Supporting information for:

Calculating Liquid-Phase Entropy using Real Gas Model within QM/PCM Framework

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Contents:

TABLE S1. Experimental *S* values for the liquefied 20 compounds investigated in this study (J mol^{-1} K^{-1}). All values were taken from Ref 32.

TABLE S2. Experimental gas-phase and solvation entropies (J mol^{-1} K^{-1}) for various compounds in different solvents. The standard conditions for the gas-phase values are 1 bar and 298.15 K and the solute concentration in each case is 1 mol dm^{-3}.

TABLE S3. Values for the coefficients a_i in the equation for density $\rho\ [\mathrm{kg\ m^{-3}}] = \sum_{i=0}^{3} a_i\{(T\ /\ \mathrm{K}) - 273.15\}^i$ taken from the Ref 54.

TABLE S4. Parameters used to calculate S_{trans} values for pure liquids based on the RGM.

TABLE S6. Computed and experimentally determined *S* values for pure liquids and the contributions of electronic, translational, rotational, vibrational and isomeric terms (S_{elec}, S_{trans}, S_{rot}, S_{vib}, S_{CD}) to computed values. All *S* values are in units of J mol^{-1} K^{-1}.

TABLE S7. Computed and experimentally determined *S* values for solute molecules in various solvents and the contributions of electronic, translational, rotational, vibrational and isomeric terms (S_{elec}, S_{trans}, S_{rot}, S_{vib}, S_{CD}) to computed values. All *S* values are in units of J mol^{-1} K^{-1}.

Fig. S1 H_2O monomer together with , dimer and various monocyclic water cluster ring structures, $(H_2O)_{3,4,5,6}$, as calculated at the *ω*B97X-D/6-311++G(d,p)/IEF-PCM level of theory.

Fig. S2 Computed *S* values for $(H_2O)_n$ structures with varying *n* values. Note that the *S* value for a lone H_2O molecule could not be obtained because the RGM generated a negative V_{free} value in this case, which is not physically possible. Contributions from stereoisomers were not considered in these *S* computations.

Fig. S3 *G* values for CH_3OH as functions of temperature. The red line corresponds to the values for a gas-phase system obtained using the IGM, the green line corresponds to those for a liquid system obtained using the CIGM and the blue line corresponds to values for a liquid system obtained from the proposed model. The two dashed blue lines represent the range of chemical accuracy (±1 kcal mol^{-1}) for the *G* computations. The intersection of the gas and liquid curves indicates the boiling point of CH_3OH.

Fig. S4 Computational *S* values for aqueous solutes obtained for various *n* values in $(H_2O)_n$.

Fig. S5 Computational V_{free} values obtained for aqueous solutes with various *n* values in $(H_2O)_n$.

Appendix 1. Calculations *S* and *G* at temperature of 298.15 K and a concentration of 1 mol dm^{-3} based on IGM and CIGM.

Appendix 2. Derivation of the pressure equation from Q_{RGM}.

Appendix 3. Determination of v_{molecule} using the QM/PCM method.

Appendix 4. Effect of atomic radii type on the accuracy of entropy calculations.

TABLE S1. Experimental *S* values for the liquefied 20 compounds investigated in this study (J mol^{-1} K^{-1}). All values were taken from Ref 32.

Species	$S_{\text{liq. expt.}}$
H_2O	69.95
CH_3OH	127.19
C_2H_5OH	159.86
1-C_3H_7OH	192.80
2-C_3H_7OH	180.58
1-C_4H_9OH	225.73
2-C_4H_9OH	213.10
HCOOH	128.95
CH_3COOH	158.00
CH_3CN	149.62
CH_3NO_2	171.75
acetone	200.40
DMSO	188.78
THF	203.80
benzene	173.26
toluene	220.96
CCl_4	214.39
C_5H_{12}	263.47
C_6H_{14}	296.06
cyclohexane	203.89

32 NIST Standard Reference Database Number 69, DOI: https://doi.org/10.18434/T4D303.

TABLE S2. Experimental gas-phase and solvation entropies (J mol^{-1} K^{-1}) for various compounds in different solvents. The standard conditions for the gas-phase values are 1 bar and 298.15 K and the solute concentration in each case is 1 mol dm^{-3}.

solute	solvent	$S°_{gas\_expt}$	$\Delta_{solv}S_{expt}$ [h]	$S°_{solute\_expt}$ [i]
1,4-Dioxane	cyclohexane	300.0 [a]	-72.0	228.0
1,4-Dioxane	C_2H_5OH	300.0 [a]	-71.5	228.5
1,4-Dioxane	C_6H_{14}	300.0 [a]	-74.1	225.9
1,4-Dioxane	toluene	300.0 [a]	-86.2	213.8
acetone	*n*-Hexane	295.5 [f]	-63.6	231.9
acetone	toluene	295.5 [f]	-77	218.5
acetone	H_2O	295.5 [f]	-119.2	176.3
CH_3CN	cyclohexane	245.6 [g]	-60.7	184.9
CH_3CN	water	245.6 [g]	-95.8	149.8
benzene	cyclohexane	269.3 [e]	-70.7	198.6
benzene	C_6H_{14}	269.3 [e]	-74.1	195.2
1-C_4H_9OH	benzene	362.1 [a]	-82.0	280.1
1-C_4H_9OH	cyclohexane	362.1 [a]	-70.3	291.8
1-C_4H_9OH	C_6H_{14}	362.1 [a]	-69.5	292.6
1-C_4H_9OH	toluene	362.1 [a]	-90.8	271.3
1-C_4H_9OH	H_2O	362.1 [a]	-146.9	215.2
butanone	C_6H_{14}	339.5 [f]	-69.9	269.6
butanone	toluene	339.5 [f]	-82.8	256.7
$CHCl_3$	C_6H_{14}	295.5 [a]	-82.4	213.2
cyclohexane	benzene	298.3 [a]	-68.6	229.7
cyclohexane	H_2O	298.3 [a]	-132.2	166.1
diethylether	cyclohexane	342.3 [a]	-61.5	280.8
diethylether	H_2O	342.3 [a]	-131.0	211.3
C_2H_5OH	benzene	282.8 [b]	-77.8	205
C_2H_5OH	cyclohexane	282.8 [b]	-51.5	231.3
C_2H_5OH	C_6H_{14}	282.8 [b]	-53.1	229.7
C_2H_5OH	toluene	282.8 [b]	-73.6	209.2
C_2H_5OH	H_2O	282.8 [b]	-132.2	150.6
ethylacetate	cyclohexane	342.3 [a]	-131	211.3
CH_3NO_2	C_2H_5OH	275.1 [c]	-73.2	201.9
CH_3NO_2	C_6H_{14}	275.1 [c]	-61.9	213.2
n-Pentane	benzene	347.9 [a]	-59	288.9
C_3H_7OH	cyclohexane	322.6 [a]	-64	258.6

