Physical properties of carboxymethyl cellulose (I): solubility, conformation and supramolecular aggregation.

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This review summarises current understanding of the solubility, supramolecular aggregation and dilute solution conformation of carboxymethyl cellulose, an ionic cellulose ether with many applications in industrial products. We focus on how substitution patterns control solubility and supramolecular structure. Experimental evidence supports the majority of CMC chains being molecularly dissolved with a smaller population co-existing as fringed micelle aggregates when there is approximately less than one carboxymethyl group per monomer. The influence of chemical heterogeneity on crystallinity, solubility and supramolecular aggregate structures discussed together with its consequences for the transition from molecular solutions to colloidally dispersed ones. Methods used to characterise CMC, including scattering, viscosimetry and osmometry are surveyed with attention to their sensitivity to substitution patterns and chain heterogeneity. Past, current and emerging applications are summarised. Recommendations for characterisation of physical properties such as molar mass and intrinsic viscosity are given.

I. INTRODUCTION

Carboxymethyl cellulose, typically used as the sodium salt, is an anionic cellulose ether and the most widely applied ionic cellulose derivative. It behaves as a weak, semiflexible polyelectrolyte and is used in many formulated products, including foods, beverages, toothpastes, adhesives and drilling muds.

Industrial production of CMC uses the slurry process: purified cellulose (typically from wood pulp or cotton linters) is suspended in an organic solvent such as isopropanol followed by the addition of NaOH.[1–5] This produces a slurry that swells but does not dissolve cellulose.[6] Chloroacetic acid or its sodium salt is added to introduce carboxymethyl groups via etherification. The structure of the NaCMC monomer is shown in Figure 1. R can be H or CH_2COONa. The number of carboxymethyl groups per monomer (maximum of 3) is known as the degree of substitution (DS).

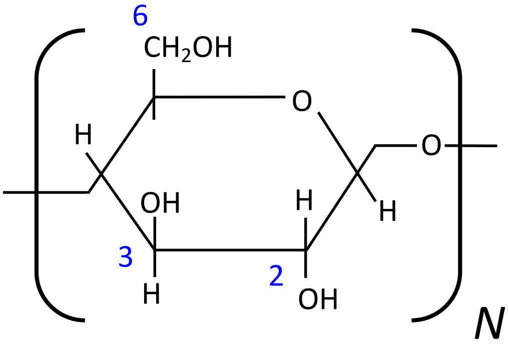

FIG. 1. Repeating unit of cellulose. The carbon to which each of the three OH is attached is labelled by the blue numbers.

Commercial NaCMC polymers typically have DS = 0.6–1.4 and molar masses of 60-1200 kg/mol. DS refers to the average over all chains in the sample, but there exists a distribution of DS values for different chains (first order heterogeneity). Further, within a single chain, different regions may exhibit different substitution patterns (second order heterogeneity). As the average DS increases, the substitution becomes more homogeneous. Samples with DS $\gtrsim 1$ are labeled 'highly substituted' and posses a relatively uniform substitution along the chain that hinders inter-chain associations. Solutions of such CMCs are shear thinning but do not gel at high concentrations and are non-thixotropic.[7–11] These are usually marketed as possessing 'smooth' flow behavior.

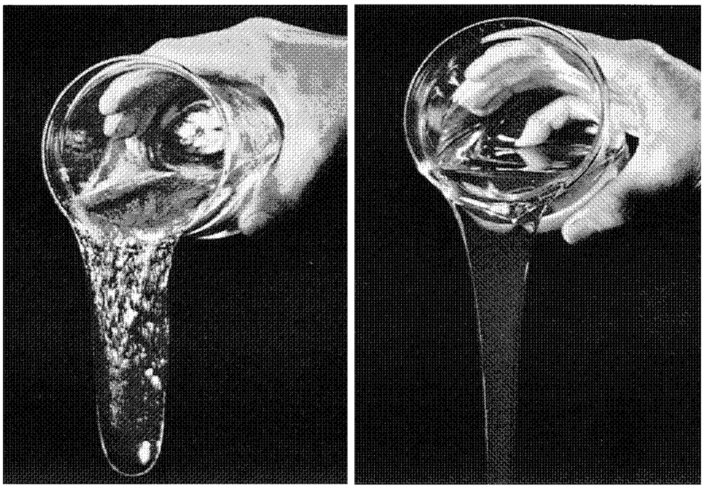

FIG. 2. Illustration of flow properties of carboxymethyl cellulose with heterogeneous (top) and homogeneous (bottom) substitution patterns. Figure reproduced from [12].

Samples with DS ≈ 0.7-0.9 typically contain around 20 to 40% unsubstituted monomers, leading to the formation of unsubstituted blocks along the chain, unless specific synthesis methods are used to ensure uniformity of substitution.[13–17] Weakly substituted samples form physical gels at high concentrations (typically above a few weight percent) and can exhibit thixotropy, where the solution viscosity depends on sample's shear history.

The difference in flow behaviour between highly substituted and weakly substituted samples can be gauged

TABLE I. Typical NaCMC quality grades and composition. Adapted from ref. [2]

Grade	Example application areas	CMC content [wt %]	Salt content [wt %]
Technical	detergents, mining flotation	< 75	> 25
Semi purified	oil and gas drilling muds	75–85	15–25
Purified	paper coating, textile sizing and printing, ceramic glazing, oil drilling muds	> 98	< 2
Extra purified	food, toothpaste, pharmaceuticals	> 99.5	< 0.5

by a simple proto-rheological experiment[18] shown in fig. 2. A solution of a highly substituted CMC flows as a homogeneous viscous liquid while that of a weakly substituted grade displays high elasticity and inhomogeneous flow behaviour.

Commercial grades of CMC are divided into technical, semi-purified, purified and extra-purified or food grade, see table I. The main impurities are sodium chloride and sodium glycoate, see refs. [2, 19] Applications in food, drinks and pharmaceutical products typically require high purity grades while detergents and drilling fluids normally employ lower purity, cheaper grades. Some physical properties of NaCMC are listed in table II

TABLE II. Properties of extra-purified commercial NaCMC grades. Data from refs. [12, 20–22]

Property	Value
Bulk Density (powder) [g/mL]	0.5-1
Monomer molar mass	$162 + 81\times\mathrm{DS}$
Partial molar volume [$\mathrm{cm^3 mol^{-1}}$]	$92.4 + 26.5\times\mathrm{DS}$
Partial molar adiabatic compressibility [$\mathrm{cm^3 mol^{-1} bar^{-1}}$]	$-(22.2 + 35.9\times\mathrm{DS})$
Length of chemical monomer	$\simeq 0.5$ nm
Intrinsic dissociation constant	3-3.4
pH (1 wt% solution)	8
Surface tension	not surface active
Refractive index	$\simeq 1.51$
Film tensile strength	$18 - 15$ kPa

Scope of this review. Several reviews have addressed aspects of CMC applications. The survey by Feddersen[12] examined a broad range of industrial uses, as did other early reviews.[23–25] Recent reviews[4, 26–32] have focused on academic research on and potential applications of CMC and its derivatives but have not examined actual industrial practices. A survey of this type would help academic researchers understand current industrial challenges. The most extensive modern review covering physical properties of CMC is ref. [33].

Here we provide an overview of how chemical composition governs solubility, aggregation and supramolecular structure. The relationship of these with the flow properties of concentrated solutions and gels will be discussed in a follow up manuscript. We emphasise areas where combining or re-analysing data from multiple sources yields new insights. Ways to improve research on CMC solutions and gels are outlined in the conclusions. Applications are summarised, from the historical development of CMC to current industrial uses.

II. HISTORICAL AND ECONOMIC ASPECTS

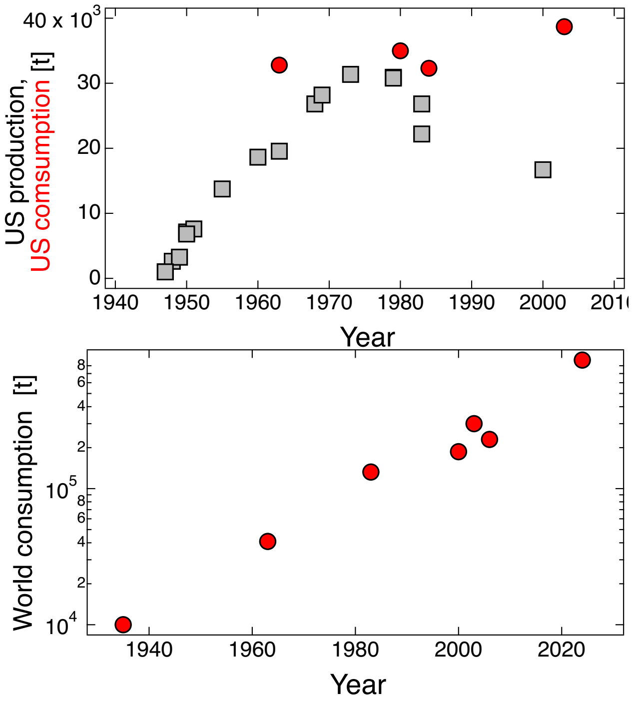

FIG. 3. CMC consumption and production in the US (top) and worldwide (bottom). Data from [24, 25, 34–39].

Sodium carboxymethyl cellulose (NaCMC), first synthesised over 100 years ago in Germany by Jansen[40] as a gelatin substitute, gained industrial relevance in the 1930s in detergent formulations under the name Tylose HBR, a low purity $\simeq 30\%$ grade, when it was found that addition of CMC to detergents reduced the amount of surfactant required for washing. During and after WWII it was used in detergent formulations in Germany[24], with an average annual production of 10^7 kg[41, 42], and in other European countries[43, 44], owing to the shortage of fatty acids[43]. A review of the academic literature and US patents up to 1945 shows a large number of proposed uses in the textile and paper industries.[23]. Many other uses, for example dye stabiliser or in paints due to its good film forming properties were also proposed. The US annual production was $\simeq 1 \times 10^6$ kg. A report by Hoyt in 1945 on the Kalle chemical plant of IG Farbenindustrie[41], and subsequent research by Vaughn and Smith[45] from Wyandotte Chemicals Corporation, led to increased NaCMC use in U.S. laundry detergents[44, 46] and a sharp rise in production. By 1951, yearly production in the U.S. had reached 8×10^6 kg, roughly two thirds of which were used in detergents[24], with additional uses in drilling fluids and textiles.

The introduction of purified NaCMC[21, 24] by Hercules in 1946 led to its use as a thickener and structuring agent in food products[25, 47], an application that persists to the present day. By the 1980s, the global consumption of NaCMC exceeded 10^8 kg/year. Today NaCMC is primarily used in food and beverage products, where it acts as a thickener, emulsifier and humectant as well as in oil drilling fluids. Other applications include its use as a structuring component in dentifrices[48, 49] and as an adhesive in the paper industry, see section III.

