Linear Solvation–Energy Relationships (LSER) and Equation-of-State Thermodynamics: On the Extraction of Thermodynamic Information from the LSER Database

Costas Panayiotou [1,*], Ioannis Zuburtikudis [2], Hadil Abu Khalifeh [2] and Vassily Hatzimanikatis [3]

[1] Department of Chemical Engineering, Aristotle University of Thessaloniki, 54624 Thessaloniki, Greece

[2] Department of Chemical Engineering, Abu Dhabi University, Abu Dhabi P.O. Box 59911, United Arab Emirates

[3] Laboratory of Computational Systems Biotechnology (LCSB), Swiss Federal Institute of Technology (EPFL), CH-1015 Lausanne, Switzerland

* Correspondence: cpanayio@auth.gr

Supplementary Material

This supplementary material consists of three parts. In part I, a brief overview of the extension of the formalism of the Lattice-Fluid with Hydrogen-Bonding (LFHB) model at infinite dilution is presented, while in part II, the LFER linearity is discussed with focus on the hydrogen-bonding contribution and examples of calculations are given. In part III, literature data for the LSER descriptors and LFER coefficients of alkanols are summarized.

Part I: Extension of the LFHB model formalism at infinite dilution and LFER linearity

This is a brief presentation of the rationale of perturbation approximation and the working equations. A detailed presentation may be found in ref. 1.

In the LFHB model [2-5] the following general equation is obeyed by the reduced numbers of hydrogen bonds for each donor-acceptor pair i,j:

$$\frac{\nu_{ij}}{\nu_{i0}\nu_{0j}} = \tilde{\rho}\exp\left(-\frac{\Delta G_{ij}}{RT}\right) \tag{S1}$$

In the limit of infinite dilution ($x_1 \rightarrow 0$, r= r2, $\tilde{\rho} = \tilde{\rho}_2$), the set of four equations (S1) become:

$$v_{11}^2 - \left(-v_{12} - v_{21} + Q_{11}\right)v_{11} + v_{12}v_{21} = 0$$

$$v_{12}^2 - \left(-v_{11} + \frac{a_2}{r_2} - v_{22} + Q_{12}\right)v_{12} - v_{11}\left(\frac{a_2}{r_2} - v_{22}\right) = 0$$

$$v_{21}^2 - \left(-v_{11} + \frac{d_2}{r_2} - v_{22} + Q_{21}\right)v_{21} - v_{11}\left(\frac{d_2}{r_2} - v_{22}\right) = 0$$
(S2)

$$v_{22}^2 - \left(\frac{d_2}{r_2} - v_{21} + \frac{a_2}{r_2} - v_{12} + Q_{22}\right)v_{22} + \left(\frac{d_2}{r_2} - v_{21}\right)\left(\frac{a_2}{r_2} - v_{12}\right) = 0$$

where, the reduced numbers of hydrogen bonds (cf. main text), in the limit of infinite dilution, are becoming: $v_{ij} = N_{ij}/r_2N_2$ and $Q_{ij} = 1/\tilde{\rho}_2 K_{ij}$.

At infinite dilution, the solution to the last of the equations S2 is essentially identical to the corresponding solution for pure solvent (component 2), or

$$r_2 v_{22}^0 = \frac{d_2 + a_2 + r_2 Q_{22} - \sqrt{\left(d_2 + a_2 + r_2 Q_{22}\right)^2 - 4d_2 a_2}}{2}$$
(S3)

Seeking an approximate solution to the set S2 by the perturbation method, we make the key assumption that the solution can be written as an expansion in terms of the near-zero perturbation parameter x_1, or: $0 < x_1 \ll 1$:

$$v_{11} = c_{01} + c_{11} x_1 + c_{21} x_1^2 + O(x_1^3) \tag{S4.1}$$

$$v_{12} = c_{02} + c_{12} x_1 + O(x_1^2) \tag{S4.2}$$

$$v_{21} = c_{03} + c_{13} x_1 + O(x_1^2) \tag{S4.3}$$

$$v_{22} = c_{04} + c_{14} x_1 + O(x_1^2) \tag{S4.4}$$

Substituting in S2, neglecting the corresponding $O(x_1^n)$ terms, we obtain a set of four polynomial expressions or a polynomial approximate system (PAS) of equations determined by nine c_{ij} coefficients. In a range of x_1 (I_1), small enough, and under a sufficient smoothness condition, these truncated polynomial expressions PAS are extremely close to zero. By imposing that each polynomial (and hence, each coefficient) of PAS is equal to zero, a system of nine polynomial equations in nine unknowns c_{ij} is obtained. This system can be partially decoupled, and the following sub-set can be first solved independently:

