

# Application of Group Additivity Approach to Polar and Polyfunctional Aqueous Solutes

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Estimates of physical or thermodynamic properties of organic compounds are often based on a group contribution approach or other quantitative structure–property relationship. Polar functional groups introduce a perturbation to intramolecular distribution of electrons, resulting in violation of a group additivity assumption known as structural or proximity effects. We propose a method for quantitative evaluation of these effects from experimental data and present the results for polar functional group contributions and their structural/proximity effects calculated for several standard thermodynamic properties of hydration at ambient conditions and at high temperatures and pressures. Recommendations are provided for further developments of group contribution methods in aqueous solutions of organics.

## 1. Introduction

The assumption central to group contribution methods is that a molecule can be reduced to a sum of its structural elements, which are independent of each other. A physical property for any molecule is then obtained as a combination of property contributions of the appropriate “building blocks”. This representation is particularly useful when a great number of molecules are composed of a limited set of structural elements (often called functional groups), as it is in case of organic compounds. The simple and powerful idea of group additivity has attracted much attention since its dawn in the 1920s and provides a basis for a multitude of estimation methods for physical and thermodynamic properties of pure substances<sup>1</sup> and mixtures.<sup>2</sup>

Despite their success, group contribution methods possess an inherent weakness stemming from the basic idea of mutual independence of structural elements. This may lead to inability of distinguishing between isomers, neglecting sterical hindrance of large molecular segments, and ignoring interactions of polar functional groups with other groups in close proximity. To overcome these structural and proximity problems, essentially three approaches have been suggested:

(1) The first approach is to add structural corrections to a simple group contribution method or applying higher-order group additivity schemes. This in principle means increasing the number of selected structural elements, which become larger and more complex, or including corrections for interactions between the functional groups in specific positions.

(2) A second approach is to use geometric or other calculated or experimental descriptors instead of the more traditional functional groups for capturing the molecular structure. The desired property is obtained as a linear combination of these descriptors.

(3) The third approach is to correct the results of a simple group or bond contribution method by quantum mechanical calculations targeted at electron distribution in the molecule of interest. While it would be possible to use first principles directly for evaluation of a given property and discard the assumption of group additivity completely, such a procedure is still limited to only small molecules due to calculation difficulties.

The main obstacle for the first mentioned approach is the limited amount of experimental data on different structures

available for model developments, resulting in corrections that depend heavily on one or a few data points and are subject to large uncertainties. Ultimately the whole molecule may be treated as one functional group in certain cases. The latter two approaches often lead to more accurate results with fewer parameters obtained from experimental data, but their application is rather difficult: that is why the group contribution methods of the first type still dominate among final users.

While the physical picture explaining qualitatively structural and proximity effects is obvious, much less is known about the actual deviations from the group contribution approximation induced by certain structural arrangements. Comparison is easily accessible only for isomers with otherwise identical functional groups such as *o*-, *m*-, and *p*-dihydroxybenzenes, 2-pentanol and 3-pentanol, etc. (another constraint is that data must be available for the same property and measured at approximately the same conditions for each isomer). However, it would be much more interesting to compare the contribution of a hydroxyl functional group at various positions in different compounds. Such information would provide a quantitative assessment of deviations from the group contribution additivity for the given functional group in different molecular structures and could serve as a signpost for possible model improvements.

In addition to intramolecular structural and proximity effects, the relative inadequacy of the group contribution method depends also on media surrounding the molecule, which can be a vacuum (i.e., ideal gas), pure fluid, or some fluid mixture. In practical applications much interest is attracted by aqueous solutions, especially at the asymmetrical standard state of infinite dilution. Thermodynamic properties of aqueous solutes at this standard state are required for modeling a variety of physicochemical transformations such as solubility, chemical reactivity, and phase partitioning for process design and cleanup of aqueous effluents and aquatic systems. Focused experimental efforts namely in the past decade or so substantially increased the amount of available data for aqueous organic solutes in a wide range of temperatures and pressures, making it possible to look in detail also at the differences introduced by functional group settings.

The main objective of this study was to evaluate quantitatively the effect of polar functional groups in various structural arrangements on group contribution predictions of standard thermodynamic properties of aqueous organic solutes. We begin with a brief overview of group contribution methods and argue for the choice

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of hydration properties as the most appropriate representation for the behavior of aqueous solutes. This is followed by a description of the procedure for extracting the group contributions for a given functional group from experimental data. The suggested method is validated with data for aqueous hydrocarbons and applied to experimental results of polar and polyfunctional compounds, both at reference conditions and at high temperatures and pressures. Analysis of the results is provided regarding the magnitude and temperature/pressure trends in needed structural and proximity corrections to the group additivity approach for standard thermodynamic properties. Based on the analysis we suggest some recommendations for the developments of the group contribution methods.

## 2. Background

**2.1. Overview of Group Contribution Methods.** In the case of aqueous solutes the group contribution concept is most often applied for a single property of practical interest, typically the Henry's law constant  $K_H$  at the reference conditions of  $T_r = 298.15$  K and  $p_r = 0.1$  MPa. Dearden and Schüürmann<sup>3</sup> reviewed over 40 such methods, tested 12 of them, and concluded that the overall best-performing one is the bond contribution method by Meylan<sup>4</sup> (bond method may be viewed as a group contribution scheme with atoms as functional groups and with corrections depending on the type of atom to which the functional group is bonded). Other popular or innovative methods for Henry's law constant or related properties should be mentioned: the original bond and group contribution approaches by Hine and Mookerjee<sup>5</sup> updated by Meylan and Howard,<sup>6</sup> the method of Cabani et al.,<sup>7</sup> prediction schemes based on so-called solvatochromic parameters<sup>8,9</sup> and topological descriptors,<sup>10,11</sup> quantum corrections to a group additivity method by Lin and Sandler,<sup>12</sup> and extensive ongoing efforts by Plyasunov et al., leading to careful reviewing of experimental data on various solute classes and development of both simple and second-order group contribution methods.<sup>13–18</sup> Some methods concentrate on accurate description of a certain solute type with environmental relevance such as PCB congeners; the molecular hologram approach applied, e.g., by Wang et al.<sup>19</sup> may serve as an example.

Limited estimation methods are available for Henry's law constant at elevated temperatures and pressures. In a rather narrow range of conditions (up to 320–350 K and at saturation pressure) the procedure could be based on a group contribution scheme for  $K_H$  as well as for its first temperature derivative  $\Delta H_h^\circ$ , which is the standard molar enthalpy of hydration, both at reference conditions  $T_r$  and  $p_r$ . Extension of predictions to at least 373 K is possible with including the second temperature derivative of  $K_H$ , the standard molar heat capacity of hydration  $\Delta C_{p,h}^\circ$ , into the scheme. Previously mentioned methods of Cabani et al.<sup>7</sup> and Plyasunov et al. include these derivative properties, and another example of this approach was presented recently by Kühne et al.<sup>20</sup> At high temperatures (over 373 K) and/or elevated pressures the modeling tools for standard thermodynamic properties are even less developed, which is understandable considering the difficulties when dealing with organic molecules whose degree of hydrophobicity changes strongly with temperature. A practical need for such predictions comes from geochemical modeling, petroleum exploration, power cycle chemistry, and technologies using hydrothermal reactions, but high-temperature data and predictions also provide an important test for thermodynamic theories and simulation pseudoexperiments. A review of high-temperature models for standard thermodynamic properties can be found in Majer et

al.<sup>21</sup> The methods applying the group contribution concept at elevated conditions were presented by Amend and Helgeson<sup>22</sup> based on the Helgeson–Kirkham–Flowers equation of state<sup>23</sup> and by Yezdimer et al.<sup>24</sup> and Sedlbauer et al.<sup>25</sup> using the Sedlbauer–O'Connell–Wood thermodynamic model.<sup>26</sup>

**2.2. Representation of Standard Thermodynamic Properties.** Arguably the most important property used in practical applications is the solute standard chemical potential (standard partial molar Gibbs energy of formation),  $\Delta G_f^\circ$ . Standard chemical potentials are easily converted to the equilibrium constants of chemical reactions involving aqueous species, and in combination with vapor pressure and other pure solid or liquid data to limiting activity coefficients, solubilities, Henry's law constants, and other vapor–liquid or air–water partition coefficients. Standard partial molar properties are in fact composed of a pure solute property (e.g., Gibbs energy of formation of pure solute,  $\Delta G_f^\circ$ ) and property change corresponding to transfer of a solute molecule from the pure state to aqueous solution (e.g., Gibbs energy of dissolution,  $\Delta G_s^\circ$ ):

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

Applying a group contribution method to this sum would be a disadvantage because of mixing two quantities for which the group contribution assumption is not exactly the same. Moreover, in the case of pure compounds plentiful experimental data and/or sophisticated estimation methods are usually available. The properties of dissolution can be successfully used for the development of a group contribution scheme if we deal with a more limited class of substances similar in nature and we require predictions at single conditions (typically 298 K and 0.1 MPa). However, for a wide range of conditions and properties the dissolution concept is also not suitable because the process of dissolution may start with the solute in solid, liquid, or gaseous state, differing by a property change during vaporization, sublimation, or melting. For convenient representation of standard thermodynamic properties, we need to select one common state of pure solute in eq 1. This state of matter should be accessible by all solutes and its properties should be well-known. A natural choice for this purpose is the ideal gas, transforming eq 1 to

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

where  $\Delta G_f^{\text{ig}}$  is the Gibbs energy of formation of a pure solute in the ideal gas standard state and  $\Delta G_h^\circ$  is the standard molar Gibbs energy of hydration, which is indeed accepted as the most appropriate measure of solute interaction with aqueous media.<sup>27</sup> The process of hydration consists of three steps: (i) transferring the material point from ideal gas standard state to aqueous solution, (ii) creating a cavity in the solution to mimic the volume and geometry of a solute molecule, and (iii) allowing the solute molecule to interact with the surrounding water. While the first term is universal, depending only on thermophysical properties of pure solvent,<sup>28</sup> it is the second and most of all the third terms that are sensitive to structural and proximity effects.

