Macromol. Symp. ***171****, 189–200 (2001)*

Crosslink Nature in Cr(III)-Polyacrylamide Gels

Klaas te Nijenhuis

Laboratory of Polymer Materials and Polymer Engineering, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, NL 2628 BL, Delft, The Netherlands

SUMMARY: The equilibrium constants of various candidates for the crosslinking reaction between chromium(III) and partly hydrolysed polyacrylamide have been calculated. For this purpose use has been made of a) the crosslinking index in gels to calculate the concentration of crosslinks, b) pH-dependent concentrations of various hydrolysis products of Cr^{3+} ions and c) pH-dependent concentration of free carboxylic acid anions. The conclusion is that the crosslinks consist of two carboxylic acid anions coordinated with the dimerisation product of the Cr^{3+} ions.

Introduction

The purpose of the present paper is to gain new insights into the network properties of partially hydrolysed polyacrylamides (HPAAm) crosslinked in an aqueous solution of a chromium(III) salt, and especially into the crosslink nature. This system has already been investigated extensively in the literature, in particular by those involved in the oil producing industry.[1-12] Hydrophilic high molecular weight polymer solutions are used in the shut-off of highly permeable rocks, in order to prevent permeation of the water that is used in the production of crude oil. Hence, networks have to be formed just there where they are needed and not at an early time during flow of the polymer solution to its proper place. For this reason, crosslinking processes with a certain time delay have been sought, in order to be sure that crosslinking does not already proceed in rock formations where it is not desired. Several methods have been proposed to achieve the required time delay. One of them makes use of ammonium or sodium dichromate, $(NH_4)_2Cr_2O_7$ or $Na_2Cr_2O_7$, respectively, which in the presence of a reducing agent like sodium hydrogen sulfite, $NaHSO_3$, produces Cr(III) at a certain rate. Another method is the addition of Cr(III) in the presence of sodium acetate or sodium citrate. It is known that Cr^{3+} forms complexes with these species, called ligands and abbreviated as L. The Cr^{3+} ion forms an octahedral complex with the ligands, in which six ligands are at the vertices of an octahedron.[13] Also, water molecules form those complexes with Cr^{3+} ions. Hence, in principle, water molecules have to be incorporated into the chemical reaction equations:

CCC 1022-1360/00/$ 17.50+.50/0

$$\mathrm{Cr(H_2O)_6} + n\,\mathrm{L} \rightleftharpoons \mathrm{Cr(H_2O)_{6\text{-}\mathit{n}}(L)_\mathit{n}} + n\,\mathrm{H_2O}$$

For the sake of simplicity we will henceforth omit the presence of the water ligands in the Cr(III) complexes, but we have to bear in mind that they are present to complete the octahedral complex. The complex constants may be rather high, depending on the kind of ligand. If the complexation of Cr^{3+} with the COO^- groups of HPAAm, that form the crosslinks, is strong enough, then gels may be formed with Cr^{3+} still present in the solution, Hence, the chromium/ligand complex will dissociate and crosslinks will be formed. In that case the overall reaction will be:11)

$$\mathrm{Cr(L)_\mathit{m}} + m\,\mathrm{P\text{-}COO} \rightleftharpoons \mathrm{Cr(P\text{-}COO)_\mathit{m}} + m\,\mathrm{L}$$

If the decomplexation reactions are slow reactions, then the crosslinking process will be delayed. It is understandable that the crosslinking reactions are relatively slow because the concentration of free Cr^{3+} ions is very low.

Nature of the Crosslinks

The nature of the crosslinks is still a matter of debate. Crosslinks are formed by a complexation of some Cr(III) ion with the acrylamide polymer. As it is known that crosslinking does not proceed in unhydrolysed polyacrylamide, the conclusion must be that carboxylic acid groups are involved in the complexation between Cr(III) and HPAAm. Moreover, crosslinking does not proceed at low pH, further supporting the conclusion that carboxylic anions are the source of the crosslinking process between Cr(III) and HPAAm. On the other hand, networks are not formed at high pH, where Cr(III) is hydrolysed to $Cr(OH)_3$ and $Cr(OH)_4^-$ ions and eventually to CrO_3^{3-} ions.

