behavior was observed in the case of *p*-toluidine where the solubilities were measured at two temperatures only. The difference between the values at 298.15 and 313.15 K is much higher compared to two other isomers. Yet our value at the lower temperature is considerably higher than the literature value (Hashimoto et al., 1984) and the one at the upper temperature is reasonably consistent with the value for *m*-toluidine. So there is no indication of a possible systematic error in our measurements and the difference in solubility is apparently

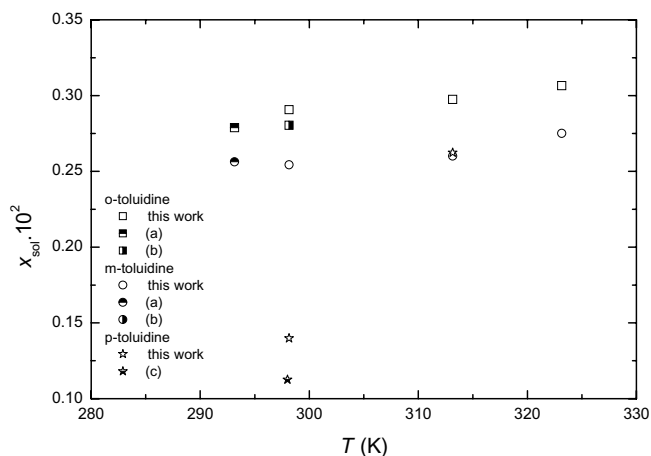


Fig. 2. Experimental data on solubility of the three toluidines: ref a, Chiou et al. (1982); ref b, Huyskens et al. (1975); ref c, Hashimoto et al. (1984).

due to the fact that *p*-toluidine is solid at the lower temperature and subcooled liquid at the upper one. It is apparent from the text below (see Section 4.1.1) that while the Henry's law constant and the activity coefficient are a continuous function of temperature independent of the physical state of pure solute, the solubility is strongly affected by the solute's state. Tables 1a–1c list also for the three toluidines the values of vapor pressures and of the resulting Henry's law constants k_H obtained by the procedure described below (see Section 4.1.1).

3.2. Volumetric measurements

The standard partial molal volumes were evaluated from the density differences between aqueous solutions of phenol or cresols and water measured on a vibrating tube flow densimeter (Hynek et al., 1997). The densities are obtained from the oscillation periods of a “U” tube, vibrating in a field of a permanent magnet. Since this is a comparative method a calibration experiment with two fluids of well-known density is necessary. The temperature within one experiment was stable to 0.01 K and was measured with an accuracy of 0.03 K using a secondary standard platinum thermometer (Burns, 500 Ω). Pressure was maintained stable to ± 0.02 MPa by means of a back-pressure regulator (Circle Seal) and read by means of an electronic manometer (DPI 260 Druck) with an expected accuracy of 0.05 MPa.

The difference between the densities of a solution ρ and deionized water ρ_w is calculated as

$$\Delta\rho = \rho - \rho_w = K(\tau^2 - \tau_w^2), \quad (9)$$

where τ and τ_w are the periods of vibration of the tube filled successively with solution and water. Calibration constant K was obtained by measurements with water and nitrogen.

Densities were obtained at target temperatures of 573, 598, and 623 K and at a pressure close to the saturation pressure of water. Determinations at the two higher tem-

peratures were also performed at a pressure near 30 MPa. Measurements were carried out at up to five concentrations between 0.15 and 0.75 m for phenol and at two target concentrations (0.1 and 0.2 m) for cresols, the upper concentration limit being a function of the solubility. Two to three experiments were performed with each solution at a given temperature and pressure. The measured density differences were converted to the apparent molar volumes (Majer et al., 2004)

$$V_\phi = M_s/(\rho_w + \Delta\rho) - \Delta\rho/(m\rho_w(\rho_w + \Delta\rho)), \quad (10)$$

where M_s and m are molar mass of water and molality of the solute, respectively. The extrapolation to zero concentration allows to obtain the partial molar volume of solute at infinite dilution that has the meaning of the standard partial molal volume

$$V^\circ = \lim_{m \rightarrow 0} V_\phi = M_s/\rho_w - \lim_{m \rightarrow 0} (\Delta\rho/m)/\rho_w^2. \quad (11)$$

In the case of phenol the limiting value of the ratio $\Delta\rho/m$ was obtained by fitting the experimental data to a linear relationship

$$\Delta\rho/m = a + bm \quad (12)$$

using the weighted least-squares regression. The reproducibility of measurements and the expected error in the calibration constants served for determining the weighting factors. In the case of cresols, for which the concentration range is limited, it was not possible to determine the intercept a with a good accuracy. It was preferred to take as the V° value the arithmetic average of the apparent molar volumes that were obtained at sufficiently low concentrations to allow an approximation of infinite dilution. The expected errors in V° were 2–3 $\text{cm}^3 \text{mol}^{-1}$ for phenol and somewhat higher for cresols (3–4 $\text{cm}^3 \text{mol}^{-1}$). The differences between volumes for the three isomers were lower than the expected uncertainty of the standard partial molal volumes. For that reason, we present only the averaged values considered as representative for all three cresols. These values are listed in Table 2 together with three literature values available close to our experimental conditions and resulting from highly reliable sources (listed below Table 2). The volumetric properties of phenol and the three cresols are available from Hynek et al. (1997) and from Hnedkovsky et al. (1998) at the lower temperature limit of our measurements; the differences with our values are below 1 $\text{cm}^3 \text{mol}^{-1}$, which confirms our error estimation. Criss and Wood (1996) reported the standard partial molal volume of phenol at 598 K and 28 MPa that is 2.4 $\text{cm}^3 \text{mol}^{-1}$ higher than our value measured at 31.4 MPa. Since the standard partial molal volume of aqueous nonelectrolytes generally decreases with increasing pressure the two values can be considered as consistent. New results and the values determined earlier at lower temperatures at the Institute of Chemical Technology in Prague are plotted in Fig. 3 that illustrates the reasonable agreement of results from

Table 2
Standard partial molal volumes of aqueous phenol and cresols at high temperatures and pressures, new measurements and literature data

T (K)	p (MPa)	V° (phenol) ($\text{cm}^3 \text{mol}^{-1}$)	V° (cresols) ^a ($\text{cm}^3 \text{mol}^{-1}$)
573.3	10.1	144.0	171.5
573.2	9.4	143.4 ^b	172.7 ^c
597.9	13.6	160.2	192.4
597.9	31.2	137.7	164.2
598.2	28.0	140.2 ^d	—
623.4	20.8	193.3	233.3
623.4	31.4	150.7	176.9

^a Averaged value for *o*-, *m*-, and *p*-cresols.

^b Hynek et al. (1997).

^c Degrange (1998) reported 172.4, 172.7, and 172.9 $\text{cm}^3 \text{mol}^{-1}$ for *o*-, *m*-, and *p*-cresols, respectively.

^d Criss and Wood (1996).

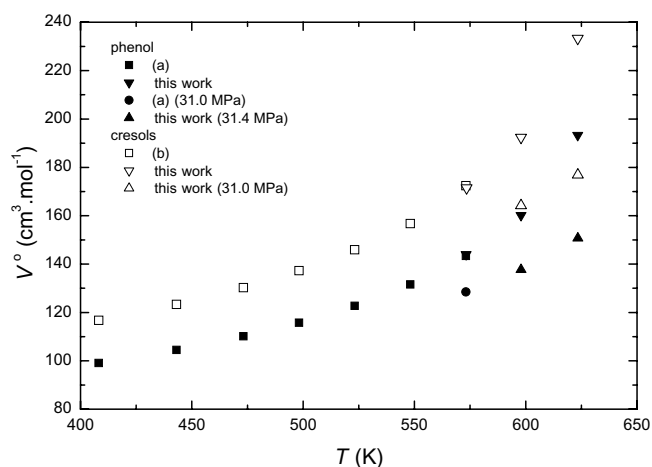


Fig. 3. Standard partial molal volumes as a function of temperature ($T > 400$ K) and pressure. The values were obtained close above the saturation pressure of water when not otherwise indicated: ref a, Hynek et al. (1997); ref b, Hnedkovsky et al. (1998).

different data sources as a function of temperature and pressure.

4. Thermodynamic properties of aqueous alkylphenols and alkylanilines

4.1. Review of experimental data

The sources of experimental data directly related to the Gibbs energy of hydration and its temperature and pressure derivatives for the studied classes of solutes are listed in Tables 3–6. These sources were used to constitute a database of 160, 17, 156, and 264 data points leading, respectively, to $\Delta_{\text{h}}G^\circ$, $\Delta_{\text{h}}H^\circ$, $\Delta_{\text{h}}C_p^\circ$, and V° values used in the simultaneous correlation. Beside the solution properties, the data on pure solutes are also needed for conversion between the solution and hydration properties. This is namely the case of vapor pressures, enthalpies of vaporization and sublimation and ideal gas heat capacities whose sources are also specified below.

It is apparent that a considerable amount of data is available on the Gibbs energy level at temperatures below

373 K resulting from a variety of literature sources. On the other hand, only few enthalpic values were reported for a limited number of solutes at or near 298 K. The volumetric and heat capacity data are available for both hydroxy and aminoderivatives over a wide range of temperatures and pressures thanks to recent campaigns of measurements at the Prague Institute of Chemical Technology (Czech republic) and at the Blaise Pascal University Clermont-Ferrand (France). Phenol, cresols, and aniline are the solutes for which the highest number of data is available in the literature. It can be noted that for solutes containing two polar groups (dihydroxybenzenes, diamino-benzenes, and aminophenols) no data are available for the Gibbs energy and enthalpy while sufficient information is available for the volumes and heat capacities.

4.1.1. Gibbs energy of hydration

The Gibbs energy of hydration is directly related to the Henry's law constant k_{H}

$$\Delta_{\text{h}}G^\circ = RT \ln(k_{\text{H}}/p_{\text{r}}) + RT \ln(M_{\text{w}}m_{\text{o}}) \quad (13)$$

in which $p_{\text{r}} = 0.1$ MPa, $m_{\text{o}} = 1$ mol kg^{-1} , and k_{H} is defined as the limiting ratio of the fugacity to the mole fraction of a solute in an aqueous phase:

$$k_{\text{H}} = \lim_{x \rightarrow 0} (f/x). \quad (14)$$

The term containing the molar mass of water M_{w} is the conversion term between the molar fraction and molality standard state conventions. The Henry's law constant can be obtained for the studied class of solutes from different types of experimental data characterizing dilute aqueous solutions at near ambient conditions. It is simply related to the vapor–liquid distribution constant (equal to the limiting value of the relative volatility) $K_{\text{d}} = \lim_{x \rightarrow 0} (y/x)$ where y and x are the molar fractions of a solute in coexisting vapor and liquid phases, respectively. At near ambient conditions $k_{\text{H}} \cong p_{\text{sat,w}} K_{\text{d}}$ where $p_{\text{sat,w}}$ is the vapor pressure of water. Another source is the air–water partition coefficient $K_{\text{aw}} = \lim_{x \rightarrow 0} (C_{\text{a}}/C_{\text{w}})$ where C stands for molarity. This coefficient is used in environmental chemistry for expressing the partitioning of a pollutant between atmospheric and aquatic phase; it is called sometimes the dimensionless Henry's

Table 3
Data sources leading to the Gibbs energy of hydration, $\Delta_h G^{\text{oc}}$