## 3. Calculation Procedure

Under the assumption of functional group additivity, any thermodynamic function of hydration of an aqueous organic molecule is determined as a sum of structural contributions. The basic equation takes the form

$$Y_h^\circ = Y_{\text{SS}} + \sum_{i=1}^N n_i Y_{h,i}^\circ + \delta Y_h^\circ \quad (3)$$

where  $N$  is the total number of functional groups present in a given compound,  $n_i$  is the number of occurrences of each specific functional group, and  $Y_{h,i}^\circ$  stands for the  $Y$  property of the  $i$ th group.  $Y_{SS}$  accounts for the intrinsic contribution to the  $Y$  property that is equal to the contribution of a material point and can be evaluated using only thermodynamic quantities of pure solvent.<sup>27,28</sup> If each functional group is independent of its neighbors, the first two terms define a first-order, simple group contribution method. Typical first-order functional groups are, e.g.,  $\text{CH}_3$  and  $\text{CH}_2$  groups in hydrocarbon backbones. Structural and proximity effects that are not accounted for in this approach are hidden in the last term  $\delta Y_{h,i}^\circ$ , which includes a sum of second-order (generally higher-order) corrections to a simple group additivity approximation.

One could suppose that group additivity is best obliged in homologous series such as in aliphatic hydrocarbons, so that considering  $\delta Y_{h,i}^\circ = 0$  for such molecules does not lead to any substantial error in  $Y_{h,i}^\circ$  property estimation. Let us consider some hydrocarbon substituted with one or more polar functional groups, e.g., 1-butanol, 2-butanol, and 1,4-butanediol. The property contribution for the hydroxyl functional group,  $Y_{h,\text{OH}}^\circ$ , is evaluated from experimental data as follows:

$$Y_{h,\text{OH}}^\circ + \delta Y_{h,1}^\circ = Y_{h,\text{OH}}^{\circ,\text{exp}} - Y_{SS} - Y_{h,\text{CH}_3}^\circ - 3Y_{h,\text{CH}_2}^\circ \quad \text{for 1-butanol}$$

$$Y_{h,\text{OH}}^\circ + \delta Y_{h,2}^\circ = Y_{h,\text{OH}}^{\circ,\text{exp}} - Y_{SS} - 2Y_{h,\text{CH}_3}^\circ - Y_{h,\text{CH}_2}^\circ - Y_{h,\text{CH}}^\circ \quad \text{for 2-butanol}$$

$$Y_{h,\text{OH}}^\circ + \delta Y_{h,3}^\circ = (Y_{h,\text{OH}}^{\circ,\text{exp}} - Y_{SS} - 4Y_{h,\text{CH}_2}^\circ)/2 \quad \text{for 1,4-butanediol}$$

The values of  $\delta Y_{h,1}^\circ$ ,  $\delta Y_{h,2}^\circ$ , and  $\delta Y_{h,3}^\circ$  represent higher-order corrections induced in the molecule by introduction of a hydroxyl functional group(s) into a specific position. We are unable to evaluate the “true” value of the group contribution  $Y_{h,\text{OH}}^\circ$ ; it is therefore common to postulate  $\delta Y_{h,1}^\circ = 0$  so that the first-order group is obtained from primary substituted hydrocarbons such as 1-butanol. The higher-order corrections  $\delta Y_{h,2}^\circ$ ,  $\delta Y_{h,3}^\circ$ , etc. can be then related to this value. Generally, if we know the properties of all first-order functional groups in a molecule except one, it can be evaluated from experimental data using the formula

$$Y_{h,N}^\circ + \delta Y_{h,N}^\circ = (Y_{h,\text{OH}}^{\circ,\text{exp}} - Y_{SS} - \sum_{i=1}^{N-1} n_i Y_{h,i}^\circ)/n_N \quad (4)$$

We assume in eq 4 that all structural and proximity corrections can be attributed to this  $N$ th functional group as it is in our examples of alcohols.

Only experimental data on fairly simple molecules can be used with eq 4 for extracting reasonably well-defined higher-order corrections. This reduces the number of functional groups whose properties need to be known in advance to basic hydrocarbon groups ( $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$ , and  $\text{C}$  groups in aliphatic hydrocarbons,  $\text{CH}_{2,\text{cyclo}}$  and  $\text{CH}_{\text{cyclo}}$  in aliphatic cycles, and  $\text{CH}_{\text{ar}}$  and  $\text{C}_{\text{ar}}$  in aromatic rings). In certain cases we also use the a priori evaluated contribution of the  $\text{OH}$  and  $\text{OH}_{\text{phi}}$  functional groups, obtained from a method for primary alcohols and phenols, respectively (subscript “phi” indicates a functional group that is bound directly to an aromatic ring). The calculations performed in this study at  $T_r = 298.15$  K and  $p_r = 0.1$  MPa utilized for these functional groups (except  $\text{OH}_{\text{phi}}$ ) the group contribution method by Plyasunov and Shock<sup>13</sup> and Censky et al.<sup>29</sup> (only for  $\text{OH}_{\text{phi}}$ ). At high temperatures and

**Table 1. Thermodynamic Properties of Hydrocarbon Functional Groups Calculated from the Sedlbauer et al. Model<sup>25</sup> as a Function of Temperature at  $p_{\text{sat}}$**

$T$ [K]	$V^\circ$ [cm <sup>3</sup> /mol]	$\Delta C_{p,h}^\circ$ [J/K/mol]	$\Delta H_h^\circ$ [kJ/mol]	$\Delta G_h^\circ$ [kJ/mol]
Group: $\text{CH}_3$ (Aliphatic Chains)				
298	26.6	139	-7.54 <sup>a</sup>	3.63 <sup>a</sup>
373	28.6	104	1.01	5.39
473	35.3	131	12.24	5.29
573	59.5	336	30.89	2.60
Group: $\text{CH}_2$ (Aliphatic Chains)				
298	16.0	67	-3.76 <sup>a</sup>	0.72 <sup>a</sup>
373	17.7	46	0.08	1.37
473	21.4	42	4.52	1.19
573	28.7	30	8.02	0.30
Group: $\text{CH}$ (Aliphatic Chains)				
298	5.8	-3	-0.90 <sup>a</sup>	-1.79 <sup>a</sup>
373	7.7	-5	-1.39	-1.96
473	10.1	-32	-2.73	-1.99
573	9.1	-182	-11.16	-1.15
Group: $\text{C}$ (Aliphatic Chains)				
298	-5.8	-71	2.60 <sup>a</sup>	-4.50 <sup>a</sup>
373	0.1	-49	-1.56	-5.76
473	11.4	-226	-13.20	-5.83
573	22.8	-737	-57.95	-0.61
Group: $\text{CH}_{2,\text{cyclo}}$ (Aliphatic Cycles)				
298	16.0	94	-5.36 <sup>a</sup>	0.83 <sup>a</sup>
373	17.8	54	-0.44	1.76
473	21.5	68	5.47	1.68
573	32.4	138	14.20	0.30
Group: $\text{CH}_{\text{cyclo}}$ (Aliphatic Cycles)				
298	10.0	16	-2.40 <sup>a</sup>	-1.03 <sup>a</sup>
373	10.5	66	2.15	-1.14
473	16.8	-82	2.29	-2.34
573	26.3	-353	-18.36	-1.16
Group: $\text{CH}_{\text{ar}}$ (Aromatic Cycles)				
298	13.7	53	-5.00 <sup>a</sup>	-0.65 <sup>a</sup>
373	15.0	43	-1.60	0.03
473	18.3	42	2.64	-0.03
573	26.6	62	7.05	-0.84
Group: $\text{C}_{\text{ar}}$ (Aromatic Cycles)				
298	2.3	-36	-0.67 <sup>a</sup>	-3.85 <sup>a</sup>
373	4.4	-29	-3.23	-4.34
473	6.2	-62	-7.04	-4.23
573	0.5	-280	-20.51	-2.59
Group: $Y_{SS}$ (Standard-State Term, eq 4) <sup>b</sup>				
298	1.1	0	-2.29	7.95
373	1.5	3	-2.23	10.52
473	3.5	19	-1.37	13.87
573	15.2	167	4.16	16.80

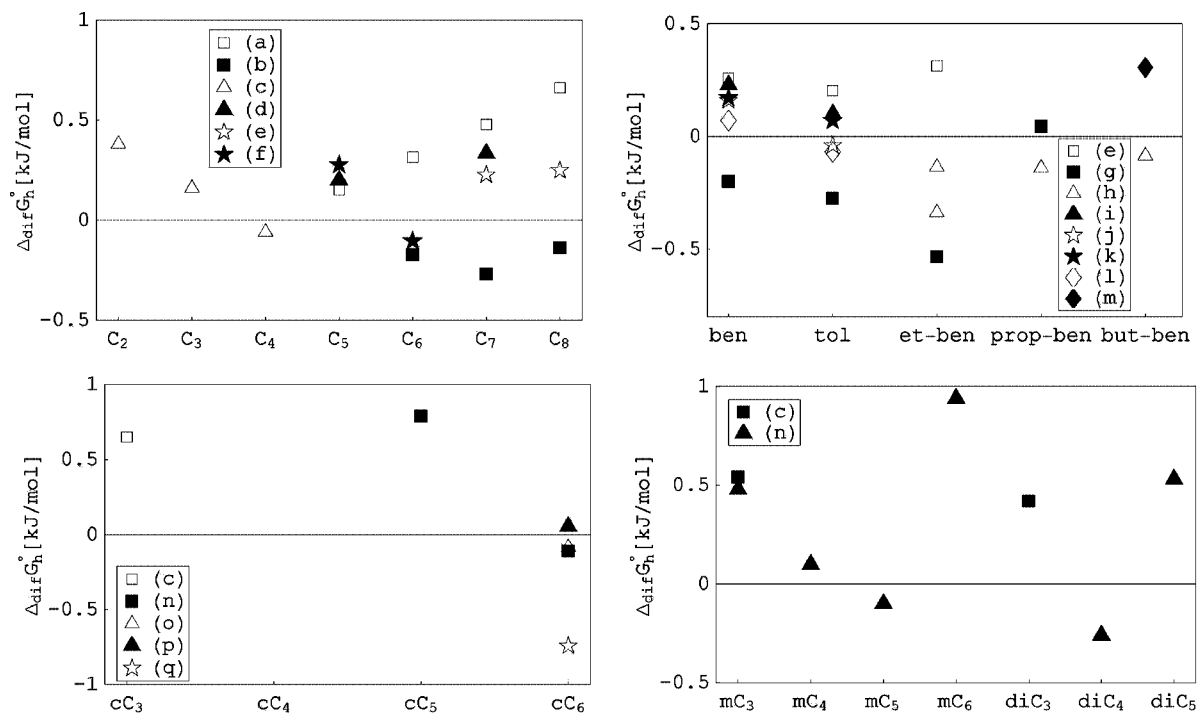
<sup>a</sup> From the method of Plyasunov and Shock.<sup>13</sup> <sup>b</sup> From the equation of state for water by Wagner and Pruss.<sup>35</sup>

pressures the thermodynamic quantities of functional groups are described by the Sedlbauer—O’Connell—Wood equation of state,<sup>26</sup> which is based on earlier results of O’Connell et al.<sup>30</sup> Appropriate functional group parameters of this model were presented by Sedlbauer et al.<sup>25</sup> (all groups but  $\text{OH}_{\text{phi}}$ ) and Censky et al.<sup>29</sup> ( $\text{OH}_{\text{phi}}$ ). Details of these methods are provided in the cited references and will not be repeated here.

