Distinct Maximum Appearing in the Viscosity Curve
of Dilute Polyelectrolyte Solutions

Hiroshi INAGAKI, Hisaya SAKURAI and Toshio SASAKI*

It is a well-known fact that the reduced viscosity *versus* concentration curve of polyelectrolyte solutions exhibits a well-defined maximum in the presence of a small amount of simple electrolytes. To ascertain this characteristic feature, viscosity measurements were made for the system of sodium carboxymethyl cellulose and several sorts of simple electrolytes, such as NaCl, NaOH, Na_2CO_3 and $MgCl_2$. A procedure for fitting numerically the viscosity curve at any extraneous electrolyte contents was developed on the basis of the experimental results obtained. The procedure was applied to the exact determination of the *position* of viscosity maximum (this is the polymer concentration where the maximum appears on the viscosity curve) and the *height* of viscosity maximum (this is the values of reduced viscosity which corresponds to the position), and it was investigated how these two quantities shifted under the variation of contents and sorts of the added electrolyte and of measuring temperature.

INTRODUCTION

One of the characteristic features of the viscosity behavior of polyelectolytes in dilute solutions comes out of the fact that the reduced viscosity η_{sp}/c *versus* concentration c curve exhibits a well-defined maximum in the presence of a small amount of simple electrolyte. Quantitative investigations have shown that the position of the maximum shifts towards higher concentrations of polymer with increasing amount of added electrolyte being accompanied with flattening of the curve. No theoretical interpretation has yet been available on the quantitative relationship between the maximum and the amount of added electrolyte. There are only some qualitative interpretations.

Fuoss[1] tried to attribute this to a mass action effect, which is based on the fact that a rise in the concentration of counterions enhances the association of counterions with the polyion. On the other hand, Pals and Hermans[2] and Basu and Gupta[4] interpreted this in terms of the effect of equivalent concentration of polyelectrolyte and evidenced this experimentally using the iso-ionic dilution method.

Uncertainty concerning the viscosity maxima in polyelectrolyte solutions mainly originates from the difficulty in viscosity measurements of the solutions at very low concentrations where the effect of shear-rate is generally remarkable. Accordingly, first of all, an intense attention should be paid to the shear-rate dependence of the solution in order to evaluate the relationship between the maximum in the viscosity curve and

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* 稲垣博，桜井久也，佐々木俊雄

the added electrolyte content for a given polyelectrolyte. We were, however, not in a position to be able to make this. So in this work, to determine unambiguously the polymer concentration where the maximum appears on the viscosity curves (hereafter referred to such a polymer concentration as the *position* of viscosity maximum), we proposed a procedure for fitting numerically the η_{sp}/c *versus c* curves of polyelectrolyte solutions at any extraneous salt contents. This procedure was applied to viscosity data of dilute solutions of sodium carboxymethyl cellulose (Na–CMC) obtained in the presence of several sorts of simple electrolytes. The factors by which the viscosity maximum would be controlled were then explored in terms of the results obtained.

CURVE-FITTING OF VISCOSITY DATA

Effective Ionic Strength

The η_{sp}/c *versus c* curve of polyelectrolyte solutions determined using the iso-ionic dilution method[3] should give a straight line for any amount of added electrolyte. As expected from the Hermans and Overbeek theory[5], this means that the molecular domain of a polyion is kept constant (irrespective of the polymer concentration) due to the iso-ionic strength of the system, which, in turn, results in a constant thickness of the electrical double layer around each polyion. Hence we may write for the iso-ionic viscosity data

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c , \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity and k' is a constant characteristic of a given system. It should be noted here that the value of $[\eta]$ and k' are essentially dependent on the *effective* ionic strength I_s as defined in a previous paper[6].

