J. CHEM. SOC. FARADAY TRANS., 1991, 87(18), 2995–2999

Thermodynamics of Solvation of Ions

Part 5.—Gibbs Free Energy of Hydration at 298.15 K†

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The standard molar Gibbs free energies of hydration, $\Delta_{hyd}G^0$, of 109 (mainly inorganic) ions ranging in their charges from -3 to $+4$ have been compiled and interpreted in terms of a model used previously for other thermodynamic quantities of hydration. The main contributions to $\Delta_{hyd}G^0$ are the electrostatic effects, resulting in solvent immobilization, electrostriction, and dielectric saturation in a hydration shell of specified thickness, and further such effects on the water that surrounds this shell. Other effects contribute to $\Delta_{hyd}G^0$ to a minor extent only.

In a recent series of papers, the standard molar heat capacity,[1] entropy,[2] and enthalpy[3] of hydration of ions at room temperature (298.15 K) were examined. The single-ion thermodynamic properties were obtained from appropriate extrathermodynamic assumptions, and the validity of the tetraphenylarsonium tetraphenylborate (TATB) assumption for this purpose was examined too.[4] These thermodynamic quantities of hydration were then interpreted on the basis of a common model.[5] This model had features that had already been suggested by others (*e.g.* Abraham and Liszi),[6] but differed in some respects, and its applicability to all these quantities as well as to other ones (*e.g.* the partial molar volume) could be demonstrated. Its applicability to the standard molar Gibbs free energy of hydration was not presented in detail, however.

Lists of standard molar Gibbs free energies of hydration of ions have been published.[7,8] A more complete data base of these quantities has been assembled recently, and it is the purpose of this paper to present it and interpret it on the basis of the above-mentioned model.

Model

The model[5] characterizes the ion by its charge, z, and its radius, r, and does not distinguish between cations ($z > 0$) and anions ($z < 0$) having the same radius and absolute values of the charge. The environment of the ion is divided into two regions: a hydration shell, in which the water is immobilized and electrostricted, and bulk water, that is, however, under the influence of the electric field of the ion. The thickness, Δr, of the hydration shell is specified as follows. The number n of water molecules in this shell is given by:

$$n = A|z|/r \tag{1}$$

where A is the fitting parameter of the model, and is equal to 0.36 nm, as found for fitting $\Delta_{hyd}H^0$ data.[5] Each of these n water molecules occupies a volume of $\pi d^3/6$, where $d = 0.276$ nm is the diameter of a water molecule. Hence the volume of the hydration shell is:

$$n\pi d^3/6 = (4\pi/3)[(r + \Delta r)^3 - r^3] \tag{2}$$

where the right-hand side is the volume of the spherical shell of thickness Δr surrounding the ion of radius r. This thickness, Δr, is obtained by algebraic manipulation of eqn. (1) and (2).

The ion interacts with its environment in a manner that provides the following independent contributions to the thermodynamic quantities of hydration. A cavity in the water of radius $r + \Delta r$ is formed, and the ion with its hydration shell is permitted to interact with the bulk water as if it were uncharged, *i.e.* by means of dispersion, dipole–induced dipole *etc.* forces. Then the charge is 'turned on', and the electric field causes dielectric saturation in the hydration shell. The permittivity of the water is considered to follow a step function, having the value $\varepsilon' = n_D^2$ (where n_D is the refractive index at the D line) in the hydration shell and its bulk value ε beyond the distance $r + \Delta r$ from the centre of the ion. Finally, effects of the ion on the structure of the water beyond those implicitly taken into account in the contributions just described are also recognized for the calculation of the standard thermodynamic functions of hydration or partial molar quantities of the aqueous ions.

For the present discussion of the standard molar Gibbs free energy of hydration, these contributions take the following form. The 'neutral term', representing the contribution of the interactions with the charge 'turned off' is taken to equal the corresponding quantity for a suitable gaseous solute (*e.g.* a noble gas):[6]

$$\Delta G_{neut}/\text{kJ mol}^{-1} = 41 - 87[(r + \Delta r)/\text{nm}] \tag{3}$$

