Group Contribution Values for the Thermodynamic Functions of Hydration at 298.15 K, 0.1 MPa. 3. Aliphatic Monoethers, Diethers, and Polyethers

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

Department of Geological Sciences and Department of Chemistry and Biochemistry, Arizona State University,
Tempe, Arizona 85287, and CrystalTech Web Hosting, Inc., Phoenix, Arizona 85014

A compilation of experimental values of the infinite dilution partial molar Gibbs energy, enthalpy, and heat capacity of hydration, together with partial molar volumes in water at 298.15 K and 0.1 MPa is presented for aliphatic monoethers, diethers, and polyethers. These data are treated in the framework of the first- and second-order group additivity methods. However, third- and higher-order effects (i.e., interactions expressed beyond the nearest neighbors) are clearly present in aqueous ethers. The effects can be accounted for by the introduction of a number of corrections. For the second-order group contribution method, numerical values are determined for the following groups: $C-(C)_2(H)(O)_{ether}$, $C-(C)_3(O)_{ether}$, $O-(C)_2$, $C-(H)_2(O)_2$, $C-(C)(O)_2(H)$, and corrections: a "ethoxyalkane" correction, $\{CH_3-CH_2-O-CH_2\}$, and a "diether" correction, $\{O-(CH_2)_2-O\}$. For the first-order group contribution method, in addition to the "ether" O group, a large number of corrections appears to be necessary for accurate reproduction of the compiled data: "ethoxyalkane", and "diether", corrections, two "acetal", $\{O-CH_2-O\}$ and $\{O-CH(CH_3)\text{-}O\}$, corrections, as well as "tertiary", $\{C_{tert}\text{-}O\}$, and "ternary", $\{HC_{tern}\text{-}O\}$, corrections, applied to monoethers that have direct contacts of tertiary and ternary carbon atom with oxygen.

Introduction

Aliphatic ethers are classes of organic compounds having the structural unit R_1-O-R_2, where R_1 and R_2 represent alkyl groups. Ethers are a comparatively well-studied group of organic substances with a very broad spectrum of practical applications. Their uses vary from major constituents in medicine and pharmacology to components of food flavoring, powerful industrial solvents, and effective fuel oxygenates. Aliphatic diethers and polyethers (glycol ethers), compounds having more than one R_1-O-R_2 structural unit, are important solvents with many technological applications. The extensive industrial use of ethers results in their abundance in waste materials harmful for environmental and human health. Thermodynamic properties of these compounds in water are of interest for environmental sciences, medicine, agriculture, chemistry, geochemistry, and biology.

This contribution is a continuation of our efforts[1−4] to provide an up-to-date compilation of 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. Initially, we planned to limit our consideration of ethers to the monoethers. However, very few calorimetric enthalpy and heat capacity data are available for aqueous solutions of monoethers. In addition, experimental determinations of the partial molar volume (V_2^∞) appear to have been made only for ethoxy ethane (diethyl ether). Therefore, we decided to include data for di- and polyethers, for which there are accurate experimental determinations of enthalpy of solution, partial molar heat capacity, and volume. The polyethers considered in this work are ethylene glycol dialkyl ethers. Nevertheless, this decision raised problems because our analysis shows that even a second-order group contribution method is not completely adequate for aqueous di- and polyethers. It appears that for these compounds the influence of neighboring atoms is felt beyond the nearest contacts, signaling the importance of third- and higher-order effects for aqueous polyethers.

This work is organized as follows. First, as for other classes of organic compounds,[3,4] we compile an extensive database of thermodynamic functions of hydration for aliphatic mono-, di-, and polyethers. Second, the database is used to derive optimal values of the contributions of the functional groups in the framework of 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 ($\Delta_h H^\infty$), heat capacity ($\Delta_h C_p^\infty$), and volume ($\Delta_h V^\infty \equiv V_2^\infty$). 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.[5]

Auxiliary Data for Pure and Aqueous Compounds

Standard Gibbs Energy of Vaporization of Pure Compounds. In this study, values of the standard Gibbs energy of vaporization ($\Delta_{vap}G^\circ$), 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}) according to

$$\Delta_{vap}G^\circ = -RT \ln\frac{P_2^*\phi_2^*}{P^\circ} \qquad (1)$$

where $P^\circ = 0.1$ MPa is the standard state pressure, and $\phi_2^* =$

---

* Corresponding author. E-mail: Andrey.Plyasunov@asu.edu. Phone: (480)-965-6033. Fax: (480)-965-8102.
† Department of Geological Sciences.
§ CrystalTech Web Hosting, Inc.
‡ Department of Chemistry and Biochemistry.

10.1021/je050390a CCC: $33.50

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

compound	A	B	C	temperature range/K	data sources
2-ethoxypropane	3.9707	1086.98	219.92	298−338	P_{s},[11] $\Delta_{\mathrm{vap}}H$[12]
1-methoxy-2-methylpropane	4.0080	1138.35	225.86	270−430	P_{s},[11,13][a] $\Delta_{\mathrm{vap}}H$[12]
2-methoxybutane	4.0030	1137.40	225.48	270−430	P_{s},[11,13][a] $\Delta_{\mathrm{vap}}H$[12]
2-propoxypropane	4.1070	1265.74	225.54	270−450	P_{s},[11,13][a] $\Delta_{\mathrm{vap}}H$[12]
1-ethoxybutane	3.9972	1217.78	212.76	298−365	P_{s},[14] $\Delta_{\mathrm{vap}}H$[12]
2-ethoxy-2-methylpropane	3.7505	1043.27	205.69	278−346	P_{s}[15,16]
2-ethoxy-2-methylbutane	4.2415	1406.22	230.53	274−412	P_{s}[16−18]
1,1′-oxybis-2-methylpropane	4.0412	1348.84	211.65	298−396	P_{s},[19] $\Delta_{\mathrm{vap}}H$[12]
1,1′-oxybisbutane	4.2866	1523.30	214.81	298−415	P_{s},[14,19−21] $\Delta_{\mathrm{vap}}H$[12]
1,2-dimethoxyethane	4.3189	1330.25	223.46	225−533	P_{s},[22−27] $\Delta_{\mathrm{vap}}H$[12]
1-ethoxy-2-methoxyethane	4.0437	1248.02	205.58	270−430	P_{s},[28,13][a] $\Delta_{\mathrm{vap}}H$[12]
1,2-diethoxyethane	4.0799	1318.51	202.59	293−394	P_{s},[29,30] $\Delta_{\mathrm{vap}}H$[12]
1-methoxy-2-propoxyethane	4.1720	1382.55	207.221	270−420	P_{s},[28,13][a] $\Delta_{\mathrm{vap}}H$[12]
1,4-dimethoxybutane	4.4087	1544.95	218.95	270−410	P_{s}[13][a]
1,3-diethoxypropane	4.5011	1620.83	220.06	270−430	P_{s},[13][a] $\Delta_{\mathrm{vap}}H$[12]
1-butoxy-2-methoxypropane	4.2204	1477.14	203.88	270−440	P_{s},[13][a] $\Delta_{\mathrm{vap}}H$[12]
1,5-dimethoxypentane	4.4973	1682.76	216.97	270−450	P_{s}[13][a]
1,4-diethoxybutane	4.5229	1704.72	214.46	270−450	P_{s},[13][a]
1,2-dipropoxyethane	4.4722	1676.34	212.29	270−470	P_{s},[28,13][a] $\Delta_{\mathrm{vap}}H$[12]
1,2-dibutoxyethane	4.7733	2012.58	216.39	270−490	P_{s},[28,13][a] $\Delta_{\mathrm{vap}}H$[12]
1,2-dimethoxymethane	4.0212	1060.48	221.75	273−357	P_{s},[24,14,31−34] $\Delta_{\mathrm{vap}}H$[12]
1,1-dimethoxyethane	4.2307	1235.34	228.59	273−478	P_{s}[35,14,26]
1,1-diethoxymethane	4.0358	1223.94	215.78	273−348	P_{s},[29,14] $\Delta_{\mathrm{vap}}H$[12]
1,1-diethoxyethane	4.2720	1370.32	217.76	273−377	P_{s}[36,37,14]

[a] Estimated by the group contribution corresponding-states method.[13]

$\exp(B_{22}P_2^*/RT)$ 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[6,7] and/or Hayden−O'Connell[8] corresponding state correlations. Values of the saturated vapor pressure of the best studied ethers were taken from the Poling et al.[7] or Reid et al.[9] handbooks. For other compounds we used experimental vapor pressure (P_2^*) and enthalpy of vaporization ($\Delta_{\mathrm{vap}}H°$) data from the literature to determine, by the simultaneous fit of these data, the parameters (A, B, C) of the Antoine equation, which was taken in the form:[7]

$$\log (P_2^*/\mathrm{bar}) = A - B/\{(T/\mathrm{K}) + C - 273.15\} \tag{2}$$

Following Majer et al.,[10] we corrected the measured enthalpy of vaporization for nonideality of the gaseous phase to extract the value of the derivative ($\mathrm{d}\ln P_2^*/\mathrm{d}T$) as follows:

$$RT^2\left(\frac{\mathrm{d}\ln P_2^*}{\mathrm{d}T}\right) = \frac{\Delta_{\mathrm{vap}}H^*}{1 + P_2^*(B_{22} - V_2^*)/RT} \tag{3}$$

The resulting parameters of the Antoine equation, together with sources of data and the temperature ranges of validity, are given in Table 1. For a number of diethers (1,4-dimethoxybutane, 1,5-dimethoxypentane, 1,4-diethoxybutane) 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[13] to estimate P_2^*. Experimental and fitted values of the vapor pressure and B_{22} of the studied compounds are accessible in our database[38] at http://orchyd.asu.edu.

Estimation of Activity Coefficients of Ethers in Aqueous Solutions. Conversion of ether−water mutual solubility data into the values of the Gibbs energy of hydration of ethers requires estimates of activity coefficients for ethers dissolved in water. For moderately soluble ethers one can use the Savage−Wood group contribution method[39,40] for estimating excess properties of organic compounds in water. This method takes into account only binary interaction contributions to the excess Gibbs energy of a system (i.e., it presupposes the linear molality dependence of $\ln \gamma_{\mathrm{m},2}$) according to

$$\ln \gamma_{\mathrm{m},2} = \frac{2g_{xx}m}{RT} \tag{4}$$

where g_{xx} is the ether−ether binary self-interaction coefficient. This linear concentration dependence of $\ln \gamma_{\mathrm{m},2}$ is a reasonable approximation for many nonelectrolytes in water up to molality one or even slightly higher. In the Savage-Wood formalism, there is the following group contribution approximation to estimate g_{xx}:

$$g_{xx} = \sum_{i,j} n_i n_j G_{ij} - \frac{RT}{2N_{\mathrm{w}}} \tag{5}$$

where n_i and n_j represent the number of groups i and j in two interacting molecules of organic compounds in water, and G_{ij} stands for the excess Gibbs energy of an $i-j$ interaction. To simplify calculations, the following counting rules are applicable:[39] the CH_3 group is equal to 1.5 CH_2 group; the CH group is equal to 0.5 CH_2 group, the C group is not counted. Therefore, the following interactions have to be considered for aqueous solutions of ethers: CH_2-CH_2, O−O, and CH_2-O. As an example, to calculate the activity coefficient of methyl isobutyl ether (1-methoxy-2-methylpropane) in water, one needs to count 36 CH_2-CH_2, 12 CH_2-O, and 1 O−O interactions. Aqueous solutions of 1,1-diethoxyethane (diethyl acetal) account for 49 CH_2-CH_2, 28 CH_2-O, and 4 O−O interactions. The numerical values of the binary parameters for the relevant interactions at 298.15 K are available[41] from freezing point and calorimetric determinations in aqueous solutions: $G(CH_2-CH_2) = -34\ \mathrm{J{\cdot}kg{\cdot}mol^{-2}}$, $G(CH_2-O) = 37\ \mathrm{J{\cdot}kg{\cdot}mol^{-2}}$, and $G(O-O) = -57\mathrm{J{\cdot}kg{\cdot}mol^{-2}}$.

For polyethers, which are derivatives of di-, tri-, and tetraethylene glycols, the Savage−Wood model predicts very strong deviations from ideality in aqueous solutions, with very low calculated values for the activity coefficients of solutes.

However, isopiestic data[42] for aqueous solutions of tetraethylene glycol diethyl ether show only moderate deviations from ideality. As discussed by the authors of the Savage−Wood model,[40] this approach may not be applicable for polyfunctional compounds. In addition, ether derivatives of glycols are highly soluble in water.[43,44] Correspondingly, we did not include mutual solubility data for water−polyether systems.

In a number of instances one needs to calculate activity coefficients of ethers at temperatures other than 298.15 K. To calculate the excess Gibbs energy at various temperatures, one needs to know the excess enthalpy of $i-j$ interactions (H_{ij}):

$$H_{ij} = -T^2\left(\frac{\partial(G_{ij}/\mathrm{T})}{\partial T}\right)_{\mathrm{P}} \tag{6}$$

These values are determined from excess enthalpy measurements for water−ether mixtures, and numerical values of the binary parameters for the relevant interactions at 298.15 K are as follows:[41] $H(CH_2-CH_2) = 36$ J·kg·mol^{-2}, $H(CH_2-O) = 60$ J·kg·mol^{-2}, and $H(O-O) = -104$ J·kg·mol^{-2}. Recalculations to other temperatures can be done assuming that H_{ij} are temperature independent over a limited temperature range:

$$G_{ij}(T) = T\left(\frac{G_{ij}(T_{\mathrm{r}})}{T_{\mathrm{r}}} + H_{ij}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{r}}}\right)\right) \tag{7}$$

where $T_{\mathrm{r}} = 298.15$ K.

Specifics of Aliphatic Mono-, Di-, and Polyethers in Aqueous Solution. Ethers are strongly polar compounds and are generally inert in chemical reactions in water and aqueous solutions, except for solutions of mineral acids, where ethers react producing an alcohol and an alkene. Ethers do not exhibit any acidic properties and tend to be extremely weak bases. One of the most important characteristics of ethers is their reaction with atmospheric oxygen to form peroxides, especially in sunlight (auto-oxidation).[45] Once exposed to the atmosphere even for a short period of time ethers of any type will contain some amount of peroxide. This raises an issue of possible sample contamination that one should be aware of when considering results of experimental studies. We found a very large discrepancy in data for aqueous ethers, much larger than that previously found for aqueous aliphatic alcohols[1], ketones,[2] or esters.[3] For example, most results for solubility of 2-methoxy-2-methylpropane (methyl *tert*-butyl ether) at 298.15 K cluster around the value of 0.5 mol·kg^{-1}; however, values as high as 1.86[46] mol·kg^{-1} and as low as 0.33[47] mol·kg^{-1} are reported in peer-reviewed journals. It is not clear whether such strong scatter should be attributed only to the instability of ethers in aqueous solutions.

Data Compilation

A major part of this contribution is the compilation of a representative database of thermodynamic properties of aliphatic ethers in aqueous solution at infinite dilution. As before, we worked with primary sources of data that report original experimental values, avoiding literature compilations, which are often mixtures of data from primary and secondary sources. Our established procedures for converting primary data of different types into functions of hydration, as well as their critical evaluation, were described earlier[3]. All of the primary data on the functions of hydration for aliphatic mono-, di-, and polyethers are accessible through the ORCHYD database.[38] The database also includes recommended properties of hydration, standard thermodynamic properties in aqueous solution, 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.

Standard Partial Molar Enthalpy of Hydration at 298.15 K, 0.1 MPa. The most accurate values of the standard partial molar enthalpy of hydration ($\Delta_{\mathrm{h}}H^{\infty}$) can be obtained by combining the calorimetrically determined molar enthalpy of solution in water ($\Delta_{\mathrm{sol}}H^{\infty}$) and the standard molar enthalpy of vaporization ($\Delta_{\mathrm{vap}}H^{\circ}$) according to the relation

$$\Delta_{\mathrm{h}}H^{\infty} = \Delta_{\mathrm{sol}}H^{\infty} - \Delta_{\mathrm{vap}}H^{\circ} \tag{8}$$

The value of the enthalpy of solution in water, if determined at temperatures other than 298.15 K, can be recalculated to $T_{\mathrm{r}} = 298.15$ K as follows:

$$\Delta_{\mathrm{sol}}H^{\infty}(T_{\mathrm{r}}) = \Delta_{\mathrm{sol}}H^{\infty}(T) - \Delta_{\mathrm{sol}}C_p^{\ \infty}(T - T_{\mathrm{r}}) \tag{9}$$

where the standard partial molar heat capacity of solution is defined as $\Delta_{\mathrm{sol}}C_p^{\infty} = C_{p,2}^{\infty} - C_p^{\circ}(\mathrm{l})$, with $C_{p,2}^{\infty}$ being the standard partial molar heat capacity of a compound in water and $C_p^{\circ}(\mathrm{l})$ being the molar heat capacity of a pure compound in the liquid state. Over a limited temperature range, say (273 to 323) K, one can assume that $\Delta_{\mathrm{sol}}C_p^{\infty}$ is constant. In the absence of calorimetric values of $C_{p,2}^{\infty}$ one can use a group contribution estimate without introducing serious error into the temperature dependence of $\Delta_{\mathrm{sol}}H^{\infty}$.

