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$[\eta]$-M-Relationship for Polyacrylamide in Aqueous 0.1 M Na_2SO_4 Solution

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Summary

The intrinsic viscosity $[\eta]$ and the molecular weight M_w of 8 pure, unbranched polyacrylamide (PAAm) samples - prepared in our laboratory - were determined and lead to the following formula

$$[\eta] = 0{,}0194 \cdot M_w^{0{,}70} (cm^3/g)$$

Solvent: aqeous 0.1 M Na_2SO_4 solution; $T=298K$; $M_w/M_n \simeq 2{,}5$.
In addition a comparison to the $[\eta]$-M-relationships of PAAm in other solvents is given.

Introduction and Results

Although a great number of $[\eta]$-M-relationships exists for polyacrylamide (PAAm) in different solvents$^{1)}$, there were some reasons for a new $[\eta]$-M-dependence in 0.1 M Na_2SO_4 solution.

Firstly, this solvent was found to be a less corroding agent than aqueous salt solutions containing halogen anions. This circumstance is of practical importance i.e. for the lifetime of pumps in gel permeation chromatography (GPC) apparatus$^{2)}$. Secondly, the coil expansion is smaller than in pure water and therefore the molar mass range accessible in GPC-experiments is greater. The adsorption tendency to the stationary phase is lower$^{2)}$. Thirdly, the abnormal viscosity-time-dependence in 0.1 M Na_2SO_4 solution is much smaller.

It is well known that the solution viscosity of aqueous PAAm solutions decreases with time in the scale of weeks$^{3,4,5,6)}$. Simultaneously a loss of flocculation activity occurs$^{7)}$. With increasing M_w this unusual viscosity drop increases and a maximum viscosity loss of about 30% ($M_w = 6 \cdot 10^6$ g·mol^{-1}) has been observed Aqueous solutions of other polymers exhibit this abnormal visco-

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sity behaviour too and a viscosity loss of more than 90% can be observed[8]. To interpret this peculiar behaviour some detailed investigations were made, from which was concluded that conformational transitions within single polymer chains - controlled via intramolecular H-Bonds - and not chain scission is causing the viscosity decrease[1,8]. However a sample with $M_w = 7.9 \cdot 10^6$ $g \cdot mol^{-1}$ exhibits in 0.1 M Na_2SO_4 aqueous solution a decrease in viscosity of 9% only.

Fourthly, suitable solvents for PAAm are water, aqueous salt solution, ethylene glycol and formamide, but in case of high molar masses there exist some problems in handling formamide or ethylene glycol i.e. carrying out light scattering measurements[1,9].

These are the reasons to present a new$[\eta]$-M-relationship for PAAm.

Tab. 1 covers the experimental data. The intrinsic viscosity increases with M_w, the second virial coefficient A_2 decreases

M_w /$(g \cdot mol^{-1})$	$[\eta]$ /$(cm^3 \cdot g^{-1})$	dn/dc /$(cm^3 \cdot g^{-1})$	A_2 /$(bar \cdot cm^6 \cdot g^{-2})$	$d_{equ,[\eta]}$ /(nm)
9 269 000	1573	0.172	5.96	263.8
7 967 000	1407	0.175	7.16	241.7
4 261 000	873	0.177	6.40	167.3
2 023 000	530	0.180	6.88	110.5
1 705 000	445	0.177	7.87	98.5
1 425 000	380	0.177	10.40	88.0
766 000	285	0.174	13.04	65.0
158 000	88	-	-	26.0

Tab. 1 Experimental data of polyacrylamide in 0.1 M Na_2SO_4 solution at 289 K.

with M_w and the refractive index increment dn/dc has a constant value of 0.176 $cm^3 \cdot g^{-1}$. By plotting log$[\eta]$as a function of log M_w a straight line (s. Fig. 1) with a slope of 0.70 has been calculated. A comparison to other mixed solvents can be made from [1].

