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# Calculation of Relative Humidity in Equilibrium with Strong Electrolyte Solutions by Thermodynamic Data

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## Abstract

In order to estimate concentrations of electrolyte layers formed on metal surface in atmospheric environment, relative humidity,  $RH$ , in equilibrium with various concentrations of strong electrolyte solutions were calculated using available thermodynamic data. The activity coefficient of water,  $f_w(X)$ , for the solution with molar fraction of water,  $X$ , could be given as a function of ionic strength of the solution, which was determined using the mean activity coefficient data available in literature for electrolytes in the solution.  $RH$  values obtained as  $RH(\%) = 100 \times f_w(X) \cdot X$  agreed well with the measured values reported in the literature for solutions with individual electrolytes, for example  $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Mg}(\text{NO}_3)_2$  and so on.  $RH$  values for solutions with various concentrations of sea salt were also calculated as those for solutions with  $\text{NaCl}$ – $\text{MgCl}_2$  mixed electrolytes. In this case also the calculated  $RH$  values agreed well with the measured ones. It was confirmed that composition of water film formed as a solution of

sea salt could be estimated when amount of deposited sea salt,  $Ws$ , was  $Ws \geq 10^{-2} \text{g/m}^2$ .

**Keywords:** atmospheric corrosion, water film, relative humidity, activity of water, strong electrolyte, mean activity coefficient

## Introduction

Atmospheric corrosion is known to progress under a thin water film deposited on a metal surface. The thin water film is formed as a solution of strong electrolyte, for example deposited sea salt, by absorbing moisture in air. The relative humidity,  $RH [\%]$ , of air in equilibrium with a thin water film is given by  $RH [\%] = 100a_w$ ; where  $a_w$  is the activity of water in the electrolyte solution or thin water film. A few researchers [1, 2] have made thermodynamic analyses for compositions of the thin water films with NaCl and/or  $\text{MgCl}_2$ . However, many kinds of strong electrolyte particles are deposited on the metal surfaces in the actual atmospheric environment. In this study, calculation methods for estimation of  $RH$  in equilibrium with various concentrations of strong electrolyte solutions are suggested where these  $RH$  values are calculated by using available thermodynamic data [3].

## Relationship between Activity Coefficient of Water And That of Solute Species

Consider a mixed aqueous solution containing  $n$  number of solute species. Activity,  $a_i$ , of solute  $i$  ( $i = 1, 2, \dots, n$ ) in such a solution is related to  $a_w$  by the Gibbs–Duhem relation:

$$x_w d(\ln a_w) + \sum_{i=1}^n x_i d(\ln a_i) = 0$$

This relation is rewritten as

$$d(\ln a_w) = - \sum_{i=1}^n (x_i / x_w) d(\ln a_i) \quad (1)$$

where  $x_w$  and  $x_i$  are the mole fractions of water and solute  $i$  with reference to the Raoult standard. The expression for  $d(\ln a_i)$  in terms of activity coefficient  $f_i$  is given by

$$d(\ln a_i) = d(\ln f_i x_i) = d(\ln f_i) + d(\ln x_i) = d(\ln f_i) + (1/x_i) dx_i$$

Substituting this equation into Eq. (1), following equation is obtained

$$\begin{aligned}
d \ln(f_w) + (1/x_w) dx_w &= - \sum_{i=1}^n (x_i/x_w) d(\ln f_i) - \sum_{i=1}^n (x_i/x_w) (1/x_i) dx_i \\
&= - \sum_{i=1}^n (x_i/x_w) d(\ln f_i) - (1/x_w) \sum_{i=1}^n dx_i \quad (2)
\end{aligned}$$

