

Viscosity of Dilute Solutions of Polyelectrolytes

By

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The viscosity measurements were performed with poly (vinyl alcohol) partially acetalized with glyoxylic acid, in solutions of a simple electrolyte, and Pals and Hermans' method of dilution was used. It was found that the extension of a macro-ion on the dilution line was kept constant over the polymer concentration range covered, utilizing our treatment as previously reported.⁵⁾ A parameter, m , introduced in the method of dilution was known to be not far from the ratio of activity coefficients of polymeric and simple electrolytes. The "effective ionic strength" proposed by Pals and Hermans was suggested to be a significant quantity in dilute solutions of polyelectrolytes.

1. Introduction

It has been well-known that the reduced viscosity of dilute solutions of polyelectrolytes shows a remarkably different concentration dependence from that of neutral polymer solutions. It is observed to increase so steeply with decreasing concentration in salt-free solutions that the limiting viscosity number $[\eta]$ can not be determined with high accuracy.

The proposed methods of extrapolation for determining $[\eta]$ can be classified into two groups. The first is the method of Fuoss and Strauss¹⁾ that utilizes a linear relation between the reduced viscosity, η_{sp}/C_p , and the square root of the polymer concentration, $\sqrt{C_p}$. As pointed out recently by many authors, however, the $\eta_{sp}/C_p - C_p$ curve has a distinct maximum at a very low concentration²⁾ so that this method of extrapolation seems definitely dubious. The second method, in contrast to the first which employs an empirical relation, is based on the choice of a parameter by which the experimental data can be rearranged so that the linearity between η_{sp}/C_p and C_p can be secured. (The detailed discussion of these methods of extrapolation was given by Terayama and Wall³⁾). Some parameters were chosen, which can be distinguished by their physical significance to each other. However not all of them are valid over a wide range such that they can give the linear relation desired. The method of dilution proposed by Pals and Hermans⁴⁾ is interesting in some respects: though the

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original intention to determine $[\eta]$ in salt-free solutions was not satisfactorily attained, the method seems to contain useful suggestions for interpretation of the concentration dependence of viscosity. In this report, attention will be focused on this method of dilution, and some analyses will be given.

2. Preliminary Considerations

Pals and Hermans (P-H) have defined a quantity, X_0 , which was given the name of "effective ionic strength", for polyelectrolyte solutions. This quantity is clearly an extension of "ionic strength" for simple electrolyte solutions. According to them, X_0 is related to the concentration of foreign salt (mol./l), X , the concentration of polymer (g/l), C_p , and the number of equivalents per gram of the polymer, γ , by the relation

$$X_0 = X + \gamma C_p m, \quad (1)$$

where m denotes the number of moles of foreign salt which is required to replace one equivalent of the polyelectrolyte. This method of dilution is to determine the parameter m so as to obtain the straight $\eta_{sp}/C_p - C_p$ line, keeping X_0 constant.

It is noteworthy that the first term in eq. (1) reduces to the usual "ionic strength" when the foreign salt is of 1-1 type and the second expresses polymer concentration effects. Apart from the arbitrariness in determining the value of m , it is of great significance that this effect was introduced into a parameter chosen for description of the polyelectrolyte solutions. We mentioned in another report⁵⁾ that theories or interpretations on the solutions previously published have not considered the presence of more than one macro-ion with a few exceptions. This omission has made the treatments unnecessarily intricate and as a result the theories have failed to give an adequate interpretation, from a unified stand-point, regarding the many varieties of properties. Whether the "effective ionic strength," defined on the ground of the assumption of an equivalency of simple and polymeric electrolytes, is a characteristic quantity for polyelectrolyte solutions, just as the "ionic strength" is for simple electrolyte solutions, will be determined by the physical implications of the parameter m .

The linear relation between η_{sp}/C_p and C_p , from which m can be determined, was originally discovered for neutral polymer solutions. It can be approximately admitted that the extension of the polymer is kept constant on this line. From the similarity of the situation, we could expect that the extension of a macro-ion on the the P-H dilution line is independent of the concentrations of both polymer and foreign salt. We will, in the following considerations, regard this expectation as a criterion for judging the validity of the treatment employed for the purpose of exploring the character of m .

3. Experimental

(A) **Material.** The material used was poly (vinyl alcohol) partially acetalized with glyoxylic acid (PVAG). The details of the method of preparation are found elsewhere.⁶⁾

(B) **Viscosity Measurements.** The viscosity measurements were carried out at $30 \pm 0.1^\circ\text{C}$ with an Ostwald viscosimeter, the characteristics of which were described in another paper.⁷⁾ Potassium chloride was chosen as a foreign salt.

