J Solution Chem (2015) 44:2258–2265
DOI 10.1007/s10953-015-0402-5

# The Effect of Complex Anions on the Structure of Water

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Received: 16 June 2015 / Accepted: 1 September 2015 / Published online: 27 October 2015

**Abstract** The microscopic ionic volumes, $v_A$, of complex inorganic anions, obtained from crystal unit cell volumes, as well as their standard molar volumes, $V_A^\infty$, in aqueous solutions serve to establish whether these anions are water-structure-breakers or -makers. This is done via correlations with well known criteria for such effects, namely the ionic viscosity *B*-coefficients and the structural entropies. Complex anions with charges $z_A$ are structure-breakers if $v_A > 0.1|z_A|\ \text{nm}^3\cdot\text{ion}^{-1}$ or $V_A^\infty > 35|z_A|^{4/3}\ \text{cm}^3\cdot\text{mol}^{-1}$ and structure-makers if otherwise.

**Keywords** Microscopic ionic volumes · Standard partial molar volume · Viscosity *B*-coefficient · Structural entropy · Complex anions · Water structure

## 1 Introduction

The effects of ions on the structure of water beyond their hydration shells, whether they destroy it (structure-breaking or chaotropic ions) or enhance it (structure-making or cosmotropic ions), have been recently reviewed by the author [1, 2]. The anions considered there included only very few complex anion with inorganic ligands, whereas their effects could be of considerable interest. Two quantities pertaining to the behavior of ions in aqueous solutions have mainly been employed for ascertaining the effects of the ions on the structure of the water. One is the ionic *B*–coefficient of the viscosity of aqueous solutions, $B_\eta$, the other is the ionic structural entropy, $\Delta_{\text{str}}S^\infty$.

Electrolyte *B*-coefficients are obtained as the slope of plots of the left hand side of:

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Presented at the 34th International Conference on Solution Chemistry in Prague, September 2015.

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$$(\eta - \eta_W)/\eta_W c_E^{1/2} = A_\eta + B_\eta c_E^{1/2} \quad (1)$$

against the square root of the electrolyte concentration, $c_E^{1/2}$. Here $\eta$ is the dynamic viscosity of the $c_E$ molar electrolyte solution ($c_E < 1$ mol·dm$^{-3}$) and $\eta_W$ is the viscosity of pure water at the same temperature. The units of $B_\eta$ are dm$^3$·mol$^{-1}$ and the values for common electrolytes are in the tenths of units. The electrolyte values are additive in the ionic contributions and are split into them on the assumption that the *B*-coefficients of the aqueous rubidium and bromide ions are equal [3]:

$$B_\eta(\mathrm{Rb}^+, \mathrm{aq}) = B_\eta(\mathrm{Br}^-, \mathrm{aq}) \quad (2)$$

justified by the mobilities of these ions being equal over a considerable temperature range around ambient. Ions that reduce the viscosity and for which $B_\eta < 0$ are structure-breaking or chaotropic and those that enhance the viscosity and for which $B_\eta > 0$ are structure-making or cosmotropic. Values for many aqueous ions at 298.15 K are listed in the review [3], but only few complex anions are included.

The ionic structural entropy, $\Delta_{\mathrm{str}}S^\infty$, is that part of the standard molar entropy of hydration of an ion, $\Delta_{\mathrm{hyd}}S^\infty$, from which entropic effects not pertaining to the water structure-making and -breaking have been deducted:

$$\Delta_{\mathrm{str}}S^\infty = \Delta_{\mathrm{hyd}}S^\infty - [\Delta S_{\mathrm{nt}} + \Delta S_{\mathrm{el\,1}} + \Delta S_{\mathrm{el\,2}}] \quad (3)$$

The terms on the right side of Eq. 3 denote the standard molar ionic entropies of hydration, $\Delta_{\mathrm{hyd}}S^\infty$, a neutral term, $\Delta S_{\mathrm{nt}}$, and two electrostatic terms, $\Delta S_{\mathrm{el\ 1}}$, and $\Delta S_{\mathrm{el\ 2}}$, which are described in detail in the following.

