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Hydrophobic Microphase Formation in Surfactant Solutions Containing an Amphiphilic Graft Copolymer

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ABSTRACT: Strong association between the hydrophobic side chains on water-insoluble C_{12}-grafted hydroxyethyl cellulose and sodium dodecyl sulfate in aqueous solution is reported. This association gives rise to viscoelastic solutions and hydrogels with dispersed hydrophobic microdomains, indicating that intermolecular surfactant bridges are linking alkyl chains from more than one macromolecule. The solutions were characterized using conductivity, viscosity, and pyrene fluorescence measurements.

Introduction

Considerable effort has been devoted toward understanding the bulk and microscopic properties of aqueous solutions containing surfactants and water-soluble polymers. This work has made use of a variety of experimental techniques including neutron scattering,[1] NMR,[2] fluorescence spectroscopy,[3-5] dye solubilization,[5,6] viscosity,[6,7] and ESR spin probe techniques[8] and has focused on determining the types of structures that form as a result of interactions between the polymer segments and the surfactant molecules. Both polymer/surfactant interactions and self-aggregation of surface-active copolymers have been studied.

Results on water-soluble homopolymers like poly(ethylene oxide)[1-4] and poly(vinylpyrrolidone)[3,9-12] in sodium dodecyl sulfate (SDS) indicate that initially surfactant molecules prefer to adsorb onto the polymer chain rather than aggregate into micelles. These interactions occur on uniform hydrophilic polymer backbones where there is no preferred site for adsorption. The adsorbed surfactant aggregates have aggregation numbers reported to be 30–50% lower than pure surfactant micelles,[4] but which in fact increase with increasing total surfactant concentration. Beyond a certain concentration of the surfactant that is higher than the critical micelle concentration (cmc), the system favors aggregation of any additional surfactant molecules into free micelles. This transition occurs because Coulombic repulsion among the adsorbed surfactant aggregates precludes any additional adsorption on the polymer.[1]

With water-soluble surface-active copolymers in pure water, self-aggregation has been observed that is reminiscent of the process of micellization in monomeric surfactants. The formation of these aggregates depends on the free energies of the hydrophilic and hydrophobic groups in water. Self-aggregation has been demonstrated using water-soluble copolymers composed of long chain alkenes alternating with maleic anhydride (poly(1-alkene-*co*-(maleic anhydride))).[13-16] They form structures described as polymeric micelles, with "aggregation numbers" comparable to those of surfactants with the same alkyl groups in certain concentration regimes. These polymeric aggregates may form either intra- or intermolecularly depending on the length of the hydrophobic side chains and the flexibility of the polymer, as governed in this case by the charge density of its backbone. Also, the shape of the resulting aggregates has been shown to vary with side chain length.[15]

The present study is an investigation of the properties of water-insoluble surface-active copolymers in aqueous surfactant solutions. We have investigated the properties of a hydrophobically modified water-soluble polymer to determine the effects of alkyl grafts on the asso-

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ciation of the polymer with surfactant and with itself. The polymer used in this study is hydrophobically modified hydroxyethyl cellulose (HMHEC). Its hydroxyethyl cellulose (HEC) backbone is highly soluble in water and has been shown to interact only very weakly with SDS.[6] However a small degree of alkyl substitution on the polymer main chain renders it insoluble in water. Other studies on less substituted water-soluble HMHECs have shown evidence of both polymer/surfactant association and self-aggregation of the polymer via intra- and intermolecular association of the hydrophobes.[8,17,18] Also, in general surfactant has been found to solubilize the polymer by preventing unfavorable interactions between the side chains and water.[18]

In the present work, we will show that self-aggregation among HMHEC chains also occurs in water-insoluble HMHECs in the presence of surfactant. Moreover, beyond a critical surfactant concentration, the polymer separates into two distinct macroscopic phases—a water-rich solution and a polymer-rich hydrogel—both of which are characterized by dispersed hydrophobic microphases made up of surfactant molecules and polymer side chains. These dispersed-phase polymer networks are expected to retain permeants in proportion to their hydrophobicity and should therefore have applications in separations and controlled delivery technology.

