

Group Contribution Method for Aqueous Nitro-, Chloro-, and Phenolate- Substituted Aromatics at Elevated Temperatures

Josef Sedlbauer

Department of Chemistry, Technical University of Liberec, 46117 Liberec, Czech Republic
Email: josef.sedlbauer@tul.cz

The article presents a method for predicting the standard partial molar Gibbs energy (standard chemical potential) and related derivative properties of aqueous nitro- and chloro- derivatives of aromatic hydrocarbons over a wide range of temperature and pressure. A thorough literature overview was conducted for collecting the available experimental data resulting from phase equilibrium, calorimetric and volumetric measurements that lead to the thermodynamic properties of hydration. A group contribution scheme was developed based on the acquired database both at reference conditions (298 K, 0.1 MPa) and at high temperatures and pressures, with predictions valid up to at least 523 K and 50 MPa. In connection with our previous results, the method allows calculating the standard thermodynamic properties of aqueous aromatic hydrocarbons substituted with any combination of nitro-, chloro-, hydroxy-, amino-, and alkyl-functional groups. Combined with the experimental data on ionization of phenols and phenol derivatives, the methods also makes it possible to determine the contribution of the phenolate (charged) functional group.

Introduction

Aromatic nitro- and chloro- compounds are often applied technologically and their effluents belong among the most environmentally sensitive systems. Phenolates appear in large amounts namely as intermediates in the production of phenol and due to their solubility constitute an important part of wastewaters from such processes. Assessment of environmental partition and the design of remediation technologies for these solutes require the knowledge of their standard thermodynamic properties. These can be obtained for individual compounds directly from phase equilibrium and ionization experiments, but a more efficient approach is based on generalization of experimental data using an equation-of-state for standard thermodynamic properties and some form of group additivity approximation. There are several substantial advantages of such modeling procedure: all available experimental results can be used for development of a thermodynamic model, including the often-measured volumetric and calorimetric data, and predictions can be made also for structurally similar compounds for which little or no experimental information is accessible. An example of such approach is the group contribution scheme utilizing the Sedlbauer-O'Connell-Wood (SOCW)

equation-of-state [1] for the description of standard thermodynamic properties in a wide range of temperature and pressure. Structural groups evaluated within this method include so far the hydrocarbon backbone groups [2] (aliphatic saturated and unsaturated, cyclic, aromatic), alcohols, (alkyl)phenols and (alkyl)anilines [3].

The purpose of this work is to extend the existing SOCW-based high-temperature group contribution scheme by addition of nitro-, chloro-, and phenolate-(charged) functional groups directly bound to an aromatic ring. The procedure included three steps: (i) Compilation and evaluation of literature results for standard thermodynamic properties and the properties of ionization for solutes, containing at least one of the functional groups of interest (nitro-, chloro- or phenolate-) in addition to the already established structural groups. Collected data have to include results at high temperatures as well as at the reference conditions (298 K, 0.1 MPa), which are used as integration constants in the SOCW model. (ii) Supplementing the existing experimental database with targeted measurements. New ionization and calorimetric data have been obtained recently for aqueous isomeric nitrophenols and chlorophenols in the laboratories at the University of Guelph and at the Technical University of Liberec.

Nitrophenols and chlorophenols were selected as suitable key-compounds mainly due to their higher solubility compared e.g. to nitrobenzene or chlorobenzene.

(iii) Simultaneous correlation of all available standard thermodynamic data for nitro-, chloro-, and phenolate aqueous systems, using the group contribution assumption for the nitro-, chloro- and phenolate- functional groups. The results of this treatment are presented and discussed in terms of hydrophobic/hydrophilic behavior of the resulting groups and higher-order structural effects induced in molecules with several functional groups bound to the aromatic ring.

Background

The standard¹ partial molar 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 obtained by integration using the known values of ΔG_f° and S° (standard partial molar entropy) at selected reference conditions T_r and p_r

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

To evaluate the integrals in Eq. (1), expressions for the standard partial molar volume $V^\circ = V^\circ[T, p]$ and for the standard partial molar 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. This concept has been widely utilized in geochemistry namely in connection with the revised Helgeson-Kirkham-Flowers equations [4]. A new generation of thermodynamic models appeared in the last decade that was inspired by the Fluctuation Solution Theory and based on the work of O'Connell and collaborators [1,5,6]. The approach presented by Sedlbauer, O'Connell and Wood [1] has been since applied for data representation and for predictions in a variety of aqueous systems, nonelectrolyte and ionic, e.g. [2,3,7].