The standard molar ionic entropies of hydration, $\Delta_{\mathrm{hyd}}S^\infty$, is the difference between the standard molar entropy of the aqueous ion, $S^\infty$(ion, aq), and that of the ion in the ideal gaseous phase, $S^{\mathrm{o}}$(ion, ig). The former of which is based on the assumption that $S^\infty$(H$^+$, aq) = −22.2 J·K$^{-1}$·mol$^{-1}$, and the values of $\Delta_{\mathrm{hyd}}S^\infty$ at 298.15 K are listed, e.g., in [4], where the justification for this assumption is briefly described and annotated. The terms in the square brackets of Eq. 3 have the following meanings.

The neutral term, $\Delta S_{\mathrm{nt}}$, describes the entropic effect of the compression of the ion from the ideal gas phase to the standard concentration in the aqueous solution:

$$\Delta S_{\mathrm{nt}} = -3 - 600(r_A/\mathrm{nm})\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} \quad (4)$$

where $r_A$ is the ionic radius [5]. The first electrostatic term, $\Delta S_{\mathrm{el\ 1}}$, describes this entropic effect in the hydration shell of the ion of charge number $z_A$ having the permittivity of the electrostricted water, $\varepsilon' = n_D^2$, and the corresponding temperature derivative of the refractive index squared.

$$\Delta S_{\mathrm{el1}} = \left(N_A e^2/8\pi\varepsilon_0\right) z_A^2 \left[\Delta r_A (r_A + \Delta r_A)^{-1}\right] \varepsilon'^{-2} (\partial\varepsilon'/\partial T)_p \quad (5)$$

The width, $\Delta r_A$, of this shell is obtained from its volume and the number of water molecules in this shell, $h_A = 0.360|z_A|/(r_A/\mathrm{nm})$, where $d_W = 0.276$ nm is the diameter of a water molecule [6]:

$$(4\pi/3)\left[(r_A + \Delta r_A)^3 - r_A^3\right] = h_A \pi d_W^3/6 \quad (6)$$

The second electrostatic term, $\Delta S_{\mathrm{el\ 2}}$, describes this entropic effect beyond the first hydration shell [5], where the water has its bulk relative permittivity, $\varepsilon_r$:

$$\Delta S_{\mathrm{el}\,2} = \left(N_{\mathrm{A}}e^2/8\pi\varepsilon_0\right)z^2(r_{\mathrm{A}} + \Delta r_{\mathrm{A}})^{-1}\varepsilon_{\mathrm{r}}^{-2}(\partial\varepsilon_{\mathrm{r}}/\partial T)_p \tag{7}$$

Ions for which the structural entropy obtained from Eqs. 3 to 7 is $\Delta_{\mathrm{str}}S^{\infty} > 20\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ are structure-breaking or chaotropic and those for which $\Delta_{\mathrm{str}}S^{\infty} < -20\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ are structure-making or cosmotropic. Ions with values of $-20 < \Delta_{\mathrm{str}}S^{\infty}/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} < 20$ are borderline ones, having little effect on the structure of the water. Although ionic $\Delta_{\mathrm{str}}S^{\infty}$ values have been obtained for some 150 ions with charge numbers $-4 \le z_{\mathrm{A}} \le 4$, which are linearly correlated with the ionic viscosity $B$–coefficients, very few complex anions are included.

It is, therefore necessary, for ascertaining the effects of complex anions on the structure of water, to find measures for these effects alternative to $B_{\eta}$ and $\Delta_{\mathrm{str}}S^{\infty}$, or such measures from which these two criteria can be estimated. The volume based thermodynamics promoted in recent years [7, 8] provide such a route that is followed in this paper. The correlation of the sizes of anions with their effects on the structure of the water depends on whether they may fit into the naturally occurring cavities, of average volume 0.0094 nm$^3$, or not, although thermal agitation produces larger as well as smaller cavities. This average cavity size is estimated as the difference of the volume per water molecule of water at ambient temperatures, $1.807 \times 10^{-5}/N_{\mathrm{A}}\ \mathrm{m^3{\cdot}mol^{-1}}$, and the van der Waals volume of the latter, $1.24 \times 10^{-5}/N_{\mathrm{A}}\ \mathrm{m^3{\cdot}mol^{-1}}$. An anion, if too large, would disrupt some of the hydrogen-bonded structure of the water, whereas smaller anions re-arrange the water around them by forming hydrogen bonds with its molecules.

