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Group Contribution Values for the Thermodynamic Functions of Hydration at 298.15 K, 0.1 MPa. 2. Aliphatic Thiols, Alkyl Sulfides, and Polysulfides

Natalia V. Plyasunova,*,† Andrey V. Plyasunov,† and Everett L. Shock†,‡

Department of Geological Sciences and Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287

Group additivity contributions are evaluated for normal and branched thiols (mercaptans), alkyl sulfides, and polysulfides on the basis of a compilation of experimental values of the infinite dilution partial molar Gibbs energy, enthalpy, and heat capacity of hydration, together with molar volumes in aqueous solution at 298.15 K and 0.1 MPa. The thermodynamic data were treated using both first- and second-order group additivity methods. Numerical values of the contributions to each of the thermodynamic properties are obtained for the following first-order S-containing groups: SH, S, S_2, and S_3 as well as for the C−SH correction for the attachment of the thiol group to the tertiary carbon atom. In the case of the second-order group contribution method, numerical values are determined for the groups C−(S)(H)$_3$, C−(C)(S)(H)$_2$, C−(C)$_2$(S)(H), C−(C)$_3$(S), S−(H)(C), S−(C)$_2$, S−(S)(C), and S−(S)$_2$.

Introduction

Aliphatic thiols, alkyl sulfides, and polysulfides are widely dispersed in natural materials. They are constituents of many well-known aromas, such as onions, garlic, cheese, and coffee; pure aliphatic thiols of higher molecular mass (C > 4) are characterized by offensive odors. Disulfides are components of many biologically active substances including peptides. The most important industrial application of aliphatic thiols, sulfides, and polysulfides is in the production of agricultural chemical agents and pharmaceuticals and as additives in the rubber and plastic industries; polysulfides are used in ore flotation and petroleum refining. Thiols, sulfides, and disulfides are among the organosulfur compounds found in petroleum and other fossil fuels; they are pollutants, widespread in industrial waste systems, and are toxic. Thiols can be major organic ligands for metals in natural waters. Thermodynamic properties of these compounds in water are of special interest for environmental sciences, agriculture, chemistry, geochemistry, biology, and medicine. Nevertheless, these compounds are relatively poorly studied, especially in aqueous media; the representative sets of data are available only for the smallest homologues of normal thiols, alkyl sulfides, and disulfides. Consequently, a variety of group additivity methods are especially helpful when estimating and/or correlating properties of these compounds.

This contribution is a continuation of our efforts[1−3] to provide an up-to-date compilation of the thermodynamic properties of hydration of organic compounds and to determine functional group contributions to the functions of hydration of these compounds at 298.15 K and 0.1 MPa. The current study involves thermodynamic properties of hydration of sulfur-containing organic compounds: aliphatic thiols, alkyl sulfides, and polysulfides. We also include data for aqueous carbon disulfide. Although this compound cannot be represented by the groups composing thiols and alkyl sulfides, it is an important industrial and natural chemical. The database of compiled data on sulfur-containing substances is used to derive the optimal values of the contributions of the functional groups in the framework of the first- and second-order group contribution methods.

The following standard partial molar thermodynamic functions of hydration are the focus of this study: the Gibbs energy, $\Delta_h G^\infty$, enthalpy, $\Delta_h H^\infty$, entropy, $\Delta_h S^\infty$, heat capacity, $\Delta_h C_p^\infty$, and volume, $\Delta_h V^\infty$. Any thermodynamic function of hydration for a compound represents the difference between the value of the property for this compound in the state of a standard aqueous solution and that in the ideal gas state. The standard state conventions adopted in this study for gaseous, liquid, and aqueous compound are those recommended by IUPAC.[4] A detailed discussion of relations among the thermodynamic functions of hydration and the methods of their evaluation from various types of experimental data is given in a previous publication.[1] If necessary, a recalculation of $\Delta_h G^\infty$ to $T_r = 298.15$ K can be done using the approximation that $\Delta_h C_p^\infty$ is constant, yielding the expression for the temperature dependence of $\Delta_h G^\infty$ given by

$$\Delta_h G^\infty(T_r) = \Delta_h G^\infty(T)\frac{T_r}{T} + \Delta_h H^\infty(T_r)\frac{T - T_r}{T} + \Delta_h C_p^\infty \frac{T_r}{T}\left(T \ln \frac{T}{T_r} - T + T_r\right) \quad (1)$$

which provides an excellent reproduction of $\Delta_h G^\infty$ at temperatures between 273.15 and 333.15 K or even higher.

Auxiliary Data for Pure Compounds

Standard Gibbs Energy of Vaporization of Pure Compounds. In this study, values of the standard Gibbs

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* Corresponding author. E-mail: natalia.plyasunova@asu.edu. Phone: (480) 965-9436. Fax: (480)-965-8102.
† Department of Geological Sciences.
‡ Department of Chemistry and Biochemistry.

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Table 1. Antoine Constants in the Equation $\log(P_s/\text{bar}) = A - B/(T/\text{K} + C - 273.15)$

compound	A	B	C	temperature range/K	data sources
1-propanethiol	4.0770	1196.50	226.16	218−375	P_s[9,10,11,12], $\Delta_{vap}H$[8]
1-butanethiol	4.0320	1271.18	217.34	298−409	P_s[9,11], $\Delta_{vap}H$[8]
1-pentanethiol	4.1050	1400.73	215.05	298−440	P_s[11], $\Delta_{vap}H$[8]
1-hexanethiol	4.0753	1456.35	205.22	298−467	P_s[11], $\Delta_{vap}H$[8]
1-heptanethiol	4.1168	1552.51	200.72	298−471	P_s[11], $\Delta_{vap}H$[8]
2-methyl-2-propanethiol	3.9099	1114.16	221.16	275−372	P_s[13,14,15,11], $\Delta_{vap}H$[8]
2-butanethiol	4.0080	1228.07	221.86	298−394	P_s[11], $\Delta_{vap}H$[8]
methyl propyl sulfide	4.0609	1275.25	218.88	298−378	P_s[16], $\Delta_{vap}H$[8]
dipropyl sulfide	4.1750	1487.15	213.88	298−426	P_s[16], $\Delta_{vap}H$[8]
diisopropyl sulfide	4.0230	1343.22	214.34	298−432	P_s[11,16], $\Delta_{vap}H$[8]
dimethyl disulfide	4.2108	1414.13	226.53	273−401	P_s[17,11,16]
diethyl disulfide	4.2110	1558.46	216.66	273−434	P_s[11,16], $\Delta_{vap}H$[8]
dipropyl disulfide	4.3244	1761.50	212.30	298−455	P_s[11,16], $\Delta_{vap}H$[8]
dimethyl trisulfide	4.5220	1769.60	226.93	273−438	P_s[18,a]