The purpose of the present paper is a) to gain insight into the nature of the crosslinks, i.e. the complexation between Cr(III) and HPAAm, and b) to calculate the equilibrium constant of the crosslink formation, which in general is given by:

$$K_{crl} = \frac{[\text{crosslink}]}{[\mathrm{Cr}_p(\mathrm{OH})_q^{(3p-q)}]^a[\mathrm{COO}^-]^b}$$

Calculation of the Equilibrium Constant

In order to be able to determine the values of *a*, *b*, *p* and *q* in the preceeding equation and to calculate the equilibrium constant, one has to calculate a) the concentration of crosslinks present in the network formed, b) the concentration of COO^- groups and c) the concentration of the involved free Cr^{3+} ions or other Cr(III) ions. In the literature, several Cr(III) species were mentioned as candidates for the crosslinking reaction: free Cr^{3+} ions (e.g. ref.[9)]), colloidal $Cr(OH)_3$ (e.g. refs.[7)] and [9)]) and the dimer $Cr_2(OH)_2^{4+}$ (e.g., refs.[7)] and [14)]). Also, see Fig. 1. Our aim is to distinguish between the involvment of the various Cr(III) species.

The concentration of crosslinks can be calculated from network models developed for the calculation of network parameters during the crosslinking of high molecular weight polymers. The concentration of Cr(III)-species present in solution may be calculated from protolysis or hydrolysis constants of the Cr^{3+} ions, known from literature.[14-19)] The concentration of COO^- may be calculated if one knows the (apparent) protolysis constant of the carboxylic acid groups along the polymer chain and if the ionic strength is high enough to protect the ions against mutual interaction.

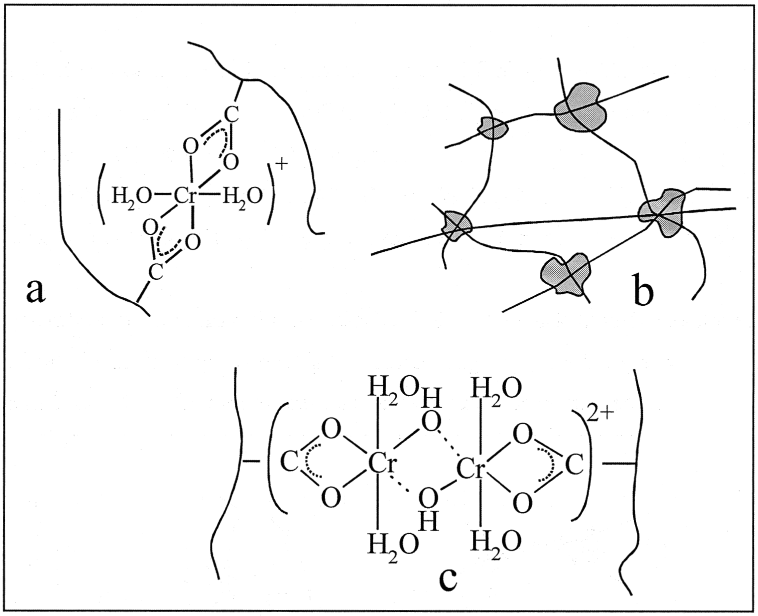

Fig. 1: Three crosslink structures in Cr(III)-HPAAm gels, as found in literature: a) mentioned by Lockhart[9)]; b) crosslinks are formed on colloidal particles of chromium(III) hydroxyde[9)]; c) dimeric chromium, mentioned by several authors as a crosslinking candidate.[1,7,14,34,35)]

Calculation of Concentration of Crosslinks

The molar concentration of crosslinks follows from the crosslinking index:

$$[\text{crosslinks}] = \bar{\gamma}_w \times \frac{2}{f} \times \frac{c}{\overline{M}_w} \tag{1}$$

where $\bar{\gamma}_w$ = weight-average crosslinking index;

f = crosslink functionality;

c = polymer concentration /kg m^{-3};

$\overline{M}_w$ = weight-average molecular mass /kg mol^{-1}.