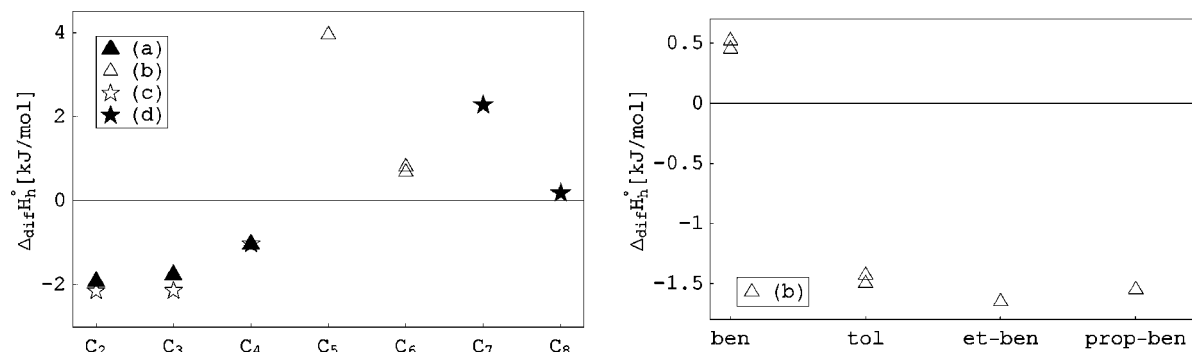
## 4. Results and Discussion

**4.1. Experimental Database.** Our collections of experimental results on standard thermodynamic properties of hydration include almost 13000 data points retrieved from original literature sources. Recalculations of the published results were needed in some cases, especially for  $\Delta G_h^\circ$ , which is presented in the literature in various formats of the Henry’s law constant, as a limiting activity coefficient, or as an equilibrium constant, or it can be extracted from data on solubility and vapor pressure. The standard molar enthalpy of hydration is usually obtained from the enthalpy of dissolution and vaporization/sublimation of the pure solute:

$$\Delta H_h^\circ = \Delta H_s^\circ - \Delta H_{\text{vap/sub}}^\circ \quad (5)$$



**Figure 1.** Difference between experimental standard molar property and its prediction by first-order group additivity approximation. Standard molar Gibbs energy of hydration for aliphatic hydrocarbons (ethane, C<sub>2</sub>, to octane, C<sub>8</sub>), alkylbenzenes (benzene to butylbenzene), cyclic hydrocarbons (cyclopropane, cC<sub>3</sub>, to cyclohexane, cC<sub>6</sub>), and branched aliphatic hydrocarbons (2-methylpropane, mC<sub>3</sub>, to 2-methylhexane, mC<sub>6</sub>; 2,2-dimethylpropane, diC<sub>3</sub>, to 2,2-dimethylpentane, diC<sub>5</sub>). All data correspond to 298.15 K and 0.1 MPa. Experimental data: (a) Jönsson et al.;<sup>36</sup> (b) Polak and Lu;<sup>37</sup> (c) Wilhelm et al.;<sup>38</sup> (d) Nelson and de Ligny;<sup>39</sup> (e) Ryu and Park;<sup>40</sup> (f) Tewari et al.;<sup>41</sup> (g) Dewulf et al.;<sup>42</sup> (h) Owens et al.;<sup>43</sup> (i) Görgényi et al.;<sup>44</sup> (j) Bakierowska and Trzeczynski;<sup>45</sup> (k) Dohnal and Hovorka;<sup>46</sup> (l) Peng and Wan;<sup>47</sup> (m) Sutton and Calder;<sup>48</sup> (n) Mackay and Shiu;<sup>49</sup> (o) Dewulf et al.;<sup>50</sup> (p) de Hemptinne et al.;<sup>51</sup> (q) Mc Bain and Lissant.<sup>52</sup>



**Figure 2.** Difference between experimental standard molar property and its prediction by first-order group additivity approximation. Standard molar enthalpy of hydration for aliphatic hydrocarbons (ethane, C<sub>2</sub>, to octane, C<sub>8</sub>) and alkylbenzenes (benzene to propylbenzene). All data correspond to 298.15 K and 0.1 MPa. Experimental data: (a) Olofsson et al.;<sup>53</sup> (b) Gill et al.;<sup>54</sup> (c) Dec and Gill;<sup>55</sup> (d) Nelson and de Ligny.<sup>39</sup>

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

$$\Delta C_{p,h}^{\circ} = C_p^{\circ} - C_p^{\text{ig}} \quad (6)$$

We obtain  $C_p^{\text{ig}}$  from the extensive compilation by Frenkel et al.<sup>31</sup> or estimate it using the group contribution method by Joback.<sup>1</sup> The standard molar volume of hydration is identical to the experimentally accessible standard molar volume (it follows from the pressure derivative of eq 2 where  $\Delta G_i^{\text{ig}}$  is at constant pressure).

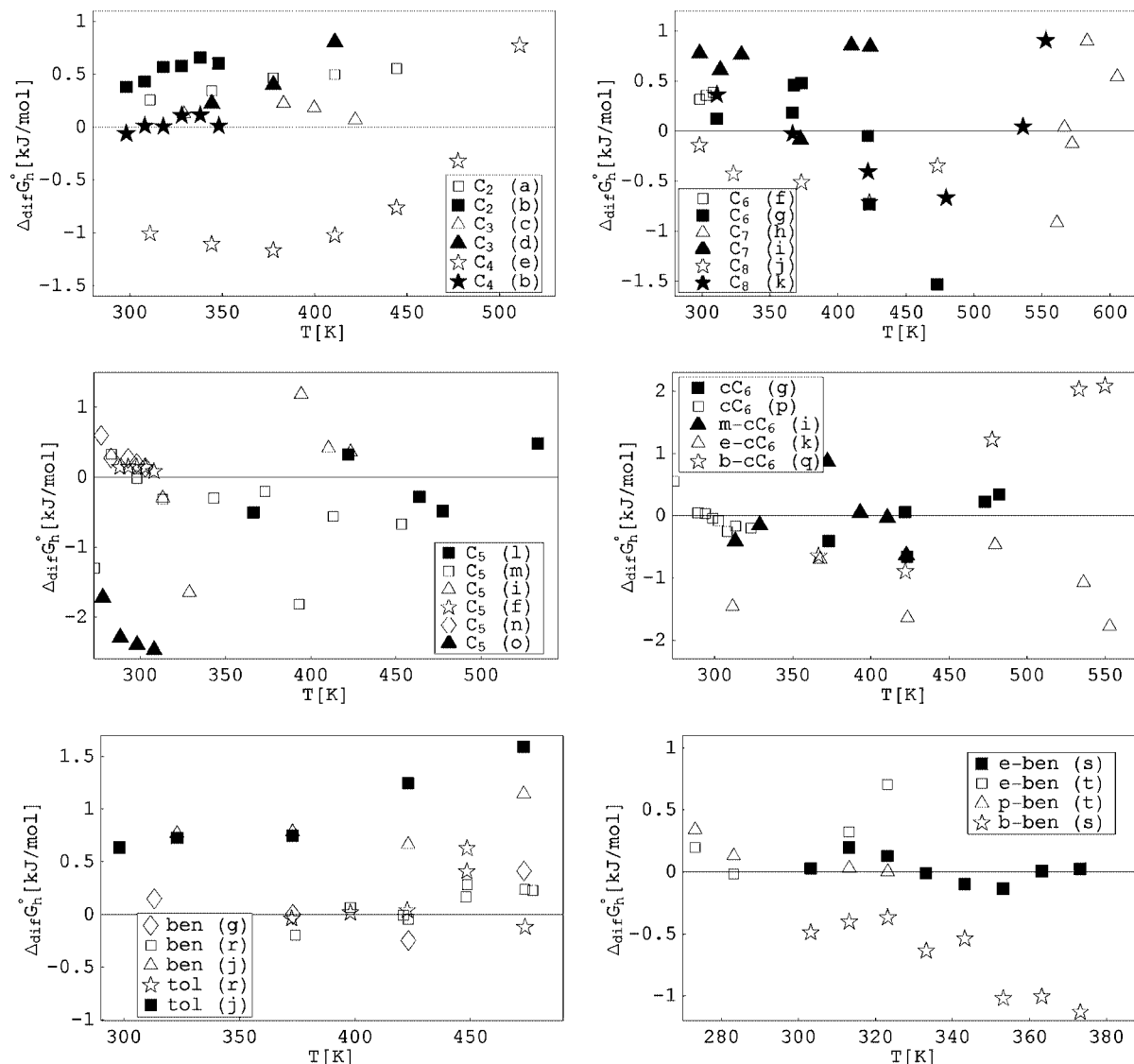
The results are presented in this study mainly in a graphical form. For the sake of visual convenience we could not include all available results into the figures. Selected representative data sets were used for evaluations, covering major and reliable literature sources. Numerical values of the hydration properties

for hydrocarbon functional groups calculated from Plyasunov and Shock<sup>13</sup> and Sedlbauer et al.<sup>25</sup> methods are provided in Table 1 at selected temperatures along the saturation line of water. The table may serve as a handy tool for making simplified estimations of the structural and/or proximity effects for solutes not included in our tests.

