Effect of electric field induced within rain drops on acid rain formation

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Abstract

In order to take account of the effect of the electric potential ϕ induced by charged chemical species in rain drops on acid rain formation, a new mathematical model, which contains the electro-migration term in addition to the conventional terms, has been constructed. The electric field in rain drops is brought about by the movement of ions which is produced by the absorption of acidic atmospheric pollutant. The ions undergo the electric force caused by the electic field in rain drops and they move toward the certain direction depending on their charge. The numerical simulations by the new model developed here discloses that: (1) the electro-migration of ions makes H^+ concentration higher than that estimated neglecting the electro-migration; (2) the distibution of H^+ concentration tends to uniform under the elecric potential field; and (3) the electric potential is higher at the drop center than at the drop surface.

1 Introduction

There are various interactions between aquatic enviromnent and atmospheric envionment. Rain is an important mediator which brings about interactions between the two envionments. Among the interactions the transfer of anthropogenic atmospheric pollutant, especially acidic substances, from the air to rain water is paid great attention in these days, because it gives rise to deterioration of water and soil, which causes a lot of damage to human health and various ecosystems as lakes, forest, and so on. Therfore, it is very important to estimate the rain water acidity precisely and to clear the mechanisms of the acidification of rain water.

Conventioal mathematical models used to estimate the rain water acidity usually include drop-phase diffusion, drop-phase reaction, and mass trasfer between rain drops and the air (Shiba, 1992). However, when acidic atmospheric pollutant as sulfur dioxide is absorbed into rain drops, it dissociates to produce such cahrged species (ions) as H^+, HSO_3^-, and SO_3^{2-}. These ions are transported by not only the diffusion process but also their individual velocity acquired under the electric potential field.

This movement of ions in rain drops is driven by the electric potential difference and it is called elecro-migration, which brings about recurrently the new state of electric field within the rain drops. That is, ions undergo the time varying electric force induced by the non-steady electric potential due to their own movement. Thus obtained elecro-migration velocity should affect the rate of the transport of ions and acordingly the dynmics of rain drop acidification caused by the absorption of the acidic pollutants. The dynamics of the distribution of their concentration under the electric field may be different from those ignoring the electric field.

2 Drop-phase chemistry of acidification

After absorption of $SO_2(g)$ into rain drops, physically dissolved sulfur dioxide $SO_2 \cdot H_2O$ is dissociated to form bisulfite ion HSO_3^-, sulfite ion SO_3^{2-}, and hydrogen ion H^+. The dissociation process is typically quite rapid compared with such processes as oxidation and diffusion. After two steps of dissociation, the resulting concentrations in rain drops reach equilibrium with a given air-phase concentration. For $SO_2(g)$ the absorption and desorption process can be represented as follows (Liss and Slinn, 1983):

$$SO_2(g) + H_2O \rightleftharpoons SO_2 \cdot H_2O \qquad (\mathcal{H}_1) \qquad (1)$$

$$SO_2 \cdot H_2O \rightleftharpoons HSO_3^- + H^+ \qquad (K_1) \qquad (2)$$

$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+ \qquad (K_2) \qquad (3)$$

where $\mathcal{H}_1$ = distibution coefficient (= 30.32); K_1 and K_2 = first and second dissociation constants, respectively (= 1.74×10^{-2}M and 6.24×10^{-8}M). These values of coefficient and constants are measured at 25 Cels. $SO_2 \cdot H_2O$, HSO_3^-, and SO_3^{2-} form a particular class that is in rapid equilibrium and they usually represented as a sulfur group S(IV).

The acidification due to physical absorption and abovementioned dissociation is limited to the equilibrium concentration to the ambient $SO_2(g)$ and in that case usually pH does not get so low value (e.g., $pH < 4.0$). Then, it is considered that before rain drops reach the ground the sulfur species S(IV) in rain drops are oxidized to sulfate SO_4^{2-}, i.e., a species of group S(VI), after the dissociation. SO_4^{2-} is more powerful for the acidification of rain drops than HSO_3^- [the major species of S(IV)].

The highly soluble hydrogen peroxide $H_2O_2(g)$ is a common species found in the atmosphere and can work for S(IV) oxidation in rain drops. O_3 and O_2 also can work to oxidize S(IV), but hydrogen peroxide is the most effective in the pH

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range of 3-6 (Pandis and Seinfeld, 1989). This pH range observed in usual acid rain.

