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Review

A simple empirical model describing the thermodynamics of hydration of ions of widely varying charges, sizes, and shapes

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Abstract

Cations and anions and small and large ions are hydrated in different manners, due to the orientation of water molecules around them. Still, a very simple model accounts reasonably well for the thermodynamics of hydration of ions with charges z varying from ± 1 to ± 4, depending only on z and their radii r, when taken as spheres. The model specifies the width of the hydration shell, Δr, the number n of water molecules immobilized and electrostricted in it, proportional to $|z|/r$, and the bulk and high-field dielectric properties of the water. It accounts for the Gibbs energy, enthalpy, entropy, heat capacity of hydration and the partial molar volumes of the ions.

Key words: Model for ion hydration; Thermodynamic functions of hydration; Electrostriction; Water structure making, breaking

1. Introduction

Cations and anions are hydrated in different manners, due to the different orientations of the water molecules in their first hydration shells [1]. Water molecules turn their oxygen atoms, with one of the two lone pairs of electrons, towards cations, at least the monoatomic ones. The water molecules act as donors and the cations as acceptors of coordinative bonds in the cases of transition metal cations (with participation of d-orbitals) and even the smaller main group cations, resulting in a definite geometry in the first hydration shell. They turn one of their hydrogen atoms towards anions, forming hydrogen bonds with them, unless the anions are hydrophobic. Very large ions, such as quaternary alkyl- or aryl-substituted ammonium, phosphonium, borate, etc. ions, are hydrated differently from monoatomic ones due to hydrophobic hydration. Protic ions, such as hydroxylammonium and hydrogensulfate, will donate hydrogen bonds to the oxygen atoms of the water molecules near their protic hydrogen atoms. It is, therefore, to be expected that as many models would be required for the description of the thermodynamic functions of hydration of the ions as there are different manners of hydration. Furthermore, different thermodynamic functions, such as the enthalpy, the entropy, and the volume change due to hydration, should per-

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haps not be expected a priori to be described by the same model, since a model tends to stress certain features of the interactions and neglect others, being an approximation to the true state of the ion in its aqueous environment, rather than a rigorous description.

Still, a very simple model [2] has been found to account reasonably well for the thermodynamics of hydration of ions with charges z ranging from -4 to -1 and from 1 to 4, monoatomic and polyatomic, depending only on z and on their radius r, when taken as spheres, ranging from 0.06 to 0.43 nm. The model is restricted to ions where the charge is localized to a large extent in the center of the ion. It has been tested for the standard molar Gibbs energy [3], enthalpy [2,4], entropy [2,5], and heat capacity changes [6] of hydration and the standard partial molar volumes [7] of the ions. (The model was similar in its earlier form to, but not exactly the same as, that adopted later.) The epithet 'reasonably' means that the errors in the fit of the predicted with the experimental thermodynamic quantities are not as small as the uncertainties of the data would warrant, but no more than a small multiple of them.

The model specifies the width Δr of the first hydration shell and the number n of water molecules translationally immobilized in it as functions of z and r. The size of the hydrated ion (only to the edge of the first shell) and the 'hydration number' obtained in this manner [8] are compatible with similar quantities obtained from the mobilities and other properties of dilute solutions of electrolytes [8]. The model utilizes beside z and r of the ions only the known dielectric and light-refraction properties of bulk water and their temperature and pressure derivatives.

The development of the model dependes on an extrathermodynamic assumption necessary for the division of the observed standard molar thermodynamic functions of electrolytes into their ionic contributions. Due to the additivity of these standard molar quantities, however, the results of the predictions of the model can be added for the stoichiometric quantities of cations and anions to be compared directly with observable thermodynamic quantities, without recourse to an extrathermodynamic assumption. Similarly, differences of quantities for electrolytes with a common ion and unlike counter-ions of the same charge number (or, if of different charges, the quantities weighted by the reciprocals of the charges) are assumption-free quantities and can be compared with predictions from the model.

2. Thermodynamics of hydration

Hydration, like any solvation process, is defined [9] as the transfer of a solute particle from a fixed position in the ideal gas to a fixed position in the solvent, i.e. in water in the present case. This definition specifies infinite dilution in the resulting solution, precluding solute–solute interactions. The fixed positions in the gas and solution phases remove complications from the translational degrees of freedom of the solute particle. The latter, if present, would require consideration of the change of the volume available to the solute on its transfer, and possibly a consideration of the ill-defined 'free volume'. The process as defined describes the net changes in the thermodynamic functions due to the interactions of the hydrating solute with its new environment, i.e. what 'hydration' really is about, since there are no interactions in the ideal gas phase. These interactions include eventual changes in the internal degrees of freedom of the solute (vibrations, internal rotations and rotation as a whole), the interactions with the water molecules in the immediate environment of the solute and also with more remote ones (mainly due to the electrical field, in the case that the solute is charged), and changes in the mutual molecular orientations and hydrogen-bonding ('structure') of the water surrounding the solute.

Tabulated standard molar thermodynamic quantities of hydration, denoted as a generalization by $\Delta\text{hyd}Y^0$, are the differences between the corresponding standard molar quantities of formation of the aqueous and gaseous solute, in the cases of the Gibbs energy and enthalpy [10], and between the partial molar quantity of the aqueous solute at infinite dilution and the molar quantity for the gaseous solute in the cases of the entropy [5,11], heat capacity [6], and volume [7],

$$\Delta\text{hyd}Y^0 = \Delta_f Y^0(\text{aq}) - \Delta_f Y^0(\text{g}),\quad (Y = G \text{ and } H), \tag{1a}$$

$$\Delta\text{hyd}Y^0 = \bar{Y}^\infty(\text{aq}) - Y^0(\text{g}),\quad (Y = S,\ C_\text{p}, \text{ and } V). \tag{1b}$$

These quantities, however, do not conform to the definition of hydration given above, but include contributions from the compression of the space available to the solute from that in the ideal gas phase at $P_0 = 0.1$ MPa (1 bar) pressure to the 1 mol dm^{-3} aqueous solution. Also, in the entropy, enthalpy and heat capacity terms appears the isobaric expansibility of water, α, and in the volume appears a term in the isothermal compressibility, κ in addition to the interaction term proper. It is, therefore, necessary to 'correct' the tabulated standard molar thermodynamic functions (marked by ^{0}) to those pertaining to hydration as defined above (marked by *) as follows [9]:

$$\Delta\text{hyd}G^* = \Delta\text{hyd}G^0 + RT\ \ln(RT/0.001\ P_0) = \Delta\text{hyd}G^0 + 7.93 \text{ kJ mol}^{-1}, \tag{2a}$$

$$\Delta\text{hyd}H^* = \Delta\text{hyd}H^0 + RT(1 - \alpha T) = \Delta\text{hyd}H^0 + 2.29 \text{ kJ mol}^{-1}, \tag{2b}$$

$$\Delta\text{hyd}S^* = \Delta\text{hyd}S^0 + R[1 - \alpha T - \ln(RT/0.001\ P_0)] = \Delta\text{hyd}S^0 - 18.9 \text{ J K}^{-1} \text{ mol}^{-1} \tag{2c}$$

$$\Delta\text{hyd}C_p^* = \Delta\text{hyd}C_\text{p}^0 + R(1 - 2\alpha T) = \Delta\text{hyd}C_\text{p}^0 + 7.0 \text{ J K}^{-1} \text{ mol}^{-1}, \tag{2d}$$

$$\Delta\text{hyd}V^* = \Delta\text{hyd}V^0 + RT/P_0(-1 + \kappa P_0) = \Delta\text{hyd}V^0 + 24464 \text{ cm}^3 \text{ mol}^{-1}. \tag{2e}$$

The numerical constants pertain to 298.15 K and the corrections are independent of the solutes.

Tabulated standard molar thermodynamic functions of hydration of ions (or of their formation [10] or their standard partial molar quantities) are apt to be 'conventional' values, based on the convention of assigning to one particular ion, generally the hydrogen ion, H$^+$, a particular value, generally zero, unless a specific value is provided by theory. The principle of the additivity of the (stoichiometrically weighted) quantities for the cation and the anion is then invoked in order to obtain conventional values for all the ions that constitute those electrolytes, for which the thermodynamic quantities have been determined by experiment. If a different assignment were made for a particular ion, then all the values have to be adjusted by the corresponding difference, weighted by the (algebraic value of the) charge of this ion.