[a] Estimated with a group contribution corresponding-states method.[18]

energy of vaporization, which give the difference between the Gibbs energy of a pure compound in the ideal gas state and in the liquid state, were calculated from vapor pressures, P_2^*, and second virial coefficients, B_{22}, of pure thiols, sulfides, and polysulfides according to

$$\Delta_{vap}G^o = -RT \ln \frac{P_2^* \phi_2^*}{P^o} \tag{2}$$

where $P^o = 0.1$ MPa is the standard state pressure and ϕ_2^* represents the fugacity coefficient of a pure compound as calculated from the virial equation of state (EoS) truncated at the second virial coefficient using values of B_{22} evaluated with the Tsonopouolos[5] and/or Hayden−O'Connell[6] corresponding state correlations. Values of the saturated vapor pressure of the best-studied thiols, sulfides, and disulfides were taken from the Poling et al.[7] handbook. For other compounds, we used experimental vapor pressure, P_2^*, and enthalpy of vaporization, $\Delta_{vap}H^o$, data from the literature to determine, by the simultaneous fit of these data, the parameters of the Antoine equation, which was taken in the form[7]

$$\log(P_2^*/\text{bar}) = \frac{A - B}{(T/\text{K}) + C - 273.15} \tag{3}$$

Following Majer et al.,[8] we corrected the measured enthalpy of vaporization for the nonideality of the gaseous phase; see refs 8 and 1 for relevant relations. The resulting parameters of the Antoine equation, together with sources of data and the temperature ranges of validity, are given in Table 1. In the case of dimethyl trisulfide, for which precise experimental vapor pressure data are unavailable, we employed the boiling-point values reported in Chemical Abstracts and by Sigma-Aldrich (http://www.sigmaaldrich.com) together with a group contribution corresponding-states method[18] to estimate P_2^*. Experimental and fitted values of the vapor pressure and B_{22} of the compounds included in this study are accessible in the ORCHYD database[19] (http://orchyd.asu.edu).

Specifics of Aliphatic Thiols, Alkyl Sulfides, and Polysulfides in Aqueous Solution. Normal and branched thiols are weak acids; for example, for ethanethiol pK_a = 10.61 at 25 °C according to Tsonopoulos et al.[20] The ionization of *n*-alkyl thiols is expected to be only slightly dependent on molecular weight, decreasing as molecular weight increases.[20] It follows that the dissociation of thiols in pure water can be neglected because the contribution of ionized species to the total concentration of a dissolved thiol would exceed 3% only in solutions with pH > (9.0 to 9.3). This was confirmed experimentally for methanethiol[21] by studying the vapor−liquid partitioning as a function of pH.

Data Compilation

A central part of this contribution is the compilation of a representative database of the partial molar thermodynamic properties of aliphatic thiols, alkyl sulfides, and polysulfides in aqueous solution at infinite dilution. Unlike our previous efforts,[1−3] where large representative databases could be compiled for hydrocarbons, alcohols, ketones, and esters, in this study we encountered significant challenges in composing the database. First, the number of sulfur-containing organic compounds for which experimental data in aqueous media are available is rather limited. Second, the data for this limited number of compounds are scarce and often inconsistent. As before, we worked with primary sources of data that report original experimental values, avoiding numerous literature compilations, which are often mixtures of data from primary and secondary (other compilations) sources. Our established procedures for converting primary data of different types into functions of hydrations as well as their critical evaluation were described earlier.[1] All of the primary data on the functions of hydration for aliphatic thiols, alkyl sulfides, and polysulfides are accessible through the ORCHYD database.[18] The database also includes dynamically evaluated recommended properties of hydration, standard thermodynamic properties in aqueous solution, properties along the vapor saturation curve of pure water, and thermodynamic properties of pure compounds in the ideal gas state and in the state of condensed phases stable at 298.15 K, 0.1 MPa as well as properties of vaporization and auxiliary properties of pure compounds. The following sections provide discussions of each of the thermodynamic properties used in the present study.

Enthalpy of Hydration at 298.15 K, 0.1 MPa. Calorimetric values[22] of the enthalpy of solution in water, $\Delta_{sol}H^\infty$, are available for a number of sulfides and disulfides. These values were combined with standard enthalpy of vaporization, $\Delta_{vap}H^o$, data, which represent the difference between the enthalpy of a compound in the ideal gas state and in the liquid state, to give the standard enthalpy of hydration according to the relation

$$\Delta_h H^\infty = \Delta_{sol}H^\infty - \Delta_{vap}H^o \tag{4}$$

Table 2. Standard Enthalpy of Hydration, $\Delta_h H^{\infty}$, and Vaporization, $\Delta_{vap}H^{\circ}$, of Aliphatic Thiols, Alkyl Sulfides, and Polysulfides at 298.15 K and 0.1 MPa, Experimental and Group Contribution (GC) Values for First (I) and Second (II) Order Additivity Methods, and the Difference between Experimental and GC Values, Δ.