For $H_2O_2(g)$ the sequence of absorption and dissociation can be described as follows:

$$H_2O_2(g) + H_2O \rightleftharpoons H_2O_2 \cdot H_2O \qquad (\mathcal{H}_5) \qquad (4)$$

$$H_2O_2 \cdot H_2O \rightleftharpoons HO_2^- + H^+ + H_2O \qquad (K_5) \qquad (5)$$

where $\mathcal{H}_5$ = distribution coefficient ($= 1.73 \times 10^6$); and K_5 = dissociation constant ($= 1.84 \times 10^{-12}$M). Since $SO_2(g)$ and $H_2O_2(g)$ are absorbed concurrently, HSO_3^- is oxidized by $H_2O_2 \cdot H_2O$ in rain drops and is transformed to sulfate SO_4^{2-} as follows (Maahs, 1983):

$$HSO_3^- + H_2O_2 \cdot H_2O \rightarrow SO_4^{2-} + 2H_2O + H^+ \qquad (k^* = k[H^+]) \qquad (6)$$

where k^* = reaction rate; and k = reaction rate constant ($= 5.2 \times 10^7 s^{-1} M^{-2}$). Comparing with the time scale of oxidation [Eq.(6)], the time scale of the dissociation [Eqs.(1)-(5)] is very short and the dissociation is considered to be instantaneously accomplished in rain drops. In Fig.1 the sequence of the poduction of sulfate ion SO_4^{2-} described by Eqs.(1)-(6) is schematized.

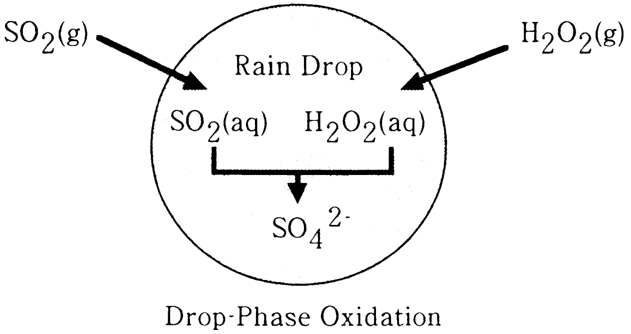

Figure 1: Production of Sulfate Ion SO_4^{2-} from Sulfur Dioxide Gas $SO_2(g)$

It should be noted that the oxidation rate of Eq.(6) is propotional to the concentration of produced H^+. This means that SO_4^{2-} and H^+ increase autocatalytically and that the production rate of SO_4^{2-} is dependent on the initial concentration of H^+.

Although nitrogen oxide is also considered to cause acid rain, NO and NO_2 play no direct role in the acidification or formation of NO_3^- or SO_4^{2-} (Durham et al., 1981). Furthermore, from the global point of view the amount of the emission of sulfur oxide to the air is much greater than that of nitrogen oxide and it is still increasing year by year especially in Asia. Therefore, in this study the acidification of rain drops due to sulfur dioxide is exclusively treated.

3 Governing equations for rain drop acidification

The washout of gaseous pollutants by rain drops is effected by various physical and chemical factors. Therefore the acidification process due to the washout is very complex. However, in this study the washout process is represented by a simple diffusion equation, equilibrium relations, and electro-neutrality condition, providing that non-circurating spherical rain drops fall with terminal velocity through the air of uniform gas concentration.

The notations for the concentrations of the chemical species in rain drops and in the air are defined as follows:

$$(C_1, C_2, C_3, C_4, C_5, C_6, C_7)$$

$$= ([SO_2 \cdot H_2O], [HSO_3^-], [SO_3^{2-}], [SO_4^{2-}], [H_2O_2 \cdot H_2O], [H^+], [HO_2^-]) \qquad (7)$$

$$(C_{1G}, C_{5G}) = ([SO_2(g)], [H_2O_2(g)]) \qquad (8)$$

From the two step dissociation of $SO_2 \cdot H_2O$ described by Eqs.(2) and (3), equilibrium relations can be taken as:

$$K_1 \cdot C_1 = C_2 \cdot C_6 \quad ; \quad K_2 \cdot C_2 = C_3 \cdot C_6 \qquad (9), (10)$$

Similarly, from the dissociation of $H_2O_2 \cdot H_2O$ described by Eq.(5), an equilibrium relation is given as:

$$K_5 \cdot C_5 = C_7 \cdot C_6 \qquad (11)$$

The electro-neutrality condition, which must be satisfied among the concentrations of anios and cations in rain drops, is:

$$C_6 - C_2 - 2C_3 - 2C_4 - C_7 - K_W / C_6 = \alpha \qquad (12)$$

where K_W = dissociation constant for water (= $10^{-14}M^2$); α = constant to be estimated by initial concentrations of ions in rain drops.