Standard chemical potential is the crucial property for predicting thermodynamic constants characterizing chemical equilibrium in systems

involving aqueous species. However, for data representation and modeling of phase equilibrium it is convenient to work in terms of the Gibbs energy of hydration, defined as

$$\Delta G_{\text{hyd}}^\circ = \Delta G_f^\circ[T, p] - \Delta G_f^{\text{ig}}[T, p_r] \quad (2)$$

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. $\Delta G_{\text{hyd}}^\circ$ 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 temperature and pressure derivatives of $\Delta G_{\text{hyd}}^\circ$ provide a link with the corresponding standard derivative properties: enthalpy of hydration $\Delta H_{\text{hyd}}^\circ$, heat capacity of hydration $\Delta C_{p,\text{hyd}}^\circ$, and standard partial molar volume V°

$$T^2 \left(\frac{\partial(\Delta G_{\text{hyd}}^\circ / T)}{\partial T} \right)_p = -\Delta H_{\text{hyd}}^\circ \quad (3)$$

$$\left(\frac{\partial}{\partial T} \left[T^2 \frac{\partial(\Delta G_{\text{hyd}}^\circ / T)}{\partial T} \right] \right)_p = -\Delta C_{p,\text{hyd}}^\circ \quad (4)$$

$$\left(\frac{\partial \Delta G_{\text{hyd}}^\circ}{\partial p} \right)_T = V^\circ \quad (5)$$

The new thermodynamic models [1,3] are based on a hydration approach because this representation of thermodynamic properties naturally follows from the underlying theory and because most data for nonelectrolyte solutes such as Henry's law constant, limiting activity coefficient, solubility, enthalpy of solution etc. are actually obtained in experiments closely related to the 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 molar properties of formation requires only ideal gas phase properties that are well known.

Methodology

For generalization of the properties of organic compounds, it is often useful to adopt a group additivity scheme. The reason is obvious: while the number of organic structures is large, they consist of just a few constituent groups. In the thermodynamics of dilute aqueous solutions, this principle has been adopted with success at the temperature of 298 K and several methods are available varying in the set of selected structural groups and in the type of evaluated thermodynamic properties, e.g. [8-10]. This approach can be applied also at elevated

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

temperatures and pressures, where the structural group contributions need to be expressed in terms of an equation-of-state such as the SOCW model [2,3,7].

The fundamental group additivity scheme applies a general equation

$$\Delta X_{\text{hyd}}^{\circ} = X_{\text{SS}} + \sum_{i=1}^N n_i X_i^{\circ} \quad (6)$$

where N is the total number of structural groups present in a given solute, n_i is the number of occurrences of each specific constituent 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 and can be evaluated using only thermodynamic functions of pure solvent [1]. Structural 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 conditions T_r, p_r from the relatively abundant data at near-ambient conditions. Thermodynamic consistency of the resulting values can be assured by applying van't Hoff-type equations. Simple approximation, which is realistic to at least 373 K, assumes constant (temperature independent) heat capacity of hydration. For the Gibbs energy of hydration, this leads to a simplified version of Eq. (1)

$$\Delta G_{\text{hyd}}^{\circ}[T] = \Delta H_{\text{hyd}}^{\circ}[T_r] + (T - T_r) \Delta C_{p,\text{hyd}}^{\circ}[T_r] - T \left(\frac{\Delta H_{\text{hyd}}^{\circ}[T_r] - \Delta G_{\text{hyd}}^{\circ}[T_r]}{T_r} + \ln(T/T_r) \Delta C_{p,\text{hyd}}^{\circ}[T_r] \right) \quad (7)$$

where Eq. (7) is considered at a saturation pressure p_r and the substitution was applied

$$\Delta S_{\text{hyd}}^{\circ}[T_r] = (\Delta H_{\text{hyd}}^{\circ}[T_r] - \Delta G_{\text{hyd}}^{\circ}[T_r]) / T_r. \quad (8)$$

The same assumptions as in Eq. (7) yield for the enthalpy and heat capacity of hydration (see Eqs. 3,4)

$$\Delta H_{\text{hyd}}^{\circ}[T] = \Delta H_{\text{hyd}}^{\circ}[T_r] + (T - T_r) \Delta C_{p,\text{hyd}}^{\circ}[T_r] \quad (9)$$

$$\Delta C_{p,\text{hyd}}^{\circ}[T] = \Delta C_{p,\text{hyd}}^{\circ}[T_r]. \quad (10)$$

The available experimental data for $\Delta G_{\text{hyd}}^{\circ}$ and $\Delta H_{\text{hyd}}^{\circ}$ to 373 K and $\Delta C_{p,\text{hyd}}^{\circ}$ at ≈ 298 K for aqueous nitro-, chloro- and phenolate- substituted aromatic hydrocarbons can be decomposed to structural contributions with Eq. (6) and then used in the simultaneous weighted regression with Eqs. (7-10), producing thermodynamically consistent values of

$\Delta G_{\text{hyd}}^{\circ}[T_r, p_r]$, $\Delta H_{\text{hyd}}^{\circ}[T_r, p_r]$ and $\Delta C_{p,\text{hyd}}^{\circ}[T_r, p_r]$ for each of the structural groups occurring in the included compounds.