compound	$\Delta_{vap}H^{\infty}$/ kJ·mol^{-1}	$\Delta_h H^{\infty}$/kJ·mol^{-1}	accepted value	I order GCvalue	Δ/kJ·mol^{-1}	II order GC value	Δ/kJ·mol^{-1}
methanethiol		$-23.30G^{\infty}(T)$[23], $-23.90G^{\infty}(T)$[21], $-25.80G^{\infty}(T)$[24], $-25.90G^{\infty}(T)$[25]	-24.37 ± 1.0	-24.61	0.24	-24.45	0.08
ethanethiol	27.52 ± 0.14[8]	$-29.70G^{\infty}(T)$[9 a], $-28.50G^{\infty}(T)$[24]	-28.87 ± 1.0	-28.24	-0.63	-28.40	-0.47
1-propanethiol	32.05 ± 0.16[8]	$-30.70G^{\infty}(T)$[9 a], $-29.70G^{\infty}(T)$[24]	-30.20 ± 2.0	-31.87	1.67	-31.92	1.72
1-butanethiol	36.70 ± 0.19[8]	$-31.70G^{\infty}(T)$[24], $-40.90G^{\infty}(T)$[26 b]	-36.29 ± 4.6	-35.50	-0.79	-35.44	-0.85
dimethyl sulfide	27.99 ± 0.15[8]	$\mathbf{-31.48}\Delta_{sol}H^{\infty}$[22], $-31.80G^{\infty}(T)$[21], $-28.80G^{\infty}(T)$[27], $-31.10G^{\infty}(T)$[24]	-31.47 ± 0.2	-32.01	0.54	-31.80	0.33
diethyl sulfide	35.88 ± 0.18[8]	$\mathbf{-40.22}\Delta_{sol}H^{\infty}$[22]	-40.22 ± 0.3	-39.27	-0.95	-39.70	-0.52
dipropyl sulfide	44.23 ± 0.45[8]	$\mathbf{-47.65}\Delta_{sol}H^{\infty}$[22]	-47.65 ± 0.6	-46.53	-1.12	-46.74	-0.91
carbon disulfide	27.65 ± 0.14[8]	$-23.00G^{\infty}(T)$[23], $-33.20G^{\infty}(T)$[28], $-29.95G^{\infty}(T)$[29]	-30.38 ± 3.0				
dimethyl disulfide	37.90 ± 0.19[8]	$\mathbf{-34.69}\Delta_{sol}H^{\infty}$[22], $-34.90G^{\infty}(T)$[21], $-33.60G^{\infty}(T)$[24]	-34.69 ± 0.2	-34.64	-0.05	-34.35	-0.34
diethyl disulfide	45.20 ± 0.46[8]	$\mathbf{-41.02}\Delta_{sol}H^{\infty}$[22], $-38.80G^{\infty}(T)$[24 c]	-40.96 ± 0.4	-41.90	0.94	-42.25	1.29
dipropyl disulfide	53.14 ± 0.54[8]	-45.14$G^{\infty}(T)$[30 d]	-45.15 ± 4.0	-49.16	4.02	-49.29	4.15

[a] Recalculated from 338.1 K. [b] Recalculated from 303.2 K. [c] Recalculated from 308.15 K. [d] Recalculated from 321.2 K.

In the absence of calorimetric data for other compounds, less-accurate values of $\Delta_h H^{\infty}$ were evaluated from temperature-dependent $\Delta_h G^{\infty}$ results by means of

$$\Delta_h H^{\infty} = -T^2 \left(\frac{\partial \Delta_h G^{\infty}/T}{\partial T} \right)_P \tag{5}$$

Results of data evaluation for $\Delta_h H^{\infty}$ are summarized in Table 2. The first column gives names of sulfur compounds. The accepted values of the standard enthalpy of vaporization of pure compounds at 298.15 K are listed in the second column. The third column gives compiled values of $\Delta_h H^{\infty}$ together with abbreviations employed to indicate the type of data converted to the $\Delta_h H^{\infty}$ value: $\Delta_{sol}H^{\infty}$ denotes values based on the enthalpy of solution, and $G^{\infty}(T)$ denotes values based on the temperature differentiation of $\Delta_h G^{\infty}$ with eq 5. Results that we consider to be the most reliable are given in bold. Our accepted values of $\Delta_h H^{\infty}$ together with their expected uncertainties are given in the fourth column.

Heat Capacity of Hydration at 298.15 K, 0.1 MPa. In the absence of direct calorimetric determinations of the heat capacity of aqueous solutions, the values of $\Delta_h C_p^{\infty}$ for a number of sulfides and disulfides were evaluated by means of

$$\Delta_h C_p^{\infty} = \Delta_{sol} C_p^{\infty} + C_{p,2}^{*}(\mathrm{l}) - C_{p,2}^{*}(\mathrm{ig}) \tag{6}$$

where $C_{p,2}^{*}(\mathrm{l})$ and $C_{p,2}^{*}(\mathrm{ig})$ are the molar heat capacity of a compound in the liquid state and in the ideal gas state, respectively. The values of

$$\Delta_{sol} C_p^{\infty} = \left(\frac{\partial \Delta_{sol} H^{\infty}}{\partial T} \right)_P$$

are determined from measurements[22] of the enthalpy of solution at different temperatures.

Results of the data evaluation for the standard partial molar heat capacity of hydration, $\Delta_h C_p^{\infty}$, are given in Table 3. The accepted values of the molar heat capacity of compounds in the ideal gas state at 298.15 K are listed in the second column. The third column gives compiled values of $\Delta_h C_p^{\infty}$, which in every case are derived from single studies; $H^{\infty}(T)$ denotes that temperature differentiation of $\Delta_{sol}H^{\infty}$ was used to obtain the $\Delta_h C_p^{\infty}$ values.

For thiols, there are no calorimetric determinations of either partial molar heat capacities or enthalpies of solution in water. The data on the Gibbs energy of hydration, available for lower homologues over an appreciable temperature range, cannot be used for a meaningful determination of $\Delta_h C_p^{\infty}$ because of the insufficient precision of $\Delta_h G^{\infty}$, as judged by comparing data from different laboratories. However, Schulte and Rogers[32] suggested that the difference between the partial molar heat capacity values for 1-propanethiol and 1-propanol is about the same as that between the amino acids cysteine and serine, or approximately 70 J·K^{-1}·mol^{-1}, because both pairs of compounds are structural analogues except for OH and HS functional groups. We accepted this suggestion to estimate the value of $\Delta_h C_p^{\infty}$ for 1-propanethiol.