Solute	Temp. range ^a	Press. range ^b	No. of data	Reference	
Phenol	329–363	0.1	3	Schreinemakers (1900)	
	318	0.1	1	Weller et al. (1963)	
	353–373	0.1	2	Hakuta (1975)	
	281–298	0.1	2	Leunberger et al. (1985)	
	277–300	0.1	3	Abd-El-Bary et al. (1986)	
	293–303	0.1	2	Tremp et al. (1993)	
	349–372	0.1	3	Dohnal and Fenclova (1995)	
	349–371	0.1	5	Moore et al. (1995)	
	313–363	0.1	6	Tabai et al. (1997)	
	293	0.1	1	Sheikheldin et al. (2001)	
	281–302	0.1	6	Harrison et al. (2002)	
	278–298	0.1	5	Feigenbrugel et al. (2004)	
	<i>o</i> -Cresol	373	0.1	1	Hakuta (1975)
		281–298	0.1	2	Leunberger et al. (1985)
293–303		0.1	2	Tremp et al. (1993)	
349–372		0.1	3	Dohnal and Fenclova (1995)	
293		0.1	1	Sheikheldin et al. (2001)	
281–302		0.1	6	Harrison et al. (2002)	
<i>m</i> -Cresol	278–298	0.1	5	Feigenbrugel et al. (2004)	
	281–298	0.1	2	Leunberger et al. (1985)	
	349–372	0.1	3	Dohnal and Fenclova (1995)	
<i>p</i> -Cresol	293	0.1	1	Sheikheldin et al. (2001)	
	281–302	0.1	6	Harrison et al. (2002)	
	278–298	0.1	5	Feigenbrugel et al. (2004)	
2,3-Dimethylphenol	281–298	0.1	2	Leunberger et al. (1985)	
	349–372	0.1	3	Dohnal and Fenclova (1995)	
	293	0.1	1	Sheikheldin et al. (2001)	
	281–298	0.1	2	Leunberger et al. (1985)	
2,4-Dimethylphenol	293–303	0.1	2	Tremp et al. (1993)	
	349–372	0.1	3	Dohnal and Fenclova (1995)	
	278–298	0.1	5	Feigenbrugel et al. (2004)	
2,5-Dimethylphenol	281–298	0.1	2	Leunberger et al. (1985)	
	349–372	0.1	3	Dohnal and Fenclova (1995)	
	281–298	0.1	2	Leunberger et al. (1985)	
2,6-Dimethylphenol	349–372	0.1	3	Dohnal and Fenclova (1995)	
	281–298	0.1	2	Leunberger et al. (1985)	
	349–372	0.1	3	Dohnal and Fenclova (1995)	
3,4-Dimethylphenol	281–298	0.1	2	Leunberger et al. (1985)	
	349–372	0.1	3	Dohnal and Fenclova (1995)	
	281–298	0.1	2	Leunberger et al. (1985)	
3,5-Dimethylphenol	349–372	0.1	3	Dohnal and Fenclova (1995)	
	281–298	0.1	2	Leunberger et al. (1985)	
	349–372	0.1	3	Dohnal and Fenclova (1995)	
Aniline	323	0.1	1	Dallos et al. (1983)	
	356–371	0.1	4	Moore et al. (1995)	
	298–353	0.1	6	Bernauer et al. (2006)	
<i>o</i> -Toluidine	293	0.1	1	Chiou et al. (1982)	
	298–323	0.1	3	This work	
<i>m</i> -Toluidine	293	0.1	1	Chiou et al. (1982)	
	298–323	0.1	3	This work	
<i>p</i> -Toluidine	298–366	0.1	4	Moore et al. (1995)	
	298–313	0.1	2	This work	

^a K.

^b MPa.

^c Additional sources with only one result at 298 K and 0.1 MPa: Parsons et al. (1971) for phenol; Parsons et al. (1972) for *o*-, *p*-cresol; Huyskens et al. (1975) for *o*-toluidine; Hashimoto et al. (1984) for *p*-toluidine; Jayasinghe et al. (1992) for aniline, *p*-toluidine, 3,4-dimethylaniline, and 2,4,5-trimethylaniline; Shiu et al. (1994) for 2,4,6-trimethylphenol, 2,4-dimethylphenol, 2,6-dimethylphenol, 4-nonylphenol, 4-octylphenol, phenol and *o*-, *m*-, and *p*-cresol; Mackay et al. (1995) for 2- and 4-ethylphenol; Altschuh et al. (1999) for *o*-, *m*-cresol, aniline and *o*-, *m*-, and *p*-toluidine.

law constant. It simply stands $k_H = K_{aw} RT/V_w$ (V_w is the molar volume of water). Values for the limiting activity coefficients $\gamma^{\text{R}\infty}$ complying with Raoult's law and derived from vapor-liquid, chromatographic or solubility experiments have been published in chemical engineering and

environmental literature at temperatures up to 373 K or so. They can be converted to the Henry's law constant by multiplication with vapor pressure of pure liquid solute (real or hypothetical) according to $k_H = p_{\text{sat}}^l \gamma^{\text{R}\infty}$. For solids or liquids sparingly soluble in water, the Henry's law

Table 4
Data sources leading to the enthalpy of hydration, $\Delta_{\text{h}}H^{\circ}$

Solute	Temp. range ^a	Press. range ^b	No. of data	Reference
Phenol	298	0.1	1	Fernandez and Hepler (1959)
	298	0.1	1	Parsons et al. (1971)
	293–305	0.1	3	Nichols and Wadsö (1975)
	298	0.1	1	Gillet (1990)
<i>o</i> -Cresol	298	0.1	1	Parsons et al. (1972)
<i>p</i> -Cresol	293	0.1	1	Parsons et al. (1972)
	293–313	0.1	4	Nichols and Wadsö (1975)
Aniline	293–313	0.1	4	Nichols and Wadsö (1975)
	298	0.1	1	Gillet (1990)

^a K.

^b MPa.

^c The enthalpies of sublimation of phenol, *o*-cresol, and *p*-cresol were obtained from Andon et al. (1960), the enthalpy of vaporization of subcooled *p*-cresol was obtained from Andon et al. (1960), the enthalpy of vaporization of aniline was from the review of Majer and Svoboda (1985), respectively.

Table 5
Data sources for the standard partial molal volume, V°

Solute	Temp. range ^a	Press. range ^b	No. of data	Reference
Phenol	298–598	28	10	Criss and Wood (1996)
	373–573	0.5–31	9	Hynek et al. (1997)
	298–338	0.1–0.2	5	Hnedkovsky et al. (1998)
	278–388	0.35	12	Origlia-Luster et al. (2003)
<i>o</i> -Cresol	298–573	0.1–10	12	Hnedkovsky et al. (1998)
	598–623	13–31	4	Censky et al. (2005a)
<i>m</i> -Cresol	298–573	0.1–10	12	Hnedkovsky et al. (1998)
	598–623	13–31	4	Censky et al. (2005a)
<i>p</i> -Cresol	278–348	0.1	4	Makhatadze et al. (1990)
	298–573	0.1–10	12	Hnedkovsky et al. (1998)
	598–623	13–31	4	Censky et al. (2005a)
<i>o</i> -Dihydroxybenzene	298–498	0.1–30	15	Jedelsky et al. (1999)
<i>m</i> -Dihydroxybenzene	298–498	0.1–30	15	Jedelsky et al. (1999)
<i>p</i> -Dihydroxybenzene	298–498	0.1–30	15	Jedelsky et al. (1999)
Aniline	298–573	0.1–30	21	Ruzicka et al. (2000a)
<i>o</i> -Toluidine	298–573	0.1–30	19	Ruzicka et al. (2000b)
<i>m</i> -Toluidine	298–573	0.1–30	19	Ruzicka et al. (2000b)
<i>p</i> -Toluidine	298–573	0.1–30	19	Ruzicka et al. (2000b)
<i>o</i> -Diaminobenzene	298–573	0.1–30	20	Hyncica et al. (2002)
<i>m</i> -Aminophenol	298–573	0.1–30	27	Striteska et al. (2003)

^a K.

^b MPa.

^c Additional sources with only one result at 298 K and 0.1 MPa: Desnoyers et al. (1973), Hamann and Linton (1974), Hamann and Lim (1954), and Hopkins et al. (1976) for phenol; Indelli (1963) for *o*-, *m*-, and *p*-dihydroxybenzene; Shahidi et al. (1977) for aniline.

constant can be also approximated by the ratio of the vapor pressure of pure solute and its solubility in water $k_{\text{H}} = p_{\text{sat}}/x_{\text{sol}}$ where x_{sol} is the mole fraction solubility. This approach is not, however, easily applicable here since most solutes are fairly soluble and the vapor pressures at near ambient conditions are often missing for these compounds of low volatility.

It should be noted that beside the rigorous thermodynamic definition of k_{H} by Eq. (14) that we strictly adopt here, other definitions are used in the literature. The Henry's law constant is considered in geochemistry and atmospheric chemistry rather as a concentration to pressure ratio and it is usually assimilated to K_{aw} by environmental chemists.

All these different data allowing the calculation of $\Delta_{\text{h}}G^{\circ}$ via k_{H} (Eq. (13)) can be found in references listed in Table 3.

It is apparent that more information is available for the hydroxyderivatives, where most of data were reported for phenol and cresols, than for solutes containing the amino group. It is practically impossible to derive k_{H} values for solutes with two polar groups on the aromatic ring that are highly soluble in water and nonvolatile (solid) at ambient conditions. For the solutes containing one polar group, Henry's law constants are published or can be derived from the reported data at 298 K or over a limited temperature interval close to and above ambient conditions. The data have been published in sources focusing on thermodynamic data for chemical engineering and in journals of environmental and atmospheric chemistry.

On the thermodynamic side, the most important contribution is that of Dohnal and Fenclova (1995) who published highly reliable Henry's law constants and limiting

Table 6
Data sources leading to heat capacity of hydration $\Delta_h C_p^{cc}$

Solute	Temp. range ^a	Press. range ^b	No. of data	Reference
Phenol	278–388	0.35	12	Origlia-Luster et al. (2003)
	298–628	0.1–30	18	Censky et al. (2005a)
<i>o</i> -Cresol	304–623	0.1–30	17	Censky et al. (2005a)
<i>m</i> -Cresol	304–623	0.1–30	17	Censky et al. (2005a)
<i>p</i> -Cresol	278–348	0.1	4	Makhatadze et al. (1990)
	304–623	0.1–30	17	Censky et al. (2005a)
<i>o</i> -Dihydroxybenzene	303–473	0.1–2.1	4	Censky et al. (2005b)
<i>m</i> -Dihydroxybenzene	303–473	0.1–2.1	4	Censky et al. (2005b)
<i>p</i> -Dihydroxybenzene	303–473	0.1–2.1	4	Censky et al. (2005b)
Aniline	303–573	0.1–30	8	Censky et al. (2005a)
<i>o</i> -Toluidine	303–574	0.1–30	8	Censky et al. (2005a)
<i>m</i> -Toluidine	303–574	0.1–30	8	Censky et al. (2005a)
<i>p</i> -Toluidine	303–574	0.1–30	8	Censky et al. (2005a)
<i>o</i> -Diaminobenzene	303–574	0.1–30	8	Censky et al. (2005b)
<i>o</i> -Aminophenol	303–473	0.1–2.1	4	Censky et al. (2005b)
<i>m</i> -Aminophenol	303–573	0.1–30	8	Censky et al. (2005b)
<i>p</i> -Aminophenol	303–473	0.1–2.1	4	Censky et al. (2005b)

^a K.

^b MPa.

^c Additional sources with only one result at 298 K and 0.1 MPa: Perron and Desnoyers (1979) and Hopkins et al. (1976) for phenol; Bernauer et al. (2006) for aniline.

Table 7
Values of group contributions for calculating thermodynamic properties of hydration of aqueous alkylphenols and alkyanilines at 298 K and 0.1 MPa

Group	$\Delta_h G^{oa}$	$\Delta_h H^{oa}$	$\Delta_h C_p^{cb}$	V^{cc}
C ^d	−4.50	2.6	−63	−3.0
CH ^d	−1.79	−0.9	−2	6.35
CH ₂ ^d	0.72	−3.76	64	15.70
CH ₃ ^d	3.63	−7.54	132	25.14
Car ^{d,e}	−3.85	−0.67	−50	4.00
CH _{ar} ^{d,e}	−0.65	−5.00	48	13.58
I(C−C) ^f	−1.01	2.0	n.e.	n.e.
OH _{phi} ^{g,h}	−19.11(0.13) ^j	−27.51(0.45) ^j	30(6) ^j	12.88(0.36) ^j
NH _{2,phi} ^{g,h}	−15.96(0.20) ^j	−26.43(0.75) ^j	49(8) ^j	16.71(0.72) ^j
I(C−OH) ^{f,h}	1.83(0.18) ^j	n.e. ^k	24(24) ^j	0.8(0.8) ^j
I(OH−OH) ^{f,h}	n.e. ^k	n.e. ^k	51(30) ^j	−2.2(1.4) ^j
I(NH ₂ −NH ₂) ^{f,h}	n.e. ^k	n.e. ^k	69(32) ^j	−3.0(2.2) ^j
X _{SS} ⁱ	7.96	−2.29	0	1.2

^a kJ mol^{−1}.