The result of the measurement is given in Fig. 1. The full curves denote the reduced viscosity curves. As is usually the case, the reduced viscosity increases

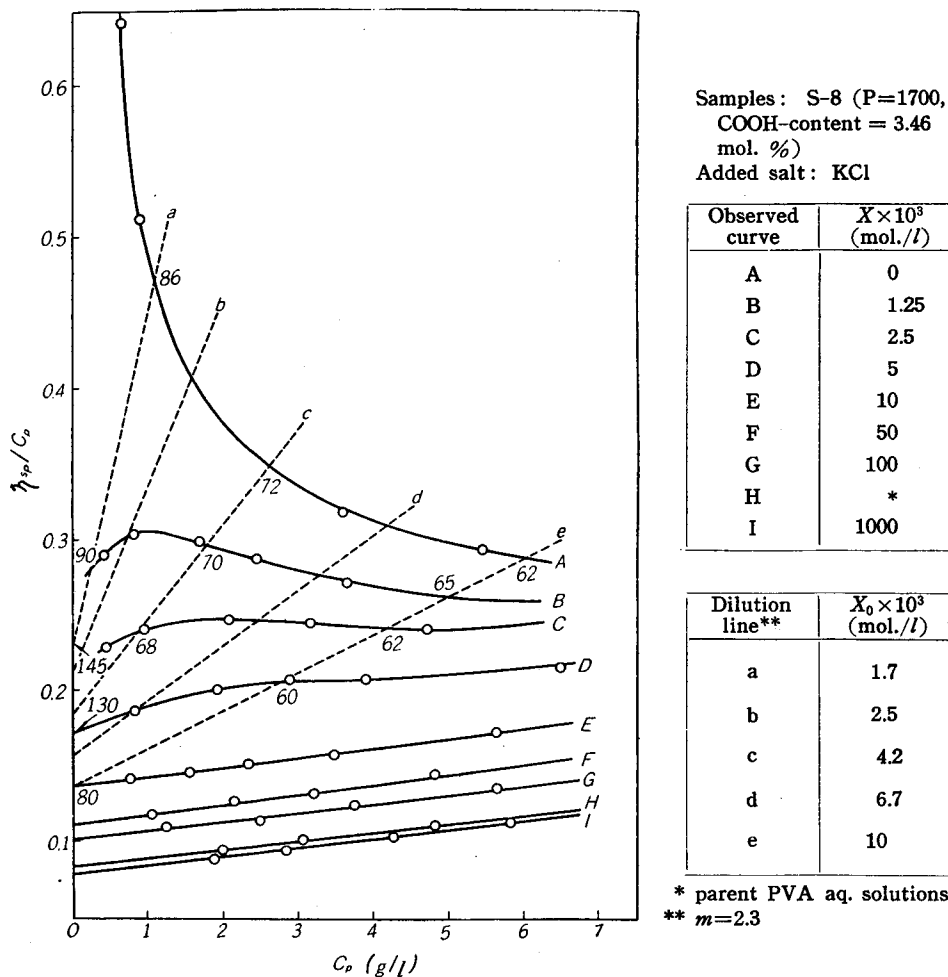


Fig. 1. Observed reduced viscosity-concentration curves of PVAG in solutions of a simple electrolyte and the Pals-Hermans dilution lines. (The figures in this fig. denote the radius of the polymer sphere estimated from titration data.)

sharply with decreasing C_p for the salt-free solution, i.e. $X=0$. [A distinct maximum as mentioned in §1 was not observed for this material, but it was observed at about 1 g/l for S-5 (degree of polymerization = 370, carboxyl group content = 2.97 mol. %). According to other reports, the concentration exhibiting the maximum reduced viscosity is much higher than ours. This discrepancy may be due to a difference in the charge density of the material used.] As X becomes greater, η_{sp}/C_p decreases and linearity is approached. Though the viscosity of aqueous solutions of the parent PVA is, as expected, strikingly low, it should be mentioned that this low viscosity is exhibited by a PVAG solution which contains a large amount of foreign salt ($X=1$). This appears to mean that the linearity can not be immediately interpreted as an indication of the disappearance of electrostatic interaction.

Applying the P-H method of dilution to our observations, we obtained a group of dilution lines (dashed lines in Fig. 1) at $m=2.3$. According to eq. (1), $X=X_0$ holds when $C_p=0$. Therefore, the intercept on the ordinate gives $[\eta]$ at the concentration of foreign salt = X .