C_3H_7OH	toluene	322.6[a]	-79.1	243.5
C_3H_7OH	H_2O	322.6[a]	-138.5	184.1
toluene	benzene	320.8[d]	-78.2	242.6
toluene	cyclohexane	320.8[d]	-75.3	245.5
toluene	C_2H_5OH	320.8[d]	-81.2	239.6
toluene	C_6H_{14}	320.8[d]	-73.2	247.6
xenon	C_2H_5OH	169.7	-46.9	122.8
xenon	H_2O	169.7[a]	-98.3	71.4

[a]Taken from ref 32, [b]Taken from ref 33, [c]Taken from ref 34, [d]Taken from ref 35, [e]Taken from ref. 36, [f]Taken from ref 37, [g]Taken from ref 38, [h]Taken from ref 12. [i]$S°_{gas} + \Delta_{solv}S$.

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TABLE S3. Values for the coefficients a_i in the equation for density $\rho\ [\mathrm{kg\ m^{-3}}] = \sum_{i=0}^{3} a_i\{(T\ /\ \mathrm{K}) - 273.15\}^i$ taken from the Ref 54.

Species	methanol	ethanol
a_0	809.983	806.594
a_1	-0.93429	-0.84589
a_2	-2.793×10^{-5}	-1.361×10^{-4}
a_3	-5.337×10^{-6}	-5.557×10^{-6}

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TABLE S4. Parameters used to calculate S_{trans} values for pure liquids based on the RGM.

Species	M_{liquid} / g mol^{-1}	ρ^{a} / g cm^{-3}	v_{liquid} / × 10^{-30} m^3	v_{molecule} / × 10^{-30} m^3	V_{free} / × 10^{-8} m^3 mol^{-1}	b / × 10^{-5} m^3 mol^{-1}
$(H_2O)_6$	108.6	0.997	180.0	149.1	2.45	10.2
CH_3OH	32.03	0.791	67.2	52.4	2.07	3.73
C_2H_5OH	46.04	0.789	96.9	74.5	3.45	5.34
C_3H_7OH	60.06	0.805	123.9	96.7	3.72	6.87
i-C_3H_7OH	60.06	0.786	127.0	96.9	4.87	6.99
n-C_4H_9OH	74.07	0.815	151.0	119.4	3.88	8.41
2-C_4H_9OH	74.07	0.806	152.6	118.7	4.76	8.45
HCOOH	46.01	1.220	62.6	27.5	0.28	2.87
CH_3COOH	60.02	1.051	94.8	38.4	1.78	4.23
CH_3CN	41.03	0.783	87.1	64.6	4.45	4.75
CH_3NO_2	61.02	1.137	89.1	71.6	1.85	4.99
acetone	58.04	0.790	122.0	88.8	7.42	6.61
DMSO	78.01	1.101	117.7	98.1	1.44	6.67
THF	72.06	0.883	135.5	104.4	4.70	7.48
benzene	78.05	0.879	147.5	104.4	11.4	7.91
toluene	92.06	0.867	176.4	133.2	7.58	9.67
CCl_4	151.88	1.594	158.2	112.9	11.5	8.51
C_5H_{12}	72.09	0.626	191.2	131.5	18.6	10.2
C_6H_{14}	46.04	0.789	96.9	74.5	3.45	5.34
cyclohexane	84.09	0.779	179.3	135.0	7.98	9.82

[a] taken from Ref 32.

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TABLE S5. Parameters used to calculate S_{trans} for solutes in solvents based on the RGM.