$$c_{01}^2 - \left(-c_{02} - c_{03} + Q_{11}\right)c_{01} + c_{02}c_{03} = 0$$

$$c_{02}^2 - \left(-c_{01} + \frac{a_2}{r_2} - c_{04} + Q_{12}\right)c_{02} - c_{01}\left(\frac{a_2}{r_2} - c_{04}\right) = 0$$

$$c_{03}^2 - \left(-c_{01} + \frac{d_2}{r_2} - c_{04} + Q_{21}\right)c_{03} - c_{01}\left(\frac{d_2}{r_2} - c_{04}\right) = 0$$
(S5)

$$c_{04}^2 - \left(\frac{d_2}{r_2} - c_{03} + \frac{a_2}{r_2} - c_{02} + Q_{22}\right)c_{04} + \left(\frac{d_2}{r_2} - c_{03}\right)\left(\frac{a_2}{r_2} - c_{02}\right) = 0$$

As seen, the set S5 represents a system of four equations in the four unknown zero-order coefficients, c_{0j}. On the basis of S4, the set of c_{0j} represents by definition the perturbation solution of S2 at $x_1 = 0$. Since S5 is formally equivalent to S4 (by replacing v_{11}, v_{12}, v_{21} and v_{22} with c_{01}, c_{02}, c_{03} and c_{04}, respectively), the consistent and unique solution for the set of c_{0j} is:

$$c_{01} = c_{02} = c_{03} = 0$$
$$c_{04} = v_{22}^0$$

(S6)

Once the set of c_{0j} has been obtained, the remaining five equations can be split into two subsets, which can be solved by a recursive method. The first subset, in the unknown c_{11}, c_{12} and c_{13}, is given by:

$$c_{11}r_2^2 Q_{11} = 0$$
$$a_2 d_1 - d_1 r_2 c_{04} - a_2 r_2 c_{11} + c_{11}r_2^2 c_{04} - a_2 r_2 c_{12} - r_2^2 c_{12}Q_{12} + c_{12}r_2^2 c_{04} = 0$$
$$a_1 d_2 - a_1 r_2 c_{04} - d_2 r_2 c_{11} + c_{11}r_2^2 c_{04} - d_2 r_2 c_{13} - r_2^2 c_{13}Q_{21} + c_{13}r_2^2 c_{04} = 0$$

(S7)

The solution to (S7) is:

$$c_{11=0}$$

$$c_{12} = d_1 \left(\frac{1}{r_2} + \frac{1}{-r_2 - a_2/Q_{12} + r_2 v_{22}^0/Q_{12}} \right) = \frac{d_1}{r_2} \left(\frac{r_2 v_{22}^0 - a_2}{r_2 v_{22}^0 - a_2 - r_2 Q_{12}} \right)$$

$$c_{13} = a_1 \left(\frac{1}{r_2} + \frac{1}{-r_2 - d_2/Q_{21} + r_2 v_{22}^0/Q_{21}} \right) = \frac{a_1}{r_2} \left(\frac{r_2 v_{22}^0 - d_2}{r_2 v_{22}^0 - d_2 - r_2 Q_{21}} \right)$$

(S8)

. Substituting for $Q_{ij} = 1/\tilde{\rho}_2 K_{ij}$, eq. S8 gives:

$$c_{11=0}$$

$$c_{12} = \frac{d_1}{r_2} \left(\frac{d_2 - a_2 + r_2 Q_{22} - \sqrt{(d_2 + a_2 + r_2 Q_{22})^2 - 4d_2 a_2}}{d_2 - a_2 + r_2 Q_{22} - \sqrt{(d_2 + a_2 + r_2 Q_{22})^2 - 4d_2 a_2} - 2r_2 Q_{12}} \right) = \frac{d_1}{r_2} \frac{W_{d2}}{W_{d2} - 2r_2 Q_{12}}$$

(S9)

$$c_{13} = \frac{a_1}{r_2} \left(\frac{a_2 - d_2 + r_2 Q_{22} - \sqrt{(d_2 + a_2 + r_2 Q_{22})^2 - 4d_2 a_2}}{a_2 - d_2 + r_2 Q_{22} - \sqrt{(d_2 + a_2 + r_2 Q_{22})^2 - 4d_2 a_2} - 2r_2 Q_{21}} \right) = \frac{a_1}{r_2} \frac{W_{a2}}{W_{a2} - 2r_2 Q_{21}}$$

In the general reference state of zero hydrogen-bonding free energies ($K_{ij} = 1$), the above equations become:

$$c_{11=0}$$

$$c_{12,0} = \frac{d_1}{r_2}\left(\frac{d_2 - a_2 + r_2/\tilde{\rho}_2 - \sqrt{(d_2 + a_2 + r_2/\tilde{\rho}_2)^2 - 4d_2 a_2}}{d_2 - a_2 - r_2/\tilde{\rho}_2 - \sqrt{(d_2 + a_2 + r_2/\tilde{\rho}_2)^2 - 4d_2 a_2}}\right)$$

