Establishing recommended data on thermodynamic properties of hydration for selected organic solutes

Appendix 1

Thermodynamic background and main classes of experimental data needed

Thermodynamic property (function) of hydration (TPH) – difference between a property in the standard state of infinite dilution (temperature and pressure of the system) and in the state of an ideal gas (temperature of the system and standard pressure of 0.1 MPa)

$$\Delta_{\rm hyd} X_2^{\rm o} = X_2^{\rm o}[T,p] - X_2^{\rm ig}[T,p_{\rm o}] \qquad p_{\rm o} = 0.1\ {\rm MPa}$$

Gibbs energy of hydration $\Delta_{\rm hyd}G_2^{\rm o}$:

Relationship with the Henry's law constant: $\Delta_{\rm hyd}G_2^{\rm o} = G_2^{\rm o} - G_2^{\rm ig} = RT\ln(k_{\rm H,2}/p_{\rm o})$

Relationship with the Gibbs energy associated with dissolution of a liquid or solid solute

$$\Delta_{\rm hyd}G_2^{\rm o} = \Delta_{\rm sol}G_2^{\rm o} + RT\ln(f_2^{\bullet}/p_{\rm o}) = \Delta_{\rm sol}G_2^{\rm o} + RT\ln(f_2^{\bullet}p_2^{\rm sat}/p_{\rm o}) + \int_{p_2^{\rm sat}}^{p} V_2^{\bullet}{\rm d}p$$

Relationship of $\Delta_{\rm sol}G_2^{\rm o}$ to the symmetric limiting activity coefficient (liquid solutes)

$$\Delta_{\rm sol}G_2^{\rm o} = G_2^{\rm o} - G_2^{\bullet \rm l} = RT\ \ln g_2^{\rm R\infty}$$

Relationship of $\Delta_{\rm sol}G_2^{\rm o}$ to the solubility (sparingly soluble liquid or solid solutes)

$$\Delta_{\rm sol}G^{\rm o} = G_2^{\rm o} - G_2^{\bullet} = -RT\ln x_2^{\rm sol} g_2^{\rm H} \cong -RT\ln x_2^{\rm sol}$$

<u>*Experimental data needed:*</u>
(aq) - Henry's law constants (gases), limiting activity coefficients (hydrophilic and moderately hydrophobic liquid solutes), solubilities (hydrophobic liquid and solid solutes)
(pure) - vapour pressures, gas nonideality corrections, densities of pure solutes

Enthalpy of hydration $\Delta_{\rm hyd}H_2^{\rm o}$:

Relationship with the enthalpy associated with dissolution

$$\Delta_{\rm hyd}H_2^{\rm o} = \Delta_{\rm sol}H_2^{\rm o} + \int_0^p (V_2^{\bullet} - T(\partial V_2^{\bullet}/\partial T)_p){\rm d}p \quad T>T_{\rm c}$$

$$\Delta_{\rm hyd}H_2^{\rm o} = \Delta_{\rm sol}H_2^{\rm o} - \Delta_{\rm vap}H_2^{\bullet} + \int_0^{p_2^{\rm sat}} (V_2^{\bullet} - T(\partial V_2^{\bullet}/\partial T)_p){\rm d}p \cong \Delta_{\rm sol}H_2^{\rm o} - \Delta_{\rm vap}H_2^{\bullet} \quad T<T_{\rm c}$$

Relationship of $\Delta_{\rm sol}H_2^{\rm o}$ to the data resulting from calorimetric experiments

$$\Delta_{\rm sol}H_2^{\rm o} = (H_2^{\rm o} - H_2^{\bullet}) = \lim_{n_2\to 0}(\Delta_{\rm sol}H/n_2)$$

Experimental data needed:
(aq) - enthalpies of solution (dilute aqueous solutions)

(pure) - residual enthalpies (enthalpic departure function resulting from *pVT* data) for gases and supercritical fluids, enthalpies of vaporization (liquids) / sublimation (solids)

Heat capacity of hydration $\Delta_{\text{hyd}} C_{p,2}^{\text{o}}$ **:**

$$\Delta_{\text{hyd}} C_{p,2}^{\text{o}} = C_{p,2}^{\text{o}} - C_{p,2}^{\text{ig}}$$

