The Mechanism of Stabilization of Hydrophobic Sols by Non-ionic Surface-Active Agents*

Yu. Glazman

Tufts and Northeastern Universities in Boston, USA

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Stabilization of hydrophobic sols by nonionic surface-active agents (NSAA) is of great theoretical and practical significance. The effect of NSAA on the stability of hydrophobic sols is discussed not as an isolated problem but it is considered as a constituent of the whole problem of the disperse systems stability. Particular attention is paid to the lyophilic colloidal dispersions. The stability of lyophilic sols is interpreted basing on the idea of the disjoining pressure of thin liquid layers and especially on its structural component. The analysis of the experimental data obtained shows that hydrophilization of the dispersed phase surface occurs as a result of oriented adsorption of the NSAA molecules by colloidal particles, and that lyophilic colloidal dispersions are formed. Another alternative interpretation of the same experimental data, based on the idea of steric stabilization mechanism, is also discussed. A certain contribution of the steric factor to the total effect of stabilization by NSAA is not excluded in some cases.

The stabilization of hydrophobic sols by nonionic surface-active agents is of great theoretical and practical significance. In order to understand the mechanism of stabilization one should consider it not as an isolated problem but as a constituent of the whole problem of the disperse systems stability which has been, as it is well known, the main problem in colloid chemistry for many years.

Colloidal dispersions are usually classified into the lyophobic and lyophilic ones. Various polymers have been formerly considered as belonging to the lyophilic colloids. This classification (with some additions and reservations) has generally been accepted for a long time. However, the situation has changed fundamentally since it was established that the spontaneously formed solutions of the high molecular compounds (at least the diluted solutions) were actually not colloidal dispersions but true solutions. The kinetic units in such systems are not the disperse particles forming a separate phase and consisting of a lot of molecules (small or big ones), but they are individual gigantic molecules (usually called macromolecules) of polymers. As a result, a somewhat vague situation has been created, and it is not clear whether the lyophilic sols do exist at all and if so, the question arises as to what systems they actually belong to and what is their true nature. It should be noted that no

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generally accepted point of view exists on this subject in modern colloid chemistry.

Some authors (see for example ref. 5—7) assume even now that the true solutions of high molecular compounds (and, besides, the typical association colloids — saops, dyes, tanning materials, etc. — as well) belong to the group of lyophilic colloids. The only reason for an approach of this kind is the fact that the molecules of the solute in these systems are big enough in terms of their dimensions to fall within the range of the colloidal degree of dispersion. Some other scientists (for example ref. 8) do not word their concepts explicitly and they practically ignore the consideration of lyophilic colloidal systems. One may guess that in all probability these authors do not admit the existence of lyophilic sols. A different approach to this subject was expressed recently\(^9\) and that is »the general usage of the terms lyophilic and lyophobic in describing colloidal systems is somewhat illogical«.

Not very long ago an idea was put forward\(^10\) that true lyophilic sols are those colloidal dispersions in which the specific free interfacial energy \(\sigma\) on the surface of dispersed particles is less than its limiting value \(\sigma_m\) (determined by the mean kinetic energy of Brownian motion) approximately equal at normal temperature to 0.1 erg. cm\(^{-2}\). Alongside with this approach other concepts have been propounded on the above subject in literature\(^11\).

Experimental data accumulated in colloid chemistry during the last decades has enriched and considerably developed the studies of lyophilicity of surfaces; in particular, it has made possible a deeper understanding of the role of lyophilicity in the problem of the disperse systems stability. The progress achieved in this area has made one point clear and that is the approach to the study and to the distinction of various colloidal systems which existed until recently has not yet lost its significance and is entirely justified. It is safe to assert now that the new concepts concerning the nature of solutions of high molecular compounds should by no means shake the foundation of the classification of colloids generally accepted previously. The only problem is to find out the right approach to the lyophilic sols corresponding to the modern level of colloid science.

