CHARACTERIZATION OF SALT STABLE, BIOLOGICALLY DEGRADABLE POLYMERS FOR COMMERCIAL APPLICATION IN EOR

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EOR encompasses a wide range of methods for recovering additional oil in place, of which polymer flooding is one special example[1]. It is applicable to oil fields with an oil viscosity of up to 150 mPas at a given oil field temperature. Although this seems to be a limitation, there are lots of important oil fields which meet these properties. Two examples are the oil fields in Libya which represent the largest resources in the Near East and the off-shore projects in the north sea. The oil of these fields is valuable because of its low sulfur content and its low viscosity which enables it to be easily processed into fuel.

In the past synthetic polymers, strictly speaking polyelectrolytes such as ionic polyacrylamide-derivatives, were used exclusively with success. The disadvantage of such polyelectrolytes however is an enormous viscosity loss in the presence of salts such as NaCl, $CaCl_2$, $MgCl_2$ etc.. Moreover, precipitation may occur in the presence of multivalent counterions like Ca^{2+} or Mg^{2+}, which may lead to reservoir plugging. An additional disadvantage is that these polymers are not biologically degradable.

In the last few years various field trials have been carried out with fermentation polymers instead of synthetic polyelectrolytes since these biopolymers do not possess the abovementioned negative properties. They stand out because of their physiological compatibility and their biological degradability. The entire production process leaves no environmentally harmful residues. Apart from this, fermentation polymers also possess extraordinary solution properties compared with synthetic polymers. For instance, xanthan exhibits a high water bonding capacity and a high viscosity yield. Meanwhile, the production costs for xanthan have been lowered considerably to a price level comparable with polyacrylamide-co-acrylates.

Depending on the fermentation conditions employed[2] (geometric ratios of reactor and stirrer, fermentation time, oxygen and nutrient supply, etc.) and the processing conditions (precipitation, purification, temperature treatment preshearing, etc.), very large differences in product properties may arise, the causes of which are not fully understood.

It was shown in contrast to previous works[3], that the xanthan molecule consists of four different monomer units and can therefore be described as a quaternary polymer[4] (fig. 1).
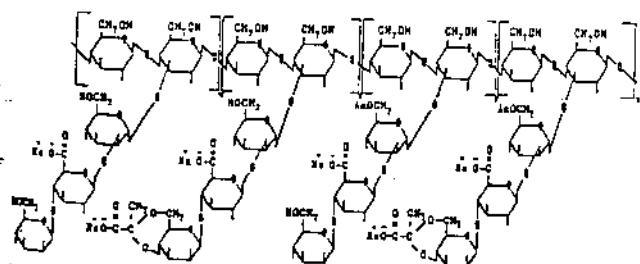
The secondary structure of native xanthan is known to be helical, but this ordered conformation is destroyed by lowering the salt content or raising the temperature of the solution. This conformational change can be detected by polarimetry and viscometry, for example in 0.01 M NaCl solution at a transition temperature of 55 °C.

To get a general idea of the influence of the chemical and steric microstructure of single molecules on the viscous and elastic solution properties, their exact determination is necessary. Although very comprehensive studies have been carried out on various xanthans by several research groups, it has not yet been possible to draw general valid conclusions about the relation between molecular parameters and solution properties, since comparability of the results is complicated by the differences in production and processing techniques.

In order to investigate the influence of the chemical structure, the acetyl and pyruvate content of more than 50 laboratory and commercially available xanthan samples from different manufacturers were determined by enzymatic analysis. Nine samples were chosen for further investigations, including more exact chemical analysis by ^1H NMR spectroscopy. In addition to the molar mass M_w, information on the solution structures of the xanthans was obtained with the aid of viscometry, low angle (LALLS) and multi-angle laser light scattering (MALLS) investigations. The results are summarized in tab. 1.

Tab. 1: Results of the acetyl (Ac) and pyruvate (Py) content determination by ^1H NMR spectroscopy and of viscometric and light scattering investigations.

Sample	Ac_{NMR} (mol%)	Py_{NMR} (mol%)	$[\eta]$ (ml/g)	$M_{w\ LALLS}$ (10^6 g/mol)	$M_{w\ MALLS}$ (10^6 g/mol)	R_G nm
A1	32	27	4225	8.8	-	-
B1	25	57	9047	5.7	4.3	240
B2	95	67	7651	5.8	5.0	183
B3	89	73	8380	5.5	4.1	243
B4	10	53	8154	6.9	5.1	157
C1	84	51	4923	6.4	-	-
C2	93	44	3803	7.4	-	-
C3	96	42	3907	5.3	-	-
C4	98	46	5142	5.6	-	-

All the angle dependent scattering curves, obtained by a Zimm evaluation of the MALLS measurements, show a prominent curvature. A comparison of these curvatures with theoretical scattering functions for different molecular structures (fig. 2) and a quantitative evaluation for semiflexible chains according to Peterlin[5], yields further information about the solution structure and the flexibility of the xanthan molecule[6].
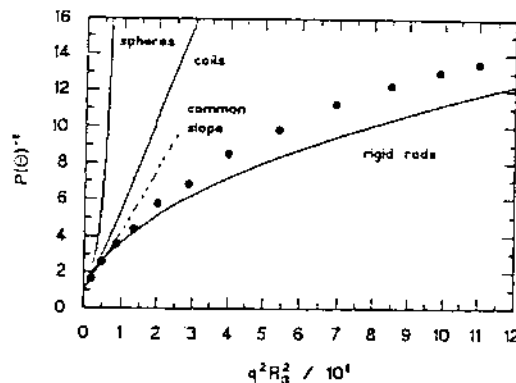

Fig. 1: Structural formula of xanthan as a quaternary polymer

Fig. 2: Comparison of the measured scattering curve with theoretical scattering functions for different molecular structures. P(θ) is the scattering function and $q=(4\pi/\lambda)\sin(\theta/2)$.

