Various Alkyl Amines and Ammonium Compounds as Accelerators for Grain Growth of Silver Chloride Suspensions in Aqueous Polyvinyl Alcohol Solution

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The physical ripening of silver chloride polyvinyl alcohol emulsion (i. e. the grain growth of silver chloride suspension in an aqueous polyvinyl alcohol solution) was found able to be accelerated by the addition of some sorts of substance[1,2,3].

Substances already reported as active comprise many sorts of substance, some of them having active sulfur atom, are so-called "sulfur-sensitizers" in photographic chemistry, e. g. inorganic thiosulfates, thiocyanates or organic derivatives of thiourea, rhodanine, or the like[1]. Some without active sulfur are those that contain a nitrogen atom together with some other nitrogen, oxygen or non-active sulfur atom in their molecule, e. g. *N*-alkyl homologues of guanidine, pyrrolidone, pyridone, quinolone or 2-imino-thiazolines[2].

In later experiments much simpler compounds which contain only one heterogeneous atom, sulfur or nitrogen, such as alkyl thiols or alkyl ammonium compounds were active. In the present paper, however, only alkyl amines such as primary, secondary, tertiary amines and some *N*-alkyl quaternary ammonium compounds (both non-cyclic and cyclic) are dealt with. Surface active properties of higher alkyl homologues of these compounds are well known, and a remarkable resemblance of the mechanism of grain growth and that of micelle formation of many of these surface active substances was also reported by one of the present authors[3].

1) Y. Oh-yama: "Science and Application of Photography" (Proceedings of the R. P. S. Centenary Conference, London 1953) 37 (1955).
2) Y. Oh-yama and K. Futaki: This Bulletin, **28**, 243 (1955).
3) Y. Oh-yama, Lectured at "Internat. Konferenz f. Wiss. Phot." Köln, 1956. (*Sci. et Ind. Phot.* [2], **27**, 390 (1956)).

Experimental

To 42 ml. of aqueous solution of an active substance of varying concentrations (10 ml. of this solution may be replaced by ethanol when necessary for sparingly soluble substance), 10 ml. of 6% solutions of polyvinyl alcohol and 4 ml. of 0.6 M sodium chloride solution are added. The mixture is heated to 70°C, and 4 ml. of 0.2 M silver nitrate solution (70°C) is added within 15 seconds.

After drawing out 2 ml. of this suspension of silver chloride at 2, 4, 8 and 16 min. after the addition of silver ions, it is diluted with 20 ml. of cold water and the turbidity is measured.

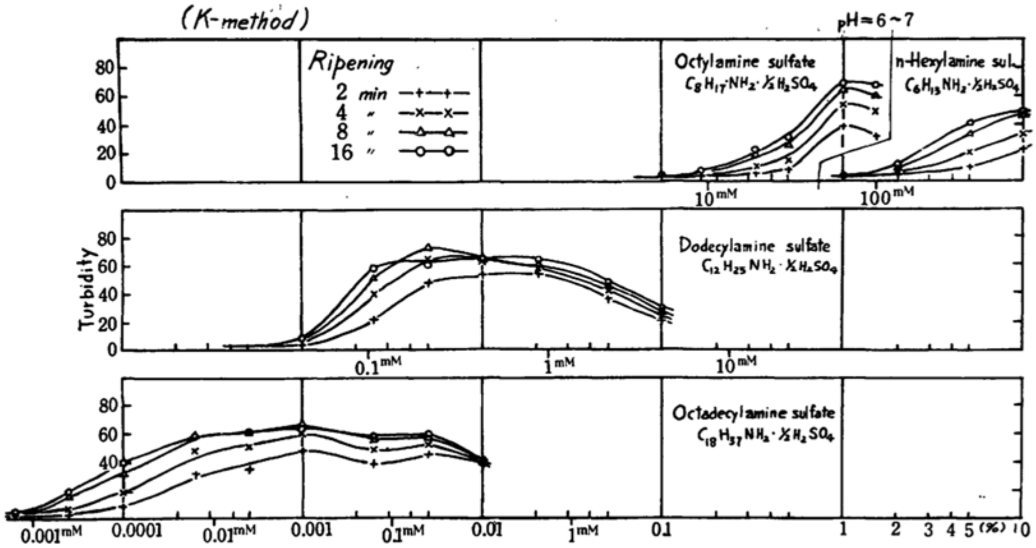
From the fact[4,5] that the turbidity of the suspension is in linear proportion to the mean diameter of grains in the region of the sizes in question ($0.05 \sim 0.25\,\mu$ in diameter), the grain growth can be traced by the nephelometric method as was previously reported[1,2]. The turbidity measurement usually adopted[1,2] (designated as K-method) was, however, altered in some cases by the method closely resembling Ammann's[6] (designated as A-method). A simpler method which was used in the previous report and designated as Transmission method (or T-method)[2], was used only in a few cases. The suspension remains almost neutral ($6 \sim 7$) without using buffer-solution.