It is understood that the concept of lyophobic and lyophilic colloids may be defined differently, and it should be emphasized that the terminology itself does not matter very much; it is in fact very insignificant. However, another point is important — the classification enabling us to characterize the peculiarities in the properties of diverse disperse systems should be created; this might facilitate the study of the effect of various factors on their behaviour. It seems that the phenomenological approach to this problem would be the most expedient and helpful at present\(^11\).

The lyophobic sols should be characterized as colloidal dispersions highly sensitive even to the smallest electrolyte additions; their coagulation obeys, as it is well known, the Shulze-Hardy rule. This regularity is the most significant one and it reflects the most typical peculiarity of lyophobic sols. The problem of stability and of the mechanism of the lyophobic sols coagulation by electrolytes has been studied intensively during the last decades. This problem is being fundamentally developed at present both theoretically and experimentally (ref 12—15 and others).
The lyophilic sols are much less explored. Not only are the quantitative theories of stability absent at the time being, but moreover, as it has already been noted even the qualitative concepts in this area are not clear enough. Still, from the phenomenological point of view the lyophilic sols, in contrast with the lyophobic ones, may be defined as colloidal systems preserving stability even in rather concentrated salt solutions; their coagulation sets in at very high concentrations of electrolytes in solution and the pattern of coagulation is completely different. The coagulating action in this case no longer depends on the sign of the ion's charge and on the ion's valence but is determined by the position of the ion in the lyotropic series. The classification of colloidal systems based on the mentioned experimental criterion has a significant virtue since it reflects the essence of distinctions in the nature of the aggregative stability of lyophobic and lyophilic colloidal dispersions and in the mechanism of their coagulation; this point is certainly the most important for any classification.

The analysis of the pattern of lyophobic sols coagulation by electrolytes entailed definite concepts concerning the formation of the ionic double layer on the surface of colloidal particles. The forces of repulsion arise when in the process of the particles approach the diffuse ionic atmospheres surrounding the particles overlap. As a result an energy barrier is created and it causes the aggregative stability of a system. Thus the stabilization of colloidal dispersion can be realized if the electric forces of repulsion acting between the disperse particles (i.e. the electric component of the disjoining pressure $P_e$) are the only ones. However, by no means can this decide beforehand whether the repulsion forces of another origin — of nonelectrostatic nature — develop between colloidal particles (even in the lyophobic systems). As a matter of principle it is also necessary to take into consideration the existence of the nonionic component of the disjoining pressure $P_0$ caused by the formation of polymolecular solvate layers at the surface of the dispersed phase. The liquid in these layers has a modified structure and hence specific properties different from those of the liquid in the bulk. The actual existence of $P_0$ was proved by direct experiments.

When ideal (i.e. extreme) lyophobic sols are under consideration one may neglect the value of $P_0$, since it is small in comparison with $P_e$. On the other hand, for typically lyophilic sols, where the value of $P_e$ may be (but not necessarily is) close to zero, the aggregative stability of a colloidal dispersion is practically solely associated with the nonionic component of the disjoining pressure $P_0$. It stands to reason that the two mentioned cases ($P_0 \approx 0$ and $P_e \approx 0$) are the limiting ones. Actually the colloidal particles are almost always solvated in real lyophobic sols (ref. 20, 21; see also 22), and this is reflected in some peculiarities of the regularities observed during coagulation of the colloidal systems investigated in the works cited above. Not dwelling on details here, we shall note only that although the solvation degree of the disperse phase surface was somewhat changed in the described cases, the systems still remained ionically stabilized and in this sense they should be regarded as the lyophobic ones. Consequently, in spite of the fact that the nonionic component of the disjoining pressure $P_0$ contributed to a certain extent to the total aggregative stability of the colloidal dispersions considered, the mechanism of their coagulation and the stability itself depended mainly on the electric forces of the particles interaction. Thereby the system's behaviour is determined
not by \( P_e \) but by \( P_o \) in the above mentioned cases. Alongside with this it is necessary to note that the electric factor of stability (i.e. \( P_o \)) may act to a certain extent in lyophilic sols as well, but the value of \( P_o \) is of decisive significance for the stability of these systems.

Some colloidal dispersions — such as silica, sulfur and others — are of special interest in view of the problems discussed here, because these sols enable us to follow various stages of transition of the disperse systems from typically lyophobic to the lyophilic ones.