The weight-average crosslinking index is equal to the average number of crosslinks per weight-average primary polymer molecule in the network system as a whole, i.e. sol fraction (w_s) + network fraction (w_n).[20-22] The crosslink functionality is equal to the number of polymeric chains leaving a crosslink. The present author extended the network model of Flory and Stockmayer of the 1940's,[20-24] where the crosslinking index was calculated for networks formed from monodisperse polymer with tetrafunctional crosslinks, to polydisperse primary polymers that are crosslinked with *f*-functional crosslinks.[25-32] For a Schulz-Flory distribution with a polydispersity index $D \equiv \overline{M}_w / \overline{M}_n = 2$, the relationship between $\bar{\gamma}_w$ and the sol fraction is found to be:

$$\bar{\gamma}_w = \frac{2 \cdot (w_s^{-0.5} - 1)}{1 - w_s^{0.5f-1}} \tag{2}$$

whereas the relationship between the equilibrium shear modulus and the sol fraction is:

$$\frac{G_e \overline{M}_w}{4cRT} = (1 - w_s^{0.5f}) \left[\frac{w_s^{-0.5}(1 - w_s^{0.5f})}{1 - w_s^{0.5f-1}} \cdot \frac{f-2}{f} - 1 \right] \tag{3}$$

Hence, from the equilibrium shear modulus, the sol fraction can be calculated and subsequently the weight-average crosslinking index. Thus, we are now able to calculate the crosslink concentration.

Calculation of the Concentrations of the Various Cr(III) Ions

In aqueous Cr(III)-solutions the Cr^{3+} ions have undergone many hydrolysis reactions, each with its own equilibrium constant. They are listed along with the pK values mentioned in ref.[19]:

$$Cr^{3+} + H_2O \rightleftharpoons Cr(OH)^{2+} + H^+ \qquad pK_1 = 4.20$$

$$Cr^{3+} + 2H_2O \rightleftharpoons Cr(OH)_2^+ + 2H^+ \qquad pK_2 = 10.40$$

$$Cr^{3+} + 3H_2O \rightleftharpoons Cr(OH)_3 + 3H^+ \qquad pK_3 = 18.70$$

$$Cr^{3+} + 4H_2O \rightleftharpoons Cr(OH)_4^- + 4H^+ \qquad pK_4 = 18.80$$

$$2Cr^{3+} + 2H_2O \rightleftharpoons Cr_2(OH)_2^{4+} + 2H^+ \qquad pK_5 = 5.30$$

$$3Cr^{3+} + 4H_2O \rightleftharpoons Cr_3(OH)_4^{5+} + 4H^+ \qquad pK_6 = 8.70$$

$$4Cr^{3+} + 6H_2O \rightleftharpoons Cr_4(OH)_6^{6+} + 6H^+ \qquad pK_7 = 13.90$$

where, e.g., pK_1 is:

$$pK_1 \equiv -\log_{10}\left[\frac{[Cr(OH)^{2+}][H^+]}{[Cr^{3+}]}\right]$$

The various equilibrium constants lead to the following pH-dependent concentration ratios:

$$\log([Cr(OH)^{2+}]/[Cr^{3+}]) = -\ 4.20 + 1 \times pH$$

$$\log([Cr(OH)_2^{+}]/[Cr^{3+}]) = -\ 10.40 + 2 \times pH$$

$$\log([Cr(OH)_3]/[Cr^{3+}]) = -\ 18.70 + 3 \times pH$$

$$\log([Cr(OH)_4^{-}]/[Cr^{3+}]) = -\ 18.80 + 4 \times pH$$

$$\log([Cr_2(OH)_2^{4+}]/[Cr^{3+}]^2) = -\ 5.30 + 2 \times pH$$

$$\log([Cr_3(OH)_4^{5+}]/[Cr^{3+}]^3) = -\ 18.70 + 4 \times pH$$

$$\log([Cr_4(OH)_6^{6+}]/[Cr^{3+}]^4) = -\ 13.90 + 6 \times pH$$

If the total Cr(III)-concentration is known, then the various concentrations of Cr(III) species can be calculated, because we also have an expression for the total Cr(III)-concentration:

$$[Cr(III)] = [Cr^{3+}]+[Cr(OH)^{2+}]+[Cr(OH)_2^{+}]+$$

$$+[Cr(OH)_3]+[Cr(OH)_4^{-}]+2[Cr_2(OH)_2^{4+}]+3[Cr_3(OH)_4^{5+}]+4[Cr_4(OH)_6^{6+}]$$

