# Reply to the discussion by C. Shi of the paper "Estimating the electrical conductivity of cement paste pore solution from OH$^-$, K$^+$, and Na$^+$ concentrations

by

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Discussion

# Reply to the discussion by C. Shi of the paper "Estimating the electrical conductivity of cement paste pore solution from OH−, K+, and Na+ concentrations"☆

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Shi et al. [1] have applied an equation for solution equivalent conductivities (denoted by $\Lambda$) to the problem of estimating species equivalent conductivities (denoted by $\lambda$), with potentially pathological consequences, as I will show. For completeness, I will address some of Dr. Shi's statements one at a time:

*Estimation of the electrical conductivity of mixed solutions... is discussed and demonstrated in most physical chemistry and electrochemistry textbooks.*

Actually, the electrical conductivity of solutions composed of binary salts is discussed in most textbooks. As these are textbooks, they typically limit the discussion to simple salts and leading order concentration dependence. Most textbooks give Kohlrausch's equation for the solution electrical conductivity $\Lambda$:

$$\Lambda = \Lambda_0 - Ac^{1/2} \tag{1}$$

The quantity $c$ refers to the concentration of the binary salt, and $\Lambda_0$ is the dilute limit ($c \to 0$) solution equivalent conductivity. The solution equivalent conductivity $\Lambda_i$ is the sum of the component species equivalent conductivities $\lambda_{i,j}$:

$$\Lambda_i = \sum \lambda_{i,j} \tag{2}$$

The index $i$ refers to a particular solution. The index $j$ refers to an ionic species in the $i$th solution. For example, $i = \text{NaCl}$ and $j = (\text{Na}^+, \text{Cl}^-)$.

But Kohlrausch's equation is only a first-order estimate for solution equivalent conductivity. As I state in the paper, "While a number of highly accurate equations containing numerous coeffcients exist for estimating the equivalent conductivity [2], a new single-parameter model is proposed for its simplicity". To put this into context, I have summarized these equations here in Table 1. The quantities A, B, C, and D are coefficients for specific salts. Our paper uses a variation on the 1924 Walden equation.

*The authors "proposed" Eq. (3) or "a single-parameter model" to estimate the concentration dependence of the individual equivalent conductivity at 25 C. However, no references or information was given how the equation was derived.*

I refer the reader to the right column on page 794 of our paper, "As a compromise, Eq. (3) is a modification of a relationship (for binary salts) by Walden ..." References to both Horvath and Walden appear in our paper.

The approach described in our paper begins with the Walden expression for a binary salt, but addresses the fact that it is to be applied to individual species in arbitrary mixtures, which had never been done before; estimating the transport parameters in arbitrary multispecies electrolytes is a deep and difficult problem. Therefore, I had to determine the species parameters in a balanced way and incorporate the overall ionic strength. As stated in our paper, "The empirical coeffcients $G_i$ are chosen to best agree with published data for the electrical conductivity of solutions". As a result, I refer to my equation as resembling Walden's, but with important differences.

*Actually, a single-parameter equation is described in most physical chemistry and electrochemistry textbooks, which appears to be obeyed to a concentration of about 0.1 M aqueous univalent ions, only slight deviations are observed for NaOH and KOH solutions up to a concentration of 1 M [3].*

I could not find this assertion in Adamson. Adamson did, however, have this to say about the 1923 Debye–Hückel

Table 1
Summary of equations for solution equivalent conductivity $\Lambda$, taken from Table 2.11.1 in Ref. [2]

| Author | Equation | Year |
|---|---|---|
| | $\Lambda = \Lambda_o - Ac^{1/2}$ | |
| | $\Lambda = \Lambda_o - (A\Lambda_o + B)c^{1/2}$ | |
| | $\Lambda = \Lambda_o/(1 + Bc^{1/2})$ | |
| | $\Lambda = \Lambda_o - Ac^{1/2} + Bc$ | |
| | $\Lambda = \Lambda_o - [Ac^{1/2}/(1 + Bc^{1/2})]$ | |
| | $\Lambda = \Lambda_o - [Ac^{1/2}/(1 + Bc^{1/2})] + Dc$ | |
| | $\Lambda = \Lambda_o - Ac^{1/2} + Bc \log c + Cc$ | |
| | $\Lambda = \Lambda - (\log c)/2$ | |