Using the relation

$$x_w + \sum_{i=1}^n x_i = 1$$

following equation is obtained

$$dx_w + \sum_{i=1}^n dx_i = 0$$

Thus, Eq . (2) is rewritten as

$$d(\ln f_w) = - \sum_{i=1}^n (x_i/x_w) d(\ln f_i) \quad (3)$$

By integration of Eq . (3) from  $x_w=1$  to  $x_w=X$ , following equation is obtained

$$\int_{x_w=1}^{x_w=X} d(\ln f_w) = - \sum_{i=1}^n \int_{x_w=1}^{x_w=X} (x_i/x_w) d(\ln f_i) \quad (4)$$

The left hand side, LHS, of this equation is expressed as

$$\text{LHS} = \ln f_w(X) - \ln f_w(1) = \ln f_w(X)$$

Thus, Eq. (4) is reduced to

$$\ln f_w(X) = - \sum_{i=1}^n \int_{x_w=1}^{x_w=X} (x_i/x_w) d(\ln f_i) \quad (5)$$

Because  $(x_i/x_w)$  in Eq.(5) is give as  $(x_i/x_w) = (m_i/M)$ , then Eq. (5) is further reduced to

$$\ln f_w(X) = - \sum_{i=1}^n \int_{x_w=1}^{x_w=X} (m_i/M) d(\ln f_i) \quad (6)$$

where  $m_i$  is the molality of solute i and  $M$  is that of water ( $M = 1000/W_0 = 55.51 \text{ mol/kg}$ ; where  $W_0$  is the molecular weight of  $\text{H}_2\text{O}$ ).

## Calculation of Activity Coefficient of Water for Strong Electrolyte Solution

### Calculation of Activity Coefficient of Water for Single Strong Electrolyte Solution

Consider an aqueous solution containing a single strong electrolyte species ( $\text{A}_{\nu+}\text{B}_{\nu-} \rightarrow \nu_+\text{A}^{z+} + \nu_-\text{B}^{z-}$ ), the activity coefficient,  $f$ , of this strong electrolyte solution is given by

$$f = f_{\pm}^{\nu}, \quad \nu = \nu_+ + \nu_-$$

Thus, Eq. (6) for this solution can be written as

$$f_w(x) = (v/M) \int_{x_w=1}^{x_w=X} m d(\ln f_{\pm}) ; \quad X = M/(M + vm) \quad (7)$$

Suffix i is not given in this formula because this solution contains only a single strong electrolyte species. The mean activity coefficient,  $f_{\pm}$ , of the strong electrolyte solution is given as a function of ionic strength,  $I$ , as follows

$$d(\ln f_{\pm}) = [\partial(\ln f_{\pm})/\partial I] dI \quad (8-1)$$

where  $I$  is further represented by

$$I = Z^* m, \quad Z^* = (z_+^2 \nu_+ + z_-^2 \nu_-) / 2 \quad (8-2)$$

Thus, by substituting Eqs. (8-1) and (8-2) into Eq. (7) under the conditions of  $I = 0$  at  $x_w = 1$  and  $I = I_x$  at  $x_w = X$ , following equation is obtained

$$\ln f_w(X) = -(v/MZ^*) \int_0^{I_x} I [\partial(\ln f_{\pm})/\partial I] dI \quad (9)$$

By applying the Debye-Hückel relation

$$\log f_{\pm} = AZ_+ z_-^{1/2} / (1 + Ba^{1/2}) \quad (10)$$

( $A = 0.5115 \text{ mol}^{-1/2} \text{ dm}^{3/2}$ ,  $B = 0.3291 \times 10^7 \text{ cm}^{-1} \text{ mol}^{-1/2} \text{ dm}^{3/2}$ )