The procedure of model regression at high temperatures and pressures is essentially similar to the reference conditions. First, each experimental value for the target solutes (nitro- and chloro-substituted aromatics) is expressed as a sum of the appropriate structural contributions with Eq. (6). Second, the database is subject to simultaneous weighted fit resulting in optimized values of structural contributions, which are represented by a selected thermodynamic model (i.e. equation-of-state which is the SOCW model in our case). The objective function for correlation has the form

$$F = \sum_{i=1}^O \left(\frac{\Delta G_{\text{hyd}}^{\circ,\text{exp}} - \Delta G_{\text{hyd}}^{\circ,\text{calc}}}{\sigma \Delta G_{\text{hyd}}^{\circ}} \right)_i^2 + \sum_{j=1}^P \left(\frac{\Delta H_{\text{hyd}}^{\circ,\text{exp}} - \Delta H_{\text{hyd}}^{\circ,\text{calc}}}{\sigma \Delta H_{\text{hyd}}^{\circ}} \right)_j^2 + \sum_{k=1}^Q \left(\frac{\Delta C_{p,\text{hyd}}^{\circ,\text{exp}} - \Delta C_{p,\text{hyd}}^{\circ,\text{calc}}}{\sigma \Delta C_{p,\text{hyd}}^{\circ}} \right)_k^2 + \sum_{l=1}^R \left(\frac{V_s^{\circ,\text{exp}} - V_s^{\circ,\text{calc}}}{\sigma V_s^{\circ}} \right)_l^2 \quad (11)$$

where the superscripts exp and calc denote experimental data and values calculated with the model, respectively, and $\sigma \Delta X_{\text{hyd}}^{\circ}$ is the estimated uncertainty of the experimental $\Delta X_{\text{hyd}}^{\circ}$ property.

Due to the lengthy equations, the SOCW model applied in this work for temperature-dependent thermodynamic properties of hydration will not be presented in any detail; a full description can be found e.g. in refs. [1-3,7]. It is sufficient to note that, within this model, each structural group is described by five group-specific adjustable parameters and any property of hydration for this structural group can be calculated from the basic SOCW model and its derivations, in accordance with Eqs. (3-5).

Experimental database

Our collection of experimental results on standard thermodynamic properties of hydration for aqueous nitro- and chloro- substituted aromatics included 342 data points retrieved from original literature sources. Recalculations of the published results were needed in some cases, especially for $\Delta G_{\text{hyd}}^{\circ}$ that is presented in the literature in various formats of Henry's law constant, as limiting activity coefficient, equilibrium constant, or it can be extracted from data on solubility and vapor pressure. Standard molar enthalpy of hydration is usually obtained from the enthalpy of dissolution and vaporization/sublimation of the pure solute

$$\Delta H_{\text{hyd}}^{\circ} = \Delta H_s^{\circ} - \Delta H_{\text{vap/sub}}^{\circ}. \quad (12)$$

Standard molar heat capacity resulting from experiments is transformed to standard molar heat capacity of hydration with the heat capacity of pure solute in the ideal gas standard state

$$\Delta C_{p,\text{hyd}}^{\circ} = C_p^{\circ} - C_p^{\text{ig}} \quad (13)$$

We estimate C_p^{ig} with the group contribution method by Joback [11]. Standard molar volume of hydration is identical to the experimentally accessible standard molar volume.

Substantial amount of data for our solutes is available for $\Delta G_{\text{hyd}}^{\circ}$ -related properties (218 data points). However, all of them were obtained at temperatures below 363 K and their significance mostly relates to the development of the method at reference conditions. Some of the more important data sources covering wider temperature range include refs. [12-17] for nitrophenols and nitrobenzenes, and refs. [18-23] for chlorophenols and chlorobenzenes. Data on the enthalpy and heat capacity of hydration [24,25] are scarce, altogether 7 data points only at 298 K are available. Standard molar volumes to 573 K obtained by Hnedkovsky and Cibulka for nitrobenzene and nitrophenols [26] and Hnedkovsky et al. for chlorophenols [27] represent the most important information on high-temperature behavior of these solutes and play a crucial role in parameterization of the high-temperature SOCW model for nitro- and chloro-functional groups.

Experimental data regarding phenolates refer again mostly to ambient conditions. As for the more important high-temperature results, the standard molar volumes and heat capacities of sodium phenolate were measured at the Brigham Young University [28] to 393 K, ionization enthalpies of chlorophenols at the Technical University of Liberec to 318 K, and mainly the ionization constants are available to 498 K by Ehlerova et al. [29] for aqueous nitrophenols and to 448 K by Uchida and Okuwaki for chlorophenols [30].

