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[報 文]

Models for Formation of Chloroform by Reaction of Linear Alkylbenzenesulfonate with Free Chlorine

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LAS의 염소와 반응에 의한 클로로포름 생성 모델

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ABSTRACT

It is very frequent that LAS meets the chlorine bleaches not only in the processes but also in the path from the sewages to the rivers. Therefore, it is not difficult to imagine that the harmful substances like DBPs are produced when LAs reacts with free chlorine. THMs are the major components of DBPs which are formed by reactions of organic substances with the chlorine oxidants. Among them, chloroform is the most noteworthy material. Since the major behavior observed was the formation of chloroform during reaction of LAS with free chlorine, the models were developed to grasp the tendency of chloroform formation depending on condition. According to these models, the effect of pH in the formation of chloroform is most grave.

Key words : LAS, free chlorine, chloroform, chemodegradation, models

INTRODUCTION

Nobody can deny that linear alkylbenzenesulfonate (LAS) has been the most important and representative surfactant. The average occupation of LAS among all surfactants consumed on worldwide is pushing to 30%. This figure is nearly close to 70% in Asia-Pacific region and 80% in Latin America respectively.[1,2] The average ratio of surfactants in mg/L to BOD in mg/L ranged between 2.5% and 5.0% in the major aquatic system suchlike rivers, streams, and drinking water sources.[3,4]

Moreover, sodium hypochlorite has been used imprudently in many countries for long time since it is relatively cheap and has the strong oxidizing power.[5]

When LAS meets free chlorine directly in the processes, water treatment plants as well as in the path from the sewages to the rivers, it is not difficult to imagine that the harmful substances like disinfection byproducts (DBPs) are formed. Many studies on the effects of surfactants themselves to environment and aquatic biomass have been published but the studies on the results of reactions in between surfactants and free chlorine were very scare. Therefore in this study, the models for the formation of chloroform by reaction of LAS with free chlorine were mainly devel-oped and examined.

EXPERIMENTAL PROCEDURES

1. Material

The glass bottles in the incubator were used as the reactors. LAS, sodium hypochlorite as the source of free chlorine and other major chemicals in these experiments were the extra pure reagents from Sigma Chemical Company.

2. Analytical methods

Chloroform and the intermediates formed were determined and identified by a GC/ECD and a GC/MSD. LAS remained was measured by a spectrophotometer in the visible region and at various wavelengths of ultraviolet region. Free chlorine was checked by a DPD Kit from Hach. The solvent for extraction of chloroform from samples was n-pentane. The detailed items and methods are shown in Table 1.

Table 1. Analytical items and methods

Item	Analytical Method
pH	pH meter (Corning pH/ion analyzer 350)
chloroform	GC (HP 5890 GC series II plus) detector; ECD oven temp; 50°C (1 min), 4°C/min, 300°C (3 min) injection temp; 150°C detector temp; 250°C flow rate; 2.99 mL/min column; Vocol, 0.53 μm, 30 m, capillary
SPA	UV-Visible spectrophotometer (Shimazu UV 1601) λ; 223 nm
MBAS	UV-Visible spectrophotometer (Shimazu UV 1601) λ; 650 nm
free chlorine	Manual Method and Hach DPD kit

Table 2. Condition of reactions between LAS and free chlorine

Item	Condition
Surfactants	sodium dodecylbenzenesulfonate (LAS) [1]
applied concentration	0.00115, 0.0115, 0.115, 1.15 mM [4]
Chlorination agent	NaOCl [1]
applied concentration (as free chlorine)	0.00563, 0.0563, 0.563, 5.63 mM [4]
Initial pH	4, 7, 10 [3]
Reaction temperature	20, 30°C [2]
Source of photolysis	UV, dark [2]
Reaction time	0, 2, 24, 48, 120, 240 h [6]

3. Experiment

When LAS meets free chlorine in cleaning processes, concentrations of both chemicals are relatively high. That is why concentrations of these chemicals in these experiments were diverse. The source of light employed was a low-pressure mercury UV lamp (λ=365 nm). The intensity of illumination at 25 cm dis-tance from the lamp was about 3.8 mW/cm^2 or 33 lux. The samples that required to be shielded were kept dark by wrapping with aluminum foil and black PE film respectively. Other conditions are illustrated in Table 2.