Figure 3 plots the consumption of CMC in the United States and world wide as a function of year. According to market reports [39, 50], global production in 2025 was approximately 8.8×10^5 tonnes per annum, which corresponds to a market value of $\simeq$ 2 billion USD. The total value of cross border trade was $\simeq$ 1.2 billion USD, with China, the Netherlands and Finland being the main three exporters.[51]

III. APPLICATIONS

CMC is an important polymer in the food and beverage industries, where high-purity NaCMC is employed as a thickener, stabiliser and emulsion modifier in baked goods, sauces, beverages and dairy formulations.[52–57] Market analyses[50, 58] indicate that the food and beverage segment accounts for the largest share of global CMC consumption ($\simeq 40\%$), reflecting its regulatory approval in major markets such as the United States, the European Union[59] and China. The use of NaCMC in processed foods dates back to the 1950s as can be seen in the extensive patent literature, including stabiliser systems for ice creams and frozen deserts[60–63], dairy products[64–66], wine clarification[67–70] and baked goods.[71–73]

CMC is also used widely in oil drilling fluids,[50, 74] where it is mixed at concentrations of a few weight percent with salty water and clays to generate viscous gels. Market reports usually assign $\simeq 20\%$ of global CMC production to oil drilling applications. Its main functions are to act as a thickener (viscosifier) that prevents fluids loss into porous rocks and stabilizer that reduces shale hydration and prevents borehole collapse. [75–78]

Beyond food and oil drilling fluids, carboxymethyl cellulose is used in detergents, personal care formulations and the paper and construction industries. In detergents, NaCMC acts as a soil suspending polymer that inhibits redeposition during washing.[79–82] In personal care and cosmetic products, CMC functions as a rheology modifier in shampoos, lotions and dentifrices, where its water-retaining (humectant) behaviour and film-forming properties are exploited.[83–85] In paper manufacture it improves fibre bonding and surface strength.[86, 87] In cement systems it is a component it serves as a water retention agent that enhances workability and adhesion.[88]

Potential uses of NaCMC in food, textiles, biomedical engineering, pharmaceutical formulations, wastewater treatment and energy storage are covered in an extensive review published recently by Rahman et al.[4]

IV. COMPOSITION OF CMC POLYMERS

A. Substitution Patterns

The Spurlin model[89] describes the kinetics of substitution of cellulose ethers, assuming that the ratio of the reaction constants (k_i) for the three positions do not change with time. The fraction of monomers with position i substituted is:

$$x_i = 1 - e^{-k_i t} \tag{1}$$

where t is the reaction time and $i = 2, 3, 6$ corresponds to each of the positions in figure 1.

The fraction of monomers which are unsubstituted (χ_0), mono-substituted (χ_1), di-substituted (χ_2) or tri-substituted (χ_3) are:

$$\chi_0 = e^{-(k_2+k_3+k_6)t} \tag{2}$$

$$\chi_1 = e^{-(k_2+k_3)t} + e^{-(k_2+k_6)t} + e^{-(k_3+k_6)t} - 3e^{-(k_2+k_3+k_6)t} \tag{3}$$

$$\begin{aligned}\chi_2 = e^{-k_2 t} + e^{-k_3 t} + e^{-k_6 t} - 2e^{-(k_2+k_3)t} - 2e^{-(k_2+k_6)t} \\ - 2e^{-(k_3+k_6)t} + 3e^{-(k_2+k_3+k_6)t}\end{aligned} \tag{4}$$

$$\begin{aligned}\chi_3 = 1 - e^{-k_2 t} - e^{-k_3 t} - e^{-k_6 t} - e^{-(k_2+k_3)t} \\ - e^{-(k_2+k_6)t} - e^{-(k_3+k_6)t} - e^{-(k_2+k_3+k_6)t}\end{aligned} \tag{5}$$

Note that we omit the last term of Eq. 17 of ref [89], which appears to be a typo.

Figure 4 considers the application of the Spurlin model to experimental data for NaCMC of different degrees of substitution. Kono et al synthesised a series of NaCMC samples by carboxymethylating fibrous cellulose with chloroacetic acid in concentrated NaOH water/isopropanol media. ^{13}C NMR was used to determine the fractions of monomers with a given substitution pattern. The Spurlin model is shown as full and dashed lines in figure 4. The ratios of reaction constants are determined by fitting the x_i data in part a. These values are then used to calculate χ_i as a function of degree of substitution in part b.

The values of x_i in figure 4a are seen to be well described by the Spurlin model. Similar agreement is observed for other systems with different ratios for the reaction constants, see for example [101]. The data in figure 4b show that the Spurlin model is less successful at predicting the values of χ_i, compared to x_i. In particular, the number of unsubstituted monomers is underestimated throughout the entire DS range. Reuben and Connor's data[96] for χ_i of CMCs over a similar DS range show better agreement with the Spurlin model. Reuben[104] modified Spurlin's model to include a k_3 constant which increases threefold for monomers where the position 2 hydroxyl has been substituted, see [103] and references therein for additional discussion of this topic.

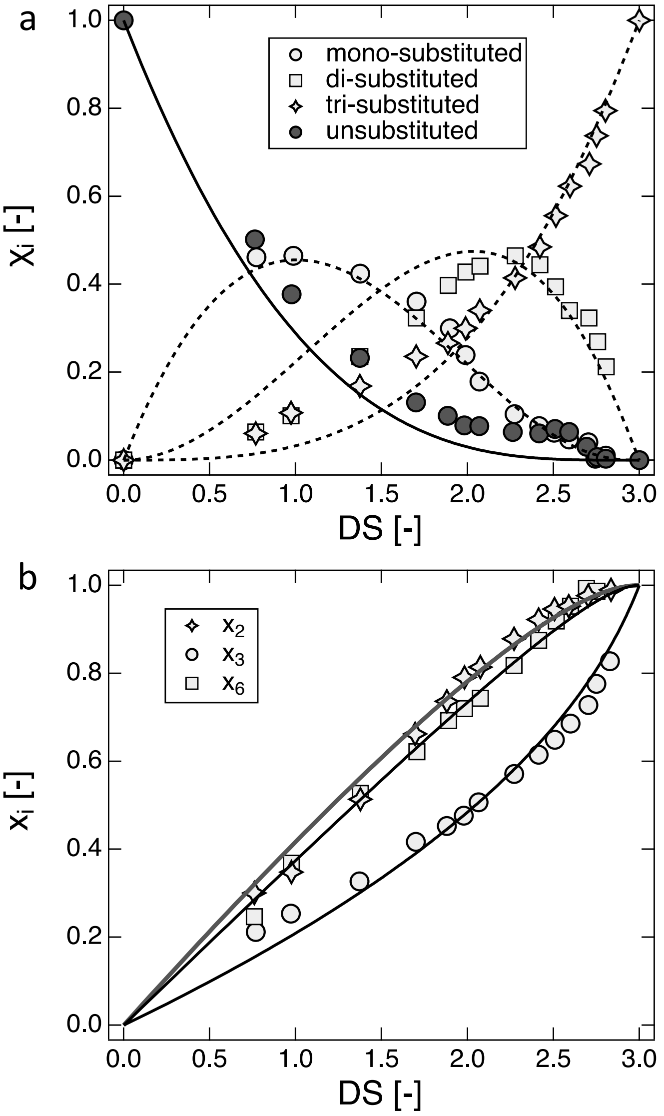

FIG. 4. a: partial degrees of substitution for each position as a function of total degree of substitution for CMC samples synthesised by carboxymethylation of cellulose with chloroacetic acid in IPA/NaOH. Data are from ref. [90]. Lines are the Spurlin model (Eq. 1). The best fit reaction constants are $k_2 : k_3 : k_6 = 2.3 : 1 : 2$. b: Fraction of monomers with varying types of substiution patterns as a function of degree of substitution for the same samples as part a. Lines are the Spurlin model (Eqs. 2-5) with the reaction constants obtained in the fit of part a.

Reference	k_2	k_3	k_6
Baar et al[91]	3	1	2.1
Kragten et al[92]	1.8	1	1.2
Kragten et al[92]	1.9	1	1.3
Kragten et al[92]	2.3	1	1.5
Zeller et al [93]^a	2.35	1	1.82
Abdel-Malik & Yalpani[94]^b	2.1	1	1.5
Niemla & Sjostrom[95] ^{c}	3.1	1	2.6
Reuben & Connor[96]^a	2.14	1	1.58
Ho & Klosiewicz[97] ^{a}	2	1	1.5
Buytenhuys & Bonn[98] ^{b}	2.5	1	1.8
Croon & Purves[99] ^{b}	4.6	1	3.6
Timell & Spurlin[100] ^{b}	2	1	2.5
Kulicke et al[101]^a	2.6	1	2.8
Adden [102]*	2.6	1	1.9
Kono et al[90]*	2.3	1	2

TABLE III. Reaction constants of Spurlin model according to various literature sources. This table follows the compilation by Baar et al[91] and Adden[103]. ^{a} obtained from a fit imposing a fixed ratio of reaction constants to a series of samples. ^{b} values quoted from 91. * Calculated from data in ref 90, see figure 4 for fits of the Spurlin model to these data. ^{c} average of values obtained for two samples: 3.3:1:2.9 and 2.8:1:2.2.

The Spurlin model has been extensively applied to describe substitution patterns of carboxymethyl cellulose in the literature, and is used as a reference for homogeneous substitution. Table III collects the reaction constants reported in various studies. These consistently show $k_2 \gtrsim k_6 > k_3$ but the specific ratios between the three constants vary by a factor of $\simeq \times$2-3 across different studies, presumably due to differences in the reaction conditions (solvent media, ratio of acetic acid to AGU etc), which are known to influence the reaction kinetics.[91, 92, 105] Note that Dapie et al's data suggest that temperature influences the overal reaction constant but not the ratio between k_is. [106]

B. Compositional heterogeneity

As early as 1950 [107], During and Banderet reported that strong centrifugation separates weakly substituted NaCMC into 'solution' and 'gel' fractions. Both fractions were found to have similar molar mass and average DS. The gel fraction displayed crystalline peaks in the x-ray diffraction pattern similar to those of mercerised cellulose, presumably arising from block-like unsubstituted groups along the chain. Cellulose being insoluble in water, these unsubstituted blocks cluster together and form crystalline cores. The experiments of Elliot and co-workers confirmed these features and showed that the solution fraction displays pseudoplastic (shear-thinning) behaviour while the gel fraction exhibits thixotropy, as shown in figure 6. The presence of a gel fraction in NaCMC samples in water is confirmed by sev-

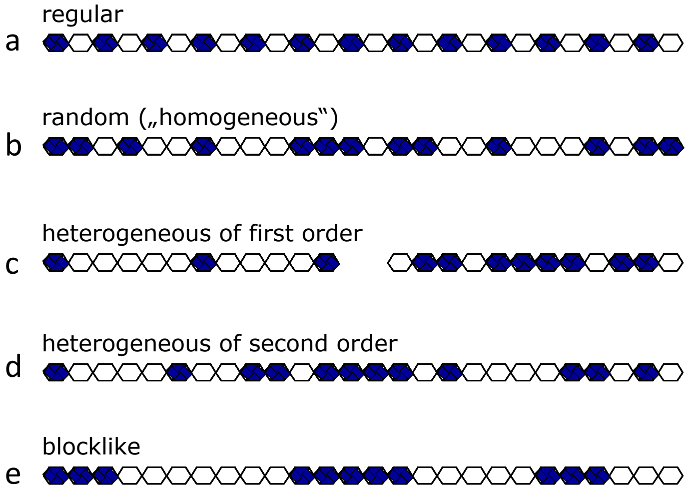

FIG. 5. Substitution patterns for CMC polymers. Blue hexagons represented substituted glucose units and hollow hexagons are unsubstituted ones. Figure adapted from [102].

eral studies.[8, 9, 108, 109]

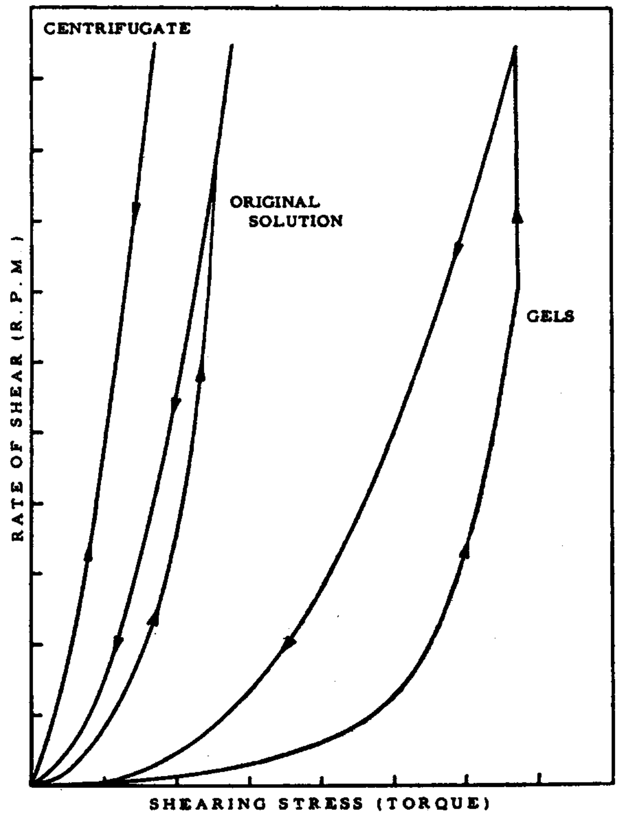

FIG. 6. Rheological properties of NaCMC solution before centrifugation (original solution) and the solution and gel fractions after separation. Figure reproduced from [8].

