Group Contribution Values for the Thermodynamic Functions of Hydration of Aliphatic Esters at 298.15 K, 0.1 MPa

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A compilation of experimental values of the infinite dilution partial molar Gibbs energy, enthalpy, and heat capacity of hydration, together with molar volumes in water at 298.15 K and 0.1 MPa, is presented for aliphatic esters. These data, combined with the related results for aliphatic hydrocarbons, monohydric alcohols, and ketones, are treated in the framework of the first- and second-order group additivity methods. Numerical values of the contributions to each of the thermodynamic properties are obtained by a least-squares procedure for the following first-order groups: CH_3, CH_2, CH, C, OH, CO, COO, and COOH as well as for the C−OH, C−CO, and C−COO corrections for the attachment of the polar groups to the tertiary carbon atom. For the case of the second-order group contribution method, numerical values are retrieved for the following groups: $C-(C)(H)_3$, $C-(C)_2(H)_2$, $C-(C)_3(H)$, $C-(C)_4$, $C-(C)(H)_2(O)$, $C-(C)_2(H)(O)_{alcohol}$, $C-(C)_3(O)_{alcohol}$, O−(H)(C), $CO-(C)_2$, $C-(CO)(H)_2(C)$, $C-(CO)(H)(C)_2$, $C-(CO)(C)_3$, $C-(C)_2(H)(O)_{ester}$, and $C-(C)_3(O)_{ester}$ and for the provisional “ester” $COO-(C)_2$ and “methanoate” HCOO−(C) groups.

Introduction

Thermodynamic properties of organic compounds in water are of interest for many applications in chemical engineering, environmental sciences, chemistry, geochemistry, biology, medicine, and so forth. There are too many organic compounds for all of them to be studied experimentally, so various group additivity methods are used for the correlation and estimation of properties of these compounds. Group additivity methods start from the consideration that a molecule can be built from smaller segments, or groups, and that the property of interest for the molecule can be calculated as the sum of the corresponding properties of the constituting groups.

There are different variants of the group contribution methods. The most accurate ones are the second-order group additivity methods[1,2] in which properties of a group are taken to depend on the surrounding atoms and groups. As a result, the effects of nearest-neighbor interactions can be accurately accounted for using these group additivity methods. However, the application of the second-order group contribution scheme requires a large matrix of accurate experimental results. An alternative but inherently less accurate approach is the first-order group contribution method, where the properties of a group, CH_2 for example, are considered to be identical in all types of organic compounds. The first-order group contribution approach is not accurate for polyfunctional compounds,[3,4] although its performance can be improved by the introduction of new groups to correct for nearest-neighbor interactions[5,6] or by an explicit consideration of the change in electrostatic interactions between the solvent and polar functional groups where the latter are in close proximity.[3,7] The first-order group contribution method is a pragmatic choice for the situation where the quantity and accuracy of experimental data preclude an accurate consideration of the second-order effects (nearest-neighbor interactions).

In 1981, Cabani et al.[5] employed the first-order method to evaluate group contribution values for the thermodynamic functions of hydration at 298.15 K, 0.1 MPa for about 80 functional groups by considering experimental data for about 400 organic compounds. A few attempts are devoted to the derivation of the second-order group contribution values for organic compounds in the state of aqueous solution. Guthrie[8] determined more than 40 group contribution values for the partial molar heat capacity in the C−H−O−N system at 298.15 K. Domalski[9] showed the pathway to derive the values of the enthalpy of formation of organic compounds at infinite dilution in water at 298.15 K by combining the experimental values of the enthalpy of solution with the enthalpy of formation in the state of liquid, solid, or gas and derived the values of about 40 functional groups in the C−H−O system.

Recently, we updated the database and group contribution values for aliphatic and monoaromatic hydrocarbons, aliphatic ketones, and monohydric alcohols.[6,10] The current contribution continues this effort by considering thermodynamic functions of hydration of aliphatic esters. The database is used to derive optimal values of functional group contributions in the frameworks of the first- and second-order group contribution schemes.

Thermodynamic Functions of Hydration under Consideration

Thermodynamic functions of hydration represent the change in those functions upon transferring one mole of a solute from an ideal gas state to a standard aqueous solution. The standard-state convention adopted here is that identical to IUPAC[11] recommendations: the standard state for a gaseous substance is the hypothetical state of the pure substance as a ideal gas at the standard-state pressure $P^o = 0.1$ MPa; the standard state for a pure liquid or a solvent is the state of the pure substance in the liquid

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phase at the standard pressure $P^o = 0.1$ MPa. (In practice, the difference between the standard-state pressure and the saturated vapor pressure over the liquid phase can be neglected.) The standard state for a solute in aqueous solution is the hypothetical state of the pure substance dissolved in pure water without dissociation at the standard molality $m^o = 1\ \text{mol}\cdot\text{kg}^{-1}$, at the standard pressure $P^o = 0.1$ MPa, and exhibiting the behavior of a solution at infinite dilution. Here and below, superscript * denotes the properties of a pure liquid, and superscript ∞ denotes the property at infinite dilution in water; subscripts 1 and 2 are used for water and a solute, respectively.

Our focus is on the following partial molar thermodynamic functions of hydration at infinite dilution: the Gibbs energy, $\Delta_h G^\infty$, enthalpy, $\Delta_h H^\infty$, entropy, $\Delta_h S^\infty$, heat capacity, $\Delta_h C_p^\infty$, and volume, $\Delta_h V^\infty$, with the following relations between them:

$$\Delta_h H^\infty = -T^2 \left(\frac{\partial \Delta_h G^\infty / T}{\partial T} \right)_P \tag{1}$$

$$\Delta_h S^\infty = \frac{\Delta_h H^\infty - \Delta_h G^\infty}{T} \tag{2}$$

$$\Delta_h C_p^\infty = \left(\frac{\partial \Delta_h H^\infty}{\partial T} \right)_P \tag{3a}$$

$$= C_{p,2}^\infty - C_p(g) \tag{3b}$$

$$\Delta_h V^\infty \equiv V_2^\infty = \left(\frac{\partial \Delta_h G^\infty}{\partial P} \right)_T \tag{4}$$

where $C_{p,2}^\infty$ and C_p(g) are the partial heat capacity at infinite dilution in water and the heat capacity in the state of an ideal gas, respectively; V_2^∞ stands for the partial molar volume of a solute.

Evaluation of the Thermodynamic Functions of Hydration from Various Types of Experimental Data

Standard Partial Molar Gibbs Energy of Hydration. There are different types of data in the literature that can be converted into the values of the standard partial molar Gibbs energy of hydration, $\Delta_h G^\infty$.

(1) Henry's constant, k_H, which is defined in the chemical engineering literature as

$$k_H = \lim_{x \to 0} \frac{f_2}{x}$$

where f_2 stands for the fugacity of a solute (2) and x is the mole fraction of a solute in a liquid phase, relates to $\Delta_h G^\infty$ according to

$$\Delta_h G^\infty = RT \ln \left(\frac{k_H}{P^o} \frac{1}{N_w} \right) \tag{5}$$

where $N_w = (1000\ \text{g})/M_w \approx 55.5084$ is the number of moles of H_2O in 1000 g of water, with $M_w = 18.0153\ \text{g}\cdot\text{mol}^{-1}$ being the molar mass of water.

(2) Gas−water distribution constant in the molarity scale, $K_{D,c}$, which is defined as

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

relates to $\Delta_h G^\infty$ (assuming ideal gas behavior for the gaseous phase) by means of

$$\Delta_h G^\infty = RT \ln \left(K_{D,c} \frac{RT}{P^o V^*_1} \frac{1}{N_w} \right) \tag{6}$$

where V_1^* is the molar volume of pure water. These types of data are common in the environmental, medical, food chemistry, and other applied science literature.

(3) Gas−water distribution constant on the mole fraction concentration scale, $K_{D,x}$, is defined as

$$K_{D,x} = \lim_{x \to 0} \frac{y}{x}$$

where y and x stand for the mole fraction concentrations of a solute in coexisting vapor and liquid phases, respectively. $K_{D,x}$ relates to $\Delta_h G^\infty$ (assuming ideal gas behavior for the gaseous phase) by means of

$$\Delta_h G^\infty = RT \ln \left(K_{D,x} \frac{P^*_1}{P^o} \frac{1}{N_w} \right) \tag{7}$$

where P_1^* is the saturated water vapor pressure. These types of data are reported in the chemical engineering literature.

(4) Activity coefficient at infinite dilution, γ^∞, for the symmetrical normalization of activity ($\gamma_i \to 1$ when $x_i \to 1$) for the mole fraction concentration scale is common in the chemical engineering literature. The following statement gives (as a reasonable approximation, ignoring small pressure corrections between the standard-state pressure $P^o = 0.1$ MPa and P_2^*, the saturated vapor pressure of liquid organic compounds) the relation between γ^∞ and $\Delta_h G^\infty$:

$$\Delta_h G^\infty = RT \ln \left(\frac{P^*_2\, \phi^*_2}{P^o} \gamma^\infty \frac{1}{N_w} \right) = -\Delta_{vap} G^o + RT \ln \left(\frac{\gamma^\infty}{N_w} \right) \tag{8}$$

where $\Delta_{vap} G^o = -RT \ln((P_2^* \phi_2^* / P^o))$ is the standard Gibbs energy of vaporization of a pure organic compound and ϕ_2^* represents the fugacity coefficient of a pure compound. Values of ϕ_2^* can be evaluated using the virial equation of state truncated at the second virial coefficient, B_{22} ($\phi_2^* = \exp(B_{22} P_2^* / RT)$), and the correction for the nonideality of the gaseous phase is insignificant at $P_2^* <$ (0.005 to 0.010) MPa.

(5) 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 (in the case of a solid compound $x_s = 1$), are reported in the chemical literature for many organic compounds in water. The following statement gives the relation between m_s, x_s, and $\Delta_h G^\infty$:

$$\Delta_h G^\infty = \Delta_{sol} G^\infty - \Delta_{vap} G^o \tag{9}$$

where the standard molar Gibbs energy of solution is given by

$$\Delta_{sol} G^\infty = -RT \ln \frac{(m_s/m_o)\gamma_{m,2}}{x_s f_{x,2}} \tag{10}$$

and $\Delta_{vap} G^o$, the standard Gibbs energy of vaporization, is defined in the previous paragraph. Here $\gamma_{m,2}$ stands for the activity coefficient of a solute in the saturated aqueous solution referenced to Henry's law[11] (unsymmetrical normalization of activity, the molality concentration scale, $\gamma \rightarrow 1$ if $m \rightarrow 0$), and $f_{x,2}$ is the activity coefficient of a liquid solute saturated with water referenced to Raoult's law (symmetrical normalization of activity, the mole fraction concentration scale, $\gamma \rightarrow 1$ if $x \rightarrow 1$). For the case of a solid compound, $f_{x,2}$=1. In general, $f_{x,2}$ can be calculated using the UNIQUAC, NRTL, ASOG, and other models. However, these models are not accurate for activity coefficients of solutes that are dilute in water[12,13] (i.e., for $\gamma_{m,2}$). In principle, values of $\gamma_{m,2}$ can be determined from the isopiestic or freezing temperature measurements for solutions of organic compounds in water, if available; however, these data are not available for every solute of interest.

