Reviews

Group Contribution Values for the Thermodynamic Functions of Hydration at 298.15 K, 0.1 MPa. 4. Aliphatic Nitriles and Dinitriles

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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 partial molar volumes in water at 298.15 K and 0.1 MPa is presented for aliphatic nitriles and dinitriles. These data are treated in the framework of the first- and second-order group additivity methods. Thermodynamic properties are determined for the first-order CN group and for the following second-order groups: C-(CN)(C)(H)$_2$, C-(CN)(C)$_2$(H), and CN-(C). The relatively long-range dipole−dipole interactions of two terminal nitrile groups require additional corrections, {CN-(CH$_2$)$_2$-CN}$_{corr}$ and {CN-(CH$_2$)$_3$-CN}$_{corr}$, for lower dinitriles. New experimental studies of aqueous branched mononitriles and lower dinitriles (particularly propanedinitrile) are required to expand the usefulness and accuracy of group contribution models for aqueous nitriles.

Introduction

Aliphatic nitriles are organic compounds having the structural unit R−C≡N, where R represents any alkyl group. Nitriles are used for production of polymers and for the synthesis of pharmaceuticals and pesticides[1] because nitrile groups can be converted relatively easily to other functional groups. Nitriles are stable in water at moderate temperatures; however, they are hydrolyzed in strong solutions of either acids or bases. 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 (see, for example, ref 2) to provide an up-to-date compilation of thermodynamic properties of hydration of organic compounds and to determine group contributions to the functions of hydration of these compounds at 298.15 K and 0.1 MPa.

This work is organized as follows. First, a database of thermodynamic functions of hydration for aliphatic mono- and dinitriles is compiled. Second, the database of compiled data is used to derive optimal values of the contributions of the functional groups in the framework of the first- and second-order group contribution methods. The following standard partial molar thermodynamic functions of hydration are the focus of this study: the Gibbs energy, $\Delta_h G^\infty$; enthalpy, $\Delta_h H^\infty$; 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 compounds are those recommended by IUPAC.[3]

Auxiliary Data for Pure and Aqueous Compounds

Standard Gibbs Energy of Vaporization of Pure Compounds. The necessary 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 saturated vapor pressures, P_s, and second virial coefficients, B_{22}, according to

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

where $P^\circ = 0.1$ MPa is the standard state pressure, and ϕ_2^* stands for the fugacity coefficient of a pure compound:

$$\phi_2^* = \exp\left(\frac{B_{22}P_s}{RT}\right) \qquad (2)$$

The values of B_{22} are evaluated from the Tsonopouolos[4] and Poling et al.[5] and/or Hayden−O'Connell[6] corresponding-states correlations. Experimental vapor pressure, P_s, and enthalpy of vaporization, $\Delta_{vap}H^*$, data from the literature were used to determine, by the simultaneous fit of these data, the parameters (A, B, C) of the Antoine equation, which was taken in the form:[5]

$$\log(P_s/\text{bar}) = A - B/\{(T/\text{K}) + C - 273.15\} \qquad (3)$$

Following Majer et al.,[7] the measured enthalpy of vaporization was corrected for nonideality of the gaseous phase to evaluate

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

compound	A	B	C	temperature range/K	data sources
acetonitrile	4.4285	1436.94	243.31	273−400	P_s[9−14]
propanenitrile	4.4366	1492.45	239.61	290−400	P_s[10,14−16]
butanenitrile	4.2816	1467.95	225.74	278−415	P_s,[14,17−19] $\Delta_{vap}H$[20]
2-methylpropanenitrile	4.5481	1566.94	241.31	298−380	P_s,[15] $\Delta_{vap}H$[20]
pentanenitrile	4.2054	1501.07	216.61	290−430	P_s,[14,16] $\Delta_{vap}H$[20]
hexanenitrile	4.2337	1593.56	213.21	290−455	P_s,[14,16,18,19] $\Delta_{vap}H$[20]
octanenitrile	4.5089	1872.05	211.69	280−480	P_s,[21,19,14] $\Delta_{vap}H$[20]
butanedinitrile (solid)	5.5854	2735.64	233.74	270−331.3	P_s[29] [a]
butanedinitrile (liquid)	4.7921	2432.84	225.38	331.3−460	P_s[a]
pentanedinitrile	4.5055	2247.15	212.36	280−370	P_s[29]
hexanedinitrile	4.7414	2497.61	219.86	280−370	P_s[29]

[a] P_s data correlated and/or predicted by the method of “thermodynamically controlled extrapolation”, see text.

the value of the derivative ($\mathrm{d}\ln P_s/\mathrm{d}T$) as follows:

$$RT^2\left(\frac{\mathrm{d}\ln P_s}{\mathrm{d}T}\right) = \frac{\Delta_{vap}H^*}{1 + P_s(B_{22} - V_2^*)/RT} \tag{4}$$

where V_2^* is the molar volume of a liquid nitrile. The resulting parameters of the Antoine equation, together with sources of data and the temperature ranges of validity, are given in Table 1. Experimental and fitted values of the vapor pressure and B_{22} of the studied compounds are accessible in the ORCHYD database[8] at http://orchyd.asu.edu.

