Group Contribution Values of the Infinite Dilution Thermodynamic Functions of Hydration for Aliphatic Noncyclic Hydrocarbons, Alcohols, and Ketones at 298.15 K and 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 noncyclic ketones. These data, combined with the related results for aliphatic noncyclic hydrocarbons and monohydric alcohols, were treated in the framework of a simple first-order group additivity scheme. Numerical values of the contributions to each of the thermodynamic properties are obtained by the least-squares procedure for the following groups: CH_3, CH_2, CH, C, OH, and CO.

Introduction

Values of thermodynamic properties of organic compounds in aqueous solutions at infinite dilution are needed for many applications in chemistry, biology, medicine, geochemistry, chemical engineering, and so forth. An experimental study of all the variety of organic compounds is out of the question: there are simply too many substances to make a comprehensive study possible. Instead, group additivity methods have been used to estimate the properties of organic species in gas, liquid, and solid phases (see refs 1−3). In 1981, Cabani et al.[4] presented an extensive database of thermodynamic functions of hydration of organic compounds at 298.15 K and derived group contribution values for many functional groups. Recently, attempts[5] have been made to update the database and group contribution values for aliphatic and monoaromatic hydrocarbons and monohydric alcohols. Here we present the results for aliphatic noncyclic ketones.

Data Compilation

The infinite dilution partial molar functions of hydration under consideration are the Gibbs energy, $\Delta_h G°$, the enthalpy, $\Delta_h H°$, the heat capacity, $\Delta_h C_p°$, and the volume, $V_2°$. The standard state adopted for gaseous species is unit fugacity of the ideal gas at any temperature and pressure $P^® = 0.1$ MPa; that for aqueous species calls for unit activity of a hypothetical 1 *m* solution referenced to infinite dilution at any temperature and pressure. The hydration process refers to transfer of 1 mol of a solute from an ideal gas to a standard 1 *m* solution. We note two main reasons to work with the functions of hydration rather than with the partial molar properties, like the Gibbs energy of formation of an aqueous compound. First, functions of hydration typically have lower uncertainties, because they do not include the uncertainties of the enthalpy of combustion measurements. Second, as discussed by Cabani et al.,[4] there is a universal contribution to the properties of aqueous species, which is seen as the nonzero intercept of a plot of properties for a homologous series versus molecular mass or number of groups. The nature of this term is obvious for the thermodynamic functions of hydration, where it arises as the functions of hydration of a material point.[6] This term can be calculated independently using the thermophysical properties of pure water, thus reducing the dimension of the fitting task.

Gibbs Energy of Hydration at 298.15 K. Literature values of the various modifications of Henry's law constants and gas/water partition coefficients were recalculated to yield equilibrium constants, $K°$, for a gas dissolution reaction A(g) ↔ A(aq), for which $\Delta_h G° = -RT \ln K° = -RT \ln(aP^®/f)$, where a and f stand for the activity and fugacity, respectively, of a solute in water, and $P^®$ is the ideal gas standard state pressure.

Results for the infinite dilution activity coefficient of a solute for the symmetrical normalization of activities, reported as γ^∞ were converted to $\Delta_h G°$ values as follows (see ref 5): $\Delta_h G° = -\Delta_{vap} G° + RT \ln \gamma^\infty - RT \ln 1000/M_w$, where M_w stands for the molecular mass of water in grams per mole; $\Delta_{vap} G° = -RT \ln(\psi P_s/P^®)$, where P_s stands for the saturated vapor pressure over the pure liquid/solid compound and ψ represents the fugacity coefficient of a pure compound, evaluated using the second virial coefficient.