Pals and Hermans[3] have introduced the total ionic strength on the usual electrochemical basis. We shall, however, define this quantity in a more material manner on the basis of the experimental results reported in a previous paper[6], in which it was shown that, so far as the present anionic polyelectrolyte is concerned, it is reasonable to introduce for the ionic strength of added electrolyte an *ionic strength calculated with respect to cations only*. We referred to it as the *effective* ionic strength of added electrolyte. It is represented by the equation :

$$I_s = \sum_j \nu_j z_j^2 m_j , \qquad (2)$$

where ν_j is the number of cations of the j-th sort whose valency is z_j, and m_j is the concentration of electrolyte in moles per liter ; and the summation extends only over the cations. (Usual factor 1/2 is dropped.) So far as our previous and present works are concerned, the introduction of the effective ionic strength seems to be advantageous over the usual ionic strength. Thus, the total effective ionic strength, I_t of the given polyelectrolyte solutions may be written :

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$$I_t = I_s + I_p , \tag{3}$$

where

$$I_p = 10 \cdot r \cdot c . \tag{4}$$

Here I_s and I_p are the effective ionic strengths of added electrolyte and polyelectrolyte, respectively, and r is a factor to convert the polymer concentration c ($g/100 \, ml$) to I_p.

Determination of $[\eta]$ and k' as Function of I_s.

First we consider to represent $[\eta]$ as a function of I_s. On the theoretical basis, Pals and Hermans[3] derived following equation :

$$[\eta] = [\eta]_\infty + B' (10^3 \, I_s)^{-1/2} , \tag{5}$$

where $[\eta]_\infty$ and B' are characteristic constants whose physical meanings may be given. It is obvious that this equation can not be applied to the region of small I_s. We here propose a modified equation to avoid the divergence at limit of zero I_s. It is

$$[\eta] = [\eta]_\infty + \beta/(I_s^{1/2} + \alpha) , \tag{6}$$

where α and β are also characteristic constants. Equation 6 is analogous to the equation of Fuoss[7] as suggested by Katchalsky[8].

We shall next proceed to determine the functional form of k'. The value of k' as a function of I_s may be evaluated when $[\eta]$-values at several extraneous salt contents and the η_{sp}/c versus c curve for electrolyte-free-solutions are obtained. The η_{sp}/c curve for $I_s = 0$ is the locus of terminal points at $I_t = 10 \cdot r \cdot c$ of the iso-ionic straight lines. Hence the k'-value at any I_s-value is given by

$$k' = \left\{ \frac{(\eta_{sp}/c)_{I_s=0} - [\eta]_{I_s}}{c \, [\eta]^2_{I_s}} \right\}_{I_s = const.} \tag{7}$$

If it were possible to derive the theoretical equation for k', the equation would be too complicated in form to be useful for practical purposes. The k'-value is dependent both on the hydrodynamic interaction between macromolecules and on the electrostatic intra- and inter- molecular interactions.[9]

If $[\eta]$ and k' can be expressed in terms of I_s, we can draw the η_{sp}/c versus c curve for a given I_s-value by solving simultaneously Equations 1 and 3.

EXPERIMENTAL

Two commercial samples of Na-CMC of low viscosity and medium viscosity were used (hereafter call CMC-L and CMC-M, respectively) ; they were thoroughly washed by a methanol-water mixture and purified using the system of ethanol-water in the manner as reported in our previous work[6]. The degree of polymerization of CMC-L and CMC-M were 175 and 430, respectively, which were estimated by referring to Pals and Hermans' results[3]. The degrees of substitution were 0.734 for CMC-L and

0.570 for CMC–M, which were determined by means of the electro-conductometric titration and also checked by the ash values.

Shift of the position of the viscosity maximum with changes in added electrolyte content and in temperature was investigated under the same cautions as was taken for the viscosity measurements in the previous work[6]. The measurements were done at temperatures of 25, 35, 45, and 55°C in a constant temperature bath controlled to within ±0.01°C.

