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Supporting Information

Unified elucidation of the entropy-driven and -opposed hydrophobic effects

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SI:1 Theories

An integral equation theory[1] consists of the Ornstein-Zernike (OZ) equation coupled with an appropriate closure equation. In the analysis of solvation properties of a solute, it is assumed that the solute is inserted into a solvent under the isochoric condition at infinite dilution. In the first step, the solvent-solvent correlation functions are calculated. In the second step, the solute-solvent correlation functions are calculated using the solvent-solvent correlation functions as part of the input data. In the third step, the potential of mean force (PMF) between solutes is calculated from the solute-solvent correlation functions. In this study, we consider two solvents. One of them is a model water and the other is a hard-sphere solvent formed by neutral hard spheres. The molecular diameter d_S and number density in the bulk ρ_S are set at those of real water at 298 K and 1 atm: d_S=0.28 nm and $\rho_S d_S^3$=0.7317. The solute is a neutral hard sphere with diameter d_U.

SI:1.1 Radial-symmetric integral equation theory (RSIET) for simple fluids

When the solvent is a simple fluid like the hard-sphere solvent and the solute is spherical, the solvent-solvent and solvent-solute correlation functions are dependent only on the distance between centers of two particles.[1] That is, they possess radial symmetry. The OZ equation can be written as

$$h(r)=c(r)+4\pi\rho_S\int_0^{\infty} c(|\boldsymbol{r}-\boldsymbol{r}'|)h_{SS}(r')r'^2dr', \tag{S1}$$

where h and c are the solute-solvent total and direct correlation functions, respectively, h_{SS} is the solvent-solvent total correlation function, and r is the distance between centers of two particles. The closure equation is given by

$$h(r)+1=\exp[-u(r)/(k_BT)+h(r)-c(r)+b(r)],$$
(S2)

where u is the solute-solvent pair potential, k_B is the Boltzmann constant, T is the absolute temperature, and b is the solute-solvent bridge function. We employ the hypernetted-chain (HNC) approximation, $b(r)\equiv 0$, in the closure equation. The OZ equation is formally exact.

For solving eqns (S1) and (S2), a sufficiently long range r_L is divided into N grid points ($r_i=i\delta r$, $i=0, 1, \ldots, N-1$; $\delta r=r_L/N$; $\delta r=0.01d_S$; $N=4096$) and all of the correlation functions are represented by their values on these points. The basic equations are then numerically solved by means of the robust, highly efficient algorithm developed by Kinoshita and coworkers.[2] Since the HNC approximation is employed, we can calculate the solvation free energy μ (i.e., excess chemical potential) of the solute from the solute-solvent correlation functions via the Morita-Hiroike formula.[3,4] For this model system, μ is given by $\mu=-TS$ where S is the solvation entropy. The solute-solvent pair correlation component of S, which is denoted by S_{PA}, is calculated from the solute-solvent pair correlation function $g(r)=h(r)+1$.[5,6] "$S-S_{PA}$" represents the solute-solvent-solvent triplet and higher-order (i.e., solute-solvent many-body) correlation components: It is denoted by S_{MB}.

The PMF between hard-sphere solutes $\Phi^{HS}(r)$ ($r\geq d_U$) (the superscript "HS" denotes "hard-sphere solvent") calculated from[7]

$$\Phi^{HS}(r)/(k_BT)=-f_{UU}(r)=h_{UU}(r)-c_{UU}(r).$$
(S3)

Here, h_{UU} and c_{UU} are the solute-solute total and direct correlation functions, respectively, and the solute-solute bridge function is neglected. The function $f_{UU}(r)$ is obtained via the back Fourier transform of $F_{UU}(k)$ expressed as[7]

$$F_{UU}(k)=\rho_S C(k)H(k)$$
(S4)

