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EFFECT OF NONIONIC SURFACTANTS ON THE STABILITY OF
HYDROPHOBIC COLLOIDS(U) TUFTS UNIV MEDFORD MA DEPT OF
CHEMICAL ENGINEERING G D BOTSARIS ET AL. 30 JUL 87
TR-2 N00014-81-K-0836

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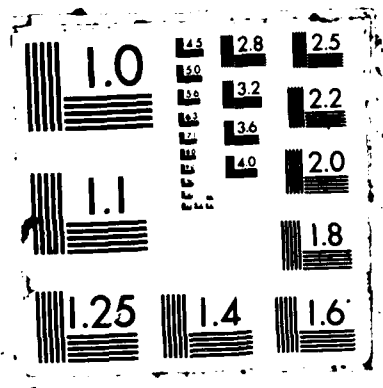
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Technical Report No. 2

Effect of Nonionic Surfactants on
the Stability of Hydrophobic Colloids

by

Gregory D. Botsaris, Yuli M. Glazman
and Gregory P. Beronja

Published in

"Surfactants in Solution" Vol. 6, 1705-1713 (1987)

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Department of Chemical Engineering
Medford, MA

July 30, 1987

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1. REPORT SECURITY CLASSIFICATION unclassified		1b. RESTRICTIVE MARKINGS	
2. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT This document has been approved for public release and sale, its distribution is unlimited	
5. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Tufts - LMI - 1987 - 4		5. MONITORING ORGANIZATION REPORT NUMBER(S) Technical Report No. 2	
6a. NAME OF PERFORMING ORGANIZATION TUFTS UNIVERSITY	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
8. ADDRESS (City, State, and ZIP Code) Medford, MA 02155		7b. ADDRESS (City, State, and ZIP Code) Arlington, Virginia 22217-5000	
9a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	9b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-81-K-0836	
10. ADDRESS (City, State, and ZIP Code) Arlington, Virginia 22217-5000		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Effect of Nonionic Surfactants on the Stability of Hydrophobic Colloids			
12. PERSONAL AUTHOR(S) Botsaris, Gregory D., Glazman, Yuli, M. and Beronja, Gregory P.			
13a. TYPE OF REPORT Technical Report	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) December 10, 1986	15. PAGE COUNT 9
16. SUPPLEMENTARY NOTATION Published in "Surfactants in Solution," Volume 6 Mittal, ed. Plenum Publishing 1987 pp 1705-1713			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Colloidal Stability, Coagulation, Solvation Stabilization, Nonionic Surfactants	
FIELD	GROUP SUB-GROUP		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) This paper reports recent findings in our continuing investigation on the preparation of stable dispersions in the presence of relatively high concentrations of electrolytes. Typical practical examples of such dispersions are those prepared with ocean water as the liquid phase. Previous investigations have shown that the nature of aggregative stability of hydrophobic sols changes drastically in the presence of nonionic surface active agents (NSAA); the ionically stabilized sols are converted into hydrophilic ones. This transition manifested by an extremely sharp rise in the resistance of the sol towards the coagulating effect of electrolytes, takes place at relatively low NSAA concentrations. This work studied the effect of a certain type of NSAA, i.e., polyoxyethylated octyl- and nonylphenols with different degrees of oxyethylation, on the stability of silver iodide hydrosols. The above mentioned steep rise in stability was observed also with this type of			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

19. Abstract (continued)

cont'd → NSAA. However, in certain cases at surfactant concentrations below those causing the steep rise, a peculiarity was discovered: a peak appeared in the curve representing the dependence of the electrolyte coagulation value on the surfactant concentration. It is important to emphasize that at these low NSAA concentrations, the sol remains hydrophobic, or in other words, it is still stabilized by an electric double layer mechanism. The phenomenon of the above peak is explained by a possible modification of the electric double layer by the benzene ring of the non-polar chain of the surfactant molecules which are adsorbed on the sol particles.

(Keywords:)

EFFECT OF NONIONIC SURFACTANTS ON THE STABILITY OF HYDROPHOBIC SOLS

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Previous investigations have shown that the nature of aggregative stability of hydrophobic sols changes drastically in the presence of nonionic surface active agents (NSAA); the ionically stabilized sols are converted into hydrophilic ones. This transition manifested by an extremely sharp rise in the resistance of the sol towards the coagulating effect of electrolytes, takes place at relatively low NSAA concentrations.