(ref. state)　　　(S10)

$$c_{13,0} = \frac{a_1}{r_2}\left(\frac{a_2 - d_2 + r_2/\tilde{\rho}_2 - \sqrt{(d_2 + a_2 + r_2/\tilde{\rho}_2)^2 - 4d_2 a_2}}{a_2 - d_2 - r_2/\tilde{\rho}_2 - \sqrt{(d_2 + a_2 + r_2/\tilde{\rho}_2)^2 - 4d_2 a_2}}\right)$$

We will specify, now, the above equations to two common cases of practical interest. In the first case, the solute and the solvent have one donor and one acceptor site, or, $a_i = d_i = 1$. In this case, eq. S9 becomes:

$$c_{11=0}$$

$$r_2 v_{22}^0 = \frac{2 + r_2 Q_{22} - \sqrt{(2 + r_2 Q_{22})^2 - 4}}{2}$$

$$c_{12} = d_1\left(\frac{1}{r_2} + \frac{1}{-r_2 - a_2/Q_{12} + r_2 v_{22}^0/Q_{12}}\right) = \frac{d_1}{r_2}\left(\frac{r_2 Q_{22} - \sqrt{(2 + r_2 Q_{22})^2 - 4}}{r_2 Q_{22} - \sqrt{(2 + r_2 Q_{22})^2 - 4} - 2\,r_2\,Q_{12}}\right)$$　(S11)

$$c_{13} = a_1\left(\frac{1}{r_2} + \frac{1}{-r_2 - d_2/Q_{21} + r_2 v_{22}^0/Q_{21}}\right) = \frac{a_1}{r_2}\left(\frac{r_2 Q_{22} - \sqrt{(2 + r_2 Q_{22})^2 - 4}}{r_2 Q_{22} - \sqrt{(2 + r_2 Q_{22})^2 - 4} - 2\,r_2\,Q_{21}}\right)$$

and in the reference state:

$$c_{11=0}$$

$$r_2 v_{22,0}^0 = \frac{2 + r_2/\tilde{\rho}_2 - \sqrt{(2 + r_2/\tilde{\rho}_2)^2 - 4}}{2}$$

$$c_{12,0} = \frac{d_1}{r_2}\left(\frac{\sqrt{(2 + r_2/\tilde{\rho}_2)^2 - 4} - r_2/\tilde{\rho}_2}{\sqrt{(2 + r_2/\tilde{\rho}_2)^2 - 4} + r_2/\tilde{\rho}_2}\right)$$　　　(ref. state; $a_i = d_i = 1$)　　　(S12)

$$c_{13,0} = \frac{a_1}{r_2}\left(\frac{\sqrt{(2 + r_2/\tilde{\rho}_2)^2 - 4} - r_2/\tilde{\rho}_2}{\sqrt{(2 + r_2/\tilde{\rho}_2)^2 - 4} + r_2/\tilde{\rho}_2}\right)$$

With the LSER assumptions of monosegmental molecules and incompressibility, the above equations become

$c_{11=0}$

$$r_2 v_{22}^0 = \frac{2 + 1/K_{22} - \sqrt{\left(2 + 1/K_{22}\right)^2 - 4}}{2}$$

$$c_{12} = d_1 \left(\frac{1/K_{22} - \sqrt{\left(2 + 1/K_{22}\right)^2 - 4}}{1/K_{22} - \sqrt{\left(2 + 1/K_{22}\right)^2 - 4} - 2/K_{12}} \right) \qquad (d_i = a_i = r_i = \tilde{\rho}_i = 1) \qquad \text{(S13)}$$

$$c_{13} = a_1 \left(\frac{1/K_{22} - \sqrt{\left(2 + 1/K_{22}\right)^2 - 4}}{1/K_{22} - \sqrt{\left(2 + 1/K_{22}\right)^2 - 4} - 2/K_{21}} \right)$$

and in the reference state, they become:

$c_{11=0}$

$$r_2 v_{22,0}^0 = \frac{3 - \sqrt{\left(3\right)^2 - 4}}{2} = \frac{3 - \sqrt{5}}{2}$$

$$c_{12,0} = d_1 \left(\frac{1 - \sqrt{5}}{1 - \sqrt{5} - 2} \right) = d_1 \left(\frac{\sqrt{5} - 1}{\sqrt{5} + 1} \right) \qquad \text{ref. state; } (d_i = a_i = r_i = \tilde{\rho}_i = 1) \qquad \text{(S14)}$$

$$c_{13,0} = a_1 \frac{\sqrt{5} - 1}{\sqrt{5} + 1}$$

The second interesting case is when $a_i = d_i = 2$. Water and glycols are typical examples of such molecules. In this case, eq. S9 becomes:

$c_{11=0}$

$$c_{12} = \frac{d_1}{r_2} \left(\frac{r_2 Q_{22} - \sqrt{\left(4 + r_2 Q_{22}\right)^2 - 16}}{r_2 Q_{22} - \sqrt{\left(4 + r_2 Q_{22}\right)^2 - 16} - 2 r_2 Q_{12}} \right)$$

$$a_i = d_i = 2 \qquad \text{(S15)}$$

$$c_{13} = \frac{a_1}{r_2} \left(\frac{r_2 Q_{22} - \sqrt{\left(4 + r_2 Q_{22}\right)^2 - 16}}{r_2 Q_{22} - \sqrt{\left(4 + r_2 Q_{22}\right)^2 - 16} - 2 r_2 Q_{21}} \right)$$

and in the reference state:

$c_{11=0}$

$$c_{12,0} = \frac{d_1}{r_2} \left(\frac{r_2 / \tilde{\rho}_2 - \sqrt{\left(4 + r_2 / \tilde{\rho}_2\right)^2 - 16}}{-r_2 / \tilde{\rho}_2 - \sqrt{\left(4 + r_2 / \tilde{\rho}_2\right)^2 - 16}} \right)$$

$$\text{ref. state; } a_i = d_i = 2 \qquad \text{(S16)}$$

$$c_{13,0} = \frac{a_1}{r_2} \left(\frac{r_2 / \tilde{\rho}_2 - \sqrt{\left(4 + r_2 / \tilde{\rho}_2\right)^2 - 16}}{-r_2 / \tilde{\rho}_2 - \sqrt{\left(4 + r_2 / \tilde{\rho}_2\right)^2 - 16}} \right)$$

With the LSER assumptions of monosegmental molecules and incompressibility, the above equations become

$c_{11=0}$

$$c_{12} = d_1 \left(\frac{1/K_{22} - \sqrt{(4+1/K_{22})^2 - 16}}{1/K_{22} - \sqrt{(4+1/K_{22})^2 - 16} - 2/K_{12}} \right)$$

$a_i = d_i = 2, \; r_i = \tilde{\rho}_i = 1$ (S17)

$$c_{13} = a_1 \left(\frac{1/K_{22} - \sqrt{(4+1/K_{22})^2 - 16}}{1/K_{22} - \sqrt{(4+1/K_{22})^2 - 16} - 2/K_{21}} \right)$$

and in the reference state:

$c_{11=0}$

$$c_{12,0} = d_1 \left(\frac{1-3}{1-3-2} \right) = \frac{d_1}{2}$$

ref. state; $a_i = d_i = 2, \; r_i = \tilde{\rho}_i = 1$ (S18)

$$c_{13,0} = \frac{a_1}{2}$$

Regarding the remaining unknowns, c_{14} will not be needed in practical applications or will be considered equal to zero, and c_{21}, is given by

$$c_{21} = \frac{(d_2 - r_2 c_{12})(a_2 - r_2 c_{13})}{r_2^2 Q_{11}}$$

(S19)

where c_{12} and c_{13} are given by S8. In fact, c_{21} is not very much needed, in practice, and the approximate solution for v_{11} is constantly set equal to zero.

Replacing from above, we obtain at infinite dilution:

$$\frac{v_{10,0}}{v_{10}} = \frac{x_1 d_1 - r v_{11,0} - r v_{12,0}}{x_1 d_1 - r v_{11} - r v_{12}} = \frac{x_1 d_1 - r x_1^2 c_{21,0} - r x_1 c_{12,0}}{x_1 d_1 - r x_1^2 c_{21} - r x_1 c_{12}} = \frac{d_1 - r_2 c_{12,0}}{d_1 - r_2 c_{12}}$$

and   (S20)

$$\frac{v_{01,0}}{v_{01}} = \frac{x_1 a_1 - r v_{11,0} - r v_{21,0}}{x_1 a_1 - r v_{11} - r v_{21}} = \frac{a_1 - r_2 c_{21,0}}{a_1 - r_2 c_{21}}$$

Part II: LFER Linearity and examples of calculations

We examine, first, the general solute – solvent case. In this general case, we will substitute from eq. S9 and S10 in eq. S20, which becomes:

$$\frac{v_{10,0}}{v_{10}} = \frac{1 - \left(\dfrac{d_2 - a_2 + r_2/\tilde{\rho}_2 - \sqrt{(d_2 + a_2 + r_2/\tilde{\rho}_2)^2 - 4d_2a_2}}{d_2 - a_2 - r_2/\tilde{\rho}_2 - \sqrt{(d_2 + a_2 + r_2/\tilde{\rho}_2)^2 - 4d_2a_2}} \right)}{1 - \left(\dfrac{d_2 - a_2 + r_2Q_{22} - \sqrt{(d_2 + a_2 + r_2Q_{22})^2 - 4d_2a_2}}{d_2 - a_2 + r_2Q_{22} - \sqrt{(d_2 + a_2 + r_2Q_{22})^2 - 4d_2a_2} - 2r_2Q_{12}} \right)} =$$