If the crosslink concentration is known and, hence, the amount of chromium needed to form the complex (in this case of Cr^{3+} and $Cr_2(OH)_2^{4+}$), then the remaining overall Cr(III) concentration can be calculated. This concentration has to be used to calculate the concentration of the eight mentioned Cr(III) species. For an aqueous solution of 100 ppm Cr(III), results are shown in Fig.2 as a function of pH. For low pH (less than 4) the concentration of Cr^{3+} is almost equal to the total Cr(III) concentration, whereas at high pH (larger than 5) this concentration decreases linearly with pH. An important conclusion is also that the concentration of uncharged $Cr(OH)_3$ is too low to precipitate colloidally from the solution, because its solubility is approximately 4.5×10^{-8} mol l^{-1}. From similar calculations it became clear that for Cr(III) concentrations smaller than 1300 ppm there will be no precipitation of $Cr(OH)_3$, and at pH=5 there will never be any precipitation of $Cr(OH)_3$. This means we can conclude that crosslinking does not proceed through colloidal chromic hydroxyde.

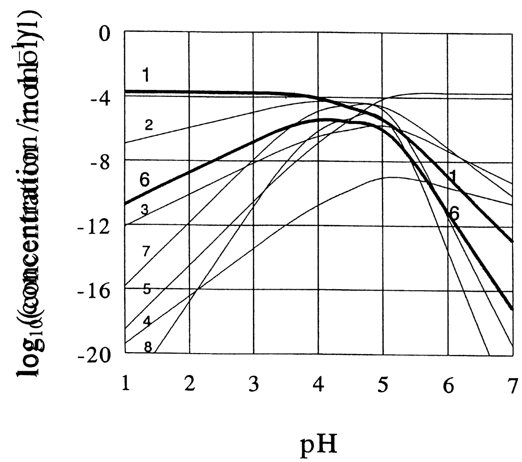

Fig. 2: pH-dependent concentrations of various hydrolysis products of Cr^{3+} in a 100 ppm aqueous Cr(III)-solution: (1) Cr^{3+}; (2) $Cr(OH)^{2+}$; (3) $Cr(OH)_2{}^+$; (4) $Cr(OH)_3$; (5) $Cr(OH)_4{}^-$; (6) $Cr_2(OH)_2{}^{4+}$; (7) $Cr_3(OH)_4{}^{5+}$ and (8) $Cr_4(OH)_6{}^{6+}$.

Calculation of the Concentration of Carboxylic Anions

In a weak monoprotic acid HA we have the equilibrium:

$$HA \rightleftharpoons H^+ + A^-$$

with the equilibrium constant:

$$pK_a = -\log_{10}\left[\frac{[A^-][H^+]}{[HA]}\right] \tag{4}$$

In partially hydrolysed polyacrylamide we have many carboxylic acid groups along the polymer chain and the ionisation of a carboxylic acid group depends on its surroundings. However, upon adding salt in order to increase the ionic strength, the ionisation of the carboxylic acid groups no longer depends on their surroundings. According to Morawetz,[33)] the so-called apparent ionisation constant of poly(acrylic acid) depends on the ionic strength and on the degree of ionisation. For an ionic strength of 0.5 (i.e., approximately 30 g NaCl l^{-1}) pK_{app} varies between 4.5 and 5.5 (pK for acetic acid is 4.75) for degrees of ionisation between 0.1 and 0.8 and, accordingly pH varies between 3.5 and 6.1. Hence, it is not unrealistic to use pK=5 for HPAAm solutions as an approximation to calculate the concentration of the carboxylic acid anions. For a concentration of p ppm (i.e. $g\,m^{-3}$) HPAAm with a degree of hydrolysis of q% the total concentration of carboxylic acid is $pq/7100000$ mol l^{-1}. The concentration of carboxylic acid anions in mol l^{-1} is then given by:

$$[\mathrm{COO^-}] = \frac{pq}{71\times10^5(1+10^{\mathrm{pK-pH}})} \qquad (5)$$

where 71 is the approximate molecular weight of a monomeric unit (in principle the average molecular weight of a monomeric unit = $0.72q+0.71(1-q)\approx71$).