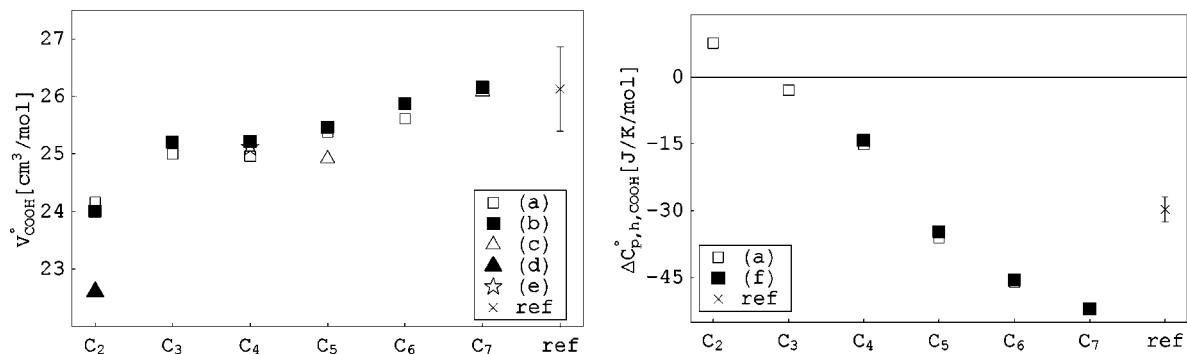
**4.2. Validation of the Applied Methods.** Before evaluating higher-order corrections from experimental data on substituted compounds, we need to investigate the expected uncertainty of the backbone hydrocarbon functional groups. The results for aqueous hydrocarbons are presented in terms of  $\Delta_{\text{dif}}Y_h^{\circ}$ , which is a difference between experimental and predicted values of the  $Y_h^{\circ}$  property:

$$\Delta_{\text{dif}}Y_h^{\circ} = Y_h^{\text{exp}} - Y_{\text{SS}} - \sum_{i=1}^N n_i Y_{h,i}^{\circ} \quad (7)$$

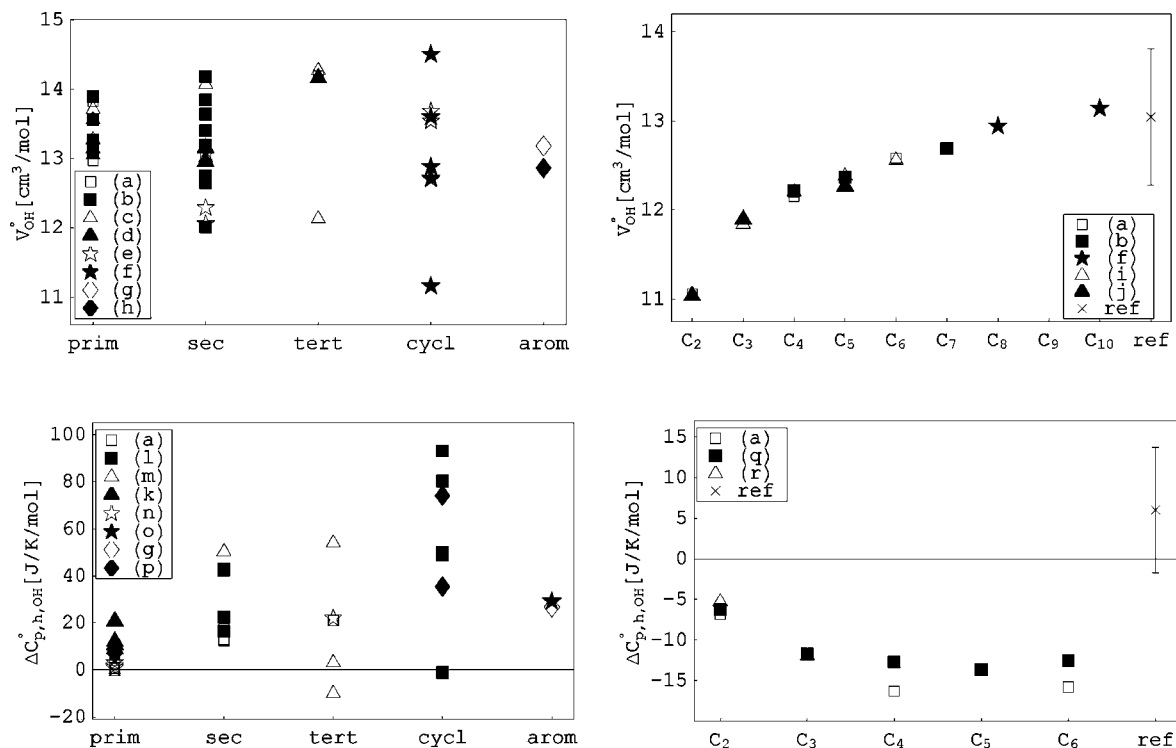
If the group additivity assumption holds for aqueous hydrocar-



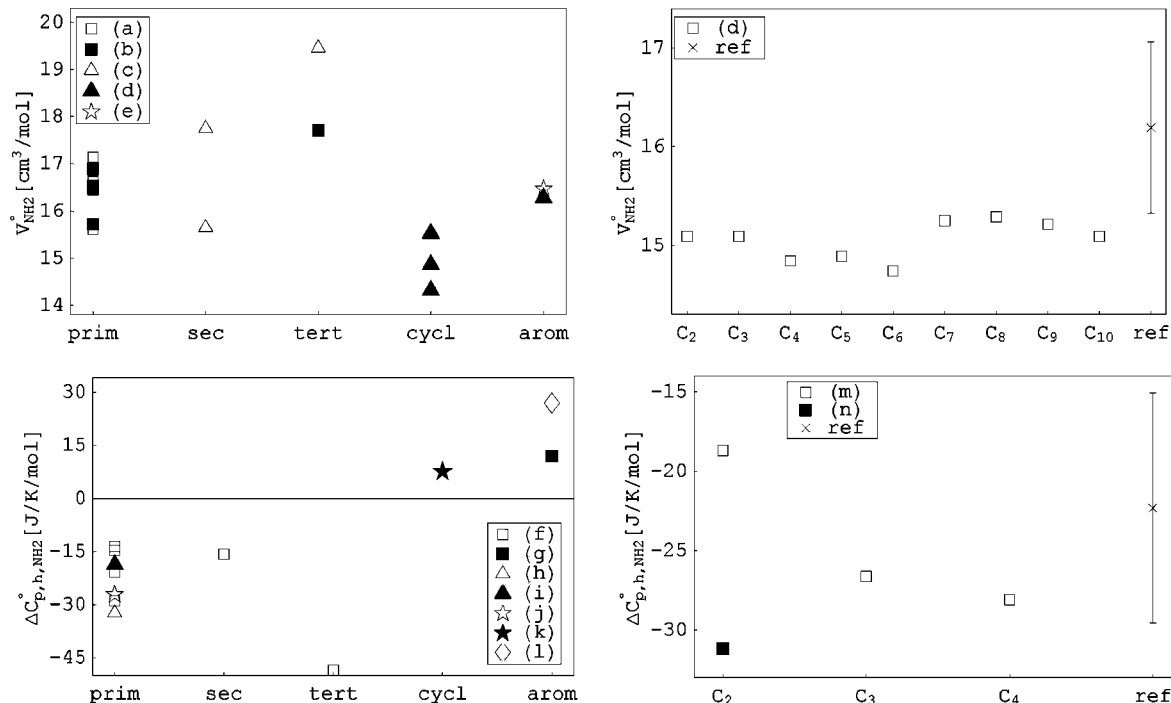
**Figure 3.** Difference between experimental standard molar property and its prediction by first-order group additivity approximation as a function of temperature. Standard molar Gibbs energy of hydration for aliphatic hydrocarbons (ethane,  $C_2$ , to octane,  $C_8$ ), alkylcyclohexanes (cyclohexane,  $cC_6$ , to butylcyclohexane,  $b-cC_6$ ), and alkybenzenes (benzene, ben, to butylbenzene,  $b$ -ben). Experimental data: (a) Culberson and McKetta<sup>56</sup> (ethane at 50.7 MPa); (b) Wilhelm et al.<sup>38</sup> (ethane and butane at  $p_{\text{sat}}$ ); (c) Kobayashi and Katz<sup>57</sup> (propane at 19.5 MPa); (d) Azarnoosh and McKetta<sup>58</sup> (propane at 0.5 MPa); (e) Reamer et al.<sup>59</sup> (butane at 50.7 MPa); (f) Jönsson et al.<sup>36</sup> (pentane and hexane at  $p_{\text{sat}}$ ); (g) Tsonopoulos and Wilson<sup>60</sup> (hexane, cyclohexane, and benzene at  $\approx p_{\text{sat}}$ ); (h) O'Grady<sup>61</sup> (heptane at 25.1 MPa); (i) Price<sup>62</sup> (pentane, heptane, and methylcyclohexane at  $\approx p_{\text{sat}}$ ); (j) Miller and Hawthorne<sup>63</sup> (octane and benzene at 6.6 MPa, toluene at 5.1 MPa); (k) Heidman et al.<sup>64</sup> (octane and ethylcyclohexane at  $\approx p_{\text{sat}}$ ); (l) Gillespie and Wilson<sup>65</sup> (pentane at 14.0 MPa); (m) Jou and Mather<sup>66</sup> (pentane at  $\approx p_{\text{sat}}$ ); (n) Nelson and De Ligny<sup>39</sup> (pentane at  $p_{\text{sat}}$ ); (o) Pierotti and Liabastre<sup>67</sup> (pentane at  $p_{\text{sat}}$ ); (p) de Hemptinne et al.<sup>51</sup> (cyclohexane at  $p_{\text{sat}}$ ); (q) Economou et al.<sup>68</sup> (butylcyclohexane at  $\approx p_{\text{sat}}$ ); (r) Anderson and Prausnitz<sup>69</sup> (benzene and toluene at  $\approx p_{\text{sat}}$ ); (s) Chen and Wagner<sup>70</sup> (ethylbenzene and butylbenzene at 0.14 MPa); (t) Sawamura et al.<sup>71</sup> (propylbenzene at 50.7 MPa).