The viscoelastic properties were examined under various conditions. One important point of interest is the behaviour of the polymer solution under injection and field conditions. Whereas the solution has to be injectable without high pressure loss at the injection well, it should keep its high viscosity level under field flow conditions. These properties can only be investigated regarding two different material functions. Under high shear rates the elastic properties, represented by the first normal stress difference, dominate the flow behaviour. Under these conditions PAAm shows very high normal stress differences. In contrast xanthan solutions show nearly no shear-induced elasticity under the same conditions (fig. 3).
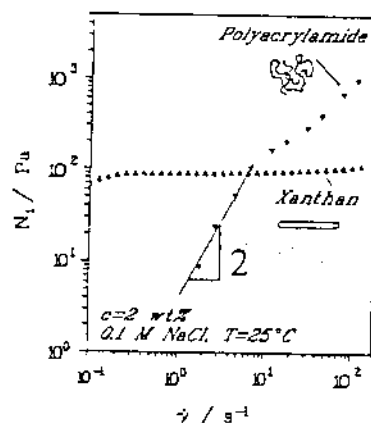

Fig. 3: Comparison of the elastic properties of polyacrylamide and xanthan.

Under field flow conditions the mobility, which depends on the viscosity, is the important property of the polymer solution.
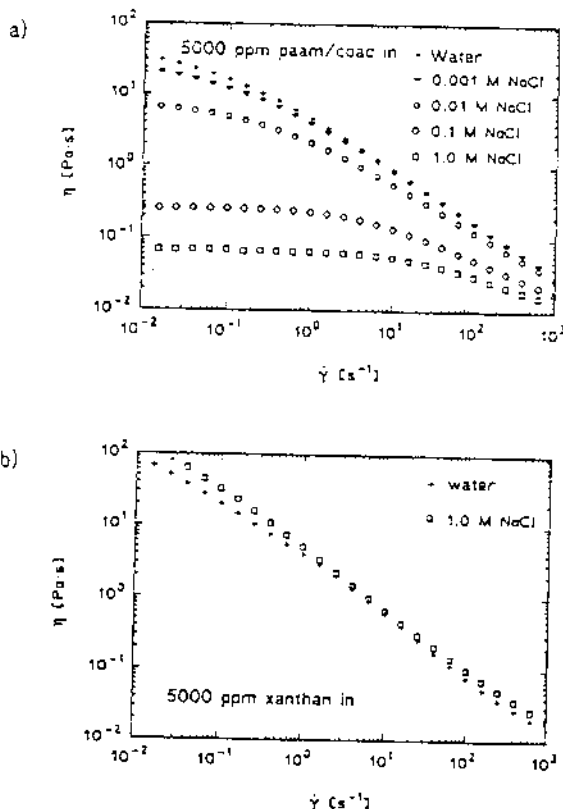
a)

b)

Fig. 4: Shear flow experiments of PAAm/AAc (a) and xanthan (b) in different salt concentrations.

Rotational shear experiments prove the extraordinary salt stability of xanthan (fig. 4 a,b). In addition to its larger viscosity yield xanthan also exhibits a better injectability compared with polyacrylamides[7] (fig. 5).
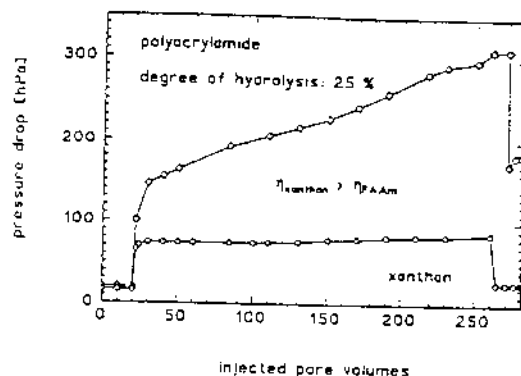

Fig. 5: Injectivity tests of xanthan and polyacrylamide.

However porous media flow cannot be quantitatively described by simple shear flow because the solution viscosity inside a porous media is the sum of the shear viscosity and the elongational viscosity. It is impossible to distinguish between viscous and elastic properties in elongational flow experiments, in which the pressure drop, being proportional to the solution viscosity, is detected over a given length of porous medium. Therefore an attempt should be made to correlate the results of the elongational flow measurements with the viscous and elastic material functions that can be obtained from oscillatory experiments.

In conclusion, this contribution shows that the structure of xanthan is more complex than has been described in the literature to date. Based on this knowledge it should be possible to establish structure property relationships to understand the macroscopic flow behaviour under field flow conditions in more quantitative terms.

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