Gibbs Energy of Hydration at 298.15 K, 0.1 MPa. Data reported as fugacity/concentration ratios for dissolved thiols, sulfides, and polysulfides in various pressure units and concentration scales were recalculated into Henry's constant values, k_H, in MPa pressure units, and converted to the standard partial molar Gibbs energy of hydration, $\Delta_h G^{\infty}$, according to

$$\Delta_h G^{\infty} = RT \ln \left(\frac{k_H}{P^o} \frac{1}{N_w} \right) \tag{7}$$

with $N_w = 1000/M_w \approx 55.5084$ being the number of moles of H_2O in 1000 g of water, where $M_w = 18.0153$ g·mol^{-1} is the molar mass of water. Many data for these compounds are reported as gas−water distribution constants, $K_{D,c}$, defined as

$$K_{D,c} = \lim_{c(\mathrm{aq}) \to 0} \frac{c(\mathrm{g})}{c(\mathrm{aq})}$$

where c stands for the concentration per 1000 cm^3 of solvent. The values of $K_{D,c}$ were converted to $\Delta_h G^{\infty}$ (assuming ideal gas behavior for the gaseous phase) by means of[1]

$$\Delta_h G^{\infty} = RT \ln \left(K_{D,c} \frac{RT}{P^o V_1^{*}} \frac{1}{N_w} \right) \tag{8}$$

where V_1^{*} is the molar volume of pure water. A few researchers report values of the activity coefficient at infinite dilution, γ^{∞}, for aqueous sulfur-containing compounds. These activity coefficients are valid for the symmetrical normalization of activity ($\gamma_i \to 1$ when $x_i \to 1$) for

Table 3. Ideal Gas Heat Capacity, C_p(g), Standard Partial Molar Heat Capacity of Hydration, $\Delta_h C_p^{\infty}$, of Aliphatic Thiols, Alkyl Sulfides, and Polysulfides at 298.15 K and 0.1 MPa, Experimental and Group Contribution (GC) Values for First (I) and Second (II) Order Additivity Methods, and the Difference between Experimental and GC Values, Δ

compound	C_p(g)/J·K^{-1}·mol^{-1}	$\Delta_h C_p^{\infty}$/J·K^{-1}·mol^{-1}	accepted value	I order GC value	Δ/J·K^{1}·mol^{-1}	II order GC value	Δ/J·K^{1}·mol^{-1}
1-propanethiol	94.9 ± 2[31] [a]	330 $H^{\infty}(T)$[32] [b]	330 ± 15	330	0	330	0
dimethyl sulfide	74.1 ± 2[31] [a]	228 $H^{\infty}(T)$[22]	228 ± 10	218	10	234	−6
diethyl sulfide	116.6 ± 2[31] [a]	320 $H^{\infty}(T)$[22]	320 ± 10	342	−22	332	−12
dipropyl sulfide	162.1 ± 2[31] [a]	487 $H^{\infty}(T)$[22]	487 ± 13	466	21	456	31
dimethyl disulfide	94.2 ± 2[31] [a]	286 $H^{\infty}(T)$[22]	286 ± 10	273	13	280	6
diethyl disulfide	141.6 ± 2[31] [a]	363 $H^{\infty}(T)$[22]	363 ± 16	397	−34	378	−15

[a] Our estimate of uncertainty. [b] See the text.

the mole fraction concentration scale, and they are converted to $\Delta_h G^{\infty}$ as follows:[1]

$$\Delta_h G^{\infty} = -\Delta_{vap} G^{\infty} + RT \ln\left(\frac{\gamma^{\infty}}{N_w}\right) \tag{9}$$

We also calculated γ^{∞} values from the experimental results of Kilner et al.,[9] who reported PX data for water−thiol (methanethiol, ethanethiol, propanethiol) mixtures at very low (x_2 < 0.01) concentrations of solutes at various temperatures. We used these data to evaluate thiol activity coefficients by Barker's method.[33] Because the solutions are very dilute, to a good approximation $\gamma_1 \approx 1$ and $\gamma_2 \approx \gamma^{\infty}$. The total pressures are small enough to justify the use of the virial EoS truncated at the second virial coefficient. Therefore, significant simplifications are possible, and the statement for the total pressure is given by

$$P = x_1 P_1^* \exp\left(\frac{V_1^*(P - P_1^*)}{RT}\right) + \gamma_2^{\infty} x_2 P_2^* \times \exp\left(\frac{B_{22}P_2^* - (2B_{12} - B_{11})P + V_2^*(P - P_2^*)}{RT}\right) \tag{10}$$

where subscripts 1 and 2 refer to water and a thiol solute, respectively; V^* stands for the molar volume of a compound in the liquid state, B_{11} is the second virial coefficient of pure water, calculated as recommended by Harvey and Lemmon;[34] and B_{12} is the second cross virial coefficient for interactions between water and an organic compound, calculated from group contribution values.[77]

The final major source of information is mutual solubility data. The compounds in this study are only slightly soluble in water. For example, at room temperature the solubility of dimethyl sulfide in water is about 0.3 mol·kg^{-1}, and the solubility of ethanethiol is less than 0.2 mol·kg^{-1}. For higher homologues, the solubility decreases sharply. Therefore, we assumed that at these low concentrations the activity coefficient of a dissolved compound, referenced to Henry's law,[4] is equal to 1, and we expect that this assumption introduces an error of less than (3 to 5)%, or less than 0.1 kJ·mol^{-1}, in the standard Gibbs energy of solution. Data on the solubility of water in the organic-rich phase are scarce, with the mole fraction of water reported to be 0.014 for dimethyl sulfide[54] and less than 0.001 for carbon disulfide[60] at room temperature. Typically, the solubility of water is the greatest in the lowest member of a homologous series. Therefore, we found that it was possible, in all cases except dimethyl sulfide, to neglect the solubility of water in the organic-rich phase, expecting that the error introduced is less than 1%, or 0.03 kJ·mol^{-1} in the standard Gibbs energy of solution. In summary, we used the simplified relation (compared with the complete relation we discuss elsewhere[1]) for converting solubility data to the Gibbs energy of hydration

$$\Delta_h G^{\infty} = \Delta_{sol} G^{\infty} - \Delta_{vap} G^{o} \approx -RT \ln(m_s) - \Delta_{vap} G^{o} \tag{11}$$

where $\Delta_{sol} G^{\infty}$ stands for the standard Gibbs energy of solution and m_s is the molality of a solute at saturation.