The Gibbs free energy of the electrostatic interactions in the hydration shell is given by:

$$\Delta G_{el1} = (N_{av}e^2/8\pi\varepsilon_0)z^2(1 - 1/\varepsilon')[\Delta r/r(r + \Delta r)] \tag{4}$$

and that for the interactions beyond it by:

$$\Delta G_{el2} = (N_{av}e^2/8\pi\varepsilon_0)z^2(1 - 1/\varepsilon)/(r + \Delta r) \tag{5}$$

For water at 298.15 K the sum of these terms is:

$$\Delta G_{el1+2}/\text{kJ mol}^{-1} = -64.5z^2[0.44(\Delta r/r) + 0.987]/(r + \Delta r) \tag{6}$$

with r and Δr expressed in nm.[5] The contribution of the effects of the ion on the structure of water to the Gibbs free energy of hydration beyond what is already specified by eqn. (3) and (6) is zero, since the structured and unstructured water around the ion are at equilibrium.[9] Hence the Gibbs free energy of interaction of the ion with its surroundings in the infinitely dilute solutions is just the sum of the contributions in eqn. (3) and (6):

$$\Delta_{hyd}G^* = \Delta G_{neut} + \Delta G_{el1+2} \tag{7}$$

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† Part 4: Y. Marcus, *J. Chem. Soc., Faraday Trans.*, 1987, **83**, 2985.

Table 1 The radius, r, width of hydration shell, Δr, number of water molecules in this shell, n, and the electrostatic contribution, ΔG_{el1+2}, calculated values [from eqn. (12)], $\Delta_{hyd}G^*_{calc}$, and experimental values, $\Delta_{hyd}G^*$, of the molar Gibbs energies of hydration of ions