$f_{\pm}$  of the strong electrolyte solution is approximated as follows [ref 04] :

$$\log f_{\pm} = \log f_{\pm \text{DH}} + CI + DI^2 \quad (11)$$

Thus, Eq. (9) is reduced to

$$\begin{aligned} \ln f_w(X) &= -2.303(v/MZ^*) \int_0^{I_x} I [\partial(\log f_{\pm})/\partial I] dI \\ &= -2.303(v/MZ^*) \{F(I_x) + CI_x^2/2 + 2DI_x^3/3\} \end{aligned} \quad (12)$$

where  $F(I_x)$  is given by

$$\begin{aligned} F(I_x) &= \int_0^{I_x} I \cdot [\partial(\log f_{\pm \text{DH}})/\partial I] dI \\ &= -[AZ_+ z_- / (Ba^{1/2})] \times [Ba^{1/2} I_x - 2 \ln(1 + Ba^{1/2} I_x) - 1/(1 + Ba^{1/2} I_x) + 1] \end{aligned} \quad (13)$$

## Calculation of Activity Coefficient of Water for Mixed Strong Electrolyte Solution

The ionic strength,  $I$ , of a mixed strong electrolyte solution is represented by

$$I = \sum_{i=1}^n Z_i^* m_i = \sum_{i=1}^n Z_i^* k_i m_1 \quad (14)$$

where  $k_i$  is the ratio of  $m_i$  against that of electrolyte  $i=1$ ,  $k_i = (m_i/m_1)$ , and  $Z_i^*$  is  $Z^*$  of the electrolyte  $i$ . Accordingly,  $m_i$  is given as :

$$m_i = k_i m_1 = k_i I / Z_i^*, \quad Z_i^* = \sum_{i=1}^n Z_i^* k_i \quad (15)$$

By substituting Eq. (15) into Eq. (6) under the assumptions of  $I = 0$  at

$x_w=1$  and  $I = I_x$  at  $x_w=X$ , following equation is obtained

$$\ln f_w(X) = -\sum_{i=1}^n \left( \nu_i k_i / MZ_t^* \right) \int_0^{I_x} I [\partial(\ln f_{iX\pm}) / \partial I] dI \quad (16)$$

$$X = M / \left( M + \sum_{i=1}^n m_i \right)$$

where  $\nu_i$  and  $f_{iX\pm}$  are  $\nu$  and  $f_{\pm}$  of the electrolyte  $i$  in the mixed strong electrolyte solution, respectively. The value of  $f_{iX\pm}$  is not available in any handbook. Hence, it was estimated under the assumption that the activity coefficient of a given ion does not vary in the solutions with the same ionic strength [ref 05, 06]. Thus, the following equation is obtained for a strong electrolyte species ( $A_{\nu+} B_{\nu-} \rightarrow \nu_+ A^{z+} + \nu_- B^{z-}$ ):

$$\begin{aligned} f_{X\pm}(I) &= [f_X(A^{z+}, I) \nu_+ \cdot f_X(B^{z-}, I) \nu_-] (1 / \nu) \\ &= [f(A^{z+}, I) \nu_+ \cdot f(B^{z-}, I) \nu_-] (1 / \nu) = f_{\pm}(I) \end{aligned} \quad (17)$$

This indicates that the activity coefficient of each ionic species in the mixed electrolyte is assumed to be the same as in the single electrolyte solution with the same ionic strength and is given by Eqs. (10) and (11). Accepting this assumption, Eq. (16) is rewritten as

$$\ln f_w(X) = -\sum_{i=1}^n \left( \nu_i k_i / MZ_t^* \right) \int_0^{I_x} I [\partial(\ln f_{i\pm}) / \partial I] dI \quad (18)$$

With reference to Eq. (9), the expression of  $f_{i,w}(X)$  in the solution containing only the electrolyte species  $i$  is given by

$$\ln f_{i,w}(I_X) = -\left( \nu_i / MZ_i^* \right) \int_0^{I_X} I [\partial(\ln f_{i\pm}) / \partial I] dI \quad (19)$$

Thus, following equation is obtained by substituting Eq. (19) into Eq.(18);

$$\ln f_w(X) = \sum_{i=1}^n \left( k_i Z_i^* / Z_i^* \right) \ln f_{i,w}(I_X) = \sum_{i=1}^n \left( Z_i^* m_i / Z_t^* m_1 \right) \ln f_{i,w}(I_X) \quad (20)$$