Results of the data evaluation for the standard partial molar Gibbs energy of hydration, $\Delta_h G^{\infty}$, are given in Table 4. Our accepted values of the standard molar Gibbs energy of vaporization of a pure compound at 298.15 K are listed in the second column. The third column gives compiled values of $\Delta_h G^{\infty}$ together with abbreviations employed to indicate the type of data converted to the $\Delta_h G^{\infty}$ value: k_H denotes Henry's constants; γ^{∞} denotes activity coefficients at infinite dilution; $K_{D,c}$ means the gas−water distribution constant in the molarity concentration scale; and Sol denotes values evaluated from the mutual solubility data. Accepted values of $\Delta_h G^{\infty}$ together with their estimated uncertainties are given in the fourth column.

Partial Molar Volumes at 298.15 K, 0.1 MPa. An experimental value of V_2^{∞} is reported in a single work for only one compound under consideration here, diethyl sulfide.[70] For carbon disulfide, two approximate values of V_2^{∞} at ambient temperatures can be calculated from the measured density and concentration of a saturated solution;[60,71] see Table 5. For propanethiol, Schulte and Rogers[32] suggested that the difference between the partial molar volumes between this thiol and 1-propanol is about the same as that between amino acids cysteine and serine, 12.87 cm^3·mol^{-1}, because both pairs of compounds are structural analogues except for OH and HS functional groups. We accepted this suggestion to estimate the value of V_2^{∞} for 1-propanethiol. The results are given in Table 5.

Determination of Group Contribution Values to the Thermodynamic Functions of Hydration at 298.15 K, 0.1 MPa

Determining group contribution values for organic sulfur-containing compounds is not a straightforward task. The problem is that for sulfides and polysulfides data are available for lower members of a homologous series, where the deviations from additivity are most profound, especially for polar compounds. For thiols, where data are available up to heptanethiol, most results come from a single study.[42] In general, for all compounds the amount and quality of data are less than satisfactory (with the notable exception of enthalpy and heat capacity data for aqueous sulfides and disulfides[22]). Therefore, we decided to reduce the dimension of the fitting task to the possible minimum and to use the compiled data to determine the properties of S-containing groups only, accepting for all other groups the values we obtained earlier.[1]

Table 4. Standard Gibbs Energy of Hydration, $\Delta_{\mathrm{h}}G^{\infty}$, and Vaporization, $\Delta_{\mathrm{vap}}G^{\circ}$, of Aliphatic Thiols, Alkyl Sulfides, and Polysulfides at 298.15 K and 0.1 MPa, Experimental and Group Contribution (GC) Values for First (I) and Second (II) Order Additivity Methods, and the Difference between Experimental and GC Values, Δ