Taking diffusion, electro-migration, drop-phase chemical reactions, and the mass trasfer between the air and rain drops into account, the non-steady equation of mass conservation for chemical species C_i can be written as follows:

$$\frac{\partial C_i}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\left\{\frac{F}{RT}\frac{\partial \phi}{\partial r} z_i \mathcal{D}_i C_i + \frac{\partial(\mathcal{D}_i C_i)}{\partial r}\right\}\right) + R_i \qquad (13)$$

where C_i = concentration of species i (mol/L); t = time (sec); r = radial coordinate (cm); $\mathcal{D}_i$ = diffusion coefficient of species i (cm^2/s); F = Faraday's constant (= 9.65×10^4erg/V/mol); R = universal gas constant (= 8.31×10^4erg/mol/K); T = absolute temperature (K); z_i = charge number of species i (-); ϕ = electric potential (V); and R_i = reaction term. The first term of the right hand side of Eq.(13) is

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due to the electro-migration of ions. The electro-migration velocity depends on $\partial\phi/\partial r$ (electric field), z_i, and $\mathcal{D}_i$. Therefore, the velocity differs for each species.

The gradient of electric potential ϕ in rain drops is given as:

$$\frac{\partial\phi}{\partial r} = -\frac{\mathrm{RT}}{\mathrm{F}}\frac{\sum(z_i\mathcal{D}_i\frac{\partial C_i}{\partial r})}{\sum(z_i^2\mathcal{D}_i C_i)} \tag{14}$$

Therefore, when all the concentration gradients $\partial C_i/\partial r = 0$, the gradient of the electric potrential $\partial\phi/\partial r = 0$ and the electro-migration velocity disappears.

The reaction terms R_i in Eq.(13) are composed of dissociation and oxidation. They are represented as:

$$R_1 = -k_{1+}C_1 + k_{1-}C_2C_6 \tag{15}$$

$$R_2 = k_{1+}C_1 - k_{1-}C_2C_6 - k_{2+}C_2 + k_{2-}C_3C_6 - kC_6C_2C_5 \tag{16}$$

$$R_3 = k_{2+}C_2 - k_{2-}C_3C_6 \quad ; \quad R_4 = kC_6C_2C_5 \tag{17), (18}$$

$$R_5 = -k_{5+}C_5 + k_{5-}C_7C_6 - kC_6C_2C_5 \tag{19}$$

$$R_6 = k_{1+}C_1 - k_{1-}C_2C_6 + k_{2+}C_2 - k_{2-}C_3C_6 + k_{5+}C_5 - k_{5-}C_7C_6 + kC_6C_2C_5 \tag{20}$$

$$R_7 = k_{5+}C_5 - k_{5-}C_7C_6 \tag{21}$$

Where k_{i+} and k_{i-} = forward and backward rate constants, respectively. k_{i+} and k_{i-} give the dissociation constant in Eqs.(2), (3), and (5) as $\mathrm{K}_i = k_{i+}/k_{i-}$.

Because C_6 in most rain water ranges from 10^{-6}M (pH 6) to 10^{-3}M (pH 3), it can be assumed that C_2 is much larger than both of C_1 and C_3. In this pH range C_5 also can be much larger than C_7. Therefore the governing equation in dimensionless form can be reduced as:

$$\frac{\partial\hat{C}_i}{\partial\hat{t}} = \frac{1}{\hat{r}^2}\frac{\partial}{\partial\hat{r}}\left(\hat{r}^2\left\{\frac{\mathrm{F}}{\mathrm{RT}}\frac{\partial\hat{\phi}}{\partial\hat{r}}z_i\hat{\mathcal{D}}_i\hat{C}_i + \frac{\partial(\hat{\mathcal{D}}_i\hat{C}_i)}{\partial\hat{r}}\right\}\right) + \hat{R}_i \quad (\mathrm{i} = 2,\ 4 \text{ and } 5) \tag{22}$$