So-called 'absolute' values of the thermodynamic quantities of concern here have been sought, since only these can be explained by physico-chemical arguments, e.g., by means of a model. They necessarily depend on extra-thermodynamic methods, since thermodynamics deals only with components, i.e. neutral entities that can be physically added to a system. The absolute values thus ignore the transfer of the charge through the phase boundary between the ideal gas and water when the process of hydration takes place. The justification for this is that in the final reckoning the absolute values can be added for the stoichiometric quantities of cations and anions correctly to yield the observable thermodynamic quantities.

Experimental methods have been devised for some of the thermodynamic quantities of concern here, which, though still dependent on extra-thermodynamic assumptions, minimize the uncertainties connected with them. Instances are the partial molar volume [12,13] and entropy [13,14], where vibration potentials and emfs of thermocells, respectively, provide some guidance. Less satisfactory are the Gibbs energies obtained from Volta potentials between streeming mercury and aqueous solutions across a gas gap [13,15], since these are not quite consistent with the entropy and enthalpy values. The latter appear to be established most satisfactorily by the extrapolation of differences between the conventional values of singly charged cations and anions of equal sizes to infinite size (actually, as a function of $[(r/\text{pm}) + 138]^{-3}$, 138 pm being the radius of a water molecule) [13,16].

If a 'reference electrolyte' is found that on the one hand has small values of $\Delta\text{hyd}Y^0$ (or of $\bar{Y}^\infty$)

relative to most ions of interest and on the other has a cation and an anion of equally large size and low charge, then the assignment of $\frac{1}{2}\Delta \mathrm{hyd}Y^0$ (or of $\bar{Y}^\infty$) to each of the cation and the anion produces only minimal errors [17]. Such is the case of tetraphenylarsonium tetraphenylborate (TATB) and the Gibbs energy and the enthalpy of hydration. However, in the case of the partial molar volumes of the aqueous ions this assumption does not hold sufficiently well, because $\bar{V}^\infty$ of the TATB ions is large relative to those of most ions and the sizes of the TATB ions are not exactly the same, a fact manifested strongly in the volumes [7]. By default of a better extra-thermodynamic assumption, the TATB one has been applied also to the partial molar heat capacities of ions, although $\bar{C}_p^\infty$ of the TATB ions is large [6]. The following expressions have been employed to convert from the conventional to the absolute values of the thermodynamic quantities of interest of ions X^z (entropies, heat capacities, and volumes of the gaseous ions are known from theory):

$$\Delta \mathrm{hyd}G^0(X^z, \mathrm{abs}) = \Delta \mathrm{hyd}G^0(X^z, \mathrm{con}) - (1056 \pm 6)z \ \mathrm{kJ\ mol^{-1}} \tag{3a}$$

$$\Delta \mathrm{hyd}H^0(X^z, \mathrm{abs}) = \Delta \mathrm{hyd}H^0(X^z, \mathrm{con}) - (1094 \pm 6)z \ \mathrm{kJ\ mol^{-1}} \tag{3b}$$

$$\bar{S}^\infty(X^z, \mathrm{abs}) = \bar{S}^\infty(X^z, \mathrm{con}) - (22.2 \pm 1.2)z \ \mathrm{J\ K^{-1}\ mol^{-1}} \tag{3c}$$

$$\bar{C}_p^\infty(X^z, \mathrm{abs}) = \bar{C}_p^\infty(X^z, \mathrm{con}) - (71 \pm 1)z \ \mathrm{J\ K^{-1}\ mol^{-1}} \tag{3d}$$

$$\bar{V}^\infty(X^z, \mathrm{abs}) = \bar{V}^\infty(X^z, \mathrm{con}) - (5.5 \pm 0.5)z \ \mathrm{cm^3\ mol^{-1}} \tag{3e}$$

The corrections from the (°) to the (*) quantities listed above can now be applied to the absolute values to give the thermodynamic functions of hydration for the individual ions. For the volumes, however, there is no point in applying this correction and to deal with the volume change of hydration [7], because of its very large value compared with the standard partial molar volume of any ion. Differences between various ions are only obscured by the large volumes of the ions in the ideal gas phase, that are all equal, hence the standard partial molar volumes of the ions will be dealt with in the following.

3. The model

The model [2] considers the ions to be spherical entities of radius r and centrally located charge z times the unit positive charge, where z is to be taken in its algebraic sense (unless $|z|$ is specified). Elongated, non-spherical ions are described by an equivalent sphere (e.g., for an elipsoid of rotation with half-diameters r_a and $r_b > r_a$, $r = (r_a^2 r_b)^{1/3}$).

The ions are surrounded by a spherical shell of width Δr, in which the water molecules are electrostricted, i.e. translationally immobilized by the electrostatic field of the ion. Although they are capable of libration and rotation around the ion–water axis, they cannot reorient themselves in an external field and are much more closely packed than in bulk water. This water is characterized by each molecule having the volume of a sphere of diameter $d = 276$ pm, the O–O distance in water, and a relative permittivity $\epsilon' = n_D^2$, the square of the refractive index of bulk water at the sodium D-line, corresponding to dielectric saturation. The pressure and temperature derivatives of ϵ' are then also those of n_D^2. These values are taken to hold throughout the hydration shell, from the surface of the ion at the distance r from its center till the edge of this shell at the distance $r + \Delta r$. Beyond the latter distance the relative permittivity reverts to its value in bulk water, ϵ_W, and so do the pressure and temperature derivatives. The values of ϵ_W and ϵ' and their temperature and pressure derivatives employed for the present model, valid for 298.15 K, are shown in Table 1.

Table 1
The parameters used for the calculation of the thermodynamic data Upper part: The relative permittivity (x) and its derivatives; Lower part: The stage II and V parameters

Function	$x=\epsilon$	$x=\epsilon'=n_D^2$	$x=\epsilon'$ (fitting)
x	78.39	1.776	1.58
$(\partial x/\partial T)_P$	-0.3595	-2.06×10^{-4}	-1.0×10^{-4}
$(\partial^2 x/\partial T^2)_P$	1.55×10^{-3}	-5.4×10^{-6}	-0.2×10^{-6}
$(\partial[1/x]/\partial P)_T$	6.0×10^{-9}	-1.24×10^{-7}	-1.24×10^{-7}

$$G^*_{II}/\mathrm{kJ\ mol^{-1}} = 41-0.087(r/\mathrm{pm})$$
$$+1.2\times10^{-3}(r/\mathrm{pm})^2+0.100(r/\mathrm{pm})z^3$$
$$H^*_{II}/\mathrm{kJ\ mol^{-1}} = 35(1+2z)-0.267(r/\mathrm{pm})$$
$$S^*_{II}/\mathrm{J\ K^{-1}\ mol^{-1}} = -22-0.600(r/\mathrm{pm})$$
$$C^*_{pII}/\mathrm{J\ K^{-1}\ mol^{-1}} = -55+1.380(r/\mathrm{pm})$$
$$\left(+4\times10^{-6}(r/\mathrm{pm})^3 \text{ for } r>250\ \mathrm{pm}\right)$$
$$V_V/\mathrm{cm^3\ mol^{-1}} = 5.4 \text{ (for } -\mathrm{CH_2}-),$$
$$6.1 \text{ (for } -\mathrm{CH_3}), 23.2 \text{ (for } -\mathrm{C_6H_5})$$

In fact, the model specifies a step function for $\epsilon(r)$ instead of the continuous function it actually has in the field of the ion, see Fig. 1. The model differs from similar ones that have been proposed previously in the manner of the specification of Δr. Although it seems in Fig. 1 that the step in $\epsilon(r)$ has been devised to take place at the inflection point of this function, this is not the case. The value of Δr is specified by the requirement that the volume of the spherical shell of immobilized water has n times the volume of an electrostricted water molecule defined above, taken to be $(\pi/6)d^3$. Here n is a 'hydration number' defined by the expression [3]

$$n=A|z|/r, \tag{4}$$

where $A=360$ pm is a fitting constant taken to be valid for all thermodynamic functions of hydration. Accordingly,

$$(4\pi/3)\left[(r+\Delta r)^3-r^3\right]=n(\pi/6)d^3. \tag{5}$$

from which Δr is readily obtained. For a given charge number z the values of Δr decrease as r increases, but $r+\Delta r$ passes through a shallow minimum. This situation is depicted schematically in Fig. 2.