This work studied the effect of a certain type of NSAA, i.e., polyoxyethylated octyl- and nonylphenols with different degrees of oxyethylation, on the stability of silver iodide hydrosols. The above mentioned steep rise in stability was observed also with this type of NSAA. However, in certain cases at surfactant concentrations below those causing the steep rise, a peculiarity was discovered: a peak appeared in the curve representing the dependence of the electrolyte coagulation value on the surfactant concentration. It is important to emphasize that at these low NSAA concentrations, the sol remains hydrophobic, or in other words, it is still stabilized by an electric double layer mechanism. The phenomenon of the above peak is explained by a possible modification of the electric double layer by the benzene ring of the non-polar chain of the surfactant molecules which are adsorbed on the sol particles.

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The effect of nonionic surfactants on the stability and coagulation of colloidal dispersions has been the subject of a large number of previous investigations. In spite of the definite conclusions reached there, a number of points have not been completely resolved yet. It is the objective of this work to deal with some of these points and attempt to provide evidence further supporting previously proposed models or fill in gaps in them. In addition, a phenomenon will be presented which occurs at very low concentrations of surfactants and has not previously been observed or reported.

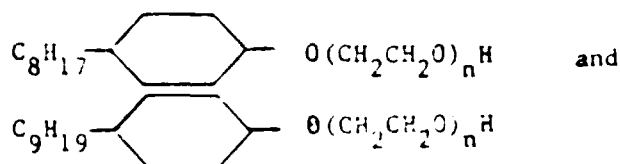
BACKGROUND-PREVIOUS INVESTIGATIONS

Previous investigations¹⁻⁹ have shown that the nature of the aggregative stability of hydrophobic sols changes fundamentally in the presence of non-ionic surface active agents (NSAA). The hydrophobic sols are actually converted to hydrophilic. The surfactant molecules, adsorbed on the colloidal particles and oriented with their polar groups towards the aqueous solution, cause hydrophilization of the particle surface. This conversion, which is realized at fairly low NSAA concentrations, is manifested by an extremely sharp rise in the resistance of the system to the coagulating action of electrolytes. The presence of NSAA raises the minimum concentration of electrolytes at which coagulation occurs by several orders of magnitude over the electrolyte concentration causing coagulation of the hydrophobic sols, i.e. in the absence of NSAA. It is important to emphasize, that while in the latter case the coagulating action of an electrolyte follows the Schulze-Hardy rule, in the former the coagulating ability of an ion is not associated anymore with its charge but it depends on the position the ion occupies in the lyotropic series. This implies that the coagulation of the NSAA protected colloidal systems at high electrolyte concentrations is caused by the breakdown of the polymolecular hydration layers surrounding the particles.

The NSAA used in our previous investigations¹⁻⁶ were different alkyl ethers of polyethylene glycol; their general formula is $C_m H_{2m+1} O (CH_2 CH_2 O)_n H$, or in the abbreviated form $C_m E_n$. The numbers m and n varied, thus both the effect of the length of the alkyl group and the effect of the oxethylene chain length on the stabilization of the sol could be examined.

EXPERIMENTAL APPROACH OF THIS INVESTIGATION

In contrast to the above investigations, in which polyoxyethylated alcohols were used, the present investigation employed polyoxyethylated alkyl phenols; in particular octyl- and nonylphenols with different degree of oxyethylation. Their formulae are



respectively and they are designated in an abbreviated form as $C_8 PE_n$ and $C_9 PE_n$. They were obtained from GAF Corporation under the trademark of ICEPAL.

All the experiments were performed with a negatively charged silver iodide sol, which was prepared using the technique described earlier¹⁰. The obtained sol was purified by a long-term dialysis accomplished through a precleaned cellophane membrane towards double distilled water. The process of the sol purification was controlled by electric conductivity measurements and was stopped when the conductivity dropped down to

5×10^{-6} ohms $^{-1}$ cm $^{-1}$. Appropriate precautions were taken to protect the sol against light during sol preparation and its use.

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The coagulation values (CV) of the electrolytes NH_4NO_3 , $\text{Ca}(\text{NO}_3)_2$ and $\text{La}(\text{NO}_3)_3$ for the above sol were obtained in the usual way.

