

**Reply to the Discussion by K. K. al-Tarawneh,
O. Buzzi, K. Krabbenh \Oft , and A. V. Lyamin on
Experimental Investigations into
Concentration-Dependent Chloride
Diffusivity in Glass Beads and Fine Sand**

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The results reported by us (Prabhakaran Nair et al., 2007) relate to the instantaneous transport pattern observed in the solute diffusion process through porous systems when a specified concentration pulse is released. Hence the experiments are conducted to determine the diffusion coefficient for the preceding situation by creating the maximum possible gradient in the diffusion cell, with the initial condition of specified concentration on one side of the cell and zero concentration on the other. It was also ensured that the porous systems considered for the experiments did not contain any traces of diffusing species before initiating the diffusion process for every solute concentration. All the results reported until now have not specified clearly the influence of solute gradient and related aspects involved in the determination of diffusion rate, the absence of which would certainly lead to serious discrepancies in the analysis and the simulation of the entire diffusion process.

The variations of the diffusion coefficient in porous systems for different concentrations of chloride ions in porous systems are explained in accordance with the change in the activity coefficient. On the basis of the observations reported from the experiments undertaken to assess the variation of the activity coefficient with the diffusion coefficient, the activity coefficient is said to lower the diffusion coefficient at lower concentrations and increase the diffusion coefficient at higher concentrations (Tang, 1999). The results presented by Tang (1999) show that a lower range of negative influence of concentration and a positive influence for higher solute concentrations on diffusion coefficients obtained. Such a variation can be attributed to the influence of the activity coefficient, which would tend to reduce the diffusion coefficient at low concentrations, but will increase the diffusion coefficient at high concentrations. The nonlinear variation of thermodynamic properties of electrolytes with ionic strength

is the prime reason for the deviations observed at high ionic concentrations. As ionic strength increases, various interactions, either ion-ion or/and ion-solvent, become significant, and the thermodynamic properties of the electrolytes gradually deviate from that of an ideal (very dilute) solution.

The concentration selected for this study is in the range 0.01 meq/cc to 0.35 meq/cc, and hence the activity coefficient of chloride ions in this concentration range could be better explained by the modified versions of Davies equation, which have shown good agreement with the activity coefficient and a higher ionic concentration (Samson et al., 1999). The modified Davies equation is represented as

$$\ln \gamma_i = -\frac{Az_i^2\sqrt{I}}{1 + (3 \times 10^{-10})B\sqrt{I}} + \frac{((-4.17 \times 10^{-15})I + 0.2)Az_i^2I}{\sqrt{1000}}$$

where A and B are constants, I is the ionic strength (mmol/l), z_i is the valance number, and γ_I is the activity coefficient. This equation has a general form of $f(\gamma_i) = A_1(I^2) + A_2(I) + A_3(\sqrt{I}) + C$. In line with these results, the chloride diffusion coefficient–concentration relationship obtained for all electrolytes shall be suitably represented as $D(C) = P(C) + Q(\sqrt{C}) + R$, where C is the chloride concentration in meq/cc, $D(C)$ is the diffusion coefficient in cm^2/s , and, P , Q , and R are constants obtained from curve fitting.

It is confirmed in our study that as the concentration of the electrolytes is increased from infinite dilution stage, the value of the diffusion coefficient will first tend to be reduced to reach a lower value that can be significantly different than at infinite dilution.

Once this critical value is reached, any subsequent increase in solution concentration will contribute to an increased diffusion coefficient. The observations are nearly identical for chloride diffusion through fine sand and glass beads. Furthermore, the $D(C)$ reported in Prabhakaran Nair et al. (2007) is able to simulate the process better. On the issues related to the tortuosity factor, the following explanations are given. The tortuosity is a lumped parameter given for representing the tortuous pathways in a porous system when compared to free solution diffusion of the solute. The equation $D = D_o\tau$ cannot be directly applied to determine the tortuosity coefficient. Here the equation needs to be modified to $D = D_o\alpha\tau$, where α is the activation correction factor for each concentration, which will ensure the constant nature of τ . This was not mentioned in Prabhakaran Nair et al. (2007) as the focus is on determining the pattern in the variation of diffusion coefficients for different solute concentrations.

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