$$= K_{12} \frac{d_2 - a_2 - r_2/\tilde{\rho}_2\left(2/K_{12} - 1/K_{22}\right) - \sqrt{(d_2 + a_2 + r_2Q_{22})^2 - 4d_2a_2}}{d_2 - a_2 - r_2/\tilde{\rho}_2 - \sqrt{(d_2 + a_2 + r_2/\tilde{\rho}_2)^2 - 4d_2a_2}} \qquad \text{(S21)}$$

and

$$\frac{v_{01,0}}{v_{01}} = K_{21} \frac{a_2 - d_2 - r_2/\tilde{\rho}_2\left(2/K_{21} - 1/K_{22}\right) - \sqrt{(d_2 + a_2 + r_2Q_{22})^2 - 4d_2a_2}}{a_2 - d_2 - r_2/\tilde{\rho}_2 - \sqrt{(d_2 + a_2 + r_2/\tilde{\rho}_2)^2 - 4d_2a_2}}$$

In the specific case, in which solute and solvent have one donor and one acceptor site, or, $a_i = d_i = 1$, eq. S21 becomes:

$$\frac{v_{10,0}}{v_{10}} = K_{12} \frac{r_2/\tilde{\rho}_2\left(2/K_{12} - 1/K_{22}\right) + \sqrt{(2 + r_2Q_{22})^2 - 4}}{r_2/\tilde{\rho}_2 + \sqrt{(2 + r_2/\tilde{\rho}_2)^2 - 4}}$$

and $\hspace{4cm} (a_i = d_i = 1) \qquad \text{(S22)}$

$$\frac{v_{01,0}}{v_{01}} = K_{21} \frac{r_2/\tilde{\rho}_2\left(2/K_{21} - 1/K_{22}\right) + \sqrt{(2 + r_2Q_{22})^2 - 4}}{r_2/\tilde{\rho}_2 + \sqrt{(2 + r_2/\tilde{\rho}_2)^2 - 4}}$$

With the LSER assumptions of monosegmental molecules and incompressibility, the above equations S22 become:

$$\frac{v_{10,0}}{v_{10}} = \frac{2}{1 + \sqrt{5}} + K_{12} \frac{\sqrt{(2 + 1/K_{22})^2 - 4} - 1/K_{22}}{1 + \sqrt{5}}$$

and $\hspace{4cm} (d_i = a_i = r_i = \tilde{\rho}_i = 1) \quad \text{(S23)}$

$$\frac{v_{01,0}}{v_{01}} = \frac{2}{1 + \sqrt{5}} + K_{21} \frac{\sqrt{(2 + 1/K_{22})^2 - 4} - 1/K_{22}}{1 + \sqrt{5}}$$

In the case of self-solvation, eq. S22 becomes:

$$\frac{v_{10,0}}{v_{10}} = \frac{r_2/\tilde{\rho}_2 + K_{22}\sqrt{(2 + r_2/\tilde{\rho}_2K_{22})^2 - 4}}{r_2/\tilde{\rho}_2 + \sqrt{(2 + r_2/\tilde{\rho}_2)^2 - 4}} = \frac{v_{01,0}}{v_{01}} \qquad \text{(self-solv.; } a_i = d_i = 1) \quad \text{(S24)}$$

With the LSER assumptions and on self-solvation, eq. S23 becomes:

$$\frac{v_{10,0}}{v_{10}} = \frac{1}{1+\sqrt{5}} + K_{22}\frac{\sqrt{\left(2+1/K_{22}\right)^2 - 4}}{1+\sqrt{5}} = \frac{v_{01,0}}{v_{01}} \quad \text{self-solv;} (d_i = a_i = r_i = \tilde{\rho}_i = 1) \text{ (S25)}$$

An approximation to eq. S25 for K_{22} values not too low could be the following:

$$\frac{v_{10,0}}{v_{10}} = \frac{v_{01,0}}{v_{01}} \simeq \frac{1+2\sqrt{K_{22}}}{1+\sqrt{5}} \qquad\qquad \text{self-solv;} (d_i = a_i = r_i = \tilde{\rho}_i = 1) \text{ (S26)}$$

Let us examine, now, the other common case, in which solute and solvent have 2 donor and 2 acceptor sites each, or, $a_i = d_i = 2$. In this case, eq. S21 becomes:

$$\frac{v_{10,0}}{v_{10}} = \frac{2r_2/\tilde{\rho}_2 + K_{12}\left(\sqrt{\left(4+r_2 Q_{22}\right)^2 - 16} - 1/K_{22}\right)}{r_2/\tilde{\rho}_2 + \sqrt{\left(4+r_2/\tilde{\rho}_2\right)^2 - 16}}$$

and $\qquad\qquad\qquad\qquad (a_i = d_i = 2) \qquad\qquad \text{(S27)}$

$$\frac{v_{01,0}}{v_{01}} = \frac{2r_2/\tilde{\rho}_2 + K_{21}\left(\sqrt{\left(4+r_2 Q_{22}\right)^2 - 16} - 1/K_{22}\right)}{r_2/\tilde{\rho}_2 + \sqrt{\left(4+r_2/\tilde{\rho}_2\right)^2 - 16}}$$