4) H. Ammann-Brass: *Sci. et Ind. Phot.* [2], **23**, 249 (1952).
5) F. Evva: *Z. wiss. Phot.*, **47**, 39 (1952).
6) H. Ammann-Brass: *Kolloid Z.*, **110**, 161 (1948).

Ripening characteristics (graphs plotting turbidities against logarithm of the concentration of added substances) were obtained as usual[1,2]. The critical concentrations for grain growth (C. C. G.) of various compounds were determined as the minimum addition concentration which caused a definite turbidity-increase (10 units above blank in the K-method or total turbidity of 35 units in the A-method after 16 minutes' ripening) on these characteristics. The reciprocal of this concentration (in millimol) defines the activity and is used for the comparison of activities of various compounds.

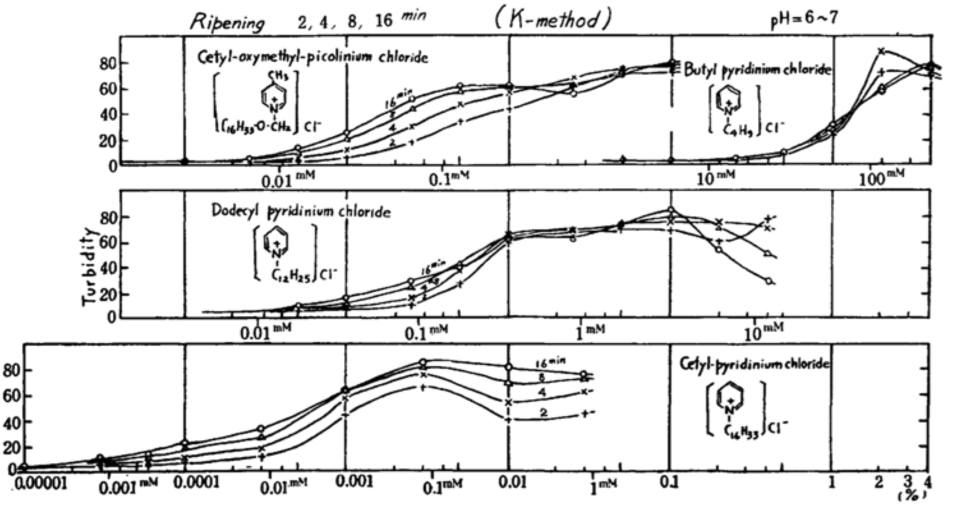
Results and Discussion

(a) Primary Alkyl and Aralkyl Amines.—Primary amines tested were benzyl, β-phenylethyl, n-hexyl, n-octyl, n-decyl, dodecyl and octadecyl amine. Some of the ripening characteristics obtained are shown in Fig. 1. The critical concentration for grain growth and activity of these compounds are computed from these curves and listed in Table I. The equivalent chain length listed in the 4th column was assumed to be counted with



Concentrationof Addition

Fig. 1. Some of the ripening characteristics of primary amines.



Concentration of Addition

Fig. 2. Some of the ripening characteristics of alkyl pyridinium and pycolinium compounds.

TABLE I

CRITICAL CONCENTRATIONS FOR GRAIN GROWTH AND ACTIVITIES OF PRIMARY AMINES AT pH 6～7

Substances tested	Mol. W.	Equiv. chain length	C. C. G. (mM)	Activity	Method of measuring turbidity	Salt used
Benzyl amine	107	4	700(?)	0.0014(?)	K	sulfate
Phenyl ethyl amine	121	5	132	0.0076	K	〃
n-Hexyl amine	101	6	135	0.0074	K	〃
n-Octyl amine	129	8	13.5	0.074	K	〃
n-Decyl amine	158	10	{ 2.8 2.8	{ 0.357 0.357	{ A K	〃
Dodecyl amine	185	12	0.0470	21.3	K	〃
Octadecyl amine	269	18	0.00130	770	K	〃

