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Concentration dependence of diffusion and migration of chloride ions
Part 2. Experimental evaluations

Luping Tang*,[1]

Department of Building Materials, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden

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Abstract

This paper series includes two parts: (1) theoretical considerations and (2) experimental evaluations. In Part 1, the chloride ion diffusion and migration processes in a pure solution system as well as in a solution-concrete system have been theoretically analyzed. The relationships between different diffusion coefficients from the conventional diffusion or migration tests have been established. In this, the second part, the parameters influencing the "effective" diffusion coefficient, such as activity coefficient, counter-electrical field, and the friction coefficient due to the ionic interaction, are quantitatively evaluated with available experimental data. The results show that the concentration dependence of chloride diffusion and migration can be quantitatively described by two decisive parameters: K_τ and f; the former describes the effect of counter-electrical field and the latter describes the friction effect. The theories fit the experimental data fairly well. Some phenomena of ion diffusion in concrete can be explained by these theories, such as the differences in diffusion coefficient between diffusion and migration tests and between cations and anions.

Keywords: Diffusion; Transport properties; Chloride; Concrete; Migration

1. Introduction

It can be seen from Part 1 [1] that the "effective" chloride diffusion coefficients of concrete determined from the conventional diffusion or migration tests are not constant but are strongly concentration dependent. A number of works [2–5] studied the use of external solutions with different chloride concentrations and have demonstrated this concentration dependence. Chatterji [6] suggested a square-root rule, similar to Kohlrausch's rule for conductivity, to describe this concentration dependence [see Eq. (1)]:

$$D = D_0(1 - K\sqrt{c}) \tag{1}$$

where K is constant. It should be noted that if not otherwise stated the definitions of symbols in this part are the same as given in Part 1 [1].

However, it seems not so easy to apply this square-root rule in concrete, as shown in Fig. 1, where the slope (K value) is different for different ranges of chloride concentration in the external solution. This implies that K in Eq. (1) is not really a constant, but instead is concentration-dependent. Therefore, Eq. (1) can only be applied to a very narrow range of concentrations. Some researchers [7,8] tried to use activity coefficient to explain the concentration-dependent diffusivity. In most cases, however, the activity coefficient of NaCl solutions changes in a range of 1 to 0.68 from a very low concentration to about 1 mol/dm^3 NaCl [7]. By using activity coefficient only, one cannot explain the large difference in chloride diffusion coefficient seen in Fig. 1. As derived in Part 1 [1], there exists not only activity coefficient, but also other decisive factors influencing the "apparent" or "effective" diffusion coefficient. The quantitative influences of these factors will be discussed in this part.

2. Effect of activity coefficient

There are many theories to describe the relationship between activity coefficient and concentration. Among these theories the Pitzer model seems most suitable for calculation of γ in concentrated solutions [8,9]. This model is, however, very complicated and the use of this model needs a lot of important experimental data, as described by Marchand et al. [8] and Hidalgo et al. [9]. In addition, it is diffi-

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* Corresponding author.

E-mail address: tang.luping@sp.se (L. Tang)

[1] Current address: SP Swedish National Testing and Research Institute, PO Box 857, SE-50115 Borås, Sweden. Tel.: +46-33-16-51-38; fax: +46-33-13-45-16.

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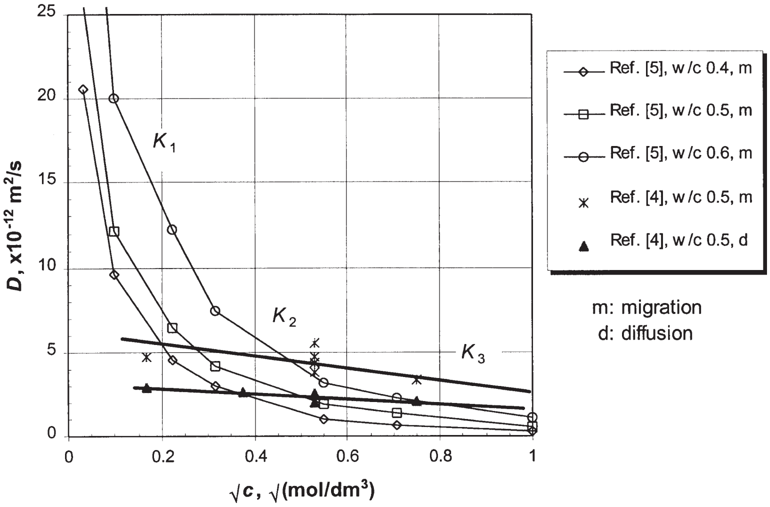