ion	r/nm	Δr/nm	n	ΔG_{el1+2}/kJ mol^{-1}	$\Delta_{hyd}G^*_{calc}$/kJ mol^{-1}	$\Delta_{hyd}G^*$/kJ mol^{-1}
H^+	0.030	0.300	12.0	−1058	−1015	−1050
Li^+	0.069	0.172	5.2	−558	−510	−475
Cu^+	0.096	0.125	3.8	−456	−400	−525
Na^+	0.102	0.116	3.5	−440	−385	−365
Ag^+	0.115	0.097	3.1	−412	−350	−430
K^+	0.138	0.074	2.6	−372	−305	−295
NH_4^+	0.148	0.065	2.4	−358	−285	−285
Rb^+	0.149	0.064	2.4	−356	−285	−275
Tl^+	0.150	0.063	2.4	−355	−280	−300
Cs^+	0.170	0.049	2.1	−328	−245	−250
$(CH_3)_4N^+$	0.280	0.014	1.3	−221	−75	−160
$(C_2H_5)_4N^+$	0.337	0.008	1.1	−186	0	0
$(C_6H_5)_4As^+$	0.425	0.004	0.8	−149	125	50
Be^{2+}	0.040	0.322	18.0	−3225	−3150	−2395
Ni^{2+}	0.069	0.233	10.4	−2111	−2005	−1980
Mg^{2+}	0.072	0.227	10.0	−2049	−1940	−1830
Cu^{2+}	0.073	0.224	9.9	−2030	−1920	−2010
Co^{2+}	0.075	0.220	9.6	−1992	−1880	−1915
Zn^{2+}	0.075	0.220	9.6	−1992	−1880	−1955
Fe^{2+}	0.078	0.213	9.2	−1940	−1825	−1840
V^{2+}	0.079	0.211	9.1	−1923	−1805	−1825
Cr^{2+}	0.082	0.205	8.8	−1876	−1755	−1850
Mn^{2+}	0.083	0.203	8.7	−1861	−1740	−1760
Pd^{2+}	0.086	0.197	8.4	−1819	−1695	−1910
Ag^{2+}	0.089	0.180	8.1	−1780	−1735	−1865
Sn^{2+}	0.093	0.183	7.7	−1731	−1600	−1490
Cd^{2+}	0.095	0.180	7.6	−1708	−1575	−1755
Ca^{2+}	0.100	0.171	7.2	−1656	−1515	−1505
Hg^{2+}	0.102	0.168	7.1	−1636	−1495	−1760
Yb^{2+}	0.105	0.163	6.9	−1608	−1460	−1510
Sr^{2+}	0.113	0.150	6.4	−1541	−1385	−1380
Eu^{2+}	0.117	0.145	6.2	−1511	−1350	−1385
Pb^{2+}	0.118	0.143	6.1	−1504	−1345	−1425
Sm^{2+}	0.119	0.138	6.1	−1497	−1335	−1375
Ba^{2+}	0.136	0.118	5.3	−1390	−1210	−1250
Ra^{2+}	0.143	0.109	5.0	−1352	−1160	−1250
Al^{3+}	0.053	0.324	20.4	−5661	−5450	−4525
Cr^{3+}	0.062	0.296	17.4	−5007	−4965	−4010
Co^{3+}	0.061	0.299	17.7	−5069	−4830	−4495
Ga^{3+}	0.062	0.296	17.4	−5006	−4765	−4515
V^{3+}	0.064	0.291	16.9	−4886	−4640	−4220
Fe^{3+}	0.065	0.288	16.6	−4829	−4580	−4265
Ti^{3+}	0.067	0.282	16.1	−4722	−4680	−4015
Au^{3+}	0.070	0.275	15.4	−4569	−4530	−4420
Sc^{3+}	0.075	0.262	14.4	−4348	−4065	−3795
In^{3+}	0.079	0.253	13.7	−4191	−3895	−3980
Lu^{3+}	0.086	0.237	12.6	−3954	−3635	−3515
Yb^{3+}	0.087	0.235	12.4	−3923	−3600	−3570
Tl^{3+}	0.088	0.233	12.3	−3893	−3565	−3970
Tm^{3+}	0.088	0.233	12.3	−3893	−3565	−3515
Er^{3+}	0.089	0.231	12.1	−2864	−3535	−3495
Y^{3+}	0.090	0.228	12.0	−3835	−3500	−3450
Ho^{3+}	0.090	0.228	12.0	−3835	−3500	−3470
Dy^{3+}	0.091	0.226	11.9	−3808	−3470	−3425
Tb^{3+}	0.092	0.223	11.7	−3780	−3440	−3400
Gd^{3+}	0.094	0.220	11.5	−3728	−3380	−3375
Eu^{3+}	0.095	0.218	11.4	−3702	−3350	−3360
Sm^{3+}	0.096	0.216	11.3	−3677	−3325	−3325
Pm^{3+}	0.097	0.214	11.1	−3653	−3295	−3250
Nd^{3+}	0.098	0.212	11.0	−3629	−3270	−3280
Pr^{3+}	0.100	0.209	10.8	−3583	−3215	−3245
Ce^{3+}	0.101	0.207	10.7	−3561	−3190	−3200
Pu^{3+}	0.101	0.207	10.7	−3561	−3190	−3235
Bi^{3+}	0.102	0.205	10.6	−3539	−3165	−3480
U^{3+}	0.104	0.201	10.4	−3497	−3115	−3205
La^{3+}	0.105	0.203	10.3	−3476	−3090	−3145
Hf^{4+}	0.071	0.306	20.3	−7892	−7305	−6965
Zr^{4+}	0.072	0.303	20.0	−7810	−7215	−6790
Ce^{4+}	0.080	0.283	18.0	−7231	−6575	−6120
Pu^{4+}	0.093	0.253	15.5	−6513	−5755	−6560
U^{4+}	0.097	0.245	14.8	−6333	−5545	−6360
Th^{4+}	0.100	0.239	14.4	−6208	5395	−5815

Table 1 (continued)