RESULTS AND DISCUSSION

1. Formation of chloroform

The most important thing found in this study is that LAS can produce chloroform evidently when it meets free chlorine.

Considering the fact that LAS is relatively abundant in the aquatic system, it must be

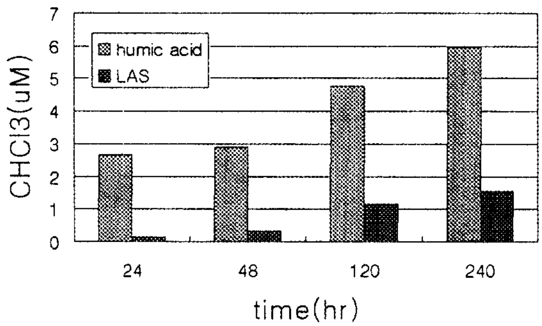

Fig. 1. Chloroform formability of LAS compared with that of humic acid
LAS; 40 mg/L
Humic acid; 40 mg/L
Free chlorine; 40 mg/L
Temp.; 30°C
pH; 7
Source of light; UV

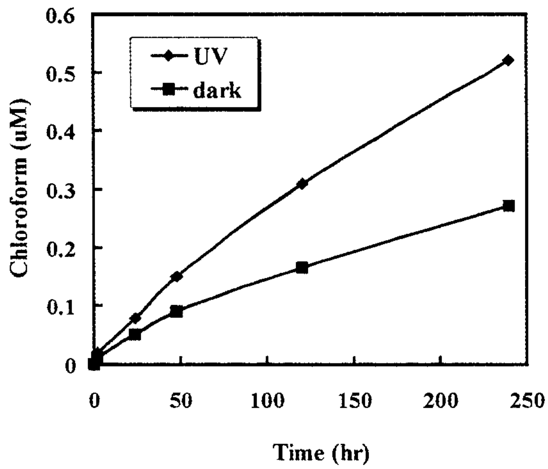

Fig. 2. Trends of chloroform formation in reaction of LAS with free chlorine depending on UV irradiation
Total run; 1,152
Sub-conditions' run
LAS; 4 (0.00115, 0.0115, 0.115, 1.15 mM)
Free chlorine; 4 (0.00563, 0.0563, 0.563, 5.63 mM),
Temp.; 2 (20, 30°C),
pH; 3 (4, 7, 10),
Reaction time; 6 (0, 2, 24, 48, 120, 240 h)

needed to pay attention when chlorine oxidants are applied not only in industrial activities but also in everyday life.

Figure 1 shows the chloroform formability of LAS compared with that of humic acid at the same condition.

As known well, the formation of THMs is effected by the substrate and its concentration, temperature, pH, concentration of chlorine dosed, contact time, and so on.[6,7,8]

According to a model that was established by Urano for humic acid, the formation of chloroform was more effected by pH and contact time than chlorine concentration.[9]

Generally the formation of chloroform is higher at higher pH. And it is commonly known that the formation of chloroform is completed within 24 hr.[7] But there are some studies that the formation of chloroform is so slow as it takes several days.[9,10,11]

In these experiments, the formation of chloroform depending on every different condition was observed.

Concentrations of chloroform formed at 1,152 different conditions were measured to find the effect of discrepancy for UV, pH, time, temperature and concentrations of LAS and free chlorine in reaction of LAS with free chlorine.

1) Effect of UV Irradiation

The effect of UV irradiation is significant not only in reaction between LAS and free chlorine but also in every reaction. That is because the activation energy can be obtained fully by UV irradiation.[12]

On the other hand, since UV irradiation makes the consumption of free chlorine itself promote, it does not always offer the affirmative effect in the formation of chloroform.[13] It is well known that hypochlorite undergoes photodecomposition in the presence of UV light.

In these experiments, the effect of UV

irradiation was very distinct even though the intensity of UV irradiation was only a few per cent of full midday sunlight. Since UV irradiation was strongly absorbed by water, this component of UV light would affect the chemistry of chlorine in reactions.[14] It was stronger than that of 10°C gap of temperature. As shown in Figure 2, the samples irradiated by UV were about 1.83 times higher on an average in the formation of chloroform than the samples in the dark.