where $C(k)$ and $H(k)$ are the Fourier transforms of $c(r)$ and $h(r)$, respectively, and k is the wave number. $\Phi^{HS}(r)$ possesses only the entropic component $\Phi_S{}^{HS}(r)$: $\Phi^{HS}(r)/(k_BT)=-\Phi_S{}^{HS}(r)/k_B$. The physical meaning of $\Phi_S{}^{HS}(r)$ is "S of two solutes separated by distance r" − "S of two solutes infinitely separated". It is known that the HNC tends to overestimate S of a solute: Both of "S of two solutes separated by distance r" and "S of two solutes infinitely separated" are somewhat overestimated, but the cancellation of errors occurs when the subtraction is taken. As a matter of fact, it was shown that the PMF thus calculated without incorporating the solvent-solvent, solute-solvent, and solute-solute bridge functions is in good agreement with the *exact* PMF.[8,9]

SI:1.2 Angle-dependent integral equation theory (ADIET) for molecular fluids

We employ a multipolar model for water: A water molecule is modeled as a hard sphere with diameter d_S=0.28 nm in which a point dipole and a point quadrupole of tetrahedral symmetry are embedded.[10,11] The ADIET[10–13] explicitly takes account of the dependence of a correlation function on the orientations of solvent molecules. The OZ equation can be written as

$$h(12)=c(12)+\{1/(8\pi^2)\}\rho_S\int c(13)h_{SS}(32)d(3), \tag{S5}$$

where h and c are the solute-water total and direct correlation functions, respectively, h_{SS} is the water-water total correlation function, (ij) represents $(\boldsymbol{r}_{ij}, \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j)$, $\boldsymbol{r}_{ij}$ is the vector connecting centers of particles i and j, $\boldsymbol{\Omega}_i$ denotes the three Euler angles describing the orientation of particle i, $\int d(3)$ represents integration over all position and angular coordinates of particle 3, and ρ_S is the water number density in the bulk. We emphasize that the OZ equation is formally exact. The closure equation is expressed by

$$c(12)=\int_r^{\infty}[h(12)\partial\{w(12)-b(12)\}/\partial r']dr'-u(12)/(k_BT)+b(12), \tag{S6a}$$

$$w(12)=c(12)-h(12)+u(12)/(k_BT), \tag{S6b}$$

where u is the pair potential, b is the bridge function, and r is the distance between centers of two particles. The closure equation is reformulated so that the rotational-invariant expansion mentioned below can be applied to it. The HNC approximation, $b(12)\equiv 0$, is employed in the closure equation.

For the numerical solution of eqns (S5) and (S6), a correlation function is expanded in a basis set of rotational invariants, and the basic equations are reformulated in terms of the projections $X^{mnl}_{\mu\nu}(r)$ occurring in the rotational-invariant expansion of $X(12)$ (X is a water-water or water-solute correlation function).[10–13] The expansion considered for m, $n\leq n_{\max}=4$ gives sufficiently accurate results for a nonpolar solute. A sufficiently long range r_L is divided into N grid points ($r_i=i\delta r$, i=0, 1, …, $N-1$; $\delta r=r_L/N$; $\delta r=0.01d_S$; N=4096) and all of the projections are represented by their values on these points. The numerical solution of the basic equations is carried out using the robust, highly efficient algorithm developed by Kinoshita and coworkers.[14]

The influence of molecular polarizability of water is taken into account by employing the self-consistent mean field (SCMF) theory.[10,11] At the SCMF level, the many-body induced interactions are reduced to pairwise additive potentials involving an effective dipole moment. At 298 K and 1 atm, the effective dipole moment thus is about 1.42 times larger than the *bare* gas-phase dipole moment. S is evaluated via the temperature derivative of μ calculated using the Morita-Hiroike formula adapted to molecular fluids[10,11] ($U=\mu+TS$; U is the solvation energy). Upon solute insertion, the translational freedom of water molecules in the entire system is restricted, and the orientational freedom of water molecules near the solute is constrained. The translational and orientational contributions are calculated using the projections of $(mnl,\mu\nu)=(000,00)$ and those of $(mnl,\mu\nu)\neq(000,00)$, respectively.[13] S_{PA} and S_{MB} are calculated by extending the procedure described above to molecular liquids.[12,13] The dielectric constant of water, which is a good measure of the validity of a theory, is calculated to be ~83 that is in good accord with the experimental value. Moreover, it was shown that the results (e.g., thermodynamic quantities of hydration such as the hydration free energy) from the ADIET using the HNC approximation and the multipolar model are in very good agreement with those from the molecular dynamics simulation employing the SPC/E and TIP4P models, for nonpolar solutes with a wide range of sizes.[13,15]

