INSTABILITY IN POLYETHYLENE OXIDE SOLUTIONS
IN A HYDRODYNAMIC FIELD

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It is found that degradation in aqueous polyethylene oxide is accompanied
by dehydration and aggregation, with deterioration in the thermodynamic
affinity for water, which is not related to molecular-mass reduction.

Instability occurs in aqueous polyethylene oxide (PEO) in that the physicochemical
and working parameters change on prolonged hydrodynamic treatment [1-8]. The reduced
turbulent friction [1-7] and the characteristic viscosity [1, 7] indicate that the macro-
molecules are damaged [6, 8], but no reduction in molecular mass (MM) has been found by
absolute methods.

We have examined the effects of hydrodynamic shear on the molecular parameters of
aqueous PEO.

The specimen had average molecular mass $M_w = 2.4 \cdot 10^6$. The solutions were prepared
in distilled water and were mixed for various periods in a thermostatic chamber at 30°C by
means of a four-blade stirrer $50 \cdot 10^{-3}$ m in diameter running at 2100 rpm. The optical
densities were monitored with a KFK-2 photoelectric colorimeter. The hydrodynamic resist-
ance coefficients were determined with an open-loop system employing automatic flow time
recording [9]. The resistance reduction was calculated for a wall stress $\tau_w = 120$ Pa.
The Reynolds number calculated from the viscosity of water ranged from 15,000 to 25,000.
The viscosity as a function of shear rate was measured with an Ostwald viscometer (capil-
lary diameter $0.56 \cdot 10^{-3}$ m) and an Eugner viscometer, which were fitted with systems for
providing additional pressure and counterpressure. The speed of ultrasound was determined
with a differential system, relative error $2 \cdot 10^{-6}$ [10]. The light scattering at concentra-
tions of 0.01-0.05% was measured with a Sofica photogoniodiffusometer at 546 nm over the
range 40-150° by a standard method [11]. The data were processed by Zimm's method. The
UV spectra were recorded with a Specord UV VIS instrument.

Figure 1 shows that high-speed stirring for a 0.1% solution for 11 h reduced [η] from
9.1 to 5.2 deciliter/g. The equation $[\eta] = 12.5 \cdot 10^{-5} M^{0.78}$ [12] indicates a reduction in the
average-viscosity molecular mass M_η from $1.71 \cdot 10^6$ to $0.83 \cdot 10^6$, but the same characteristic
viscosity can be obtained by raising the temperature from 30 to 66°C on account of reversi-
ble conformation change with an unaltered MM. The viscosity is also very much dependent on
shear rate for untreated solutions. Figure 2 shows that hydrodynamic shear reduces not
only the viscosity but also the gradient dependence. Viscometry is an indirect method of
determining the MM and cannot give an unambiguous answer on what is happening.

Hydrodynamic treatment not only reduces [η] but also the capacity of the PEO to re-
duce the resistance. Curve 2 in Fig. 1 reflects the increase in C_{opt} as the stirring time
increases. By optimal concentration is meant that giving the maximum resistance reduction.
The hydrodynamic performance is dependent not only on the MM but also on the conformation
and the thermodynamic affinity for the solvent, as is [η]. Increasing the temperature
from 6 to 80°C raises C_{opt} from 0.0003 to 0.0200% [9], i.e., by nearly two orders of
magnitude, with unaltered MM. Then hydrodynamic performance reduction, as also [η] reduc-
tion, is not adequate evidence for MM reduction in hydrodynamic treatment.

It is not usual to monitor the optical density D in instability testing, although
curve 3 of Fig. 1 indicates that D increases on stirring. The turbidity is stable and does
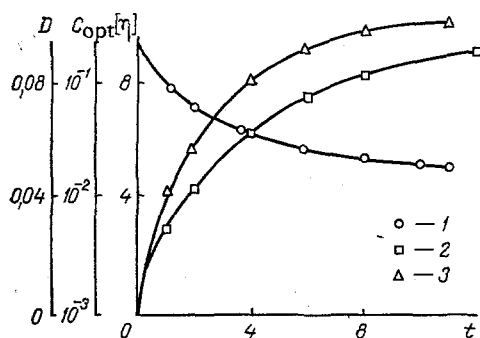
Fig. 1. Characteristic viscosity $[\eta]$ deciliter/g, optimal concentration C_{opt} (%), and optimal density D for 0.1% PEO solutions in relation to stirring time: 1) $[\eta]$; 2) C_{opt}; 3) D; t in h.
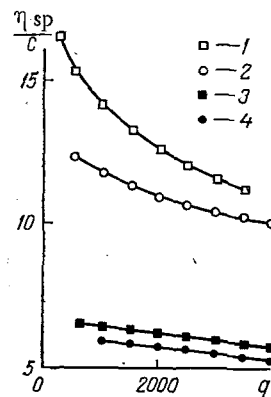
Fig. 2. Effects of shear rate q (sec^{-1}) on the reduced viscosities of initial (1 and 2) and treated (3 and 4) PEO solutions; concentrations: 1, 3) 0.1%; 2, 4) 0.04%.

not vanish on storing or on pumping off the air, so the increased D is due to colloidal particles. D has been measured at 364-590 nm and the data have been processed by means of the turbidity spectra [13], which has shown that less than 1% of the polymer is precipitated, while the colloidal-particle sizes attain $(8-10)\cdot10^2$ nm.