equation with the Onsager coefficients (the relationship used by Shi et al. [1]), "Equation 12–19 is valid for aqueous univalent ions at 25 °C at concentrations below about 0.1 M" (Ref. [3], Section 12-3.C, p. 498). This text appears in the paragraph immediately following the equation. This sentiment was reiterated by Horvath (Ref. [2], Chapter 2.11, p. 255), "The positive deviation from the theoretical conductances becomes significant at high concentrations only (above 0.1 mol/L)...".

*Actually, the estimation of electrical conductivity of cement paste pore solution has been well demonstrated in a previous publication [2] and is discussed in more details in a recent publication [3].*

The "previous publication" [1] uses the 1923 Debye–Hückel expression that appears in Table 1 and the Onsager expression for the coeffcients $A$ and $B$:

$$A = 0.2289 \quad B = 60.21 \text{ cm}^2 \text{ S mol}^{-1} \qquad (3)$$

These coeffcients are for binary salts, but Shi et al. [1] use these coeffcients, without modification, for each species in an arbitrary mixture. If this does not seem problematic, consider the following challenge: Determine the conductivity of a 0.510 mol/l NaOH solution. The *1982–1983 CRC Handbook of Chemistry and Physics* (p. D-265) reports the conductivity to be 0.0931 S/cm. The calculation, using the three approaches discussed, is tabulated as follows

$(\lambda^o_{Na^+} = 50.1 \text{ cm}^2 \text{ S/mol}; \lambda^o_{OH^-} = 198.0 \text{ cm}^2 \text{ S/mol};$

$\Lambda^o_{NaOH} = \lambda^o_{Na^+} + \lambda^o_{OH^-}):$

| | $\lambda_{Na^+}$ | $\lambda_{OH^-}$ | $\sigma$ (S/cm) |
|---|---|---|---|
| Snyder | | | |
| Shi | | | |
| Debye–Hückel | | | |

Not only is my method more accurate than either the Shi method or the Debye–Hückel equation (properly applied to a binary salt solution), the method of Shi is problematic; a negative species equivalent conductivity is unphysical, and it violates the second law of thermodynamics. The problem with Dr. Shi's method arises because the $B$ coefficient was meant to be applied to the larger solution equivalent conductivity, not the smaller species equivalent conductivities. Moreover, it points out that Dr. Shi did not make a cursory check of the equation. The telling evidence is Dr. Shi's omission of a similar calculation in his discussion, or even a comparison of his equation to the data given in our paper.

For my part, I regret not being aware of the previous publication [1] and not having referenced that paper so that I could have pointed out these problems in our paper. Unfortunately, Dr. Shi's recent publication [4] will only serve to promulgate these misconceptions to a wider readership.

The propagation of these errors through the literature highlights a growing problem in concrete materials research. It is my professional and personal opinion that concrete materials research is one of the most interdisciplinary engineering problems. Many of us have found a particular subdiscipline to study at great depth; a feature that draws people to the field. Unfortunately, limited financial support for concrete materials research has begun to isolate many of us; as a community, we have a wide breadth of knowledge, but there are very few people working deeply in the same subdiscipline. As a result, we are beginning to lose the ability to make knowledgeable decisions as to whether a particular paper should be published. This fact should make each of us pause to consider whether we have independent confirmation that our research is on a sound foundation.

## References

[1] C. Shi, J.A. Stegemann, R.J. Caldwell, Effect of supplementary cementing materials on the specific conductivity of pore solution and its implications on the Rapid Chloride Permeability Test (AASHTO T277 and ASTM C 1202) results, ACI Mater. J. 95 (1998) 389–394.
[2] A.L. Horvath, Handbook of Aqueous Electrolyte Solutions: Physical Properties, Estimation and Correlation Methods, Wiley, New York, 1985.
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[4] C. Shi, Effect of mixing proportions of concrete on its electrical conductivity and the rapid chloride permeability test (ASTM C 1202 or ASSHTO T277) results, Cem. Concr. Res. 34 (2004) 537–545.