The PMF between hard-sphere solutes $\Phi(r)$ ($r\geq d_{\mathrm{U}}$) is calculated on the basis of the extension of eqn (S4) to molecular fluids.[16] More specifically, it is calculated using the Hankel transforms of projections occurring in the rotational-invariant expansions of the solute-water correlation functions. The equation corresponding to eqn (S4) and the calculation procedure of $\Phi(r)$ were given in our earlier publication.[16] The entropic component of $\Phi(r)$, $\Phi_{\mathrm{S}}(r)$, is calculated through the temperature derivative of $\Phi(r)$, and the energetic component $\Phi_{\mathrm{E}}(r)$ is obtained as $\Phi_{\mathrm{E}}(r)=\Phi(r)+T\Phi_{\mathrm{S}}(r)$.

SI:1.3 Morphometric approach (MA)

$S_{\mathrm{PA}}/k_{\mathrm{B}}$ and $S_{\mathrm{MB}}/k_{\mathrm{B}}$ are further decomposed into the excluded-volume (EV) and solvent-accessible surface (SAS) terms. In the MA,[17,18] Z ($=S_{\mathrm{PA}}/k_{\mathrm{B}}$ or $S_{\mathrm{MB}}/k_{\mathrm{B}}$) is expressed as the linear combination of four geometric measures of a solute:

$$Z=C_1V_{\mathrm{ex}}+C_2A+C_3X+C_4Y. \tag{S7}$$

Here, eqn (S7) is referred to as the morphometric form for Z, V_{ex} is the EV, A is the SAS area, and X and Y are the integrated mean and Gaussian curvatures of the SAS, respectively. In the MA, the solute shape enters a value of Z via the four geometric measures. The four coefficients C_1–C_4 are dependent only on the solvent species and its thermodynamic state.

The solvent in the bulk (i.e., sufficiently far from the solute) contributes to the EV term "C_1V_{ex}", whereas the solvent near the solute contributes to the SAS term "$C_2A+C_3X+C_4Y$".

The C_1-C_4 are determined by the following two steps: (1) Calculate Z for hard-sphere solutes with various diameters ($0.6d_{\mathrm{S}}\le d_{\mathrm{U}}\le 10d_{\mathrm{S}}$, d_{S}=0.28 nm) using each theory; and (2) determine C_1-C_4 by means of the least square fitting applied to the following equation (i.e., eqn (S7) applied to hard-sphere solutes):

$$Z=C_1(4\pi d_{\mathrm{US}}^3/3)+C_2(4\pi d_{\mathrm{US}}^2)+C_3(4\pi d_{\mathrm{US}})+C_4(4\pi), \quad \text{(S8)}$$

where $d_{\mathrm{US}}=(d_{\mathrm{U}}+d_{\mathrm{S}})/2$. The fitting is performed so that the F_{D} defined by

$$F_{\mathrm{D}}=\sum_{d_{\mathrm{U}}}\{(Z^{\mathrm{Theory}}-Z^{\mathrm{MA}})/Z^{\mathrm{Theory}}\}^2 \quad \text{(S9)}$$

can be minimized. Here, the superscripts "Theory" and "MA", respectively, denote the values calculated by each theory and by eqn (S8), and the summation is taken over all of the values of d_{U}. We define the error E_{D} (%) as

$$E_{\mathrm{D}}=100(1/M_{\mathrm{D}})\sum_{d_{\mathrm{U}}}|(Z^{\mathrm{Theory}}-Z^{\mathrm{MA}})/Z^{\mathrm{Theory}}| \quad \text{(S10)}$$

where M_{D} is the number of the values of d_{U}. When the solvent is the model water, E_{D} is smaller than 4% for $Z=S_{\mathrm{PA}}/k_{\mathrm{B}}$ and 0.2% for $S_{\mathrm{MB}}/k_{\mathrm{B}}$. For the hard-sphere solvent, the errors are an order of magnitude smaller.[15,19]