^b J K^{−1} mol^{−1}.

^c cm³ mol^{−1}.

^d Plyasunov and Shock (2000a).

^e A group with subscript_{ar} is a part of an aromatic ring.

^f Correction for *ortho*-position on the aromatic ring: C stands for alkyl-, OH for hydroxy-, and NH₂ for amino groups.

^g A group with subscript_{phi} is directly bound to aromatic ring.

^h This work.

ⁱ Standard state term (see Eq. (8)).

^j 95% confidence limits of the parameter.

^k Not evaluated (no data available or parameters are not significant at the 95% confidence level).

activity coefficients determined in a vapor–liquid equilibrium circulation still for 10 phenolic solutes. Bernauer et al. (2006) recently reported highly reliable k_H values for aniline that are the result of a simultaneous treatment of new vapor–liquid equilibrium and calorimetric data. Other values

for phenol were measured by Abd-El-Bary et al. (1986) using the inert gas stripping method and by Tabai et al. (1997) using ebulliometry. In the latter reference are reported both the Henry's law constants and limiting activity coefficients. These data, however, are not consistent due to a calculation error in the original paper when determining k_H that we have corrected. A similar approach was used by Moore et al. (1995) who reported limiting activity coefficients and the Henry's law constants for phenol, aniline, *o*-toluidine, and *p*-toluidine determined by differential ebulliometry. However, the data for *o*-toluidine which seem to be in error were not considered. Dallos et al. (1983) published one limiting activity coefficient for aniline. All conversions between $\gamma^{R\infty}$ and k_H were performed by us using the vapor pressures reported by Dohnal and Fenclova (1995) for phenolic compounds and by Censky (2001) for solutes with the amino group. The vapor pressure data for this latter group of compounds were obtained by combining the new static measurements (Censky, 2001) with the literature data (Dreisbach and Schrader, 1949; McDonald et al., 1959; Krevor et al., 1985; Steele et al., 1994). They were correlated by the Cox equation as a function of temperature simultaneously with the ideal gas and liquid heat capacities (Frenkel et al., 1994; Zabransky et al., 1996) in order to provide a realistic extrapolation of vapor pressures towards ambient temperatures. This type of data treatment was described earlier by Ruzicka and Majer (1996).

A myriad of approaches was used by environmental and atmospheric chemists in determinations of data leading to k_H at ambient conditions. Some of these data are, however, of low reliability and striking differences are observed between the values originating from different sources. This has been recently documented in an article by Harrison et al. (2002), in which an overview table lists the Henry's

Table 8
Gibbs energy of hydration, $\Delta_h G^\circ$, and Gibbs energy of formation in the ideal gas, ΔG_f^{ig} , of aqueous alkylphenols and alkylanilines at 298.15 K and 0.1 MPa

Solute	$\Delta G_f^{\text{ig}^a}$	$\Delta_h G^\circ{}^a$	GC value ^{a,b}
Phenol	−32.5 ^c	−19.78, ^d −19.98, ^e −15.97, ^f −18.72, ^g −18.70 ^h	−18.25
<i>o</i> -Cresol	−34.3 ^c	−15.97, ^g −16.08, ^h −16.68, ⁱ −17.24, ^e −15.07, ^f −16.01 ^j	−15.99
<i>m</i> -Cresol	−40.1 ^c	−16.59, ^f −17.44, ^g −17.00, ^h −17.51 ^j	−17.82
<i>p</i> -Cresol	−31.5 ^c	−17.44, ^f −17.25, ^g −18.22, ^h −17.77 ⁱ	−17.82
2-Ethylphenol	−25.7 ^f	−15.79 ^k	−15.27
4-Ethylphenol	−25.7 ^f	−16.47 ^k	−17.10
4-Octylphenol	24.8 ^f	−13.21 ^h	−12.78
4-Nonylphenol	33.2 ^f	−10.34 ^h	−12.06
2,3-Dimethylphenol	−33.2 ^c	−17.25 ^g	−16.57
2,4-Dimethylphenol	−41.1 ^c	−14.83, ^g −15.68 ^h	−15.56
2,6-Dimethylphenol	−38.9 ^c	−12.77, ^g −13.87 ^h	−13.73
3,4-Dimethylphenol	−34.1 ^c	−19.25 ^g	−18.40
3,5-Dimethylphenol	−39.3 ^c	−18.14 ^g	−17.39
2,4,6-Trimethylphenol	118.0 ^f	−14.88 ^h	−13.30
Aniline	−7.0 ^c	−15.52, ^j −15.42, ^l −15.19 ^m	−15.10
<i>o</i> -Toluidine	167.6 ^c	−15.43, ^j −14.81, ⁿ −14.72 ^o	−14.67
<i>m</i> -Toluidine	165.4 ^c	−15.86, ^j −14.9 ⁿ	−14.67
<i>p</i> -Toluidine	167.7 ^c	−17.81, ^{j,q} −15.14, ^l −14.39, ⁿ −13.88 ^p	−14.67
3,4-Dimethylaniline	176.1 ^f	−15.98 ^l	−15.25
2,4,5-Trimethylaniline	174.9 ^f	−14.80 ^l	−14.82

^a kJ mol^{−1}.

^b Group contribution value.

^c Frenkel et al. (1994).

^d Parsons et al. (1971).

^e Harrison et al. (2002).

^f Feigenbrugel et al. (2004).

^g Leunberger et al. (1985).

^h Shiu et al. (1994).

ⁱ Parsons et al. (1972).

^j Altschuh et al. (1999).

^k Mackay et al. (1995).

^l Jayasinghe et al. (1992).

^m Bernauer et al. (2006).

ⁿ This work.

^o Huyskens et al. (1975).

^p Hashimoto et al. (1984).

^q Excluded from evaluation.

^r Estimated from Joback's group contribution scheme (Poling et al., 2001).

Table 9
Enthalpy of hydration, $\Delta_h H^\circ$, and enthalpy of formation in the ideal gas, ΔH_f^{ig} , of aqueous alkylphenols and alkylanilines at 298.15 K and 0.1 MPa

Solute	$\Delta H_f^{\text{ig}^a}$	$\Delta_h H^\circ{}^a$	GC value ^{a,b}
Phenol	−96.4 ^c	−55.94, ^d −55.96, ^e −55.69, ^f −55.73 ^h	−55.47
<i>o</i> -Cresol	−128.6 ^c	−60.75 ^g	−58.68
<i>p</i> -Cresol	−125.3 ^c	−59.79, ^g −58.16 ^h	−58.68
Aniline	−87.5 ^c	−53.93, ^e −54.05 ^h	−54.39

^a kJ mol^{−1}.

^b Group contribution value.

^c Frenkel et al. (1994).

^d Parsons et al. (1971).

^e Gillet (1990).

^f Fernandez and Hepler (1959).

^g Parsons et al. (1972).

^h Nichols and Wadsö (1975).

law constants of phenol at 298 K published in literature. The highest value differs from the lowest by more than one order of magnitude. In addition, some more reliable

data from thermodynamic sources were ignored. We have extracted the Henry's law constants from the data obtained recently using different vapor–liquid equilibrium techniques for several phenolic compounds (Sheikheldin et al., 2001; Harrison et al., 2002; Feigenbrugel et al., 2004). A considerable amount of k_H data was obtained at 298 K only (the references are listed at the bottom of Table 3), particularly for solutes containing NH₂ group (Jayasinghe et al., 1992; Altschuh et al., 1999). One should also mention solubility measurements by Chiou et al. (1982) and Hashimoto et al. (1984) for aniline and toluidines (see also Tables 1a–1c) that we have converted to k_H using vapor pressures of Censky (2001) as indicated above.

In Table 3 are also listed, beside primary data sources, three review articles reporting k_H values whose origin is sometimes unclear. This is the case of Henry's law constants of phenolic solutes obtained at 281 and 298 K as a ratio of different vapor pressure and solubility data by

Table 10
Standard partial molal volume, V° , of aqueous alkylphenols and alkylanilines at 298.15 K and 0.1 MPa

Solute	V° ^a	GC value ^{a,b}
Phenol	86.2, ^c 86.1, ^d 86.17, ^e 86.06, ^f 86.0 ^g	85.90
<i>o</i> -Cresol	102.26 ^c	102.26
<i>m</i> -Cresol	103.32 ^c	101.46
<i>p</i> -Cresol	100.3, ^h 103.23 ^e	101.46
<i>o</i> -Dihydroxybenzene	87.07, ⁱ 86.88 ^j	86.98
<i>m</i> -Dihydroxybenzene	88.92, ⁱ 88.8 ^j	89.20
<i>p</i> -Dihydroxybenzene	88.7, ⁱ 88.7 ^j	89.20
Aniline	89.3, ^k 89.49 ^l	89.73
<i>o</i> -Toluidine	105.14 ^m	105.29
<i>m</i> -Toluidine	106.1 ^m	105.29
<i>p</i> -Toluidine	106.2 ^m	105.29
<i>o</i> -Diaminobenzene	93.87 ⁿ	93.87
<i>m</i> -Aminophenol	92.08 ^o	93.03

^a cm³ mol⁻¹.

^b Group contribution value.

^c Hopkins et al. (1976).

^d Hamann and Linton (1974).

^e Hnedkovsky et al. (1998).

^f Desnoyers et al. (1973).

^g Hamann and Lim (1954).

^h Makhatadze et al. (1990).

ⁱ Indelli (1963).

^j Jedelsky et al. (1999).

^k Shahidi et al. (1977).

^l Ruzicka et al. (2000a).

^m Ruzicka et al. (2000b).

ⁿ Hyncica et al. (2002).

^o Sriteska et al. (2003).

Leunberger et al. (1985). Several values at 298 K were taken from the reviews of Shiu et al. (1994) and Mackay et al. (1995). The only source reporting directly $\Delta_h G^\circ$ (298 K) determined from solubilities and vapor pressures for phenol, *o*-cresol and *p*-cresol is Parsons et al. (1971, 1972).