RESULTS AND DISCUSSION

a) Coagulation Values and Appearance of "Peaks"

In the first experiments a NSAA of the type $\text{C}_{12}\text{E}_{12}$ was used as a point of comparison with data from previous investigations^{m,n} and as a point of reference for the data with the polyoxyethylated alkylphenols. The surfactant selected was the $\text{C}_{12}\text{E}_{12}$. The reason for the selection was based on an empirical fact established long ago^{7,11}; namely that the presence of the benzene ring in the nonpolar part of a surfactant molecule is equivalent in terms of surfactant properties to about 3.5 carbon atoms in the aliphatic chain. That is, the C_8PE_n and C_9PE_n are equivalent to $\text{C}_{11.5}\text{E}_n$ and $\text{C}_{12.5}\text{E}_n$.

The coagulation values of $\text{C}_{12}\text{E}_{12}$ by the three electrolytes, NH_4NO_3 , $\text{Ca}(\text{NO}_3)_2$ and $\text{La}(\text{NO}_3)_3$, are presented in Figure 1 as a function of the concentration of added surfactant. The data agree in general with the results of previous studies¹⁻³ showing a sharp rise in the coagulation values. This rise occurred for this particular case at about $3 \times 10^{-3}\text{M}$ solution of surfactant; experimental limitations, associated with electrolyte solubilities, did not allow, however, to reach the expected plateau. The data indicate only that such a plateau would be at 1-1 electrolyte concentration higher than 3000 mM. The only difference with previous data is that the effect of sensitization (i.e. the reduction of stability) which was previously observed at low surfactant concentrations and in case of coagulation by monovalent counterions was not observed here in the case of NH_4NO_3 .

Similar behavior was observed in the cases with polyoxyethylated alkyl phenols which are presented in Figures 2,3, and 4. The phenomena

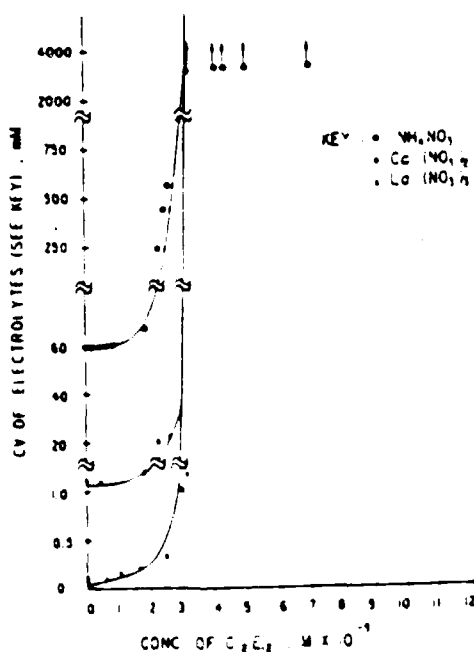


Figure 1. Coagulation values of electrolytes in the presence of $\text{C}_{12}\text{E}_{12}$.

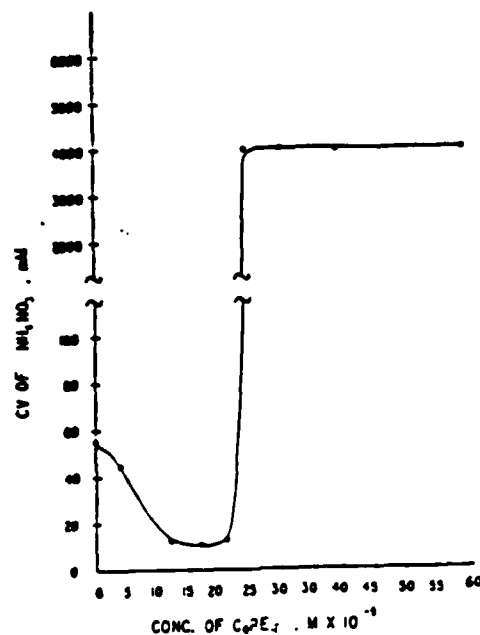


Figure 2. Coagulation values of NH_4NO_3 in the presence of C_8PE_{12} .