RESULTS AND DISCUSSION

Influence of Added Electrolytes on the Viscosity Maximum

1. Numerical Calculation of η_{sp}/c **vs.** c **Curves.** A family of the η_{sp}/c vs. c curves obtained for the system CMC–L–NaCl is shown in Figure 1. A family of the iso-ionic straight lines derived from the data in Figure 1 is given in Figure 2.
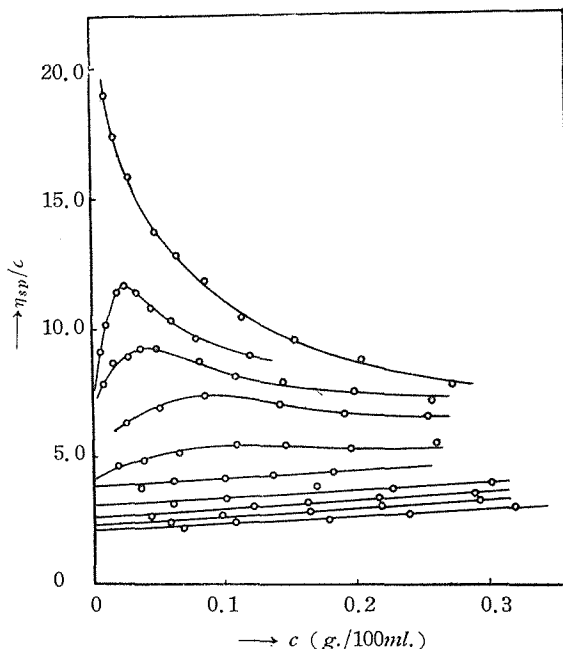

Fig. 1. The reduced viscosity *versus* concentration curves for CMC-L solutions in the presence of the following amounts of NaCl; from upper to below, nil, 5.00×10^{-4}, 1.00×10^{-3} 2.01×10^{-3}. 1.00×10^{-2}. 2.51×10^{-2}, 5.02×10^{-2}, 0.100 and 0.200 *moles/liter*.

These iso-ionic straight lines enable us to determine the functional forms of $[\eta]$ and k' in accordance with the procedure described above. First we shall describe the application of Equation 6 to the $[\eta]$-values obtained from Figure 2. In order to estimate the $[\eta]'_\infty$ in the equation, it is convenient to use Equation 5 which is applicable

with satisfactory approximation at high value of I_s. This gives 1.66 for $[\eta]'_\infty$. Then the velues of $([\eta] - [\eta]'_\infty)^{-1}$ are plotted against $I_s^{-1/2}$ as shown in Figure 3, from which the values of α and β may be determined.
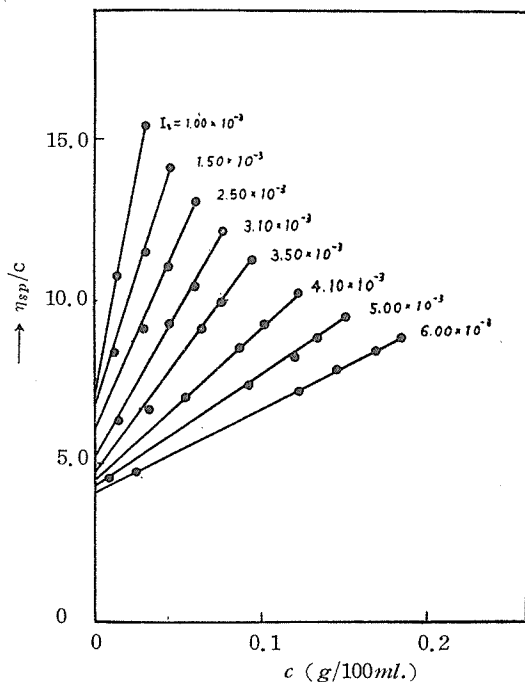

Fig. 2. Application of the iso-ionic dilution method for the system CMC-
NaCl : Numbers written at the end of each line give the total effective
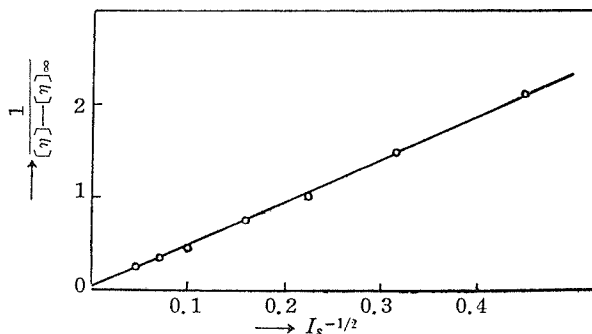ionic strength.