Krestinskaya\(^{23}\) studied the sols of silicic acid and came to the conclusion that a sol may develop properties of either hydrophobic or hydrophilic colloidal dispersion depending on the conditions in the system — first of all depending on the pH value. The state of the stabilizer changes at different values of pH and namely this (according to Krestinskaya) is of crucial importance. If the stabilizer consists of nondissociated molecules, the sol is in a hydrophilic state; on the contrary, if the molecules of a stabilizer are ionized (and hence the electrokinetic potential exists), the sol is in a hydrophobic state.

The regularities established by Krestinskaya\(^{23,24}\) and some other experimental data as well, have been interpreted\(^{20}\) on the basis of the idea that solvation of the potential-determining ions (or of the molecules of a stabilizer) directly connected with the surface of a colloid aggregate essentially affects the lyophobic sols stability in a number of cases. The formation of hydrogen bonds between the appropriate atoms of the surface layer and molecules of dispersion medium plays a significant role during the realization of such dispersed phase solvation*. The developed concepts\(^{20}\) have been confirmed later on\(^{21}\) by additional experimental data.

The dissociation of the electrical double layer surrounding the colloidal particles in silica sol becomes compressed with the hydrogen ions \( H^+ \) migrating partially from the diffuse part of the outer plate of the double layer into the adsorption layer (such a compression occurs, in particular, when the pH value is lowered). This results in the increase of the number of hydrogen bonds formed between hydrogen and oxygen atoms of silicic acid (\( H_3SiO_3 \))**, which is connected directly with the surface of the dispersed phase. The hydration of the nucleus of the colloidal particles increases accordingly. Thus both the transition of the sol of silicic acid into the hydrophilic state (when the value of pH is lowered) and the fact that the maximal stability of this colloidal dispersion towards the action of electrolytes has been achieved with the electrokinetic potential of particles equal to zero, acquire a logical interpretation. Similar reasonings may be applied to the sol of sulfur which acquires the highest stability when the dissociation of polythionic acid acting as a stabilizer in this case is completely suppressed\(^{26}\). The above concepts enable us to interpret the well known fact that in various hydroxide sols /\( Fe(OH)_3, Al(OH)_3 \) and others/, which are ioniically stabilized systems, there exists a relatively high affinity between the dispersed phase and the dispersion medium (i.e. the particles are comparatively strongly hydrated). The mentioned fact which by

* It has to be noted, however, that probably the mentioned factor should not be considered as the only one providing the formation of a solvate layer with modified structure (see, for example, ref. 25).

** The surface compounds on the particles may actually be somewhat different and have a more complicated composition. However, this does not affect the train and the essence of the above reasonings.
the way is confirmed by the new experimental data as well\(^2\) may be clarified on the basis of the views already developed\(^3\). The enhanced hydrophilicity of particles in the considered cases is associated in all probability with the formation of hydrogen bonds between OH groups (or similar groups) located on the surface of the colloidal aggregate and water molecules in the vicinity.

A number of very thorough investigations of Matijević and his co-workers\(^8\) (in which stability, electrokinetic properties and coagulation of silica sols by various electrolytes have been studied in the wide range of pH values) show that the hydration of colloidal particles is extremely essential for the stability of these systems. The sols of silica behave as lyophilic colloidal dispersions under conditions where the silanol groups located in the surface layer and hydrated owing to the hydrogen bonds formation are relatively undissociated. The ion exchange of counterions for the acidic hydrogen of the silanol surface play an important role in the destabilization process of silica sol by electrolytes. Such ion exchange can be represented schematically by the equation

\[
\equiv \text{Si-OH} + M^{n+} \not\equiv \equiv \text{SiOM}^{n+} + H^+ 
\]

where \(M^{n+}\) is an ion of charge \(n^+\).

It is easy to see that the conclusions of Matijević and his co-workers (ref. 28; compare also 29, 30) are in good agreement with the considerations expressed in ref. 20 and with the concept that solvation should be regarded as a significant factor of aggregative stability of colloidal dispersions. Essentially the same idea has been expressed recently by Ottewil\(^3\) who claims that the role of solvation is of crucial importance in many disperse systems.

