

Viscometric studies on the methyl cellulose–sodium dodecyl sulphate complex in aqueous solution

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(Received 1 July 1986; revised 4 August 1986)

Interactions between sodium dodecyl sulphate (SDS) and methyl cellulose (MC) with a molecular weight of 7.0×10^4 were studied in aqueous solution at 25°C by viscometry and equilibrium dialysis. Except for some details, the resulting adsorption isotherm was similar to that determined by Lewis *et al.* In contrast to other non-ionic polymers, the intrinsic viscosity of MC decreased to a minimum near the critical micelle concentration of SDS with increase in SDS concentration. It was concluded that the hydrophilicity of MC decreases by binding of SDS and that saturation of binding occurs at 15 mM, as correlated with peculiar Huggins plots found for this system.

(Keywords: methyl cellulose; sodium dodecyl sulphate; viscosity; complex formation; equilibrium dialysis)

INTRODUCTION

Methyl cellulose (MC) is a kind of water-soluble cellulose ether used extensively in foods, cosmetics and pharmaceutical industries, as thickeners, stabilizers, binders, swelling agents, moulding agents or suspending agents¹. Since this polymer shows interesting behaviour in aqueous media as a non-ionic and strongly water-fixed coil, or as a solute molecule which tends very much to aggregate²⁻⁴, its colloidal⁵, hydrodynamic^{6,7} and molecular^{4,8} properties have been investigated by many workers in several scientific fields. Numerous reports have been published on interactions with other materials such as ions, dyes and preservatives in aqueous MC solutions. For example, Ikawa showed that the observed decrease in the reduced viscosity of MC on adding phenol is due to a reduction in hydrophilicity of the polymer caused by complex formation⁹, while its increase on adding Congo red is due to crosslink formation among the polymer chains¹⁰.

Concerning the interaction between a non-ionic polymer and an ionic detergent, the following binding process is widely accepted. When the surfactant is added to the polymer solution, adsorption suddenly begins to occur at a certain critical concentration of the surfactant essentially by hydrophobic bonding. Subsequently, the polymer grows into a 'mature' associated chain and, after saturation, the formation of free ordinary micelles only is accelerated in the bulk. These processes have been confirmed for various systems^{11,12}. The interaction of sodium dodecyl sulphate (SDS), a typical anionic surfactant, with MC has already been reported. For example, Lewis *et al.*¹³, investigating the adsorption isotherm, showed the presence of such a critical

concentration of SDS below which no interaction with the polymer occurs, and correlated the isotherm with specific or reduced viscosity data. Goddard *et al.*¹⁴ also found SDS concentrations at which the onset and the saturation of binding occur, from dye solubilization, surface tension and specific viscosity measurements on anionic surfactant complexes with charged and uncharged cellulose ethers.

Recently Francois *et al.*¹⁵ studied in detail the hydrodynamic behaviour of a poly(ethylene oxide) (PEO) and SDS complex, and concluded from a high viscosity exponent in the Mark–Houwink–Sakurada (MHS) relation that the complex exhibits viscosity behaviour typical of a slightly charged polyelectrolyte. On the other hand, the numbers of SDS micelles adsorbed onto PEO and poly(vinyl pyrrolidone) (PVP) were determined by fluorescence quenching experiments by Lissi *et al.*¹⁶

In this work, we obtained viscosity and binding data for the MC–SDS system at 25°C, and examined whether these data can be correlated with each other.

EXPERIMENTAL

Materials and measuring solutions

Methyl cellulose 50 (Nakarai Chemical Co.) was used as a polymer sample; its solution (2%) nominally has a viscosity of 40–60 cP at 20°C. Prior to use, this was dissolved once in water in the usual manner, and any insoluble material like microgels and extraneous ionizable materials were removed by filtration and by dialysis against distilled water. Then the solution was lyophilized and dried for a prolonged time in a vacuum oven. SDS, a surfactant (which was kindly supplied by Nippon Yushi Co. Ltd), was recrystallized twice from 1-

butanol and dried *in vacuo* for 2 days. Its critical micelle concentration (c.m.c.) was found to be 8.2 mmol dm^{-3} (mM) by measuring the relative and reduced viscosities at 25°C , which agreed with those reported by Kodama *et al.*¹⁷ Distilled water used was prepared with a Yamato Auto Still WAG-28 water purifier.