Using the values of C_1-C_4 thus determined, we can obtain Z of a complexly shaped solute (e.g., a polyatomic solute) only if its V_{ex}, A, X, and Y are calculated. In this study, however, we treat a hard-sphere solute with diameter d_{U}. We define $S_{\mathrm{PA,EV}}$, $S_{\mathrm{PA,SAS}}$, $S_{\mathrm{MB,EV}}$, and $S_{\mathrm{MB,SAS}}$ as follows:

$$S_{\mathrm{PA,EV}}=C_1^{\mathrm{PA}}(4\pi d_{\mathrm{US}}^3/3), \quad \text{(S11a)}$$

$$S_{\mathrm{PA,SAS}}=C_2^{\mathrm{PA}}(4\pi d_{\mathrm{US}}^2)+C_3^{\mathrm{PA}}(4\pi d_{\mathrm{US}})+C_4^{\mathrm{PA}}(4\pi), \quad \text{(S11b)}$$

$$S_{\mathrm{MB,EV}}=C_1^{\mathrm{MB}}(4\pi d_{\mathrm{US}}^3/3), \quad \text{(S12a)}$$

$S_{\mathrm{MB,SAS}}=C_2^{\mathrm{MB}}(4\pi d_{\mathrm{US}}^2)+C_3^{\mathrm{MB}}(4\pi d_{\mathrm{US}})+C_4^{\mathrm{MB}}(4\pi)$.
(S12b)

Here, the superscripts "PA" and "MB", respectively, represent the coefficients determined for $S_{\mathrm{PA}}/k_{\mathrm{B}}$ and $S_{\mathrm{MB}}/k_{\mathrm{B}}$. ($S_{\mathrm{PA,EV}}$ can be obtained by the Asakura-Oosawa theory[20,21] without using the MA.) The solvents in the bulk (i.e., sufficiently far from the solute) and near the solute contribute to the EV and SAS terms, respectively.

SI:2 Magnitudes and signs of the four constituents of solvation entropy

SI:2.1 Hard-sphere solvent

$S_{\mathrm{PA,EV}}$, $S_{\mathrm{PA,SAS}}$, $S_{\mathrm{MB,EV}}$, and $S_{\mathrm{MB,SAS}}$ for solutes with $d_{\mathrm{U}}=d_{\mathrm{S}}$, $4d_{\mathrm{S}}$, and $10d_{\mathrm{S}}$ in the hard-sphere solvent are given in Table S1. $S_{\mathrm{MB,SAS}}/k_{\mathrm{B}}$ is positive whereas the others are negative. $|S_{\mathrm{PA,EV}}/k_{\mathrm{B}}|<<|S_{\mathrm{MB,EV}}/k_{\mathrm{B}}|$ and $|S_{\mathrm{PA,SAS}}/k_{\mathrm{B}}|<<S_{\mathrm{MB,SAS}}/k_{\mathrm{B}}$.

Table S1 The four constituents of solvation entropy.

$d_{\mathrm{U}}/d_{\mathrm{S}}$	$S_{\mathrm{PA,EV}}/k_{\mathrm{B}}$	$S_{\mathrm{PA,SAS}}/k_{\mathrm{B}}$	$S_{\mathrm{MB,EV}}/k_{\mathrm{B}}$	$S_{\mathrm{MB,SAS}}/k_{\mathrm{B}}$
1	−4.19	−2.00	−20.6	17.2
4	−65.5	−22.1	−322	138
10	−697	−127	−3430	730

SI:2.2 Water

The translational and orientational contributions to S (S^{Trans} and S^{Orient}, respectively) for solutes with $d_{\mathrm{U}}=d_{\mathrm{S}}$, $4d_{\mathrm{S}}$, and $10d_{\mathrm{S}}$ in the model water are given in Table S2. The orientational contribution is only ~2% of the total solvation entropy for a hard-sphere solute with diameter $d_{\mathrm{U}}=d_{\mathrm{S}}$ and the percentage decreases as d_{U} becomes larger.[13,22] The reason for this is the following: Upon solute insertion, the restriction of orientational freedom occurs only for the water molecules near the solute, whereas that of translational one reaches all the water molecules in the system; and the orientational contribution does not possess the EV term.