Experimental Section

The polymer hydrophobically modified hydroxyethyl cellulose (HMHEC) was obtained from Aqualon Co., Wilmington, DE. Its main chain, hydroxyethyl cellulose (HEC), is composed of anhydroglucose units rendered water soluble by addition of ethylene oxide (EO) groups. The HEC polymer is then modified with C_{12} alkyl grafts. In this study, HMHEC with a molar substitution (MS) of 3.8 EO groups per anhydroglucose unit and a degree of substitution of 1.3% (w/w) alkyl grafts, corresponding to about 1 alkyl group per 25 monomer units, was used. The viscosity average molecular weight of this polymer is 4×10^5. The HEC control polymer used here was Natrosol 250 HR, with a MS of 2.5 EO groups per anhydroglucose and a molecular weight of $\sim 10^6$. It will be seen that this higher molecular weight gives rise to similar viscosity behavior and therefore is a good control material for this study. The surfactant sodium dodecyl sulfate (SDS) (Fluka, >99% pure) was used as received. Pyrene (Aldrich, 99% pure) was recrystallized twice from ethanol.

Any conducting material was removed from the both HEC and HMHEC by batch extraction in ethanol. The ethanol does not dissolve the polymer, but the conducting impurity was soluble in the ethanol as indicated by the specific conductivity of the extract. Thus, the polymer was repeatedly washed with fresh alcohol until the specific conductance of the washing solvent fell to 2×10^{-6} mho. The polymer was then dried under vacuum and used within 2 days of purification.

Conductivity measurements on the polymer solutions were performed on a conductance–resistance meter (Yellow Springs Instrument Co., Inc., Yellow Springs, OH 45387) using a probe with a cell constant of 1.0 cm^{-1}. In the cases where the sample solutions composed of two phases (see results below), only the conductivity of the supernatant solution was measured.

All solutions were made up by weight in distilled water saturated with pyrene (3×10^{-7} M pyrene) and stirred for an hour. Fluorescence spectra of the pyrene in the solutions excited at 310 nm were obtained on a Spex Fluorolog-2 Model 112A fluorescence spectrophotometer (Spex Industries, Inc., Edison NJ). All spectral characteristics of the pyrene remained constant for at least 24 h after solution preparation. For samples in which both a gel and a supernatant had formed, this indicated that the pyrene had equilibrated between the two phases.

Viscosity of the solutions was measured using a Ubbelohde viscometer, in which the time for a liquid to flow through a cylindrical capillary under gravity is measured. The procedure was repeated three times on each solution with an accuracy greater than ±0.5%.

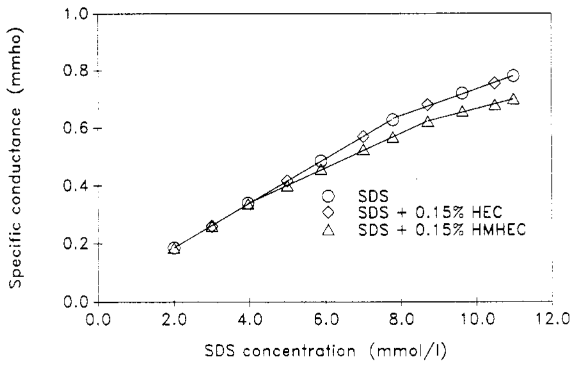

Figure 1. Specific conductance of SDS solutions with and without polymers: ○, SDS alone; ◇, SDS and HEC; △, SDS and HMHEC supernatant.

Results

We observed first of all that on addition of 0.15% (w/w) HMHEC to pure water without any surfactant present, the polymer precipitates in the form of individual swollen globules. Up to 1×10^{-3} M SDS, some of the polymer forms a macroscopic layer on the surface, with the rest precipitating out as before. At higher SDS concentrations, two distinct homogeneous phases are formed. The supernatant phase is a clear solution that was found to contain most of the surfactant and a small amount of polymer. The polymer-rich phase is a one-piece flexible hydrogel that takes the shape of its container and does not swell further or disperse in pure water. The gel phase disappears, with all of the polymer becoming solubilized in the supernatant, as the surfactant level is increased above the cmc ($\sim 8 \times 10^{-3}$ M). In the region just above the cmc, the solution exhibits recoil on pouring and cannot pass through ordinary filter paper. The solution remains clear on further addition of SDS but ceases to exhibit recoil and may be poured easily through a filter. These different regions of solution and gel behavior were investigated individually to determine the nature of the polymer/surfactant interactions in each case.