2) Effect of Temperature

It was reported that the activation energy for the formation of THMs was around 10~20 KJ/mol by Kohei and Peter. Of course, there are also some other reports that the activation energy for same reaction is lower than them.[15,16]

As in Arrhenius's Equation, the rate of chemical reaction is seriously affected by reaction temperature. It is expected that the rate of reaction is twice when reaction temperature increases by 10°C. It was proven by an ex-periment that concentration of THM produced at 40°C was 4 times higher than at 3°C.[10] By the way, the formation of chloroform is especially more sensitive to temperature than that of other THMs. According to a study, chloroform production at 48 h was approximately 4 times higher at 25°C than at 10°C, whereas dibromochloromethane was only approximately 40% higher at same condition.[17] But as shown in Figure 3, the formation of chloroform between LAS and free chlorine at 30°C was only around 1.5 times higher on an average than that at 20°C. It means that the effect of temperature gap is not great in the formation of chloroform in reaction of LAS with free chlorine. In other words, LAS can form chloroform relatively well even at low tem-perature.

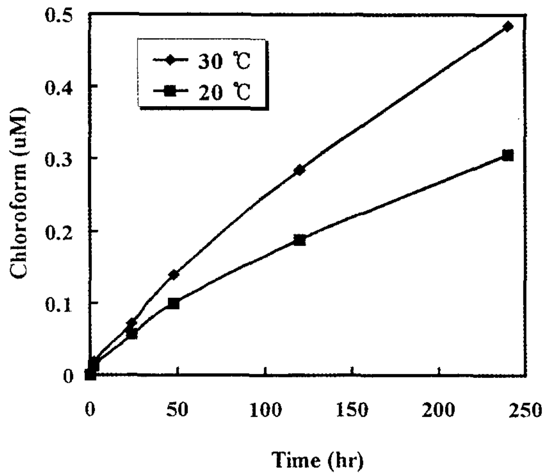

Fig. 3. Trends of chloroform formation in reaction of LAS with free chlorine depending on temperature
Total run: 1,152
Sub-conditions' run
LAS: 4 (0.00115, 0.0115, 0.115, 1.15 mM)
Free chlorine: 4 (0.00563, 0.0563, 0.563, 5.63 mM),
pH: 3 (4, 7, 10),
Source of light: 2 (dark, UV)
Reaction time: 6 (0, 2, 24, 48, 120, 240 h)

3) Effect of Concentration of LAS

It is well known that the relationship between concentration of THM produced and that of precursors (TOC) dosed is directly proportional.[7] But in these experiments, the relationship between concentration of chloroform and that of LAS was not proportional directly since LAS produced chloroform in a very limited portion.

Adin and his coworkers suggested that two competitive pathways were involved in the formation of THM from humic acid. They are a direct route and a route via organochlorine intermediates. In the former route, concentration of humic acid could contribute to the formation of THMs directly. And in the latter route, since the intermediates should be produced first and then these materials are not converted to THMs until they are accumulated, the rate for the formation of chloroform at the early stage of reaction is very low. Accordingly, when concentration of free chlorine is extremely low compared with that of humic acid, the formation of THMs is very inactive because free chlorine is consumed to produce the organochlorine intermediates in the first place.[18]

On the other hand, if concentration of substrate increases when concentration of free chlorine is constant, the consumption of free chlorine also should increase. However concentration of THMs formed could increase or decrease depending on the type of substrate.[19]

As shown in Figure 4, when concentration of LAS increased by 10 times from 0.0115 mM to 0.115 mM, concentration of chloroform formed increased by 3.5 times. Furthermore when concentration of LAS increased by 10 times again from 0.115 mM to 1.15 mM, concentration of chloroform formed only increased by 1.56 times. The formation of chloroform was poor at the beginning of reaction when concentration of LAS was exceedingly high cimpared with that of free chlorine, since concentrations of LAS and free chlorine were very relative to each other in the formation of chloroform. It was estimated that free chlorine was consumed more in the beginning of oxidation for LAS. However concentration of chloroform formed by reaction by concentrated LAS was higher naturally in progress of reaction.