The mutual solubility data were converted to $\Delta_h G°$ values as follows (see ref 5): $\Delta_h G° = \Delta_{sol} G° - \Delta_{vap} G°$, where $\Delta_{sol} G° = -RT \ln(m_s \gamma_{m,s}/X_s \gamma_{x,s})$, where m_s and $\gamma_{m,s}$ stand for the molality and the molal activity coefficient (for the unsymmetrical normalization) at saturation for an organic compound in the water-rich phase, respectively; X_s and $\gamma_{x,s}$ represent the mole fraction and the mole fraction activity coefficient (for the symmetrical normalization) of the organic compound in the coexisting organic-rich phase. The UNIQUAC model[7] was employed to evaluate $\gamma_{x,s}$. Values of $\gamma_{m,s}$ were estimated using the Savage and Wood[8] group contribution scheme. In the Savage−Wood formalism, ln $\gamma_{m,s} = 2g_{xx}m_s/RT$, where g_{xx} is the solute−solute self-interaction coefficient, given by $g_{xx} = \Sigma_{i,j} n_i n_j G_{ij} - RTM_w/2000$, where n_i and n_j represent the number of groups i and j in two interacting molecules and G_{ij} stands for the excess Gibbs energy of an i−j interaction. To characterize the ketone−ketone interactions, one needs $G_{CH_2-CH_2} = -34$

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Table 1. Values of the Gibbs Energies of Hydration of Ketones at 298.15 K and 0.1 MPa (See Text for Details)

compound	formula	$\Delta_{vap}G°$/kJ·mol^{-1}	$\Delta_{vap}G°$/kJ·mol^{-1}	accepted value	group contribution value	Δ/kJ·mol^{-1}
acetone	C_3H_6O	2.98[7,a]	−7.89,[12] −8.21,[13] −8.14,[14] −8.59,[15] −8.01,[16] −8.79,[17] −8.02,[18] −8.02,[19] −7.93,[20] −7.94,[21] −8.00,[22] −8.22,[23] −8.29,[24] −8.43[25]	−8.18 ± 0.30	−7.48	−0.70
2-butanone	C_4H_8O	5.28[7,a]	(−8.75),[12] −7.18,[11] −7.01,[16] −7.40,[17] (−5.06),[26] −7.11,[27] −6.97,[28] −6.97,[29] (−5.87),[19] −6.99,[20] −7.28,[30] −7.41,[31] −7.13,[21] −7.58[22]	−7.18 ± 0.30	−6.76	−0.42
2-pentanone	$C_5H_{10}O$	7.60[7,a]	−6.12,[32] *−6.34,*[33] *−6.19,*[34] −6.09,[16] *−6.17,*[35] −6.14,[20] −6.42,[30] −6.52,[31] *−6.21,*[36] −6.80,[22] −5.96[37]	−6.27 ± 0.40	−6.05	−0.22
3-pentanone	$C_5H_{10}O$	7.59[7,a]	*−5.82,*[34] −5.83,[16] −5.81,[20] −6.76,[31] *−5.81*[36]	−6.01 ± 0.40	−6.05	0.04
3-methyl-2-butanone	$C_5H_{10}O$	6.63[7,a]	*−5.42,*[34] *−5.61,*[38] *−5.56,*[35] *−5.29*[36]	−5.47 ± 0.30	−5.60	0.13
2-hexanone	$C_6H_{12}O$	10.35[39,a]	*−5.67,*[34] −5.64,[20] −5.48,[30] −5.67,[31] *−5.87*[36]	−5.67 ± 0.30	−5.34	−0.33
3-hexanone	$C_6H_{12}O$	9.92[39,a]	(0.63),[40] −4.95,[20] *−5.14*[36]	−5.01 ± 0.30	−5.34	0.33
4-methyl-2-pentanone	$C_6H_{12}O$	9.11[39,a]	*−4.64,*[41] *−4.81,*[34] (−2.33),[26] −4.74,[31] *−4.91*[36]	−4.78 ± 0.30	−4.88	0.10
2-methyl-3-pentanone	$C_6H_{12}O$	8.80[39,a]	*−4.12*[36]	−4.12 ± 0.60	−4.88	0.76
3-methyl-2-pentanone	$C_6H_{12}O$	9.24[39,a]	*−5.28*[36]	−5.28 ± 0.60	−4.88	−0.40
3,3-dimethyl-2-butanone	$C_6H_{12}O$	7.83[39,a]	*−3.68,*[34] −3.83,[30] *−3.63*[36]	−3.71 ± 0.40	−4.64	0.93
2-heptanone	$C_7H_{14}O$	13.04[42]	−4.38,[32] *−4.83,*[34] −4.81,[30] −5.45,[31] *−5.02,*[36] −4.77[22]	−4.88 ± 0.40	−4.63	−0.26
4-heptanone	$C_7H_{14}O$	12.54[39,a]	*−4.50*[16]	−4.50 ± 0.60	−4.63	0.13
2,4-dimethyl-3-pentanone	$C_7H_{14}O$	9.79[39,a]	*−1.89,*[34] *−2.37*[36]	−2.13 ± 0.50	−3.72	1.59
2-octanone	$C_8H_{16}O$	15.84[42]	*−4.70,*[34] *−4.28,*[43] *−4.11*[22]	−4.36 ± 0.40	−3.91	−0.45
2-nonanone	$C_9H_{18}O$	18.46[42]	*−3.53,*[44] *−3.76,*[34] −2.45[22]	−3.25 ± 0.50	−3.20	−0.05
2,6-dimethyl-4-heptanone	$C_9H_{18}O$	15.07[39,a]	*−0.73*[34]	−0.73 ± 1.00	−2.29	1.56
2-undecanone	$C_{11}H_{22}O$	24.28[39,a]	−1.09,[22] *−2.1*[22]	−1.6 ± 0.6	−1.78	0.18