Figure 1 shows plots of the specific conductance of SDS solutions with and without polymer as a function of surfactant concentration. A break in the specific conductance of pure SDS solutions appears at approximately 8×10^{-3} M, the cmc of the surfactant. This occurs because the total number of ions in the solution is reduced due to aggregation of the surfactant and the high degree of counterion binding to micelles.[19] The specific conductance of solutions containing HEC (the control polymer) and SDS coincides with that of pure SDS solutions. The presence of HMHEC, however, decreases the specific conductance of the solutions relative to controls, beginning at 4×10^{-3} M SDS. The only conducting species in the solutions are the surfactant amphiphiles and sodium counterions. Thus it is clear that the surfactant amphiphiles form aggregates in the presence of HMHEC, even below the cmc. A similar transition has also been observed in SDS/PEO solutions investigated using fluorescence[3] and surface tension[2] measurements. It has been characterized as the cmc of the surfactant in the presence of polymer. We conclude that within the sensitivity of these measurements the surfactant associates with HMHEC but not with HEC, as expected.[6] There is also a sharp break similar to that observed for pure surfactant solutions at 9×10^{-3} M surfactant. Thus micelles still form, but at a slightly higher SDS concentration in the pres-

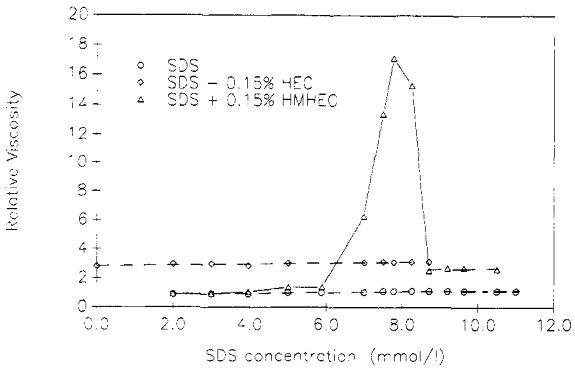

Figure 2. Viscosities of various solutions as a function of SDS concentration: ○, SDS alone; ◇, SDS and HEC; △, SDS and HMHEC supernatant.

ence of HMHEC. Similar increases in the apparent cmc of surfactants in polymer solutions have been observed elsewhere[3] and were attributed to the fact that initially surfactant prefers interacting with the polymer and only forms micelles when the former interactions become unfavorable.

Figure 2 shows the relative viscosities (compared to that of water) of the various solutions as a function of SDS concentration. For pure surfactant, the viscosity is approximately that of water and is independent of surfactant concentration even beyond the cmc. Addition of 0.15% (w/w) control polymer raises the viscosity of both the water and SDS solutions by a factor of ~3, but once again the viscosity does not vary with surfactant. For surfactant solutions containing 0.15% HMHEC the behavior is quite different. Note that HMHEC viscosity data below the cmc (where two phases formed) are for the supernatant solution only. At 4×10^{-3} M SDS, the viscosity of the solution begins to rise slowly. This is the point where conductivity results indicated the onset of association between HMHEC and the surfactant. This transition point was reproduced on three separate solutions. The observed increase in viscosity above 4×10^{-3} M is evidence that polymer has begun to enter the supernatant from the gel. However, this alone does not explain the high viscosity, since all the polymer remains in solution above the cmc where the viscosity drops off, finally leveling off close to the value for HEC in surfactant. We conclude that below the cmc, where the solutions appeared viscoelastic, polymer networks composed of surfactant-mediated hydrophobic interactions are present. These networks break down above the cmc, where the hydrophobes may be solubilized individually by surfactant micelles, making the polymer behave much like the unmodified control material.

Landoll[18] reported the effect of the degree of hydrophobic substitution on the viscosity of 2% (w/w) solutions of water-soluble HMHEC in pure water. The minimum concentration of C_{12} groups required for the intermolecular interactions to occur was found to be 2.1×10^{-3} M. By contrast, the concentration of hydrophobes in our 0.15% HMHEC solutions at the peak in the viscosity curve is only 1.15×10^{-4} M, demonstrating that the surfactant does indeed play a major role in creating the network.