The same measurements were carried out for the other two materials, and the dilution method was again used. The values of m are shown in Table 1, together with the characteristics of the materials. This table indicates that m depends on the degree of polymerization and the charge density. It has been reported that Pals and Hermans obtained $m=1.0$ for sodium carb-oxymethylcellulose, 1.5 for sodium pectinate and 1.0 for chitosan.⁸⁾ As m denotes an apparent valency of an ionized group, it might be expected to be unity in our case if the counter-ion fixation is negligible. Before asserting that this value has a sound and reasonable basis, however, a detailed discussion has to be given on the electrostatic interaction, in the field of which the ionized groups are constrained.

(C) **Potentiometric Titrations.** As stated in §2, we have to obtain information regarding the extension of a macro-ion on the dilution line. For this purpose, a method⁵⁾ using potentiometric titration data is employed here again, because no other methods are available at the present time.

The experimental procedure is the same as the one previously described⁹⁾, except

Table 1. Observed m -Values of PVAG.

Sample	P	COOH-content	m
SI-2	1420	9.46	1.0
S-8	1700	3.46	2.3
S-5	370	2.97	1.0

Table 2. pK of PVAG as a Function of Concentration of Foreign Salt.

Sample: SI-1 (P=2150, COOH-content, 7.05 mol. %)

X (mol./l)	C_p (g/l)	pK
0	1.49	3.0
0.011	1.40	3.0
0.103	1.47	3.1
0	2.98	3.0
0.013	2.90	3.0

that a pH-Meter of M-3 Type of Horiba Instruments Inc. is used and the temperature of PVAG-KCl solutions is controlled to $30 \pm 0.5^\circ\text{C}$. An example of the salt-concentration dependence of the dissociation exponent of PVAG is shown in Table 2, which shows that the presence of a foreign salt has practically no effect on the pK . This is in contradiction with the observations of Katchalsky and Spitnik and others¹⁰⁾ for poly (acrylic acid) and poly (methacrylic acid). The discrepancy appears to be due to the difference in the charge density.

4. Extension of Macro-Ion on the P-H Dilution Line and Related Problems

(A) **Extension of Macro-Ion on the P-H Dilution Line.** From the titration data, we can estimate the extension of a macro-ion at arbitrary concentrations of the polymer and the foreign salt. The results obtained by this calculation are inserted in Fig. 1. The figures at the intersecting points of the observed viscosity curves and the artificial dilution lines denote the radius (R) of the spherical macro-ion expressed in Å. Here again $pK_0=2.50$ is used.

It will be realized that the calculated value of R is nearly constant on a dilution line. (Deviation at $C_p=0$ from that constancy will be discussed later.) This is an interesting result, which agrees with an idea suggested by Pals and Hermans. Since this idea seems to be sound at present, the agreement is considered to confirm that a fundamental postulate involved in our method for estimating the extension is equivalent to that underlying the P-H method of dilution and, at the same time, assures the correctness of that postulate, i.e. the equivalency of simple and polymeric ions. This equivalency manifests itself in the viscosity behaviour: an increase in both salt-concentration and polymer-concentration gives rise to a decrease in the reduced viscosity. The P-H method can be said to be nothing but an effort to investigate the equivalency quantitatively based on this experimental fact.

Reservation has to be voiced concerning the values of R at $C_p=0$. We should like to point out some dubious points involved in the calculation. Firstly, care must be taken in the use (at $C_p=0$) of the pK -value which was practically constant over the range of finite concentrations covered. Because of the tremendous difficulties encountered in performing the titration at high dilutions, this uncertainty can not be removed. Secondly, there remains a possibility that the error involved in the treatment used for the present calculation might be fairly considerable at extreme dilution. As was already mentioned,⁵⁾ a model, similar to that of Hermans and Overbeek (H-O),¹¹⁾ was adopted for a macro-ion and the distribution formula proposed by Wicke and Eigen¹²⁾ (W-E) was assumed. Our mathematical expression naturally reduces to that obtained originally by H-O when the polymer concentration becomes extremely low. Therefore, if any disagreement or contradiction with experiment was found at great

dilutions, it can be ascribed to imperfections in the H-O model; the W-E theory simplifies to the D-H theory which is regarded as a true law in the limit of high dilution whereas an analysis of the approximations inherent in the H-O theory has not yet been extensively undertaken. The low reliability of the values of R at $C_p=0$ can be clearly understood upon considering that a spherical model has been adopted to represent the macro-ion and that a proportionality between the calculated R and the square root of the degree of polymerization does not hold at $C_p=0^{5)}$.