Fig. 1. Nonlinear relationship between diffusion coefficient and square-root concentration. Note: According to the other works [4,5] the identical concrete specimens were used in their experiments. The data [4,5] in Fig. 1 will later be used in Table 3 and Fig. 6 for demonstrating the theoretical relationships derived in Part 1 [1].

cult to solve the term ∂lnγ/∂ln*c* from such a complicated model. Another commonly used theory is the Debye-Hückel extended equation [10], as shown in Eq. (2):

$$\log\gamma = -A|z_+z_-|\frac{\sqrt{I}}{1+B\cdot a'\cdot\sqrt{I}}+B^*\cdot I \qquad (2)$$

where coefficients *A* and *B* are temperature dependent, constant *a'* is assumed to correspond to the radius of the ion, *B** is an empirical parameter depending on the type of salt solution, and *I* is the ion strength, as seen in Eq. (3).

$$I = \frac{1}{2}\cdot\sum_i z_i^2 c_i = \frac{n_+z_+^2+n_-z_-^2}{2}\cdot c \qquad (3)$$

From Eq. (2) and Eq. (3) the term ∂lnγ/∂ln*c* could be solved [see Eq. (4)]:

$$\frac{\partial\ln\gamma}{\partial\ln c} = -2.302\times\frac{n_+z_+^2+n_-z_-^2}{2}\left[\frac{A|z+z_-|}{2\sqrt{I}(1+B\cdot a'\cdot\sqrt{I})^2}-B^*\right]\cdot c \qquad (4)$$

According to Justnes and Rodum [10], for 1:1 Cl solutions at 25°C, $A = 0.509$ dm$^{1/2}$/mol$^{1/2}$, $B = 3.286$ dm$^{1/2}$/(mol$^{1/2}\cdot$ nm), and $a' = 0.4$ nm. The empirical parameter *B** could be estimated from the experimental data. Some activity coefficient data quoted from [11] for different 1:1 salt

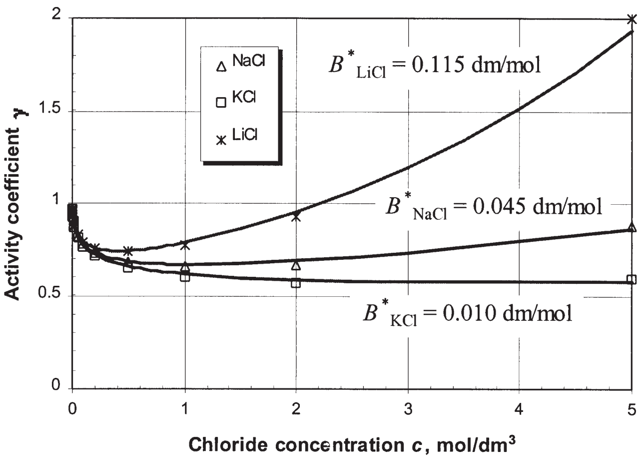

Fig. 2. Quantitative relationships between γ and *c*, where point data are quoted from a previous work [11].