The gel fraction in CMC solutions can be measured by filtration or by elution with size exclusion chromatography. These results show that the gel fraction in CMC samples produced by the slurry process decreases with increasing degree of substitution, as shown in figure 7. For DS $\gtrsim 1$, the gel fraction becomes very small, which explains the lack of gelling and thixotropic properties of highly substituted polymers. This finding is consistent with X-ray diffraction data, which show the absence of crystallinity for samples with DS $\gtrsim$ 0.9-1.1 [110, 111], as discussed below. The specific value of DS at which the cross-over between 'highly substituted' and 'weakly substituted' sample occurs depends on the specific reaction conditions used to prepare the NaCMC. The cross-over between 'high' and 'low' substitution therefore varies for samples synthesised according to different procedures. The slurry process yields as cross-over between 'gelling' and 'smooth' behaviour at around DS $\simeq 1$.

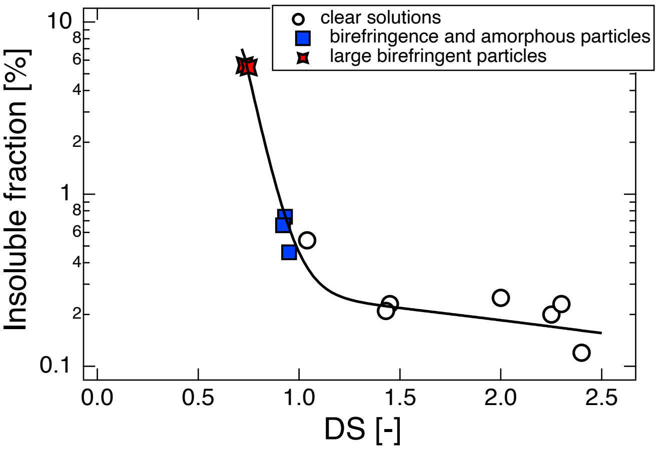

FIG. 7. Mass percentage of insoluble content in NaCMC samples as a function of degree of substitution. Samples are classified according to their appearance under the microscopy. Line is a guide to the eye. Data are from [112]

C. Heterogeneity in DS

The most commonly employed methods to determine the *average* degree of substitution of CMC are titration of the acid form and ^{1}H NMR.[90, 113, 114] Other methods, for example based on thermogravimetric analysis,[14] complexation with an oppositely charged polyelectrolyte[115] or scanning electron microscopy[116] have also been developed. NMR methods also allow to determine the partial degrees of substitution for different positions in the monomer.

The heterogeneity in degree of substitution of CMC samples has been quantified by chromatography and capillary zone electrophoresis. Shakun et al [117] used HPLC to measure the distribution of DS in CMC samples produced by the slurry process. Two starting materials were chosen for the cellulose: microcrystalline cellulose (Avicel) and cotton linters. The standard deviation of the DS distribution of each sample is plotted as a function of average degree of substitution in figure 8. The samples generated from microcrystalline cellulose display a constant standard deviation as a function of DS. By contrast, samples derived from cotton linters show a decreasing trend in standard deviation with increasing average DS, see figure 8. Oudhoff et al[118] determined the distribution of DS for commercial NaCMC samples and report that a sample with average DS $= 1.09$ displayed a DS polydispersity of Đ $= 1.04$, which corresponds a standard deviation of $\simeq 0.21$, in agreement with the results of Shakun et al, see fig. 8.[119] The starting cellulose material for their sample was not reported but is likely cotton linters or wood pulp. [120]

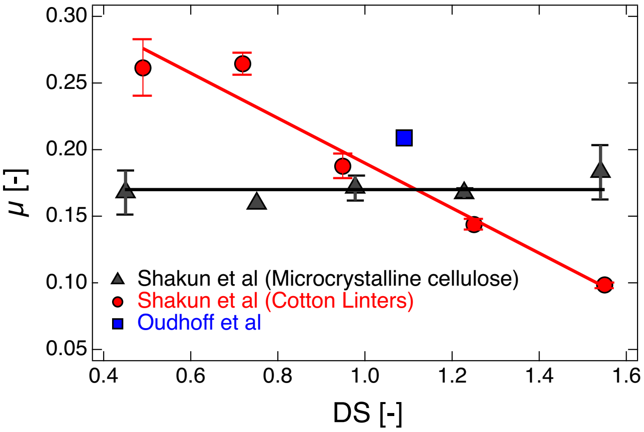

FIG. 8. Standard deviation (μ) in degree of substitution of CMCs as a function of average degree of substitution. The starting cellulose materials for Shakun et al's samples are cotton linters or microcrystalline cellulose. The starting material for Oudhoff et al's samples was not reported. Lines are guides to the eye. Data are from refs.[117, 118].

Shakun et al.'s[117, 121] chromatography results indicate that for samples produced by a single etherification step, no correlation exists between molar mass and DS of chains within a given sample. In contrast, twice-etherified samples with high substitution ($\simeq 1.5$) displayed a measurable correlation between these variables. These highly substituted samples contain essentially no chains with DS < 1, meaning that all chains are hydrophilic and their solution behaviour is largely insensitive to small variations in DS. As a result, the observed correlation between DS and molar mass in these samples is unlikely to influence their properties.

D. Random vs. block-like substitution

Methods to quantify blockiness typically rely on depolymerising the CMC chain and analysing the resulting fragments.[17, 122–124] An example is shown in figure 9. The enzyme endoglucanase (Econase CE, AB Enzyme) cleaves bonds between two unsubstituted glucose units but does not cleave bonds adjacent to substituted units. Stigsson et al define a blockiness parameter as the ratio of glucose released by enzymatic hydrolysis to that released after acid depolymerisation. This method provides a simple, although qualitative, means to characterise blockiness in substitution patterns.

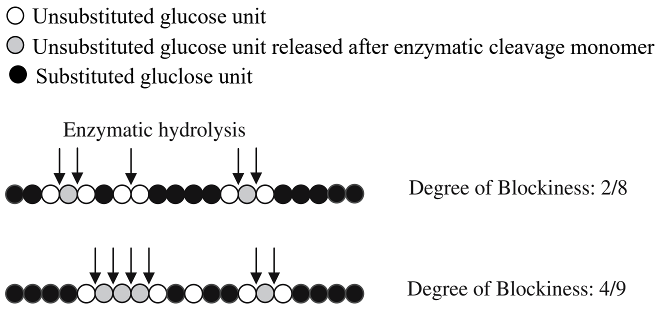

FIG. 9. Example of determination of blockiness parameter using enzymatic hydrolysis. Figure adapted from [122].

E. Crystallinity

Kamide et al[111] studied the structural and solubility properties of carboxymethyl cellulose as a function of degree of substitution. Two cellulose polymers with different crystal structures (Cell-I and Cell-II) were used as the starting polymers: the Cell-I crystal structure, where the polymer chains are aligned parallel to each other corresponds to the type of cellulose found in nature, which is used to synthesise commercial samples. The Cell-II crystal structure, where chains are aligned in an anti-parallel structure is obtained from regenerated (i.e dissolved and precipitated) cellulose. Carboxymethylation was carried out by the slurry process, using isopropanol as the non-solvent. The CMC samples derived from Cell-I were found to display $x_2+x_3 \simeq (1-1.5)x_6$. By contrast, for the CMCs synthesised from the Cell-II, some 90% of the substitution occurred at the 6 position.

X-ray diffraction (XRD) patterns for the two cellulose samples studied by Kamide et al before and after alkaline addition are shown as the top two curves in figure 10. In both cases, addition of alkali partially breaks the crystalline structure, as seen by the decrease in the prominence of the crystalline peak at $2\theta \simeq 20^\circ$. Carboxymethylation further decreases the presence of crystal regions and produces an amorphous halo at $2\theta \simeq 9^\circ$.

A separate study by Xiquan et al[110] reported different somewhat different behaviour. The XRD pattern for their starting cellulose material, shown in figure 11a closely resembles that of Kamide et al. However, as the carboxymethylation proceeds, the peak moves to lower values of $2\theta \simeq 20^\circ$ and eventually morphs into an amorphous halo centerred at $2\theta \simeq 21^\circ$ for the DS $= 1.06$ sample. Other literature studies either show no change in the crystalline peak position, close to Kamide et al's observations or a decrease in the peak position, as reported by Xiquan et al.[19, 125–129] The origin of these discrepancies is not clear at present.

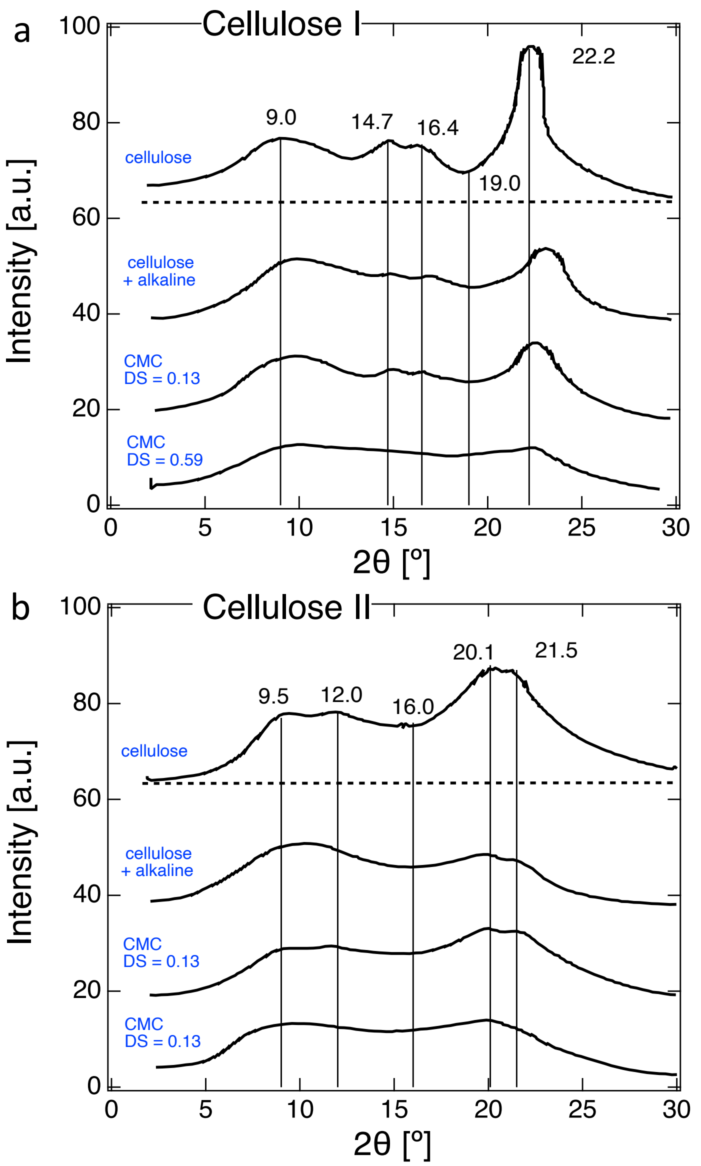

FIG. 10. X-ray diffraction patterns for cellulose with different starting crystal structure (top two curves) and resulting CMCs with DS indicated on the graph. Lines indicate position of the peaks. Dashed lines are baselines for integration. Figure adapted from [111].