For mononitriles, P_s values are available from a number of sources and are often accompanied by the calorimetrically determined enthalpy of vaporization so the consistency of data can be easily checked. The situation is different for dinitriles. Accurate vapor pressure values are available, as a rule, from a single source and over a limited temperature range. Additional data are reported as boiling points with unknown accuracy. In this situation, a method of “thermodynamically controlled extrapolation” (see refs 22−24) was employed for correlating vapor pressure data. Using this method for the process of equilibrium vaporization, one writes

$$\Delta_{vap}G^\circ(T) = \Delta_{vap}H^\circ(T_r) + \int_{T_r}^{T} \Delta_{vap}C_p^\circ(T)\,\mathrm{d}T - T\left(\Delta_{vap}S^\circ(T_r) + \int_{T_r}^{T} \frac{\Delta_{vap}C_p^\circ(T)}{T}\mathrm{d}T\right) \tag{5}$$

where the $\Delta_{vap}H^\circ(T_r)$ and $\Delta_{vap}S^\circ(T_r)$ stand for the standard enthalpy and entropy of vaporization at the reference temperature T_r = 298.15 K, and $\Delta_{vap}C_p^\circ(T)$ is the standard heat capacity of vaporization. Experience[21,24] shows that over a limited temperature range, say between 273 and 370 K, one usually can neglect the temperature dependence of the standard heat capacity of vaporization and use an approximation that $\Delta_{vap}C_p^\circ(T) \approx \Delta_{vap}C_p^\circ(T_r)$. A reliable value of $\Delta_{vap}C_p^\circ$(298.15 K) may be calculated from calorimetric data or estimated using the group contribution (GC) values for the heat capacity of a compound in the ideal gas state[25,26] and in the liquid[26−28] state. The resulting correlating equation has a form:[24]

$$R\ln\frac{P_s}{P^\circ} = a + \frac{b}{T} + \Delta_{vap}C_p^\circ \ln\frac{T}{T_r} \tag{6}$$

where $a = \Delta_{vap}S^\circ(T_r) - \Delta_{vap}C_p^\circ$ and $b = -\Delta_{vap}H^\circ(T_r) + T_r\Delta_{vap}C_p^\circ$. Only two parameters are to be determined from the fit of P_s data as compared with three parameters for the case of the Antoine equation. Therefore, eq 6 provides a more robust determination of fitting parameters, and as a thermodynamically based equation, it is better suited for the temperature extrapolation of vapor pressure values. Equation 6 can also be used for checking the consistency of data. For example, an attempt to fit together P_s data for hexanedinitrile from refs 29 and 30 over the temperature range 285 to 430 K resulted in the fitted value of $\Delta_{vap}C_p^\circ = -38$ J·K^{-1}·mol^{-1}, which is in poor agreement with the calorimetric value $\Delta_{vap}C_p^\circ(298.15) = -74 \pm 10$ J·K^{-1}·mol^{-1} calculated using GC methods.[25,27] However, P_s data for hexanedinitrile at 285 to 380 K from a single source[29] are consistent with $\Delta_{vap}C_p^\circ = -85$ J·K^{-1}·mol^{-1}, in reasonable agreement with the calorimetric value. Therefore, data from ref 30 were excluded from consideration, and the final fit was done using only P_s data of ref 29 with the fixed value of $\Delta_{vap}C_p^\circ = -74$ J·K^{-1}·mol^{-1}.

For butanedinitrile, accurate P_s values are available only below the melting point, T_m = 331.3 K.[31] These data were fitted by eq 6 with the resulting parameters a = 190.613 J·K^{-1}·mol^{-1}, b = −85317 J·K^{-2}·mol^{-1}, and $\Delta_{sub}C_p^\circ = -53.1$ J·K^{-1}·mol^{-1} (a fixed value, calculated from the experimental[31] C_p°(s, 298.15) = 145.6 J·K^{-1}·mol^{-1} and the group contribution[25] C_p°(id gas, 298.15) = 92.5 J·K^{-1}·mol^{-1}). Parameters of eq 6 for vapor pressures of butanedinitrile over the liquid phase can be predicted from $P_s = 1.63 \cdot 10^{-5}$ MPa at $T = T_m$, where vapor pressures over liquid and solid phases are equal, and the knowledge of the standard enthalpy of vaporization, $\Delta_{vap}H^\circ$, at $T = T_m$, where the following relation between $\Delta_{vap}H^\circ$, the standard enthalpy of sublimation, $\Delta_{sub}H^\circ(T = T_m)$ = 67.73 kJ·mol^{-1}, and the enthalpy of fusion, $\Delta_{fus}H$ = 3.70 kJ·mol^{-1},[31] holds:

$$\Delta_{vap}H^\circ(T_m) = \Delta_{sub}H^\circ(T_m) - \Delta_{fus}H \tag{7}$$

The resulting parameters of eq 6 for vapor pressure over liquid butanedinitrile are as follows: a = 190.955 J·K^{-1}·mol^{-1}, b = −85067 J·K^{-2}·mol^{-1}, and $\Delta_{vap}C_p^\circ = -63.5$ J·K^{-1}·mol^{-1} (a fixed value, calculated from C_p°(l, 298.15) = 156 J·K^{-1}·mol^{-1}, based on experimental[31] results after a 35 K temperature extrapolation, and the group contribution[25] C_p°(id gas, 298.15) = 92.5 J·K^{-1}·mol^{-1}). Predicted P_s values are compared in Figure 1 with results reported as boiling points in the Merck Index[32] and in ref 33. The agreement is within 6 % of P_s values at 387 K and within 12 % at 458 K, thus confirming the power of the method of “thermodynamically controlled extrapolation” of vapor pressure data.

For propanedinitrile (malononitrile), there are two sets of vapor pressure data over a solid phase.[34,35] Results of these two studies are not consistent with each other, with P_s values from ref 34 being approximately two times higher than P_s from ref 35. Neither set of data can be made consistent with boiling points reported in the literature for liquid malononitrile after applying the procedure described above for butanedinitrile, with the difference in P_s values around 400 K being approximately 2 times when using data from ref 35 and more than 3 times when

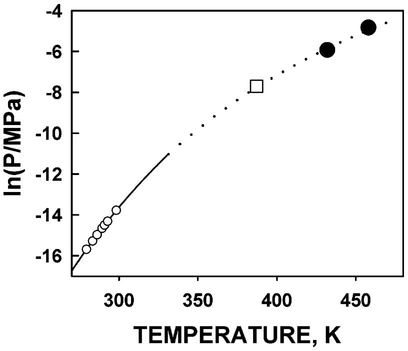

Figure 1. Vapor pressure over crystalline (solid line) and liquid (dotted line) butanedinitrile, see text: ○, Woodman et al.;[29] □, Smiley and Arnold;[33] ●, Merck Index.[32]

employing data from ref 34. The reasons for inconsistency of P_s over solid and liquid phases of malononitrile may be various: there are at least four crystalline modifications of propanedinitrile[36]and a number of premelting phenomena, including a first-order phase transition, are reported in the literature.[37] Therefore, propanedinitrile was excluded from consideration.