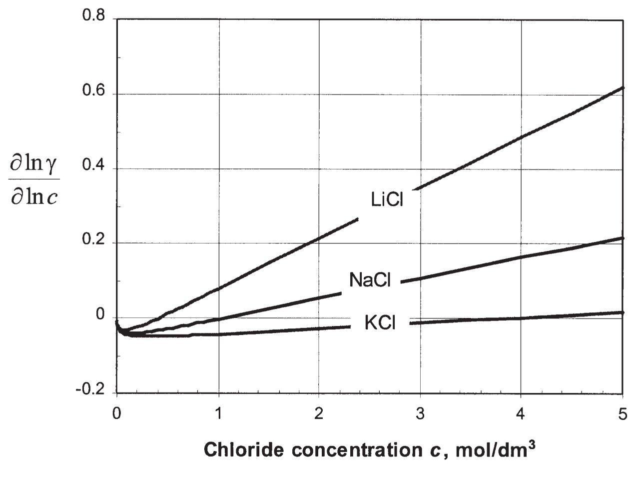

Fig. 3. Quantitative relationships between ∂lnγ/∂ln*c* and *c*.

Table 1
Values of $K_{\tau 0}$ for LiCl, NaCl, and KCl solutions

	Mobility $\times 10^{-4}$ cm^2 (s · V) [13]		
Salt	Cation	Anion	$K_{\tau 0}$
LiCl	$Li^+ = 4.01$		-0.327
NaCl	$Na^+ = 5.19$	$Cl^- = 7.91$	-0.207
KCl	$K^+ = 7.62$		-0.019

solutions as well as the quantitative relationships between γ and c, calculated from Eq. (2), are shown in Fig. 2, and the relationships between $\partial \ln\gamma/\partial \ln c$ and c, calculated from Eq. (4), are shown in Fig. 3. It can be seen from Fig. 2 that as concentration increases, activity coefficient decreases at low concentrations, but increases at high concentrations. Thus the differential term $\partial \ln\gamma/\partial \ln c$ changes its sign (from negative to positive) at a certain concentration, as shown in Fig. 3. This means that the activity coefficient tends to reduce the effective diffusion coefficient at low concentrations, but tends to increase the effective diffusion coefficient at high concentrations. For KCl, the negative influence of activity coefficient on diffusion coefficient can be found in a wide range of concentration. For LiCl, the negative influence is very limited, while a positive influence of 60% may be caused at high concentrations (e.g., 5 mol/dm^3). For NaCl, there is no influence at all when concentration is about 1 mol/dm^3, but a positive influence of 20% may be caused at a concentration of 5 mol/dm^3. For all these three types of salts, the maximal negative influence is only about a few percentage points.

3. Estimation of counter-electrical fields

3.1. Parameter $K_{\tau 0}$ caused by the source solution

According to Eq. (13) in Part 1 [1, see Eq. (5)],

$$K_{\tau 0} = \frac{u_{+0} - u_{-0}}{u_{+0} + u_{-0}} \tag{5}$$

By using the mobility data [12], the values of $K_{\tau 0}$ for LiCl, NaCl, and KCl solutions could be obtained, as listed in Table 1.

3.2. Parameter $K_{\tau m}$ caused by membrane potential

According to Eq. (22) in Part 1 [1], the value of $K_{\tau m}$ can be calculated from the measurement of membrane potential across a concrete specimen, as shown in Eq. (6):

$$K_{\tau m} = -\frac{F(\phi_2 - \phi_1)}{RT \ln\frac{\gamma_2 c_2}{\gamma_1 c_1}} \tag{6}$$

Recently, Zhang and Buenfeld [13] first reported some measured data of the membrane potential across a disc specimen of mortar with water-cement ratio of 0.45. From their experimental data the value of $K_{\tau m}$ could be estimated, as shown in Table 2.