[a] Value from the published compilation.

Table 2. Values of the Enthalpy of Hydration of Ketones at 298.15 K and 0.1 MPa

compound	formula	$\Delta_{vap}H°$/kJ·mol^{-1}	$\Delta_hH°$/kJ·mol^{-1}	accepted value	group contribution value	Δ/kJ·mol^{-1}
acetone	C_3H_6O	31.27[45,a]	−41.70,[46] −41.57,[47] −41.44,[48] −41.44,[49] −41.24,[50] −41.48,[51] −41.18[52]	−41.5 ± 0.3	−40.65	−0.85
2-butanone	C_4H_8O	34.92[45,a]	−45.64,[49] −45.42[53]	−45.5 ± 0.5	−44.37	−1.13
2-pentanone	$C_5H_{10}O$	38.46[45,a]	−48.67,[49] −49.98[54]	−49.0 ± 0.5	−48.11	−0.89
3-pentanone	$C_5H_{10}O$	38.68[45,a]	−49.58,[49] −49.56[54]	−49.6 ± 0.5	−48.11	−1.49
3-methyl-2-butanone	$C_5H_{10}O$	36.87[45,a]	−47.50[49]	−47.6 ± 1.0	−48.26	0.66
2-hexanone	$C_6H_{12}O$	43.15[45,a]	−52.61[49]	−52.6 ± 1.0	−51.86	−0.74
4-methyl-2-pentanone	$C_6H_{12}O$	40.65[45,a]	−50.15[49]	−50.2 ± 1.0	−52.00	1.80
3,3-dimethyl-2-butanone	$C_6H_{12}O$	38.00[45,a]	−47.50[49]	−47.5 ± 1.0	−51.34	3.84
2-heptanone	$C_7H_{14}O$	47.24[45,a]	−56.19,[49] −56.86[54]	−56.4 ± 0.6	−55.60	−0.80
4-heptanone	$C_7H_{14}O$	47.2[39,b]	−58.1[54]	−58.1 ± 2.0	−55.60	−2.50
2,4-dimethyl-3-pentanone	$C_7H_{14}O$	41.57[45,a]	−51.2,[49] −57.1[54]	−54.0 ± 3.0	−55.88	1.88
2-nonanone	$C_9H_{18}O$	56.44[45,a]	−62.7[54]	−62.7 ± 2.0	−63.08	0.38

[a] Recommended value from the compilation of calorimetric values of enthalpies of vaporization. [b] Estimated value from the temperature dependence of the saturated vapor pressure.