Note that the measured[29] vapor pressures over solid butanedinitrile and liquid pentanedinitrile at 298.15 K are very close: $1.02 \cdot 10^{-6}$ MPa and $1.09 \cdot 10^{-6}$ MPa, respectively. The calculated vapor pressure over liquid butanedinitrile at this temperature (with corrections for the enthalpy of fusion and the heat capacities of phases) is only 10 % higher than that for pentanedinitrile. Typically, for long-chain members of a homologous series, the addition of one methylene group decreases the P_s(298.15 K) by more than 3 times. For dinitriles, containing strongly polar terminal CN groups in close proximity, the decrease in the P_s value is expected to be much weaker. Nevertheless, a mere 10 % difference between vapor pressure of consecutive members of a series is very unusual and may call for further investigation of the thermochemical properties of lower dinitriles.

Estimation of Activity Coefficients of Nitriles in Aqueous Solutions. Conversion of nitrile−water mutual solubility data into the values of the Gibbs energy of hydration of solutes requires estimates of activity coefficients, $\gamma_{m,2}$, for nitriles dissolved in water. For moderately soluble compounds, the Savage−Wood GC method[38,39] for estimating excess properties of organic compounds in water was employed. 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 $\gamma_{m,2}$) according to

$$\ln \gamma_{m,2} = \frac{2g_{xx}m}{RT} \tag{8}$$

where g_{xx} is the nitrile−nitrile binary self-interaction coefficient. This linear concentration dependence of ln $\gamma_{m,2}$ 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 GC approximation to estimate g_{xx}:

$$g_{xx} = \sum_{i,j} n_i n_j G_{ij} - \frac{RT}{2N_w} \tag{9}$$

where n_i and n_j represent the number of groups i and j in two interacting molecules of organic compounds in water, G_{ij} stands for the excess Gibbs energy of an $i-j$ interaction, and $N_w \approx 55.5084$ is the number of moles of H_2O in 1000 g of water. To simplify calculations, the following counting rules are applicable:[38] the CH_3 group is equal to 1.5 CH_2 group; the CH group is equal to 0.5 CH_2 group. Therefore, the following interactions have to be considered for aqueous solutions of nitriles: CH_2-CH_2, CN-CN, and CH_2-CN. The numerical values of the binary parameters for the relevant interactions at 298.15 K, determined from available experimental information, are given in Table A3 of the Appendix. The temperature dependence of the G_{ij} coefficients over a limited temperature range, say at (273 to 323) K is given by

$$G_{ij}(T) = T\left(\frac{G_{ij}(T_r)}{T_r} + H_{ij}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right) \tag{10}$$

where $T_r = 298.15$ K and H_{ij} stands for excess enthalpy of $i-j$ interactions. The numerical values of H_{ij} for the CH_2-CH_2, CN-CN, and CH_2-CN interactions were determined from available calorimetric data and are given Table A3 of the Appendix.

Data Compilation

A major part of this contribution is the compilation of a database of thermodynamic properties of aliphatic nitriles in aqueous solution at infinite dilution. The procedures for converting primary data of different types into functions of hydration, as well as the critical evaluation of the data, were described earlier.[2] All of the primary data on the functions of hydration for aliphatic mono- and dinitriles are accessible through the ORCHYD database.[8] 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, and properties of vaporization and auxiliary properties of pure compounds. The following sections provide brief 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. As was discussed elsewhere,[2] the most accurate values of the standard partial molar enthalpy of hydration, $\Delta_h H^\infty$, are obtained by combining the calorimetrically determined molar enthalpy of solution in water, $\Delta_{sol} H^\infty$, and the standard molar enthalpy of vaporization, $\Delta_{vap} H^\circ$, according to the relation

$$\Delta_h H^\infty = \Delta_{sol} H^\infty - \Delta_{vap} H^\circ \tag{11}$$

In the absence of calorimetric data, the value of $\Delta_{sol} H^\infty$ may be evaluated from temperature-dependent standard molar Gibbs energy of solution, $\Delta_{sol} G^\infty$, results by means of

$$\Delta_{sol} H^\infty = -T^2 \left(\frac{\partial \Delta_{sol} G^\infty / T}{\partial T}\right)_p \tag{12}$$

Values of $\Delta_{sol} H^\infty$ obtained in this way refer to the middle of the temperature interval of the availability of $\Delta_{sol} G^\infty$, and they are recalculated to $T_r = 298.15$ K as follows:

$$\Delta_{sol} H^\infty(T_r) = \Delta_{sol} H^\infty(T) - \Delta_{sol} C_p^\infty (T - T_r) \tag{13}$$

where the standard partial molar heat capacity of solution is defined as $\Delta_{sol} C_p^\infty = C_{p,2}^\infty - C_p^\circ(l)$, with $C_{p,2}^\infty$ being the standard partial molar heat capacity of a compound in water and $C_p^\circ(l)$ 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 $\Delta_{sol} C_p^\infty$ is constant. In the absence of