A more detailed analysis of Kamide et al's data is presented in figure 12, which plots the crystalline content of NaCMC synthesised from cellulose I and cellulose II as a fraction of total degree of substitution. Crystalline fractions were obtained from the XRD data in figure 10. The sample synthesised from cellulose II displays a steady decay in X_C as function of DS, and samples retain relatively high values of $X_C \simeq 30\%$ at DS $\simeq 0.6$. By contrast, the NaCMC synthesised from cellulose I displays a step-like decrease with DS. The lower values of X_C at the highest DS studied are consistent with other reports, which do not observe measurable crystallinity for samples with DS $\simeq 0.7$.

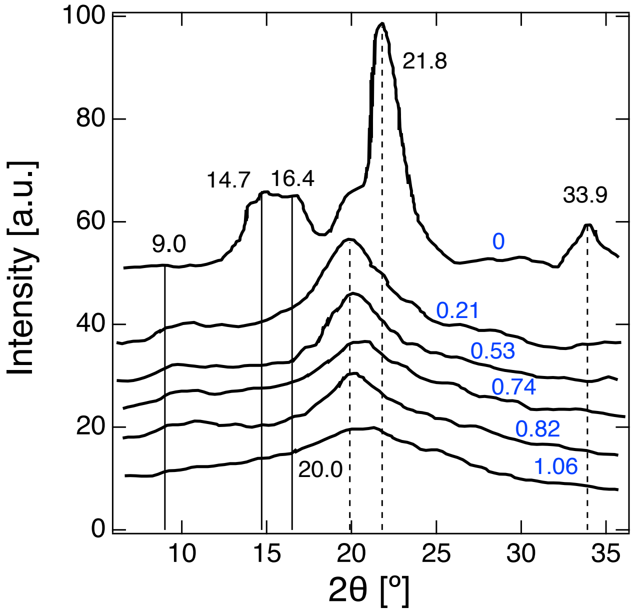

FIG. 11. XRD patterns for cellulose and CMC with varying degrees of substitution, noted in blue above the curves. Full lines are θ values in figure 10 and dashed lines indicate peak positions. Figure adapted from 110.

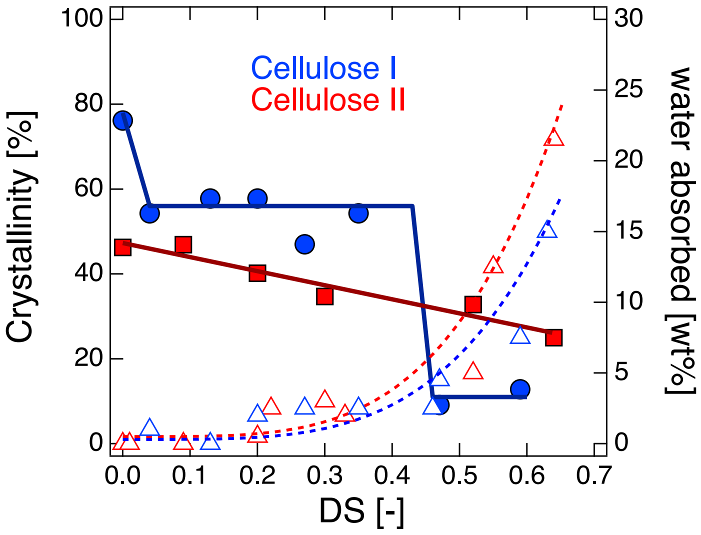

FIG. 12. Percentage of crystallinity of carboxymethyl cellulose as a function of degree of substitution for two samples, where the unsubstituted cellulose (DS = 0) has crystal form I (full blue circles) or crystal form II (full red squares). Hollow triangles are the equilibrium water absorbed relative to the polymer's dry weight. Lines are guides to the eye. Figure adapted from [111].

According to Kamide, the carboxymethylation of cellulose first occurs within the amorphous fraction and the proceeds to the crystalline parts.[111, 130] The crystalline structure of the cellulose therefore therefore influences the reaction kinetics, as well as the substitution pattern of the CMC product. This is particularly significant for weakly (DS $\lesssim 0.7$) and presumably accounts for the differences in substitution patterns and swelling behaviour observed for Kamide et al's samples.

F. Molar mass polydispersity

GPC measurements on commercial NaCMC samples show that these have molar mass polydispersities in the range of $Đ = M_w/M_n \simeq 2 - 3$[131–133] Light scattering and membrane osmometry by Brown et al gives similar values of $Đ \simeq 2 - 4$ An analytical ultracentrifugation study by Arinaitwe and Pawlik[134] reported more disperse distributions $M_z/M_w \simeq 2 - 4.5$. These values are incompatible with the Schulz-Zimm (Gamma) distribution, which Brown and Henley used to estimate M_z for their samples as this distribution allows for a maximum value of M_z/M_w of 2

Studies often rely on molar mass values reported by manufacturers but these are often not accurate. Figure 13 plots the reported molar mass of some 40 commercial NaCMC samples. Large deviations from reported and measured values are observed. These deviations are random. For example, Sigma-Aldrich grades with nominal 250kg/mol have been found to display between 170 and 390 kg/mol. Particularly for studies reported rheological or other dynamic properties, manufacturer values should not be regarded as accurate (because these parameters such as viscosity depend on molar mass).

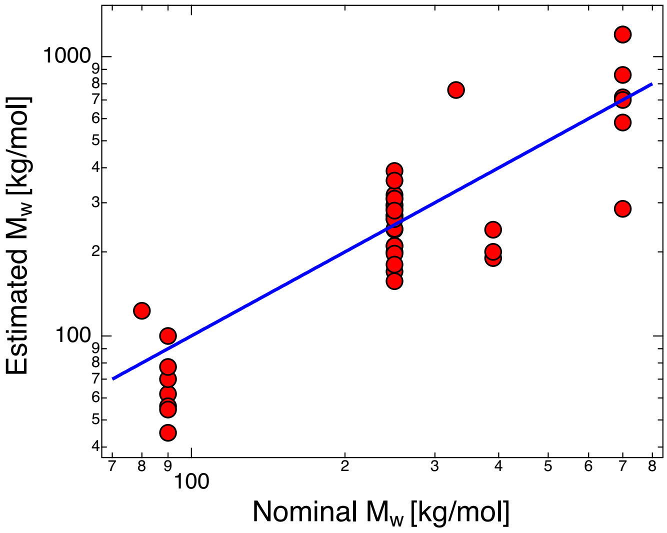

FIG. 13. Estimated molar mass of commercial CMC samples as a function of their nominal molecular weight, as reported by the manufacturer. Data are from refs. [134], compiled in [135] and refs. 10, 133, 136–141. The estimated molar masses are obtained from the references where reported or from $\eta_{sp} - N$ relations in [135] otherwise. Blue line is 1:1 correspondence.

V. SOLUBILITY

Hydrogen bonding an hydrophobic interactions are recognised to contribute to the insolubility of cellulose in water.[144–147] Solubilisation in water can be promoted by increasing the pH or by substituting the cellulose with functional groups. For carboxymethyl cellulose synthesised via the slurry process, Feddersen reports that a degree of substitution of $\simeq 0.4$ is required for full solubility in water.[12] Water-soluble samples with DS as low as 0.2 have been reported.[148]. Non-random substitution patterns can significantly alter the critical DS values required for solubility. For example Liu et al[149] report that regioselective NaCMC with $x_6 = 0$, $x_2 \simeq (1-1.5)x_3$ becomes soluble when the degree of substitution exceeds DS $\simeq 0.3$. On the other hand, CMCs synthesised with via the induced phase separation approach, which results in high values of χ_0 and χ_3 and a blocky substitution patters were found to be insoluble up to degrees of substitution as high as 1.2.[148] The water sorption data in fig. 12 also indicate that Kamide's are not soluble up to at least DS $\simeq 0.6$. Solubility of low DS samples can be enhanced by using cellulose solvents such as concentrated NaOH or cadoxen.[150, 151]

Even for a specific starting material and/or reaction protocol, the definition of a solubility threshold is not trivial because different fractions of the cellulose will coexist in different states. Reports of solubility of NaCMC in water are usually qualitative, and are based on whether the sample appears clear to the eye. While this serves as a goods starting point to characterise solubility, more detail methods are required to quantify CMC solubility.

Microscopy[143, 152] and filtration tests typically reveal the presence of some insoluble residues for NaCMC samples in the soluble DS range.[153] GPC experiments reveal similar trends to those observed in figure 7 trends but much higher fractions of non-filterable material.[129, 153] Such tests probably overestimate the fraction of insoluble matter. Filtration though 0.1 μm pores of a DS = 1.3 NaCMC sample has been shown to lead to little or no mass loss.[154] In addition to insoluble gel particles, a polymer can be *molecularly dissolved* when its chains are well dispersed and solvated, in contrast to *colloidally dissolved*, where a large fraction of the chains associate into large aggregates.[155–158]

A. Cellulose fibers

Early microscopy work by Hoppler and Stawitz and Kage established the presence of large, undissolved fibres in solutions of CMC, see figure 14. There are conjectured to arise from '*wood cells that react more slowly during the etherification due to their large dimensions or more dense structure*'.[159] Jardeby et al[152, 159, 160] later performed more detailed investigations on the influence of the starting cellulose materials and reaction conditions on the resulting fibres. They measured the degree of substitution for several CMC samples and reported values between 0.12 and 0.66. The fibre length distribution, measured by optical microscopy in refs. [152, 160], was found to be polydisperse and peaked at approximately 0.2–2 mm, depending on the sample. The fibre width also showed high dispersity, with a mean value at ~ 20