Fixed concentration and stirring conditions mean that MM reduction causes slower increase in D, so the largest particles are primarily deposited. The colloidal-phase formation is retarded at lower concentrations, but even at 0.001%, there is an appreciable increase in D.

The colloidal phase indicates altered molecular interactions and structure; it has been found [14, 15] that raising the temperature disrupts the hydrate shells and adversely affects the thermodynamic affinity. The similarity to phase separation under static conditions leads one to expect that such changes occur under hydrodynamic shear, which has been tested by measuring the speed of ultrasound in a 1% solution before and after treatment, where it fell from 1501.83 to 1501.43 m/sec, which is only a small change, since the PEO concentration was low, as was the proportion of deposited polymer, although it could be determined reliably because the change exceeded the error of measurement by two orders of magnitude. The ultrasound speed indicates the hydration on the basis of Pasynskii's method [16] or the method of [10]. In either case, the reduced ultrasound speed indicates dehydration, as it is independent of the MM [14].

The same conclusion follows from the changes in the UV spectra. The initial solution had a single characteristic band corresponding to an $n \to \sigma^*$ transition for the unshared electron pair on the ether oxygen at 212.7 nm. Stirring for 11 h did not produce new UV bands, while the $n \to \sigma^*$ band showed a bathochromic shift (red shift) to 236.2 nm. The first indicates that there are no new polar groups absorbing at 185-357 nm formed on stirring, while the second must be considered as dehydration arising from weakened interaction between the ether oxygen atoms and water molecules [17, 18].

The changes in MM, macromolecule size, and second virial coefficient A_2 on stirring were monitored by light scattering, which is a direct method of MM measurement. To improve the removal of dust and colloidal particles, 10 vol.% acetone was added, after which the solutions were centrifuged at 14,000 rpm for 90 min. Figure 3 shows that the scattering intensity increased at all angles on treatment. Zimm's method showed that M_w increased from $2.4\cdot10^6$ to $10\cdot10^6$, while the mean-square radius of inertia increased from 1550 to 3020 Å. The solvent affinity deteriorated, as A_2 fell from $18.5\cdot10^{-4}$ to $5.2\cdot10^{-4}$ $cm^3/g^2\cdot$ mole.

Zimm's method was designed for scattering in molecularly dispersed solutions, but recently it has been increasingly used for systems containing aggregates as well [15,
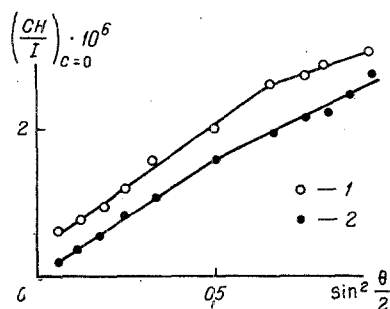
Fig. 3

Fig. 4

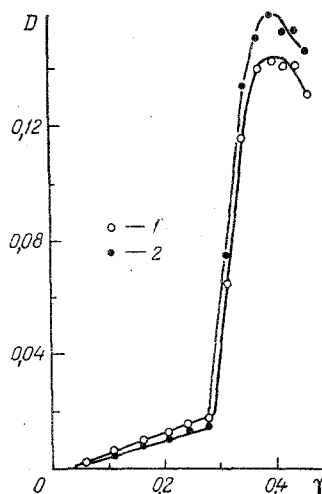Fig. 3. Light-scattering indicatrix for initial PEO (1) and treated (2).

Fig. 4. Optical density D of initial solution (1) and treated solution (2) as a function of volume precipitant fraction γ; temperature 30°C, wavelength 400 nm.

19-21]. Here the processing has been carried through to numerical values in order to indicate the changes produced by the treatment.

Turbidimetric titration [22] gives useful although ambiguous stability information for comparative purposes. There are no such data for PEO, and thus no recommendations on suitable precipitants. Simple electrolytes have a salting-out action, so we used 2 M $MgSO_4$, and as colloidal particles are formed on stirring, which may influence the deposition on titration, the solutions were purified by centrifugation at 7000 rpm for 10 min.

Figure 4 shows turbidimetric titration curves for solutions containing 0.005% PEO. The treated solution precipitates the PEO more readily, which is ascribed to increased MM, and adversely affected interaction with the water, but this conflicts with the suggestion of macromolecule breakage, since reduced MM improves the stability and shifts the D-γ curve towards the larger γ.

The data can be explained if there are intramolecular and intermolecular polymer-polymer links formed by the treatment, which may be physical (orientational crystallization [23]) or chemical, which involves radical transformations [24]. The intramolecular cross links produce stearic screening for some of the ether oxygen atoms, which become inaccessible to water molecules, i.e., dehydration occurs, as the speed of ultrasound is reduced and there is a red shift in the UV spectra. These cross links make the macromolecules kinetically more rigid and cause the gradient dependence of the viscosity to degenerate.

The intermolecular links cause aggregation and increase the MM as observed by light scattering; this adversely affects the affinity for the solvent, as A_2 is reduced, and the same is indicated by turbidimetric titration. The solution becomes cloudy because the highest-molecular part of the PEO is deposited as colloidal particles.

NOTATION

M_w, mean-mass molecular weight; τ_w, wall shear stress; [η], characteristic viscosity; M_η, mean-viscosity molecular mass; D, optical density; A_2, second virial coefficient; I, reduced scattering intensity; H, optical constant; θ, scattering angle; C, PEO concentration; γ, precipitant volume fraction; t, mixing time.

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