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Goodbye to S^{2-} in Aqueous SolutionP. M. May,^{a*} D. Batka,^a G. Hefter,^a E. Königsberger,^a and D. Rowland^{a,b}Received 00th January 2018,
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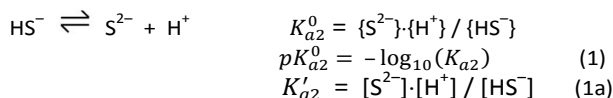
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New Raman spectra of Na_2S dissolved in hyper-concentrated $NaOH(aq)$ and $CsOH(aq)$ cast serious doubt on the widely-assumed existence of $S^{2-}(aq)$. Literature references to this species are problematic for numerous environmental and industrial applications and thus should be abandoned. Thermodynamic databases involving sulfide minerals also need to be carefully revised.

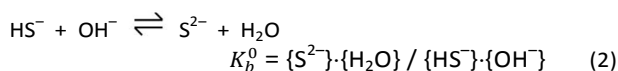
A simple chemical problem that defies the best that modern instrumentation can provide is rare nowadays. A widespread, ongoing misadventure in science is even rarer. However, both have happened over the assumed existence of the chemical species $S^{2-}(aq)$. This species appears in respected inorganic chemistry treatises,¹⁻⁴ reference works,⁵⁻⁹ introductory textbooks,¹⁰⁻¹⁵ innumerable research papers (ESI), and many widely-used thermodynamic databases. It is a pillar in classroom teaching of elementary solubility equilibria and it is commonly invoked in analytical, environmental and hydrometallurgical investigations (ESI). Yet the presence of significant amounts of S^{2-} in aqueous solution was ruled out over 30 years ago.¹⁶ New Raman spectroscopic measurements[†] presented below cast serious doubt on the formation of any $S^{2-}(aq)$ whatsoever. While it is impossible to *prove* that a chemical species never exists, we demonstrate that there is no credible experimental evidence to support the existence of $S^{2-}(aq)$ even when conditions are most favourable. Adopting the proposition that $S^{2-}(aq)$ does not exist would eliminate a great deal of confusion in the literature and counteract the ruinous effects on thermodynamic modelling of aquatic sulfide systems caused by previous interpretations. Significant benefits from improved understanding can thus be expected in a variety of environmental and industrial applications.

The most influential works to date on hydrogen sulfide

deprotonation at high pH are those of Giggenbach¹⁷ and Meyer *et al.*¹⁸ Both show conclusively that there is no significant formation of $S^{2-}(aq)$ at $[NaOH(aq)] \lesssim 5$ M (where the square brackets denote concentration and M is the concentration unit $mol.L^{-1}$). These observations are in accord with the value of $pK_{a2}^0 \geq 17$ which these investigators derive for the presumed second acid dissociation constant of $H_2S(aq)$:



where braces, $\{\}$, represent activities and K'_{a2} is the corresponding conditional equilibrium constant (when the activity coefficients are constant). At higher $[NaOH(aq)]$, where significant formation of $S^{2-}(aq)$ might be expected, the data in both of these papers are equivocal. Giggenbach,¹⁷ using UV-absorption spectroscopy, proposed a lower limit of $pK_{a2}^0 = 17.1 \pm 0.2$ from a shoulder attributed to S^{2-} on the intense HS^- absorbance band centred at 260 nm. Tellingly, however, even in saturated $NaOH(aq)$ solutions (*ca.* 23 M), the equilibrium (Equation 2) could not be forced so far to the right that the HS^- signal disappeared completely.



Meyer *et al.*¹⁸ employed Raman spectroscopy to calculate pK_{a2}^0 using the H–S stretching mode at ~ 2600 cm^{-1} . The intensity of this mode started to decrease at about 8.9 M $NaOH$ and reached *ca.* 50% in 16.9 M $NaOH$. From a limited analysis of their measurements Meyer *et al.* selected $pK_{a2}^0 = 17 \pm 1$, in accord with Giggenbach's estimate. Relevantly, both Giggenbach and Meyer *et al.* relied on numerical fitting processes to compare simulated and measured data even though it is clear from their accompanying Figures that the effect being quantified falls worryingly close to some limiting experimental conditions.