Stock solutions of MC were prepared with continuous stirring first by dispersing the required quantity of the polymer in about a half of the requisite volume of distilled water with warming and then by adding cold water up to the requisite volume, when the polymer dissolved completely. The solutions were allowed to cool in a refrigerator in line with the findings of Neely⁴. Measuring solutions were prepared before use by fully mixing each aliquot of the stock solution and of the aqueous SDS solution with the required concentration.

Measurements

Light scattering was measured at $25 \pm 0.5^\circ\text{C}$ using unpolarized mercury light of 436 nm on a Shimadzu PG-21 light scattering photometer equipped with a thermo-controlling jacket. The specific refractive index increment was determined under the same conditions using a Shimadzu DR-3 differential refractometer. The optical clarification of measuring solutions was performed by filtration through double sheets of Solvinert UH and UG filters (purchased from Nippon Millipore, Ltd). Techniques and other details have been previously described¹⁸.

Dialysis experiments were done at 25°C in an agitated water bath for 3 days in a manner similar to that reported by Lewis *et al.*¹³ and by Nakagaki *et al.*¹⁹ A Visking cellophane tube (No. 20/32 of Union Carbide Co.) was used as the semipermeable membrane. Each dialysis bag filled with 10 ml of the solution, which contains the polymer at a concentration of 0.385 g dl^{-1} in SDS solutions of a given concentration, was fully immersed in glass test tubes with the same solution volume and SDS concentration as in the bag. After equilibrium had been attained, the concentration of the SDS solution outside the membrane (with no polymer) was determined by titration using a 2 mM cetylpyridinium chloride solution according to the Epton method²⁰.

Solution viscosities were measured in a water bath at $25 \pm 0.01^\circ\text{C}$, using several Ubbelohde-type dilution viscometers with a flow time of 98–250 s for the water. The polymer concentration was $\sim 0.2 \text{ g dl}^{-1}$ at most. The viscosity of such dilute MC solutions changed little with increasing rate of shear, so that its shear-rate effect was ignored.

RESULTS AND DISCUSSION

Molecular weight and intrinsic viscosity

In his work on the molecular properties of MC in aqueous solutions by light scattering and viscometry, Neely observed distorted Zimm plots. According to his assertion, this was due to polydispersity brought about by aggregation of MC, and indicated that the methods of preparation and storage of MC solutions are critical, for MC molecules tend to aggregate with one another⁴. In contrast to Neely, we have obtained normal rectilinear Zimm plots from light scattering measurements on our MC sample in water, although Zimm plots with a

downward curvature were sometimes observed perhaps because of residual dust in the solutions. An example is shown in Figure 1, where R_θ is the reduced intensity of light scattered at an angle θ and K is the optical constant (the refractive index increment was 0.152 ml g^{-1}). This plot yields a weight-average molecular weight $M_w = 7.0 \times 10^4$ for our sample, and suggests that the aggregation of MC is not appreciable.

The intrinsic viscosity $[\eta]$ of MC in water at 25°C was found to be $2.56 \pm 0.05 \text{ dl g}^{-1}$ by repeated measurements (cf. Figure 3). When applied to the MHS equation proposed by Neely⁴, this $[\eta]$ value gives a molecular weight 2.7 times the M_w determined above. Hence, Neely's MHS relation should be accepted with reservation. Marriott *et al.*²¹ obtained a normal Zimm plot for aqueous MC solutions and pointed out that the Zimm plots obtained by Neely might be due to the presence of dust. However, comparison of their and our $[\eta]$ values reveals that their reported M_w values are much larger than ours. Similar light scattering data have also been reported by Das *et al.*²² for six fractions of MC ranging in molecular weight from 8×10^4 to 111×10^4 together with the viscosity data. These data give $[\eta] = 1.07 \times 10^{-3} M_w^{0.61}$ (by our calculation), but are inconsistent with our results. The M_w of our sample is rather consistent with the MHS equations established earlier at 30°C by Gibbons²³ and by Uda²⁴, since our $[\eta]$ measured at 30°C was 2.43 dl g^{-1} . Establishment of the MHS equation for this system seems difficult but highly desirable, since the presence of aggregates in aqueous MC influences to a great extent the estimation of M_w (but not so that of $[\eta]$)²⁵.

