Critical Chain Length in the Amphiphile-induced Coagulation of Silver Iodide

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The coagulation of AgI sols in water is accelerated by quaternary ammonium ions $RNMe_3^+$ if R is comprised of five or more carbon atoms.

Properties of AgI sols in water depend upon the ionic makeup of the solution. Positive AgI sols form when the $[Ag^+]$ exceeds the $[I^-]$. Sols assume a negative charge in an excess of I^-. Such negative sols adsorb cations whereupon they coagulate rapidly owing to charge neutralization. Large cations (Rb^+) bind more effectively than small ones (Na^+).[1—4]

The experiments in the present communication were prompted by our observing a remarkable coagulation effect. Addition of $AgNO_3$ to either NaI, n-$C_4H_9NMe_3I$, or n-$C_5H_{11}NMe_3I$ gives, under certain conditions, rapid coagulation only with n-$C_5H_{11}NMe_3I$. The photograph in Figure 1 illustrates the difference. A qualitative understanding of its origin is now in hand.

AgI sols were generated *in situ*† by adding aqueous $AgNO_3$ to aqueous solutions of $RNMe_3I$ where R = $[CH_2]_nMe$, n = 1—5. Concentrations of $AgNO_3$ were chosen so as to give (a) excess of I^- over Ag^+; (b) equimolar amounts of I^- and Ag^+; and (c) excess Ag^+ over I^-. Quaternary salts were carefully purified, and all solutions were used immediately after

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† We purposely formed the AgI sols *in situ* (as opposed to forming them from NaI and $AgNO_3$ prior to addition of $RNMe_3I$) in order to keep our systems sodium-free.[3] As a consequence of this procedure, however, it is not possible to determine what stage of particle growth (early or late) is affected by the $RNMe_3^+$.

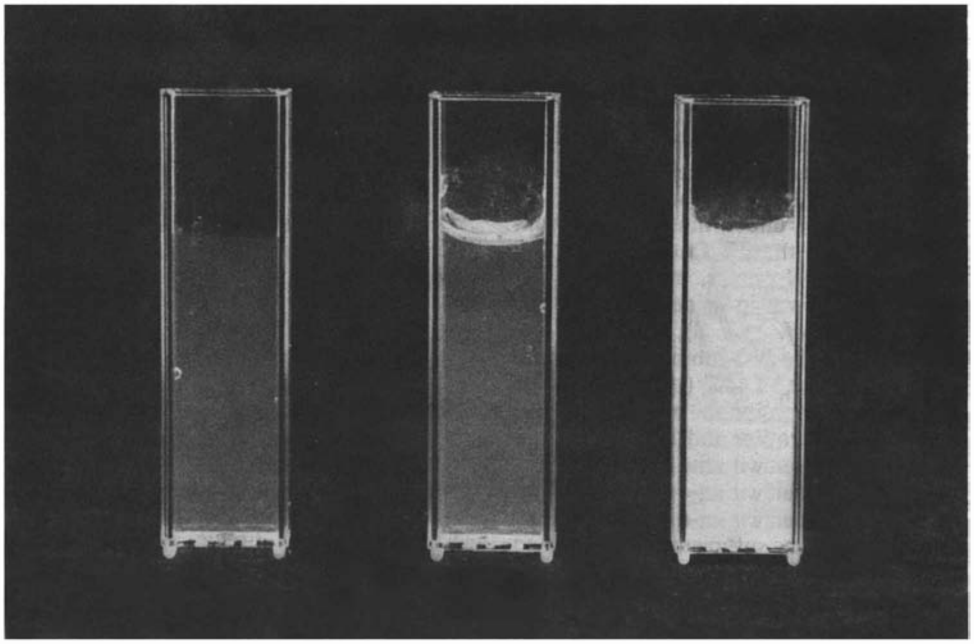

Figure 1. Cuvettes containing 1.35 mM $AgNO_3$ and (left to right) 1.49 mM NaI, $C_4H_9NMe_3I$, or $C_5H_{11}NMe_3I$. Photographs were taken 10 min after mixing the $AgNO_3$ with the iodides.

Table 1. Coagulation rates of AgI in the presence of quaternary ammonium salts.

Salt	$[RNMe_3I]$/mM	$[AgNO_3]$/mM	Turbidity[a]
$C_2H_5NMe_3I$	1.50	1.16	0.03
	1.49	1.47	0.23
	1.49	1.77	0.03
n-$C_3H_7NMe_3I$	1.49	1.13	0.03
	1.49	1.50	1.70
	1.48	1.87	0.04
n-$C_4H_9NMe_3I$	1.49	1.35	0.06
	1.49	1.50	1.80
	1.49	1.87	0.06
n-$C_5H_{11}NMe_3I$	1.49	1.13	0.8
	1.49	1.43	2.6
	1.49	1.87	0.06
n-$C_6H_{13}NMe_3I$	1.49	1.13	2.35
	1.49	1.43	2.60
	1.49	1.87	0.02
NaI	1.49	1.16	0.02
	1.49	1.47	0.08
	1.49	1.77	0.04

[a] Scattering at 500 nm of aqueous solutions (25.0 ± 0.1 °C) measured 10.0 min after mixing.

preparation. Coagulation rates, listed in Table 1, are defined as the turbidity (500 nm) 10 min after mixing.‡

Three salient facts emerge from Table 1. (i) When $RNMe_3I$ is in excess over $AgNO_3$, coagulation is slow for R = n-butyl, n-propyl, and ethyl, but fast for R = n-pentyl and n-hexyl. (ii) Coagulation is accelerated for any given $RNMe_3I$ when it is equimolar with $AgNO_3$. (iii) Coagulation is slow for all systems if $AgNO_3$ exists in excess over the salts.

The results can be explained by a combination of electrostatic and hydrophobic effects. Positive sols do not bind the quaternary ammonium cations and thus are little affected by their presence. This is not true for negative sols. Negative sols bind the n-pentyl and n-hexyl cations and then, being charge-neutralized, coagulate. Additional salts not mentioned in Table 1 (where R = cyclohexyl and benzyl) will do the same thing. Since high concentrations of n-hexanol were found not to coagulate AgI, both a cationic head-group and a hydrophobic moiety must be present on the additive. However, the latter must also possess a minimum size as shown by the n-butyl salt, and its shorter homologues, which fail to perturb the coagulation rates under the experimental conditions. The 'critical' chain-length can be understood if it is recognized that the binding equilibria depend on *both* the affinity to AgI and the aversion to water. Although the entire series of quaternary ammonium cations should be similar in the former regard, only the cations with the longer chains are sufficiently hydrophobic to partition effectively onto the negative AgI sols. It is surprising that (a) the demarcation between binding and non-binding structures is so sharp and (b) the critical chain-length is so short.

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‡ Turbidity data in Table 1 are meant for qualitative comparisons only; fortunately, differences are sufficiently large that meaningful conclusions can be drawn.