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The above conclusions appear to be supported by the work of Licht *et al.*^{19,20} who reported values of pK_{a2}^0 in good agreement with the spectroscopic estimates: 17.6 ± 0.3 from pH measurements with a glass electrode¹⁹ and 17.0 ± 0.3 from differential density measurements.²⁰ Unfortunately, given the well-known limitations²¹ of even the best glass electrodes at $pH > 12$ and the general inapplicability of density measurements to the quantification of chemical speciation, little reliance can be placed on these results.

Usually such good agreement between independent investigators, using different techniques, would be considered as strong evidence for the existence of a proposed chemical species. In this case, however, there is a simpler and more compelling explanation. Hyper-alkaline metal hydroxide solutions are radically different from their dilute counterparts,^{22,23} which is not being properly taken into account. At the molecular level, the interactions between water-depleted ions become determined by packing and other structural factors, rather than the electrostatic forces that dominate in more dilute electrolyte solutions. Such effects render the notion of a related pK_{a2}^0 meaningless because there is no reasonable way to extrapolate the activity of a chemical species in $[NaOH(aq)] > 10$ M back to infinite dilution. The idea that this can be done *even approximately* is fallacious. The conceivable effects of ion interactions in concentrated electrolyte solutions are non-trivial^{24,25} and far beyond any current theoretical treatment. To be fair, Giggenbach¹⁷ and Meyer *et al.*¹⁸ carried out high quality work and they were well aware of the limitations of their methods, pointedly expressing doubts over the physical significance of their pK_{a2}^0 estimates. Regrettably, their concerns have largely been ignored.

Appropriate analytical probes for sulfide species, particularly in chemically-aggressive hyper-alkaline solutions, are almost non-existent. There is none at present that can be used to observe $S^{2-}(aq)$ directly so numerical fitting had to be employed in all of the above studies. However, much has been learned about the dangers of such fitting procedures in recent years.^{25,26} Co-incidences arising from physical artefacts and/or misinterpretations can occur all too easily. For example, take the earlier erroneous agreement ($pK_{a2}^0 \approx 14$) between Ellis and Golding²⁷ and Widmer and Schwarzenbach²⁸ (ESI). Changes in bulk properties such as density, viscosity, refractive index and water activity, as well as impurity co-factors²⁹, may well obscure, or be mistaken for, changes in chemical speciation. Unless HS^- deprotonation is believed *a priori*, there are other possible interpretations of the experimental observations in high $[OH^-]$.

Great improvements have been made in Raman spectroscopy technology since the study of Meyer *et al.*¹⁸ Nevertheless, our experimental findings are similar to those reported by them for the same $NaOH(aq)$ medium: at room temperature (*ca.* 22 °C) the intensity of the HS^- band (Figure 1) drops significantly only when $[NaOH] \geq 7$ mol.kg⁻¹. Moreover, the intensity remains at >50 %, even at $[NaOH] \approx 20$ mol.kg⁻¹. Adjustment of band intensity using $ClO_4^-(aq)$ as an internal standard made little difference, further confirming the reliability of these observations.

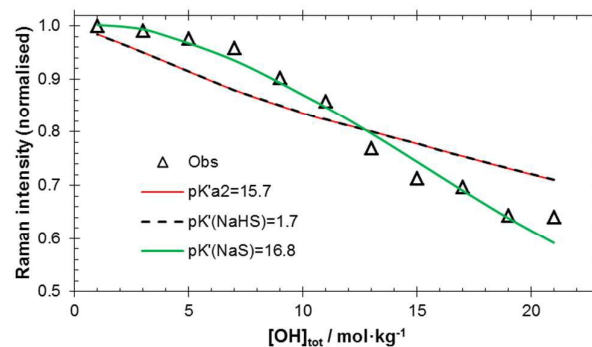
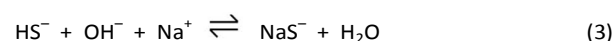