Adsorption isotherms derived from equilibrium dialysis

The amount adsorbed, x , in moles of SDS per base mole of MC, was calculated from equilibrium dialysis data using equation (5) in ref. 19. Figure 2 shows a plot of

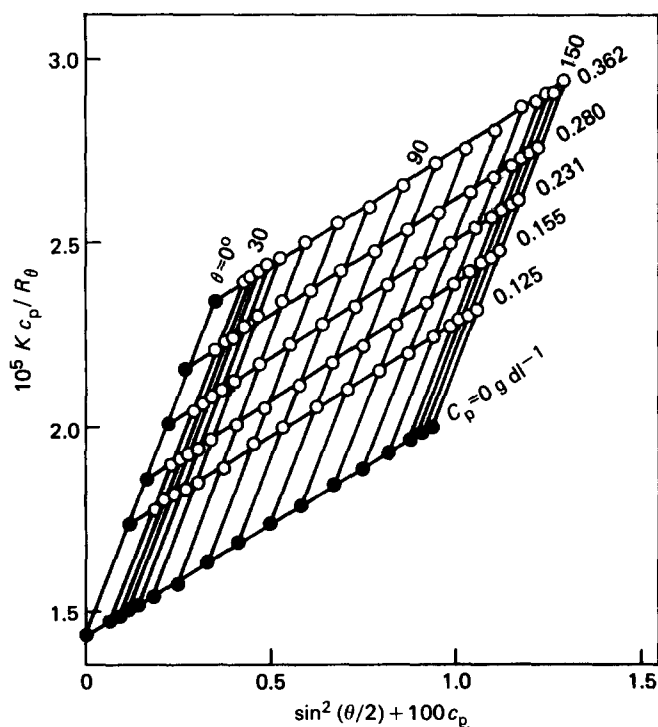


Figure 1 Zimm plot for methyl cellulose in water at 25°C . Scattering angles and polymer concentrations measured are shown

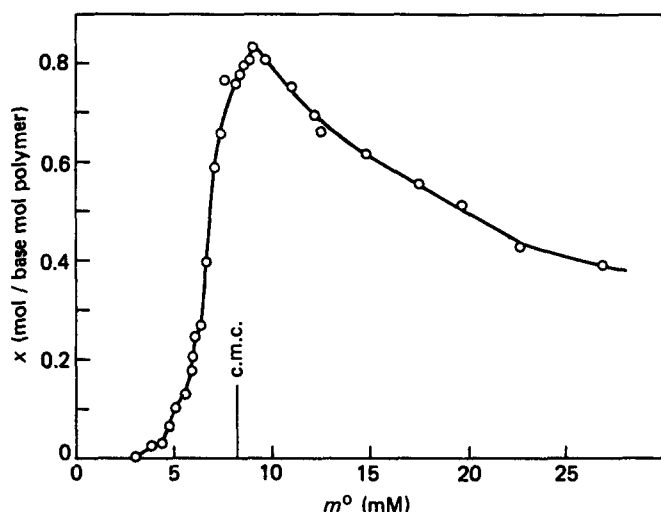


Figure 2 Adsorption isotherm for methyl cellulose in aqueous sodium dodecyl sulphate at 25°C. The thin line indicates the critical micelle concentration