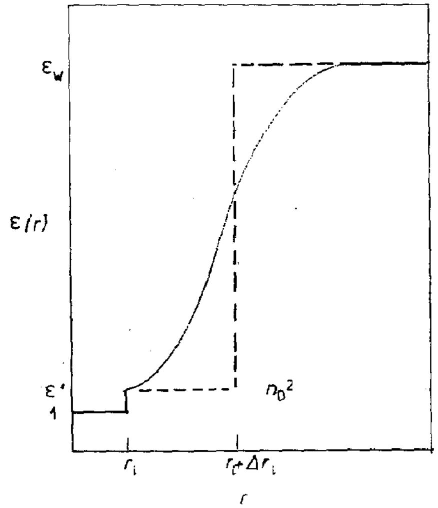

Fig. 1. The relative permittivity of the water in the field of an ion of radius r_i (continuous curve) and the step function approximating it (dashed lines), as functions of the distance r from the center of the ion. (The ordinate is not to scale.)

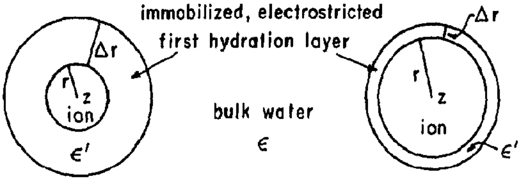

Fig. 2. Schematic representation of hydrated ions with high (left) and low (right) electrostatic fields, $|z|/r$. (from ref. [2], by permission.)

Application of the model considers the hydration process to take place in several conceptual stages. The ion in the ideal gas phase is first (stage I) localized in a fixed position and its charge is 'switched off' without changing its size. A cavity, the size of the ion, is created at a fixed position in the water and the now neutral ion is transfered into it and dispersion forces and (water) dipole-induced dipole (in the ion) interactions are allowed to take place (stage II). The charge is 'switched on' again at the center of the ion and the first hydration shell of width Δr and dielectric properties ϵ' is then built around the ion (stage III) in response to the strong electrostatic field. This electrostatic field then produces also effects in the water beyond the distance $r+\Delta r$ from the center of the ion (stage IV). Finally structural effects in the water, due to orientation of the water molecules in the near vicinity of the ion take place (stage V).

The work involved in stage I is purely electrostatic (the immobilization at a fixed position is compensated in stage II) and is temperature and pressure independent. It is equal and opposite in sign to the decrement in potential electrostatic energy as small amounts of charge are removed from the surface of the (conducting sphere) ion to infinity in the gas phase (vacuum). According to the Born model [18], it is given, per mole of ions, by the change in Gibbs free energy:

$$\Delta G_{\mathrm{I}}^{*} = -\left(N_{\mathrm{Av}} e^{2}/8\pi\epsilon_{0}\right) z^{2}/r, \tag{6}$$

where N_{Av} is Avogadro's number, e is the unit charge, and ϵ_0 is the permittivity of vacuum.

The change in the thermodynamic functions involved in stage II is calculated as if the ion were an inert gas atom or a spherical hydrocarbon molecule. As a first approximation this is taken to be linear with the size of the bare ion, r,

$$\Delta Y_{\mathrm{II}}^{*} = a_{\mathrm{II}} - b_{\mathrm{II}} r, \tag{7}$$

with the coefficients a_{II}, and b_{II} obtained from fits of actual data for such neutral species [19,20]. Conceptually, the size of the cavity and the interactions are more appropriately taken for the ion with its first hydration shell, i.e. with $r + \Delta r$ instead of r. This, however, would not take the variability of the sizes of the ions sufficiently into account. In the case of the partial molar volume, the appropriate term is not linear with the size but is the volume of the hydrated ion itself,

$$\bar{V}_{\mathrm{II}} = (4\pi N_{\mathrm{Av}}/3)(r+\Delta r)^{3}. \tag{8}$$

The electrostatic work done in stage III is given by:

$$\Delta G_{\mathrm{III}}^{*} = \left(N_{\mathrm{Av}} e^{2}/8\pi\epsilon_{0}\right) z^{2}(1/\epsilon') \times\left[\Delta r/r(r+\Delta r)\right]. \tag{9}$$

This is the reverse of the discharging in stage I, except that the increments of charge are brought from the distance $r + \Delta r$ up to the surface of the conducting ion at distance r through the medium of relative permittivity ϵ', considered as a continuum. Again, according to the Born model, this is taken to be the only work involved in stage III, all the other aspects of the ion–water intimate binding taking place in the first hydration shell being taken care of by the specifications of ϵ' and Δr.

In this expression ϵ' is the only temperature and pressure dependent quantity, hence replacement of $1/\epsilon'$ with its derivatives serves to obtain: the entropy (with $\epsilon'^{-2}\ (\partial\epsilon'/\partial T)_{\mathrm{P}}$), the enthalpy (with $\epsilon'^{-1}[1 + T\epsilon'^{-1}\ (\partial\epsilon'/\partial T)_{\mathrm{P}}]$), and heat capacity (with $T\epsilon'^{-2}[(\partial^2\epsilon'/\partial T^2)_{\mathrm{P}} - 2\epsilon'^{-1}\ (\partial\epsilon'/\partial T)_{\mathrm{P}}^2]$ changes and the partial molar volume (with $[\partial(1/\epsilon')/\partial P]_{\mathrm{T}}$) for stage III. It was found [7], however, that $\bar{V}_{\mathrm{III}}$ calculated in this manner grossly overestimates the electrostriction taking place in this hydration shell, and that it must be multiplied by the empirical factor 6.9×10^{-3} $(r/\mathrm{pm})/|z|$ in order to produce reasonable results.

The electrostatic work involved in stage IV (no other work being involved in this stage) is similarly given by

$$\Delta G_{\mathrm{IV}}^{*} = \left(N_{\mathrm{Av}} e^{2}/8\pi\epsilon_{0}\right) z^{2}(1/\epsilon) \times\left[1/(r+\Delta r)\right]. \tag{10}$$

This is the work of bringing the increments of charge from infinity through the medium of relative permittivity ϵ, considered as a continuum, to the distance $r + \Delta r$ from the charging ion according to the Born model. Again, replacement of $1/\epsilon$ by its derivatives yields the other thermodynamic functions. The difference in the distance factors between the expressions for stages III and IV reflects the fact that the former applies between the distances r and $r + \Delta r$ from the center of the ion whereas the latter applies from the distance $r + \Delta r$ to infinity.