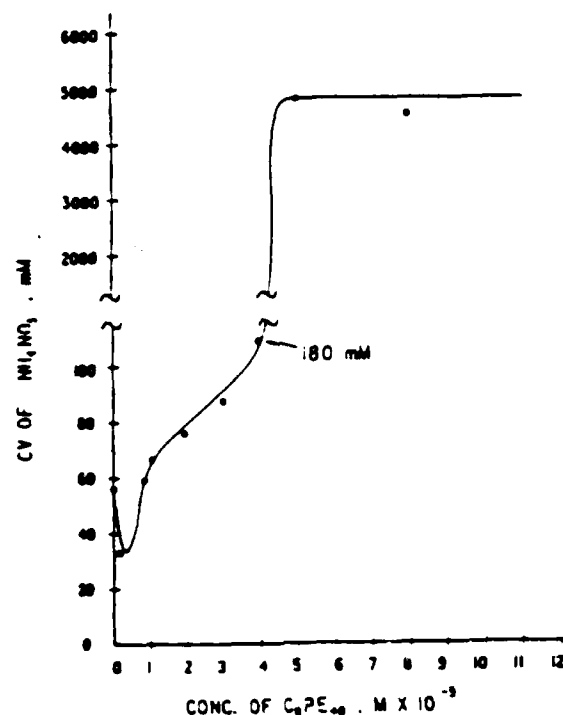


Figure 3. Coagulation values of NH_4NO_3 in the presence of C_8PE_{40} .

of sensitization (with NH_4NO_3), of the sharp rise to high electrolyte concentration level and of the subsequent attainment of a plateau of CV are clearly observed in these graphs. Experimental limitations again prevented the attainment of a plateau in the case of $\text{Mg}(\text{NO}_3)_2$.

What is noteworthy, however, is a peculiarity observed with certain alkyl phenol based surfactants. This peculiarity is exemplified by the data in Fig. 5 with $\text{C}_9\text{PE}_{7.5}$ and NH_4NO_3 . It can be seen there that a peak in the curve representing the dependence of the electrolyte's CV on the surfactant's concentration appears in the range of very low SAA concentrations; actually at the concentration range at which sensitization (i.e. a minimum) is observed for other systems.

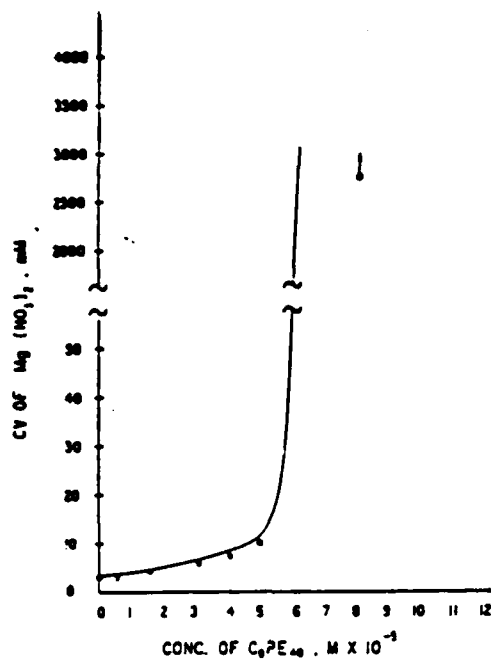


Figure 4. Coagulation values of $\text{Mg}(\text{NO}_3)_2$ in the presence of C_8PE_{40} .

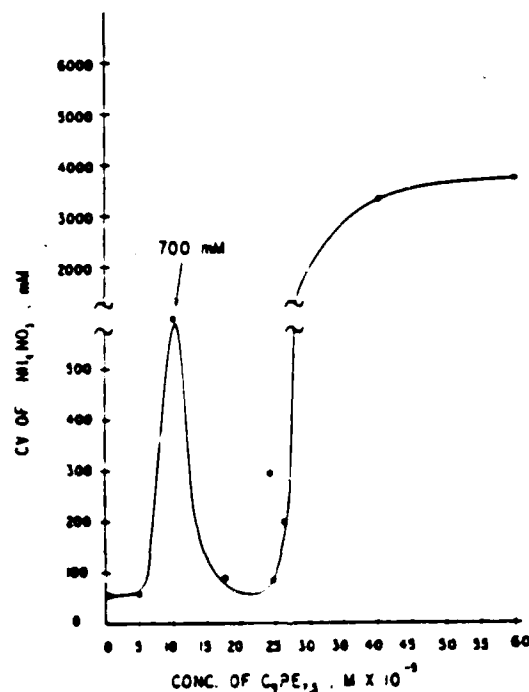


Figure 5. Coagulation values of NH_4NO_3 in the presence of $\text{C}_9\text{PE}_{7.5}$.