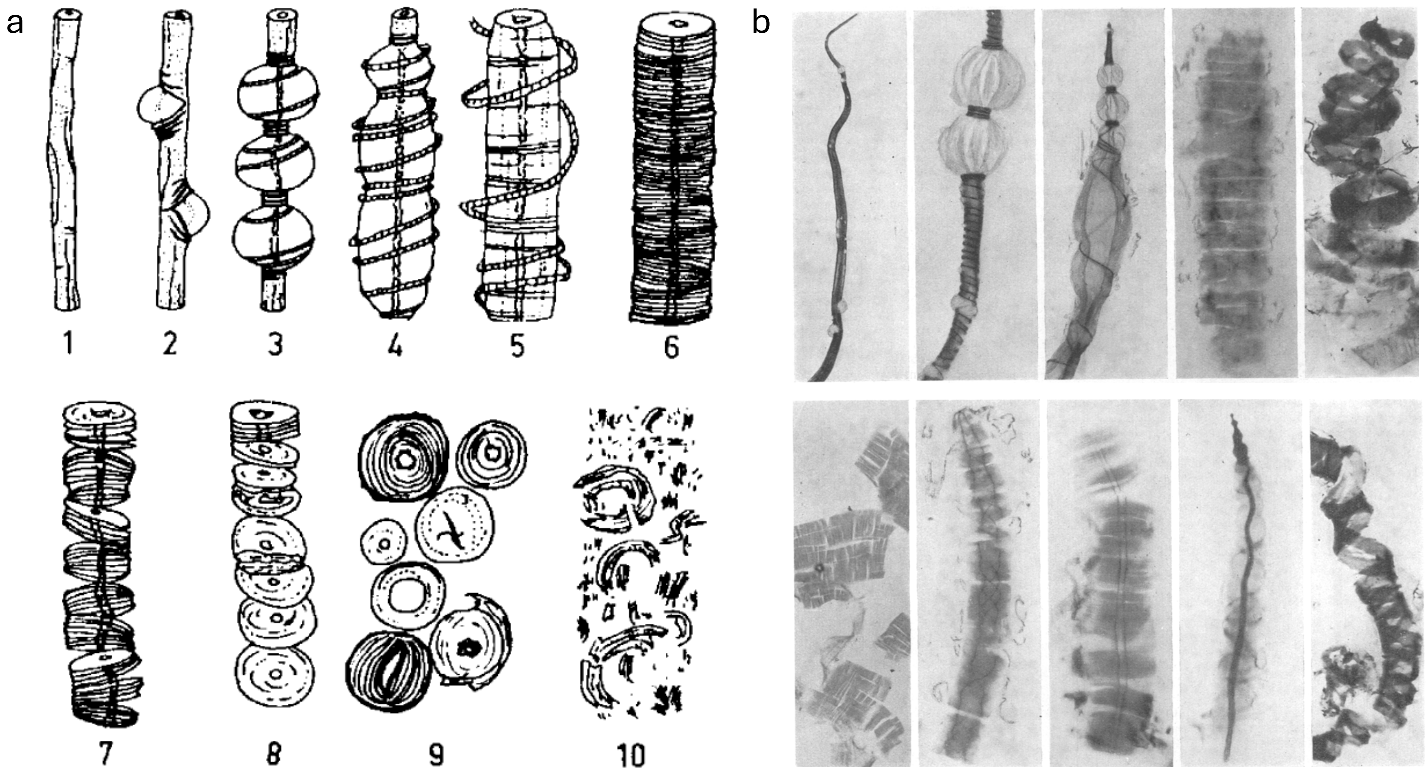

FIG. 14. a: classification of fibers by Stawitz and Kage. [142] b: Optical microscopy images from ref. [143].

μm.

Based on the above observations, Jardeby et al proposed a general mechanism of fibre dissolution that depends on the substitution level. Jardeby et al propose the following 3-step dissolution of the fibres: At low substitution (DS $\simeq 0.1$) the fibres remain largely crystalline, which is consistent with the XRD data discussed above. At intermediate substitution (DS $\simeq 0.3$ to 0.5) the fibres swell and display the ballooned morphology shown in figure 14a, 3. As the substitution increases to DS $\simeq 0.5$ to 0.6 the swollen fibres convert into gel particles, and at still higher DS a clear solution forms. These gel particles are macroscopic and distinct from the microgel-like aggregates discussed in the following section. Chapter 2 of ref. [33] contains a more detailed discussion of these studies.

B. CMC in the acid form

When excess acid is added directly to a NaCMC solution, the sample becomes turbid. If the acid is subsequently removed by dialysis against deionised water, the resulting HCMC remains in solution and typically shows a slight opalescence. Once it is dried however, HCMC does not re-dissolve in water, presumably because it remains kinetically trapped in the solid form. A moderately concentrated alkali solution is usually required to solubilise it. As with NaCMC, the solubility of HCMC in water increases with increasing degree of substitution.

The degree of substitution of NaCMC is commonly determined by converting the sample to the acid form and performing a potentiometric titration. In the standard approach, the HCMC polymer is dissolved in excess alkali, then back-titrated to pH $\simeq 8$.[113] The ASTM procedure specifies conversion to the acid form by adding nitric acid and ethanol to the a solid NaCMC powder to produce a slurry, followed by repeated washing with deionised water to remove low-molar-mass salts.

Because highly substituted HCMC is partially soluble in water, some of this fraction can be lost during the repeated washing steps of the ASTM procedure, which leads to artificially low measured degrees of substitution.[161] Conversion by addition of excess acid followed by dialysis against deionised water is less likely to remove the highly substituted material and is therefore preferable to the ethanol/nitric-acid method described in the ASTM standard.

C. Solubility in non-aqueous media

Commercial grades of NaCMC are insoluble in most common organic solvents, with a few exceptions such as glycerol. Formic acid and some ionic liquids can also dissolve CMC.[162, 163] An early patent[164] reported that NaCMC with high degree of substitution is soluble in organic solvents but this has not been reproduced to date. Mixtures of water with non-solvents can dissolve NaCMC,[139] Dissolution can be slow, particularly for viscous solvent mixtures.[165] Solubility increases with degree of substitution: highly substituted grades (DS $\simeq$ 1-1.2) dissolve readily, whereas weakly substituted grades (DS $\simeq$ 0.7-0.9) tend to form gels which slows down the dissolution process.[133, 166] As a general rule, NaCMC has higher tolerance for solvents of higher dielectric permittivity, presumably due to the entropy gain upon dissolution from dissociated counterions. NaCMC is more soluble in salt-free media, and can be salted out with added NaCl, especially in water/non-solvent mixtures.[167]

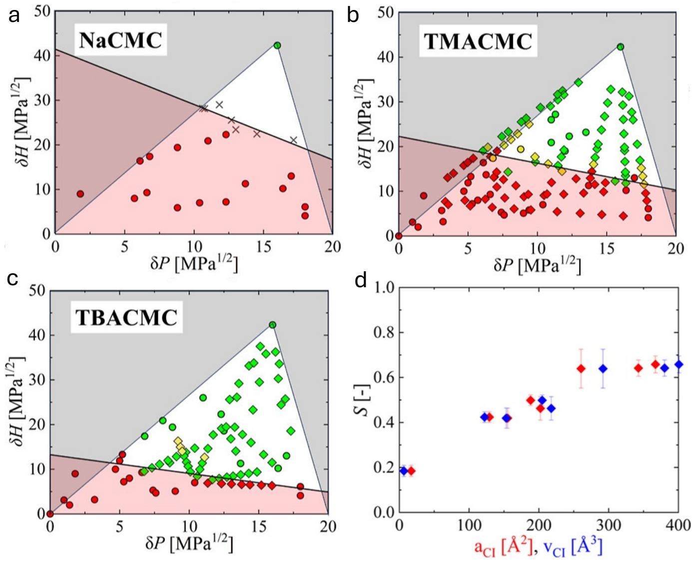

FIG. 15. Hansen solubility diagrams for a) sodium, b) tetra-methyl ammonium (TMA) and c) tetrabutylammonium (TBA) salts of CMC. The x and y-axis are the Hansen polarity and hydrogen bonding solubility parameters respectively. Red symbols indicate non-solvents and green symbols indicate solvents. Water corresponds to the (16,42) point. A triangle is drawn between the origin, (0,20) and the water datum and the ratio of soluble area to the total area is plotted in the d) panel as a function of counterion area (red symbols) and volume (blue symbols) for various counterions. Figure adapted from [168].

Substituting organic counterions for sodium ones leads to large increases in the solubility of CMC in non-aqueous solvents.[168, 169] A systematic study of the solubility of various salts of CMC was carried out by Hou and coworkers, who showed that Hansen solubility can be used to empirically describe the solubility of CMC polymers in solution, as shown in figure 15.

In brief, the Hansen approach, developed for non-ionic polymers, assigns solvents three solubility parameters: δ_D, δ_P and δ_H, which separate the solvent's cohesive energy, into dispersion, polar and hydrogen-bonding interactions. Figure 15a-c plots δ_H against δ_P for some 50 solvents. Most solvents are contained inside a triangle with vertices (0,0), (0,20) and (16,42), with the last point corresponding to (δ_P, δ_H) for water. Solvents located in the top part of the triangle, corresponding to polar and protic media are able to dissolve CMC, and are indicated by green symbols. Solvents at the bottom part of the triangle, corresponding to apolar, aprotic media do not dissolve CMC and are shown by red points. Solvents that swell but do not dissolve the polymer are shown as yellow symbols.

CMC with organic counterions such as TMA$^+$ or TBA$^+$ display greater solubility in organic media than NaCMC, as reflected by the larger area of the Hansen triangle covered by green symbols. A dimensionless parameter S can be defined that corresponds to the ratio of the soluble region of the Hansen diagram to the total area of the triangle. This is plotted as a function of counterion volume and counterion area on figure 15d.

VI. DILUTE SOLUTION PROPERTIES

Solutions below the overlap concentration c^* are in the dilute regime meaning that chains do not interpenetrate. Data in this regime allow extrapolation of physical quantities to the $c \to 0$ limit, which correspond to single chain properties.

A. Light scattering

Static light scattering can be used to measure the radius of gyration of a polyelectrolyte chain in the infinite dilution limit.[170]. In contrast to the more common measurement of chain size such as the hydrodynamic (R_H) or viscosimetric (R_η) radii, the radius of gyration is purely a geometric quantity, which is not influenced, for example by hydrodynamic draining.

The scattering intensity of a dilute polyelectrolyte solution with excess added salt ($c_S \gg fc_P/2$) can be described by the Zimm equation:

$$\frac{KC}{\Delta R(q)} = \frac{1}{M_w}\left(1 + \frac{q^2 R_{g,z}^2}{3}\right) + 2A_2 C \qquad (6)$$

where C is the concentration in mass per unit volume, M_w the weight-averaged molar mass, $R_{g,z}$ the z-averaged radius of gyration, A_2 the second virial coefficient[171], ΔR the excess Raleigh ratio (i.e. the Raleigh ratio of the solution minus that of the solvent), $q = \frac{4\pi n}{\lambda} sin(\theta/2)$ is the scattering vector with λ the wavelength of light and K is a contrast factor, given by:

$$K = \frac{4\pi^2 n_0^2}{\lambda^4 N_A}\left(\frac{dn}{dC}\right)_\mu^2 \qquad (7)$$

here n_0 is the refractive index of the solvent and dn/dC the refractive index increment. The subscript μ indicates that dn/dC must be measured at constant chemical potential of the salt. In practice, this is done by dialysing the polyelectrolyte solution against a salt solution, see refs. [172, 173] for details.

Values of $\frac{dn}{dC}$ have been determined in multiple studies,[131, 154, 167, 174–182] and are collected in table VI. These data do not show any clear trend with

DS or added salt concentration. The only measurements $(dn/dC)_\mu$ for NaCMC have been carried out by Brown et al.[183] and their results are compiled in table IV. As expected, $(dn/dC)_\mu < dn/dC$. However, other studies[173] have reported the ratio of $(dn/dC)_\mu$ to dn/dC to increase as the salt concentration increases, which is not observed in Brown et al's results. Additional measurements of these parameters as a function of added salt concentration and degree of substitution would be very useful to improve the molar mass determination of NaCMC polymers.