compound	$\Delta_{\mathrm{vap}}G^{\circ}/\mathrm{kJ{\cdot}mol^{-1}}$	$\Delta_{\mathrm{h}}G^{\infty}/\mathrm{kJ{\cdot}mol^{-1}}$	accepted value	I order GC value	$\Delta/\mathrm{kJ{\cdot}mol^{-1}}$	II order GC value	$\Delta/\mathrm{kJ{\cdot}mol^{-1}}$
methanethiol		$3.08k_{\mathrm{H}}^{36}$, $3.22k_{\mathrm{H}}^{36}$, $3.92k_{\mathrm{H}}^{23}$, $3.80K_{\mathrm{D,c}}^{37\,a}$, $2.28\gamma^{\infty 9b}$, 3.45 $\mathrm{Sol}^{38\,a}$, $3.09k_{\mathrm{H}}^{21}$, $2.27K_{\mathrm{D,c}}^{24}$, $2.02K_{\mathrm{D,c}}^{39\,a}$, $3.40\alpha^{25\,c}$, $3.17K_{\mathrm{D,c}}^{40\,d}$, $2.78k_{\mathrm{H}}^{41}$	3.20 ± 0.40	3.19	0.01	3.46	−0.26
ethanethiol	0.94 ± 0.05^{7}	$3.06\gamma^{\infty 9\,b}$, $3.17K_{\mathrm{D,c}}^{24}$, $3.69K_{\mathrm{D,c}}^{39\,a}$, $4.11K_{\mathrm{D,c}}^{39\,a}$, $4.23K_{\mathrm{D,c}}^{42\,a}$, $4.52\mathrm{Sol}^{43\,a}$, $2.91\mathrm{Sol}^{44}$, $2.62\mathrm{Sol}^{45\,a}$	3.69 ± 0.66	3.89	−0.20	3.89	−0.20
1-propanethiol	3.95 ± 0.10^{e}	$4.33K_{\mathrm{D,c}}^{46\,f,g}$, $3.63\gamma^{\infty 9\,b}$, $3.51\,K_{\mathrm{D,c}}^{24}$, $5.20K_{\mathrm{D,c}}^{39\,a}$, $5.96K_{\mathrm{D,c}}^{47}$, $5.23\mathrm{Sol}^{43\,a}$	4.36 ± 0.67	4.59	−0.23	4.57	−0.21
1-butanethiol	6.94 ± 0.15^{e}	$4.51K_{\mathrm{D,c}}^{46\,f,g}$, $3.78K_{\mathrm{D,c}}^{24}$, $6.55K_{\mathrm{D,c}}^{39\,a}$, $4.08\mathrm{Sol}^{26\,a}$, $4.94\mathrm{Sol}^{48}$, $5.72\mathrm{Sol}^{43\,a}$	4.96 ± 0.71	5.29	−0.33	5.25	−0.29
1-pentanethiol	9.88 ± 0.15^{e}	$5.88K_{\mathrm{D,c}}^{46\,f,g}$, $6.22\mathrm{Sol}^{43\,a}$	6.05 ± 0.40	5.99	0.06	5.93	0.12
1-hexanethiol	12.85 ± 0.15^{e}	$7.38K_{\mathrm{D,c}}^{46\,f,g}$, $0.73\mathrm{Sol}^{26\,a}$	7.31 ± 0.70	6.69	0.62	6.61	0.70
1-heptanethiol	15.76 ± 0.20^{e}	$7.88\mathrm{Sol}^{43\,a}$	7.88 ± 0.70	7.39	0.49	7.29	0.59
2-methyl-2-propanethiol	3.56 ± 0.10^{e}	$7.69\mathrm{Sol}^{43\,a}$	7.69 ± 0.80	7.69	0.00	7.69	0.00
2-butanethiol	5.54 ± 0.15^{e}	$4.98\mathrm{Sol}^{26\,a}$	4.98 ± 1.00	5.84	−0.86	5.05	−0.07
3-methylbutanethiol	9.50 ± 0.15^{7}	$5.95\mathrm{Sol}^{49}$, $2.98\mathrm{Sol}^{26\,a}$	5.84 ± 2.00	6.54	−1.31	6.36	−1.13
dimethyl sulfide	1.14 ± 0.05^{33}	$1.84K_{\mathrm{D,c}}^{50}$, $-0.39K_{\mathrm{D,c}}^{51\,f}$, $2.13\,\gamma^{\infty 52}$, $-1.19K_{\mathrm{D,c}}^{52}$, $1.66K_{\mathrm{D,c}}^{53}$, $1.69k_{\mathrm{H}}^{36}$, $1.83K_{\mathrm{D,c}}^{23}$, $1.44k_{\mathrm{H}}^{37\,a}$, $1.64k_{\mathrm{H}}^{21}$, $1.63\mathrm{Sol}^{54}$, $1.42k_{\mathrm{H}}^{27\,h}$, $1.44K_{\mathrm{D,c}}^{24}$, $1.42K_{\mathrm{D,c}}^{42\,a}$, $1.44\mathrm{Sol}^{24}$	1.59 ± 0.40	0.58	1.01	1.15	0.44
diethyl sulfide	6.35 ± 0.05^{7}	$1.50K_{\mathrm{D,c}}^{24}$, $2.03\mathrm{Sol}^{48}$, $2.08\mathrm{Sol}^{55\,a}$	1.89 ± 0.40	1.98	−0.09	2.01	−0.12
methyl propyl sulfide	6.68 ± 0.10^{e}	$2.08K_{\mathrm{D,c}}^{47}$	2.08 ± 0.80	1.98	0.10	2.26	−0.18
dipropyl sulfide	11.71 ± 0.15^{e}	$2.74K_{\mathrm{D,c}}^{24}$	2.74 ± 0.60	3.38	−0.64	3.37	−0.63
diisopropyl sulfide	9.08 ± 0.10^{e}	$2.99K_{\mathrm{D,c}}^{24}$	2.99 ± 0.60	4.48	−1.49	2.97	0.02
carbon disulfide	1.85 ± 0.05^{33}	$7.23K_{\mathrm{D,c}}^{23}$, $7.30\mathrm{PX}^{28\,i}$, $6.77K_{\mathrm{D,c}}^{28\,i}$, 6.28^{56}, $8.32\gamma^{\infty 57\,a}$, $6.47\mathrm{Sol}^{58\,j}$, $7.41K_{\mathrm{D,c}}^{58\,f}$, $6.25\mathrm{Sol}^{60\,a}$, $7.58\mathrm{Sol}^{61}$, $7.37\mathrm{Sol}^{62\,k}$	7.21 ± 0.42				
dimethyl disulfide	8.06 ± 0.05^{e}	$0.59K_{\mathrm{D,c}}^{63}$, $1.25K_{\mathrm{D,c}}^{50}$, $0.81\mathrm{Sol}^{64\,c}$, $1.25K_{\mathrm{D,c}}^{65\,f}$, $-1.71\mathrm{Sol}^{66\,c}$, $0.50K_{\mathrm{D,c}}^{67\,l}$, $0.83k_{\mathrm{H}}^{21}$, $0.12K_{\mathrm{D,c}}^{24}$, $0.37K_{\mathrm{D,c}}^{47}$, $1.06K_{\mathrm{D,c}}^{42\,a}$	0.73 ± 0.40	0.80	−0.07	1.01	−0.28
diethyl disulfide	12.78 ± 0.10^{e}	$1.12K_{\mathrm{D,c}}^{24}$, $2.60K_{\mathrm{D,c}}^{42\,a}$	2.30±0.59	2.20	0.10	1.87	0.43
dipropyl disulfide	17.69 ± 0.15^{e}	$-1.45K_{\mathrm{D,c}}^{47}$, $3.82\mathrm{Sol}^{62\,m}$	3.78±1.00	3.60	0.18	3.23	0.55
dimethyl trisulfide	14.3 ± 0.5^{e}	$-0.91K_{\mathrm{D,c}}^{63}$, $0.15\mathrm{Sol}^{64\,n}$, $-1.79\mathrm{Sol}^{66\,n}$, $-2.44K_{\mathrm{D,c}}^{69\,n}$	−0.55±1.00	−0.55	0.00	−0.56	0.01

[a] Recalculated from 293.15 K. [b] Recalculated from 323.15 K. [c] Recalculated from 303.15 K. [d] Recalculated from 333.15 K. [e] Calculated from P_{s} values (Table 1) and second virial coefficients.[5,6] [f] Recalculated from 310.15 K. [g] Medium is saline (~0.15 M NaCl). [h] Recalculated from 297.35 K. [i] Recalculated from 297.15 K. [j] Recalculated from 298.65 K. [k] Recalculated from 276.55. [l] Recalculated from 313.2 K. [m] Recalculated from 299.15 K. [n] Recalculated from 303.15 K.

Table 5. Standard Partial Molar Volumes, V_2^{∞}, of Aliphatic Thiols and Alkyl Sulfides at 298.15 K and 0.1 MPa and Experimental and Group Contribution (GC) Values for the First (I) Order Additivity Method

compound	$V_2^{\infty}/\mathrm{cm^3{\cdot}mol^{-1}}$	accepted value	I order GC value
1-propanethiol	$83.6^{32\,a}$	83.6 ± 1.0	83.6
diethyl sulfide	99.5^{70}	99.5 ± 1.0	99.5
carbon disulfide	$76.7^{60\,b,c}$, $72.8^{71\,b,d}$	74.8 ± 2.0	

[a] Our calculation assuming that the difference in V_2^{∞} between cysteine and serine (12.87 $\mathrm{cm^3{\cdot}mol^{-1}}$) is the same as that between propanethiol and propanol.[32] [b] Our calculation of the apparent molar volume from the density of the saturated solution. [c] Value at 293.15 K. [d] Value at 295.15 K.