With the LSER assumptions of monosegmental molecules and incompressibility, the above equations S27 become:

$$\frac{v_{10,0}}{v_{10}} = \frac{2 + K_{12}\left(\sqrt{\left(4+1/K_{22}\right)^2 - 16} - 1/K_{22}\right)}{4}$$

and $\qquad\qquad\qquad (a_i = d_i = 2;\ r_i = \tilde{\rho}_i = 1) \qquad \text{(S28)}$

$$\frac{v_{01,0}}{v_{01}} = \frac{2 + K_{21}\left(\sqrt{\left(4+1/K_{22}\right)^2 - 16} - 1/K_{22}\right)}{4}$$

In the case of self-solvation, eq. S27 become:

$$\frac{v_{10,0}}{v_{10}} = \frac{v_{01,0}}{v_{01}} = \frac{2r_2/\tilde{\rho}_2 - 1 + K_{22}\sqrt{\left(4+r_2/\tilde{\rho}_2 K_{22}\right)^2 - 16}}{r_2/\tilde{\rho}_2 + \sqrt{\left(4+r_2/\tilde{\rho}_2\right)^2 - 16}} \quad \text{(self-solv.; } a_i = d_i = 2) \text{ (S29)}$$

In the case of self-solvation, eq. S28 become:

$$\frac{v_{10,0}}{v_{10}} = \frac{v_{01,0}}{v_{01}} = \frac{1 + K_{22}\sqrt{\left(4+1/K_{22}\right)^2 - 16}}{4} \quad \text{(self-solv.; } a_i = d_i = 2;\ r_i = \tilde{\rho}_i = 1) \text{ (S28)}$$

An approximation to eq. S28 for K_{22} values approaching unity, and meeting the symmetry criterion, could be the following:

$$\frac{v_{10,0}}{v_{10}} = \frac{v_{01,0}}{v_{01}} = \frac{1+3\sqrt{K_{22}}}{4} \qquad \text{(self-solv.; } a_i = d_i = 2; \ r_i = \tilde{\rho}_i = 1 \text{)} \quad \text{(S29)}$$

But the following alternative is significantly better for not too low K_{22} values:

$$\frac{v_{10,0}}{v_{10}} = \frac{v_{01,0}}{v_{01}} = \frac{1+\sqrt{8K_{22}}}{4} \quad \text{(self-solv.; } a_i = d_i = 2; \ r_i = \tilde{\rho}_i = 1 \text{)} \quad \text{(S29a)}$$

Example: *Solvent Methanol*

From the scaling constants for the solvent methanol, we obtain: $r_2 = 3{,}715229$, $\rho_2 = 0{,}8921906$, and $K_{22} = 1035{,}7$. Replacing in the above equations S24, we obtain for the hydrogen-bonding contribution to self-solvation free-energy:

$$F_{12} = \frac{v_{10,0}}{v_{10}} = \frac{r_2/\tilde{\rho}_2 + K_{22}\sqrt{\left(2+r_2/\tilde{\rho}_2 K_{22}\right)^2 - 4}}{r_2/\tilde{\rho}_2 + \sqrt{\left(2+r_2/\tilde{\rho}_2\right)^2 - 4}} = \frac{4.164 + 1035.7 x 0.1269}{4.164 + 5.8307} = 13{,}56$$

With the LSER assumption, this gives

$$F_{12} = \frac{v_{10,0}}{v_{10}} = \frac{1 + K_{22}\sqrt{\left(2+1/K_{22}\right)^2 - 4}}{1+\sqrt{5}} = \frac{1 + 1035.7 x 0.06215}{4.164 + 5.8307} = 13{,}56$$

When methanol is the solvent, we obtain from eq. S22 for the hydrogen-bonding contribution to solvation free-energy in the solute-methanol (solvent):

$$F_{12} = \frac{v_{10,0}}{v_{10}} = \frac{\left(r_2/\tilde{\rho}_2\right)\left[2-\left(K_{12}/K_{22}\right)\right] + K_{12}\sqrt{\left(2+r_2/\tilde{\rho}_2 K_{22}\right)^2 - 4}}{r_2/\tilde{\rho}_2 + \sqrt{\left(2+r_2/\tilde{\rho}_2\right)^2 - 4}} =$$

$$= \frac{4.164\left[2-\left(K_{12}/1035.7\right)\right] + 0.1269 K_{12}}{9.995} = \frac{8.329 + 0.1229 K_{12}}{9.995} = 0.833 + 0.0123 K_{12}$$

or

$$\log\left(F_{12} - 0.833\right) + 1.91 = \log K_{12}$$
and
$$\log\left(F_{21} - 0.833\right) + 1.91 = \log K_{21}$$