Standard Partial Molar Enthalpy of Hydration. For gases, the values of the standard partial molar enthalpy of hydration, $\Delta_h H^\infty$, can be measured directly by calorimetry. For compounds existing as liquids or solids, the values of $\Delta_h H^\infty$ are usually calculated as

$$\Delta_h H^\infty = \Delta_{sol} H^\infty - \Delta_{vap} H^o \qquad (11)$$

where $\Delta_{sol} H^\infty$ is the standard molar enthalpy of solution of a (liquid or solid) compound in water and $\Delta_{vap} H^o$ is the standard molar enthalpy of vaporization ($\Delta_{sub} H^o$, the standard molar enthalpy of sublimation for the case of a solid) of a pure compound. Reliable values of $\Delta_{vap} H^o$ are obtained by calorimetry or are evaluated from the temperature dependence of the vapor pressure of a pure organic compound; see the review in ref 14. Values of the enthalpy of solution can be obtained calorimetrically as the heat effect of adding a small amount of a pure compound to water. Another method for evaluating $\Delta_{sol} H^\infty$ is by differentiating the excess enthalpies, H^E:

$$\Delta_{sol} H^\infty = \left(\frac{\partial H^E}{\partial x}\right)_{T,P,x=0} \qquad (12)$$

In practice, this can be done by representing H^E data by the following analytical form: $(H^E/x(1-x)) = \Delta_{sol} H^\infty + bx + cx^2 + ...$ In addition, values of $\Delta_h H^\infty$ can be evaluated from the temperature dependence of $\Delta_h G^\infty$; see eq 1. Typically, this is a less accurate method for determining $\Delta_h H^\infty$.

Partial Molar Entropy of Hydration. $\Delta_h S^\infty$ is usually calculated from experimental $\Delta_h G^\infty$ and $\Delta_h H^\infty$ results according to eq 2.

Standard Partial Molar Heat Capacity of Hydration. For gases, the values of the standard partial molar heat capacity of hydration, $\Delta_h C_p^\infty$, can be evaluated from the temperature dependence of $\Delta_h H^\infty$; see eq 3a. Usually the most accurate values of $\Delta_h C_p^\infty$ are calculated by means of eq 3b. Reliable values of the heat capacity of organic compounds in the ideal gas state are available in thermodynamic tabulations (see ref 15) or can be estimated using group contribution methods.[1,2] Many experimental papers report the values of the apparent molar heat capacity of a solute, $C_{p,\phi}$, calculated from measurements of the heat capacity of solutions as follows:

$$C_{p,\phi} = M_2 c_p + \frac{1000(c_p - c^*_{p,1})}{m} \qquad (13)$$

where M_2 is the molar mass of a solute, c_p is the $(J \cdot K^{-1} \cdot g^{-1})$ heat capacity of a solution with respect to mass, and $c^*_{p,1}$ is the $(J \cdot K^{-1} \cdot g^{-1})$ heat capacity of pure water with respect to mass. The values of the partial molar heat capacity of an aqueous solute at infinite dilution, $C^\infty_{p,2}$, are typically obtained by expanding $C_{p,\phi}$ into a molality series:

$$C_{p,\phi} = C^\infty_{p,2} + am + bm^2 + ... \qquad (14)$$

Another method for evaluating $C^\infty_{p,2}$ is by composition differentiation of the excess heat capacities of water + organic mixtures, C_p^E, which can be done in the following form:

$$\frac{C_p^E}{x(1-x)} = (C^\infty_{p,2} - C^*_{p,2}) + bx + cx^2 + ... \qquad (15)$$

The necessary values of the molar heat capacity of a pure organic compound in the liquid state, $C^*_{p,2}$, are available from calorimetric determinations. C_p^E data are available only for a few systems.

Values of $C^\infty_{p,2} - C^*_{p,2}$ can also be evaluated from the temperature dependence of $\Delta_{sol} H^\infty$.

Standard Partial Molar Volume of a Solute. Many experimental papers report the values of the apparent molar volumes, V_ϕ, of aqueous organic solutes, calculated as follows:

$$V_\phi = \frac{M_2}{\rho} - \frac{1000(\rho - \rho_1^*)}{m\rho\rho^*{}_1} \qquad (16)$$

where ρ and ρ_1^*stand for the densities of a solution and pure water, respectively. The partial molar volumes of a solute at infinite dilution in water, V_2^∞, are calculated by expanding V_ϕ into a molality series:

$$V_\phi = V_2^\infty + am + bm^2 + ... \qquad (17)$$

Modern works on mixtures of water with liquid solutes usually report the excess volumes of mixtures, V^E. Values of V_2^∞ can be obtained by composition differentiation of V^E, which can be done in the following form:

$$\frac{V^E}{x(1-x)} = (V_2^\infty - V_2^*) + bx + cx^2 + ... \qquad (18)$$

The necessary values of the molar volume of a pure organic compound in the liquid state, V_2^*, are available from density determinations.

Values of V_2^∞ and $V_2^\infty - V_2^*$ can also be evaluated from the pressure dependence of the Gibbs energy of hydration and solution, respectively. Typically, these values are rare and less reliable.

Temperature Corrections to the Standard Partial Molar Gibbs Energy and the Enthalpy of Hydration

In cases where experimental data are reported at temperatures others than 298.15 K, the resulting values of $\Delta_h G^\infty$ can be recalculated to 298.15 K using the approximation that $\Delta_h C_p^\infty(T) = \Delta_h C_p^\infty(298.15\ K) = const.$ This approximation is much more accurate than the assumption usually made in the environmental chemistry field that the enthalpy of hydration is constant or, in other words, that $\Delta_h C_p^\infty(T) = 0$ because in practically all experimentally studied cases $\Delta_h C_p^\infty(T)$ is positive and quite large, in excess of (100 to 200) $J \cdot mol \cdot K^{-1}$. The following relations are consistent with the approximation that $\Delta_h C_p^\infty = const$:

$$\Delta_h H^\infty(T_r) = \Delta_h H^\infty(T) - (T - T_r)\Delta_h C_p^\infty \qquad (19)$$

and

$$\Delta_h G^\infty(T_r) = \Delta_h G^\infty(T)\frac{T_r}{T} + \Delta_h H^\infty(T_r)\frac{T - T_r}{T} + \Delta_h C_p^\infty \frac{T_r}{T}\left(T \ln\frac{T}{T_r} - T + T_r\right) \quad (20)$$

where $T_r = 298.15$ K.

Estimation of the Activity Coefficients of Aqueous Organic Solutes

An important generalization for estimating $\gamma_{m,2}$ of organic compounds in water was proposed by Wood and coworkers,[16,17] which is called the Savage−Wood group contribution method for excess properties of organic compounds in water. This method takes into account only binary interaction contributions to the excess Gibbs energy of a system; in other words, it presupposes the linear molality dependence of ln $\gamma_{m,2}$ according to

$$\ln \gamma_{m,2} = \frac{2 g_{xx} m}{RT} \quad (21)$$

where g_{xx} is the solute−solute binary self-interaction coefficient. This linear concentration dependence of ln $\gamma_{m,2}$ is a reasonable approximation for many nonelectrolytes in water up to a molality of 1 or even slightly higher. In the Savage−Wood formalism, there is the following group contribution approximation to estimate g_{xx}:

$$g_{xx} = \sum_{i,j} n_i n_j G_{ij} - RT\frac{2}{N_w} \quad (22)$$

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. The following counting rules[16] are applicable for esters to simplify calculations: the CH_3 group is equal to 1.5 CH_2 groups; the CH group is equal to 0.5 CH_2 group; the C group is not counted; H in the methanoate group is considered equal to 0.5 CH_2 group; and COO is taken as a separate ester group. As an example, isopropyl acetate (2-propyl ethanoate), consisting of 3 CH_3, 1 CH, and 1 COO functional groups, in the Savage−Wood formalism is considered to consist of 5 CH_2 and 1 COO groups. To calculate g_{xx} for aqueous solutions of isopropyl acetate, one needs to count 25 CH_2−CH_2, 10 CH_2−COO, and 1 COO−COO interactions. Although the Savage−Wood formalism cannot distinguish between isomers, it is a sound and useful tool for estimating activity coefficients of organic compounds in water.

Auxiliary Data for Esters

Standard Gibbs Energy of Vaporization of Esters. The values of the standard Gibbs energy of vaporization are calculated from vapor pressures, P_2^*, and second virial coefficients, B_{22}, of pure esters; see eq 8. The Tsonopouolos[18] and Hayden−O'Connell[19] corresponding state correlations are employed to evaluate values of B_{22}. The necessary values of the saturated vapor pressure of esters are taken from the Poling et al.[20] handbook, if available. Otherwise, we simultaneously fit published experimental vapor pressure, P_2^*, and enthalpy of vaporization, $\Delta_{vap}H^*$ (at low pressures, $\Delta_{vap}H^*$ is close to $\Delta_{vap}H°$; see ref 14), data to determine the parameters of the Antoine equation, which was used in the form[20]

$$\log (P_2^*/\text{bar}) = A - \frac{B}{(T/\text{K}) + C - 273.15} \quad (23)$$

Following Majer et al.,[14] we corrected the measured enthalpy of vaporization for the nonideality of the gaseous phase to extract the value of (d ln P_2^*/dT) as follows:

$$RT^2\left(\frac{d \ln P_2^*}{dT}\right) = \frac{\Delta_{vap}H^*}{\Delta Z} = \frac{\Delta_{vap}H^*}{1 + P_2^*(B_{22} - V_2^*)/RT} \quad (24)$$

The resulting parameters of the Antoine equation and the sources of data and the temperature ranges of validity are given in Table 1. In a few cases where we could not locate experimental vapor pressure data, we employed a group contribution corresponding-states method[21] to estimate P_2^* values. Note that for some esters vapor pressure measurements were made only in the 19th century. An additional problem is that the well-known compilation of Stull[22] is based on both measured and extrapolated values, and for some esters the extrapolated values do not appear to be reliable. (At least the calculated $\Delta_{vap}H°$ and $\Delta_{vap}G°$ values do not always exhibit regularities expected in homologous series.) Therefore, in some cases, where experimental data are available only at $T > 298$ K, we add to the fit the value of $\Delta_{vap}H^*$(298.15 K), which was obtained by extrapolating the corresponding values for lower members of the corresponding homologous series. (Extensive data for ethanoates indicate that the CH_2 group contribution for esters is about 4.1 kJ·mol^{-1} for $\Delta_{vap}H°$(298.15 K).) A comparison of experimental and fitted values of the vapor pressure of esters is presented in the online ORganic Compounds HYDration database (ORCHYD) at http://orchyd.asu.edu. This site also offers online calculation of P_2^* and B_{22} of esters as well as other compounds already present in the database.

Estimation of Activity Coefficients of Esters in Aqueous Solutions. For some acetates (ethanoates), the values of activity coefficients in water are available from measurements of freezing points of aqueous solutions.[57,58] These data, combined with the compositions of coexisting phases at 273.15 K,[59,60] are used to calculate the Gibbs energy of solution of esters in water by means of eq 10. The necessary values of the activity of an ester in the organic-rich phase are calculated using the UNIQUAC model, with the UNIQUAC parameters taken from ref 61, if available, or otherwise evaluated by us from the compositions of coexisting phases at 273.15 K.