Application to Literature Results

In order to calculate the equilibrium constant of the crosslinking process, values of the equilibrium shear modulus are needed in a HPAAm/Cr(III)-system without the addition of complexing agents like, e.g., acetate or citrate. Moreover, Cr(III) must not be added as $CrCl_3$, because Cr^{3+} forms also complexes with the chloride ion.3,4) It is known that chromic nitrate is a good candidate, because the nitrate ions do not act as ligands for the chromic cation3). Hence, use has been made of measurements as published by

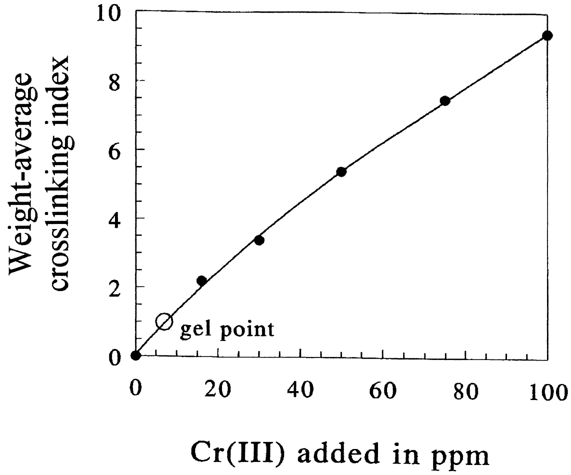

Fig. 3: Weight-average crosslinking index, $\bar{\gamma}_w$, of aqueous Cr(III)-HPAAm gels vs. amount of Cr(III) concentration added. Calculated from measurements reported by Gallino, Molinari and Lockhart.10) The gel point is reached at 7 ppm Cr(III), where $\bar{\gamma}_w$ =1.

Gallino, Molinari and Lockhart10) in their paper concerning "*Rheological studies of the gelation kinetics of Cr^{3+}- polyacrylamide solutions*". In their Figure 5, are presented equilibrium shear moduli of aqeous gels formed from 8000 ppm of 2.2% hydrolysed polyacrylamide with a weight-average molecular weight of 6×10^6 g mol^{-1} in the presence of 15 to 100 ppm Cr(III) at a pH varying from 4.8 to 5. From their reported values of G_e, the crosslinking index is calculated, assuming the polydispersity index to be 2. Results for $\bar{\gamma}_w$ are shown in Fig. 3 as a function of Cr(III) added. In this figure, the point (0,0) has also been added, because no crosslinks are formed (i.e. $\bar{\gamma}_w=0$) without addition of Cr(III). It appears that the gel point is reached ($\bar{\gamma}_w=1$) at a Cr(III) concentration of 7 ppm. Moreover, from the Cr(III) concentrations are calculated the concentrations of free chromic ion and of dimer. With the aid of Eq. (4), the concentration of the carboxylic acid anions at pH=5 is calculated to be 1.24×10^{-3} mol l^{-1}. The results of calculations are shown in Table 1.