Solutes	Solvents	M_{solute} / g mol^{-1}	$M_{solvent}$ / g mol^{-1}	$\rho_{solvent}$ ^{a} / g cm^{-3}	$v_{liquid,solvent}$ / × 10^{-30} m^3	$v_{molecule,solvent}$ / × 10^{-30} m^3	$b_{solvent}$ / × 10^{-5} m^3 mol^{-1}	$v_{molecule,solute}$ / × 10^{-30} m^3	V_{free} / × 10^{-6} m^3 mol^{-1}
1,4-dioxane	cyclohexane	88.1	84.1	0.779	179.3	135.0	9.82	113.9	3.25
1,4-dioxane	C_2H_5OH	88.1	46.0	0.789	96.9	74.5	5.34	113.9	2.74
1,4-dioxane	C_6H_{14}	88.1	86.2	0.659	217.1	153.4	11.6	113.9	5.02
1,4-dioxane	toluene	88.1	92.1	0.867	176.4	133.2	9.67	113.9	3.16
benzene	cyclohexane	78.0	84.1	0.779	179.3	135.0	9.82	110.8	3.34
benzene	C_6H_{14}	78.0	86.2	0.659	217.1	153.4	11.64	110.8	5.15
toluene	benzene	92.1	78.0	0.879	147.5	110.9	8.08	133.2	2.81
toluene	cyclohexane	92.1	84.1	0.779	179.3	135.0	9.82	133.2	2.80
toluene	C_2H_5OH	92.1	46.0	0.789	96.9	74.5	5.34	133.2	2.35
toluene	C_6H_{14}	92.1	78.0	0.659	196.6	110.9	9.78	133.2	12.41
acetone	C_6H_{14}	58.0	86.1	0.659	216.9	153.4	11.6	88.8	6.24
acetone	toluene	58.0	92.1	0.867	176.4	133.2	9.67	88.8	4.02
acetone	$(H_2O)_6$	58.0	108.1	0.997	180.0	149.1	10.18	88.8	1.67
$CHCl_3$	C_6H_{14}	117.9	86.2	0.659	217.1	153.4	11.6	94.9	5.91
ethylacetate	cyclohexane	88.1	84.1	0.779	179.3	135.0	9.82	122.2	3.04
C_2H_5OH	benzene	46.0	78.0	0.879	147.5	110.9	8.08	74.6	4.89
C_2H_5OH	cyclohexane	46.0	84.1	0.779	179.3	135.0	9.82	74.6	4.87
C_2H_5OH	C_6H_{14}	46.0	86.1	0.659	216.9	153.4	11.6	74.6	7.26
C_2H_5OH	toluene	46.0	86.1	0.867	165.0	153.4	9.70	74.6	0.20
C_2H_5OH	$(H_2O)_6$	46.0	108.1	0.997	180.0	149.1	10.2	74.6	2.02
diethylether	cyclohexane	74.1	84.1	0.779	179.3	135.0	9.82	120.2	3.09
diethylether	$(H_2O)_6$	74.1	108.1	0.997	180.0	149.1	10.2	120.3	1.20
C_2H_7OH	cyclohexane	60.1	84.1	0.779	179.3	135.0	9.82	96.7	3.81
C_2H_7OH	toluene	60.1	92.1	0.867	176.4	133.2	9.67	96.7	3.70
C_2H_7OH	$(H_2O)_6$	60.1	108.1	0.997	180.0	149.1	10.18	96.7	1.52
C_4H_9OH	benzene	74.1	78.0	0.879	147.5	110.9	8.08	119.4	3.13
C_4H_9OH	cyclohexane	74.1	84.1	0.779	179.3	135.0	9.82	119.4	3.11
C_4H_9OH	C_6H_{14}	74.1	86.2	0.659	217.1	153.4	11.64	119.4	4.81
C_4H_9OH	toluene	74.1	92.1	0.867	176.4	133.2	9.67	119.4	3.02
C_4H_9OH	$(H_2O)_6$	74.1	108.1	0.997	180.0	149.1	10.18	119.4	1.21
butanone	C_6H_{14}	72.1	86.2	0.659	217.1	153.4	11.64	110.6	5.16
butanone	toluene	72.1	92.1	0.867	176.4	133.2	9.67	110.6	3.25
CH_3NO_2	C_2H_5OH	61.0	46.0	0.789	96.9	74.5	5.34	71.6	4.31
CH_3NO_2	C_6H_{14}	61.0	86.2	0.659	217.1	153.4	11.64	71.6	7.56
C_6H_{12}	benzene	72.1	78.0	0.879	147.5	110.9	8.08	131.5	2.85
xenon	C_2H_5OH	131.9	46.0	0.789	96.9	74.5	5.34	44.7	6.65
xenon	$(H_2O)_6$	131.9	108.1	0.997	180.0	149.1	10.18	44.7	3.43

[a] taken from ref 32

32 NIST Standard Reference Database Number 69, DOI: https://doi.org/10.18434/T4D303 (Final accessed; 20 Mar. 2019).

TABLE S6. Computed and experimentally determined *S* values for pure liquids and the contributions of electronic, translational, rotational, vibrational and isomeric terms (S_{elec}, S_{trans}, S_{rot}, S_{vib}, S_{CD}) to computed values. All *S* values are in units of J mol^{-1} K^{-1}.

Species	Model	S_{elec}	S_{trans}	S_{rot}	S_{vib}	S_{CD}	S_{calc}	S_{exp}
H_2O [a]	CIGM	0	18.1	18.0	49.6	0	85.6	69.95
H_2O [a]	RGM	0	8.7	18.5	45.1	0	72.3	69.95
CH_3OH	CIGM	0	98.7	79.4	7.3	0	185.4	127.19
CH_3OH	RGM	0	35.7	79.4	7.3	0	122.4	127.19
C_2H_5OH	CIGM	0	106.3	93.5	20.6	9.1	229.5	159.86
C_2H_5OH	RGM	0	44.5	93.5	20.6	9.1	167.8	159.86
1-C_3H_7OH	CIGM	0	111.7	107.6	42.6	14.8	276.6	192.8
1-C_3H_7OH	RGM	0	48.4	107.6	42.6	14.8	213.4	192.8
2-C_3H_7OH	CIGM	0	111.9	107.8	37.9	5.8	263.3	180.58
2-C_3H_7OH	RGM	0	50.7	107.8	37.9	5.8	202.1	180.58
1-C_4H_9OH	CIGM	0	116.0	114.4	66.1	21.2	317.6	225.7
1-C_4H_9OH	RGM	0	51.4	114.4	66.1	21.2	253.0	225.7
2-C_4H_9OH	CIGM	0	116.0	108.3	60.7	17.4	302.5	214.5
2-C_4H_9OH	RGM	0	53.1	108.3	60.7	17.4	239.5	214.5
HCOOH	CIGM	0	58.5	87.9	4.4	0	146.2	131.84
HCOOH	RGM	0	23.6	87.9	4.4	0	115.9	131.84
CH_3COOH	CIGM	0	61.9	99.7	27.1 [b]	0	191.2	158
CH_3COOH	RGM	0	42.3	99.7	27.1	0	169.1	158
CH_3CN	CIGM	0	103.9	77.4	10.4	0	191.7	149.62
CH_3CN	RGM	0	45.2	77.4	10.4	0	133.0	149.62
CH_3NO_2	CIGM	0	109.1	98.4	17.0[b]	0	224.5	171.75
CH_3NO_2	RGM	0	42.8	98.4	17.0	0	158.3	171.75
acetone	CIGM	0	111.2	95.2	42.8	0	249.1	200.4
acetone	RGM	0	53.8	95.2	42.8	0	191.7	200.4
DMSO	CIGM	0	114.5	104.2	42.6	0	261.4	188.78
DMSO	RGM	0	43.8	104.2	42.6	0	190.7	188.78
THF	CIGM	0	114.6	104.1	44.6	0	263.4	203.8
THF	RGM	0	52.7	104.1	44.6	0	201.4	203.8
benzene	CIGM	0	116.3	86.6	20.6 [b]	0	223.5	173.26
benzene	RGM	0	61.0	86.6	20.6	0	168.3	173.26
toluene	CIGM	0	119.9	112.8	44.2	0	277.0	220.96
toluene	RGM	0	59.7	112.8	44.2	0	216.7	220.96
CCl_4	CIGM	0	125.3	98.8	40.5	0	264.6	214.39
CCl_4	RGM	0	69.4	98.8	40.5	0	208.7	214.39
C_5H_{12}	CIGM	0	117.5	103.3	70.6	12.2	303.6	263.47
C_5H_{12}	RGM	0	64.1	103.3	70.6	12.2	250.1	263.47
C_6H_{14}	CIGM	0	120.8	108.3	95.8	19.6	344.5	296.06
C_6H_{14}	RGM	0	65.5	108.3	95.8	19.6	289.2	296.06
cyclohexane	CIGM	0	118.9	101.1	40.5	0	260.5	203.89
cyclohexane	RGM	0	59.0	101.1	40.5	0	200.6	203.89