x against the equilibrium concentration of SDS, m° , of the outer solution at 25°C. Lewis *et al.*¹³ have reported an adsorption isotherm for the same system at room temperature ($\sim 22^\circ\text{C}$), and determined m° from the measured electric conductivity, which showed a maximum adsorption, x_{max} (≈ 1.6 mol/base mol polymer) at an SDS concentration of m_{max}° (≈ 6 mM). The isotherm in Figure 2 is similar to that of Lewis *et al.*, except that $x_{\text{max}} = 0.83$ at $m_{\text{max}}^\circ = 9.0$ mM. It is likely that the differences in both x_{max} and m_{max}° are primarily due to a difference in the amount of aggregates in solution, since the fact that the solution concentrations used, the molecular weights of MC samples and the measuring temperatures differ somewhat from each other does not seem to have much effect^{13,19}. Nakagaki *et al.*¹⁹ published isotherms for PVP–SDS and poly(vinyl alcohol) (PVA)–SDS systems at 30°C and 37°C. The observed monotonic decline of the adsorption curve following saturation was ascribed to the depression of activity of DS anions (DS^-) in water. From comparison of x_{max} we found that the MC polymer interacts with SDS molecules far more strongly than do PVP and PVA. The Donnan effect was ignored in this work for the same reason as described by Lewis *et al.*¹³, although it would give a small effect on x ¹⁹.

Variation of $[\eta]$ with SDS concentration

All the viscosity data were analysed by the Huggins equation:

$$\eta_{\text{sp}}/c_p = [\eta] + k_1[\eta]^2 c_p$$

where η_{sp} is the specific viscosity of MC, c_p the polymer concentration in g dl^{-1} and k_1 the Huggins constant. Representative Huggins plots for SDS solutions of molar concentrations m_s below and above the c.m.c. ($= 8.2$ mM) of pure SDS are depicted in Figures 3 and 4 without taking into account the molecular weight increase due to the SDS fixation. In the m_s range of 0–6.2 mM, the plots in Figure 3 give straight lines, whose slopes are steeper for higher m_s . Above 16 mM, where the data points on the lines A, B and C in Figure 4 are not shown for simplicity, linear relations can also be seen. The $[\eta]$ values estimated

from the intercepts of these plots are plotted against m_s in Figure 5. However, the Huggins plots for m_s between 7.5 and 14.0 mM in Figures 3 and 4 are curved intricately at high dilution, exhibiting behaviour similar to that often observed for polyelectrolytes at low ionic strength. Thus, the determination of $[\eta]$ in this m_s region was impossible by the Huggins plot and any other viscosity relations already published. It may only be stated from the $[\eta]$ behaviour in Figure 5 that, in the range of m_s considered here, the hydrodynamic volume of the polymer must reach a minimum near the c.m.c. (indicated by the thin line) and then expand abruptly with increase in m_s . We note that in the range of m_s from 3.7 to 14.0 mM the true m_s value for the solution surrounding MC chains should be somewhat smaller and thus the viscosity evaluated above might be underestimated a little, because the adsorption of SDS molecules onto polymer chains occurs to saturation. Such a consideration was made by Francois *et al.*¹⁵ on the hydrodynamic behaviour of the well investigated PEO–SDS system, but not made here owing to lack of detailed information for this system.