It should be noted that the disperse system acquires the properties of a lyophilic dispersion in the case when the colloidal particles become coated with polymolecular solvate layers to a certain extent, enough to prevent the aggregation of these particles. In addition, it should be emphasized that this mechanism does not depend on the cause of the dispersed phase interaction with the surrounding liquid. Different ways may be used to get such systems and one of them is the effect of nonionic surface-active agents (NSAA) on the hydrophobic sols. A number of investigations on this subject have been performed and a comprehensive review has been published about ten years ago\(^3\). For this reason we shall mostly dwell now on our own results only, obtained during the last 15 years.

We systematically studied hydrophobic colloidal dispersions containing various polyethylene glycol (PEG) alkyl ethers\(^9\). We investigated stability and coagulation by electrolytes of the hydrosols of silver halides (bromide and iodide) and of arsenic trisulfide\(^13\); besides, adsorption of the surface-active agents\(^34\), their action on the electrokinetic potential of the particles\(^35\) and some other phenomena\(^36\) have also been explored. The results obtained (see also ref. 37—39) show that modification (the hydrophilization) of the dispersed phase surface occurs as a result of oriented adsorption of the NSAA molecules by colloidal particles\(^40\). A number of experimental facts favor the concept of hydrophilization of colloidal particles by the investigated surface-active compounds. These are:

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* The general formula of the investigated compounds is \(C_mH_{2m+1}O(CH_2CH_2O)_nH\) or in the abbreviated form \(C_mE_n\).
1. very high concentrations of coagulating electrolytes; these concentrations do not depend on the valencies of counterions;
2. intensified coagulating action of sulfates;
3. reversibility of coagulation (before SAA have been added the sols coagulated irreversibly);
4. coagulation upon successive addition of ethanol and a small quantity of electrolyte;
5. regular increase of the stabilization effect with the lengthening of the oxyethylene chain in the SAA molecules;
6. coagulating action of electrolytes along with their salting out effect on the SAA solutions;
7. dependence of the permanent dipole moment of the colloidal particles on the SAA concentration in solution;
8. the plane of shear during the electrophoresis is located farther from the surface of the dispersed phase than the »axial length« of the adsorbed molecules of PEG alkyl ethers.

Thus, it may be concluded that the hydrophobic sols are converted into the hydrophilic ones under the action of nonionic surface-active agents. The polymolecular boundary layers i.e. »boundary phases« are formed around the disperse particles, and the aggregative stability of such hydrophilic colloidal systems is associated with the nonionic (i.e. structural) component of the disjoining pressure. Approach of particles of the dispersed phase entails in this case an overlapping of structure-modified polymolecular hydrate layers surrounding these particles. Repulsion forces of the nonionic origin arise accordingly, and they impart stability to the colloidal dispersion. It is necessary to emphasize that such a mechanism of the disperse system stabilization is realized when the material itself forming the particle’s core is hydrophilic, and when only the surface layer is hydrophilic. As we have already mentioned above, the high hydrophilicity of colloidal particles is acquired in the considered case owing to the adsorption of NSAA molecules and to their orientation at the interface.

The pattern of coagulation of the sols stabilized by NSAA in highly concentrated salt solutions is also consistent with the concepts expressed above. It was established experimentally that the addition even of considerable amounts of electrolytes to the system does not entail desorption of the NSAA from the surface (moreover, their adsorption is even somewhat increased). Thus the mechanism of coagulation of the lyophilic sols formed in the presence of nonionic surface-active agents is associated with the destruction of polymolecular boundary hydrate layers surrounding the colloidal particles.

It should be noted, however, that the obtained results cannot be regarded as unambiguous proof of the solvation mechanism of stabilization only. As a matter of principle the possibility of another approach has to be also taken into consideration. Although one can hardly agree with the assertion that »the distinction between a »polymer« and a »surfactant« is, of course, purely arbitrary« still, it must be admitted that the experimental data concerning the effect of NSAA on the stability and coagulation of hydrophobic sols can be interpreted by means of the mechanism of steric stabilization as well.
HYDROPHOBIC SOLS

It is very difficult to distinguish and to decide between the two mentioned mechanisms of stabilization in this case.