Most reliable aqueous solubility values for esters refer to 298.15 K. The necessary values of activity coefficients of an ester in the ester-rich phase are calculated using the UNIQUAC model, with the UNIQUAC parameters taken from ref 61 or evaluated by us from compositions of coexisting phases. In most cases, the deviations from ideality for the organic-rich phase are within (1 to 2)%. Activity coefficients of esters in aqueous solutions at 298.15 K are estimated by the Savage−Wood model, with the following numerical values of the binary parameters for the relevant interactions: CH_2−CH_2 with $G_{CH_2-CH_2} = -34$ J·kg·mol^{-2},[62] CH_2−COO with $G_{CH_2-COO} = 82$ J·kg·mol^{-2},[57] and COO−COO with $G_{COO-COO} = -240$ J·kg·mol^{-2}.[57] The last two values refer to 273.15 K; however, as a reasonable approximation, they can be used at 298.15 K because these "interactions are not very temperature dependent".[57]

Specifics of Esters. It is known[63] that in water esters eventually undergo hydrolysis and split into acids and

Table 1. Antoine Constants in the Equation $\log(P_2^*/\mathrm{bar}) = A - B/(T/\mathrm{K} + C - 273.15)$

compound	A	B	C	temperature range/K	data sources
2-propyl methanoate	4.3848	1332.88	235.68	221−342	P_2^* [22]
butyl methanoate	3.9803	1212.06	198.97	295−386	P_2^*,[23−25] $\Delta_{\mathrm{vap}}H^*$ [26]
2-methylpropyl methanoate	4.4172	1437.16	227.65	240−395	P_2^* [22,27]
pentyl methanoate	4.5287	1597.0	222.70	270−410	P_2^* [21,a]
3-methylbutyl methanoate	4.3627	1509.61	222.42	256−397	P_2^* [22,27]
hexyl methanoate	4.5909	1714.64	220.11	270−430	P_2^* [21,a]
2-propyl ethanoate	4.2880	1327.01	221.26	294−385	P_2^*,[23] $\Delta_{\mathrm{vap}}H^*$ [26]
2-butyl ethanoate	4.0863	1280.04	202.48	298−404	P_2^*,[28,29] $\Delta_{\mathrm{vap}}H^*$ [b]
1,1-dimethylethyl ethanoate	4.0005	1219.44	207.41	283−363	P_2^* [30]
2-methylpropyl ethanoate	4.3701	1468.45	220.18	295−411	P_2^*,[31,32] $\Delta_{\mathrm{vap}}H^*$ [c]
pentyl ethanoate	4.3107	1539.67	208.26	298−449	P_2^*,[33,34] $\Delta_{\mathrm{vap}}H^*$ [35]
3-methylbutyl ethanoate	4.5224	1630.06	219.67	273−415	P_2^* [22,23,35]
hexyl ethanoate	4.4502	1690.85	209.76	298−459	P_2^* [36−38]
propyl propanoate	4.1222	1344.42	204.18	270−412	P_2^*,[39,40,22] $\Delta_{\mathrm{vap}}H^*$ [26]
2-propyl propanoate	4.1180	1304.24	207.16	270−390	P_2^* [21,a]
butyl propanoate	4.3880	1559.61	210.99	298−431	P_2^*,[23,41] $\Delta_{\mathrm{vap}}H^*$ [c]
2-methylpropyl propanoate	4.2591	1468.66	208.56	298−433	P_2^*,[31,42] $\Delta_{\mathrm{vap}}H^*$ [b]
pentyl propanoate	4.2728	1588.05	203.53	270−450	P_2^* [21,a]
ethyl butanoate	4.2110	1393.11	210.30	270−404	P_2^*,[39,43] $\Delta_{\mathrm{vap}}H^*$ [26]
propyl butanoate	4.3700	1548.69	211.99	298−430	P_2^*,[31,32,39,40,44] $\Delta_{\mathrm{vap}}H^*$ [c]
2-propyl butanoate	4.1580	1397.12	205.93	270−410	P_2^* [21,a]
butyl butanoate	4.1959	1534.58	201.36	298−450	P_2^*,[44,45] $\Delta_{\mathrm{vap}}H^*$ [c]
methyl 2-methylpropanoate	4.3297	1362.69	222.91	239−390	P_2^*,[46,31,22] $\Delta_{\mathrm{vap}}H^*$ [26]
ethyl 2-methylpropanoate	4.1888	1363.47	215.75	270−409	P_2^*,[22] $\Delta_{\mathrm{vap}}H^*$ [26]
2-methylpropyl 2-methylpropanoate	4.4722	1656.03	223.37	278−441	P_2^* [29,31,47]
methyl pentanoate	4.6583	1668.54	231.28	293−417	P_2^*,[48,49] $\Delta_{\mathrm{vap}}H^*$ [26]
ethyl pentanoate	4.4041	1575.15	213.58	270−420	P_2^*,[21,a] $\Delta_{\mathrm{vap}}H^*$ [26]
butyl pentanoate	4.0187	1492.93	185.15	291−460	P_2^* [50,21,a]
methyl 2,2-dimethylpropanoate	3.9024	1180.99	201.97	298−374	P_2^*,[51] $\Delta_{\mathrm{vap}}H^*$ [26]
ethyl 3-methylbutanoate	4.1683	1415.36	205.73	270−410	P_2^* [21,a]
ethyl 2-methylbutanoate	4.1567	1424.13	210.20	278−406	P_2^* [52,53]
methyl hexanoate	4.6797	1741.69	223.28	290−378	P_2^*,[23,48] $\Delta_{\mathrm{vap}}H^*$ [26]
ethyl hexanoate	4.5217	1713.40	212.59	279−449	P_2^*,[35,36,43] $\Delta_{\mathrm{vap}}H^*$ [26]
methyl heptanoate	4.5778	1793.74	218.11	298−450	P_2^*,[48,21,a] $\Delta_{\mathrm{vap}}H^*$ [26]
methyl octanoate	4.8794	2007.38	220.92	298−419	P_2^*,[48,23,54,55] $\Delta_{\mathrm{vap}}H^*$ [26]
ethyl octanoate	4.7444	1993.65	214.31	298−479	P_2^*,[36,56] $\Delta_{\mathrm{vap}}H^*$ [56]
methyl nonanoate	4.5637	1907.50	203.87	298−358	P_2^*,[48] $\Delta_{\mathrm{vap}}H^*$ [26]

[a] Estimated by a group contribution corresponding-states method.[21] [b] Value at 298.15 K estimated by the Ducros group contribution method.[14] [c] Value at 298.15 K extrapolated from the values for the lower member of the corresponding homologous series.

alcohols. This hydrolysis is catalyzed by acids and bases and accelerated by higher temperatures. Stephenson and Stuart[64] reported a significant hydrolysis of some methanoates in aqueous solutions; however, other authors[65−67] found it is possible to obtain reliable experimental data for esters, including methanoates, by controlling the pH of solutions and avoiding long-term experiments.

Data Compilation

The central part of this work is the compilation of a representative database for thermodynamic properties of aliphatic esters in standard aqueous solution. The large number of entries in the database serves two chief purposes: first, to provide uncertainty estimates for the properties of each ester in the database, and second, to cover a variety of structures of esters. The latter is important to judge the need for introducing second-order groups or corrections. We worked with primary sources of data, reporting original experimental values of properties of interest and ignored numerous literature compilations, which are often mixtures of data from primary and secondary (other compilations) sources. An exception is for mutual solubility data in water, where we accepted for some esters the recommended values from the Solubility Data Series compilation[59,60] as the source of solubility data published before 1990. (However, we included solubility data that were overlooked by the authors of this compilation.)

There is a large number of ingenious experimental methods and their variations proposed over several decades for measuring the chemical potential and its derivatives for an aqueous solute. In many cases, it is difficult, if not impossible, to give a fair expert evaluation of the quality of an experimental measurement based solely on the description of the experimental device and data treatment procedure given in the original papers. Therefore, the following method was adopted: we convert the measured properties into values of the thermodynamic functions of hydration and compare them for each of the solutes we considered. Typically, most results cluster around a single value with a few obvious outliers. These outliers are given in parentheses among the data in Tables 2 to 5. A few results are considered to be the most reliable and are given in bold in the Tables. The decision to rate a value as the most reliable is subjective and typically is based on a number of considerations: good agreement between the results and reliable data for well-studied systems, a detailed and careful description of the methods and results, low values claimed for uncertainties, the authority of an experimental group, and so forth. More information related to our critical data evaluation (the method used, primary

Table 2. Standard Enthalpies of Hydration, $\Delta_{h}H^{\infty}$, and Vaporization, $\Delta_{vap}H^{\circ}$, of Esters at 298.15 K and 0.1 MPa, Experimental and Group Contribution (GC) Values for I and II Order Additivty Methods, and the Difference between Experimental and GC Values, Δ