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

	$\Delta_{vap}H°$	$\Delta_h H°$			Δ		Δ
compound	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	accepted value	1st order GC value	$kJ \cdot mol^{-1}$	2nd order GC value	$kJ \cdot mol^{-1}$
acetonitrile	33.40 ± 0.67[20]	−34.90 Cal,[40] −34.91 H^{ex},[41] −35.01 Cal,[42] −34.84 Cal,[43] −35.0 H^{ex},[44] −34.66 Cal,[45] −34.89 H^{ex},[46] −34.94 H^{ex},[47] −34.96 Cal,[48] −34.99 Cal[49]	−34.91 ± 0.70	−35.34	0.43	−34.91	0.00
propanenitrile	36.19 ± 0.37[20]	−39.56 H^{ex},[41] −39.48 H^{ex} [46]	−39.52 ± 0.40	−38.96	−0.55	−39.21	−0.31
butanenitrile	39.41 ± 0.40[20]	−41.80 H^{ex},[46] −42.56 Cal[50]	−42.12 ± 0.60	−42.60	0.48	−42.73	0.61
2-methylpropanenitrile	37.22 ± 0.37[20]	−40.02 $G^\infty(T)$[51]	−40.02 ± 1.5	−42.22	2.20	−40.02	0.00
pentanenitrile	43.64 ± 0.22[20]	−45.64 $G^\infty(T)$[51]	−45.64 ± 1.5	−46.23	0.59	−46.25	0.61
butanedinitrile	66.0 ± 2.0[a] 69.5 ± 1.0[a,b]	−58.2 $G^\infty(T)$[52]	−58.2 ± 2.5	−58.2	0.0	−58.2	0.0
pentanedinitrile	67.9 ± 1.0[a]	−65.6 $G^\infty(T)$,[53] −62.4 $G^\infty(T)$[54]	−63.5 ± 2.5	−63.2	−0.3	−63.3	−0.2
hexanedinitrile	70.9 ± 1.5[a]	−66.6 $G^\infty(T)$[55]	−66.6 ± 2.5	−66.9	0.3	−66.8	0.2

[a] Evaluated from $P_s(T)$ data, see Table 1. Our estimate of uncertainty. [b] Sublimation data.

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

	$C_p(g)$	$\Delta_h C_p$			Δ		Δ
compound	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	accepted value	1sr order GC value	$J \cdot K^{1} \cdot mol^{-1}$	2nd order GC value	$\Delta J \cdot K^{1} \cdot mol^{-1}$
acetonitrile	52.3[56]	**138** Cal[57], **138** Cal[58], 158[a]Cal[59]	140 ± 7	140	−6	140	0
propanenitrile	73.8[56]	211Cal[57]	211 ± 6	211	3	211	0
hexanenitrile	141[b25]	399 Cal[60]	399 ± 16	394	5	397	2

[a] Estimated from the plot in the paper. [b] Group contribution method.

calorimetric values of $C_{p,2}^{\infty}$, one can use a GC estimate without introducing a serious error into the temperature dependence of $\Delta_{sol}H^{\infty}$.

Results of data evaluation for $\Delta_h H^{\infty}$ are summarized in Table 2. The third column gives compiled values of $\Delta_h H^{\infty}$ together with abbreviations employed to indicate the type of data converted to the $\Delta_h H^{\infty}$ value: $\Delta_{sol}H^{\infty}$ denotes values based on the enthalpy of solution, H^{ex} stands for values obtained from excess enthalpy of mixing, $G^{\infty}(T)$ denotes values based on temperature differentiation of $\Delta_{sol}G^{\infty}$ with eq 12. The accepted values of $\Delta_h H^{\infty}$ 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. The values of the partial molar heat capacity of hydration, $\Delta_h C_p^{\infty}$, are calculated as

$$\Delta_h C_p^{\infty} = C_{p,2}^{\infty} - C_p^{*}(\mathrm{ig}) \tag{14}$$

where $C_{p,2}^{\infty}$ is the partial molar heat capacity of a nitrile at infinite dilution in water, evaluated from calorimetric determinations, and $C_{p,2}^{*}(\mathrm{ig})$ is the molar heat capacity of a compound in the ideal gas state, which is available from thermodynamic tabulations[56] or can be estimated using GC methods.[25,26] The results of data evaluation for the standard partial molar heat capacity of hydration, $\Delta_h C_p^{\infty}$, are given in Table 3. Values that are considered to be the most reliable are given in bold.

Standard Partial Molar Gibbs Energy of Hydration at 298.15 K, 0.1 MPa. The primary data related to the standard partial molar Gibbs energy of hydration, $\Delta_h G^{\infty}$, of nitriles are reported as mutual solubility values, activity coefficients at infinite dilution, γ^{∞}, gas−water distribution constants in the molarity concentration scale, $K_{D,c}$, and Henry's law constant, k_H. The following relations connect the reported quantities and $\Delta_h G^{\infty}$, see[2]:

$$\Delta_h G^{\infty} = -\Delta_{vap}G° + RT \ln\left(\frac{\gamma^{\infty}}{N_w}\right) \tag{15}$$

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

$$\Delta_h G^{\infty} = RT \ln\left(K_{D,c}\frac{RT}{P° V_1^{*}}\frac{1}{N_w}\right) \tag{16}$$

where $K_{D,c}$ is defined as

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

with c standing for the concentration per 1000 cm^3 of solvent, V_1^{*} being the molar volume of pure water, $P° = 0.1$ MPa is the standard pressure, and

$$\Delta_h G^{\infty} = RT \ln\left(\frac{k_H}{P°}\frac{1}{N_w}\right) \tag{17}$$

with

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

where f_2 stands for the fugacity of a solute (2), and x is the mole fraction of a solute in the liquid phase.