Indeed, the regular change of hydrophilicity in series of the PEG alkyl ethers (with increase of the number \( n \), for example, in \( C_mE_n \) molecules) is accompanied inevitably by the similar change in their efficiency as steric stabilizers. On the other hand, it is well known that the efficiency of steric stabilization does not depend only on the nature of the polymer and on the extent of particles coating but it also depends on the dispersion medium (first of all on its solvency properties for a given polymer) as well\(^{46,47}\).

According to Napper's assertion\(^{48}\) the simplest way to induce instability in sterically stabilized dispersions is to reduce the solvency of the dispersion medium for the stabilizing species. This can be achieved, in particular, by adding a nonsolvent for the stabilizing moities to the dispersion medium\(^{48}\).

It should be noted, however, that the same inferences may be drawn if one proceeds from the above concepts of the solvation mechanism of stabilization as, for example, when coagulation takes place in high concentrated solutions of electrolytes owing to the destruction of the stabilizing boundary hydrate layers occuring in this case. In connection with the discussion on this subject it is of interest to mention in somewhat more detail the results of some experiments performed. When ethanol was added to the lyophilic sols of silver iodide or and arsenic trisulfide formed in the presence of various PEG alkyl ethers, these dispersions acquired properties typical of the hydrophobic colloids: they became highly sensitive to the electrolytes and coagulated under the action of their smallest concentrations. It is worthwhile to note that ethanol cannot be regarded as a nonsolvent for the PEG alkyl ethers (since they are readily soluble in ethanol) and still, it is well known that ethanol acts as a dehydrator and, accordingly, as an agent destroying the boundary hydrate layers which surround the colloidal particles.

In any case it seems evident that the stabilization by means of steric mechanism can be efficient in that case only when the solvency of the dispersion medium for the stabilizing chains is pronounced. At the same time, as it follows from the literature mentioned before (see also ref. 49) and considerations expressed above, the formation of structure modified hydrate boundary layers on hydrophilic surfaces is by no means associated generally with adsorption of polymers at the interface (in some specific cases it can certainly be so). In this respect the solvation mechanism of disperse system stabilization should be regarded as having a wider meaning than the steric mechanism.

All our experimental data concerning the action of nonionic surface-active agents on hydrophobic sols speak well for the solvation mechanism of stabilization. However, it does not exclude the fact that a certain contribution to the total effect of the stabilization observed has been made by a steric factor as well. This contribution may be different in various cases: first of all it should depend probably on the length of the oxyethylene chain in the molecules of the PEG alkyl ethers. In connection with this it should be noted that some of the surfactants investigated are of low molecular weight and can by no means be regarded as high polymers.

In conclusion I would like to share the opinion expressed recently\(^{50}\), that it is generally almost impossible to completely separate the entropic repulsion and solvation interactions.
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SAŽETAK
Mehanizam stabilizacije hidrofobnih solova neionskim tenzidima
Yu. Glazman

Prikazan je pregled 50 radova o stabilnosti liofobnih i liofilnih disperzija.

Dio članka je poseban autorski pregled i diskusija o solvatnom i steričkom mehanizmu stabilizacije. Tako se solvatni mehanizam stabilizacije zasniva na konceptima razbijanja stabilizirajućih graničnih hidratih građeva oko koloidnih čestica, zatim hidrofilizacije koloidnih čestica površinsko-aktivnim supstancama i orijentirane adsorpcije, tj. presvlačenja površine koloidnih čestica strukturno modificiranim polimolekularnim solvatnim slojevima površinski aktivnih supstancija.

Mogućnost drugog pristupa koloidnoj stabilnosti u prisutnosti površinski aktivnih supstancija interpretirana je kao mehanizam steričke stabilizacije.

TUFTS AND NORTHEASTERN UNIVERSITIES IN BOSTON, USA

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