In order to increase the number of $\Delta_h G^\circ$ data for toluidines, we have determined the Henry's law constants at three temperatures by combining the results of solubility measurements presented above with vapor pressures of pure solutes. Since toluidines are only moderately hydrophobic and hence relatively soluble, we did not approximate k_H as the vapor pressure to solubility ratio but preferred to convert first the solubility to limiting activity coefficient $\gamma^{R\infty}$ complying with Raoult's law. While the relationship is trivial between solubility and activity coefficient in the case of liquid solutes ($\gamma^R = 1/x_{\text{sol}}$), conversion is more complex in the case of *p*-toluidine that is solid at the lowest temperature:

$$\gamma^R = F/x_{\text{sol}} \quad F = p_{\text{sat}}^s/p_{\text{sat}}^l = \exp(\Delta_m S(1 - T_m/T)), \quad (15)$$

where the entropy of melting $\Delta_m S$ (54.22 J K⁻¹ mol⁻¹) at the melting point temperature $T_m = 317$ K was determined by Censky et al. (2001). Once the activity coefficient is determined, its limiting value is obtained by approximating its concentration dependence using the Margules equation as proposed by Wright et al. (1992)

Table 11
Heat capacity of hydration, $\Delta_h C_p^\circ$, and heat capacity of the ideal gas, C_p^{ig} , of aqueous alkylphenols and alkylanilines at ≈ 298.15 K and ≈ 0.1 MPa

Solute	C_p^{ig} ^a	$\Delta_h C_p^\circ$ ^a	GC value ^{a,b}
Phenol	102.9 ^c	212.9, ^d 210.5, ^e 222.1, ^f 217.9, ^g	220
<i>o</i> -Cresol	127.6 ^c	279.5 ^f	278
<i>m</i> -Cresol	124.6 ^c	272.8 ^f	254
<i>p</i> -Cresol	124.9 ^c	275.8, ^f 254.8 ^h	254
<i>o</i> -Dihydroxybenzene	119.7 ^c	203.0 ⁱ	203
<i>m</i> -Dihydroxybenzene	123.7 ^c	151.1 ⁱ	152
<i>p</i> -Dihydroxybenzene	123.3 ^c	151.7 ⁱ	152
Aniline	107.6 ^c	229.1, ^f 214.4 ^j	239
<i>o</i> -Toluidine	129.9 ^c	281.4 ^f	273
<i>m</i> -Toluidine	125.2 ^c	280.6 ^f	273
<i>p</i> -Toluidine	125.9 ^c	275.6 ^f	273
<i>o</i> -Diaminobenzene	128.3 ^k	258.2 ⁱ	258
<i>p</i> -Diaminobenzene	128.3 ^k	213.0 ⁱ	189
<i>o</i> -Aminophenol	123.0 ^k	141.1 ⁱ	171
<i>m</i> -Aminophenol	123.0 ^k	162.0 ⁱ	171
<i>p</i> -Aminophenol	123.0 ^k	143.4 ⁱ	171

^a J K⁻¹ mol⁻¹.

^b Group contribution value.

^c Frenkel et al. (1994).

^d Perron and Desnoyers (1979).

^e Hopkins et al. (1976).

^f Censky et al. (2005a), at 303.55 K.

^g Origlia-Luster et al. (2003) at 0.35 MPa.

^h Makhatadze and Privalov (1990).

ⁱ Censky et al. (2005b), at 303.55 K.

^j Bernauer et al. (2006).

^k Estimated from Joback's group contribution scheme (Poling et al., 2001).

$$\ln \gamma^{R\infty} = \ln \gamma^R (1 - x_{\text{sol}})^{-2}. \quad (16)$$

Then the Henry's law constant was calculated by multiplying the $\gamma^{R\infty}$ value by the vapor pressure of liquid toluidines determined by Censky (2001). In all calculations of the limiting activity coefficients for toluidines, it was assumed that their activity in the organic phase is unity. Despite the non-negligible solubility of water in the liquid organic phase, generally higher than that of organic solute in water, this approximation is generally considered as reasonable at near ambient conditions. This is due to the fact that the activity coefficient (complying with the Raoult's law) of a hydrophobic organic compound saturated by water is always slightly higher than unity compensating thus approximately solubility of water in the organic phase.

4.1.2. Enthalpy of hydration

The enthalpy of hydration is obtained by combining the enthalpies of solution $\Delta_s H^\circ$ obtained from calorimetric dissolution experiments with the enthalpies of vaporization or sublimation $\Delta_v H^\circ$ of pure liquid or solid solutes:

$$\Delta_h H^\circ = \Delta_s H^\circ - \Delta_v H^\circ. \quad (17)$$

Both $\Delta_s H^\circ$ and $\Delta_h H^\circ$ are published in literature and the inconsistency between different sources can be due to the different $\Delta_v H^\circ$ values. For that reason we have used systematically as input exclusively the calorimetric enthalpies

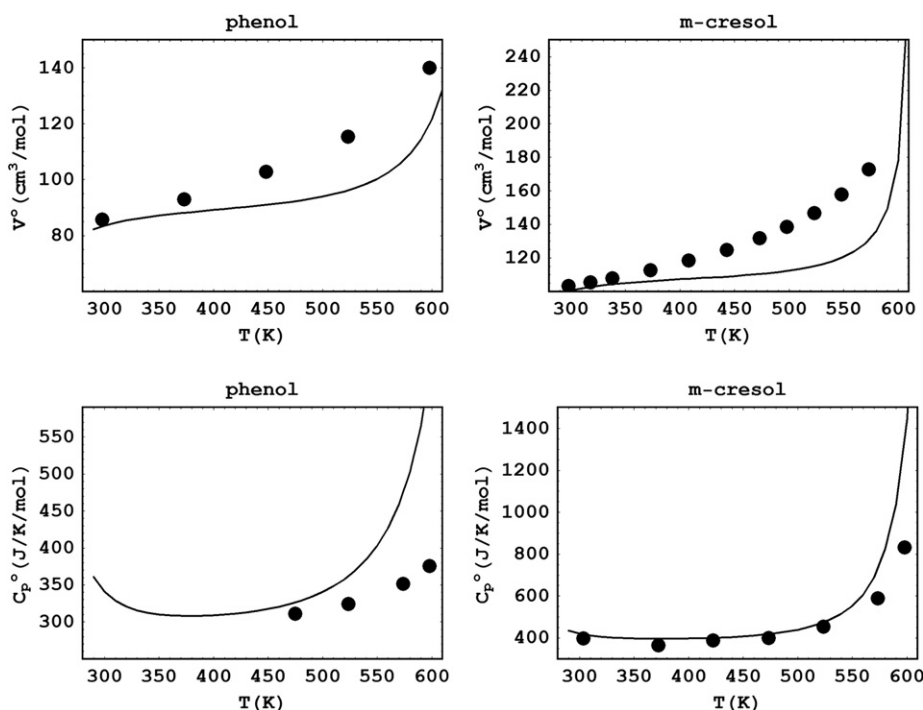


Fig. 4. Standard partial molal volume and standard partial molal heat capacity for phenol and *m*-cresol. Data for phenol: Criss and Wood (1996) for V° at 28 MPa, Čenský et al. (2005a) for C_p° at 30 MPa. Data for *m*-cresol: Hnedkovsky et al. (1998) for V° at $p \approx p_{\text{sat,w}}$, Čenský et al. (2005a) for C_p° at $p \approx p_{\text{sat,w}}$. Lines were calculated from the HKF model with parameters from Dale et al. (1997).

Table 12

Summary of standard partial molal thermodynamic properties at 298 K and 0.1 MPa calculated with the group contribution values (Table 7) and HKF parameters for selected aqueous alkylphenols and alkylanilines

Solute	$\Delta G_f^{\circ a}$	$\Delta H_f^{\circ a}$	$C_p^{\circ b}$	$S^{\circ c}$	$V^{\circ d}$	a_1^e	$10^{-3}a_2^c$	$10^{-3}a_3^f$	$10^{-5}a_4^g$	$10^{-2}c_1^b$	$10^{-4}c_2^g$	$10^{-5}\omega^c$
Phenol	-50.8	-151.9	323	190.0	86.0	7.3406	4.8168	5.4259	-3.1830	3.0787	5.9057	-0.3675
<i>o</i> -Cresol	-50.3	-187.3	406	206.0	102.3	8.6946	5.8445	6.4745	-3.9002	3.8615	7.8245	-0.4306
<i>m</i> -Cresol	-57.9	-191.0	379	219.1	101.5	8.6610	5.7094	6.4360	-3.8395	3.6273	6.2708	-0.3793
<i>p</i> -Cresol	-49.1	-184.0	379	213.0	101.5	8.6610	5.7094	6.4360	-3.8395	3.6273	6.2708	-0.3793
Aniline	-22.1	-141.9	346	185.8	89.7	7.6153	5.1674	5.6511	-3.3757	3.2540	8.5801	-0.4562
<i>o</i> -Toluidine	152.9	-1.17	403	207.3	105.3	8.9263	6.0845	6.6622	-4.0503	3.7615	8.9452	-0.4688
<i>m</i> -Toluidine	150.7	-2.97	398	208.6	105.4	8.9263	6.0845	6.6622	-4.0503	3.7615	8.9452	-0.4688
<i>p</i> -Toluidine	153.0	-2.27	399	203.3	105.3	8.9265	6.0840	6.6623	-4.0501	3.7297	8.9367	-0.4684
<i>o</i> -Dihydroxybenzene	-223.7	-351.6	323	202.6	87.0	7.7940	3.9439	5.6653	-3.0204	3.5034	-13.035	0.1390
<i>m</i> -Dihydroxybenzene	-229.9	-354.4	276	214.1	89.2	7.9909	4.0436	5.8075	-3.0948	3.0334	-13.035	0.1390
<i>p</i> -Dihydroxybenzene	-216.6	-341.2	276	213.7	89.2	7.9909	4.0436	5.8075	-3.0948	3.0334	-13.035	0.1390
<i>o</i> -Diaminobenzene ^h	235.3	125.5	386	380.5	93.9	8.2985	4.5393	6.0630	-3.3266	4.0304	-7.6867	0.1429
<i>m</i> - <i>p</i> -Diaminobenzene ^h	235.3	125.5	317	380.5	96.9	8.5635	4.6842	6.2574	-3.4347	3.3404	-7.6867	0.1429
Aminophenols ^h	23.9	-74.2	294	361.2	93.0	8.2794	4.3581	6.0322	-3.2604	3.1570	-10.361	0.7816

^a kJ mol⁻¹.

^b J K⁻¹ mol⁻¹.

^c J mol⁻¹.

^d cm³ mol⁻¹.

^e J mol⁻¹ MPa⁻¹.

^f J K mol⁻¹ MPa⁻¹.

^g J K mol⁻¹.

^h Ideal gas properties for diaminobenzenes and aminophenols were estimated from the Joback's group contribution scheme (Poling et al., 2001); different isomers are undistinguishable in this method.

of solution published in literature combined with the representative enthalpies of vaporization for their conversion to the enthalpy of hydration. In the case of phenolic com-

pounds the enthalpies of vaporization and sublimation were obtained from the vapor pressure data published by Andon et al. (1960) and in the case of aniline we used the

Table 13

Parameters for calculating group contributions in the T, p dependent SOCW model for hydration properties of aqueous alkylphenols and alkylanilines

Group	$10^3 a^a$	$10^4 b^a$	$10^6 c^a$	d	$10 e^b$
C ^c	-34.6310	9.4034	-53.9212	-7.3260	-13.7921
CH ^c	-6.5437	1.8156	-16.9215	-0.9492	-3.9136
CH ₂ ^c	-0.0244	0.7216	-8.9576	0.3416	-1.8264
CH ₃ ^c	7.2778	-0.1571	-1.9499	1.4268	-0.0177
Car ^c	-9.1549	2.2106	-21.3460	-1.3723	-4.9993
CH _{ar} ^c	0.6924	0.5168	-5.0903	0.3337	-1.0754
OH _{phi} ^d	10.9493	-3.1873	15.0667	3.2721	3.6873
NH _{2,phi} ^d	9.7888	-2.6612	21.2513	2.9503	4.7834
I(C-OH) ^d	3.9277	-1.0866	15.7086	0.7662	3.3560
I(OH-OH) ^d	-11.3296	3.1447	-3.9242	-2.6087	-1.3348

See Table 7 for group descriptions.

^a m³ kg⁻¹.

^b J K⁻² mol⁻¹.

^c Sedlbauer et al. (2002).

^d This work.

recommended $\Delta_v H^\circ$ values of Majer and Svoboda (1985) resulting from calorimetric measurements.

As apparent from Table 4, the enthalpies of solution are available only for four solutes (phenol, *o*-cresol, *p*-cresol, and aniline). The most important source of information and the only one presenting $\Delta_s H^\circ$ at several temperatures is that of Nichols and Wadsö (1975) where measurements were performed on a precision isothermal calorimeter of LKB (Sweden). Their values are in good agreement with those published by Gillet (1990) for phenol and aniline at 298 K, using the same type of calorimeter. These data were complemented by earlier determinations of Fernandez and Hepler (1959) and Parsons et al. (1971, 1972) that were obtained using relatively simple instrumentation but agree reasonably well with the above data. The values of Arnett et al. (1976) for phenol and three cresols have been omitted because they are systematically lower by at least 10% compared to other data.