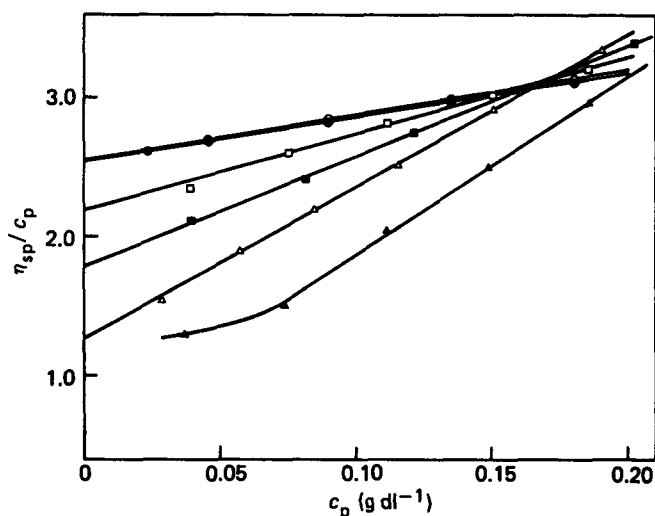


Figure 3 Huggins plots for aqueous methyl cellulose solutions below the c.m.c. of sodium dodecyl sulphate at 25°C. Concentration of sodium dodecyl sulphate (in mM): ○, 0; ●, 1.0; □, 3.7; ■, 5.0; △, 6.2; ▲, 7.5

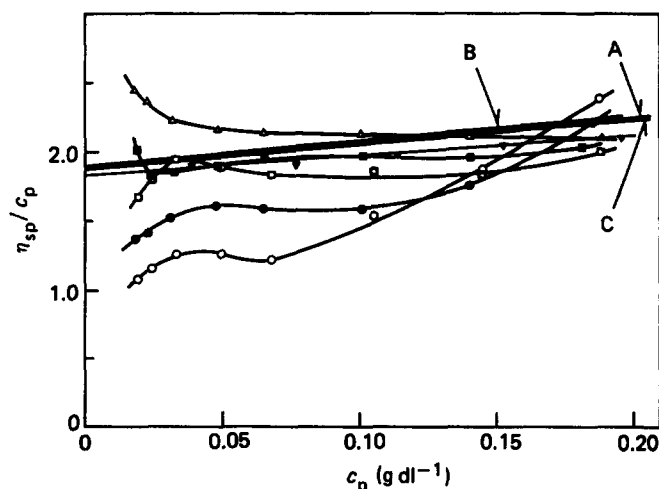


Figure 4 Huggins plots for aqueous methyl cellulose solutions above the c.m.c. of sodium dodecyl sulphate. Concentration of sodium dodecyl sulphate (in mM): ○, 8.6; ●, 10.0; □, 12.1; ■, 13.0; △, 14.0; line A, 16.6; line B, 20.0; line C, 24.9; ▼, 33.2

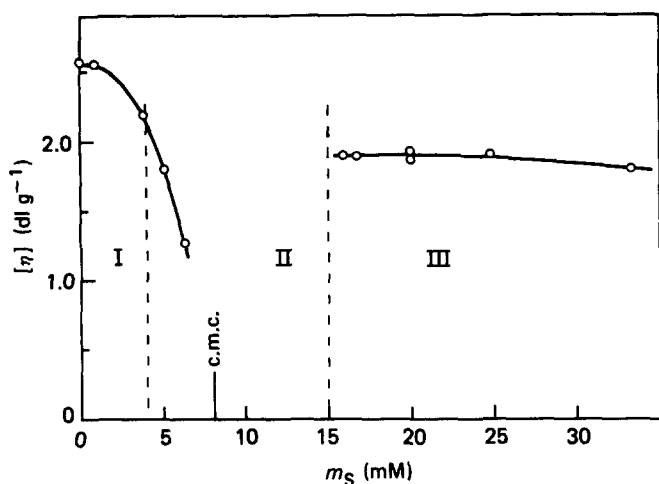


Figure 5 Variation of $[\eta]$ with m_s in aqueous solution at 25°C. The Roman numerals indicate three regions for binding