There are only a few calorimetric data for the enthalpy of solution in water ($\Delta_{\mathrm{sol}}H^{\infty}$) for monoethers. Arnett et al.[48] provided measurements for ethoxyethane, and the only other source is the International Critical Tables,[49] citing 19th century data of Berthelot for methoxymethane and ethoxyethane. More calorimetric measurements of the enthalpy of solution are available for di- and polyethers.

Another method for evaluating $\Delta_{\mathrm{sol}}H^{\infty}$ is by differentiating the excess enthalpies (H^{E}) of water-ether mixtures:

$$\Delta_{\mathrm{sol}}H^{\infty} = \left(\frac{\partial H^{\mathrm{E}}}{\partial x}\right)_{\mathrm{T,P},x=0} \tag{10}$$

Less accurate values of $\Delta_{\mathrm{sol}}H^{\infty}$ for monoethers and 1,2-dimethoxymethane may be evaluated from temperature-dependent $\Delta_{\mathrm{sol}}G^{\infty}$results by means of

$$\Delta_{\mathrm{sol}}H^{\infty} = -T^2\left(\frac{\partial \Delta_{\mathrm{sol}}G^{\infty}/T}{\partial T}\right)_{\mathrm{P}} \tag{11}$$

Values of $\Delta_{\mathrm{sol}}H^{\infty}$ obtained in this way refer to the middle of the temperature interval of the availability of $\Delta_{\mathrm{sol}}G^{\infty}$, and they are recalculated to 298.15 K using a relation analogous to eq 9.

Gniazdowska and Narbutt[50] determined the enthalpy of partition ($\Delta_{\mathrm{p}}H^{\infty}$) of a number of ethers between water and *n*-heptane from the temperature dependence of the corresponding partition coefficients. The values of $\Delta_{\mathrm{sol}}H^{\infty}$ can be evaluated from these data provided that the standard partial molar enthalpies of solution of ethers in *n*-heptane ($\Delta_{\mathrm{sol}}H_{\mathrm{hept}}^{\infty}$) are known:

$$\Delta_{\mathrm{sol}}H^{\infty} = \Delta_{\mathrm{sol}}H_{\mathrm{hept}}^{\infty} - \Delta_{\mathrm{p}}H^{\infty} \tag{12}$$

The necessary values of $\Delta_{\mathrm{sol}}H_{\mathrm{hept}}^{\infty}$ for a few ethers can be evaluated from excess enthalpy measurements in the corresponding systems[51] or estimated from the temperature depen-

Table 2. Enthalpy of Hydration of Ethers at 298.15 K and 0.1 MPa, Experimental and Group Contribution (GC) Values

compound	$\Delta_{\text{vap}}H°$ kJ·mol^{-1}	$\Delta_{\text{h}}H°$ kJ·mol^{-1}	accepted value	I order GC value	Δ/kJ·mol^{-1}	II order GC value	Δ/kJ·mol^{-1}
methoxymethane		−36.80 G$^{\infty}$(T)[50], −30.9 G$^{\infty}$(T)[52], −36.9 G$^{\infty}$(T)[53], −33.3 Cal[49]	−33.97 ± 2.0	−33.34	−0.63	−32.44	−1.53
methoxyethane		−33.50 G$^{\infty}$(T)[50]	−33.5 ± 4.0	−36.97	3.47	−37.61	4.10
1-methoxypropane	29.50 ± 0.15[12]	−36.80 G$^{\infty}$(T)[50], −39.2 G$^{\infty}$(T)[54]	−38.0 ± 4.0	−40.60	2.60	−41.13	3.13
2-methoxypropane	26.78 ± 0.14[12]	−38.08 G$^{\infty}$(T)[54]	−38.1 ± 4.0	−41.83	3.75	−40.63	2.55
ethoxyethane	27.37 ± 0.14[12]	−48.07 G$^{\infty}$(T)[55], −36.47 G$^{\infty}$(T)[50], −46.40 G$^{\infty}$(T)[56], −**46.0**7 H$^{\text{ex}}$[57], −**46.57** Cal[48], −49.07 Cal[49]	−46.41 ± 1.0	−46.10	−0.31	−46.11	−0.30
2-ethoxypropane	30.32 ± 0.16[12]	−46.12 G$^{\infty}$(T)[54]	−46.12 ± 4.0	−45.46	−0.66	−45.80	0.32
1-methoxy-2-methylpropane	30.31 ± 0.31[12]	−46.21 G$^{\infty}$(T)[54]	−46.21 ± 4.2	−43.85	−2.36	−43.46	−2.75
2-methoxy-2-methylpropane	30.04 ± 0.16[12]	−41.2 G$^{\infty}$(T)[58], −52.34 G$^{\infty}$(T)[55], −48.6 G$^{\infty}$(T)[56], −**48.44** H$^{\text{ex}}$[59], −46.94 G$^{\infty}$(T)l[60], −45.74 G$^{\infty}$(T)[61], −51.84 G$^{\infty}$(T)[54]	−48.68 ± 2.0	−48.89	0.21	−48.82	0.14
1-methoxybutane	32.53 ± 0.17[12]	−41.53 G$^{\infty}$(T)[50], −54.33 G$^{\infty}$(T)[54]	−47.13 ± 4.0	−44.23	−2.90	−44.65	−2.48
2-methoxybutane	30.41 ± 0.31[12]	−42.71 G$^{\infty}$(T)[54]	−42.71 ± 4.2	−45.46	2.75	−44.15	1.44
1-methoxypentane	36.91 ± 0.40[12]	−45.91 G$^{\infty}$(T)[50]	−45.91 ± 5.0	−47.86	1.95	−48.17	2.26
2-ethoxy-2-methylpropane	32.97 ± 0.33[12]	−56.70 G$^{\infty}$(T)[58], −44.17 G$^{\infty}$(T)[62] , −52.40 G$^{\infty}$(T)[63]	−53.4 ± 4.0	−52.52	−0.88	−53.99	0.59
2-propoxypropane	33.95 ± 0.34[12]	−52.15 G$^{\infty}$(T)[54]	−52.15 ± 4.2	−49.09	−3.06	−49.32	−2.83
1,1′-oxybispropane	35.79 ± 0 × 10[12]	−50.49 G$^{\infty}$(T)[55], −44.69 G$^{\infty}$(T)[50], −52.19 G$^{\infty}$(T)[54]	−49.88 ± 3.0	−47.86	−2.02	−49.82	−0.06
2,2′-oxybispropane	32.26 ± 0.17[12]	−54.80 G$^{\infty}$(T)[58], −55.86 G$^{\infty}$(T)[55], −50.70 G$^{\infty}$(T)[56], −42.06 G$^{\infty}$(T)[50]	−51.74±2.0	−50.33	−1.41	−48.82	−2.92
1-ethoxybutane	36.41 ± 0 × 10[12]	−46.41 G$^{\infty}$(T)[50], −48.31 G$^{\infty}$(T)[60], −48.71 G$^{\infty}$(T)[54]	−48.43 ± 4.0	−53.36	4.93	−53.15	4.72
2-methoxy-2-methylbutane	35.2 ± 0.6[a]	−51.70 G$^{\infty}$(T)[58], −56.50 G$^{\infty}$(T)[55], −55.20 G$^{\infty}$(T)l[60], −46.60 G$^{\infty}$(T)[64]	−52.50 ± 4.0	−52.52	0.02	−52.34	−0.16
1-propoxybutane	40.26 ± 0.41[12]	−49.76 G$^{\infty}$(T)[50]	−49.76 ± 5.0	−51.49	1.73	−53.34	3.58
1-methoxyhexane	42.10 ± 0.43[12]	−51.9 G$^{\infty}$(T)[50]	−51.9 ± 5.0	−51.49	−0.41	−51.69	−0.21
1,2-dimethoxyethane	36.47 ± 0.19[12]	−**59.42** Cal[65], −**59.42** Cal[66], −58.83 H$^{\text{ex}}$[67], −59.67 H$^{\text{ex}}$[68], −**59.42** Cal[69]	−59.37±0.50	−62.04	2.67	−60.34	0.97
1-ethoxy-2-methoxyethane	39.87 ± 0.20[12]	−**66.08** Cal[69]	−66.08±0.50	−65.67	−0.41	−65.51	−0.57
1-methoxy-2-propoxyethane	43.65 ± 0.22[12]	−**69.09** Cal[69]	−69.09 ± 0.50	−69.30	0.21	−69.03	−0.06
1,2-diethoxyethane	43.27 ± 0.22[12]	−**71.99** Cal[69], −72.27 Cal[70]	−72.00 ± 0.40	−69.30	−2.70	−70.68	−1.32
1-butoxy-2-methoxypropane	47.84 ± 0.24[12]	−**72.49** Cal[69]	−72.49 ± 0.50	−72.93	0.44	−72.55	0.06
1,2-dipropoxyethane	50.62 ± 0.26[12]	−**76.79** Cal[69]	−76.79 ± 0.50	−76.56	−0.23	−77.72	0.93
1,2-dimethoxymethane	29.17 ± 0.21[34]	−36.80 G$^{\infty}$(T)[31], −41.77 Cal[49]	−41.12 ± 2.0	−41.12	0	−41.12	0
1,1-diethoxyethane	39.4 ± 0.5[a]	−61.24 Cal[71], −59.05 Cal[72]	−59.86 ± 1.50	−59.86	0	−59.86	0
1,1′-oxybis(2-methoxy) ethane	44.70 ± 0.13[12]	−**74.61** H$^{\text{ex}}$[67], −71.01 Cal[73], −75.50 H$^{\text{ex}}$[68], −74.90 H$^{\text{ex}}$[74]	−74.70 ± 1.0				
3,6,9-trioxaundecane	58.4 ± 0.3[12]	−92.66 Cal[73], −**96.50** H$^{\text{ex}}$[75], −**96.3** Cal[70]	−96.19 ± 1.50				
2,5,8,11-tetraoxadodecane	63.7 ± 3.3[76]	−**102.29** H$^{\text{ex}}$[67], −102.52 Cal[73], −102.31 H$^{\text{ex}}$[68]	−102.35 ± 0.3				
2,5,8,11,14-pentaoxapentadecane	79.6 ± 2.6[76]	−125.70 H$^{\text{ex}}$[77], −**125.85** H$^{\text{ex}}$[67], −127.10 H$^{\text{ex}}$[78], −122.20 Cal[73], −126.50 H$^{\text{ex}}$[68]	−125.76 ± 1.5				

[a] Evaluated from P_s(T) data, see Table 1.

dence of the infinite dilution activity coefficients of ethers in heptane ($\gamma_{\text{hept}}^{\infty}$) estimated using the UNIFAC model[7] as follows:

$$\Delta_{\text{sol}}H_{\text{hept}}^{\infty} = R\left(\frac{\partial \ln \gamma_{\text{hept}}^{\infty}}{\partial(1/T)}\right) \tag{13}$$

Values of $\Delta_{\text{sol}}H^{\infty}$ evaluated from the temperature dependence of solubility in water or water-heptane partition data suffer from low accuracy, but they are employed because of the scarcity of calorimetric information.

Results of data evaluation for $\Delta_{\text{h}}H^{\infty}$are summarized in Table 2. The first column gives names of ethers. 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 $\Delta_{\text{h}}H^{\infty}$ together with abbreviations employed to indicate the type of data converted to the $\Delta_{\text{h}}H^{\infty}$ value: $\Delta_{\text{sol}}H^{\infty}$ denotes values based on the enthalpy of solution, H^{E} stands for values obtained from excess enthalpy of mixing, $G^{\infty}(T)$ denotes values based on temperature differentiation of $\Delta_{\text{h}}G^{\infty}$ with eq 11 or eq 13. Results that we consider to be the most reliable are given in bold. Our accepted values of $\Delta_{\text{h}}H^{\infty}$ together with their expected uncertainties are given in the fourth column.

Standard Partial Molar Heat Capacity of Hydration at 298.15 K, 0.1 MPa. A number of reports of experimental work present calorimetric measurements of heat capacity of solution in water, mainly for di- and polyethers. From these data, values of the heat capacity of hydration ($\Delta_{\text{h}}C_p^{\infty}$) were evaluated for a number of ethers by means of

$$\Delta_{\text{h}}C_p^{\ \infty} = \Delta_{\text{sol}}C_p^{\ \infty} + C_{p,2}^{*}(\text{l}) - C_{p,2}^{*}(\text{ig}) \tag{14}$$

where $C_{p,2}^{*}(\text{l})$ and $C_{p,2}^{*}(\text{ig})$ are the molar heat capacity of a compound in the liquid state and in the ideal gas state, respectively. In the absence of direct calorimetric determinations, values of the heat capacity of solution were obtained from the temperature dependence of the enthalpy of solution:

$$\Delta_{\text{sol}}C_p^{\infty} = \left(\frac{\partial \Delta_{\text{sol}}H^{\infty}}{\partial T}\right)_{\text{P}} \tag{15}$$

or, in the case of tetraglyme (2,5,8,11,14-pentaoxapentadecane) and methyl *tert*-butyl ether, evaluated from measurements of H^{E} at different temperatures.[59,78]

The results of data evaluation for the standard partial molar heat capacity of hydration ($\Delta_{\text{h}}C_p^{\infty}$) 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 $\Delta_{\text{h}}C_p^{\infty}$ with the following abbreviations: Cal stands for values based on calorimetric measurements of the heat capacity of solutions, H^{∞}(*T*) and H^{E}(*T*) denote that temperature differentiation of $\Delta_{\text{sol}}H^{\infty}$ or H^{E} were used to obtain the $\Delta_{\text{h}}C_p^{\infty}$ values.

Standard Partial Molar Gibbs Energy of Hydration at 298.15 K, 0.1 MPa. The ethers in this study vary greatly in

Table 3. Partial Molar Heat Capacity of Hydration of Ethers at 298.15 K and 0.1 MPa, Experimental and Group Contribution (GC) Values

compound	C_p(g) $\text{J·K}^{-1}\text{·mol}^{-1}$	$\Delta_h C_p$ $\text{J·K}^{-1}\text{·mol}^{-1}$	accepted value	I order GC value	Δ $\text{J·K}^{1}\text{·mol}^{-1}$	II order GC value	Δ $\text{J·K}^{1}\text{·mol}^{-1}$
ethoxyethane	120 ± 1[79]	304 Cal[80]	304 ± 15	304	0	304	0
2-methoxy-2-methylpropane	134 ± 2[79]	330 $H^E(T)$[59]	330 ± 40	330	0	330	0
1,2-dimethoxyethane	122 ± 2[81][a]	242 Cal[82], **258** $H^\infty(T)$[69]	253 ± 10	266	−13	259	−6
1-ethoxy-2-methoxyethane	142 ± 2[81][a]	321 $H^\infty(T)$[69]	321 ± 16	328	−7	327	−6
1-methoxy-2-propoxyethane	165 ± 2[81][a]	398 $H^\infty(T)$[69]	398 ± 16	390	8	389	9
1,2-diethoxyethane	163 ± 2[81][a]	408 Cal[83], 407 $H^\infty(T)$[69]	407 ± 10	390	17	395	12
1-butoxy-2-methoxypropane	188 ± 2[81][a]	464 $H^\infty(T)$[69]	464 ± 16	452	12	451	13
1,2-dipropoxyethane	209 ± 2[81][a]	492 $H^\infty(T)$[69]	492 ± 16	514	−22	519	−27
1,2-dimethoxymethane	209 ± 2[81][a]	180 Cal[80]	180 ± 16	196	−16	190	−10
1,1-diethoxymethane	134 ± 2[7][a,b]	335 Cal[80]	335 ± 16	320	15	326	9
2,5,8,11-tetraoxadodecane	233 ± 3[81][a]	413 Cal[85]	413 ± 20				
3,6,9-trioxaundecane	219 ± 2[81][a]	479 Cal[85]	479 ± 16	482	−3	486	−7
2,5,8,11,14-pentaoxapentadecane	288±3[81][a]	547 $H^E(T)$[78]	547 ± 40	541	6	532	15

[a] Our estimate of uncertainty. [b] Benson group contribution method.[84]

their solubility in water. Some of the lower carbon number compounds are totally miscible with water at ambient conditions, for example, ethoxyethane, 1,2-dimethoxyethane, 1,2-dimethoxymethane. For higher homologues, like 1,1′-oxybisbutane, the solubility is very low. For ethers with infinite or very high aqueous solubility, the Gibbs energy of hydration was evaluated from the activity coefficient at infinite dilution (γ^∞), gas−water distribution constants in the molarity concentration scale ($K_{D,c}$), and Henry's law constants (k_H) according to the following relations, see ref 3:

$$\Delta_h G^\infty = -\Delta_{vap} G^\circ + RT \ln\left(\frac{\gamma^\infty}{N_w}\right) \tag{16}$$

where $N_w = 1000/M_w \approx 55.5084$ is the number of moles of H_2O in 1000 g of water, $M_w = 18.0153\ \text{g·mol}^{-1}$ is the molar mass of water:

$$\Delta_h G^\infty = RT \ln\left(K_{D,c} \frac{RT}{P^\circ V_1^*} \frac{1}{N_w}\right) \tag{17}$$

where $K_{D,c}$ is defined as $K_{D,c} = \lim_{c(aq)\to 0} c(g)/c(aq)$, with c standing for the concentration per 1000 cm^3 of solvent, V_1^* being the molar volume of pure water, $P^\circ = 0.1$ MPa is the standard pressure, and

$$\Delta_h G^\infty = RT \ln\left(\frac{k_H}{P^\circ} \cdot \frac{1}{N_w}\right) \tag{18}$$

with $k_H = \lim_{x\to 0} f_2/x$, where f_2 stands for the fugacity of a solute (2), and x is the mole fraction of a solute in the liquid phase.