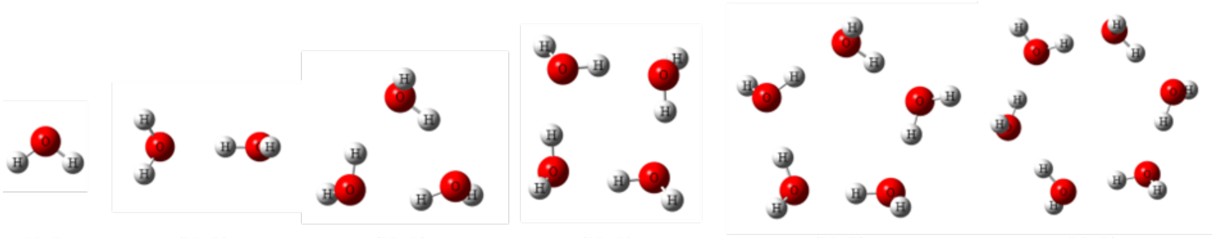
[a] The *S* values for $(H_2O)_6$ were divided by six to obtain the *S* per one H_2O.

[b] Vibrational mode derived from rotation of CH_3- was treated as the free rotor.

TABLE S7. Computed and experimentally determined S values for solute molecules in various solvents and the contributions of electronic, translational, rotational, vibrational and isomeric terms (S_{elec}, S_{trans}, S_{rot}, S_{vib}, S_{CD}) to computed values. All S values are in units of J mol^{-1} K^{-1}.

Solutes	Solvent	S_{elec}	S_{trans}	S_{rot}	S_{vib}	S_{CD}	S_{calc}	S_{exp}
1,4-dioxane	cyclohexane	0	90.4	103.0	32.7	0	226.0	228.0
1,4-dioxane	C_2H_5OH	0	89.0	103.0	32.8	0	224.7	228.5
1,4-dioxane	C_6H_{14}	0	94.0	103.0	32.6	0	229.6	225.9
1,4-dioxane	toluene	0	90.1	103.0	32.7	0	225.8	213.8
benzene	cyclohexane	0	89.1	86.6	20.6	0	196.3	198.6
benzene	C_6H_{14}	0	92.7	86.6	20.6	0	199.9	195.2
toluene	benzene	0	89.7	112.8	44.2	0	246.7	242.6
toluene	cyclohexane	0	89.7	112.8	44.2	0	246.7	245.5
toluene	C_2H_5OH	0	88.2	112.8	44.2	0	245.2	239.6
toluene	C_6H_{14}	0	102.1	112.8	44.2	0	259.1	247.6
acetone	C_6H_{14}	0	90.6	95.2	43.6	0	229.3	231.9
acetone	toluene	0	86.9	95.2	43.1	0	225.2	218.5
acetone	$(H_2O)_6$	0	79.6	95.2	42.8	0	217.6	176.3
$CHCl_3$	C_6H_{14}	0	99.0	105.1	23.0	0	227.0	213.2
ethylacetate	cyclohexane	0	89.8	111.9	78.2	5.3	285.3	292.5
C_2H_5OH	benzene	0	85.7	93.3	22.2	9.1	210.4	205.0
C_2H_5OH	cyclohexane	0	85.6	93.3	22.2	9.1	210.3	231.3
C_2H_5OH	C_6H_{14}	0	89.0	93.3	22.2	9.1	213.6	229.7
C_2H_5OH	toluene	0	59.2	93.3	22.2	9.1	183.9	209.2
C_2H_5OH	$(H_2O)_6$	0	78.3	93.3	22.4	9.1	203.2	150.6
diethylether	cyclohexane	0	87.8	101.9	67.2	7.4	264.3	280.8
diethylether	$(H_2O)_6$	0	79.9	101.9	68.0	7.7	257.5	211.3
C_2H_7OH	cyclohexane	0	86.9	107.6	42.4	17.2	254.2	258.6
C_2H_7OH	toluene	0	86.7	107.6	42.5	16.1	252.9	243.5
C_2H_7OH	$(H_2O)_6$	0	79.3	107.6	42.6	16.1	245.5	184.1
C_4H_9OH	benzene	0	87.9	114.4	65.9	23.1	291.2	280.1
C_4H_9OH	cyclohexane	0	87.9	114.4	65.9	23.1	291.2	291.8
C_4H_9OH	C_6H_{14}	0	91.5	114.4	65.9	23.1	294.8	292.6
C_4H_9OH	toluene	0	87.6	114.4	65.9	23.1	290.9	271.3
C_4H_9OH	$(H_2O)_6$	0	80.0	114.4	65.8	23.0	283.1	215.2
butanone	C_6H_{14}	0	91.7	107.2	63.7	5.8	268.4	269.6
butanone	toluene	0	87.9	107.2	63.2	6.0	264.3	256.7
CH_3NO_2	C_2H_5OH	0	88.1	98.4	17.0	0	203.6	201.9

CH_3NO_2	C_6H_{14}	0	92.8	98.4	17.0	0	208.3	213.2
C_6H_{12}	benzene	0	86.8	103.3	70.1	12.4	272.6	288.9
xenon	C_2H_5OH	0	101.4	0	0	0	101.4	122.8
xenon	$(H_2O)_6$	0	95.9	0	0	0	95.9	71.4



H_2O $(H_2O)_2$ $(H_2O)_3$ $(H_2O)_4$ $(H_2O)_5$ $(H_2O)_6$

Fig. S1 H_2O monomer together with, dimer and various monocyclic water cluster ring structures, $(H_2O)_{3,4,5,6}$, as calculated at the ωB97X-D/6-311++G(d,p)/IEF-PCM level of theory.