## 2 Anion Property Database

Ionic volumes are obtained from the unit cell volume $v_{\mathrm{uc}}$ of crystalline salts $\mathrm{C}_p\mathrm{A}_q$, involving the cations C and anions A in question, obtained from X-ray diffraction, and the number of formula units of the salt per unit cell, $Z$. The volumes of cations and anions are assumed to be additive:

$$v_{\mathrm{uc}} = Z(pv_{\mathrm{C}} + qv_{\mathrm{A}}) \tag{8}$$

where $v_{\mathrm{C}}$ and $v_{\mathrm{A}}$ are the microscopic ionic volumes of the cation and anion. Assignment of the Goldschmidt radii $r_{\mathrm{A}}^{\mathrm{G}}$ to the alkali metal and alkaline earth metal cations leads to $v_{\mathrm{C}} = (4\pi/3)\left(r_{\mathrm{A}}^{\mathrm{G}}\right)^3$ and to derived values of $v_{\mathrm{A}}$. Lists of $v_{\mathrm{A}}$ for many common anions, including a few complex ones, are available in [9] (under the heading $v_{\mathrm{J}}$) and in particular the $v_{\mathrm{A}}$ of inorganic complex anions are reported in [10]. It is assumed that these ionic volumes obtained in crystalline solids are also pertinent to the anions in aqueous solutions.

Another measure of ionic volumes, directly pertinent to aqueous solutions, are their standard partial molar volumes, $V_{\mathrm{A}}^{\infty}$. These should describe the actual volume, per mole, that the ions occupy in the solution. For electrolytes the $V_{\mathrm{E}}^{\infty}$ are obtained from the densities, $\rho$, of salt solutions:

$$V_{\mathrm{E}}^{\infty} = \lim(c_{\mathrm{E}} \to 0)[M_{\mathrm{E}}/\rho_{\mathrm{W}} + 1000(\rho - \rho_{\mathrm{W}})/\rho_{\mathrm{W}}c_{\mathrm{E}}] \tag{9}$$

where $M_{\mathrm{E}}$ is the molar mass of the electrolyte (in $\mathrm{g{\cdot}mol^{-1}}$) and $\rho_{\mathrm{W}}$ is the density of pure water (in $\mathrm{g{\cdot}cm^{-3}}$), yielding $V_{\mathrm{E}}^{\infty}$ in $\mathrm{cm^3{\cdot}mol^{-1}}$. The ionic values $V_{\mathrm{A}}^{\infty}$ are obtained from the conventional ionic volumes, listed [11] on the basis that $V^{\mathrm{conv}\ \infty}(\mathrm{H^+, aq}) = 0$, and Eq. 10 by setting $V_{\mathrm{ion}}^{\infty}(\mathrm{H^+,\ aq}) = -\ 5.4\ \mathrm{cm^3{\cdot}mol^{-1}}$ at 298.15 K [11].

$$V_{\mathrm{A}}^{\infty} = V_{\mathrm{A}}^{\mathrm{conv}\,\infty} + z_i V^{\infty}(\mathrm{H}^+,\ \mathrm{aq}) \tag{10}$$

A list of $V_{\mathrm{A}}^{\infty}$ of anions is available in [4], but few values for complex anions are available.