4.1.3. Standard partial molal volume

The standard partial molal volumes are obtained from the density measurements, using typically a vibrating tube densimeter, by extrapolation to infinite dilution as described above (Eq. (9)). The bulk of high-temperature data are the measurements up to 573 K from the Prague Institute of Chemical Technology (Hynek et al., 1997; Hnedkovsky et al., 1998; Jedelsky et al., 1999; Ruzicka et al., 2000a,b; Hyncica et al., 2002; Striteska et al., 2003). The only measurements performed above 573 K are those of Criss and Wood (1996) for phenol and the new results presented above for phenol and cresols. Two additional sources present data over a limited temperature interval at near ambient conditions as apparent from Table 5. Several values were reported exclusively at 298 K.

4.1.4. Heat capacity of hydration

The heat capacities of hydration $\Delta_h C_p^\circ$ are obtained as the difference between the standard partial molal heat

capacity C_p° of a solute in aqueous solution and the heat capacity of an ideal gas C_p^{ig} . The standard partial molal heat capacities are extracted from experimental data *via* the apparent molar heat capacities that are calculated as

$$C_{p\phi} = M_s(c_{pw} + \Delta c_p) + \Delta c_p/m. \quad (18)$$

It is apparent that $C_{p\phi}$ is closely related to the heat capacity difference per unit mass Δc_p between solution and water. A relationship analogous to that for the standard volumes (Eq. (11)) is used for extrapolation to infinite dilution

$$C_p^\circ = \lim_{m \rightarrow 0} C_{p\phi} = c_{pw}M_s + \lim_{m \rightarrow 0} (\Delta c_p/m). \quad (19)$$

where c_{pw} is the heat capacity of pure water per unit mass. The heat capacity differences Δc_p are typically (but not exclusively) obtained from flow calorimetric experiments using the Picker type flow calorimetry. The bulk of high-temperature data has been obtained recently at the Blaise Pascal University in Clermont-Ferrand. These values are complemented for phenols by nano-DSC (differential scanning calorimetry) measurements of Origlia-Luster et al. (2003) and other data measured at 298 K or at near ambient conditions.

The ideal gas heat capacities tabulated by Frenkel et al. (1994) were used for calculation of heat capacities of hydration. The estimation method of Joback as presented by Poling et al. (2001) was used for estimation when C_p^{ig} were not available from literature.

4.2. Thermodynamic properties at ambient conditions: a group contribution approach

Available experimental data at 298 K and 0.1 MPa refer to a limited number of compounds, while many more structurally similar solutes may be of interest for geochemical modeling. In most cases there is only single experimental determination, or the various results for a solute differ significantly, such as for $\Delta_h G^\circ$ of phenol as commented above. It is therefore useful to look for a method that allows estimation of thermodynamic properties of solutes not yet measured, as well as assessment of thermodynamic consistency of experimental results obtained for different compounds in different laboratories. A group additivity concept can be used most conveniently for this purpose. Following previous efforts (Hine and Mookerjee, 1975; Cabani et al., 1981; Meylan and Howard, 1991; Amend and Helgeson, 1997; Plyasunov and Shock, 2000a) we have adopted a group contribution scheme based on Eq. (8) to calculate thermodynamic properties of hydration at $T_r = 298.15$ K and $p_r = 0.1$ MPa. Group contributions of hydrocarbon segments (parts of aromatic rings and alkyl groups) were taken from Plyasunov and Shock (2000a), because these values were obtained recently from the comprehensive literature evaluation of thermodynamic data for hydrocarbons. It should be noted that this approach has already been used as a basis for further extensions, for aqueous alcohols and ketones (Plyasunov and Shock, 2001a),

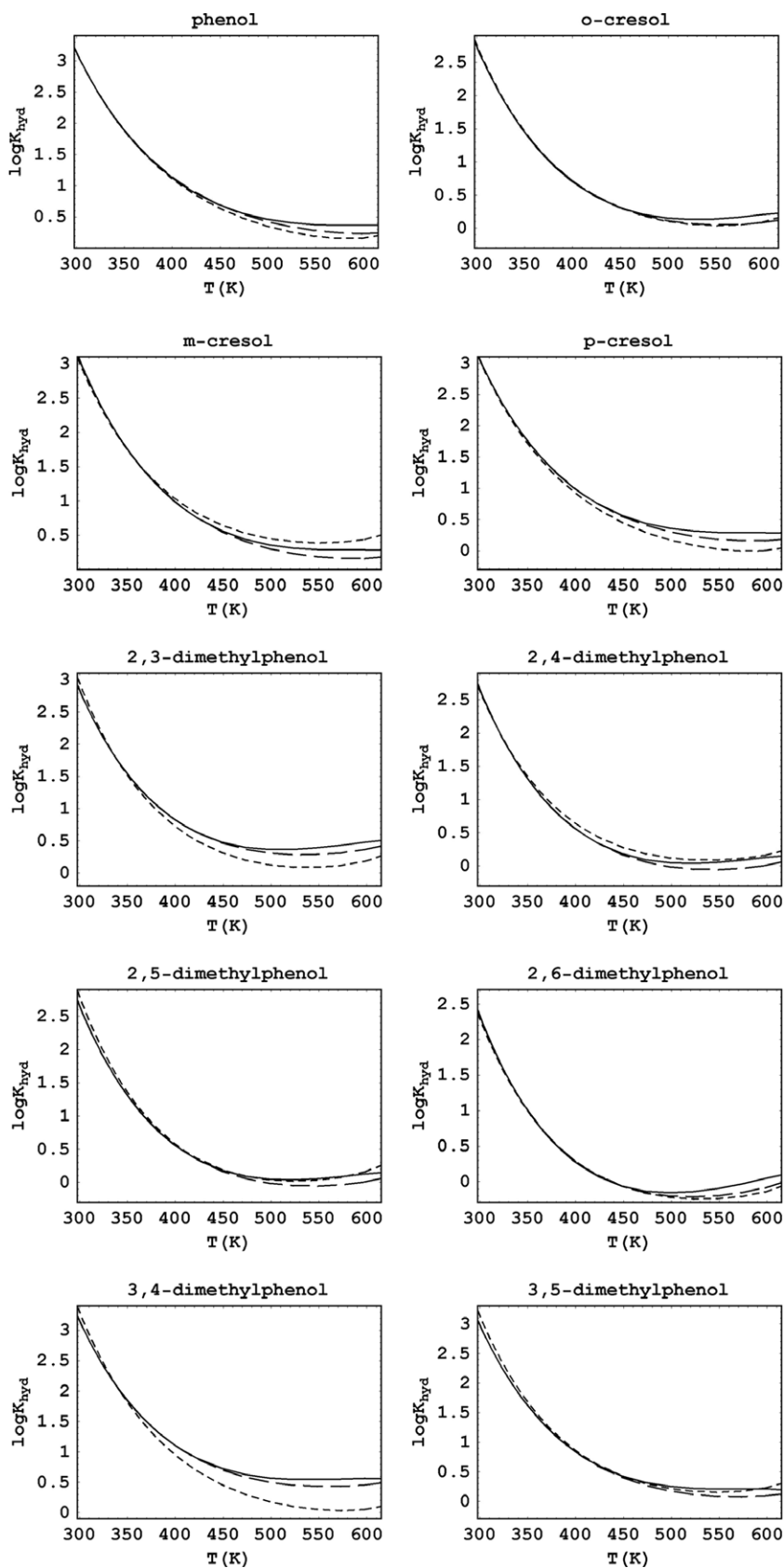


Fig. 5. Logarithmic equilibrium constants for the hydration reaction $solute(\text{ig}, T, p_i) \rightarrow solute(\text{aq}, T, p_{\text{sat},w})$ where $p_{\text{sat},w}$ is the saturation pressure of water for alkylphenols covered by Dale et al. (1997). Comparison of $\log K_{\text{hyd}}$ calculated from the group contribution SOCW model (full line); HKF model with parameters obtained with the correlation algorithm of Plyasunov and Shock, 2001b (long-dashed line); HKF model with parameters by Dale et al., 1997 (short-dashed line).

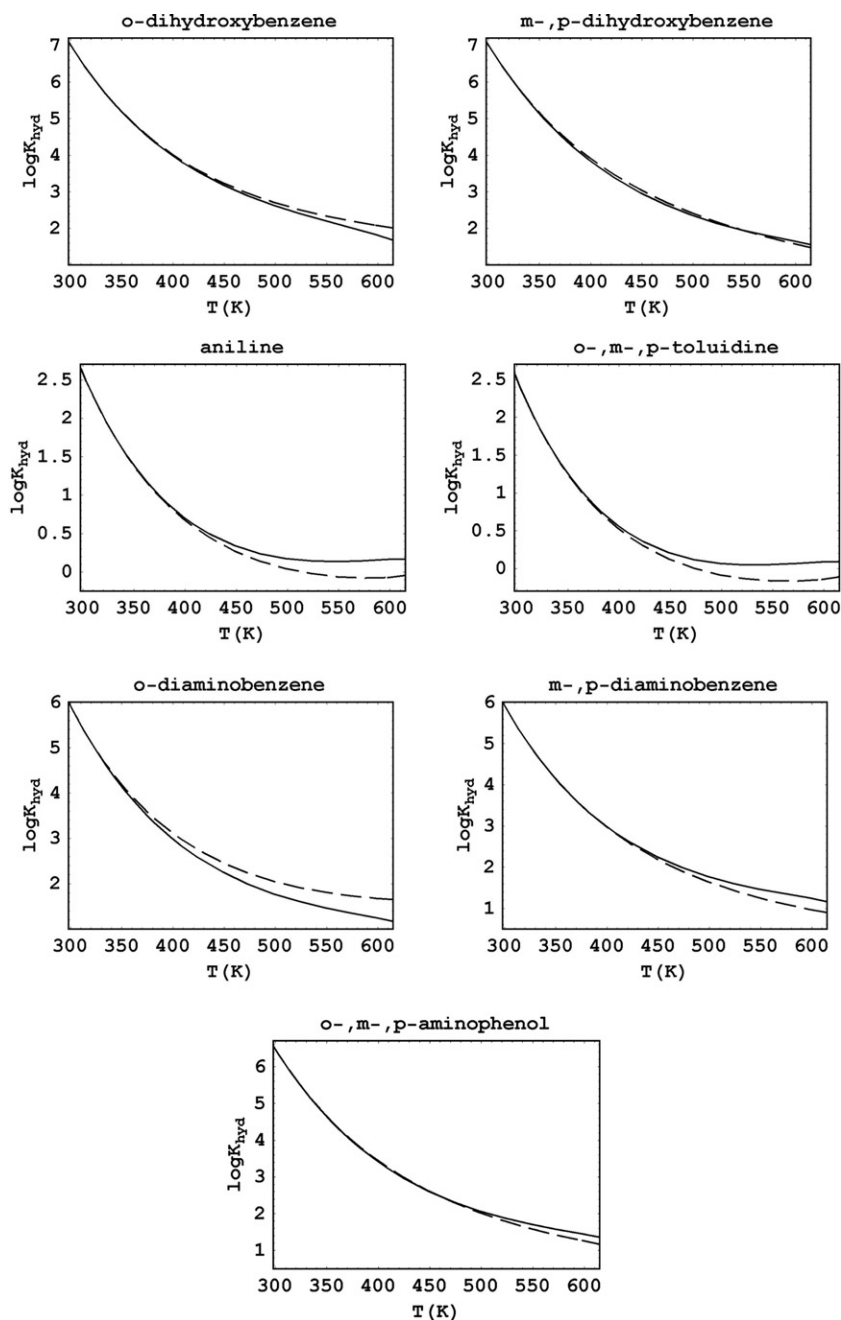


Fig. 6. Predictions of logarithmic equilibrium constants for the hydration reaction $solute(ig, T, p_r) \rightarrow solute(aq, T, p_{sat,w})$ where $p_{sat,w}$ is the saturation pressure of water for selected alkylanilines, aminophenols and dihydroxybenzenes. Comparison of $\log K_{hyd}$ calculated from the group contribution SOCW model (full line); HKF model with parameters obtained with the correlation algorithm of Plyasunov and Shock, 2001b (dashed line).

esters (Plyasunov et al., 2004), thiols and sulfides (Plyasunova et al., 2005), and ethers (Plyasunov et al., 2006).