Provided that the ionic strength of the electrolyte  $i$  is represented by  $I_i = Z_i^* m_i$ , Eq. (20) is reduced to

$$\ln f_w(X) = \sum_{i=1}^n \left( I_i / I_X \right) \ln f_{i,w}(I_X) \quad (21)$$

Thus, if  $f_w$  of the solution containing only one electrolyte species is known,  $f_w$  of the mixed electrolyte solution can be estimated.

## **RH of Atmosphere in Equilibrium with Strong Electrolyte Solution**

### **RH of Atmosphere in Equilibrium with Aqueous Solution Containing a Single Strong Electrolyte Species**

To carry out the calculation of Eq. (12), the value of  $\hat{a}$  in Eq. (10) must be determined in addition to those of C and D. The values for these parameters were found as follows. First, the relationship between  $f_{\pm}$  and  $I$  was derived from the relationship between mean activity coefficient,  $\gamma_{\pm}$ , and concentration,  $m$  [mol/kg], in literatures [03]. The values of  $f_{\pm}$  and  $I$  were input by taking into account Eq. (8-2) and the following relationship [03]:

$$f_{\pm} = \gamma_{\pm} (1 + \nu W_0 m / 1000)$$

Next, the relationship between  $\Delta = \log f_{\pm} - \log f_{\pm DH}$  and  $I$  was derived under the condition of  $\hat{a} = 0 \sim 10^{-7} \text{cm}$ , and this relationship was fitted as a second order equation of  $I$ ,  $(CI + DI^2)$ , by the least squares method. The values for  $\hat{a}$ , C, and D yielding the largest correlation coefficient were taken as the acceptable parameter values. The values of  $\gamma_{\pm}$  used in following calculations are the ones at 25 °C [03]. Fig. 1 shows the results for  $\text{MgCl}_2$ . The largest correlation coefficient was obtained with  $\hat{a} = 4.5 \times 10^{-8} \text{cm}$ , as shown in the figure. The approximate expression of  $f_{\pm}$  is given on top of the figure. Using this equation and Eqs. (12) and (13),  $f_w(X)$  was calculated. Fig. 2 shows the results of a similar calculation for NaCl and for  $\text{MgCl}_2$  together with the available values in the literature ([03] for NaCl and [01] for  $\text{MgCl}_2$ ). For NaCl, the  $RH$  was obtained as the  $a_w$  value calculated from the osmotic pressure. The calculation results for both NaCl and  $\text{MgCl}_2$  agreed well with the corresponding values in the literature.

Similar calculations were carried out for various strong electrolyte solutions. The  $m$ - $RH$  relationships for chloride and sulfate solutions are shown in Fig. 3 and 4. Table 1 shows the  $RH$  values for saturated solutions with those in the literature [03, 07, 08, 09]. The

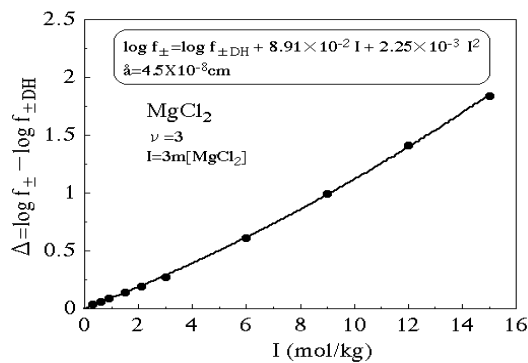


Fig. 1 The best fit for the estimated result of the relationship between  $\log f_{\pm}$  and  $I$ , using the parameters  $\hat{a}$ , C and D values for  $\text{MgCl}_2$  solution.