compound	$\Delta_{vap}H^{\circ}$ kJ·mol^{-1}	$\Delta_{h}H^{\infty}$ kJ·mol^{-1}	accepted value	I order GC value	Δ kJ·mol^{-1}	II order GC value	Δ kJ·mol^{-1}
methyl methanoate	28.60 ± 0.29[26]	−32.1 $\Delta_{sol}H^{\infty}$,[68,a] H^{E},[24,a] −31.4 $G^{\infty}(T)$[69]	−32.02 ± 2.0	−33.06	1.04	−32.29	0.27
ethyl methanoate	32.11 ± 0.33[26]	−38.4 $\Delta_{sol}H^{\infty}$,[68,a] H^{E},[24,a] −35.6 $G^{\infty}(T)$[69]	−38.09 ± 2.0	−36.70	−1.39	−37.47	−0.62
propyl methanoate	37.61 ± 0.18[26]	−40.6 $G^{\infty}(T)$[59]	−40.51 ± 2.0	−40.33	−0.18	−40.99	0.48
2-methylpropyl methanoate	38.0 ± 1.0[b]	−43.0 $G^{\infty}(T)$[64]	−43.0 ± 2.2	−43.57	0.57	−43.32	0.32
pentyl methanoate	44.2 ± 1.5[b]	−48.1 $G^{\infty}(T)$[64]	−48.1 ± 2.5	−47.60	−0.50	−48.04	−0.06
3-methylbutyl methanoate	41.8 ± 1.0[b]	−47.7 $G^{\infty}(T)$[64]	−47.7 ± 2.2	−47.21	−0.49	−46.84	−0.86
methyl ethanoate	32.50 ± 0.17[26]	**−39.96** $\Delta_{sol}H^{\infty}$,[70] (−42.33) $\Delta_{sol}H^{\infty}$,[71] (−42.33) $\Delta_{sol}H^{\infty}$,[72] −41.60 $\Delta_{sol}H^{\infty}$,[73] **−40.10** $\Delta_{sol}H^{\infty}$,[74] **−40.31** $\Delta_{sol}H^{\infty}$,[75] −39.61 $\Delta_{sol}H^{\infty}$,[76] −41.33 H^{E} [77]	−40.13 ± 0.5	−40.92	0.79	−40.18	0.05
ethyl ethanoate	35.69 ± 0.18[26]	**−45.22** $\Delta_{sol}H^{\infty}$,[78] −45.04 $\Delta_{sol}H^{\infty}$,[79] −45.44 $\Delta_{sol}H^{\infty}$,[71] −45.44 $\Delta_{sol}H^{\infty}$,[72] **−45.39** $\Delta_{sol}H^{\infty}$,[73] **−45.38** $\Delta_{sol}H^{\infty}$,[74] **−45.48** $\Delta_{sol}H^{\infty}$,[80,c] −45.61 H^{E},[77] (−46.19) $\Delta_{sol}H^{\infty}$,[81] −45.02 $\Delta_{sol}H^{\infty}$,[82] −45.02 $\Delta_{sol}H^{\infty}$,[83] −45.02 $\Delta_{sol}H^{\infty}$,[84] −45.65 $\Delta_{s}H^{\infty}$,[85] −45.21$\Delta_{sol}H^{\infty}$ [86,d]	−45.32 ± 0.5	−44.56	−0.76	−45.35	0.03
propyl ethanoate	39.77 ± 0.10[26]	−49.61 $G^{\infty}(T)$,[87] −47.87 $G^{\infty}(T)$,[59] **−49.07** $\Delta_{sol}H^{\infty}$,[73] −45.9 $G^{\infty}(T)$,[88] −47.42 $\Delta_{sol}H^{\infty}$[76,e]	−48.66 ± 1.0	−48.19	−0.47	−48.88	0.22
2-propyl ethanoate	37.27 ± 0.19[26]	−46.52 $\Delta_{sol}H^{\infty}$,[80,c] −47.06 $\Delta_{sol}H^{\infty}$[82]	−46.79 ± 0.5	−47.80	1.01	−46.88	0.09
butyl ethanoate	43.89 ± 0.22[26]	−53.62 $\Delta_{sol}H^{\infty}$,[71] −52.72 $\Delta_{sol}H^{\infty}$,[72] −51.72 $\Delta_{sol}H^{\infty}$,[76] −53.28 H^{E} [77]	−52.66 ± 1.0	−51.83	−0.83	−52.40	−0.26
1,1-dimethylethyl ethanoate	38.03 ± 0.20[26]	−45.85 $G^{\infty}(T)$,[87] −47.78 $G^{\infty}(T)$,[64] −45.38 $\Delta_{sol}H^{\infty}$,[76] −46.92 $\Delta_{sol}H^{\infty}$,[89,f] (−43.47) $\Delta_{sol}H^{\infty}$[82]	−46.22 ± 1.0	−46.56	0.34	−46.22	0.00
2-methylpropyl ethanoate	41.4 ± 1.0[b]	−50.62 $G^{\infty}(T)$,[77] (−55.94) $\Delta_{sol}H^{\infty}$,[71] −52.08 $\Delta_{sol}H^{\infty}$,[72] −51.9 $G^{\infty}(T)$[64]	−51.84 ± 1.0	−51.43	−0.41	−51.20	−0.64
2-butyl ethanoate	42.1 ± 1.0[b]	−51.35 $G^{\infty}(T)$,[77] −52.2 $G^{\infty}(T)$[64]	−51.9 ± 2.0	−51.43	−0.46	−50.41	−1.49
pentyl ethanoate	48.0 ± 0.8[b]	(−48.6) $\Delta_{sol}H^{\infty}$,[71] −56.6 $G^{\infty}(T)$,[64] −56.3 $G^{\infty}(T)$,[90] −54.1 $G^{\infty}(T)$,[88] −54.9 H^{E} [77]	−55.34 ± 1.5	−55.46	0.12	−55.92	0.58
3-methylbutyl ethanoate	46.3 ± 0.6[b]	(−45.9) $\Delta_{sol}H^{\infty}$,[71] −55.9 $G^{\infty}(T)$,[64] −54.8 $G^{\infty}(T)$[91]	−53.83 ± 1.5	−55.07	1.24	−54.72	0.89
hexyl ethanoate	48.0 ± 0.8[b]	−60.8 $G^{\infty}(T)$[64]	−60.8 ± 2.2	−59.10	−1.70	−59.45	−1.35
methyl propanoate	35.95 ± 0.18[26]	**−44.60** $\Delta_{sol}H^{\infty}$,[75] −41.95 $G^{\infty}(T)$[59]	−44.54 ± 0.5	−44.56	0.02	−44.12	−0.42
ethyl propanoate	39.27 ± 0.10[26]	**−49.52** $\Delta_{sol}H^{\infty}$,[74] −47.77 $G^{\infty}(T)$[64]	−49.52 ± 0.5	−48.19	−1.33	−49.29	−0.23
propyl propanoate	43.48 ± 0.25[26]	−51.18 $G^{\infty}(T)$[64]	−51.18 ± 2.0	−51.83	0.65	−52.81	1.63
butyl propanoate	47.6 ± 0.5[b]	−57.8 $G^{\infty}(T)$[64]	−57.8 ± 2.1	−55.46	−2.34	−56.34	−1.46
2-methylpropyl propanoate	45.7 ± 1.0[b]	−54.7 $G^{\infty}(T)$[92]	−54.7 ± 2.2	−55.07	0.37	−55.14	0.44
methyl butanoate	39.33 ± 0.40[26]	**−47.66** $\Delta_{sol}H^{\infty}$,[74] −47.37 $\Delta_{sol}H^{\infty}$,[75] −47.1 $\Delta_{sol}H^{\infty}$[93]	−47.53 ± 0.5	−48.19	0.66	−47.64	0.11
ethyl butanoate	42.71 ± 0.13[26]	**−52.60** $\Delta_{sol}H^{\infty}$,[74] −54.11 $G^{\infty}(T)$[64]	−52.67 ± 0.5	−51.83	−0.84	−52.81	0.14

Table 2. (Continued)

compound	$\Delta_{\mathrm{vap}}H^\circ$ $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{\mathrm{h}}H^\infty$ $\mathrm{kJ \cdot mol^{-1}}$	accepted value	I order GC value	Δ $\mathrm{kJ \cdot mol^{-1}}$	II order GC value	Δ $\mathrm{kJ \cdot mol^{-1}}$
propyl butanoate	46.8 ± 0.5[b]	−54.9 $G^\infty(T)$[64]	−54.9 ± 2.1	−55.46	0.56	−56.34	1.44
butyl butanoate	50.9 ± 1.0[b]	−63.5 $G^\infty(T)$[64]	−63.5 ± 3.2	−59.10	−4.40	−59.86	−3.64
methyl 2-methyl-propanoate	37.42 ± 0.38[26]	**−46.04** $\Delta_{\mathrm{sol}}H^\infty$,[75] −45.12 $G^\infty(T)$[64]	−45.96 ± 1.0	−47.80	1.84	−45.98	0.02
ethyl 2-methyl-propanoate	39.88 ± 0.20[26]	−51.28 $G^\infty(T)$[64]	−51.28 ± 2.0	−51.43	0.15	−51.16	−0.12
2-methylpropyl 2-methylpropanoate	45.7 ± 2.0[b]	−55.3 $G^\infty(T)$[64]	−55.3 ± 3.6	−58.31	3.01	−57.01	1.70
methyl pentanoate	43.13 ± 0.22[26]	**−50.41** $\Delta_{\mathrm{sol}}H^\infty$,[75] −50.63 $G^\infty(T)$[64]	−50.42 ± 0.5	−51.83	1.41	−51.17	0.75
ethyl pentanoate	47.01 ± 0.10[26]	**−56.52** $\Delta_{\mathrm{sol}}H^\infty$[74]	−56.52 ± 0.5	−55.46	−1.06	−56.34	−0.18
methyl 2,2-dimethylpropanoate	38.82 ± 0.20[26]	**−46.14** $\Delta_{\mathrm{sol}}H^\infty$,[75] −47.62 $G^\infty(T)$[64]	−46.21 ± 0.5	−46.56	0.35	−45.76	−0.45
ethyl 2,2-dime-thylpropanoate	41.29 ± 0.42[26]	**−50.32** $\Delta_{\mathrm{sol}}H^\infty$,[74] −51.09 $G^\infty(T)$[64]	−50.33 ± 0.5	−50.20	−0.13	−50.93	0.60
ethyl 3-methylbutanoate	45.1 ± 1.0[b]	−56.0 $G^\infty(T)$[64]	−56.0 ± 2.2	−55.07	−0.93	−55.14	−0.86
ethyl 2-methylbutanoate	43.8 ± 1.0[b]	−55.4 $G^\infty(T)$[92]	−55.4 ± 2.2	−55.07	−0.33	−54.68	−0.72
methyl hexanoate	48.04 ± 0.25[26]	**−54.74** $\Delta_{\mathrm{sol}}H^\infty$,[74] −56.04 $G^\infty(T)$[64]	−54.74 ± 0.5	−55.46	0.72	−54.69	−0.05
ethyl hexanoate	51.72 ± 0.10[26]	**−60.17** $\Delta_{\mathrm{sol}}H^\infty$,[74] −59.82 $G^\infty(T)$[64]	−60.17 ± 0.6	−59.10	−1.07	−59.86	−0.31

[a] See text. [b] Evaluated from P_2^*(T) data, see Table 1. [c] Medium is 0.1 HCl. [d] Medium is 0.2 M NaCl. [e] Recalculated from 297.05 K. [f] Recalculated from 296.7 K.

Table 3. Ideal Gas Heat Capacity, C_p(g), Standard Partial Molar Heat Capacity of Hydration, $\Delta_{\mathrm{h}}C_p^\infty$, of Esters at 298.15 K and 0.1 MPa, Experimental and Group Contribution (GC) Values for I and II Order Additivity Methods, and the Difference between Experimental and GC Values, Δ

compound	C_p(g) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\Delta_{\mathrm{h}}C_p^\infty$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	accepted value	I order GC value	Δ $\mathrm{J \cdot K^{1} \cdot mol^{-1}}$	II order GC value	Δ $\mathrm{J \cdot K^{1} \cdot mol^{-1}}$
methyl methanoate	66.6 ± 3[15,a]	176 $H(T)$[30,68,b]	176 ± 30	170	6	166	10
ethyl methanoate	92 ± 3[a,c]	225 $H(T)$[30,68,b]	225 ± 30	231	−6	235	−10
methyl ethanoate	86 ± 3[a,c]	**213** cal,[95] 204 $H(T)$,[74] 215 cal,[96] **212** cal,[97] 197 cal[98]	210 ± 7	206	4	202	8
ethyl ethanoate	114 ± 3[a,c]	270 $H(T)$,[74] 281 cal,[96] 259 cal,[99] **283** cal,[97] 260 cal[98]	275 ± 10	267	8	271	4
ethyl propanoate	139 ± 3[a,c]	335 $H(T)$[74]	335 ± 7	329	6	331	4
methyl butanoate	141 ± 3[a,c]	319 $H(T)$[74]	319 ± 7	329	−10	325	−6
ethyl butanoate	162 ± 3[a,c]	392 $H(T)$[74]	392 ± 10	391	1	393	−1
ethyl 2,2-dimethylpropanoate	186 ± 3[a,c]	433 $H(T)$[74]	433 ± 10	434	−1	433	0
ethyl pentanoate	185 ± 3[a,c]	457 $H(T)$[74]	457 ± 12	453	4	455	2
methyl hexanoate	187 ± 3[a,c]	444 $H(T)$[74]	444 ± 10	453	9	449	−5
ethyl hexanoate	208 ± 3[a,c]	491 $H(T)$[74]	491 ± 12	515	−24	517	−26

[a] Our estimate of uncertainty. [b] See text. [c] Benson group contribution method.[94]

data reported, estimated uncertainty, and comments) is available in our online database at http://orchyd.asu.edu.

Standard Molar Enthalpy of Hydration at 298.15 K, 0.1 MPa. Table 2 gives the results of our evaluation for $\Delta_{\mathrm{h}}H^\infty$. The first column lists names of esters. Our accepted values of the standard enthalpy of vaporization of the pure compound at 298.15 K are listed in the second column. The third column gives the compiled values of $\Delta_{\mathrm{h}}H^\infty$ together with abbreviations employed to indicate the type of data converted to the $\Delta_{\mathrm{h}}H^\infty$ value: $\Delta_{\mathrm{sol}}H^\infty$ denotes values based on the enthalpy of solution; H^{E} denotes values based on the composition differentiation of the excess enthalpy of mixing; and $G^\infty(T)$ denotes values based on the temperature differentiation of $\Delta_{\mathrm{h}}G^\infty$ or $\Delta_{\mathrm{sol}}G^\infty$. Accepted values of $\Delta_{\mathrm{h}}H^\infty$ together with their estimated uncertainties are given in the fourth column.