TABLE II

CRITICAL CONCENTRATIONS FOR GRAIN GROWTH AND ACTIVITIES OF *N*-ALKYL PYRIDINIUM AND PYCOLINIUM COMPOUNDS AT pH 6～7

Substances tested	Equiv. W.	Equiv. chain length	C. C. G. (mM)	Activity	Method of measuring turbidity	Salt used
n-Butyl pyridinium ion	136	6	36.0	0.028	K	chloride
n-Octyl 〃 〃	192	10	{ 3.95 4.00	{ 0.253 0.250	{ A K	〃
n-Decyl 〃 〃	220	12	{ 1.40 1.63	{ 0.714 0.613	{ A K	〃
Dodecyl 〃 〃	248	14	0.0250	40.0	K	〃
Hexadecyl 〃 〃	304	18	0.00146	685	K	〃
Octadecyl 〃 〃	332	20	0.00106	942	K	bromide
Hexadecyl oxymethyl-pycolinium ion	348	21(?)	0.0125	80	K	chloride

TABLE III

CRITICAL CONCENTRATIONS FOR GRAIN GROWTH AND ACTIVITIES OF *N*-ALKYL QUINOLINIUM COMPOUNDS AT pH 6～7

Substances tested	Equiv. W.	Equiv. chain length	C. C. G. (mM)	Activity	Method of measuring turbidity	Salt used
n-Butyl quinolinium ion	186	10	{ 5.00 4.50	{ 0.200 0.223	{ A K	chloride
Benzyl quinolinium ion	220	10	{ 3.30 3.50	{ 0.303 0.285	{ A K	〃
n-Octyl quinolinium ion	242	14	{ 0.222 0.230	{ 4.56 4.35	{ A K	〃
Decyl quinolinium ion	270	16	{ 0.072 0.074	{ 13.9 13.5	{ A K	〃
Dodecyl quinolinium ion	298	18	{ 0.0064 0.0063	{ 147 159	{ A K	〃

their real number of carbon atoms in the simple alkyl amines and phenyl group in benzyl or phenyl-ethyl radicals was counted as 3, and in some other cases it will be discussed later in detail.

(b) *N*-Alkyl Pyridinium, Pycolinium and Quinolinium Compounds.—Some of the ripening characteristics are shown in Fig 2, and all of the substances tested are listed in Tables II and III.

(c) Relations between Activity and Molecular Weight or Chain Length.—The activity increases as a whole with increase in the molecular weight as shown in Fig. 3, yet the relation is not so simple as was in the case with guanidine, pyridone, pyrrolidone or quinolones which was reported before.[2]

(d) The Concept of Equivalent Chain Length.—The fact that the activities are related intrinsically to the chain length of the linear alkyl radical attaching to the nitrogen atom of these amines rather than to the molecular weight itself, was demonstrated in Fig. 4. Although there is a "break" or a sudden rise of activity

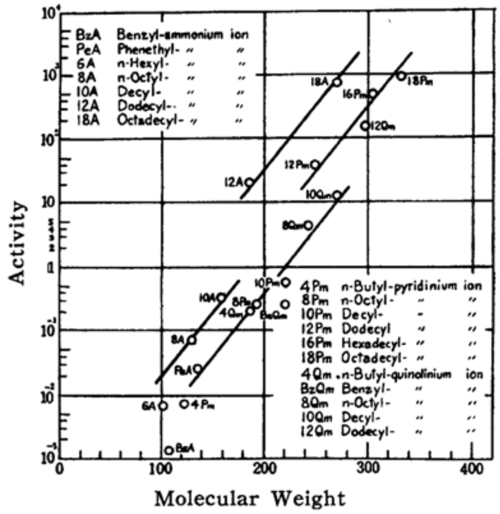


Fig. 3. Relation between activities and molecular weights of primary alkyl amines and N-alkyl homologues of pyridinium and quinolinium compounds.