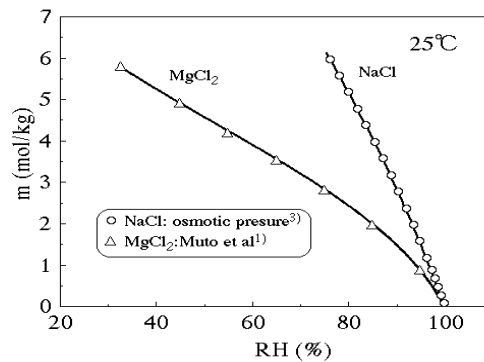


Fig. 2 Comparison of calculated results with measured data in literature on the relationship between concentrations and  $RH$  values for NaCl and  $\text{MgCl}_2$ .

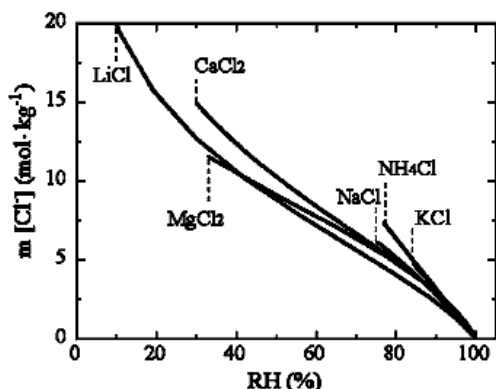


Fig. 3 Calculated results of molality of chloride ion in terms of relative humidity ( $RH$ ) for various chloride salts.

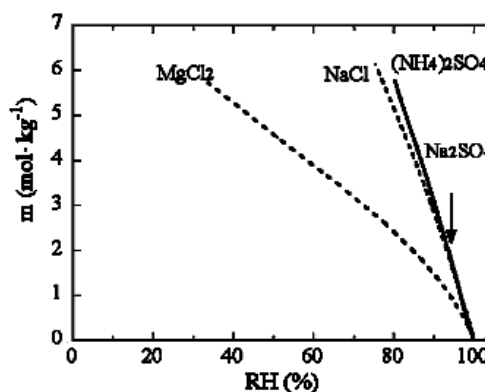


Fig. 4 Calculated results of molality of sulphate ion in terms of relative humidity ( $RH$ ) for  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ .

Table1. Comparison of the calculated relative humidity values of various saturated salt solutions with the reported values in the literature.

	Calculated	Literature		
	25°C	25°C <sup>3)</sup>	15°C <sup>7)</sup>	25°C
$\text{Na}_2\text{SO}_4$	93.6	93	93	
KCl	84.1		86	
$(\text{NH}_4)_2\text{SO}_4$	78.5	81.1		
NaCl	75.2		76	
$\text{NH}_4\text{Cl}$	76.8	79.3	79.2	
$\text{Mg}(\text{NO}_3)_2$	53.7	52		
$\text{CaCl}_2$	28.1	31	32.3	
$\text{MgCl}_2$	32.9		34	
LiCl	11.4	15	11.3	
KOH	10.1*			9.2 <sup>8)</sup>
NaOH	6.6*			7.2 <sup>8)</sup>
LiBr	4.2			3.6 <sup>9)</sup>

calculation results for these strong electrolytes also agreed well with the corresponding values in the literature.

### ***RH* of Atmosphere in Equilibrium with Mixed Strong Electrolyte Solution**

In the atmospheric environment, water film is formed by absorption of moisture by sea salt particle, which contains mainly NaCl and  $\text{MgCl}_2$ .

