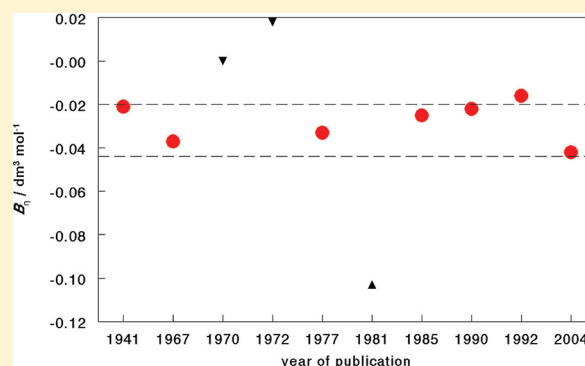# The Viscosity *B*-Coefficient of the Thiocyanate Anion

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ABSTRACT: The value of the viscosity *B*-coefficient of the thiocyanate anion reported in the biophysical literature, $B_\eta(SCN^-)$ = -0.103 $dm^3 \cdot mol^{-1}$, is erroneous. It is not derived from direct viscosity measurements. It should be replaced by -0.032 ± 0.006 $dm^3 \cdot mol^{-1}$ at 25 °C, the average from values derived from viscosity measurements.

■ INTRODUCTION

The viscosity *B*-coefficients of ions play an important role in the examination of the biophysical and colloid chemical effects ions have in aqueous solutions. Ions with large negative values of these coefficients are deemed to be water-structure-breaking, chaotropic, and "tail anions" (denaturing, salting-in) in the Hofmeister series. The *B*-coefficients of aqueous electrolytes are derived from the Jones−Dole equation:[1]

$$\eta = \eta_W[1 + A_\eta c^{1/2} + B_\eta c + ...] \tag{1}$$

that can be rewritten as:

$$(\eta/\eta_W - 1)/c^{1/2} = A_\eta + B_\eta c^{1/2} + ... \tag{2}$$

Here η is the dynamic viscosity of the electrolyte solution of concentration c, η_W that of pure water, A_η and B_η are temperature (and pressure) dependent coefficients, and up to moderately high values of c (several $mol \cdot dm^{-3}$) no further terms in eqs 1 and 2 are required. The B_η coefficients are the limiting slopes of plots of the left side of eq 2 against $c^{1/2}$ and are thus valid at infinite dilution, hence are additive in the contributions of the constituent ions of the electrolyte. Individual ionic values are obtained by splitting the electrolyte B_η values in a conventional manner, based on the relative mobility of the ions. The convention $B_\eta(Rb^+) = B_\eta(Br^-) = -0.033$ $dm^3 \cdot mol^{-1}$ is adopted here, following Jenkins and Marcus,[2] being justified over a wider temperature range near ambient than the convention $B_\eta(K^+) = B_\eta(Cl^-) = -0.007$ $dm^3 \cdot mol^{-1}$ that has been often employed in the literature. The differences in the conventions lead to $B_\eta(K^+) = -0.009$ rather than -0.007 $dm^3 \cdot mol^{-1}$, a change that is negligible in view of the assigned uncertainties, $\pm$ 0.002 $dm^3 \cdot mol^{-1}$.

■ DATA

For the aqueous thiocyanate anion the large negative value $B_\eta(SCN^-) = -0.103$ $dm^3 \cdot mol^{-1}$ has been quoted even recently by biochemists and biophysicists, for example, Collins,[3] as well as by physical chemists, for example, Kunz[4] and Lopez-Leon et al.,[5] but it is erroneous. This value is traceable to Robinson et al.,[6] who measured elution concentrations of enzymes by a variety of aqueous salts from dextrane−Sepharose. These concentrations were correlated with the viscosity *B*-coefficients obtained from the literature (four specified books), and from this correlation they deduced the above-mentioned $B_\eta(SCN^-)$ = -0.103 $dm^3 \cdot mol^{-1}$ value. These authors did not show their correlation expression but supported this value as being already available from references to the four books; however, none of these books contains this or any value at all for thiocyanate or one of its salts. (The book by Stokes and Mills[7] has an entry in the appendix for NaSCN with a reference to Miller and Doran[8] but with no numerical value in either source.) Furthermore, although there is agreement between the elution volume for SCN^- with the purported B_η from the literature, for some other ions (Li^+, $CH_3CO_2^-$, NH_4^+, SO_4^{2-}, Mg^{2+}, NO_3^-, among others) no such agreement was obtained.[6] Hence, the value $B_\eta(SCN^-)$ = -0.103 $dm^3 \cdot mol^{-1}$ has no basis whatsoever and should be completely disregarded.