Using the same group contribution scheme as Plyasunov and collaborators with their hydrocarbon contributions fixed, we evaluated the contributions of hydroxy and amino functional groups bound to an aromatic ring. However, unlike Plyasunov et al. we did not regress each thermodynamic property separately, but applied a simultaneous fit using the van't Hoff-type equation to assure thermodynamic consistency of the resulting values. This relation follows from the equivalent of Eq. (1), stated for the Gibbs energy

of hydration instead of the Gibbs energy of formation, at constant pressure $p_r = 0.1$ MPa:

$$\Delta_h G^\circ[T] = \Delta_h G^\circ[T_r] + (T_r - T) \cdot \Delta_h S^\circ[T_r] + \int_{T_r}^T \Delta_h C_p^\circ dT - T \cdot \int_{T_r}^T \Delta_h C_p^\circ d \ln T. \quad (20)$$

Simple approximation, which is realistic to at least 373 K, assumes constant (temperature independent) heat capacity of hydration. Substituting the entropy of hydration from $\Delta_h S^\circ[T_r] = (\Delta_h H^\circ[T_r] - \Delta_h G^\circ[T_r])/T_r$ and applying the

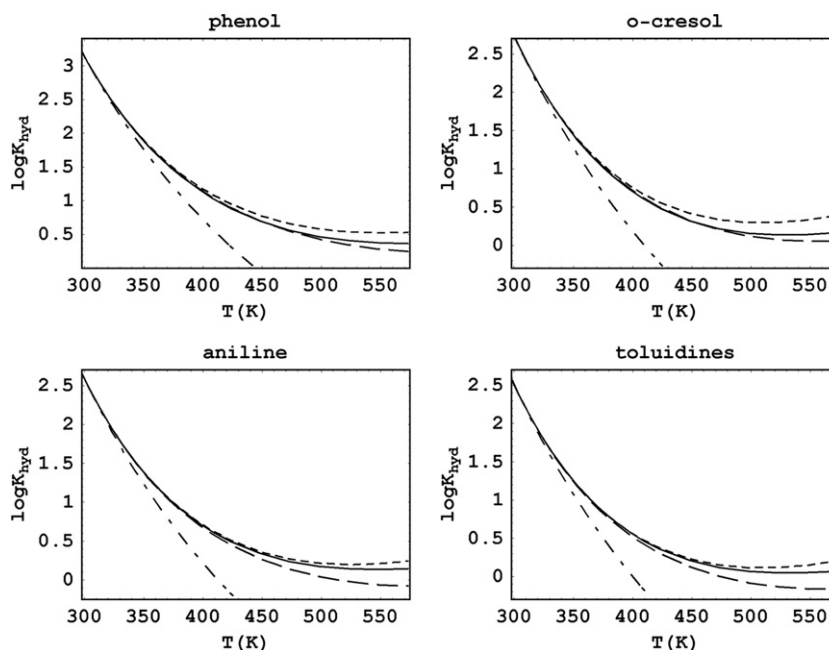


Fig. 7. Predictions of logarithmic equilibrium constants of phenol, *o*-cresol, aniline, and toluidines for the hydration reaction $\text{solute}(\text{ig}, T, p_T) \rightarrow \text{solute}(\text{aq}, T, p_{\text{sat},w})$ where $p_{\text{sat},w}$ is the saturation pressure of water. Comparison of $\log K_{\text{hyd}}$ calculated from the group contribution SOCW model (full line); HKF model with parameters obtained with the correlation algorithm of Plyasunov and Shock, 2001b (long-dashed line); Eq. (21) (short-dashed line); and Eq. (24) (dashed-dot line).

Table 14

Logarithmic equilibrium constants $\log K_{\text{hyd}}$ of selected solutes for the hydration reaction $\text{solute}(\text{ig}, T, p_T) \rightarrow \text{solute}(\text{aq}, T, p)$ along the saturation line of water and at elevated pressures

T (K)	298	373	423	473	523	573
p_{sat}						
Phenol	3.20	1.48	0.89	0.56	0.41	0.36
<i>o</i> -Cresol	2.80	1.04	0.48	0.21	0.13	0.16
<i>m,p</i> -Cresol	3.12	1.34	0.75	0.44	0.31	0.29
Aniline	2.65	1.02	0.50	0.24	0.14	0.14
Toluidines	2.57	0.88	0.36	0.12	0.05	0.07
Diaminobenzenes	6.00	3.54	2.60	1.99	1.61	1.34
Aminophenols	6.56	4.01	2.99	2.32	1.88	1.58
<i>o</i> -Dihydroxybenzene	7.11	4.56	3.56	2.89	2.41	2.02
<i>m,p</i> -Dihydroxybenzene	7.11	4.48	3.38	2.64	2.14	1.80
20 MPa						
Phenol	2.90	1.23	0.65	0.34	0.22	0.22
<i>o</i> -Cresol	2.45	0.74	0.20	-0.05	-0.09	-0.01
<i>m,p</i> -Cresol	2.77	1.03	0.46	0.18	0.08	0.11
Aniline	2.34	0.75	0.25	0.01	-0.06	-0.01
Toluidines	2.21	0.56	0.06	-0.16	-0.19	-0.12
Diaminobenzenes	5.67	3.26	2.34	1.76	1.42	1.23
Aminophenols	6.24	3.73	2.74	2.09	1.69	1.45
<i>o</i> -Dihydroxybenzene	6.80	4.30	3.32	2.67	2.22	1.90
<i>m,p</i> -Dihydroxybenzene	6.80	4.21	3.14	2.43	1.96	1.68
40 MPa						
Phenol	2.60	0.97	0.41	0.11	-0.01	-0.02
<i>o</i> -Cresol	2.09	0.43	-0.09	-0.32	-0.37	-0.29
<i>m,p</i> -Cresol	2.42	0.72	0.17	-0.10	-0.20	-0.17
Aniline	2.02	0.48	0.00	-0.23	-0.30	-0.26
Toluidines	1.84	0.24	-0.24	-0.45	-0.48	-0.41
Diaminobenzenes	5.34	2.98	2.08	1.52	1.18	1.00
Aminophenols	5.92	3.46	2.49	1.86	1.46	1.24
<i>o</i> -Dihydroxybenzene	6.50	4.04	3.08	2.44	2.01	1.69
<i>m,p</i> -Dihydroxybenzene	6.49	3.95	2.90	2.20	1.75	1.48

approximation of constant heat capacity of hydration, Eq. (20) transforms to

$$\Delta_{\text{h}}G^{\circ}[T] = \Delta_{\text{h}}H^{\circ}[T_{\text{r}}] + (T - T_{\text{r}})\Delta_{\text{h}}C_{\text{p}}^{\circ}[T_{\text{r}}] - T\left(\frac{\Delta_{\text{h}}H^{\circ}[T_{\text{r}}] - \Delta_{\text{h}}G^{\circ}[T_{\text{r}}]}{T_{\text{r}}} + \ln(T/T_{\text{r}})\Delta_{\text{h}}C_{\text{p}}^{\circ}[T_{\text{r}}]\right). \quad (21)$$

Following from Eqs. (5), (6), and (21), the enthalpy and heat capacity of hydration are then given by

$$\Delta_{\text{h}}H^{\circ}[T] = \Delta_{\text{h}}H^{\circ}[T_{\text{r}}] + (T - T_{\text{r}})\Delta_{\text{h}}C_{\text{p}}^{\circ}[T_{\text{r}}], \quad (22)$$

$$\Delta_{\text{h}}C_{\text{p}}^{\circ}[T] = \Delta_{\text{h}}C_{\text{p}}^{\circ}[T_{\text{r}}]. \quad (23)$$

The more common, but rather inaccurate assumption of constant enthalpy of hydration leads to zero for the heat capacity of hydration and to the following relation for the Gibbs energy of hydration:

$$\Delta_{\text{h}}G^{\circ}[T] = \Delta_{\text{h}}H^{\circ}[T_{\text{r}}] - T((\Delta_{\text{h}}H^{\circ}[T_{\text{r}}] - \Delta_{\text{h}}G^{\circ}[T_{\text{r}}])/T_{\text{r}}). \quad (24)$$

Eqs. (20), (21) or (24) represent various forms of the van't Hoff equation, expressing (in connection with Eq. (4)) the temperature dependence of the equilibrium constant of a hydration reaction. The data for $\Delta_{\text{h}}G^{\circ}$ and $\Delta_{\text{h}}H^{\circ}$ to 373 K and $\Delta_{\text{h}}C_{\text{p}}^{\circ}$ at ≈ 298 K were used in the simultaneous weighted regression with Eqs. (8) and (20)–(22). The weights were originally assigned as experimental uncertainties reported by authors or estimated by us when missing. During correlation they were usually modified by a property-specific multiplication factor in order to describe each property by the group contribution model, on average, within the prescribed accuracy. In other words, we required the value of average $|\Delta|/\sigma$, Δ being the difference between experimental and calculated value and σ the appropriate uncertainty, to be equal or close to unity for each property data set in the final regression. This dynamic method of error assignment allows the simultaneous multiproperty fit without a danger of some property being over- or underweighted, it also at the same time offers an information about the average accuracy of model description for any property included in regression. The average values of σ were found to be 0.5 kJ mol^{-1} for $\Delta_{\text{h}}G^{\circ}$, 0.6 kJ mol^{-1} for $\Delta_{\text{h}}H^{\circ}$, and $10 \text{ J K}^{-1} \text{ mol}^{-1}$ for $\Delta_{\text{h}}C_{\text{p}}^{\circ}$. The results for group contributions obtained from the regression are presented in Table 7. Values of V° at ambient conditions were regressed separately in a single property fit and their average σ was found to be $0.4 \text{ cm}^3 \text{ mol}^{-1}$. The first-order group contribution scheme does not account for sterical hindrance of two substituents in neighbor positions, which is typically not negligible for two groups in *ortho*-position on an aromatic ring. Plyasunov and Shock (2000a) calculated the correction contribution for this effect of two alkyls, noted $I(\text{C}-\text{C})$ in Table 7. We used the same approach and established the corrections for various combinations of *ortho*-substituents. The amount of available data, however, does not allow their evaluation for all pairs and properties, only the values significant at 95% confidence levels were finally accepted and are listed in Table 7. Corrections for *meta*-substituents were not

obtained for the same reason, but they also could be established when sufficient and reliable data become available.

It should be noticed that the group contributions are not confined to predictions exclusively at T_{r} and p_{r} ; they can be used in combination with Eq. (21) for realistic predictions of the Gibbs energy of hydration as a function of temperature up to at least 370 K and possibly higher. Since the standard partial molal volume does not change much with pressure and temperature up to 373 K, the availability of group contributions for V° allows to calculate also the pressure effect on $\Delta_{\text{h}}G^{\circ}$ by integration of Eq. (7). The predictive capability of Eq. (21) is further discussed below.

Experimental data, appropriate ideal gas formation properties and group contribution predictions for the Gibbs energy, enthalpy and heat capacity of hydration and for the standard partial molal volume at 298 K and 0.1 MPa are presented in Tables 8–11.