Table 1: Data needed to calculate crosslink equilibria according to measurements reported in ref.[10)]

[Cr(III) added] /ppm	100	75	50	30	15
G_e /N m^{-2}	19.8	14.2	8.2	3.2	0.9
$\bar{\gamma}_w$	9.4	7.5	5.4	3.4	2.2
$10^6\cdot$[crosslinks] /mol l^{-1}	6.27	5.00	3.60	2.27	1.47
$10^4\cdot$[Cr(III) added] /mol l^{-1}	19.2	14.2	9.62	5.77	2.88
$10^6\cdot[Cr^{3+}]$ /mol l^{-1}	11.2	10.1	8.87	7.38	5.56
$10^7\cdot[Cr_2(OH)_2^{4+}]$ /mol l^{-1}	62.1	51.1	39.2	27.1	15.5
$10^3\cdot[COO^-]$ /mol l^{-1}	1.24	1.24	1.24	1.24	1.24

We now are able to calculate equilibrium constants of possible crosslinking equilibria:

$$K_1 = \frac{[\text{crosslinks}]}{[\text{Cr}^{3+}][\text{COO}^-]^2} \tag{6}$$

$$K_2 = \frac{[\text{crosslinks}]}{[\text{Cr}^{3+}]^2[\text{COO}^-]^2} \tag{7}$$

$$K_3 = \frac{[\text{crosslinks}]}{[\text{Cr}_2(\text{OH})_2^{4+}][\text{COO}^-]^2} \tag{8}$$

Table 2: Equilibrium constants of the formation of various crosslinks.

[Cr(III) added] /ppm	100	75	50	30	15
$10^{-5}\cdot K_1$ /l^2 mol^{-2}	3.7	3.2	2.6	2.0	1.7
$10^{-10}\cdot K_2$ /l^3 mol^{-3}	3.3	3.2	3.0	2.7	3.1
$10^{-5}\cdot K_3$ /l^2 mol^{-2}	6.6	6.4	6.0	5.5	6.1

In Table 2, the values of the three candidate equilibrium constants are shown for the various amounts of Cr(III) added. It is clear that K_1 does not have a constant value. Hence, the corresponding reaction drops out as a candidate for the crosslinking mechanism. K_2 and K_3 have more constant values. Their average values are:

$K_2 = 3.1 \times 10^{10}$ l^3 mol^{-3} with a standard deviation of 0.2×10^{10}

$K_3 = 6.1 \times 10^{5}$ l^2 mol^{-2} with a standard deviation of 0.4×10^{5}

According to these equilibrium constants, the crosslink concentration is proportional to $[Cr^{3+}]^2$ or to $[Cr_2(OH)_2{}^{4+}]$. Because the concentration of the carboxylate anions is almost constant (only a very small fraction of the anions are used to form crosslinks), double logarithmic plots of the crosslink concentration versus the free chromic cation or dimer concentrations should yield straight lines with slopes equal to 2 or 1, respectively. In Fig. 4 those plots are shown. The slopes of the straight lines are equal to 2.12 and 1.06, respectively. From these results we can conclude that the equilibrium constant of the crosslinking reaction is proportional to $[Cr^{3+}]^2$ or to $[Cr_2(OH)_2{}^{4+}]$. Because of the quadratic dependence of the chromic dimer on $[Cr^{3+}]$, it is obvious that both K_2 and K_3 can be the real equilibrium constant. However, if one of the two is really the equilibrium constant, then the other one will be pH-dependent.

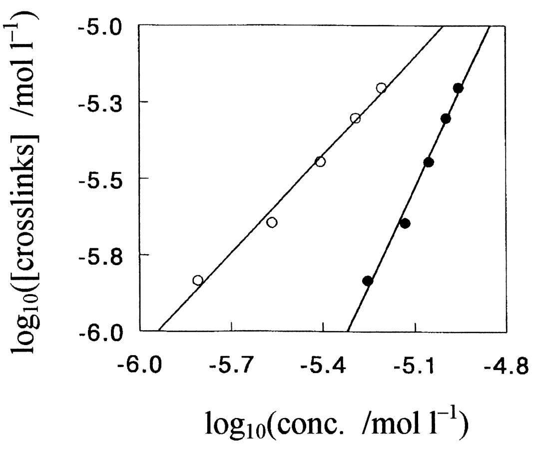

Fig. 4: Double logarithmic plot of crosslink concentration in the gels mentioned in Fig. 3 vs. Cr^{3+} concentration (●) and vs. $Cr_2(OH)_2{}^{4+}$ concentration (O).