Determination of First-Order Group Contribution Values to the Thermodynamic Functions of Hydration at 298.15 K, 0.1 MPa

Preliminary Calculations. Preliminary runs showed that the HS group in *tert*-butanethiol (2-methyl-2-propanethiol) is energetically different from the same group in other linear and branched thiols, at least for the Gibbs energy of hydration. We found similar behavior[1] for other polar groups (OH, CO, COO) attached to the tertiary carbon atom. Therefore, by analogy, we introduced a second-order correction to account for the contact of the SH group with a tertiary carbon atom.

It is impossible to describe the Gibbs energy of hydration of sulfides and polysulfides by characterizing the groups SS (S_2) and SSS (S_3) as the sums of two and three S groups. Therefore, we have to introduce S, SS (S_2), and SSS (S_3) groups as independent entities. Among trisulfides, data are available only for dimethyl trisulfide and only for the Gibbs energy of hydration. For the evaluation of other properties of dimethyl trisulfide, we used the observation that in the series dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide the addition of a new S atom decreases the values of $\Delta_{\mathrm{h}}G^{\infty}$ and $\Delta_{\mathrm{h}}H^{\infty}$ by approximately 0.9 kJ·mol−1 and 3.2 kJ·mol−1, respectively, and increases the value of $\Delta_{\mathrm{h}}C_p^{\infty}$ by about 58 J·mol−1·K−1. These values can be used, in the absence of experimental information, for rough estimates of the properties of higher aqueous polysulfides.

Optimal Values of the Contributions of First-Order Groups to Thermodynamic Functions of Hydration at 298.15 K, 0.1 MPa. The main assumption behind group additivity for thermodynamic functions of hydration is that a property, Y, of a compound is given by

$$Y = Y_{\mathrm{o}} + \sum_i n_i Y_i + \sum_j n_j Y_j \tag{12}$$

Table 6. Numerical Values of the Group Contributions to Each Thermodynamic Function of Hydration at 298.15 K and 0.1 MPa Together with Their Uncertainties at the 0.95 Confidence Level for the First-Order Method^{a}

group or correction	$\Delta_{h}G^{o}$/kJ·mol^{-1}		$\Delta_{h}H^{o}$/kJ·mol^{-1}		$\Delta_{h}C_{p}^{o}$/J·K^{-1}·mol^{-1}		V_{2}^{o}/cm^{3}·mol^{-1}	
Y_o	7.95^{b}		-2.29^{b}		0^{b}		1.12^{b}	
HS	-8.43 ± 0.48	(10)	-14.30 ± 1.86	(4)	75(1)		25.5	(1)
S	-14.71 ± 0.53	(5)	-13.68 ± 0.45	(3)	-44 ± 14	(3)	15.9	(1)
S_2	-14.49 ± 0.74	(3)	-16.31 ± 0.55	(3)	-11 ± 19	(2)		(0)
S_3	-15.84	(1)	*−19.5*^{c}	(0)	*47*^{c}	(0)		(0)
C−HScorr	1.67	(1)				(0)		(0)
CH_3	3.67 ± 0.07^{b}		-8.02 ± 0.25^{b}		131 ± 4^{b}		25.49 ± 0.79^{b}	
CH_2	0.70 ± 0.04^{b}		-3.63 ± 0.13^{b}		62 ± 2^{b}		15.73 ± 0.13^{b}	
CH	-1.72 ± 0.16^{b}		1.14 ± 0.63^{b}		-6 ± 8^{b}		6.43 ± 0.86^{b}	
C	-4.51 ± 0.31^{b}		10.39 ± 0.99^{b}		-96 ± 11^{b}		-3.50 ± 1.66^{b}	

[a] The number of compounds containing the selected group for each of the property is given in parentheses. [b] Values from Plyasunov et al.[1] [c] Estimated values; see the text.

Table 7. Numerical Values of the Group Contributions to Each Thermodynamic Function of Hydration at 298.15 K and 0.1 MPa Together with Their Uncertainties at the 0.95 Confidence Level for the Second-Order Method^{a}

group	$\Delta_{h}G^{o}$/kJ·mol^{-1}		$\Delta_{h}H^{o}$/kJ·mol^{-1}		$\Delta_{h}C_{p}^{o}$/J·K^{-1}·mol^{-1}	
Y_o	7.95^{b}		-2.29^{b}	(7)	0^{b}	
C−(C)(S)$(H)_2$	$+0.43 \pm 0.30$	(12)	-3.95 ± 0.36		49 ± 10	(4)
C−$(C)_2$(S)(H)	-2.81 ± 0.53	(2)		(0)		(0)
C−$(C)_3$ (S)	-3.21	(1)		(0)		(0)
S−(H)(C)	-8.21 ± 0.40	(10)	-13.97 ± 2.02	(4)	87	(1)
S−$(C)_2$	-14.24 ± 0.53	(5)	-13.13 ± 0.57	(3)	30 ± 15	(3)
S−(S)(C)	-7.19 ± 0.28	(4)	-7.84 ± 0.28	(3)	8 ± 8	(2)
S−$(S)_2$	-1.57	(1)	*−3.2*^{c}	(0)	*58*^{c}	(0)
C−(C)$(H)_3$	3.72 ± 0.07^{b}		-8.19 ± 0.18^{b}		132 ± 4^{b}	
C−$(C)_2(H)_2$	0.68 ± 0.03^{b}		-3.52 ± 0.09^{b}		62 ± 2^{b}	
C−$(C)_3$(H)	-1.93 ± 0.16^{b}		2.34 ± 0.54^{b}		-17 ± 10^{b}	

[a] The number of compounds containing the selected group for each of the properties is given in parentheses. [b] Values from Plyasunov et al.[1] [c] Estimated values; see the text.

The first summation (the running index i) is for the first-order functional groups. In this case, the groups are CH_3, CH_2, CH, C, HS, S, S_2, and S_3. The second summation (the running index j) is for the corrections for the attachment of the polar groups to the tertiary carbon atom. In this work, the only such correction is C−HS for 2-methyl-2-propanethiol. The first term on the right-hand side of eq 12, Y_o, is equal to Y for an imaginable compound without any groups at all (i.e., for a material point). Y_o values for various functions of hydration can be calculated from the thermophysical properties of pure water;[72] see Plyasunov et al.[1] for details.