An examination of the literature for papers reporting actual measurements of the viscosity of aqueous thiocyanate salts yielded rather widely varying values for $B_\eta(MSCN)$, where M^+ is a univalent cation, from which, however, a fairly consistent value for $B_\eta(SCN^-)$ could be distilled. Bingham[9] was the first to have measured a relevant quantity, namely, the fluidity of 1 $mol \cdot dm^{-3}$ aqueous KSCN at 25 °C: Φ = 115.4 "rhes", compared with Φ_W = 111.91 "rhes", for pure water. The fluidity is the reciprocal of the viscosity, hence $\eta/\eta_W - 1 = \Phi_W/\Phi - 1 = -0.0302$. On neglecting the small A_η term, this value is $B_\eta(KSCN)$ in $dm^3 \cdot mol^{-1}$ from eq 2, because $c^{1/2} = 1^{1/2} = 1$. The

subtraction of $B_\eta(K^+) = -0.009$ yields $B_\eta(SCN^-) = -0.021$ dm^3·mol^{-1}. Eisenstadt and Friedman[10] reported $B_\eta(SCN^-) = -0.039$ dm^3·mol^{-1} on the basis $B_\eta(K^+) = -0.007$ dm^3·mol^{-1}, that becomes $B_\eta(SCN^-) = -0.037$ dm^3·mol^{-1} on the basis $B_\eta(K^+) = -0.009$ dm^3·mol^{-1} preferred here. These authors did not, however, report the experimental details on which they based their listed value. Miller and Doran[8] reported η/η_W data for 29.87 °C in a figure, showing only two points below $c(NaSCN) = 1$ mol·dm^{-3}, from which no useful value for $B_\eta(NaSCN)$ could be deduced. Janz et al.[11] provided a fitting expression for $\eta(NaSCN)/\eta_W$ at 25 °C using eight points for $0.1 \leq c(NaSCN)/mol·dm^{-3} \leq 4.0$, that for four points ≤ 1.4 mol·dm^{-3} is linear with $c^{1/2}$, yielding from eq 2 the slope $B_\eta(NaSCN) = 0.0854$ dm^3·mol^{-1}. The subtraction of $B_\eta(Na^+) = 0.085$ dm^3·mol^{-1} from $B_\eta(NaSCN)^2$ then yields $B_\eta(SCN^-) = 0.000$ dm^3·mol^{-1}. Moulik[12] reported a fitting expression for $[\eta(NaSCN)/\eta_W]^2$ at 25 °C, from which a linear dependence of $\eta(NaSCN)/\eta_W$ on $c^{1/2}$ over the range $0.5 \leq c(NaSCN)/mol·dm^{-3} \leq 1.7$ could be deduced, yielding $B_\eta(NaSCN) = 0.1028$ dm^3·mol^{-1}. The subtraction of $B_\eta(Na^+) = 0.085$ dm^3·mol^{-1} then yields $B_\eta(SCN^-) = 0.018$ dm^3·mol^{-1}.

Tikoo and Singh[13] reported values of $B_\eta(KSCN)$ in aqueous N,N-dimethylacetamide mixtures at 25 °C. Their value for pure aqueous solutions is -0.0419 ± 0.0019 dm^3·mol^{-1}, from which, on subtraction of $B_\eta(K^+) = -0.009$, the value $B_\eta(SCN^-) = -0.033 \pm 0.002$ dm^3·mol^{-1} results. Mitchell et al.[14] reported viscosity data for aqueous KSCN at 25 °C that for the five points up to $c = 1.03$ mol·dm^{-3} yield from eq 2 $B_\eta(KSCN) = -0.0246$ dm^3·mol^{-1}, and on subtraction of $B_\eta(K^+) = -0.009$ $B_\eta(SCN^-) = -0.016$ dm^3·mol^{-1} results. Wadi and Goyal[15] showed a figure for $\eta(KSCN)/\eta_W$ for (15, 25, and 35) °C, and the three points for $c \leq 0.6$ mol·dm^{-3} (converted from molalities with the density functions provided) yield $B_\eta(KSCN) = 0.0311$ dm^3·mol^{-1}, and $B_\eta(SCN^-) = -0.022$ dm^3·mol^{-1}. The most recent useful information is from Tsierkezos and Molinou[16] who reported the viscosities of NaSCN, KSCN, and NH$_4$SCN in aqueous N,N-dimethylformamide mixtures at 20 °C. The B_η coefficients for these salts in pure water are 0.032, -0.063, and -0.026 (all ± 0.001) yielding the $B_\eta(SCN^-)$ values of (-0.053, -0.054, and -0.018) dm^3·mol^{-1}, the value from the ammonium salt not agreeing with those from the sodium and potassium salts.

Marcus[17,18] selected the value $B_\eta(SCN^-) = -0.025$ dm^3·mol^{-1} at 25 °C from the data available to him in the literature at the time. Jenkins and Marcus[2] erroneously left a misprinted value (0.022) for $B_\eta(SCN^-)$ in their table for ionic B-coefficients at 25 °C, instead of its negative, the parentheses signifying a "tentative" value where no agreement of values reported in the literature within 0.005 dm^3·mol^{-1} was found. They also provided a wrong reference for Moulik, instead of the correct one given here.