A combination of the values of the ionic $B$–coefficients, $B_{\eta}$, and ionic structural entropies, $\Delta_{\mathrm{str}}S^{\infty}$, with the ionic anion volumes, $v_{\mathrm{A}}$, and alternatively with the ionic standard partial molar volumes of anions, $V_{\mathrm{A}}^{\infty}$, leads to the following linear correlations for a large number of common uni-, di-, and trivalent anions for which these quantities are known.

$$B_{\eta/}\mathrm{dm}^3{\cdot}\mathrm{mol}^{-1} = 0.195|z_{\mathrm{A}}| - 2.76|z_{\mathrm{A}}|^{-2/3}\left(v_{\mathrm{A}}/\mathrm{nm}^3{\cdot}\mathrm{ion}^{-1}\right) \tag{11}$$

$$B_{\eta}/\mathrm{dm}^3{\cdot}\mathrm{mol}^{-1} = 0.118|z_{\mathrm{A}}|^{4/3} - 0.00385|z_{\mathrm{A}}|^{-1/3}\left(V_{\mathrm{A}}^{\infty}/\mathrm{cm}^3{\cdot}\mathrm{mol}^{-1}\right) \tag{12}$$

$$\Delta_{\mathrm{str}}S^{\infty}/\mathrm{J}{\cdot}\mathrm{K}^{-1}{\cdot}\mathrm{mol}^{-1} = -87.5|z_{\mathrm{A}}|^{5/2} + 2350|z_{\mathrm{A}}|^{1/4}\left(v_{\mathrm{A}}/\mathrm{nm}^3\right) \tag{13}$$

$$\Delta_{\mathrm{str}}S^{\infty}/\mathrm{J}{\cdot}\mathrm{K}^{-1}{\cdot}\mathrm{mol}^{-1} = -33.7|z_{\mathrm{A}}|^{3} + 2.61|z_{\mathrm{A}}|^{1/4}\left(V_{\mathrm{A}}^{\infty}/\mathrm{cm}^3{\cdot}\mathrm{mol}^{-1}\right) \tag{14}$$

Plots of Eqs. 11 and 12 are shown in Fig. 1 and those of Eqs. 13 and 14 are shown in Fig. 2. Although these plots have considerable scatter around the correlation lines, they serve well for the present purpose, in view also of the uncertainties in the so-called experimental values, as discussed below.

## 3 Complex Anions

Many complex anions with halide and cyanide ligands have been prepared, but only some of them are sufficiently stable in aqueous solutions for their effects on the structure of the water to be of interest. A representative list of such complex anions is shown in Table 1

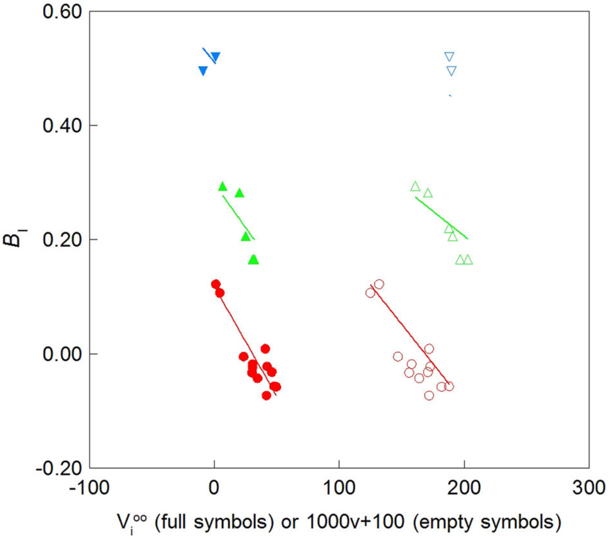

**Fig. 1** The ionic viscosity coefficients $B_i$/dm$^3$·mol$^{-1}$ (i.e., $B_{\eta}$) of common anions versus their ionic standard molar volumes $V_i^{\infty}$/cm$^3$·mol$^{-1}$ (i.e., $V_{\mathrm{A}}^{\infty}$) (*filled symbols*) and microscopic ionic volumes 1000$v_{\mathrm{A}}$/nm$^3$ (*empty symbols*, displaced by 100 units for the sake of clarity). Univalent anions in *circles*, divalent ones in *upright triangles* and trivalent ones in *downward triangles*