Some comments are necessary to explain our selection of $\Delta_{\mathrm{h}}H^\infty$ for methyl and ethyl methanoates. For methyl methanoate, there is an old (19th century) value of the enthalpy of solution in water, $\Delta_{\mathrm{sol}}H^\infty(288.2\ \mathrm{K}) = -4.73\ \mathrm{kJ \cdot mol^{-1}}$, as given in the International Critical Tables.[68] In addition, the value of $\Delta_{\mathrm{sol}}H^\infty(323.15\ \mathrm{K}) = -0.41\ \mathrm{kJ \cdot mol^{-1}}$ was evaluated by us from enthalpy of mixing measurements[24] at 323.15 K and 1.755 MPa; the pressure correction between $P^\circ = 0.1$ and $P = 1.755$ MPa, equal to

$$-\int_{P_0}^{P} \left\{ V_2^\infty - T\left(\frac{\partial V_2^\infty}{\partial T}\right) \right\} \mathrm{d}P$$

is expected to be less than 0.1 kJ·mol^{-1} and was neglected. These data, treated using the assumption that $\Delta_{\mathrm{h}}C_p^\infty$ = const and combined with the accepted values of C_p(g) and $\Delta_{\mathrm{vap}}H^\circ$ at 298.15 K (Tables 2 and 3), result in values of $\Delta_{\mathrm{h}}H^\infty(298\ \mathrm{K}) = -32.1\ \mathrm{kJ \cdot mol^{-1}}$ with an expected uncertainty of about 1 kJ·mol^{-1} and $\Delta_{\mathrm{h}}C_p^\infty(298\ \mathrm{K}) = 176\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ with an expected uncertainty of about 30 J·K^{-1}·mol^{-1}. Values of $\Delta_{\mathrm{h}}H^\infty$ and $\Delta_{\mathrm{h}}C_p^\infty$ for ethyl methanoate are evaluated in a similar way; see Tables 2 and 3.

Standard Molar Heat Capacity of Hydration at 298.15 K, 0.1 MPa. Table 3 gives results of the data

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

compound	$\Delta_{\mathrm{vap}}G^{\circ}$	$\Delta_{\mathrm{h}}G^{\infty}$	accepted value	I order GC value	Δ	II order GC value	Δ
	$\mathrm{kJ{\cdot}mol^{-1}}$	$\mathrm{kJ{\cdot}mol^{-1}}$			$\mathrm{kJ{\cdot}mol^{-1}}$		$\mathrm{kJ{\cdot}mol^{-1}}$
methyl methanoate	0.69 ± 0.05^{20}	$-\mathbf{3.53}\ \gamma^{\infty},^{24}\ -3.85\ \gamma^{\infty},^{100}$ $-3.49\ K_{\mathrm{D},c},^{102}\ (-7.49)\ K_{\mathrm{D},c},^{103,a}$ $-3.42\ \gamma^{\infty},^{104}\ -3.43\ K_{\mathrm{D},c},^{69,b}$ $-3.55\ \gamma^{\infty}\ ^{105,c}$	-3.53 ± 0.20	-3.70	0.17	-3.75	0.23
ethyl methanoate	2.84 ± 0.05^{20}	$-\mathbf{3.10}\ \gamma^{\infty},^{24}\ -3.42\ \gamma^{\infty},^{106}$ $-3.24\ \gamma^{\infty},^{100}\ -3.35\ \mathrm{sol},^{59}$ $-2.77\ \gamma^{\infty},^{107,d}\ -2.72\ k_{\mathrm{H}},^{108,d}$ $-2.93\ K_{\mathrm{D},c},^{103,a}\ (4.14)\ K_{\mathrm{D},c},^{69,b}$ $-3.15\ \gamma^{\infty}\ ^{105}$	-3.11 ± 0.24	-3.01	0.10	-2.99	-0.12
propyl methanoate	5.57 ± 0.05^{20}	$-2.80\ \gamma^{\infty},^{100}\ -2.75\ \mathrm{sol},^{59}$ $-2.30\ K_{\mathrm{D},c},^{103,a}\ -2.85\ \gamma^{\infty},^{105}$ $-2.64\ \mathrm{sol}^{65,e}$	-2.57 ± 0.30	-2.31	0.26	-2.30	0.37
2-propyl methanoate	4.20 ± 0.15^{f}	$-1.60\ K_{\mathrm{D},c}^{103,a}$	-1.60 ± 0.30	-1.75	0.15	-1.50	-0.10
butyl methanoate	8.17 ± 0.15^{f}	$-1.50\ \gamma^{\infty},^{24}\ -1.63\ K_{\mathrm{D},c},^{103,a}$ $-1.83\ \mathrm{sol},^{109,g}\ -1.89\ \mathrm{sol},^{65,e}$ $-1.45\ \mathrm{sol}^{110}$	-1.62 ± 0.30	-1.62	0.00	-1.62	-0.00
2-methylpropyl methanoate	7.28 ± 0.15^{f}	$-1.39\ \mathrm{sol},^{64,h}\ -0.83\ K_{\mathrm{D},c},^{103,a}$ $-1.53\ \mathrm{sol}^{111,i}$	-1.09 ± 0.4	-1.05	-0.04	-1.19	0.10
pentyl methanoate	10.96 ± 0.30^{f}	$-1.69\ \mathrm{sol},^{64,j}\ -0.90\ K_{\mathrm{D},c}^{103,a}$	-1.11 ± 0.5	-0.92	-0.19	-0.94	-0.17
3-methylbutyl methanoate	9.93 ± 0.15^{f}	$1.69\ \mathrm{sol},^{64,k}\ -0.43\ K_{\mathrm{D},c},^{103,a}$ $-0.32\ \mathrm{sol},^{67,c}\ -1.31\ \mathrm{sol},^{65,l}$ $-1.53\ \mathrm{sol}^{111,i}$	-0.52 ± 0.5	-0.36	-0.16	-0.51	0.01
hexyl methanoate	13.73 ± 0.30^{f}	$(-1.93)\ \mathrm{sol},^{64,m}\ 0.00\ K_{\mathrm{D},c}^{103,a}$	-0.11 ± 0.5	-0.23	0.12	-0.25	0.14
methyl ethanoate	3.12 ± 0.05^{20}	$-\mathbf{5.23}\ \gamma^{\infty},^{4}\ -4.87\ \mathrm{sol},^{87}$ $-\mathbf{5.19}\ \mathrm{sol},^{58,n}\ -5.07\ K_{\mathrm{D},c},^{112,a}$ $-5.35\ \gamma^{\infty},^{100}\ -4.42\ \gamma^{\infty},^{113}$ $-5.06\ K_{\mathrm{D},c},^{114}\ -5.25\ \gamma^{\infty},^{115,o}$ $-5.06\ K_{\mathrm{D},c},^{103,a}\ -5.05\ \gamma^{\infty},^{104}$ $-5.05\ K_{\mathrm{D},c},^{88}\ -5.40\ \gamma^{\infty},^{116,\mathrm{c}}$ $-5.34\ K_{\mathrm{D},c},^{55}\ -5.91\ k_{\mathrm{H}},^{117}$ $-5.23\ k_{\mathrm{H}}^{118}$	-5.18 ± 0.20	-4.87	-0.31	-5.15	-0.03
ethyl ethanoate	5.16 ± 0.05^{20}	$-4.90\ \mathrm{sol},^{119,a}\ -5.09\ K_{\mathrm{D},c},^{120,a}$ $-4.70\ \mathrm{sol},^{121,p}\ -4.93\ \mathrm{sol},^{87}$ $-4.42\ K_{\mathrm{D},c},^{122,a}\ -4.99\ K_{\mathrm{D},c},^{123,a}$ $-4.24\ \mathrm{sol},^{58,n}\ -4.93\ \mathrm{sol},^{124}$ $(-0.02)\ K_{\mathrm{D},c},^{125}\ -4.81\ \mathrm{sol},^{126}$ $-4.65\ \gamma^{\infty},^{127}\ -3.01\ K_{\mathrm{D},c},^{128}$ $-3.91\ \gamma^{\infty},^{129}\ -4.37\ \gamma^{\infty},^{130}$ $-4.64\ \mathrm{sol},^{131,c}\ -4.24\ K_{\mathrm{D},c},^{112,a}$ $-4.73\ \gamma^{\infty},^{100}\ -4.61\ \gamma^{\infty},^{132}$ $-4.93\ \mathrm{sol},^{59}\ -4.70\ \gamma^{\infty}\ ^{133}$ $-4.42\ \gamma^{\infty},^{134,q}\ -4.27\ K_{\mathrm{D},c},^{135,r}$ $-5.03\ \mathrm{sol},^{136,c}\ -5.35\ K_{\mathrm{D},c}\ ^{137,a}$ $-4.51\ K_{\mathrm{D},c},^{138}\ -4.92\ \mathrm{sol},^{139}$ $-3.99\ \gamma^{\infty},^{140}\ -4.50\ \mathrm{sol}\ ^{57,n}$ $-4.41\ \gamma^{\infty},^{107,d}\ -3.53\ \gamma^{\infty},^{141}$ $-4.31\ k_{\mathrm{H}},^{108,d}\ -4.65\ K_{\mathrm{D},c}\ ^{114,q}$ $-4.45\ K_{\mathrm{D},c},^{103,a}\ -4.51\ \gamma^{\infty},^{104}$ $-4.37\ K_{\mathrm{D},c},^{88}\ -4.65\ \gamma^{\infty},^{116,c}$ $-4.44\ K_{\mathrm{D},c},^{142,s}\ -4.65\ k_{\mathrm{H}},^{89}$ $(-2.76)\ \gamma^{\infty},^{143,t}\ -4.74\ K_{\mathrm{D},c},^{144,u}$ $-4.98\ k_{\mathrm{H}}^{117}$	-4.56 ± 0.28	-4.17	-0.39	-4.38	-0.18
propyl ethanoate	7.73 ± 0.05^{20}	$-5.20\ K_{\mathrm{D},c},^{120,a}\ -3.25\ K_{\mathrm{D},c},^{122,a}$ $-3.98\ \mathrm{sol},^{87}\ -3.50\ \mathrm{sol},^{58,n}$ $-3.98\ \mathrm{sol},^{124}\ -3.22\ K_{\mathrm{D},c},^{128}$ $-3.57\ K_{\mathrm{D},c},^{112,a}\ -4.08\ \gamma^{\infty},^{70}$ $-4.04\ \mathrm{sol},^{59}\ -3.62\ \gamma^{\infty},^{107,d}$ $-3.53\ \gamma^{\infty},^{141}\ -3.55\ k_{\mathrm{H}},^{108,d}$ $-3.61\ K_{\mathrm{D},c},^{103,a}\ -3.85\ \gamma^{\infty},^{104}$ $-3.75\ K_{\mathrm{D},c},^{88}\ -3.62\ \gamma^{\infty}\ ^{116,c}$	-3.72 ± 0.26	-3.48	-0.24	-3.69	-0.03
2-propyl ethanoate	6.25 ± 0.05^{f}	$-3.11\ \mathrm{sol},^{145}\ -3.57\ K_{\mathrm{D},c},^{112,a}$ $-3.19\ \gamma^{\infty},^{100}\ -3.02\ \mathrm{sol},^{59}$ $-2.51\ \gamma^{\infty},^{141}\ -2.69\ K_{\mathrm{D},c},^{103,a}$ $-2.44\ \gamma^{\infty 116,c,e}$	-2.95 ± 0.40	-2.91	-0.04	-2.89	-0.06
butyl ethanoate	10.40 ± 0.15^{f}	$-4.50\ K_{\mathrm{D},c},^{120,a}\ -3.29\ K_{\mathrm{D},c},^{122,a}$ $-3.17\ \mathrm{sol},^{87}\ -2.68\mathrm{sol},^{58,n}$ $-3.17\ \mathrm{sol},^{124}\ -3.56\ \mathrm{sol},^{146,d}$ $-2.45\ K_{\mathrm{D},c},^{128}\ -2.56\ K_{\mathrm{D},c},^{112,a}$ $-4.52\ \mathrm{sol},^{147,d}\ -3.74\ \gamma^{\infty},^{100}$ $-2.87\ K_{\mathrm{D},c},^{135,r}\ -3.49\ \mathrm{sol},^{59}$ $-3.99\ \mathrm{sol},^{136,c}\ -3.09\ \gamma^{\infty},^{141}$ $-3.12\ K_{\mathrm{D},c},^{114}\ -2.96\ K_{\mathrm{D},c},^{103,a}$ $-3.12\ K_{\mathrm{D},c},^{88}\ -2.84\ \gamma^{\infty},^{116,c}$ $-3.48\ \gamma^{\infty},^{148,v}\ -3.19\ \mathrm{sol}^{110}$	-3.09 ± 0.40	-2.78	-0.31	-3.01	-0.08
1,1-dimethylethyl ethanoate	7.13 ± 0.10^{f}	$-0.34\ \mathrm{sol},^{87}\ 1.22\ \mathrm{sol},^{58,n}$ $-0.34\ \mathrm{sol},^{124}\ -0.45\ \mathrm{sol}^{64,w}$	-0.30 ± 0.40	0.05	-0.35	-0.3	0.00
2-methylpropyl ethanoate	9.25 ± 0.15^{f}	$-2.14\ \mathrm{sol},^{87}\ -1.29\ \mathrm{sol},^{58,n}$ $-2.14\ \mathrm{sol},^{124}\ -1.93\ K_{\mathrm{D},c},^{112,a}$ $-2.32\ \mathrm{sol},^{149}\ -2.50\ \gamma^{\infty},^{100}$ $-2.28\ \mathrm{sol},^{59}\ -1.97\ K_{\mathrm{D},c},^{103,a}$ $-2.08\ \gamma^{\infty}\ ^{116,c,e}$	-2.13 ± 0.30	-2.22	0.09	-2.58	0.45
2-butyl ethanoate	8.81 ± 0.20^{f}	$-2.37\ \mathrm{sol},^{87}\ -1.51\ \mathrm{sol},^{58,n}$ $-2.37\ \mathrm{sol},^{124}\ -2.28\ \mathrm{sol},^{64,x}$ $-2.09\ K_{\mathrm{D},c}^{103,a}$	-2.06 ± 0.36	-2.22	0.16	-2.21	0.15

