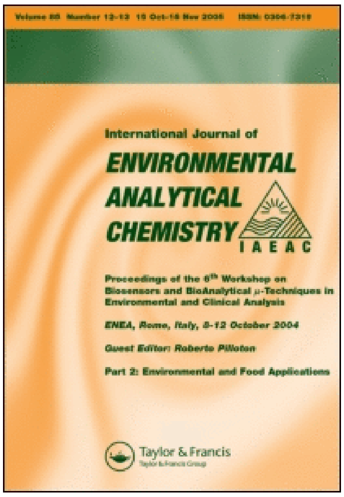

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ESTIMATION OF ALUMINUM SPECIATION IN SURFACE WATERS OF LOW IONIC STRENGTH BY A SIMPLE COMPUTER MODEL

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A simple computer model based on chemical equilibrium calculation for evaluating the aluminum speciation in surface waters of low ionic strength ($I < 1 \times 10^{-4}$ M) was presented in this paper. The speciations of aluminum obtained by this model have been compared with those obtained experimentally and the reasons for the observed differences have been discussed. This model has been applied to the estimation of aluminum speciation in practical surface waters sampling from areas of the United Kingdom, United States and People's Republic of China. Some valuable conclusions are obtained.

Keywords: Aluminum speciation; computer simulation; surface water

INTRODUCTION

Aluminum is an important parameter in the study of environmental acidification processes. [1] Dissolved aluminum at elevated concentrations is found to be toxic to aquatic and terrestrial biota. [2, 3] The development of methods for the determination of aluminum in surface waters has therefore received considerable attention. [4-9] However, the chemical speciation of aluminum in natural waters is complicated because Al^{3+} forms complexes with OH^-, F^-, SO_4^{2-} and organic compounds. It is generally recognized that dissolved aluminum species differ greatly in toxicity. Therefore, the evaluation of potential environmental impacts of aqueous aluminum must include speciation, rather than simply total

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concentration. Analytically, there are many problems associated with a determination of the speciation of Al in a natural water samples: (1) sampling and sample storage, where the dynamic equilibria in the natural water are easily perturbed; (2) speciation methodology where any reaction used to detect a specific form of Al will upset the equilibrium, it is further difficult to ascertain what is actually measured with a given method. Computer simulation models based on chemical equilibrium calculations are very useful tools for investigation of metal speciation in the aquatic environment. They have been essential in increasing the understanding of the interactions between hydrological and geochemical processes. Many models have been developed on this subject, such as, MINEQL, GEOCHEM, WHAM and ALCHEMI. [10-13] However, different models will provide acceptable fits to data sets covering limited ranges of conditions even though they are based on different precepts. There are still some problems in the practical use of these models: (1) most models are designed only for general analysis of water quantity data involving too many variables. Modeling of the organic complexation of aluminum is too complicated, due to the wide range of organics with different complexing abilities; (2) the aluminum is often modeled assuming an equilibrium between aluminum in solution and Al in a solid phase (e.g. in equilibrium with an Al trihydroxide mineral phase). However, in many cases, disequilibrium occurs and the Al water chemistry may be controlled by a kinetic process which is in marked departure from $Al(OH)_3$ solubility; [14-18] We contend that, for practical purposes, it is worth sacrificing some goodness-of-fit in order to obtain a model that is easily usable but retains the basic physicochemical attributes of the system. In this present paper, we would like to:

(1) Set up a simple model describing the aluminum speciation in surface waters of low ionic strength. Special attention is focused on the minimization of the number of model parameters in a reasonablely straight-forward as well as a predictive sense;

(2) Verify the accuracy of this model by comparing the speciations obtained by this model with those obtained experimentally and investigate the reasons for those observed differences;

(3) Apply this model to analyse the aluminum species and concentrations in practical sampling of surface waters.

THEORY

Firstly, we make the following assumptions:

(1) the surface water studied is a dilute solution of low ionic strength (generally $I < 1 \times 10^{-4}$ M). Al concentration is not in equilibrium with the mineral phase, such as gibbsite;

(2) naturally occurring organic solutes are presented as a triprotic acid as proposed by Driscoll[18];

(3) Fe and Mn are at trace level, their influences are insignificant; [19]

(4) adsorption of SO_4^{2-} and F^- are not taken into account. Polymeric aluminum species are not considered either.

The mass balance equations for aluminum can be written as:

$$C^*_{Al} = [Al^{3+}] + [Al\text{-}OH] + [Al\text{-}F] + [Al\text{-}SO_4] + [Al\text{-}Org] \tag{1}$$

The meanings of the parameters throughout this paper is explained in Appendix A. We express the various aluminum speciation $[Al^{3+}]$, [Al-OH], [Al-F], $[Al\text{-}SO_4]$ and [Al-Org] as the functions of the fluoride $[F^-]$ (See Appendix B). Let,

$$CN = [Al^{3+}] + [Al\text{-}OH] + [Al\text{-}F] + [Al\text{-}SO_4] + [Al\text{-}Org] - C^*_{Al} \tag{2}$$

where CN is the discrepancy in concentrations of aluminum speciations. We assume that C^*_{Al} is constant under the condition of fixed pH. Thus, $\frac{\partial CN}{\partial C^*_{Al}} = 0$. By differentiating eqn(1):

$$CN' = \frac{\partial CN}{\partial F} = \frac{\partial [Al]}{\partial F} + \frac{\partial [Al\text{-}OH]}{\partial F} + \frac{\partial [Al\text{-}F]}{\partial F} + \frac{\partial [Al\text{-}SO_4]}{\partial F} + \frac{\partial [Al\text{-}Org]}{\partial F} \tag{3}$$

For simplicity, all charges in the partial derivative of each component are omitted. Each component in eqn. (3) can be solved by mass balance equations of C^*_F, C^*_{SO4} and C^*_{Org} respectively (Appendix B). The Newton-Raphson method is employed to calculate free $[F^-]$:

$$[F^-_{i+1}] = [F^-_i] - \frac{CN}{CN'} \tag{4}$$

where $[F^-_i]$ is the fluoride ion concentration at the i th iteration and $[F^-_{i+1}]$ the fluoride concentration at the $i + 1$ th iteration. Convergence is reached when $|[F^-_{i+1}] - [F^-_i]| < 1 \times 10^{-10}$ M. It should be emphased that the selection of a suitable initial value $[F^-]_0$ is very important. If inappropriate values are used, the

TABLE I Equilibrium constants, ΔH values and standard deviation used in Monte Carlo analysis [13, 24, 27]