TABLE IV. Refractive index increment of NaCMC in 0.2 M and 0.005 M NaCl. Results in units of mL/g. Data from [183]

Solvent	Dialysed: $\left(\frac{dn}{dc}\right)_\mu$	Non-dialysed: $\left(\frac{dn}{dc}\right)$
0.2 M NaCl	0.132	0.140
0.005 M NaCl	0.136	0.144

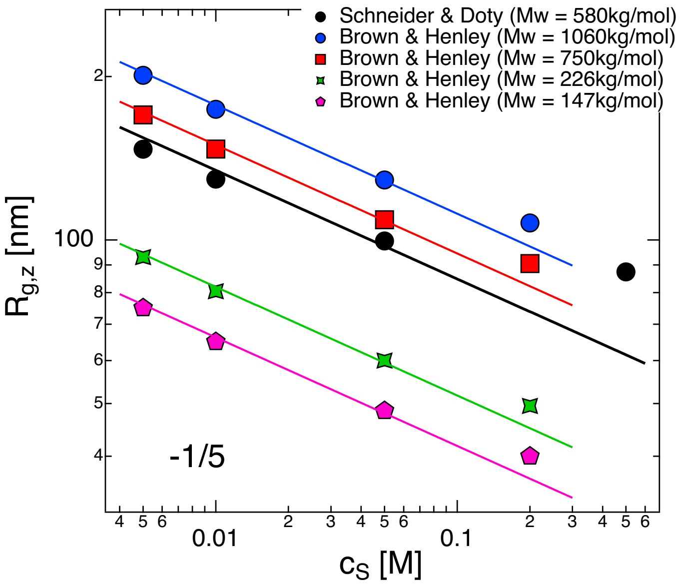

FIG. 16. z-averaged radius of gyration of NaCMC as a function of added salt concentration. Results are data by Bown and co-workers[181, 185] and Schneider and Doty. Lines are predicted power-laws of -1/5.

1. *Dependence of chain dimensions on added salt*

Figure 16 plots the radius of gyration of NaCMC with DS $\simeq 1$ as a function of NaCl concentration. Data from Brown and Henley and from Schneider and Doty were largely collected outside the $qR_g < 1$ regime where the Zimm approximation is valid, as noted by Davis.[184] However, the molar masses measured by light scattering for these samples agree with values calculated from the intrinsic viscosities, indicating that their extrapolation to zero scattering angle was carried out correctly despite working at $qR_g > 1$. This outcome is consistent with the fact that Eq. 6 remains accurate for polydisperse wormlike chains for values of qR_g up to about 2–3.

The radius of gyration decreases with increasing salt concentration following the $R_g \propto c_S^{-1/5}$ dependence predicted by scaling theory for flexible polyelectrolytes. At high salt concentrations, the datasets deviate systematically above this exponent because the intrinsic chain rigidity limits further contraction as screening increases. Brown an Henley reported that their samples displayed turbidity at salt concentrations higher than 0.2 M added NaCl, which is not expected for their samples with DS = 1.06. Usually such samples are single-phase up to molar concentrations of added NaCl. Studying the M–dependence of R_g is difficult because the available studies[139, 176, 181, 185] used polydisperse samples but do not measure the $z-$averaged molar mass.

The persistence length of polyelectrolytes contains intrinsic and electrostatic contributions. For semiflexible polyelectrolytes such as CMC, the intrinsic term dominates once the added salt concentration exceeds roughly 0.1 M.[186] Hoogendam et al.[131] analysed NaCMC chain dimensions using size exclusion chromatography and fitted the R_g–M data to the expanded wormlike chain model, obtaining an intrinsic persistence length of $l_{p,0} \simeq 15$ nm. By contrast, Lopez's analysis of intrinsic viscosity data found a smaller value of $l_{p,0} \simeq 5$ nm.[187] For other polymers, persistence length estimates obtained from light scattering and viscosity typically agree to within ten percent. The light scattering data of Brown and Henley, Schneider and Doty, Hou et al.[139] and Yoshida et al.[176] are all incompatible with the value obtained by Hoogendam et al.[188] It may be tempting to discard the data of Hoogendam et al., but these align closely with the R_g–M results of Barba et al.[153] and Shakun et al.[180], also obtained by GPC coupled with light scattering. The discrepancy between these sets of studies remains unresolved and needs to be addressed in future work.

B. Viscosimetry

At c^* the viscosity is about twice that of the solvent ($\eta_{sp} \simeq 1$).[189, 190] The overlap concentration is reached when the 'self concentration' of a chain matches the solution concentration,

$$c^* \simeq \frac{N}{R^3}, \tag{8}$$

where N is the degree of polymerisation and R the end-to-end distance, so that R^3 represents the pervaded volume of a chain. Added salt screens the electrostatic interactions reducing R along with the corresponding increase in c^*. The overlap concentration can be experimentally measured as the reciprocal of the intrinsic viscosity $[\eta]$.

In excess salt, that is when the concentration of salt ions ($2c_S$) is much larger than that of free counterions fc, the viscosity follows the Huggins and Kraemer equations:

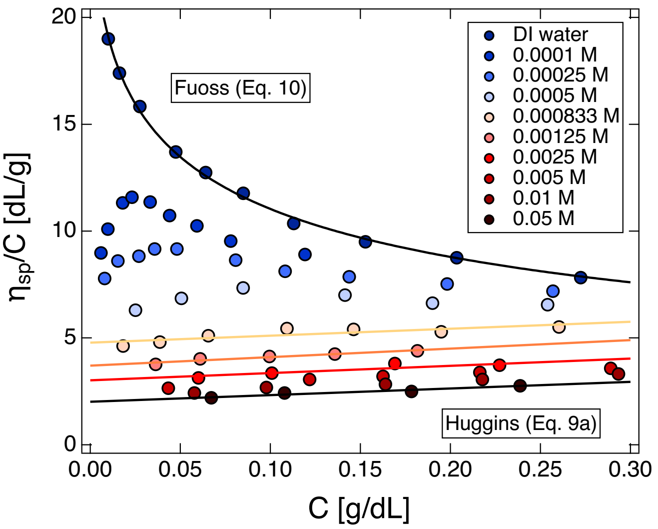

FIG. 17. Reduced viscosity of NaCMC as a function of concentration in DI water and NaCl solutions. Data from ref. [191], see ref. [192] for correct labels. Curves are fits to the Huggins and Fuoss equations (eqs. 9 and 10).

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c, \tag{9a}$$

$$\ln(\eta_{sp})/c = [\eta] - k_K[\eta]^2 c. \tag{9b}$$

where k_H and k_K are the Huggins and Kraemer's coefficients and $k_H - k_H = 1/2$. Equation 9 should generally be applied for $c \lesssim [\eta]^{-1}$, corresponding to $\eta_{sp} \lesssim 1.3 - 1.5$. Hydrophobic moieties on the polymer cause a strong concentration-dependence of the dilute solution viscosity and limit the concentration range of both equations, particularly the Huggins equation, see refs. [193–195] for details. For sufficiently dilute solutions, both equations apply.

In low salt solutions ($2c_S \ll fc$), the reduced viscosity increases upon dilution (figure 17) due to chain expansion, inter-chain repulsion, and ionic friction.[186] Fuoss proposed the empirical form:

$$\frac{\eta_{sp}}{c} = \frac{A}{1 + Bc^{1/2}}, \tag{10}$$

where A corresponds to $\lim_{c\to 0} \eta_{red}$ and B correlates with the effective chain charge. Equation 10 overestimates $[\eta]$ because a viscosity maximum appears at sufficiently low concentrations, first noted by Inagaki et al. The maximum occurs when $2c_S$ becomes comparable to the free counterion concentration fc. For NaCMC in aqueous solution, there is roughly one free counterion per two monomers,[139, 196] so in DI water ($c_S \simeq 5 \times 10^{-6}$ M) the maximum appears near $c_{max} \simeq 10^{-5}$ M ($\simeq 2.5 \times 10^{-3}$ g/L). Below c_{max} it is difficult to obtain accurate extrapolations of η_{red}.

The use of Fedors or Wolff equations[197, 198] to evaluate the intrinsic viscosity of NaCMC[134, 199] in salt-free or low salt solvents are not recommended as they do not correctly capture the concentration dependence of the specific viscosity at low concentrations.[186, 200]

Figure 18 shows the overlap concentration of CMC in salt-free water and in 0.1 M NaCl as a function of degree of polymerisation. In DI water, which contains only $\simeq 4 \times 10^{-6}$ M residual salt from carbonic acid, electrostatic interactions remain long-ranged in the dilute regime and chains adopt rod-like conformations. This gives $R \propto N$ and $c^* \propto N^{-2}$.[186] In 0.1 M NaCl, electrostatics are short-ranged and act similarly to excluded volume in neutral polymers, leading to $R \propto N^{0.59}$ and $c^* \propto N^{-0.78}$, in agreement with observations for other polyelectrolytes.[201–204]

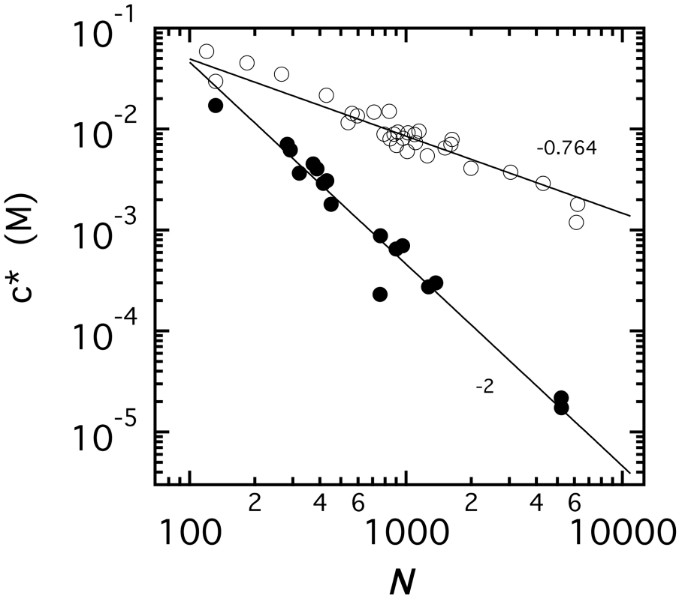

FIG. 18. Overlap concentration of CMC as a function of degree of polymerisation N in DI water and 0.1 M aqueous NaCl. In DI water, the overlap concentration is obtained from the $\eta_{sp}(c^*)$ criterion. In excess salt, c^* is estimated as the reciprocal of the intrinsic viscosity. Lines are power-laws with theoretical exponents[205] for polyelectrolytes in salt-free and excess salt regime. Figure reproduced from [187], see also [135] for selection of data.

C. Experimental artefacts

Ordinary capillary viscometers impose shear rates of order 10^3 s^{-1}. For low-salt and high-molar-mass NaCMC, these conditions fall in the non-Newtonian regime, and shear-dilution viscometers are required to measure the viscosity as a function of shear rate. This limitation has been noted repeatedly in the polyelectrolyte literature for decades,[135, 186, 204, 206–210] but viscometry studies on polyelectrolytes often overlook it, with some studies implausibly claiming that capillary viscosimetry data for high molar mass samples are not influenced by shear thinning[199]. Coupled with the lack of adequate determination of the molar mass, this renders a significant number of viscosimetry studies unreliable. A survey the literature, indicating which measurements are affected, is given in the supplementary information of [135].

VII. SOLUBILITY AND SUPRAMOLECULAR AGGREGATION

Significant discussion in the literature has taken place on the question of whether carboxymethyl cellulose in aqueous solution is dissolved at a *molecular* or colloidal level, with many apparently contradictory results.[132, 211, 212] Here, we restrict our discussion to dilute solutions, where chains do not overlap. Following the scheme Burchard and co-workers,[156] molecular dissolution corresponds to a state where chains are individually dispersed and well-solvated. Colloidal dissolution corresponds to when most chains are aggregated into multichain clusters. It is often the case, that a fraction of the polymer is molecularly dissolved while the rest is aggregated. This can be especially pronounced for polymers like CMC, where the second order heterogeneity in chemical composition results in chains with varying tendencies to aggregate.