Results and discussion

At first, the experimental data to 373 K for $\Delta G_{\text{hyd}}^{\circ}$, $\Delta H_{\text{hyd}}^{\circ}$ and at ≈ 298 K for $\Delta C_{p,\text{hyd}}^{\circ}$ were regressed with Eqs. (7-10) to obtain the values of hydration properties at reference conditions for the nitro-, chloro- and phenolate- functional groups. The data also allowed evaluation of several second-order group contributions, namely for the interaction of two substituents in ortho- position. Similarly to the previous work on (alkyl)phenols where the o-corrections were obtained for OH-alkyl and OH-OH

interaction [3], we were able to extract the values of NO₂-OH, Cl-OH and Cl-Cl corrections for the o-interaction. A particularly large correction of this type was found for the NO₂-OH interaction, which applies in compounds derived from o-nitrophenol. The resulting values of hydration properties at reference conditions (298 K and 0.1 MPa) are summarized in Table 1, along with the values of group contributions for several other structural groups that appear in our compounds. These group contributions were taken from previous publications [3,10] and were fixed in our data treatment.

Table 1. Values of group contributions for calculating thermodynamic properties of hydration of aqueous substituted aromatic hydrocarbons at 298 K and 0.1 MPa.

Group	$\Delta G_{\text{hyd}}^{\circ}$ ^a	$\Delta H_{\text{hyd}}^{\circ}$ ^a	$\Delta C_{p,\text{hyd}}^{\circ}$ ^b	V° ^c
C _{ar} ^{d,e}	-3.85	-0.67	-50	4.00
CH _{ar} ^{d,e}	-0.65	-5.00	48	13.58
CH ₃ ^d	3.63	-7.54	132	25.14
I(C-C) ^f	-1.01	2.0	n.e. ^g	n.e. ^g
OH _{phi} ^{h,i}	-19.11	-27.51	30	12.88
I(CH ₃ -OH) ^{f,i}	1.83	n.e. ^g	24	0.8
I(OH-OH) ^{f,i}	n.e. ^g	n.e. ^g	51	-2.2
NH _{2,phi} ^{h,i}	-15.96	-26.43	49	16.71
I(NH ₂ -NH ₂) ^{f,i}	n.e. ^g	n.e. ^g	69	-3.0
NO _{2,phi} ^{h,j}	-7.90	-17.03	115	23.08
I(NO ₂ -OH) ^{f,j}	18.51	n.e. ^g	24	n.e. ^g
Cl _{phi} ^{h,j}	2.71	-0.95	-104	21.24
I(Cl-OH) ^{f,j}	4.04	n.e. ^g	n.e. ^g	0.7
I(Cl-Cl) ^{f,j}	-0.49	n.e. ^g	n.e. ^g	n.e. ^g
O _{phi} ^{h,j}	19.25	-3.82	-115	2.0
X _{SS} ^k	7.96	-2.29	0	1.2

(a) kJ/mol. (b) J/K/mol. (c) cm³/mol. (d) Plyasunov and Shock [10]. (e) A group with subscript _{ar} is a part of an aromatic ring. (f) Correction for *ortho*-position on the aromatic ring: CH₃ stands for alkyl-, OH for hydroxy-, NH₂ for amino-, NO₂ for nitro-, and Cl for chloro- groups. (g) Not evaluated (no data available or parameter not significant at the 95% confidence level). (h) A group with subscript _{phi} is directly bound to aromatic ring. (i) Censky et al. [3]. (j) This work. (k) Standard-state term (see Eq. 6).

Table 1 also includes the values at reference conditions for V° , obtained from regressing the data on this property at ≈ 298 K with an analogue of Eq. (10).

Using the results for $\Delta G_{\text{hyd}}^{\circ}$ and $\Delta H_{\text{hyd}}^{\circ}$ from Table 1 as integration constants, all data on nitro-

and chloro- substituted aromatic hydrocarbons were applied in the simultaneous weighted correlation (Eq. 11) to evaluate parameters of the SOCW model for $\text{NO}_{2,\text{phi}}$ and Cl_{phi} functional groups (subscript phi refers to a group directly bound to an aromatic ring). No other groups or second-order corrections were included in the fit. There are not enough appropriate experimental data for this purpose and we assume that most differences among the isomers are already contained in the reference values of $\Delta G_{\text{hyd}}^\circ$ and $\Delta H_{\text{hyd}}^\circ$ that are included in the SOCW model. The parameters of the SOCW equations are reported in Table 2, again with the parameters for other structural groups that appear in our compounds and were obtained previously [2,3] and used here as fixed constants.

Table 2. Parameters for calculating group contributions in the T, p dependent SOCW model for hydration properties of aqueous substituted aromatic hydrocarbons. See Table 1 for group descriptions.

Group	$10^3 a^a$	$10^4 b^a$	$10^6 c^a$	d	$10 e^b$
CH_3^c	7.278	-0.157	-1.950	1.427	-0.018
C_{ar}^c	-9.155	2.211	-21.35	-1.372	-4.999
CH_{ar}^c	0.692	0.517	-5.090	0.334	-1.075
OH_{phi}^d	10.949	-3.187	15.067	3.272	3.687
$\text{I}(\text{CH}_3\text{-OH})^d$	3.928	-1.087	15.709	0.766	3.356
$\text{I}(\text{OH-OH})^d$	-11.33	3.1447	-3.924	-2.609	-1.335
$\text{NH}_{2,\text{phi}}^d$	9.789	-2.661	21.251	2.950	4.783
$\text{NO}_{2,\text{phi}}^e$	4.4194	-0.141	-25.10	1.6485	-4.437
Cl_{phi}^e	8.041	-0.575	-5.529	1.627	-2.136

(a) m^3/kg . (b) $\text{J}/\text{K}^2/\text{mol}$. (c) Sedlbauer et al. [2]. (d) Censky et al. [3]. (e) This work.

