Polymer Bulletin 12, 327–330 (1984)

Polymer Bulletin

Evidence by Light Scattering of Hydroxyethylcellulose Aggregation Induced by Solution Filtrations

Y. Boscher[1], F. Lafuma[1], C. Quivoron[1], J.C. Mileo[2], and B. Sillion[2]

[1] Laboratoire de Physico-Chimie Macromoléculaire, Université Pierre et Marie Curie
Ecole Superieure de Physique et de Chimie Industrielles de la Ville de Paris
10, rue Vauquelin – 75231 Paris Cedex 05, France

[2] Institut Français du Pétrole C.E.D.I. – B.P. n°3, 69390 Vernaison, France

ABSTRACT

It is reported from light-scattering results that a thermoreversible aggregation may occur when hydroxyethylcellulose (HEC) solutions are filtered. The aggregation extent depends on concentration and filter porosity but not on filtration pressure. The aggregates are in part responsible for filter plugging and could arise from a cellulose type interchain association of unsubstituted anhydroglucose units.

INTRODUCTION

Filterability of water soluble polymer solutions is of high importance for their applications in oil recovery processes. For this purpose, a standard laboratory procedure of filtration has been developed (1) so as to improve the absence of microgels in such solutions. However, numerous papers have pointed out the occurrence of structural modifications in polymer solutions during filtrations (2). In order to get better understanding of these mechanisms, light-scattering was used to follow the physico-chemical behaviour of macromolecules submitted to every step of those filtration tests in the case of hydroxyethylcellulose (HEC) solutions.

EXPERIMENTAL

Materials

HEC (WP 100 MH grade) was synthetized by BP Chemicals for the Institut Français du Pétrole. Its weight average molecular weight $\bar{M}w$ is $1.28\ 10^6$ as measured by light-scattering and its limiting viscosity number 141 g^{-1} at 30°C ($\bar{G} = 1\ 800\ s^{-1}$). The z-average of the radius of gyration, $\langle \bar{R}^2_z \rangle^{1/2}$ is 1 400 Å.
All solutions were made in distilled water containing 400ppm of NaN_3 as a bactericide.

Light-scattering experiments

They were performed at 25°C over the angular range 30°–150° with a FICA 40 000 apparatus, home-modified with a red laser source (632nm). Refractive-index increments were measured on a differential Brice-Phoenix refractometer provided with a similar laser.

Solutions were freed from dust just before light-scattering measurements by centrifugation at high speed (18 000g) for two hours without reduction of concentration.

Reduced scattered intensities for zero concentration an angle were obtained by the Zimm method.

Standard filterability test

It is the one developed at the Institut Français du Pétrole which has been quite described elsewhere (3). It consists in two main steps :

(1) clarification by two successive filtrations through 3 and 0.8μ Millipore filters under 1 bar pressure drop ;

(2) injection at constant and very low flow rate (0.25m/d) of the clarified solution through on line 3μ Millipore filters plus measurement of pressure drops during flow. Mobility reduction (Rm) (i.e. the ratio of pressure drops between solution and solvent flow for a given flow rate) is then plotted against the cumulative injected volume.

RESULTS AND DISCUSSION

We recently showed (4) that the plugging behaviour of HEC solutions is highly concentration and temperature dependent. Indeed quite good filterability was observed for solutions up to 700ppm while plugging solutions (C > 1 000ppm) were found to become filterable when heated at 60°C just before injection (fig. 1, curve (d)).

All clarified solutions exhibited an increase in their light-scattering parameters ($\bar{M}w$, $\langle \bar{R}^2_{Gz} \rangle^{1/2}$) which occurred without any measurable change in concentration or intrinsic viscosity ; after 5 h heating at 60°C the initial $\bar{M}w$ and $\langle \bar{R}^2_{Gz} \rangle^{1/2}$ of the sample were recovered.

Such a thermoreversible aggregation depends on the filter porosity : being greater through 0.8μ filters ($\bar{M}w \sim 1.9\ 10^6$, $\langle \bar{R}^2_{Gz} \rangle^{1/2} \sim 1\ 800$ Å) than through 3 μ ones ($\bar{M}w \sim 1.6\ 10^6$, $\langle \bar{R}^2_{Gz} \rangle^{1/2} \sim 1\ 600$ Å).

Influence of filtration pressure was not found to be very important between 0.1 bar and 1 bar for clarification steps. In the same way, when previously thermally disaggregated solutions were injected through the 3μ filter of the test itself (i.e. at a very low pressure drop), as for curve (c) of fig.1, they displayed afterwards $\bar{M}w$ and $\langle \bar{R}^2_{Gz} \rangle^{1/2}$ values very close to those of 3μ clarified solutions.

All the above results are summarized in table I.