No generally applicable expression was found to be usable in stage V. In the case of the Gibbs free energy it was argued [21] that the equilibrium between hydrogen-bonded and non-bonded water molecules, perturbed by the intrusion of the ion, is restored with exact compensation between the entropy and enthalpy terms, so that $\Delta G_{\mathrm{V}}^{*} = 0$. Although consequently $\Delta H_{\mathrm{V}}^{*} \neq 0$, it is small with respect to $\Delta H_{\mathrm{III}}^{*}$, hence can be neglected. In the cases of the entropy and the heat capacity, however, this term is significant, describing the effect of the ion on the structure of

Table 2
The radius r (and derived Δr and n) and the molar Gibbs free energy, enthalpy, entropy, and heat capacity of hydration and the standard partial molar volume of ions

Ion	r (pm)	Δr (pm)	n	$-\Delta \mathrm{hyd}G^*$ kJ/mol	$-\Delta \mathrm{hyd}H^*$ (kJ/mol)	$-\Delta \mathrm{hyd}S^*$ (J/K/mol)	$-\Delta \mathrm{hyd}C_p^*$ (J/K/mol)	$\bar{V}^\infty$ (cm^3/mol)
Li^+	69	172	5.2	475	530	161	23	−6.4
Na^+	102	116	3.5	365	415	130	42	−6.7
K^+	138	74	2.6	295	330	93	72	3.5
Rb^+	149	64	2.4	275	305	84	94	8.6
Cs^+	170	49	2.1	250	280	78	108	15.8
Cu^+	77	156	4.7	525	585	162	28	−13.5
Ag^+	115	97	3.1	430	480	136	59	−6.2
Au^+	137	75	2.6	575	585	163	82	5.6
Tl^+	150	63	2.4	300	335	91	103	5.4
H_3O^+	112	78	2.7			163	85	−5.5
NH_4^+	148	65	2.4	285	325	131	29	12.4
$MeNH_3^+$	200	33	1.8	295	310	131	6	30.6
Me_4N^+	280	14	1.3	160	215	163	−74	84.1
Et_4N^+	337	8	1.1	0	205	241	−259	143.6
Pr_4N^+	379	5	0.9				−576	208.9
Bu_4N^+	413	4	0.9		225		−900	270.2
Pe_4N^+	443	3	0.8				−1143	333.7
Ph_4P^+	424	4	0.8		45		−779	285.8
Ph_4As^+	425	4	0.8	−50	45	321	−803	295.2
Be^{2+}	45	303	16.0	2395	2510	329	72	−23.4
Mg^{2+}	72	227	10.0	1830	1945	350	172	−32.2
Ca^{2+}	100	171	7.2	1505	1600	271	183	−28.9
Sr^{2+}	113	150	6.4	1380	1470	261	191	−29.2
Ba^{2+}	136	118	5.3	1250	1330	224	202	−23.5
Ra^{2+}	143	109	5.0	1250	1320	186	215	−21.6
V^{2+}	79	212	9.1	1825	1690	319		
Cr^{2+}	82	205	8.8	1850	1930	327		
Mn^{2+}	83	203	8.7	1760	1870	311	168	−28.7
Fe^{2+}	78	213	9.2	1840	1970	381	202	−30.2
Co^{2+}	75	220	9.6	1915	2035	356	183	−35.0
Ni^{2+}	69	233	10.4	1980	2115	370	198	−35.0
Cu^{2+}	73	224	9.9	2010	2120	339	176	−36.0
Zn^{2+}	75	220	9.6	1955	2070	337	178	−32.6
Pd^{2+}	86	197	8.4	1910	2050	432	182	−31.8
Ag^{2+}	89	180	8.1	1850			178	−30.3
Cd^{2+}	95	178	7.6	1755	1830	304	164	−31.0
Sn^{2+}	93	183	7.7	1490	1575	249	203	−26.5
Pt^{2+}	80	209	9.0	1960	2060	337		
Hg^{2+}	102	168	7.1	1760	1850	194	147	−30.3
Pb^{2+}	118	143	6.1	1425	1570	228	209	−26.5
Sm^{2+}	119	138	6.1	1375	1460	294	141	−16.7
Eu^{2+}	117	145	6.2	1385	1480	283	131	−13.2
Yb^{2+}	102	168	7.1	1510	1600	306	153	−21.3
Hg_2^{2+}	190	66	3.8			270	100	3.4
UO_2^{2+}	175	78	4.1		1360	422	167	−5.1
Al^{3+}	53	324	20.4	4525	4715	557	363	−58.7
Sc^{3+}	75	262	14.4	3795	3965	497	233	−58.4
Y^{3+}	90	228	12.0	3450	3590	502	234	−57.3
La^{3+}	105	203	10.3	3145	3310	474	353	−55.6
Ce^{3+}	101	207	10.7	3200	3365	476	329	−56.3

Table 2 (continued)

Ion	r (pm)	Δr (pm)	n	$-\Delta\text{hyd}G^*$ kJ/mol	$-\Delta\text{hyd}H^*$ (kJ/mol)	$-\Delta\text{hyd}S^*$ (J/K/mol)	$-\Delta\text{hyd}C_p^*$ (J/K/mol)	$\bar{V}^\infty$ (cm^3/mol)
Pr^{3+}	100	209	10.8	3245	3410	484	392	−59.0
Nd^{3+}	98	212	11.0	3280	3445	482	381	−59.8
Pm^{3+}	97	214	11.1	3250	3465	485	318	−58.7
Sm^{3+}	96	216	11.3	3325	3490	484	376	−58.8
Eu^{3+}	95	218	11.4	3360	3535	488	365	−57.2
Gd^{3+}	94	220	11.5	3375	3545	481	345	−56.4
Tb^{3+}	92	223	11.7	3400	3580	506	354	−56.7
Dy^{3+}	91	226	11.9	3425	3600	512	348	−57.3
Ho^{3+}	90	228	12.0	3470	3635	509	353	−58.3
Er^{3+}	89	231	12.1	3495	3670	526	366	−59.4
Tm^{3+}	88	233	12.3	3515	3695	523	350	−59.9
Yb^{3+}	87	235	12.4	3570	3740	515	364	−60.7
Lu^{3+}	86	237	12.6	3515	3695	523	353	−61.5
U^{3+}	104	201	10.4	3205	3435	459	329	
Pu^{3+}	101	207	10.7	3235	3525	464	322	
Ti^{3+}	67	282	16.1	4015	4340	602		
V^{3+}	64	291	16.9	4220	4450	571		
Cr^{3+}	62	296	17.4	4010	4670	533	208	−53.2
Mn^{3+}	65	288	16.6	4410	4640	636		
Fe^{3+}	65	288	16.6	4265	4460	576	218	−53.0
Co^{3+}	61	299	17.7	4495	4690	570	220	−60.4
Ga^{3+}	62	296	17.4	4515	4305	579	214	−61.4
Rh^{3+}	67	282	16.1	4350		567		−60.0
In^{3+}	79	253	13.7	3980	4125	405	231	−58.7
Au^{3+}	70	275	15.4	4420			237	−57.8
Tl^{3+}	89	233	12.3	3970	4125	453	249	−55.8
Bi^{3+}	102	205	10.6	3480	3625	413		
Zr^{4+}	72	303	20.0	6790	6990	782	356	
Ce^{4+}	80	283	18.0	6120	6325	580	394	
Hf^{4+}	71	306	20.3	6965	7155	738		
Th^{4+}	94	251	15.3	5815	6055	707	441	−75.5
U^{4+}	89	262	16.2	6360	6570	708	418	
Pu^{4+}	86	269	16.7	6560	6765	688	406	
F^-	133	79	2.7	465	510	156	59	4.3
Cl^-	181	43	2.0	340	365	94	70	23.3
Br^-	196	35	1.9	315	335	78	74	30.2
I^-	220	26	1.6	275	290	55	64	41.7
OH^-	133	79	2.7	430	520	180	91	−0.2
HS^-	207	31	1.7	295	340	117	45	26.2
HSe^-	205	32	1.8	360	395	121	4	24.5
ClO^-	161	55	2.2			299	161	15.5
BrO^-	168	50	2.1			310	161	15.5
IO^-	180	43	2.0					4.2
CN^-	191	38	1.9	295	345	99		29.7
OCN^-	203	32	1.8	365	395	109		31.6
SCN^-	213	29	1.7	280	310	85	−6	41.2
N_3^-	195	35	1.9	295	300	101		30.5
Br_3^-	270	15	1.3			108	−30	57.0
I_3^-	285	13	1.3		173	92	−57	62.7
HF_2^-	172	47	2.1		640	116	95	27.6
HO_2^-	158	57	2.3			202	84	11.2
BO_2^-	150	63	2.4	460	535	250	131	−9.0

Table 2 (continued)