The evolution of $\text{NO}_{2,\text{phi}}$ and Cl_{phi} functional groups with temperature and at saturation pressure can be found in Figure 1 for all hydration properties. The curves corresponding to OH_{phi} and $\text{NH}_{2,\text{phi}}$ groups from ref. [3] were also added to the graphs for comparison. The figures indicate generally lower polarity of the $\text{NO}_{2,\text{phi}}$ and Cl_{phi} functional groups compared to the OH_{phi} and $\text{NH}_{2,\text{phi}}$ groups.

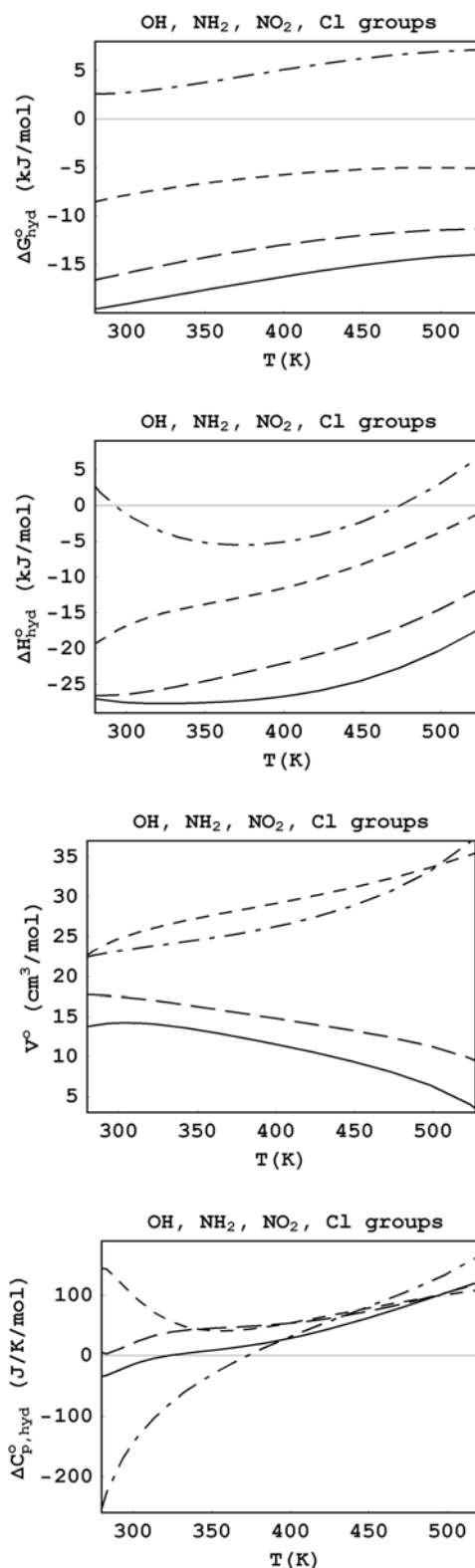


Figure 1. Temperature evolution of functional group contributions to the standard partial molar Gibbs energy of hydration and its T, p derivatives. Full line: OH_{phi} group; long-dashed line: $\text{NH}_{2,\text{phi}}$ group; short-dashed line: $\text{NO}_{2,\text{phi}}$ group; dashed-dot line: Cl_{phi} group.

Assessment of accuracy of the group contribution method is provided in Figures 2-4 for representative high-temperature data. While the standard molar volumes of nitrophenols and chlorophenols in Figure 2 are not much different for the various isomers and the model does not include any second-order correction, significant differences are observed in the case of $\Delta G_{\text{hyd}}^{\circ}$ for o- substituted solutes and the second-order correction (hidden in the value of $\Delta G_{\text{hyd}}^{\circ}[T_r, p_r]$) is clearly needed.