ion	r/nm	Δr/nm	n	$\Delta G_{\mathrm{el1+2}}$/kJ mol^{-1}	$\Delta_{\mathrm{hyd}}G^*_{\mathrm{calc}}$/kJ mol^{-1}	$\Delta_{\mathrm{hyd}}G^*$/kJ mol^{-1}
F^-	0.133	0.079	2.7	−380	−345	−465
OH^-	0.133	0.079	2.7	−380	−345	−430
HCO_3^-	0.156	0.059	2.3	−346	−310	−335
$CH_3CO_2^-$	0.162	0.055	2.2	−338	−300	−365
HCO_2^-	0.169	0.050	2.1	−329	−290	−395
NO_3^-	0.179	0.044	2.0	−317	−275	−300
IO_3^-	0.181	0.043	2.0	−315	−270	−400
Cl^-	0.181	0.043	2.0	−315	−270	−340
BrO_3^-	0.191	0.038	1.9	−303	−260	−330
CN^-	0.191	0.038	1.9	−303	−260	−295
NO_2^-	0.192	0.037	1.9	−302	−255	−330
N_3^-	0.195	0.035	1.9	−299	−250	−295
Br^-	0.196	0.035	1.8	−297	−250	−315
ClO_3^-	0.200	0.033	1.8	−293	−245	−280
$H_2PO_4^-$	0.200	0.033	1.8	−293	−245	−465
OCN^-	0.203	0.032	1.8	−290	−240	−365
SeH^-	0.205	0.032	1.8	−288	−240	−360
SH^-	0.207	0.031	1.7	−285	−235	−295
SCN^-	0.213	0.029	1.7	−279	−230	−280
I^-	0.220	0.026	1.6	−272	−220	−275
BF_4^-	0.232	0.023	1.6	−261	−205	−190
MnO_4^-	0.240	0.021	1.5	−253	−195	−235
ClO_2^-	0.240	0.021	1.5	−253	−195	−205
BO_2^-	0.240	0.021	1.5	−253	−195	−460
ClO_4^-	0.250	0.019	1.4	−245	−180	−430
ReO_4^-	0.260	0.017	1.4	−237	−170	−330
$B(C_6H_5)_4^-$	0.421	0.004	0.9	−150	15	50
CO_3^{2-}	0.178	0.076	4.0	−1195	−1300	−1315
S^{2-}	0.184	0.070	3.9	−1171	−1280	−1315
SO_3^{2-}	0.200	0.059	3.6	−1112	−1230	−1295
SO_4^{2-}	0.230	0.043	3.1	−1010	−1145	−1080
CrO_4^{2-}	0.240	0.039	3.0	−979	−1120	−950
SeO_4^{2-}	0.243	0.038	3.0	−970	−1110	−900
SiF_6^{2-}	0.259	0.032	2.8	−923	−1075	−930
$PtCl_6^{2-}$	0.313	0.020	2.3	−787	−955	−685
$PdCl_6^{2-}$	0.319	0.018	2.3	−744	−945	−695
PO_4^{3-}	0.238	0.054	4.5	−2153	−2835	−2765

Data Base

Most of the values of the standard molar Gibbs free energy of hydration of the ions, $\Delta_{\mathrm{hyd}}G^0$, at 298.15 K have been presented previously,[7] based on the conventional values ($\Delta_{\mathrm{hyd}}G^0_{\mathrm{conv}}[\mathrm{H}^+] = 0$) in the NBS compilation.[10] They are converted to the absolute values by means of the expression:

$$\Delta_{\mathrm{hyd}}G^0 = \Delta_{\mathrm{hyd}}G^0_{\mathrm{conv}} - 1056z \text{ kJ mol}^{-1} \qquad (8)$$

corresponding to the choice $\Delta_{\mathrm{hyd}}G^0[\mathrm{H}^+] = -1056$ kJ mol^{-1}. This choice, in turn, is based on the choices[7] of the values $\Delta_{\mathrm{hyd}}H^0[\mathrm{H}^+] = -1094$ kJ mol^{-1} and $\Delta_{\mathrm{hyd}}S^0[\mathrm{H}^+] = -131$ J K^{-1} mol^{-1} or $\bar{S}^\infty[\mathrm{H}^+(\mathrm{aq})] = -22.2$ J k^{-1} mol^{-1}. The uncertainty in $\Delta_{\mathrm{hyd}}G^0[\mathrm{H}^+]$ is ±6 kJ mol^{-1} and is the same as that of $\Delta_{\mathrm{hyd}}H^0[\mathrm{H}^+]$. The latter value is consistent, though not identical, with the value preferred later,[3] -1103 ± 7 kJ mol^{-1}, based on the TATB assumption. Conway[11] in his examination of the single-ion thermodynamic values of solvation chose the value $\Delta_{\mathrm{hyd}}G^0[\mathrm{H}^+] = -1066 \pm 17$ kJ mol^{-1} on the basis of the data known at the time, consistent with our choice of -1056 ± 6 kJ mol^{-1}. Therefore the conversion expression (8) is employed in the present study.