Reaction equations	lgK	ΔH (cal/mol)	Literature error (logK ± s.d.)	Symbol
$Al^{3+} + H_2O = AlOH^{2+} + H^+$	−4.99	11,900	−4.987 ± 0.306	K_1
$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$	−10.00	22,000	−9.613 ± 0.690	K_2
$Al^{3+} + 3H_2O = Al(OH)_3 + 3H^+$	−16.76	39,345	−16.62 ± 0.739	K_3
$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	−23.00	44,060	−23.284 ± 1.603	K_4
$Al^{3+} + F^- = AlF^{2+}$	7.02	1,100	6.5780 ± 0.395	K_{F1}
$Al^{3+} + 2F^- = AlF_2^+$	12.76	2,000	11.626 ± 1.107	K_{F2}
$Al^{3+} + 3F^- = AlF_3$	17.03	2,500	16.080 ± 0.785	K_{F3}
$Al^{3+} + 4F^- = AlF_4^-$	19.73	2,200	18.746 ± 0.747	K_{F4}
$Al^{3+} + 5F^- = AlF_5^{2-}$	20.92	1,800	19.902 ± 0.651	K_{F5}
$Al^{3+} + SO_4^{2-} = AlSO_4^+$	3.01	2,150	3.342 ± 0.267	K_{S1}
$Al^{3+} + Org^{3-} = AlOrg$	8.39	-	-	K_{O1}
$Al^{3+} + H^+ + Org^{3-} = AlHOrg^+$	13.09	-	-	K_{O2}
$H_3Org = H^+ + H_2Org^-$	−1.76	-	-	K_{g1}
$H_2Org^- = H^+ + HOrg^{2-}$	−5.90	-	-	K_{g2}
$HOrg^{2-} = H^+ + Org^{3-}$	−6.83	-	-	K_{g3}
$Org^{3-} + H^+ = HOrg^{2-}$	-	-	6.860 ± 0.353	
$Org^{3-} + 2H^+ = H_2Org^-$	-	-	12.800 ± 0.450	
$Org^3 + 3H^+ = H_3Org$	-	-	14.90 ± 3.02	
$H^+ + F^- = HF$	3.17	3,460	3.112 ± 0.122	K_{HF}
$H_2O = H^+ + OH^-$	−14.00	13,340	-	K_W

iterative sequence will be divergent. We designed a program to select the suitable initial value automatically and the convergence solutions can be easily obtained.

A GW-BASIC computer program was developed to perform the necessary calculation of the solution speciation by an IBM-PC/386 computer. Inputs for the calculations are pH, total concentrations of C^*_{Al}, C^*_{SO4} and C^*_{Org}. In surface waters of low ionic strength, their concentrations are generally: [20-24] $C^*_{Al} \sim 10\ \mu M$, $C^*_{SO4} \sim 100\ \mu M$ and $C^*_{Org} \sim 10\ \mu M$. The concentrations of various forms of Al can be easily calculated by the equilibrium equations listed in Appendices A and B. Chemical reaction equations assumed to be involved in the speciation of aluminum are given in Table I, together with the corresponding equilibrium constants, enthalpy values and standard deviations.

RESULTS AND DISCUSSION

Assess the Accuracy of the Model

We compare the results of two methods, the chemical equilibrium calculation by our model and the PCV method proposed by Sullivan *et al.*, for surface water samples from southern Norway. [25] Figure 1 shows that there is little difference between these two independent methods for Al_i (labile monomeric aluminum, mainly inorganic Al^{3+}, Al-OH, $Al\text{-}SO_4$ and Al-F) and Al_0 (non-labile monomeric aluminum, mainly organic Al-ORG), as the slopes are close to 1.00 and the intercepts do not deviate much from zero. This indicates that our simplified model is accuracy and acceptable. What we should emphasize is that the close agreement between methods for analysis of inorganic monomeric Al is particularly important, as this fraction is considered to include the toxic species. [26]

Error Analysis

Except for the reasons of approximation of this model (without considering the significance of complexation reactions involving Ca, Mg, Fe and Mn with various ligands and adsorption of F^- and SO_4^{2-}), some important environmental factors, such as, temperature, the concentrations of aluminum-binding ligands (particularly organic matter and fluoride) and equilibrium constants, also have

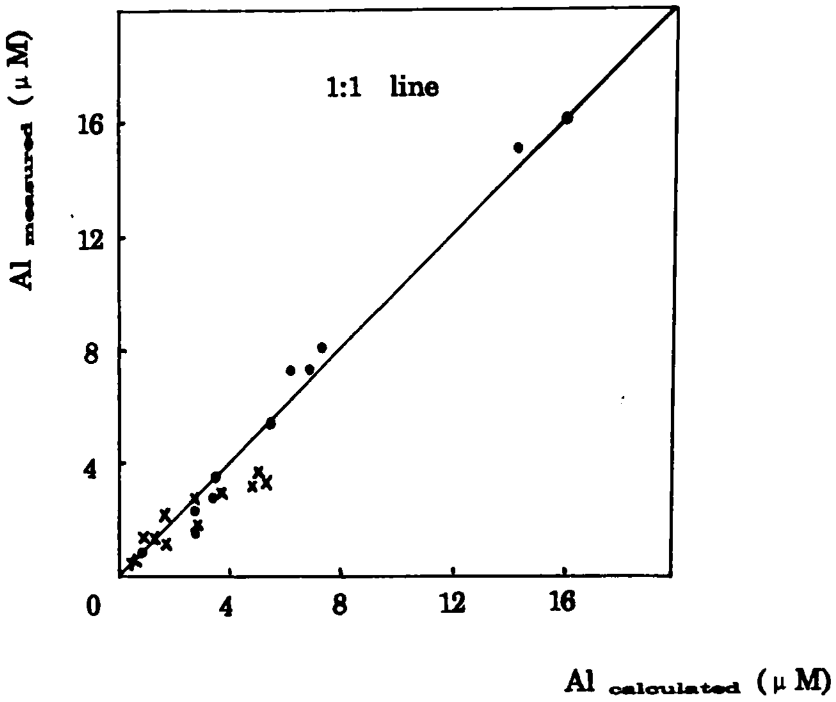

FIGURE 1 Comparison of the results between two methods .... inorganic monomeric aluminum x x x x organic monomeric aluminum

substantial influences on the inorganic and inorganic equilibrium compositions. Therefore, considerable errors in model predication might be result from these factors. The pH values of the natural surface waters are generally falling in the range of 4 ~ 7. [27, 28] For the sake of simplicity, we investigate the influences of these factors on aluminum speciation by the theoretical calculation results at a fixed pH value of 5.5. Most attention is paid to illustrate how those factors (temperature, complexing ligands and equilibrium constants of chemical reactions) affect the distribution of aluminum in surface waters.