As has commonly been shown for systems like ours, the viscosity increases, in general, with increasing detergent concentration by electrostatic repulsion between dissociated detergent ions fixed on the polymer. Such an increase in $[\eta]$ or η_{sp}/c_p with m_s was shown for PVA and PVP¹⁹ or for PEO¹⁵. However, the results in Figure 5 are the opposite. Similar viscosity behaviour was observed by Lewis *et al.*¹³, who found an abrupt decrease in relative viscosity η_r for various SDS solutions containing 0.05% MC. For an aqueous 0.1% MC solution at 25°C, Goddard *et al.*¹⁴ reported a variation of η_r (to water) with SDS concentration, which showed a plateau up to 4 mM SDS, a subsequent decrease to a minimum at 8 mM and an increase with a definite levelling off at 15 mM. They suggested from this finding that the onset and the saturation of binding occur at m_s of 4 and 15 mM, respectively. The former is nearly equal to the results from our adsorption isotherms and those of Lewis *et al.*¹³, but the latter is not decisive since it is different from the aforementioned x_{max}° . However, the results in Figure 4 support this m_s of 15 mM for the reason mentioned in the last paragraph of this text; we have found recovery to linear Huggins plots above ~15 mM. Thus the three non-interacting, premature and saturated regions for binding may be indicated, respectively, by I, II and III, as shown in Figure 5.

Some considerations on viscometric behaviour in each region

In region II of Figure 5, premature micelles or clusters may first be formed on MC chains and then grow to mature ones by filling up the possible remaining binding sites to saturation¹⁴. In the former domain of this region, Lewis *et al.*¹³ have concluded that, from the standpoint of the many aggregates of MC present in the aqueous solutions, the abrupt viscosity decrease mentioned above results from the disaggregation of associated MC molecules. We suppose that the decrease of $[\eta]$ may be due to a decrease in the hydrophilicity of MC caused by partially associated SDS molecules, in addition to the dehydration capacity of Na^+ dissociated into the bulk, since electrostatic repulsion is not predominant in this domain yet, as seen from the linear Huggins plots in Figure 3. We disagree with the disaggregation of MC for the reason mentioned below. Contrary to the normal k_1

values of 0.48 to 0.61 obtained in the regions I and III, the k_1 value calculated from the straight lines for 3.7, 5.0 and 6.2 mM solutions were 1.2, 2.5 and 11, respectively, which are much larger than those (≤ 0.7) usually reported for many polymer–solvent systems. This may not be altered even if the ‘true’ solvent mentioned above is considered. According to the equation of Sakai²⁶, a large k_1 is expected for a flexible chain polymer far below the theta state, but as argued by him the equation may be of less significance in such a state. Recently Wolff *et al.*²⁷ have shown theoretically that, when aggregates of a polymer are present in a solution, a curve of η_{sp}/c_p vs. c_p has a convex curvature and results in $k_1 \gg 0.5$. Huggins plots with k_1 larger than unity were observed for aqueous MC at 45°C near the cloud point²⁸. In these circumstances we consider that aggregation should be more pronounced in the domain under consideration than in region I and that the hydrodynamic volume of MC should be influenced more strongly by the hydration state of the chain; we note that MC appears to aggregate side by side and thus the viscosity should be insensitive to aggregation²⁵.

The abrupt increase in viscosity at higher m_s in region II may be, as commonly explained, due to the DS^- fixed on the polymer, which may enhance the hydrophilicity of MC chains, leading to chain expansion due to electrostatic repulsion between them.

When Huggins plots are considered based on the above hypothesis for the formation of saturated polymer complexes above $m_s = 15$ mM, their recovery to the normal ones can be understood by the idea that the chain expansion of such a polyelectrolyte-like polymer with a certain charge density may be largely suppressed by dilution with solvents of high ionic strengths containing Na^+ , DS^- and anions of micelles. Anyhow it is apparent that the hydrodynamic dimensions ($[\eta] = \sim 1.9$) of the polymer fully adsorbed by SDS are definitely smaller than those ($[\eta] = 2.56$) of the MC molecule in water in spite of a possible increase of the molecular weight. Thus we may conclude that the binding of SDS molecules diminishes the hydrophilicity of MC and this is characteristic of the MC–SDS system. A quantitative discussion remains until more detailed data have been accumulated.

ACKNOWLEDGEMENTS

The author wishes to express his deep thanks to Professor Masayuki Nakagaki of Kyoto University and to Professor Shizuo Arichi of Kumamoto University for their continuous advice and encouragement during this work.

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