This phenomenon has not previously been reported. Further tests showed that other phenoxy type surfactants demonstrate the same phenomenon. Figures 6, 7, and 8 represent the low-NSAA-concentration portion of the CV curves for the systems $\text{C}_8\text{PE}_{12}\text{-Ca}(\text{NO}_3)_2$, $\text{C}_8\text{PE}_{12}\text{-Mg}(\text{NO}_3)_2$ and $\text{C}_9\text{PE}_{7.5}\text{-Ca}(\text{NO}_3)_2$ respectively. A peak was observed also in the system $\text{C}_8\text{PE}_{12}\text{-La}(\text{NO}_3)_3$. Since the existence of these peaks was unexpected, we considered it necessary to have a second experimenter confirming the results by parallel independent tests.

It should be emphasized that the above peak appears at NSAA concentration ranges at which the dispersions are still electrostatically

stabilized and is observed only with surfactants containing a phenoxy group in the nonpolar chain. The peak is, therefore, the result of the electric double layer modification by the benzene ring of the surfactant. One can conclude from the literature ^{12, 13} that aromatic compounds prefer to adsorb at interfaces in such a way that the benzene ring lies flat. Thus the question is what effect this particular mode of adsorption would have on the electric double layer?

Two such effects are plausible. First, the adsorbed surfactant molecules displace counterions from the Stern layer¹⁴ causing an increase in Stern potential, in zeta potential and consequently in the stability of dispersion. One may expect that the adsorption of polyoxyethylated alkylphenols, with the aromatic ring lying flat on the solid surface, would be more effective in displacing counterions from the Stern layer and thereby increasing the dispersion stability. However, as the surfactant concentration increases another effect is developed at the same time and it

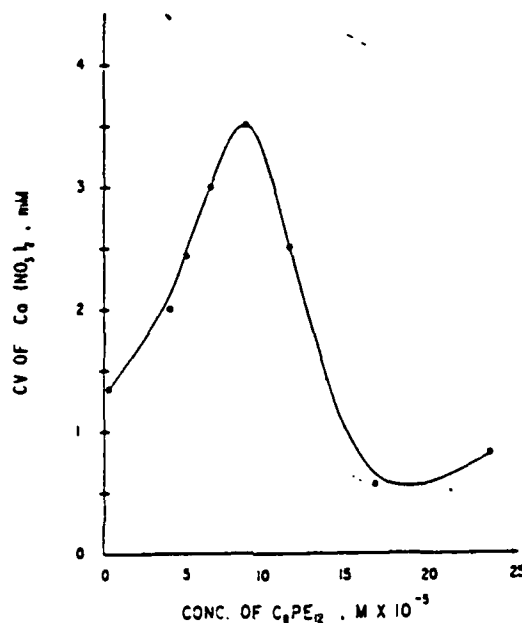


Figure 6. Coagulation values of $Ca(NO_3)_2$ in the presence of C_8PE_{12} .

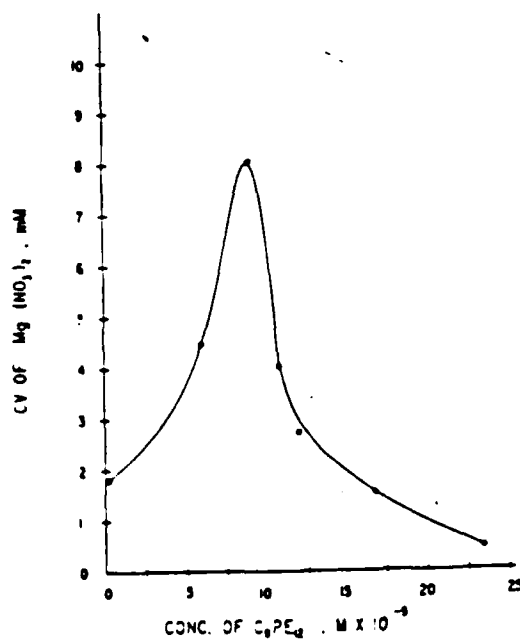


Figure 7. Coagulation values of $Mg(NO_3)_2$ in the presence of C_8PE_{12} .