Table S2 Translational and orientational contributions to solvation entropy.

$d_{\mathrm{U}}/d_{\mathrm{S}}$	$S^{\mathrm{Trans}}/k_{\mathrm{B}}$	$S^{\mathrm{Orient}}/k_{\mathrm{B}}$
1	−8.95	−0.14
4	−234	−2.60
10	−2820	−14.8

$S_{\mathrm{PA,EV}}$, $S_{\mathrm{PA,SAS}}$, $S_{\mathrm{MB,EV}}$, and $S_{\mathrm{MB,SAS}}$ for solutes with $d_{\mathrm{U}}=d_{\mathrm{S}}$, $4d_{\mathrm{S}}$, and $10d_{\mathrm{S}}$ in the model water are given in Table S3. Both of the translational and orientational contributions are included. The orientational contribution is significant only in $S_{\mathrm{PA,SAS}}/k_{\mathrm{B}}$: In a strict sense, $S_{\mathrm{PA,SAS}}$ is attributed a decrease in not only the translational freedom but also the orientational freedom of each solvent particle near the solute. $S_{\mathrm{MB,SAS}}/k_{\mathrm{B}}$ is positive whereas the others are negative. $|S_{\mathrm{PA,EV}}/k_{\mathrm{B}}|<<|S_{\mathrm{MB,EV}}/k_{\mathrm{B}}|$ and $|S_{\mathrm{PA,SAS}}/k_{\mathrm{B}}|<<S_{\mathrm{MB,SAS}}/k_{\mathrm{B}}$.

Table S3 The four constituents of solvation entropy.

$d_{\mathrm{U}}/d_{\mathrm{S}}$	$S_{\mathrm{PA,EV}}/k_{\mathrm{B}}$	$S_{\mathrm{PA,SAS}}/k_{\mathrm{B}}$	$S_{\mathrm{MB,EV}}/k_{\mathrm{B}}$	$S_{\mathrm{MB,SAS}}/k_{\mathrm{B}}$
1	−4.19	−0.82	−14.0	9.95
4	−65.5	−3.59	−219	51.9
10	−697	−16.2	−2330	212

SI:3 Entropic and enthalpic components of potential of mean force under isobaric condition

SI:3.1 Relation between components of potential of mean force (PMF) under isochoric condition and those under isobaric one

For the PMF between solutes in water, $\Phi_{\mathrm{S}}(r)$ and $\Phi_{\mathrm{E}}(r)$ are calculated under the isochoric condition. The entropic and enthalpic components under the isobaric condition ($\Phi_{\mathrm{SP}}(r)$ and $\Phi_{\mathrm{EP}}(r)$, respectively) are related to $\Phi_{\mathrm{S}}(r)$ and $\Phi_{\mathrm{E}}(r)$ through (also see Section 2.4, “Contribution from structure and properties of bulk water to thermodynamic quantities of solvation”, in the main article)[12,23]

$$\Phi_{\mathrm{SP}}(r)/k_{\mathrm{B}}=\Phi_{\mathrm{S}}(r)+\Delta\Omega(r), \tag{S13a}$$

$$\Phi_{\mathrm{EP}}(r)/(k_{\mathrm{B}}T)=\Phi_{\mathrm{E}}(r)/(k_{\mathrm{B}}T)+\Delta\Omega(r), \tag{S13b}$$

$$\Delta\Omega(r)=(\alpha^*/\kappa_{\mathrm{T}}^*)\Delta V_{\mathrm{P}}(r)/d_{\mathrm{S}}^3. \tag{S13c}$$