The effect of temperature on the aluminum speciation is essential, but is most often ignored. Temperature exerts a strong effect on the distribution of Al because the equilibrium constants are temperature dependent. [29, 30] It is convenient to express the temperature dependence of Ks as following:

$$\log Ks = \log K^*s + \Delta H/(2.303R)(1/T^* - 1/T) \qquad (5)$$

where T is the temperature of interest (in K), T* a reference temperature, ΔH the enthalpy change and R the gas constant. In writing this equation, we assumed that ΔH for the reaction does not vary with temperature. Figure 2 indicates that temperature plays a very important role in Al distribution: free Al, Al-F, Al-SO_4 and Al-Org complexes decline as the temperature increases. On the other hand, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3$ increase with the increase of temperature;

Aluminum can form complexes with the ligands fluoride, sulphate and organic acids. However, most naturally occurring organic substances are present in the

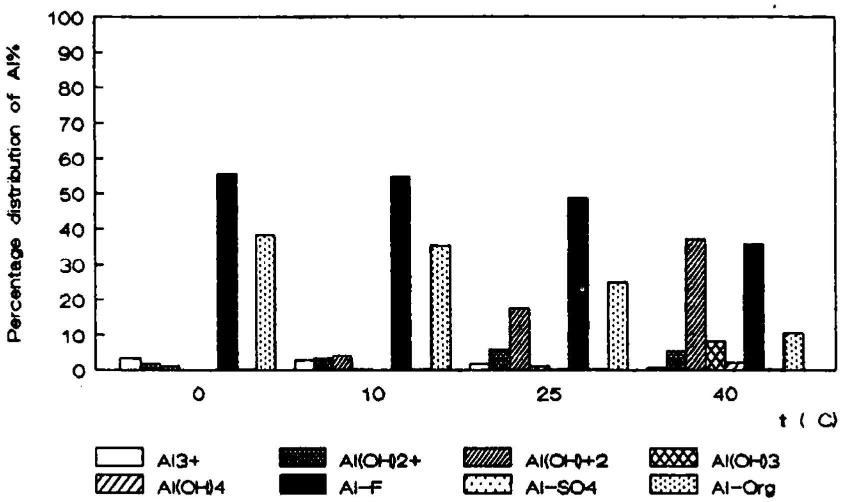

FIGURE 2 Influence of the temperature on the distribution of aluminum speciation ($C^*_{Al} = 5 \times 10^{-6}$ M, $C^*_F = 5 \times 10^{-6}$ M, $C^*_{SO4} = 1 \times 10^{-4}$ M, $C^*_{Org} = 5 \times 10^{-6}$ M, pH = 5.5)

form of humic compounds. It is difficult to estimate the equilibrium constant for the formation of Al-humate complexes. The best way is to represent the organic acid chemistry of all natural waters in terms of a hypothetical homogeneous compound. A method has been proposed by treating the organic solute as a triprotic acid. [13] Data from the large and diverse Adirondack lake survey were used to calibrate from simple organic acid analog models in an effort to quantify the influence of naturally occurring organic acids on lake water pH. The organic acid analog models were calibrated to observations from a reduced data set representing 1128 individual lake samples. Of the four organic analog approaches examined, including the Oliver[31] *et al* model, as well as monoprotic, diprotic and triprotic representations, the triprotic analog model was qualitatively consistent with observed patterns of change in organic solute charge density as a function of pH. [32] Figure 3 depicts the effect of organic acids on Al distribution. It shows that at a fixed pH, increasing organic acid concentration will result in the increase of Al-Org and the reduction of Al^{3+}, Al-OH and Al-SO_4, and especially Al-F complex.

Similarly, increasing C^*_F will result in the increase of Al-F compounds and decrease of Al-Org, free Al and Al-OH complexes. See Figure 4.

The theoretical calculation above also indicates that the Al-F and Al-Org complexes are the main constituents in Al speciation, Al-SO_4 complexes are insignificant and do not exceed 4%, although C^*_{SO4} is much higher than C^*_{Org} and C^*_F.

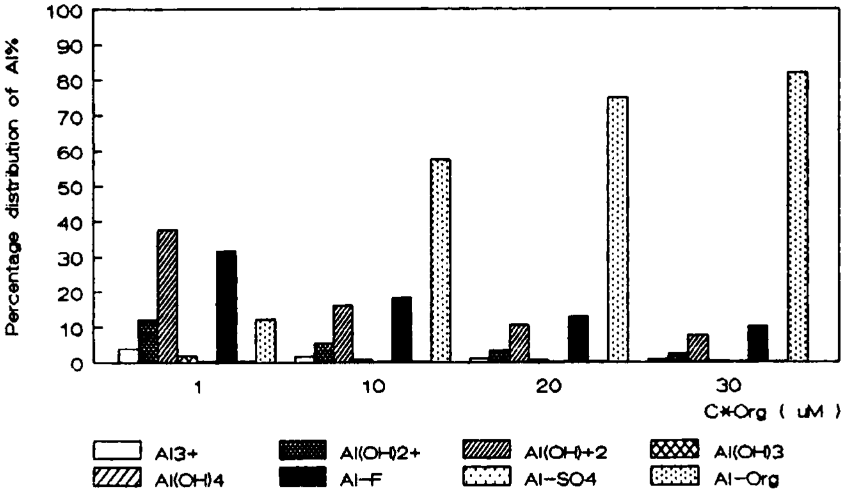

FIGURE 3 Effect of organic acids on the distribution of aluminum speciation ($C^*_{Al} = 5 \times 10^{-6}$ M, $C^*_F = 5 \times 10^{-6}$ M, $C_{SO4} = 1 \times 10^{-4}$ M, t = 25°C, pH = 5.5)

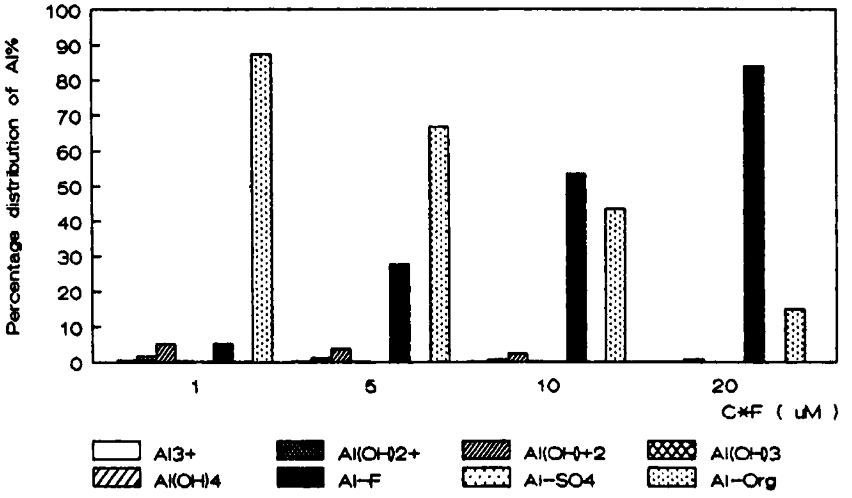

FIGURE 4 Effect of fluoride on the distribution of aluminum speciation ($C^*_{Al} = 5 \times 10^{-6}$ M, $C^*_{org} = 5 \times 10^{-5}$ M, $C^*_{SO4} = 1 \times 10^{-4}$ M, t = 25°C, pH = 5.5)