Ion	r (pm)	Δr (pm)	n	$-\Delta \mathrm{hyd}G^*$ kJ/mol	$-\Delta \mathrm{hyd}H^*$ (kJ/mol)	$-\Delta \mathrm{hyd}S^*$ (J/K/mol)	$-\Delta \mathrm{hyd}C_p^*$ (J/K/mol)	$\bar{V}^\infty$ (cm^3/mol)
NO_2^-	192	37	1.9	330	410	110	47	31.7
AlO_2^-	180	43	2.0			235	18	15.5
ClO_2^-	240	21	1.5	205	475	153	95	33.4
NO_3^-	179	44	2.0	300	310	95	39	34.5
ClO_3^-	200	33	1.8	280	295	99	38	42.2
BrO_3^-	191	38	1.9	330	375	114	74	40.8
IO_3^-	181	43	2.0	400	450	167	59	30.8
BF_4^-	232	23	1.6	190	225	85	13	49.7
ClO_4^-	250	19	1.4	205	245	76	9	49.6
BrO_4^-	254	18	1.4			79	−7	53.2
IO_4^-	271	15	1.3			72	−31	58.5
MnO_4^-	240	21	1.5	235	250	83	5	48.0
TcO_4^-	265	16	1.4	245		88		53.4
ReO_4^-	267	15	1.3	330	360	90	3	53.7
$B(OH)_4^-$	230	23	1.6			166		30.0
$Al(OH)_4^-$	265	16	1.4			151		47.8
$AuCl_4^-$	330	8	1.1	120	180	94		
HCO_2^-	169	50	2.1	395	430	121	46	31.8
$MeCO_2^-$	190	39	1.9	365	425	189	−43	46.2
HCO_3^-	185	41	2.0	335	380	156	26	28.9
HSO_3^-	200	33	1.8			124		38.8
HSO_4^-	230	23	1.6	330		148		37.1
$HSeO_4^-$	243	20	1.5			143		36.6
$H_2PO_4^-$	238	21	1.5	465	520	290	19	34.6
BPh_4^-	421	4	0.9	−50	45	327	−781	283.1
S^{2-}	184	70	3.9	1315	1345	141		2.8
Se^{2-}	198	61	3.6			168		9.6
Te^{2-}	221	47	3.3	1260				24.0
CO_3^{2-}	178	76	4.0	1315	1395	264	196	6.7
SO_3^{2-}	200	59	3.6	1295	1375	268	222	16.6
SiO_3^{2-}	214	51	3.4					7.2
SO_4^{2-}	240	38	3.0	1080	1035	219	193	25.0
SeO_4^{2-}	257	33	2.8	900	960	202		32.0
CrO_4^{2-}	255	33	2.8	950	1010	206	177	30.7
MoO_4^{2-}	268	29	2.7			239	127	39.9
WO_4^{2-}	271	28	2.7			231	114	43.2
$C_2O_4^{2-}$	210	53	3.4		1260	224		27.0
$S_2O_3^{2-}$	250	35	2.9			199	163	38.2
$S_2O_4^{2-}$	250	35	2.9			192	183	40.9
$S_2O_6^{2-}$	270	29	2.7			187		68.1
$S_2O_8^{2-}$	300	22	2.4			72	76	90.0
$S_4O_6^{2-}$	310	20	2.3			74	75	80.4
$Cr_2O_7^{2-}$	320	18	2.3			92	77	84.4
HPO_4^{2-}	238	40	3.0			291	163	18.7
SiF_6^{2-}	259	32	2.8	930	980	162	161	50.5
$PdCl_6^{2-}$	385	10	1.8	695	730	115		
$PtCl_6^{2-}$	395	10	1.8	685	740	182		161.0
PO_4^{3-}	238	54	4.5	2765	2875	440	341	−14.1
AsO_4^{3-}	248	51	4.4			404		0.9
$Fe(CN)_6^{3-}$	380	16	2.8			165	443	137.3
$Co(CN)_6^{3-}$	370	17	2.9			185		132.0
$Fe(CN)_6^{4-}$	343	29	4.2			305	249	96.0
$Mo(CN)_8^{4-}$	390	20	3.7					151.2
$P_2O_7^{4-}$	300	41	4.8			391		24.6

water, but the only way to obtain it is by subtraction of the sum of the contributions from terms I to IV from the observed $\Delta\text{hyd}S^*$ and $\Delta\text{hyd}C_p^*$. In the case of the partial molar volume a definite $\bar{V}_V$ was assigned per methyl, methylene, and phenyl group of the ion to give the total for this stage.

4. The fit of the thermodynamic functions

The values of the permittivity ϵ and n_D^2 of water and their temperature and pressure derivatives are shown in Table 1. Table 2 shows the radii r used for the ions (z is specified by their formulas), the derived values of Δr and n, and the experimental values of $-\Delta\text{hyd}Y^*$, for $Y = G$, H, S and C_p and of $\bar{V}^\infty$.

The values of the coefficients a_{II}, and b_{II} for the various thermodynamic functions that are employed for the calculations are shown in Table 1. In the case of Y being the Gibbs free energy, a better approximation acknowledges the fact that a positive term $c_{II}\, r^2$ has to be added for fitting the data to include also the larger neutral molecules, and this should be applicable to the ions too. Furthermore, the different modes of orientation of the water molecules towards cations and anions can be recognized by the addition of an empirical term dependent on the sign of the charge: $d_{II}\, r\, z^3$. The final form in this case is then

$$\Delta G_{II}^* = a_{II} - b_{II}r + c_{II}r^2 + d_{II}rz^3 \tag{11}$$

The third and fourth terms on the rhs of this expression have not been employed for Y not being the Gibbs free energy, partly because data had not been available for very large spherical ions or neutral species. Another way of saying this is that the temperature coefficients of c_{II} and d_{II} have arbitrarily been set equal to zero. On the other hand, in the case of Y being the heat capacity, a term $c_{II}\, r^3$ has to be added for $r > 250$ pm to accomodate large neutral or charged particles. For the enthalpies, a_{II} depends on z for the best fit. See Table 1 for the values of the extra terms.

It turned out that setting $\epsilon' = n_D^2$ (and the corresponding derivatives) does not reproduce the experimental data sufficiently well. Much improved fitting can be achieved by the use of empirical quantities, as shown in Table 1. There is no *a priori* theoretical requirement that n_D^2 and its derivatives should represent the relative permittivity and its derivatives for the electrostricted water in the first hydration shell. This was a choice of convenience, and can be replaced by other choices, although the elegance of the model suffers from ad hoc choices of these parameters.

The quantities obtained by calculation with the expressions shown above and the parameters in Table 1 are shown and compared with the experimental values in Fig. 3 for $\Delta\text{hyd}G^*$, Fig. 4 for $\Delta\text{hyd}H^*$, and Fig. 5 for $\bar{V}^\infty$.

The Gibbs free energies and enthalpies (in kJ/mol) of hydration of monoatomic cations range from -530 to -270 for $z = 1$, from -1940 to -1250 for $z = 2$, from -4690 to -3130 for $z = 3$ and from -7480 to -5430 for $z = 4$ as r increases. The deviations from the fit (in kJ/mol) average ±20 for $z = 1$ and ±50 for $z = 2$ or 3, but are worse for $z = 4$ and for certain groups of ions. It should be noted that for $r = 65$ pm $\text{d}[\Delta\text{hyd}G^*$ (or H^*)$/\text{kJ mol}^{-1}]/\text{d}(r/\text{pm})$ is 5 for $z = 1$, 23 for $z = 2$, 57 for $z = 3$, and 90 for $z = 4$, decreasing to about half these values for $r = 100$ pm. Hence, some of the deviations could be due to uncertainties in the ionic radii. The Gibbs free energies and enthalpies of hydration of anions (in kJ/mol) range from -510 to -180 for $z = -1$, from -1430 to -700 for $z = -2$, and are -2770 and -2880 for PO_4^{3-}, the only trivalent anion for which the data are available. The average deviations (in kJ/mol) are worse than for the cations, being ±50 for $z = -1$ and the smaller anions with $z = -2$. Note that $\Delta\text{hyd}H^*$ is always somewhat more negative than $\Delta\text{hyd}G^*$ ($\Delta\text{hyd}S^*$ being negative for all the ions).