4) Effect of Concentration of Free Chlorine

It is natural that chlorine dose effects the distribution between THMs and NPTOX. At

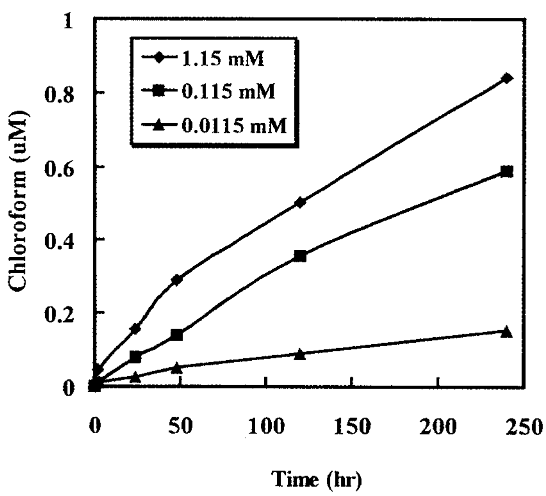

Fig. 4. Trends of chloroform formation in reaction of LAS with free chlorine depending on concentration of LAS
Total run; 1,152
Sub-conditions' run
Free chlorine; 4 (0.00563, 0.0563, 0.563, 5.63 mM),
Temp.; 2 (20, 30°C),
pH; 3 (4, 7, 10),
Source of light; 2 (dark, UV)
Reaction time; 6 (0, 2, 24, 48, 120, 240 h)

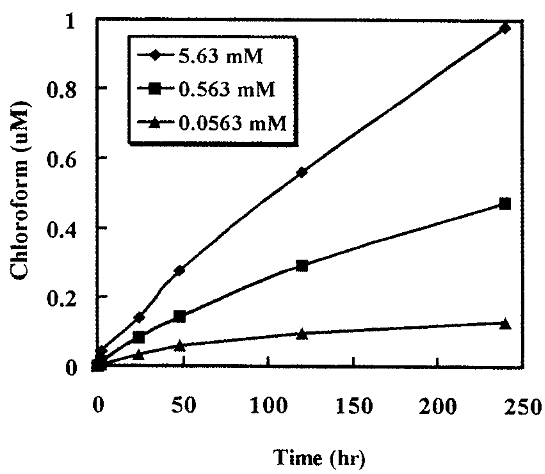

Fig. 5. Trends of chloroform formation in reaction of LAS with free chlorine depending on concentration of free chlorine
Total run; 1,152
Sub-conditions' run
LAS; 4 (0.00115, 0.0115, 0.115, 1.15 mM)
Temp.; 2 (20, 30°C),
pH; 3 (4, 7, 10),
Source of light; 2 (dark, UV)
Reaction time; 6 (0, 2, 24, 48, 120, 240 h)

low chlorine doses, the substituted products dominate. At higher chlorine doses, the oxidized or cleaved products and ultimately THMs become more important.[6] It is supported by the fact that with a low chlorine dose, high molecular weight chlorinated products are formed more, while at a high chlorine dose, low molecular weight chlorinated products and aromatic acids are formed more.[20]

It was reported that when THMFP was kept up steadily, the formation of THMs was not affected by additional chlorine doses after adequacy of chlorine demand. Combined residual chlorine was also not able to affect the formation of THMs.[10,21]

However in reaction between LAS and free chlorine, the influence of free chlorine was more immense than that of LAS. It means that LAS is very stable and resistant to free chlorine compared with other substrates.

5) Effect of Reaction Time

It is known that a great part of THM formations is completed within 24 h. For instance, the formation of THM was completed within 24 h by chlorination of dissolved organic materials in sewages and effluents.[7]

But the formation of chloroform increased gradually and steadily up to 240 h in these experiments. Naturally there were some cases in which the formation of chloroform within 24 or 48 h reached 65~75% of that in 240 h, but in the most cases, the formation of chloroform showed a consistent increase in progress of reaction. This coincides to the result of a study that usually. takes many days to reach the maximum formation of THMs at a given condition.[10]

6) Effect of pH

Since it is considered that haloform reaction is a main route of the formation of chloroform, it is affected greatly by pH. For example, the formation of chloroform at pH 9 was 8 times higher than that at pH 5 when a source of drinking water was chlorinated.[22] The phenomenon like above was proven by Stevens, Rook *et al.*[23] Because haloform reaction is promoted by basic catalysts, OH^- is required indispensably in hydrolysis which is a very important step in haloform reaction. It is also noted that the final products of haloform reaction are THMs and carboxylic acids. In addition, the macromolecules are disintegrated to the small molecules by mutual repulsion at a high pH range. Accordingly new and different reactions are introduced into this process by natural.[10]