Some discrepancies may depend on uncertainties in the equilibrium constants. The selection of equilibrium constants is a potentially important but generally ignored factor which contributes to uncertainty in model predication. Significant differences in the speciation of aluminum might arise from using different published values for the stability constants of the common aqueous complexes. Schecher and Driscoll[27] found a wide discrepancy in reported values for the aqueous Al equilibrium constants. In order to evaluate the uncertainties caused by the variation in equilibrium constants, we use the Monte Carlo method to perform the sensitivity analysis. The equilibrium constants are assumed to have uncertainties which are normally distributed. Large normally distributed samples of each equilibrium constant are developed with a random normal variate generator. [33] The randomly selected values from each synthetic distribution are inserted into the equations in the model to generate a predicted species distribution. Table II indicates that selection of equilibrium constants has a remarkable effect on the aluminum distribution.

Analysis of the Aluminum Speciation of Surface Water

We applied our model to the practical analysis of surface water samples. The water quality data are cited from the literature. [34-43] The study sites are:

(I) the United Kingdom.

TABLE II Confidence limit (98%) for mean model output due to variations of equilibrium constants from the literatures (C^*_{Al} = 5 μ M, C^*_F = 5 μ M, C^*_{Org} = 50 μ M, C^*_{SO4} = 100 μ M, t = 25°C)

pH	%	Al^{3+}	$AlOH^{2+}$	$Al(OH)_2^+$	$Al(OH)_3$	$Al(OH)_4^-$	Al-F	Al-SO_4	Al-Org
	max	10.54	9.98	28.21	57.68	0.03	81.05	6.44	60.30
4.5	mean	6.47	2.11	1.58	0.04	0	53.19	1.42	35.37
	min	2.11	0.19	0.02	0	0	24.86	0.21	16.52
	max	0.52	7.89	76.43	100	48.79	36.45	0.43	93.64
5.5	mean	0.44	1.43	10.69	2.70	0.02	10.76	0.10	75.76
	min	0.08	0.04	0.01	0	0	1.26	0	16.04
	max	0.02	2.23	96.44	100	99.63	7.97	0	71.23
6.5	mean	0.01	0.35	26.44	66.20	5.64	0.33	0	35.49
	min	0	0	0.05	0.06	0	0	0	0.34

Svartberget Catchment Stream (July, 1986). [34]

(II) the United States.

Coxingkill stream, [35] situated in the northern Shawangunk Mts, Ulster County, NY (January 1990).

White Oak Run Watershed, [36] located within the Shenandoah National Park, VA. (1986)

The Rhode River Watershed, [37] a subestuary on the western shoreline of Chesapeake Bay about 20 km south of Annapolis, MD. (Feb, 1984-April, 1985)

(III) the People's Republic of China.

Chongqing Coniferous Forest Streams, Sichuan Province. [38, 39] (1986, May, 1991)

Guangyuang City and E-Mei Mountain Streams, Sichuan Province. (April, 1988) [40]

Yang-Zi River, Nanjing City, Jiangsu Province. (June, 1995) [41]

Le-An River, Jiangxi Province. (September, 1989) [42]

The aluminum speciation in surface waters of these sampling areas is listed in Table III.

Aluminum toxicity to some aquatic plants and animals strongly depends on aqueous Al speciation. It was demonstrated that the positively charged aluminum hydroxy species are much more toxic to fish than the organic complexes, and fluoride may reduce aluminum toxicity. Laboratory bioassay studies have shown fish mortality to occur at aquo plus OH-complexed Al (Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$) concentrations as low as $4 \sim 8\ \mu M$. [43] Our model simulation results indicate that concentrations of toxic forms of Al^{3+} plus Al-OH complexes changes with pH: (a) In the acidified surface waters (pH < 5), the sum of Al^{3+} and Al-OH concentrations may be up to $4 \times 10^{-6} \sim 1 \times 10^{-4}$ M, which exceeds the critical level of 7.5 μM and could be potentially toxic to fish. This situation is

TABLE III(1) Practical analysis of aluminum speciation in surface waters (concentration in M)

No	pH	Al^{3+}	$AlOH^{2+}$	$Al(OH)_2^+$	$Al(OH)_3$	$Al(OH)_4^-$	Al-F	$Al\text{-}SO_4$	Al-Org
Norway [25]									
(1)	4.4	3.04×10^{-6}	7.81×10^{-7}	1.92×10^{-7}	8.37×10^{-10}	1.21×10^{-11}	2.46×10^{-6}	1.89×10^{-7}	3.83×10^{-6}
(2)	4.9	3.00×10^{-6}	2.44×10^{-6}	1.90×10^{-6}	2.62×10^{-8}	1.20×10^{-9}	6.60×10^{-6}	2.33×10^{-7}	5.23×10^{-6}
(3)	4.4	7.86×10^{-6}	2.02×10^{-6}	4.96×10^{-7}	2.16×10^{-9}	3.13×10^{-11}	4.65×10^{-6}	6.98×10^{-7}	5.11×10^{-6}
the United Kingdom [34]									
(4)	4.7	2.26×10^{-6}	1.16×10^{-6}	5.67×10^{-7}	4.94×10^{-9}	1.42×10^{-10}	3.59×10^{-6}	1.20×10^{-7}	9.95×10^{-7}
the United States									
White Oak Run Watershed [36]									
(5)	4.32	2.34×10^{-6}	5.01×10^{-7}	1.02×10^{-7}	3.71×10^{-10}	4.46×10^{-12}	4.09×10^{-6}	1.26×10^{-7}	1.34×10^{-6}
Coxingkill Stream [35]									
(6)	6.6	2.46×10^{-10}	1.00×10^{-8}	3.90×10^{-7}	2.70×10^{-7}	6.18×10^{-7}	4.99×10^{-8}	2.51×10^{-11}	3.95×10^{-8}
Rhode River Watershed [37]									
(7)	5.56	2.20×10^{-9}	2.82×10^{-9}	4.04×10^{-9}	5.41×10^{-11}	7.41×10^{-12}	4.06×10^{-7}	1.67×10^{-10}	7.34×10^{-7}
(8)	5.71	1.11×10^{-9}	2.00×10^{-9}	4.07×10^{-9}	7.67×10^{-11}	1.48×10^{-11}	5.81×10^{-7}	8.18×10^{-11}	8.22×10^{-7}
(9)	5.29	6.22×10^{-9}	4.28×10^{-9}	3.30×10^{-9}	2.37×10^{-11}	1.74×10^{-12}	1.87×10^{-6}	5.96×10^{-10}	1.41×10^{-6}
(10)	5.41	5.70×10^{-9}	1.50×10^{-8}	3.76×10^{-8}	1.68×10^{-9}	2.49×10^{-10}	1.36×10^{-6}	4.98×10^{-10}	3.71×10^{-6}
(11)	5.14	1.53×10^{-8}	2.16×10^{-8}	2.91×10^{-8}	6.98×10^{-10}	5.55×10^{-11}	2.18×10^{-6}	1.53×10^{-9}	3.36×10^{-6}
(12)	5.35	2.67×10^{-9}	6.12×10^{-9}	1.33×10^{-8}	5.21×10^{-10}	6.71×10^{-11}	8.48×10^{-7}	1.74×10^{-10}	8.73×10^{-7}