**Figure 4.** Contribution of carboxylic group to standard molar volume and standard molar heat capacity of hydration for  $\alpha,\omega$ -dioic acids (ethanedioic acid,  $C_2$ , to heptanedioic acid,  $C_7$ ). All data correspond to 298.15 K and 0.1 MPa; "ref" is the average contribution of carboxylic group obtained from experimental results on aliphatic primary acids. Experimental data: (a) Sijpkes et al.;<sup>72</sup> (b) Stokes;<sup>73</sup> (c) Apelblat and Manzurola;<sup>74</sup> (d) Apelblat and Manzurola;<sup>75</sup> (e) Manzurola and Apelblat;<sup>76</sup> (f) Nichols et al.<sup>77</sup>



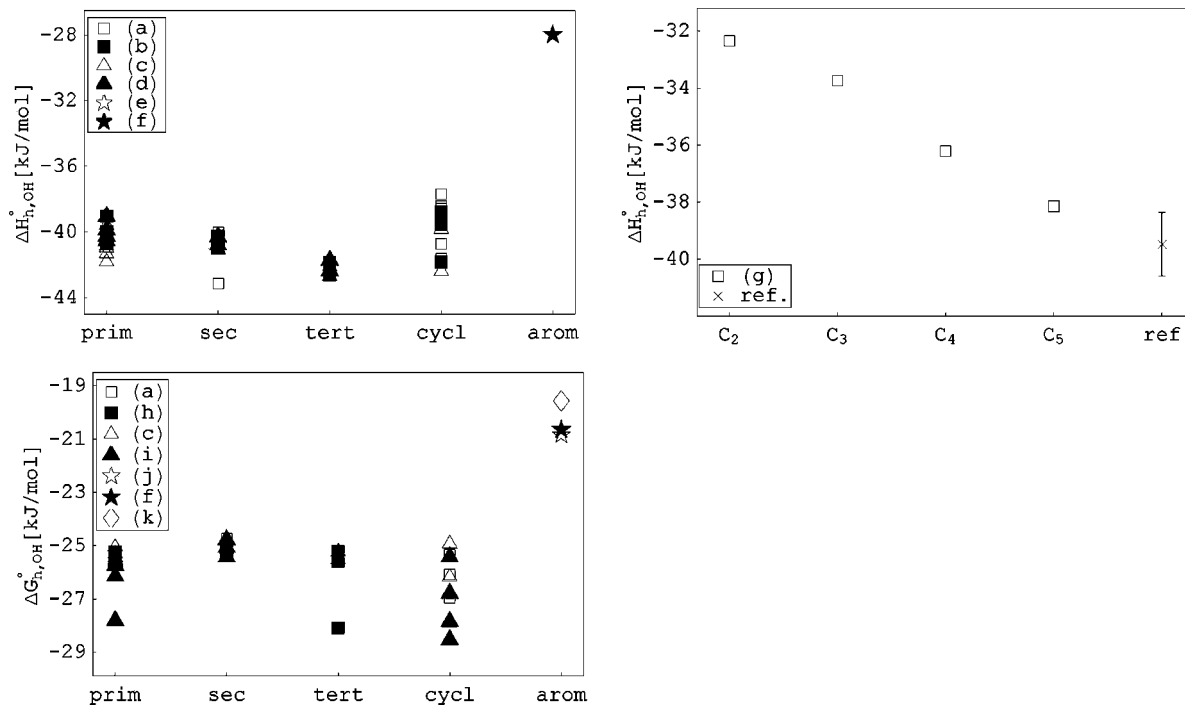
**Figure 5.** Contribution of hydroxyl group to standard molar volume and standard molar heat capacity of hydration for primary, secondary, tertiary, cyclic, and aromatic alcohols and  $\alpha,\omega$ -diols (ethanediol,  $C_2$ , to decanediol,  $C_{10}$ ). All data correspond to 298.15 K and 0.1 MPa; "ref" is the average contribution of hydroxyl group obtained from experimental results on aliphatic primary alcohols. Experimental data: (a) Jolicoeur and Lacroix;<sup>78</sup> (b) Hoiland and Vikingstad;<sup>79</sup> (c) Sakurai et al.;<sup>80</sup> (d) Origlia and Woolley;<sup>81</sup> (e) Cabani et al.;<sup>82</sup> (f) Edward et al.;<sup>83</sup> (g) Hopkins et al.;<sup>84</sup> (h) Origlia-Luster et al.;<sup>85</sup> (i) Nakajima et al.;<sup>86</sup> (j) Wurzburg et al.;<sup>87</sup> (k) Conti et al.;<sup>90</sup> (l) Arnett et al.;<sup>88</sup> (m) Makhatadze et al.;<sup>89</sup> (n) Perron and Desnoyers;<sup>91</sup> (o) Perron and Desnoyers;<sup>92</sup> (p) Hovorka et al.;<sup>93</sup> (q) Nichols et al.;<sup>77</sup> (r) DiPaola and Belleau.<sup>94</sup>



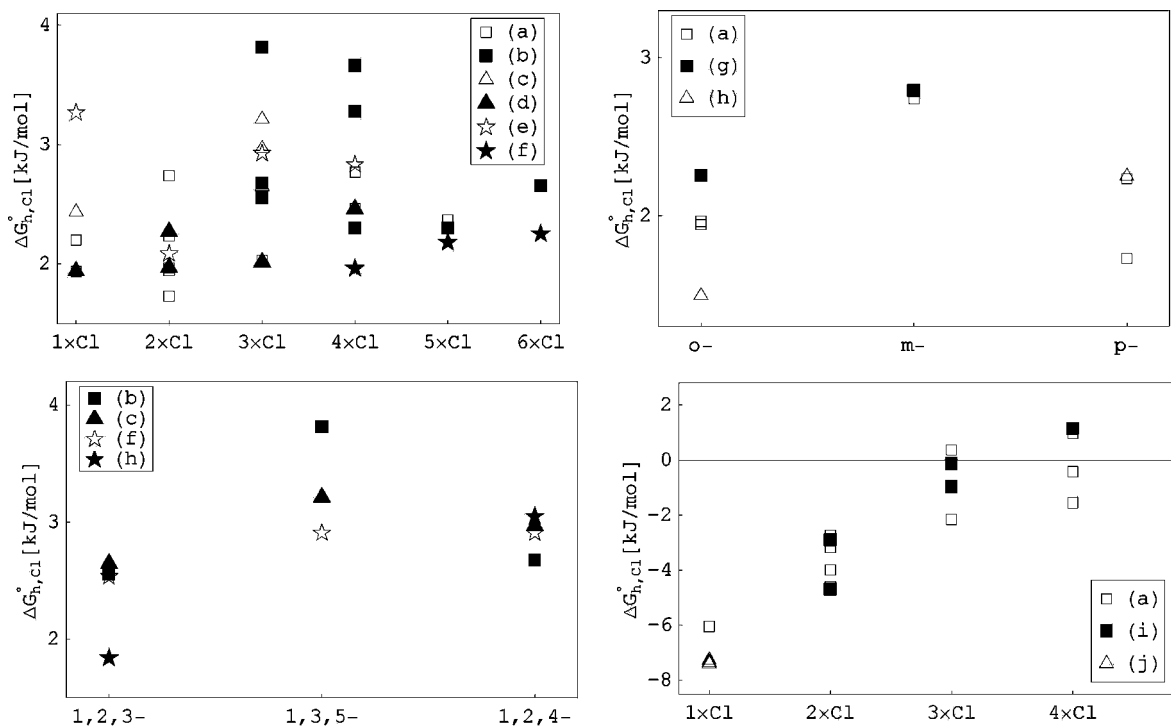
**Figure 6.** Contribution of amino group to standard molar volume and standard molar heat capacity of hydration for primary, secondary, tertiary, cyclic, and aromatic amines and  $\alpha,\omega$ -diamines (ethanediamine,  $C_2$ , to decanediamine,  $C_{10}$ ). All data correspond to 298.15 K and 0.1 MPa; "ref" is the average contribution of amino group obtained from experimental results on aliphatic primary amines. Experimental data: (a) Cabani et al.;<sup>82</sup> (b) Kaulgud et al.;<sup>95</sup> (c) Kaulgud and Patil;<sup>96</sup> (d) Shahidi et al.;<sup>97</sup> (e) Ruzicka et al.;<sup>98</sup> (f) Konecny and Wadso;<sup>99</sup> (g) Nichols and Wadso;<sup>100</sup> (h) Makhatadze and Privalov;<sup>101</sup> (i) Riedl and Jolicoeur;<sup>102</sup> (j) Cabani et al.;<sup>103</sup> (k) Bergstrom and Olofsson;<sup>104</sup> (l) Bernauer et al.;<sup>105</sup> (m) Nichols et al.;<sup>77</sup> (n) Cabani et al.<sup>106</sup>

bons and the hydrocarbon functional groups were correctly evaluated by Plyasunov and Shock<sup>13</sup> (reference conditions) or Sedlbauer et al.<sup>25</sup> (high temperatures and pressures), the value

of  $\Delta_{\text{dif}}Y_h^o$  should be zero. Its nonzero value indicates either experimental scatter of the data or violation of one or both of the above statements. In Figure 1 the results are given in terms