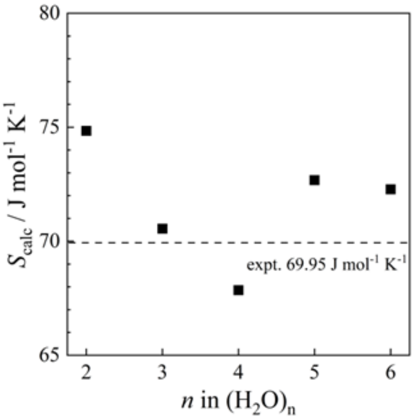


Fig. S2 Computed *S* values for $(H_2O)_n$ structures with varying *n* values. Note that the *S* value for a lone H_2O molecule could not be obtained because the RGM generated a negative V_{free} value in this case, which is not physically possible. Contributions from stereoisomers were not considered in these *S* computations.

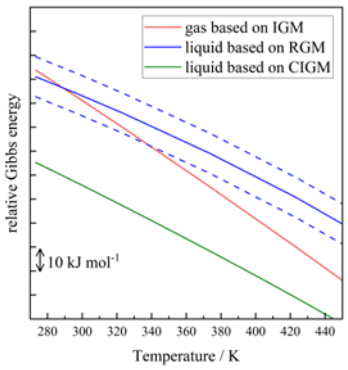


Fig. S3 *G* values for CH_3OH as functions of temperature. The red line corresponds to the values for a gas-phase system obtained using the IGM, the green line corresponds to those for a liquid system obtained using the CIGM and the blue line corresponds to values for a liquid system obtained from the proposed model. The two dashed blue lines represent the range of chemical accuracy (±1 kcal mol^{-1}) for the *G* computations. The intersection of the gas and liquid curves indicates the boiling point of CH_3OH.

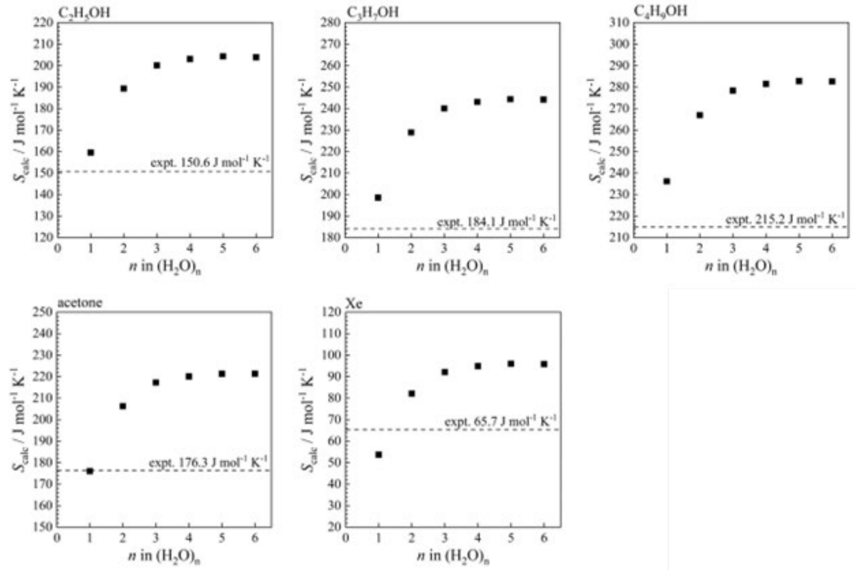


Fig. S4 Computational S values for aqueous solutes obtained for various n values in $(H_2O)_n$.

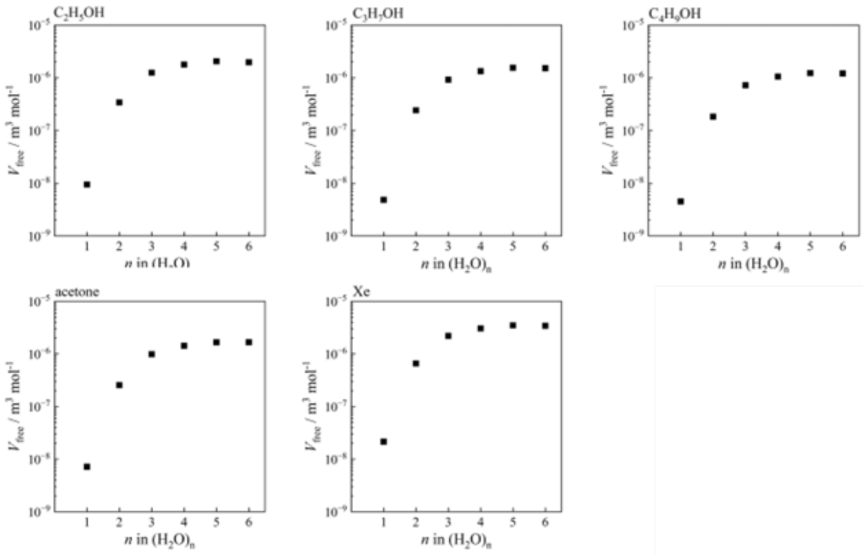


Fig. S5 Computational V_{free} values obtained for aqueous solutes with various *n* values in $(H_2O)_n$.

Appendix 1. Calculations *S* and *G* at temperature of 298.15 K and a concentration of 1 mol dm^{-3} based on IGM and CIGM.

The partition function and entropy at 1 atm and 298.15 K can be written as:

$$q_{\text{trans\_IGM at 1 atm}} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} = \frac{RT}{p}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} = \frac{8.314\times 298.15}{101300}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}},$$

$$S_{\text{trans\_IGM at 1 atm}} = R\left[\ln\left\{\frac{8.314\times 298.15}{101300\times N_{\text{A}}}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right\} + \frac{5}{2}\right].$$

A pressure of 24.5 (24.47) atm in a volume of 1 dm^3 corresponds to a concentration of 1 mol dm^{-3} at 298.15 K based on the ideal gas equation of state.

$$q_{\text{trans,CIGM}} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} = \frac{8.314\times 298.15}{24.47\times 101300}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} = 0.001\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}$$

$$S_{\text{trans,CIGM}} = R\left[\ln\left\{\frac{0.001}{N_{\text{A}}}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right\} + \frac{5}{2}\right].$$

Consequently, the *S* and *G* corrections for converting the state at 1 atm to 1 mol dm^{-3} at 298.15 K can be calculated as -26.78 J mol^{-1} K^{-1} and +7.98 Jmol^{-1}.