Allowance for stage V in the case of the standard partial molar volume of large, hydrophobic ions is made by the assignment of the $\bar{V}_V$ shown in Table 1 per methylene, methyl, or phenyl group. In the cases of $\Delta\text{hyd}S^*$ and $\Delta\text{hyd}C_p^*$ no allowance for stage V can be made on an indepen-

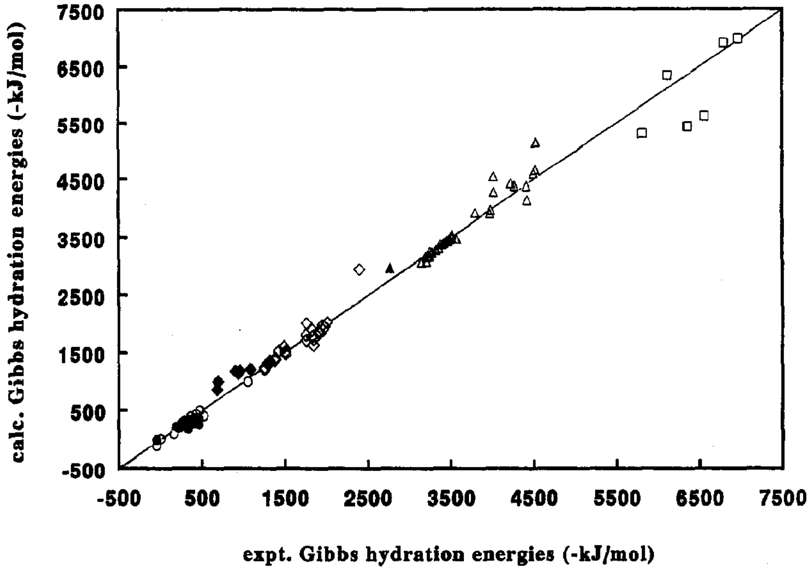

Fig. 3. Calculated versus experimental values of $-\Delta\text{hyd}G^*$. Empty symbols: cations, filled symbols: anions; circles: univalent, diamonds: divalent, triangles: trivalent, squares: quadrivalent.

dent basis, and the procedure is inverted: $S^*_V = \Delta\text{hyd}S^* - (S^*_{II} + S^*_{III} + S^*_{IV})$ (note that $S^*_I = 0$) and similarly for C^*_{pV}. The correlation between values of S^*_V and C^*_{pV} is shown in Fig. 6. Ions with $S^*_V \geq 20$ J K^{-1} mol^{-1} are considered to be definitely 'structure-breaking', those with $S^*_V \leq -20$ J K^{-1} mol^{-1} are 'structure-making' and those in between are 'border-line' ions. Similarly,

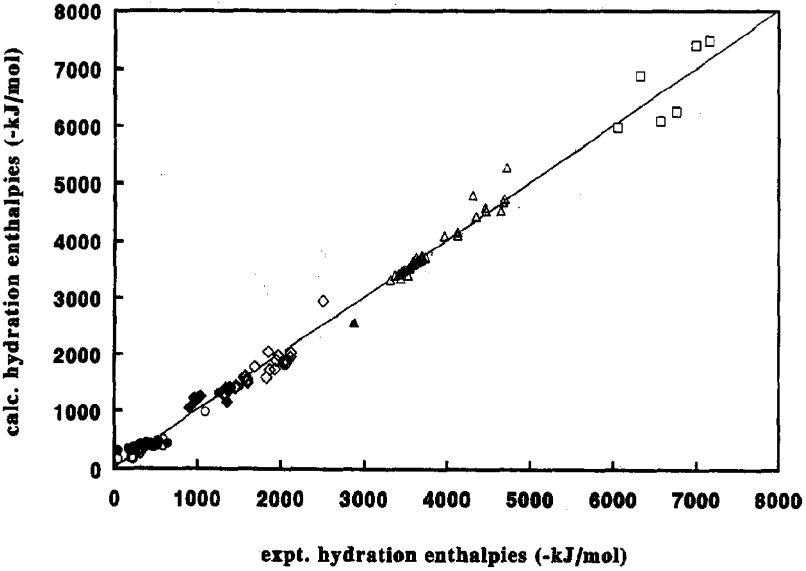

Fig. 4. Calculated versus experimental values of $-\Delta\text{hyd}H^*$. Empty symbols: cations, filled symbols: anions; circles: univalent, diamonds: divalent, triangles: trivalent, squares: quadrivalent.

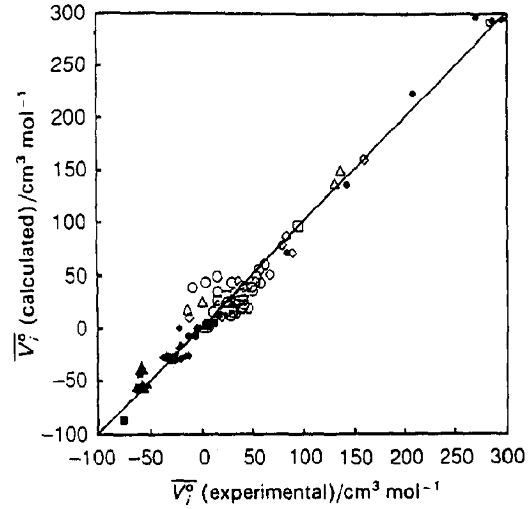

Fig. 5. Calculated versus experimental values of $\overline{V}^\infty$. Filled symbols: cations, empty symbols: anions; circles: univalent, diamonds: divalent, triangles: trivalent, squares: quadrivalent. (From ref. [7], by permission.)

ions with $C^*_{pV} \leqslant 150$ J K^{-1} mol^{-1} are considered to be definitely 'structure-breaking', those with $C^*_{pV} \geqslant 200$ J K^{-1} mol^{-1} are 'structure-making' and those in between are 'border-line' ions. If the premise [21] that $G^*_V = 0$ is accepted, then $H^*_V = TS^*_V$ and is completely negligible compared with the other terms making up ΔhydH^*, its omission from Fig. 4 thus being justified.

5. Failures of the model and/or the data

Figs. 3, 4, and 5 show an overall good fit of the calculated values with the experimental data. The structure-making and structure-breaking properties of the ions deduced from Fig. 6 are also reasonable. There are, however, instances where the fit is not good, that ought to be explained.

Among ions that exhibit deviations of the calculated from the experimental ΔhydG^* or ΔhydH^* should be mentioned the 'soft' cations, and their fit can be considerably improved (and brought into line with the above-mentioned average deviations) if $-400\sigma_M$ is added, where σ_M is their softness parameter [22]. The softness of the cations implies some covalent character to the bonding with the nearest water molecules, causing ΔhydH^* (and ΔhydG^*) to become more negative, but no similar correction need be in-

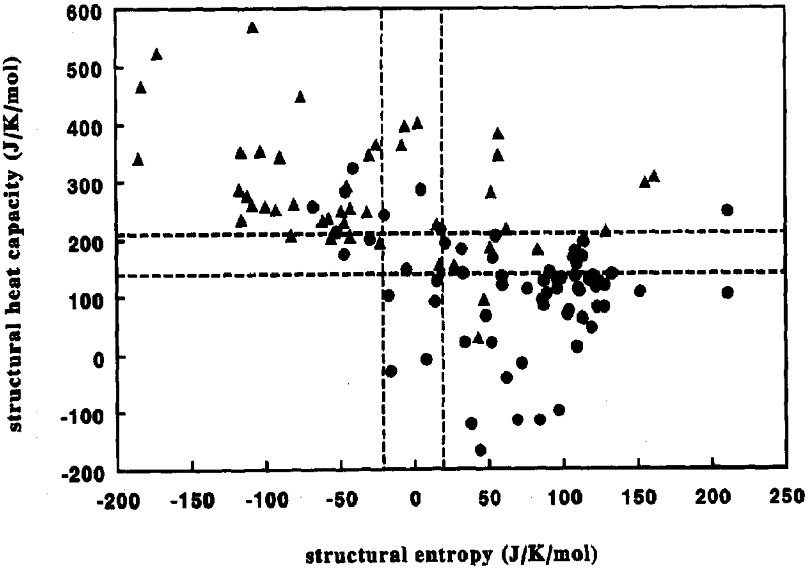

Fig. 6. The values C^*_{pV} plotted against S^*_V. Circles: cations, triangles: anions. The upper left-hand quarter pertains to structure-breaking ions, the lower right-hand one to structure-making ions, and the regions between the dashed lines to borderline ones.

cluded for 'hard' ions, where electrostatic binding of the water is already implied in the stage III term. From this added softness term profit the fits of Ag^+, Au^+, Cu^{2+}, Zn^{2+}, Pt^{2+}, Pd^{2+}, Cd^{2+}, Tl^{3+}, and Bi^{3+} (as well as Pb^{2+} for $\Delta \text{hyd} H^*$), but those of Tl^+, Sn^{2+}, Hg^{2+} (and Pb^{2+} for $\Delta \text{hyd} G^*$) become somewhat worse. In the case of $\Delta \text{hyd} H^*$ of Ga^{3+} the fit on correction for softness becomes quite bad, leading to the suspicion that the reported experimental data are incorrect. No reliable values of σ_M are available for the soft Cu^+, Ag^{2+}, and Au^{3+} ions, but the deviations between the experimental and calculated values are all in the direction that the fit would improve if reasonable values of σ_M were assigned to these cations.