However, despite their formation concentration dependence (table II) and the best filterability results observed after thermal treatments (fig.1, curves (c) and (d)), the filtration-induced aggregates account only partly for plugging phenomena, since otherwise 0.8μ clarified solutions would have been less filterable than 3μ ones. Besides, there should be some differences in the filtration behaviour of e.g. two 400ppm solution obtained from dilution of the same 1 500ppm, one before (no aggregation, $\bar{M}w = 1.2\ 10^6$) or after clarification steps ($\bar{M}w \simeq 2\ 10^6$) and nothing of that kind could be observed. Anyway, no obvious correlation was found between the quantity of eluted aggregates and the filtered volume before plugging.

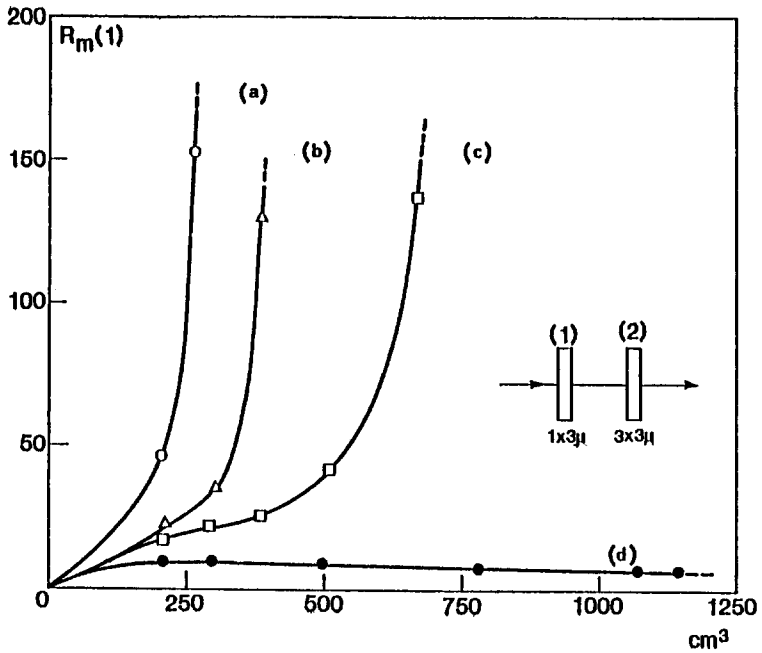

Figure 1

Mobility reduction Rm(1) through the first 3µ filter of the filtration test as function of the injected volume for a 1 500ppm HEC solution in pure water previously treated as follows :

(a) ○ Clarification through one 3µ Millipore filter - Filtration at 30°C.

(b) △ Clarifications through one 3µ plus one 0.8µ filter - Filtration at 30°C.

(c) □ Same clarifications as (b) - 5h heating 60°C - Cooling - Filtration test at 30°C.

(d) ● Same clarifications as (b) - Solution injected at 60°C.

From the lack of viscosity change and the relatively low increase in $\langle \bar{R}^2_{Gz} \rangle^{1/2}$ with regards to $\bar{M}w$, we think that the light-scattering detected aggregates are very compact and in very low proportion. Similar observation have been made for other systems where aggregation occurs through filtrations (2).

Therefore, it can be assumed that HEC aggregates must arise from interchain association through the unsubstituted anhydroglucose units, leading to some super-molecular structure of cellulosic type displaying a rather low accessibility to water (5).

Compte information about experimental work and interpretation will be given in a forthcoming paper (4).

Clarification	3μ	3μ + 0.8μ or 0.8μ alone		3μ + 0.8μ + 5h 60°C	
Injection temperature °C	-	30	60	30	60
$\langle \frac{\Delta \bar{M}_w}{\bar{M}_w} \rangle \times 100$ before test	25	55	55	0	0
after test	-	55	30	30	15
Filtered volume (cm^3) for Rm(1)= 100	250	375	>1 000	650	>1 000

TABLE I

Mean relative increase in $\bar{M}w$ for the various steps of the test and corresponding filterability results in function of clarification and temperature C = 1 500ppm - $\bar{M}w$ = 1.28 10^6 - Average was done over 5 different solutions.

Porosity / Concentration	3μ	0.8μ
1 500ppm	30 %	55 %
800ppm	12 %	25 %
400ppm	-	< 4 %

TABLE II

Relative increase in $\bar{M}w$ (1.28 10^6) as function of filter porosity and initial concentration.

BIBLIOGRAPHY

(1) KOHLER, N. and CHAUVETEAU, G., J. Pet. Techn., 349 (1981).
(2) ELIAS, J.G. and SCHLUMPF, H., Makromol. Chem., 85, 118 (1965).
STRAZIELLE, C., Makromol. Chem., 119, 50 (1968).
SUZUKI, J., MURAKOVA, Y. SAITO, M. and KAMIDE, K., Eur. Polym. J., 18, 831 (1982).
(3) KOHLER, N., Note Institut Français du Pétrole, n°505 NK/PC (1978).
(4) BOSCHER, Y., LAFUMA, F., QUIVORON, C., MILEO, J.C. and SILLION, B., to be published.
(5) GLASS, J.E., Paper SPE 7871 presented at the 1979 SPE International Symposium on Oil Field and Geothermal Chemistry, HOUSTON, Texas, January 22-24 1979.

Accepted August 8, 1984