The similarity in behavior between HMHEC and HEC at high surfactant concentration is reasonable in light of the findings of Cabane and Duplessix.[1] Their work shows that the minimum intermicellar distance over which adsorbed SDS micelles do not interact either electrostatically or sterically corresponds to 60 PEO monomer units, which is equivalent to approximately 25 HEC units. The HMHEC used here has an average distribution of 1 alkyl side chain per 25 monomer units, so SDS micelles adsorbed on the side chains will be separated enough not to affect the dimensions of the polymer and hence the viscosity of polymer solutions.

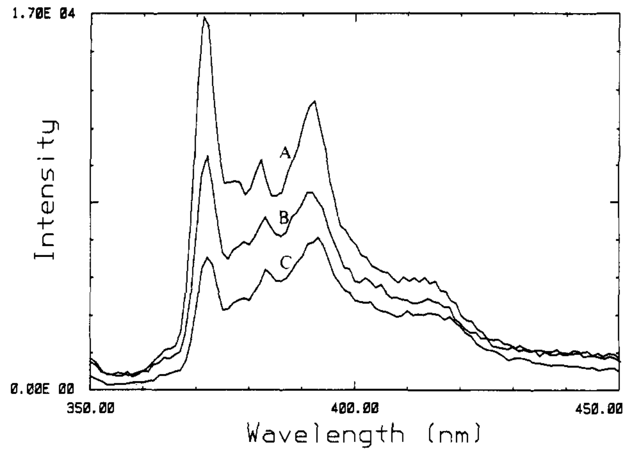

Figure 3. Typical spectra of pyrene in (A) water, (B) HEC/SDS, and (C) HMHEC gel (λ_{exc} = 310 nm).

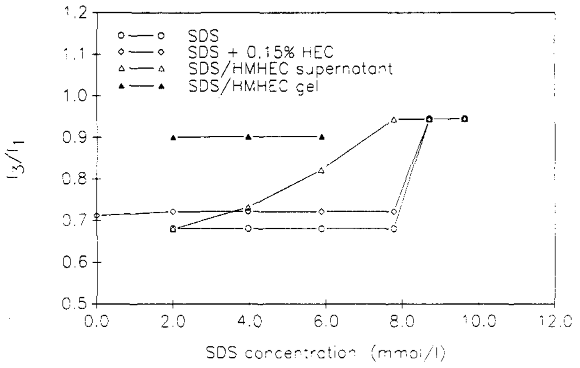

Figure 4. Relative hydrophobicities of aqueous SDS/polymer solutions: ○, SDS alone; ◇, SDS and HEC; △, SDS and HMHEC supernatant; ▲, HMHEC gel.

The relative intensities of the vibronic bands of pyrene fluorescence spectra are closely related to the polarity of the pyrene's environment. The spectra are characterized by five distinct peaks; the ratio of the intensities of peaks 3 and 1 (I_3/I_1) has been shown[20] to be a direct function of the hydrophobicity of the pyrene's environment. We used this property to probe the microscopic structure of the aggregates that gave rise to the bulk properties described above. Pyrene is only sparingly soluble (~3×10^{-7} M) in water and will partition into any nonpolar regions in a solution or dispersion.

Typical pyrene spectra in HMHEC/surfactant solutions are shown in Figure 3. Figure 4 gives values for the I_3/I_1 ratio for aqueous SDS/polymer solutions containing pyrene as a function of SDS concentration. For SDS in water, I_3/I_1 assumes two different values above and below the cmc, as expected. Below the cmc, the pyrene resides in the bulk (aqueous) solution, with I_3/I_1 = 0.68 (I_3/I_1 (water) = 0.63[3,20]); above the cmc the pyrene partitions into micelles, and the value of I_3/I_1 goes to 0.94, reflecting a more hydrophobic environment. Solutions containing 0.15% (w/w) HEC produced similar results, with I_3/I_1 values depending only on whether or not free surfactant micelles are present. The slightly higher hydrophobicity of the solutions below the cmc of SDS may be attributed to the presence of the polymer. With HMHEC, on the other hand, the environment of the pyrene in the supernatant solution becomes increasingly hydrophobic on addition of SDS, leveling off at the cmc of pure surfactant. Recall that in these solutions the total HMHEC concentration in the supernatant phase goes up with increasing SDS. However, here again the observed increase in hydrophobicity of the solution with SDS cannot be due to the increase in polymer concentration alone, as discussed below. Thus we have evidence that hydrophobic regions have begun to form in the supernatant phase of HMHEC/SDS solutions even below the cmc. Results on the gel phase are even more dramatic. Here we see that regardless of either surfactant or polymer concentration, hydrophobic regions are present and their average polarity remains constant until all of the polymer leaves the gel to dissolve in the supernatant. Thus the microscopic composition of the gel is independent of its bulk composition.