The model fails seriously (considerably more negative calculated $\Delta \text{hyd} G^*$ and $\Delta \text{hyd} H^*$ values than the experimental ones) for the very small Be^{2+}, Al^{3+}, Cr^{3+}, Hf^{4+} and Zr^{4+} (for the latter two only $\Delta \text{hyd} H^*$) cations, as well as (considerably less negative calculated $\Delta \text{hyd} G^*$ and $\Delta \text{hyd} H^*$ values than the experimental ones) for the larger tetravalent cations. In the cases of the more highly charged cations that are liable to hydrolyze one may suspect the reliability of the data. An explanation that was advanced for the discrepancy with the small cations is their large n values (see Table 2). These cause some of the water in the hydration shell to be more remote from the ion, so that a lower field is 'seen' by them. This means that a larger ϵ' applies, and consequently a more positive G^*_{III} and H^*_{III}, leading to less negative calculated $\Delta \text{hyd} G^*$ and $\Delta \text{hyd} H^*$. For the divalent first row transition metal cations the calculated $\Delta \text{hyd} H^*$ (but not $\Delta \text{hyd} G^*$) values are less negative than they should have been by 170 to 190 kJ/mol, outside of the average deviations noted for other divalent cations and difficult to explain.

The model yields $\Delta \text{hyd} G^*$ and $\Delta \text{hyd} H^*$ values too negative by 100 to 200 kJ/mol for the larger divalent anions ($r \geqslant 240$ pm) deviating more seriously than the average deviation shown by smaller divalent and the monovalent anions. On the other hand, a series of monovalent anions (F^-, HSe^-, OCN^-, BO_2^-, IO_3^-, ReO_4^-, HSO_4^-, and $H_2PO_4^-$) have calculated values of $\Delta \text{hyd} G^*$ not sufficiently negative by 100-150 kJ/mol. No ready explanation is apparent for these discrepancies: problems with hydrolysis of anions of the weaker acids may have caused some errors in the data, but it is impossible to pinpoint such definite errors. Among those anions that have relatively large negative deviations of $\Delta \text{hyd} H^*$ (about -100 kJ/mol) are anions of strong acids (I^-, NO_3^-, BF_4^-, MnO_4^-, and ClO_4^-) and these cases cannot be explained away in terms of hydrolysis.

Since the model has been very recently applied [7] to the partial molar volumes, with comments about eventual discrepancies, no further comments are required at this point.

A point that ought to be noted concerning the entropy of hydration is that the thermodynamic identity $\Delta \text{hyd} G^* = \Delta \text{hyd} H^* - T \Delta \text{hyd} S^*$ must be obeyed, as it does for the experimental values. This is the case also with the expressions for stages I, III, and IV of the model, but not, however, for stage II. The dependencies in this stage on the size and charge of the ions have been 'tailored' empirically to obtain good fits for the various thermodynamic functions, with coefficients based on the behavior of the uncharged analogs: noble gas atoms and approximately spherical hydrocarbon molecules.

The calculated values of the entropy and the heat capacity of hydration lack the contribution from stage V, that is not known independently but constitutes an important part of the whole. It is, therefore, impossible to point out discrepancies, unless the structure-making or structure-breaking behavior predicted from the model (see above) is inconsistent between the entropy and the heat capacity or with what is known from other kinds of data, e.g., the Dole-Jones B coefficients of viscosity [8,23]. The following ions that are deemed to be structure-breaking according to one criterion are borderline according to the other: K^+, Ba^{2+}, IO_3^-, SO_4^{2-}, MoO_4^{2-}, and WO_4^{2-}, or structure-making and borderline: Au^+, $(C_2H_5)_4N^+$, Hg^{2+}, In^{3+}, Sm^{3+}, Nd^{3+}, Pr^{3+}, La^{3+}, F^-, OH^-, and AlO_2^-. The deviations (in J K^{-1} mol^{-1}) in these cases are ± 20 for S^*_V and ± 50 for C^*_{pV}. More serious are the cases where one criterion designates ions to be structure-making and the other structure-breaking: these are rare among cations (Hg_2^{2+} and UO_2^{2+}) but more common among anions: ClO^-, BrO^-, HO_2^-, BO_2^-, $H_2PO_4^-$, HPO_4^{2-}, CO_3^{2-}, SO_3^{2-}, and PO_4^{3-}. There are good reasons to suspect the accuracy of some of the data that lead to these discrepancies.

6. Discussion

Table 2 presents a large amount of thermodynamic data concerning the hydration of ions. Included are ions ranging in charge from ±1 to ±4, and in size from 40 to 440 pm (as the radius of the equivalent sphere). In shape they vary from spherical (monoatomic ions) or nearly so (symmetrical tetrahedral or octahedral ions) to elongated (e.g., Br_3^-) or flat (e.g., $AuCl_4^-$) ellipsoids of rotation or with pendant atoms (e.g., HSO_4^-). Some of the ions are not particularly stable in aqueous solutions (e.g., Ag^{2+}) or are readily hydrolyzed (e.g., Zr^{4+}), and for these the data are possibly inaccurate. It is attempted to present as full a picture as could be obtained from the literature at the time of writing. It should be noted that many ions of possible interest are missing altogether from the table, as are data of some thermodynamic functions for ions that are included. These gaps are challenges for experimentalists in the future, but it is hoped that the model presented here gives some guidelines for the approximate numerical values that can be expected.

The model presented above was anticipated by others, although not for all the thermodynamic functions and not for the variety of ions discussed here, and not in the details concerning the width of the hydration shell. The latter point is, perhaps, the crucial one in distinguishing the present model from its predecessors. That the values of Δr employed here are realistic is shown by their relationship to values obtained by neutron diffraction [24] for Ni^{2+} and Dy^{3+} and to molar conductivities of uni- and di-valent cations and anions, as shown previously [3,7].

For the Gibbs free energy and enthalpy of hydration of the monoatomic cations and the smaller anions (up to, say, $r = 230$ pm) the terms for stages I and III are the major contributions. These together constitute the Born expression [18] (for the Gibbs free energy), albeit for the modified radius $r + \Delta r$, rather than the ionic radius r of the original expression. Over half a century ago, Latimer, Pitzer and Slansky [25] recognized the dielectric saturation near the ion (implicitly specifying the temperature-independent $\epsilon' = 1$) and the necessity of adding a quantity Δr to the ionic radius, since otherwise the Born expression over-estimates the work done by the hydration of the ion. They confined their treatment to the alkali metal cations and halide anions, and specified $\Delta r = 85$ pm for the former and 10 pm for the latter (cf. the values in Table 2) to obtain the best fit of $\Delta \mathrm{hyd} G^0$ and $\Delta \mathrm{hyd} S^0$.