Several further values are included in the data base, that are not available from the NBS compilation.[10] These pertain to V^{2+}, V^{3+} Ag^{2+}, Ti^{3+}, Cr^{3+}, and Au^{3+}, taken from Bartsch and Lagowski,[12] and several further values calculated from

$$\Delta_{\mathrm{hyd}}G^0 = \Delta_{\mathrm{hyd}}H^0 - T[\bar{S}^\infty(\mathrm{aq}) - S^0(\mathrm{g})] \qquad (9)$$

for $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(C_6H_5)_4As^+$, Sm^{2+}, Yb^{2+}, U^{4+}, Pu^{4+}, SeH^- OCN^-, BO_2^-, ClO_2^-, IO_3^-, ReO_4^-, $(C_6H_5)_4B^-$, HCO_2^-, $CH_3CO_2^-$, HCO_3^-, $H_2PO_4^-$, CO_3^{2-}, SO_3^{2-} SeO_4^{2-}, CrO_4^{2-}, SiF_6^{2-}, $PdCl_6^{2-}$, $PtCl_6^{2-}$, and PO_4^{3-}, with values of $\Delta_{\mathrm{hyd}}H^0$, $\bar{S}^\infty$ (aq), and S^0(g) from previous publications.[2,3,13] Altogether the data base included 109 ions, with charges, z, ranging from −3 to +4. For several further ions: $C_2H_5NH_3^+$, $(CH_3)_2NH_2^+$, $(C_4H_9)_4N^+$, Mn^{3+}, PO_3^- and SbF_6^-, although $\Delta_{\mathrm{hyd}}H^0$ is known,[3,14] either $\bar{S}^\infty$(aq) or S^0(g) or both are unknown, so that $\Delta_{\mathrm{hyd}}G^0$ could not be calculated.

The standard molar Gibbs free energy of hydration, $\Delta_{\mathrm{hyd}}G^0$, includes a term for the compression of the space available to the ion on its transfer from its gaseous to its aqueous standard states, that is foreign to the solvation (hydration) process proper. This process, that pertains directly to the interactions of the ion with its surroundings as specified by eqn. (7), is the transfer of the ion from a fixed point in the gas to a fixed point in the solution.[15] Hence it is necessary to add $RT\ln[RT/V_0P_0] = 7.93$ kJ mol^{-1} at 298.15 K to $\Delta_{\mathrm{hyd}}G^0$, irrespective of the charge of the ion, to give $\Delta_{\mathrm{hyd}}G^*$. In this expression $V_0 = 0.001$ m^3 (1 dm^3) is the standard volume of the aqueous solution and $P_0 = 0.1$ MPa is the relevant pressure. Admittedly, this correction is negligible in practice, but has to be applied in principle.

The values of $\Delta_{\mathrm{hyd}}G^*$ are shown in Table 1, along with the values of r^{13} and the derived values of Δr and n from eqn. (1) and (2). Since it is claimed that the model employed pertains to all the thermodynamic functions of hydration, the value of A in eqn. (1) obtained from the fitting of $\Delta_{\mathrm{hyd}}H^0$ data should

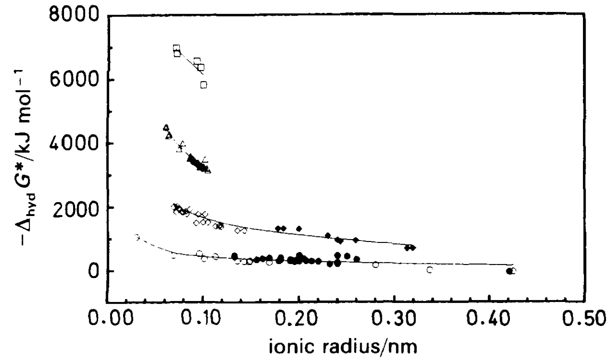

Fig. 1 Values of the experimental $-\Delta_{hyd}G^*$ (symbols) and calculated $-\Delta G_{el1+2}$ (lines) plotted against the radii r of ions: ○, $z = 1$; ●, $z = -1$; ◇, $z = 2$; ◆, $z = -2$; △, $z = 3$; □, $z = 4$

also be applicable to the fitting of the $\Delta_{hyd}G^0$. Eqn. (6) was used in order to obtain values of ΔG_{el1+2}, and these are also shown in Table 1. The neutral term, ΔG_{neut}, according to eqn. (3) is between 15 kJ mol^{-1} for the smallest ion to 3 kJ mol^{-1} for the largest. The fit of the electrostatic term (continuous lines) to the experimental values of $\Delta_{hyd}G^*$ (symbols) is shown graphically in Fig. 1.