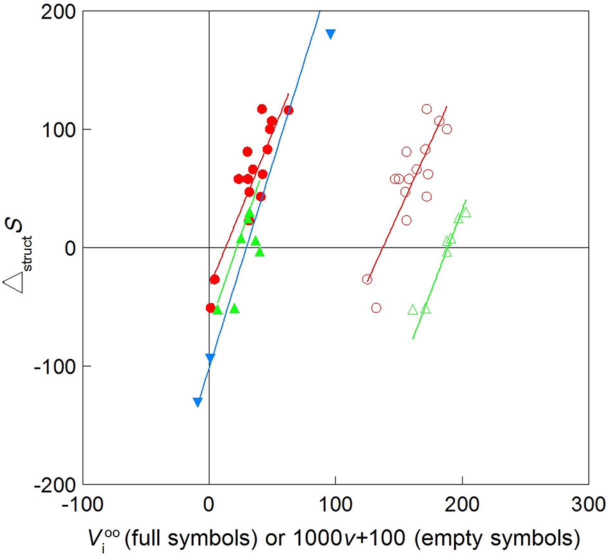

**Fig. 2** The ionic structural entropies $\Delta_{str}S$/J·K$^{-1}$·mol$^{-1}$ of common anions versus their ionic standard molar volumes $V_i^{\infty}$/cm$^3$·mol$^{-1}$(i.e., $V_A^{\infty}$) (*filled symbols*) and microscopic ionic volumes 1000$v_A$/nm$^3$ (*empty symbols*, displaced by 100 units for the sake of clarity). Univalent anions in *circles*, divalent ones in *upright triangles* and trivalent ones in *downward triangles*

with the values of $B_\eta$ and $\Delta_{str}S^{\infty}$ derived from the microscopic anion volumes $v_A$, Eqs. 11 and 13, and consequently their effects on the structure of the water in their dilute aqueous solutions. As mentioned in the Introduction, the criteria are $B_\eta > 0$ and $\Delta_{str}S^{\infty} < -20$ J·K$^{-1}$·mol$^{-1}$ for structure-making anions and $B_\eta < 0$ and $\Delta_{str}S^{\infty} > 20$ J·K$^{-1}$·mol$^{-1}$ for structure-breaking ones. These effects are presented symbolically as in Tables 1 and 2 ++ for strongly structure-breaking (very chaotropic), + for mildly structure-breaking (mildly chaotropic), 0 for indifferent or borderline, − for mildly structure-making (mildly cosmotropic) and −− for strongly structure-making (strongly cosmotropic).

Only few standard partial molar volumes, $V_A^{\infty}$, are available for complex aqueous anions, but application of Eqs. 12 and 14 to these data, shown in Table 2, produce similar results to those from the equations pertaining to the ionic volumes $v_A$.

## 4 Discussion

Table 1 shows that the moderately charged complex inorganic anions considered are too large to fit into naturally occurring cavities in water, so that they are water structure-breakers (chaotropic), unless they are sufficiently highly charged, so that they turn to be water structure-makers (cosmotropic). There is good agreement between the consequent criteria posed by the calculated viscosity $B$-coefficients and the structural entropy of the anions. These criteria may be turned around to yield that an anion would be water-structure-breaking if its microscopic volume is $v_A > 0.1|z_A|$ nm$^3$·ion$^{-1}$ and structure-making otherwise (an exception is the mildly structure-breaking $BF_4^-$). Alternatively, an