*(1) Hogkleinvatn $C^*_{Al} = 1.07 \times 10^{-5}$ M, $C^*_{SO4} = 6.10 \times 10^{-5}$ M, $C^*_F = 3.16 \times 10^{-6}$ M, $C^*_{Org} = 1.89 \times 10^{-5}$ M (2) Bie-01-lowflow $C^*_{Al} = 1.94 \times 10^{-5}$ M, $C^*_{SO4} = 7.60 \times 10^{-5}$ M, $C^*_F = 7.42 \times 10^{-6}$ M, $C^*_{Org} = 9.30 \times 10^{-6}$ M (3) Bie-01-highflow $C^*_{Al} = 2.11 \times 10^{-5}$ M, $C^*_{SO4} = 8.75 \times 10^{-5}$ M, $C^*_F = 4.84 \times 10^{-6}$ M, $C^*_{Org} = 1.29 \times 10^{-5}$ M (4) Svartberget $C^*_{Al} = 8.53 \times 10^{-6}$ M, $C^*_{SO4} = 5.25 \times 10^{-5}$ M, $C^*_F = 4.00 \times 10^{-6}$ M, $C^*_{Org} = 3.04 \times 10^{-6}$ M (5) White Oak Run $C^*_{Al} = 8.33 \times 10^{-6}$ M, $C^*_{SO4} = 5.25 \times 10^{-5}$ M, $C^*_F = 4.57 \times 10^{-6}$ M, $C^*_{Org} = 10.0 \times 10^{-6}$ M$^+$ (6) Coxingkill $C^*_{Al} = 1.50 \times 10^{-6}$ M, $C^*_{SO4} = 10.0 \times 10^{-5}$ M, $C^*_F = 5.00 \times 10^{-6}$ M, $C^*_{Org} = 2.00 \times 10^{-6}$ M$^+$ (7) Pastureland $C^*_{Al} = 1.15 \times 10^{-6}$ M, $C^*_{SO4} = 8.96 \times 10^{-5}$ M, $C^*_F = 5.84 \times 10^{-6}$ M, $C^*_{Org} = 7.28 \times 10^{-5}$ M (8) Forest 109 $C^*_{Al} = 1.41 \times 10^{-6}$ M, $C^*_{SO4} = 8.75 \times 10^{-5}$ M, $C^*_F = 1.00 \times 10^{-5}$ M, $C^*_{Org} = 9.62 \times 10^{-5}$ M (9) Forest 110 $C^*_{Al} = 3.30 \times 10^{-6}$ M, $C^*_{SO4} = 1.14 \times 10^{-4}$ M, $C^*_F = 1.03 \times 10^{-5}$ M, $C^*_{Org} = 1.31 \times 10^{-4}$ M (10) 109 (1984) $C^*_{Al} = 5.11 \times 10^{-6}$ M, $C^*_{SO4} = 8.54 \times 10^{-5}$ M, $C^*_F = 7.89 \times 10^{-6}$ M, $C^*_{Org} = 2.45 \times 10^{-4}$ M (11) 110 (1984) $C^*_{Al} = 5.59 \times 10^{-6}$ M, $C^*_{SO4} = 9.79 \times 10^{-5}$ M, $C^*_F = 7.89 \times 10^{-5}$ M, $C^*_{Org} = 2.21 \times 10^{-4}$ M (12) 111 (1984) $C^*_{Al} = 1.74 \times 10^{-6}$ M, $C^*_{SO4} = 6.35 \times 10^{-4}$ M, $C^*_F = 7.89 \times 10^{-5}$ M, $C^*_{Org} = 1.52 \times 10^{-4}$ M

TABLE III(2) Practical analysis of aluminum speciation in surface waters (concentration in M)

No	pH	Al^{3+}	$AlOH^{2+}$	$Al(OH)_2^+$	$Al(OH)_2$	$Al(OH)_4^-$	Al-F	$Al\text{-}SO_4$	Al-Org
the People's Republic of China									
Chongqing Coniferous Forest Areas [38, 39]									
(13)	4.8	4.80×10^{-7}	3.10×10^{-7}	1.91×10^{-7}	2.10×10^{-9}	7.61×10^{-11}	1.49×10^{-5}	1.40×10^{-6}	1.27×10^{-6}
(14)	5.1	6.72×10^{-10}	8.65×10^{-10}	1.06×10^{-9}	2.32×10^{-11}	1.69×10^{-12}	2.50×10^{-7}	3.40×10^{-10}	5.85×10^{-9}
(15)	5.0	1.34×10^{-9}	1.37×10^{-9}	1.34×10^{-9}	2.33×10^{-11}	1.34×10^{-12}	3.20×10^{-6}	1.58×10^{-9}	8.15×10^{-9}
(16)	5.2	7.50×10^{-10}	1.22×10^{-9}	1.88×10^{-9}	5.19×10^{-11}	4.73×10^{-12}	3.21×10^{-6}	2.27×10^{-10}	9.40×10^{-9}
(17)	5.65	6.72×10^{-8}	3.07×10^{-7}	1.34×10^{-6}	1.04×10^{-7}	2.68×10^{-8}	5.80×10^{-6}	1.31×10^{-8}	2.99×10^{-6}
(18)	5.48	1.77×10^{-7}	5.46×10^{-7}	1.61×10^{-6}	8.46×10^{-8}	1.47×10^{-8}	5.35×10^{-6}	3.61×10^{-8}	3.80×10^{-6}
(19)	6.41	2.52×10^{-9}	6.62×10^{-8}	1.66×10^{-6}	7.42×10^{-7}	1.10×10^{-6}	2.26×10^{-6}	3.11×10^{-10}	1.24×10^{-6}
Guangyuang City and E-Mei Mountain Streams [40]									
(20)	8.5	1.12×10^{-15}	3.61×10^{-12}	1.12×10^{-8}	6.13×10^{-7}	1.12×10^{-4}	0	2.63×10^{-16}	2.68×10^{-12}
(21)	8.5	1.07×10^{-15}	3.32×10^{-12}	9.80×10^{-9}	5.14×10^{-7}	8.93×10^{-5}	0	2.76×10^{-16}	2.58×10^{-12}
(22)	8.2	3.11×10^{-15}	4.82×10^{-12}	7.13×10^{-9}	1.87×10^{-7}	1.63×10^{-5}	0	1.71×10^{-15}	7.32×10^{-12}
(23)	6.5	1.11×10^{-9}	3.85×10^{-8}	1.28×10^{-6}	7.52×10^{-7}	1.47×10^{-8}	1.53×10^{-7}	8.51×10^{-11}	7.41×10^{-7}
(24)	6.9	4.43×10^{-12}	3.86×10^{-10}	3.21×10^{-8}	4.75×10^{-8}	2.33×10^{-7}	0	1.25×10^{-12}	5.86×10^{-9}