Table 3. Values of the Heat Capacity of Hydration of Ketones at 298.15 K and 0.1 MPa

compound	formula	$C_p(ig)$/J·K^{-1}·mol^{-1}	$\Delta_hC_p°$/J·K^{-1}·mol^{-1}	accepted value	group contribution value	Δ/J·K^{-1}·mol^{-1}
acetone	C_3H_6O	74.5[3]	150,[55] 166[56]	158 ± 10	163	−5
2-butanone	C_4H_8O	103.3[3]	234,[57] 233[58]	234 ± 5	230	4
3-pentanone	$C_5H_{10}O$	129.9[3]	298[58]	298 ± 10	297	1

Table 4. Values of $V_2°$ of Ketones in Water at 298.15 K and 0.1 MPa

compound	formula	$V_2°$/cm^3·mol^{-1}	accepted value	group contribution value	Δ/cm^3·mol^{-1}
acetone	C_3H_6O	66.92,[59] 66.8,[60] 66.92,[61] 67.0[62]	66.9 ± 0.3	66.80	0.10
2-butanone	C_4H_8O	82.44,[57] 82.56,[63] 82.52,[58] 82.9,[60] 82.5[62]	82.5 ± 0.3	82.51	−0.01
2-pentanone	$C_5H_{10}O$	98.0[60]	98.0 ± 2.0	98.21	−0.21
3-pentanone	$C_5H_{10}O$	98.08[58]	98.1 ± 1.0	98.21	−0.11
3-methyl-2-butanone	$C_5H_{10}O$	95.0[60]	95.0 ± 2.0	98.41	−3.41

J·mol^{-1},[9] G_{CH_2-CO} = 41 J·mol^{-1}, and G_{CO-CO} = −64 J·mol^{-1}; the two later values were evaluated from the g_{xx} values for acetone[10] and 2-butanone.[11]

The values of $\Delta_hG°$ obtained for ketones are presented in Table 1. Where necessary, results measured within (10−20) K from 298.15 K were recalculated to this temperature using the approximation that $\Delta_hH°$ is constant. Results based on mutual solubility studies are given in italics.

Values considered unreliable are given in parentheses and were excluded from consideration.

Enthalpy and Heat Capacity of Hydration, and Partial Molar Volume at 298.15 K and 0.1 MPa. Calorimetric values of the standard enthalpy of solution of a pure liquid ketone in water, $\Delta_sH°$, were converted to $\Delta_hH°$ by means of $\Delta_hH° = \Delta_sH° − \Delta_{vap}H°$, where $\Delta_{vap}H°$

Table 5. 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[a]

group	$\Delta_h G°/kJ \cdot mol^{-1}$	$\Delta_h H°/kJ \cdot mol^{-1}$	$\Delta_h C_p°/J \cdot K^{-1} \cdot mol^{-1}$	$V_2°/cm^3 \cdot mol^{-1}$
CH_3	3.62 ± 0.15 (79)	-7.55 ± 0.58 (40)	128 ± 5 (26)	25.46 ± 0.89 (30)
CH_2	0.71 ± 0.07 (66)	-3.74 ± 0.29 (29)	67 ± 2 (19)	15.70 ± 0.15 (22)
CH	-1.74 ± 0.30 (43)	-0.08 ± 1.44 (13)	9 ± 11 (6)	6.15 ± 0.98 (12)
C	-4.41 ± 0.54 (12)	4.39 ± 2.30 (4)	-42 ± 15 (4)	-3.46 ± 1.85 (4)
OH	-25.34 ± 0.23 (32)	-40.47 ± 1.09 (16)	1 ± 7 (16)	12.63 ± 0.97 (20)
CO	-22.68 ± 0.31 (18)	-23.24 ± 1.25 (12)	-93 ± 11 (3)	14.76 ± 1.82 (5)
Y_o	7.96	-2.29	0	1.12

[a] The number of compounds containing the selected groups for each of the properties is given in parentheses.

stands for the standard enthalpy of vaporization of a pure compound. Results are presented in Table 2.