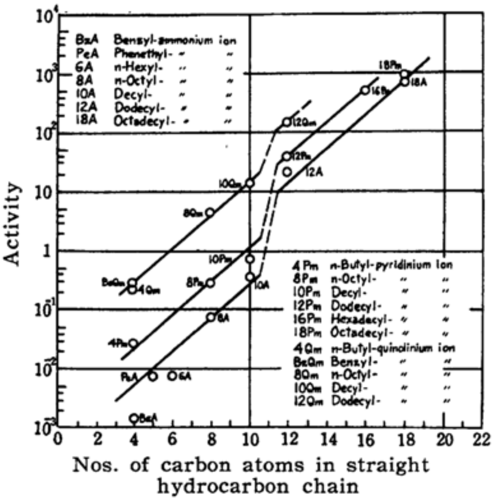


Fig. 4. Relation between activities and alkyl chain-length of primary alkyl amines and N-alkyl cyclo-ammonium compounds.

between 10 and 12 carbon atoms, the parallel relation among these three lines is quite clear. It is also clear that the number of carbon atoms of these cyclic hydrocarbon chains of pyridinium or quinolinium nucleus would participate in the activities with the linear alkyl carbon chains.

If we assume an adequate chain length for these cyclic nuclei for example, 1 for pyrrole, 2 for pyridine, 6 for quinoline respectively, and define the equivalent chain length (n_E) of a certain active compound as the sum of the number of carbon atoms of linear alkyl chain and that of the chain length of the nucleus assumed as above, the relation between activity (or the critical concentration of grain growth) and the chain length will be expressed in the following equation as shown in Fig. 5,

$$-\log_{10} C_g = \log_{10} A = \frac{n_E - \beta}{3.50}$$

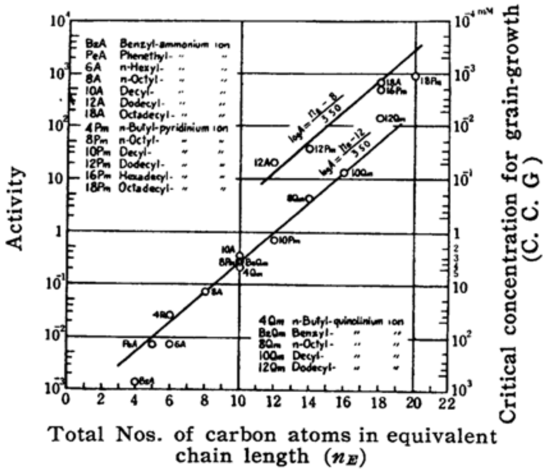


Fig. 5. Relation between activities and equivalent chain lengths of various primary amines and cyclo ammonium compounds.

where C_g is the critical concentration for grain growth (in mM), A the activity and β a constant. Three lines in Fig. 4 now coincide with one another and the sudden increase in activitys between 10 and 12 carbon atoms of linear alkyl chains is now turned to decrease in β from 12 to 8 abruptly.

Assumed chain lengths of these cyclic unclei are only empirical, yet the equivalent chain length of these compounds seems to be able to be calculated according to the following equation,

$$n_E = n_A + (n_C - 3)$$

where n_A is the number of carbon atoms in the alkyl chain attached directly to the central nitrogen atom, and n_C that of carbon atoms in the cyclic nucleus containing the nitrogen atom.

(e) Coincidences of the Relation with that of Guanidine. Pyridone-quinolone, and Imino-pyridine Series.—The concept of equivalent chain length is also held well as shown in Fig. 6 for guanidine and pyridone, quinolone series, whose relations between activity and molecular weight were already reported[2]. In Fig. 6, the case of imino-pyridines is also included.

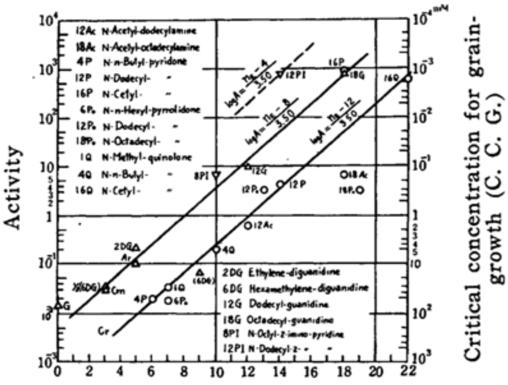


Fig. 6. Relation between activities and equivalent chain lengths of various compounds of guanidine-, pyridone- and quinolone series.

The coincidence of Fig. 5 and Fig. 6 is most striking, considering that they were derived from results of independent experiments. The reason for this coincidence and the intimate relationship between the grain growth of silver halide in this case and the micelle formation of surface active substances was already discussed in another report in connection with the mechanism of these two phenomena[3].