Many other authors have since tried to improve on this and consider a wider choice of ions, as data became available. Most directly influencing the present model was the work of Abraham and co-workers [19,20,26]. They first specified $\epsilon' = 2$, then modified it to $\epsilon' = 1.05\ n_D^2 = 1.87$, and $(\partial \epsilon'/\partial T)_P = -1.60 \times 10^{-3}\ K^{-1}$ (the value for nonpolar solvents with $\epsilon = 2$), then modified this to $-0.24 \times 10^{-3}\ K^{-1}$, and also $(\partial^2 \epsilon'/\partial T^2)_p = 0$. They took for Δr the radius of a water molecule, 155 pm, obtained from the molar volume, then adjusted it to 147 pm, or let it vary between 92 and 162 pm as a fitting parameter for $\Delta \mathrm{hyd} G^0$. They applied their treatment to several other solvents besides water (yielding better results for the thermodynamics of solvation than of hydration), but considered only sodium, potassium, rubidium, cesium, chloride, bromide, iodide and perchlorate ions, employing radii r for the cations that are at variance with those employed here [11]. They did not consider water-structural effects in $\Delta \mathrm{hyd} S^0$, and indeed found for aqueous solutions a large discrepancy between the values given by their model and the observed data. This omission was corrected in the case of the heat capacity of hydration [6].

Further recent work that has been of influence is that of Rashin and co-workers [27-29], who consistently applied the continuum model with the Born approach to the energetics. A major difference is in the specification of Δr, based in Rashin's work on the minimum in the electron density map in ionic crystals. This leads to cavity radii for cations being their covalent radii, rather than the ionic radii used for anions, with a 7% correction for both kinds of ions [27]. Specifications for the calculation of the cavity radius for non-spherical ions, based on the individual atoms in the ion, were given [28] but the calculations are much more complicated than the simplistic model of an equivalent sphere based on the half-diameters of the ellipsoids of rotation used here. The entropies of hydration do take into account the number of water molecules affected by interaction with the ion, [29] but again in a manner different from that employed here. The entropy and enthalpy calculations, thus, do not relate to the same model.

Other authors have dealt with a wider choice of ions in their treatments, but the purpose of this paper is not to review previous work; that was done elsewhere [1–8,11]. The simplicity of the present model speaks for itself, although it carries with it the inadequacy to deal as accurately as the experimental data warrant with the thermodynamic functions studied. The representation of non-spherical ions as equivalent spheres and the assignment of radii to them is a major source of possible error. Other reasons for discrepancies that are noted are discussed above.

7. Conclusions

As mentioned at the beginning of the introduction, it is hardly to be expected that a simple model would be able to account quantitatively for all the studied thermodynamic functions of hydration of ions varying in charge from -4 to $+4$, in radius (if spherical) from 40 to >400 pm, and in shape from spherical to elongated elipsoids of rotation. It is remarkable, however, how effectively the model does account for the data, see Figs. 3–6. The main features of the original ideally conceived model are retained: the five stages in the process of hydration with the corresponding expressions and the width Δr of the hydration shell and the number $n = A|z|/r$ of water molecules in it (involving the fitting parameter $A = 360$ pm). Some features have to be discarded: the use of $\epsilon' = n_D^2$ and its derivatives for the hydration shell in stage III, the systematic use of data for particles with $z = 0$ for stage II, and independent estimates of the contributions from stage V. The first of these, ϵ', requires replacement with *ad hoc* fitting parameters, except for $\bar{V}^\infty$, where a more far reaching modification is required to account for the packing of the water molecules. The data for stage II are augmented by further empirical fitting parameters, while for stage V, in the cases of the entropy and heat capacity of hydration, only qualitative results are provided by the model. Correlation of S_V^* and C_{pV}^* with other, independent, measures of water structure-making and structure-breaking may eventually lead to predictive abilities of the model for these functions too [30].

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Discussion to the paper by Y. Marcus

Comments

By A. Rashin

(1) Your paper is an excellent source of experimental data for your fellow theoreticians, in addition to being a theoretical exercise itself. Therefore, my first set of questions addresses the data collected in your review.

(a) The set of hydration entropies in your Table 2 (especially for alkali and halide ions) seems more acceptable to me than the one in Table 2.25 of the "Solvation thermodynamics" by Ben-Naim (the data in that table are taken from ref. [1]). While hydration enthalpy e.g., for KI in Ben-Naim's compilation and in yours is about the same: −620.25 kJ/mol (Ben-Naim) and −620 kJ/mol (in yours), hydration entropies for KI are drastically different: −50.9 J/K/mol (Ben-Naim) and −148 J/K/mol (in yours). Similar differences are found for other alkali-halide pairs. Can you explain the difference? Readers will use both sources as authoritative and will be confused.

(b) What is your assessment of the accuracy of different types of data included in your Table 2? It would be very handy if you could provide a little table as an answer to be published. It could be used and referenced by many researchers.

(2) I find some difficulties in your five-stage process.

(a) Words "without changing its size" are rather tricky. When in the second stage you allow neutral "ion-size" particle to interact through dispersion forces and through water-dipole induced dipole (on neutral ion) interactions, I would expect you to find a substantial repulsion (positive energy). This is because the size of the ion in water is determined by a balance of the electrostatic attraction between water and the charged ion (which is zero at stage 2) and all other interactions (most if not all of which are included at this stage). The sizes of ionic and neutral particles with the same Lennard-Jones parameters are different, and one would have to push to keep the size of a neutral particle the same as that of an ion. This positive enthalpic term cannot be extracted from the data on hydrocarbon transfer, and, thus, is ignored. This may make your scheme less consistent. It seems like approximating stage 2 by transfer of a somewhat larger hydrocarbon would be more consistent.

(b) It looks like you complicate the process by first creating a cavity for a hydrophobic particle. Such cavities have their peculiar characteristics not easy to understand. Then you transform them into the cavities for ions which have their peculiar characteristics. Thus, we have to deal with shifting reference states, each of them with its own problem. I do not claim that I have a much better solution, and I do not know, for example, whether for ions the Born entropy and that calculated from probability functions [2] should be added together, or the Born term is just a part of that calculated from probability distributions.

If you could offer some clarifying comments on the physics of your five stages, or any other subdivisions of the total transfer, it would be very valuable.

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Response by Y. Marcus, to Comments

To A. Rashin

(1a, 1b) The source of the (conventional) $\Delta_{\mathrm{hyd}}H^0$ data for most of the ions (in particular, the alkali metal and halide ones) is the differences between the $\Delta_f H^0$ of the (aq) and (g)-standard states of the ions in my ref. [10]: the NBS Tables. This is the most authoritative and internally consistent source of such data. Their accuracy is specified there by the number of significant digits reported. Often to two decimal places in e.g. $\Delta_{\text{hyd}}H^0/\text{kJ mol}^{-1}$, and an uncertainty of 8 to 80 in the last digit reported. The $\Delta_{\text{hyd}}S^0$ are the differences between the S^0 data of the ions in these states from my ref. [11], where for the (aq) state the source is, again, the NBS Tables and for the (g) state the calculations specified there or in A. Loewenschuss and Y. Marcus, J. Phys. Chem. Ref. Data 16 (1987) 61. Then $\Delta_{\text{hyd}}G^0 = \Delta_{\text{hyd}}H^0 - T\,\Delta_{\text{hyd}}S^0$ was obtained. For a discussion of the uncertainties and sources of data for ions not in the NBS Tables, see refs. [3–7]. The conversion to the *absolute* values adds small uncertainties, as specified in Eqs. (3a)–(3e). In the specific case of KI, these sources yield $\Delta_{\text{hyd}}S^0$ of $K^+ = -52.1$, that of $I^- = -58.1$, together -110.2 J K^{-1} mol^{-1}. Conversion to the *-quantities (transfer from fixed position in the gas to fixed position in the solution, Eq. (2c), then adds -18.9 J K^{-1} mol^{-1} per ion, giving together $-110.2 - 2 \times 18.9 = -148$ J K^{-1} mol^{-1}, the value given in the paper.

I cannot answer for the source of Ben-Naim's hydration entropies in the reference quoted by you.

(2a, 2b) I tried to keep the model 'simple', hence had knowingly to gloss over such difficulties as you mention. These are reflected by the necessity to add empirical terms to ΔY_{II} (beyond the $a_{\text{II}} - b_{\text{II}}r$ that apply to inert gas atoms) and to replace $\epsilon' = n_D^2$ and its temperature and pressure derivatives by empirical fitting quantities. These empiricisms take care – to a certain extent – of the points that you rightly raise in criticism of the model.