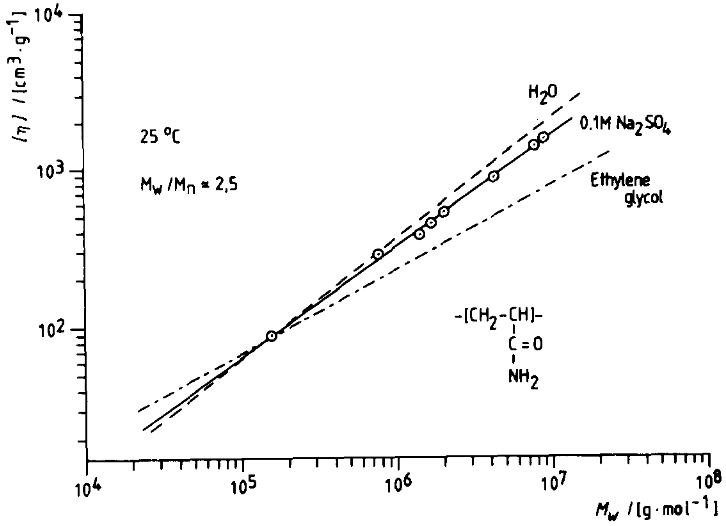

Fig. 1 Intrinsic viscosity $[\eta]$ as a function of molecular weight M_w in aqueous 0.1 Na_2SO_4 solution. In addition the $[\eta]$-M-relationships in H_2O and ethylene glycol are plotted too, to demonstrate that an intersection point at unusual high molecular weight exists (~180 000 g/mol).

Therefore the thermodynamic quality of this solvent is better than ethylene glycol but not as good as H_2O. An intersection point at unusual high molecular mass region M = 150 000 - 200 000 g·mol^{-1} from the relationship for water, ethylene glycol and 0.1 M Na_2SO_4 can be seen from Fig. 1. It has been shown that the point of intersection between the relationships for H_2O, ethylene glycol and formamide is in the same range[1,11]. For most polymer solvent systems this intersection point is normally observed at a molecular mass region of about 10 000 g/mol. The interpretation of this effect is based on the assumption, that a more rigid chain conformation of considerable chain length may exist, where the conformational stabilization is caused by intramolecular hydrogen bonds. Only samples of rather high molar mass provide flexibility enough to obtain a solution structure which reflects the the thermodynamic quality of the solvent.

Experimental

Preparation of Polymers : The polymers used for this investigation were prepared by free radical polymerization of acrylamide with H_2O_2 as initiator in water or a mixture of water and methanol. The conversion was kept below 25% to prevent branching or imidization. For details see[1,10]. To the 0.1 M Na_2SO_4 aqueous solution one drop of the biocide KATHON WT, Röhm GmbH, F.R.G., per liter was added. This is only necessary when GPC-experiments are carried out at the same time with the same solution to prevent a clogging of the GPC-columns[2].

Determination of the intrinsic viscosity: The $[\eta]$-values are determined in rotational viscosimeters (Zimm-Crothers and Low-Shear 100, Contraves AG, Zürich, CH.). These instruments are appropriate to measure at low shear rates (between 10^{-4} and 5 sec^{-1}) which is important, because a sample with $M_w = 7.9 \cdot 10^6 g \cdot mol^{-1}$ and c = 0.1 % in water exhibits a viscosity dependence on shear rate already at 70 sec^{-1} [1]. Capillary viscosimeters are working ordinary at higher shear rates (about at 2000 sec^{-1}).

Determination of M_w and dn/dc: The contamination of the aqueous solutions with dust, fibres and particles accumulated throughout the preparation of the samples and the solution is a main problem of light scattering. Therefore, a general applicable filtration method was tested and details are given elsewhere[9]. Using membrane filters the pore size should be about 2.5 times greater than $d_{equ,[\eta]}$, for details see[9].

Due to its rather high affinity to water, care has been taken to use dried samples for the dn/dc determination. Further, these solutions require dialysis equilibrium, because of the preferential adsorption of the specific components to the polymer in such mixed solvents. This has been done using collodium hulls (SM 13200, Sartorius, Göttingen, F.R.G.). Equilibrium requires a minimum dialysis time of 7 hours, therefore a dialysis time of about 12 hours was chosen.

To determine the correct dn/dc value, it is required for each concentration to measure the polymer solution inside against the corresponding solvent outside of the collodium hulls. The measurements were carried out with a Brice-Phoenix Diffential Refractometer at λ_0 = 632.8 nm and 298 K. The light scattering measurements were carried out with a low angle laser light scattering photometer KMX-6 (Chromatix, Sunny Vale, Calif., USA). In case of the sample with the lowest molar mass the determination of M_w was carried out in pure water using a wide angle photometer (Sofica-Photo-Gonio-Diffusometer 42000). Therefore the values of dn/dc and A_2 are not comparable with the other samples.

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