Figure 1. Variation of the Raman intensity (in normalised units) of the $HS^-(aq)$ mode at ~ 2600 cm⁻¹ with the molal concentration of $NaOH(aq)$, also showing three simple fits as described in the text and ESI. The only adjusted parameters were $pK'_{a2} = 15.7$ for $HS^- - H^+ = S^{2-}$; $pK'(NaS) = 16.8$ for $HS^- + Na^+ - H^+ = NaS^-$; and $pK'(NaHS) = 1.7$ for $HS^- + Na^+ = NaHS^0$.

While the variation of the intensity of the H–S mode with $[NaOH]$ superficially resembles that expected from a simple deprotonation equilibrium (Equation (2)), it is quantitatively inconsistent with such a reaction. The data are inherently difficult to interpret because in these highly concentrated solutions $\{H_2O\}$ will decrease in parallel with any supposed change in $[HS^-]$. Nevertheless, three simple simulations using the ESTA package (ESI), each with *one* (conditional) equilibrium constant as an adjusted variable, suggests that the formation of $NaS^-(aq)$ matches the observed data better (green line) than would the formation of either $S^{2-}(aq)$ (red line) or $NaHS^0(aq)$ (dashed black line).

An even more instructive result was obtained from analogous measurements in $CsOH(aq)$. The Raman intensity, adjusted using $SO_4^{2-}(aq)$ as the internal standard ($CsClO_4(s)$ is sparingly soluble), showed no decrease at all (Figure 2) up to the approximate solubility limit of $CsOH(s)$.

The displacement of H^+ from $HS^-(aq)$ by Na^+ in concentrated $NaOH(aq)$ is consistent with all this evidence. Equation (3) is therefore more pertinent than Equation (2), although even this would still be an over-simplification (ignoring the possible weak binding of HS^- and OH^- by Na^+ , for example). We note, in particular, that there is no spectral signal to confirm $NaS^-(aq)$.



Importantly, however, if HS^- deprotonation occurs in $NaOH(aq)$ it is unequivocally due to the presence Na^+ as is evident from a comparison of Figure 1 and Figure 2 (inset). Values of K'_{a2} obtained from measurements in $NaOH(aq)$ thus refer to a medium in which the critical effect is dominated by strong Na^+ interactions and, as such, cannot be characterised by any method currently available. Every connection between a putative S^{2-} species in concentrated $NaOH(aq)$ and other sulfide species *in aqueous solution* is therefore refuted.