Discussion

Examination of Fig. 1 and of Table 1 shows that the model fits the experimental results remarkably well, considering its simplicity and the wide range of ionic charges, −3 to 4, and sizes, 0.030–0.425 nm, included. However, a detailed look at the entries in Table 1 shows some discrepancies.

One source of discrepancy is the linear decrease of ΔG_{neut} specified in eqn. (3), according to Abraham and Liszi.[6] Inspection of their paper, however, shows that this trend is valid only for the noble gases, but that for hydrocarbons and similar large and globular molecules the dependence of $\Delta_{hyd}G^*$ of the non-electrolytes on their radii has an upward swing. These data conform rather to:

$$\Delta G'_{neut}/\text{kJ mol}^{-1} = 41 - 87(r/\text{nm}) + 1200(r/\text{nm})^2 \qquad (10)$$

This leads to non-negative values of $\Delta_{hyd}G^*$ for the largest ions, as is indeed observed. For such ions the amount of work done to create the cavity in the water in which the ion finds itself is larger than the Gibbs free energy released when the large ion interacts with the water through its charge and through dispersion and induced dipole interactions.

Note that if for the ions the bare ionic radius r is used in eqn. (10) instead of $r + \Delta r$ specified in eqn. (3), this will have a negligible effect for the largest ions. However, this expedient is necessary for ordinary ions (with $r < 0.25$ nm), since otherwise (use of $r + \Delta r$) an over-correction results. This makes this correction empirical, since the cavity should have the size specified by $r + \Delta r$ rather than by r.

Another systematic discrepancy can be noted when the sum of the contributions from eqn. (6) and (10) is compared with the experimental values, mainly for the multi-charged ions. The cations tend to have more negative and the anions more positive calculated values. This tendency could have its origin from the fact that the water molecules in the hydration shell between r and $r + \Delta r$ are oriented differently towards cations and anions. This fact has not been taken into account[5] in the model, and is also at variance with the more simple-minded version of the TATB assumption. Empirical cognizance of this unsymmetric charge effect can be made by inclusion of the term:

$$\Delta G_{unsym} = 120(r/\text{nm})z^3 \qquad (11)$$

on the right-hand side of eqn. (7), producing the values of

$$\Delta_{hyd}G^*_{calc} = \Delta G'_{neut} + \Delta G_{el1+2} + \Delta G_{unsym} \qquad (12)$$

shown in Table 1. The odd power of z in eqn. (11) causes the charge-unsymmetry correction to be negative for anions and positive for cations, and to be more pronounced for the more highly charged ions (and also the larger ones). This correction removes most of the systematic discrepancies, with fits generally to considerably better than $\pm 100|z|$ kJ mol^{-1}. This leaves only more or less non-systematic cases to be explained on an *ad hoc* basis.

These cases include the smallest cations: Be^{2+}, Al^{3+}, Cr^{3+}, Ti^{3+} and Fe^{3+}, that show large negative deviations of the calculated from the experimental values, as well as some larger ions: Cu^+, Hg^{2+}, Tl^{3+}, Bi^{3+}, Pu^{4+}, U^{4+}, IO_3^-, $H_2PO_4^-$, BO_2^-, ClO_2^-, ReO_4^-, $PtCl_6^{2-}$ and $PdCl_6^{2-}$. A plausible explanation in the case of the smallest cations is that some of the many water molecules ($n > 16$) are sufficiently remote from the ion because of the crowding of the first shell, so that a larger ε' than n_D^2 applies to them. Hence a less negative value of ΔG_{el1+2} should have been used. Relatively large positive deviations of the calculated from the experimental values are shown by the four cations, Cu^+, Hg^{2+}, Tl^{3+} and Bi^{3+}, that belong to the very soft group of cations (even Ag^+ that belongs to this group shows a positive deviation, though <100 kJ mol^{-1}). However, no good reason is apparent why water, that is a hard ligand, would cause more negative values of $\Delta_{hyd}G^*$ than the model allows. Reasons for the remaining outlying values could be inaccuracies in the ionic radius or the $\Delta_{hyd}G^*$ employed. The former inaccuracy may apply in particular to the anions, where so-called thermochemical radii have been used.

A case of good conformity of the calculated with the experimental value should be pointed out, since it is artificial, in the sense that the radius r was arbitrarily assigned. This is the case of the hydrogen ion, H^+. Fine-tuning of r might have caused even better agreement, but was considered unnecessary.