*(13) Nanlouquan (up) $C^*_{Al} = 1.85 \times 10^{-5}$ M, $C^*_{SO4} = 2.84 \times 10^{-8}$ M, $C^*_F = 1.79 \times 10^{-5}$ M, $C^*_{Org} = 1.00 \times 10^{-5}$ M+(14) Nanlouquan (down) $C^*_{Al} = 2.57 \times 10^{-7}$ M, $C^*_{SO4} = 4.94 \times 10^{-4}$ M, $C^*_F = 7.37 \times 10^{-6}$ M, $C^*_{Org} = 1.00 \times 10^{-5}$ M+(15) Guanyingqiao $C^*_{Al} = 3.22 \times 10^{-6}$ M, $C^*_{SO4} = 1.15 \times 10^{-8}$ M, $C^*_F = 2.42 \times 10^{-5}$ M, $C^*_{Org} = 1.00 \times 10^{-5}$ M+(16) Jingyunsan $C^*_{Al} = 3.22 \times 10^{-6}$ M, $C^*_{SO4} = 1.88 \times 10^{-4}$ M, $C^*_F = 2.96 \times 10^{-6}$ M, $C^*_{Org} = 1.00 \times 10^{-5}$ M+(17) JO5 $C^*_{Al} = 1.06 \times 10^{-5}$ M, $C^*_{SO4} = 1.91 \times 10^{-4}$ M, $C^*_F = 1.27 \times 10^{-5}$ M, $C^*_{Org} = 1.00 \times 10^{-5}$ M+(18) JO6 $C^*_{Al} = 1.16 \times 10^{-5}$ M, $C^*_{SO4} = 2.00 \times 10^{-4}$ M, $C^*_F = 8.26 \times 10^{-6}$ M, $C^*_{Org} = 1.00 \times 10^{-5}$ M+(19) JO3 $C^*_{Al} = 7.07 \times 10^{-6}$ M, $C^*_{SO4} = 1.21 \times 10^{-4}$ M, $C^*_F = 1.53 \times 10^{-5}$ M, $C^*_{Org} = 1.00 \times 10^{-5}$ M+(20) Guangyuan 1 $C^*_{Al} = 1.12 \times 10^{-4}$ M, $C^*_{SO4} = 2.31 \times 10^{-4}$ M, $C^*_F = 2.11 \times 10^{-6}$ M, $C^*_{Org} = 1.00 \times 10^{-5}$ M+(21) Guangyuan 2 $C^*_{Al} = 2.39 \times 10^{-5}$ M, $C^*_{SO4} = 4.37 \times 10^{-4}$ M, $C^*_F = 4.21 \times 10^{-6}$ M, $C^*_{Org} = 1.00 \times 10^{-5}$ M+(22) Guangyuan 3 $C^*_{Al} = 1.65 \times 10^{-5}$ M, $C^*_{SO4} = 5.36 \times 10^{-4}$ M, $C^*_F = 5.26 \times 10^{-6}$ M, $C^*_{Org} = 1.00 \times 10^{-5}$ M+(23) E-Mei 1 $C^*_{Al} = 4.43 \times 10^{-6}$ M, $C^*_{SO4} = 7.48 \times 10^{-5}$ M, $C^*_F = 4.21 \times 10^{-6}$ M, $C^*_{Org} = 1.00 \times 10^{-5}$ M+(24) E-Mei 2 $C^*_{Al} = 3.19 \times 10^{-7}$ M, $C^*_{SO4} = 2.75 \times 10^{-4}$ M, $C^*_F = 4.21 \times 10^{-6}$ M, $C^*_{Org} = 1.00 \times 10^{-5}$ M+

TABLE III(3) Practical analysis of aluminum speciation in surface waters (concentration in M)

No	pH	Al^{3+}	$AlOH^{2+}$	$Al(OH)_2^+$	$Al(OH)_3$	$Al(OH)_4^-$	Al-F	$Al\text{-}SO_4$	Al-Org
the People's Republic of China									
Yang-Zhi river, Nanjing [41]									
(25)	7.2	1.16×10^{-11}	1.79×10^{-9}	2.65×10^{-7}	6.97×10^{-7}	6.07×10^{-6}	0	2.95×10^{-12}	1.93×10^{-9}
Le-An River [42]									
(26)	7.5	1.02×10^{-13}	4.17×10^{-11}	1.57×10^{-8}	1.21×10^{-7}	2.42×10^{-6}	0	1.70×10^{-15}	2.06×10^{-11}
(27)	7.1	5.22×10^{-12}	8.49×10^{-10}	1.27×10^{-7}	3.91×10^{-7}	3.11×10^{-6}	0	2.55×10^{-13}	8.18×10^{-10}
(28)	7.4	1.13×10^{-12}	3.42×10^{-10}	9.56×10^{-8}	5.47×10^{-7}	8.09×10^{-6}	0	2.51×10^{-13}	2.14×10^{-10}
(29)	7.0	5.27×10^{-11}	7.47×10^{-9}	9.75×10^{-7}	2.61×10^{-6}	1.85×10^{-5}	0	7.91×10^{-12}	7.76×10^{-9}
(30)	7.5	2.74×10^{-13}	1.17×10^{-10}	4.62×10^{-8}	3.73×10^{-7}	7.80×10^{-6}	0	5.54×10^{-14}	5.56×10^{-11}
(31)	7.2	5.95×10^{-12}	1.34×10^{-9}	2.77×10^{-7}	1.17×10^{-6}	1.29×10^{-5}	0	1.19×10^{-12}	1.04×10^{-9}
(32)	7.3	2.14×10^{-12}	5.52×10^{-10}	1.31×10^{-7}	6.39×10^{-7}	8.04×10^{-6}	0	2.76×10^{-13}	3.89×10^{-10}
(33)	7.8	1.55×10^{-14}	1.27×10^{-11}	9.52×10^{-9}	1.47×10^{-7}	5.84×10^{-6}	0	2.70×10^{-15}	3.44×10^{-12}
(34)	7.7	1.84×10^{-14}	1.19×10^{-11}	7.12×10^{-9}	8.71×10^{-6}	2.76×10^{-6}	0	2.56×10^{-15}	3.98×10^{-12}