Here, $\Delta V_{\mathrm{P}}(r)$ is the change in system volume caused when the distance between centers of two solutes changes from ∞ to r under the isobaric condition. The dimensionless parameters, α^* and κ_{T}^*, which depend only on the properties of pure bulk water, are defined as $\alpha^*=\alpha T$ and $\kappa_{\mathrm{T}}^*=\kappa_{\mathrm{T}}k_{\mathrm{B}}T/d_{\mathrm{S}}^3$ where α is the isobaric thermal expansion coefficient and κ_{T} is the isothermal compressibility. $\alpha^*/\kappa_{\mathrm{T}}^*=-0.208$, 0.0, 0.894, and 2.43 at T=273, 277, 298, and 373 K, respectively.[24,25]

$\Phi_{SP}(r)$, for example, is equivalent to "S_P of a pair of solutes separated by distance r" – "S_P of a pair of solutes infinitely separated". Since "V_P of a pair of solutes separated by distance r" is not significantly different from "V_P of a pair of solutes infinitely separated", $\Delta V_P(r)$ is very small. Therefore, $\Delta\Omega(r)$ is very small irrespective of the value of α^*/κ_T^*: $\Phi_{SP}(r)$ and $\Phi_{EP}(r)$ are almost equal to $\Phi_S(r)$ and $\Phi_E(r)$, respectively. It follows that $\Phi_{SP}(r)$ and $\Phi_{EP}(r)$ are largely dependent on the change in the structure and properties of bulk water just as $\Phi_S(r)$ and $\Phi_E(r)$.

$\Delta V_P(r)$ can approximately be calculated in the following manner.

(1) The MA is applied to the solute-solute pair:

$$\Delta V_P(r)/d_S^3=C_1\Delta V_{ex}(r)+C_2\Delta A(r)+C_3\Delta X(r)+C_4\Delta Y(r). \tag{S14}$$

Here, $\Delta V_{ex}(r)$, for example, is the EV change caused when the distance between centers of two solutes changes from ∞ to r. It follows that $\Delta V_{ex}(r)$, $\Delta A(r)$, $\Delta X(r)$, and $\Delta Y(r)$ are all zero for $r-d_U \geq d_S$.

(2) The four coefficients (C_1–C_4) are determined beforehand by treating the partial molar volumes of hard-sphere solutes with various diameters ($0.6d_S \leq d_U \leq 30d_S$, d_S=0.28 nm) (see section SI:1.3).

(3) ΔV_{ex}, ΔA, ΔX, and ΔY are expressed as functions of r. ΔV_{ex}, ΔA, ΔX, and ΔY are all negative for $r-d_U<d_S$.

(4) Using the values of C_1–C_4 determined in step (3) and eqn (S12), we can calculate $\Delta V_P(r)/d_S^3$.

SI:3.2 Entropic and enthalpic components of potential of mean force between hard-sphere solutes in water under isobaric condition

$\Delta\Omega(r)$ is zero for $r-d_U \geq d_S$ and negative for $r-d_U<d_S$. When "$r-d_U$" becomes smaller than d_S, the compression of bulk water occurs under the isobaric condition. Consequently, the entropic and energetic components of the PMF, which would arise under the isochoric condition, exhibits slight downward shifts (i.e., they shift in negative directions). In Fig. S1, Φ_{SP}/k_B and $\Phi_{EP}/(k_BT)$ are compared with Φ_S/k_B and $\Phi_E/(k_BT)$, respectively. These are components of the PMF between hard-sphere solutes with diameter d_U immersed in the model water (d_S=0.28 nm and $\rho_S d_S^3$=0.7317): (a) $d_U=d_S$, (b) $d_U=4d_S$, and (c) $d_U=30d_S$. As observed in the figure, Φ_{SP}/k_B and $\Phi_{EP}/(k_BT)$ are almost indistinguishable from Φ_S/k_B and $\Phi_E/(k_BT)$, respectively. Therefore, in the main text we refer to Φ_S/k_B and $\Phi_E/(k_BT)$ as the entropic and enthalpic components of the PMF, respectively.

