Supporting Information

Table S1. Experimental molar volume of water (from reference 18 of the text), V_w, effective hard sphere diameter of water molecules, σ_w, determined by fitting the experimental β_T values with respect to the theoretical SPT formula, the corresponding values of volume packing density ξ_w, values of ΔG_c to create in water a spherical cavity of radius a = 10 Å, corresponding to the N-state, and a spherocylindrical cavity of radius a = 4 Å and cylindrical length l = 78 Å, corresponding to the D-state; values of $\Delta\Delta G_c = \Delta G_c(D) - \Delta G_c(N)$, of $T\cdot\Delta S_{conf}$, calculated according to eqn. (6), and of $\Delta G_d = \Delta\Delta G_c - T\cdot\Delta S_{conf}$. These same values were used to construct Figures 2 and 3 in reference 7 of the text.

T	V_w	σ_w	ξ_w	$\Delta G_c(N)$	$\Delta G_c(D)$	$\Delta\Delta G_c$	$T\cdot\Delta S_{conf}$	ΔG_d
°C	$cm^3\ mol^{-1}$	Å		kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
-30	18.316	2.6104	0.30622	282.4	498.1	215.7	238.6	-22.9
-20	18.137	2.6616	0.32780	325.0	573.0	248.0	248.4	-0.4
-10	18.054	2.6885	0.33939	356.4	628.2	271.8	258.3	13.5
-5	18.033	2.6972	0.34309	369.4	651.0	281.6	263.2	18.4
0	18.023	2.7034	0.34566	380.6	670.8	290.1	268.1	22.0
5	18.021	2.7085	0.34766	391.1	689.1	298.0	273.0	25.0
10	18.025	2.7117	0.34880	400.0	704.9	304.9	277.9	27.0
20	18.052	2.7153	0.34967	415.3	731.8	315.5	287.7	27.8
30	18.099	2.7158	0.34897	427.5	753.3	325.8	297.5	28.3
40	18.161	2.7137	0.34696	436.7	769.6	332.9	307.3	25.6

50	18.238	2.7095	0.34389	443.5	781.6	338.1	317.1	21.0
60	18.328	2.7037	0.34002	448.1	789.9	341.8	327.0	14.8
70	18.430	2.6964	0.33541	450.7	794.6	343.9	336.8	7.1
80	18.543	2.6880	0.33025	451.8	796.6	344.8	346.6	-1.8
90	18.667	2.6778	0.32433	450.8	795.0	344.2	356.4	-12.2
100	18.803	2.6666	0.31797	448.5	791.1	342.6	366.2	-23.6

Supporting Information

Table S2. Aqueous 2M MeOH solution is treated as a slightly modified water: (1) it is considered a uniform liquid with the same density values of neat water for temperatures above TMD, but shifted by 2 °C toward lower temperatures, because TMD = 2.23 °C for aqueous 2M MeOH solution, whereas for neat water TMD = 3.98 °C (see references 17 and 18 of the text); (2) at temperatures below TMD, the density of aqueous 2M MeOH solution is assumed to decrease to a slightly lesser extent than that of neat water, because for common organic liquids, such as alcohols, the density increases on decreasing temperature. Effective values for the hard sphere diameter of solvent molecules, σ, correspond to those of neat water, but they are simply attributed to temperatures lower by 2 °C with respect to the neat water case; the corresponding values of volume packing density ξ; values of ΔG_c to create in aqueous 2M MeOH solution a spherical cavity of radius a = 10 Å, corresponding to the N-state, and a spherocylindrical cavity of radius a = 4 Å and cylindrical length l = 78 Å, corresponding to the D-state; values of $\Delta\Delta G_c = \Delta G_c(D) - \Delta G_c(N)$, of $\Delta\Delta G_c + \Delta E_a$, where ΔE_a = 5 kJ mol^{-1} independent of temperature, of $T{\cdot}\Delta S_{conf}$, calculated according to eqn. (6), and of $\Delta G_d = \Delta\Delta G_c + \Delta E_a - T{\cdot}\Delta S_{conf}$.

T	σ	ξ	$\Delta G_c(N)$	$\Delta G_c(D)$	$\Delta\Delta G_c$	$\Delta\Delta G_c + \Delta E_a$	$T{\cdot}\Delta S_{conf}$	ΔG_d
°C	Å		kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
-32	2.6104	0.31522	296.7	523.2	226.5	231.5	236.7	-5.2
-22	2.6616	0.33080	328.6	579.2	250.6	255.6	246.5	9.1
-12	2.6885	0.34039	355.9	627.3	271.4	276.4	256.3	20.1
-7	2.6972	0.34409	368.9	650.1	281.2	286.2	261.2	25.0
-2	2.7034	0.34666	380.2	670.0	289.8	294.8	266.1	28.7

3	2.7085	0.34766	388.2	684.1	295.9	300.9	271.0	29.9
8	2.7117	0.34880	397.2	699.9	302.7	307.7	275.9	31.8
18	2.7153	0.34967	412.5	726.8	314.3	319.3	285.7	33.6
28	2.7158	0.34897	424.6	748.3	323.7	328.7	295.5	33.2
38	2.7137	0.34696	433.9	764.7	330.8	335.8	305.4	30.4
48	2.7095	0.34389	440.7	776.7	336.0	341.0	315.2	25.8
58	2.7037	0.34002	445.4	785.1	339.7	344.7	325.0	19.7
68	2.6964	0.33541	448.1	790.0	341.9	346.9	334.8	12.1
78	2.6880	0.33025	449.2	792.1	342.9	347.9	344.6	3.3
88	2.6778	0.32433	448.3	790.6	342.3	347.3	354.4	-7.1
98	2.6666	0.31797	446.1	786.8	340.7	345.7	364.2	-18.5