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Gibbs energy of solvation of organic ions in aqueous and dimethyl sulfoxide solutions

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The Gibbs energy of solvation of several ions in water and dimethyl sulfoxide (DMSO) solutions was obtained through the use of thermodynamic equations relating $\Delta G_{\mathrm{solv}}*$ of the ion with gas phase basicity, pK_a, $\Delta G_{\mathrm{solv}}*$ of neutral species and the Gibbs energy of solvation of the proton. We have used the most accurate and recent values for these properties, and this report provides 56 Gibbs energy of solvation values in aqueous solution and 30 in DMSO solution. Our results support the general view that anions are much better solvated in aqueous solution than in DMSO. An important example is the hydroxide ion for which the Gibbs energy of transfer from water to DMSO is 26 kcal mol^{-1}. The majority of anions have a Gibbs energy of transfer in the range 10 to 15 kcal mol^{-1}. In the case of cations, DMSO has a larger solvation ability but the difference in the Gibbs energy of solvation between water and DMSO is not greater than 5 kcal mol^{-1}. The present data can be very useful for the development of continuum solvation models.

Introduction

Many basic concepts and generalisations regarding the behaviour of chemical systems are based on the correlation between molecular structure and chemical reactivity. While solvent effects on reaction rates have been recognised for over a century,[1] some of the most dramatic illustrations of the effect of solvation on chemical reactivity have emerged from gas phase ion chemistry.[2] Contributions from different laboratories have shown that intrinsic reactivity in a solvent-free environment can be quite different from that observed in solution. This is well exemplified by such a classical reaction as the basic hydrolysis of methyl formate. Whereas the reaction in aqueous solution proceeds through the well known $B_{AC}2$ mechanism,[3] two others pathways are also important in the gas phase reaction: an α-elimination leading to the decarbonylation of the ester (the so-called Riveros reaction) and an S_N2 mechanism resulting from attack at the methyl group.[4] Thus, chemical properties of molecules and ions can be strongly influenced by the surrounding solvent.

The early theoretical explanations of solvent effects were based on the primitive model of solutions. The solvent was viewed as a dielectric continuum interacting with the solute molecules, and simple continuum models such as those proposed by Born and Onsager were used to account for medium effects.[1] However, these models cannot fully account for solvent effects such as the rate enhancement observed for nucleophilic reactions upon transferring the reaction system from a protic solvent to dipolar aprotic media.[5,6] While solvents such as DMSO and water are characterized by high relative permittivities, their solvation ability differs considerably due to specific (hydrogen bond) solute–solvent interactions. It is well known that small, or charge localised, anions are better solvated in protic solvents than in dipolar aprotic ones.[7–10]

Thermochemical information obtained from gas phase ion-chemistry such as proton affinities[11,12] has also had an important impact on the thermodynamics of ion solvation.[13] In fact, proton affinities when coupled with the pK_as of the conjugate acids and the standard Gibbs energy of solvation ($\Delta G_{\mathrm{solv}}°$) of the respective neutral species were used by Taft *et al.*[14] to derive the relative $\Delta G_{\mathrm{solv}}°$ of several protonated organic species in aqueous solution. These thermodynamic parameters are very important for evaluating the ability of a given solvent to stabilise organic ions and for determining the importance of the medium in acid–base equilibria. Almost a decade later, Pearson[15] reported absolute $\Delta G_{\mathrm{solv}}°$ for several organic cations and anions in aqueous solution based on gas phase proton affinity data, pK_a, Gibbs energy of solvation of neutral species, and an estimated $\Delta G_{\mathrm{solv}}°$ (H^+) of -259.5 kcal mol^{-1}. More recently, reports of more accurate pK_a values have led to a set of new values for the Gibbs energy of solvation of organic cations.[16,17] In the meantime, the Gibbs energy of hydration of important organic ions has been reported by Florian and Warshel.[18] This data was used in the parameterisation of their Langevin dipole model.

Calculating absolute Gibbs energies of solvation for ions from experimental data is usually dependent on the absolute Gibbs energy of solvation chosen for the proton which is considered as the anchor ion. Unfortunately, considerable uncertainty[19] has surrounded this value in the past with values ranging from -250 kcal mol^{-1} to -260 kcal mol^{-1}. This issue seems to have been finally resolved by Tissandier *et al.*[20] who have used the cluster-pair-based approximation to obtain $\Delta G_{\mathrm{solv}}°$ (H^+) = -264.0 kcal mol^{-1}. Using this new and more reliable value as a reference point, we have recently reported the calculation of the absolute Gibbs energy of solvation for several organic ions in aqueous solution.[19] Our data revealed some important differences with previous compilations that are partly due to the new value for $\Delta G_{\mathrm{solv}}°$ (H^+) and to some more recent and accurate proton affinity data.