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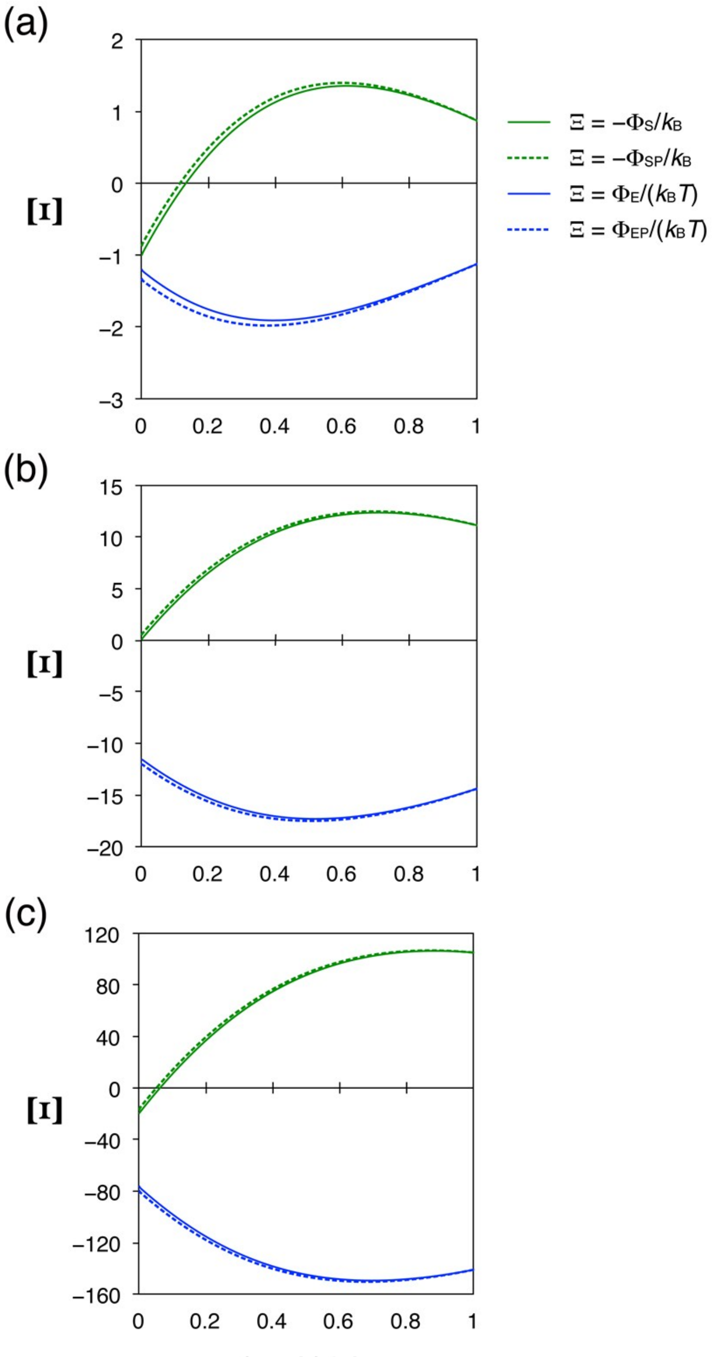

Fig. S1 Comparison between Φ_S/k_B and Φ_{SP}/k_B and that between $\Phi_E/(k_BT)$ and $\Phi_{EP}/(k_BT)$. Φ_S/k_B and $\Phi_E/(k_BT)$ are the entropic and energetic components of the PMF scaled by k_BT under the isochoric condition, respectively. Φ_{SP}/k_B and $\Phi_{EP}/(k_BT)$ are the entropic and enthalpic components of the PMF scaled by k_BT under the isobaric condition, respectively. The quantities are calculated for hard-sphere solutes with diameter d_U immersed in the model water (d_S=0.28 nm and $\rho_S d_S^3$=0.7317): (a) d_U=d_S, (b) d_U=4d_S, and (c) d_U=30d_S. Note that the entropic component is plotted as its negative so that the entropy-energy or entropy-enthalpy compensation can be emphasized.