Table 4. (Continued)

compound	$\Delta_{\mathrm{vap}}G^{\mathrm{o}}$ kJ·mol^{-1}	$\Delta_{\mathrm{h}}G^{\infty}$ kJ·mol^{-1}	accepted value	I order GC value	Δ kJ·mol^{-1}	II order GC value	Δ kJ·mol^{-1}
pentyl ethanoate	13.10 ± 0.15^{f}	$(-7.30)\ K_{\mathrm{D},}c,^{150,d}\ -2.70\ K_{\mathrm{D},}x,^{151,o}$ -2.29 sol,^{124} $-1.89\ K_{\mathrm{D},}c,^{112,a}$ $-3.00\ \gamma^{\infty},^{100}$ -2.57 sol,^{60} $-2.23\ K_{\mathrm{D},}c,^{103,a}\ -2.54\ K_{\mathrm{D},}c,^{88}$ $-2.40\ \gamma^{\infty\ 116,c}$	-2.43 ± 0.30	-2.09	-0.34	-2.33	-0.10
3-methylbutyl ethanoate	12.22 ± 0.10^{f}	$(-6.28)\ K_{\mathrm{D},}c,^{150,d}\ -1.37\ \gamma^{\infty},^{152}$ $-1.67\ K_{\mathrm{D},}c,^{112,a}$ -2.07 sol,^{60} $-1.53\ K_{\mathrm{D},}c^{103,a}$	-1.69 ± 0.40	-1.52	-0.17	-1.90	0.21
hexyl ethanoate	15.71 ± 0.20^{f}	$-1.01\ K_{\mathrm{D},}c,^{153}$ -1.31 sol,^{124} $-2.28\ \gamma^{\infty},^{100}$ -1.86 sol,^{60} $-0.93\ K_{\mathrm{D},}c^{103,a}$	-1.29 ± 0.40	-1.39	0.10	-1.64	0.35
methyl propanoate	5.39 ± 0.05^{20}	-4.61 sol,^{59} $-3.97\ \gamma^{\infty},^{113}$ $-4.12\ K_{\mathrm{D},}c,^{114}\ -4.13\ K_{\mathrm{D},}c,^{103,a}$ $-4.12\ \gamma^{\infty},^{116,\mathrm{c}}$ -4.21 sol,^{154,c} $-4.31\ K_{\mathrm{D},}c^{55}$	-4.21 ± 0.30	-4.17	-0.04	-4.00	-0.21
ethyl propanoate	7.45 ± 0.05^{20}	$-3.66\ \gamma^{\infty},^{100}$ -3.63 sol,^{59} $-3.39\ K_{\mathrm{D},}c,^{103,a}$ -3.13 sol^{110}	-3.51 ± 0.30	-3.48	-0.03	-3.23	-0.28
propyl propanoate	9.96 ± 0.15^{f}	-2.76 sol,^{59} $-2.44\ K_{\mathrm{D},}c^{103,a}$	-2.60 ± 0.40	-2.78	0.18	-2.55	-0.05
2-propyl propanoate	8.38 ± 0.30^{f}	$-1.51\ K_{\mathrm{D},}c^{103,a}$	-1.51 ± 0.6	-2.22	0.71	-1.75	0.24
butyl propanoate	12.68 ± 0.15^{f}	-2.20 sol,^{64,y} $-1.65\ K_{\mathrm{D},}c,^{103,a}$ -1.22 sol^{110}	-1.68 ± 0.50	-2.09	0.41	-1.86	0.18
2-methylpropyl propanoate	11.59 ± 0.25^{f}	-1.42 sol,$^{92,}z$ $-0.67\ K_{\mathrm{D},}c^{103,a}$	-1.04 ± 0.50	-1.52	0.48	-1.44	0.40
pentyl propanoate	15.28 ± 0.30^{f}	-2.83 sol,^{60} $-0.30\ K_{\mathrm{D},}c^{103,a}$	-1.56 ± 1.3	-1.39	-0.17	-1.18	-0.38
methyl butanoate	7.82 ± 0.05^{20}	$(-4.86)\ K_{\mathrm{D},}c,^{124,a}$ -3.60 sol,^{59} $-3.62\ \gamma^{\infty},^{113}\ -3.20\ K_{\mathrm{D},}c,^{114}$ $-3.12\ \gamma^{\infty},^{116,c}$ -3.38 sol,^{154,c} $-3.90\ K_{\mathrm{D},}c^{55}$	-3.55 ± 0.4	-3.48	-0.07	-3.32	-0.23
ethyl butanoate	$9.77\ \pm 0.15^{f}$	-2.23 sol,^{119,a} $-3.85\ K_{\mathrm{D},}c,^{120,a}$ $-3.05\ K_{\mathrm{D},}c,^{122,a}\ (-4.35)\ K_{\mathrm{D},}c,^{123,a}$ $-2.71\ K_{\mathrm{D},}c,^{155}\ -2.25\ K_{\mathrm{D},}c,^{130}$ $-2.21\ \gamma^{\infty},^{129}\ -3.38\ \gamma^{\infty},^{100}$ $-3.15\ \gamma^{\infty},^{132}$ -2.32 sol,^{132} -2.69 sol,^{59} $-2.59\ \gamma^{\infty 116,c}$	-2.63 ± 0.4	-2.78	0.19	-2.55	-0.04
propyl butanoate	12.36 ± 0.15^{f}	-2.10 sol,^{64,aa} -1.69 sol^{156,bb}	-1.97 ± 0.4	-2.09	0.12	-1.86	-0.11
2-propyl butanoate	10.81 ± 0.30^{f}	(-6.62) sol,^{64,x} -1.38 sol^{157,d}	-1.47 ± 1.0	-1.52	0.05	-1.07	-0.40
butyl butanoate	14.75 ± 0.25^{f}	-1.34 sol,^{64,c} -0.66 sol^{158,c}	-1.20 ± 0.5	-1.39	0.19	-1.18	-0.02
methyl 2-methyl-propanoate	6.68 ± 0.10^{f}	-2.52 sol,^{64,cc} $-2.27\ \gamma^{\infty 116,c}$	-2.40 ± 0.40	-2.91	0.51	-2.31	-0.09
ethyl 2-methyl-propanoate	8.43 ± 0.10^{f}	$-1.98\ \gamma^{\infty},^{132}$ -0.88 sol,^{132} -1.24 sol^{64,dd}	-1.33 ± 0.6	-2.22	0.89	-1.54	0.21
2-methylpropyl 2-methylpropanoate	12.53 ± 0.15^{f}	$+1.33$ sol,^{64,z} $-0.03\ K_{\mathrm{D},}c^{159}$	0.63 ± 0.83	-0.26	0.89	0.25	0.38
methyl pentanoate	10.58 ± 0.10^{f}	-2.37 sol,^{161,ee} $(-5.10)\ \gamma^{\infty},^{113}$ -2.85 sol,^{64,x} $-2.70\ \gamma^{\infty},^{116,c}$ (-0.79) sol,^{157,d} -2.61 sol,^{154,d} $-2.81\ K_{\mathrm{D},}c^{55}$	-2.69 ± 0.3	-2.78	0.09	-2.64	-0.05
ethyl pentanoate	12.55 ± 0.20^{f}	$(-7.49)\ K_{\mathrm{D},}c,^{150,d}$ -2.78 sol,^{157,c} -1.56 sol^{161}	-2.10 ± 0.64	-2.09	-0.01	-1.86	-0.24
butyl pentanoate	17.61 ± 0.15^{f}	-0.87 sol,^{157,c} 0.96 sol^{110}	0.04 ± 1.0	-0.70	0.74	-0.50	0.54
methyl 2,2-dimethylpropanoate	7.44 ± 0.15^{f}	$+0.14$ sol^{64,m}	0.14 ± 0.5	0.05	0.09	-0.21	0.35
ethyl 2,2-dimethylpropanoate	9.29 ± 0.05^{f}	$+1.39$ sol^{64,c}	1.39 ± 0.6	0.74	0.65	0.56	0.83
ethyl 3-methylbutanoate	11.23 ± 0.20^{f}	-0.98 sol,^{64,z} -0.39 sol^{162}	-0.78 ± 0.5	-1.52	0.74	-1.44	0.66
ethyl 2-methylbutanoate	10.84 ± 0.15^{f}	$0.32\ K_{\mathrm{D},}c,^{163}\ -3.31\ K_{\mathrm{D},}c,^{164,d}$ -0.58 sol,^{165} -0.87 sol^{92,ff}	-0.76 ± 0.5	-1.52	0.76	-0.86	0.10
methyl hexanoate	13.33 ± 0.10^{f}	-1.55 sol,^{161,ee} $-3.24\ \gamma^{\infty},^{113}$ -2.46 sol,^{64,c} $-2.61\ \gamma^{\infty},^{116,c}$ -2.22 sol,^{154,c} $-2.46\ K_{\mathrm{D},}c,^{55}$ -1.90 sol^{166,c}	-2.36 ± 0.4	-2.09	-0.27	-1.95	-0.41
ethyl hexanoate	15.36 ± 0.15^{f}	-1.67 sol,^{119,a} $-1.78\ \gamma^{\infty},^{152}$ $-0.43\ K_{\mathrm{D},}c,^{155}\ (+0.11)\ K_{\mathrm{D},}c,^{130}$ $-1.29\ \gamma^{\infty},^{132}$ -1.51 sol,^{132} -2.48 sol,^{64,m} -2.12 sol,^{161} -1.80 sol^{167,c}	-1.65 ± 0.5	-1.39	-0.26	-1.18	-0.47
methyl heptanoate	15.99 ± 0.15^{f}	-0.55 sol,^{160,ee} -3.43 sol,^{64,y} -2.23 sol^{168,gg}	-1.45 ± 0.9	-1.39	-0.06	-1.27	-0.18
methyl octanoate	18.74 ± 0.15^{f}	0.12 sol,^{160,ee} $-0.58\ K_{\mathrm{D},}c,^{55}$ -0.52 sol,^{55} 0.64 sol^{166,c}	-0.36 ± 0.5	-0.70	0.34	-0.59	0.23
ethyl octanoate	20.47 ± 0.30^{f}	(-6.07) sol,^{64,k} -1.32 sol,^{161} -1.07 sol^{167,c}	-1.29 ± 2.0	0.00	-1.29	0.19	-1.48
methyl nonanoate	21.52 ± 0.15^{f}	(-7.53) sol,^{168,gg} 0.51 sol^{169}	0.49 ± 1.0	0.00	0.49	0.10	0.39
ethyl decanoate	25.86 ± 0.3^{f}	-0.3 sol,^{161} -2.10 sol^{167}	-0.55 ± 2.0	1.39	-1.94	1.55	-2.10