Where $\hat{R}_i$ and z_i are given as:

$$(\hat{R}_2,\ \hat{R}_4,\ \hat{R}_5) = (-\hat{k}\hat{C}_6\hat{C}_2\hat{C}_5,\ \hat{k}\hat{C}_6\hat{C}_2\hat{C}_5,\ -\hat{k}\hat{C}_6\hat{C}_2\hat{C}_5) \tag{23}$$

$$(z_2,\ z_4,\ z_5) = (-1,\ -2,\ 0) \tag{24}$$

The dimensionless variables and numbers are defined as follows:

$$\hat{C}_i = \frac{C_i}{\mathcal{H}_1 C_{1\mathrm{G}}} \quad ; \quad \hat{t} = \frac{4t\mathcal{D}_1}{D^2} \quad ; \quad \hat{r} = \frac{2r}{D} \tag{25), (26), (27}$$

$$\mathrm{Bi}_i = \frac{k_{\mathrm{G}i}D}{2\mathcal{H}_i\mathcal{D}_i} \quad ; \quad \hat{k} = k\frac{D^2(\mathcal{H}_1 C_{1\mathrm{G}})^2}{4\mathcal{D}_1} \tag{28), (29}$$

$$\hat{\mathcal{H}}_i\hat{C}_{i\mathrm{G}} = \frac{\mathcal{H}_i C_{i\mathrm{G}}}{\mathcal{H}_1 C_{1\mathrm{G}}} \quad ; \quad \hat{\mathrm{K}}_i = \frac{\mathrm{K}_i}{\mathcal{H}_1 C_{1\mathrm{G}}} \quad ; \quad \hat{\mathcal{D}}_i = \frac{\mathcal{D}_i}{\mathcal{D}_1} \tag{30), (31), (32}$$

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Where $\mathrm{Bi_i}$ = Biot Number which can be estimated by Eqs.(37)-(40) as shown later.

The initial condition for the governing equation Eq.(22) is given as:

$$\widehat{C}_\mathrm{i} = \widehat{C}_\mathrm{i0} \quad \text{at} \quad \widehat{t} = 0 \qquad (\mathrm{i} = 2, 4 \text{ and } 5) \tag{33}$$

$\widehat{C}_\mathrm{i0}$ is the concentration of the rain drop at the time the rain drop leaves the cloud bottom. That is, $\widehat{C}_\mathrm{i0}$ is identical to the concentration of the cloud water.

The boundary conditions for Eq.(22) are given at rain drop center and surface. They prescibe the mass flux at the boundaries and are described as:

$$-\frac{\partial(\widehat{\mathcal{D}}_\mathrm{i}\widehat{C}_\mathrm{i})}{\partial\widehat{r}} = 0 \quad \text{at} \quad \widehat{r} = 0 \quad ; \quad -\frac{\partial(\widehat{\mathcal{D}}_\mathrm{i}\widehat{C}_\mathrm{i})}{\partial\widehat{r}} = J_\mathrm{i} \quad \text{at} \quad \widehat{r} = 1 \qquad (\mathrm{i} = 2, 4 \text{ and } 5) \qquad (34), (35)$$

$$(J_2,\ J_4,\ J_5) = \left[\frac{\mathbf{Bi}_1}{\widehat{\mathcal{D}_2}}\left(\frac{\widehat{C}_{6\mathrm{i}}}{\widehat{\mathbf{K}}_1}\widehat{C}_2 - \mathcal{H}_1\widehat{C}_{1\mathrm{G}}\right),\ 0,\ \widehat{\mathcal{D}}_5\mathbf{Bi}_5\left(\widehat{C}_5 - \mathcal{H}_5\widehat{C}_{5\mathrm{G}}\right)\right] \tag{36}$$