In a few cases we treated the primary vapor−liquid equilibrium[52,63,86−88] experimental data to calculate and extrapolate to infinite dilution either activity coefficients or fugacity/concentration ratios for aqueous methoxymethane and ethoxyethane. For these volatile compounds the fugacity coefficients in the gas phase were calculated using the virial equation of state truncated at the second virial coefficient. The necessary values of the second virial coefficient of pure water were calculated as recommended by Harvey and Lemmon;[89] those of pure ethers were evaluated using either the Tsonopouolos[6,7] or Hayden−O'Connell[8] corresponding state correlations. The second cross virial coefficients for interactions between water and ethers were calculated from group contribution values.[90]

Some authors[53,91,92] have reported gas−liquid distribution constants for ethers in physiological saline solution (approximately 0.15 M NaCl aqueous solution). To recalculate these values into a pure water medium, one has to know the salting-out (Setschenow) coefficients for ethers in water. Xie et al.[93] observed a quasi-universal linear correlation between the salting-out coefficients in NaCl solutions and LeBas[7] molar volumes for a variety of organic compounds. This correlation was used by us to estimate the Setschenow coefficients for aqueous ethers and extrapolate observed distribution constants to pure water.

A major source of information is the ether−water mutual solubility data m_s and x_s, where m_s stands for the molal solubility of a compound dissolved in water, and x_s stands for the mole fraction of a solute liquid saturated with water. The following statement[3] gives the relation between m_s, x_s, and $\Delta_h G^\infty$:

$$\Delta_h G^\infty = \Delta_{sol} G^\infty - \Delta_{vap} G^\circ \tag{19}$$

where the standard molar Gibbs energy of solution ($\Delta_{sol}G^\infty$) is given by

$$\Delta_{sol} G^\infty = -RT \ln (m_s/m_o)\gamma_{m,2}/x_s f_{x,2} \tag{20}$$

where $\gamma_{m,2}$ stands for the activity coefficient of a solute in the saturated aqueous solution referenced to Henry's law,[5] and $f_{x,2}$ is the activity coefficient of a liquid solute saturated with water referenced to Raoult's law ($m_o = 1\ \text{m·kg}^{-1}$). Values of $f_{x,2}$ were calculated using the UNIQUAC[7] model, with the UNIQUAC parameters taken from ref 94 or evaluated by us from compositions of coexisting phases. The values of $\gamma_{m,2}$ were calculated using the Savage−Wood[39,40] model, as explained above. In general, mutual solubility data were employed only for the binary water + ether systems with m$_s$ less than 1 m·kg^{-1}, the expected concentration range of validity of the Savage−Wood group contribution model. For water + monoether systems calculated values of $f_{x,2}$ deviate from 1 by not more than 2%. However, the calculated values of $\gamma_{m,2}$ in saturated aqueous solutions of 1- and 2-methoxypropanes, for example, are as low as 0.6−0.7, indicating the importance of the concentration/activity correction for these solutes. For aqueous mixtures with diethers, deviations from ideality are significantly larger for both the water-rich and organic-rich coexisting phases, making estimates of $\Delta_{sol}G^\infty$ more uncertain.

Another source of data, which was not previously employed by our group, is water−alkane partition data for organic compounds. Such data are reported for ethers by a number of research groups.[95−97,50] Water−solvent partition coefficients are usually[98,99] designated by the symbol P (we use the abbreviation P^∞ to escape confusion with the symbol for pressure), and they are defined as the ratio of molar concentrations of a solute in coexisting organic and aqueous phases, respectively:

$$P^\infty = \lim_{c(\mathrm{aq})\to 0} \frac{c(\mathrm{org})}{c(\mathrm{aq})} \qquad (21)$$

where c stands for the concentration per 1000 cm^3 of solvent. There are two main pathways to convert data on water−solvent partition coefficients to the values of the Gibbs energy of hydration of a solute.

First, P^∞ data can be combined with values of the gas-solvent partition coefficients (L) defined as $L = \lim_{c(\mathrm{org})\to 0} c(\mathrm{org})/c(\mathrm{g})$, to give values of the gas−water distribution constants ($K_{\mathrm{D,c}}$):

$$K_{\mathrm{D,c}} = \frac{P^\infty}{L} \qquad (22)$$

The relation between $K_{\mathrm{D,c}}$ and $\Delta_h G^\circ$ is given by eq 17. Equation 22 is especially useful for the case of water−hexadecane partitioning, because accurate values of the gas−hexadecane partition coefficients are determined for many hundreds of organic compounds by Abraham and co-workers.[96,100−102] Note that the occasionally used assumption that water-alkane partition coefficients are independent of the nature of an alkane contradicts the UNIFAC model and can result in an error of up to 30 rel. % in the P^∞ value or about 1 $\mathrm{kJ{\cdot}mol^{-1}}$ in the calculated $\Delta_h G^\circ$ value.

Second, P^∞ data can be used to calculate the value of the infinite dilution activity coefficient of a solute in water (γ^∞) according to the relation:

$$\gamma^\infty = P^\infty\left(\frac{N_{\mathrm{w}}}{N_{\mathrm{org}}}\right)\gamma^\infty_{\mathrm{org}} \qquad (23)$$

where $\gamma^\infty_{\mathrm{org}}$ stands for the infinite dilution activity coefficient of a solute in an organic solvent, and N_{w} and N_{org} designate of the number of moles of water and an organic solvent in 1000 cm^3 of pure water or the organic solvent, respectively. The factor $N_{\mathrm{w}}/N_{\mathrm{org}}$ simply converts the partition constant from the molarity concentration scale to the mole fraction concentration scale. For ethers, $\gamma^\infty_{\mathrm{org}}$ values are experimentally determined[24,29] for a few ether + alkane systems. These values were employed by us, after recalculating, if necessary, to 298.15 K by means of eq 13. In most cases the values of $\gamma^\infty_{\mathrm{org}}$ were estimated using the group contribution UNIFAC model.[7] We checked that for experimentally studied ether + alkane systems the UNIFAC estimates are in very good agreement with the measured values. Relations given by eqs 22 and 23 are only valid in cases where water and another solvent are practically immiscible. This circumstance determined our decision to employ only data for partition of ethers between water and alkanes.

Results of data evaluation for the standard partial molar Gibbs energy of hydration ($\Delta_h G^\infty$) at 298.15 K, 0.1 MPa are given in Table 4. The 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: γ^∞ denotes the activity coefficient at infinite dilution; $K_{\mathrm{D,c}}$ means the gas−water distribution constant in the molarity scale; Sol denotes values evaluated from mutual solubility data; k_{H} denotes Henry's constants; P^∞ stands for water−alkane partition coefficients. Accepted values of $\Delta_h G^\infty$, together with their estimated uncertainties, are given in the fourth column. For most compounds the assigned uncertainty represents our judgment of the accuracy of the available data. More information related to our critical data evaluation (the method used, primary data reported, estimated uncertainty, comments) is available in our online database at http://orchyd.asu.edu.

Temperature Corrections to the Standard Partial Molar Gibbs Energy of Hydration. In cases where experimental data are reported at temperatures others than 298.15 K, the resulting values of $\Delta_h G^\infty$ were recalculated to 298.15 K using the approximation that $\Delta_h C_p^\infty(T) = \Delta_h C_p^\infty(298.15\ \mathrm{K}) = \mathrm{const}$. The following relation is consistent with this approximation[3]:

$$\Delta_h G^\infty(T_{\mathrm{r}}) = \Delta_h G^\infty(T)\frac{T_{\mathrm{r}}}{T} + \Delta_h H^\infty(T_{\mathrm{r}})\frac{T - T_{\mathrm{r}}}{T} + \Delta_h C_p^\infty \frac{T_{\mathrm{r}}}{T}\left(T \ln\frac{T}{T_{\mathrm{r}}} - T + T_{\mathrm{r}}\right) \qquad (24)$$

where $T_{\mathrm{r}} = 298.15$ K.

Standard Partial Molar Volumes at 298.15 K, 0.1 MPa. Results of data evaluation for the standard partial molar volumes (V_2^∞) are given in Table 5. Accepted values of V_2^∞ together with their estimated uncertainties are given in the third column.

Determination of Group Contribution Values to the Thermodynamic Functions of Hydration Aliphatic Ethers at 298.15 K, 0.1 MPa: Preliminary Analysis. At the start of this discussion it should be emphasized that we assume that the estimated uncertainties of the thermodynamic functions of hydration of ethers, given in Tables 2 to 5, are close to their true uncertainties. Among different group contribution methods,[198] the simplest is the first-order group contribution method. This method assumes that the properties of a group, $\mathrm{CH_2}$ for example, are identical in all types of organic compounds, independent of its neighbors. In the framework of the simplest first-order method, ethers can be constructed from $\mathrm{CH_3}$, $\mathrm{CH_2}$, CH, C, and O groups. However, such an attempt reproduces thermodynamic properties of aqueous ethers with errors that often grossly exceed the expected uncertainties of the experimental data.

At first sight, the whole concept of group contribution has only a limited application to aqueous ethers. For example, one can consider the change of the Gibbs energies of hydration in the series methoxymethane−ethoxyethane−1,1′-oxybispropane−1,1′-oxybisbutane. Each next member of this series is obtained by addition of two $\mathrm{CH_2}$ groups to the previous one. From our treatment[3] of numerous data for the Gibbs energy of hydration for aliphatic hydrocarbons, alcohols, ketones, and esters, the contribution of one $\mathrm{CH_2}$ group to the $\Delta_h G^\infty$ function is 0.7 $\mathrm{kJ{\cdot}mol^{-1}}$. Therefore, the addition of two $\mathrm{CH_2}$ groups is expected to increase the values of the Gibbs energy of hydration by 1.4 $\mathrm{kJ{\cdot}mol^{-1}}$. However, the following values of $\Delta_h G^\infty$ (in $\mathrm{kJ{\cdot}mol^{-1}}$) are obtained, see Table 4, for the series methoxymethane−ethoxyethane−1,1′-oxybispropane−1,1′-oxybisbutane: 0.05 ± 0.20; -0.13 ± 0.30; 2.85 ± 0.40; and 3.97 ± 1.00. It appears that ethoxyethane does not belong to this series, being rather the first member of another series: ethoxyethane−1-ethoxypropane−1-ethoxybutane ..., where the change of $\Delta_h G^\infty$ along the series approximately corresponds to the contribution of one $\mathrm{CH_2}$ group. Other examples include attempts to "build" 1,2-dimethoxymethane and 1,2-dimethoxyethane from the O group, evaluated from methoxymethane, by adding $\mathrm{CH_2}$ groups and subtracting $\mathrm{CH_3}$ groups. Estimated in this way the values of $\Delta_h G^\infty$are approximately 10 and 2 $\mathrm{kJ{\cdot}mol^{-1}}$ more negative than the experimental data for 1,2-dimethoxymethane and 1,2-dimethoxyethane, respectively. The physical reason for this behavior is expected to be the mutual polarization of oxygen molecules in diethers, which decreases the strength of oxygen-water interactions. The effect is particularly strong in acetals, where two oxygen molecules are separated by a single methylene group. Dipole−dipole interactions are of relatively short range, but the magnitude of the effect is so large that it is clearly

Table 4. Gibbs Energy of Hydration of Ethers at 298.15 K and 0.1 MPa. Experimental and Group Contribution (GC) Values