A major source of information is the nitrile−water mutual solubility data, m_s and x_s, where m_s stands for the molality of a compound dissolved in water and x_s stands for the mole fraction of a solute liquid saturated with water. The following statement[2] gives the relation between m_s, x_s, and $\Delta_h G^{\infty}$:

$$\Delta_h G^{\infty} = \Delta_{sol}G^{\infty} - \Delta_{vap}G° \tag{18}$$

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

$$\Delta_{\mathrm{sol}}G^{\infty} = -RT\ln\frac{(m_{\mathrm{s}}/m_{\mathrm{o}})\gamma_{\mathrm{m},2}}{x_{\mathrm{s}}\, f_{x,2}} \qquad (19)$$

where $\gamma_{\mathrm{m},2}$ stands for the activity coefficient of a solute in the saturated aqueous solution referenced to Henry's law,[3] and $f_{x,2}$ is the activity coefficient of a liquid solute saturated with water referenced to Raoult's law, $m_{\mathrm{o}} = 1\ \mathrm{m{\cdot}kg^{-1}}$. Values of $f_{x,2}$ were calculated using the UNIQUAC[5] model, with the UNIQUAC parameters taken from ref 61 or evaluated by us from compositions of coexisting phases. The values of $\gamma_{\mathrm{m},2}$ were calculated using the Savage−Wood[29,38] model, as explained above. In general, the Savage−Wood GC model should not be used for systems where the concentration of a solute in the water-rich phase exceeds 1 $\mathrm{m{\cdot}kg^{-1}}$; however, it was employed for the treatment of data in the butanedinitrile−water systems, where the saturation molalities may approach 2 $\mathrm{m{\cdot}kg^{-1}}$. In this case, the uncertainty in the correction for nonideality of the aqueous phase may result in an error of up to ± 1 $\mathrm{kJ{\cdot}mol^{-1}}$ in the calculated $\Delta_{\mathrm{h}}G^{\infty}$ value.

In cases where experimental data are reported at temperatures others than 298.15 K, the resulting values of $\Delta_{\mathrm{h}}G^{\infty}$ were recalculated to 298.15 K using the approximation that $\Delta_{\mathrm{h}}C_p^{\infty}(T) = \Delta_{\mathrm{h}}C_p^{\infty}(298.15\ \mathrm{K}) = \mathrm{const}$. The following relation[2] is consistent with the approximation that $\Delta_{\mathrm{h}}C_p^{\infty} = \mathrm{const}$:

$$\Delta_{\mathrm{h}}G^{\infty}(T_{\mathrm{r}}) = \Delta_{\mathrm{h}}G^{\infty}(T)\frac{T_{\mathrm{r}}}{T} + \Delta_{\mathrm{h}}H^{\infty}(T_{\mathrm{r}})\frac{T - T_{\mathrm{r}}}{T} + \Delta_{\mathrm{h}}C_p^{\infty}\frac{T_{\mathrm{r}}}{T}\left(T\ln\frac{T}{T_{\mathrm{r}}} - T + T_{\mathrm{r}}\right) \qquad (20)$$

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

Results of data evaluation for the standard partial molar Gibbs energy of hydration, $\Delta_{\mathrm{h}}G^{\infty}$, at 298.15 K, 0.1 MPa are presented in Table 4. The third column gives compiled values of $\Delta_{\mathrm{h}}G^{\infty}$ together with abbreviations employed to indicate the type of data converted to the $\Delta_{\mathrm{h}}G^{\infty}$ value: γ^{∞} denotes 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. Accepted values of $\Delta_{\mathrm{h}}G^{\infty}$, 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 the critical data evaluation (the method used, primary data reported, estimated uncertainty, comments) is available in the online database at http://orchyd.asu.edu.[8]

Standard Partial Molar Volumes at 298.15 K, 0.1 MPa. Published values of the standard partial molar volumes, V_2^{∞}, obtained using the vibrating-tube densimeter, 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 of Aliphatic Nitriles at 298.15 K, 0.1 MPa

First-Order Method. In the framework of the first-order method, in which the properties of a group are assumed to be independent of the neighboring groups and atoms, aliphatic nitriles under consideration can be constructed from CH_3, CH_2, CH, and CN groups. The thermodynamic properties of the CH_3, CH_2, and CH groups were determined earlier,[2] and those of the nitrile, CN, group were found by least-squares fit of compiled data for mononitriles using the relation:

$$Y = Y_{\mathrm{o}} + \sum_i n_i Y_i \qquad (21)$$

where n_i stands for the number of times the ith group is present in the compound, and Y_i is the contribution of the ith group to a thermodynamic property, Y. The first term on the right-hand side of eq 21, 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 (see Plyasunov et al.[2] for details). Results are presented in Table 6. For each group, the value of the GC is given together with its uncertainty at the

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

	$\Delta_{\mathrm{vap}}G^{\circ}$	$\Delta_{\mathrm{h}}G^{\circ}$			Δ		Δ
compound	$\mathrm{kJ{\cdot}mol^{-1}}$	$\mathrm{kJ{\cdot}mol^{-1}}$	accepted value	1st order GC value	$\mathrm{kJ{\cdot}mol^{-1}}$	2nd order GC value	$\mathrm{kJ{\cdot}mol^{-1}}$
acetonitrile	5.36 ± 0.05[a]	−9.02 k_{H},[62] **−9.01** k_{H},[41 b] −9.65 K_{D},[63] −9.17 γ^{∞},[64 c] −8.72 K_{D},[65] −9.11 γ^{∞},[66 b] −9.84 k_{H},[67 d] −9.59 γ^{∞},[68] −9.35 γ^{∞},[69] **−9.10** γ^{∞},[70 e] −8.72 K_{D},[71] **−8.79** γ^{∞},[72 b] −9.82 k_{H},[73 d] −8.66 γ^{∞},[74 b], −9.10 γ^{∞},[75 f] −8.81 k_{H}[76]	−9.04 ± 0.25	−8.57	−0.47	−9.04	0.00
propanenitrile	6.90 ± 0.10[a]	**−7.87** k_{H},[41 g] −7.95 Sol,[77] −7.23 Sol,[51 g] −7.86 γ^{∞},[68] −8.02 γ^{∞},[69] −8.04 Sol,[68 g] −7.96 Sol,[79 d] −8.06 Sol,[80] −8.11 k_{H}[81]	−7.91 ± 0.20	−7.87	−0.04	−7.90	−0.01
butanenitrile	9.00 ± 0.10[a]	−6.4 K_{D},[82] −7.02 Sol,[51 d] −7.25 γ^{∞},[68] −7.14 γ^{∞},[69] −7.16 Sol,[83] −7.30 k_{H}[81]	−7.18 ± 0.30	−7.17	−0.01	−7.22	0.04
2-methylpropanenitrile	7.66 ± 0.15[a]	−5.91 Sol,[51 d] −5.46 γ^{∞},[68] −5.81 γ^{∞} [69]	−5.70 ± 0.30	−6.62	0.92	−5.70	0.00
pentanenitrile	11.46 ± 0.15[a]	−6.83 Sol,[51 d] −6.48 γ^{∞},[68] −6.55 γ^{∞},[69] −6.05 Sol[84]	−6.50±0.30	−6.47	−0.03	−6.54	0.04
hexanenitrile	14.02 ± 0.15[a]	**−6.02** γ^{∞},[69] −6.90 Sol[60]	−6.14 ± 0.60	−5.77	−0.37	−5.86	−0.28
octanenitrile	19.41 ± 0.10[a]	−3.08 Sol,[51 h] −9.24 Sol[85 d]	−4.3 ± 2.5	−4.37	0.07	−4.50	0.20
butanedinitrile	28.11 ± 0.30[a] 28.47 ± 0.15[a,i]	−28.30 Sol,[53 j] −28.17 Sol[52 k]	−28.2 ± 0.8	−28.2	0.0	−28.2	0.0
pentanedinitrile	28.11 ± 0.15[a]	−28.00 Sol,[53] −27.86 Sol[54 l]	−27.93 ± 0.7	−27.9	0.0	−27.9	0.0
hexanedinitrile	31.16 ± 0.15[a]	−29.29 Sol,[86] −29.56,[87 d] −29.59 Sol[55 m]	−29.47 ± 0.7	−29.6	0.1	−29.8	0.3