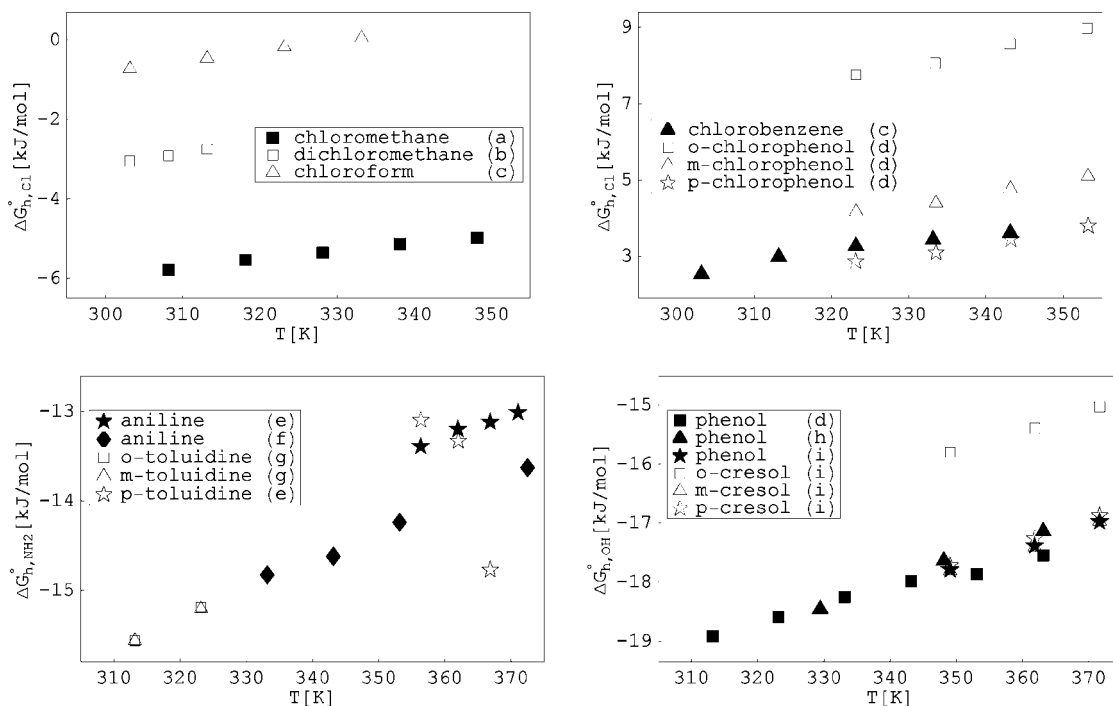
**Figure 7.** Contribution of hydroxyl group to standard molar enthalpy of hydration and standard molar Gibbs energy of hydration for primary, secondary, tertiary, cyclic, and aromatic alcohols and  $\alpha,\omega$ -diols (ethanediol, C<sub>2</sub>, to pentanediol, C<sub>5</sub>). All data correspond to 298.15 K and 0.1 MPa, "ref" is the average contribution of hydroxyl group obtained from experimental results on aliphatic primary alcohols. Experimental data: (a) Cabani et al.;<sup>107</sup> (b) Arnett et al.;<sup>88</sup> (c) Bocek;<sup>108</sup> (d) Row and Somsen;<sup>109</sup> (e) Gillet;<sup>110</sup> (f) Parsons et al.;<sup>111</sup> (g) Nichols et al.;<sup>77</sup> (h) Merk and Riederer;<sup>112</sup> (i) Stephenson and Stuart;<sup>113</sup> (j) Harrison et al.;<sup>114</sup> (k) Shiu et al.<sup>115</sup>



**Figure 8.** Contribution of chloride group to standard molar Gibbs energy of hydration for chlorinated benzene (monochlorobenzene to hexachlorobenzene); *o*-, *m*-, and *p*-dichlorobenzenes; trichlorobenzenes; and chlorinated methane and ethane. All data correspond to 298.15 K and 0.1 MPa. Experimental data: (a) Mackay and Shiu;<sup>49</sup> (b) Bobra et al.;<sup>116</sup> (c) Dewulf et al.;<sup>50</sup> (d) Shiu and Mackay;<sup>117</sup> (e) Ryu and Park;<sup>40</sup> (f) Hulscher et al.;<sup>118</sup> (g) Suntio et al.;<sup>119</sup> (h) Calamari et al.;<sup>120</sup> (i) Dewulf et al.;<sup>42</sup> (j) Sarraute et al.<sup>121</sup>

of  $\Delta_{\text{dif}}G_{\text{h}}^\circ$  at  $T_{\text{r}} = 298.15$  K and  $p_{\text{r}} = 0.1$  MPa for homologous series of aliphatic and aromatic hydrocarbons (ethane to octane, benzene to butylbenzene), for aliphatic cycles (cyclopropane to cyclohexane), and for selected isomeric alkanes (2-methylpropane to 2-methylhexane; 2,2-dimethylpropane to

2,2-dimethylpentane). Most  $\Delta_{\text{dif}}G_{\text{h}}^\circ$  values fall within 0.5 kJ/mol with the exception of the values for cycloalkanes, which is not surprising because of nonnegligible sterical hindrance, namely in short cycles. It is important that there is no clear evidence of systematic deviation from functional group addi-



**Figure 9.** Contribution of a functional group to standard molar Gibbs energy of hydration as a function of temperature: chloride group in chlorinated methane; chloride group in chlorophenols; amino group in aminobenzenes; hydroxyl group in phenols. Experimental data: (a) Wilhelm et al.<sup>38</sup> (chloromethane at  $p_{\text{sat}}$ ); (b) Tse et al.<sup>122</sup> (dichloromethane at  $p_{\text{sat}}$ ); (c) Görgényi et al.<sup>44</sup> (chloroform and chlorobenzene at  $p_{\text{sat}}$ ); (d) Tabai et al.<sup>123</sup> (*o*-, *m*-, and *p*-chlorophenols and phenol at  $p_{\text{sat}}$ ); (e) Moore et al.<sup>124</sup> (aniline and *p*-toluidine at  $p_{\text{sat}}$ ); (f) Bernauer et al.<sup>105</sup> (aniline at  $p_{\text{sat}}$ ); (g) Censky et al.<sup>125</sup> (*o*- and *m*-toluidines at  $p_{\text{sat}}$ ); (h) Schreinemakers<sup>126</sup> (phenol at  $p_{\text{sat}}$ ); (i) Dohnal and Fenclova<sup>127</sup> (phenol, *o*-, *m*-, and *p*-cresols at  $p_{\text{sat}}$ ).

tivity for  $\text{C}_2\text{--C}_8$  hydrocarbon chains, at least within the 0.5 kJ/mol scatter of the data. Underestimation of the property for short chains and overestimation for longer chains is, on the other hand, obvious in case of  $\Delta H_h^\circ$  at  $T_r$ ,  $p_r$  in Figure 2. The observed prediction error for this quantity is about 2 kJ/mol for hydrocarbon chains with up to eight carbon atoms. The results for (alkyl)benzenes correspond closely to those for alkanes (negative value of  $\Delta_{\text{diff}}H_h^\circ$  for benzene substituted by short alkyls). The results for other hydration properties of aqueous hydrocarbons are not presented; their experimental data are very scarce because of extremely low solubilities of hydrocarbons, which complicates the measurements of derivative properties.

At elevated temperatures and pressures the data are abundant for  $\Delta G_h^\circ$ , extracted from published Henry's law constants and from mutual solubility of water and hydrocarbon phases.<sup>25,32</sup> Representative results at high temperatures and at selected isobars are given in Figure 3 for ethane to octane, (alkyl)cyclohexanes, and (alkyl)benzenes. Similar to reference conditions, no systematic deviations are observed either with temperature or with chain length. Differences among data sets and therefore also expected uncertainty of predictions is larger, at least 1 kJ/mol.

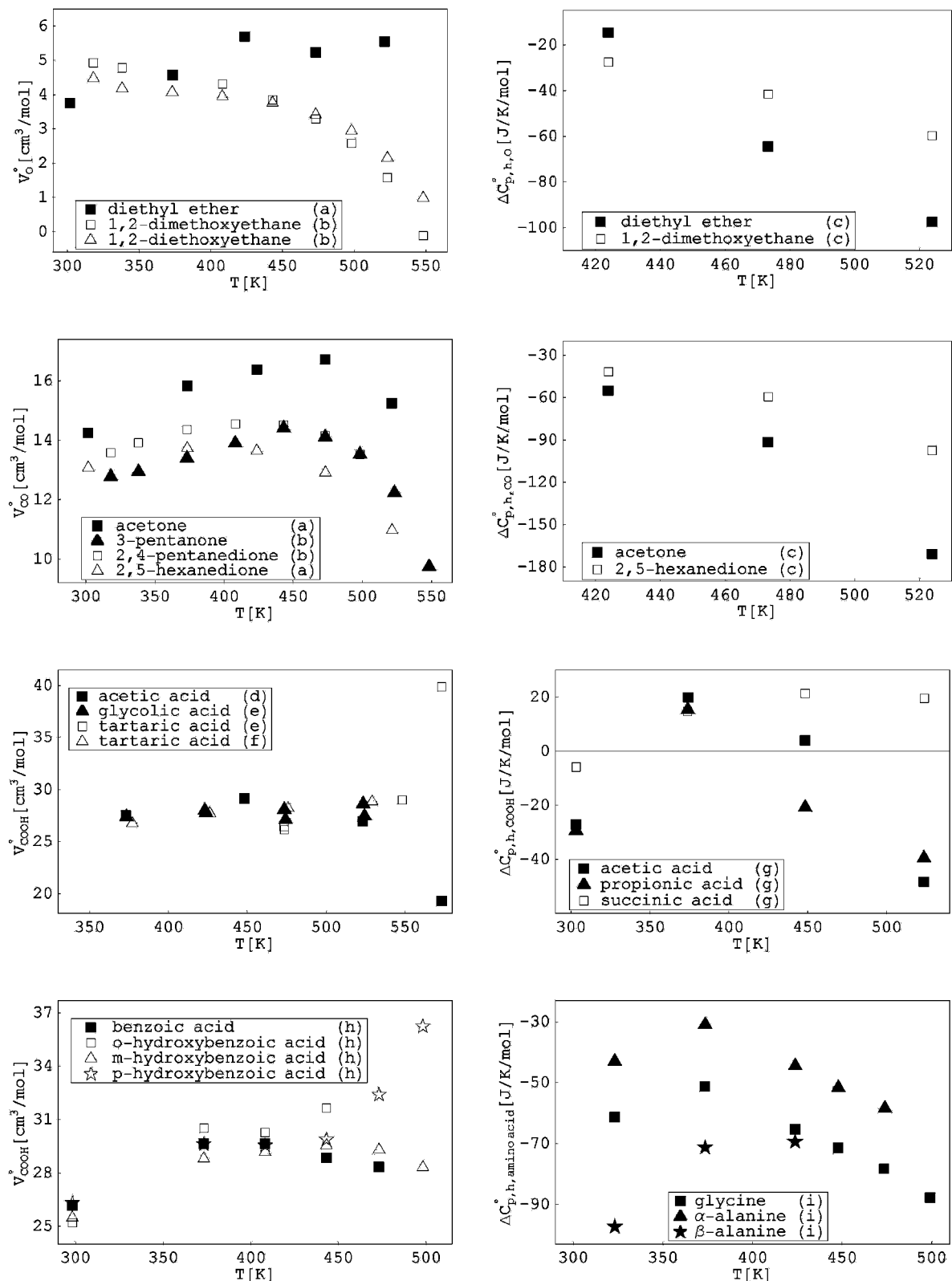
The above test calculations with the Plyasunov and Shock<sup>13</sup> and Sedlbauer et al.<sup>25</sup> methods provide reasonable assurance that the polar functional group contributions and induced structural/proximity effects calculated from data on  $\Delta G_h^\circ$  of substituted hydrocarbons shall not be subject to method bias other than the scatter of experimental data. Systematic deviations of our backbone group contribution methods need to be considered in the case of  $\Delta H_h^\circ$  and possibly also for other derivative properties.