compound	$\Delta_{vap}G^o$ kJ·mol^{-1}	Δ_hG^o kJ·mol^{-1}	accepted value	I order GC value	Δ kJ·mol^{-1}	II order GC value	Δ kJ·mol^{-1}
methoxymethane		0.30 $P^{\infty 50\,a}$, 0.10 $k_H^{86\,b}$, 0.30 $k_H^{52\,b}$, −0.32 $k_H^{87\,c}$, −0.21 $K_{D,c}^{53\,d,e}$, **0.05** k_H^{103}	0.05 ± 0.20	−0.11	0.16	−0.13	0.18
methoxyethane		0.56 $P^{\infty 50\,a}$	0.56 ± 0.50	0.59	−0.03	0.64	−0.08
1-methoxypropane	1.27 ± 0.05^9	0.19 $P^{\infty 50\,a}$, 1.09 Sol^{11}, 0.95 Sol^{104}, 1.22 Sol^{54}	0.93 ± 0.40	1.29	−0.36	1.32	−0.39
2-methoxypropane	0.58 ± 0.05^9	0.48 Sol^{11}, 0.37 Sol$^{105\,f}$, 0.52 Sol^{54}	0.46 ± 0.40	0.78	−0.32	0.77	−0.31
ethoxyethane	0.91 ± 0.05^7	−**0.02** $\gamma^{\infty 55\,g}$, −0.41 $P^{\infty 50\,a}$, −**0.11** $\gamma^{\infty 56}$, −**0.04** $k_H^{106\,h}$, −0.49 $K_{D,c}^{107\,i}$, −0.63 $K_{D,c}^{107\,j}$, −0.13 $P^{\infty 108\,k,b}$, -0.63 $K_{D,c}^{109\,l}$, 0.10 $K_{D,c}^{91\,l,e}$, −0.05 $P^{\infty 96\,m}$, **0.02** $\gamma^{\infty 57\,n}$, −0.03 $\gamma^{\infty 110\,b}$, −0.03 $K_{D,c}^{111\,l,o}$, −0.32 $K_{D,c}^{112}$, −**0.25** $P^{\infty 95\,p}$, −0.05 $K_{D,c}^{53\,q,e}$, −0.22 $K_{D,c}^{113\,n}$, 0.18 $\gamma^{\infty 88}$, −0.18 $K_{D,c}^{114\,l}$, −0.20 $K_{D,c}^{115}$, −0.06 $K_{D,c}^{116\,l}$, −0.43 $K_{D,c}^{117\,q}$, −0.19 $K_{D,c}^{118\,r}$	-0.13 ± 0.30	−0.03	−0.10	−0.01	−0.12
1-ethoxypropane	$3.56 \pm 0 \times 10^9$	0.62 $P^{\infty 50\,a}$, 0.50 Sol^{11}, 1.29 Sol^{119}, 0.50 Sol^{54}	0.73 ± 0.4	0.67	0.06	0.67	0.06
2-ethoxypropane	2.72 ± 0.10^s	0.87 Sol^{11}, 0.87 Sol^{54}	0.87 ± 0.6	1.48	−0.61	1.54	−0.67
1-methoxy-2-methyl-propane	3.07 ± 0.15^s	1.24 Sol^{11}, 0.95 Sol^{120}, **2.08** Sol^{54}	1.90 ± 0.5	2.54	−0.64	2.43	−0.53
2-methoxy-2-methyl-propane	2.77 ± 0.05^9	−**0.34** Sol^{121}, −**0.44** Sol^{122}, −0.81 $K_{D,c}^{123}$, −**0.55** $\gamma^{\infty 55\,g}$, 0.51 $K_{D,c}^{58}$, −**0.57** $K_{D,c}^{124\,t}$, −**0.75** $\gamma^{\infty 56}$, −0.01 Sol$^{125\,u}$, −1.25 Sol^{46}, −**0.66** $K_{D,c}^{126}$, 0.76 $K_{D,c}^{127}$, −0.10 Sol^{128}, −0.84 $K_{D,c}^{129\,h}$, −0.57 $K_{D,c}^{130\,l}$, 0.45 Sol^{131}, −2.11 $K_{D,c}^{132}$, 0.06 Sol^{133}, −0.12 Sol^{134}, −0.67 $K_{D,c}^{92\,l,e}$, 0.41 Sol^{47}, −1.56 $K_{D,c}^{135}$, −1.02 $\gamma^{\infty 136}$, 0.03 Sol$^{60\,v}$, −0.37 Sol^{137}, −**0.34** Sol^{61}, −0.66 Sol^{11}, −0.58 Sol^{120}, −0.26 Sol$^{138\,b}$, −0.77 Sol^{54}	-0.48 ± 0.4	−0.46	−0.04	−0.46	0.04
1-methoxybutane	4.22 ± 0.05^9	1.28 $P^{\infty 50\,a}$, 1.52 Sol^{11}, 1.52 Sol^{54}	1.44 ± 0.4	1.99	−0.55	2.00	−0.56
2-methoxybutane	3.12 ± 0.10^s	2.04 Sol^{11}, 0.80 Sol^{54}	1.42 ± 0.7	1.48	−0.06	1.45	−0.03
1-methoxypentane	7.10 ± 0.30^s	2.02 $P^{\infty 50\,a}$	2.02 ± 1.0	2.69	−0.67	2.68	−0.66
2-propoxypropane	5.42 ± 0.15^s	1.99 Sol^{11}, 2.85 Sol^{54}	2.42 ± 0.5	2.18	0.24	2.22	0.20
1-ethoxybutane	6.44 ± 0.10^s	1.76 $K_{D,c}^{139\,b}$, 1.92 $P^{\infty 50\,a}$, 1.48 $K_{D,c}^{129\,h}$, 0.75 Sol$^{60\,b}$	1.57 ± 0.5	1.37	0.20	1.35	0.22
1-propoxybutane	9.22 ± 0.30^s	1.38 $P^{\infty 50\,a}$	1.38 ± 2.0	3.39	−2.01	3.45	−2.07
1-methoxyhexane	10.03 ± 0.30^s	2.52 $P^{\infty 50\,a}$	2.52 ± 1.0	3.39	−0.87	3.36	−0.84
1,1′-oxybispropane	6.18 ± 0.05^9	**2.99** $\gamma^{\infty 55\,g}$, 1.38 $P^{\infty 50\,a}$, **2.95** γ^{∞} **140**, **2.69** $\gamma^{\infty 110\,b}$, −1.03 Sol$^{141\,l}$, 2.90 $K_{D,c}^{142\,w}$, 3.98 Sol^{143}, 3.02 Sol$^{54\,x}$, 1.40 Sol$^{54\,y}$	2.85 ± 0.40	2.69	0.16	2.77	0.08
2,2′-oxybispropane	$4.05 \pm 0 \times 10^9$	2.35 $K_{D,c}^{58}$, 2.50 Sol$^{144\,b}$, **2.03** $\gamma^{\infty 55\,g}$, 0.48 $P^{\infty 50\,a}$, **1.84** $\gamma^{\infty 56}$, 1.60 Sol^{145}, 4.45 $K_{D,c}^{146}$, 2.42 $K_{D,c}^{129\,h}$, −0.60 Sol^{147}, **1.92** $\gamma^{\infty 148\,z}$, **1.83** $\gamma^{\infty 148\,aa}$, **2.18** $k_H^{106\,h}$, **1.96** $\gamma^{\infty 149}$, **2.11** $\gamma^{\infty 140}$, 2.76 Sol$^{60\,b}$, 1.16 $K_{D,c}^{109\,l}$, 2.40 Sol^{150}, **1.89** $\gamma^{\infty 110\,b}$, 1.82 Sol$^{151\,b}$, 1.65 Sol$^{141\,l}$, 1.10 Sol$^{152\,bb}$, 1.18 Sol^{153}, 1.74 Sol^{154}, 1.55 Sol^{11}, 1.62 Sol^{155}, 2.43 Sol$^{156\,b}$, 1.50 Sol$^{157\,cc}$	1.91 ± 0.40	1.68	0.23	1.67	0.24
2-methoxy-2-methyl-butane	5.74 ± 0.10^s	**0.01** $\gamma^{\infty 55\,g}$, **0.72** $K_{D,c}^{58}$, −1.25 Sol^{46}, 1.98 $K_{D,c}^{129\,h}$, −**0.32** $K_{D,c}^{130\,l}$, **0.25** Sol^{64}, −**0.12** $\gamma^{\infty 148\,z}$, −**0.01** $\gamma^{\infty 148\,aa}$, 0.87 $K_{D,c}^{132}$, −0.40 $K_{D,c}^{92\,l,e}$, −0.40 Sol^{133}, −0.73 Sol^{134}, −0.14 Sol^{158}, −0.01 Sol^{47}, 0.36 Sol$^{60\,dd}$, 1.29 Sol^{137}, 0.24 Sol$^{159\,b}$, 0.04 Sol$^{138\,b}$	0.03 ± 0.40	0.24	−0.21	0.22	−0.19
2-ethoxy-2-methyl-propane	4.44 ± 0.05^s	**1.25** $K_{D,c}^{58}$, 1.39 Sol$^{125\,u}$, 2.51 $K_{D,c}^{129\,h}$, **0.17** $K_{D,c}^{130\,l}$, **0.31** $\gamma^{815\,ee}$, −0.76 Sol^{160}, 2.78 Sol$^{64\,ff}$, −0.20 Sol^{62}, **0.57** $\gamma^{\infty 63\,gg}$, 0.62 $K_{D,c}^{92\,l,e}$, −1.25 Sol^{137}, 1.37 Sol$^{138\,b}$	0.68 ± 0.60	0.24	0.44	0.31	0.37
2-ethoxy-2-methyl-butane	7.22 ± 0.10^s	3.90 Sol^{161},−0.03 Sol$^{64\,hh}$, 1.61 Sol$^{159\,b}$	1.36 ± 1.00	0.94	0.42	0.99	0.37
1,1′-oxybis-2-methyl-propane	9.47 ± 0.15^s	1.33 Sol^{162}	1.33 ± 3.00	5.19	−3.86	4.99	−3.66
1,1′-oxybisbutane	11.79 ± 0.10^s	1.83 $P^{\infty 50\,a}$, **4.93** $\gamma^{\infty 149}$, **3.65** $\gamma^{\infty 140}$, **4.04** Sol$^{60\,dd}$, 0.54 Sol^{163}, 3.39 Sol$^{164\,b}$, 3.76 Sol$^{165\,bb}$, 6.12 Sol$^{166\,b}$, −1.95 Sol$^{141\,l}$, −1.22 Sol^{153}, 2.84 Sol^{167}, 2.13 Sol$^{30\,b}$, −1.48 Sol$^{157\,hh}$	3.97 ± 1.00	4.09	−0.12	4.13	−0.16
1,2-dimethoxyethane	5.93 ± 0.10^s	−11.45 $P^{\infty 97\,a}$, −12.27 $\gamma^{\infty 168}$, −11.73 $\gamma^{\infty 169\,ii}$	-12.11 ± 0.5	−11.82	−0.29	−11.90	−0.21
1,3-dimethoxypropane	8.07 ± 0.30^s	−9.96 $P^{\infty 50\,a}$	-9.96 ± 3.0	−13.41	3.45	−13.44	3.48
1,2-diethoxyethane	9.78 ± 0.15^s	−10.47 $P^{\infty 97\,a}$, −10.08 Sol$^{43\,jj}$, −9.86 Sol$^{170\,c}$	-10.23 ± 0.4	−10.42	0.19	−10.36	0.13
1,4-dimethoxybutane	10.99 ± 0.30^s	−10.99 $P^{\infty 97\,a}$, −9.78 Sol^{171}	-10.76 ± 1.5	−12.71	1.95	−12.76	2.00
1,3-diethoxypropane	12.06 ± 0.30^s	−9.19 $P^{\infty 97\,a}$, −7.15 Sol^{171}	-8.78 ± 1.5	−12.01	3.23	−11.90	3.12
1,5-dimethoxypentane	14.03 ± 0.40^s	−12.55 $P^{\infty 97\,a}$, −11.40 Sol^{171}	-11.98 ± 1.0	−12.01	0.03	−12.08	0.10
1,4-diethoxybutane	14.82 ± 0.40^s	−11.02 $P^{\infty 97\,a}$, −8.92 Sol^{171}	-9.24 ± 1.5	−11.31	2.07	−11.22	1.98
1,2-dibutoxyethane	20.34 ± 0.40^s	−**6.82** Sol$^{43\,i}$, −9.35 Sol^{171} , −8.85 Sol$^{172\,c}$	-7.58 ± 1.5	−7.62	0.04	−7.64	0.06
1,2-dimethoxymethane	1.65 ± 0.10^s	−4.92 $\gamma^{\infty 31\,kk}$, −4.21 $P^{\infty 97\,a}$, −4.33 $\gamma^{\infty 173\,ll}$	-4.80 ± 0.50	−4.96	0.16	−5.03	0.23
1,1-diethoxymethane	6.00 ± 0.10^s	−3.52 Sol^{174} , −4.25 $P^{\infty 97\,a}$, −4.69 Sol$^{30\,i}$	-3.72 ± 0.50	−3.56	−0.16	−3.49	−0.23
1,1-diethoxyethane	7.85 ± 0.15^s	−6.03 Sol^{175}, −**4.94** Sol$^{176\,mm}$, −5.13 Sol$^{30\,nn}$, −4.96 Sol$^{177\,nn}$	-5.19 ± 0.50	−5.19	0	−5.19	0.00

[a] Water−heptane partition. [b] Recalculated from 293.15 K. [c] Recalculated from 323.15 K. [d] Recalculated from 293.5 K. [e] Data are reported for physiological saline and recalculated to a pure water medium as explained in the text. [f] Recalculated from 301.2 K. [g] Recalculated from 303.25 K. [h] Recalculated from 296.15 K. [i] Recalculated from 303.15 K. [j] Recalculated from 318.15 K. [k] Water−octane partition. [l] Recalculated from 310.2 K. [m] Water−hexadecane partition. [n] Recalculated from 308.15 K. [o] Data are reported for Krebs solution and recalculated to a pure water medium using the authors[111] statement that $K_{d,c}$ in water average 0.92 of value in Krebs solution. [p] Water−cyclohexane partition. [q] Recalculated from 293.3 K. [r] Recalculated from 299.2 K. [s] Calculated according to eq 1 from P_s values; see Table 1 and second virial coefficients.[6,8] [t] Recalculated from 294.65 K. [u] Recalculated from 295.35 K. [v] Recalculated from 292.9 K. [w] Recalculated from 285.7 K. [x] Synthetic method of solubility determination. [y] Volumetric method of solubility determination. [z] Inert gas stripping method. [aa] Exponential saturation method. [bb] Recalculated from 297.8 K. [cc] Recalculated from 297.2 K. [dd] Recalculated from 293.1 K. [ee] Recalculated from 313.15 K. [ff] Recalculated from 300.65 K. [gg] Recalculated from 293.42 K. [hh] Recalculated from 297.95 K. [ii] Recalculated from 373.15 K. [jj] Recalculated from 333.8 K. [kk] Recalculated from 293.4 K. [ll] Recalculated from 297.3 K. [mm] Medium is 0.001 M NaOH to prevent hydrolysis. [nn] Temperature is not specified, assumed to be 293.2 K

seen in compounds where oxygen molecules are separated by two methylene groups. Similar problems were encountered by Cabani et al.[199] in their group contribution analysis of the thermodynamic functions of hydration of a large database of organic compounds. These authors introduced O−$(CH_2)_n$−O corrections for diethers, stating that the values of the corrections

Table 5. Standard Partial Molar Volumes of Ethers at 298.15 K and 0.1 MPa. Experimental and Group Contribution (GC) Values

compound	V_2° / $cm^3 \cdot mol^{-1}$	accepted value	I order GC value	Δ / $cm^3 \cdot mol^{-1}$	II order GC value	Δ / $cm^3 \cdot mol^{-1}$
ethoxyethane	90.40[178], 90.50[179], 89.90[180], 90.40[181][a], 89.30[182][a]	90.4 ± 0.3	90.4	0	90.4	0.0
2,2-oxybispropane	115.0[178], 117.20[154][a]	115.4 ± 1.0	115.4	0	115.4	0.0
1,2-dimethoxyethane	95.06[183], 95.26[184], 94.84[185], 94.72[186], 96.08[187], 95.59[188], 95.89[189], 95.88[190], 95.85[191], 95.70[178] 95.45[179], 95.60[192], 95.60[193]	95.5 ± 0.4	95.46	0.04	94.25	1.25
1,2-diethoxyethane	126.34[188], 127.29[190]	126.8 ± 0.5	126.92	−0.12	128.75	−1.95
1,2-dimethoxymethane	80.47[187], 80.42[190], 80.50[178], 80.86[179]	80.6 ± 0.3	81.17	−0.57	80.36	0.24
1,1-dimethoxyethane	101.54[187]	101.5 ± 1.0	101.5	0	101.5	0.0
1,1-diethoxymethane	113.88[190], 114.59[179]	114.2 ± 0.5	112.63	1.57	114.86	−0.66
1,1′-oxybis(2-methoxy) ethane	132.42[184], 132.90[194], 132.69[189], 132.72[191], 132.40[178], 131.60[192]	132.6 ± 0.3	132.58	0.02	132.01	0.59
3,6,9-trioxaundecane	162.86[188], 164.16[85], 165.00[178]	164.1 ± 0.8	164.04	0.06	166.51	−2.41
2,5,8,11-tetraoxadodecane	169.6[195], 169.36[184], 170.3[196], 169.90[197], 169.18[188], 170.30[194], 169.63[189], 169.83[191], 169.00[193]	169.7 ± 0.5	169.70	−0.00	169.57	0.13
2,5,8,11,14-pentaoxapentadecane	205.95[184], 207.0[196], 207.30[197], 206.56[188], 207.10[194], 206.66[189], 206.88[191]	206.8 ± 0.5	206.83	−0.02	207.12	−0.32

[a] Our calculation of V_ϕ from published density of saturated solution.

decrease with increasing distance between O atoms "following an exponential law".

These examples demonstrate the limitations of the first-order group contribution method for reproducing the thermodynamic properties of aqueous ethers and, particularly, polyethers. It is important to note that the mutual effect of oxygen atoms is seen even beyond the nearest neighbors. Usually, the suggested remedy to improve the performance of the first-order method is to select larger groups, which include fragments of molecules containing atoms with strong mutual interactions. Within the framework of the first-order group contribution method there are too many choices to select a new set of groups. Therefore, we started our quantitative data treatment employing the second-order group contribution method, which explicitly accounts for nearest-neighbor interactions.

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:[84,200] 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 $O{-}(C)_2$ represents the O group connected to two C atoms. The groups necessary to represent the selected set of compounds are $C{-}(C)(H)_3$, $C{-}(C)_2(H)_2$, $C{-}(C)_3(H)$, $C{-}(O)(H)_3$, $C{-}(C)(O)(H)_2$, $C{-}(C)_2(O)(H)$, $C{-}(C)_3(O)$, $C{-}(C)(O)_2(H)$, $C{-}(H)_2(O)_2$, $O{-}(C)_2$. Following existing practice,[200,3] we accepted the identity of the second-order groups $C{-}(O)(H)_3 = C{-}(C)(H)_3$. We call this set "minimal", because the analysis of data may show the need for adding new groups or corrections.

Preliminary Calculations. For a number of groups, $C{-}(C)(H)_3$, $C{-}(C)_2(H)_2$, $C{-}(C)_3(H)$, $C{-}(C)(O)(H)_2$, we employed values from Plyasunov et al.[3], determined by fitting a large database of aliphatic hydrocarbons, alcohols, ketones and esters. The attempt to describe the whole dataset of mono-, di-, and polyethers by the "minimal" set of groups for the second-order group contribution method listed above worked well for the partial molar volumes, but failed for all caloric properties of hydration. The greatest disagreement between compiled experimental and group contribution values of the functions of hydration was observed for the series ethoxyethane−1-ethoxypropane−1-ethoxybutane, diethers, and polyethers. Calculated values of the Gibbs energy of hydration for the ethoxyalkanes were systematically more positive (by more than 2 $kJ \cdot mol^{-1}$) than experimental determinations; for polyethers the difference exceeded 4 $kJ \cdot mol^{-1}$. In contrast, for diethers group contribution values of $\Delta_h G^\infty$ were more negative and, for the case of 1,2-dimethoxyethane, by as much as 3 $kJ \cdot mol^{-1}$. Although the datasets for the enthalpy and heat capacity of hydration are generally less representative, they also demonstrated a systematic disagreement between experimental and calculated values of the functions of hydration using the overall fit for ethers. The disagreement observed for the properties of hydration is caused by third- or higher-order effects, which are noted and discussed above. The simplest way to account for the third-order effects in the framework of the second-order group contribution method is to add corresponding corrections.