[a] Calculated from P_{s} data from Table 1 and values of B_{22} evaluated using corresponding-states correlations.[4−6] Our estimate of uncertainty. [b] Recalculated from 323.15 K. [c] Recalculated from 310.15 K. [d] Recalculated from 293.15 K. [e] Recalculated from 308.15 K. [f] Recalculated from 333.15 K. [g] Recalculated from 303.15 K. [h] Recalculated from 353.15 K. [i] Sublimation value. [j] Recalculated from 305 K. [k] Recalculated from 290.15 K. [l] Recalculated from 308.0 K. [m] Recalculated from 294.75 K.

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

compound	V_2°/cm^3·mol^{-1}	accepted value	1storder GC value	Δ/cm^3·mol^{-1}	2nd order GC value	Δ/cm^3·mol^{-1}
acetonitrile	**47.41**,[57] 46.90,[88] **47.33**,[89] 47.42,[90] 47.40[59]	47.35 ± 0.2	48.02	−0.68	47.34	0.0
propanenitrile	64.40,[57] 64.34[90]	64.37 ± 0.3	63.75	0.62	64.70	−0.33
butanenitrile	80.59[90]	80.59 ± 0.5	79.48	1.11	80.31	0.28
pentanenitrile	96.73[90]	96.73 ± 1.0	95.21	1.52	95.92	0.81
hexanenitrile	111.6,[60] 111.91[90]	111.76 ± 0.5	110.94	0.82	111.53	0.23
octanenitrile	146.18[90]	146.18 ± 2.0	142.40	3.78	142.75	3.43

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	$\Delta_h G^\circ$ 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]	
CN	−20.19 ± 0.42	(7)	−25.03 ± 0.66	(5)	15 ± 5	(3)	22.31 ± 0.80	(6)
{CN-$(CH_2)_2$-CN}$_{corr}$	2.83 ± 1.0	(1)	1.4 ± 2.7	(1)	no data		no data	
{CN-$(CH_2)_3$-CN}$_{corr}$	2.40 ± 0.9	(1)	∼0	(1)	no data		no data	
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]	

[a] The number of compounds containing the selected group for each property is given in parentheses. [b] Values from Plyasunov et al.[2]

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 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		−2.29		0		1.12	
C-(CN)(C)$(H)_2$	1.14 ± 0.20	(5)	−4.30 ± 1.44	(3)	71 ± 2	(2)	17.36 ± 0.79	(5)
C-(CN)$(C)_2$(H)	−0.38 ± 0.28	(1)	3.08 ± 3.09	(1)	no data		no data	
CN-(C)	−20.71 ± 0.18	(7)	−24.43 ± 1.31	(5)	8 ± 1 (3)		20.66 ± 0.53 (6)	
{CN-$(CH_2)_2$-CN}$_{corr}$	2.99 ± 0.9	(1)	1.6 ± 3.2	(1)	no data		no data	
{CN-$(CH_2)_3$-CN}$_{corr}$	2.58 ± 0.8	(1)	∼0	(1)	no data		no data	
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]	

[a] The number of compounds containing the selected group for each property is given in parentheses; [b] Values from Plyasunov et al.[2]

0.95 confidence level. In parentheses, the number of compounds containing the selected group is listed.

Dinitriles were intentionally excluded from the first-order fit of data. The problem is that the polyfunctional compounds may successfully be "constructed" from the first-order groups only in cases where polar groups are widely separated from each other in the structure of a compound. Wide separation is necessary owing to the multipole (mainly dipole−dipole) interactions between polar groups in polyfunctional compounds (i.e., interactions that are absent in monofunctional compounds). The dipole−dipole interactions are expected to fall off approximately as the inverse cube of the distance between dipoles, and, as experience shows, may be neglected in cases where polar groups in the structure of an organic compound are separated by more than four or five methylene, CH_2, groups. The interactions between dipoles decrease the strength of their binding with water, and as a result, the Gibbs energy of hydration of short-chain polyfunctional compounds is more positive than the corresponding sum of the first-order groups. The magnitude of the dipole−dipole effects in nitriles can be calculated as the difference between experimental thermodynamic functions and values calculated using "mononitrile" group contributions. For the Gibbs energy of hydration, the difference is 2.83 ± 1.0, 2.40 ± 0.9, and 0.16 ± 0.9 kJ·mol^{-1} for butane-, pentane-, and hexanedinitrile, respectively. As expected, the difference is minimal for hexanedinitrile, where two polar nitrile groups are separated by four methylene groups. Results for the enthalpy of hydration have larger uncertainties, and the calculated dipole−dipole contributions are equal to 1.4 ± 2.7, −0.3 ± 2.7, and 0.4 ± 2.7 kJ·mol^{-1} for butane-, pentane-, and hexanedinitrile, respectively. In principle, theoretically based terms for multipole interactions can be added into GC models,[91,92] although the implementation is not simple. In this work, the choice was made to introduce the corrections to the properties of lower dinitriles (see Table 6).