The dimensionless number $\mathrm{Bi_i}$ controls the mass transfer rate at rain drop surface. $\mathrm{Bi_i}$ is estimated as:

$$\mathrm{Bi_i} = \mathrm{Sh_{iG}}\frac{\mathcal{D}_\mathrm{iG}}{\mathcal{D}_\mathrm{i}}\frac{1}{2\mathcal{H}_\mathrm{i}} \quad ; \quad \mathrm{Sh_{iG}} = 2 + 0.6\mathrm{Re}_\mathrm{G}^{1/2}\cdot\mathrm{Sc}_\mathrm{iG}^{1/3} \qquad (37), (38)$$

$$\mathrm{Re_G} = \frac{uD}{\nu_\mathrm{G}} \quad ; \quad \mathrm{Sc_{iG}} = \frac{\nu_\mathrm{G}}{\mathcal{D}_\mathrm{iG}} \qquad (39), (40)$$

where $\mathrm{Sh_{iG}}$ = Sherwood Number; $\mathrm{Re_G}$ = Reynolds Number; $\mathrm{Sc_{iG}}$ = Schmidt Number; ν_G = kinematic viscosity of gas; and u = falling velocity of rain drop. u in cm/s is geven as:

$$u(D) = 958\left\{1 - \exp\left[-(D/0.177)^{1.147}\right]\right\} \tag{41}$$

Once $\widehat{C}_2$, $\widehat{C}_4$, and $\widehat{C}_5$ are known, the remainders $\widehat{C}_1$, $\widehat{C}_3$, $\widehat{C}_6$, and $\widehat{C}_7$ are easily calculated from the charge neutrality condition and the equilibrium relations. They are given as follows:

$$\widehat{C}_6 = \frac{1}{2}\left(\widehat{C}_2 + 2\widehat{C}_4 + \widehat{\alpha} + \sqrt{(\widehat{C}_2 + 2\widehat{C}_4 + \widehat{\alpha})^2 + 4(2\widehat{\mathbf{K}}_2\widehat{C}_2 + \widehat{\mathbf{K}}_5\widehat{C}_5 + \widehat{\mathbf{K}}_\mathrm{W})}\right) \tag{42}$$

$$(\widehat{C}_1,\ \widehat{C}_3,\ \widehat{C}_7) = (\widehat{C}_6\widehat{C}_2/\widehat{\mathbf{K}}_1,\ \widehat{\mathbf{K}}_2\widehat{C}_2/\widehat{C}_6,\ \widehat{\mathbf{K}}_5\widehat{C}_5/\widehat{C}_6) \tag{43}$$

The algorithm of the computation of the rain drop concentrations at $t = t_\mathrm{i}$ is summarized as: (a) obtain $\widehat{C}_2$, $\widehat{C}_4$, and $\widehat{C}_5$, integrating Eq.(22) with known values of C_i's at $t = t_{\mathrm{i}-1}$; (b) compute $\widehat{C}_6$, substituting thus obtained new $\widehat{C}_2$, $\widehat{C}_4$, and $\widehat{C}_5$ into Eq.(42), ; and (c) calculate $\widehat{C}_1$, $\widehat{C}_3$, and $\widehat{C}_7$ by Eq.(43), using these new $\widehat{C}_2$, $\widehat{C}_4$, $\widehat{C}_5$, and $\widehat{C}_6$.

4 Effect of electric field on rain drop acidification

In order to investigate the characteristics of rain drop acidification process under the influence of the elecric field induced in rain drops, numerical simulations of rain drop acidification have been carried out. The initial concentraions of rain drops are: $C_2 = 10^{-7}$(M); $C_4 = 10^{-10}$(M); $C_5 = 10^{-6}$(M); $C_6 = 2.5 \times 10^{-6}$(M) (pH = 5.6). The ambient concentration of SO_2(g) is 50 ppb and that of H_2O_2(g) is 0.1 ppb.