After a number of trials we selected the following corrections and rules for their implementation. First, we introduce the "ethoxyalkane", $\{CH_3{-}CH_2{-}O{-}CH_2\}$ correction, which should be applied to monoethers containing this structural unit. This correction should not be used for di- and polyethers. Second, for diethers and polyethers we introduce a "diether", $\{O{-}(CH_2)_2{-}O\}$ correction, which should be applied for compounds having this structural fragment. There are indications that the O−O interaction is strong enough even when the oxygen atoms are separated by 3 or even more methylene groups, however, available data are not sufficiently accurate to justify the corresponding corrections. In any case it is expected that the effects of the mutual polarization of the oxygen atoms would strongly diminish with additional CH_2 groups.

By including these corrections, the resulting fit was statistically much better for all the thermodynamic functions of hydration. Nevertheless, the experimental values of the enthalpy hydration of polyethers could not be satisfactorily reproduced. Finally, we decided to exclude $\Delta_h H^\infty$ data for polyethers from the fitted dataset. Quantitative description of these properties have to wait until we have examine data for other derivatives of glycols. In any case, the ordering placement of oxygen atoms in the structure of these compounds significantly changes their properties compared to those of mono- and diethers. For the partial molar heat capacity of hydration we did not observe a significant improvement of the fit by excluding polyethers. This might be due to the scarcity of the data and bigger uncertainties in the experimental values. On the other hand, the effects seen

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 Second Order Method[a]

group	$\Delta_h G°$ kJ·mol^{-1}	$\Delta_h H°$ kJ·mol^{-1}	$\Delta_h C_p°$ J·K^{-1}·mol^{-1}	$V_2°$ cm^3·mol^{-1}
Y_o	7.95	−2.29	0	1.12
$C-(C)_2(H)(O)_{ether}$	−2.82 ± 0.30 (5)	0 fixed (5)	(0)	3.69 (1)
$C-(C)_3(O)_{ether}$	−7.77 ± 0.46 (4)	0 fixed (3)	−102 (1)	(0)
$O-(C)_2$	−15.52 ± 0.20 (34)	−13.76 ± 1.39 (27)	−96 ± 9 (12)	4.65 ± 0.89 (11)
$C-(H)_2(O)_2$	10.63 ± 0.72 (2)	5.08 (1)	118 ± 20 (2)	18.81 ± 1.85 (2)
$C-(C)(H)(O)_2$	5.21 (1)	4.87 (1)	(0)	14.39 (1)
$\{CH_3\text{-}CH_2\text{-}O-CH_2\}$	−1.42 ± 0.41 (3)	−3.34 ± 2.11 (2)	0 fixed (1)	−0.99 (1)
$\{O-(CH_2)_2-O\}$	2.22 ± 0.65 (3)	−3.79 ± 2.81 (6)	1 ± 16 (8)	−1.60 ± 1.25 (6)
$C-(C)(H)_3$	3.72 ± 0.07[b]	−8.19 ± 0.18[b]	132 ± 4[b]	25.56 ± 0.64[b]
$C-(C)_2(H)_2$	0.68 ± 0.03[b]	−3.52 ± 0.09[b]	62 ± 2[b]	15.61 ± 0.11[b]
$C-(C)_3(H)$	−1.93 ± 0.16[b]	2.34 ± 0.54[b]	−17 ± 10[b]	5.96 ± 0.80[b]
$C-(C)(H)_2(O)$	0.77 ± 0.20[b]	−5.17 ± 0.40[b]	68 ± 6[b]	17.25 ± 0.50[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.[3]

in the Gibbs energy and enthalpy of hydration might have less influence on the heat capacity of hydration, the next derivative function. In fitting the overall set of partial molar volumes, including polyethers, we found that assuming the identity of the groups $C-(O)(H)_3$ and $C-(C)(H)_3$ worsens the agreement between the experimental and fitted values compared to the case where the groups are considered different. The latter gives for $C-(O)(H)_3$ $V_2^\circ = 26.7 \pm 0.2$ cm^3·mol^{-1}; the value for $C-(C)(H)_3$ from our previous study[3] is 25.56 ± 0.64 cm^3·mol^{-1}. The two values appear to be statistically different, however, the result for V_2° of the $C-(O)(H)_3$ group is obtained from only 3 compounds. We decided to not separate these groups in this study, especially taking into account that no such differences in values for $C-(O)(H)_3$ and $C-(C)(H)_3$ groups were observed for the other thermodynamic functions of hydration. Consideration of other derivatives of glycols may clarify this situation.

Optimal Values of the Contributions of Second-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

$$Y = Y_o + \sum_i n_i Y_i + \sum_j n_j Y_j \qquad (25)$$

The first summation (the running index i) is for the second-order functional groups. The second summation (the running index j) is for the corrections for third- or higher-order effects (i.e., for effects that are expressed beyond the nearest neighbors). The first term on the right-hand side of eq 25 (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[201] (see Plyasunov et al.[3] for details).

Values of Y_i and Y_j of eq 25 for ether groups were obtained by a weighted least-squares fitting procedure. Results for the O-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. No determinations of the second-order group contribution values are possible for V_2^∞ of the group $C-(C)_3(O)$, and for $\Delta_h C_p^\infty$ of the groups $C-(C)(H)(O)_2$ and $C-(C)_2(H)(O)$ due to the absence of data. It should be emphasized that the Gibbs energy and enthalpy of hydration of individual groups listed in Table 6 were obtained without consideration of polyethers and, therefore, should not be used to calculate these properties for polyethers.

Determination of the First-Order Group Contribution Values to the Thermodynamic Functions of Hydration at 298.15 K, 0.1 MPa: Optimal Values of the Contributions of First-Order Groups to Thermodynamic Functions of Hydration at 298.15 K, 0.1 MPa. As in the case of the second-order approach, we used eq 25 as a basis for evaluating the properties of individual groups. As described above, an attempt to reproduce the thermodynamic properties of ethers using only one "ether", O, group, was completely unsuccessful. Analysis of data in the framework of the second-order group contribution method called for introduction of a number of corrections in addition to the O group. These corrections are also necessary to improve the performance of the first-order group contribution method.

First, we introduce two "acetal" corrections, $\{O-CH_2-O\}$ and $\{O-CH(CH_3)\text{-}O\}$, for compounds having these structural fragments. Then, as in the case of the second-order method, we accept the "diether", $\{O-CH_2)_2-O\}$, and the "ethoxyalkane", $\{CH_3-CH_2-O-CH_2\}$, corrections. Finally, we introduce "tertiary", $\{C_{tert}\text{-}O\}$, and "ternary", $\{HC_{tern}\text{-}O\}$, corrections, applied to compounds with direct contacts of tertiary and ternary carbon atom with oxygen. The last two structural variations are present in the current database only for monoethers, and it is unclear if their use should be extended for diethers and polyethers. Note that the necessity of the correction for the contact of a tertiary carbon atom with a polar functional group was found previously for aqueous alcohols, ketones and esters[3] and thiols.[4] However, ethers are the first class of compounds where we have to introduce the "ternary" correction.

As in the case of the second-order method, preliminary runs showed very poor reproduction of experimental values of $\Delta_h G^\infty$ and $\Delta_h H^\infty$ in the overall fit including polyethers. Thus, polyethers were excluded from the fitting procedure for the Gibbs energy and enthalpy of hydration. The final results for the first-order group contribution properties of hydration of individual groups are shown in Table 7. As before, we applied a weighted least-squares fitting procedure to derive numerical values for the contributions, and 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.

Discussion

Aqueous aliphatic mono- and polyethers represent classes of organic compounds, for which both the first- and the second-order group contribution methods appear inadequate for accurate reproduction of thermodynamic functions of hydration. It

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 First-Order Method[a]

group or correction	$\Delta_h G^\circ$ kJ·mol^{-1}	$\Delta_h H^\circ$ kJ·mol^{-1}	$\Delta_h C_p^\circ$ J·K^{-1}·mol^{-1}	V_2° cm^3·mol^{-1}
Y_o	7.95[b]	−2.29[b]	0[b]	1.12[b]
O	−15.40 ± 0.21 (34)	−15.60 ± 2.88 (27)	−88 ± 14 (12)	6.24 ± 0.51 (11)
$(HC_{ter}\text{-}O)_{corr}$	−1.05 ± 0.31 (5)	0 fixed (5)	(0)	−3.39 (1)
$(C_{tert}\text{-}O)_{corr}$	−3.17 ± 0.47 (4)	−9.32 ± 5.50 (3)	−10 (1)	(0)
$\{CH_3\text{-} CH_2\text{-}O-CH_2\}_{corr}$	−1.31 ± 0.42 (3)	−4.91 ± 4.01 (2)	6 (1)	0.60 (1)
$\{O-(CH_2)_2-O\}_{corr}$	−2.30 ± 0.67 (3)	−5.25±5.80 (6)	56 ± 24 (6)	−0.57 ± 0.72 (2)
$\{O-CH_2-O\}_{corr}$	9.85 ± 0.73 (2)	12.04 (1)	47 ± 29 (2)	1.87 ± 1.06 (2)
$\{O-CH(CH_3)\text{-}O\}_{corr}$	6.97 (1)	3.81 (1)	(0)	5.01 (1)
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.[3]

appears that the regular placement of O atoms in the structure of diethers and polyethers changes the properties of the structural units constituting a compound. This effect is clearly seen in diethers, with two O atoms separated by two methylene groups, and it may be present in compounds where the distance between O atoms is even greater. The cause of this phenomenon, the mutual polarization of oxygen molecules, decreases the strength of oxygen-water interactions. As a result, one has to account for third- and perhaps higher- order effects, which are expressed beyond the nearest neighbors. In the current study these effects are included through the introduction of a number of corrections.

For the second-order group contribution method there are two additional corrections: the "ethoxyalkane" correction, $\{CH_3-CH_2-O-CH_2\}$, applicable for monoethers only, and the "diether" correction, $\{O-(CH_2)_2-O\}$. However for diethers with 3 and 4 CH_2 groups separating the oxygen atoms (1,4-dimethoxybutane, 1,4-diethoxybutane and 1,3-diethoxypropane) the differences between experimental and fitted values for $\Delta_h G^\infty$- were larger than the accepted uncertainties. This may signal the necessity to introduce corrections even for 3 and 4 carbon groups between the O atoms, but the amount and quality of the corresponding experimental data so far available would not justify such corrections. The "diether" correction improves the reproduction of the properties of polyethers as well, but is insufficient on its own to yield a quantitative reproduction of the enthalpy of hydration for polyethers. The problem of description of $\Delta_h G^\infty$ and $\Delta_h H^\infty$ for these compounds has to wait until we can incorporate other derivatives of glycols.

We found it possible to fix the values of the properties of hydration for the group $C-(C)(H)_2(O)$ at the results obtained previously[3] by fitting a large dataset of organic oxygen-containing compounds including alcohols, ketones and esters. However, for the groups $C-(C)_2(H)(O)$ and $C-(C)_3(O)$ the absolute values of the functions of hydration, determined in this work, appear to be very different from those for aqueous alcohols and esters[3], thus the groups are assigned "ether" subscripts in the current study. The differences among these stoichiometrically identical groups in the three classes of compounds stems from different oxygen atom environments: the "ester", $COO-(C)_2$, group in esters, hydrogen atom in alcohols, and hydrocarbon groups in ethers. Thus, the difference in absolute values of the functions of hydration for these groups is caused by effects of third-order interactions.

The first-order group contribution method, in its simplest formulation, shows clear and expected limitations in the reproduction of the thermodynamic properties of aqueous mono- and polyethers. For example, its application to acetals, compounds having the structural unit $O-CH_2-O$, is accompanied by an error of up to 10 kJ·mol^{-1} in the value of the Gibbs energy of hydration. In fact, only linear monoethers without the "ethoxyalkane" group can be described more or less accurately using the first-order group contribution approach. The performance of this additivity method can be considerably improved by introduction of specific corrections. However, the list of these corrections is large, see above. The reader may check our selection of groups for each of the compounds in this study at http://orchyd.asu.edu.

Our result for the first-order group contribution value for the Gibbs energy of hydration of the oxygen group, O, is similar to that of Cabani et al.:[199] (−15.40 ± 0.21) kJ·mol^{-1} in this study versus −15.77 kJ·mol^{-1} in ref 199. However, the results for enthalpy, heat capacity and molar volume are rather different, which is not surprising given that only 1 primary source was used by Cabani et al. for evaluation of these functions. In contrast, we used 27 primary data sources for $\Delta_h H^\infty$, 12 primary data sources for $\Delta_h C_p^\infty$, and 11 data sources for V_2°. We would like to emphasize the importance of working with a large and diverse set of compounds when determining the values of the group contributions to the thermodynamic properties. Many deficiencies of the first- and second-order group contribution methods would have been overlooked had we been dealing only with monoethers, or with a smaller overall set of compounds.

Additional experimental studies are needed for aqueous ethers. As already mentioned, no determinations were possible for V_2^∞ of the second-order group $C-(C)_3(O)$, and for $\Delta_h C_p^\infty$ of the groups $C-(C)(H)(O)_2$ and $C-(C)_2(H)(O)$, and their corresponding first-order corrections due to the absence of data. To cover the existing gaps in data, additional measurements of all properties for acetals, containing the groups $C-(H)_2(O)_2$ and $C-(H)(C)(O)_2$, would be helpful. Precise measurements of the heat capacity and density of aqueous solutions of ethers with ternary and tertiary carbon atoms are also needed, as well as measurements for ethoxyalkanes different from ethoxyethane. We could not find in the open literature any information leading to the evaluation of the Gibbs energy of hydration for glymes (di-, tri-, and tetraethylene glycol dimethyl ethers). Experimental studies of these properties would expand the usefulness and accuracy of group contribution models.

Future Directions

Thermodynamic properties of aqueous organic compounds are of great technological and societal importance. Perhaps the most useful applications of these properties are for understanding the fate of organic pollutants in an aqueous environment (Henry's constant, solubility) and for discovery of drugs with favorable ADME (absorption, distribution, metabolism, and excretion) properties (first of all solubility). These are areas of very active research programs that are oriented to predicting properties using many types of experimentally and theoretically derived descriptors combined with sophisticated computer algorithms for data treatment.[202] The shortcoming of these efforts for aqueous systems is the lack of properly documented and verifiable databases of properties together with uncertainty estimates. As a rule, researchers themselves compile data sets necessary for their work, usually from secondary sources. The estimates of uncertainties of experimental and predicted data differ widely. Some authors[203] state that "the estimated uncertainty of the experimental data is no less than 0.5 log unit", which may be too pessimistic for many aqueous compounds. Other groups[204] achieve correlation of Henry's law constant "with average absolute errors of 0.03 log units", which, in our opinion, is significantly less than the uncertainty of data for most organic chemicals in water. Tests of different predictive schemes against properly documented and verifiable database, containing reliable uncertainties estimates, will be useful to clarify the situation and objectively evaluate the merits of various proposed methods. Goldberg et al.[205] discussed this problem and emphasized the importance of a truly representative database: "It is these tables of thermodynamic data that can most profitably be used for the development of estimation methods. ... These thermodynamic tables are useful not only for reproducing the experimental results ..., but also for the calculation of thermodynamic quantities that have not been directly measured. Therefore, the more extensive these tables are, the more valuable they become".