Fig. 3. Plot of $[\eta]$ against $I^{-1/2}$ according to Eqation 6.

Equation 7 shows that the k'-value for any given I_s-value can be evaluated when the viscosity curve for the electrolyte-free-solutions and the $[\eta]$ for the I_s-value are obtained. The plot of k' $vs.$ $I_s^{-1/2}$ obtained by applying this method to the data on CMC-L is similar to that obtained by Pals and Hermans[3] as shown in Figure 4, but

does not make it possible to extrapolate to $I_s = 0$. It is seen from the figure that the k'-value tends to approach a limiting value k'_∞ at $I_s = \infty$; the limiting value is within $0.2 - 0.6$ in agreement with those usually encountered for neutral polymer solutions. The value of k'_∞ was determined by the trial and error method so that the plots of $log(k' - k'_\infty + 1)^{-1}$ against I_s may become a staight line. (See Figure 5.) The empirical formula thus obtained for k' is represented in the form :

$$k' - k'_\infty = exp\left(\frac{b}{I_s+a}\right) - 1 , \tag{8}$$
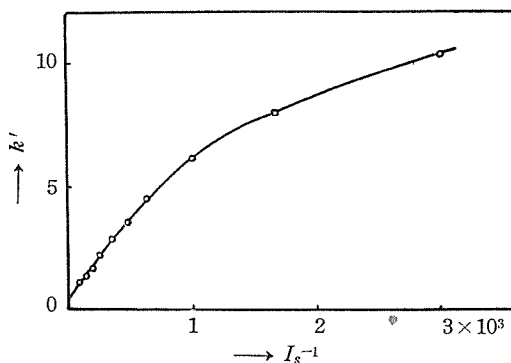
where a and b are experimental constants.
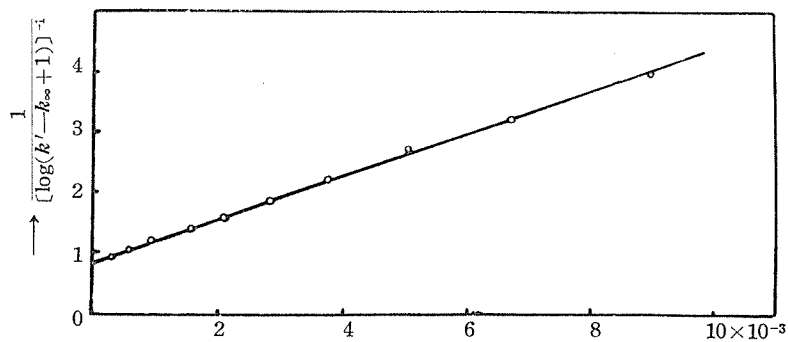

Fig. 4. Plot of k' against I_s^{-1}.

Fig. 5. Linearized relation of k' and I_s according to Equation 8.

Table 1.

$[\eta]_\infty$	1.66
α	8.3×10^{-3}
β	2.075×10^{-1}
r	3.3×10^{-3}
k'	0.34
a	2.28×10^{-3}
b	6.33×10^{-3}

Table 2.

$I_s \times 10^3$	$[\eta]$	k'
0.80	7.33	7.14
1.00	6.86	6.24
1.50	6.08	4.68
2.10	5.50	3.58
2.50	5.22	3.10
3.10	4.90	2.58
3.50	4.74	2.33
4.10	4.53	2.04
5.00	4.29	1.73