[a] Recalculated from 310.15 K. [b] Recalculated from 285.65 K. [c] Recalculated from 293.15 K. [d] Recalculated from 303.15 K. [e] Recalculated from 305.15 K. [f] Calculated from P_2^{*} values (Table 1) and second virial coefficients.[18,19] [g] Recalculated from 303.65 K. [h] Recalculated from 293.95 K. [i] Recalculated from 295.15 K. [j] Recalculated from 293.05 K. [k] Recalculated from 292.75 K. [l] Recalculated from 305.65 K. [m] Recalculated from 292.85 K. [n] Recalculated from 273.15 K. [o] Recalculated from 323.15 K. [p] Recalculated from 308.15 K. [q] Recalculated from 288.15 K. [r] Recalculated from 313.15 K. [s] Value is taken from the figure in original reference. [t] Recalculated from 297.4 K. [u] Recalculated from 301.2 K. [v] Recalculated from 317.6 K. [w] Recalculated from 292.35 K. [x] Recalculated from 292.65 K. [y] Recalculated from 292.45 K. [z] Recalculated from 292.55 K. [aa] Recalculated from 293.25 K. [bb] Recalculated from 290.15 K. [cc] Recalculated from 292.05 K. [dd] Recalculated from 292.95 K. [ee] Recalculated from 283.15 K. [ff] Recalculated from 291.85 K. [gg] Recalculated from 294.15 K.

evaluation for the standard partial molar heat capacity of hydration, $\Delta_{\mathrm{h}}C_p^{\infty}$. The accepted values of the molar heat capacity of a compound in the ideal gas state at 298.15 K are listed in the second column. The third column gives

Table 5. Standard Partial Molar Volumes, V_2^{∞}, of Esters at 298.15 K and 0.1 MPa, Experimental and Group Contribution (GC) Values for I and II Order Additivity Methods, and the Difference between Experimental and GC Values, Δ

compound	V_2^{∞} $\mathrm{cm^3 \cdot mol^{-1}}$	accepted value	I order GC value	Δ $\mathrm{cm^3 \cdot mol^{-1}}$	II order GC value	Δ $\mathrm{cm^3 \cdot mol^{-1}}$
methyl methanoate	55.27[170]	55.3 ± 0.3	55.45	−0.15	55.32	−0.02
ethyl methanoate	72.8[171]	72.8 ± 1.0	71.18	1.62	72.57	0.23
methyl ethanoate	72.36,[95] 72.23,[172] 72.26,[173] 72.46[97]	72.3 ± 0.2	73.59	−1.29	72.28	0.02
ethyl ethanoate	88.87,[172] 89.05,[173] 88.93,[170] 88.8,[171] 88.97[97]	89.0 ± 0.2	89.92	−0.32	89.53	−0.53
propyl ethanoate	104.90,[124,a] 105.12,[172] 105.24[173]	105.1 ± 0.2	105.05	0.05	105.14	−0.04
2-propyl ethanoate	106.21[173]	106.2 ± 0.2	105.51	0.69	106.27	−0.07
butyl ethanoate	121.02,[124,a] 121.17,[172] 121.14[173]	121.1 ± 0.2	120.78	0.32	120.75	0.35
2-methylpropyl ethanoate	121.32,[124,a] 121.43,[172] 121.71[173]	121.6 ± 0.3	121.25	0.36	121.05	0.55
2-butyl ethanoate	(119.47),[124,a] 121.73,[172] 122.10[173]	122.0 ± 0.4	121.25	0.76	121.88	0.12
1,1-dimethylethyl ethanoate	122.07,[124,a] 121.27,[172] 122.11[173]	122.1 ± 0.4	122.1	0.00	122.1	0.00

[a] Our calculation of V_{ϕ} from the published density of the saturated solution.

the compiled values of $\Delta_h C_p^{\infty}$ together with abbreviations employed to indicate the type of data converted to the $\Delta_h C_p^{\infty}$ value: cal denotes values based on calorimetric measurements of the heat capacity of solutions, and $H(T)$ denotes values based on the temperature differentiation of $\Delta_{sol}H^{\infty}$. Accepted values of $\Delta_h C_p^{\infty}$ together with their estimated uncertainties are given in the fourth column.

Gibbs Energy of Hydration of Esters at 298.15 K, 0.1 MPa. Table 4 gives the results of the data evaluation for the standard partial molar Gibbs energy of hydration, $\Delta_h G^{\infty}$. 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 the compiled values of $\Delta_h G^{\infty}$ together with abbreviations employed to indicate the type of data converted to the $\Delta_h G^{\infty}$ value: k_H denotes Henry's constants; γ^{∞} denotes the activity coefficient at infinite dilution; $K_{D,c}$ is the gas−water distribution constant on the molarity scale; and sol denotes values evaluated from mutual solubility data. Accepted values of $\Delta_h G^{\infty}$ together with their estimated uncertainties are given in the fourth column. For compounds with many $\Delta_h G^{\infty}$ values derived from experiment, the assigned uncertainty is equal to one standard deviation. For most compounds, the assigned uncertainty represents our judgment of the accuracy of the available data.

Partial Molar Volumes of Esters in Water at 298.15 K, 0.1 MPa. Table 5 gives the results of the data evaluation for the standard partial molar volumes, V_2^{∞}. All experimental data cited are obtained using the vibrating-tube densimeter, and they are given in the second column. Accepted values of V_2^{∞} together with their estimated uncertainties are given in the third column.

Online Database of the Thermodynamic Properties of Aqueous Organic Compounds

The thermodynamic properties of aliphatic esters in the ideal gas state, in the state of condensed phases stable at 298.15 K, 0.1 MPa, and in the state of standard aqueous solution as well as the thermodynamic functions of hydration at 298.15 K, 0.1 MPa are available in the online ORganic Compounds HYDration database (ORCHYD) described elsewhere.[174] A system was developed for the storage, manipulation, retrieval, and presentation of data that allows for the dynamic evaluation of the properties of hydration of an individual compound based on the current state of experimental coverage for the properties of that compound. The database stores primary experimental data from which the thermodynamic functions of hydration can be derived (solubility in water, Henry's constants, gas−water distribution constants, activity coefficients at infinite dilution, enthalpies of solution, etc.), relevant comments, and the properties of hydration evaluated according to the procedures outlined above (eqs 1 to 18). In most cases, the uncertainties of the values of the properties of hydration are assigned on the basis of a critical evaluation, but original experimental uncertainties, if given, are documented as well. The recommended values of the properties of hydration are then calculated dynamically at the time of retrieval as the weighted mean values of the corresponding set for an individual compound. The uncertainty of the recommended value is given as the standard deviation of the weighted mean value if a large number of experimental determinations are available, or more often, the uncertainty value reflects our estimate of the reliability of the data set for a given compound. As more experimental data become available for the compounds in the database, the values of the properties of hydration may change, along with the thermodynamic properties in the state of the aqueous solution, which are calculated dynamically from the functions of hydration and properties of the ideal gas state. This system not only provides a useful mechanism for up-to-date property evaluations but also ensures the internal consistency of the data while facilitating rapid updates and easy output.

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

Preliminary Runs. The values of the thermodynamic functions of hydration of esters were combined with those for aliphatic saturated hydrocarbons, alcohols, and ketones, both studied earlier[6,10] and for those added recently to our online database. Preliminary runs showed the necessity of separating the ester, COO, and the methanoate, COOH, groups. (Note that this was not done by Cabani and coworkers.[5]) In addition, it was found that the first-order group contribution method involving only CH_3, CH_2, CH, C, OH, CO, COO, and COOH groups was not capable of accurately reproducing $\Delta_h H^{\infty}$ values. For example, deviations between experimental and fitted values of $\Delta_h H^{\infty}$ could exceed 5 $\mathrm{kJ \cdot mol^{-1}}$, which is more than 5 to 10 times higher than the expected accuracy of calorimetric values. Similar, although less convincing, behavior was noticed for $\Delta_h G^{\infty}$ values. An attempt to introduce additional groups, for example, $C(CH_3)_2$, resulted in only a modest improvement of the goodness of the fit and was deemed not to be worthwhile.

We note that these large discrepancies are almost always found for organic compounds containing a tertiary carbon atom connected to polar groups. Therefore, we introduced second-order corrections to account for the presence of polar groups OH, CO, COO, and COOH(methanoate) attached to the tertiary carbon atom. The presence of these second-order corrections decreases the sums of the squared errors (SSE) for the Gibbs energy and enthalpy of hydration by about 28% and 57%, respectively (i.e., considerably improving the goodness of the fit). These results clearly demonstrate the limitations of the first-order group contribution method without nearest-neighbor corrections.

Optimal Values of the Contributions of the First-Order Groups to the Various Thermodynamic Functions of Hydration at 298.15 K, 0.1 MPa. Assuming group additivity for the thermodynamic functions of hydration, a property Y of a compound is given as

$$Y = Y_o + \sum_i n_i Y_i + \sum_j n_j Y_j \tag{25}$$

The first summation (with running index i) is for the first-order functional groups. In this case, these groups are CH_3, CH_2, CH, C, OH, CO, COO, and COOH(methanoate). The second summation (with running index j) accounts for corrections for the attachment of polar groups to the tertiary carbon atom. In this work, these corrections are C−OH, C−CO, C−COO, and C−COOH(methanoate). 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, a hypothetical substance devoid of size and interactions with anything). It follows from theoretical models[175,176] that the transfer of a material point from an ideal gas to the standard aqueous solutions is accompanied by the following nonzero change of the Gibbs energy:

$$\Delta_h G^\infty_{mp} = RT \ln\frac{RT}{P^o V^*_1} - RT \ln N_w \approx 7.95\ \mathrm{kJ \cdot mol^{-1}} \tag{26}$$

where the subscript mp denotes the material point and V^*_1 stands for the molar volume of water at some T and P (298.15 K, 0.1 MPa in our case). The second term is needed if (as in our case, see above) the molality concentration scale is employed. (It would be equal to zero if the mole fraction concentration scale were employed.) The numerical value, 7.95 kJ·mol^{-1}, is valid at 298.15 K, 0.1 MPa.