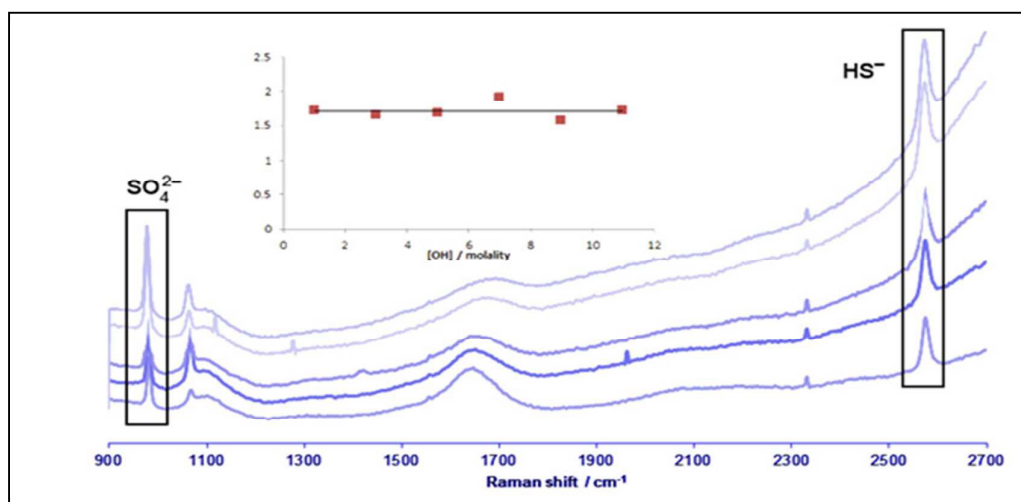


Figure 2. Raman spectra at $1 \leq [\text{CsOH(aq)}]/(\text{mol.kg}^{-1}) \leq 11$ (increasing from bottom to top) at $\sim 22^\circ\text{C}$. Inset shows the invariance of the Raman intensity of the $\text{HS}^-(\text{aq})$ mode at $\sim 2600\text{ cm}^{-1}$ over the entire range of CsOH concentration.

There is not just this inability to extrapolate to infinite dilution (*i.e.*, by appropriately defining activity coefficients in concentrated solutions), on top of the chaotic history of reported pK_{a2}^0 values (ESI). Even more compellingly, there is no practical difference between the above experimental estimates of 17, the OECD Nuclear Energy Agency recommendation³⁰ of 19 or any other even-higher (order of magnitude) value. In other words, there is no relationship between independent and dependent observations. Sustaining the present situation by adding and then subtracting the same pK_{a2}^0 value is purely artificial.

We specifically do not depend here on any fundamental explanation for the difference found between NaOH(aq) and CsOH(aq) other than to note that structural causes (such as changes in hydration and packing) are likely, permitting a stronger interaction of S^{2-} with $\text{Na}^+(\text{aq})$ than $\text{Cs}^+(\text{aq})$. A valuable conclusion can nonetheless be drawn with confidence: it is implausible to suggest that $\text{S}^{2-}(\text{aq})$ forms *via* Equilibrium (2) in NaOH(aq) but not in CsOH(aq) . Hydroxide alone is evidently insufficient. Such reasoning, on the other hand, is not proof: $\text{S}^{2-}(\text{aq})$ *might* exist in 'regular aqueous solutions' at negligibly low concentrations, even if it were of no practical interest (ESI). The issue is not just philosophical. It also has widespread tangible consequences.

A better understanding of equilibria in sulfide solutions can only be achieved by a major shift in thinking and practice in all relevant fields of chemical research and teaching, as required (ESI) by our 'null hypothesis': the sulfide dianion, S^{2-} , does not exist in aqueous solution. Previous attempts to deprecate this species have failed spectacularly. Just emphasising that pK_{a2}^0 is

uncertain and/or that $\text{S}^{2-}(\text{aq})$ is unimportant, as Myers did¹⁶, **will not suffice**. $\text{S}^{2-}(\text{aq})$ should no longer be tolerated (unless and until there is solid evidence to the contrary). It is easy enough to avoid by writing the reaction equations differently (ESI).

Our findings have significant ramifications, most notably for thermodynamic databases in which reliable older data of many chemical reactions become inconsistent with more-recent estimates based on differing values of pK_{a2} . Errors so arising tend to become embedded in derived thermodynamic parameters in ways that are not easy to reverse (ESI). All thermodynamic calculations of sulfide solutions, *even under acidic conditions*, must therefore be treated with more-than-usual caution.³¹ Note, for instance, the major differences in Gibbs energies of formation for $\text{H}_2\text{S(aq)}$ between recent evaluations,^{32,33} and when compared with traditional values. Modellers can ensure that these confounding knock-on effects are minimised by working only with well-characterised equilibria established between chemical species at realistic concentrations. Experimentalists can help by proving the existence of putative chemical species beyond reasonable doubt. As shown above, no experimental investigation of $\text{S}^{2-}(\text{aq})$ to date has met this critical standard. The sorry caravan of confusion over pK_{a2}^0 will roll on until $\text{S}^{2-}(\text{aq})$ is comprehensively banished by the chemical community.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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