4.3. Calculation of thermodynamic properties at high temperatures and pressures

4.3.1. Predictions with the HKF model

Dale et al. (1997) adjusted the HKF parameters of several alkylphenols using experimental data at ambient conditions and solubility results of Dohnal and Fenclova (1995) at temperatures to 373 K. Since then new results became available namely for standard partial molal volumes and heat capacities to 623 K, which are indicative of extrapolation ability of the model to elevated conditions (see Tables 5 and 6 for references regarding the new data). Therefore, we wanted to assess the performance of Dale et al. (1997) calculations for derivative properties. Fig. 4 compares some of the new experimental V° and C_{p}° with the predictions of Dale et al. HKF parameterization. It is obvious that the agreement is semiquantitative particularly at higher temperatures, where the changes in derivative properties are driven by rapidly increasing compressibility of the solvent. Nevertheless, the extrapolated chemical potentials calculated with HKF and parameters by Dale et al. (1997) are probably satisfactory up to about 450 K due to relative insensitivity of this integral property to the values of V° and C_{p}° . It is apparent from Eq. (1) that the first two terms dominate the calculations at lower temperatures and any model is in fact used to calculate just a *deviation* of the chemical potential from the linear temperature dependence whose intercept is $G_{\text{f}}^{\circ}[T_{\text{r}}, p_{\text{r}}]$ and the slope is given by $S^{\circ}[T_{\text{r}}, p_{\text{r}}]$.

New experiments at superambient conditions should allow re-adjustment of parameters in the HKF equations to account also for the high-temperature region. However, it was argued before (Sedlbauer and Majer, 2000; Plyasunov and Shock, 2001b) that the HKF model is unsuitable for such simultaneous correlations including large body of derivative data over a wide range of conditions. This is due to the empirical character of the HKF model for aqueous nonelectrolytes, which cannot account for all these properties simultaneously with sufficient accuracy.

Including derivative data at high temperatures thus typically leads to only marginal improvement of correlation for derivative properties and at the same time to poor predictions of integral functions such as the Gibbs energy of hydration. The same was proved by our preliminary fits for phenols and anilines and we decided to adopt a different path.

A successful approach to HKF parameterization, established by Shock and Helgeson (1988) and later improved by Plyasunov and Shock (2001b), applies only thermodynamic functions at 298 K and 0.1 MPa for estimation of the parameters. We have used these parameter inter-correlations and calculated the parameters a_1 , a_2 , a_4 , c_2 , and ω with group additivity estimates of $\Delta_h G^\circ$ and V° from Table 7. Parameters a_3 and c_1 were then set consistently with the group additivity estimates of V° and C_p° , as suggested by Plyasunov and Shock (2001b). Parameters of the HKF equation of state obtained by this procedure for alkylphenols and alkylanilines are presented in Table 12 along with the needed thermodynamic properties at 298 K and 0.1 MPa calculated from Tables 8–11 as a sum of the appropriate property of hydration and the ideal gas formation property. Summary of the HKF model equations and parameter inter-correlations is provided in Appendix A.

4.3.2. Predictions with the group contribution SOCW model

The group contribution approach was also applied by Sedlbauer et al. (2002) to aqueous hydrocarbons, using for T , p description of functional groups the SOCW equation of state (Sedlbauer et al., 2000). Explicit forms of the equations within this framework are presented in Appendix A. Compared to HKF, the SOCW model provides sufficient flexibility for the description of various thermodynamic properties of hydration of nonelectrolytes and therefore is suitable for the task of simultaneous regression of all available experimental data. This has been done by minimizing an objective function written in the form:

$$\begin{aligned}
 F = & \sum_{i=1}^O \left(\frac{\Delta_h G^{\circ, \text{exp}} - \Delta_h G^{\circ, \text{calc}}}{\sigma \Delta_h G^\circ} \right)_i^2 \\
 & + \sum_{j=1}^P \left(\frac{\Delta H^{\circ, \text{exp}} - \Delta_h H^{\circ, \text{calc}}}{\sigma \Delta_h H^\circ} \right)_j^2 \\
 & + \sum_{k=1}^Q \left(\frac{\Delta_h C_p^{\circ, \text{exp}} - \Delta_h C_p^{\circ, \text{calc}}}{\sigma \Delta_h C_p^\circ} \right)_k^2 \\
 & + \sum_{l=1}^R \left(\frac{V_s^{\circ, \text{exp}} - V_s^{\circ, \text{calc}}}{\sigma V_s^\circ} \right)_l^2, \quad (25)
 \end{aligned}$$

where the superscripts exp and calc denote experimental data (see sources in Tables 3–6) and values calculated with the model, respectively.

Using the group contributions for $\Delta_h G^\circ[T_r, p_r]$ and $\Delta_h H^\circ[T_r, p_r]$ presented in Table 7 and replacing the integrals in Eq. (1) by a combination of three terms (denoted with superscript SOCW), $\Delta_h G^{\circ, \text{calc}}$ was calculated as follows

$$\begin{aligned}
 \Delta_h G^{\circ, \text{calc}}[T, p] = & \Delta_h G^\circ[T_r, p_r] + (T_r - T)\Delta_h S^\circ[T_r, p_r] \\
 & + (\Delta_h H^{\circ, \text{SOCW}}[T, p_r] - \Delta_h H^{\circ, \text{SOCW}}[T_r, p_r]) \\
 & - T(\Delta_h S^{\circ, \text{SOCW}}[T, p_r] - \Delta_h S^{\circ, \text{SOCW}}[T_r, p_r]) \\
 & + (\Delta_h G^{\circ, \text{SOCW}}[T, p] - \Delta_h G^{\circ, \text{SOCW}}[T_r, p_r]). \quad (26)
 \end{aligned}$$

After a rearrangement, Eq. (26) can be expressed in a compact form

$$\begin{aligned}
 \Delta_h G^{\circ, \text{calc}}[T, p] = & \Delta_h G^\circ[T_r, p_r] + (T_r - T)\Delta_h S^\circ[T_r, p_r] \\
 & - \Delta_h G^{\circ, \text{SOCW}}[T_r, p_r] \\
 & - (T_r - T)\Delta_h S^{\circ, \text{SOCW}}[T_r, p_r] \\
 & + \Delta_h G^{\circ, \text{SOCW}}[T, p]. \quad (27)
 \end{aligned}$$

The expressions for the Gibbs energy and entropy of hydration from the high-temperature SOCW model are given by Eqs. (A.3) and (A.5) in Appendix A. Analogously the enthalpy of hydration is constrained by the value of $\Delta_h H^\circ[T_r, p_r]$ obtained from Table 7 as follows

$$\begin{aligned}
 \Delta_h H^{\circ, \text{calc}}[T, p] = & \Delta_h H^\circ[T_r, p_r] - \Delta_h H^{\circ, \text{SOCW}}[T_r, p_r] \\
 & + \Delta_h H^{\circ, \text{SOCW}}[T, p], \quad (28)
 \end{aligned}$$

where the SOCW enthalpy term is obtained from Eq. (A.4). Relationships for the standard partial molal volume $V^{\circ, \text{calc}}[T, p]$ and heat capacity of hydration $\Delta_h C_p^{\circ, \text{calc}}[T, p]$ are stated as Eqs. (A.1) and (A.6), respectively.

Group contributions obtained from the simultaneous regression, including two proximity corrections, are listed in Table 13. The values of σ used as weighting factors correspond to experimental uncertainties according to original sources at temperatures 523–623 K where the thermodynamic properties change rapidly and the same holds true for the associated uncertainties. At temperatures below 523 K we used the same method as described above for the low temperature regression, i.e., we required the value of average $|\Delta|/\sigma$, with Δ being the difference between experimental and calculated value, to be equal or close to unity for each property data set in the final regression. Not surprisingly, σ values were higher than those obtained in the low temperature fit, namely for V° and $\Delta_h C_p^\circ$ for which the data at high temperatures are the most abundant. The average σ values were 0.5 kJ mol⁻¹ for $\Delta_h G^\circ$, 0.6 kJ mol⁻¹ for $\Delta_h H^\circ$, 20 J K⁻¹ mol⁻¹ for $\Delta_h C_p^\circ$, and 0.6 cm³ mol⁻¹ for V° . It should be noted again that resulting values of σ provide at the same time an estimate of expected uncertainties when the model is used for predictions of thermodynamic properties of solutes with molecular structures similar to compounds in our training set.

5. Discussion and conclusions

The results of both high-temperature predictions (HKF and SOCW) are compared in Figs. 5 and 6 for the equilibrium constant of the hydration reaction defined by Eq. (4). Fig. 5 for alkylphenols includes also the HKF calculations

using parameters by Dale et al. (1997). As expected, the lines calculated from HKF and SOCW models mostly overlap at temperatures below 400 K. At higher temperatures the two calculated curves (three in case of alkylphenols) diverge, more substantially at $T > 450$ K. Logically, the results of the SOCW model are assumed to be more reliable at elevated conditions, because they are strictly constrained by experimental data on V° and $\Delta_h C_p^\circ$ at temperatures to 623 K.

It is apparent that while in certain cases the two types of prediction schemes give similar results, at temperatures above 573 K the results can differ in some cases by more than 100% in K_{hyd} . In addition, in the case of alkylphenols the new set of parameters for the HKF model gives the results generally (but not always) closer to the SOCW predictions compared to those by Dale et al. (1997).

Widely used low temperature geochemical packages PHREEQC, MINTeq or Geochemists Workbench are supplied with databases of standard chemical potentials and enthalpies at 298 K and 0.1 MPa. The standard chemical potentials and subsequently thermodynamic equilibrium constants of aqueous species at other temperatures are therefore calculated using Eq. (24), which is a simplified form of Eq. (21) neglecting the value of the heat capacity of hydration. Even with carefully constructed and internally consistent database, this approximation leads to large errors if the software is used outside the limit of its applicability, which is about ± 30 K from the reference temperature. This is documented in Fig. 7 on the examples of phenol, *o*-cresol, aniline, and toluidines. The reason for such a failure of the simple form of van't Hoff equation is obvious—while the values of $\Delta_h C_p^\circ$ do not change much with temperature to 500–550 K (see, e.g., Fig. 4) and can be fairly approximated as constant, they are certainly not equal to zero, as imposed by Eq. (24) (see Table 11).

As follows from Fig. 7, results obtained with the HKF model are typically lower compared to those obtained with the group contribution SOCW model, the maximum difference being 0.25 $\log K_{\text{hyd}}$ units for toluidines at 573 K. Agreement is better in most cases, differences usually stay within 0.1–0.2 $\log K_{\text{hyd}}$ units corresponding approximately to differences between 30% and 60% in K_{hyd} . Predictions of Eq. (24) are out of consideration at higher temperatures with differences from the other methods of the order of 0.2–0.3 $\log K_{\text{hyd}}$ units even at 373 K and failing completely at more elevated temperatures. Eq. (21) performs reasonably, with differences from the group contribution SOCW model comparable in magnitude to the HKF predictions, except that the difference is usually of the opposite sign. These results suggest that thermodynamic data at reference conditions—with consideration of the hydration heat capacity—can be used with confidence for approximate calculation of thermodynamic properties to elevated temperatures. At pressures other than saturation, the pressure correction must be applied via Eq. (7). It was shown recently (Sedlbauer and Majer, 2004) that this correction is large for nonelectrolyte solutes (up to several hundred per cent

of K_{hyd} at 100 MPa, even at temperatures not far from ambient T). On the other hand, evaluating the pressure correction with only the value of V° at reference conditions leads to acceptable results at temperatures below 500 K (Sedlbauer and Majer, 2004). The above discussion thus further documents the importance of data on derivative properties for modeling aqueous systems of geochemical interest.

Finally, we provide in Table 14 a grid of $\log K_{\text{hyd}}$ values for phenol, cresols, aniline, toluidines, aminophenols, diaminobenzenes and dihydroxybenzenes, calculated at several temperatures and isobars from the group contribution SOCW model. Table 14 may serve as a reference when implementing the method, but can be used also directly for evaluation of hydration properties by interpolation of the presented values.

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Appendix A

A.1. Summary of the SOCW thermodynamic model

SOCW equation of state is based on a volumetric formula inspired by the Fluctuation Solution Theory (Sedlbauer et al., 2000)

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

where V_w , ρ_w , and κ_w are molar volume, specific density, and isothermal compressibility of water, respectively, and general coefficients valid for all solutes are $v = 0.005 \text{ m}^3 \text{ kg}^{-1}$, $\theta = 1500 \text{ K}$, $\lambda = -0.01 \text{ m}^3 \text{ kg}^{-1}$. Adjustable parameters are a , b , c , and d , parameter δ is determined depending on the charge of a particle ($\delta = 0.35a$ for neutral molecules). Eq. (A.1) is in fact modeling the hydration process by a series of perturbation effects due to insertion of an ideal gas molecule into water solvent ($RT\kappa_w$), growing it to a “water-like” molecule with size adjusted to mimic the intrinsic volume of a solute ($d(V_w - RT\kappa_w)$), and then changing its potential field from solvent–solvent to

solute–solvent interaction (the third term on the right-hand side of Eq. (A.1)).