**Table 1** Ionic $B_\eta$ coefficients and structural entropies $\Delta_{str}S^\infty$ calculated from ionic volumes $v_A$ of inorganic complex anions by Eqs. 11 and 13 and the deduced effects on the structure of water

| Anion | $v_A$/nm$^{3a}$ | $B_{\eta\ calc}$/dm$^3$·mol$^{-1}$ | $\Delta_{str}S^\infty_{calc}$/J·K$^{-1}$·mol$^{-1}$ | Effect on water structure |
|---|---|---|---|---|
| $BF_4^-$ | 0.073$^b$ | −0.106 | 84 | + |
| $PF_6^-$ | 0.109$^c$ | −0.206 | 168 | ++ |
| $AsF_6^-$ | 0.116 | −0.225 | 185 | ++ |
| $SbF_6^-$ | 0.121 | −0.236 | 196 | ++ |
| $NbF_6^-$ | 0.125 | −0.250 | 206 | ++ |
| $SiF_6^{2-}$ | 0.112 | 0.106 | −182 | −− |
| $ZrF_6^{2-}$ | 0.121 | 0.090 | −157 | −− |
| $PtF_6^{2-}$ | 0.119 | 0.094 | −163 | −− |
| $AlCl_4^-$ | 0.156 | −0.336 | 279 | ++ |
| $FeCl_4^-$ | 0.155 | −0.333 | 276 | ++ |
| $AuCl_4^-$ | 0.157 | −0.338 | 281 | ++ |
| $TaCl_6^-$ | 0.206 | −0.474 | 396 | ++ |
| $PdCl_4^{2-}$ | 0.183 | −0.017 | 16 | 0 |
| $PtCl_4^{2-}$ | 0.184 | −0.019 | 19 | 0 |
| $PdCl_6^{2-}$ | 0.218 | −0.078 | 114 | + |
| $PtCl_6^{2-}$ | 0.219 | −0.080 | 117 | + |
| $IrCl_6^{2-}$ | 0.229 | −0.082 | 140 | + |
| $AlBr_4^-$ | 0.198 | −0.451 | 377 | ++ |
| $AuBr_4^-$ | 0.177 | −0.394 | 328 | ++ |
| $BiBr_4^-$ | 0.177 | −0.394 | 328 | ++ |
| $HgBr_4^{2-}$ | 0.216 | −0.075 | 109 | + |
| $PdBr_6^{2-}$ | 0.247 | −0.129 | 195 | ++ |
| $PtBr_6^{2-}$ | 0.258 | −0.148 | 226 | ++ |
| $IrBr_6^{2-}$ | 0.248 | −0.131 | 198 | ++ |
| $HgI_4^{2-}$ | 0.245 | −0.125 | 190 | ++ |
| $Ag(CN)_2^-$ | 0.110 | −0.209 | 171 | ++ |
| $Au(CN)_2^-$ | 0.109$^b$ | −0.206 | 168 | ++ |
| $Au(CN)_4^-$ | 0.171 | −0.377 | 314 | ++ |
| $Ni(CN)_4^{2-}$ | 0.171 | −0.004 | −17 | 0 |
| $Fe(CN)_6^{3-}$ | 0.284$^b$ | 0.215 | −486 | −− |
| $Co(CN)_6^{3-}$ | 0.263$^b$ | 0.243 | −551 | −− |
| $Ir(CN)_6^{3-}$ | 0.271 | 0.233 | −526 | −− |
| $Fe(CN)_6^{4-}$ | 0.246 | 0.687 | −1983 | −− |
| $Mo(CN)_8^{4-}$ | 0.333 | 0.592 | −1693 | −− |

[a] Except where noted, the $v_A$ values are from [10]

[b] From [9]

[c] From [12]

**Table 2** Ionic $B_\eta$ coefficients and structural entropies $\Delta_{\rm str}S^\infty$ calculated from ionic standard partial molar volumes $V_{\rm A}^\infty$ of inorganic complex anions by Eqs. 11 and 13 and the deduced effects on the structure of water