Second-Order Method. The Benson notation for the second-order GC method[26,93] is used: 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 CN-(C) represents the nitrile group connected to a C atom. The groups necessary to represent the selected set of compounds are as follows: C-(C)$(H)_3$, C-$(C)_2(H)_2$, C-$(C)_3$(H), C-(CN)(C)$(H)_2$, C-(CN)$(C)_2$(H), and CN-(C). Following existing practice,[2,26] the identity of the second-order groups C-(CN)$(H)_3$ and C-(C)$(H)_3$ was accepted.

The thermodynamic properties of the C-(C)$(H)_3$, C-$(C)_2(H)_2$, and C-$(C)_3$(H) groups were determined earlier,[2] and those of the remaining groups were found by least-squares fit of compiled data for mononitriles using the relation given by eq 21. The results are presented in Table 7. Again, for each group the value of the group contribution together is listed together with its uncertainty at the 0.95 confidence level. In parentheses, the number of compounds containing the selected group is given. The quality of data description is higher in the case of the second-order method because three new groups are employed for in the fit rather than one as in the case of the first-order method.

For reasons outlined above, a quantitative description of data for dinitriles requires introduction of corrections for dipole−dipole interactions between terminal nitrile groups. The magnitudes of these corrections are close to those obtained for the first-order method. These corrections, which are necessary for butane- and pentanedinitrile, are listed in Table 7.

Discussion and Recommendations

Thermodynamic properties of straight-chain mononitriles in aqueous solution are relatively well investigated. However, for branched aqueous nitriles data are reported only for 2-methylpropanenitrile and only for the Gibbs energy. (Stephenson[51] measured aqueous solubility for 4-methylpentanonitrile, but the sample studied was a mixture of isomers with less than 80 % 4-methylpentanonitrile, so these data were not considered.) Additional experimental investigations of aqueous branched nitriles would be useful for the determination of the contributions of the second-order groups C-(CN)(C)$_2$(H) and C-(CN)(C)$_3$.

All experimental data for dinitriles are limited to mutual solubilities of water-dinitrile systems. The concentrations of water and solutes in coexisting phases are high; therefore, the corrections for nonidealities of coexisting solutions are rather uncertain. For propanedinitrile and butanedinitrile an organic-rich liquid-phase exists below the melting temperature of the pure dinitrile. All these circumstances limit the usefulness of solubility data for the determination of the standard thermodynamic functions of hydration of dinitriles. In such a situation, experimental determinations of Henry's constants or gas−water partition constants, which can be performed in dilute solutions and do not require the knowledge of the vapor pressure of a pure compound, will be particularly valuable. Calorimetric and densimetric studies of aqueous solutions of dinitriles are also needed. It is expected that the thermodynamic properties of hexanedinitrile and higher dinitriles can be predicted without any additional corrections for dipole−dipole interactions of CN groups; however, additional data would be useful for lower dinitriles to quantify the dipole−dipole corrections for these solutes. In this respect, a compound of particular interest is propanedinitrile (malononitrile), where two terminal nitrile groups are separated by a single methylene group. Additional experimental studies of aqueous mono- and dinitriles would expand the usefulness and accuracy of GC models.

Appendix: Values of the Enthalpic and Gibbs Energy Second Virial Coefficients for Aqueous Nitriles

As follows with a good approximation from the theory of McMillan and Mayer,[94] the concentration dependence of the excess Gibbs energy, G^{ex}, of an aqueous solution of a single nonelectrolyte A is given by the power series in molality of the solute species:

$$\frac{G^{ex}}{W} = m^2 \cdot g_{AA} + m^3 \cdot g_{AAA+...} \tag{A1}$$

where W stands for the mass of water (1 kg) and g_{AA} and g_{AAA} are the second and third virial coefficients arising from binary and ternary interactions between solutes A.

Straightforward thermodynamic manipulations give the following relations for the osmotic coefficient of a solution, ϕ:

$$\phi = 1 + \frac{1}{RT}(m \cdot g_{AA} + 2 \cdot m \cdot g_{AAA} + ...) \tag{A2}$$

for the activity coefficient, γ_A (referenced to Henry's law):

$$RT \ln \gamma_A = 2 \cdot m \cdot g_{AAA} + 3 \cdot m^2 \cdot g_{AAA} + ... \tag{A3}$$

and for the activity coefficient, f_A (referenced to Raoult's law and the mole fraction concentration scale):

$$RT \ln f_A = RT \ln \gamma^{\infty} + RT \ln\left(1 + \frac{m}{N_w}\right) + 2 \cdot m \cdot g_{AA} + 3 \cdot m^2 \cdot g_{AAA} + ... \tag{A4}$$

where γ^{∞} is the activity coefficient at infinite dilution, $N_w \approx 55.5084$ is the number of moles of H_2O in 1000 g of water. The second term on the right-hand side of eq A4 is the conversion factor from the mole fraction to the molality concentration scale.