Non-conformity of the calculated values for the tetraphenylarsonium and tetraphenylborate ions, 125 and 15 kJ mol^{-1}, with the TATB model, that calls in its simplest version to equal values (here $\Delta_{hyd}G^* = 50$ kJ mol^{-1}) requires some comment. These values of 50 kJ mol^{-1} were obtained by eqn. (9) from $\Delta_{hyd}H^0 = -47$ kJ mol^{-1} [3] and $\Delta_{hyd}S^0 = -302$ J K^{-1} mol^{-1}.[16] The former of these appears to be better established than the latter, that is based on the application of the TATB assumption to $\bar{S}^\infty(MPh_4)$. Whereas the standard molar entropy of a solid compound of Ph_4B^- is known, hence also the corresponding entropy of solution and $\bar{S}^\infty$ for this compound, this is not the case for any compound of Ph_4As^+ (or Ph_4P^+). Therefore this assumption cannot be checked with respect to its conformity with the established value of $\bar{S}^\infty(H^+) = -22.2$ J K^{-1} mol^{-1} on which eqn. (8) is based. An uncertainty therefore is connected with the 'experimental' $\Delta_{hyd}G^*$ values for the tetraphenylarsonium and tetraphenylborate ions. This uncertainty is not expected to be sufficiently large, however, to explain the difference of 110 kJ mol^{-1} between the calculated values, that arises directly from the factor r in the empirical eqn. (11), that appears to require it for ions with $r \leqslant 0.3$ nm. No manipulation of the simple form of this expression is warranted, however, for the special cases of the tetraphenyl ions.

On the whole, however, the model permits remarkably good predictions of $\Delta_{hyd}G^*$ of the ions, given the empirical adjustments in eqn. (10) and (11) relative to the simpler model used previously for fits of $\Delta_{hyd}H^*$ *etc.* Therefore some physical meaning may be ascribed to the parameters of the model, in particular to n and Δr. 'Hydration numbers' are defined

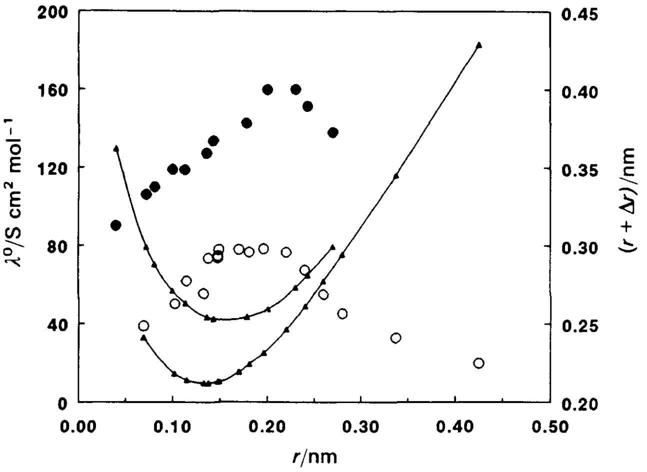

Fig. 2 The molar conductivities and 'hydrated radii' of ions plotted against their radii: circles, λ^0; triangles, $r + \Delta r$; empty, $z = \pm 1$; filled, $z = \pm 2$

operationally only with respect to the method by means of which they are determined. The values of n resulting from the model can be considered as useful 'hydration numbers', combining for multi-charged ions the values for the nearest neighbours with those of the next-nearest neighbours, as determined by X-ray diffraction and similar methods.[17]

The physical significance of Δr, or rather $r + \Delta r$, can be seen in Fig. 2, where the molar conductivity of the uni- and di-valent ions of both kinds of sign and their values of $r + \Delta r$ are plotted against their r values. The former dependent variable shows a maximum approximately where the latter one has a minimum, implying the well known fact that it is the hydrated ion that moves in the electric field. It is significant, however, that the conductivities of cations and anions fall on the same curve and that the equivalent conductivities of all the ions would nearly do so. The non-coincidence of the extrema for the two variables may be due to the fact that the anions are generally larger than the cations, and that structure-making by the larger ions would affect the conductivity but not $\Delta_{\text{hyd}} G^*$.

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Paper 1/02148F; *Received* 8*th May*, 1991