$$\Delta S(1\text{ atm } \rightarrow 1\text{ mol dm}^3) = S_{\text{trans,CIGM}} - S_{\text{trans,IGM}}$$

$$= R\ln\frac{100000\times 0.001}{8.314\times 298.15} = -26.69\ [\text{J mol}^{-1}\ \text{K}^{-1}]$$

$$\Delta G(1\text{ atm } \rightarrow 1\text{ mol dm}^3) = -T\Delta S(1\text{ atm } \rightarrow 1\text{ mol dm}^3) = -298.15\ \times -26.69 = 7.958\ [\text{kJ mol}^{-1}]$$

Appendix 2. Derivation of the pressure equation from Q_{RGM}.

$$p = k_{\mathrm{B}}T\left(\frac{\partial \ln Q_{\mathrm{RGM}}}{\partial V_{\mathrm{liquid}}}\right) = k_{\mathrm{B}}T\left(\frac{\partial \ln \frac{1}{N_{\mathrm{A}}!} q_{\mathrm{RGM}}^{N_{\mathrm{A}}}}{\partial V_{\mathrm{liquid}}}\right) = k_{\mathrm{B}}T\left(\frac{\partial \ln \frac{1}{N_{\mathrm{A}}!} q_{\mathrm{trans}}^{N_{\mathrm{A}}}}{\partial V_{\mathrm{liquid}}}\right) = k_{\mathrm{B}}T\left(N_{\mathrm{A}}\frac{\partial \ln q_{\mathrm{trans}}}{\partial V_{\mathrm{liquid}}}\right) = RT\left(\frac{\partial \ln q_{\mathrm{trans}}}{\partial V_{\mathrm{liquid}}}\right)$$

$$= RT\left(\frac{\partial \ln q_{\mathrm{trans}}}{\partial V_{\mathrm{liquid}}}\right) = RT\left(\frac{\partial \ln V_{\mathrm{free}}}{\partial V_{\mathrm{liquid}}}\right) = RT\left(\frac{1}{V_{\mathrm{free}}} \cdot \frac{\partial V_{\mathrm{free}}}{\partial V_{\mathrm{liquid}}}\right)$$

$$\frac{\partial V_{\mathrm{free}}}{\partial V_{\mathrm{liquid}}} = \frac{\partial}{\partial V_{\mathrm{liquid}}} N_{\mathrm{A}}\left(\left(\frac{V_{\mathrm{liquid}}}{N_{\mathrm{A}}}\right)^{\frac{1}{3}} - v_{\mathrm{molecule}}^{1/3}\right)^{3} = 3N_{\mathrm{A}}\left(\left(\frac{V_{\mathrm{liquid}}}{N_{\mathrm{A}}}\right)^{\frac{1}{3}} - v_{\mathrm{molecule}}^{1/3}\right)^{2} \cdot \frac{1}{3N_{\mathrm{A}}} V_{\mathrm{liquid}}{}^{-\frac{2}{3}}$$

$$= \left(\left(\frac{V_{\mathrm{liquid}}}{N_{\mathrm{A}}}\right)^{\frac{1}{3}} - v_{\mathrm{molecule}}^{1/3}\right)^{2} \cdot V_{\mathrm{liquid}}{}^{-\frac{2}{3}}$$

$$\frac{1}{V_{\mathrm{free}}}\frac{\partial V_{\mathrm{free}}}{\partial V_{\mathrm{liquid}}} = \frac{1}{N_{\mathrm{A}}\left(\left(\frac{V_{\mathrm{liquid}}}{N_{\mathrm{A}}}\right)^{\frac{1}{3}} - v_{\mathrm{molecule}}^{1/3}\right)^{3}} \cdot \left(\left(\frac{V_{\mathrm{liquid}}}{N_{\mathrm{A}}}\right)^{\frac{1}{3}} - v_{\mathrm{molecule}}^{1/3}\right)^{2} \cdot V_{\mathrm{liquid}}{}^{-\frac{2}{3}}$$

$$= \frac{1}{N_{\mathrm{A}}\left(\left(\frac{V_{\mathrm{liquid}}}{N_{\mathrm{A}}}\right)^{\frac{1}{3}} - v_{\mathrm{molecule}}^{1/3}\right)V_{\mathrm{liquid}}{}^{\frac{2}{3}}} = \frac{1}{N_{\mathrm{A}}\left(\frac{V_{\mathrm{liquid}}}{N_{\mathrm{A}}} - v_{\mathrm{molecule}}^{1/3} \cdot \left(\frac{V_{\mathrm{liquid}}}{N_{\mathrm{A}}}\right)^{\frac{2}{3}}\right)} = \frac{1}{V_{\mathrm{liquid}} - N_{\mathrm{A}} \cdot v_{\mathrm{molecule}}^{1/3} \cdot v_{\mathrm{liquid}}^{2/3}}$$

