Journal of Porous Media 12(3), 289–291 (2009)

Discussion of the Paper "Experimental Investigation into Concentration-Dependent Chloride Diffusivity in Glass Beads and Fine Sand" by K. Prabhakaran Nair, A. Praveen, and S. Chandrakaran

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The article under discussion deals with the classical topic of electrolyte diffusion in porous media. Special attention is given to the concentration dependence of the effective diffusion coefficient. The findings of the article are, in many ways, rather unusual. First, a concentration dependence far exceeding that reported in the literature is found, and second, the apparent tortuosities are, in most cases, of such a magnitude that their physical meaning must be seriously questioned.

The authors (Prabhakaran Nair et al., 2007) report effective diffusion coefficients for separate assemblies of glass beads and fine sand, for which four common electrolytes (NaCl, KCl, $CaCl_2$, and $MgCl_2$) were used. The experimentally determined effective diffusion coefficients all appear to increase significantly with concentration, and some, but not all, data display a slight initial decrease with increasing concentration. The ratio of the diffusion coefficients in the concentration intervals considered (approximately 0.02 M to 0.55 M) in some cases amount to almost a factor of 10. Although it is well known that the diffusion coefficient does depend on the electrolyte concentration, the variation measured by the authors is far beyond that reported in benchmark literature on the subject (see, e.g., Mills, 1957; Mills and Lobo, 1989; Rard and Miller, 1979; Robinson and Stokes, 1959; Stokes et al., 1957). For instance, results obtained by Robinson and Stokes (1959) are shown in Fig. 1. More recent results have largely confirmed these well-established trends (Ahl, 2004; Ahl and Lü, 2007; Leaist and Curtis, 1999; Tang, 1999).

It should be noted that the concentration range shown in Fig. 1 (up to 4 M) is approximately a factor of 8 larger than that considered in the article under

Received November 19, 2007; Accepted January 16, 2008

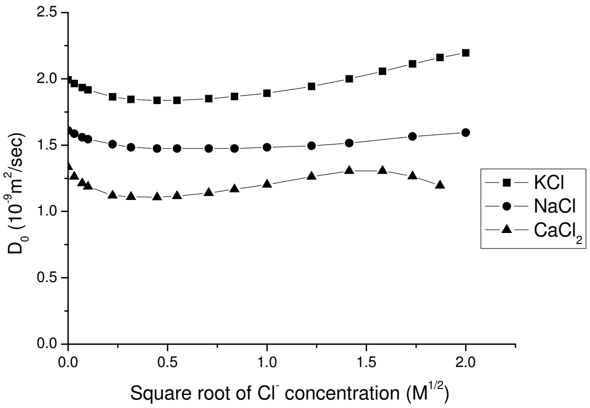

Figure 1. Concentration dependence of free diffusion coefficients for three different electrolytes (after Robinson and Stokes, 1959)

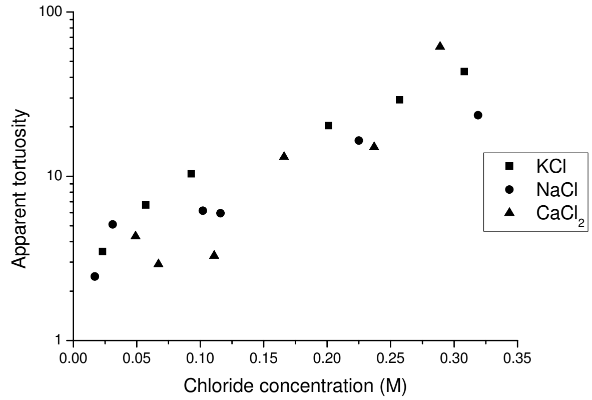

Figure 2. Apparent tortuosity of glass bead assembly as function of chloride concentration back calculated using the effective diffusion coefficients provided by Prabhakaran Nair et al. (2007) and according to Eq. (1)

discussion. Also, it appears that for the narrower concentration range studied by Prabhakaran Nair et al. (2007), the effective diffusion coefficients should largely be expected to decrease slightly.

In accordance with the authors, the effective diffusion coefficient can be defined as

$$D_{\text{eff}} = \tau_a D_0 \tag{1}$$

where τ_a is the apparent tortuosity, D_0 is the free (solute) diffusion coefficient, and D_{eff} is the effective diffusion coefficient. Note that the apparent tortuosity by definition is less than unity. Using the effective diffusion coefficients provided by the authors for the glass bead assembly, the tortuosity can be calculated according Eq. (1). The value of D_0 at a given concentration has been estimated on the basis of the Robinson and Stokes (1959) results shown in Fig. 1. The tortuosities so determined are shown in Fig. 2. Remarkably, these are all significantly greater than unity, with a trend to increase with concentration (consistent with the results already discussed). The authors do not attempt to explain these definitely unphysical results. In view of the inertness of the materials used, it is difficult to see that these results can be caused by anything other than errors in the experimental protocol.

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