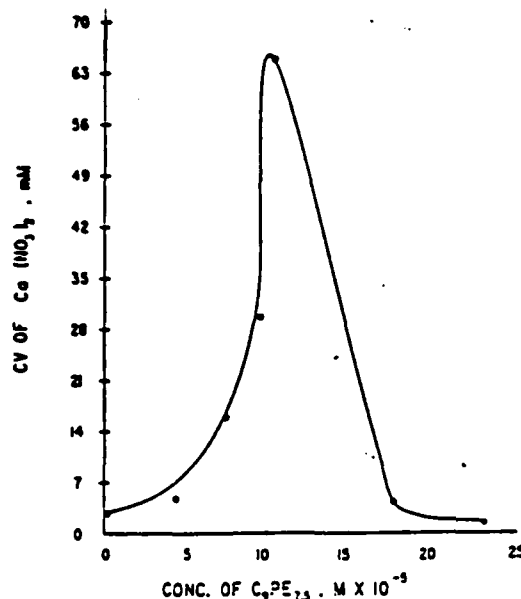


Figure 8. Coagulation values of $\text{Ca}(\text{NO}_3)_2$ in the presence of $\text{C}_9\text{PE}_{7.5}$.

eventually prevails. This is the displacement of the original plane of shear caused by the adsorbed bulky surfactant molecules. The above effect inevitably would decrease the zeta potential⁵ and, consequently, the dispersion stability as long as the system remains electrostatically stabilized. The competition of these two effects, acting in opposite directions, accounts for the appearance of the peak in the curve.

b) Adsorption Mode of C_nPE_m Compounds on AgI Particles

As was pointed out in the beginning of this paper, the initially hydrophobic sol (in our case the AgI sol) is converted into the hydrophilic one as the surfactant concentration in the solution increases. This happens as a result of the oriented adsorption^{3,4} of SAA molecules; the nonpolar part of the surfactant molecule is attached to the solid surface and the hydrophilic oxyethylene chain is extended into the aqueous solution. The transition of AgI sol from hydrophobic to hydrophilic is assumed to occur in the region of the steep rise of stability towards the coagulating action of the electrolytes. A comparison of the steep rise in the stabilization plots of the surfactants with the phenoxy group in the nonpolar chain with the plots of those without the aromatic ring in the molecule, leads to the conclusion that the former are less effective than the latter. For example, if one compares the stabilization plots of $\text{C}_{12}\text{E}_{12}$ and C_8PE_{12} , it becomes evident that the steep rise occurs at a concentration equal roughly to 0.03 mM for $\text{C}_{12}\text{E}_{12}$ and at approximately 0.3 mM C_8PE_{12} with NH_4NO_3 . In all probability this can be explained by the stipulation that the benzene ring in the nonpolar part of the molecule C_8PE_{12} is located flat on the AgI surface, and because of this the oxyethylene chain is prevented from extending very far into solution. It was suggested earlier² on the basis of the concepts of van der Waals attraction between the particles on the one hand, and the repulsion forces arising as a result of overlapping of polymolecular hydration layers on the other, that the stabilizing action of hydration sheaths depends on their distance from the "support", i.e. the surface of the particle. The greater the distance of the hydration barrier from the particle surface, the more effective hydration is in increasing the stability of the disperse system². Thus, it is probably this mode of adsorption of C_nPE_m on the AgI particles which may account for the lower effectiveness of these surfactants as stabilizers in comparison to those with the straight alkyl chain.

There is a disagreement in the literature concerning the question, whether or not the surfactant concentration at which a sol becomes relatively insensitive to the coagulating action of electrolytes (i.e. the region of "steep rise") coincides with the critical micelle concentration (CMC) of the surfactant (compare for example refs. 1-3 and ref.8). Table 1 presents the CMC values of the surfactants used in this study which were determined from the surface tension measurements*, and the corresponding concentrations at "steep rise".

Table 1. Comparison of CMC and Surfactant Concentration at "Steep Rise"
Surfactant Concentration (mM)
Corresponding to the "Steep Rise"

Surfactant	in the Stabilization Plots	CMC, mM
C_8PE_{12}	0.2-0.7	0.16
C_8PE_{40}	0.05	0.20
$G_9PE_{7.5}$	0.2-0.8	0.08
$C_{12}E_{12}$	0.03	0.06

It is evident from the data presented, that there is no correspondence between the CMC values and the surfactant concentration at the "steep rise". This confirms earlier findings^{1-3,5}.

In conclusion, it should be noted that the mechanism of hydrophobic sols stabilization by the nonionic SAA has not been definitively and unambiguously clarified by the above findings, and it is still open to discussion (see ref. 15).

ACKNOWLEDGEMENTS

This work was supported by the Office of Naval Research of the U.S. under Award No. N00014-81-K-0836.

*The surface tension of C_8PE_{40} was not measured. Instead, the information provided by GAF was utilized.

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