The values of Y_i and Y_j of eq 12 for S-containing groups were obtained by a weighted least-squares fitting procedure. The necessary values of Y_i for CH_3, CH_2, CH, and C groups were taken from our previous study[1], where they were determined by fitting a large database including aliphatic hydrocarbons, alcohols, ketones, and esters. Results for the S-containing groups are presented in Table 6. For each group, we list the value of the group contribution together with its uncertainty at the 0.95 confidence level. In parentheses, we give the number of compounds containing the selected group. Our estimated values of $\Delta_{h}H^{\infty}$ and $\Delta_{h}C_{p}^{\infty}$ for the trisulfide group, S_3, obtained by employing the regularities in the series dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide (see above), are shown in italics.

Determination of Second-Order Group Contribution Values to the Thermodynamic Functions of Hydration at 298.15 K, 0.1 MPa

In the following discussion, we use the Benson notation for the second-order group contribution method:[73,74] first the polyvalent atom (or group of atoms) is identified, followed by its "ligands" or immediate neighbors. For example, C−$(H)_3$(C) represents a C atom connected to three H atoms and another C atom, and S−(H)(C) represents the S group connected to one H and one C atoms.

Preliminary Calculations. The groups necessary to represent the selected set of compounds are C−(C)$(H)_3$, C−$(C)_2(H)_2$, C−$(C)_3$(H), C−$(C)_4$, C−(S)$(H)_3$, C−(C)(S)$(H)_2$, C−$(C)_2$(S)(H), C−$(C)_3$(S), S−(H)(C), S−$(C)_2$, S−(S)(C), and S−$(S)_2$. Following existing practice,[74,1] we accepted the identity of the second-order groups C−$(H)_3$(S) = C−$(H)_3$(C). For the CH groups (i.e., C−(C)$(H)_3$, C−$(C)_2(H)_2$, C−$(C)_3$(H), and C−$(C)_4$), we employed values from Plyasunov et al.,[1] determined by fitting a large database of aliphatic hydrocarbons, alcohols, ketones, and esters.

Optimal Values of the Contributions of Second-Order Groups to Thermodynamic Functions of Hydration at 298.15 K, 0.1 MPa. As in the case of the first-order method, we applied a weighted least-squares fitting procedure to derive numerical values for contributions of the S-containing groups. Results are given in Table 7. As in the case of the first-order method, for each group we give the value of the group contribution together with its uncertainty at the 0.95 confidence level. In parentheses, we give the number of compounds containing the selected group. No determinations of the second-order group contribution values are possible for V_{2}^{∞} owing to the scarcity of data. The values of $\Delta_{h}H^{\infty}$ and $\Delta_{h}C_{p}^{\infty}$ for the S−$(S)_2$ group were determined "manually" by employing the regularities in the series dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide; see above. These estimated values are shown in italics.

Discussion

Our result for the first-order group contribution value for the Gibbs energy of hydration of the sulfide group, S, is rather similar to that of Cabani et al.:[75] (-14.71 ± 0.53) kJ·mol^{-1} versus -14.36 kJ·mol^{-1} in ref 75. However, the corresponding results for the thiol group, HS, are different: (-8.43 ± 0.48) kJ·mol^{-1} versus -9.91 kJ·mol^{-1} in Cabani et al.[75] This difference can partially be traced to the large (up to 1.1 kJ·mol^{-1}) difference in the values accepted for the Gibbs energy of hydration of methanethiol and ethanethiol between ref 75 and this study. Cabani et al.[75] quote data from the compilation of Hine and Mookerjee,[76] which gives only one primary data source for methanethiol[41] and for ethanethiol quotes only one secondary data source. In contrast, we used 12 primary data sources for methanethiol, 8 primary data sources for ethanethiol, and, in addition, data for 8 other aliphatic thiols. We emphasize the importance of a truly representative database for deriving reliable group contribution values.

One of the conclusions from this study is that the first-order disulfide (S_2) and trisulfide (S_3) groups have to be introduced because these groups cannot be represented as sums of two and three S groups. We also found that for the Gibbs energy of hydration it is necessary to introduce a C−SH correction, 1.67 kJ·mol^{-1}, for thiol groups attached to the tertiary carbon atom. This value is close to values of the corresponding corrections for the attachment to the tertiary carbon of the ketone (0.87 kJ·mol^{-1}) and the ester (2.08 kJ·mol^{-1}) polar functional groups; see ref 1. We expect that a corresponding correction would be necessary for the case of the sulfide group; however, no data are available for sulfides containing a tertiary carbon atom.

Only a few second-order group contribution values can be determined for the standard partial molar enthalpy and heat capacity of hydration of S-containing compounds, and none can be determined for the partial molar volumes.

Clearly, more experimental data are needed for these important classes of organic substances. Data leading to the evaluation of the partial molar volumes of the S-containing organic compounds are virtually nonexistent; any direct experimental determinations of densities and excess volumes of their dilute aqueous solutions would be helpful. Calorimetric measurements of the heat capacity of aqueous solutions, lacking for all of the compounds considered in this study, would be a major contribution, as would calorimetric determinations of the enthalpy of solution of normal and branched thiols. Measurements of solubility, activity coefficients, air−water distribution constants, and Henry's law constants, necessary for the evaluation of the Gibbs energy of hydration, are more or less representative only for the lower normal thiols (through 1-butanethiol), thus limiting the reliability of group contribution methods, especially second-order methods. For sulfides and polysulfides, the situation is even worse: only the first homologues (dimethyl) of sulfides and disulfides have been comparatively well studied experimentally, and it is the first homologues that usually show the greatest deviations from group-additivity relations. The amount of data drops off sharply even for diethyl compounds. Only one or two independent measurements are available for each of the higher sulfides, disulfides, and dimethyl trisulfide; very often, when there are two independent data sets, they disagree. (See Table 4 for details.) It should be kept in mind that the present study relies on the data available so far; any new experimental measurements for higher homologues could change, maybe significantly, the absolute values of the functions of hydration for S-containing groups but, at the same time, would dramatically improve the reliability of the group contribution determinations.

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