Corresponding change in the Gibbs energy of hydration is expressed by

$$\Delta_{\text{h}}G^{\circ} = \int_{p_{\text{r}}}^0 RT \, d \ln p + \int_0^p V_{\text{s}}^{\circ} \, dp + \Delta_{\text{h}}G^{\circ\text{cor}}, \quad (\text{A.2})$$

where $p_{\text{r}} = 0.1$ MPa is the standard pressure. Correction term $\Delta_{\text{h}}G^{\circ\text{cor}}$ applies at temperatures below critical temperature of water $T_{\text{c}} = 647.126$ K and arises due to inadequacy of the simple volumetric Eq. (A.1) to describe accurately pressure change of hydration Gibbs energy in both gas and liquid phases in a two-phase subcritical region. Full form of Eq. (A.2) in the framework of the SOCW model and in the adopted standard state is given by

$$\begin{aligned} \Delta_{\text{h}}G^{\circ} &= \Delta_{\text{h}}G^{\circ\text{cor}} + RT \ln \left[\frac{\rho_{\text{w}}RT}{p_{\text{ref}}} \right] \\ &+ d \left(G_{\text{w}} - G_{\text{w}}^{\text{ig}} - RT \ln \left[\frac{\rho_{\text{w}}RT}{p_{\text{ref}}} \right] \right) \\ &+ RT \left(\rho_{\text{w}}(a + c \exp[\theta/T] - b - \delta) + \frac{b}{\vartheta} (\exp[\vartheta\rho_{\text{w}}] - 1) \right. \\ &\left. + \frac{\delta}{\lambda} (\exp[\lambda\rho_{\text{w}}] - 1) \right). \end{aligned} \quad (\text{A.3})$$

Appropriate derivations of $\Delta_{\text{h}}G^{\circ}$ lead to other thermodynamic properties of hydration

$$\begin{aligned} \Delta_{\text{h}}H^{\circ} &= \Delta_{\text{h}}H^{\circ\text{cor}} + RT(\alpha - 1) \\ &+ d(H_{\text{w}}^{-}H_{\text{w}}^{\text{ig}} - RT(\alpha - 1)) + RT\theta c \\ &\times \exp[\theta/T] \frac{\rho_{\text{w}}}{T} - RT^2 \left(\frac{\partial \rho_{\text{w}}}{\partial T} \right)_{\text{p}} \\ &\times (a + b(\exp[\vartheta\rho_{\text{w}}] - 1) + c \exp[\theta/T] \\ &+ \delta(\exp[\lambda\rho_{\text{w}}] - 1)), \end{aligned} \quad (\text{A.4})$$

$$\Delta_{\text{h}}S^{\circ} = (\Delta_{\text{h}}H^{\circ} - \Delta_{\text{h}}G^{\circ})/T, \quad (\text{A.5})$$

$$\begin{aligned} \Delta_{\text{h}}C_{\text{p}}^{\circ} &= \Delta_{\text{h}}C_{\text{p}}^{\circ\text{cor}} + \left(2RT\alpha_{\text{w}} + RT^2 \left(\frac{\partial \alpha_{\text{w}}}{\partial T} \right)_{\text{p}} - R \right) \\ &+ d \left(C_{\text{p,w}}^{-} C_{\text{p,w}}^{\text{ig}} - \left(2RT\alpha_{\text{w}} + RT^2 \left(\frac{\partial \alpha_{\text{w}}}{\partial T} \right)_{\text{p}} - R \right) \right) \\ &- T \left(\begin{aligned} &2R \left(\frac{\partial \rho_{\text{w}}}{\partial T} \right)_{\text{p}} (a + b(\exp[\vartheta\rho_{\text{w}}] - 1) + c \exp[\theta/T] \\ &+ \delta(\exp[\lambda\rho_{\text{w}}] - 1) - c \exp[\theta/T] \frac{\theta}{T}) \\ &+ Rc \exp[\theta/T] \theta^2 \frac{\rho_{\text{w}}}{T} + RT \left(\frac{\partial \rho_{\text{w}}}{\partial T} \right)_{\text{p}}^2 \\ &\times (\vartheta b \exp[\vartheta\rho_{\text{w}}] + \lambda \delta \exp[\lambda\rho_{\text{w}}]) \\ &+ RT \left(\frac{\partial^2 \rho_{\text{w}}}{\partial T^2} \right)_{\text{p}} (a + b(\exp[\vartheta\rho_{\text{w}}] - 1) + c \exp[\theta/T] \\ &+ \delta(\exp[\lambda\rho_{\text{w}}] - 1)) \end{aligned} \right), \end{aligned} \quad (\text{A.6})$$

where G_{w} , H_{w} , and $C_{\text{p,w}}$ are the molar Gibbs free energy, enthalpy, and heat capacity of water, G_{w}^{ig} , H_{w}^{ig} , and $C_{\text{p,w}}^{\text{ig}}$ are the same properties of water in ideal gas standard state at temperature T , and $\alpha_{\text{w}} = -\frac{1}{\rho_{\text{w}}} \left(\frac{\partial \rho_{\text{w}}}{\partial T} \right)_{\text{p}}$ is the coefficient of thermal expansion. Thermodynamic properties of pure water needed in calculations were obtained in this study

from the equation of state by Hill (1990). Correction terms in Eqs. (A.2)–(A.6) are for nonelectrolyte solutes expressed by an empirical function with one additional adjustable parameter, e

$$\Delta_{\text{h}}S^{\circ\text{cor}} = e \left(T - T_{\text{c}} - \frac{T_{\text{c}}^2}{\Phi} \ln \left[\frac{T}{T_{\text{c}}} \right] + \frac{(T_{\text{c}} - \Phi)^2}{\Phi} \ln \left[\frac{T - \Phi}{T_{\text{c}} - \Phi} \right] \right), \quad (\text{A.7})$$

$$\begin{aligned} \Delta_{\text{h}}H^{\circ\text{cor}} &= e \left((2T_{\text{c}} - \Phi)(T_{\text{c}} - T) + 1/2(T^2 - T_{\text{c}}^2) \right. \\ &\left. + (T_{\text{c}} - \Phi)^2 \ln \left[\frac{T - \Phi}{T_{\text{c}} - \Phi} \right] \right), \end{aligned} \quad (\text{A.8})$$

$$\Delta_{\text{h}}G^{\circ\text{cor}} = \Delta H_{\text{hyd}}^{\circ\text{cor}} - T \Delta S_{\text{hyd}}^{\circ\text{cor}}, \quad (\text{A.9})$$

$$\Delta_{\text{h}}C_{\text{p}}^{\circ\text{cor}} = \frac{e(T - T_{\text{c}})^2}{(T - \Phi)}, \quad (\text{A.10})$$

where $\Phi = 228$ K is a general constant. Correction functions are zero by definition at $T \geq T_{\text{c}}$. All thermodynamic properties that appear in the above equations should be applied in their basic SI units when using parameters from Table 13 in the text.

For use with the group contribution scheme, the model is applied most easily by calculating each parameter as a sum of parameters for functional groups present in the solute of interest, e.g.

$$a = \sum_{i=1}^N n_i a_i, \quad (\text{A.11})$$

where a_i is the parameter for i th functional group, taken from Table 13.

A.2. Summary of the revised HKF thermodynamic model for neutral species

In the revised HKF equation of state (Tanger and Helgeson, 1988) the standard partial molal thermodynamic properties are considered as sum of solvation and nonsolvation contributions, represented by Born equation and by an empirical function, respectively. In case of nonelectrolyte aqueous solutes the Born equation is simplified and the expressions for standard partial molal volume and heat capacity at reference pressure 0.1 MPa are

$$\begin{aligned} V^{\circ} &= a_1 + \frac{a_2}{\psi + p} + \left(a_3 + \frac{a_4}{\psi + p} \right) \left(\frac{1}{T - \Theta} \right) \\ &- \frac{\omega}{\varepsilon_{\text{w}}^2} \left(\frac{\partial \varepsilon_{\text{w}}}{\partial p} \right)_{\text{T}}, \end{aligned} \quad (\text{A.12})$$

$$C_{\text{p,r}}^{\circ} = c_1 + \frac{c_2}{(T - \Theta)^2} + \omega T \left(\frac{\partial}{\partial T} \frac{1}{\varepsilon_{\text{w}}^2} \left(\frac{\partial \varepsilon_{\text{w}}}{\partial T} \right) \right)_{\text{p}}. \quad (\text{A.13})$$

The symbols a_i and c_i stand for six adjustable parameters in the nonsolvation part, ω is the only adjustable parameter in the solvation part of the equation, ε_{w} is the dielectric con-

stant (relative permittivity) of water, $\Theta = 228$ K and $\psi = 260$ MPa. When used with Eq. (1), the standard partial molal Gibbs energy of formation follows:

$$\begin{aligned} G_f^\circ[T, p] &= G_f^\circ[T_r, p_r] + (T_r - T) \cdot S^\circ[T_r, p_r] \\ &- c_1 \left[T \ln \frac{T}{T_r} - T + T_r \right] \\ &- c_2 \left[\left(\frac{1}{T - \Theta} - \frac{1}{T_r - \Theta} \right) \frac{\Theta - T}{\Theta} - \frac{T}{\Theta^2} \ln \frac{T_r(T - \Theta)}{T(T_r - \Theta)} \right] \\ &+ a_1(p - p_r) + a_2 \ln \frac{\psi + p}{\psi + p_r} \\ &+ \frac{1}{T - \Theta} \left[a_3(p - p_r) + a_4 \ln \frac{\psi + p}{\psi + p_r} \right] \\ &+ \omega \left(\frac{1}{\varepsilon_w} - \frac{1}{\varepsilon_w[T_r, p_r]} + \frac{(T - T_r)}{\varepsilon_w^2[T_r, p_r]} \left(\frac{\partial \varepsilon_w[T_r, p_r]}{\partial p} \right) \right). \end{aligned} \quad (\text{A.14})$$

Eq. (2) is used for conversion of G_f° to $\Delta_h G^\circ$ and Eqs. (5)–(7) can be then applied for calculation of the other properties of hydration.

Parameters of the HKF equations are often estimated with only the thermodynamic functions at 298 K and 0.1 MPa. This approach was established for organic species by Shock and Helgeson (1990) and later improved by Plyasunov and Shock (2001b), who suggested as the most appropriate measure of the solute–solvent interaction the Gibbs energy of hydration. Empirical inter-correlations for the HKF parameters were proposed by Plyasunov and Shock (2001b) in the form:

$$a_1 = 10^{-1} V^\circ[T_r, p_r] (0.820 - 1.85 \cdot 10^{-3} \Delta_h G^\circ[T_r, p_r]), \quad (\text{A.15})$$

$$a_2 = 10^2 V^\circ[T_r, p_r] (0.648 + 4.81 \cdot 10^{-3} \Delta_h G^\circ[T_r, p_r]), \quad (\text{A.16})$$

$$a_4 = 10^4 (8.10 - 0.746 \cdot 10^{-2} a_2 + 0.219 \Delta_h G^\circ[T_r, p_r]), \quad (\text{A.17})$$

$$c_2 = 10^4 (21.4 + 0.849 \Delta_h G^\circ[T_r, p_r]), \quad (\text{A.18})$$

$$\omega = 10^5 \left(2.61 + \frac{324.1}{\Delta_h G^\circ[T_r, p_r] - 90.6} \right). \quad (\text{A.19})$$

Remaining parameters a_3 and c_1 are then obtained consistently with the values of $V^\circ[T_r, p_r]$ and $\Delta_h C_p^\circ[T_r, p_r]$.

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