Table 1 summarizes the experimental values of constants appearing in Equations 4, 6 and 8. The values of $[\eta]$ and k' are listed in Table 2. Putting these values into Equation 1 and using Equation 3, we can draw the η_{sp}/c *vs.* c curves for any desired I_s-values. The results are shown in Figure 6. In the figure, some of the observed data obtained for the system CMC–L – NaCl are plotted for comparison.
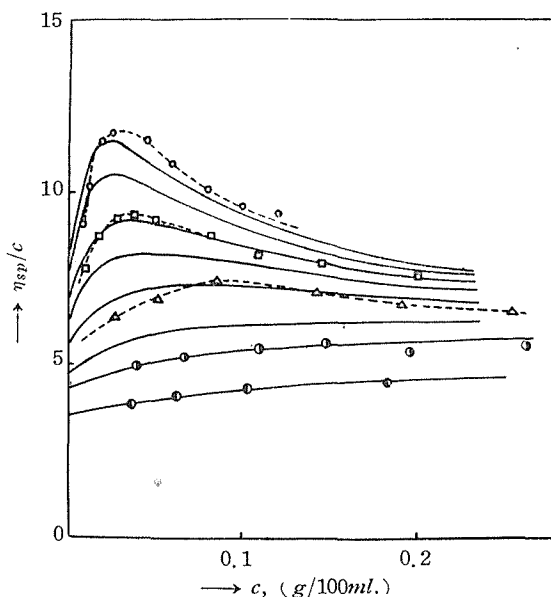

Fig. 6. Calculated reduced viscosity *versus* concentration curves : Solid curves are calculated at I_s-values, 5.00, 6.67, 10.0, 13.3, 20.0, 33.0, 50.0, and 100. (*moles/liter* $\times 10^4$), respectively. Dashed curves show the observed for the system CMC–L–NaCl.

Table 3.

Simple Electrolyte	Concentration of Electrolyte ($moles/l$) $\times 10^3$	Position of Maximum $(I_p)_m \times 10^3$	Height of Maximum $(\eta_{sp}/c)_m$	$(I_p)_m/I_s$
NaCl	0.500	1.0	11.7	2.0
	1.003	1.3	9.3	1.3
	2.01	2.9	7.4	1.5
Na$_2$CO$_3$	0.200	0.45	12.5	1.1
	0.33	0.6	11.1	1.1
	0.50	1.0	9.9	1.1
	0.84	2.0	7.4	1.2
MgCl$_2$	0.314	1.5	8.9	1.1
	0.517	2.6	7.6	1.3
	0.676	3.9	7.0	1.4
Alkali–I*	1.000	1.7	8.3	1.5
	2.000	2.6	6.5	1.2
Alkali–II*	1.000	1.8	7.6	1.2
	2.000	2.5	6.3	0.8

* Mixture of NaOH and Na$_2$CO$_3$; Mole fraction of NaOH, "p" is 0.922.
** Mixture of Na$_2$CO$_3$; p=0.442.

2. Comparison with Experimental Data. In this part, we shall compare the positions of viscosity maximum in η_{sp}/c read off the calculated curves in Figure 6 with those found experimentally. The experimental η_{sp}/c *versus* c curves obtained with either Na_2CO_3 or $MgCl_2$ as added electrolyte are presented in Figures 7 and 8. In Table 3, the positions of viscosity maximum estimated from the experimental curves are listed with a heading $(I_p)_m$. The table also lists the values of η_{sp}/c corresponding to the positions of viscosity maximum $(I_p)_m$ in the column headed by $(\eta_{sp}/c)_m$. Hereafter we shall call $(\eta_{sp}/c)_m$ as the *height* of viscosity maximum.
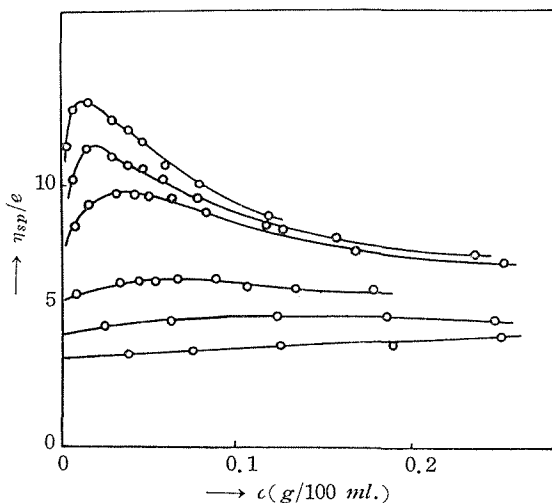

Fig. 7. Observed viscosity curves with Na_2CO_3: The curves, from upper to below, correspond to the added amounts, 2.00, 2.30, 5.50, 8.40, 13.4 and 20.0 (*moles/liter* $\times 10^1$), respectively.