In order to distinguish between them, measurements are needed at a different pH. Such measurements were reported by Allain and Salomé$^{6)}$ in their paper concerning *"The critical behaviour of the rheological properties versus crosslink concentration"*. They reported for a

2500 ppm aqueous solution of 24% hydrolysed HPAAm, with a weight-average molecular weight of 6×10^6, equilibrium values of the shear modulus for Cr(III) concentrations varying from 4 to 5×10^{-4} mol l^{-1} (see their Fig. 6b). Unfortunately, they did not mention the pH of the solutions. However, the concentration of acid groups in the HPAAm solutions is equal to *pq*/71000 (see earlier), corresponding to 8.45×10^{-3} mol l^{-1}. By making use of Eq. (4) and again assuming pK=5, it is easy to calculate that for the solutions $[H^+]=[COO^-]=2.96\times10^{-4}$ mol l^{-1} and pH=3.5. We now are able to calculate the various concentrations needed to calculate K_2 and K_3. The results of the calculations are shown in Table 3. From the results presented, it appears that the average values of K_2 and K_3 are:

$K_2 = 2.9 \times 10^7$ $l^3 mol^{-3}$ with a standard deviation of 0.2×10^7

$K_3 = 5.7 \times 10^5$ $l^2 mol^{-2}$ with a standard deviation of 0.5×10^5

By comparing these results with the previous results we come to the conclusion that K_2 is pH-dependent and that K_3 is independent of pH. Hence, K_3 is the real equilibrium constant with a value of $(6\forall0.5)\times10^5$ $l^2 mol^{-2}$. It is amazing that the values of the equilibrium constants from both series of measurements, with such clear differences in conditions, are so closely in agreement.

Table 3: Data needed to calculate crosslink equilibria according to measurements reported in ref.$^{6)}$

[Cr(III) added] /ppm	26	23.4	20.8
$10^2 \cdot G_e$ /N m^{-2}	4.8	2.2	0.9
$\bar{\gamma}_w$	1.55	1.40	1.28
$10^7\cdot$[crosslinks] /mol l^{-1}	3.23	2.92	2.67
$10^4\cdot$[Cr(III) added] /mol l^{-1}	5.0	4.5	4.0
$10^4\cdot[Cr^{3+}]$ /mol l^{-1}	3.77	3.44	3.10
$10^6\cdot[Cr_2(OH)_2^{4+}]$ /mol l^{-1}	7.12	5.93	4.81
$10^4\cdot[COO^-]$ /mol l^{-1}	2.96	2.96	2.96
$10^{-7}\cdot K_2$ /l^3 mol^{-3}	2.6	2.8	3.2
$10^{-5}\cdot K_3$ /l^2 mol^{-2}	5.2	5.6	6.3

Thus, we now come to the important conclusion that the crosslinks consist of a complex of $Cr_2(OH)_2^{4+}$ and two COO^- ions (see Fig. 1c). It is not clear, however, whether the crosslinks are formed via a mechanism where first two Cr^{3+} ion complexes react, each with a COO^- anion of a polymer chain, followed by the formation of a crosslink via so-called olation and oxalation reactions,$^{1)}$ or whether the $Cr_2(OH)_2^{4+}$ cation reacts directly with two COO^-anions to form the crosslink. This problem cannot be solved from equilibrium thermodynamics, but from the kinetics of the crosslinking process. This in general can be done by measurement of the gel shear modulus as a function of time, assuming that the number of crosslinks is proportional to this equilibrium modulus. It would be more realistic, however, to make use of the crosslinking index, as calculated from the gel shear modulus, because this parameter really is proportional to the number of crosslinks.

Conclusions

A method has been described to calculate the equilibrium constant of the crosslinking reaction in the aqueous system Cr(III)/HPAAm and to determine the nature of the crosslinks formed. It appears that the crosslinks consist of a complex of the dimerisation product of Cr^{3+} ions and two carboxylic acid anions. This is one of the candidates mentioned in literature for the crosslink structure. This structure is also assumed to be the structure formed during the chromium(III) tanning process of leather at low pH.$^{34,35)}$

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