Adopting the universal constant (cf. eq. 29 of main text) at 298.15K, *kRT = 84000* J/mol, or $\Delta G_{ij}^{hb} = -kRT A_i B_j = -84000 A_i B_j = -RT \ln K_{ij}$, we obtain:

$$\log K_{ij} = \frac{84000 A_i B_j}{2{,}303 RT} = 14.7 A_i B_j$$

For methanol $A_2 = 0{,}43$ and $B_2 = 0{,}47$. Thus, the above equations become:

$$\log\left(F_{12}-0.833\right)+1.91=14.71A_1B_2=14.71x0.47A_1=6.91A_1$$
and
$$\log\left(F_{21}-0.833\right)+1.91=14.71B_1A_2=14.71x0.43B_1=6,33B_1$$

Alternatively, we obtain for the hydrogen bonding contributions in solvent methanol:

$$F_{12}=0.833+10^{(6.91A_1-1.91)}$$
and
$$F_{21}=0.833+10^{(6.33B_1-1.91)}$$

The general equation is:

$\log(F_{12}-c_1) + c_2 = c_3A_1$ (S30)

and

$\log(F_{21}-c_1) + c_2 = c_4B_1.$ (S31)

The values of the constants for alkanols are reported in table S1 and S2.

Table S1: The constants of equation S30 – S31 for hydrogen bonding contributions to the free-energy of solvation in alkanol solvents

Alkanol	c_1	c_2	c_3	c_4
METHANOL	0.833	1.91	6.91	6.33
ETHANOL	0.873	1.86	7.06	5.44
1-PROPANOL	0.896	1.89	7.06	5.44
1-BUTANOL	0.912	1.91	7.09	5.42
1-PENTANOL	0.923	1.93	7.09	5.42
1-HEXANOL	0.932	1.95	7.14	5.40
1-HEPTANOL	0.939	1.97	7.10	5.41
1-OCTANOL	0.945	1.98	7.14	5.38
1-DECANOL	0.950	1.99	7.22	5.40
2-PROPANOL	0.954	2.00	7.17	5.36
2-PENTANOL	0.898	1.91	8.24	4.51

Table S2: The hydrogen bonding contributions to the free-energy of solvation in alkanol solvents

Alkanol	Self-Solv	F_{12}	F_{21}
METHANOL	13.55	$0.833+10^{6.91A1\,-1.91}$	$0.833+10^{6.33B1\,-1.91}$
ETHANOL	9.16	$0.873+10^{7.06A1\,-1.86}$	$0.873+10^{5.44B1\,-1.86}$
1-PROPANOL	8.12	$0.896+10^{7.06A1\,-1.89}$	$0.896+10^{5.44B1\,-1.89}$
1-BUTANOL	7.24	$0.912+10^{7.09A1\,-1.91}$	$0.912+10^{5.42B1\,-1.91}$
1-PENTANOL	6.58	$0.923+10^{7.09A1\,-1.93}$	$0.923+10^{5.42B1\,-1.93}$
1-HEXANOL	6.05	$0.932+10^{7.14A1\,-1.95}$	$0.932+10^{5.40B1\,-1.95}$
1-HEPTANOL	5.62	$0.939+10^{7.10A1\,-1.97}$	$0.939+10^{5.41B1\,-1.97}$
1-OCTANOL	5.24	$0.945+10^{7.14A1\,-1.98}$	$0.945+10^{5.38B1\,-1.98}$
1-DECANOL	4.89	$0.950+10^{7.22A1\,-1.99}$	$0.950+10^{5.40B1\,-1.99}$
2-PROPANOL	4.60	$0.954+10^{7.17A1\,-2.00}$	$0.954+10^{5.36B1\,-2.00}$
2-PENTANOL	8.35	$0.898+10^{8.24A1\,-1.91}$	$0.898+10^{4.51B1\,-1.91}$

Part III: Literature data

Table S3: LSER descriptors and LFER coefficients for alkanols [10-11]