Another question relates to the application of the second order (Benson) group contribution method to aqueous organic compounds. "...the Benson group estimation method ... has proved extremely useful for gaseous and condensed-phase organic compounds ...".[205] It is safe to say that modern thermochemical studies of organic compounds are systematically aimed at the determination of numerical values for new functional groups or on revision of older and less accurate values, see Steele et al.[206] and Roganov et al.[207] as relevant examples. It is somewhat surprising that among the bewildering variety of methods proposed to correlate and predict properties of organic compounds in water the Benson method, with few exceptions,[208−210] has not received the attention it deserves. Our previous studies[1−4] were concerned mainly with monofunctional compounds. The current work is our first systematic account of polyfunctional compounds, di- and polyethers. We have found, in agreement with earlier tests,[211] that the first-order group contribution method without corrections for the intramolecular interaction of groups is very inaccurate, with errors in the Gibbs energy as high as 10 $\mathrm{kJ \cdot mol^{-1}}$ (see above). However, the necessary number of corrections is very large (see Table 7), and it appears that further development of the first-order method may be not worthwhile. A very large number of errors is intrinsically impossible for the second-order method. Nevertheless, dipole−dipole O−O intramolecular interactions are expressed beyond the nearest neighbors, which is the range of interaction explicitly accounted for by the second-order group contribution method. The corrections for higher-order effects are as large as 2 and 4 $\mathrm{kJ \cdot mol^{-1}}$ for the Gibbs energy and enthalpy of hydration of diether, respectively, see Table 6.

Summing up our experience, we note that a representative database of properties, containing compounds with various structures, is necessary to find out the minimal set of groups capable of an accurate reproduction of thermodynamic properties, especially for polyfunctional compounds. It appears that in addition to the traditional Benson groups, corrections for higher-order effects are necessary for the thermodynamic function of hydration of organic compounds containing several polar functional groups.

Acknowledgment

The authors are grateful to Dr. N. W. Boaz (Eastman Chemical Company, USA) for providing us with additional information regarding the diethoxymethane aqueous solubility data reported in ref 174. We also thank Prof. Ming-Jer Lee (National Taiwan University of Science & Technology) for allowing our access to vapor pressure data from his laboratory in advance of publication.

Literature Cited

(1) Plyasunov, A. V.; Shock, E. L. Thermodynamic functions of hydration of hydrocarbons at 298.15 K and 0.1 MPa. *Geochim. Cosmochim. Acta* **2000**, *64*, 439−468.

(2) Plyasunov, A. V.; Shock, E. L. Group contribution values of the infinite dilution thermodynamic functions of hydration for aliphatic non-cyclic hydrocarbons, alcohols and ketones at 298.15 K and 0.1 MPa. *J. Chem. Eng. Data* **2001**, *46*, 1016−1019.

(3) Plyasunov, A. V.; Plyasunova, N. V.; Shock, E. L. Group contribution values for the thermodynamic functions of hydration of aliphatic esters at 298.15 K, 0.1 MPa. *J. Chem. Eng. Data* **2004**, *49*, 1152−1167.

(4) Plyasunova, N. V.; Plyasunov, A. V.; Shock, E. L. Group contribution values for the thermodynamic functions of hydration at 298.15 K, 0.1 MPa. 2. Aliphatic thiols, alkyl sulfides and polysulfides *J. Chem. Eng. Data* **2005**, *50*, 246−253.

(5) Mills, I.; Cvita, T.; Homann, K.; Kallay, N.; Kuchitsu, K. *Quantities, Units and Symbols in Physical* Chemistry; Blackwell Science: Oxford, 1993.

(6) Tsonopoulos, C. An empirical correlation of second virial coefficients. *AIChE J.* **1974**, *20*, 263−272.

(7) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids;* McGraw-Hill: New York, 2001.

(8) Hayden, J. G.; O'Connell, J. P. A generalized method for predicting second virial coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209−216.

(9) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1987.

(10) Majer, V.; Svoboda, V.; Pick, J. *Heats of Vaporization of Fluids;* Elsevier: Amsterdam, 1989.

(11) Marsh, D. F.; Leake, C. D. The comparative anesthetic activity of the aliphatic ethers. *Anesthesiology* **1950**, *11*, 455−463.

(12) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds*; Blackwell: Oxford, 1985.

(13) Li, P.; Ma, P.-S.; Yi, S.-Z.; Zhao, Z.-G.; Cong, L.-Z. A new corresponding-states group-contribution method (CSGC) for estimating vapor pressures of pure compounds. *Fluid Phase Equilib.* **1994**, *101*, 101−119.

(14) Boublik, T.; Fried, V.; Hala, E. *The Vapour Pressures of Pure Substancse*; Elsevier: Amsterdam, 1984.

(15) Rarey, J.; Horstmann, S.; Gmehling, J. Vapor−liquid equilibria and vapor pressure data for the system ethyl *tert*-butyl ether + ethanol and ethyl *tert*-butyl ether + water. *J. Chem. Eng. Data* **1999**, *44*, 532−538.

(16) Krahenbuhl, M. A.; Gmehling, J. Vapor pressures of methyl *tert*-butyl ether, ethyl *tert*-butyl ether, isopropyl *tert*-butyl ether, *tert*-amyl methyl ether, and *tert*-amyl ethyl ether. *J. Chem. Eng. Data* **1994**, *39*, 759−762.

(17) Verevkin, S. P. Thermochemistry of branched ethers: experimental study of chemical equilibrium in the reacting system of *tert*-amyl alkyl ether synthesis. *J. Chem. Eng. Data* **2004**, *49*, 576−581.

(18) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. DIPPR project 821. Vapor pressure of organic chemicals of industrial interest. The 1991 project results. *DIPPR Data Ser.* **1994**, *2*, 154−173.

(19) Greune, G.; Kehlen, H. Liquid−vapor equilibrium of butanol−butyl ether mixtures. *Z. Phys. Chem.* (*Leipzig*) **1977**, *258*, 913−925 (in German).

(20) Ott, J. B.; Marsh, K. N.; Richards, A. E. Excess enthalpies, excess Gibbs free energies, and excess volumes for (di-*n*-butyl ether + benzene) and excess Gibbs free energies and excess volumes for (di-*n*-butyl ether + tetrachloromethane) at 298.15 and 308.15 K. *J. Chem. Thermodyn.* **1981**, *13*, 447−455.

(21) Marsh, K. N.; Ott, J. A.; Costigan, J. B. Excess enthalpies, excess volumes, and excess Gibbs free energies for *n*-hexane + di-*n*-butyl ether at 298.15 and 308.15 K. *J. Chem. Thermodyn.* **1980**, *12*, 857−862.

(22) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Smith, N. K. Thermodynamic properties and ideal-gas enthalpies of formation for butyl vinyl ether, 1,2-dimethoxyethane, methyl glycolate, bicyclo-[2.2.1]hept-2-ene, 5-vinylbicyclo[2.2.1]hept-2-ene, *trans*-azobenzene, butyl acrylate, di-*tert*-butyl ether, and hexane-1,6-diol. *J. Chem. Eng. Data* **1996**, *41*, 1285−1302.

(23) Aizawa, K.; Kato, M. Vapor−liquid equilibrium determination by total pressure measurements for three binary systems made of 1,2-dimethoxyethane with toluene, methylcyclohexane, or (trifluoromethyl) benzene. *J. Chem. Eng. Data* **1991**, *36*, 159−161.

(24) Treszczanowicz, T.; Lu, B. C.-Y. Isothermal vapour−liquid equilibria for 11 examples of (an ether + a hydrocarbon). *J. Chem. Thermodyn*. **1986**, *18*, 213−220.

(25) Treszczanowitcz, T. Vapour−liquid equilibrium of binary systems formed by aliphatic ethers with aliphatic hydrocarbons. *Bull. Acad. Pol. Sci., Ser. Sci. Chim*. **1973**, *21*, 107−111.

(26) Kobe, K. A.; Ravitcz, A. E.; Vohra, S. P. Critical properties and vapor pressures of some ethers and heterocyclic compounds. *J. Chem. Eng. Data* **1956**, *1*, 50−56.

(27) Stull, D. R. Vapor pressure of pure pubstances. *Ind. Eng. Chem*. **1947**, *39*, 517−550.

(28) Kusano, K. Densities, refractive indexes, and normal boiling points of 1,2-disubstituted ethylene glycol derivatives. *J. Chem. Eng. Data* **1978**, *23*, 141−143.

(29) Treszczanowicz, T. (Vapor + liquid) equilibria of (3,6-dioxaoctane + *n*-heptane) at 343.15 K. *J. Chem. Thermodyn*. **1987**, *19*, 391−394.

(30) Scheflan, L.; Jacobs, M. B. *The Handbook of Solvents*; Van Nostrand: New York, 1953.

(31) Alberth, M.; Hahnenstein, I.; Hasse, H.; Maurer, G. Vapor−liquid and liquid−liquid equilibria in binary and ternary mixtures of water, methanol, and methylal. *J. Chem. Eng. Data* **2001**, *46*, 897−903.

(32) Brazhnikov, M. M.; Peshchenko, A. D.; Ral'ko, O. V. Heats of vaporization of C1−C4 aliphatic aldehydes and of dimethoxymethane. *Russ. J. Appl. Chem*. **1976**, *49*, 1083−1085.

(33) Kobe, K. A.; Mathews, J. F. Critical properties and vapor pressures of some organic nitrogen and oxygen compounds. *J. Chem. Eng. Data* **1970**, *15*, 182−186.

(34) McEachern, D. M.; Kilpatrick, J. E. Entropy and related thermodynamic properties of dimethoxymethane. *J. Chem. Phys*. **1964**, *41*, 3127−3131.

(35) Figurski, G. The vapor−liquid equilibria of the binary systems methanol/2-methyl-1,3-dioxolane and acetaldehyde−dimethylacetal/methanol in the low-pressure region. *Chem. Technol*. **1992**, *44*, 27−29 (in German).

(36) Verevkin, S. P. Improved Benson increments for the estimation of standard enthalpies of vaporization of alkyl ethers, acetals, ketals, and ortho esters. *J. Chem. Eng. Data* **2002**, *47*, 1071−1097.

(37) Daubert, T. E.; Danner, R. P.; Sibil, H. M.; Stebbins, C. C. *Physical and Thermodynamic Properties of Pure Chemicals. Data Compilation. Parts I−V*; Taylor and Francis: Philadelphia, 1997.

(38) Plyasunova, N. V.; Plyasunov, A. V.; Shock, E. L. Database of thermodynamic properties for aqueous organic compounds. *Int. J. Thermophys*. **2004**, *25*, 351−360.

(39) Savage, J. J.; Wood, R. H. Enthalpy of dilution of aqueous mixtures of amides, sugars, urea, ethylene glycol, and pentaerythritol at 25 °C: enthalpy of interaction of the hydrocarbon, amide, and hydroxy functional groups in dilute aqueous solutions. *J. Solution Chem*. **1976**, *5*, 733−750.

(40) Okamoto, B. Y.; Wood, R. H.; Thompson, P. T. Freezing points of aqueous alcohols. Free energy of interaction of the CHOH, CH_2, CONH and $C{=}C$ functional groups in dilute aqueous solutions. *J. Chem. Soc., Faraday Trans. I* **1978**, *74*, 1990−2007.

(41) Suri, S. K.; Spitzer, J. J.; Wood, R. H.; Abel, E. G.; Thompson, P. T. Interactions in aqueous nonelectrolyte systems. Gibbs energy of interaction of the ether group with the hydroxy group and the amide group. *J. Solution Chem*. **1985**, *14*, 781−794.

(42) Nakayama, H. Thermodynamic properties of an aqueous solution of tetraethylene glycol diethyl ether. *Bull. Chem. Soc. Jpn*. **1972**, *45*, 1371−1375.

(43) Stephenson, R. M. Mutual solubilities: water−glycol ethers and water−glycol esters. *J. Chem. Eng. Data* **1993**, *38*, 134−138.

(44) Li, X.-X.; Liu, Y.-X.; Wei, X.-H. Density, viscosity and surface tension at 293.15 K and liquid−liquid equilibria from 301.15 to 363.15 K under atmospheric pressure for the binary mixture of diethylene glycol diethyl ether + water. *J. Chem. Eng. Data* **2004**, *49*, 1043−1045.

(45) Heitmann, W.; Hüls, A. G.; Strehlk, G.; Mayer, D. Ethers, Aliphatic. In *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed.; Wiley-Interscience: New York, 2003 (online edition).

(46) Tamura, K.; Chen, Y.; Yamada, T. Liquid−liquid equilibria of oxygenate fuel additives with water at 25 °C: ternary and quaternary aqueous systems of methyl *tert*-butyl ether and *tert*-amyl methyl ether with methanol or ethanol. *J. Solution Chem*. **2001**, *30*, 291−305.

(47) Arce, A.; Blanco, A.; Blanco, M.; Soto, A.; Vidal, I. Liquid−liquid equilibria of water + methanol + (MTBE or TAME) mixtures. *Can. J. Chem. Eng*. **1994**, *72*, 935−938.

(48) Arnett, E. M.; Burke, J. J.; Carter, J. V.; Douty, C. F. Solvent effects in organic chemistry. XV. Thermodynamics of solution for nonelectrolytes in aqueous acid and salt solutions. *J. Am. Chem. Soc*. **1972**, *94*, 7837−7852.

(49) Anderson, E. Heats of solution of organic substances. *Int. Crit. Tables* **1928**, *5*, 148−160.

(50) Gniazdowska, E.; Narbutt, J. Thermodynamics of liquid−liquid partition and hydration of aliphatic ethers. *Pol. J. Chem*. **2002**, *76*, 111−116.

(51) Marongiu, B.; Dernini, S.; Lepori, L.; Matteoli, E.; Kehiaian, H. V. Thermodynamics of binary mixtures containing ethers or acetals. 1. Excess enthalpies of linear ethers or acetals + heptane or + cyclohexane mixtures. *J. Chem. Eng. Data* **1988**, *33*, 118−122.

(52) Holldorff, H.; Knapp, H. Binary vapor−liquid−liquid equilibrium of dimethyl ether−water and mutual solubilities of methyl chloride and water: experimental results and data reduction. *Fluid Phase Equilib*. **1988**, *44*, 195−209.

(53) Brody, A. W.; Lyons, K. P.; Kurowski, J. L.; McGill. J. J.; Weaver, M. J. Analysis and solubility of dimethyl and diethyl ether in water, saline, oils, and blood. *J. Appl. Physiol*. **1971**, *31*, 125−131.

(54) Bennett, G. M.; Philip, W. G. The influence of structure on the solubilities of ethers. Part I. Aliphatic ethers. *J. Chem. Soc*. **1928**, *131*, 1930−1937.

(55) Atik, Z.; Gruber, D.; Krummen, M.; Gmehling, J. Measurement of activity coefficients at infinite dilution of benzene, toluene, ethanol, esters, ketones, and ethers at various temperatures in water using the dilutor technique. *J. Chem. Eng. Data* **2004**, *49*, 1429−1432.

(56) Fukuchi, K.; Miyoshi, K.; Watanabe, T.; Yonezawa, A.; Arai, Y. Measurement and correlation of infinite dilution activity coefficients of alkanol or ether in aqueous solution. *Fluid Phase Equilib*. **2002**, *194−197*, 937−945.

(57) Villamanan, M. A.; Allawi, A. J.; Ness, H. C. V. Vapor/liquid/liquid equilibrium and heats of mixing for diethyl ether/water at 35 °C. *J. Chem. Eng. Data* **1984**, *29*, 431−435.

(58) Arp, H. P. H.; Schmidt, T. C. Air−water transfer of MTBE, its degradation products, and alternative fuel oxygenates: the role of temperature. *Environ. Sci. Technol*. **2004**, *38*, 5405−5412.

(59) Rehak, K.; Novak, J. P.; Konetzna, J.; Heintz, A.; Vonka, P.; Matous, J. Excess enthalpy in the systems nitromethane−water and methyl *tert*-butyl ether−water. Employing data on excess enthalpy for thermodynamic description of heterogeneous systems. *Collect. Czech. Chem. Commun*. **1999**, *64*, 1393−1411.

(60) Stephenson, R. Mutual solubilities: water−ketones, water−ethers, and water−gasoline−alcohols. *J. Chem. Eng. Data* **1992**, *37*, 80−95.

(61) Zikmundova, D.; Matous, J.; Novak, J. P.; Kubicek, V.; Pick, J. Liquid−liquid and vapour−liquid equilibria in the system methyl *tert*-butyl ether + tetrahydrofuran + water. *Fluid Phase Equilib*. **1990**, *54*, 93−110.

(62) Quitain, A. T.; Goto, S. Liquid−liquid equilibria of ternary ETBE-EtOH−H_2O and Quaternary ETBE-EtOH−H_2O−TBA mixtures. *Can. J. Chem. Eng*. **1998**, *76*, 828−831.

(63) Clark, A. Q.; McBain, S. E.; Kilner, J. (Vapour + liquid) equilibria of (alkoxyalkanes−alkanes, or *o*-xylene, or water, or methanol) for ether mole fractions 0 to 0.5, between temperatures 293 K and 323 K. *J. Chem. Thermodyn*. **1997**, *29*, 441−446.