(f) Secondary and Tertiary Amines and Quaternary Ammonium Salts.— These compounds tested are listed in Table IV, and some of the ripening characteristics are shown in Fig. 7. They are also as powerful as primary amines, yet somewhat less powerful when compared on the basis of the molecular weight. It will be easily deduced from the above mentioned results regarding cyclic ammonium compounds, that the concept of equivalent chain length holds well. Because of lack of examples and exactness, the calculating method of the equivalent chain length for them, however, could not be found out from the experimental results.

Fortunately the critical micelle concentration (C. M. C.) of various surface active substances can be determined much more exactly, so the calculation of the equivalent chain length could be easily deduced from these data, and at first the equivalent chain length (n_E) of these compounds is assumed to be expressed by the following equation,

$$n_E = n_1 + \alpha(n_2 + n_3 + n_4)$$

where n_1, n_2, n_3 and n_4 are the numbers of carbon atom in four alkyl chains attached to the central nitrogen atom of these ammonium ions and there exist $n_1 \geqq n_2 \geqq n_3 \geqq n_4$ (of course for tertiary amines $n_4 = 0$, and for secondary amines $n_3 = n_4 = 0$).

The constant α calculated from the data plotted from the curves determined by

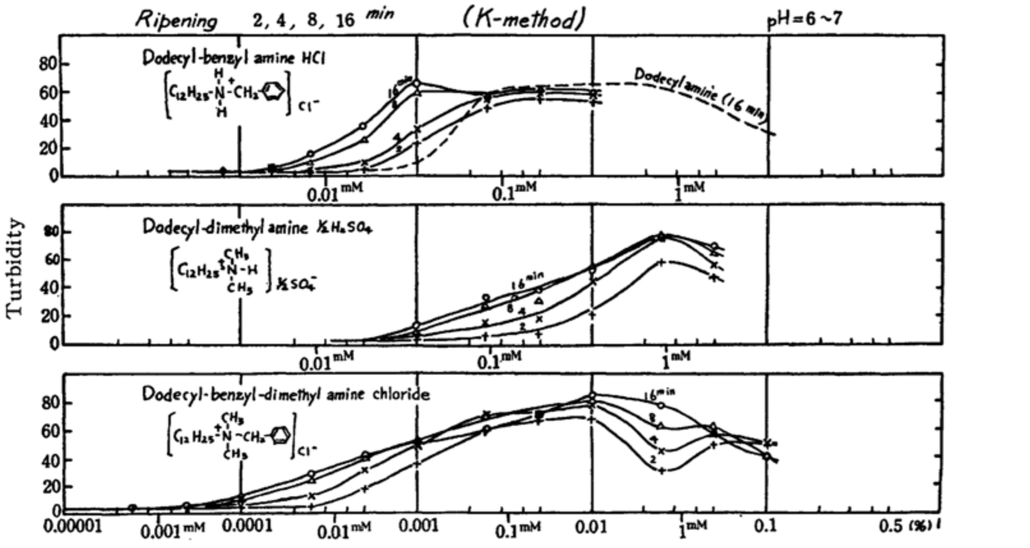


Fig. 7. Some of the ripening characteristics of secondary, tertiary amines and quaternary ammonium salts.

TABLE IV

CRITICAL CONCENTRATIONS FOR GRAIN GROWTH AND ACTIVITIES OF VARIOUS SECONDARY, TERTIARY AND QUATERNARY AMMONIUM SALTS AT pH 6~7

Substances tested	Equiv. W.	Equiv. chain length	C. C. G. (mM)	Activity	Method of measuring turbidity	Salt used
Benzyl diethyl-ammonium ion	164	6.20	{56.0 44.0	{0.0175 0.0227	{A K	chloride
Dodecyl dimethyl-ammonium ion	214	13.10	{0.044 0.038	{22.7 26.3	{T K	sulphate
Dodecyl benzyl-ammonium ion	275	15.85	0.0073	137	K	chloride
Dodecyl benzyl dimethyl-ammonium ion	304	16.95	0.0032	313	K	〃
Hexadecyl trimethyl ammonium ion	284	17.65	0.0035	286	K	bromide
Octadecyl dimethyl-ammonium ion	298	19.10	{0.0130 0.0103	{77.0 97.0	{T K	sulfate
Octadecyl trimethyl-ammonium ion	312	19.65	0.0040	250	K	chloride
Octadecyl benzyl-ammonium ion	359	21.85	0.00102	980	K	〃