Alkanol	E	S	A	B	V_x	L	c	e	s	a	b	l
METHANOL	0.28	0.44	0.43	0.47	0.31	0.97	0.039	0.338	1.317	3.826	1.396	0.773
ETHANOL	0.25	0.42	0.37	0.48	0.45	1.50	0.017	0.232	0.867	3.894	1.192	0.846
1-PROPANOL	0.23	0.42	0.37	0.48	0.59	2.04	0.042	0.246	0.749	3.888	1.076	0.874
1-BUTANOL	0.22	0.42	0.37	0.48	0.73	2.60	0.004	0.285	0.768	3.705	0.879	0.890
1-PENTANOL	0.22	0.42	0.37	0.48	0.87	3.10	0.002	0.161	0.535	3.778	0.960	0.900
1-HEXANOL	0.21	0.42	0.37	0.49	1.01	3.61	0.014	0.205	0.583	3.621	0.891	0.913
1-HEPTANOL	0.21	0.42	0.37	0.48	1.15	4.11	0.056	0.216	0.554	3.596	0.803	0.933
1-OCTANOL	0.20	0.42	0.37	0.49	1.30	4.61	0.147	0.214	0.561	3.507	0.749	0.943
1-DECANOL	0.19	0.42	0.36	0.49	1.58	5.62	0.139	0.090	0.356	3.547	0.727	0.958
2-PROPANOL	0.21	0.37	0.31	0.56	0.59	1.78	0.048	0.324	0.713	4.036	1.055	0.884
2-PENTANOL	0.20	0.37	0.33	0.56	0.87	2.84	0.031	0.325	0.496	3.792	1.024	0.934

Data for figure 3 of the main text are reported in table S4.

Table S4: Experimental [12] and calculated solvation free energies of various solutes in 1-octanol solvent

Solute	ΔG_{12}^{S} exp/ Jmol^{-1}	ΔG_{12}^{S} LSER/ Jmol^{-1}	F_{12}	F_{21}	ΔG_{12}^{S} LFHB/ Jmol^{-1}
1-butanol	-24602	-25877	0,734	0,703	-24645
1-pentanol	-26485	-28601	0,734	0,703	-27369
1-propanol	-21046	-22908	0,743	0,694	-21655
2-butanone	-15774	-17805	-0,020	0,827	-20235

2-propanone	-13347	-15424	-0,015	0,752	-16720
nitromethane	-14560	-16870	-0,012	0,158	-15173
water	-17364	-20622	3,464	0,316	-25322
THF	-16318	-18954	-0,020	0,690	-20734
CHCl3	-15941	-19337	0,029	-0,018	-16307
pyridine	-22259	-22702	-0,020	0,839	-25191
pentane	-11088	-12488	-0,020	-0,020	-12262
octane	-19497	-20666	-0,020	-0,020	-20440
toluene	-18828	-21745	-0,020	0,001	-21054
methanol	-16234	-18409	1,122	0,651	-17916
heptane	-16694	-17915	-0,020	-0,020	-17689
ethanol	-18954	-19994	0,743	0,694	-18741
cyclohexanol	-29204	-31886	0,420	1,139	-32144
cyclohexane	-15690	-17492	-0,020	-0,020	-17266
benzene	-16108	-18839	-0,020	0,002	-18139
butanal	-19414	-17268	-0,020	0,569	-18479
2-propanol	-19330	-20366	0,408	1,069	-20270
2-penntanone	-18159	-20181	-0,020	0,826	-22608
1-pentanol	-26485	-28601	0,734	0,703	-27369
ethylacetate	-15774	-17406	-0,020	0,569	-18617

In figure 2 of the main text, only the experimental data [12] at 298.15 K are shown. However, the same reference [12] reports also data on enthalpies and entropies of self-solvation of 1-alkanols, which may be converted to free-energies of self-solvation at 298.15 K, through the equation: $\Delta G_{22}^{S} = \Delta H_{22}^{S} - 298.15 \Delta S_{22}^{S}$. These converted data are reported in table S5 along with the original temperature, T_{or}, for which the enthalpy and entropy data are known [12]. As shown in the table, almost always, the discrepancies of the experimental data are less than 1%.

Table S5: Experimental data [12] for the self-solvation free energy of 1-alkanols at 298.15 K. Original data on solvation enthalpy and entropy, at other temperatures, Tor, were converted to 298.15 K through the equation $\Delta G_{22}^{S} = \Delta H_{22}^{S} - 298.15 \Delta S_{22}^{S}$

Solvent	T_{or}/ K	ΔG_{22}^{S} / kJ/mol		Solvent	T_{or}/ K	ΔG_{22}^{S} / kJ/mol
Methanol	294	-20.25		1-Hexanol	298	-30.29
	298	-20.29			305	-30.29
	353	-20.17				
				1-Heptanol	298	-32.97
Ethanol	285	-21.21			318	-32.89
	298	-21.25				
	348	-21.13		1-Octanol	258	-34.64
					298	-35.1
1-Propanol	298	-23.22			336	-34.77
	302	-23.3				
				1-Nonanol	269	-37.57
1-Butanol	259	-25.27			298	-37.87
	298	-25.56			349	-37.32

	315	-25.31				
				1-Decanol	281	-39.87
1-Pentanol	274	-27.45			298	-39.96
	298	-27.61				

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