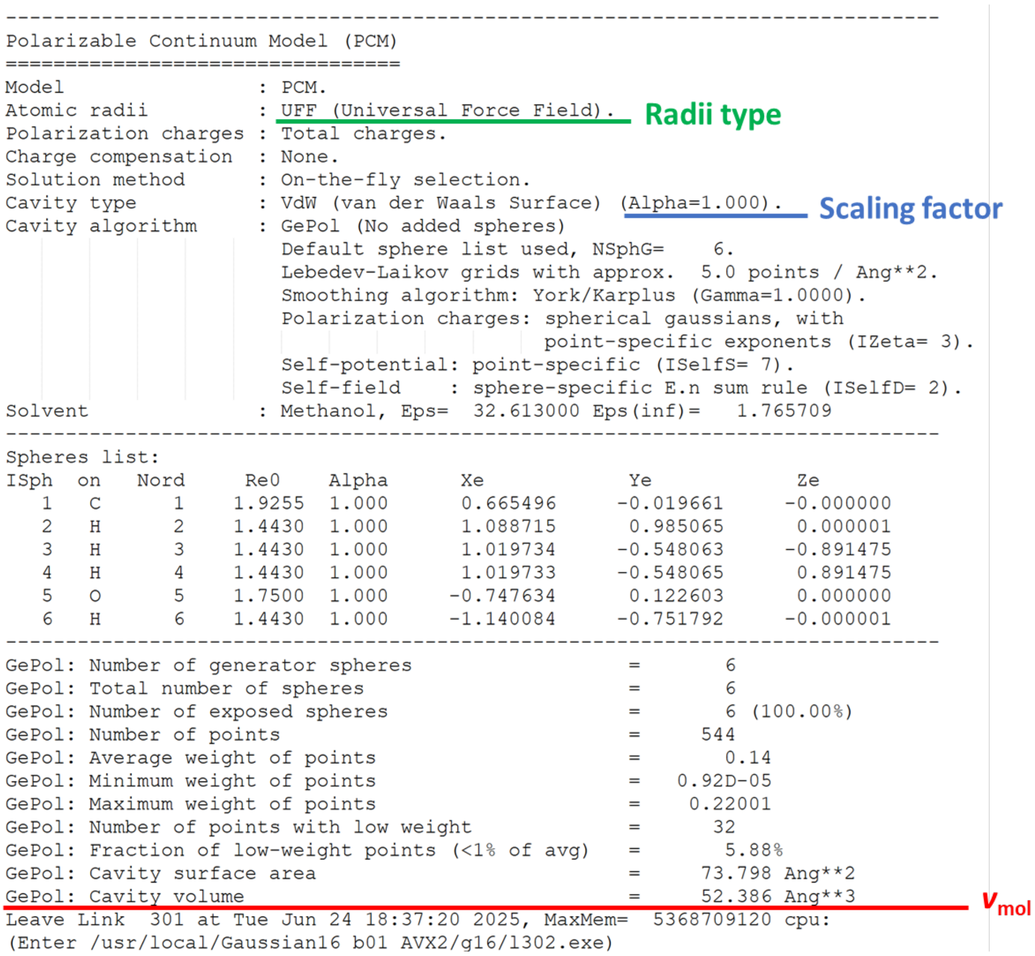
$$\therefore\ p = RT\left(\frac{1}{V_{\mathrm{free}}} \cdot \frac{\partial V_{\mathrm{free}}}{\partial V_{\mathrm{liquid}}}\right) = RT\left(\frac{1}{V_{\mathrm{free}}} \cdot \frac{\partial V_{\mathrm{free}}}{\partial V_{\mathrm{liquid}}}\right) = \frac{RT}{V_{\mathrm{liquid}} - N_{\mathrm{A}} \cdot v_{\mathrm{molecule}}^{1/3} \cdot v_{\mathrm{liquid}}^{2/3}}$$

$$\begin{cases} p = \dfrac{RT}{V - b} \\ b = N_{\mathrm{A}} \cdot v_{\mathrm{liquid}}^{2/3} \cdot v_{\mathrm{molecule}}^{1/3} \end{cases}$$

Appendix 3. Determination of v_{molecule} using the QM/PCM method.

In this study, the v_{molecule} was evaluated using the cavity volume obtained from QM/PCM calculations. In the PCM framework, the cavity volume is defined as the volume generated by a superposition of atom-centered spheres and is determined by the cavity scaling parameter *f*, which acts as a multiplicative factor applied to the atomic spherical radii. By performing QM/PCM calculations with the scaling parameter set to *f* =1.0, the resulting cavity volume corresponds directly to the v_{molecule}.