The present work is a considerable extension of our preliminary publication. We have increased the number of ions

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to 56 as opposed to the initial 30 and we have adopted more accurate pK_a values for very weak bases and very weak acids. It is known that this latter property cannot be adequately measured in aqueous solution when the pK_a is out of the 1 to 16 range due to the levelling effect of the solvent. Thus, a different approach is required for such species. For positive ions, strongly protonating media must be used to generate the cations. In the comprehensive review of Arnett,[21] pK_as were obtained by using acidity functions of these media. However, strongly acidic media can display different solvation ability for ions and neutral species when compared with dilute aqueous solutions and thus result in different Gibbs energies of transfer. As a consequence, the acidity function method does not work properly and the pK_as determined by this procedure can be in considerable error.[22,23]To overcome these difficulties more reliable procedures have been proposed such as the Bunnet–Olsen and the Yates–McClelland equations.[23–26] New measurements were then carried out and with the help of these more accurate schemes, good quality pK_a data have been determined.[16,17,27,28] Similarly, weak bases have had their pK_as obtained by extrapolation schemes that can lead to considerable errors. More recently, the pK_as of several important organic species were determined from kinetic measurements,[29–35] resulting in more accurate data that have been adopted in our present work.

While values for the $\Delta G_{solv}*$ (see eqn. (1)) of organic ions in aqueous solution are now available, the situation is quite different for organic solvents for which very few data exist. Studies of solvation in organic solvents have been restricted to inorganic ions for which a reasonable set of data is available.[7–10,36] The determination of $\Delta G_{solv}*$ of organic ions in a variety of solvents depends critically on the availability of pK_as and $\Delta G_{solv}*$ for the respective neutral species in the corresponding solvents. Thanks to the work of Bordwell and his group[37–40] there is considerable knowledge about the pK_a of organic species in an important organic solvent such as DMSO. Likewise, the pK_a of some amines in DMSO solution is known.[41] By comparison, values for the $\Delta G_{solv}*$ of neutral species in DMSO solution are scarce although some important data have appeared in the recent literature.[42–44] Given the present availability of these properties for organic species in DMSO and the importance of this solvent in the study of organic reactions we have evaluated for the first time the Gibbs energy of solvation of several organic ions in this solvent.

The knowledge of the absolute Gibbs energy of solvation of organic ions is of great relevance to chemistry. This property is very important in evaluating the influence of solvents on chemical behaviour and serves to parametrise continuum models used in the modelling of chemical reactions in the liquid phase. It should be remembered that no continuum model has used the Gibbs energy of solvation of organic ions in DMSO or other organic solvents in its parametrisation. By the same token, no parametrisation of a continuum model is able to predict the rate enhancement of S_N2 reactions on going from protic to dipolar aprotic solvents. The present paper reporting 56 values of $\Delta G_{solv}*$ for ions in aqueous solution and 30 values of $\Delta G_{solv}*$ for ions in dimethyl sulfoxide solution will hopefully bridge this gap.

Calculation of the Gibbs energy of solvation of ions

The general theoretical approach to the calculation of the Gibbs energy of solvation of ions using pK_as, gas phase basicities, the Gibbs energy of solvation of neutral molecules and the absolute Gibbs energy of solvation of the proton has been explained in our previous work.[19] It must be remembered that two definitions are usually employed in discussing the Gibbs energy of ions: (a) the standard Gibbs energy of solvation, $\Delta G_{solv}°$, corresponding to the process (ideal gas, 1 atm) → (ideal dilute solution, 1 mol L^{-1}), and (b) the Gibbs energy of solvation defined by Ben-Naim,[45] $\Delta G_{solv}*$, corresponding to the process (ideal gas, 1 mol L^{-1}) → (ideal dilute solution, 1 mol L^{-1}). These two properties are related by eqn. (1),

$$\Delta G_{solv}* = \Delta G_{solv}° - RT\ \ln(\tilde{R}T) \qquad (1)$$

with $\tilde{R} = 0.082053\ K^{-1}$. In this work, we adopt $\Delta G_{solv}*$ as our reference Gibbs energy of solvation.