The $B_\eta(SCN^-)$ values at 25 °C available from measured viscosity data are summarized in Table 1.

■ DISCUSSION

Neither the positive value nor the near zero value of $B_\eta(SCN^-)$ deduced from the data and fitting expressions reported by Moulik[12] and by Janz et al.,[11] respectively, can be correct, in view of the behavior of thiocyanate as a definitely chaotropic anion. The unweighted average of the eight negative values of $B_\eta(SCN^-)$ in Table 1 resulting from direct experimental measurements is -0.032 ± 0.006 dm^3·mol^{-1}. The estimate

Table 1. $B_\eta(SCN^-)$ Values at 25 °C Available from Measured Viscosity Data

author(s)	ref	salt used	$B_\eta(SCN^-)$ dm^3·mol^{-1}
Bingham	9	KSCN	−0.021
Eisenstadt and Freidman	10	(Na)SCN	−0.037
Janz et al.	11	NaSCN	0.000
Moulik	12	NaSCN	0.018
Tikoo and Singh	13	KSCN	−0.033 ± 0.002
Mitchell et al.	14	KSCN	−0.016
Wadi and Goyal	15	KSCN	−0.022
Tsiekezos and Molinou (20 °C)	16	NaSCN	−0.053
		KSCN	−0.054
		NH$_4$SCN	−0.018
Marcus	17, 18	(literature)	−0.025

suggested by Marcus,[17,18] -0.025 dm^3·mol^{-1}, is thus of a reasonable magnitude.

It is unfortunate that the misprint "(0.022)" in the review by Jenkins and Marcus[2] has not been corrected up to now, since this value was quoted by Bilaničová et al.,[19] although attributed to a wrong reference (Ru et al.,[20] who did not deal with the SCN$^-$ anion). On the other hand, Salomäki et al.[21] correctly listed $B_\eta(SCN^-)$ as "uncertain" according to the information they had at the time.

Various physicochemical properties of aqueous ions have been correlated with their B_η coefficients. Among these properties is the structural entropy, $\Delta_{struc}S$, the remainder from the entropy of hydration after the ion size and electrostatic effects have been subtracted. The correlation expression[18] can be written as:

$$B_\eta/dm^3·mol^{-1} = [20(z^2 + |z|) - \Delta_{struc}S/J·K^{-1}·mol^{-1}]/605 \tag{3}$$

where z is the ionic charge number. The values of $\Delta_{struc}S(SCN^-) = 83$ and $\Delta_{struc}S(Br^-) = 81$ J·K^{-1}·mol^{-1} indicate that these two anions should according to eq 3 have similar values of B_η, and also $B_\eta(Br^-) = -0.033$ dm^3·mol^{-1} is well-established.[2] Hence, the average of the negative entries in Table 1, -0.032 dm^3·mol^{-1}, agrees with this expectation. Another correlation expression is with the NMR relaxation data of Engel and Herz.[22] This can be written as:

$$B_\eta/dm^3·mol^{-1} = (-0.002 \pm 0.005) + (0.696 \pm 0.063) (B_{NMR}/dm^3·mol^{-1}) \tag{4}$$

The B_{NMR} values are listed to only one significant digit, unfortunately, so that from the correlation eq 4 and $B_{NMR}(SCN^-) = -0.07$ dm^3·mol^{-1} the value $B_\eta(SCN^-) = -0.05$ dm^3·mol^{-1} results (the value for $B_{NMR}(Br^-) = -0.04$ dm^3·mol^{-1} corresponds then to $B_\eta(Br^-) = -0.03$ dm^3·mol^{-1}, agreeing with the established value).

In conclusion, although the results of correlations such as these or the one used by Robinson et al.[6] (but not shown explicitly) may be useful, they should never replace directly measured values of the required quantity. The average of the negative values for $B_\eta(SCN^-)$ in Table 1, namely, $= -0.032 \pm 0.006$ dm^3·mol^{-1}, should be adopted as the correct value to use

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(rather than $B_\eta(SCN^-) = -0.103$ dm^3·mol^{-1} appearing in the biophysical literature).

It still remains baffling why thiocyanate anions should be so strongly protein denaturing that it is placed at the very end of the Hofmeister series, being the "tip of its tail" so to say. However, it must be realized that the effects of ions on biomolecules and colloids in general are very complicated and have multiple causes acting together and sometimes antagonistically.[4,23] The ion effects on the structure of water, designating them as kosmotropic or chaotropic, are measurable by their viscosity B-coefficients or their structural entropy among several other properties manifested in dilute homogeneous solutions.[24] These effects are just one aspect of the complicated interactions taking place in more concentrated solutions in the presence of surfaces that biomolecules and colloids manifest. The cause of the specific effects of the thiocyanate anion on biomolecules must be sought elsewhere, perhaps in direct interactions, than in its effect on the structure of water.

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