As it was expected the formation of chloroform is greatly affected by pH in these experiments. Total volume of chloroform formed at higher pH was far larger than that at

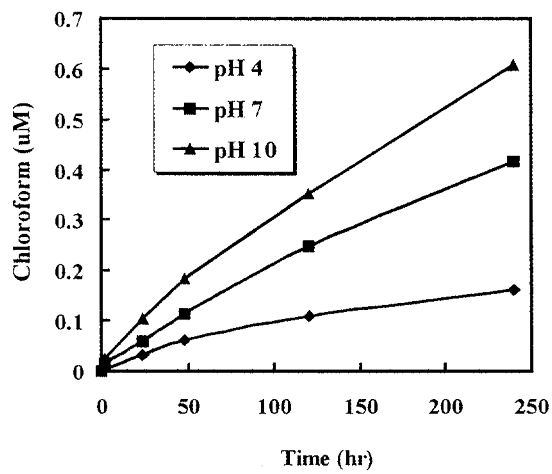

Fig. 6. Trends of chloroform formation in reaction of LAS with free chlorine depending on pH
Total run: 1,152
Sub-conditions' run
LAS: 4 (0.00115, 0.0115, 0.115, 1.15 mM)
Free chlorine: 4 (0.00563, 0.0563, 0.563, 5.63 mM),
Temp.: 2 (20, 30°C),
Source of light: 2 (dark, UV),
Reaction time: 6 (0, 2, 24, 48, 120, 240 h)

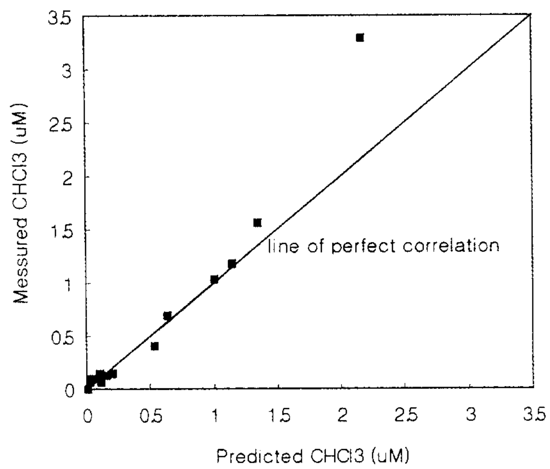

Fig. 7. Predicted chloroform vs measured chloroform by internal data simulation via this study in reactions of LAS with free chlorine (under UV irradiation)

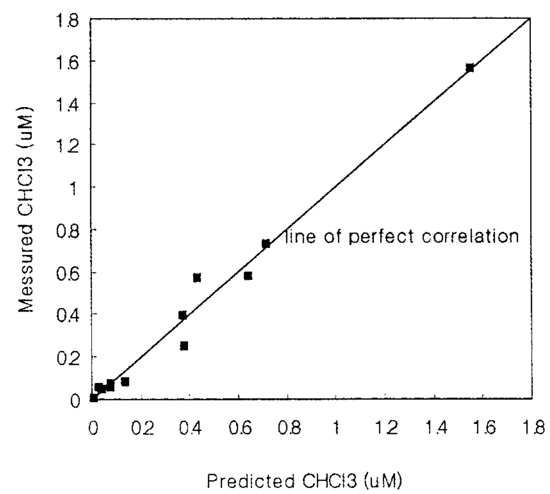

Fig. 8. Predicted chloroform vs measured chloroform by internal data simulation via this study in reactions of LAS with freechlorine (in the dark)

lower pH. But in some cases, of course, it was few and far between, chloroform was formed more at pH 7.0 than at a higher pH range.

2. Models for Formation of Chloroform

It has been commonly known that the models for the formation of THMs in reactions of the organic substance as TOC, DOC or humic acid with chlorine oxidants were developed.

In this study, the models for the formation of chloroform in reaction of LAS with free chlorine were induced to clearly understand the effect of every condition and their relationships at a glance. The models under UV irradiation and in the dark were created respectively by the Regression Analysis of SAS using total 1,152 data that were obtained from various conditions.