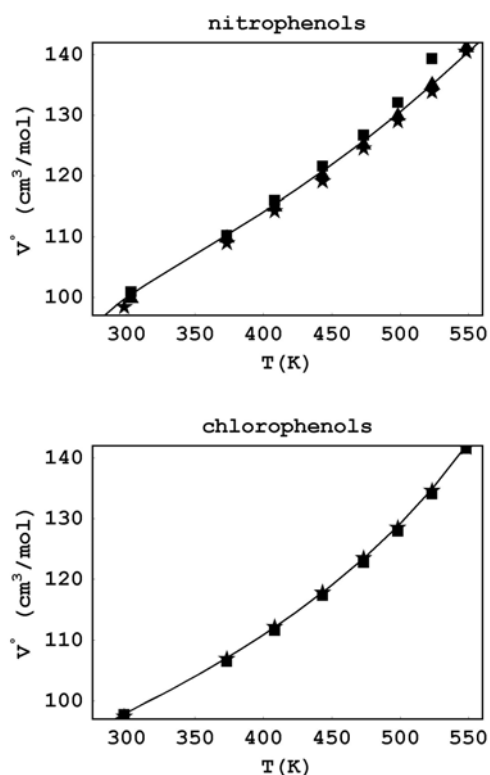


Figure 2. Standard molar volume of aqueous nitrophenols [26] and chlorophenols [27] at 30 MPa isobar. Full line: predictions of the SOCW model with parameters from Table 2; boxes: o-isomers; triangles: m-isomers (only m-nitrophenol); stars: p-isomers.

Figures 3 and 4 illustrate the major problem of data quality that hinders the development of a reliable model for standard thermodynamic properties of many organic solutes. The data are retrieved from a variety of sources (environmental, chemical engineering, atmospheric, physical, solution and food chemistry etc.) and were obtained by different techniques and with different quality standards. Their treatment therefore requires some experience with data handling, transformed into justified uncertainty estimates that are used as weights in the correlations. On the other hand, the important advantage of the group contribution

approach combined either with the van't Hoff approximation (at low temperatures) or with the SOCW model (at high temperatures) is that the method identifies suspect experimental data and allows (namely in the high-temperature model) to utilize the relatively abundant and accurate data on derivative properties such as the standard molar volumes in the case of nitro- and chloro- substituted aromatics in this study.

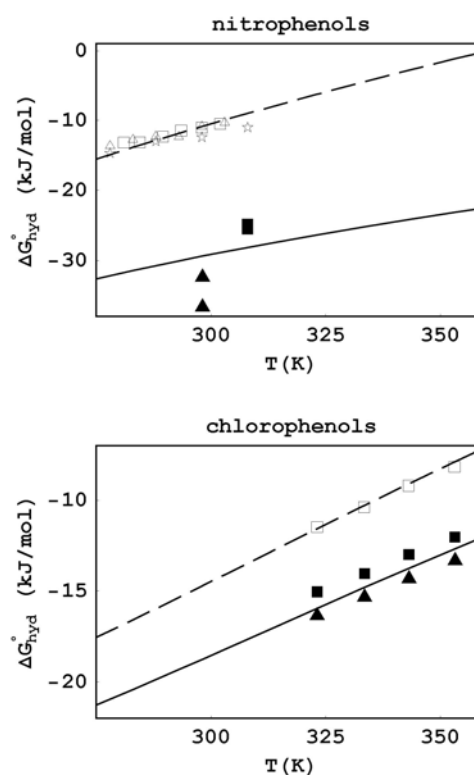


Figure 3. Standard molar Gibbs energy of hydration of aqueous nitrophenols and chlorophenols at saturation pressure. Full line: predictions of the SOCW model with parameters from Tables 1 and 2 for m- and p-isomers; dashed line: predictions of the SOCW model with parameters from Tables 1 and 2 for o-isomers. Data for nitrophenols: refs. [8,15] for m-, p-isomers (triangles and boxes, respectively); refs. [13-15] for o-isomer (open boxes, triangles and stars, respectively). Data for chlorophenols: ref. [22] for all isomers (open boxes for o-chlorophenol, boxes for m-chlorophenol, triangles for p-chlorophenol).

The data on ionization of phenols and substituted phenols such as in refs. [29,30] can be in principle applied in the same procedure leading to the parameters of the SOCW model for phenolate functional group. However, we did not attempt this calculation. The challenge of this approach lies mainly in the strong intramolecular interactions of the phenolate functional group with the rest of the molecule. As observed e.g. for nitrophenols [29], the

electron-withdrawing effect of the nitro- group stabilizing the O_{phi}^- anion is much stronger than the proximity effects in a neutral molecule. Moreover, it applies not only to o-, but also to p- isomers (much less than to m- isomers) and therefore requires a different setup of second-order corrections compared to neutral solutes. Ignoring this fact, as we did in the case of evaluating the reference values of standard-state properties for phenolate functional group in Table 1, leads to only semi-quantitative estimates. E.g. the ionization constant at 298 K of any (substituted) phenol is predicted the same value using the properties from Table 1, which is obviously not true. For instance, the p*K* of ionization for phenol and p-nitrophenol differs by almost 3 p*K* units [31].