A. Experimental evidence for well-dispersed chains

Many osmotic pressure[213–218] and light scattering[139, 176, 181, 183, 219] studies for NaCMC with $0.45 \leq$ D.S. ≤ 1.7 in excess salt solutions show positive second virial coefficients and molecular weights matching those of single chains. These features are characteristic of molecularly dissolved polymers. The variation of intrinsic viscosity[187, 220] and radii of gyration (R_g)[131, 180, 221, 222] with degree of polymerisation and salt concentration, discussed above, are also typical of semiflexible polymers in good solvents. We note that light scattering experiments are usually performed after filtration and/or centrifugation to remove dust particles. These procedures can also lead to the removal of aggregates. As we have seen in sec. IV B, the mass loss upon filtration for DS$\gtrsim 0.9$ is small (less than 1%), meaning that the well-dispersed fraction measured by light scattering corresponds to the majority of chains. Such results are also consistent with SANS and SAXS data on semidilute solutions.[10, 132, 139, 223, 224]

B. Experimental evidence for aggregation

Four types of supramolecular structures have been observed for NaCMC, we classify them as follows:

I. Regions of unreacted or weakly reacted cellulose present in NaCMC form large fibers [159, 160, 179], easily removed by filtration and/or centrifugation, see the discussion above. These aggregates are found for low DS samples and can be dissolved by addition of NaOH.[151]

II. Smaller aggregates, typically sub-micron have also been observed by light scattering[167, 225], AFM [226] and SANS [155, 227]. These aggregates are probably not of a unique kind but may rather correspond to different aggregation mechanisms depending on D.S., salt concentration etc. A possible structure is that of the fringed micelle[226, 228–230], which is supported by the AFM [226] data on dried NaCMC and by the GPC-light scattering results of Kötz [222] et al which show $R_g \sim M_w^0 \simeq 56$ nm (see fig. 20), this variation is characteristic of elongated objects undergoing lateral aggregation [156, 231, 232]. Given that several light scattering studies[131, 180, 181, 183, 219] on NaCMC with D.S. in the range of 0.7-1.1 report no aggregation for filtered and/or centrifuged aqueous salt solutions, it seems likely that if these aggregates are common, they are at least in part removable by filtration/centrifugation and/or addition of salt.

III. Liebert et al [226] report the formation of large network structures upon solution drying for NaCMC samples with non-random substitution. Gel formation in concentrated solutions have been observed in a number of other studies[8, 11, 112, 228, 233].

IV. Polyelectrolyes in salt-free or low salt solutions are known to display a slow mode in their DLS autocorrelation function. While the precise mechanism driving this kind of aggregation remains unclear[186], the strong sensitivity of aggregates on added salt concentration establishes that this kind of assembly is electrostatically driven. No systematic study on the characteristic of this kind of aggregation has been performed for NaCMC. The slow mode observed by dynamic light scattering by Lopez and Richtering[138] and Behra et al[174] in salt-free solution likely contains a contribution from these and type II aggregates.

1. *Fringed micelles*

For cellulose derivatives, intermolecular clusters are usually thought to form ‘fringed micelles’. Possible structures for these fringed micelles are shown in 19. The common feature is the presence of segments of unsubstituted cellulose, which form a crystalline core out of which dangling chains emanate. A detailed mathematical treatment of the scattering properties of the fringed micelle was developed by Burchard.[230] In practice, accurate fitting of a form factor to scattering data is difficult, but the basic features of the model can be elucidated. As we will see below, experimental evidence, in our view, favours the structures schematised in panels c and d of figure 19.

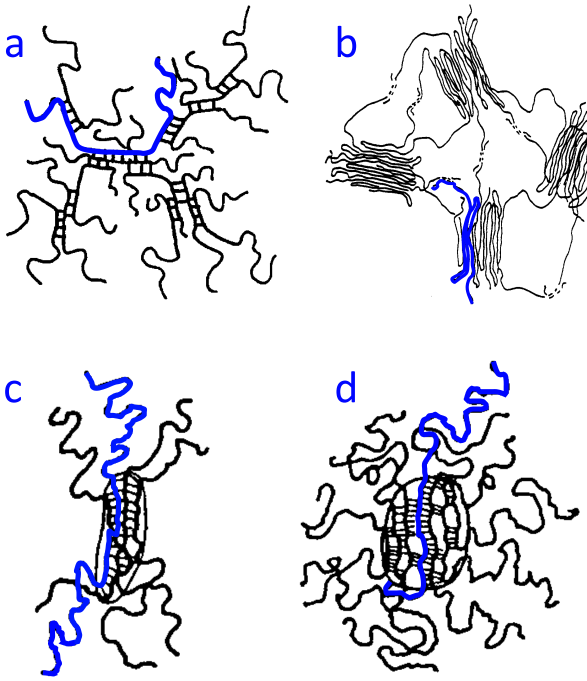

FIG. 19. Possible structures of fringed micelles. Sections where chains are aligned in parallel are the crystalline cores. Schematics are adapted from refs. 156, 231, 234. Blue lines are single chains within an aggregate.

Experimental evidence for fringed micelles

While most published light scattering studies are consistent with NaCMC being molecularly soluble, a few studies give evidence supporting strong inter-molecular aggregation. Figure 20 plots the radius of gyration of CMC solutions where aggregation is apparent. Buchard et al[231, 234] and Sitaramaiah and Goring[167, 235] (SG) performed static light scattering on solutions of NaCMC in 0.1 M NaCl for samples of varying molar mass.[236]. SG's samples have DS $\simeq 0.62 - 0.74$, Burchard et al do not report the DS of their polymers. Both datasets display a scaling relationship of $R_{g,z} \propto M_w^{1/3}$ as expected for compact objects (fractal dimension $d_F = 3$) with constant polydispersity.[237] The 1/3 exponent contrasts with the larger values observed for CMC samples in samples of higher degree of substitution.

The molar mass measured by SG using static light scattering was found to be $\simeq \times 4$ larger than the molar mass calculated from the intrinsic viscosities in 0.1 M NaCl using the MHS relationship reported in 220 or from their sedimentation-diffusion estimates. This difference persisted despite extensive centrifugation of their samples. The results suggest the coexistence of a fraction of chains which are molecularly dissolved, and a fraction which is highly aggregated. The aggregated fraction makes a large contribution to M_w and $R_{g,z}$ but not to the intrinsic viscosity because their compact size results in a low hydrodynamic volume relative to their mass ($[\eta] \propto R_H^3/M_w$, where R_H^3 is the hydrodynamic volume of the chain). The $M-$dependence for the diffusion coefficient, intrinsic viscosity and sedimentation coefficient in SG's study are also consistent with the scaling relationships observed for molecularly dissolved polymers in good solvent, indicating the aggregates do not strongly contribute to these quantities.

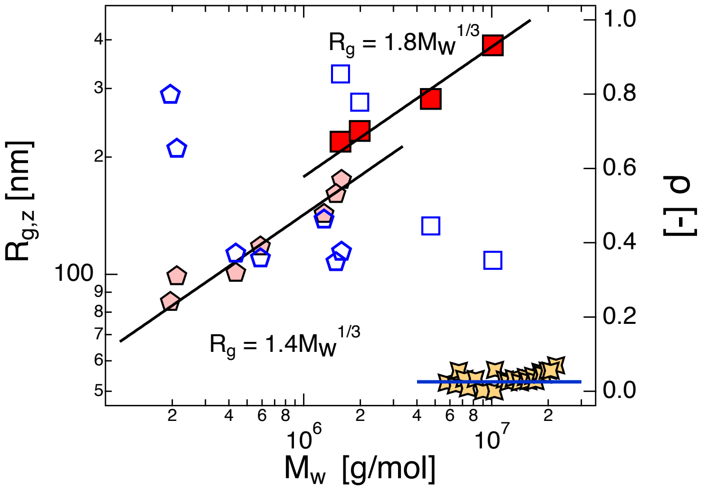

FIG. 20. Light scattering results on fringed micelles. Red/Orange symbols are radius of gyration: Data are by Burchard et al (DS not given) in 0.1 M NaCl (red squares), Sitaramaiah and Goring for DS = 0.66-0.74 in 0.1 M NaCl (pentagons) and Kotz et al (stars, measured by SEC). Black lines are power-laws with exponents forced to 1/3, as expected for compact objects. Blue line is $R_g = 53$ nm. Blue hollow symbols are $\rho = R_g/R_H$. R_H for Sitaramaiah and Goring's samples was estimated from the intrinsic viscosity, an therefore correspond to the hydrodynamic radii of a single chain and not of an aggregate, see the text for details.

Further evidence supporting the fringed micelle structures in figure 20 comes from the dimensionless ratio ρ reported by Burchard et al. Polyelectrolytes in excess salt or polydisperse polymers in good solvent typically display $\rho \simeq 1.5 - 2$. For compact spheres $\rho = 0.78$. Buchard et al's data at high M_w display values of $\rho \simeq 0.4$, below those of hard spheres, which are characteristic of objects with a dense core and dangling chains such as heterogeneously cross-linked microgels.[238, 239]

Following the preceding discussion, we assume that the intrinsic viscosity of SG's samples contains a negligible contribution from aggregates. The universal ratio $U_{\eta,f}$ is given by:

$$U_{\eta,f} = 6\pi \Big(\frac{[\eta] M}{N_A R_H^3} \Big)^{1/3} \tag{11}$$

where $[\eta]$ is the intrinsic viscosity, R_H the hydrodynamic radius, M the molar mass and N_A Avogadros's constant.

$U_{\eta,f}$ is known to take a value of $\simeq 0.12$ for polymers in solution.[186] Using the intrinsic viscosity values given in refs. [167, 235], the hydrodynamic radius of individual chains are calculated, see table V. Furthermore, assuming a value of $\rho = 2$ for well dispersed chains, $R_{g,z}$ for a

Sample	DS [-]	N_w^{LS} [-]	$R_{g,z}^{LS}$ [nm]	$[\eta]_{0.1M}$ [M^{-1}]	N_η [-]	R_H^* [nm]	R_g^* [nm]	$\sigma^* = R_{g,z}^{LS}/R_g^*$ [-]
H1	0.66	7460	175	262	2500	45	91	1.9
H2	0.62	7070	161	256	2430	45	89	1.8
H3	0.63	2790	118	160	1420	32	64	1.8
M1	0.72	5880	143	151	1330	31	61	2.3
M2	0.72	2000	101	127	1080	27	54	1.9
L1	0.7	3700	-	111	935	25	49	-
L2	0.74	960	99	56.3	427	15	30	3.3
L3	0.73	890	85	34.3	241	11	21	4

TABLE V. Measured and calculated parameters for Sitaramaiah and Goring's samples. N_w^{LS} and $R_{g,z}^{LS}$ are the weight averaged degree of polymerisation and z-averaged radius of gyration measured by SLS. $\eta]_{0.1M}$ is the intrinsic viscosity measured in 0.1 M NaCl and N_η is the degree of polymerisation calculated using the MHS relationship reported in 135. R_H^* is the hydrodynamic radius of a single chain estimated from Eq. 11 and the measured intrinsic viscosities, and R_g^* is the radius of gyration of a single chain calculated as $R_g^* = \rho R_H^*$ with $\rho = 2$. The parameter σ^* is an estimate of the radius of gyration of a chain to that of the fringed micelle.

single chain, is estimated. These values are listed as R_g^* in table V. Then, taking the light scattering radius of gyration to correspond to that of the fringed micelle[240], we estimate the ratio of the R_g of a single chain to that of the multi-chain aggregate, and find values of $\sigma^* \simeq$ 2-4 for SG's samples. Noting that our coarse estimates for σ^* are likely underestimates, we judge they support the structures sketched in panels a and d of figure 19.