Discussion

HMHEC/surfactant solutions will be characterized by interactions between surfactant molecules and the polymer backbones, between surfactant and polymer side chains, and among several side chains. The first of these will also be present in HEC/surfactant solutions; thus any unusual behavior observed with HMHEC may be attributed directly to the presence of the hydrophobes on the polymer.

The possible types of interactions involving the hydrophobes are as follows:

1. Intramolecular associations of alkyl grafts from the same polymer chain, giving rise to polymer chains with a relatively coiled configuration. Intramolecular micelles of this type are likely to be characterized by a well-defined aggregation number, much like the case of monomeric surfactant micelles,[15,16] although this has not yet been demonstrated conclusively. This constant composition is required in order to exclude water completely and provide maximum contact among the hydrophobes in the aggregates. The HMHEC polymer used here is not soluble at all in water, indicating that either the polymer chains cannot assume a conformation in which intramolecular "micelles" form or else the hydrophobe content of the chains is high enough that hydrophobes make significant contact with water regardless of the chain conformation. Landoll[18] has shown that the limiting C_{12} content per polymer chain which permits solubility in water is 17.5 ± 1. The HMHEC used here has ~31 alkyl groups per polymer molecule.

2. Intermolecular associations among hydrophobic grafts from several polymer chains. Intermolecular interactions in polymer solutions give rise to non-Newtonian behavior and a high bulk viscosity. Such interactions have been observed in water-soluble poly(1-alkene-*co*-(maleic anhydride)),[13-15] maleic anhydride–hexyl vinyl ether copolymer,[21] and water-soluble HMHEC both with[7,8,17]and without surfactant.[7,18] They have been described as polymeric micelles with relatively bulky "head groups" made up of the main chains of the polymer. However, they did not form spontaneously with our water-insoluble HMHEC but required the intervention of surfactant.

3. Alkyl grafts solubilized by SDS. When the surfactant concentration has reached a high enough level, there is enough surfactant present to solubilize most or all of the polymer side chains individually. Thus intermolecular interactions disappear, leading to a decrease in the bulk viscosity of the solution. This explanation is supported by the fact that the surfactant concentration at which the interactions begin to break down is a linear function of the total HMHEC concentration in the solution.[17]

Thus the following picture of HMHEC/surfactant interactions emerges. In the presence of some small but finite amount of surfactant, surfactant molecules begin to adsorb onto the polymer chain from the bulk phase. This can be seen from the decrease in the specific conductance of the solution with polymer (Figure 1). It is known[1-4,9-12] that in aqueous solutions of PEO and PVP, for example, surfactant molecules adsorb on the polymer backbone even below the cmc. This initial binding is seen in our HMHEC/SDS solutions at 4×10^{-3} M SDS. However, in PEO and PVP, as with our control polymer, the adsorption process is not site-specific and the viscosity did not vary with surfactant concentration as it does with HMHEC. With HMHEC the side chains provide a nucleus for surfactant adsorption. The resulting side chain/surfactant complexes are hydrophobic and micelle-like in nature and can solubilize pyrene readily. Note that when all of the HMHEC is solubilized (0.15% w/w), the total moles of C_{12} contributed by the polymer is 1.15×10^{-4} mol/L. This is over an order of magnitude less than the starting C_{12} concentration from the surfactant, which we have seen has almost no effect on the pyrene fluorescence signal until micelles begin to form. Thus the presence of the additional hydrophobe from the polymer cannot by itself be responsible for the observed higher hydrophobicity in the supernatant phase. Moreover, a steady increase in the I_3/I_1 ratio with SDS concentration has been reported[4] in SDS/PEO solutions at constant polymer concentration and was attributed to growth of bound SDS micelles. The limit of the size of SDS/HMHEC aggregates appears to be equal to the size of free SDS micelles (Figure 4).