The Gibbs energy of solvation of an anion A^- can be determined from eqn. (2)[19]

$$\begin{aligned}\Delta G_{solv}*(A^-) = 2.303\ RT\ pK_a(HA) - \Delta G_{bas}°(A^-)\\ + \Delta G_{solv}*(HA) - \Delta G_{solv}°(H^+)\end{aligned} \qquad (2)$$

while for BH^+ cations the following equation is used:

$$\begin{aligned}\Delta G_{solv}*(BH^+) = 2.303\ RT\ pK_a(BH^+) + (B)\\ + \Delta G_{solv}*(B) - \Delta G_{solv}°(H^+)\end{aligned} \qquad (3)$$

where $\Delta G_{bas}°$ is the gas phase basicity and $\Delta G_{solv}°(H^+)$ is the standard Gibbs energy of solvation of the proton. In these equations, a value of −264.0 kcal mol^{-1} is used for $\Delta G_{solv}°(H^+)$ in water in agreement with the most recent data.[20] For DMSO solutions, the $\Delta G_{solv}°(H^+)$ was calculated by adding −4.6 kcal mol^{-1} to the $\Delta G_{solv}°(H^+)$ in water corresponding to the Gibbs energy associated with transfer of a proton from water to DMSO.[36] This results in a standard Gibbs energy of solvation of −268.6 kcal mol^{-1} for the proton in DMSO.

The solvation of the protonated solvent molecule SH^+ in S (H_3O^+ in water and $(CH_3SOCH_3)H^+$ in DMSO solution) was computed from eqn. (4).

$$\begin{aligned}\Delta G_{solv}*(SH^+) = \Delta G_{solv}*(H^+) + \Delta G_{bas}°(S) + \Delta G_{solv}*(S)\\ + RT\ \ln(\tilde{R}T) + RT\ \ln[S]\end{aligned} \qquad (4)$$

Compilation of experimental data

The data required for using the equations above had to be critically analysed and collected from different sources. A large part of the pK_a data in water is based on the compilation of Albert and Serjeant.[46] For protonated weak bases such as alcohols, ketones, esters, amides, dimethyl sulfide and dimethyl sulfoxide, the pK_a data were taken from the work of Scorrano and co-workers.[16,17,27,28] For weak acids such as aldehydes, ketones, esters, nitriles and acetylene, we have used values derived from kinetic data as reported by several authors.[29–34] For dimethyl sulfoxide solutions, we have adopted the previously mentioned pK_a values.[37–41]

In our previous report on the $\Delta G_{solv}*$ of ions[19] we made use of experimental gas phase data involving primarily proton affinities available in the literature.[11,12] In the present work, we have used a revised compilation of the gas phase basicity scale[47] with the exception of PH_2^- and CH_3COO^- whose basicities were obtained from *ab initio* calculations.

Gibbs energies of solvation for neutral species in aqueous solution were obtained from the compilations of Ben-Naim and Marcus,[48] Cabani *et al.*,[49] and Hine and Mookerjee[50] while for aniline we adopted the value reported by Truhlar *et al.*[51] Finally, the Gibbs energy of solvation of dimethyl sulfoxide in aqueous solution was calculated from eqn. (5)

$$\Delta G_{solv}* = -RT\ln\left(\frac{x_A C_{solv}}{p_A}\right) - RT\ln(\tilde{R}T) \qquad (5)$$

where x_A is the molar fraction of the dimethyl sulfoxide solute in aqueous solution, p_A is the partial pressure(in atmospheres) of the solute in equilibrium with the solution, and C_{solv} stands for the concentration of the solvent in mol L^{-1} ($C_{solv} = 55.5$ mol L^{-1} for water). This equation is valid in the limit

$x_A \rightarrow 0$. The experimental data available for water–dimethyl sulfoxide systems[44] was then used in eqn. (5). For several other solutes, ΔG_{solv}* was obtained from the Henry's law constant (k_H) and the relationship between the concentration of the solute (C_A) at infinite dilution and its partial pressure (p_A):

$$C_A = k_H p_A \qquad (6)$$

Values for k_H were obtained from ref. 47*a* and they can be related to ΔG_{solv}* by,

$$\Delta G_{\text{solv}}^* = -RT\ \ln(k_H) - RT\ \ln(\tilde{R}T) \qquad (7)$$

with k_H in units of mol L^{-1} atm^{-1}.