**4.3. Higher-Order Corrections to Polar and Polyfunctional Solutes.** Due to increased solubility of polar-substituted hydrocarbons, the data are more easily obtained for

derivative properties of hydration (most frequently published are experimental standard molar volumes at reference and at elevated conditions). Figures 4–8 display the values of polar functional group contributions calculated from experimental data using eq 4 at  $T_r$  and  $p_r$ . Presented group contributions include higher-order effects induced by the polar group in the specific position. In some figures the results for various structures are compared to the “reference” value of the functional group retrieved from primary substituted alkanes: error bars on this quantity are its standard deviation. Calculated group contributions lying outside the interval of error bars thus indicate a higher-order effect corresponding to a given structure. The temperature evolution of group contributions is shown in Figures 9–11. At high temperatures we used representative data sources, from which we have selected results along some isobar (usually the one with most data available). The temperature range is typically from 298 to 523 K due to a high-temperature limitation of the applied method for hydrocarbon functional groups.<sup>25</sup> As an exception, the data for cresols in Figure 11 are extended to 623 K. The range of pressures is from  $p_{\text{sat}}$  (saturation line of water) to 30 MPa. Appropriate isobars are noted in the figure captions.

Group contributions to standard molar volume and standard molar heat capacity of hydration are shown in Figures 4–6 for COOH, OH, and  $\text{NH}_2$  functional groups, calculated from  $\alpha,\omega$ -disubstituted solutes (e.g.,  $\text{C}_2$  in Figure 5 is 1,2-ethanediol,  $\text{C}_3$  is 1,3-ethanediol, etc.). In the case of  $\text{V}^\circ$  the proximity effect of two polar groups is obvious for short chains (up to 3  $\text{cm}^3/\text{mol}$  for oxalic acid) and becomes negligible only at separations by six to eight carbons. A second-order correction would not be sufficient for capturing this difference, although it would improve the results at least for 1,2-disubstituted solutes that show the largest deviation from group additivity. Results for diamines in Figure 6 seem not to limit to the reference value, but there

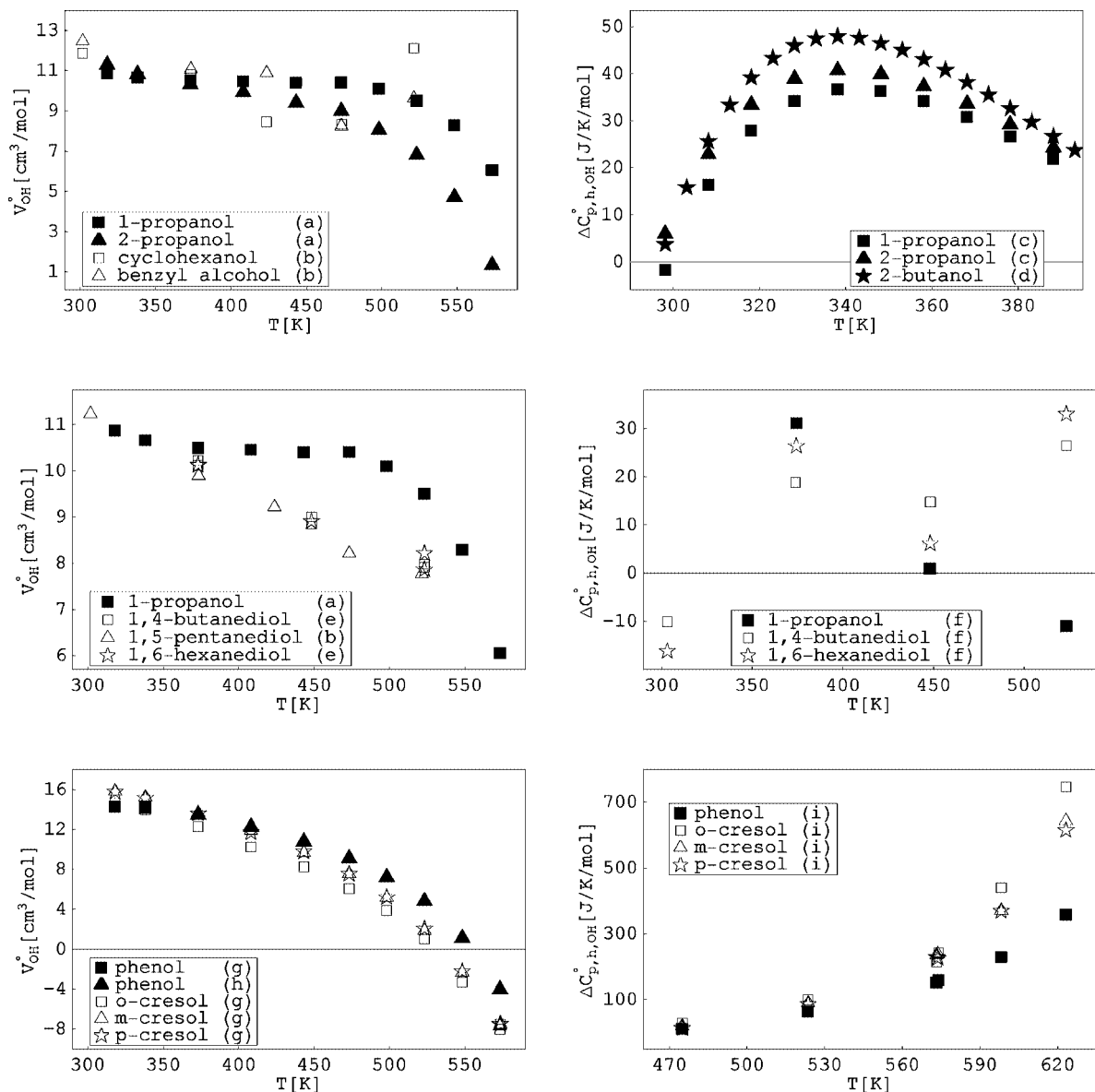




**Figure 10.** Contribution of a functional group to standard molar volume and standard molar heat capacity of hydration as a function of temperature: ether group in ethers and diethers; carbonyl group in ketones and diketones; carboxyl group in carboxylic acids and hydroxyacids; amino acid group (combination of COOH and NH<sub>2</sub> groups) in amino acids. Experimental data: (a) Schulte et al.<sup>128</sup> (diethyl ether, acetone, and 2,5-hexanedione at 28 MPa); (b) Cibulka and Hnedkovsky<sup>129</sup> (1,2-dimethoxyethane, 1,2-diethoxyethane, 3-pentanone, and 2,4-pentanedione at 30 MPa); (c) Slavik et al.<sup>130</sup> (diethyl ether, 1,2-dimethoxyethane, acetone, and 2,5-hexanedione at 10 MPa); (d) Majer et al.<sup>131</sup> (acetic acid at 10 MPa); (e) Bulemela and Tremaine<sup>132</sup> (glycolic and tartaric acids at 11 MPa); (f) Xie et al.<sup>34</sup> (tartaric acid at  $\approx 10$  MPa); (g) Inglese et al.<sup>133</sup> (acetic, propionic, and succinic acids at 28 MPa); (h) Jedelsky et al.<sup>134</sup> (benzoic, *o*-, *m*-, and *p*-hydroxybenzoic acids at 30 MPa); (i) Clarke et al.<sup>135</sup> (glycine,  $\alpha$ - and  $\beta$ -alanines at 30 MPa).

is just one literature source and the calculated higher-order effects are all within about 1 cm<sup>3</sup>/mol. Unexpected behavior is observed for polar group contributions obtained from  $\Delta C_{p,h}^\circ$

of disubstituted compounds: their tendency to reach the reference value is not clear even for long chains (C<sub>7</sub>) and the proximity effect of 1,2-disubstituted solutes is not necessarily the most



**Figure 11.** Contribution of a functional group to standard molar volume and standard molar heat capacity of hydration as a function of temperature: hydroxyl group in alcohols, diols, and phenols. Experimental data: (a) Hyncica et al.<sup>136</sup> (1-propanol and 2-propanol at 30 MPa); (b) Schulte et al.<sup>128</sup> (cyclohexanol, benzyl alcohol, and 1,5-pentanediol at 28 MPa); (c) Origlia and Woolley<sup>137</sup> (1-propanol and 2-propanol at 0.35 MPa); (d) Origlia and Woolley<sup>81</sup> (2-butanol at 0.35 MPa); (e) Criss and Wood<sup>138</sup> (1,4-butanediol and 1,6-hexanediol at 28 MPa); (f) Inglese and Wood<sup>139</sup> (1-propanol, 1,4-butanediol, and 1,6-hexanediol at 28 MPa); (g) Hnedkovsky et al.<sup>140</sup> (phenol, *o*-, *m*-, and *p*-cresols at  $p_{sat}$ ); (h) Hynek et al.<sup>141</sup> (phenol at  $p_{sat}$ ); (i) Censky et al.<sup>142</sup> (phenol, *o*-, *m*-, and *p*-cresols at 30 MPa).

prominent. Maximum deviation from the reference value is about 30 J/K/mol (oxalic acid), which is considerably more than the typical experimental uncertainty.