Once the parameters $K_{\tau 0}$ and $K_{\tau m}$ are known, the ratio of cation velocity to anion velocity can be calculated by Eq. (30) in Part 1 [1], and here as Eq. (7):

$$\beta_v = \frac{v_+}{v_-} = \frac{1 + (K_{\tau 0} + L_{\tau m})}{1 - (K_{\tau 0} + K_{\tau m})} \tag{7}$$

4. Estimation of friction coefficient *f*

4.1. Pure solution system

According to Part 1 [1], the effective chloride diffusion coefficient D_d in a pure solution system is shown in Eq. (8).

$$D_d = D_{-0}(1 - z_- K_{\tau 0})\left(1 + \frac{\partial \ln\gamma}{\partial \ln c}\right) \cdot \frac{2c + c_0}{f(1 - \beta_v)c + c_0} \tag{8}$$

In the above equation, $D_{-0} = 2.03 \times 10^{-9}$ m^2/s for Cl$^-$ [12, 13]. The values of $K_{\tau 0}$ have been listed in Table 1 and $\partial \ln\gamma/\partial \ln c$ can be determined by Eq. (4). β_v $(= v_{+0}/v_{-0} = u_{+0}/u_{-0})$ can be calculated from the values of mobility (see Table 1) and the solvent concentration c_0 can be calculated by Eq. (9) in Part 1 [1]. Therefore, the only unknown parameter in Eq. (8) is *f*. The values of *f* could be found by curve-fitting the experimental data of D_d. Some calculated results are shown in Fig. 4. It can be seen that the theoretical Eq. (8) fits the reported data [14,15] fairly well for the three types of common chloride salts.

It should be noted that for a salt solution, D_d represents the effective diffusion coefficient of salt. In other words, the anions and cations have the same effective diffusion coefficient in a pure solution system. At the infinite dilute concentration, Eq. (8) becomes Eq. (9),

$$D_d = D_{-0}(1 - z_- K_{\tau 0}) = D_{-0}\frac{2u_{+0}}{u_{+0} + u_{-0}} = \frac{2D_{-0}D_{+0}}{D_{+0} + D_{-0}} \tag{9}$$

which is in accordance with the diffusion coefficient for 1:1 salts [11].

Table 2
Values of $K_{\tau m}$ for NaCl and KCl solutions

	Concentration [9]		Activity coefficient [12]			
Salt	c_1	c_2	γ_1	γ_2	$(\phi_2 - \phi_1)$ [9]	$K_{\tau m}$
KCl	1 M	0.1 M	0.604	0.768	−21 mV	−0.397
NaCl	1 M	0.1 M	0.657	0.779	−22 mV	−0.402

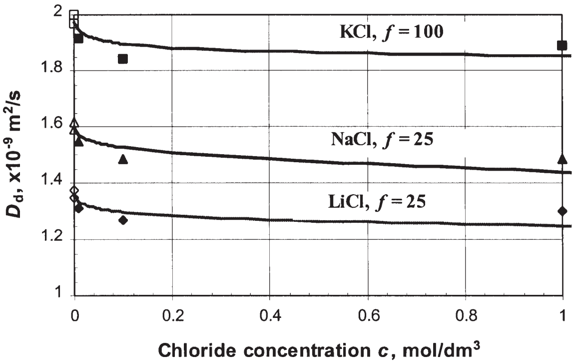

Fig. 4. Effective chloride diffusion coefficient D_d in a pure solution system. Data with hollow points are quoted from another work [14]. Data with solid points are also quoted from another work [15].

4.2. Solution-concrete system

According to Eq. (28) in Part 1 [1], the friction coefficient f can be expressed as shown in Eq. (10).

$$f = \frac{\varepsilon(2c + c_0)D_{-0} - c_0 D_{ssm}}{(1 + |\beta_\nu|)cD_{ssm}} \tag{10}$$

Recently, Zhang [5] reported a series of experimental data of chloride migration coefficient in concrete measured from the steady-state procedures. These data covered two magnitude orders of concentrations (i.e., from 0.01 to 1 mol/dm^3 NaCl). Zhang [5] also measured the water content of the specimens that could represent the diffusible porosity ε. Therefore, his data are suitable for the estimation of the f values. The calculated results are listed in Table 3. It is obvious that only those values in the concentration range 0.1 to 1 mol/dm^3 appear very close. Considering the larger uncertainties in the chloride measurement at low concentrations and the chloride concentration in reality (e.g., seawater), the values obtained from the concentration $<$0.1 mol/dm^3 were excluded in averaging.