Specifically, a single-point PCM calculation was carried out for geometries optimized using the same set of van der Waals radii scaled by *f* =1.0. In the Gaussian program, the corresponding information is reported in the output (.log or .out) file, as illustrated in the figure below. The green-highlighted line indicates the selected radii type, the blue-highlighted line specifies the scaling parameter *f*, and the red-highlighted line reports the cavity volume, which is taken as the v_{molecule} in this work.



```
 ------------------------------------------------------------------------------
 Polarizable Continuum Model (PCM)
 =================================
 Model                : PCM.
 Atomic radii         : UFF (Universal Force Field).
 Polarization charges : Total charges.
 Charge compensation  : None.
 Solution method      : On-the-fly selection.
 Cavity type          : VdW (van der Waals Surface) (Alpha=1.000).
 Cavity algorithm     : GePol (No added spheres)
                        Default sphere list used, NSphG=    6.
                        Lebedev-Laikov grids with approx.  5.0 points / Ang**2.
                        Smoothing algorithm: York/Karplus (Gamma=1.0000).
                        Polarization charges: spherical gaussians, with
                                              point-specific exponents (IZeta= 3).
                        Self-potential: point-specific (ISelfS= 7).
                        Self-field    : sphere-specific E.n sum rule (ISelfD= 2).
 Solvent              : Methanol, Eps=  32.613000 Eps(inf)=   1.765709
 ------------------------------------------------------------------------------
 Spheres list:
 ISph   on   Nord     Re0    Alpha      Xe            Ye            Ze
    1   C       1    1.9255  1.000     0.665496     -0.019661     -0.000000
    2   H       2    1.4430  1.000     1.088715      0.985065      0.000001
    3   H       3    1.4430  1.000     1.019734     -0.548063     -0.891475
    4   H       4    1.4430  1.000     1.019733     -0.548065      0.891475
    5   O       5    1.7500  1.000    -0.747634      0.122603      0.000000
    6   H       6    1.4430  1.000    -1.140084     -0.751792     -0.000001
 ------------------------------------------------------------------------------
 GePol: Number of generator spheres                  =       6
 GePol: Total number of spheres                      =       6
 GePol: Number of exposed spheres                    =       6 (100.00%)
 GePol: Number of points                             =     544
 GePol: Average weight of points                     =       0.14
 GePol: Minimum weight of points                     =    0.92D-05
 GePol: Maximum weight of points                     =     0.22001
 GePol: Number of points with low weight             =      32
 GePol: Fraction of low-weight points (<1% of avg)   =       5.88%
 GePol: Cavity surface area                          =     73.798 Ang**2
 GePol: Cavity volume                                =     52.386 Ang**3
 Leave Link  301 at Tue Jun 24 18:37:20 2025, MaxMem=   5368709120 cpu:
 (Enter /usr/local/Gaussian16 b01 AVX2/g16/l302.exe)
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Appendix 4. Effect of Atomic Radii Type on the Accuracy of Entropy Calculations.

The influence of the choice of atomic radii type on the accuracy of entropy calculations was examined. Several atomic radii types available in the Gaussian program were tested to evaluate their impact on the calculated entropies of pure liquids. Geometry optimizations and vibrational frequency analyses were performed at the ωB97X-D/6-311++G(d,p) level using three atomic radii types: Bondi, and Klamt. Translational entropies were evaluated following the procedure described in the main text, and total entropies were subsequently calculated. The isomeric entropy contribution, S_{isom}, was taken from values obtained using UFF radii.

Because the molecular volumes calculated using the Bondi radii are smaller than those obtained with the UFF and Klamt radii, the resulting free volumes are correspondingly larger, leading to systematically higher entropy values. Among the atomic radii types examined, the entropy values computed using UFF radii exhibited the best agreement with experimental data and therefore provided the highest overall accuracy.

TABLE A3-1. Computed and experimentally determined *S* values for pure liquids. All *S* values are in units of J mol^{-1} K^{-1}.

Species	S_{calc} UFF	S_{calc} Bondi	S_{calc} Klamt	S_{exp}
H_2O [a]	72.3	75.7	76.2	69.95
CH_3OH	122.4	143.9	130.2	127.19
C_2H_5OH	167.8	187.4	176.4	159.86
1-C_3H_7OH	213.4	232.5	220.5	192.8
2-C_3H_7OH	202.1	220.6	208.9	180.58
1-C_4H_9OH	253.0	272.5	260.8	225.7
2-C_4H_9OH	239.5	259.6	247.0	214.5
HCOOH	115.9	115.9	124.1	131.84
CH_3COOH	169.1	191.4	175.1	158
CH_3CN	133.0	151.0	134.4	149.62
CH_3NO_2	158.3	179.9	163.1	171.75
acetone	191.7	206.4	198.6	200.4
DMSO	190.7	213.2	193.5	188.78
THF	201.4	218.8	207.0	203.8
benzene	168.3	179.7	164.9	173.26
toluene	216.7	233.0	218.8	220.96
CCl_4	208.7	223.5	203.0	214.39
C_5H_{12}	250.1	264.2	255.8	263.47
C_6H_{14}	289.2	304.3	295.4	296.06
cyclohexane	200.6	217.3	207.4	203.89
RMSD	13.4	23.8	16.1	-

[a] The *S* values for $(H_2O)_6$ were divided by six to obtain the *S* per one H_2O.

[b] Vibrational mode derived from rotation of CH_3- was treated as the free rotor.

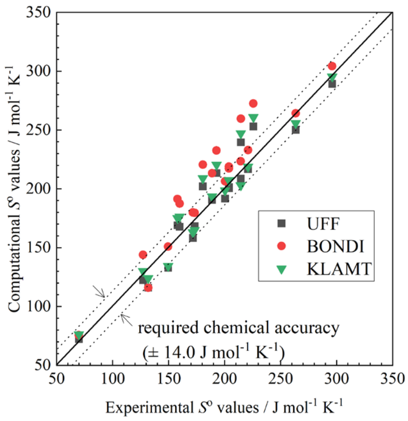

Fig. A3-1 Correlations between experimentally determined and computed S values for 20 pure liquids.

TABLE A3-2. Computed and experimentally determined *S* values for solute molecules in various solvents. All *S* values are in units of J mol^{-1} K^{-1}.

Solutes	Solvent	S_{calc} UFF	S_{calc} Bondi	S_{calc} Klamt	S_{exp}
1,4-dioxane	cyclohexane	226.0	240.1	231.6	228.0
1,4-dioxane	C_2H_5OH	224.7	240.5	230.3	228.5
1,4-dioxane	C_6H_{14}	229.6	241.9	234.2	225.9
1,4-dioxane	toluene	225.8	239.6	227.9	213.8
benzene	cyclohexane	196.3	210.2	201.5	198.6
benzene	C_6H_{14}	199.9	212.1	202.8	195.2
toluene	benzene	246.7	260.6	247.9	242.6
toluene	cyclohexane	246.7	261.0	251.9	245.5
toluene	C_2H_5OH	245.2	261.2	250.6	239.6
toluene	C_6H_{14}	259.1	260.4	250.3	247.6
acetone	C_6H_{14}	229.3	240.4	232.9	231.9
acetone	toluene	225.2	237.8	226.5	218.5
acetone	$(H_2O)_1$	172.3	234.4	172.6	176.3
$CHCl_3$	C_6H_{14}	227.0	239.0	244.4	213.2
ethylacetate	cyclohexane	285.3	299.6	290.8	292.5
C_2H_5OH	benzene	210.4	223.3	211.9	205.0
C_2H_5OH	cyclohexane	210.3	223.6	215.6	231.3
C_2H_5OH	C_6H_{14}	213.6	225.3	218.1	229.7
C_2H_5OH	toluene	183.9	221.4	208.0	209.2

C_2H_5OH	$(H_2O)_1$	158.6	220.1	159.7	150.6
diethylether	cyclohexane	264.3	278.6	271.7	280.8
diethylether	$(H_2O)_1$	211.0	275.6	212.0	211.3
C_2H_7OH	cyclohexane	254.2	268.0	259.7	258.6
C_2H_7OH	toluene	252.9	266.5	255.1	243.5
C_2H_7OH	$(H_2O)_1$	199.8	263.1	201.0	184.1
C_4H_9OH	benzene	291.2	305.1	292.9	280.1
C_4H_9OH	cyclohexane	291.2	305.4	297.0	291.8
C_4H_9OH	C_6H_{14}	294.8	307.3	299.7	292.6
C_4H_9OH	toluene	290.9	305.0	293.2	271.3
C_4H_9OH	$(H_2O)_1$	236.6	301.1	237.8	215.2
butanone	C_6H_{14}	268.4	280.8	273.0	269.6
butanone	toluene	264.3	278.2	266.4	256.7
CH_3NO_2	C_2H_5OH	203.6	218.3	208.7	201.9
CH_3NO_2	C_6H_{14}	208.3	219.8	212.4	213.2
C_6H_{12}	benzene	272.6	286.7	274.3	288.9
xenon	C_2H_5OH	101.4	113.5	104.5	122.8
xenon	$(H_2O)_1$	53.7	109.8	51.2	71.4
RMSD		11.3	31.5	11.7	-

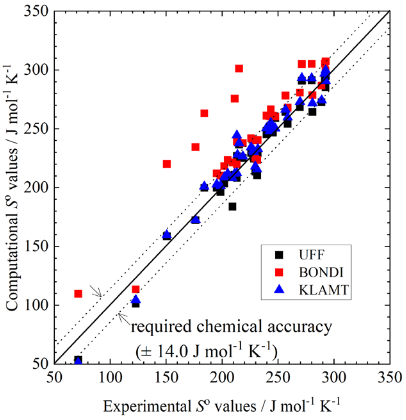

Fig. A3-2 Correlations between experimentally determined and computed S values for solute molecules in various solvents.