As the surfactant concentration is increased, surfactant molecules replace polymer side chains in the aggregates. A relatively high ratio of surfactant molecules to polymer side chains in these aggregates is favored because it permits denser packing of the hydrophobes. Once the intermolecular associations are disrupted, the HMHEC in solution resembles HEC, the backbone polymer, with the hydrophobes completely shielded from the water phase and therefore not contributing at all to the bulk solution properties. This can be seen from Figures 2 and 4.

Conclusions

Strong site-specific adsorption of surfactant occurs on the hydrophobic side chains of water-insoluble HMHEC. The resulting interactions give rise to a network composed of hydrophobic microdomains dispersed throughout an aqueous polymer solution or gel, depending on the composition of the system.

The hydrogel phase that forms from HMHEC below the cmc of the surfactant appears to be an important new material that bears further investigation. It is clear, flexible, viscoelastic, and homogeneous and contains hydrophobic regions in an aqueous network. This material may have numerous applications in separations technology and controlled release and is under detailed investigation in our laboratory.

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Registry No. SDS, 151-21-3.

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Static Structure Factors of Compressible Polymer Blends and Diblock Copolymer Melts

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ABSTRACT: The incompressibility constraint is removed within the random-phase approximation (RPA). We thereby derive a set of three static structure factors for monomer-monomer correlations within a binary polymer blend as a function of the three excluded-volume interactions that are required for compressible blends. The results are compared to the conventional RPA structure factor. It is shown that the incompressible limit of the blend structure factors recovers the conventional RPA scattering functions when the intrachain excluded-volume parameters are equal. Otherwise, the usual empirical definition of the Flory interaction parameter is a function of all three excluded-volume parameters, the composition of the blend, and the scattering wavevector. Introducing compressibility into the RPA is, however, shown not to alter usual RPA predictions about the behavior of the structure factor and correlation length near the spinodal. The compressible RPA structure factors are also compared with those emerging from integral equation approaches. A brief outline is given of the extensions of the compressible RPA theory to block copolymer melts. We discuss the manner in which overall density fluctuations might affect some experiments on melts and blends and theories of microphase separation in block copolymers.

I. Introduction

Theories of the structure and thermodynamics of polymer blends[1-4] generally place an incompressibility constraint on the monomer concentration fluctuations. These physically motivated approaches have their roots in de Gennes' random-phase approximation (RPA)[1] for the static structure factor of one of the two polymer species. This assumption is entirely adequate for many applications, and the RPA structure factor and free energy of blends have been used to predict their phase diagrams and to determine the Flory–Huggins effective interaction parameter χ from small-angle neutron-scattering (SANS) experiments.[5-7] Similarly, RPA structure factors of block copolymers[8,9] have been inserted into theories of their microphase separation.

Polymer melts, however, are at least as compressible as ordinary liquids or liquid mixtures. It is well appreciated that the latter undergo small, but nonnegligible, density changes upon freezing or phase separation. The incompressibility constraint of the RPA theory nevertheless demands that phase-separated blends occupy the same volume as the unseparated mixture. A related problem concerns block copolymers that undergo *microphase* separations[8,9,11-14] to periodically ordered structures. In this case, it might be expected that the predicted morphology depends crucially on whether or not the theory includes the melt's compressibility in the analysis of monomer–monomer correlations. In order to address this problem, it is at least necessary to generalize the RPA theory to include blend incompressibility. Whereas the description of the structure factor of an incompressible blend requires the use of only a single interaction parameter χ, when the incompressibility constraint is lifted, the structure factor, in principle, may depend on three different interaction parameters. This raises questions about the proper analysis and interpretation of extrapolated zero-angle neutron-scattering data.

Some recent work has investigated the effects that *nonzero* wavevector concentration fluctuations have on polymer blend thermodynamics. Olvera de la Cruz et al.[4] demonstrate that such fluctuations decrease the stabil-

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