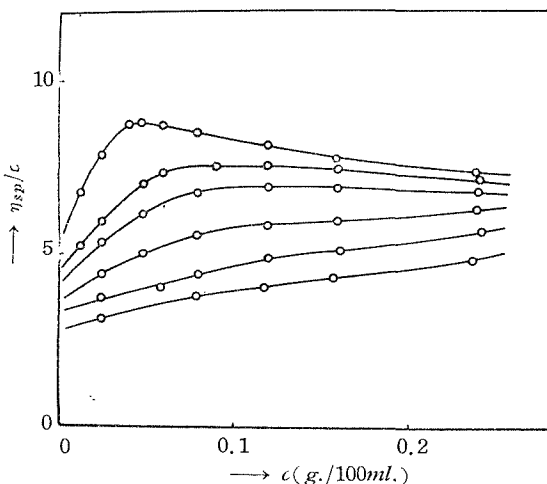Fig. 8. Observed viscosity curves with $MgCl_2$: The added amounts are, from upper to below, 3.30, 5.67, 10.1, 13.5 and 2.53 (*moles/liter* $\times 10^1$), respectively.

To put the observed results in more tractable form, the ratios $(I_p)_m/x$, where x is the usual ionic strength, and $(I_p)_m/I_s$ are plotted against x and I_s in Figures 9a and 9b, respectively. In Figure 9b, the soild line shows the relation derived from the calculated curves in Figure 6. It is seen from these figures that the introduction of
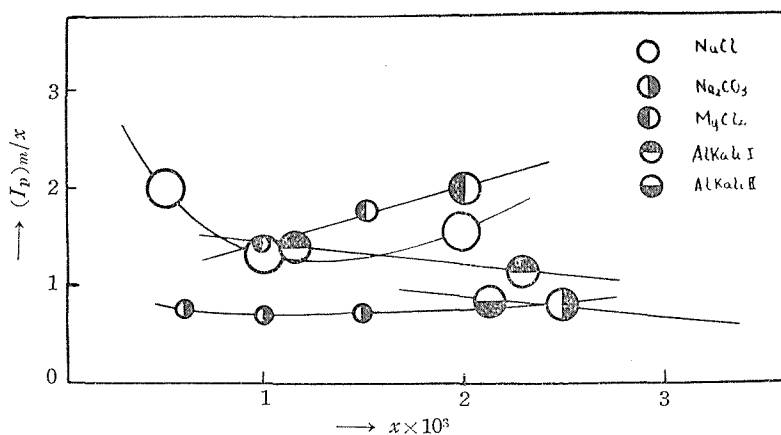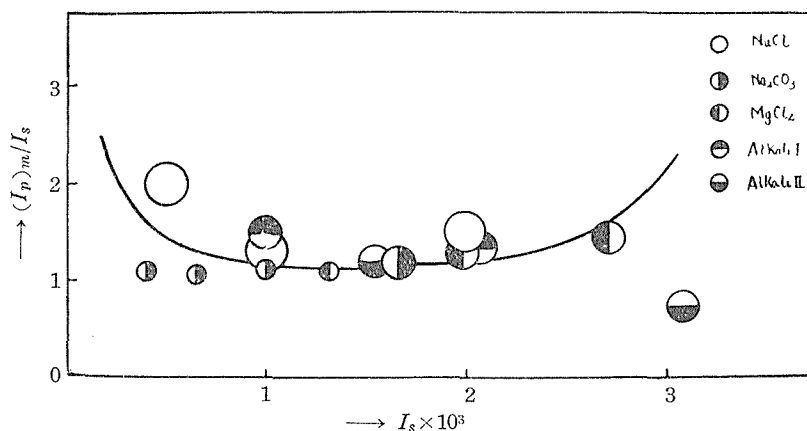
Fig. 9a. Plot of $(I_p)_m/x$ versus x.

Fig. 9b. Plot of $(I_p)_m/I_s$ versus I_s.