The Gibbs energy of solvation of neutral molecules in DMSO solution is a difficult problem because of the lack of data. Truhlar *et al.*[51] have made an extensive compilation of $\Delta_{\text{solv}}G^*$ for several molecules in different solvents including DMSO. However, only five $\Delta_{\text{solv}}G^*$ values in DMSO were found. We have used their value for toluene in this work. For the solvation of water and DMSO in DMSO, the corresponding $\Delta_{\text{solv}}G^*$s were determined from eqn. (5) using the data obtained in the study of water–DMSO systems.[44] A somewhat different approach was used for methanol, ethanol, isopropanol and acetone based on experimental data. For these cases, infinite dilution activity coefficients (γ^{∞})[42] coupled to the vapour pressure of the pure liquid $(P_A{}^{\circ})$[52] (in atm) led us to calculate the Gibbs energy of solvation of these molecules in DMSO through eqn. (8),

$$\Delta G_{\text{solv}}^* = RT\ \ln\left(\frac{P_A{}^{\circ}\gamma^{\infty}}{C_{\text{solv}}}\right) - RT\ \ln(\tilde{R}T) \qquad (8)$$

where we have used $C_{\text{solv}} = 14.0$ mol L^{-1}. For species such as HCN, HN_3, CH_3SO_3H and NH_3, results from an unpublished set of Monte Carlo free energy perturbation calculations[53] were used to estimate ΔG_{solv}*. Finally, theoretical calculation using the continuum SM5.42R/HF/6-31G* model of Cramer and Truhlar[51] in conjunction with HF/6-31+G(d,p) optimised geometries were used for all other species. These calculations were carried out with the Gamess[54] and Gamesol[55] program systems.

Although the use of accurate ΔG_{solv}* for neutral species would be highly desirable, the lack of this data and its great importance led us to estimate these values theoretically for several molecules. Since this property represents a small contribution to the final Gibbs energy of solvation of the ion we believe this procedure to be justifiable. Considering an error ±2 kcal mol^{-1} for the gas phase basicity data, and ±2 kcal mol^{-1} for the theoretically determined Gibbs energy of solvation of neutral species, we estimate our final ΔG_{solv}* of ions to have an

Table 1 Properties of HA acids in the gas phase, water and in DMSO solutions[a]