(64) Domanska, U.; Morawski, P.; Malanowski, S. K. Phase equilibria and volumetric properties in binary mixtures containing branched chain ethers (methyl 1,1-dimethylethyl ether or ethyl 1,1-dimethylethyl ether or methyl 1,1-dimethylpropyl ether or ethyl 1,1-dimethylpropyl ether). *J. Chem. Eng. Data* **1999**, *44*, 974−984.

(65) Kustov, A. V.; Antonova, O. A.; Korolev, V. P. Enthalpies of 1,4-dioxane, 1,2-dimethoxyethane, and ethylacetate solutions in the water−1-propanol and water−glycerol binary mixtures. *J. Solution Chem*. **2002**, *31*, 671−680.

(66) Kustov, A. V.; Volkova, E. Yu.; Korolev, V. P. Enthalpies of dissolution and specific features of interparticle interactions in the system water−alcohol−ether. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*. **2001**, *44*, 25−28 (in Russian).

(67) Dohnal, V.; Roux, A. H.; Hynek, V. Limiting partial molar excess enthalpies by flow calorimetry: some organic solvents in water. *J. Solution Chem*. **1994**, *23*, 889−900.

(68) Biros, J.; Pouchly, J.; Zivny, A. A Calorimetric investigation of interactions in aqueous solutions of poly(oxyethylene). 1. *Makromol. Chem*. **1987**, *188*, 379−394.

(69) Kusano, K.; Suurkuusk, J.; Wadso, I. Thermochemistry of solutions of biochemical model compounds. 2. Alkoxyethanols and 1,2-dialkoxyethanes in water. *J. Chem. Thermodyn*. **1973**, *5*, 757−767.

(70) Nakayama, H. Temperature dependence of the heats of solution of poly(ethyleneglycol) and of related compounds. *Bull. Chem. Soc. Jpn*. **1970**, *43*, 1683−1685.

(71) Cox, B. G. Free energies, enthalpies, and entropies of transfer of non-electrolytes from water to mixtures of water and dimethyl sulphoxide, water and acetonitrile, and water and dioxan. *J. Chem. Soc., Perkin Trans. 2* **1973**, 607−610.

(72) Tong, K. K. J.; Olson, A. R. A study of the dilatometric method of measuring rates of reactions: the application to the determination of the rate of hydrolysis of acetal. *J. Am. Chem. Soc*. **1943**, *65*, 1704−1707.

(73) Cifra, P.; Romanov, A. Enthalpies of solution of methoxy and ethoxy end group oligomers of poly(ethylene glycol) in binary solvent water−dimethylformamide. Study of hydrophobic hydration. *Chem. Pap.* **1987**, *41*, 395−400.

(74) Wallace, W. J.; Vellenga, Th. J. Heat of mixing of water and diethylene glycol dimethyl ether. *J. Chem. Eng. Data* **1971**, *16*, 331−333.

(75) Nakayama, H.; Shinoda, K. Enthalpies of mixing of water with some cyclic and linear ethers. *J. Chem. Thermodyn*. **1971**, *3*, 401−405.

(76) Nichols, G.; Orf, J.; Reiter, S. M.; Chickos, J.; Gokel, G. W. The vaporization enthalpies of some crown and polyethers by correlation gas chromatography. *Thermochim. Acta* **2000**, *346*, 15−28.

(77) Lopez, E. R.; Garcia, J.; Legido, J. L.; Coronas, A.; Fernandez, J. Experimental and predicted excess enthalpies of the 2,2,2-trifluoroethanol−water−tetraethylene glycol dimethyl ether ternary system using binary mixing data. *Chem. Soc., Faraday Trans. 1* **1995**, *91*, 2071−2079.

(78) Krumbeck, M.; Schulz, S. Excess enthalpies of binary polar mixtures. *Thermochim. Acta* **1989**, *151*, 109−130.

(79) Frenkel, M.; Marsh, K. N.; Wilhoit, R. C.; Kabo, G. I.; Roganov, G. N. *Thermodynamics of Organic Compounds in the Gas State*, Vols. I, II.; Thermodynamics Research Center, Texas A&M University System: College Station, TX, 1994.

(80) Cabani, S.; Conti, G.; Matteoli, E. Adiabatic and isothermal apparent molal compressibilities of organic compounds in water. I. Cyclic and open-chain secondary alcohols and ethers. *J. Solution Chem.* **1979**, *8*, 11−23.

(81) Stein, S. E.; Brown, R. L. *Structures and Properties Group Additivity Model. NIST Chemistry WebBook*; NIST Standard Reference Database 69; National Institute of Standards and Technology: Gaithersburg, MD, 2003.

(82) Cabani, S.; Lobo, S. T.; Matteoli, E. Apparent molal heat capacities of organic solutes in water. V. Aminoalcohols, amonoethers, diamines, and polyethers. *J. Solution Chem.* **1979**, *8*, 5−10.

(83) Suurkuusk, J.; Wadso, I. Design and testing of an improved precise drop caloriemter for the measurement of the heat capacity of small samples. *J. Chem. Thermodyn.* **1974**, *6*, 667−669.

(84) Benson, S. W. *Thermochemical Kinetics;* John Wiley & Sons: New York, 1976.

(85) Roux, G.; Perron, G.; Desnoyers, J. E. The heat capacities and volumes of some low molecular weight amides, ketones, esters, and ethers in water over the whole solubility range. *Can. J. Chem.* **1978**, *56*, 2808−2814.

(86) Dahlhoff, G.; Pfennig, A.; Hammer, H.; van Oorschot, M. Vapor−liquid equilibria in quarternary mixtures of dimethyl ether + *n*-butane + ethanol + water. *J. Chem. Eng. Data* **2000**, *45*, 887−892.

(87) Pozo, M. E.; Street, W. B. Fluid phase equilibria for the system dimethyl ether/water from 50 to 220 °C and pressures to 50.9 MPa. *J. Chem. Eng. Data* **1984**, *29*, 324−329.

(88) Signer, R.; Arm, H.; Daeniker, H. Behavior of organic mixed phases. VIII. Vapor pressures, densities, thermodynamic mixing functions, and refractive indexes of the binary systems water−tetrahydrofuran and water−ethyl ether at 25 °C. *Helv. Chim. Acta* **1969**, *52*, 2347−2351 (in German).

(89) Harvey, A. H.; Lemmon, E. W. Correlation for the second virial coefficient of water. *J. Phys. Chem. Ref. Data* **2004**, *33*, 369−376.

(90) Plyasunov, A. V.; Shock, E. L. Second cross virial coefficients for interactions involving water. Critical data compilation. *J. Chem. Eng. Data* **2003**, *48*, 808−821.

(91) Gargas, M. L.; Burgess, R. J.; Voisard, D. E.; Cason, G. H.; Andersen, M. E. Partition coefficients of low-molecular-weight volatile chemicals in various liquids and tissues. *Toxicol. Appl. Pharmacol.* **1989**, *98*, 87−99.

(92) Nihlen, A.; Lof, A.; Johanson, G. Liquid/air partition coefficients of methyl and ethyl *tert*-butyl ethers, *tert*-amyl methyl ether, and *tert*-butyl alcohol. *J. Exposure Anal. Environ. Epidemiol.* **1995**, *5*, 573−583.

(93) Xie, W.-H.; Shiu, W.-Y.; Mackay, D. A review of the effect of salts on the solubility of organic compounds in seawater. *Mar. Environ. Res.* **1997**, *44*, 429−444.

(94) Sorensen, J. M.; Arlt, W. *Liquid−Liquid Equilibrium Data Collection. Binary Systems*; Chemistry Data Series, Vol. V, Part 1; DECHEMA: Frankfurt/Main, 1979.

(95) Huyskens, P. L.; Tack, J. J. Specific interactions of phenols with water. *J. Phys. Chem.* **1975**, *79*, 1654−1658.

(96) Abraham, M. H.; Grellier, P. L.; McGill, R. A. Determination of olive oil−gas and hexadecane−gas partition coefficients, and calculation of the corresponding olive oil−water and hexadecane−water partition coefficients. *J. Chem. Soc., Perkin Trans. 2* **1987**, 797−803.

(97) Gniazdowska, E.; Narbutt, J. Hydration of dioxaalkanes in aqueous solution. *J. Mol. Liq.* **2000**, *84*, 273−278.

(98) Leo, A.; Hansch, C.; Elkins, D. Partition coefficients and their uses. *Chem. Rev.* **1971**, *71*, 525−616.

(99) Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology;* John Wiley & Sons: New York, 1979.

(100) Abraham, M. H.; Whiting, G. S.; Doherty, R. M.; Shuely, W. J. Hydrogen bonding. XVI. A new solute solvation parameter, π_2^{H}, from gas chromatographic data. *J. Chromatogr.* **1991**, *587*, 213−228.

(101) Abraham, M. H.; Whiting, G. S. Hydrogen bonding. XXI. Solvation parameters for alkylaromatic hydrocarbons from gas−liquid chromatographic data. *J. Chromatogr.* **1992**, *594*, 229−241.

(102) Abraham, M. H. Hydrogen bonding. XXVII. Solvation parameters for functionally substituted aromatic compounds and heterocyclic compounds, from gas−liquid chromatographic data. *J. Chromatogr.* **1993**, *644*, 95−139.

(103) Hine, J.; Weimar, R. D., Jr. Carbon basicity. *J. Am. Chem. Soc.* **1965**, *87*, 3387−3396.

(104) Krantz, J. C.; Evans, W. E.; Carr, C. J.; Kibler, D. V. Anesthesia. XIX. The anesthetic action of *n*-propyl methyl ether. *J. Pharmacol. Exp. Ther.* **1946**, *86*, 138−144.

(105) Krantz, J. C.; Carr, C. J.; Evans, W. E.; Musser, R. Anesthesia. XXII. The anesthetic action of isopropyl methyl ether. *J. Pharmacol. Exp. Ther.* **1946**, *87*, 132−137.

(106) Nielsen, F.; Olsen, E.; Fredenslund, A. Henry's law constants and infinite dilution activity coefficients for volatile organic compounds in water by a validated batch air stripping method. *Environ. Sci. Technol*. **1994**, *28*, 2133−2138.

(107) Guitart, R. Solubility of six gases in blood and various liquid media. *Rev. Esp. Fisiol.* **1993**, *49*, 195−202 (in Spanish).

(108) Leshechev, S. M.; Rakhman'ko, E. M.; Onishchuk, V. I. Assessment of the hydrophobicity of molecules and functional groups of organic nonelectrolytes. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* **1990**, *33*, 46−50 (in Russian).

(109) Guitart, R.; Puigdemont, A.; Arboix, M. Rapid headspace gas chromatographic method for the determination of liquid/gas partition coefficients. *J. Chromatogr.* **1989**, *491*, 271−280.

(110) Aarna, A. Ya.; Melder, L. I.; Ebber, A. V. Gas-chromatographic determination of thermodynamic functions of solution of ketones and ethers. *J. Appl. Chem. USSR* **1979**, *52*, 1640−1642.

(111) Renzi, F.; Waud, B. E. Partition coefficients of volatile anestetics in krebs solution. *Anesthesiology* **1977**, *47*, 62−63.

(112) Bocek, K. Relationships among activity coefficients, partition coefficients and aolubilities. *Experientia Suppl.* **1976**, *23*, 231−240.

(113) Bachofen, H.; Farhi, L. E. Simple manometric apparatus for measuring partition coefficients of highly soluble gases. *J. Appl. Physiol.* **1971**, *30*, 136−139.

(114) Lowe, H. J.; Hagler, K. Determination of volatile organic anaesthetics in blood, gases, tissues and lipids: partition coefficients. *Gas Chromatogr. Biol. Med., Ciba Found. Symp.* **1969**, 86−112.

(115) Lowe, H. J. Determination of volatile organic anesthetics in gases, blood and tissues. *Theory Appl. Gas Chromatogr. Ind. Med., 1st Hahnemann Symp.* **1968**, 194−209.

(116) Eger, E. I.; Shagel, R.; Merkel, G. Solubility of diethyl ether in water, blood and oil. *Anesthesiology* **1963**, *24*, 676−678.

(117) Shaffer, P. A.; Ronzoni, E. Ether anesthesia. I. The determination of ethyl ether in air and in blood, and its distribution ratio between blood and air. *J. Biol. Chem.* **1923**, *57*, 741−760.

(118) Haggard, H. W. An accurate method of determining small amounts of ethyl ether in air, blood, and other fluids, together with a determination of the coefficient of distribution of ether between air and blood at various temperatures. *J. Biol. Chem.* **1923**, *55*, 131−143.

(119) Cone, N. M.; Forman, S. E.; Krantz, J. C. Relationship between anesthetic potency and physical properties. *Proc. Soc. Exp. Biol. Med.* **1941**, *48*, 461−463.

(120) McBain, J. W.; Richards, P. H. Solubilization of insoluble organic liquids by detergents. *Ind. Eng. Chem.* **1946**, *38*, 642−646.

(121) Susilo, R.; Lee, J. D.; Englezos, P. Liquid−liquid equilibrium data of water with neohexane, methylcyclohexane, *tert*-butyl methyl ether, *n*-heptane and vapor-liquid−liquid equilibrium with methane. *Fluid Phase Equilib.* **2005**, *231*, 20−26.

(122) Chen, Y.; Dong, Y.; Pan, Z. Quaternary (liquid + liquid) equilibria for (water + 1,1-dimethylethyl methyl ether + diisopropyl ether + toluene) at the temperature 298.15 K. *J. Chem. Thermodyn*. **2005**, *37*.

(123) Fisher, A.; Muller, M.; Klasmeier, J. Determination of Henry's law constant for methyl *tert*-butyl ether (MTBE) at groundwater temperatures. *Chemosphere* **2004**, *54*, 689−694.

(124) Caires, J. P.; Suzuki, M.; Kibbey, T. C. G. Counterflow method for measurement of Henry's law constants. *J. Environ. Eng.* **2003**, *129*, 1169−1175.

(125) Noureddini, H. Ethyl *tert*-butyl ether amd methyl *tert*-butyl ether: status, review, and alternative use: exploring the environmental issues of mobile, recalcitrant compounds in gasoline. *ACS Symp. Ser.* **2002**, *799*, 107−124.

(126) Callender, T.; Davis, L. C. Environmental behavior of methyl *tert*-butyl ether: a study of Henry's law constant and the dispersion of MTBE through river bottom sand and soil. *Proceedings of the Conference on Environmental Research: New Approaches to Managing Environmental Quality in the Heartland*, May 21−24, 2001, Manhattan, KS; pp 137−146.

(127) Bierwagen, B. C.; Keller, A. A. Measurement of Henry's law constant for methyl *tert*-butyl ether using solid-phase microextraction. *Environ. Toxicol. Chem.* **2001**, *20*, 1625−1629.

(128) Alkandary, J. A.; Aljimaz, A. S.; Fandary, M. S.; Fahim, M. A. Liquid−liquid equilibria of water + MTBE + reformate. *Fluid Phase Equilib.* **2001**, *187*−*188*, 131−138.

(129) Miller, M. E.; Stuart, J. D. Measurement of aqueous Henry's law constants for oxygenates and aromatics found in gasolines by the static headspace method. *Anal. Chem.* **2000**, *72*, 622−625.

(130) Kaneko, T.; Wang, P.-Y.; Sato, A. Partition coefficients for gasoline additives and their metabolites. *J. Occup. Health* **2000**, *42*, 86−87.

(131) Arce, A.; Blanco, M.; Soto, A. Liquid−liquid equilibria of 1-octanol + 2-methoxy-2-methylpropane + water + methanol at 25 °C. *J. Chem. Eng. Data* **1998**, *43*, 255−258.

(132) Park, S.-J.; Han, S.-D.; Ryu, S.-A. Measurement of air/water partition coefficient (Henry's law constant) by using UEPICS method and their relationship with vapor pressure and water solubility. *Hwahak Konghak*, **1997**, *35*, 915−920 (in Korean).

(133) Arce, A.; Blanco, M.; Riveiro, R.; Vidal, I. Liquid−liquid equilibria of (MTBE or TAME) + ethanol + water mixtures. *Can. J. Chem. Eng.* **1996**, *74*, 419−422.

(134) Peschke, N.; Sandler, S. I. Liquid−liquid equilibria of fuel oxygenate + water + hydrocarbon mixtures. 1. *J. Chem. Eng. Data* **1995**, *40*, 315−320.

(135) Robbins, G. A.; Wang, S.; Stuart, J. D. Using the static headspace method to determine Henry's law constants. *Anal. Chem.* **1993**, *65*, 3113−3118.

(136) Dallas, A. J. Solvatochromic and Thermodynamic Studies of Chromatographic Media. Ph.D. Thesis, University of Minnesota, Minneapolis, MN, 1993.