The model under UV irradiation is as follow;

$$\ln[X]_{UV} = -0.2933 + 0.356\ \ln[L] + 0.363\ \ln[Ch] + 0.708\ \ln[t] + 0.713\ \ln[T] + 0.763\ \ln[pH-2.6]$$

$R^2 = 0.8991$ $SSE = 66.6782$

$F = 452.732$ $MSE = 0.2623$

And the model in the dark is as follow;

$$\ln[X]_{D} = 0.1070 + 0.309\ \ln[L] + 0.363\ \ln[Ch] + 0.623\ \ln[t] + 0.623\ \ln[T] + 0.670\ \ln[pH-2.6]$$

$R^2 = 0.9073$ $SSE = 45.3168$

$F = 487.246$ $MSE = 0.1820$

The full log models in their formats can be amended by antilogs. The resultant multiple parameter power functions that can calculate concentration of chloroform directly are

$$[X]_{UV} = 0.74578\ [L]^{0.356} \cdot [Ch]^{0.363} \cdot [t]^{0.708} \cdot [T]^{0.713} \cdot [pH-2.6]^{0.763}$$

$$[X]_{D} = 1.11289\ [L]^{0.309} \cdot [Ch]^{0.363} \cdot [t]^{0.623} \cdot [T]^{0.623} \cdot [pH-2.6]^{0.670}$$

in which [X] is concentration of chloroform formed in μM, [L] is concentration of LAS dosed in mM, [Ch] is concentration of free

Table 3. Comparison of data used in several models for formation of THM(s)

$[X]=k[S]^a \cdot [Ch]^b \cdot [t(oC)]^c \cdot [T(h)]^d \cdot [pH-2.6]^e \cdot [Br-+1]^f$

Designer	k	a	b	c	d	e	f	substrate & product
Amy, G. *et al.*	0.00309	0.440	0.409	0.265	1.06	0.715	0.036	UV_{254}(cm^{-1}) · TOC(mg/L), F · Ch(mg/L) vs TTHM(μM)
Greiner, A *et al.*	0.27800	0.616	0.391	0.265	1.15	0.800	−2.230	UV_{254}(cm^{-1}) TOC(mg/L), F · Ch(mg/L) vs $CHCl_3$(μM)
Harrington, G. *et al.*	0.00309	0.440	0.409	0.265	1.06	0.715	0.036	UV_{254}(cm^{-1}) DOC(mg/L), F · Ch(mg/L) vs TTHM(μM)
Urano	0.00083	2.800	0.250	0.360	–	–	–	humic sub.(mg/L), F · Ch(mg/L) vs TTHM(mg/L)
In this study								
UV	0.74578	0.356	0.363	0.708	0.71	0.763	–	LAS(mM), F · Ch(mg/L)
dark	1.11289	0.309	0.363	0.623	0.62	0.670		vs $CHCl_3$(μM)

chlorine dosed in mM, [t] is reaction temperature in °C, [T] is reaction time in h. And pH=(pH-2.6), with 2.6 representing a statistically determined minimum pH at which the formation of THM commences.[24]

The comparisons of concentrations between predicted chloroform and measured chloroform via the models developed in this study are displayed in Figure 7 and Figure 8.

The comparison of the constants and exponents in these models with them in the existing models which were established between the organic substances as TOC, DOC, UV_{254} and chlorine is shown in Table 3.[6,21,24,25,26]

CONCLUSIONS

When LAS meets free chlorine in everyday life and industrial activities, it can be fully imagined that some harmful substances suchlike DBPs are formed.

In spite of the chemical structure of LAS that does not retain the adequate property as the precursors of THMs, chloroform was formed remarkably by reaction with free chlorine.

In order to grasp and predict the tendency of chloroform formation in reaction of LAS with free chlorine depending on condition at a glance, the models were developed.

The models that were obtained from 1,152 different sub-conditions for the formation of chloroform under UVirradiation and in the dark are asfollows;

$$[X]_{UV}=0.74578\ [L]^{0.356} \cdot [Ch]^{0.363} \cdot [t]^{0.708} \cdot [T]^{0.713} \cdot [pH-2.6]^{0.763}$$

$$[X]_{D}=1.11289\ [L]^{0.309} \cdot [Ch]^{0.363} \cdot [t]^{0.623} \cdot [T]^{0.623} \cdot [pH-2.6]^{0.670}$$

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