Figures 5 and 6 include also the group contributions calculated from (mono)substituted compounds with a polar group bound to a primary, secondary, or tertiary carbon, to an aliphatic cycle, or to an aromatic ring. The scatter of results is large for cyclic structures, but the differences in this case are probably mostly due to violation of group additivity in the hydrocarbon cycle. An interesting point is that there is no significant difference between polar group contributions to standard molar volumes of aliphatic and aromatic compounds (indeed the values for OH and OH<sub>phi</sub> groups reported by Plyasunov and Shock<sup>13</sup> and Censky et al.<sup>29</sup> differ just by 0.2 cm<sup>3</sup>/mol). The standard molar heat capacity of hydration is again very sensitive to molecular arrangement: structural effects are up to 90 J/K/mol.

Figure 7 extends the calculated OH group contributions to standard molar enthalpy and Gibbs energy of hydration. The

largest scatter is observed for aliphatic cycles: group contributions bound to aliphatic and aromatic hydrocarbons are distinctly different (by 12 kJ/mol in case of  $\Delta H_h^o$  and 6 kJ/mol for  $\Delta G_h^o$ ). The differences between other structures are much lower. The results in Figure 8 correspond to  $\Delta G_{h,Cl}^o$  group contribution obtained from (poly)chlorinated benzenes and (poly)chlorinated aliphatic hydrocarbons (last graph, which includes mainly derivatives of methane and ethane, but also 1-chlorooctane). Proximity effects for polychlorinated benzenes look randomly scattered within 2 kJ/mol, but closer examination reveals that the main differences are due to changes in the molecular resonance structures of ortho, meta, and para isomers. Values for these compounds are presented in the second graph, and the third one depicts group contributions from isomeric trichlorobenzenes. 1,2,3-Trichlorobenzene (two ortho pairs) provides a group contribution essentially the same as *o*-dichlorobenzene, 1,3,5-trichlorobenzene (all meta positions) is close to *m*-dichlorobenzene, and 1,2,4-trichlorobenzene (one

ortho and one meta pair) is at about the average of ortho- and meta-group contributions. Most important is the fact that only the meta position introduces higher-order effects large enough to require correction. Typically this need for proximity corrections is expected for ortho isomers, which does not seem true in the case of chlorobenzenes. Higher-order effects for (poly-)chlorinated alkanes are much larger and reflect increasing hydrophobicity with increasing number of chlorine atoms in the compound. There is up to 7–8 kJ/mol difference between group contributions calculated from monochloroalkanes and those calculated from tetrachloroalkanes, which would lead to a huge error in predictions of  $\Delta G_h^\circ$  based on the first-order additivity for molecules with several chlorine substituents.

The results on  $\Delta G_h^\circ$  group contributions in Figure 9 are extended to temperatures of about 373 K and at  $p_{\text{sat}}$ . (Poly-)chloromethanes display in this temperature range almost constant differences; the same holds true also for isomeric substituted benzenes in the other graphs. The temperature evolution of  $\Delta G_h^\circ$  is described from the definition of Gibbs energy:

$$\Delta G_h^\circ(T, p) = \Delta G_h^\circ(T_r, p_r) + [\Delta H_h^\circ]_{T_r, p_r}^{T, p} - [T\Delta S_h^\circ]_{T_r, p_r}^{T, p} \quad (8)$$

which, after some rearrangements, leads to a common formula:

$$\Delta G_h^\circ(T, p) = \Delta G_h^\circ(T_r, p_r) + (T_r - T)\Delta S_h^\circ(T_r, p_r) + \int_{T_r}^T \Delta C_{p, h}^\circ dT - T \int_{T_r}^T \Delta C_{p, h}^\circ d \ln T + \int_{p_r}^p V^\circ dp \quad (9)$$

It is obvious that accuracy of predictions at temperatures close to  $T_r$  crucially depends on the quality of  $\Delta G_h^\circ(T_r, p_r)$ , at more elevated temperatures and also on the slope  $\Delta S_h^\circ(T_r, p_r)$  ( $\Delta S_h^\circ(T_r, p_r) = (\Delta H_h^\circ(T_r, p_r) - \Delta G_h^\circ(T_r, p_r))/T_r$ ). The integrals using some  $T$ ,  $p$ -dependent thermodynamic models become important only at high temperatures and/or at elevated pressures. If the values of  $\Delta G_h^\circ(T_r, p_r)$  and  $\Delta S_h^\circ(T_r, p_r)$  (or  $\Delta H_h^\circ(T_r, p_r)$ ) are known with good precision, the results suggest only a small relevance of higher-order corrections in models of  $\Delta C_{p, h}^\circ$  and  $V^\circ$  in eq 9 to the quality of calculated  $\Delta G_h^\circ$ . As shown below, these higher-order corrections to  $\Delta C_{p, h}^\circ$  and  $V^\circ$  may be large, but still they become only marginally important when integrated to obtain the target property, which is most often  $\Delta G_h^\circ$ . Another appealing feature of Figure 9 is the deviation of polar group contributions obtained from ortho-disubstituted benzenes with unlike groups (chlorophenols, toluidines, cresols). This is in contrast to the results on dichlorobenzenes in Figure 7, where the largest higher-order effect was observed for meta position.

Figures 10 and 11 concentrate on derivative properties of hydration, namely  $V^\circ$  and  $\Delta C_{p, h}^\circ$ . Generous experimental record allows investigation of several polar groups and different structures: O in ethers and diethers; CO in ketones and diketones; COOH in carboxylic acids, hydroxyacids, diacids, and amino acids (in this case the zwitterions are considered as one functional group; they are not separated to COOH and  $\text{NH}_2$  groups). Figure 11 provides the results on the hydroxyl functional group in a variety of structural arrangements. General conclusions from these figures are that both derivative properties are sensitive to higher-order effects; deviations are typically increasing with temperature and in the case of polyfunctional compounds the proximity effects even may lead to a reverse in the high-temperature limiting behavior of the polar functional group (from hydrophilic to hydrophobic). Specifically we notice the large isomeric effect on  $\Delta C_{p, h}^\circ$  of alanine, showing that it is not possible to treat COOH and  $\text{NH}_2$  groups as one universal zwitterionic functional group as it was assumed, e.g., in the

group contribution method by Yezdimer et al.<sup>24</sup> (the distance between both parts of the zwitterion matters). It is also confirmed that higher-order effects are found at ortho- and para-disubstituted benzenes with unlike substituent functional groups.

## 5. Conclusions

The method was presented for evaluation of structural and/or proximity effects of polar functional groups from experimental data. Some “backbone” group contribution scheme is required for its application, allowing estimation of the thermodynamic properties of all parts of the molecule except the polar functional group and corresponding higher-order effects. We used for this purpose the group contribution methods by Plyasunov and Shock<sup>13</sup> at 298.15 K and 0.1 MPa and Sedlbauer et al.<sup>25</sup> at elevated temperatures and pressures. Another choice of the backbone schemes is certainly possible. The method provides quantitative assessment of the structural and/or proximity effects induced by specific structural arrangements and could be useful in further development of group contribution schemes with unbiased selection of structural features that need to be accounted for at a required level of prediction accuracy. It can also be used for an easy check of consistency of experimental results obtained on similar structures (i.e., not necessarily for the same compounds). Some conclusions regarding data examined here and recommendations for further development can be summarized as follows:

(a) The group contributions calculated from polyfunctional solutes vary from their values obtained from monofunctional compounds. The difference was found at ambient conditions up to 3 cm<sup>3</sup>/mol for  $V^\circ$ , 30 J/K/mol for  $\Delta C_{p, h}^\circ$ , 7 kJ/mol for  $\Delta H_h^\circ$ , and 4 kJ/mol for  $\Delta G_h^\circ$  of disubstituted solutes, increasing with more polar groups in the molecule and (usually) with temperature. Such a difference leads to an error in the calculated Henry's law constant of up to 150%.

(b) The differences depend on structural arrangement. Typically they decrease with the distance between the polar groups (not in the case of  $\Delta C_{p, h}^\circ$ ). The differences are larger than experimental uncertainties even if the substituents are separated by several C atoms: second-order corrections to a simple group contribution method are therefore not sufficient for the description of experimental data within the uncertainty limits.

(c) Aromatic solutes with substituents of unlike polarity in the ortho position need correction for second-order effects. The para position has lower impact; its trend is the same as with the ortho position. In polychlorinated benzenes (with the same polarity of substituents) the higher-order correction is needed for the meta position, but not for the ortho position.

(d) Hydrophilic character of the polar functional groups is suppressed in polyfunctional solutes, leading in some cases even to a reversed near-critical divergence for the compound. This behavior was observed, e.g., by Cibulka et al.<sup>33</sup> for polyhydric alcohols and by Xie et al.<sup>34</sup> for tartaric acid.

(e) Derivative standard thermodynamic properties of hydration appear more sensitive to higher-order effects than  $\Delta G_h^\circ$ : the largest structural/proximity deviations are observed for  $\Delta C_{p, h}^\circ$ .

(f) An accurate prediction scheme is needed for  $\Delta G_h^\circ(T_r, p_r)$  and  $\Delta H_h^\circ(T_r, p_r)$ . The properties at reference conditions provide reasonable estimates of the practical property ( $\Delta G_h^\circ$ ) to at least 370–400 K since they are used as integration constants in the high-temperature models.

(g) There are at least two promising strategies for the development of the group contribution scheme at reference conditions: (i) The first is using a simple group contribution method with various structural corrections, accounting for the

most prominent higher-order effects that were identified by the procedure presented above. Such a scheme is relatively simple to use, it can be applied in "levels" of accuracy, and it is extendable when new data appear. (ii) The second strategy is to develop a quantum mechanical based scheme, which takes into account geometry, ligand size, and charge distribution. For instance, the approach of Lin and Sandler<sup>12</sup> could be a basis for such a method, extended to other hydration properties and revised with updated databases of experimental results. The method would be more difficult to use, but it could be applied for generating a database of recommended values (e.g., for compounds from the EPA list of priority pollutants).

(h) A first-order method seems to be satisfactory for high-temperature predictions, if the main purpose is calculating  $\Delta G_h^\circ$ . Most structural/proximity effects are in such a case already contained in the reference properties  $\Delta G_h^\circ(T_r, p_r)$  and  $\Delta H_h^\circ(T_r, p_r)$ .

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**Note Added after ASAP Publication:** Reference 16 in the version of this paper that was published on the Web February 27, 2008 was incorrect. The correct version of this paper was reposted to the Web July 30, 2008.

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