I_s in place of x makes the plots of $(I_p)_m$ vs. x for different electrolytes closer and allows the data to approach the theoretical soild line. Figure 10 shows that the data for the height of viscosity maximum, $(\eta_{sp}/c)_m$, plotted agaist $(I_p)_m$ fall, irrespective of the sort of electrolyte added, on a single curve drawn by referring to the data in Figure 6. The facts demonstrated in these figures may be mentioned as follows : For a given sample of polyelectrolyte, the position of viscosity maximum is independent of the sort of added electrolyte, if the comparison is made with respect to the effective ionic strength I_s ; and the height of viscosity maximum is not affected by the sort of added electrolyte. Therefore, there is no doubt that, whatever mechansim may be
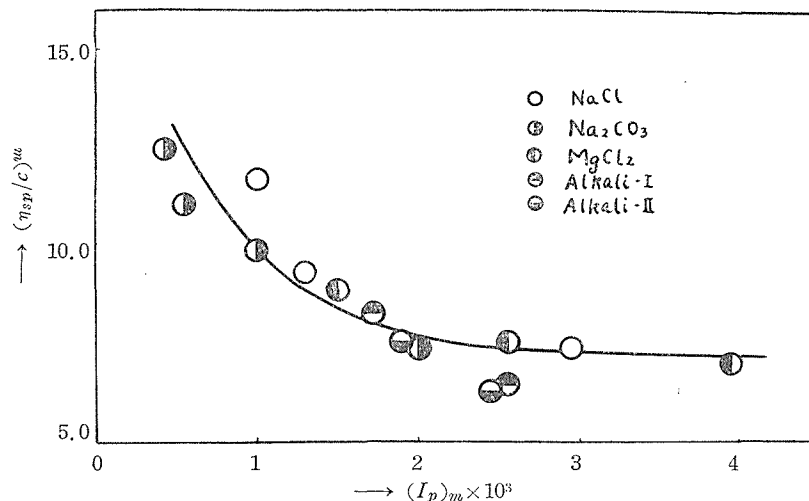
Fig. 10. Observed relation between the position and the height of viscosity
maximum : Solid curve is drawn by referring to Fig. 6.

operating, the appearance of the viscosity maximum is due to a combined effect of
$[\eta]$, k' and c and the shift of its position is caused by the dependence of $[\eta]$ and k'
on I_s.

If we confine the discussion to the electrolytes used here, it may be inferred that
only cation of added electrolyte will have an effective influence on the values of $[\eta]$
and k' in solutions of a given anionic polyelectrolyte and that 2-1 electrolytes such as
MgCl₂ will much more suppress the dissociation of polyion than do 1-1 electrolytes.
Divalent cations behave as if they are four times stronger than univalent cations in
the power of suppressing the ionization of the polyelectrolyte molecule. In fact, to in-
terpret the observed relation between $[\eta]$ and $I_s^{-1/2}$ for the system Na–CMC–MgCl₂,
the number of ionizable groups on the macromolecule had to be estimated much
smaller than that calculated from the stoichiometric base[6].

It is of interest to examine whether the addition of simple electrolyte is necessary
in order to give rise the viscosity maximum. Up to recent years, it has been believed
that the η_{sp}/c in electrolyte-free-solutions of a polyelectrolyte continues to increase
monotonously with increasing dilution and reaches finally a limiting value at $c = 0$.
However, several recent works demonstrated that the viscosity maximum can be ob-
tained even in the absence of added electrolyte[10,11,12,13].

Of these observations, Fujita and Homma[13] ascertained a maximum at an extremely
high dilution of about $5 \times 10^{-3} g./100ml.$ on the viscosity curve for electrolyte-free-
solutions of CMC-L, the same sample as used here. While, at the present situation,
we can not interpret the appearence of the viscosity maximum in salt-free-solutions
of polyelectrolytes in terms of the "molecular" mechanism, we point out that the k'
value observed by Fujita and Homma for CMC-L in salt-free-solutions was about 10,

very close to 15 which is expected from Equation 8 at $I_s = 0$.