From $[\eta]$ at an effective ionic strength, the radius under this condition of a macro-ion assumed to be a rigid sphere can be estimated by means of Einstein's equation. The values calculated are 180, 160 and 130 Å for $X_0=1.7 \times 10^{-3}$, 4.2×10^{-3} and 10^{-2} respectively, about twice as large as the R obtained above at $C_p \neq 0$. This discrepancy may come from the omission of the electroviscous effect in Einstein's theory. As clearly expected, taking this effect into consideration would result in a smaller radius.

(B) Consideration about m . As mentioned above, m was introduced as a parameter denoting an equivalency of the charge of the ionized group and that of a simple ion. In our case, the ionized group carries a monovalent charge just as the foreign salt used. Therefore $m=1$ can be taken for granted. Experimentally, however, we have a value other than unity sometimes, as stated above. Stoichiometric considerations, thus, are supposed not to be applicable: the deviation from unity appears to mean that the charge of an ionized group and that of a simple ion can not electrochemically have an effect equivalent to the analytical valency. It is not absurd to ascribe this to the electrostatic interaction by which the ionized groups and simple ions are always influenced.

This interaction can be measured in terms on the activity coefficient of the solute (or the solvent). It is evident that the choice of a standard state common to both polymeric and simple electrolytes is necessary and convenient for further discussion of the present problem. As the standard state, the ideal state of simple electrolyte solutions should be chosen. It should be mentioned here, that the activity coefficients calculated previously⁵⁾ are really based on this state. Accordingly, for interpreting the character of m , it will be useful to compare m with $\gamma_{p\pm}/\gamma_{s\pm}$, where $\gamma_{p\pm}$ denotes the **mean** activity coefficient of the polyelectrolyte and $\gamma_{s\pm}$ that of a simple electrolyte.

$\gamma_{p\pm}$ can be formulated using the expressions for the ionic activity coefficient (eqs. (17) and (18) in Ref. 5) and $\gamma_{s\pm}$ is given, in the low concentration range of the foreign salt, by the relation

$$\log \gamma_{s\pm} = 2 \log \gamma_g \quad (2)$$

where γ_g denotes the activity coefficient of gegen-ions.

Using the value of R inserted in Fig. 1, $\gamma_{p\pm}$, $\gamma_{s\pm}$ and the ratio can be evaluated for a sample, S-8. The results are tabulated in Table 3, from which the ratio is seen to be about 1.6 (compare with $m=2.3$) except when $X_0=1.7\times 10^{-3}$ and $C_p=0$. It will

Table 3. Mean Activity Coefficients of Polyelectrolyte and Simple Electrolyte on the Dilution Line and the Ratio.
Sample: S-8, $m=2.3$.

$X_0 \times 10^3$ (mol./l)	C_p (g/l)	$X \times 10^3$ (mol./l)	R (Å)	$\gamma_{p\pm}$	$\gamma_{s\pm}$	$\gamma_{p\pm}/\gamma_{s\pm}$
1.7	1	0	86	1.1	0.8	1.4
	0.25	1.25	90	1.2	0.9	1.3
	0	1.7	145 (90)	0.5 (1.2)	0.9 (0.9)	0.6 (1.3)
4.2	2.5	0	72	1.2	0.8	1.6
	1.75	1.25	70	1.2	0.8	1.6
	1	2.5	68	1.3	0.8	1.6
	0	4.2	130 (70)	0.3 (1.1)	0.9 (0.9)	0.4 (1.3)
10	6	0	62	1.2	0.7	1.7
	4.5	2.5	62	1.2	0.7	1.7
	3	5	60	1.1	0.7	1.5
	0	10	80 (60)	0.3 (0.7)	0.8 (0.8)	0.4 (0.8)

be noticed that, at $C_p=0$, the calculated value of the ratio has a rather small value for all X_0 's when use is made of the value of R shown in Fig. 1. This value, however, becomes greater, approaching to 1.6, when the value of R obtained at $C_p \neq 0$ is used, for example 70 Å for $X_0=4.2 \times 10^{-3}$. This appears to support the view that the value of R has a low reliability at $C_p=0$ as mentioned above. When the estimate of the ratio at $X_0=1.7 \times 10^{-3}$ is evaluated, the experimental difficulties in the viscosity measurements at such a high dilution have to be taken into consideration. Thus it can be supposed that the parameter, m , might be giving the ratio of the activity coefficient of the polyelectrolyte to that of a simple electrolyte. This supposition, while not too firmly established at present, can be examined by direct measurement of the mean activity coefficient of polyelectrolytes, which was undertaken for the first time by Chadwick and Neale most recently.¹³⁾