HA	pK_a(HA) (Water)	Ref.	pK_a(HA) (DMSO)	Ref.	$\Delta G_{\text{bas}}{}^{\circ}(A^-)$	Ref.	ΔG_{solv}*(HA) (Water)	Ref.	ΔG_{solv}* (HA) (DMSO)	Ref.
HF	3.18	46	15	37	365.8	47*a*	−7.57	47*a*	−5.89	63
HCl	−6.1	46	–	–	328.1	47*a*	−2.2	47*a*	–	–
HBr	−8	46	–	–	318.3	47*a*	−3.4	47*a*	–	–
HI	−9	46	–	–	309.2	47*a*	−2.4	47*a*	–	–
HOCl	7.54	56	–	–	349.2	47*a*	−5.74	47*a*	–	–
HOBr	8.60	57	–	–	347.1	47*a*	−4.58	47*a*	–	–
HOI	11.64	58	–	–	347.4	47*a*	(−4)	61	–	–
HCN	9.22	46	12.9	37	341.0	47*a*	−3.21	47*a*	(−3.15)	62
HN_3	4.70	15	7.9	37	337.9	47*a*	−3.25	47*a*	(−7.05)	62
H_2O	15.74	46	31.4	40	384.1	47*a*	−6.32	48	−6.3	44
H_2O_2	11.65	46	–	–	368.6	47*a*	−8.59	47*a*	–	–
MeOH	15.50	59	29.0	40	375.2	47*a*	−5.10	48	−5.08	42,52
EtOH	15.9	59	29.8	40	371.7	47*a*	−5.05	48	−5.19	42,52
isoPrOH	–		3.03	40	368.5	47*a*	–	–	−5.12	42,52
tert-BuOH	–	–	32.2	40	367.7	47*a*	–	–	(−4.27)	63
PhOH	9.99	46	18.0	37	342.3	47*a*	−6.62	49	(−7.56)	63
HCOOH	3.75	46	–	–	338.3	47*a*	−6.99	47*a*	–	–
CH_3COOH	4.76	46	12.3	37	341.1	60	−6.70	49	(−6.99)	63
PhCOOH	4.20	46	–		333.1	47*a*	−7.87	47*a*	–	–
CH_3SO_3H	−1.2	46	1.6	37	315.0	47*a*	−19.10	47*a*	(−11.76)	62
CH_3NO_2	10.21	46	17.2	37	349.7	47*a*	−4.15	47*a*	(−4.24)	63
CH_3CHO	16.73	32	–	–	359.0	47*a*	−3.50	49	–	–
CH_3COCH_3	19.16	33	26.5	37	361.9	47*a*	−3.85	49	−3.76	42,52
$PhCOCH_3$	18.24	34	–	–	354.5	47*a*	−4.58	49	–	–
CH_3COOEt	25.60	30	–	–	362.2	47*a*	−3.10	49	–	–
H_2S	7.05	46	–	–	344.8	47*a*	−0.44	47*a*	–	–
CH_3SH	10.33	46	–	–	350.6	47*a*	−1.24	49	–	–
PhSH	6.62	46	10.3	39	333.8	47*a*	−2.55	49	(−3.73)	63
CH_3SOCH_3	–	–	35.1	40	366.4	47*a*	–	–	−7.68	44
PH_3	(27)	46	–	–	361.2	19	0.96	47*a*	–	–
NH_3	(33)	46	(41)	38	396.9	47*a*	−4.31	48	(−1.96)	62
$PhNH_2$	(27)	46	30.6	38	359.1	47*a*	−5.49	51	(−6.50)	63
$HCONH_2$	–	–	23.5	37	352.8	47*a*	–	–	(−6.73)	63
CH_3CONH_2	15.1	46	25.5	37	355.0	47*a*	−9.71	49	(−7.63)	63
CH_3CN	28.9	29	3.13	37	365.2	47*a*	−3.89	49	(−3.30)	63
CH_3CH_2CN	30.9	29		–	367.9	47*a*	−3.85	49		–
HCCH	21.7	31	–	–	369.7	47*a*	−0.01	49	–	–
$PhCH_3$	–	–	(43)	38	373.7	47*a*	–	–	−4.42	51

[a] Gibbs energy in units of kcal mol^{-1}. $T = 298.15$ K. Values in parentheses account for theoretically estimated Gibbs energy of solvation or pK_a obtained by extrapolation procedures.

Table 2 Properties of B bases in the gas phase, water and in DMSO solutions[a]

BH^+	$pK_a(BH^+)$ (Water)	Ref.	$pK_a(BH^+)$ (DMSO)	Ref.	$\Delta G_{bas}°(B)$	Ref.	$\Delta G_{solv}*(B)$ (Water)	Ref.	$\Delta G*_{solv}*(B)$ (DMSO)	Ref.
H_3O^+	–	–	–	–	157.7	47*b*	−6.32	48	–	–
$CH_3OH_2^+$	−2.05	28	–	–	173.2	47*b*	−5.10	48	–	–
$CH_3CH_2OH_2^+$	−1.94	28	–	–	178.0	47*b*	−5.05	48	–	–
$(CH_3)_2OH^+$	−2.48	28	–	–	182.7	47*b*	−1.90	50	–	–
$(CH_3CH_2)_2OH^+$	−2.39	28	–	–	191.0	47*b*	−1.75	50	–	–
$(CH_3)_2C{=}OH^+$	−3.06	17	–	–	186.9	47*b*	−3.85	49	–	–
$(PhCOCH_3)H^+$	−3.87	17	–	–	198.2	47*b*	−4.58	49	–	–
$(CH_3COOEt)H^+$	−4.61	27	–	–	192.3	47*b*	−3.10	49	–	–
$(CH_3)_2SH^+$	−6.99	28	–	–	191.5	47*b*	−1.54	50	–	–
$(CH_3SOCH_3)H^+$	−1.54	28	–	–	204.0	47*b*	−10.3	44	−7.68	44
NH_4^+	9.25	46	10.5	37	195.7	47*b*	−4.31	48	(−1.96)	62
$CH_3NH_3^+$	10.66	46	–	206.6	47*b*	−4.57	48	–	–	
$(CH_3)_2NH_2^+$	10.73	46	–	–	214.3	47*b*	−4.28	50	–	–
$(CH_3)_3NH^+$	9.80	46	–	–	219.4	47*b*	−3.23	50	–	–
$EtNH_3^+$	10.65	46	–	–	210.0	47*b*	−4.51	48	–	–
$(Et)^+NH_2^+$	10.84	46	–	–	219.7	47*b*	−4.08	48	–	–
$(Et)_3NH^+$	10.75	46	9.07	41	227.0	47*b*	−3.04	48	(−2.06)	63
$PrNH_3^+$	10.54	46	–	–	211.3	47*b*	−4.40	48	–	–
$nBuNH_3^+$	10.66	46	11.12	41	211.9	47*b*	−4.30	48	(−3.37)	63
$PhNH_3^+$	4.87	46	3.82	41	203.3	47*b*	−5.49	51	(−6.50)	63
$PyridineH^+$	5.23	46	5.2	41	214.7	47*b*	−4.69	50	(−4.32)	63
$HCONH_3^+$	−1.47	16	–	–	189.1	47*b*	(−9.61)	64	–	–
$CH_3CONH_3^+$	−0.66	16	–	–	199.0	47*b*	−9.71	49	–	–