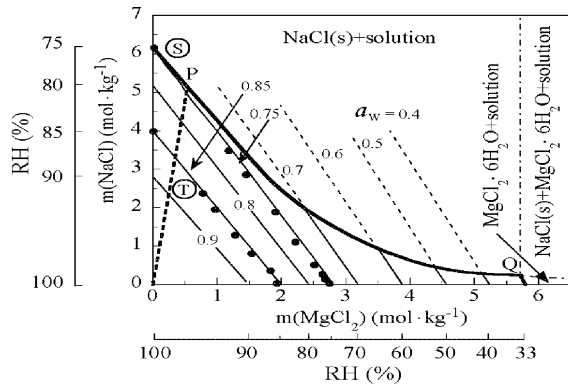


Fig. 5 Chemical composition of NaCl and MgCl<sub>2</sub> which gives prescribed  $a_w$  with measured one (•) in phase diagram of the Na-Mg-Cl system.

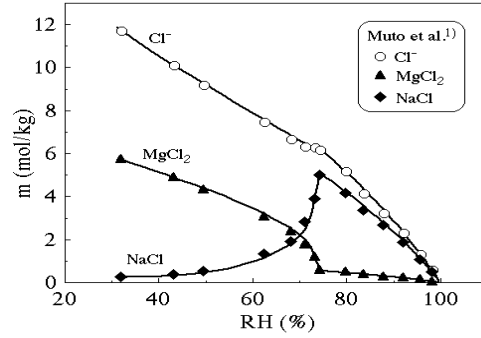


Fig. 6 Comparison of calculated results with measured data in literature for relationship between partial molality of NaCl and MgCl<sub>2</sub> and chloride ion in sea salt and relative humidity ( $RH$ ).

The values of  $f_{\pm}$  and  $a_w$  for solutions containing NaCl and MgCl<sub>2</sub> were calculated, and the results are plotted in the phase diagram of the Na-Mg-Cl system in Fig. 5. The results in the region where NaCl is precipitated, “NaCl(s)+solution”, are indicated by dotted lines. The calculated results for  $a_w=0.75$  and  $0.85$  are fitted well with measured ones (•, #ref01).

In the calculation for the solution of sea salt, it was assumed that  $m[\text{MgCl}_2]/m[\text{NaCl}] = m[\text{Mg}^{2+}]/m[\text{Na}^+] = 0.11$  [#ref01] where sea salt is fully dissolved – line T in the figure –, and  $m[\text{MgCl}_2]$  and  $m[\text{NaCl}]$  were determined from the available solubility curve where NaCl is precipitated– line S in the figure –. The calculated concentrations of NaCl, MgCl<sub>2</sub> and Cl<sup>-</sup>,  $m[\text{NaCl}]$ ,  $m[\text{MgCl}_2]$  and  $m[\text{Cl}^-] = m[\text{NaCl}] + 2m[\text{MgCl}_2]$ , respectively, are shown in Fig.6 with measured results. The calculated results were fitted well with the available measured data, and it is confirmed that the  $RH$  value for mixed electrolyte solutions also can be estimated with available thermodynamic data.

To confirm the relationships between chemical composition of water film and  $RH$ , amount of absorbed moisture was measured. Stainless steel sheets with area of 100cm<sup>2</sup> and QCM, Quartz Crystal Microbalance, were covered with simulated sea salt, which contains NaCl and MgCl<sub>2</sub>·6H<sub>2</sub>O;  $m[\text{Mg}^{2+}]/m[\text{Na}^+] = 0.11$  [#ref01], and were exposed in the constant humidity chamber for 2~4h. The amount of absorbed moisture,  $W_{ab}$ , was determined as weight change during the exposure.

The QCM was an AT-cut quartz crystal with gold platings on both sides. The surface on one side was to be exposed, while the other



side was covered with silicone sealant forming a closed compartment filled with dry air. The frequency change,  $\Delta q$  (Hz) was converted to the weight change,  $\Delta w$  (g/m<sup>2</sup>), by the following equation:

$$\Delta q = -(q_0^2 u / N \rho) \cdot \Delta w \quad (22)$$

where  $q_0$  is a reference resonant frequency ( $q_0 = 5.88$  MHz),  $N$  is a fixed frequency coefficient of the crystal ( $N = 1.67 \times 10^{-5} \text{ cm} \cdot \text{Hz}$ ),  $\rho$  is the density of the crystal ( $\rho = 2.65 \text{ g/cm}^3$ ), and  $u$  is the number of exposed surface ( $u = 1$ ). Thus, a frequency change of 1 (Hz) was converted to weight change of  $1.28 \times 10^{-4} \text{ g/m}^2$ .