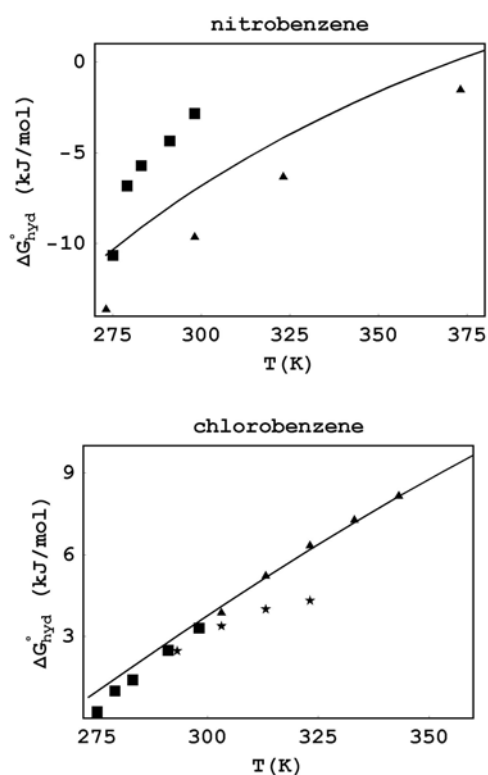


Figure 4. Standard molar Gibbs energy of hydration of aqueous nitrobenzene and chlorobenzene at saturation pressure. Full line: predictions of the SOCW model with parameters from Tables 1 and. Data for nitrobenzene: refs. [17,19] (triangles and boxes, respectively). Data for chlorobenzene: refs. [16,19,23] (triangles, boxes and stars, respectively).

Summary and Conclusions

The data on various thermodynamic properties related to the process of hydration of nitro-, chloro- and phenolate- substituted aromatic hydrocarbons were retrieved from the literature, recalculated to a common format of standard properties of hydration

and used in the evaluation of appropriate functional group models. Along with the previous results, the new group contribution scheme allows calculations of hydration properties of aqueous aromatic hydrocarbons substituted with any combination of nitro-, chloro-, hydroxy-, amino-, and alkyl-functional groups up to at least 523 K and 50 MPa.

Acknowledgement: This work was supported by the Research Center “Advanced Remedial Technologies and Processes” at TU Liberec.

Literature

- [1] *J. Sedlbauer, J.P. O’Connell and R.H. Wood:* A new equation of state for correlation and prediction of standard molal thermodynamic properties of aqueous electrolytes and nonelectrolytes at high temperatures and pressures. *Chem. Geol.* 163: 43-63 (2000).
- [2] *J. Sedlbauer, G. Bergin and V. Majer:* Group contribution method for the Henry’s law constant of aqueous hydrocarbons. *AIChE J.* 48: 2936-2959 (2002).
- [3] *M. Censky, J. Sedlbauer, V. Majer and V. Ruzicka:* Standard partial molal properties of aqueous alkylphenols and alkyanilines over a wide range of temperatures and pressures. *Geochim. Cosmochim. Acta* 71: 580-603 (2007).
- [4] *J.C. Tanger and H.C. Helgeson:* Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Revised equations of state for the standard partial molal properties of ions and electrolytes. *Amer. J. Sci.* 288: 19-98 (1988).
- [5] *J.P. O’Connell, A.V. Sharygin and R.H. Wood:* Infinite dilution partial molar volumes of aqueous solutes over wide ranges of conditions. *Ind. Eng. Chem. Res.* 35: 2808-2812 (1996).
- [6] *A.V. Plyasunov, J.P. O’Connell, R.H. Wood and E.L. Shock:* Infinite dilution partial molar properties of aqueous solutions of nonelectrolytes. II. Equations for the standard thermodynamic functions of hydration of volatile nonelectrolytes over wide ranges of conditions including subcritical temperatures *Geochim. Cosmochim. Acta* 64: 2779-2795 (2000).
- [7] *E.M. Yezdimer, J. Sedlbauer and R.H. Wood:* Predictions of thermodynamic properties at infinite dilution of aqueous organic species at high temperatures via functional group additivity. *Chem. Geol.* 164: 259-280 (2000).
- [8] *S. Cabani, P. Gianni, V. Mollica and L. Lepori:* Group contributions to the thermodynamic properties of non-ionic organic solutes in dilute aqueous solution. *J. Solution Chem.* 10: 563-595 (1981).