[a] Gibbs energy in units of kcal mol^{-1}. $T = 298.15$ K. Values in parentheses account for theoretically estimated Gibbs energy of solvation or pK_a obtained by extrapolation procedures.

uncertainty of ±3 kcal mol^{-1} in DMSO solution, and of ±2 kcal mol^{-1} in aqueous solution.

Results and discussion

The data used in our present work are tabulated in Tables 1 and 2, while Table 3 shows the Gibbs energy of solvation obtained for anions and cations. In aqueous solution, the present solvation data are very close to our previous report and do not differ by more than 2 kcal mol^{-1} with some notable exceptions. The cyanide ion is an example where the difference amounts to 4.4 kcal mol^{-1} with respect to our previous value. This is due to the use of a more accurate value for the gas phase basicity and the Gibbs energy of solvation of HCN. For the PhO^- ion, the use of a revised value for the gas phase basicity is the source of the 2.6 kcal mol^{-1} difference in Gibbs energy of solvation. A very high difference of 6.6 kcal mol^{-1} is noticeable for the acetate ion, that is due to the incorrect value for its proton affinity value extracted from ref. 11 in our previous report. In this work we have used a high level *ab initio* calculation to obtain the basicity of this species.[60] The CH_2CN^- ion is another species with a large difference of 5.5 kcal mol^{-1}. Here, the discrepancy arises from the pK_a value used in our previous work that was obtained by an approximate scheme. The new pK_a adopted in this work was obtained by a kinetic method[29] and we consider this to be more reliable. The differences of 3.7 kcal mol^{-1} for HCC^- and 5.4 kcal mol^{-1} for $(CH_3COCH_3)H^+$ have the same origin.

Few values of $\Delta_{solv}G*$ are available in the literature for comparison of our results regarding solvation in DMSO solution. Using the Gibbs energy of solvation in aqueous solution presented in this work and the Gibbs energy of transfer from water to DMSO compiled by Marcus,[9] we can calculate the Gibbs energy of solvation of CN^-, N_3^- and CH3COO$^-$ ions in DMSO as being −59.2, −64.5 and −65.3 kcal mol^{-1}, respectively. The values for CN^- and N_3^- ions are in excellent agreement with our data shown in Table 3, namely −58.0 and −65.6 kcal mol^{-1}. For acetate, the deviation is 2.6 kcal mol^{-1}, well inside our estimated uncertainty of ±3 kcal mol^{-1}. The good agreement encountered for these species is encouraging and supports the quality of the present data.

The Gibbs energy of solvation of ions reported for water and DMSO solutions is also in agreement with the view that anions are better solvated in aqueous solution than in DMSO. In the case of small and hard ions such as F^- and OH^-, the difference in $\Delta_{solv}G*$ is greater than 20 kcal mol^{-1}. The same large variation is observed for CH_3O^-, EtO^- and CH_3CONH^- ions. For other species, the variation is around 10 to 15 kcal mol^{-1}. Exceptions are the Br^-, I^- and N_3^- ions that have a Gibbs energy of transfer of ~5 kcal mol^{-1} or less. Species with high positive Gibbs energy of transfer from water to dimethyl sulfoxide can become very powerful nucleophiles (or bases) in DMSO. In the case of positive ions, the DMSO solution has a slightly better solvation power than water, and differences in Gibbs energy of solvation do not exceed 5 kcal mol^{-1}.