Stainless steel sheets were used for the measurement under conditions where amount of deposited sea salt,  $W_s$ , was  $W_s \geq 1 \text{ g/m}^2$ . The QCM was used under conditions where  $W_s = 10^{-3} \sim 10^{-2} \text{ g/m}^2$ , because the oscillations of QCM were unstable under conditions where  $W_s > 10^{-2} \text{ g/m}^2$ .

Relationships between  $W_{ab}$  and  $RH$  measured by QCM and stainless steel sheets are shown in Fig.7, and the ratios of ( $W_{ab} / W_s$ ) for the data in Fig. 7 are shown in Fig.8. The weight of NaCl, MgCl<sub>2</sub> and water,  $W[\text{NaCl}]$ ,  $W[\text{MgCl}_2]$  and  $W_w$ , respectively, in the deposited sea salt with weight of  $W_s$  are determined as follows:

$$W[\text{NaCl}] = (M[\text{NaCl}] / M_t) \cdot W_s \quad (23-1)$$

$$W[\text{MgCl}_2] = (s M[\text{MgCl}_2] / M_t) \cdot W_s \quad (23-2)$$

$$W_w = (6 s M[\text{H}_2\text{O}] / M_t) \cdot W_s \quad (23-3)$$

$$M_t = M[\text{NaCl}] + s M[\text{MgCl}_2] + 6 s M[\text{H}_2\text{O}]$$

where  $M[\text{NaCl}]$ ,  $M[\text{MgCl}_2]$  and  $M[\text{H}_2\text{O}]$  are molecular weights of NaCl, MgCl<sub>2</sub> and water, respectively, and  $s = m[\text{Mg}^{2+}] / m[\text{Na}^+] = 0.11$ . It is considered that MgCl<sub>2</sub>·6H<sub>2</sub>O is fully dissolved under the conditions of  $RH \geq 40\%$ . Thus, concentration of MgCl<sub>2</sub>,  $m[\text{MgCl}_2]$ , is obtained as

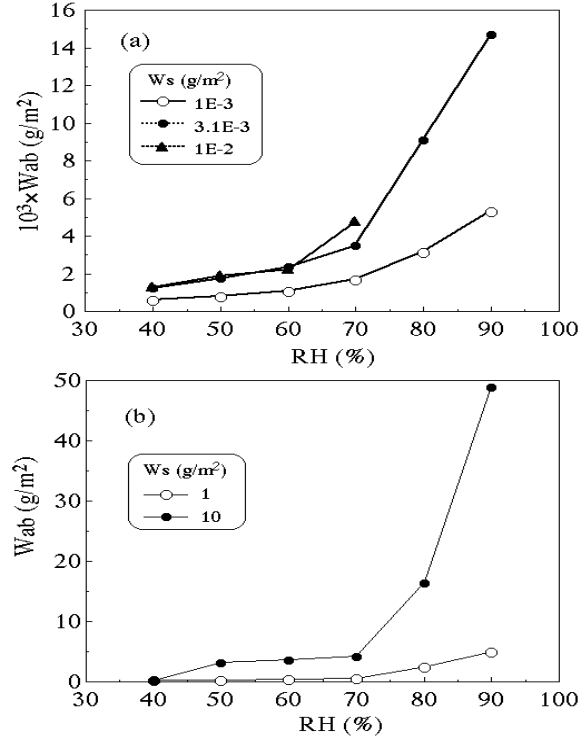


Fig. 7 Relationship between amount of absorbed moisture,  $W_{ab}$ , and  $RH$  measured with simulated sea salt.