*(25) Yang-Zi River $C^*_{Al} = 7.04 \times 10^{-6}$ M, $C^*_{SO4} = 2.49 \times 10^{-4}$ M, $C^*_F = 1.58 \times 10^{-5}$ M, $C^*_{Org} = 1.00 \times 10^{-6}$ M$^+$ (26) Haikou $C^*_{Al} = 2.56 \times 10^{-6}$ M, $C^*_{SO4} = 1.56 \times 10^{-5}$ M, $C^*_F = 1.05 \times 10^{-5}$ M, $C^*_{Org} = 1.00 \times 10^{-6}$ M$^+$ (27) Gouku $C^*_{Al} = 3.63 \times 10^{-6}$ M, $C^*_{SO4} = 4.58 \times 10^{-3}$ M, $C^*_F = 1.05 \times 10^{-5}$ M, $C^*_{Org} = 1.00 \times 10^{-6}$ M$^+$ (28) Xiangtun $C^*_{Al} = 8.74 \times 10^{-6}$ M, $C^*_{SO4} = 2.08 \times 10^{-4}$ M, $C^*_F = 1.05 \times 10^{-5}$ M, $C^*_{Org} = 1.00 \times 10^{-6}$ M$^+$ (29) Daichun $C^*_{Al} = 2.17 \times 10^{-5}$ M, $C^*_{SO4} = 1.41 \times 10^{-4}$ M, $C^*_F = 1.05 \times 10^{-5}$ M, $C^*_{Org} = 1.00 \times 10^{-6}$ M$^+$ (30) Laosan $C^*_{Al} = 8.22 \times 10^{-6}$ M, $C^*_{SO4} = 1.90 \times 10^{-4}$ M, $C^*_F = 1.05 \times 10^{-5}$ M, $C^*_{Org} = 1.00 \times 10^{-6}$ M$^+$ (31) Jiedu $C^*_{Al} = 1.43 \times 10^{-5}$ M, $C^*_{SO4} = 1.88 \times 10^{-4}$ M, $C^*_F = 1.05 \times 10^{-5}$ M, $C^*_{Org} = 1.00 \times 10^{-6}$ M$^+$ (32) Hanjiadu $C^*_{Al} = 8.81 \times 10^{-6}$ M, $C^*_{SO4} = 1.21 \times 10^{-4}$ M, $C^*_F = 1.05 \times 10^{-6}$ M, $C^*_{Org} = 1.00 \times 10^{-6}$ M$^+$ (33) Shizhen $C^*_{Al} = 6.00 \times 10^{-6}$ M, $C^*_{SO4} = 1.63 \times 10^{-4}$ M, $C^*_F = 1.05 \times 10^{-6}$ M, $C^*_{Org} = 1.00 \times 10^{-6}$ M$^+$ (34) Caijiawan $C^*_{Al} = 2.85 \times 10^{-6}$ M, $C^*_{SO4} = 1.30 \times 10^{-4}$ M, $C^*_F = 1.05 \times 10^{-6}$ M, $C^*_{Org} = 1.00 \times 10^{-6}$ M$^+$ (+ estimated)

occurring in the United Kingdom, Norway and Chongqing area of China; (b) In the pH range of 5 $\sim$ 7, aluminum species were dominated by organic monomeric and Al-F complexes, the total concentration of free Al and Al hydroxides is smaller than 1×10^{-6} M. (c) When pH > 7, the dominant form of aluminum is $Al(OH)_4^-$, like in the areas of Le-An River of China.

CONCLUSIONS

A simple chemical equilibrium model is presented which can be employed to estimate the Al speciation in surface waters of low ionic strength. Results obtained from analysis of surface water samples in this simple model compared favorably with those obtained experimentally. Although chemical equilibrium calculation can only provide a gross picture of aluminum speciation in surface waters because the natural waters are very complicated, it can still offer a way to account for these factors and allow a general characterization of the chemical speciation. All of this should prove to be useful guide for assessing the actural speciation of aluminum for field condition with the merit of simplicity. It may be used to intercept data obtained from water quality monitoring programs. For example, calculations of the distribution of Al may be useful in assessing biogechemical pathways, as well as potential toxicity to auqatic organisms.

APPENDIX A

C^*_{Al}: total concentration of aluminum

C^*_{SO4}: total concentration of sulphate $C^*_{SO4} = [SO_4^{2-}] + [AlSO_4^+]$ (6)

C^*_F: total concentration of fluoride $C^*_F = [F^-] + [HF] + [F\text{-}Al]$ (7)

C^*_{Org}: total concentration of organic acids

$$C^*_{Org} = [Org^{3-}] + [HOrg^{2-}] + [H_2Org^-] + [H_3Org] + [AlOrg] + [AlHOrg^+]$$

$$[Al\text{-}OH] = [AlOH^{2+}] + [Al(OH)_2^+] + [Al(OH)_3] + [Al(OH)_4^-] \quad (8)$$

$$= \frac{K_1[Al^{3+}]}{[H^+]} + \frac{K_2[Al^{3+}]}{[H^+]^2} + \frac{K_3[Al^{3+}]}{[H^+]^3} + \frac{K_4[Al^{3+}]}{[H^+]^4} \quad (9)$$

$$[Al\text{-}F] = [AlF^{2+}] + [AlF_2^+] + [AlF_3] + [AlF_4^-] + [AlF_5^{2-}]$$
$$= K_{F1}[Al^{3+}][F^-] + K_{F2}[Al^{3+}][F^-]^2 + K_{F3}[Al^{3+}][F^-]^3 + K_{F4}[Al^{3+}][F^-]^4$$
$$+ K_{F5}[Al^{3+}][F^-]^5 \quad (10)$$

$$[\text{F-Al}] = [\text{AlF}^{2+}] + 2[\text{AlF}_2^+] + 3[\text{AlF}_3] + 4[\text{AlF}_4^-] + 5[\text{AlF}_5^{2-}]$$

$$= K_{F1}[\text{Al}^{3+}][\text{F}^-] + 2K_{F2}[\text{Al}^{3+}][\text{F}^-]^2 + 3K_{F3}[\text{Al}^{3+}][\text{F}^-]^3 + 4K_{F4}[\text{Al}^{3+}][\text{F}^-]^4$$

$$+ 5K_{F5}[\text{Al}^{3+}][\text{F}^-]^5 \qquad (11)$$

$$[\text{Al-Org}] = [\text{AlOrg}] + [\text{AlHOrg}^+] = K_{O1}[\text{Al}^{3+}][\text{Org}^{3-}] + K_{O2}[\text{Al}^{3+}][\text{H}^+][\text{Org}^{3-}] \qquad (12)$$

$$[\text{Al-SO}_4] = [\text{AlSO}_4^+] \qquad (13)$$

[ ]: component's concentration (M).