(137) Piel, W. J.; Thomas R. X. Oxygenates for reformulated gasoline. *Hydrocarbon Process.* **1990**, *69*, 68−73.

(138) Evans, T. W. The Hill method for solubility determinations. *Ind. Eng. Chem.* **1936**, *8*, 206−208.

(139) Bakierowska, A.-M.; Trzeszczcynski, J. Dependence of the water/gas partition coefficient of volatile organic compounds on the ionic strength of sodium chloride solution. *J. Solution Chem.* **2004**, *33*, 329−338.

(140) Li, J.; Carr, P. W. Measurement of water−hexadecane partition coefficients by headspace gas chromatography and calculation of limiting activity coefficients in water. *Anal. Chem.* **1993**, *65*, 1443−1450.

(141) Evans, B. K.; James, K. C.; Luscombe, D. K. Quantitative structure−activity relationships and carminative activity. *J. Pharm. Sci.* **1978**, *67*, 277−278.

(142) Hartkopf, A.; Karger, B. L. Study of the interfacial properties of water by gas chromatography. *Acc. Chem. Res.* **1973**, *6*, 209−216.

(143) Krupatkin, I. L.; Shcherbakova, T. A. Extraction systems of phosphoric acid with ethers. *J. Appl. Chem. USSR* **1971**, *44*, 1652−1654.

(144) Harrison, C. H.; Roquero, P. Liquid−liquid equilibria of the system water/phosphoric acid/diisopropyl ether at (273.15, 283.15, and 293.15) K. *J. Chem. Eng. Data* **2004**, *49*, 218−220.

(145) Arce, A.; Marchiaro, A.; Rodriguez, A.; Soto, A. Liquid−liquid equilibrium of diisopropyl ether + ethanol + water system at different temperatures. *J. Chem. Eng. Data* **2002**, *47*, 529−532.

(146) Park, Y.-S.; Part, S.-J. Determination and prediction of octanol/water partition coefficients and air/water partition coefficients for environmental toxic chemicals. *Kongop Hwahak* **2000**, *11*, 773−779 (in Korean).

(147) Arce, A.; Arce, A., Jr.; Martinez-Ageitos, J.; Rodil, E.; Rodriguez, O.; Soto, A. Physical and equilibrium properties of diisopropyl ether + isopropyl alcohol + water system. *Fluid Phase Equilib.* **2000**, *171*, 113−126.

(148) Dohnal, V.; Hovorka, S. Exponential saturator: a novel gas−liquid partitioning technique for measurement of large limiting activity coefficients. *Ind. Eng. Chem. Res.* **1999**, *38*, 2036−2043.

(149) Li, J.; Dallas, A. J.; Eikens, D. I.; Carr, P. W.; Bergmann, D. L.; Hait, M. J.; Eckert, C. A. Measurement of large infinite dilution activity coefficients of nonelectrolytes in water by inert gas stripping and gas chromatography. *Anal. Chem.* **1993**, *65*, 3212−3218.

(150) Tewari, Y. B.; Martire, D. E.; Wasik, S. K.; Miller, M. M. Aqueous solubilities and octanol−water partition coefficients of binary liquid mixtures of organic compounds at 25 °C. *J. Solution Chem.* **1982**, *11*, 435−445.

(151) Lozano, F. J.; Garfias, F. J. Phase equilibrium of the system phosphoric acid−water−diisopropyl ether at 20 °C. *Rev. Soc. Quim. Mex.* **1978**, *22*, 436−437 (in Spanish).

(152) Hlavaty, K.; Linek, J. Liquid−liquid equilibria in four ternary acetic acid−organic solvent−water systems at 24.6 °C. *Collect. Czech. Chem. Commun.* **1973**, *38*, 374−378.

(153) Krupatkin, I. L.; Shcherbakova, T. A. Liquid-phase equilibrium in ternary systems containing phosphoric acid, water, and ethers. *J. Appl. Chem. USSR* **1972**, *45*, 1897−1900.

(154) Donahue, D. J.; Bartell, F. E. The boundary tension at water−organic liquid interfaces. *J. Phys. Chem.* **1952**, *56*, 480−484.

(155) Frere, F. J. Ternary system diisopropyl ether−isopropyl alcohol−water. *Ind. Eng. Chem.* **1949**, *41*, 2365−2367.

(156) Krupatkin, I. L.; Bodin, M. A. Homogenization of binary layering by a third component. *Zh. Obshchei Khim.* **1947**, *17*, 1993−1998 (in Russian).

(157) Othmer, D. F.; White, R. E.; Trueger, E. Liquid−liquid extraction data. *Ind. Eng. Chem.* **1941**, *33*, 1240−1248, 1513.

(158) Hellinger, S.; Sandler, S. I. Liquid−liquid equilibria of fuel oxygenate + water + hydrocarbon mixtures. 2. *J. Chem. Eng. Data* **1995**, *40*, 321−325.

(159) Evans, T. W.; Edlund, K. R. Tertiary alkyl ethers. Preparation and properties. *Ind. Eng. Chem.* **1936**, *28*, 1186−1188.

(160) Fandary, M. S. H.; Aljimaz, A. S.; Al-Kandary, J. A. Liquid−liquid equilibria for the system water + ethanol + ethyl *tert*-butyl ether. *J. Chem. Eng. Data* **1999**, *44*, 1129−1131.

(161) Arce, A.; Martinez-Ageitos, J.; Rodriguez, O.; Soto, A. (Liquid + liquid) equilibria of (*tert*-amyl ethyl ether + ethanol + water) at several temperatures. *J. Chem. Thermodyn.* **2001**, *33*, 139−146.

(162) Marcilla, A. F.; Ruiz, F.; Sabater, M. C. Two-phase and three-phase liquid−liquid equilibrium for bis(2-methylpropyl) ether + phosphoric acid + water. *J. Chem. Eng. Data* **1994**, *39*, 14−18.

(163) Marcilla, A.; Ruiz, F.; Campos, J.; Asensio, M. Purification of wet process phosphoroc acid by solvent extraction with dibutyl ether. Part I. Liquid−liquid equilibrium of the water−phosphoric acid−dibutyl ether at 25 °C. *Solvent Extr. Ion Exch.* **1989**, *7*, 201−210.

(164) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*; Wiley: New York, 1986.

(165) Tapper, M. B.; Engelhardt, C. E.; Schechter, B. A.; Fried, V. Liquid−liquid equilibrium in the water/*n*-dibutyl ether system. *AIChE Symp. Ser.* **1985**, *81*, 142−143.

(166) Logutov, V. I.; Danov, S. M.; Chubarov, G. A.; Tomashchuk, V. I. Liquid−liquid equilibria in certain systems containing acrylic acid and butyl acrylate. *J. Appl. Chem. USSR* **1983**, *56*, 214−216.

(167) Kakovsky, I. A. Physicochemical properties of some flotation reagents and their salts with ions of heavy non-ferrous metals. *Proceedings of the Second International Congress of Surface Activity*, London, 1957; pp 225−237.

(168) Cabani, S.; Mollica, V.; Lepori, L. Thermodynamic study of dilute aqueous solutions of organic compounds. Part 5. Open-chain saturated bifunctional compounds. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2667−2671.

(169) Gmehling, J.; Onken, U. *Vapor−Liquid Equilibrium Data Collection. Aqueous−Organic Systems. Vol.1, Part 1*; DECHEMA: Frankfurt, 1977.

(170) Wormuth, K. R.; Kaler, E. W. Microemulsifying polar oils. *J. Phys. Chem.* **1989**, *93*, 4855−4861.

(171) Burger, L. L. Dialkyl diethers in solvent extraction. *J. Chem. Eng. Data* **1964**, *9*, 112−114.

(172) Curme, G. O., Jr.; Johnston, F. *Glycols*; American Chemical Society Monograph Series; Reinhold: New York, 1952.

(173) Shaffer, D. L.; Daubert, T. E. Gas−liquid chromatographic determination of solution properties of oxygenated compounds in water. *Anal. Chem.* **1969**, *41*, 1585−1589.

(174) Boaz, N. W.; Venepali, B. Applications of diethoxymethane as a versatile process solvent and unique reagent in organic synthesis. *Org. Process Res. Dev.* **2001**, *5*, 127−131.

(175) Tewari, Y. B.; Miller, M. M.; Wasik, S. P.; Martire, D. E. Aqueous solubility and octanol/water partition coefficient of organic compounds at 25.0 °C. *J. Chem. Eng. Data* **1982**, *27*, 451−454.

(176) Salomaa, P.; Kankaanpera, A. Thermodynamic characterization of the initial and transition states for the hydrolyses of vinyl ethers and acetals. *Acta Chem. Scand.* **1966**, *20*, 1802−1810.

(177) Adkins, H.; Nissen, B. H. A study of catalysis in the preparation of acetal. *J. Am. Chem. Soc.* **1922**, *44*, 2749−2755.

(178) Edward, J. T.; Farrell, G.; Shahidi, F. Partial molar volumes of organic compounds in water. Part 1. Ethers, ketones, esters, and alcohols. *J. Chem. Soc., Faraday Trans. 1* **1977**, 705−714.

(179) Cabani, S.; Conti, G.; Matteoli, E. Partial molal expansibilities of organic compounds in aqueous solution. I. Alcohols and ethers. *J. Solution Chem.* **1976**, *5*, 751−763.

(180) Chadwell, H. M. The viscosities of several aqueous solutions of organic substances and the polymerization of water. *J. Am. Chem. Soc.* **1926**, *48*, 1912−1925.

(181) Kablukov, I. A.; Malischeva, V. T. The volumetric method of measurement of the mutual solubility of liquids. The mutual solubility of the systems ethyl ether−water and iso-amyl alcohol−water. *J. Am. Chem. Soc.* **1925**, *47*, 1553−1561.

(182) Hill, A. E. The mutual solubility of liquids. I. The mutual solubility of ethyl ether and water. II. The solubility of water in benzene. *J. Am. Chem. Soc.* **1923**, *45*, 1143−1155.

(183) George, J.; Sastry, N. V. Partial excess molar volumes, partial excess isentropic compressibilities and relative permittivities of water + ethane-1,2-diol derivative and water + 1,2-dimethoxyethane at different temperatures. *Fluid Phase Equilib.* **2004**, *216*, 307−321.

(184) Douheret, G.; Reis, J. C. R.; Davis, M. I.; Fjellander, I. J.; Hoiland, H. Aggregative processes in aqueous solutions of mono- to tetra-ethylene glycol dimethyl ether at 298.15 K. *Phys. Chem. Chem. Phys.* **2004**, *6*, 784−792.

(185) Marchetti, A.; Tassi, L.; Ulrici, A. Density and volumetric behavior of 1,2-dimethoxyethane + water binary mixtures from −10 to 80 °C. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 987−991.

(186) Douheret, G.; Davis, M. I.; Hernandez, M. E.; Flores, H. Excess molar volumes of some polyether + water systems. *J. Indian Chem. Soc.* **1993**, *70*, 395−401.

(187) Akers, H. A.; Gabler, D. G. The molar volume of solutes in water. *Naturwissenschaften* **1991**, *78*, 417−419.

(188) Sikora, A. Volume properties of dilute aqueous solutions of poly-(oxyethylene) and its low molecular models. *Collect. Czech. Chem. Commun.* **1985**, *50*, 2146−2158.

(189) Lepori, L.; Mollica, V. Volumetric properties of dilute aqueous solutions of poly(ethylene glycols). *J. Polym. Sci*. **1978**, *16*, 1123−1134.

(190) Lepori, L.; Mollica, V. Densities of dilute aqueous solutions of selected ethers. *J. Chem. Eng. Data* **1978**, *23*, 65−68.

(191) Harada, S.; Nakajima, T.; Komatsu, T.; Nakagawa, T. Apparent molal volumes and adiabatic compressibilities of ethylene glycol derivatives in water at 5, 25, and 45 °C. *J. Solution Chem*. **1978**, *7*, 463−474.

(192) Terasawa, S.; Itsuki, H.; Arakawa, S. Contribution of hydrogen bonds to the partial molar volumes of nonionic solutes in water. *J. Phys. Chem.* **1975**, *79*, 2345−2351.

(193) Wallace, W. J.; Mathews, A. L. Densities, refractive indices, molar refractions, and viscosities of ethylene glycol dimethyl ether−water solutions at 25 °C. *J. Chem. Eng. Data* **1963**, *8*, 496−498.

(194) Dethlefsen, C.; Hvidt, A. Densities and derived volume functions of binary mixtures: (an ethylene glycol derivative + water) at 298.15 K. *J. Chem. Thermodyn.* **1985**, *17*, 193−199.

(195) Schrödle S.; Hefter G.; Buchner R. Effects of hydration on the thermodynamic properties of aqueous ethylene glycol ether solutions. *J. Chem. Thermodyn*. **2005**, *37*, 513−522.

(196) Bernal, P.; McCluan, J. Apparent molar volumes and adiabatic compressibilities of crown ethers and glymes in H_2O and D_2O at 25 °C. *J. Solution Chem.* **2001**, *30*, 119−131.

(197) Bernal, P.; Bunn, A.; Logan, J.; McCluan, J. Apparent molar volumes and adiabtic compressibilities of crown ethers and glymes in aqueous solutions at various temperatures. *J. Solution Chem*. **2000**, *29*, 651−665.

(198) Benson, S. W.; Buss, J. H. Additivity rules for the estimation of molecular properties. thermodynamic properties. *J. Chem. Phys.* **1958**, *29*, 546−572.

(199) Cabani, S.; Gianni, P.; Mollica, V.; Lepori, L. Group contributions to the thermodynamic properties of non-ionic organic solutes in dilute aqueous solution. *J. Solution Chem.* **1981**, *10*, 563−595.

(200) Domalski, E. S.; Hearing, E. D. Estimation of the thermodynamic properties of C−H−N−O−S−halogen compounds at 298.15 K. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805−1159.

(201) Wagner, W.; Pruss, A. The IAPWS formulation for the thermodynamic properties of ordinary water substances for general and scientific use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387−535.

(202) Reinhard, M.; Drefahl, A. *Handbook for Estimating Physicochemical Properties of Organic Compounds;* John Wiley & Sons: New York, 1999.

(203) Liu, R.; So, S.-S. Development of quantitative structure−property relationship models for early ADME evaluation in drug discovery. 1. Aqueous solubility. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 1633−1639.

(204) Yaffe, D.; Cohen, Y.; Espinosa, G.; Arenas, A.; Giralt, F. A Fuzzy ARTMAP-based quantitative structure−property relationship (QSPR) for the Henry's law constant of organic compounds. *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 85−112.

(205) Goldberg, R. N.; Kishore, N.; Tewari, Y. B. Enzyme-catalyzed reactions. In *Chemical Thermodynamics*; Letcher, T. M., Ed.; Blackwell Science: London, 1999; pp 291−300.

(206) Steele, W. V.; Chirico, R. D.; Cowell, A. B.; Knipmeyer, S. E.; Nguyen, A. Themodynamic properties and ideal-gas enthalpies of formation for 1,4-diisopropylbenzene, 1,2,4,5-tetraisopropylbenzene, cyclohexanone oxime, dimethyl malonate, glutaric acid, and pimelic acid. *J. Chem. Eng. Data* **2002**, *47*, 725−739.

(207) Roganov, G. N.; Pisarev, P. N.; Emel'yanenko, V. N.; Verevkin, S. P. Measurement and prediction of thermochemical properties. Improved Benson-type increments for the estimation of enthalpies of vaporization and standard enthalpies of formation of aliphatic alcohols. *J. Chem. Eng. Data* **2005**, *50*, 1114−1124.

(208) Guthrie, J. P. Additivity schemes permitting the estimation of partial molar heat capacities of organic compounds in aqueous solution. *Can. J. Chem.* **1977**, *55*, 3700−3706.

(209) Guthrie, J. P. A group equivalents scheme for free energies of formation of organic compounds in aqueous solution. *Can. J. Chem.* **1992**, *70*, 1042−1054.

(210) Domalski, E. S. Estimation of enthalpies of formation of organic compounds at infinite dilution in water at 298.15 K. A pathway for estimation of enthalpies of solution. *ACS Symp. Ser.* **1998**, *No. 677*, 47−62.

(211) Hovorka, S.; Dohnal, V.; Roux, A. H.; Roux-Desgranges, G. Determination of temperature dependence of limiting activity coefficients for a group of moderately hydrophobic organic solutes in water. *Fluid Phase Equilib*. **2002**, *201*, 135−164.

Received for review September 26, 2005. Accepted October 29, 2005. Support of this work by the Department of Energy (DOE) under Grant DE-FG02-92ER14297 is acknowledged.

JE050390A