Conclusion

We have reported the Gibbs energy of solvation of several ions in aqueous and dimethyl sulfoxide solutions. The data utilised to calculate $\Delta G_{solv}*$ are the most accurate available in the literature, although the Gibbs energy of solvation of some neutral species in DMSO were obtained theoretically due to lack of data. However, our values are sufficiently accurate to be useful in the evaluation of solvent effects in chemistry as well as in the development of continuum solvation models that are applied in the modelling of liquid phase chemical reactions.

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Table 3 Gibbs energy of solvation of A^- and BH^+ ions in aqueous and DMSO solutions[a]

A^-	ΔG_{solv}*(A^-) (Water)	ΔG_{solv}*(A^-) (DMSO)	BH^+	ΔG_{solv}*(BH^+) (Water)	ΔG_{solv}*(BH^+) (DMSO)
F^-	−105.0	−82.6	H_3O^+	−110.2	–
Cl^-	−74.6	−65.0[b]	$CH_3OH_2^+$	−93.1	–
Br^-	−68.6	−62.1[b]	$(CH_3)CH_2OH_2^+$	−88.4	–
I^-	−59.9	−57.4[b]	$(CH_3)_2OH^+$	−79.8	–
OCl^-	−80.7	–	$(CH_3CH_2)_2OH^+$	−71.5	–
OBr^-	−75.9	–	$(CH_3)_2C{=}OH^+$	−76.8	–
OI^-	−71.5	–	$(PhCOCH_3)H^+$	−65.1	–
CN^-	−67.6	−58.0	$(CH_3COOEt)H^+$	−68.5	–
N_3^-	−70.7	−65.6	$(CH_3)_2SH^+$	−64.5	
OH^-	−105.0	−79.0	$(CH_3SOCH_3)H^+$	−68.2	−69.6
HO_2^-	−97.3	–	NH_4^+	−85.2	−89.2
MeO^-	−95.2	−72.1	$CH_3NH_3^+$	−76.5	–
EtO^-	−91.1	−67.6	$(CH_3)_2NH_2^+$	−68.6	–
$isoPrO^-$	–	−63.7	$(CH_3)_3NH^+$	−61.2	–
tert-BuO^-	–	−59.4	$EtNH_3^+$	−73.0	–
PhO^-	−71.3	−56.7	$(Et)^+NH_2^+$	−63.2	–
$HCOO^-$	−76.2	–	$(Et)_3NH^+$	−54.7	−56.0
CH_3COO^-	−77.3	−62.7	$PrNH_3^+$	−71.5	–
$PhCOO^-$	−71.2	–	$nBuNH_3^+$	−70.9	−75.2
$CH_3SO_3^-$	−71.7	−56.0	$PhNH_3^+$	−72.8	−77.0
$CH_2NO_2^-$	−75.9	−61.9	pyridineH^+	−61.1	−65.3
CH_2CHO^-	−75.7	–	$HCONH_3^+$	−82.5	–
$CH_3COCH_2^-$	−75.6	−60.9	$CH_3CONH_3^+$	−73.8	–
$PhCOCH_2^-$	−70.2	–			
CH_2COOEt^-	−66.4	–			
HS^-	−71.6	–			
CH_3S^-	−73.7	–			
PhS^-	−63.3	−54.9			
$CH_3SOCH_2^-$	–	−57.6			
PH_2^-	−59.4	–			
NH_2^-	−92.2	−74.3			
$PhNH^-$	−63.8	−55.3			
$HCONH^-$	–	−58.9			
CH_3CONH^-	−80.1	−59.2			
CH_2CN^-	−65.7	−57.2			
CH_3CHCN^-	−65.6	–			
HCC^-	−76.1	–			
$PhCH_2^-$	–	−50.9			

[a] Gibbs energy in units of kcal mol^{-1}. $T = 298.15$ K. Values calculated from data of Tables 1 and 2 and using $\Delta_{solv}G^0\ (H^+)_{water} = -264.0$ kcal mol^{-1} and $\Delta_{solv}G^0\ (H^+)_{DMSO} = -268.6$ kcal mol^{-1} [b] Values obtained from the present Gibbs energy of solvation in water in water plus the Gibbs energy of transfer from water to DMSO solution taken from ref. 9.

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63 Theoretical calculation using the SM5.42R/HF/6-31G* continuum model.
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