On the basis of these results it may be concluded that, on the contrary to the previous findings, the η_{sp}/c *versus* c curve for electrolyte-free-solutions of any polyelectrolyte does not necessarily show a continuous steep rise with decreasing polymer concentration.

Influence of Temperature on Maximum of η_{sp}/c

The position of viscosity maximum for the CMC-M solution was determined in the presence of a certain amount of sodium chloride as a function of temperature. The values obtained for the positions and heights of the maximum are tabulated in Table 4. It is seen from the table that the viscosity maximum shifts slightly towards

Table 4.

Concentration of NaCl ($moles/l.$) $\times 10^3$	Temperature °C	Position of Maximum $(I_p)_m \times 10^3$	Height of Maximum $(\eta_{sp}/c)_m$
0.501	55	0.49	25.2
	45	0.48	26.0
	35	0.47	26.8
	25	0.45	27.4
0.667	55	0.74	21.0
	45	0.68	21.8
	35	0.63	22.9
	25	0.60	24.7
1.001	55	1.2	17.6
	45	1.1	18.0
	35	1.0	20.0
	25	1.0	21.9
1.335	55	1.9	16.4
	45	1.7	16.9
	35	1.6	17.5
	25	1.5	18.8
2.002	55	3.3	14.7
	25	2.5	16.5

higher concentration of the polymer with increase in temperature. The shifts were too slight to discuss quantitatively, but showed a certain distinct tendency, differing from the results of Mock and Marshall[14].

The results show that the elevation of temperature may apparently be equivalent to the addition of more amount of sodium chloride. According to Fuoss' mass action effect, it may be presumed that the amount of Na-ion dissociated from the polymer salt would be reduced as a consequence of the elevation of temperature. Figure 11 shows, however, that the plots form independent curves corresponding to each temperature. This suggests that the variation of temperature would induce not only the effect equivalent to the additon of more amount of sodium chlorid but also have an influence
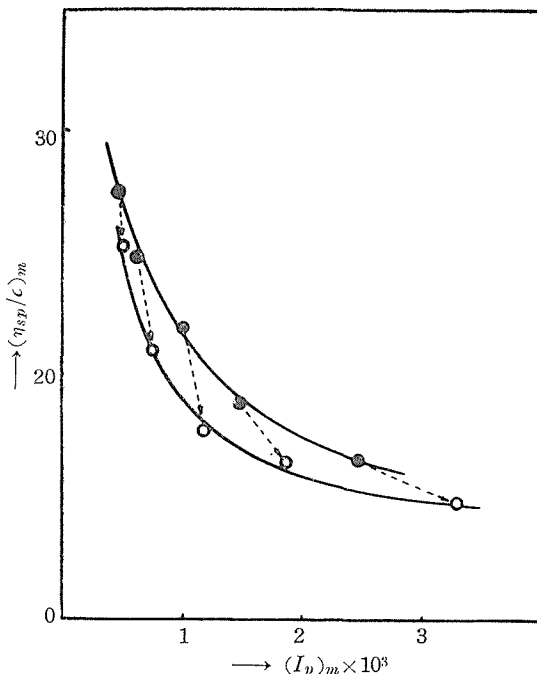
Maximum in the Viscosity Curve

Fig. 11. Temperature dependence of the relation between the position
and the height of viscosity maximum: Solid circles and open circles
are the plots at 25 and 55°C, respectively.

upon the electrostatic interaction between the polyion and its counterions or between the polyions. From the macroscopic viewpoint, the elevation of temperature brings about a decrease in dielectric constant of the medium, which, in turn, results in an increase in the electrostatic potential energy among the ions. However, all "molecular" theories hitherto developed in this field have not been concerned with this problem, only assuming that the dielectric constant of the solution has a constant value averaged over the medium and the solute at a certain temperature. Our finding will, therefore, set forth a problem as to the effect brought about by the temperature dependence of the dielectric constant of the system. The calculation of entropy of the system will have to be modified to a certain extent by taking this effect into account.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Professor M. Horio for his interest toward this work. They also thank Dr. H. Fujita for reading this manuscript.

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