APPENDIX B

Solving of the partial derivative of each component:

(1)

$$\frac{\partial[\text{Al-OH}]}{\partial F} = K_{OH}\frac{\partial[\text{Al}]}{\partial F} \qquad (14)$$

where

$$K_{OH} = \frac{K_1}{[\text{H}^+]} + \frac{K_2}{[\text{H}^+]^2} + \frac{K_3}{[\text{H}^+]^3} + \frac{K_4}{[\text{H}^+]^4} \qquad (15)$$

(2)

$$\frac{\partial[\text{Al-SO}_4]}{\partial F} = K_{S1}[\text{SO}_4^{2-}]\frac{\partial[\text{Al}]}{\partial F} + K_{S1}[\text{Al}^{3+}]\frac{\partial[\text{SO}_4]}{\partial F} \qquad (16)$$

where from eqn. 6,1

$$[\text{SO}_4^{2-}] = \frac{C^*_{SO4}}{1 + K_{S1}[\text{Al}^{3+}]} \qquad (17)$$

$$\frac{\partial[\text{SO}_4^{2-}]}{\partial F} = \frac{\partial[\text{SO}_4^{2-}]}{\partial \text{Al}}\frac{\partial[\text{Al}]}{\partial F} = -\frac{C^*_{SO4}}{(1 + K_{S1}[\text{Al}^{3+}])^2}\frac{\partial[\text{Al}]}{\partial F} \qquad (18)$$

(3)

$$\frac{\partial[\text{Al-Org}]}{\partial F} = K_{O1}[\text{Al}^{3+}]\frac{\partial[\text{Org}]}{\partial F} + K_{O1}[\text{Org}^{3-}]\frac{\partial[\text{Al}]}{\partial F}$$

$$+ K_{O2}[\text{Org}^{3-}][\text{H}^+]\frac{\partial[\text{Al}]}{\partial F} + K_{O2}[\text{Al}^{3+}[\text{H}^+]\frac{\partial[\text{Org}]}{\partial F} \qquad (19)$$

where

$$[\text{Org}^{3-}] = \frac{C^*_{Org}}{K_G} \qquad (20)$$

$$K_G = 1 + \frac{[H^+]}{K_{g3}} + \frac{[H^+]^2}{K_{g3}K_{g2}} + \frac{[H^+]^3}{K_{g3}K_{g2}K_{g1}} + K_{O1}[Al^{3+}] + K_{O2}[H^+][Al^{3+}] \quad (21)$$

$$\frac{\partial[Org]}{\partial F} = \frac{\partial[Org]}{\partial Al}\frac{\partial[Al]}{\partial F} = -\frac{C^*_{Org}}{K_G^2}(K_{O1} + K_{O2}[H^+])\frac{\partial[Al]}{\partial F} \quad (22)$$

(4) Al-F complexes are more complicated because step-wise complexes are formed. When n = 1, AlF^{2+} occurs,

$$C^*_F = [F^-] + [HF] + [AlF^{2+}] = [F^-] + K_{HF}[H^+][F^-] + K_{F1}[Al^{3+}][F^-] \quad (23)$$

then,

$$[Al^{3+}] = \frac{C^*_F - [F^-] - K_{HF}[H^+][F^-]}{K_{F1}[F^-]} \quad (24)$$

$$\frac{\partial[Al]}{\partial F} = \frac{C^*_F}{K_{F1}[F^-]^2} \quad (25)$$

$$\frac{\partial[Al\text{-}F]}{\partial F} = K_1[Al^{3+}] + K_{F1}[F^-]\frac{\partial[Al]}{\partial F} \quad (26)$$

when n≥2, the general equations are:

$$\begin{aligned} C^*_F &= [F^-] + [HF] + [AlF^{2+}] + 2[AlF_2^+] + 3[AlF_3] + 4[AlF_4^-] + 5[AlF_5^{2-}] \\ &= [F^-] + K_{HF}[H^+][F^-] + K_{F1}[Al^{3+}][F^-] + 2K_{F2}[Al^{3+}][F^-]^2 \\ &\quad + 3K_{F3}[Al^{3+}][F^-]^3 + 4K_{F4}[Al^{3+}][F^-]^4 + 5K_{F5}[Al^{3+}][F^-]^5 \end{aligned} \quad (27)$$

$$[Al^{3+}] = \frac{C^*_F - [F^-] - K_{HF}[H^+][F^-]}{K_F} \quad (28)$$

in which,

$$K_F = K_{F1}[F^-] + 2K_{F2}[F^-]^2 + 3K_{F3}[F^-]^3 + 4K_{F4}[F^-]^4 + 5K_{F5}[F^-]^5 \quad (29)$$

$$\frac{\partial[Al]}{\partial F} = -\frac{(1 + K_{HF}[H^+])}{K_F} - \frac{K_{FF}[Al^{3+}]}{K_F} \quad (30)$$

in which,

$$K_{FF} = K_{F1} + 4K_{F2}[F^-]^2 + 9K_{F3}[F^-]^2 + 16K_{F4}[F^-]^3 + 25K_{F5}[F^-]^4 \quad (31)$$

$$\frac{\partial[Al\text{-}F]}{\partial F} = K_{FA}[Al^{3+}] + K_{FH}\frac{\partial[Al]}{\partial F} \quad (32)$$

in which,

$$K_{FA} = K_{F1} + 2K_{F2}[F^-] + 3K_{F3}[F^-]^2 + 4K_{F4}[F^-]^3 + 5K_{F5}[F^-]^4 \quad (33)$$

$$K_{FH} = K_{F1}[F^-] + K_{F2}[F^-]^2 + K_{F3}[F^-]^3 + K_{F4}[F^-]^4 + K_{F5}[F^-]^5 \quad (34)$$

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