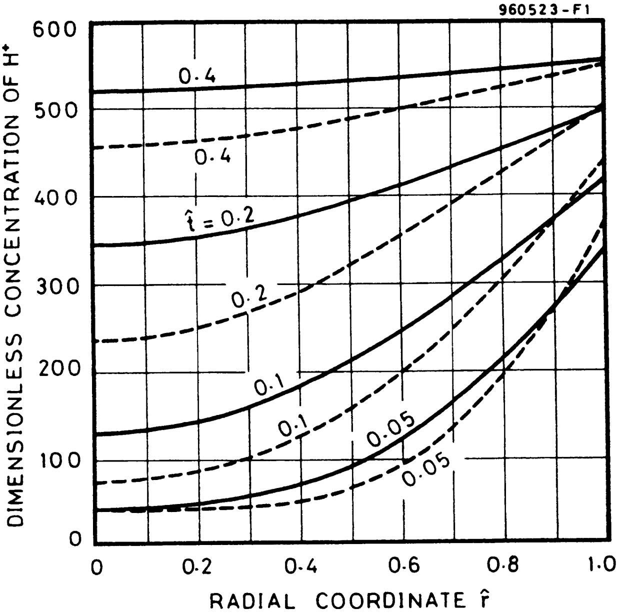

Figure 2: Time Variation of Distribution of H^+ Concentraion in Rain Drop

The distribution of dimensionless H^+ concentration at various time in a rain drop of 0.1 cm diameter are shown in Fig.2. The distributions are represented parametrically in dimensionless time $\hat{t}$. Solid curves (this work) are for the case considered the electro-migration of ions due to the electric field induced by the ions, and the broken curves (Shiba, 1992) are for the case without the elecro-migration of ions. In both cases the concentration distributions approach to the same quasi-equilibrium distribution (the true equilibrium value is not shown on account of the oxidation by hydrogen peroxide). However, at any time the concentration taking the electro-migration of ions into account is higher than that neglecting the electro-migration, except for the vicinity of drop surface in early stage of the acidification process. The slope of the concentration distribution considering the electro-migration is gentler than that neglecting the electro-migration. In other words, the electro-migration tends to make the concentration distributions uniform. The tendency to uniform the distribution is especially notable in early stage of the acidification. This feature of the concentration distributions shows that the electro-migration of ions accelerates the mass transfer from the air to rain drops.

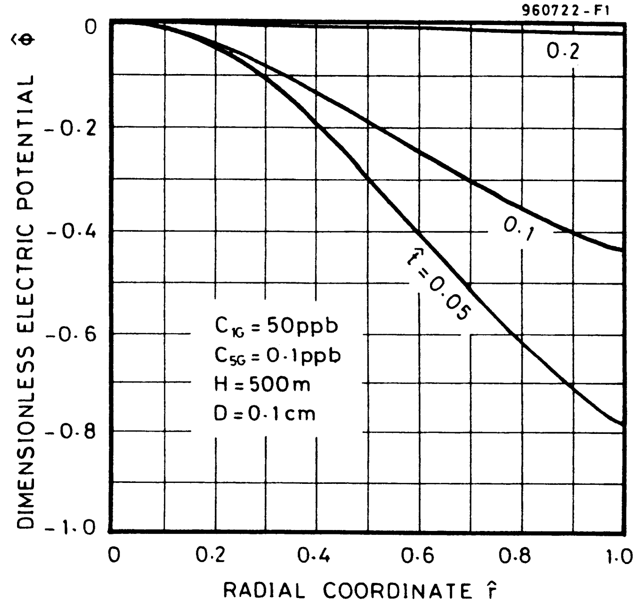

Figure 3: Time Variation of Distribution of Electric Potential $\hat{\phi}$ in Rain Drop

The time variations of the dimensionless electric potential $\hat{\phi}$ in rain drops are shown in Fig.3 parametrically in the dimensionless time $\hat{t}$. The reference point of the potential is set tentatively at the drop center $\hat{r} = 0$. Then $\hat{\phi}$ is negative-valued. If the point is set at the drop surface $\hat{r} = 1$, the potential $\hat{\phi}$ becomes positive-valued. In short the electric potential is higher at the drop center than at the drop surface and $\hat{\phi}$ decreases monotonously from the center to the surface. The slope of the potential distribution becomes gentle with lalpse of time and the slope is almost horizontal at $\hat{t} = 0.2$, i.e., the potential distribution will be unform ultimately.

Shown in Fig.4 is the time variation of the increment of volume averaged H^+ concentration ΔC_6(M) defined as follows:

$$\Delta C_6 = C_6 - C_6^0 \tag{44}$$

where C_6^0(M) is H^+ concentration estimated ignoring the effect of the electric potential ϕ. ΔC_6 is mono-peaked and has the maximum value at around $\hat{t} = 0.2$.