| Anion | $V_{\rm A}^\infty$/cm$^3$·mol$^{-1}$ [4] | $B_{\eta\ \rm calc}$/dm$^3$·mol$^{-1}$ | $\Delta_{\rm str}S_{\rm calc}^\infty$/J·K$^{-1}$·mol$^{-1}$ | Effect on water structure |
|---|---|---|---|---|
| $BF_4^-$ | 50.6 | −0.077 | 98 | + |
| $PF_6^-$ | 58 | −0.105 | 118 | + |
| $SiF_6^{2-}$ | 53.6 | 0.132 | −104 | −− |
| $Fe(CN)_6^{3-}$ | 137.6 | 0.144 | −439 | −− |
| $Co(CN)_6^{3-}$ | 131.9 | 0.159 | −458 | −− |
| $Fe(CN)_6^{4-}$ | 96.0 | 0.516 | −1503 | −− |

anion breaks the water structure if $V_{\rm A}^\infty > 35|z_{\rm A}|^{4/3}$ cm$^3$·mol$^{-1}$ and enhances it if otherwise, as shown in Table 2.

Some comments on the reliability of the input data, $v_{\rm A}$ and $V_{\rm A}^\infty$, and on the ionic viscosity data $B_\eta$ available in the literature are in place here. The uncertainties ascribed to the $v_{\rm A}$ values in [10] range from 0.005 to 0.010 nm$^3$ but may be as large as 0.020 nm$^3$. Furthermore, there are discrepancies between the $v_{\rm A}$/nm$^3$ values reported from the same laboratory in different publications. Such are the cases of $AlCl_4^-$, for which 0.156 and 0.161 are in the same publication [10], $Au(CN)_2^-$ 0.092 [12] and 0.109 [9], $Ni(CN)_4^{2-}$ 0.195 [12] and 0.171 [10], and $Fe(CN)_6^{3-}$ 0.284 [9] and 0.265 [12]. The value 0.299 for $IrCl_6^{2-}$ in [10] is much too large, possibly a misprint in view of 0.229 reported in [12]. These discrepancies and the probable uncertainties in the $v_{\rm A}$ values do not change the qualitative picture of the anion effects on the structure of water.

The $V_{\rm I}^\infty$ values have the inherent uncertainty of ± $0.2z_{\rm ion}$ cm$^3$·mol$^{-1}$, due to the choice of $V_{\rm ion}^\infty({\rm H}^+, {\rm aq})$ [11], but this is immaterial for the present purposes. The agreement between the calculated values of the viscosity and structural entropy for complex anions between Tables 1 and 2 is satisfactory. It remains to compare the values of the calculated viscosity *B*-coefficients with experimental values where available [3]. This compilation of experimental values lists 'selected' values when data from various sources are in agreement with each other, within an uncertainty of ± $0.005z_{\rm i}$ dm$^3$·mol$^{-1}$. The $B_\eta$ value for $SCN^-$ has since this publication been revised to −0.032 dm$^3$·mol$^{-1}$ [13]. These values then served for the establishment of correlations (Eqs. 11 and 12). For complex anions no 'selected' values are available, and the reliability of the reported values is difficult to judge. The following values of $B_\eta$/dm$^3$·mol$^{-1}$ have been reported (for references see [3]): $BF_4^-$ −0.093, $PF_6^-$ −0.21, $Ag(CN)_2^-$ −0.038, $Au(CN)_2^-$ −0.040, $SiF_6^{2-}$ 0.374, $PtCl_6^{2-}$ 0.218, $Fe(CN)_6^{3-}$ 0.129, $Co(CN)_6^{3-}$ 0.146, $Fe(CN)_6^{4-}$ 0.342 and 0.400, and $Mo(CN)_8^{4-}$ 0.230. These experimental values for $BF_4^-$ and $Fe(CN)_6^{4-}$ are in-between the calculated values from $v_{\rm A}$ and $V_{\rm A}^\infty$, those for $Fe(CN)_6^{3-}$ and, $Co(CN)_6^{3-}$ agree with the values calculated from $V_{\rm A}^\infty$ rather than those calculated from $v_{\rm A}$, and agreement only with respect to sign pertains to the other complex anions (except for $PtCl_6^{2-}$, where the sign is wrong). However, the so-called experimental values have not been confirmed by workers other than those responsible for the values recorded (as non-selected) in [3], and could be due for revision, as was the case for $SCN^-$ mentioned above.

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