

THE VISCOSITY OF EXTREMELY LOW CONCENTRATED ANIONIC POLYELECTROLYTE SOLUTIONS

BERNHARD GAMPERT, CHRISTOPH WILKES AND THOMAS EICH

Applied Mechanics, University of Essen, Schützenbahn 70, D-45127 Essen, Germany
e-mail: bernhard.gampert@uni-essen.de
Fax: x49.201.183.2909

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ABSTRACT

Polyelectrolytes are macromolecules which carry a large quantity of ionizable groups along their chains. By dissolving them in suitable solvents, for example water, these groups dissociate in highly charged macroions and an equivalent quantity of low-molecular counter ions. Through the connection between polymer and electrolyte properties this class of materials obtains its peculiar characteristic behaviour. The experiments undertaken here, were carried out using a commercial, anionic polyacrylamide with different hydrolysis factors in aqueous solutions. The reduced viscosity reaches a maximum which depends on the polymer concentration. The maximum also depends on the molar mass and is a function of the hydrolysis factor of the polymer.

KURZFASSUNG

Polyelektrolyte sind Makromoleküle, die entlang ihrer Ketten eine große Anzahl ionisierbarer Gruppen tragen. Beim Auflösen in geeigneten polaren Lösungsmitteln, wie zum Beispiel Wasser, dissoziieren diese Gruppen in hoch geladene Makroionen und eine äquivalente Anzahl niedermolekularer Gegenionen. Durch die Verbindung von Polymer- und Elektrolyteigenschaften erhält diese Stoffklasse ihr eigentümliches Verhalten. Für diese Arbeit wurde die Viskosität von Polyacrylamiden mit unterschiedlichen Verseifungsgraden in wässrigen Lösungsmitteln untersucht. Es wurden reduzierte Viskositäten ermittelt, die in Abhängigkeit der Konzentration ein Maximum aufweisen. Das Maximum ist abhängig vom Molekulargewicht und steht in direktem Zusammenhang mit dem Verseifungsgrad des Polymers.

RÉSUMÉ

Les polyélectrolytes sont des macromolécules qui portent de nombreux groupes ionisés le long de leurs chaînes. En les diluant à l'aide d'un solvant adéquat, comme l'eau par exemple, ces groupes se dissocient en macroions fortement chargés et en un nombre équivalent d'ions de charges contraires. Le couplage entre les propriétés polymères et électrolytiques confère à ces matériaux leur comportement particulier. L'étude suivante consiste à chercher la viscosité de polyacrylamides anioniques commerciaux en solutions aqueuses avec différents degrés d'hydrolyse. L'évolution de la viscosité réduite en fonction de la concentration atteint un maximum, qui dépend du poids moléculaire et est en rapport direct avec le degré d'hydrolyse du polymère.

KEY-WORDS:

polyelectrolytes, polyacrylamides, reduced viscosity, intrinsic viscosity

1 INTRODUCTION

For the characterisation of the phenomenological effects of polyelectrolyte solutions, viscometric methods were exclusively applied for this paper. For the characterisation of the polymer solutions, the intrinsic viscosity was used. The intrinsic viscosity is a measure of the space requirement of a polymer molecule in a solution and it is required to determine the solution-structure range and the average molar mass.

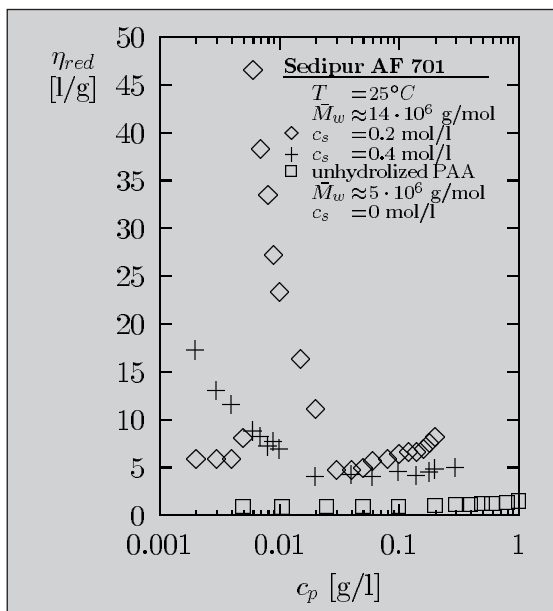
In order to determine the intrinsic viscosity one first attempts to eliminate the influence of the viscosity of the solvent. This leads to a specific viscosity, which represents the relationship between the viscosity of the solution to the viscosity of the solvent:

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} \quad (1)$$

The specific viscosity is divided by the polymer concentration to give the following equation for the reduced viscosity:

$$\eta_{red} = \frac{\eta_{sp}}{c_p} = \frac{\eta - \eta_s}{\eta_s} \frac{1}{c_p} \quad (2)$$

The reduced viscosity, η_{red} , is a characteristic of the material. In this case, c_p represents the polymer concentration in the solution, η the shear viscosity of the solution and η_s the shear viscosity of the solvent. The reduced viscosity relates to



follows a 20% increase in the concentration. Supplementary investigations with the polyacrylamide Sedipur AF 701 dissolved in highly pure water and an addition of salt of 0.1 mol/l NaCl gave the maximum at the same position again, contrary to the results of Cohen and Priel [1] as well as de Gennes *et al.* [10]. This probably refers to the relatively high salt concentrations and the polydispersion of the polymer in use. No maximum could be detected for this polymer dissolved in highly pure water without the addition of low-molecular counter ions and for solutions

with salt concentrations $c_s < 0.01$ mol/l NaCl. This refers to a displacement of the maximum to lower concentrations with the decrease of the counter ions in the solution. The theoretical maximum therefore lies outside the measuring range.

6 SUMMARY

It can be seen that a maximum appears in the curve of the reduced viscosity as a function of the polymer concentration for solutions of ionic polyacrylamides. As for polyelectrolytes which have a molar mass greater than 10^6 g/mol, the determination of the maximum is not always possible as there are influences which result in an especially strong anisotropy and the maximum is then displaced to lower polymer concentrations. A simple extrapolation is connected with large uncertainties, since the maximum of the reduced viscosity is not taken into consideration. Another method to calculate the intrinsic viscosity is only possible for commercially ionic polyacrylamides because of the experimental, only partially accessible Bjerrum radius and the polydispersion.

Author	Polymer	[M_w] g/L	Solvent	Salt	Peak	Tendency
Antonietti <i>et al.</i> [18]	linear PSS acids	$6.1 \cdot 10^4 - 1.07 \cdot 10^6$	highly pure water	low M_w salt	yes	1 & 3
Antonietti <i>et al.</i> [19]	PSS	$4.96 \cdot 10^5 - 3.07 \cdot 10^6$	highly pure water	-	yes	-
Borsali and Rinaudo [16]	NaPSS	$4 \cdot 10^5 - 10^6$	bidest. water	NaCl	yes	1, 2 & 3
Borsali <i>et al.</i> [17]	NaPSS	$4 \cdot 10^5 - 10^6$	bidist. water	NaCl	yes	1, 2 & 3
Cohen and Priel [1]	NaPSS	$1.6 \cdot 10^5 - 7 \cdot 10^5$	bidist. water	NaCl	yes	1, 2 & 3
Cohen <i>et al.</i> [14]	NaPSS	$1.6 \cdot 10^5 - 7 \cdot 10^5$	bidist. water	NaCl	yes	1, 2 & 3
Fujita [3]	Na-CMC		water	-	yes	-
Fuoss and Stauss [6]	Poly-4-vinylpyridine Poly-N-n-butyl-4-vinylpyridonium bromide	$2 \cdot 10^5$	dest. water - ethanol ethanol-water		no (yes)	1 & 2
Kaji <i>et al.</i> [11]	NaPSS	$1.8 \cdot 10^3 - 1.2 \cdot 10^6$	highly pure water	-	yes	-
Vink [5]	NaPSS	$4.7 \cdot 10^4 - 3.7 \cdot 10^6$	highly pure water	NaCl	yes	-
Wolff [13]		theoretical work			yes	-

Figure 5:
The reduced viscosity as a function of the polymer concentrations for different polymer solvent systems.

Table 1:
The employed polymer solvent system from the quoted literature with reference to the detection of a maximum of the reduced viscosity as a function of the polymer concentration and its tendency ($c_{p,max}$ = polymer concentration at the maximum of the reduced viscosity; In column Tendency "1" denotes $\bar{M}_w \rightarrow \eta_{red,max}$, "2" denotes $\bar{M}_w \rightarrow c_{p,max}$, while "3" denotes $c_s \rightarrow c_{p,max}, \eta_{red,max}$).

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