(C) **On the Slope of the Dilution Line.** According to Huggins, the slope S of the viscosity-concentration curve is related to the so-called Huggins constant, k' , by the following relation,

$$S = [\eta]^2 k'. \quad (3)$$

k' of the dilution line can be estimated for our three kinds of materials and is plotted against $1/X_0$ in Fig. 2. From this figure, it is realized that (1) k' of the dilution line is much greater than that usually found for neutral polymers, (2) k' increases linearly with decreasing X_0 and (3) all of our materials have the same linearity.

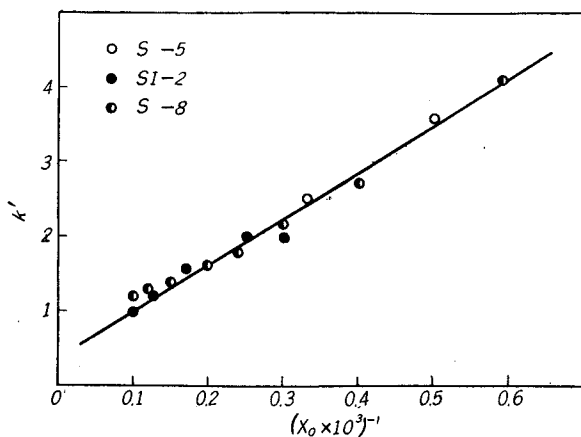


Fig. 2. Variation of k' of the Pals-Hermans dilution line with effective ionic strength, X_0 .

Facts, (1) and (2), were observed by Pals and Hermans for sodium carboxymethylcellulose, but the slope of the dilution line varied depending on the degree of polymerization and on the charge density. If our experiments are not in error, it is tempting to conclude that X_0 , depending on a characteristic parameter of the polyelectrolyte, i.e. m , has considerable significance. As X_0 becomes greater, we can

say that the solvent power is lowered. If this expression is permitted, the tendency of k' mentioned in (2) is in complete contradiction with the trend of this constant observed for neutral polymers.¹⁴⁾ Our present observations, however, should be interpreted in terms of the surface potential of the macro-ion which decreases with increasing concentration of foreign salt so that interionic interaction is diminished and k' also becomes smaller. Of course, k' depends also on the segment-density and the flexibility of the chain, which could be neglected in polyelectrolyte solutions according to the data presented here.

5. Discussion

In the above sections, it was pointed out that the effective ionic strength of polyelectrolyte solutions has an important physical significance. So far, it has been introduced and discussed only in connection with the viscosity of the solutions. It is expected that it will be subject to extensive examination in the light of other experimental evidence. The diffusion characteristics of polyelectrolytes might be a pertinent source of information.

We showed that the parameter, m , was approximately close to the ratio of the mean activity coefficients of the polyelectrolyte and a simple electrolyte. The variation of m with charge density and the degree of polymerization as illustrated in Table 1 is interesting and can be interpreted at least qualitatively in terms of the dependence of $\gamma_{p\pm}/\gamma_{s\pm}$ upon these characteristics of the materials used. $\gamma_{s\pm}$, as the numerical calculation shows, is not influenced to as great an extent as $\gamma_{p\pm}$, by the character of the macro-ions. Therefore we can omit $\gamma_{s\pm}$ in the following considerations. Generally, $\gamma_{p\pm}$ increases with the degree of polymerization and charge density, according to our calculations.⁵⁾ The charge densities of the materials used here are in the order,

S-5 < S-8 < SI-2, and the degree of polymerization increases in the order S-5 < SI-2 < S-8. Since the volume effect on the activity coefficient is much greater than the effect of charge density, $\gamma_{p\pm}$ of S-8 (and therefore m) has the greatest value, as experimentally observed. (Care must be paid to a fact that the calculated activity coefficient is for systems in thermodynamic equilibriums. To be correct, it should be applied to irreversible process, such as viscosity or diffusion, only after the entropy production has been estimated.)

It is to be noted that the dilution lines can be distinguished from each other by the extension of a macro-ion, though a value which is to be determined by the nature of the material used is assigned to m irrespective of the effective ionic strength. The insensitivity of m towards these ionic strengths appears rather curious at first glance. It is not clear whether this property of m will be observed in a wide range of concentrations or not.

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