Relationship of $\Delta_{\text{hyd}} C_{p,2}^{\text{o}}$ to the data resulting from calorimetric experiments

$$C_{p,2}^{\text{o}} = c_{p,1} \cdot M_2 + \lim_{m_2 \to 0} \left(\frac{c_p - c_{p,1}}{m_2} \right)$$

Experimental data needed:
(aq)- specific heat capacities (heat capacity differences) of dilute aqueous solutions
(pure)- ideal gas heat capacities of solute

Partial molar volume at infinite dilution V_2^{o}**:**

$$V_2^{\text{o}} = \frac{M_2}{r_1} - \frac{1}{r_1^2} \lim_{m_2 \to 0} \left(\frac{r - r_1}{m_2} \right)$$

Experimental data needed:
(aq) - densities (density differences) of dilute aqueous solutions

Relationship between individual TPH:

$$\Delta_{\text{hyd}} G_2^{\text{o}} = \Delta_{\text{hyd}} G_2^{\text{o}}[T_{\text{r}}, p_{\text{r}}] - (T - T_{\text{r}}) \Delta_{\text{hyd}} S_2^{\text{o}}[T_{\text{r}}, p_{\text{r}}] +$$
$$+ \int_{T_{\text{r}}}^{T} \left(\Delta_{\text{hyd}} C_{\text{p},2}^{\text{o}} \right)_{p_{\text{r}}} \mathrm{d}T - T \int_{T_{\text{r}}}^{T} \left(\Delta_{\text{hyd}} C_{\text{p},2}^{\text{o}} \right)_{p_{\text{r}}} \mathrm{d}\ln T + \int_{p_{\text{r}}}^{p} \left(V_2^{\text{o}} \right)_T \mathrm{d}p$$

where

$$\Delta_{\text{hyd}} S_2^{\text{o}}[T_{\text{r}}, p_{\text{r}}] = (\Delta_{\text{hyd}} H_2^{\text{o}}[T_{\text{r}}, p_{\text{r}}] - \Delta_{\text{hyd}} G_2^{\text{o}}[T_{\text{r}}, p_{\text{r}}]) / T_{\text{r}}$$

T_{r}=298.15 K, $p_{\text{r}} = p_{\text{o}}$ = 0.1 MPa

Symbols : 2 solute, 1 solvent ; superscript • - pure solute property, superscript °- standard state of infinite dilution, superscript ig – ideal gas
Note: thermodynamic properties of water are obtained from the equation of state for ordinary water substance (IAPWS-95 formulation)

Appendix 2

Classes of compounds covered and tentative numbers of solutes included

Compounds of carbons and hydrogen (C-H)	55
Alkanes	
Cycloalkanes	
Unsaturated aliphatic hydrocarbons	
Aromatic and unsaturated monocyclic hydrocarbons	
Polycyclic hydrocarbons	
Compounds of carbon, hydrogen and halogen (C-Hal, C-H-Hal)	20
Fluoroderivatives	
Chloroderivatives	
Bromoderivatives	
Iododerivatives	
Mixed halogen derivatives	
Compounds of carbon, hydrogen and nitrogen (C-H-N)	30
Amines	
Nitriles	
Heterocyclic nitrogen compounds	
Miscellaneous nitrogen compounds	
Compounds of carbon, hydrogen and oxygen (C-H-O)	60
Ethers	
Alcohols and phenols	
Carbonyl compounds	
Acids	
Esters	
Heterocyclic oxygen compounds	
Miscellaneous oxygen compounds	
Compounds of carbon, hydrogen and sulphur (C-H-S)	15
Sulphides	
Thiols	
Heterocyclic sulphur compounds	
Other organic compounds	10
Compounds of carbon, hydrogen, halogen and oxygen (C-H-Hal-O)	
Compounds of carbon, hydrogen, nitrogen and oxygen (C-H-N-O)	
Compounds of carbon, hydrogen, oxygen and sulphur (C-H-O-S)	
Miscellaneous compounds	
Inorganic gases (H_2 O_2, N_2, He, Ar, CO_2, NH_3, H_2S, …)	10