It can be seen from Table 3 that the value of f increases with decrement of water-cement ratio, implying larger friction in dense concrete than in poor concrete. Compared with those values in Fig. 4, the values of f for concrete are two to three magnitude orders larger than those for pure solution, indicating much larger friction in the pore solution than in the external source solution.

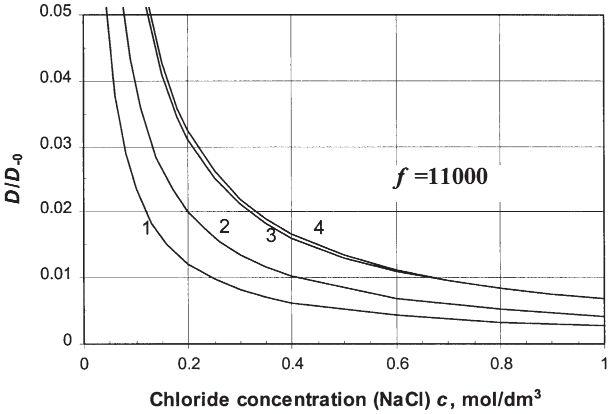

Fig. 5. Comparison between different curves of D/D_0 versus c. Curve 1: diffusion according to Eq. (27) in Part 1 [1] with $K_{\tau 0} = -0.207$ (Table 1) and $K_{\tau m} = -0.402$ (Table 2). Curve 2: migration according to Eq. (28) in Part 1 [1]. Curve 3: diffusion assuming $K_{\tau 0} = K_{\tau m} = 0$. Curve 4: diffusion assuming $\partial \ln\gamma/\partial \ln c = 0$ and $K_{\tau 0} = K_{\tau m} = 0$.

5. Comparison between different effects

By inserting various parameters into Eq. (27) and Eq. (28) in Part 1 [1], one can obtain different curves of effective diffusion coefficient, as shown in Fig. 5. It can be seen from curves 3 and 4 that the influence of activity coefficient does not seem significant for NaCl. Comparing curve 3 with curve 1, one can find that the parameter K_τ has a very strong influence on chloride diffusion.

6. Relationship between diffusion and migration coefficients

It can be seen from Fig. 5 that in the absence of counter-electrical fields (i.e., $K_\tau = 0$, curve 3), the diffusion coeffi-

Table 3
Values of f for ordinary Portland cement concrete*

	w/c = 0.4, ε = 0.05		w/c = 0.5, ε = 0.067		w/c = 0.6, ε = 0.064	
c (mol/dm^3)	D_{ssm}	f	D_{ssm}	f	D_{ssm}	f
0.01	9.6	42700**	12.1	45700**	20.0	24500**
0.05	4.5	19300**	6.4	18100**	12.2	8622**
0.1	3.0	14700	4.2	14000	7.4	7400
0.3	1.0	15000	1.9	10600	3.2	5900
0.5	0.6	15200	1.4	8700	2.3	5000
1.0	0.3	15300	0.5	12300	1.1	5300
Average f		15000		11000		5900

*Data except for f values are quoted from [5] with D_{ssm} in $\times 10^{-12}$ m^2/s.
**Excluded in the averaging.
w/c = water/cement ratio.

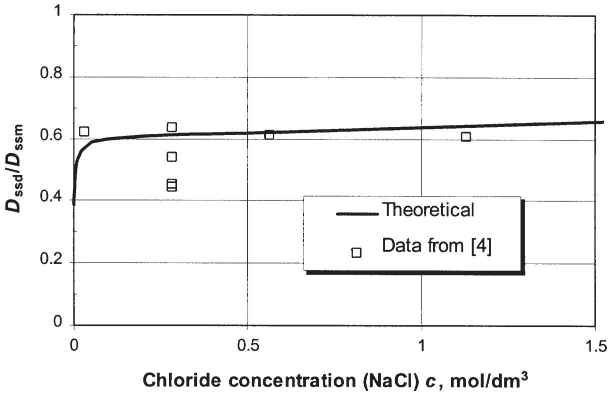

Fig. 6. Relationship between diffusion coefficient D_{ssd} and migration coefficient D_{ssm}, with $f = 11000$ (Table 3, water-cement ratio 0.5), $K_{\tau 0} = -0.207$ (Table 1) and $K_{\tau m} = -0.402$ (Table 2).