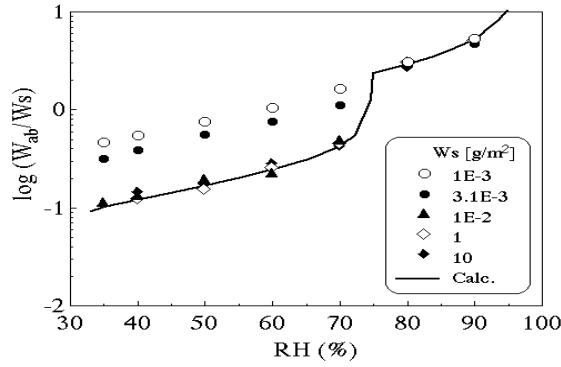


Fig. 8 Relationship between  $(W_{ab}/W_s)$  and  $RH$  for measured results in Fig. 7 with calculated result.

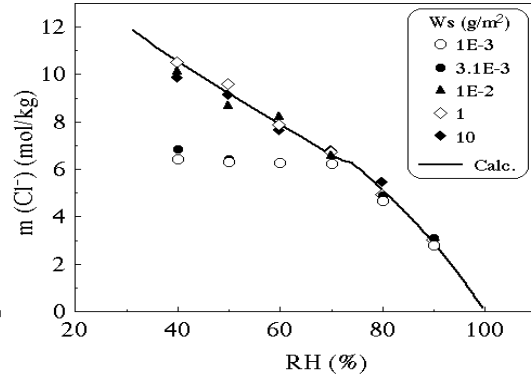


Fig. 9 Dependence of  $m(Cl^-)$  on  $RH$  for measured results in Fig. 7 with calculated result.

$$\begin{aligned} m[MgCl_2] &= 1000 W[MgCl_2] / M[MgCl_2] \cdot (W_{ab} + W_w) \\ &= 1000 s / \{6 s M[H_2O] + M_t (W_{ab} / W_s)\} \end{aligned} \quad (24)$$

By resolving Eq.24,  $(W_{ab} / W_s)$  is obtained as :

$$(W_{ab} / W_s) = \{ (1000 s / m[MgCl_2]) - 6 s M[H_2O] \} / M_t \quad (25)$$

This estimated value of  $(W_{ab} / W_s)$  is also plotted in Fig. 8.

For NaCl, concentration,  $m^*[NaCl]$ , is calculated temporarily as follows;

$$\begin{aligned} m^*[NaCl] &= 1000 W[NaCl] / M[NaCl] \cdot (W_{ab} + W_w) \\ &= 1000 / \{6 s M[H_2O] + M_t (W_{ab} / W_s)\} \end{aligned} \quad (26)$$

If the composition of  $\{m[MgCl_2], m^*[NaCl]\}$  is plotted in the “NaCl(s)+solution” region in the phase diagram in Fig. 5, actual concentration,  $m[NaCl]$ , must be obtained based on solubility curve, line S given in Fig. 5, and  $m[MgCl_2]$ , while  $m[NaCl] = m^*[NaCl]$  if the composition of  $\{m[MgCl_2], m^*[NaCl]\}$  is plotted in the “solution” region. The concentrations of  $Cl^-$ ,  $m[Cl^-] = m[NaCl] + 2 m[MgCl_2]$ , obtained for the data in Fig. 7 are plotted in Fig. 9 along with calculated line given in Fig. 6. For water film, calculated results also agreed well with the measured data, when  $W_s \geq 10^{-2} g/m^2$ , as shown in Figs. 8 and 9. Thus, it is confirmed that composition of water film formed as a solution of sea salt can be estimated when  $W_s \geq 10^{-2} g/m^2$ . Concentrations of water film are diluted than estimated ones when  $W_s < 10^{-2} g/m^2$ , because water adsorbs on metal surface without sea salt particle and its weight is not neglected [ref 10].

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