Thermodynamic manipulations of eq 26 result in the other thermodynamic functions of hydration of the material point:

$$\Delta_h H^\infty_{mp} = -T^2\left(\frac{\partial}{\partial T}\left[\frac{\Delta_h G^\infty_{mp}}{T}\right]\right)_P = RT(\alpha T - 1) \approx -2.29\ \mathrm{kJ \cdot mol^{-1}} \tag{27}$$

$$\Delta_h C^\infty_{p,mp} = \left(\frac{\partial}{\partial T}\Delta_h H^\infty_{mp}\right)_P = R\left(T^2\left(\frac{\partial \alpha}{\partial T}\right)_P + 2\alpha T - 1\right) \approx 0.08\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \cong 0 \tag{28}$$

$$\Delta_h V^\infty_{mp} \equiv V^\infty_{2,mp} = \left(\frac{\partial}{\partial P}\Delta_h G^\infty_{mp}\right)_T = RT\kappa_T \approx 1.12\ \mathrm{cm^3 \cdot mol^{-1}} \tag{29}$$

where the thermal expansion of water, α, is defined as

$$\alpha = \left(\frac{\partial \ln V^*_1}{\partial T}\right)_P \tag{30}$$

and the isothermal compressibility of water, κ_T, is given by

$$\kappa_T = -\left(\frac{\partial \ln V^*_1}{\partial P}\right)_T \tag{31}$$

The numerical values on the right-hand sides of eqs 27 to 29 are valid at 298.15 K, 0.1 MPa and were calculated from the IAPWS-95 equation of state for pure water.[177]

The values of Y_i and Y_j in eq 25 were obtained by using a weighted least-squares fitting procedure. Some remarks about the selection of weights are necessary. The most accurate values of the thermodynamic properties are obtained for the lowest members of a homologous series. However, it is well known that the lowest members of a homologous series show the greatest deviations from additivity. To reduce the possible effects of this conflict, we accepted as minimal uncertainties the following values: ±0.15 kJ·mol^{-1} and ±0.5 kJ·mol^{-1} for $\Delta_h G^\infty$ and $\Delta_h H^\infty$data, respectively; ±10 J·K^{-1}·mol^{-1} for $\Delta_h C^\infty_p$ values; and ±0.3 cm^3·mol^{-1} for V^∞_2 data. In addition, we excluded methanol from the fit because it alone contributed more than 25% to the SSE (sum of squared errors) value in the case of the enthalpy of hydration data.

Results are given in Table 6. For each group, we give the value of the group contribution together with its uncertainty at the 0.95 confidence level. The value of Y_j given in the Table as "0 fixed" means that it is statistically indistinguishable from zero. In parentheses, we give the number of compounds containing the selected group.

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

We assume that the reader is familiar with the Benson notation for the second-order group contribution method.[1,2] In the nomenclature used, the polyvalent atom (or group of atoms) is first identified and then 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 $CO-(C)_2$ represents the CO group connected to two C atoms.

Preliminary Runs. Preliminary runs showed that the existing practice[2] of accepting the identities of the following second-order groups $C-(H)_3(C) = C-(H)_3(CO) = C-(H)_3(O)$ can be safely extended to the thermodynamic functions of hydration as well because treating these groups separately resulted in only a modest improvement in the goodness of the fit. We also found that it makes little sense to include the "tertiary" and "quaternary" corrections for the attachment of the methyl, CH_3, group to a tertiary or quaternary carbon atom. However, we emphasize that these conclusions are valid for the current database and can be changed when a much larger number of organic compounds will be available to work with.

The following groups are necessary to represent compounds in the database: $C-(C)(H)_3$, $C-(C)_2(H)_2$, $C-(C)_3(H)$, $C-(C)_4$, $C-(C)(H)_2(O)$, $C-(C)_2(H)(O)_{alcohol}$, $C-(C)_3(O)_{alcohol}$, $O-(H)(C)$, $CO-(C)_2$, $C-(CO)(H)_2(C)$, $C-(CO)(H)(C)_2$, $C-(CO)(C)_3$, $C-(C)_2(H)(O)_{ester}$, $C-(C)_3(O)_{ester}$, $CO-(C)(O)$, $CO-(H)(O)$, and $O-(CO)(C)$. However, the contributions of the second-order groups $CO-(C)(O)$, $CO-(H)(O)$, and $O-(C)(O)$ cannot be separated because they are always present as the following combinations: $CO-(C)(O) + O-(CO)(C)$ for the case of esters and $CO-(C)(H) + O-(CO)(C)$ for the case of methanoates. Therefore, we introduced provisional "ester" and "methanoate" groups, namely, $COO-(C)_2$ and $HCOO-(C)$, respectively. Separating these groups will have to wait for a considerable extension of the database with the inclusion of polyfunctional compounds.

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

group or correction	$\Delta_h G^o$ / kJ·mol^{-1}	$\Delta_h H^o$ / kJ·mol^{-1}	$\Delta_h C_p^o$ / J·K^{-1}·mol^{-1}	V_2^∞ / cm^3·mol^{-1}
Y_o	7.95	−2.29	0	1.12
CH_3	3.67 ± 0.07 (136)	−8.02 ± 0.25 (99)	131 ± 4 (38)	25.49 ± 0.79 (52)
CH_2	0.70 ± 0.04 (116)	−3.63 ± 0.13 (81)	62 ± 2 (29)	15.73 ± 0.13 (39)
CH	−1.72 ± 0.16 (55)	1.14 ± 0.63 (42)	−6 ± 8 (5)	6.43 ± 0.86 (22)
C	−4.51 ± 0.31 (16)	10.39 ± 0.99 (13)	−96 ± 11 (5)	−3.50 ± 1.66 (9)
OH	−25.40 ± 0.15 (37)	−40.29 ± 0.53 (33)	17 ± 5 (15)	12.52 ± 0.86 (27)
CO	−22.74 ± 0.22 (19)	−23.15 ± 0.65 (16)	−92 ± 8 (3)	14.45 ± 1.63 (10)
COO	−20.17 ± 0.17 (40)	−22.60 ± 0.50 (29)	−28 ± 4 (9)	21.48 ± 1.59 (8)
HCOO	−15.33 ± 0.20 (9)	−22.76 ± 2.06 (6)	39 ± 16 (2)	28.83 ± 0.95 (2)
C−OHcorr	0 fixed (5)	−8.01 ± 1.06 (5)	34 ± 8 (2)	0 fixed (5)
C−COcorr	0.87 ± 0.79 (1)	0 fixed (1)	0 fixed (0)	0 fixed (1)
C−COOcorr	2.08 ± 0.56 (3)	0 fixed (3)	0 fixed (1)	1.03 ± 0.86 (1)
SSE[b]	105.5	153.0	17.4	106.8

[a] The number of compounds containing the selected group for each of the property is given in parentheses. [b] SSE stands for the sum of the squared errors.

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

group	$\Delta_h G^o$ / kJ·mol^{-1}	$\Delta_h H^o$ / kJ·mol^{-1}	$\Delta_h C_p^o$ / J·K^{-1}·mol^{-1}	V_2^∞ / cm^3·mol^{-1}
Y_o	7.95	−2.29	0	1.12
$C-(C)(H)_3$	3.72 ± 0.07 (136)	−8.19 ± 0.18 (99)	132 ± 4 (38)	25.56 ± 0.64 (52)
$C-(C)(H)_2$	0.68 ± 0.03 (96)	−3.52 ± 0.09 (63)	62 ± 2 (20)	15.61 ± 0.11 (29)
$C-(C)(H)$	−1.93 ± 0.16 (32)	2.34 ± 0.54 (22)	−17 ± 10 (2)	5.96 ± 0.80 (8)
$C-(C)_4$	−4.60 ± 0.32 (7)	10.87 ± 1.00 (4)	−97 ± 12 (2)	−4.08 ± 1.41 (2)
$C-(C)(H)_2(O)$	0.77 ± 0.20 (50)	−5.17 ± 0.40 (40)	68 ± 6 (16)	17.25 ± 0.50 (16)
$C-(C)_2(H)(O)_{alcohol}$	−1.64 ± 0.28 (13)	−1.88 ± 0.65 (12)	6 ± 10 (3)	7.48 ± 0.86 (10)
$C-(C)_3(O)_{alcohol}$	−4.58 ± 0.35 (5)	0.88 ± 0.85 (5)	−56 ± 12 (2)	−2.43 ± 1.43 (5)
$O-(C)(H)$	−25.46 ± 0.24 (37)	−38.34 ± 0.52 (33)	9 ± 7 (15)	11.35 ± 0.83 (27)
$CO-(C)_2$	−23.46 ± 0.27 (19)	−22.76 ± 0.59 (23)	−92 ± 9 (3)	14.81 ± 1.68 (10)
$C-(CO)(H)_2(C)$	+1.15 ± 0.28 (37)	−3.94 ± 0.38 (16)	61 ± 4 (8)	15.43 ± 0.82 (7)
$C-(CO)(H)(C)_2$	−0.88 ± 0.29 (8)	2.39 ± 0.92 (8)	(0)	4.12 ± 2.03 (3)
$C-(CO)(C)_3$	−2.50 ± 0.49 (3)	10.81 ± 0.72 (3)	−102 ± 14 (1)	−4.75 ± 3.44 (1)
$COO-(C)_2$[b]	−20.53 ± 0.22 (40)	−21.50 ± 0.54 (29)	−62 ± 8 (9)	20.05 ± 1.35 (8)
$HCOO-(C)$[c]	−15.43 ± 0.22 (9)	−21.81 ± 1.41 (6)	34 ± 16 (2)	28.64 ± 0.77 (2)
$C-(C)_2(H)(O)_{ester}$	−1.46 ± 0.34 (5)	1.49 ± 0.86 (2)	(0)	8.43 ± 0.85 (2)
$C-(C)_3(O)_{ester}$	−2.58 ± 0.67 (1)	10.34 ± 1.58 (1)	(0)	−1.30 ± 1.48 (1)
SSE[d]	72.5	64.0	14.6	66.6

[a] The number of compounds containing the selected group for each of the properties is given in parentheses. [b] Provisional ester group; see text. [c] Provisional methanoate group; see text. [d] SSE stands for the sum of the squared errors.

Optimal Values of the Second-Order Group Contributions to the Various Thermodynamic Functions of Hydration at 298.15 K, 0.1 MPa. As in the case of the first-order method, we employed a weighted least-squares fitting procedure to obtain values of second-order group contributions. To make the results of the two group contribution methods comparable, we used identical weights for the least-squares procedure. As in the case of the first-order method, we excluded methanol from the fit.

The results are given in Table 7. As in the case of the first-order method, for each group we give the value of the group contribution together with its uncertainty at the 0.95 confidence level. In parentheses, we give the number of compounds containing the selected group.

Discussion

Our results using the first-order group contribution method are rather similar to the results of Cabani et al.[5] For example, Cabani et al. found for the COO group the following values of contributions to the Gibbs energy and heat capacity of hydration: −20.34 kJ·mol^{-1} and −37 J·K^{-1}·mol^{-1} as compared with (−20.17 ± 0.17) kJ·mol^{-1} and (−28±4) J·K^{-1}·mol^{-1}, respectively, obtained in this study. Our results are based on a larger database for esters, which allows estimates of uncertainties of both accepted values for individual compounds and for derived group contributions. However, a direct comparison of our values with those of Cabani et al. cannot be made because of the different number and stoichiometry of groups employed; we found it is necessary to distinguish the ester and methanoate groups, and we also introduced some corrections for the presence of polar groups OH, CO, and COO attached to the tertiary carbon atom. In addition, we prefer to fix contributions from Y_o at their theoretical values (eqs 25 to 29) rather than treat them as adjustable parameters, as done by Cabani et al.[5]

Our experience shows that the second-order method provides significant improvement in the goodness of the fit, which can be seen by comparing the SSE (sum of squared errors) in Tables 6 and 7.

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