The temperature dependence of the Gibbs energy virial coefficients g_{AA} and g_{AAA} is given by the following relations:

$$h_{AA} = -T^2\left(\frac{\partial(g_{AA}/T)}{\partial T}\right)_p \tag{A5}$$

and

$$h_{AAA} = -T^2\left(\frac{\partial(g_{AAA}/T)}{\partial T}\right)_p \tag{A6}$$

where the enthalpic virial coefficients h_{AA} and h_{AAA} appear in the statement for the excess enthalpy of an aqueous solution of a solute A. Parameters h_{AA} and h_{AAA} are usually determined from the concentration dependence of the apparent molar enthalpy, $^{\phi}L_A$, of solution of a solute A (from enthalpy of dilution measurements):

$$^{\phi}L_A = h_{AA}m + h_{AAA}m^2 + ... \tag{A7}$$

or from measurements of the excess enthalpy of mixing, H^{ex}, of water and a liquid A (see, for example, refs 41 and 44):

$$\frac{H^{ex}}{x_1 x_2} = \Delta_{sol}H^{\circ} + b \cdot x_2 + c \cdot {x_2}^2 + ... \tag{A8}$$

where $\Delta_{sol}H^{\circ}$ is the standard enthalpy of solution of a solute A in water, and

$$h_{AA} = \frac{b}{N_w} \tag{A9}$$

The practical utility of eqs A1 to A9 is in the fact that for many aqueous nonelectrolytes only binary interactions are important in dilute solutions. Therefore, the variants of eqs A1 to A4, truncated at the second virial coefficient g_{AA}, are often adequate up to a molality of dissolved species of about one. Over the temperature range (273 to 323) K, one can neglect the (usually weak) temperature dependence of h_{AA} and obtain the following relation for the temperature dependence of g_{AA}:

$$g_{AA}(T) = T \cdot \left[\frac{g_{AA}(T_r)}{T_r} + h_{AA} \cdot \left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \tag{A10}$$

Table A1. Compiled and Group Contribution (GC) Values of the Enthalpic Second Virial Coefficients of Aqueous Nitriles

h_{AA}/J·kg·mol^{-2}			
exptl value	Savage−Wood GC value	method	comments
Acetonitrile			
840 ± 6[41]	843	enthalpy of mixing	authors' value of $b = 46.9 \pm 0.3$ kj·mol^{-1}, see eq A9
860[44]	843	enthalpy of mixing	authors' value of $b = 48$ kJ·mol^{-1}, see eq A9
840[95]	843	enthalpy of dilution	authors' value
Propanenitrile			
1570 ± 30[41]	1611	enthalpy of mixing	authors' value of $b = 86.9 \pm 1.5$ kJ·mol^{-1}, see eq A9
1900[95]	1611	enthalpy of dilution	authors' value
2-Propenenitrile			
1670 ± 20[41]	1611	enthalpy of mixing	authors' value of $b = 92.8 \pm 1.0$ kJ·mol^{-1}, see eq A9
Butanenitrile			
2560[95]	2452	enthalpy of dilution	authors' value
Pentanenitrile			
3300[95]	3365	enthalpy of dilution	authors' value

Table A2. Compiled and Group Contribution (GC) Values of the Gibbs Energy Second Virial Coefficients of Aqueous Nitriles

T	g_{AA}/J·kg·mol^{-2}				
K	exptl value	recalculated to 298.15 K	Savage−Wood GC value	method	comments
Acetonitrile					
310.15	−148 ± 48[64]	−110 ± 48	−162	*PX*	$m < 0.95$; ln γ^{∞} in eq A4 is a fitting parameter
323.15	−220 ± 50[66]	−138 ± 50	−162	*PXY*	$m < 1.5$; ln γ^{∞} in eq A4 is fixed[41]
273.15	−85 ± 17[96]	−170 ± 17	−162	freezing temperature	$m < 0.55$
2-Propenenitrile					
323.15	−390 ± 50[66]	−231 ± 50	−232	*PXY*	$m < 1.2$; ln γ^{∞} in eq A4 is fixed[41]
298.15	−238 ± 68[97]	−238 ± 68	−232	partial pressures	$m < 1.47$; ln γ^{∞} in eq A4 is a fitting parameter
Butanedinitrile					
273.15	−342 ± 120[52]	−551 ± 130	−542	freezing temperature	$m = 0.725$; GC value of h_{AA} was employed for recalculation to 298.15 K

Table A3. Values of the Gibbs Energy and Enthalpic Second Virial Coefficients of Group Interactions Relevant for Aqueous Nitriles

groups $i-j$	G_{ij}/J·kg·mol^{-2}	H_{ij}/J·kg·mol^{-2}
CH_2-CH_2	−34[a]	36[a]
CH_2-CN	33 ± 31[b]	312 ± 28[b]
CN-CN	−162 ± 96[b]	−175 ± 90[b]

[a] Value from ref 98, fixed in the fitting procedure; [b] Uncertainty at the 0.95 confidence level.

where for the reference temperature T_r the value of 298.15 K was selected.

Values of h_{AA} for aqueous nitriles, compiled or evaluated from literature data, are given in Table A1. Table A2 lists values of g_{AA} for aqueous nitriles evaluated from experimental data.

Determination of the Savage−Wood GC Values for Aqueous Nitriles

In the Savage−Wood formalism,[38] there is the following GC approximation to estimate h_{AA}:

$$h_{AA} = \sum_{i,j} n_i n_j H_{ij} \tag{A11}$$

where n_i and n_j represent the number of groups i and j in two interacting molecules of organic compounds in water, and H_{ij} stands for the excess enthalpy of an $i-j$ interaction. To simplify calculations, the following counting rules are applicable:[38] the CH_3 group is equal to 1.5 CH_2 group; the CH group is equal to 0.5 CH_2 group. 2-Propenenitrile is considered identical to propanenitrile. Therefore, the following interactions have to be considered for aqueous solutions of nitriles: CH_2-CH_2, CN-CN, and CH_2-CN. Values of H_{ij} were obtained by a weighted least-squares fitting procedure and the results are presented in Table A3.

The Savage-Wood model employs the following relation for the Gibbs energy second virial coefficient,[39] g_{AA}:

$$g_{AA} = \sum_{i,j} n_i n_j G_{ij} - \frac{RT}{2N_w} \tag{A12}$$

where G_{ij} stands for the excess Gibbs energy of an $i-j$ interaction. Values of G_{ij} at 298.15 K were obtained by a weighted least-squares fitting procedure, and the results are presented in Table A3.

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