- [9] *W.M. Meylan and P.H. Howard*: Bond contribution method for estimating Henry's law constants. *Environ. Toxicol. & Chem.* 10: 1283-1293 (1991).
- [10] *A.V. Plyasunov and E.L. Shock*: Thermodynamic functions of hydration of hydrocarbons at 298.15 K and 0.1 MPa. *Geochim. Cosmochim. Acta* 64: 439-468 (2000).
- [11] *B.E. Poling, J.M. Prausnitz and J.P. O'Connell*: The Properties of Gases and Liquids, Fifth edition, McGraw-Hill (2001).
- [12] *J. Tremp, P. Mattrel, S. Fingler and W. Giger*: Phenols and nitrophenols as tropospheric pollutants: Emissions from automobile exhausts and phase transfer in the atmosphere. *Water, Air, and Soil Pollution* 68: 113-123 (1993).
- [13] *M.A.J. Harrison, J.N. Cape and M.R. Heal*: Experimentally determined Henry's law coefficients of phenol, 2-methylphenol and 2-nitrophenol in the temperature range 281-302 K. *Atmospheric Environ.* 36: 1843-1851 (2002).
- [14] *B. Muller and M.R. Heal*: The Henry's law coefficient of 2-nitrophenol over the temperature range 278-303 K. *Chemosphere* 45: 309-314 (2001).
- [15] *X.X. Guo and P. Brimblecombe*: Henry's law constants of phenol and mononitrophenols in water and aqueous sulfuric acid. *Chemosphere* 68, 436-444 (2007).
- [16] *M. Görgényi, J. Dewulf and H. Langenhove*: Temperature dependence of Henry's law constant in an extended temperature range. *Chemosphere* 48: 757-762 (2002).
- [17] *M. Bernauer, V. Dohnal, A.H. Roux, G.R. Desgranges and V. Majer*: Temperature dependences of limiting activity coefficients and Henry's law constants for nitrobenzene, aniline, and cyclohexylamine in water. *J. Chem. Eng. Data* 51, 1678-1685 (2006).
- [18] *T. Hulscher, L. Velde and W. Bruggeman*: Temperature dependence of Henry's law constants for selected chlorobenzenes, polychlorinated biphenyls and polycyclic aromatic hydrocarbons. *Environ. Toxicol. Chem.*, 11: 1595-1603 (1992).
- [19] *J. Dewulf, H. Van Langenhove and P. Everaert*: Determination of Henry's law coefficients by combination of the equilibrium partitioning in closed systems and solid-phase microextraction techniques. *J. Chromatography A* 830: 353-363 (1999).
- [20] *S. Hovorka and V. Dohnal*: Determination of air-water partitioning of volatile halogenated hydrocarbons by the inert gas stripping method. *J. Chem. Eng. Data* 42: 924-933 (1997).
- [21] *C. Leuenberger, M.P. Ligocki and J.F. Pankow*: Trace organic compounds in rain. 4. Identities, concentrations, and scavenging mechanisms for phenols in urban air and rain. *Environ. Sci. Technol.* 19: 1053-1058 (1985).
- [22] *S. Tabai, M. Rogalski, R. Solimando and S.K. Malanowski*: Activity coefficients of chlorophenols in water at infinite dilution. *J. Chem. Eng. Data* 42: 1147-1150 (1997).
- [23] *B. Khalfaoui and D.M.T. Newsham*: Determination of infinite dilution activity coefficients and second virial coefficients using gas-liquid chromatography - I. The dilute mixtures of water and unsaturated chlorinated hydrocarbons and of water and benzene. *Journal Chromatography A* 673: 85-92 (1994).
- [24] *E.M. Arnett, L.E. Small, D. Oancea and D. Johnston*: Heats of ionization of some phenols and benzoic acids in dimethyl sulfoxide. Heats of solvation of oxyanions in dimethyl sulfoxide and water. *J. Am. Chem. Soc.* 98: 7346-7350 (1976).
- [25] *H.P. Hopkins, W.C. Duer and F.J. Millero*: Heat capacity changes for the ionization of aqueous phenols at 25 C. *J. Solution Chem.* 5: 263-268 (1976).
- [26] *L. Hnedkovský and I. Cibulka*: Partial molar volumes of organic solutes in water. VIII. Nitrobenzene and nitrophenols at T = 298 K to T = 573 K and pressures up to 30 MPa. *J. Chem. Thermodyn.* 35: 1185-1197 (2003),.
- [27] *L. Hnedkovsky, I. Cibulka and V. Hnyek*: Partial molar volumes of organic solutes in water. VI. o-chlorophenol and p-chlorophenol at temperatures from T=298 K to 573 K and pressures up to 30 MPa. *J. Chem. Thermodyn.* 33: 1049-1057 (2001).
- [28] *M.L. Origlia-Luster, K. Ballerat-Busserolles, E.D. Merkley, J.L. Price, B.R. McRae and E.M. Woolley*: Apparent molar volumes and apparent molar heat capacities of aqueous phenol and sodium phenolate at temperatures from 278.115 to 393.15 K and at the pressure 0.35 MPa. *J. Chem. Thermodyn.* 35: 331-347 (2003).
- [29] *J. Ehlerova, L. Trevani, J. Sedlbauer and P.R. Tremaine*: Spectrophotometric determination of the ionization constants of aqueous nitrophenols at temperatures up to 225 C. *J. Solution Chem.* 37: 857-874 (2008).
- [30] *M. Uchida and A. Okuwaki*: UV-Vis Spectrophotometric determination of the dissociation constants for monochlorophenols in aqueous solution at elevated temperatures. *J. Solution Chem.* 32: 19-39 (2003).
- [31] *G.H. Parsons, C.H. Rochester and C.E.C. Wood*: Effect of four-substitution on the thermodynamics of phenol and the phenoxide anion. *J. Chem. Soc. B*, 533-536 (1971).