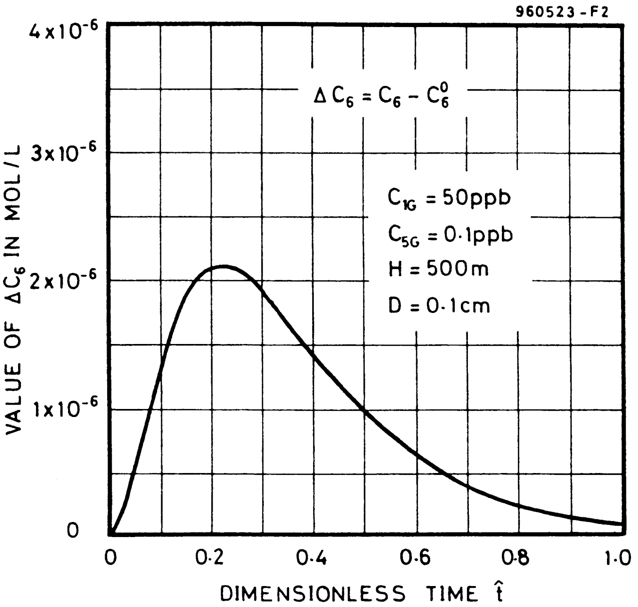

Figure 4: Time Variation of Increment of Volume Averaged H^+ Concentration ΔC_6 in Rain Drop

In other words the enhacement of rain drop acidification by the electric potential ϕ keeps increasing from zero (at $\hat{t} = 0$) to a maximum value (at about $\hat{t} = 0.2$) and then it starts decreasing. As can be seen from Eq.(13), the electro-migration of ions in rain drops is controlled by the electric gradient $\partial\phi/\partial r$. Then, the increase or decrease of ΔC_6 behaves in the same manner as that of $\partial\phi/\partial r$ does. This can be ascertained by comparing the variation of ΔC_6 in Fig.3 with that of $\partial\phi/\partial r$ in Fig.4.

5 Conclusions

From the numerical simulations with the model developed here, the following conclusions may be drawn:

1. A mathematical model, which takes electro-migration of ions into account in addition to such factors for non-charged chemical species as diffusion and drop-phase chemical reaction, has been constructed [Eq.(13)].
2. The electric potential field caused by ions accelerates the pollutant mass transfer from the air to the rain drops. That is, the electro-migration of ions quicken the dynamic responce of the acidification to the gas absorption (Fig.2).
3. Electric potential tends to make the slope of the transient distributions of the concentrations gentler, although the steady (equilibrium) state concentrations seem to be not changed by the electro-migration (Fig.2).
4. The electric potential is high at the rain drop center and low at the drop surface, i.e., the potential gradient is negative-valued. The slope decreases with lapse of time, although the slope is supposed to increse in very early stage of the acidification (Fig.3).
5. The enhancement of rain drop acidity due to the electric potential increases gradually till it gets to the maximum. After the maximum the enhancement decreases monotonously and becomes zero ultimately (Fig.4).

References

1. Durham, J. L., Overton, J. H., and Aneja, V. P. (1981). Influence of Gaseous Nitric Acid on Sulfate Production and Acidity in Rain, *Atmospheric Environment*, Vol.15, No.6, pp. 1059-1068.
2. Maahs, H. G. (1983). Kinetics and Mechanism of the Oxidation of S(IV) by Ozone in Aqueous Solution with Particular Reference to SO_2 Conversion in Nonurban Tropospheric Clouds, *J. Geophysical Research*, Vol.88 (C15), pp.10721-10732.
3. Liss, P. S., and Slinn, W. G. N. (1983). *Air-Sea Exchange of Gases and Particles*, NATO ASI Series, Series C, Mathematical and Physical Series No.108, D. Reidel Publishing Co., Dordrecht, p.206.
4. Pandis, S. N., and Seinfeld, J. H. (1989). Sensitivity Analysis of a Chemical Mechanism for Aqueous-Phse Atmospheric Chemistry, *Journal of Geophysical Research*, Vol.94 (D1), pp.1105-1126.
5. Shiba, S. (1992). Acid Rain Formation by $SO_2 - H_2O_2$ Absorption with Sequential Drop-Phase Chemical Reactions, *Computer Techniques in Environmental Studies IV*, Zannetti, P. (Ed.), Computational Mechanics Publications, Southampton, pp.45-60.