cient D_{ssd} from a diffusion process should always be larger than D_{ssm} from a migration process (curve 2), because the counter-flow of cations in the migration process should have larger friction effect on the anions than in the diffusion process in which both the cations and anions move in the same direction. Due to the existence of counter-electrical fields, however, the actual D_{ssd} may become less than D_{ssm}, as shown by curve 1 in Fig. 5. The experimental data reported by Arsenault et al. [4] from their steady-state diffusion and migration tests have shown that D_{ssd} is really less than D_{ssm}. This might be additional evidence of the existence of counter-electrical fields in an ion diffusion process.

The theoretical relationship between D_{ssd} and D_{ssm} has been expressed by Eq. (29) in Part 1 [1]. A comparison of this theoretical relationship with the measured data [4] is shown in Fig. 6. It is very surprising that the experimental data fit the theoretical curve fairly well.

7. Diffusion coefficient of coexisting cations

In the literature, the reported diffusion coefficients of cations or anions are often a simple measure of ion flux, as seen in Eq. (11):

$$D_{d+} = \frac{J_+}{-\frac{\partial c}{\partial x}} \quad \text{and} \quad D_{d-} = \frac{J_-}{-\frac{\partial c}{\partial x}} \tag{11}$$

Therefore, under the same diffusion experiment [see Eq. (12)],

$$\frac{D_{d+}}{D_{d-}} = \frac{J_+}{J_-} = \frac{v_+}{v_-} = \beta_v \tag{12}$$

Inserting Eq. (7) into Eq. (12) gives Eq. (13).

$$\frac{D_{d+}}{D_{d-}} = \frac{1 + (K_{\tau 0} + K_{\tau m})}{1 - (K_{\tau 0} + K_{\tau m})} = \frac{1 + K_\tau}{1 - K_\tau} \tag{13}$$

Some calculated values and measured data are listed in Table 4. It can be seen that the measured data are close to the calculated values.

8. Conclusions

The quantitative analyses of various factors influencing chloride diffusion show that the parameter K_τ, which describes the effect of counter-electrical fields, has a great influence on chloride diffusion, while the influence of activity coefficient does not appear significant for NaCl and KCl. The friction coefficient f influences both diffusion and migration. The values of f for concrete are two to three magnitude orders larger than those for pure solution, indicating much larger friction in the pore solution than in the external source solution.

The theories established in this paper series for ion diffusion and migration in concentrated solutions describe well the behaviors of ion transport through concrete. According to the theories, the concentration dependence of chloride diffusion and migration can be quantitatively determined by two decisive parameters: K_τ and f; the former may be estimated by measuring membrane potential across a concrete disc specimen, while the latter should be based on the measurement of migration coefficient at different concentrations. The experimental data fit the theories fairly well. Some phenomena of ion diffusion in concrete can be explained by these theories, such as the differences in effective diffusion coefficient between diffusion and migration tests and between cations and anions.

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Table 4
Comparison between calculated and measured ratios of D_+/D_{Cl^-}

Source of chloride	Measured D_+/D_{Cl^-}	Calculated D_+/D_{Cl^-}	$K_\tau = K_{\tau 0} + K_{\tau m}$*
LiCl	0.209 [16]	0.157	−0.729
NaCl	0.272 [16]	0.243	−0.609
	0.196 [17]		
KCl	0.438 [16]	0.408	−0.421

*See Table 1 for the values of $K_{\tau 0}$ and Table 2 for the values of $K_{\tau m}$.

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