Published values of the infinite dilution partial molar heat capacity of aqueous solutes, $C_{p,2}°$, were used to calculate $\Delta_h C_p$ as follows: $\Delta_h C_p = C_{p,2}° - C_p(ig)$, where $C_p(ig)$ represents the heat capacity of a compound in the ideal gas state. Results are given in Table 3.

Literature values of the infinite dilution partial molar volumes of ketones in water are presented in Table 4.

Group Contribution Values

The values of the thermodynamic functions of hydration of ketones at 298.15 K and 0.1 MPa were combined with those for aliphatic noncyclic hydrocarbons and monohydric alcohols, which were presented elsewhere.[5] The first-order group additivity scheme, in which the properties of a group are assumed to be independent of the group's neighbors, was chosen to treat the data. The following groups are necessary to represent the selected compounds: CH_3, CH_2, CH, C, OH, and CO. Assuming the properties of the groups are additive, any thermodynamic property of interest, Y, can be estimated from $Y = Y_o + \Sigma_i n_i Y_i$, where n_i stands for the number of times the i-th group is present in the compound, Y_i designates the contribution to the Y property of the i-th group, and Y_o represents the values of thermodynamic functions of hydration of a material point, that is, an imaginable compound without any groups at all. Values of Y_o can be calculated independently using the thermophysical properties of water (ref 6; for details see ref 5). The numerical values of the group contributions given in Table 5 were derived by a weighted least-squares fit of the selected data set.

Our results can be compared only with those of Cabani et al.,[4] who also determined the group contribution values for the thermodynamic functions of hydration of organic compounds. However, direct comparison of results is senseless, because of different values of the Y_o term accepted here and in ref 4 (the difference is large; for instance, $Y_o = 1.12$ cm$^3 \cdot$mol^{-1} in our method versus 13.41 cm$^3 \cdot$mol^{-1} [4] for the partial molar volumes, or -2.29 kJ$\cdot$mol^{-1} versus -13.87 kJ$\cdot$mol^{-1} in ref 4 for the partial molar enthalpies of hydration). The latter authors treated the Y_o term as an adjustable parameter in the fit; however, we accepted it to represent the thermodynamic functions of hydration of a material point. In defense of our position, there is greater theoretical clarity in our decision to choose a material point as a limiting case of a compound without any groups at all. In addition, our experience shows that fixing Y_o at its theoretical value results in a relatively small sacrifice in the goodness of the fit.[5] Besides, the potential extension of group contribution methods to other temperatures, where experimental data are not as extensive as at 298 K, will be easier to implement with the independently known value of Y_o. Of course, the different values of Y_o will translate into different values of the group contributions

even when the identical database is used to derive them. As every group contribution method has to reproduce data for the hydrocarbon backbone, then the effect of the Y_o variations is larger for values of CH_3, CH_2, CH, and C groups and smaller for the values of functional groups, like CO and OH. Indeed, the value of the Gibbs energy of hydration for the CO group obtained here, -22.68 ± 0.31 kJ$\cdot$mol^{-1}, is close to -23.06 kJ$\cdot$mol^{-1}, given by Cabani et al.;[4] however, these values should not be compared directly, for reasons discussed above. An essential feature of this work is a comprehensive update of the database for the thermodynamic functions of hydration for ketones (see Tables 1–4), which may be valuable for many applications besides the determination of the group contribution values.

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