The size exclusion chromatography data of Kotz et al[222], plotted in figure 20 show $R_g \sim M_w^0 \simeq 53$ nm. Unlike the data from refs. [167, 231, 234, 235], each point here corresponds to a monodisperse fraction of aggregates, with no contribution from the molecularly dispersed chains, which elute at earlier times and show $R_g \sim M_w^{1/2}$ (see fig 3 of ref. [222]). The unusual independence of R_g on molar mass is consistent with laterally aggregated chains, where the molar mass increases proportionally with the number of chains in the cluster, but the longest dimension of the aggregate is largely unchanged. This supports the pictures in panels c and d of figure 20.

In summary, the data of Burchard et al and Sitaramaiah and Goring are broadly consistent with the fringed micelle model. Though the specific structure of the micelles cannot be resolved in any detail, the experimental evidence are most consistent with structures a and d of figure 20. A more quantitative evaluation of the fringed micelle model is not possible from the present data.

2. *Evidence from atomic force microscopy*

Representative examples type II and type III aggregates obtained by atomic force microscopy are shown on figure 21. The microscopy work on these type of aggregates is more sparse than for type I aggregates and no systematic studies has have performed to clearly distinguish the effect of different parameters (salt concentration, temperature, pH etc) on aggregate formation. Further, it is not known if the observed structures are thermodynamically stable or whether they correspond to kinetically trapped assemblies. So far, the best evidence for fringed-micelle structures comes from the light scattering work discussed above.

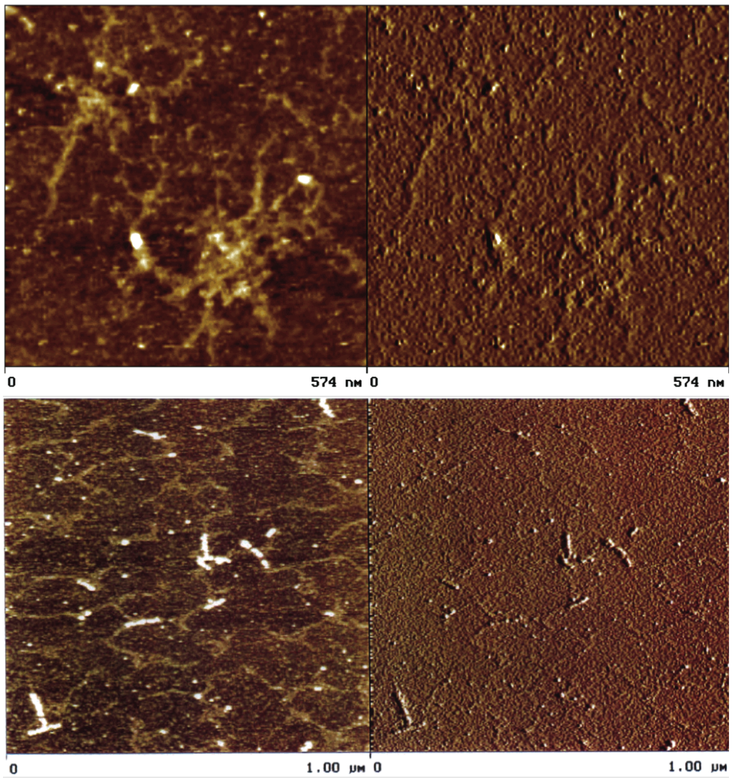

FIG. 21. AFM images of CMC supramolecular assemblies. Top panels: fringed-micelle like aggregates observed by Liebert et al, from reference [226]. Bottom: Type III aggregates, also Libert et al.

C. The slow mode and low-q upturn

Long-ranged inhomogeneities are commonly reported in polyelectrolyte solutions, even though their existence is difficult to reconcile with the high osmotic pressure and correspondingly low osmotic compressibility of salt-free systems is expected to suppress such inhomogeneities. Dynamic light scattering often reveals a slow relaxation mode, and small angle scattering profiles frequently display a low-q upturn, both features suggesting fluctuations or structures on length scales of hundreds of nanometers. These observations are therefore surprising from a theoretical standpoint and remain the subject of debate.[186, 241–244]

Carboxymethyl cellulose solutions exhibit the same behaviour. Dynamic light scattering measurements on several NaCMC salts[138, 174, 179] show a pronounced slow mode whose apparent size depends on the pore size used during filtration. Changes that occur within a week of filtration indicate that the relevant structures are not at equilibrium, consistent with findings for polystyrene sulfonate.[245] Small angle neutron scattering data likewise reveal large-scale inhomogeneities in CMC solutions.[10, 132, 224, 246]

Because multiple types of aggregates are present in typical CMC samples, it is difficult to attribute the slow DLS mode and the low-q excess scattering solely to these long-ranged 'polyelectrolyte inhomogeneities'. The overlap between different populations obscures the origin of these signals and complicates interpretation.

VIII. CONCLUSIONS

Solubility, conformation and supramolecular aggregation: Carboxymethyl cellulose displays a wide range of solubility and supramolecular behaviour that reflects its substitution pattern, molar mass distribution and the crystalline parts of the starting cellulose material. First and second order heterogeneity in substitution determine whether chains dissolve molecularly or assemble into colloidal aggregates. Weakly substituted samples contain unsubstituted blocks that promote association into macroscopic fibres, gel particles or fringed micelles with crystalline cores. Highly substituted samples (DS $\gtrsim$ 1) dissolve molecularly with negligible gel fractions and no detectable crystallinity.

Dilute-solution measurements in excess salt yield single-chain properties consistent with the scaling theory of Dobrynin et al. The radius of gyration decreases with added salt as $c_S^{-1/5}$ and the overlap concentration follows the expected molar mass scaling in salt-free and excess-salt regimes. Data for the persistence length of CMC are contradictory and additional light scattering experiments on samples with well characterised molar mass distributions would be helpful in this regard.

Needed improvements in characterisation and sample preparation: Purification by dialysis is standard practice for many commercial polyelectrolytes and is, in general, necessary to obtain reproducible results. The high purity of food-grade CMC means that as-received samples often contain relatively low levels of residual salt, typically below one salt ion per 50 monomers, and can sometimes be used without further purification. For technical and semi-purified grades, however, purity cannot be assumed. Dialysis against DI water followed by freeze-drying would help improve reproducibility.

Work on CMC would benefit from characterisation of the degree of substitution and the molar mass. Many authors rely on manufacturer specifications for DS and M_w. DS values are usually accurate to within $\simeq 20\,\%$, but reported molar masses can deviate by factors of up to two, and batches sold under the same nominal molar mass do not necessarily exhibit consistent M_w. A survey of recent work shows that reliance on manufacturer data is the rule rather than the exception.[54, 136, 247–258] As a result, many reported correlations between physical properties, for example solution viscosity, and molar mass [199, 259–261] are likely to be only qualitatively correct. Since the average DS can be measured by simple titration methods, authors should determine these values rather than rely on manufacturer specifications. Determination of the intrinsic viscosity in excess salt to obtain the molar mass is straightforward. Static light scattering can provide additional information, but, as discussed above, accurate values of $(dn/dC)_\mu$ need to be determined first.

The heterogeneity in degree of substitution and the specific substitution pattern plays a central role in determining the rheological and associative behaviour of CMC. Despite this, studies that quantify DS polydispersity or substitution pattern remain rare.[262] Systematic characterisation of these features would allow for better interpretation of the flow behaviour of CMC solutions and gels. Experimental techniques such as XRD are easy to perform and allow for at least some qualitative information on the substitution pattern of the polymers. More involved methods such as enzymatic depolymerisation followed by residue analysis provide greater detail but require considerably more work. Similar considerations apply to the molar mass polydispersity, which, while important to understand flow properties, is not usually quantified in rheological studies.[10, 11, 133, 135–139, 166, 174] The development of methods to quantify molar mass distribution from rheological properties of salt-free polyelectrolytes should be helpful in this direction.[263]

Outlook: The economic importance of NaCMC has resulted in considerable academic research into the physical properties of this polymer. However, given its complexity and inherent heterogeneity, many questions about its conformation and aggregation state in dilute solution remain unresolved. The collected data allow for a qualitative description of aggregation phenomena, and Burchard's fringed micelle model appears to correctly capture the experimental observations. Systematic light scattering studies on samples of various degrees of substitution in particular would be of interest to resolve some of the questions raised here.

IX. DISCLOSURE STATEMENT

The author reports there are no competing interests to declare.

APPENDIX A: REFRACTIVE INDEX OF SOLUTIONS

TABLE VI. Refractive index increment of NaCMC in various salt solutions. The added salt is NaCl except for ref. [175] [a] TBACMC [b] presumably 0.02 or 0.1 M NaCl [c] added salt is NH_4NO_3

Ref.	c_S [M]	$\frac{dn}{dc}$ [mL/g]	DS [-]	λ [nm]
[174]	no salt	0.17	0.8	-
[154] [a]	no salt	0.168	1.3	633
[175]	0.1 mM [c]	0.145	DS-independent (1-2.9)	-
[176]	0.05	0.137	0.66, 0.69	488
[177]	no salt	0.144	1.23	950
[178]	0.1	0.147	1	-
[179]	0.1	0.141	0.7	-
[176]	0.1	0.139	1.2	488
[180]	0.1*	0.156	DS-independent (0.8–2.9)	-
[167]	0.1	0.147	0.66–0.77	546.1
[131]	- [b]	0.163	DS-independent (0.75-1.25)	632.8
[181]	0.5	0.154	1.15	436
[182]	-	0.138	0.8	690

APPENDIX B: LIST OF SYMBOLS

- A_2 - second virial coefficient
- b - length of chemical monomer ($\simeq 5$ Å for CMC)
- B - stretch parameter
- c - polymer concentration in units of moles of repeating units per volume
- C - polymer concentration in units of mass per volume
- c_S - concentration of added salt in units of salt molecules per volume
- Đ - dispersity or polydispersity
- e - elementary unit of charge
- K - optical contrast factor (Eq. 7)
- k_B - Boltzmann's constant
- k_H - Huggins constant
- k_K - Kraemers constant
- l_K - Kuhn length
- M_0 - Molar mass of a monomer
- M_n - number average molar mass
- M_w - weight average molar mass
- M_z - z-average molar mass
- M_{z+1} - (z+1)-average molar mass
- n - refractive index of solution
- n_0 - refractive index of solvent
- N_A - Avogadro's constant
- N_K - number of Kuhn segments per chain
- $P(q)$ - Form factor of a chain
- q - scattering wave-vector
- R - end-to-end distance of a chain
- R_g - radius of gyration of a chain
- R_H - Hydrodynamic radius
- R_η - Viscosimetric radius ($R_\eta \equiv [\eta]^{1/3}$)
- T - Absolute Temperature
- x_i - fraction of monomers with with position i substituted ($i = 2, 3, 6$, see fig 1)
- χ_i - fraction of monomers which are unsubstituted ($i = 0$), mono-substituted ($i = 1$), di-substituted ($i = 2$) or tri-substituted ($i = 3$)
- ΔR - excess Raleigh ratio
- ϵ_0 - vacuum permittivity
- ϵ_r - relative permittivity
- κ^{-1} - Debye screening length
- λ - wavelength of scattering radiation
- η_{inh} - inherent viscosity
- η_{rel} - relative viscosity
- η_{red} - reduced viscosity
- η_{sp} - specific viscosity
- $[\eta]$ - Intrinsic Viscosity
- θ - scattering angle
- μ - mean of DS distribution

APPENDIX C: LIST OF ABBREVIATIONS

- AGU - anhydrous glucose unit
- Cell - Cellulose
- CMC - carboxymethyl cellulose
- DS - degree of substitution
- IPA - Isopropanol
- TMA - tetramethyl ammonium
- TBA - tetrabutyl ammonium

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