TABLE V

ESTIMATION OF THE EQUIVALENT CHAIN LENGTH OF SOME ALIPHATIC QUATERNARY AMMONIUM SALTS

Substances(1)	C.M.C.(2) (mM)	−log (C.M.C.)	n_E(3)	n_1	$n_2+n_3+n_4$	n_E-n_1	$n_E-n_1/n_2+n_3+n_4$	$n'_E=n_1+0.55(n_2+n_3+n_4)$ Calc.	Deviation
8- 8-1-1-Am	28.3	−1.450	13.42	8	10	5.42	0.542	13.50	−0.08
10-10-1-1-Am	2.16	−0.334	17.33	10	12	7.33	0.611	16.60	+0.73
12- 1-1-1-Am	23.2	−1.365	13.73	12	3	1.73	0.577	13.65	+0.08
12- 8-1-1-Am	1.69	−0.226	17.71	12	10	5.71	0.571	17.50	+0.21
12-12-1-1-Am	0.760	+0.119	18.92	12	14	6.92	0.495	19.70	−0.78
16- 1-1-1-Am	1.77	−0.247	17.63	16	3	1.63	0.543	17.65	−0.02
						mean	0.5565	mean	0.316

(1) Names of substances are abbreviated by the numbers of carbon atoms in alkyl chains, e. g. Di-octyl-dimethyl ammonium ion is shown by 8-8-1-1-Am.

(2) Deta from Ralston et al.[7]

(3) n_E are calculated from the equation; $-\log(\text{C. M. C.}) = \frac{n_E - 18.50}{3.50}$

Ralston et al.[7] is 0.55 as shown in Table V. This table would also prove the validity of the above mentioned assumption.

In Table IV, together with the experimental data there also are shown the equivalent chain lengths of compounds tested, calculated by the above mentioned method. The relation between the activity and the equivalent chain-length is plotted in Fig. 8. Two straight lines drawn in the figure are identical with those of Fig. 5.

It is interesting to know that the activity of the compound, whose solubility in water is very great, e. g. dodecylbenzyldimethyl ammonium salt (10% solution is quite clear), is much higher than those scarcely soluble compounds such as decyl- or dodecylamine, and is almost comparable with that of octadecyl amine which is not completely soluble in less than 0.001%.

7) A. W. Ralston, D. N. Eggenberger and P. L. Du. Brow. *J. Am. Chem. Soc.*, **70**, 977 (1948).

Summary

Various alkyl amines and ammonium compounds (non-cyclic and cyclic) were tested as accelerators for the grain growth of silver chloride suspension in aqueous polyvinyl alcohol solution.

The relation previously found between the molecular weight and the grain growth acceleration activity (A) of various organic *N*-derivatives did not exactly hold for these series of compounds.

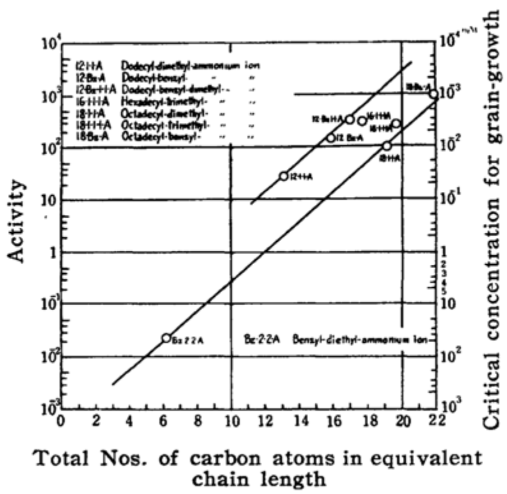


Fig. 8. Relation between activities and equivalent chain lengths of various secondary, tertiary amines and quaternary ammonium salts.

Instead, when the concept of the equivalent chain length is introduced, the data were able to be represented by:

$\log A = -\log C_g = (n_E - \beta)/3.50$, where C_g is the critical concentration for grain growth (in millimol), n_E the equivalent chain length and β 8 or 12.

This equation quite resembles the relation between chain length and critical micelle concentration of many surface active compounds. The fact leads to the author's assumption that the mechanism of grain growth of silver chloride would be intrinsically identical with that of micelle formation and this was discussed in another paper.

The equivalent chain lengths of some of these active substances were able to be derived empirically from the number of carbon atoms in the molecule.

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